INTERNATIONAL CONFERENCE ON THEORETICAL PHYSICS

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Science Council of Japan

Abstract Book

Section B and C

Kyoto and Tokyo, September 1953

TENTATIVE PROGRAMME OF SYMPOSIUM ON PHOTOGRAPHIC SENSITIVITY

(*Hakone Hotel Sept. 16, 1 p. m.*)

Section A

Physical Properties

Presiding : Prof. *T. Muto* (University of Tokyo)

(*Titles of lectures*)

A1. *F. Seitz :* The Properties of Silver Halides (*30 min.*)
A2. *H. Kanzaki :* Lattice Defects in Silver Halides (*30 min.*)

(*Titles of 5 minutes comments*)

A3. *C. Yamashita :* On the Formation Energy of the Lattice Defects in Silver Halides.
A4. *S. Suzuki :* Photoconductivity of Silver Halides.
A5. *M. Tamura :* Photoconductivity in Silver Bromide Polycrystallin Films Prepared by Precipitation Method at Room Temperature.
A6. *N. Suita :* Breakdown and Photochemistry of Silver Halides.
A7. *S. Sonoike :* Orientation of the Photolytic Silver.
A8. *S. Fujisawa :* A Note on the Print-out Effect.
A9. *K. Kamiyoshi :* Preliminary Experiments on the Dielectric Properties of Silver Chloride.
A10. *S. Makishima :* A Note on Low Temperature Fluorescence of Silver Halides.
A11. *S. Miyake :* Crystal Structure of α-Silver Iodide.

Section B

Photographic Emulsion

Presiding : Director *S. Fujisawa* (Fuji Photo Film Co., Ltd.)

(*Titles of lectures*)

B1. *N. F. Mott :* The Mechanism of Photographic Sensitivity (*30 min.*)
B2. *E. Mizuki :* Sensitization and Sensitivity of Photographic Emulsions (*30 min.*)

(*Titles of 5 minutes comments*)

B3. *A. Sasai :* The Influence of Ripening and Chemical Sensitization on the Hershell Effect.
B4. *A. Miyauchi :* The Influence of After-ripening on the X-ray Sensitivity.
B5. *H. Goto :* A Note on the Photoconductivity of Photographic Emulsions.
B6. *M. Tamura :* The Mechanism of Desensitization by Dyes.
B7. *S. Umano :* Contribution of the Triplet State in Dye Sensitization.
B8. *Y. Oyama :* Pressure After Effect on Solarization of Photographic Emulsion.
B9. *S. Sugai :* On the Activation Energy of Photographic Chemical Development.

INTERNATIONAL CONFERENCE ON THEORETICAL PHYSICS

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for
SECTION B

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SECTION B

CRYSTAL DISLOCATION

— Sept. 18 (Fri.) Morning —

POLYMERS

— Sept. 18 (Fri.) Afternoon —

LIQUID

— Sept. 19 (Sat.) Morning —

TRANSPORT PHENOMENA

— Sept. 21 (Mon.) Morning —

IRREVERSIBLE PROCESSES

— Sept. 21 (Mon.) Afternoon —

GENERAL METHODS IN STATISTICAL MECHANICS

— Sept. 22 (Tues.) Morning —

Difficulties in the Theory of Dislocations

N. F. Mott

H. H. Wills Loboratory, Bristol, England

My aim in this lecture is to describe some of the difficulties at present encountered in the application of the theory of dislocations to the mechanical properties of solids. I shall assume in the lecture that my audience is familiar with the many observations[1,2] of slip lines on the surface of metals, and with the explanation of slip lines given recently by Frank and Read[3]. I shall however give some evidence that the "sources" postulated by Frank and Read actually exist. The most direct evidence I consider is provided by the work of Mitchell and Hedges[4], who have succeeded in photographing dislocations in the interior of silver-halide crystals, the dislocations being made visible by metallic silver which has precipitated along them.

I think, then, that we are on firm ground in developing a theory of the mechanical properties of metals, if we assume that slip has its origin in Frank-Read sources, and that they are distributed at random throughout the material in a way that depends on the method of preparation. I think, too, that it is fair to say that dislocations generated by the Frank-Read sources do not normally pass out of the crystal, except in "easy glide", but pile up against grain boundaries or other barriers (sessile dislocations). Also that work-hardening is mainly due to the interaction between these retained dislocations, as suggested originally by Taylor[5] and in the more detailed model given by the present author[6].

The main problem, to my mind, is to explain the amount of slip in each slip line. Here the experimental evidence is not entirely consistent. Yamaguchi[1] was the first to make a detailed examination of the number and rate of growth of slip lines on a metal surface. He showed that, as the degree of cold-work increased, so did the number of slip lines, and that the intensity or amount of slip on each line also increased. More recently the electron microscope has been applied to the problem. Heidenreich and Shockley[7] and Brown[1] showed that all slip lines had roughly the same height, 1000—2000 Ångstrom Units, that they were formed suddenly, and that the increase of height during deformation of the crystal observed by Yamaguchi was in reality due to the formation and widening of a "cluster" of these elementary lines, each 200—400 Ångstron apart. However there are various difficulties in accepting this model, and it is certainly not universally valid. One curious result, unexplained up to the present, is that if the surface has not been subjected to mechanical polishing, the slip is finer (more lines of smaller height) than would otherwise be the case. In hexagonal crystals very large number of fine lines are observed which gradually grow in height as the crystal is deformed. The same appears to be true of cubic crystals when deformed in creep under constant stress. Moreover the recent work of Wilsdorf and Kuhlmann-Wilsdorf[8] has shown that fine slip is observed even in cubic metals deformed at room temperature at normal rates. These workers use electropolished surfaces on aluminium and silver; and a silica replica to allow examination with the electron microscope. According to them, all slip in the pure metals investigated consists of fine slip lines of from 50—200 Ångstrom in height, and the coarse slip observed by other authors must, if their results are of general applicability, consist of clusters of such lines. Only in alloys (alpha brass) could they observe slip over 100 Ångstrom or more on one plane.

Now according to the model of Frank and Read it is quite true that some "sources" of dislocations will generate dislocations for lower stresses than others. But as soon as a source has generated a few dislocations, the stress from these would prevent it from generating any more, and another source would come into play. Thus we should expect "fine slip", the early formation of a large number of steps on the surface, new steps gradually increasing in height, as in hexagonal crystals. The distance between them is expected to be L^2/N where L is the "slip distance", and N the number of scurces per unit volume. Taking frequently accepted values, $L=10^{-2}\,cm$ and $N=10^{10}\,cm^{-3}$, this gives $10^{-6}\,cm$ for the distance between slip lines.

Whether "coarse slip" consists of single steps 2000 Ångstrom high, or a cluster of steps as maintained by Wilsdorf, some hypothesis is required to explain it. One needs some mechanism to explain why a source, once it starts to generate dislocations, should continue to do so rather than handing over the task to others. The main hypothesis have been put forward.

(a) The dynamic hypothesis of Fisher, Hart and Pry[9] and of the present author[6]. These authors suggest that dislocations can move with a speed near to the velocity of sound, and that once they are set in motion their momentum allows the source to continue. This hypothesis may well contain elements of truth, but there are objections to it. The analysis of Fisher, Hart and Pry[9] does not really yield enough dislocations to account for coarse slip; there is much doubt as to whether a dislocations can in fact move fast; and there is evidence that slip lines are not always formed in a short period of time. Certainly, if the dynamic hypothesis is adopted, one will have to admit the simultaneous non-dynamic behavior of Frank-Read sources to account for fine slip. A theory of how both may arise has been given by the present author[10].

(b) Coarse slip is due to "locking" of the sources by impurities; when once slip has begun, it continues from the same source because the locking mechanism cannot operate again until the dislocation comes to rest. This hypothesis is perhaps supported by the observation of Wildsdorf in brass quoted above. On the other land, if it were correct, the pattern of slip lines on polycrystalline metals as well as on single crystals would be very sensitive to purity. In my view, the work-hardening and ductility would in that case depend essentially on hardening also, and this does seem to be the case.

I do not think, then, that we yet have a wholly satisfactory explanation of the formation of slip lines.

Another problem of great interest is that of fracture in metals. Most metals in a tensile test show a reduction of area of about fifty per cent prior to fracture. The crack starts in the middle of the specimen, and spreads to the outside. It must start at some point whether the internal stress approaches the theoretical fracture stress, say ten per cent of the shear modulus. It is difficult to see where this can be, other than at the ends of slip lines, where it is easy to show that very high stresses must exist. A piled up group of 1000 dislocation may be shown to provide a big enough concentration of stress to initiate fracture. But 100 would not be enough; if fine slip is all that occurs, it is difficult to understand fracture.

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Dislocation Networks in Crystals

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The hexagonal form of dislocation network was first predicted in the lecture made by Mott[1] two years ago. His prediction, following a suggestion by Frank, was brought into close-up by the very recent success of J. W. Mitchell[2] in making dislocation lines visible in a transparent silver bromide crystal. The theory is still in its infancy, however. The aim of this report is to construct the elementary concepts of the dislocation network and to give some critical discussions on the bases of experimental results performed recently in our laboratory.

As easily shown, the most fundamental network in a face-centred cubic crystal is made of three dislocations, of which Burgers vectors are all in the same plane. It forms a hexagonal network in a mechanical equilibrium. If the dislocations of the same Burgers vector are all parallel to each other, it is called a regular hexagonal network. When four dislocations meet at a node, two regular polyhedral networks can be defined. The one is realized in a face-centred cubic crystal and the other in a body-centred cubic crystal. A mechanical equilibrium, however, is maintained only in the second case. The transposition of dislocations and the transformation from the one scheme to another are possible in both cases of regular hexagonal networks under two definite conditions: the community of the dislocation line and the conservation of its Burgers vector.

Any dislocation network, which can be realized, must have a sufficiently long life time. Thus it necessitates at least a local mechanical equilibrium and the driving force for the vacancy diffusion tending to turn its structure must be sufficiently small. From such suppositions we can find the most stable network in a face-centred cubic crystal in {113} planes. In it a mechanical equilibrium is possible only when two dislocations are edge type, each in two {111} planes neighbouring to their vector plane and the rest is screw type in the latter.

Some possible origins of dislocation network will be described. Real crystals are supposed to contain a number of networks of different schemes, though separate considerations are needed to decide how the domain structure is connected with annealing process. An interaction between domains will result in some deviation from the regular {113} network.

A recent powerful experimental method advanced by Mitchell as stated before has succeeded in giving a visual evidence to the reality of both plane and polyhedral networks in a silver bromide crystal. Some observations of the surface structure of α-brass single crystal revealed by thermal etching will also give somewhat useful knowledge for the underlying structures.

The motion of a dislocation node in {113} network necessarily accompanies climb motion of one or more dislocation segments. Then on each dislocation a number of jogs will be formed. This leads to an alternative mechanism for the micro-creep of metal crystals. Most important differences from Cottrell's theory³⁾ are in the order of micro-creep rate and in its dependency on temperature and on crystal orientation. A situation will be reached at the steady state of micro-creep, where a chemical potential over each dislocation line is almost constant. The shearing rate at this stage is found to be of the order $10^4 D\mu/kT\ sec^{-1}$, where D means the diffusion coefficient. A chemical potential, μ, given by the osmotic force, can be calculated under a condition of energy balance between the increase of line energy of dislocation and the decrease of potential energy owing to slip and climb motion. The rate of micro-creep in the steady state thus obtained is of the order of 10^{-8} sec^{-1} for copper at 500°C in good agreement with our experimental results. Such mechanisms will also provide a theory for the micro-creep at the transient stage.

It must be of importance to examine whether the micro-creep of metal crystals accelerates the vacancy diffusion as the theory predicted or not. Really, the predicted increase of disorder-order transformation rate in a Cu_3Au single crystal was observed under very small stress at 200°C.

Face-centred cubic metal crystals have also been found to yield as in tin crystals observed by Chalmers⁴⁾. If we increased the loads progressively with very slow rate (of the order of 1 gr/mm^2 per hour), however, they did not show any yield point and continued to creep at the steady-state rate of micro-creep decided by applied stress so far as we experienced. We may call such treatments stress-annealing. Its effect on stress-strain curves of high purity aluminium single crystals will be described. Those are to be compared with the effect of nuclear radiation on plastic properties of metals⁵⁾.

If the present idea proposed for dislocation networks is valid, it gives rise to some difference in slip mechanism from that of Frank and Read⁶⁾. As reasonably supposed in the case of alloy, pole dislocations will remain at their original positions when a sufficient stress needed for the multiplication is applied. Each dislocation loop thus formed is expected to be in every parallel slip plane, because the Burgers vector of pole dislocation of {113} network has a component equal to one atomic distance normal to the operative slip plane. On the other hand, pole dislocations in metals are comparatively easy to move and besides, they are both capable of sessile reaction with the active one. That means, there will be a chance forming immobile dislocation segments at a node and it provides a stable source of slip band.

Electron-microscopic observations made by Fujita in our laboratory really show a very homogeneous distribution of slip bands in α-brass crystals, each of which seems to give a shear nearly equal to unity. It is also possible that the micro-slip found in aluminium originates in the same mechanism. Furthermore, the present mechanism can give a reasonable number of vacancies left behind sweeping dislocations, which were estimated in different manner by Seitz⁷⁾ and in later by Mott⁸⁾

It must be stressed, furthermore, that the linear hardening rate of high purity aluminium single crystals ("easy glide") has been found to vary regularly with crystallographic orientation to tension axis, which will be discussed somewhat quantitatively on the basis of the present view as well as the orientation dependency of stress-annealing effect.

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Internal Friction of Metals due to Crystal Imperfections.

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Many kinds of crystal imperfections contribute to the internal friction of metals. Attention is focused here to the dislocations and the lattice defects produced by cold-working.

Internal friction due to dislocations was studied by many authors(1-5). There are two kinds of internal frictions when viewed as a function of temperature of measurement. The one is temperature dependent internal friction and the other is temperature independent one. The former was found and interpreted qualitatively in terms of dislocation theory by Nowick(3). The latter was recently found in our laboratory(6).

It was pointed out by the author(7) that pairs of vacancies or interstitials produced during cold-working would contribute to the internal friction of metals. The direct experimental evidences for this process were recently found also in our laboratory(6)

The aims of this paper are (1) to extend Koehler and Weertman-Koehler's theory(4,5) to explain temperature dependent and temperature independent internal frictions due to dislocations, (2) to develop the theory of reorientation of vacancy or interstitial pairs, and (3) to show the experimental evidences for the reorientation theory.

(1) According to Weertman and Koehler internal friction ϕ is express by

$$\phi=\text{const.}\,N/(GN+G_0)^2, \tag{1}$$

where N is the length of dislocation line per unit volume of the metal, G is a constant which depends sensitively on the particular type of dislocation array considered, and G_0 is a coefficient of restoring force for vibrating dislocations which is caused by impurities or any agency other than dislocation interactions. Now we consider a temperature range where no irreversible phenomenon such as annealing takes place to a measurable amount within a length of time considered. G and N are undoubtedly independent of temperature, while G_0 depends on temperature, because the dislocations break away more often from anchoring entities such as impurities, vacancies and interstitials at higher temperatures, decreasing the value of G_0.

In the case of annealed or slightly cold-worked crystals, where $G_0>GN$, a predominant effect of temperature dependent G_0 results in a temperature dependent internal friction. In other words the higher the temperature, the larger the internal friction.

On the other hand in heavily cold-worked crystals, G_0 is much smaller than GN, hence the effect of temperature independent GN predominates. The internal friction of heavily cold-worked copper single crystals was found quite independent of temperature from about 0°C down to about −100°C(6).

(2) When a metal crystal is subjected to a plastic deformation, many atomic vacancies and interstitials are formed, of which mechanisms of formation were considered in terms of dislocations by various authors(8-10). For example a moving jog of screw dislocation leaves behind it either a line of vacancies or a line of interstitials according to the sign. It is possible that some of them will agglomerate. Thus is considered that a cold-worked metal crystal contains a fairly high density of many kinds of groups of vacancies and interstitials, if the temperature is not too high for them to remain without diffusing out of the crystal. In the following discussion, pairs of vacancies will be chosen for simplicity to represent groups of vacancies or interstitials which show non-cubic symmetry of stress field(7) around them in a cubic crystal. But it should be kept in mind that various kinds of groups other than vacancy pairs would contribute to the internal friction under discussion.

If a vacancy pair has a non-cubic symmetrical stress field around it, the reorientation of pair axis will occur, resulting in a non-elastic strain, when a vibrational external stress is applied, just as an impurity atom pair of larger size reorientates in Cu–Zn or Ag–Zn solid solution alloy(11-12). Internal friction ϕ due to vacancy pair is related to the relaxation time τ of reorientation and the angular frequency ω of vibration by the equation

$$\phi=\Delta_M\,\tau\omega/(1+\tau^2\omega^2), \tag{2}$$

whrre Δ_M is the relaxation strength. τ changes with absolute temperature T, according to the equation

$$\tau=\tau_0\exp(\mathcal{E}/kT), \tag{3}$$

where τ_0 is a constant, k is Boltzmann's constant, and $\mathcal{E}$ is the activation energy of reorientation of vacancy pair. From equations (2) and (3), we obtain a peak of internal friction when measured as a function of temperature.

(3) An above mentioned peak was found6) around room temperatures in a heavily cold-worked single crystal of copper under the vibration of 10 kilocycle frequency range. The heights of peaks are different from specimen to specimen. This fact shows that the density of vacancy pairs in a particular specimen is different according to the condition of specimen. The skirt of peak curve ranges about ten degrees of temperature, which is rather narrow. This is not surprising, because the peak is buried in the background of internal friction due to dislocations.

The peak disappears when a specimen is kept at room temperature for a day or so. As the time of relaxation at the temperature of peak is about 10^{-4} sec., a vacancy pair will make about 10^9 atomic jumps in a day, resulting in a migration of about 10^{4-5} atomic distances. This may be large enough for a vacancy pair to migrate to mosaic or grain boundaries to be absorbed there.

Zener13) suggested to the present author that a peak found by Bordoni(14) in cold-worked materials at a temperature of about 1/2 their Debye characteristic temperature may be due to the vacancy pairs. Here the Debye temperature has no particular meaning, because the peak temperature depends on the external vibrational frequency. It is easy to shift the peak temperature about 150°C, if the vibrational frequency is changed by a factor of 1000. (Bordoni's paper was not available for the present author at the time when this abstract was written.)

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On the Theory of the Kirkendall Effect

Frederick SEITZ

The Kirkendall experiment demonstrates that there may be a net current of atoms flowing relative to the crystal lattice in a region where a concentration gradient exists. Thus diffusion does not occur exclusively by the interchange of atoms in the lattice. In fact, the most careful experiments carried out on systems such as copper-zinc, copper-nickel and silver-gold show that direct interchange must be nearly negligible in many interesting systems. Presumably, diffusion occurs in the main, in such cases, either as a result of interstitial or vacancy migration. There is strong evidence, principally of a theoretical nature, to support the view that the vacancy mechanism prevails. However, it must be admitted that conclusive experimental proof is still lacking. Most phenomena observed to date can be explained with the use of either an interstitial or a vacancy mechanism.

The Kirkendall effect has received the benefit of a great deal of careful experimental and theoretical work. For example, Smigelskas and Kirkendall, Correa da Silva and Mehl, Alexander Balluffi and Kuczynski, Barnes, Buckel and Blin, and Seith and Kottman, have confirmed and amplified the original measurements with a number of couples composed almost exclusively of face-centered cubic metals.

Darken first proposed a purely macroscopic formalism to describe the Kirkendall effect. He assumed that each constituent atom in the diffusion couple must be given its own characteristic diffusion coefficient with the auxilialy condition that if an excess of atoms diffuse into or out of a given volume of the lattice the volume expands or contracts in order to preserve the equilibrium atomic density for the local composition. Subsequently the writer made the first attempt to interpret the Kirkendall effect on an atomic basis, using the vacancy theory. He arrived at a system of relations more general than Darken's for he did not assume that the vacancy current is in equilibrium with the crystal. Bardeen then demonstrated that Darken's equations can be derived with the use of vacancy theory if one assumes that the vacancies are in local equilibrium. Subsequently the writer showed that his equations contained Bardeen's solution as a special case. He also demonstrated that exactly the same relations could be derived using the interstitial mechanism, although he expressed preference for the vacancy mechanism.

Bardeen and Herring summarized the existing situation in 1950. They expressed the view that one should expect the dislocations present in the crystal to provide ample sources and sinks for vacant lattice sites so that equilibrium should be easy to attain. They estimated that a vacancy should have a lifetime of the order of 10^9 jumps from source to sink.

More recent experimental work shows that porosity develops on the side of the diffusion couple toward which the vacancy current flows. This indicates that the vacancies may have considerable difficulty in coming to equilibrium in the regions into which they are pumped in consequence of the concentration gradient. The experiments of Barnes on the copper-nickel system show, in fact, that as many as half the vacancies may end in pores.

There is a possibility that relatively large inclusions, perhaps 1000 atoms distances on an edge, act as much better sinks for vacancies than the dislocation network. Inclusions of this size would permit pores to form for superconcentrations of vacancies of the order of 1% or even less. However, this proposal remains highly hypothetical.

The writer has demonstrated that in cases where a typical strong Kirkendall effect is observed it would be perfectly possible for the pumping action of the concentration gradient to produce a superconcentration of vacancies in the neighborhood of twice the equilibrium value if no 'easy' nuclei are present. Such high superconcentrations could cause vacancies to condense at relatively tiny inclusions, only about 10 atomic diameters in size. If such superconcentrations actually do occur in the cases where pores are observed, one would be compelled to conclude that the dislocation network provides exceedingly poor sinks for vacancies and that the lifetime of vacancies in such metals probably is much longer than the 10^9 jumps estimated by Bardeen and Herring as a reasonable value.

The writer has attempted to survey evidence concerning the superconcentrations of vacancies that actually are achieved in metals. None of the available experiments provide a conclusive answer to the question. There are, however, several experiments, in particular, the observations of Buffington and Cohen on the increase in self-diffusion in alpha-iron during creep, which indicate that the lifetime of vacancies may be longer than 10^{10} jumps.

It has been suggested that the dislocations in face-centered cubic metals may be poor sources or sinks for vacancies because they split into twin dislocations. Thus other imperfections take over most of the burden. Actually, Balluffi has observed porosity during the dezincification of beta brass. This observation, in addition to those of Buffington and Cohen concerning evidence for long lifetimes of vacancies in alpha-iron, suggest that the factors producing superconcentrations are quite general. In addition, it is not clear why vacancies should be produced so profusely in face-centered cubic metals if the geometry of dislocations prevents them from being absorbed.

The Configuration and Properties of Polymer Molecules in Dilute Solution

Paul J. Flory

The closely related problems will be discussed in this paper. One of these pertains to the configuration of a flexible, long chain polymer molecule and the other to the thermodynamic properties of dilute solutions of such molecules. Both depend on interactions between segments of ploymer chains. The configuration of such a molecule in an infinitely dilute solution is modified significantly by its *intramolecular* interactions; the thermodynamic properties of the dilute polymer solution depend similarly on the *intermolecular* interactions between chain segments belonging to a pair of molecules in proximity in the solution.

The analogy between the configuration of a polymer chain and the path of a random flight has long been recognized. The configuration of a real polymer chain generally departs appreciably from the corresponding random flight, however, owing to the finite volume (i. e., the "volume effect") occupied by a chain segment. Various estimates of the factor α by which an average linear dimension of the randomly coiled molecule (e.g., its root-mean-square end-to-end distance r) exceeds that which would prevail if this volume were zero have led to discordant results. Extension of the theory of random flights seemed at first to indicate that α is an asymptotic function of the chain length, or of the molecular weight M. More recent treatments carried out in better approximation have shown on the contrary that α should increase slowly with M but without limit.

A more satisfactory solution of the problem has been obtained by considering the intramolecular interactions to be those of a cloud of chain segments distributed about the molecular center of gravity. This density distribution may be approximated by a Gaussian function. In the interests of expressing these interactions in a most general manner which is also useful in treating the intermolecular interaction problem, the chemical potential of the solvent in a volume element in which the volume fraction of polymer chain segments is v_2 may be written

$$[\mu_1-\mu_1^\circ]=RT(\kappa_1-\psi_1)v_2^2=-RT\psi_1(1-\Theta/T)v_2^2$$

where ψ_1 and κ_1 are entropy and heat of dilution parameters and $\Theta=\kappa_1 T/\psi_1$. Higher terms in the concentration are unnecessary and lower terms are absent since the segments are not independent of one another. By considering the molecule as a small thermodynamic system, the average linear dilatation α may be shown to be given by

$$\alpha^5-\alpha^3=2C_M\psi_1(1-\Theta/T)M^{1/2}$$

where C_M is a constant characteristic of the polymer chain type and M is the molecular weight. Experimental observations related to the molecular size are thus satisfactorily described as a function of the chain length (M) and of the thermodynamic interactions. In a poor solvent κ_1 is potitive and the repulsion between chain segments is reduced. At the characteristic temperature Θ, corresponding to the Boyle point of a real gas, this repulsion vanishes and ideal behavior ($\alpha=1$) prevails.

Pursuant to the treatment of the intermolecular interactions in a dilute polymer solution, the potential of average force for a pair of "cloud" molecules may be calculated as a function of the distance of separation of the pair. Then, by a treatment analogous to that widely used in the treatment of imperfect gases, the following expression may be derived for the excluded volume u for the pair of molecules:

$$u=2\psi_1(1-\Theta/T)(\bar{v}^2M^2/NV_1)F(X)$$

where $\bar{v}$ is the specific volume of the polymer, V_1 is the molar volume of the solvent, N is Avogadro's number, and $F(X)$ is a function of the molecular configuration and the interaction parameters. The second virial coefficient in the osmotic expansion

$$\pi/c=(\pi/c)_0[1+\Gamma_2c+\cdots\cdots]$$

is given by

$$\Gamma_2=Nu/2M.$$

We thus achieve a formulation of the intra- and inter-molecular interaction problems in terms of the same set of parameters. Experiments bear out the expected intimate relationship between the two, and they confirm the essential validity of the approach described.

The Theory of Visco-Elastic Properties of High Polymers

J. G. Kirkwood

(The abstract is not yet received, Aug. 28)

Statistical Mechanics of Rubber Elasticity

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The statistical theories of rubber-like elasticity have been developed more or less connected with the random flight problem. If we adopt for a model of a well-vulcanized rubber-samples, an ideal network of non-interacting chains, we arrive at a Gaussian type distribution function for end to end distance of the chains. By calculating the effect of the deformation of the sample on this distribution function, we can obtain the stress-strain equation, which reproduces successfully the main features of the rubber elasticity. However, this equation only fits the experiments at small elongations and cannot reproduce the upward turning of the Gaussian theory. This is one of the important failures of the Gaussian theory, but within the limit of the small elongations, there are still several unsettled problems and misunderstandings. Amongst these, the problem of the dependence of the elastic properties of vulcanized rubbers on the degree of crosslinking, seems to be important. As it is known, there are two expressions for the elastic modulus, one is characterized by the molecular weight of a chain, whereas the other is characterized by the molecular weight of a kinetic unit of the chain, and the difference in the modulus with different magnitudes of vulcanization is, in turn, characterized by the mean extensibility of chains in the network of the rubber samples. However, if we assume the number distribution of various kinds of chains, which have different chain length, is given by a Gaussian function, and take the mean value of the expression of the latter theory for the modulus, this coincides with the modulus of the former theory. Thus from the theoretical point of view, the problem lies whether the above assumption is legitimate or not, which in turn must be proved by experiments. Very recently, Flory has made (in 1949) very interesting experiments on this point. He has observed that the magnitudes of the force of retraction were close to the prediction of his theory, but the change in the force with the degree of cross-linking was different, the force being higher than the theory for low degrees of cross-linking, while the reverse was true at high degrees. Moreover, the dependence of the tensile strength on the degree of cross-linking was not simple. On the other hand, Gee's experiment (in 1947) shows that the theoretical expression does not completely reproduce the experimental curve of the stress-strain relation even at small elongation.

Now, in addition to these points, Treloar has found (in 1948) another failure of the statistical theory, which seems very important: the deviation was not only quantitative but also qualitative. He has found that the Gaussian theories are totally inadequate to explain his experiment on the two dimensional stretching of rubber. In this case, let the stresses in the plane of a rubber sheet be t_1 and t_2 and perpendicular to the plane be t_3, and let the corresponding strains be λ_1, λ_2 and λ_3. The Gaussian theories predict that a plot of t_1 or t_2 against $\lambda_1^2-\lambda_3^2$ and $\lambda_2^2-\lambda_3^2$ respectively should yield a straight line of slope equal to the rigidity of the sample. However, Treloar's experiment shows that the theoretical relation breaks down and the points fall not on a single straight line but on a series of discrete linear arrays. In any one of these arrays the force corresponding to one stress is kept constant whereas the other is varied.

This fact together with the failure of the Gaussian theory, that it cannot explain the upward bending of the stress-strain curve (S-shape), has made the present author to develop a non-Gaussian theory of rubber-elasticity. Different from the theories which use the result of the random flight problem, let us consider the orientation distributions of segments or kinetic units referred to the axes connecting end to end of chains. The distribution function $n_1(\omega)$ of single segment is the simplest one among the distribution functions. If we use this, and consider the segments, of which orientations fall in the solid angle between ω and $\omega+d\omega$, to be indistinguishable with each other, we can develop a non-Gaussian theory with no interaction, which not only explains the failure found by Treloar but reproduces the S-shape as well. However, from the investigation of Wang-Guth (in 1952), there still remains a small discrepancy between the theoretical and experimental stress-strain curve. They consider that this may be originated from the neglection of the interactions of segments in our theories.

Unfortunately, the nature of the interaction of intra- and inter-chains are not known and that there is no theory which calculates the stress-temperature relation, especially at low temperatures where the interactions prevail with no doubt. If we adopt the simplified model in which the interaction of interchain molecules is neglected and only take account for the interaction of the neighoring two segments of the same chain, we can go a little ahead.

Let us introduce the distribution function $n_2(\omega_1,\omega_2)$ of two neighboring segments in the same chain having the orientations of ω_1 and ω_2 respectively. $n_2(\omega_1,\omega_2)$ is reduced to the distribution function $n_1(\omega_1)$ of single chain stated above by integrating the former over all the values of ω_2. Both distribution functions $n_2(\omega_1,\omega_2)$ and $n_1(\omega_1)$ must of course satisfy the normalizing conditions. The interaction of the two neighboring kinetic units is considered to be a function between the angles of these kinetic units. From the condition of the free energy minimum, we can obtain an integral equation which determines the distribution function $n_2(\omega_1,\omega_2)$. If we designate the square root of the distribution function $n_1(\omega_1)$ by $g(\omega_1)$, the latter function is shown to satisfy the integral equation of Fredholm's first kind:

$$g(\omega)=\lambda\int H(\omega_1,\omega_2)\,g(\omega_2)\,d\omega_2,$$

where λ is the eigen value and the kernel $H(\omega_1,\omega_2)$ is a symmetrical function of the orientations ω_1 and ω_2 of the kinetic units. An approximate solution of this integral equation shows that the stress temperature curve turns upward at a certain temperature which may be connected with the second order transition of the rubber samples. With respect to the stress-strain relation, the inclusion of the interaction energy of the above type does not alter the theoretical form obtained previously, but in this case the modulus is not a linear function of temperature which is zero at 0°K.

Apart from the theory of rubber elasticity, some remarks will be given on the relation to the elasticity of fiberous protein such as keratine.

Statistical Theory of Chain Polymers

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In 1951 the author and M. Yamamoto developed the statistical mechanical theory of a long chain molecule, especially concerning the volume interferences between chain elements7, 8, 9, 10). Two different approaches were made to this problem and led to the same expression of mean square end-to-end distance proportional to $N^{3/2}$, where N is total number of chain elements. Although the similar results have recently been obtained also by R. J. Rubin16), F. Bueche19), T. B. Grimley18) and N. Saito20), there have not yet been any reliable experimental foundation, so it seems worth while again to try to summarize and partially extend our considerations. Thus here we shall give an outline of early developed methods and next some considerations about the classification of chain-like problems in parallel with the discussion of various investigations carried out by many authors, and lastly several data of an artificial experiment of square lattice chains will be presented.

Model used here is a " pearl necklace model " composed of N beads. These beads with diameter b are chained one after the other with a constant bond length a, and are attached numbers 0, 1, 2, . . ., N from one end to the other. The first method7, 8, 11) is based on the formal expansion of its partition which is derived in the same manner as that of imperfect gas theory, namely in the form

$$\Omega(R, N, T)=\sum_{\mu=0}^{N} B_{\mu}(T, R), \tag{1}$$

where first several terms are given explicitly by

$$\begin{aligned}
B_0(T, R)&=\Omega_0(R, N)\\
B_1(T, R)&=\sum_{(N(ij))}\iint f_{ij}\Omega_2(R, (i), (j))d(i)d(j)\\
&=\sum_{(N(ij))}\iint f_{ij}\Omega_0(r_{0i}, i)\Omega_0(r_{ij}, j-i)\Omega_0(r_{jN}, N-j)d(i)d(j)\\
B_2(T, R)&=\sum_{(N(ijk))}\iiint (f_{ij}f_{jk}+f_{ik}f_{ki}+f_{ki}f_{ij}+f_{ij}f_{jk}f_{ki}) \qquad (2)\\
&\quad\times\Omega_0(r_{0i}, i)\Omega_0(r_{ij}, j-i)\Omega_0(r_{jk}, k-j)\Omega_0(r_{kN}, N-k)d(i)d(j)d(k)\\
&\quad+\sum_{(N(ijkl))}\iiiint (f_{ij}f_{kl}+f_{ik}f_{jl}+f_{il}f_{jk})\Omega_0(r_{0i}, i)\Omega_0(r_{ij}, j-i)\Omega_0(r_{jk}, k-j)\\
&\quad\times\Omega_0(r_{kl}, l-k)\Omega_0(r_{lN}, N-l)d(i)d(j)d(k)d(l)\,.\\
f_{ij}&=e^{-\phi(r_{ij})/kT}-1
\end{aligned}$$

Function $\Omega_0(r, n)$ is the partition function of an ideal random flight chain and is sufficiently approximated by Gaussian distribution function

$$\Omega_0(r, n)=(4\pi a^2)^n(2\pi na^2/3)^{-3/2}\exp(-3r^2/2na^2), \tag{3}$$

for large value of n. Using these expressions, the mean square end-to-end distance is evaluated and becomes

$$\begin{aligned}
<R^2>&=\int R^4\,\Omega(R, N)dR\Big/\int R^2\Omega(R)dR\\
&=Na^2\left[1+\frac{4}{3}\sqrt{\frac{6}{\pi}}\sqrt{N}\left(\frac{b}{a}\right)^3+0\left(\left(\frac{b}{a}\right)^4\right)\right]
\end{aligned} \tag{4}$$

neglecting the higher terms than $\left(\frac{b}{a}\right)^4$.

Another method9, 10) is more intuitive and simple, namely each order overlaps between beads are excluded separately and successively, using an assumption " superposition of corrections." Here order of overlaps is defined in such a way that for an overlap of any bead i and $i+s$ or $i-s$, we give order s. After such successive calculations, it follows that

$$\begin{aligned}
<R^2>&=Na^2\prod_{l=1}^{N}\left[1+\sqrt{\frac{6}{\pi}}\frac{1}{\sqrt{l+1}}\left(1-\frac{l}{N}\right)\left(\frac{b}{a}\right)^3\right]\\
&=Na^2\left[1+\frac{4}{3}\sqrt{\frac{6}{\pi}}\sqrt{N}\left(\frac{b}{a}\right)^3\right]
\end{aligned} \tag{5}$$

This result is just the same with that obtained previously. According to this result, the correction term due to the volume interference is proportional to $N^{1/2}$ and does not converge as the number of beads tend to infinite, consequently it would seem that the expansion form developed in this article is not so profitable as that of imperfect gas theory, and it is desirable to devise the new method to study this problem in more closed form.

It seems that various chain-like problems can be classified into three types, and these three types of problems must be distinguished from each other from the mathematical point of view. We shall illustrate these types in the following.

(1) Random Flight Type (Markoff Chain) This first class involves such problems, as random walk problem, diffusion problem and statistical mechanical problem of a chain molecule with zero volume or with the interactions of finite order. A common characteristic of this type is that mathematically they can be exactly reduced to the problem of Markoff chain, so that their solutions can be obtained by solving the diffusion equation, Fokker-Planck equation or eigen value problem as developed by R. Kubo1) concerning the linear polymer and by E. Montroll3) for lattice chains. Thus for the chain system of this class, the mean square end-to-end distance proportional to N will be obtained by the central limit theorem of regular Markoff chain in a sense of Frechet.

(2) Production Type As a representative problem of second class, there is a quasi random walk problem in which a new addition of a jump is decided dependently on the whole way already passed. In other words, in the first type the present event depends upon the history of only near past, but in the second type depends upon the history of the whole past from the beginning. And strictly speaking, these problems of second type are not Markoff chain but they can be treated approximatly as Markoff chain as developed by J. J. Hermans, M. S. Klamkin, R. Rubin14) and H. Hadwiger5), concerning the excluded volume effect of chain molecules. If one applies the calculation of this second type to the pearl necklace

model, one will obtain an answer to the question: if one attaches the beads successively one after the other with a constant bond length, then after the attachment of all N beads have finished, what probability distribution of end point does result? And they do not reply to the probability distribution of the shape of chain molecule in solutions. Accordingly the calculation adopted by these authors seems to be inappropriate to study the excluded volume effect of real polymer chain, and in order to study the feature of a chain molecule in solutions one must adopt the third type of chain like problem.

(3) Real Chain Type In the first and second type a word "chain" is used to represent the phenomena emphasizing its successive occurrence, or to represent the systems which can be reduced mathematically to this chain like phenomena. On the other hand, statistical thermodynamical problems of a real chain molecule with the complete interaction (or complete volume interference) can not be reduced to chain like phenomena or Markoff chain in closed form, so one must calculate its partition function or the distribution function of the whole system as exactly as possible, for which several attempts were made in this article and also by R. J. Rubin[16], T. B. Grimley[18], F. Bueche[19], and N. Saito[20], and led to the similar expressions of end-to-end distance proportional to $N^{3/2}$. Lastly we shall give one of data of an artificial experiment in Fig. 1 in which it will be seen that $<R^2>/N$ calculated with the probability of second type, curve 2, is always smaller than that of third type, curve 1, and curve 2 has little tendency to converge to a saturated value.

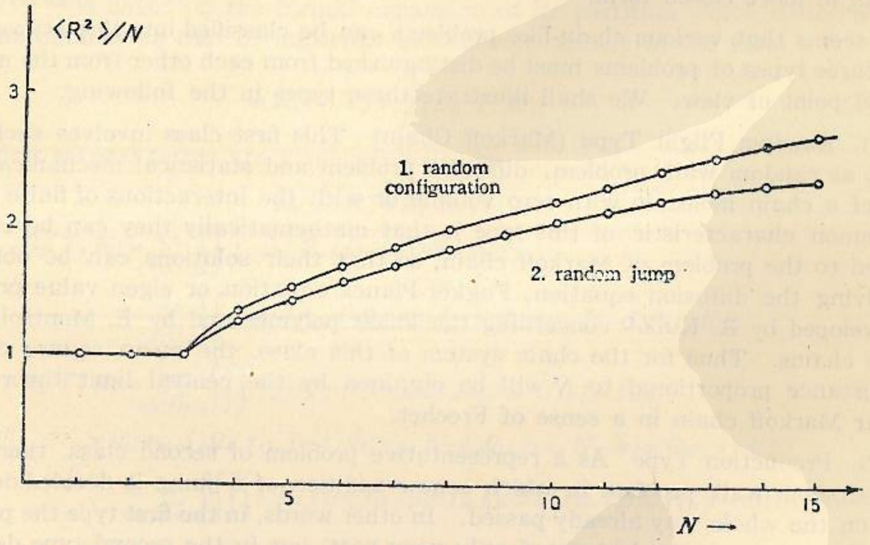

Fig. 1. Mean square end-to-end distance of two dimensional square chain

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Theory of Liquids

J. E. MAYER

(The abstract will be found on page 41)

The Statistical Mechanical Theory of the Liquid State

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The statistical mechanical theory of liquids and liquid solutions provides relations between the thermodynamic functions of the system and the potential of intermolecular force, which involve distribution functions for sets of n molecules, for example singlets, pairs, triplets, which form subsets of the total number of molecules of which the system is composed. The distribution function $\rho^{(n)}$ is defined as the average density of ordered sets n in the n-dimensional sub-configuration space of such sets. If the potential of intermolecular force has the form

$$V_N=\sum_{i<j} V(R_{ij}, \xi_i\xi_j) \tag{1}$$

and the potential $V(R_{ij}, \xi_i, \xi_j)$ of the force between the molecular pair ij is assumed to be a symmetric function of two parameters ξ_i and ξ_j, the theories of Kirkwood¹⁾, Born-Green²⁾, and Yvon³⁾, as generalized by Mayer⁴⁾ lead to the following set of integro-differential equations for the densities $\rho^{(n)}$.

$$\frac{\partial\rho^{(n)}}{\partial\xi_i}=-\beta\left(\sum_{k=1}^{n}\frac{\partial V_{ik}}{\partial\xi_i}\right)\rho^{(n)}-\beta\sum_{j=n+1}^{N}\int\frac{\partial V_{ij}}{\partial\xi_i}\rho^{(n+1)}(1\ldots n, j)dv_j \tag{2}$$

$$\beta=1/kT$$

For systems possessing the potential of intermolecular force, Eq. (1), the pair density $\rho^{(2)}$ and the associated radial distribution function $g(R)$, defined by the relation,

$$\rho^{(2)}(R)=\left(\frac{N}{v}\right)^2 g(R) \tag{3}$$

are of special importance. The equation of state and the internal energy of the system are related to the potential of intermolecular force and the radial distribution function in the following manner,

$$\frac{pv}{NkT}=1-\frac{2\pi N}{3vkT}\int_0^\infty R^3\frac{dV}{dR}g(R)dR$$

$$E/NkT=\frac{3}{2}+\frac{2\pi N}{vkT}\int_0^\infty R^2V(R)g(R)dR \tag{4}$$

where p is the pressure, v the molal volume, N is Avogadro's number, k Boltzmann's constant and T the thermodynamic temperature.

When the system of integro-differential equations (2) is closed by the superposition approximation in the space of molecular triplets, the radial distribution function is found to satisfy the following integral equation,

$$\log g(R)=-\beta V(R)+\frac{\pi N}{vR}\int_0^\infty\{K(R-r)-K(R+r)\}r[g(r)-1]dr$$

$$K(t)=-2\beta\int_0^1\int_{|t|}^\infty sV(s)g(s, \xi)ds\, d\xi\text{ ; } K \tag{5}$$

$$K(t)=\beta\int_{|t|}^\infty(s^2-t^2)\frac{dV}{ds}g(s)ds\text{ ; } BGY.$$

where the first form of the kernel corresponds to the Kirkwood formulation and the second form to the Born-Green-Yvon formulation.

The integral equation, Eq. (5), for the radial distribution function has been solved numerically with the use of I.B.M. equipment for fluids possessing the Lennard-Jones potential of intermolecular force. With the use of the radial distribution functions so obtained, the equation of state and the thermodynamic functions of the Lennard-Jones fluid have been calculated and tabulated. Moderately good agreement with experiment is obtained when the theory is applied to the noble gases.

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Statistical Mechanics of Surface Tension

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In this report a brief review of the development of the theory of surface tension of pure liquids in Japan will be given and then a simplified method of deriving the expression for surface tension, together with some detailed discussions of the assumption of mathematical surface of density discontinuity will be given.

Historical Review: In 1940 we attempted to find an expression for the surface energy of a liquid in which molecules interact with each other with a potential of the form

$$\phi=\phi_0\{(r_0/r)^{12}-2(r_0/r)^6\}. \tag{1}$$

Assuming a quasicrystalline structure we obtained the following expression for the surface energy U.

$$U=2\phi_0/a^2\{3.0(r_0/a)^6-1.08(r_0/a^{12})\},$$

where a is the distance between nearest neighbor molecules. Further, for the relation between the surface energy and the heat of vaporization Q, we obtained

$$(Q+1/2\cdot RT)/UV^{2/3}=2.3\times10^8,$$

$$Q\text{ in ergs/mol, }U\text{ in ergs/cm}^2\text{, }V\text{ in cm}^3\text{/mol.} \tag{2}$$

This relation could be considered as a version of Stefan's law.

The theory of surface tension was later attacked by Ono in 1947 on the basis of the lattice theory. He determined the ratio of the number of the holes to that of the molecules on each layer parallel to the interface by the condition of minimization of the free energy and obtained results in good agreement with observed values.

A Simplified Method: In 1949 Kirkwood and Buff developed a general theory of surface tension by calculating the stress transmitted across a strip of unit width, normal to a Gibbs dividing surface. Attempts to obtain surface tension as Helmholtz's free energy per unit area were made by MacLellan and Harasima. The procedure followed by the latter will be given here.

Let us consider a system of N molecules enclosed in a cubic vessel of edge length a and let the system consist of a liquid film which is stretched parallel to the $x-y$ plane, the other parts (above and under the film) of the vessel being filled with the vapor of the liquid. The free energy F is given by

$$\exp(-F/kT)=\frac{1}{N!}(2\pi mkT/h^2)^{3N/2}\iint\cdots\int\exp(-\Phi/kT)\prod_{i=1}^{N}d\boldsymbol{r}_i\,, \qquad (3)$$

where $\boldsymbol{r}_i$ is the position vector of the i-th molecule and Φ is the potential energy of the system which we assume to be of the form $\Phi=\sum_{i>j}\phi_{ij}$.

Now we shift one of the planes, perpendicular to the x-axis, outward by a length $a\varepsilon$, and simultaneously shift one, perpendicular to the z-axis, inward by a length $a\varepsilon$, this being conducted under isothermal conditions. By a procedure similar to that adopted by Born and Green in deriving the equation of state, we can calculate the increase in free energy per unit area,

$$\gamma=\frac{1}{2}\iiiint\frac{d\phi_{12}}{dR_{12}}(x_{12}{}^2-z_{12}{}^2)/R_{12}\cdot\rho^{(2)}(z_1,\boldsymbol{R}_{12})dz_1\,dv_{12}. \qquad (4)$$

This expression can be transformed into the following form:

$$\gamma=\int(p_N-p_T)dz_1\,,$$

where,

$$\left.\begin{aligned}p_N(z_1)&=kT\rho^{(1)}(z_1)-\frac{1}{2}\iiint dv_{12}\int_{z_1-z_{12}}^{z_1}\frac{d\phi_{12}}{dR_{12}}\frac{z_{12}}{R_{12}}\rho^{(2)}(\zeta,\boldsymbol{R}_{12})d\zeta\\ p_T(z_1)&=kT\rho^{(1)}(z_1)-\frac{1}{2}\iiint dv_{12}\frac{d\phi_{12}}{dR_{12}}\frac{x_{12}{}^2}{R_{12}}\rho^{(2)}(z_1,\boldsymbol{R}_{12})\end{aligned}\right\} \qquad (6)$$

The result coincides with that of Kirkwood and Buff which was derived by calculating the stresses. It made the calculations much simpler that we considered a thin film of liquid instead of assuming the liquid to occupy the lower part of the vessel as done by MacLellan.

Assumption of Mathematical Surface of Density Discontinuity: The pressure P_N must be independent of z_1, and this can easily be justified by the well-known integral equation

$$kT\frac{d\rho^{(1)}(z_1)}{dz_1}=\iiint dv_{12}\frac{d\phi_{12}}{dR_{12}}\frac{z_{12}}{R_{12}}\rho^{(2)}(z_1,\boldsymbol{R}_{12}). \qquad (7)$$

Now, the liquid-vapor interface is often assumed to be a mathematical surface of density discontinuity. In that case, as was derived by Fowler, we have

$$\gamma=\frac{\pi}{8}\int_0^\infty R^4\frac{d\phi}{dR}\rho^{(2)}(R)dR\,. \qquad (8)$$

But if we calculate P_N and P_T, we obtain on this supposition

$$\begin{aligned}p_N=p_0+\frac{2\pi}{3}p_\alpha{}^{(1)2}\int_{-z_1}^\infty R^3\frac{d\phi}{dR}g(R)dR&\\ -\frac{\pi}{3}\rho_\alpha{}^{(1)2}z_1{}^3\int_{-z_1}^\infty\frac{d\phi}{dR}g(R)\,dR+\pi z_1\rho_\alpha{}^{(1)2}\int_{-\infty}^\infty R_2\frac{d\phi}{dR}g(R)dR,&\end{aligned} \qquad (9)$$

$$\begin{aligned}p_T=p_0+\frac{\pi}{3}p_\alpha{}^{(1)2}\int_{-z_1}^\infty R^3\frac{d\phi}{dR}g(R)dR&\\ -\frac{\pi}{6}\rho_\alpha^{(1)2}z_1{}^3\int_{-z_1}^\infty\frac{d\phi}{dR}g(R)dR+\frac{\pi}{2}z_1\rho_\alpha^{(1)2}\int_{-z_1}^\infty R^2\frac{d\phi}{dR}g(R)dR\,.&\end{aligned} \qquad (10)$$

Calculated values of P_N and P_T for liquid argon will be shown by a figure. P_N-P_0 is 200 atm. at $z_1=0$, and attains its maximum value 660 atm. at $z_1=-0.7\mathring{A}$

Quantum Theory of Transport Processes

J. de Boer

(The abstract will be found on page 45)

Quantum-Statistical Theory of Transport Phenomena

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About twenty years ago Uehling and Uhlenbeck established the fundamental equation for quantum theory of transport in gases, by physical argument which would seem to be plausible. In spite of rather obscure points left in the derivation given by Uehling and Uhlenbeck, the subsequent theories on transport in quantum fluids have been based on this equation.

On the other hand, several years ago, Kirkwood succeeded in analytical derivation of the classical Boltzmann equation from the Liouville equation, by using the time-averaging procedure and the postulate of molecular chaos at the initial time. And Mori and I derived analytically the Uehling-Uhlenbeck equation from the Irving-Zwanzig equation in the similar manner. This method is essentially based on the time-averaging procedure and the postulate of random a priori phases, which would correspond to the postulate of molecular chaos in Kirkwood's theory. But their derivation of the fundamental equation is not completely rigorous, because the assumption of random a priori phases destroys the dependence of the inital distribution on coordinates.

In order to avoid the above-mentioned difficulties it seems to be necessary to use an orthonormal set other than the set of plane waves. And, then, the Wigner distribution function becomes inadequate in such cases. To obtain suitable description for systems in which the density distribution is not uniform we shall generalize the Wigner distribution function by means of the quantized density matrix and the integral transformation which is not the Fourier transformation. Such generalized phase-space distribution function was used by Mori in analytical derivation of the Bloch equation in the theory of metallic conductivity from the quantum mechanical Liouville equation.

Let us consider a system composed of N identical Bose or Fermi particles. Let $\boldsymbol{x}_i$ be the coordinates of the i-th particle and q^N be the set of the coodinates of all particles of the system. A complete orthonormal set of symmetrized or anti-symmetrized functions of the set of the coordinates of N particles is given by

$$\Psi^{(\pm)}_{n_1,n_2,\cdots}(q^N)=\det{}^{(\pm)}[\psi_{t_1}(\boldsymbol{x}_1)\cdots\psi_{t_N}(\boldsymbol{x}_N)], \tag{1}$$

where $\Psi_t(\boldsymbol{x})$ is a function belonging to a complete orthonormal set of single-particle functions, and n_t is the number of particles in the state represented by $\Psi_t(\boldsymbol{x})$. If we introduce annihilation operator a_t and creation operator $a_t{}^*$, both acting upon $\Psi^{(\pm)}_{n_1,n_2,\cdots}(q^N)$, the quantized wave function of the system may be written as

$$\psi(\boldsymbol{x})=\sum_t a_t\,\psi_t(\boldsymbol{x}). \tag{2}$$

According to Husimi and Nisiyama's method the reduced density matrix in the x-representation for $n(<N)$ particles is given by

$$\rho^{(n)}(\boldsymbol{x}_1,\cdots,\boldsymbol{x}_n;\boldsymbol{x}_1',\cdots\boldsymbol{x}'_n)=\mathrm{trace}\,[\psi^*(\boldsymbol{x}_1')\cdots\psi^*(\boldsymbol{x}_n')\psi(\boldsymbol{x}_1)\cdots\psi(\boldsymbol{x}_n)\rho], \tag{3}$$

ρ being the density operator of the system. And we shall define the following function:

$$\begin{aligned} &g^{(n)}(\boldsymbol{x}_1,\cdots,\boldsymbol{x}_n\,.\,k_1,\cdots,k_n;t)\\ &=\int\overset{(n)}{\cdots}\int\varphi_{k1}{}^*\Big(\boldsymbol{x}_1-\frac{\boldsymbol{y}_1}{2}\Big)\cdots\varphi_{kn}{}^*\Big(\boldsymbol{x}_n-\frac{\boldsymbol{y}_n}{2}\Big)\rho^{(n)}\Big(\boldsymbol{x}_1-\frac{\boldsymbol{y}_1}{2},\cdots,\boldsymbol{x}_n-\frac{\boldsymbol{y}_n}{2};\boldsymbol{x}_1+\frac{\boldsymbol{y}_1}{2},\cdots,\boldsymbol{x}_n+\frac{\boldsymbol{y}_n}{2};t\Big)\\ &\qquad\times\varphi_{k1}\Big(\boldsymbol{x}_1+\frac{\boldsymbol{y}_1}{2}\Big)\cdots\varphi_{kn}\Big(\boldsymbol{x}_n+\frac{\boldsymbol{y}_n}{2}\Big)d\boldsymbol{y}_1\cdots d\boldsymbol{y}_n\,. \end{aligned} \tag{4}$$

Then, we have immediately the relations,

$$\sum_{k_1}\sum_{k_2}\cdots\int g^{(n)}(\boldsymbol{x}_1,\cdots,\boldsymbol{x}_n;k_1,\cdots,k_n;t)=\rho^{(n)}(\boldsymbol{x}_1,\cdots,\boldsymbol{x}_n;\boldsymbol{x}_1,\cdots,\boldsymbol{x}_n;t) \tag{5}$$

and

$$\int\cdots\int d\boldsymbol{x}_1\cdots d\boldsymbol{x}_n g^{(n)}(\boldsymbol{x}_1,\cdots,\boldsymbol{x}_n;k_1,\cdots,k_n;t)=n_{k1}n_{k2}\cdots n_{kn}\,. \tag{6}$$

And, therefore, we may regard $g^{(n)}(\boldsymbol{x}_1,\cdots,\boldsymbol{x}_n;k_1\cdots,k_n;t)$ defined by (4) as a generalization of the phase-space distribution function.

If we choose the plane waves, $h^{-3/2}exp(-\boldsymbol{p}\cdot\boldsymbol{x}/i\hbar)$, as the complete orthonormal set, (4) becomes

$$\begin{aligned} &g^{(n)}(\boldsymbol{x}_1,\cdots,\boldsymbol{x}_n;\boldsymbol{p}_1,\cdots\boldsymbol{p}_n;t)\\ &=h^{-3n}\int\overset{(n)}{\cdots}\int e^{-\boldsymbol{p}\cdot\boldsymbol{y}/i\hbar}\rho^{(n)}\Big(\boldsymbol{x}_1-\frac{\boldsymbol{y}_1}{2},\cdots,\boldsymbol{x}_n-\frac{\boldsymbol{y}_n}{2};\boldsymbol{x}_1+\frac{\boldsymbol{y}_1}{2},\cdots,\boldsymbol{x}_n+\frac{\boldsymbol{y}_n}{2};t\Big) \end{aligned} \tag{7}$$

where $\boldsymbol{p}\cdot\boldsymbol{y}=\sum_i \boldsymbol{p}_i\boldsymbol{y}_i$. This function is identical with the Wigner distribution function apart from the normalization factor.

From the Schrödinger equation for the quantized wave function, we obtain the equation of motion for the generalized phase-space distribution function of a single particle. This equation serves the present theory as the fundamental equation, and agrees with the Irving-Zwanzig equation if we adopt the plane waves as the orthonormal functions. In order to take into account non-uniformity of the phase-space distribution function with respect to the coordinates, we divide the space into a number of cells. And we shall denote coordinate vectors of the center of cubes by $\boldsymbol{X}$, whose components assume integral multiples of a, a^3 being the cell volume.

Then, one may define the characteristic function such that

$$E(\boldsymbol{X},\boldsymbol{x})=\begin{cases}1, & \text{if } \boldsymbol{x} \text{ belongs to the interior points of the cell whose}\\ & \text{center is } \boldsymbol{X}.\\ 0, & \text{otherwise}\end{cases}$$

Then we can employ the complete orthonormal set of the following functions:

$$\varphi(\boldsymbol{X},\boldsymbol{P};\boldsymbol{x})=a^{-3/2}e^{-\frac{\boldsymbol{X}\boldsymbol{P}}{i\hbar}}E(\boldsymbol{X},\boldsymbol{x}), \tag{8}$$

where

$$\boldsymbol{P}=h\boldsymbol{k}/a \tag{9}$$

$\boldsymbol{k}$ being a set of positive or negative integers or zero.

To this case we cannot apply the ordinary method of perturbation theory, because φ given by (8) is not eigenfunction of any unperturbed Hamiltonian. But we may develop the theory in the same way as in the time-dependent perturbation theory. As a result it is concluded that the Uehling-Uhlenbeck equation may be derived from the generalized Liouville equation in equation in quantum mechanics in the case where the cell length, a, is sufficiently large as compared with the range of intermolecular forces. And, furthermore, the variation of the distrbution function in the momentum space is assumed to be not so rapid as in condensed Bose-Einstein gas in this derivation.

Finally, the transport equation in phonon gases is derived by the same method. Let us denote the coordinate and the momentum of the oscillator corresponding to a normal mode of vibration k, j by $x_{k,j}$ and $p_{k,j}$, respectively. Then these variables are assumed to satisfy the following quantum conditions:

$$x_{kj}p_{k'j'}-p_{k'j'}x_{kj}=i\hbar\delta_{kk'}\delta_{jj'}, \tag{10}$$

where j indicates the direction of the polarization.

Introducing the operators a_{kj} and $a_{kj}{}^*$ defined as

$$\left.\begin{aligned} x_{kj}&=\sqrt{\frac{\hbar}{2Ma_{kj}}}(a_{kj}+a_{kj}{}^*)\\ p_{kj}&=\sqrt{\frac{\hbar M\omega_{kj}}{2}}(a_{kj}{}^*-a_{kj}), \end{aligned}\right\} \tag{11}$$

we may define a function $\psi_j(X)$ by

$$\psi_j(X)=G^{-3/2}\sum_k a_{kj}\,e^{-\frac{2\pi kX}{iGa}} \tag{12}$$

where Ga is the period concerning the Born-v. Kármán periodicity condition and X indicate the coordinates of a lattice point.

If we regard (12) as a quantized wave function in the ordinary gas, the reduced density matrix of an assembly of phonons is obtained, where the density matrix in the N-respresentation may correspond to the density matrix represented by the set of quantum numbers of normal oscillators. Thus using (4) to define the phase-space distribution function of phonon, we obtain the fundamental equation for the kinetic theory of phonon gases.

Statistical Mechanics of Irreversible Phenomena

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Some contributions recently made in this country to the statistical mechanical theory of irreversible processes are reviewed.

Suppose an isolated dynamical system with a large number of degrees of freedom, of which the representative point in the phase space is denoted by $X=\{X_i\}$, $i=1\ldots\ldots N$. Its classical motion is given by Liouville's equation:

$$\frac{\partial F(X,t)}{\partial t}=-\sum_{r=1}^{N}\frac{\partial}{\partial X_r}\{U_r(X)F(X,t)\}, \tag{1}$$

$$U_r(X)=dX_r/dt, \tag{2}$$

where $F(X,\ t)$ is the distribution function of a Gibbsian ensemble.

Now let us follow the motion of this ensemble through measurement with less than the greatest admissible accuracy (Yamamoto, 1952, 1953). That is, we arbitrarily choose a set of independent phase functions $A_1(X)\ldots\ldots A_h(X)$, $h<N$, whose values $\{a_i\}$ are now adopted as independent variables to specify the state of our system and to describe its motion. We denote by $\sum_a$ the $(N-h)$-manifold $A_i(X)=a_i$ and by $d\sum$ the element of $(N-h)$-measure within the manifold. We can find the distribution function $f(a,t)$ of our ensemble in a-sace from that in the phase space:

$$f(a,t)=\Omega(a)<F(X,t)>_{a'} \tag{3}$$

$$<F(X,t)>_a=\frac{1}{\Omega(a)}\int_{\Sigma_a}F(X,t)\frac{d\Sigma}{|\nabla A|}, \tag{4}$$

where $\Omega(a)$ is the limit of the volume of a thin shell $a_i<A_i(X)<a_i+da_i$ divided by da, and $d\sum/|\nabla A|$ is the N-measure within $\sum_a$ (Grad, 1952; Ono, 1953a).

In order to find the secular motion of $f(a,t)$ we introduce the "macroscopic time derivative" $\partial^*/\partial t$:

$$\frac{\partial^* f(a,t)}{\partial t}=\frac{1}{\tau}\{f(a,t+\tau)-f(a,t)\}, \tag{5}$$

where τ is a macroscopically small but microscopically large time interval. Using (1), (2) and (3) in (5), one obtains

$$\frac{\partial^* f(a,t)}{\partial t}=\sum_{k=1}^{h}\frac{\partial}{\partial a_k}\Big[-\Big\{<V_k>_a+\frac{1}{\Omega(a)}\sum_l\frac{\partial}{\partial a_l}[\xi_{kl}(a,\tau)\Omega(a)]\Big\}f(a,t)$$
$$+\sum_l\frac{\partial}{\partial a_l}\{\xi_{kl}(a,\tau)\,f(a,t)\}\Big] \tag{6}$$

where

$$V_k(X)=dA_k(X)/dt, \tag{7}$$

$$\xi_{kl}(a,\tau)=\frac{1}{\tau}\int_0^{\tau}ds\int_0^{s}ds'<V_k(X)V_l(X_{-s'})>_a, \tag{8}$$

and $<\ldots\ldots>_a$ denotes the phase average over $\sum_a$. In the above derivation the following conditions are necessary:

(A) The fluctuation of $A(X)$ is very small.

(B) $\bar{F}(X,t)\equiv\frac{1}{\tau}\int_0^{\tau}ds\,F(X,t+s)$ can be approximated by
$F'(X,t)\equiv f(A(X),t)/\Omega(A(X))$.

In addition, if the following condition is also satisfied:

(C) $\xi_{kl}(a,\tau)$ has a plateau value $\xi_{kl}(a)$ independent of τ,

then (5) becomes the Fokker-Planck equation already obtained by M.S. Green (1952):

$$\frac{\partial^* f(a,t)}{\partial t}=\sum_k\frac{\partial}{\partial a_k}\Big[-\Big\{<V_k>_a+\frac{1}{\Omega(a)}\sum_l\frac{\partial}{\partial a_l}[\xi_{kl}(a)\Omega(a)]\Big\}f(a,t)$$
$$+\sum_l\frac{\partial}{\partial a_l}\{\bar{\xi}_{kl}(a)f(a,t)\}\Big], \tag{9}$$

$$\bar{\xi}_{kl}=\frac{1}{2}\{\xi_{kl}(a)+\xi_{lk}(a)\} \tag{10}$$

If one remembers the fact that the usual method of measurement for large systems is gross, it is reasonable to postulate that the observed value of $A_l(X)$ is given by the time average:

$$\bar{A}_l(X)=\frac{1}{\tau}\int_0^{\tau}ds\,A_l(X_s). \tag{11}$$

On the basis of this postulate one can justify the condition (A)—in this case $A_l(X)$'s are shown to be approximately one-valued integrals of motion in M.S. Green's sense (1952) and may be called gross variables—and the idea of "macroscopic time derivative" can naturally be introduced. Furthermore the condition (B) is reduced to a "generalized ergodic theorem" which, the author believes, will substantially be equivalent to the condition (C).

For the purpose of deriving Green's equation (9) the postulate (11) may not always be necessary. S. Ono (1953a) has really shown that, if one choose as $A(X)$'s the coordinates and momenta of a molecule—they cannot be considered as gross variables—as well as the total energy and the total momentum of the whole system, Eisenschits' Fokker-Planck equation (1951, 1952) can straightforwardly be obtained.

In the above formulation we have succeeded to derive from the deterministic law of mechanics the stochastic law which describes the secular motion of large system. It is however not yet clear how and when the deterministic law turns stochastic. To this point H. Mori (1953a, b) has made a remarkable contribution. From (3) and Liouville's theorem he has found a formal expression for the transition probability $T(a,t\,;a',t')$ in a-space:

$$f(a',t')=\int_{\Sigma_{a'}}F(X,t')\frac{d\Sigma}{|\nabla A|}=\int da\int_{\Sigma_a}\delta(A(X)-a')F(X,t')\frac{d\Sigma}{|\nabla A|}$$
$$=\int da\, f(a,t)T(a,t\,;a',t'), \tag{12}$$

where

$$T(a,t\,;a',t')=\Omega(a)<\delta(A(X_{t'-t})-a')W(X/A(X)\,;t)>_a, \tag{13}$$

and

$$W(X/A(X)\,;t)=F(X,t)/f(A(X),t) \tag{14}$$

is the conditional probability finding the system in the phase X when $A(X)=a$. As is easily verified, $T(a,t\,;a',t')$ given by (13) has all the properties necessary for transition probability, in particular the Smoluchowski equation holds without any approximation:

$$T(a,t\,;a',t')=\int da''T(a,t\,;a'',t'')T(a'',t''\,;a',t'), \tag{15}$$

Thus the projected motion of our system into a-space is clearly seen to be a continuous stochastic process. This noticeable fact is due solely to the law of mechanics that the natural motion in the phase space is generated by a one-parameter linear group of unitary transformation.

Now from the definition (13) the condition for the motion to become Markoffian is obvious: when and only when the conditional probability $W(X/A(X)\,;t)$ is independent of t, the motion of $f(a,t)$ becomes Markoffian. In order to study an interesting example of such cases Mori has approximated W by its equilibrium value $1/\Omega(a)$. Then the Kolmogoroff equation corresponding to (15) is given by

$$\frac{\partial^* T(a_0,t_0\,;a,t)}{\partial t}=\sum_k\frac{\partial}{\partial a_k}\Big[-\Big\{<\dot{V}_k>_a+\frac{1}{\Omega(a)}\sum_l\frac{\partial}{\partial a_l}[\xi_{kl}(a)\Omega(a)]\Big\}T(a_0,t_0\,;a,t)$$
$$+\sum_l\frac{\partial}{\partial a_l}\{\xi_{kl}(a)T(a_0,t_0\,;a,t)\}\Big], \tag{16}$$

provided that one assumes, as before, the conditions (A) and (C), but not (B) which is now replaced by the steadiness of the conditional probability. Using the same approximation in (12) the secular motion of $f(a,t)$ can also be found in an analogous way, the result being seen to agree with (9).

However Mori's approximation does not only hold in equilibrium, but also in more general states—local equilibrium. Furthermore it can be reinterpreted as assuming an equal *a priori* probability in every $\sum_a$. Utilizing this fact S. Ono (1953b) has elegantly reformulated Mori's theory. Under the above assumption it is no longer necessary to follow the motion of $F(X,t)$ itself, but that of the "coarse-grained distribution function" $F'(X,t)$. The results given by Ono are as follows:

$$F'(X',t')=\int dXF'(X,t)S(X,t\,;X',t'), \tag{17}$$

where

$$S(X,t\,;X',t')=\Big[\frac{1}{\Omega(a')}<\delta(a'-A(X_{t'-t})>_a\Big]_{a=A(X),\ a'=A(X')} \tag{18}$$

is the "coarse-grained transition probability" in H. B. Callen's sense (1947). If one transforms the both sides of (17) into a-space by making use of (3), Mori's results again occur, at it should be. Thus one sees the Markoffian character is due to the coarse-graining procedure successively operated on $F(X,t)$ in each $\sum_a$. In the course of deriving (8), as was already stated, $\overline{F}(X,t)$, not $F(X,t)$ itself, must be approximated by $F'(X,t)$. This may be supposed as an alternative statement for Ono's assumption of equal *a priori* probability.

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Some Recent Applications of Thermodynamics of Irreversible Processes

I. PRIGOGINE

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Statistical and Formal Theories of Thermal Fluctuations

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The purpose of this paper is to obtain as general a formula as possible for the thermal fluctuation that is subject to experimental verification, rather than to derive formal equations. Therefore we shall purposely avoid the use of such restrictive assumptions as Markoff processes, and hence the Fokker-Planck equations. This is made possible by the use of the method of ensemble averages, that is, we operate on the correlation function of the form $X_i(t)u(t+\tau)$, where X_i and u are two macroscopic quantities, whose fluctuations we are dealing with. This function gives us information entirely equivalent to the solution of Fokker-Planck equation, when the latter is at all valid, but the former is more general.

The result is as follows:

$$\overline{(X_i(t)-X_i)(u(t+\tau)-\bar{u})}=kT\left\{\frac{\partial\bar{u}}{\partial x_i}-\Psi_{i,u}(\tau)\right\} \tag{1}$$

where $\Psi_{i,u}(\tau)$ in the right hand side is the after-effect function defined by the linear relation of u and x_i

$$u(t)-\bar{u}=\int_{-\infty}^{t}\Psi'_{i,u}(t-t')x_i(t')dt' \tag{2}$$

where x_i is one of the external parameters for the system, to which is associated the generalized force X_i. It will also be expressed in terms of the frequency spectrum as

$$\overline{\boldsymbol{X}_i^*(\omega)\boldsymbol{u}(\omega)}d\omega=\frac{2i\omega}{\pi}kT\,\boldsymbol{f}_i(\omega)d\omega \tag{3}$$

where $\boldsymbol{u}=\sum_i\boldsymbol{f}_i\boldsymbol{x}_i$ and black letters indicate the Fourier transforms of the corresponding time functions.

If u is put equal to X_k, another generalized force, and Z_{ik} is the impedance, we obtain

$$\overline{\boldsymbol{X}_i^*(\omega)\boldsymbol{X}_k(\omega)}d\omega=\frac{1}{\pi}kT(Z_{ik}^*+Z_{ki})d\omega \tag{4}$$

which is the extension of Nyquist's formula for thermal noises, which corresponds to $i=k$.

The formula (1) or (3) will be proved in several ways. Let us begin with the most straightforward one, which is based on a direct application of Boltzmann's distribution law.

Consider a dynamical system of many degrees of freedom with the coordinates $q_1, q_2,\cdots q_N$ and momenta $p_1,\cdots p_N$, and depending also on external parameters $x_1,\cdots x_m$. Let u be any function of p's and q's and of x's, and you will find no difficulty in finding the identity

$$\overline{(u-u)(X_i-X_i)}=kT\left(\frac{\partial\bar{u}}{\partial x_i}-\overline{\frac{\partial u}{\partial x_i}}\right)$$

where the bars denote averages over a canonical ensemble. If we notice that $u(t+\tau)$ which is a function of $p(t+\tau)$ and $q(t+\tau)$ is after all a function of $p(t)$ and $q(t)$, and denote it as u^τ, we obtain

$$\overline{(u^\tau-\bar{u})(X_i-X_i)}=kT\left(\frac{\partial\bar{u}}{\partial x_i}-\overline{\frac{\partial u^\tau}{\partial x_i}}\right) \tag{5}$$

If the average over a canonical ensemble can be identified with the value really observed in experiment, equation (5) will become (1).

This proof seems to be quite satisfactory, since it is based on a widely accepted atomistic principle. Nevertheless, there are a number of limitations. First, it is a classical theory. A quantum-mechanical counterpart of the theory could be worked out if a definite expression of averages in an ensemble were given. Unfortunately, the instrument available nowadays in quantum theory seems to be insufficient for this purpose.

The second point concerns the doubt raised by Casimir as to the legitimacy of the identification of derivatives in the right hand side of (5) with the observable after-effect function, which is really concerned with an absurdly large deviations. This necessitates some further investigation. These limitations seem to justify my appending the following proofs, which are, however, of less fundamental value.

This time we shall show the transformed equation (3), assuming that the original Nyquist formula is known.

Let the equations between $\boldsymbol{x}$'s and $\boldsymbol{X}$'s be

$$\boldsymbol{x}_i=\frac{1}{i\omega}\sum Y_{ik}\boldsymbol{X}_k \tag{6}$$

neglecting fluctuation. Nyquist formula gives

$$\overline{|\boldsymbol{x}_1|^2}d\omega=\frac{2}{\pi}kTY_{11}d\omega,\qquad \overline{|\boldsymbol{x}_2|^2}d\omega=\frac{2}{\pi}kTY_{22}d\omega \tag{7}$$

for the fluctuation of $\boldsymbol{x}_1$ and $\boldsymbol{x}_2$ in the absence of external forces. Now suppose we apply a restoring force $\boldsymbol{X}_2=-c\boldsymbol{x}_2$ on the coordinate $\boldsymbol{x}_2$. The fluctuation of $\boldsymbol{x}_1$ and $\boldsymbol{x}_2$ will change due to the change in the admittances. If we mark the new values by primes, we have for $\boldsymbol{x}_1'$

$$\overline{|\boldsymbol{x}_1'|^2}d\omega=\frac{2}{\pi}kT\left(Y_{11}-\frac{Y_{12}Y_{21}}{1+cY_{22}/i\omega}\right)d\omega \tag{8}$$

Alternatively, we can suppose this change as caused by the fluctuating force on $\boldsymbol{x}_2$, and then we have

$$\overline{|\boldsymbol{x}_1'|^2}d\omega=\left|\boldsymbol{x}_1-\frac{cY_{12}/i\omega}{1-cY_{22}/i\omega}\boldsymbol{x}_2\right|^2d\omega. \tag{9}$$

Comparison of (8) with (9) will lead to (4).

This proof, being purely phenomenological, will be of unrestricted generality, as compared with the first one, without no question as to classical or quantum.

This is therefore considered as a sufficient guarantee for the correctness of (2) or (4).

The third proof is somewhat restricted in so far as it assumes a finite number of macroscopic parameters x_i satisfying the equations

$$X_i=\sum(m_{ik}\ddot{x}_k+(r_{ik}+g_{ik})\dot{x}_k+c_{ik}x_k) \tag{10}$$

Some of x's may be external parameters, and others internal ones, to which the corresponding forces X_i will be zero. The three tensors m_{ik}, r_{ik} and c_{ik} are symmetric, while the gyroscopic term g_{ik}, which is usually caused by a magnetic field, is anti-symmetric.

We assume the Nyquist formula for pure "viscosity"

$$\overline{X_i^*X_k}d\omega=\frac{2}{\pi}kTr_{ik}d\omega \tag{11}$$

and show the general formula (4). Put

$$Z_{ik}{}^0=im_{ik}\omega+g_{ik}+c_{ik}/i\omega$$

for brevity, and let the inverted form of (10) be

$$x_i=\frac{1}{i\omega}\sum_k Y_{ik}X_k$$

hence

$$\overline{x_i^*x_k}d\omega=\frac{2}{\omega^2\pi}kV\sum\sum r_{jh}Y_{ij}{}^*Y_{kh} \tag{12}$$

Then we have

$$\sum(r_{kj}+Z_{kj}{}^0)Y_{ik}=\delta_{ij}$$

from which we obtain

$$\left.\begin{aligned}&\sum\sum(r_{kj}+Z_{kj}{}^0)Y_{ik}Y_{hj}{}^*=Y_{k}{}^*\\ &\text{and its complex conjugate}\\ &\sum\sum(r_{jk}-J_{jk}{}^{0*})Y_{ik}Y_{hj}{}^*=Y_{ih}\end{aligned}\right\} \tag{13}$$

Adding these together and we have

$$\sum r_{jk}Y_{ik}Y_{hj}{}^*=\frac{1}{2}(Y_{hi}{}^*+Y_{ih}) \tag{14}$$

Putting (14) in (12), we at once obtain the dual form of (4).

Thermal Fluctuations in Linear Dissipative Systems

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The thermodynamics of irreversible processes was recently built up by Prigogine and others, using the reciprocal relations of Onsager. We can formally insert small fluctuations into this thermodynamics on the basis of a principle, which was also proposed by Onsager. The statistical theory thus obtained is found to be essentially the same as that developed by Kirkwood, Green and others. We shall give the method of Onsager in a somewhat generalized form.

1. *Thermodynamics of irreversible processes.*

Let us consider a thermodynamic system, each macroscopic state of which is specified by a set of varirbles $\alpha=(\alpha_1,\cdots\cdots,\alpha_N)$ and has an entropy $S(\alpha)$. Then the rate of entropy production will be given in the form

$$\left(\frac{dS}{dt}\right)_{irr}=\sum_j\frac{A_i(\alpha)}{T_i{}^0}\left\{\frac{d\alpha_i}{dt}-V_i(\alpha)\right\} \tag{1}$$

where A_i denotes the affinity associated with α_i, $T_i{}^\circ$ the temperature of the part of the system, to which α_i belongs, and V_i the rate of change of α_i due to the effects of the environment of that part, which vanishes at complete equilibrium. In the thermodynamics of irreversible processes we assume the phenomenological linear relations

$$\frac{d\alpha_i}{dt}=V_i(\alpha)+\sum_j L_{ij}A_j(\alpha) \tag{2}$$

where L_{ij} are the kinetic coefficients. Onsager proved the reciprocity theorem

$$G_{ij}\equiv T_j{}^0L_{ij}=G_{ji} \tag{3}$$

(for a simplest case), which has been generalized by Casimir and others. In general the coefficients G_{ij} may contain their symmetric and antisymmetric parts, $G_{ij}{}^{(s)}$ and $G_{ij}{}^{(a)}$. Then (1) may be written in the form

$$\left(\frac{dS}{dt}\right)_{irr}=\sum_i\frac{A_i(\alpha)}{T_i{}^0}\left(\frac{d\alpha_i}{dt}\right)_{irr} \tag{4}$$

where

$$\left(\frac{d\alpha_i}{dt}\right)_{irr}\equiv\frac{d\alpha_i}{dt}-\sum_j G_{ij}{}^{(a)}\frac{A_j(\alpha)}{T_j{}^0}. \tag{5}$$

2. *The method of Onsager for introducing fluctuations.*

Onsager found that the linear relations (2) could be derived from the variation principle, the principle of the least dissipation of energy,

$$I(\alpha,\dot{\alpha})\equiv\left(\frac{dS}{dt}\right)_{irr}-\Phi(\dot{\alpha},\dot{\alpha})=\text{maximum}, \tag{6}$$

where the variation should be taken with respect to $\dot{\alpha}=d\alpha/dt$, α being fixed, and Φ denotes the dissipation function (devided by temperature)

$$\Phi(\dot{\alpha},\dot{\alpha})\equiv\frac{1}{2}\sum_{ij}(G^{(s)-1})_{ij}\left(\frac{d\alpha_i}{dt}\right)_{irr}\left(\frac{d\alpha_j}{dt}\right)_{irr}. \tag{7}$$

Noticing the fact that the principle (6) is a generalization of that of Boltzmann in statistical mechanics, Onsager further proceeded, and proposed as a statistical interpretation of (6) the transition probability from a state α' to a state $\alpha''\equiv\alpha'+\Delta\alpha$ during a small time Δt

$$\Psi(\alpha',t;\alpha'',t+\Delta t)=N(\alpha',\Delta t)\exp\left\{\frac{1}{2k}\int_t^{t+\Delta t}I(\alpha,\dot{\alpha})\,dt\right\}, \tag{8}$$

N being the normalization factor. If we assume the stochastic process concerned to be Markoffian, (8) gives for a finite time interval $t''-t'$

$$\Psi(\alpha',t';\alpha'',t'')=\int N\exp\left\{\frac{1}{2k}\int_{t'}^{t''}I(\alpha,\dot{\alpha})\,dt\right\}d(\text{paths}),\tag{9}$$

where the integration should be taken over all possible paths $\alpha(t)$ that satisfy the condition $\alpha(t')=\alpha'$ and $\alpha(t'')=\alpha''$. k denotes the Boltzmann constant, i.e., the parameter closely connected with the order of magnitude of the fluctuations. If we would remove fluctuations, we should, formally, make it negligibly small. Then the transition probability (8) would vanish for all values of α'' except the one that is determined by the condition

$$\begin{aligned}I(\alpha,\dot{\alpha})&\simeq\frac{1}{\Delta t}\int_t^{t+\Delta t}I(\alpha,\dot{\alpha})\,dt\\&\simeq\sum_i\frac{A_i}{T_i^0}\left(\frac{\Delta\alpha_i}{\Delta t}\right)_{irr,}-\frac{1}{2}\sum_{ij}(G^{(s)-1})_{ij}\left(\frac{\Delta\alpha_i}{\Delta t}\right)_{irr,}\left(\frac{\Delta\alpha_j}{\Delta t}\right)_{irr,}\\&=-\frac{1}{2}\sum_{ij}(G^{(s)-1})_{ij}\left\{\frac{\Delta\alpha_i}{\Delta t}-[V_i+\sum_l L_{il}A_l]\right\}\left\{\frac{\Delta\alpha_j}{\Delta t}-[V_j+\sum_m L_{jm}A_m]\right\}\\&\quad+\text{a term independent of }\Delta\alpha/\Delta t\\&=\text{maximum}.\end{aligned}\tag{10}$$

That is to say, only the path determined by the phenomenological relation (2) would have a non-zero transition probability.

3. *Generalized Fokker-Planck and Langevin equations.*

We obtain from the transition probability (8) or (9) the Fokker-Planck equation, which is essentially the same as that derived by Green and others,

$$\frac{\partial W}{\partial t}=\sum_i\frac{\partial}{\partial\alpha_i}\left[-(V_i+\sum_l L_{il}A_l)W+\sum_j\frac{\partial}{\partial\alpha_j}(D_{ij}W)\right],\tag{11}$$

where the generalized diffusion coefficient D is defined by

$$D_{ij}\equiv kG_{ij}^{(s)}.\tag{12}$$

This seems to serve for a theoretical justification of the validity of (8).

It will be more intuitive to make use of the Langevin equations, which are obtained by adding fluctuating terms to the phenomenological relations (2):

$$\frac{d\alpha_i}{dt}=V_i+\sum_j L_{ij}A_j+\mathfrak{F}_i(t).\tag{13}$$

The statistical property of $\mathfrak{F}$ is determined by the transition probability (8) under the usual assumptions:

$$<\mathfrak{F}_i(t)>_\alpha=0,\tag{14}$$

$$\int_{-\infty}^{\infty}<\mathfrak{F}_i(t)\mathfrak{F}_j(t+s)>_\alpha ds=2D_{ij}.\tag{15}$$

4. *An example. Thermal noise in metals.*

The thermal noise arises from the fluctuation in electronic distribution $f(\boldsymbol{x},\boldsymbol{p};\,t)$. We wish to determine this fluctuation. According to the free electron model, each local electron gas has a heat-reservoir formed by a crystal lattice of temperature $T(\boldsymbol{x})$ and a mass-reservoir of Fermi-sea with chemical potential $\mu(\boldsymbol{x})$ which determine essentially the state of the gas. Since these local gases are quasi-independent of each other, we may apply our general theory. The generalized affinity associated with the state variable $f(\boldsymbol{x},\boldsymbol{p})$ is found to be

$$\begin{aligned}A(\boldsymbol{x},\boldsymbol{p})&\equiv-\frac{\delta}{\delta f(\boldsymbol{x},\boldsymbol{p})}\{U(\boldsymbol{x})-T(\boldsymbol{x})S(\boldsymbol{x})-\mu(\boldsymbol{x})N(\boldsymbol{x})\}\\&=\mu(\boldsymbol{x})-\mathcal{E}(\boldsymbol{p})kT(\boldsymbol{x})\log-\frac{f(\boldsymbol{x},\boldsymbol{p})}{1-f(\boldsymbol{x},\boldsymbol{p})}\\&\simeq-\frac{kT}{f^0(1-f^0)}(f-f^0),\end{aligned}\tag{16}$$

where

$$f^0(\boldsymbol{x},\boldsymbol{p})\equiv\frac{1}{\exp\dfrac{\mathcal{E}(\boldsymbol{p})-\mu(\boldsymbol{x})}{kT(\boldsymbol{x})}+1}.\tag{17}$$

On the other hand, according to the Lorentz theory of metals, the function f should satisfy the equation of Boltzmann:

$$\frac{\partial f}{\partial t}+\left\{\frac{\boldsymbol{p}}{m}\cdot\frac{\partial}{\partial\boldsymbol{x}}+e\left(\boldsymbol{E}+\frac{\boldsymbol{p}}{mc}\times\boldsymbol{H}\right)\cdot\frac{\partial}{\partial\boldsymbol{p}}\right\}f=-\frac{f-f^0}{\tau}\tag{18}$$

where the mean free time τ is assumed to be a function of $\mathcal{E}$ and $T(\boldsymbol{x})$ only. Comparing (18) with the linear relations (2), we obtain the diffusion coefficient

$$D(\boldsymbol{x},\boldsymbol{p};\boldsymbol{x}',\boldsymbol{p}')=\frac{kT(\boldsymbol{x})}{\tau(\mathcal{E})}\left\{-\frac{\partial f^0}{\partial\mathcal{E}}\right\}\delta(\boldsymbol{x}-\boldsymbol{x}')\delta(\boldsymbol{p}-\boldsymbol{p}').\tag{19}$$

Thus the Langevin equation becomes

$$\left\{\frac{\partial}{\partial t}+\frac{\boldsymbol{p}}{m}\cdot\frac{\partial}{\partial\boldsymbol{x}}+e\left(\boldsymbol{E}+\frac{\boldsymbol{p}}{mc}\times\boldsymbol{H}\right)\cdot\frac{\partial}{\partial\boldsymbol{p}}\right\}f=-\frac{f-f^0}{\tau}+\mathfrak{F}_t(\boldsymbol{x},\boldsymbol{p}),\tag{20}$$

where

$$<\mathfrak{F}_t(\boldsymbol{x},\boldsymbol{p})>_f=0,\tag{21}$$

$$\int_{-\infty}^{\infty}<\mathfrak{F}_t(\boldsymbol{x},\boldsymbol{p})\mathfrak{F}_{t+s}(\boldsymbol{x}',\boldsymbol{p}')>_f ds=2D(\boldsymbol{x},\boldsymbol{p};\boldsymbol{x}'.\boldsymbol{p}').\tag{22}$$

The solution corresponding to that of Lorentz is given by

$$f\simeq f^0-\tau\frac{\partial f^0}{\partial\mathcal{E}}\left\{e\boldsymbol{E}-T\frac{\partial}{\partial\boldsymbol{x}}\left(\frac{\mu}{T}\right)-\mathcal{E}\frac{\partial\log T}{\partial\boldsymbol{x}}\right\}\cdot\frac{\boldsymbol{p}}{m}+\tau\mathfrak{F}_t,\tag{23}$$

which gives the electronic flow and the electronic energy flow:

$$\begin{pmatrix}\boldsymbol{I}\\\boldsymbol{Q}\end{pmatrix}\simeq\begin{pmatrix}K_1&K_2\\K_2&K_3\end{pmatrix}\begin{pmatrix}e\boldsymbol{E}-T\dfrac{\partial}{\partial\boldsymbol{x}}\left(\dfrac{\mu}{T}\right)\\-\dfrac{\partial\log T}{\partial\boldsymbol{x}}\end{pmatrix}+\begin{pmatrix}\mathfrak{J}_t\\\mathfrak{Q}_t\end{pmatrix},\tag{24}$$

and the statistical properties of their fluctuating parts:

$$<\mathfrak{J}_{ti}(\boldsymbol{x})>_f=0,\qquad(\mathfrak{Q}_{ti}>_f=0,\tag{25}$$

$$\begin{aligned}\int_{-\infty}^{\infty}ds&\begin{pmatrix}<\mathfrak{J}_{t,i}(\boldsymbol{x})\mathfrak{J}_{t+s,j}(\boldsymbol{x}')>_f&<\mathfrak{J}_{t,i}(\boldsymbol{x})\mathfrak{Q}_{t+s,j}(\boldsymbol{x}')>_f\\<\mathfrak{Q}_{t,i}(\boldsymbol{x})\mathfrak{J}_{t+s,j}(\boldsymbol{x}')>_f&<\mathfrak{Q}_{t,i}(\boldsymbol{x})\mathfrak{Q}_{t+s,j}(\boldsymbol{x}')>_f\end{pmatrix}\\&=2kT\begin{pmatrix}K_1&K_2\\K_2&K_3\end{pmatrix}\delta_{ij}\delta(\boldsymbol{x}-\boldsymbol{x}'),\quad(i,j=x,y,z),\end{aligned}\tag{26}$$

where

$$K_\gamma \equiv -\frac{2}{3m}\int \tau(\varepsilon)\,\varepsilon^\gamma \frac{\partial f^0}{\partial \varepsilon}\, 2\frac{d\boldsymbol{p}}{h^3}, \quad (\gamma=1, 2, 3) \tag{27}$$

If we assume the white spectrum

$$<\mathfrak{F}_t(\boldsymbol{x}, \boldsymbol{p})\,\mathfrak{F}_{t+s}(\boldsymbol{x}', \boldsymbol{p}')>_f = 2D(\boldsymbol{x}, \boldsymbol{p}; \boldsymbol{x}', \boldsymbol{p}')\,\delta(s), \tag{28}$$

we obtain the well-known Nyquist formula, and if we assume the spectrum of the type

$$<\mathfrak{F}_t(\boldsymbol{x}, \boldsymbol{p})\,\mathfrak{F}_{t+s}(\boldsymbol{x}', \boldsymbol{p}')>_f = 2D(\boldsymbol{x}, \boldsymbol{p}; \boldsymbol{x}', \boldsymbol{p}')\frac{e^{-|s|/\tau}}{2\tau}, \tag{29}$$

we obtain the result of Bakker-Heller theory.

Theoretical Treatment of the Quantum Properties of Condensed Systems

J. de Boer

(The abstract will be found on page 48)

Statistical Mechanics of Condensation

K. Husimi

(The abstract will be found on page 50)

On the Theory of Cooperative Phenomena

Shigetoshi Katsura
Department of Applied Science, Tohoku University

Statistical treatment of the Ising model is a common problem through ferromagnetic lattice, alloy, imperfect gas and liquid (lattice gas). In the general case under arbitrary magnetic field and three-dimensional lattice, it is remained to obtain a solution in a closed form. Meanwhile, on the theory of condensation by cluster integrals, it is doubtful whether the smallest real positive singularity of the analytic function continued from the power series $\sum_{l=1}^{\infty} b_l z^l$, would give the point of condensation or not.$^{1)}$

We consider the square lattice (cube lattice) which has a small number (m, n or l, m, n) of lattice point on each side (edge). The partition function of such system can be obtained in a closed form as a binary function of temperature and external field. We represent the nearest neighbour interaction by J, spin magnetic moment by μ_0, external magnetic field by $\boldsymbol{H}$, and $H=J/2kT$, $I=\mu_0\boldsymbol{H}/kT$, $\beta=e^{-2H}$, $\alpha=e^I$.

The partition function of such system $\Xi(\alpha,\beta)$ are as follows:

$$\begin{aligned}(3\times3)\Xi &= \beta^{-9}(\alpha^9+\alpha^{-9})+9\beta^{-5}(\alpha^7+\alpha^{-7})+(18\beta^{-3}+18\beta^{-1})(\alpha^5+\alpha^{-5})\\ &\quad +(6\beta^{-3}+36\beta^{-1}+36\beta+6\beta^3)(\alpha^3+\alpha^{-3})+(45\beta^{-1}+36\beta+45\beta^3)(\alpha+\alpha^{-1})\\ (3\times3\times2)\Xi &= \beta^{-27}(\alpha^{18}+\alpha^{-18})+18\beta^{-21}(\alpha^{16}+\alpha^{-16})+(9\beta^{-19}+36\beta^{-17}+108\beta^{-15})(\alpha^{14}+\alpha^{-14})\\ &\quad +\cdots\cdots+(314\beta^{-9}+576\beta^{-7}+2754\beta^{-5}+4464\beta^{-3}+7830\beta^{-1}+9216\beta\\ &\quad +10782\beta^3+6480\beta^5+3618\beta^7+1458\beta^9+936\beta^{11}+102\beta^{15})\end{aligned}$$

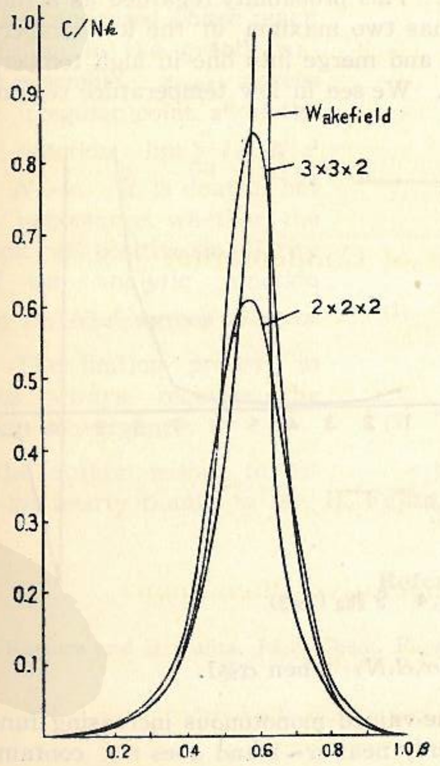

Fig. 1

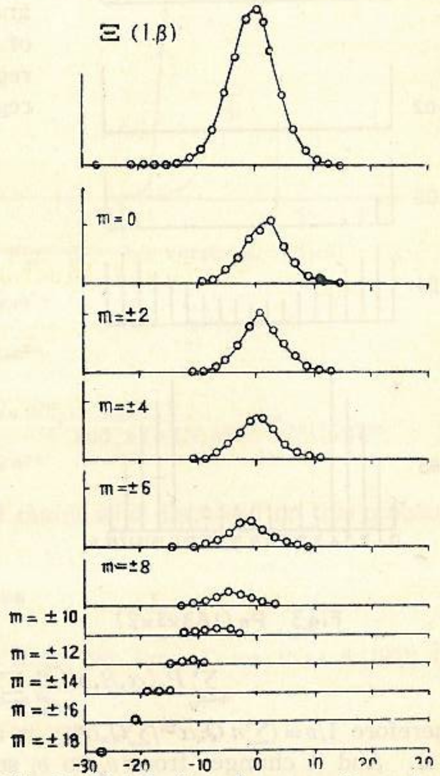

Fig. 2 Distribution of energy eigenvalues. The ordinate represents the coefficient of $\alpha^m\beta^{-n}$. The abscissa represents n.

The results of free energy, energy and specific heat are compared with the results of Onsager and Wakefield. In two dimensional lattice the specific heat has a maximum nearly at $\beta=0.42$ when $\alpha=1$, and that of the three dimensional lattice lies nearly at $\beta=0.57\sim0.58$. These values of β may be considered as an approximation of the Curie point. That of the three-dimensional lattice is somewhat lower than the value of Wakefield (0.641) and Oguchi (0.62∼0.66), and is nearly equal to the value of the plane triangular lattice (0.577).

The coefficient of β^n in $\Xi(\alpha,\beta)$ regarded as a function of n shows a distribution of energy eigenvalues. We see this function can be well approximated by Gaussian distribution.

The relation to the case of imperfect gas is given by Rushbrooke, Yang and Lee.

$$\Xi_{gas}=\sum_{n=1}^{N}\Omega_n z^n=\sum_{n=1}^{N}Q_n\alpha^{2n}=\alpha^N\beta^N\Xi(\text{or } c^N\beta^{3/2N}\Xi)$$

where Ω_n is the configurational partition function and Ξ_{gas} is a grand partition function, z is a fugacity. $Q_n(\beta,N)\alpha^{2n}=P_n(\alpha,\beta,N)$ is a probability of finding a system which contains n particles in N sites under given β and α. This probability regarded as a function of n, has two maxima in the low temperature region and merge into one in high temperature region. We see in low temperature region

$$\sum_{n\sim n_g}P_n(\alpha,\beta,N)\gtreqless\sum_{n\sim n_l}P_n(\alpha,\beta,N)\quad\text{when } \alpha\lesseqgtr1.$$

Therefore $1/v=(\sum n\,Q_n\alpha^{2n}/\sum Q_n\alpha^{2n})$ is a one-valued monotonous increasing function of α. And it changes from v_g to v_l suddenly near $\alpha\sim1$ and does not contain the unstable state. The supersaturation is interpreted by the inhibition to the second maximum of $P_n(\alpha,\beta,N)$.

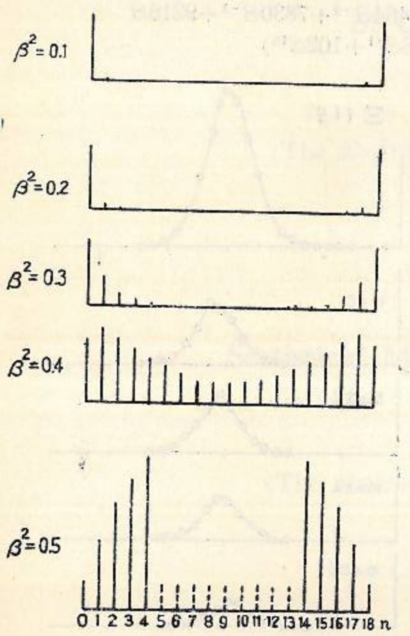

Fig.3 Pn (1.β3×3×2)

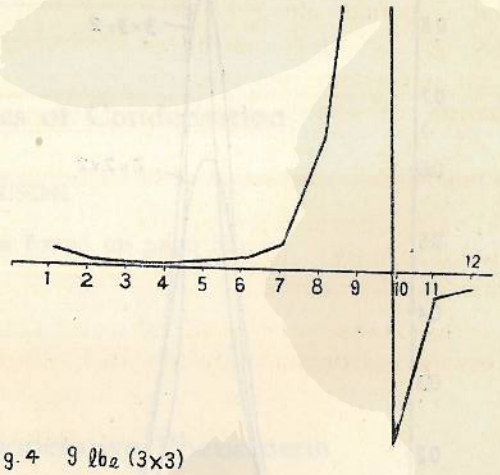

Fig. 4 9 lb_l (3×3)

The cluster integrals $b_l(N)$ can be calculated by

$$b_l(N)=-\frac{1}{N}\sum_{n=1}^{N}\cos l\,\theta_n(N)$$

where $\theta_n(N)$ is the argument of the zeros of $\sum_{n=0}^{N}Q_n(N)\alpha^{2n}$ which lie on the unit circle in the complex α–plane. The calculated behaviour of $b_l(N)$ (as a function of l) is not a monotonous function but shows an irregular behaviour near $l\sim N$, as supposed by the author and Fujita[1]. The irregular part is due to the second maximum of $Q_n(N)$. Indeed, the numerical calculation of $1/v=\sum_{l=1}^{\infty}l\,b_l(N)\alpha^{2l}$ shows the steep change at $\alpha\sim1$ while $1/v=\sum_{l=1}^{\infty}l\,b_l(\infty)\alpha^{2l}$ is extended beyond $\alpha>1$ and shows the state of supersaturation. The singularity of the latter is considered to be given by the zero of $\sum_{n=0}^{N}Q_n'\alpha^{2n}=\sum_{n=0}^{N/2}Q_n(N)\alpha^{2n}$, which does not lie on the unit circle.

Thus we see that the volume dependency of cluster integrals plays a dominant role in the condensation. The point of condensation $z_{\text{cond.}}$ is the point where the gaseous phase and the condensed phase reach equilibrium in the grand canonical ensemble. $z_{\text{cond.}}$ agrees to the irregular point z^* of the limit function $\lim\sum_{l=1}^{\infty}l\,b_l(N)z^l$ when $N\to\infty$. It is doutful but of no importance whether the smallest real positive singularity z_s of the analytic function $\sum_{s=1}^{\infty}\lim l\,b_l(N)z^l$ agrees to z^* or not. The limting process in physics always requires the uniform convergence.

The author wishes to express his hearty thanks to Mr. H. Fujita and many who discussed on this problem.

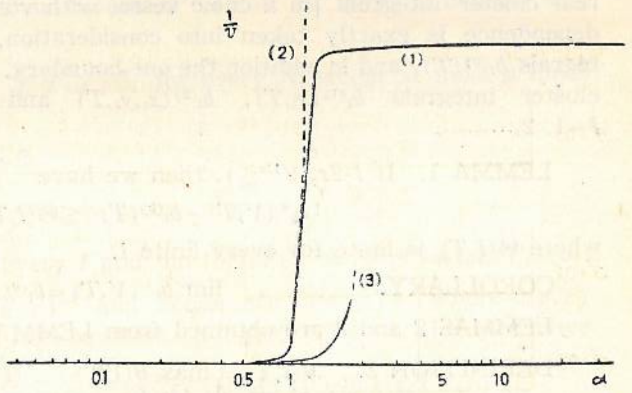

Fig. 5 $1/v$ versus α. (3×3)

(1) $\dfrac{\sum_{n=0}^{N}nQ_n\alpha^{2n}}{\sum_{n=0}^{N}Q_n\alpha^{2n}}$ (2) $\sum_{l=1}^{\infty}l\,b_l(N)\alpha^{2l}$

(3) $\dfrac{\sum_{n=0}^{N}nQ_n'\alpha^{2n}}{\sum_{n=0}^{N}Q_n'\alpha^{2n}}$ and $\sum_{l=1}^{n'}l\,b_l(N)\alpha^{2l}\sim\sum_{l=1}^{\infty}l\,b_l(\infty)\alpha^{2l}$

References

1) S. Katsura and H. Fujita, Jour. Chem. Phys., **19** (1951) 799; Prog. Theor. Phys. **6** (1951) 498.

On the Theory of Condensation

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By a rigorous mathematical method we argue about the connection between the phase transitions and the singular points and criticize the Mayer theory of condensation.

DEFINITION 1. For the system of interacting particles, whose potential energy is $U=\sum u(r_{ij})$ where $u(r)>-\infty$ for $r\geqq 0$ and $u(r)=0$ for $r\geqq r_0>0$, we define the real cluster integrals [in a cubic vessel with volume V] $b_l{}^{+}(V,T)$, whose volume dependence is exactly taken into consideration, and the non-boundary cluster integrals $b_l{}^{(0)}(T)$, and in addition the one-boundary, two-boundary and three-boundary cluster integrals $b_l{}^{(1)}(x_l,T)$, $b_l{}^{(2)}(x_l,y_l,T)$ and $b_l{}^{(3)}(x_l,y_l,z_l,T)$ respectively, for $l=1, 2, \ldots\ldots\ldots$

LEMMA 1. If $l\cdot 2r_0/V^{1/3}\leqq 1$, then we have

$$|b_l{}^{+}(V,T)-b_l{}^{(0)}(T)|\leqq\Theta(l,T)\cdot 8lr_0/V^{1/3},$$

where $\Theta(l,T)$ is finite for every finite l.

COROLLARY. $$\lim_{V\to\infty} b_l{}^{+}(V,T)=b_l{}^{(0)}(T).$$

LEMMAS 2 and 3 are obtained from LEMMA 1, but are omitted here.

DEFINITION 2. $$\bar{\theta}(l,T)=\max_{1\leqq l'\leqq l}\theta(l'T)\qquad(l=1, 2, \ldots\ldots),$$

where $$\theta(l',T)=\Theta(l',T)/|b_{l'}{}^{(0)}(T)|\qquad(l'=1, 2, \ldots\ldots).$$

LEMMA 4. If the radius of convergence of the power series $\sum_{l=1}^{\infty}b_l{}^{(0)}(T)z^l$ is not zero and the lower limit of the sequence $\{|b_l{}^{(0)}(T)|^{1/l}\}_{l=1}^{\infty}$ is not zero, then we can find a function $l^*(N)$ of $N(=1, 2, \ldots\ldots)$ which satisfies the following five conditions simultaneously.

1° $l^*(N)$ assumes a positive integral value for every N.
2° $l^*(N)\cdot 2r_0/(N^{1/3}v^{1/3})\leqq 1$ for all N except at most a finite number of N.
3° There exists a constant $\alpha(0<\alpha<1)$ such that $l^*(N)\bar{\theta}(l^*(N),T)\cdot 8r_0/(N^{1/3}v^{1/3})\leqq\alpha$ for all N except at most a finite number of N.

4° There exists a constant $K(>0)$ such that $\ln N/l^*(N)\leqq K$ for all N.
5° $\lim_{N\to\infty}\{\bar{\theta}(l^*(N),T)/N^{1/3}\}=0$.

DEFINITION 3. For any given T and v, we take any one of the functions which satisfy the five conditions above-mentioned, and we denote it by $l^*(N)$.

DEFINITION 4. The configurational part of the partition function of the real system is

$$\Omega_N^{+}(Nv,T)=\frac{1}{N!}\int_{V=Nv}e^{-\frac{U}{kT}}d\{N\}=\sum_{m_l\geqq 0}\Bigl(\sum_{l=1}^{N}lm_l=N\Bigr)\prod_{l=1}^{N}\frac{\{Nvb_l{}^{+}(Nv,T)\}^{m_l}}{m_l\,!},$$

and that of the (0)-system is defined to be

$$\Omega_N^{(0)}(Nv,T)=\sum_{m_l\geqq 0}\Bigl(\sum_{l=1}^{N}lm_l=N\Bigr)\prod_{l=1}^{N}\frac{\{Nvb_l^{(0)}(T)\}^{m_l}}{m_l\,!}.$$

Now we write*) $$\Omega_N^{+}(Nv,T)=\sum_i\widetilde{T}^{+}_{i,N}+\sum_j\widetilde{\widetilde{T}}{}^{+}_{j,N}$$

where $$\widetilde{T}^{+}_{i,N}=\prod_{l=1}^{l^*(N)}\frac{\{Nvb_l^{+}(Nv,T)\}^{m_l}}{m_l\,!}$$

and $$\widetilde{\widetilde{T}}{}^{+}_{j,N}=\prod_{l=1}^{l^*(N)}\frac{\{Nvb_l^{+}(Nv,T)\}^{m_l}}{m_l\,!}\prod_{l=l^*(N)+1}^{N}\frac{\{Nvb_l^{+}(Nv,T)\}^{m_l}}{m_l\,!}.$$

Here, in each $\widetilde{\widetilde{T}}{}^{+}_{j,N}$, $m_l\geqq 1$ for at least one value of l such that $N\geqq l\geqq l^*(N)+1$.

Similarly we write $\Omega_N^{(0)}(Nv,T)=\sum_i\widetilde{T}{}^{(0)}_{i,N}+\sum_j\widetilde{\widetilde{T}}{}^{(0)}_{jN}$

where $\widetilde{T}{}^{(0)}_{i,N}$ and $\widetilde{\widetilde{T}}{}^{(0)}_{j,N}$ correspond to $\widetilde{T}^{+}_{i,N}$ and $\widetilde{\widetilde{T}}{}^{+}_{j,N}$ respectively.

LEMMA 5. For any value of T such that $b_l^{(0)}(T)>0$ for every l, and for any assigned value of v,

(i) $\widetilde{T}^{+}_{i,N}>0$ for each i and hence $\sum_i\widetilde{T}^{+}_{i,N}>0$, for every N except at most a finite number of N.

(ii) $\lim_{N\to\infty}\dfrac{1}{N}\Bigl(\ln\sum_i\widetilde{T}^{+}_{i,N}-\ln\sum_i\widetilde{T}{}^{(0)}_{i,N}\Bigr)=0$.

[Proof] by LEMMAS 3 and 4.

LEMMA 6. Let $b_l^{(0)}(T)>0$ for every l and $\lim_{l\to\infty}\{b_l^{(0)}(T)\}^{1/l}=b_0^{(0)}(T)=1/z_s(T)<\infty$. Now if $v>v_s(T)\equiv\{\sum_{l=1}^{\infty}l\,b_l^{(0)}(T)\,(z_s(T))^l\}^{-1}$ and hence $z(v,T)<z_s(T)$, where $z(v,T)$ is the least real positive root of the equation $\sum_{l=1}^{\infty}lvb_l^{(0)}(T)z^l=1$, i.e. we have

$$\lim_{N\to\infty}\frac{1}{N}\ln\Omega_N^{(0)}(Nv,T)=\omega^{(0)}(v,T)=\sum_{l=1}^{\infty}vb_l^{(0)}(T)\,(z(v,T))^l-\ln z(v,T),$$

then we have $$\lim_{N\to\infty}\frac{1}{N}\ln\sum_i\widetilde{T}{}^{(0)}_{i,N}=\omega^{(0)}(v,T).$$

[Proof] using LEMMA 4.

The theorem on the equality and inequality of the thermodynamic functions of the real system and the (0)-system :——

THEOREM. For any value of T such that $b_l^{(0)}(T)>0$ for every l and any value of v such that $v>v_s(T)$;——

[I] The necessary and sufficient condition that $\lim_{N\to\infty}\frac{1}{N}\ln\Omega_N^{+}(Nv,T)=\omega^{+}(v,T)$ should exist and $\omega^{+}(v,T)=\omega^{(0)}(v,T)$ is that

$$\limsup_{N\in E(+),\,N\to\infty}\frac{1}{N}\Bigl(\ln\sum_j\widetilde{\widetilde{T}}{}^{+}_{j,N}-\ln\sum_i\widetilde{T}^{+}_{i\,N}\Bigr)\leqq 0$$

when the set $\boldsymbol{E}_{(+)}=\boldsymbol{E}\{\text{positive integers } N;\ \sum_j\widetilde{\widetilde{T}}{}^{+}_{j,N}>0\}$ is an infinite set, and

$$\ln\{1+\bigl(\sum_j\widetilde{\widetilde{T}}{}^{+}_{j,N}/\sum_i\widetilde{T}^{+}_{i,N}\bigr)\}^{-1}=o(N)\quad\text{for } N\in\boldsymbol{E}_{(-)}$$

when the set $\boldsymbol{E}_{(-)}=\boldsymbol{E}\{\text{positive integers } N;\ \sum_j\widetilde{\widetilde{T}}{}^{+}_{j,N}\leqq 0\}$ is an infinite set.

[II] When $\boldsymbol{E}_{(+)}$ is an infinite set, we have

$$\lim_{N\in E(+),\,N\to\infty}\sup \frac{1}{N}\Big(\ln\sum_j \tilde{\tilde{T}}{}^+_{j,N}-\ln\sum_i \tilde{T}{}^+_{i,N}\Big)=\lim_{N\in E(+),\,N\to\infty}\sup\frac{1}{N}\Big(\ln\sum_j \tilde{\tilde{T}}{}^+_{j,N}-\ln\sum_i \tilde{T}{}^{(0)}_{i,N}\Big)$$

$$\leqq \lim_{N\in E(+),\,N\to\infty}\sup\frac{1}{N}\Big(\ln\sum_j \tilde{\tilde{T}}{}^+_{j,N}-\ln\sum_j \tilde{\tilde{T}}{}^{(0)}_{j,N}\Big).$$

[III] The necessary and sufficient condition that $\lim_{N\to\infty}\frac{1}{N}\ln\Omega^+_N(Nv,T)=\omega^+(v,T)$ should exist and $\omega^+(v,T)>\omega^{(0)}(v,T)$ is that $\sum_j \tilde{\tilde{T}}{}^+_{j,N}>\sum_i \tilde{T}{}^+_{i,N}>0$ for every N except at most a finite number of N and $\lim_{N\to\infty}\frac{1}{N}\big(\ln\sum_j \tilde{\tilde{T}}{}^+_{j,N}-\ln\sum_i \tilde{T}{}^+_{i,N}\big)=\lambda_1$ should exist and $\lambda_1>0$.

[iv] The necessary and sufficient condition that $\lim_{N\to\infty}\frac{1}{N}\ln\Omega^+_N(Nv,T)=\omega^+(v,T)$ should exist and $\omega^+(v,T)<\omega^{(0)}(v,T)$ is that $-\sum_i \tilde{T}{}^+_{i,N}<\sum_j \tilde{\tilde{T}}{}^+_{j,N}<0$ for every N except at most a finite number of N and $\lim_{N\to\infty}\frac{1}{N}\ln\{1+(\sum_j \tilde{\tilde{T}}{}^+_{j,N}/\sum_i \tilde{T}{}^+_{i,N})\}=\lambda_2$ should exist and $\lambda_2<0$.

[Proof] Notice the identity

$$\frac{1}{N}\ln\Omega^+_N(Nv,T)=\frac{1}{N}\ln\sum_i \tilde{T}{}^+_{i,N}+\frac{1}{N}\ln\{1+(\sum_j \tilde{\tilde{T}}{}^+_{j,N}/\sum_i \tilde{T}{}^+_{i,N})\}$$

and the similar identity for the (0)-system, and use LEMMAS 5 and 6.

COROLLAY. For any value of T such that $b_l^{(0)}(T)>0$ for every l and any value of v such that $v>v_s(T)$, a sufficient condition that $\lim_{N\to\infty}\frac{1}{N}\ln\Omega^+_N(Nv,T)=\omega^+(v,T)$ should exist and $\omega^+(v,T)=\omega^{(0)}(v,T)$ is that, for every N except at most a finite number of N,

$$0\leqq b_l^+(Nv,T)\leqq b_l^{(0)}(T) \qquad \text{provided that} \quad l\leqq N.$$

[Proof] by [I] and [II] of the theorem.

In the condensation theory by Born, Fuchs, Kahn, Uhlenbeck and Mayer the (0)-system is treated. But in reality we should treat not the (0)-system but the real system that is the system for which volume dependence of the cluster integrals is exactly taken into consideration. Using our theorems we argue about the condensation phenomenon of the real system and the analytical properties**) of the singular points with which the condensation is connected.

References

*) A similar technique was used in a theory of condensing systems: K. Ikeda *Busseiron Kenkyu* **52**, 21 (1952).

) K. Ikeda *Busseiron Kenkyu* **57, 77 (1952).

Equation of State Calculations by Fast Computing Machines

M. N. and A. W. Rosenbluth

(The abstract will be found on page 129)

Theoretical Treatments of Liquids

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(Received on Aug. 28)

In the description of a thermodynamic system, either in complete equilibrium, or also in some state of flux near local equilibrium, it is often convenient to regard the usual thermodynamic potentials such as free energy, or pressure, as the zero'th member of a set of a function depending on the coordinates of n molecules each; the specification of the set for all values of n constituting a complete description of an ensemble of which the system is a member.

For instance, define a "distribution function," $F_n(\mathbf{x}^{(n)})$, of the coordinates, $\mathbf{x}^{(n)}$, of n molecules as being proportional to the probability density of finding n molecules at the position $\mathbf{x}^{(n)}$. If the system consists of several kinds of molecules we must extend the stipulation to what kinds of molecules are at the various coordinate positions, but for the sake of simplicity we shall restrict ourselves to systems of one chemical component. The coordinate $\mathbf{x}^{(n)}$ may include internal degrees of freedom as well as the $3n$ coordinates of the centers of mass, or may even include momenta components. For our example, however, we shall discuss only the case that $\mathbf{x}^{(n)}$ has $3n$ cartesian components. The normalization of F_n is conveniently so chosen that its average value in infinite space is unity,

$$lim\, V\to\infty\Big[V^{-n}\iiint\cdots\int_V F_n(\mathbf{x}^{(n)})\,d\mathbf{x}^{(n)}\Big]=1.$$

If the system is in complete equilibrium its state will be determined by two intensive thermodynamic parameters which we could choose as temperature, T, and number density, $\rho=N/V$, or T and chemical potential μ. It is often convenient to substitute for μ the activity, $z=exp\ (\mu-\mu_0)/kT$ with μ_0 so chosen that $\lim \rho\to 0\ [z/\rho]=1$.

Now the "natural" thermodynamic potential for a system of fixed T and z is the negative pressure volume product, $-PV$. However if we define functions,

$W_n(z, T, x^{(n)})$ as

$$W_n(z,T,x^{(n)}) = -kT \ln F_n(z,T,x^{(n)}), \tag{1}$$

then the set, $-PV$, $-kT\,ln\,\rho + W_1(z, T, x^{(1)})$, $W_2(z, T, x^{(2)})$, W_3, ……, $W_n(z, T, x^{(n)})$, can be regarded as a set of functions of which P is only the zero'th member, which describe the condition of the system in increasing detail as the set is extended to higher and higher n-values.

In the case of an ensemble of systems each consisting of single crystals with the same fixed orientation of axes and phase of the positions of the lattice sites $W_1(z, T, x^{(1)})$ is triply periodic in space and describes the crystal lattice, as well as the average distribution of atoms around the lattice sites. In this case $W_2(z, T, x^{(2)})$ is approximately $W_1(z, T, x_1) + W_1(z, T, x_2)$ when $x^{(2)} = x_1, x_2$, the difference giving the correlation in the vibration of two atoms on different sites.

In the case of a fluid (glass, liquid or gas) the function W_1 is identically zero and the first significant member of the series, besides $-kT\,ln\,\rho$, is the function W_2 of the coordinates of a pair of particles. This function, or more directly $F_2 = exp\,(-W_2/kT)$, which depend only on the distance r between the two molecules, can be obtained experimentally from an X-ray diffraction study of the fluid.

It is easy to prove theoretically that, for a classical system, these functions, $W_n(z, T, x^{(n)})$ have the significance of a potential of average force, That is, if in the fluid n molecules are at the coordinate position $x^{(n)}$, then the average force, $f_{x_i}(z, T, x^{(n)})$ along any coordinate x_i of one of the molecules, averaged over the positions of all other molecules in the fluid of activity z, and temperature T, is

$$\overline{f}_{x_i}(z,T,x^{(n)}) = -\partial W_n(z,T,x^{(n)})/\partial x_i. \tag{2}$$

In the limit of zero activity, when no other than the n particles will be present, it follows that for a classical system

$$\lim_{z\to 0}[W_n(z,T,x^{(n)})] = U(x^{(n)}), \tag{3}$$

W_n becomes the direct potential energy, U_n of the n molecules.

There is no similar simple significance to the meaning of W_n for a quantum mechanical system.

The normalization of F_n as having average unit value in infinite space fixes the zero of W_n for a fluid by its value when all molecules are at infinite distance from each other.

It is commonly assumed that for a fluid,

$$W_n(z,T,x^{(n)}) \cong \sum_{n\geq i>j\geq 1}\sum W_2(z,T,(x_i,x_j)), \tag{4}$$

an assumption sometimes called "superposition" or the "Kirkwood assumption." Unfortunately there is little or no direct evidence for or against its validity. It is not correct for an ensemble of crystals of random orientation and phase, for which W_1 is also identically zero.

These functions, or the equivalent distribution functions, F_n, related to W_n by Fq. (1), usually play a predominant role in liquid theories. They may be defined for the equilibrium ensemble, or for an ensemble in some steady state of flux, and may be defined as functions of momentum as well as coordinate space.

In most theoretical work the Canonical Ensemble of systems of fixed V, T, and number of particles N, or of the Grand Canonical Ensemble of systems of fixed V, T, and chemical potential μ or activity z is used. It is usually easy to convert any particular method from one formulation into the other, but in my opinion the Grand Canonical Ensemble usually leads to an easier formulation. The fundamental equation relating the distribution functions, $F_n(z_2, T, x^{(n)})$ of one activity, z_2, to those, $F_N(z_1, T, x^{(N)})$ of another activity is

$$e^{P_2V/kT}(\rho_2/z_2)^n F_n(z_2,T,x^{(n)}) = e^{P_1V/kT}\sum_{N\geq 0}\frac{(z_2-z_1)^N}{N!}\iint_V\cdots\int\left(\frac{\rho_1}{z_1}\right)^{n+N}F_{n+N}(z_1,T,x^{(N)},x^{(n)})\,dx^{(N)}, \tag{5}$$

where P_1 and ρ_1 are pressure and number density at z_1 and P_2, ρ_2 at z_2. The particular case $z_1=0$, $P_1=0$, $(\rho_1/z_1)=1$ with $F_n(z_1, T, x^{(n)}) = \exp\,[-U_n(x^n)/kT]$, is that usually considered.

The methods employed by various authors can usually be classified as belonging into either of 3 general categories:

1) The development as a power series of Δz.
2) The method of integral equations.
3) The cell method or free volume method.

1) Equation (5) gives the exponent of P, and W_n as a power series of $z_2 - z_1$. If one uses the fact that F_N of z_1, appearing on the right is equal to the product of F_1's for all N particles at large distances for all pairs, and in general to $F_{n1}\,F_{n2}\,F_{n3}\cdots\cdots$, $\sum n_1 = N$, when the different subsets n_i are distant from each other, the integrals on the right can be written as products of integrals.

The numerical coefficients occurring are such that the logarithm of the sum is a simple power series in $z_2 - z_1$, so that $P_2 - P_1$ and $W_n(z_2, T) - W_n(z_1, T)$ are given by the series. The coefficients of Δz^n are simple integrals over the coordinates of n molecules.

Since it is a series development this fails if z_2 and z_1 are two activities separated by a phase transition at the same temperature. One may, therefore, not use this method for a liquid with $z_1=0$. One may, however, derive certain useful relations in terms of the distribution functions of the liquid, especially for solutions of several chemical components.

2) The method of integral equations makes use of (5) by carrying out some operation on the exponents occurring in both sides of the equation, for instance differentiation with respect to one of the coordinates of one of the particles occurring in the set $\{n\}$ on the left. The operation nust be such that it multiplies the terms on the right by a sum of terms $\psi_m(x^{(m)})$ depending on the coordinates of a small number, m, of molecules, Grouping the similar terms for all values of N in which they occur, and integration over all molecules *not* occurring in the set $\{m\}$ the sum over N leads to distribution functions of the activity z_2 on the right hand side. One thus obtains a set of integral equations with combinations of the distribution functions at z_2 as kernels, and the results, $\psi_m(z_1, T, x^{(m)})$, of the operation

at z_1 under the integrand. The functions $\psi_m(z_2, T, x^{(m)})$ obtained by the same operation at z_2 occur on the left.

One may choose either z_1 or z_2 as zero. In the former case the kernels are unknown, but related to the also unknown $\psi_m(z_2, T)$ by some defined non-linear relationship. In the latter case the kernels are known.

Comparison of the two cases show that the kernels at z_1 and z_2 are related in the same manner that the kernel and reciprocal kernel are related in a simple Fredholm integral equation.

This method has been used numerically by Kirkwood. Unfortunately, although completely rigorous in its general formulation, it is necessary to terminate the series of equations obtained by something like the superposition principle, in order to actually make use of the set to find solutions.

3) The cell method is that most frequently used to find approximate equations of state. Originally more intuitive than formal in its derivation, the method can be regarded as a formal use of the principle that a real system at equilibrium always adjusts its distribution to give the minimum value of the appropriate thermodynamic potential.

If the distribution functions at zero activity, $z_1=0$, are assumed to be of such a form that no two molecules can be in the same cell of a lattice of contiguous cells, then the integrals of Eq. (5) become more tractable. In the particular case that the distribution within a cell is independent of the position of molecules, or even occupancy, of neighboring cells, the integration is trivial. The entropy, which depends only on the distribution, the energy, and the pressure can be computed. Any parameters in the assumed distribution can then be adjusted to give minimum thermodynamic potential. Kirkwood has shown that the original Lennard-Jones Devonshire formulation was equivalent to this with some additional approximation in the solution of the minimization.

Most early computations depended on the assumption of an equal number of cells and molecules. Permitting a new parameter of the ratio of cells to molecules always improves the result by giving a lower, and hence more nearly correct thermodynamic potential, providing the original calculation did not introduce approximate compensations for errors. New parameters describing correlations between cell occupancy in neighboring cells, or even between positions in neighboring cells, can be introduced by use of the order-disorder methods. At a cost of considerble labor one might expect the method to become reasonably good numerically.

Quantum Theory of Transport Phenomena

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The object of the lecture is to summarise the results obtained in the quantum theory and the numerical evaluation of the transport coefficients. The discussion will be limited to the case of gases under normal pressure, this being the only case for which exact theoretical calculations have at present been made. As much of the considerations are formally the same in classical and in quantum theory, we will start with summarising the classical treatment of *Chapman and Enskog.*

1. *The classical theory of the transport phenomena* is based on the Boltzmann equation:

$$\frac{\partial f}{\partial t}+\frac{\boldsymbol{p}}{m}\cdot\frac{\partial f}{\partial \boldsymbol{r}}=\int(ff_1-f'f_1')2\pi g\,bdb \tag{1}$$

where $f=f(\boldsymbol{p},\boldsymbol{r})$ is the number density in μ-space. The derivation of the equation is based on the "collision-hypothesis" ("Stosszahl-Ansatz"), that $f\,f_1\,g\,2\pi\,b\,db\,d\boldsymbol{p}\,d\boldsymbol{p}_1$ is the number of collisions per unit volume and time specified by the momenta $\boldsymbol{p}$ and $\boldsymbol{p}_1$ and the collision parameter b, g being the relative velocity. This limits the applicability of the results to dilute gases for which only bimolecular collisions are of importance (i.e. $n\sigma^3\ll 1$; σ is the diameter of the molecules.)

The solution of the integral equation requires the introduction of the classical angle of deflection $\chi(b,g)$ for a two molecule collision, which is given by:

$$\chi(b_1g)=\pi-2b\int_{r_m}^{\infty}\frac{dr/r^2}{\sqrt{1-F(r)}}\qquad F(r)=\frac{b^2}{r^2}+\frac{4\varphi(r)}{mg^2} \tag{2a, b}$$

in terms of which one defines the cross-section:

$$Q^{(s)}(g)=\int_0^{\infty}(1-\cos^s\chi)2\pi bdb \tag{3}$$

In terms of this cross-section, which is a function, of the relative velocity g one defines an average cross-section

$$P_{(r)}^{(s)}(T)=\int_0^{\infty}e^{-\gamma^2}\gamma^{2r+3}Q^{(s)}(g)\,d\gamma \tag{4}$$

where $\gamma^2=mg^2/4kT$. The transport coefficients can immediately expressed in these average cross-sections:

$$\frac{D_{11}}{S}=\frac{3}{8}\frac{(\pi mkT)^{1/2}}{P_{(1)}^{(1)}(T)}\qquad \mu=\frac{2}{5}\frac{\lambda}{c_v}=\frac{5}{8}\frac{(\pi mkT)^{1/2}}{P_{(2)}^{(2)}(T)} \tag{5, 6}$$

This expression of Chapman and Enskog is, except for a correction of minor importance, an *exact* expression for the density independent part of the viscosity and heat conductivity coefficients, μ and λ, but it should be reminded, that the derivation is based on the assumption, that the relative change of the macroscopic local quantities temperature, mean velocity and density over the range of one "free path" is small compared to unity, which excludes the application at very low densities, where the transport coefficients become density dependent.

1a) *Numerical calculations:* Calculations, based on the Lennard-Jones potential for the molecular interaction: $\varphi(r)=4\varepsilon[(\sigma/r)^{12}-(\sigma/r)^{6}]$, where ε and σ are two constants of the dimension of an energy (the depth of the potential field) and a length (the distance where the potential is zero), which vary from substance to substance, have been carried out by *Kihara and Kotani* (1942) and independently by *de Boer and van Kranendonk* (1948) and by *Hirschfelder, Bird and Spotz* (1949) for a large range of temperatures.

2) The *quantum theory of the transportphenomena*, has to be based on the quantum theoretical version of the Boltzmann equation, which according to *Uehling and Uhlenbeck* (1933) differs only in two respect from the classical analogue:

A) The classical scattering differential cross-section *2 b db* should be replaced by the quantum-mechanical analogue: $\sigma(g,\chi)2\pi\sin\chi\,d\chi$, which accounts for the *diffraction effects* resulting from the quantum-mechanical treatment of the two molecule collision. The well-known expression of the differential cross-section in the phase shifts $\eta_l(k)$, characterising the asymptotic behaviour of the wave function of relative motion, is:

$$\sigma(g,\chi)=\frac{1}{4k^2}\left|\sum_l(2l+1)\left(e^{2i\eta_l(k)}-1\right)P_l(\cos\chi)\right|^2 \tag{7}$$

where the state of the two molecule system is now characterized by the wave number $k={}^1/_2\,mg/\hbar$ (instead of g) and the angular momentum quantum number l (instead of b).

B) The collision hypothesis has to be modified by replacing every f by: $f(1\pm h^3f')$, f' being the distribution function in the final state. This accounts for the *influence of the statistics* but, as has been shown by Uehling and Uhlenback these terms give rise only to density dependent terms in the transport coefficients. As we are interested at present only in the density *in*dendent part, these factors $(1\pm h^3f')$ will be disregarded here.

Introduction of the differential cross-section (7), multiplied by $2\pi\sin\chi\,d\chi$, instead of the classical expression, $2\pi b\,db$, in equ. (3) for the cross-section, leads to

$$Q^{(1)}(k)=\frac{4\pi}{k^2}\sum_l(l+1)\sin^2(\eta_{l+1}-\eta_l) \tag{8a}$$

$$Q^{(2)}(k)=\frac{4\pi}{k^2}\sum_l\frac{(l+1)(l+2)}{2l+3}\sin^2(\eta_{l+2}-\eta_l) \tag{8b}$$

2a) *Very low temperatures* $\left(\text{where: } k\leq\frac{1}{\sigma}\right)$

All calculations based on the Lennard-Jones potential require the numerical evaluation of the phase shifts from the wave equation for the relative motion of two molecules. Calculations have been carried out by *de Boer* (1943) for ${}^4He$ (up to 3 °K), by *de Boer and Cohen* (1951) for ${}^3He$ (up to 5 °K) and by *Miyako* (1942) for H_2 and D_2 (at 15 and 20 °K).

2b) *Relatively high temperatures* $\left(\text{where } k\gg\frac{1}{\sigma}\right)$

Extension of the numerical method to higher temperatures seems inpracticable because of the large number of phase shifts which is required. Therefore *de Boer and Bird* (1951) used the results of the application of the W. K. B. method for the calculation of the phases. After transforming the result using the substitutions $k=\frac{1}{2}mg/h$ and $l(l+1)=\frac{1}{2}mbg/h$ one obtaines the following expressions:

$$\eta(b,g)=\eta^{\mathrm{I}}(b,g)+\eta^{\mathrm{II}}(b,g) \tag{9}$$

$$\eta^{\mathrm{I}}(b,g)=\frac{\mu g}{\hbar}\Omega(b,g),\qquad \Omega(b,g)=\frac{\pi}{2}+\frac{1}{b}\int_{r_m}^{\infty}\left[\sqrt{1-F(r)}-1\right]dr \tag{9a}$$

$$\eta^{\mathrm{II}}(b,g)=\frac{\hbar}{\mu g}\Psi(b,g),\qquad \Psi(b,g)=\pi-\frac{2}{3}b\int\frac{F'''/F'-(F''/F')^2}{\sqrt{1-F(r)}}\,dr \tag{9b}$$

where $F(r)$ is the function defined already in (2b).

Introduction of (9) in the cross-section (8) and making a systematic transformation of difference and summations into differential quotients and integrals then gives:

$$\begin{aligned}Q^{(1)}(g)&=4\pi\int_0^\infty\sin^2\frac{1}{2}\chi\,b\,db+\\&+\frac{\pi\hbar^2}{m^2g^2}\int_0^\infty\left[\chi-\Psi+b\Psi'+b\chi'+\frac{1}{3}b^2\chi''\right]\sin\chi\frac{db}{b}+\ldots\text{terms in }\hbar^4\ldots\end{aligned} \tag{10a}$$

$$\begin{aligned}Q^{(2)}(g)&=2\pi\int_0^\infty\sin^2\chi\,b\,db+\\&+\frac{\pi\hbar^2}{m^2g^2}\int_0^\infty\left[\left(\chi-\Psi+b\Psi'+\frac{4}{3}\chi''b^2\right)\sin 2\chi-2\sin^2\chi\right]\frac{db}{b}+\ldots\text{terms in }\hbar^4\ldots\end{aligned} \tag{10b}$$

where $\chi(b,g)=2d(b\Omega)/db$ is exactly the classical angle of deflection, equ (2a). One thus obtains a systematic series expansion in powers of h^2/mkT of which the first term independent of h is exactly the classical expression for the cross-section (3). Because of the fact, that in the temperature region, where the present series development applies, the attractive forces do not contribute to the transport coefficients, the cross-sections have been evaluated by *de Boer and Bird* (1953) for a repulsive field alone: $\varphi(r)=4\varepsilon\sigma^{12}/r^{12}$ numerically. Substitution of the result in (4) to obtain the average cross-section and finally in (5) to give the transport coefficients has the following result:

$$D_{11}=D_{11}^{(\mathrm{class.})}]1+0.00597\Lambda^{*2}/T^{*5/6}+\ldots\text{terms in }\Lambda^{*4}\ldots] \qquad (11a)$$

$$\mu=\mu^{(\mathrm{class.})}[1-0.01025\Lambda^{*2}/T^{*5/6}+\ldots\text{terms in }\Lambda^{*4}\ldots] \qquad (11b)$$

where $\Lambda^*=h/\sigma\sqrt{m\varepsilon}$ and $T^*=kT/\varepsilon$.

2c. Comparison with experiment.

The experimental data with which the quantum mechanical calculation can be compared are rather scarce. At very low temperatures there seems to be a satisfactory agreement with data on the viscosity as well as on the heat conductivity of gaseous ^{4}He. At high temperatures however, there is not much experimental evidence, which is accurate enough to test the small deviations, which are calculated above by the W.K.B. method.

Summarising, it may be concluded, that as far as the density independent part of the viscosity and heat conductivity is concerned, the quantum-theoretical treatment differs only from the classical treatment in the method of calculating the cross-section as a function of the relative velocity of a pair of molecules, a conclusion, which follows also from the recent considerations of *Mori and Ono* (1952). The experimental evidence, if available, is in agreement with the theoretical results.

Quantum Properties of the Condensed State.

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The quantum-theoretical treatment of a condensed system of interacting molecules meets with so much mathematical difficulties, that at present only a few methods of approximation are available, none of which gives a really accurate description of the condensed state.

1) Non interacting molecules (Ideal gas)

For a system of non interacting molecules the quantummechanical treatment can be given for *all* temperatures and densities. The theory includes the exchange effects, due to the symmetrisation of the wavefunctions. These exchange effects, which occur at such high densities and low temperatures, that $n\lambda^3$ becomes of the order of magnitude of unity and larger, ($n\lambda^3\geqq1$, where $\lambda=h/(2\pi mkT)^{1/2}\approx$ the De Broglie wavelength and $n=N/V=$ the number density). In particular for the symmetrical case there occurs the phenomenon of the Bose Einstein condensation at such high densities and low temperatures that $n\lambda^3=2.615$.

2) Interacting molecules (Real gases)

a) It is tempting to try whether the real system of interacting molecules cannot be treated by *perturbation theory* using the ideal gas as a first approximation. The actual interaction, in particular the repulsive field between the molecules is so large however, that so far this method has not been succesfull in obtaining quantitative results.

b) An accurate treatment is possible by developing the properties of the condensed state in a *power series of powers of the density*. This treatment includes the ordinary quantal *diffraction effects* in the molecular interaction, occurring at such low temperatures, that $\lambda\geqq\sigma$ (where λ is the De Broglie wavelength and σ is the diameter of the molecules) and also the *exchange effects*. The exchange effects, which in the case of the ideal gas are the only cause for the remarkable deviations from classical behaviour, are overshadowed however in the present case of real gases by the effect of the large repulsive field. Quantitative calculations, on the basis of the Lennard Jones potential field for the intermolecular interaction have been made for He for the terms in the series proportional to the density for very low temperatures (where $\lambda\geqq\sigma$) as well as for relatively high temperatures (where $\lambda\ll\sigma$). Here satisfactory agreement with the experimental data exists. The present method however only converges when $n\sigma^3\ll1$, which makes this treatment unsatisfactory at the highly condensed or liquid state where $n\sigma^3\approx1$.

c) An approximate treatment at high densities, where $n\sigma^3\approx1$, is the quantum mechanical version of the *cell-method*, originated by Lennard-Jones, in which every molecule is supposed to move in a cell formed by the repulsive potential field of the surrounding molecules. Already in the classical theory this is a suitable approximation only at high densities and low temperatures and only for those properties, which are insensitive for the entropy of disorder, which is not properly accounted for in this model. Quantitative calculations show, that the model accounts in first approximation for the quantum properties of the condensed state. However the model, being a one particle model does not account for any exchange effects. This is not a serious objection, because there are experimental indications, that most of the quantum deviations from the classical behaviour are not influenced very much by the exchange effects. It is possible however, to generalise the cell method so as to take into account the exchange effects also.

Statistical Mechanics of Condensation

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Although the theory of gaseous condensation has been essentially achieved by J. E. Mayer in orthodox statistical mechanics, it cannot be denied that there are some ambiguous points in his arguments. One of the defects in his theory lies in the neglect of volume-dependence of the cluster integrals, which results in the vanishing extension of the liquid phase. This, however, seems not to invalidate the theory in its essential point so far as we confine ourselves to the immediate neighbourhood of beginning condensation, since the volume of the gas enclosure may be imagined as large as we please compared with liquid droplets. A second point of difficulty concerns with an apparently inadequate treatment in the asymptotic evaluation of the configurational partition function. If we plot the molecular density ($1/v$) against the fugacity Z, then the very relation

$$1/v=\sum_l lb_lZ^l$$

is a result of that asymptotics, and one must be careful in drawing conclusions from the relation, in order not to step out beyond the validity of the relation. We may in general expect that $1/v$ increases without bound just beyond a critical value (Z_s) of Z, where, however, the relation itself ceases to have a meaning.

There has been a considerable controversy with respect to whether the condensation occurs just at the singular point of the gaseous phase function or the latter can be analytically continued to the region of supersaturation without encountering with a singular point. If we adhere to the older view points and want to describe the condensation phenomenon as a two phase equilibrium between the branches of a van der Waals loop, then we are apt to accept the second possibility. In this respect Mr. Katsura, Tohoku University, strongly supports the second point of view on the basis of his rather extended numerical computations on a lattice gas model consisting of finite, in fact very small, number of atoms. But it may depend on the inadequacy of inference from the small number case to the infinite number case.

Mr. Ikeda of Kyusyu University attempts to overcome Mayer's difficulty in the manner Dingle has done in his criticism of London's theory of Einstein-Bose condensation. Consider the Ursell-Mayer expansion

$$\Omega_N=\sum_{\Sigma lm_l=N}\Pi\frac{(Nvb_l)^{m_l}}{m_l\,!}$$

of the configurational partition function. Ikeda suggests to discriminate "large" clusters ($l=L\sim N$) from "small" clusters ($l\ll N$):

$$N=N_1+N_2=\sum lm_l=\sum Lm_L.$$

Large clusters are expected to exist only in small numbers, although the atoms in them may make up a large number N_2, and these should be treated separately from

small ones. If we make use of Mayer's asymptotic estimation $b_L\sim b_0{}^L$, it turns out to be irrelevant to decide how many large clusters there are, and one may suppose only one cluster b_{N_2} present. After this discrimination we can apply the usual method of searching for the maximum term in Ω_N. If

$$1/v<1/v_s\equiv\sum^{\infty}lb_lZ_s{}^l,$$

when $Z_s\equiv b_0{}^{-1}$, then there is no difference from the accepted part of Mayer's theory and here we have a gaseous phase. On the contrary, if

$$1/v>1/v_s,$$

the large cluster comes in and we have the relations

$$\log\Omega_N\sim N\sum^{\infty}vb_lZ_s{}^l-N\ln Z_s$$

Z_s being the fugacity of the condensing system and constant.

Ikeda's argument certainly puts one step forward, but as it appears to me, it contains one weak point in clear-cut separation between "large" and "small" clusters. There may be contributions from clusters of intermediate size.

Mr. Ikeda also prepared a very rigorous proof for the validity of replacing $b_l(V,T)$ by $b_l(\infty,T)$. On the usual assumption of hard core repulsion and finite short range (r_0) of molecular interaction, he first establishes the inequality

$$\left|\frac{1}{l}\ln\frac{b_l(V,T)}{b_l(\infty,T)}\right|\leq\frac{8\theta(l,T)r_0}{(1-\alpha)V^{1/3}},$$

where $b_l(\infty,T)$ are supposed all positive and

$$2r_0l/V^{1/3}\leq1,\quad 8lr_0\theta(l,T)/V^{1/3}\leq\alpha<1$$

and θ's are certain finite quantities connected with the behaviour of b's near the boundary of the gas enclosure. He further introduces a certain $l^*(N)$, which should serve to discriminate between large and small l, the cluster size. $l^*(N)$ should increase more rapidly than $\ln N$, but more slowly than $N^{1/3}$. After these and other preparatory considerations, he proceeds to treat the configurational partition function Ω_N expressed in terms of volume-dependent cluster integrals $b_l(Nv,T)$ in comparison with the ideal one $\Omega_N{}^\circ$ where all b's are replaced by their limiting value $b_l(\infty,T)$. The terms in Ω_N are classified according to whether it contains large clusters ($l>l^*$) or not:

$$\Omega_N=\Omega_{NS}+\Omega_{NL},$$
$$\Omega_N{}^\circ=\Omega_{NS}{}^\circ+\Omega_{NL}{}^\circ.$$

It is first shown that the small cluster part Ω_{NS} is positive and may be replaced by the small cluster part $\Omega_{NS}{}^\circ$ of the ideal system:

$$\lim_{N\to\infty}\frac{1}{N}(\ln\Omega_{NS}-\ln\Omega_{NS}{}^\circ)=0.$$

Then it is rigorously proved that for the ideal system and for $v>v_s$ the small cluster part only accounts for the entire partition function

$$\lim_{N\to\infty}\frac{1}{N}\ln\Omega_{NS}{}^\circ=\lim_{N\to\infty}\frac{1}{N}\ln\Omega_N{}^\circ(Nv,T)[\equiv\omega^\circ(v,T)]$$

Mr. Ikeda's main theorem reads as follows: The necessary and sufficient condition for the existence and coincidence of the limit

$$\lim_{N\leftarrow\infty}\frac{1}{N}ln\Omega_N(Nv,\,T)\equiv\omega(v,\,T)=\omega^\circ(v,\,T)$$

is given by the following: if the set of natural numbers N for which $\Omega_{NL}>0$ is infinite, then

$$\lim\sup\frac{1}{N}(ln\Omega_{NL}-ln\Omega_{NS})\leq 0,$$

if the set of numbers N for which $\Omega_{NL}<0$ is infinite, then

$$ln\left(1+\frac{\Omega_{NL}}{\Omega_{NS}}\right)^{-1}=o(N)\quad .$$

A sufficient condition for the validity of the theorem is

$$0\leq b_l(Nv,\,T)\leq b_l(\infty,\,T),\quad \text{for}\quad l\leq N.$$

The theorem has the following physical bearing: Since the ideal system has been proved to exhibit an analytical singularity at the condensation point, the same is true for the real system.

TIME TABLE

for

SECTION C

18th (Fri.) 9.00—12.00 a.m. **Molecules**

(1)	M. Kotani :	20 m
(2)	P. O. Löwdin :	30 m
(3)	J. C. Slater :	30 m
(4)	R. Mulliken :	30 m

18th (Fri.) 2.00—5.00 p.m. **Metals**

(1)	C. A. Coulson :	25 m
(2)	J. H. Van Vleck :	25 m
(3)	E. Wigner :	25 m
(4)	L. Onsager :	20 m
(5)	A. Morita :	10 m
(6)	R. Peierls :	5 m

19th (Sat.) 9.00—12.00 a.m. **Electron Theory of Intrinsic Magnetization**

(1)	J. C. Slater :	45 m
(2)	T. Matsubara & T. Yokota :	30 m

21st (Mon.) 9.00—12.30 a.m. **Antiferro- and Ferrimagnetism**

(1)	L. Néel :	20 m
(2)	T. Nagata :	10 m
(3)	H. Watanabe :	10 m
(4)	T. Okamura :	25 m
(5)	T. Nagamiya :	30 m
(6)	K. Yosida :	20 m
(7)	C. G. Gorter :	10 m

21st (Mon.) 2.00—5.00 p.m. **Magnetic Resonance Absorption and Relaxation**

(1)	N. Bloembergen :	30 m
(2)	T. Muto and M. Watanabe :	10 m
(3)	R. Kubo and K. Tomita :	25 m
(4)	H. Kumagai	25 m
(5)	K. Tomita and S. Koide :	10 m

22nd (Tue.) 9.00—12.00 a.m. **Dielectrics**

(1)	H. Fröhlich :	20 m
(2)	J. Yamashita :	25 m
(3)	K. S. Krishnan :	15 m
(4)	Y. Takagi :	30 m
(5)	H. Kawamura :	20 m

22nd (Tue.) 1.00—4.00 p.m. **Colour Centres**

(1)	F. Seitz :	30 m
(2)	Y. Uchida and M. Ueta :	25 m
(3)	T. Inui and Y. Uemura :	30 m
(4)	T. Nagamiya, T. Kojima, Z. Kanamori and T. Morita :	5 m

23rd (Wed.) 9.00—12.00 a.m. **Liquid Helium**

(1)	L. Onsager :	20 m
(2)	C. J. Gorter :	30 m
(3)	S. Nakajima :	20 m
(4)	R. P. Feynman :	20 m
(5)	T. Nishiyama and K. Kamiya :	10 m
(6)	K. Husimi :	10 m

23rd (Wed.) 2.00—5.00 p.m. **Superconductivity**

(1)	H. Fröhlich :	30 m
(2)	Y. Kitano, H. Nakano, S. Nakajima and S. Hayakawa :	15 m
(3)	Y. Kitano :	20 m
(4)	M. Toda :	20 m
(5)	H. Ichimura :	10 m

SECTION C

MOLECULES

— Sept. 18 (Fri.) Morning —

METALS

— Sept. 18 (Fri.) Afternoon —

ELECTRON THEORY OF INTRINSIC MAGNETIZATION

— Sept. 19 (Sat.) Morning —

ANTIFERRO- AND FERRIMAGNETISM

— Sept. 21 (Mon.) Morning —

MAGNETIC RESONANCE ABSORPTION AND RELAXATION

— Sept. 21 (Mon.) Afternoon —

DIELECTRICS

— *Sept. 22 (Tues.) Morning* —

COLOUR CENTRES

— *Sept. 22 (Tues.) Afternoon* —

LIQUID HELIUM

— *Sept. 23 (Wednes.) Morning* —

SUPERCONDUCTIVITY

— *Sept. 23 (Wednes.) Afternoon* —

Recent Simplifications in the Molecular-Orbital Theory of Calculating Energy Levels

Per-Olov Löwdin

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University of Uppsala, Uppsala, Sweden.

In the ASP–MO–LCAO method of treating the electronic structure of molecules and crystals, there is a characteristic difficulty connected with the fact that the energy expression contains a large number of atomic two-, three-, and four-center integrals.[1)] In the polyatomic case, the difficulty is twofold, since the number of terms is so enormous that, even if the numerical values of all the occurring integrals would be explicitly known, it is practically almost hopeless to get the energy by summing "term by term".

In order to solve this problem, we would here like to propose another approach: we will try to derive formulas for the molecular integrals of such a type as will permit the summations in the energy expression to be conveniently factorized and sometimes carried out analytically in a closed form. In this way, we will obtain new expressions for the energy levels as sums of only certain basic coulomb integrals, multiplied by matrix elements describing the bonding, the overlapping, and the asymmetry of the atomic orbitals involved.

The unrelativistic Hamiltonian operator for a molecular or crystal system with "fixed" nuclei is of the form

$$\boldsymbol{H}_{op}=W+\sum_{i}\boldsymbol{H}_i+\sum_{ik}{}' G_{ik}, \tag{1}$$

where W is the nuclear repulsion energy, $\boldsymbol{H}_i$ is the operator for the kinetic and potential energy of the electron i in the field of the nuclei, and $G_{ik}=e^2/2r_{ik}$ represents the electronic repulsion energy. For the sake of simplicity, let us consider a non-degenerate state, where each molecular orbital is occupied by two electrons having antiparallel spins. Approximating the total wave function by a single Slater determinant of the occupied MSO, we obtain for the energy[2)]

$$E=W+\sum_{\mu\nu}R_{\nu\mu}(\mu|\boldsymbol{H}|\nu)+\sum_{\mu\nu\kappa\lambda}\left(R_{\nu\mu}R_{\lambda\kappa}-\frac{1}{2}R_{\lambda\mu}R_{\nu\kappa}\right)(\mu\kappa|G|\nu\lambda), \tag{2}$$

where $(\mu|\boldsymbol{H}|\nu)$ and $(\mu\kappa|G|\nu\lambda)$ are the conventional matrix elements of the given (ordinary or eventually hybridized) atomic orbitals ϕ_μ, ϕ_ν, etc. with respect to the operators $\boldsymbol{H}_i$ and G_{ik}, respectively. R is further the bonding-overlapping matrix, defined by

$$R=\Delta^{-1/2}Q\Delta^{-1/2}, \tag{3}$$

where Δ is the overlapping matrix[3)] constituted by the elements

$$\Delta_{\mu\nu}=\delta_{\mu\nu}+S_{\mu\nu}=\int\phi_\mu\phi_\nu d\tau, \tag{4}$$

and $\boldsymbol{Q}$ is the charge-order and bond-order matrix[4] characteristic for the state under consideration.

The direct evaluation of the four-dimensional sum in the electronic repulsion energy in (2) is a formidable task, and, in order to avoid it, we will develop the AO's ϕ_ν and ϕ_λ in the complete orthonormalized systems $(\phi_{\mu'})$ and $(\phi_{\kappa'})$ of AO's associated with the same nuclei as the given AO's ϕ_μ and ϕ_κ, respectively:

$$\phi_\nu=\sum_{\mu'}\phi_{\mu'}\Delta_{\mu'\nu},\quad \phi_\lambda=\sum_{\kappa'}\phi_{\kappa'}\Delta_{\kappa'\lambda} \tag{5}$$

The expansion coefficients are here just the overlap integrals[5]. Substitution of (5) into the expressions for the matrix elements of $\boldsymbol{H}_i$ and G_{ik} will render the formulas[5]

$$\left.\begin{aligned}(\mu\,|\,\boldsymbol{H}\,|\,\nu)&=\sum_{\mu'}(\mu\,|\,\boldsymbol{H}\,|\,\mu')\,\Delta_{\mu'\nu},\\ (\mu\kappa\,|\,G\,|\,\nu\lambda)&=\sum_{\mu'\kappa'}(\mu\kappa\,|\,G\,|\,\mu'\kappa')\,\Delta_{\mu'\nu}\Delta_{\kappa'\lambda},\end{aligned}\right\} \tag{6}$$

which are of such a form as will permit the summations in (2) to be conveniently simplified. After introducing the new *rectangular* matrix

$$\bar{Q}_{\mu'\mu}=\sum_{\alpha}\Delta_{\mu'\alpha}R_{\alpha\nu} \tag{7}$$

we obtain in this way

$$E=W+\sum_{\mu\mu'}\bar{Q}_{\mu'\mu}(\mu\,|\,\boldsymbol{H}\,|\,\mu')+\sum_{\mu\mu'\kappa\kappa'}\left(\bar{Q}_{\mu'\mu}\bar{Q}_{\kappa'\kappa}-\frac{1}{2}\bar{Q}_{\mu'\kappa}\bar{Q}_{\kappa'\mu}\right)(\mu\kappa\,|\,G\,|\,\mu'\kappa') \tag{8}$$

For the square part of $\bar{\boldsymbol{Q}}$, which corresponds to the given AO's, we have simply $\bar{\boldsymbol{Q}}=\boldsymbol{\Delta}^{1/2}\boldsymbol{Q}\boldsymbol{\Delta}^{1/2}$ ($=\boldsymbol{Q}$, if $\boldsymbol{\Delta}$ and $\boldsymbol{Q}$ commutes). On the other hand, we note that the higher AO's $\phi_{\mu'}$ are in general essential in (8), since they preserve the three- and four-body character of the energy (2), which is of direct physical importance in many cases. For the alkali halide crystals, for instance, it has been shown that the many-body character of the cohesive energy (corresponding to the occurrence of many-center integrals) gives a reasonable explanation of the actual deviations from the Cauchy relations for the elastic constants.[6]

The expression (8) is really useful only if the higher overlap and coulomb integrals occurring are tabulated in advance in the literature. For practical applications, we have therefore also developed a modified form, where merely the given AO's are involved. Let us try to approximate the given charge density $\phi_\mu\phi_\nu$ by an expression of the form

$$\phi_\mu(1)\,\phi_\nu(1)=\frac{1}{2}\{M^{\mu}{}_{\mu\nu}\phi_\mu(1)\,\phi_\mu(1)+M^{\nu}{}_{\mu\nu}\phi_\nu(1)\,\phi_\nu(1)\} \tag{9}$$

The total charge of the distribution is preserved if

$$\frac{1}{2}(M^{\mu}{}_{\mu\nu}+M^{\nu}{}_{\mu\nu})=\Delta_{\mu\nu}=\delta_{\mu\nu}+S_{\mu\nu}, \tag{10}$$

and the individual values of the two coefficients in (9) should further be chosen to give a description of the "center of gravity" etc. of the distribution as correct as possible. By using (9), we obtain the approximate formula[7]

$$\left.\begin{aligned}(\mu\kappa\,|\,G\,|\,\nu\lambda)=\frac{1}{4}\{&M^{\mu}{}_{\mu\nu}M^{\kappa}{}_{\kappa\lambda}(\mu\kappa\,|\,G\,|\,\mu\kappa)+M^{\mu}{}_{\mu\nu}M^{\lambda}{}_{\kappa\lambda}(\mu\lambda\,|\,G\,|\,\mu\lambda)\\ &+M^{\nu}{}_{\mu\nu}M^{\kappa}{}_{\kappa\lambda}(\nu\kappa\,|\,G\,|\,\nu\kappa)+M^{\nu}{}_{\mu\nu}M^{\lambda}{}_{\kappa\lambda}(\nu\lambda\,|\,G\,|\,\nu\lambda)\},\end{aligned}\right\} \tag{11}$$

which is a generalization of previous formulas by Sklar[8] and Mulliken[9]. For angular dependent AO's formula (11) may be further improved by introducing additional terms which make it invariant with respect to the axes of quantization of the atoms involved. The form of (11) is analogous to (6), but the use of the multiplicators $\boldsymbol{M}$ has apparently strongly increased the convergency, since tests of (11) on two-center integrals by using Kotani's tables[10] for hydrogen-like functions have shown a surprisingly high accuracy (95–100%).

Let us further introduce the new square matrices

$$U_{\mu\nu}=\sum_{\alpha}M^{\mu}{}_{\mu\alpha}R_{\alpha\nu},\quad V_{\mu\nu}=\sum_{\alpha\beta}M^{\mu}{}_{\mu\alpha}R_{\alpha\beta}M^{\nu}{}_{\beta\nu}=V_{\nu\mu} \tag{12}$$

Here $\boldsymbol{U}$ is usually unsymmetric, $U_{\nu\mu}\neq U_{\mu\nu}$, and satisfies the relation $\sum_{\mu}U_{\mu\mu}=\sum_{\mu}Q_{\mu\mu}$. By substituting (11) into (2), we obtain finally for the energy

$$E=W+\sum_{\mu\nu}R_{\nu\mu}(\mu\,|\,\boldsymbol{H}\,|\,\nu)+\sum_{\mu\kappa}\left\{U_{\mu\mu}U_{\kappa\kappa}-\frac{1}{4}(U_{\mu\kappa}U_{\kappa\mu}+V_{\mu\kappa}R_{\kappa\mu})\right\}(\mu\kappa\,|\,G\,|\,\mu\kappa), \tag{13}$$

where the four-dimensional sum in the electronic repulsion energy has now been transformed into a two-dimensional sum containing only the simplest coulomb integrals. We note that also part of the second sum may be treated analogously.

Comparison with some previous results on aromatic molecules, ionic crystals, and alkali metals has shown that the numerical accuracy of formula (13) is remarkably good. In the π-electron approximation for treating conjugated compounds, this formula gives also a deeper understanding of some results recently intuitively obtained by Parr[11] by using a "rigid-sphere" model.

Further applications of formula (13) are now in progress.

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Work on Molecular Theory in the Solid State and Molecular Theory Group, M.I.T.

J. C. SLATER

The primary interest of this group is in solid-state theory, and our molecular work is aimed primarily at problems which can throw light on solid-state theory. First, we may mention the study of oxygen by Meckler, using configuration interaction methods. Our interest there was to study the correlation effect in a magnetic problem. A single determinantal function using molecular orbitals gives an energy for a non-magnetic state which lies above the energy of the magnetic state, either in O_2 or a ferromagnetic solid, at infinite internuclear distance. This is wrong, arising because the single determinantal function allows electrons of opposite spin to be close together, a difficulty which is removed by considering the interaction of a sufficient number of configurations. Meckler used 9 configurations for his triplet state, 12 for his singlet, and got good results.

Next we have studied the number of configurations required to give a similar treatment of other molecules, since we wish to know how important such configuration interactions are. In methane we should require 104 configurations to get comparable results, in water 18. We want particularly to study the question as to how much the various covalent bonds interact with each other in a complicated molecule: how important are the configurations with 0, 1, 3, or 4 electrons in a covalent bond, as compared to those with just 2 electrons in each bond? If only those with 2 electrons per bond were important, this would result in a large decrease in the number of configurations required: in methane from 104 to 22, in water from 18 to 12. Koster and Schweinler are studying the question by making a very careful configuration interaction study of water, using the 18 required configurations; they will find how important the 12 configurations with 2 electrons per bond are in comparison with the 6 which have different numbers of electrons.

If a complete configuration interaction is carried out, it is not necessary to get good molecular orbitals, but if only an incomplete problem is carried through, good molecular orbitals are essential. The determination of molecular orbitals, by Roothaan's method, has been very tedious. Consequently Meckler and Kaplan are looking into a method of carrying out the solution of the self-consistent LCAO method on the Whirlwind digital computer at M.I.T. They propose to use this method to study the ammonia molecule by a molecular orbital method.

Several other molecular studies are in progress, all aimed as these are toward an understanding of general methods of solving molecular and solid-state problems, rather than toward molecules of special chemical interest.

Methods of Approximation in the Theory of Electronic Structure of Molecules

Masao KOTANI

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(Abstract will be found on page 128)

Intermolecular Charge-Transfer Forces

R. MULLIKEN

(Abstract is not yet received, Aug. 28)

A New Approach to the Theory of Solids

C. A. COULSON

(Abstract will be found on page 130)

The Cohesive Energies of Alkali Metals

J. H. VAN VLECK

Harvard University

The standard method of computing the cohesive energies of alkali metals is one developed by Wigner and Seitz. The energy per conduction electron may be divided into three parts (a) the energy of an electron in the ground state (b) the promotional or "Fermi" energy which arises because the exclusion principle restricts the number of electrons to a state (c) numerous corrections, notably correlation, internuclear repulsion, etc. The present paper is concerned entirely with methods of computing (a) and (b).

In the Wigner-Seitz procedure, the ground energy (a) is determined by specifying that the radial derivative of the wave function vanish at the boundary of the unit cell. The wave functions originally employed by Wigner and Seitz were obtained by numerical integration of the wave equation appropriate to a Hartree or Prokofjew field. However, in the region where the boundary condition is applied, the force field is almost perfectly hydrogenic, and the wave functions are confluent hypergeometric functions. The one consequential parameter is that which determines the mixing ratio of the two linearly independent solutions of the hydrogenic wave equation, which is conditioned by what happens to the electron when it penetrates into the non-hydrogenic region of the atom. The idea occurred to the writer that this parameter could be determined by using the empirical quantum defects, thereby avoiding the labor and uncertainty involved in constructing wave functions for the non-hydrogenic portions of the force field.

The detailed working-out of this idea was essayed by Kuhn. He first utilized what may be called the function-matching method. He found that there was a region of values of the radius r relative to a given nucleus such that the field is sensibly hydrogenic and such that at the same time the logarithmic derivative is a fairly continuous function of the energy. By extrapolation of the values obtained from the observed spectroscopic quantum defects of the free atom, Kuhn determined this logarithmic derivative as a function of the energy over the range needed in computing cohesive energies. By the matching of logarithmic derivatives, the appropriate linear combination of confluent hypergeometric functions could be estimated. The computation of these functions themselves is not too easy a task numerically, and Kuhn found that the best way of computing these functions was as a series in the energy parameter. This procedure for calculating confluent hypergeometric functions is an amplification of one previously used by Wannier and Jastrow. The coefficients in this development are expressible essentially in terms of Bessel functions in their dependence on the radius, and hence are not too difficult to calculate once the appropriate expansions have been developed.

The conventional W.K.B. method of approximating wave functions does not have sufficient refinement to permit the calculation of cohesive binding energies. However, after Kuhn had completed his calculations by the function-matching method, an important improvement of the W.K.B.-Langer method was developed by a Japanese physicist, Imai. The great advantage of the Imai formulas is that they provide quite good representations of the wave functions near the turning points, where the conventional W.K.B. method fails. Kuhn found that with Imai's method he could avoid the labor of the function-matching method in determining the energy of the ground state, and could obtain substantially as good agreement with experiment.

Kuhn's work has recently been extended by Brooks. He developed a formula expressing the proper linear combination of the two confluent hypergeometric functions in terms of the quantum defect. The formula itself is amazingly simple, but the underlying theory is fairly intricate, and perhaps somewhat lacking in rigor. This procedure makes the calculation of the energy of the ground state quite easy once tables of confluent hypergeometric functions are available.

In many ways the calculation of the Fermi energy is trickier and more difficult than that of the ground state. Brooks found with his new formulas that some of the original calculations of Kuhn of the Fermi energy were rather inaccurate and as a result was able to improve considerably the agreement with experiment. The question arises whether the Imai method can also be used to calculate the Fermi energy. This question has been investigated by Kambe at Harvard. The computations involve some subtleties not encountered in the calculations of the ground state because it is necessary to work with p wave-functions which in most cases have no turning points at the relevant range for energy values. Kambe finds that with the Imai method the calculated Fermi energy can apparently be computed considerably more accurately than in Kuhn's original work, but perhaps not as precisely as with the formulas of Brooks.

With the most refined forms of the various methods based on quantum defects which we have described, the calculated densities and binding energies for the various alkali metals agree with experiment much better than in the case of the earlier work of Wigner, Seitz, and others who employed explicit non-hydrogenic wave functions. In fact, the agreement is, if anything, better than one has any right to expect in view of the many corrections (c) which have to be applied, especially as regards the correlation energy. The observed and calculated cohesive energies are as follows:

	Li	*Na*	*K*	*Rb*	*Cs*	
Obs.	36.5	26.0	22.6	18.9	18.8	*Kg cal/mol*
Calc.	38.7	26.5	22.2	20.8	19.7	

The compressibilities can also be calculated fairly well, but this is a more difficult assignment, as it requires computation of the second derivative of the energy with respect to the distance.

Qualitative Theory of the Cohesion in Metals

E. P. Wigner

Professor Van Vleck told us of a way to describe the difference between the electronic energy in the free atom and in the crystal. This energy difference manifests itself as the cohesive energy. It consists of four parts. The first part, E_b, could be called the boundary condition correction. It is the lowering of the energy of the crystal electron due to the fact that the normal derivative of the wave function vanishes at the cell boundary while it is, at the same distance, negative in the atom. Professor Van Vleck told us about an accurate method to calculate this energy difference. It is easy to see that E_b is always negative and

$$E_b < \frac{\hbar^2}{2m}\int \overline{\psi}\, \mathrm{grad}_n\, \psi\, dS = \frac{\hbar^2}{2m}\int \frac{1}{2}\, \mathrm{grad}_n |\psi|^2\, dS \qquad (1)$$

where ψ is the atomic wave function and the integration is over the cell boundary.

The above expression gives, at the same time, an approximate value for E_b.

The second part in the energy difference is the Fermi energy E_f, i.e. the kinetic energy of the motion of free electrons. The third part is the exchange energy E_e. The last part E_4 contains a number of correction terms, all due to the interaction of electrons which, on the whole, compensate E_e. We have seen that a calculation of the four terms has been successfully carried out for the alkali metals and gave quite accurate values for the lattice constant and the cohesive energy. The latter turns out to be, essentially, equal to $|E_b+E_f|$. The E_b is negative and provides the binding which is, however, much diminished by the positive E_f.

One is tempted to extend these considerations to other metals. The total cohesive energy is much larger for these, and a less accurate calculation of E_b and E_f may therefore be expected to provide already some insight into the problem. The phenomenon of several allotropic modifications with only little different cohesive energies further strengthens the impression that the details of the structure do not affect the cohesive energy critically. On the other hand, this same phenomenon shows that yielding a good value for the cohesive energy should not be considered as proof that the underlying structure is correct.

There is a complicating factor in the consideration of solids formed by atoms with several valence electrons which does not appear in the case of alkalis: the interaction of the valence electrons already takes place in the free atom. This interaction leads, furthermore, to statistical correlations between the positions of the valence electrons which manifest themselves also in the configuration's leading to several terms of the atom. (This complication did not yet occur in the work of Herring and Hill.) These correlations are undoubtedly preserved to some degree also in the crystal but they are difficult to reproduce analytically and this could be done, so far, only very incompletely. For this reason one may just as well use the approximation $E_e+E_4=0$, i.e. take only E_b and E_f into account.

This was done recently by F. Stern in the case of Fe. He found that the Fermi energy is very much smaller than it would be for free electrons. The reason herefor is partly that the energy bands of the d electrons are degenerate and can accommodate 6 and 4 electrons, respectively, instead of the 2 electrons of s bands. In addition, the bands are much narrower than the s bands. The increased cohesive energy of iron is principally the result of this decrease of the Fermi energy.

One can arrive on the basis of these calculations to the following interpretation of the variations of the cohesive energy. The boundary correction increases as one goes along the series s, p, d, because the value of the expression (1) increases along this series. Furthermore, one obtains the largest boundary correction only in the case of s electrons by choosing the wave vector $k=0$; for p and d electrons the lowest state lies at the boundary of the Brillouin zone. This follows from earlier calculations of various authors and also from the way the wave functions at the various lattice points piece together most naturally to give a large value to (1). This fitting together can be done less perfectly for p and f than for s and d electrons.

The width of the band decreases along the series s, p, d. This results principally from the degeneracy of the p and d bands but also from the fact that, in the case of the s band, all the surface of the Brillouin zone lies high, in the case of the d band in particular, only relatively small parts of the band.

It follows that the cohesive energy is smallest if the valence electron is an s electron and the binding due to the second s electron should be very small indeed. It is likely, therefore, and this again follows also from earlier calculations, that a large part of the cohesive energy of the earth alkalies is due to p and d electrons. It is in agreement with this picture that the cohesive energy increases much more from the s to the s^2 configuration if the next electron is a d electron than if it is a p electron.

The cohesive energy is larger in the p zone but because of the relatively large Fermi energy decreases rather fast as one fills up the zone. Furthermore, there is no unfilled level close to the p level in the way in which a p or d level is close to the s level. As a result, the cohesive energy of the metallic lattice decreases rapidly as one approaches the end of the p zone. The phenomenon of decreasing cohesive energy is much less pronounced in the d zone and is manifest only at the end of it where the small high region of the zone has to be filled. The fluctuations of the cohesive energy toward the middle of the d zones appear to be connected with statistical correlations of the valence electrons in the atom which cannot be quite duplicated in the lattice.

Diamagnetism of Metals

L. Onsager

(Abstract is not yet received, Aug. 28)

Band Structure of Semi-Metals

Akira Morita

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We use the word "semi-metals" for the cases where the number of valence electrons present is just sufficient to fill the first zone, and some of the energy levels of the second zone lie lower than the highest levels of the first zone, or the energy gap between the first zone and the second zone is small.

The crystal structure of semi-metals has rather low crystal symmetry. Furthermore, even if the crystals are constituted of one kind of atom, they are constructed by two or more sub-lattices with the same structure and there is no any primitive translation of the lattice which put the one of them on the other. These properties have close relations to the band structure of semi-metals. On account of them, the energy bands become to be divided into two groups which slightly overlap each other, or are separated by a narrow gap from each other. And the lower group is almost or completely filled and the upper one is almost or completely empty. In order to make the circumstance clear, it is convenient to use the tight-binding approximation.[1-5].

In the tight-binding approximation, the energy $E(\boldsymbol{K})$ is given as the root of the secular equation

$$|H_{i\alpha,\, i'\alpha'} - E\Delta_{i\alpha,\, i'\alpha'}| = 0, \tag{1}$$

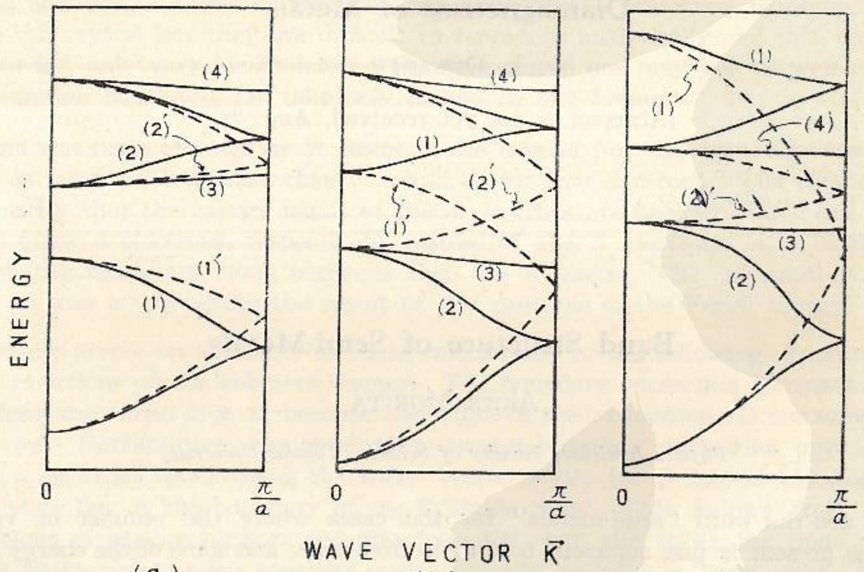
where

$$H_{i\alpha,\, i'\alpha'} = \int \varphi_{i\alpha}{}^{*} H \varphi_{i'\alpha'}\, d\tau$$

$$\Delta_{i\alpha,\, i'\alpha'} = \int \varphi_{i\alpha}{}^{*} \varphi_{i'\alpha'}\, d\tau.$$

H is the one-electron Hamiltonian of the crystal and $\varphi_{i\alpha}$ is the Bloch function, constructed by the normalized i-orbital of an atom, concerning sub-lattice a. Here we discuss the energy $E(\boldsymbol{K})$ of the crystals with diamond structure and bismuth structure.

In the case of diamond structure, which is constructed by two f.c.c. sub-lattices and the first Brillouin zone contains one level per atom, the results obtained from (1) are shown by solid curves in Fig. 1 for $\boldsymbol{K}=(K_x,\ 0,\ 0)$ schematically. In the figures, dotted curves show the energy bands obtained by neglecting combinations between different orbitals. For example the curves (1′) and (2′) corresponds to $(\varphi_{sa}+\varphi_{sb})$ and $(\varphi_{p_x a}-\varphi_{p_x b})$ respectively. The energy bands (3) and (4) are doubly



(a)　(b)　(c)

Fig. 1.

degenerate. (a) corresponds to large interatomic distance, and in this case, the crystal becomes to be metallic. (b) and (c) correspond to small interatomic distance, and in these cases, the crystal becomes to be semi-metallic. The energy width of the forbidden zone is given, in the case (b), by

$$4(\gamma_s+\gamma_p)-(E_p-E_s)$$

and is given, in the case (c), by $8\gamma_p$, where E_s and E_p are the energy of separated atomic s- and p-orbitals in the crystal respectively, and γ_s and γ_p are the resonance energy of them between nearest neighbour sites. The results obtained recently by Herman[6] by using orthogonalized plane wave corresponds to the case (c).

In the case of bismuth structure, the first zone is, as shown in Fig. 2, a slightly deformed truncated octahedron with a three-fold rotational symmetrical axis (OA in the figure). Calculation by tight-binding approximation shows that energy contours characteristic to bismuth structure appear at points A, B, C and D in the figure. The energy contour at the point A has the form

$$\mathcal{E}_A(\boldsymbol{K}) = E_A + \frac{\hbar^2}{2m}(\alpha_1 k_\xi{}^2 + \alpha_1 k_\mu{}^2 + \alpha_2 k_\zeta{}^2)$$

and the others have the form

$$\mathcal{E}_C(K) = E_C + \frac{\hbar^2}{2m}(\alpha_2' k_\xi'^2 + \alpha_1' k_\mu'^2 + \alpha_1' k_\zeta'^2)$$

where

$$\alpha_1 = \frac{\pi m}{6\mathcal{E}\Gamma_A\hbar^2}(\gamma_1-\gamma_2)^2,$$

$$\alpha_2 = \frac{\pi m}{3\mathcal{E}\Gamma_A\hbar^2}(\gamma_1+2\gamma_2)^2,$$

$$\alpha_2' = \alpha_2\Gamma_A/\Gamma_C, \quad \alpha_1' = \alpha_1\Gamma_A/\Gamma_C,$$

$$\Gamma_A = |4(\gamma_1-\gamma_2)-(2\gamma_1'+4\gamma_2')|,$$

$$\Gamma_C = |4(\gamma_1-\gamma_2)-2\gamma_1'| > \Gamma_A,$$

$$E_A < E_C,$$

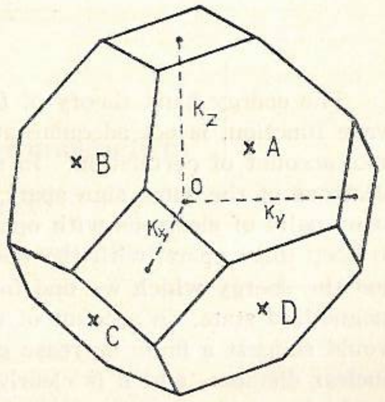


Fig. 2.

$\gamma_1, \gamma_2, \gamma_1'$ and γ_2' are quantities concerning resonance energies of p-orbital between nearest neighbour sites and $\mathcal{E}$ is small number dependent of crystal structure, for example $\mathcal{E}=0{,}0548$ for bismuth. $\mathcal{E}_A(\boldsymbol{K})$ corresponds to the energy contour which H. Jones[7] introduced to explain magnetic behaviours of bismuth at room temperature. $\mathcal{E}_C(\boldsymbol{K})$ corresponds to the ones which Blackman,[8] Schoenberg[9] and others introduced to explain de Haas-vom Alphen effect of bismuth. If we assume $|\gamma_2|/\gamma_1=4/11$, our results reproduce experimental results fairly good. This value is adopted by considering the nature of γ_1 and γ_2.

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On Diamagnetism of Metals

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Configuration Interaction and Ferromagnetism

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The energy band theory of ferromagnetism, depending on a single determinantal wave function, is not adequate at large internuclear distances, because it does not take account of correlation. In the magnetized state the exclusion principle keeps electrons of the same sign apart, while in the non-magnetized state, where we have many pairs of electrons with opposite spins, the exclusion principle does not operate to keep them apart, with the result that they are often found on the same atom, and the energy which we find for the unmagnetized state lies above that for the magnetized state, on account of the existence of positive and negative ions. This would suggest a finite decrease of energy on magnetization even at infinite internuclear distance, which is clearly incorrect. The discrepancy can be removed by combining various configurations, thus leading to a wave function taking proper account of correlation. Such correlation calculations are well known in molecular problems; the best known one is on hydrogen as solved by the molecular orbital method, and a similar calculation for oxygen has recently been made by Meckler. We might fear that since correlation exactly cancels the exchange effect at large internuclear distances, the same thing might happen at smaller distances too, invalidating the energy band theory of ferromagnetism, but the results on oxygen show that this is not the case.

The writer, Statz, and Koster, have tried to apply configuration interaction in a case of crystalline ferromagnetism, to see if we can investigate the correctness of the energy band method in this case. We have taken the simple case of a filled band (like the 3*d* band in a transition group element) lacking only two electrons. We then ask whether the lowest state of the system corresponds to the spins of the two holes being parallel (ferromagnetic case) or antiparallel (non-magnetic case). Fortunately this problem, being essentially a two-body problem, is simple enough to solve rather completely. We find that if the band is non-degenerate (for instance, a band formed from *s* orbitals), the non-magnetic state always lies lower; but if it is degenerate (for instance, the 3*d* band, formed from the 5-fold degenerate atomic orbitals), we can well have a ferromagnetic ground state. The energy difference between magnetic and non-magnetic states vanishes as it should at infinite internuclear distance; also, as in the elementary energy band theory, the ferromagnetic effect vanishes if the atoms are too close together, or the energy bands too broad.

The mechanism of ferromagnetism, from this study, is an intra-molecular one. With a degenerate band, it is possible for the two holes to be simultaneously on the same atom, in different atomic orbitals, with the same spin. By Hund's rule, the energy is lower if their spins are parallel than if they are anti-parallel. They retain their spin as they travel away from each other and normally they are found in distant parts of the crystal, where their spins do not affect each other. The model shows us how correlation comes in. At infinite internuclear distance, electrostatics makes it impossible for the two holes to be found on the same atom in the ground state, so that the energy difference between ferromagnetic and non-magnetic states disappears. At ordinary internuclear distance, however, they can often be found on the same atom, and ferromagnetism arises much as in the simple energy band theory.

Band Theory of Antiferromagnetism

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A collective electron theory of antiferromagnetism is developed along the line suggested by Slater.[1] This theory may be applicable to Cr and Mn which have been experimentally proved to have antiferromagnetic superstructures.[2]

We consider a crystal lattice composed of N atoms each having one s electron. Let $U_0(\boldsymbol{r})$ be the Hartree potential for an electron moving in this lattice, and $\varepsilon(\kappa)$ and $u(\kappa, \boldsymbol{r})$ be the energy band and the Bloch function respectively. κ is the wave vector of the electron. We introduce the Wannier function defined by

$$\phi(\boldsymbol{r}-\boldsymbol{R}) = \frac{1}{\sqrt{N}}\sum_{\kappa} e^{-i\kappa\cdot R}\, u(\kappa, \boldsymbol{r}), \qquad (1)$$

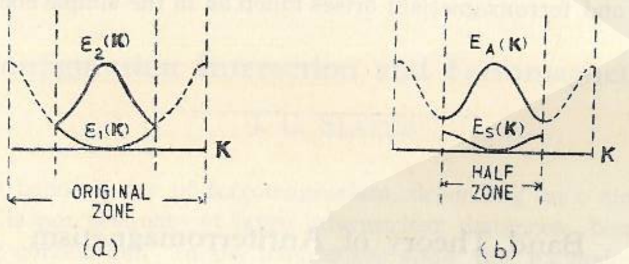
$\boldsymbol{R}$ being the positional vector of an atomic nucleus. As was pointed out by Slater,[3] the Hartree-Fock potential for an electron may be different for different direction of the spin in virtue of Pauli principle, which makes two electrons with parallel spins keep apart from each other. Then if the crystal lattice can be divided into two inter-penetrating sublattices, I and II, we may suppose Hartree-Fock potentials $U_+(\boldsymbol{r})$ and $U_-(\boldsymbol{r})$ which make + and − spin electrons move preferably on I and II sublattices respectively. In the absence of external field, it can be assumed further that $U_-(\boldsymbol{r})=U_+(\boldsymbol{r}+\boldsymbol{a})$, where $\boldsymbol{a}$ is a primitive translation vector of the lattice. Since $U_\pm(\boldsymbol{r})$ have a periodicity twice as large as that of $U_0(\boldsymbol{r})$, the energy band of electrons moving in these potential $U_\pm(\boldsymbol{r})$ will be split into two bands as in Fig. 1 (b). In the reduced zone scheme, these two bands are given by

$$E(\boldsymbol{\kappa})=\frac{1}{2}\left[\{\mathcal{E}_1(\boldsymbol{\kappa})+\mathcal{E}_2(\boldsymbol{\kappa})\}\pm\sqrt{\Delta^2+\{\mathcal{E}_1(\boldsymbol{\kappa})-\mathcal{E}_2(\boldsymbol{\kappa})\}^2}\right], \tag{2}$$

where

$$\Delta=\int\phi^*(\boldsymbol{r})\left[U_+(\boldsymbol{r})-U_-(\boldsymbol{r})\right]\phi(\boldsymbol{r})\,d\boldsymbol{r}, \tag{3}$$

and $\mathcal{E}_1(\boldsymbol{\kappa})$ and $\mathcal{E}_2(\boldsymbol{\kappa})$ represent respectively each of two different branches of $\mathcal{E}(\boldsymbol{\kappa})$ regarded as a two-valued function of the reduced wave vector $\boldsymbol{\kappa}$ (Fig. 1).



(a)　　(b)

Fig. 1. Energy as a function of κ, in (a) potential $U_0(r)$; (b) potential $U_\pm(r)$.

In deriving (2), we have made an approximation to neglect the overlapping between two different Wannier functions $\phi(\boldsymbol{r}-\boldsymbol{R})$ and $\phi(\boldsymbol{r}-\boldsymbol{R}')$ $(\boldsymbol{R}\neq\boldsymbol{R}')$. If we denote the lower energy band given by (2) as $E_S(\boldsymbol{\kappa})$ and the higher one as $E_A(\boldsymbol{\kappa})$, the corresponding eigenfunctions for the +spin are obtained as

$$\left.\begin{aligned}\Psi_{+S}(\boldsymbol{\kappa},\boldsymbol{r})&=\cos\theta_\kappa\psi_1(\boldsymbol{\kappa},\boldsymbol{r})+\sin\theta_\kappa\psi_2(\boldsymbol{\kappa},\boldsymbol{r}),\\ \Psi_{+A}(\boldsymbol{\kappa},\boldsymbol{r})&=\sin\theta_\kappa\psi_1(\boldsymbol{\kappa},\boldsymbol{r})-\cos\theta_\kappa\psi_2(\boldsymbol{\kappa},\boldsymbol{r}),\end{aligned}\right\} \tag{4}$$

where

$$\left.\begin{aligned}\psi_1(\boldsymbol{\kappa},\boldsymbol{r})&=\sqrt{\frac{2}{N}}\sum_{\substack{\text{Sublattice}\\ \text{I}}}e^{i\boldsymbol{\kappa}\boldsymbol{R}_{\text{I}}}\phi(\boldsymbol{r}-\boldsymbol{R}_{\text{I}}),\\ \psi_2(\boldsymbol{\kappa},\boldsymbol{r})&=\sqrt{\frac{2}{N}}\sum_{\substack{\text{Sublattice}\\ \text{II}}}e^{i\boldsymbol{\kappa}\boldsymbol{R}_{\text{II}}}\phi(\boldsymbol{r}-\boldsymbol{R}_{\text{II}}),\end{aligned}\right\} \tag{5}$$

and

$$\cot 2\theta_\kappa=\frac{\Delta}{\mathcal{E}_1(\boldsymbol{\kappa})-\mathcal{E}_2(\boldsymbol{\kappa})}. \tag{6}$$

For the −spin, the energy band are the same as (2) and the eigenfunctions are obtained by interchanging $\psi_1(\boldsymbol{\kappa},\boldsymbol{r})$ and $\psi_2(\boldsymbol{\kappa},\boldsymbol{r})$ in (4). When all the electrons of + and − spins fill the lower bands, we get a state having antiferromagnetic superstructure. The width of the energy gap between the lower and higher bands is given by Δ, which can be determined as a function of temperature in the following way. In our approximation, the probability of finding out a + spin electron on one of I-sublattice points will be given by

$$A=\frac{2}{N}\sum_\kappa\left\{\frac{\cos^2\theta_\kappa}{e^{\alpha+\beta E_S(\kappa)}+1}+\frac{\sin^2\theta_\kappa}{e^{\alpha+\beta E_A(\kappa)}+1}\right\} \tag{7a}$$

and that on one of II-sublattice points by

$$B=\frac{2}{N}\sum_\kappa\left\{\frac{\sin^2\theta_\kappa}{e^{\alpha+\beta E_S(\kappa)}+1}+\frac{\cos^2\theta_\kappa}{e^{\alpha+\beta E_A(\kappa)}+1}\right\} \tag{7b}$$

where $\beta=1/kT$ and α is a constant determined from the condition

$$\frac{N}{2}=\sum_\kappa\left\{\frac{1}{e^{\alpha+\beta E_S(\kappa)}+1}+\frac{1}{e^{\alpha+\beta E_A(\kappa)}+1}\right\}. \tag{8}$$

Therefore, if we denote the 'intra-atomic' exchange integral by I_0 and the 'inter-atomic' exchange integral between nearest neighbors by I_1, then the mean exchange energy of a + spin electron on one of I−sublattice points is given by

$$AI_0+zBI_1 \tag{9}$$

and that on one of II-sublattice points by

$$BI_0+zAI_1, \tag{10}$$

where z is the number of nearest neighbors to an atom. The difference (9)−(10) is just equal to Δ because of the definition (3). Thus we have

$$\begin{aligned}\Delta&=(A-B)\,(I_0-zI_1)\\ &=\frac{2(I_0-zI_1)}{N}\sum_\kappa\cos 2\theta_\kappa\left\{\frac{1}{e^{\alpha+\beta E_S(\kappa)}+1}-\frac{1}{e^{\alpha+\beta E_A(\kappa)}+1}\right\}.\end{aligned} \tag{11}$$

It is not difficult to show that if

$$J=(I_0-zI_1)>0 \tag{12}$$

Δ determined from (11) is finite at 0°K and it decreases with increasing temperature until the antiferromagnetic superstructure breakes down at a critical temperature, above which the splitting of the energy band disappears. Accordingly (12) is the necessary condition for antiferromagnetism to occur, but not a sufficient condition, because for a sufficiently narrow band the ferromagnetic state is proved to have lower energy than the antiferromagnetic state at 0°K. The theory above presented will be easily extended to the case of the degenerate d bands.

An interesting result concerning the mean magnetic moment of atom will be brought about by our theory. From our point of view, electrons of both spins can migrate on the I-sublattice points as well as on the II-sublattice points, though there exists a slight difference in electron's preference for stay on each of two sublattice points, and therefore both spins cancel with each other on each lattice point, leaving but a small fractional net moment per atom. In fact, we can easily see that the mean magnetic moment per electron μ is given by

$$\mu=(A-B)\,\mu_0=\frac{\Delta}{J}\,\mu_0, \tag{13}$$

where μ_0 is the Bohr magneton. Basing upon the formula (13), we can show that the larger is the width of the energy band the smaller μ/μ_0 becomes, and that μ/μ_0 is always smaller than unity and decreases with increasing temperature. In this way the fractional magnetic moment observed in the experiments of neutron diffraction on Cr and Mn[2] may be interpreted by our theory.

The magnetic properties calculated from our model are also of some interest. Above the critical temperature we have nothing but an ordinary paramagnetic metal, whereas below the critical temperature our model gives rise to a parallel susceptibility $\chi_\parallel$ which decreases to zero with decreasing temperature and a perpendicular susceptibility $\chi_\perp$ which is nearly constant.

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A Prepared Discussion

J. H. Van Vleck

(The title is not known, Aug. 28)

Ferrimagnetism

L. Néel

(Abstract is not yet received, Aug. 28)

Antiferromagnetism of $CuCl_2 \cdot 2H_2O$

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When Néel published his theory of antiferromagnetism in 1936,[1] he assumed in his computation an anisotropy energy of uniaxial symmetry and derived the susceptibility as a function of applied field strength and the orientation of the applied field with respect to that symmetry axis. A striking result he obtained is that, when the field is applied along the direction of easy magnetization (that is, parallel to that symmetry axis) and exceeds a certain critical value H_c, the antiparallel system of spins turns from that direction to the one perpendicular to it. This is because the difference of the free energies $-1/2(\chi_\perp-\chi_\parallel)H^2$ due to the applied field H perpendicular and parallel to the spin direction is negative and overcomes the anisotropy energy for higher field strengths. Néel confined this computation to absolute zero.

In 1941 van Vleck[2] formulated the Weiss-type theory of antiferromagnetism and derived the parallel and perpendicular susceptibilities for an arbitrary temperature, but he did not explicitly take into account the anisotropy energy. In 1951[3] I introduced it explicitly into theory and discussed the susceptibilities and also the resonance phenomenon for an oscillating external magnetic field. In the same year, Yosida[4] extended my theory and treated the anisotropy of the susceptibility of MnF_2 as well as Néel's flopping of spins at an arbitrary temperature. Meanwhile we became very much interested in the report of the experiment on $CuCl_2 \cdot 2H_2O$ done at Leiden, and Yosida[5] (1952) worked out a theory applicable to this substance. This case is a bit different from other cases in that the magnetic ions Cu^{++} carry a spin of magnitude 1/2 and that the crystal possesses an orthorhombic symmetry. The anisotropy energy for spins of magnitude greater than 1/2 and a crystal of tetragonal or hexagonal symmetry may be assumed in the form $-DS_z^2$, but this is merely a constant for spin 1/2. He took according to van Vleck[6] (1937) the interaction between spins l and m as

$$\begin{aligned}-2J_{lm}\sum_{x,y,z} S_{lx}S_{mx}+C_{lm}(2S_{lz}S_{mz}-S_{lx}S_{mx}-S_{ly}S_{my})+D_{lm}(S_{lx}S_{mx}-S_{ly}S_{my})\\+E_{lm}(S_{lx}S_{my}+S_{ly}S_{mx})+F_{lm}(S_{lz}S_{mx}+S_{lx}S_{mz})+G_{lm}(S_{ly}S_{mz}+S_{lz}S_{my}),\end{aligned}\tag{1}$$

where J_{lm}, C_{lm}, D_{lm}, E_{lm}, F_{lm}, G_{lm} are coupling constants which depend on the vectorial distance between l and m. If this expression is averaged over the orientations of the spin m and summed over the lattice sites m surrounding l, we have an anisotropic Weiss-type Hamiltonian for the spin l of the form

$$\begin{aligned}a_xS_x^+<S_x^->+a_yS_y^+<S_y^->+a_zS_z^+<S_z^->\\+c_xS_x^+<S_x^+>+c_yS_y^+<S_y^+>+c_zS_z^+<S_z^+>,\end{aligned}\tag{2}$$

where S^+ outside $< >$ stands for S_l and $< >$ means the thermal average. The indices + and − mean the two sublattices of the antiferromagnetic arrangement of spins.

Another complicacy in $CuCl_2 \cdot 2H_2O$ is that the g-factor for each spin is a tensor. Paramagnetic resonance measurement by Itoh[7] at room temperature provides us data for that. Taking all these into account, Yosida computed the susceptibility and also the resonance frequency of this salt. In particular, his computation of the resonance frequency could explain the majority of Ubbink's[8] observations.

In the mean time, Gorter[9] (1952) published a paper in which he stressed the importance of the anisotropy of the Weiss-field factor, that is, the unequalness of a_x, a_y, a_z (and also of c_x, c_y, c_z) in (2), as well as the anisotropic character of the spin moment, that is, the tensor character of g. The latter has actually been neglected in Yosida's computation below the Curie point. However, I can show that these two theories are equivalent if the notations used in Yosida's paper

$\boldsymbol{M}^+$, $\boldsymbol{M}^-$ (magnetization vectors of the + and − sublattices) and $\boldsymbol{H}$ (applied static field)

are read as

$N\mu_B\langle \boldsymbol{S}^+\rangle$, $N\mu_B\langle \boldsymbol{S}^-\rangle$ (μ_B: Bohr magneton, N: number of spins per cm^3) and $\boldsymbol{H}'$ defined by

$$H_x'=(g_x/2)\,H_x,\quad H_y'=(g_y/2)\,H_y,\quad H_z'=(g_z/2)\,H_z, \tag{3}$$

and $\chi_\parallel$ and $\chi_\perp$ are related with the observed susceptibility by

$$\chi_\parallel=(2/g_x)^2\chi_{aa} \tag{4}$$

(χ_{aa}: both the applied field and the spin direction are parallel to a),

$$\chi_\perp=(2/g_y)^2\chi_{ba}=(2/g_x)^2\chi_{ab} \tag{5}$$

(χ_{ba}: applied field parallel to b and spin direction parallel to a, χ_{ab}: a and b interchanged).

The a-axis is the easiest direction of the spins and b is the intermediate axis in $CuCl_2{\cdot}2H_2O$. By the way, it will be remarked that the experimental data[10] do not fit in very well to the second equality of (5), especially when the temperature is close to the Curie point.

Eqs. (4) and (5) are easy to see, but other things become clear only when we construct the equation of motion with the Hamiltonian (2):

$$i\hbar\dot{\boldsymbol{S}}^\pm=[\boldsymbol{S}^\pm,\,(2)\,], \tag{6}$$

which can be written as

$$\dot{\boldsymbol{S}}^\pm=\gamma\boldsymbol{S}^\pm\times\boldsymbol{H}^\pm{}_{\text{eff}}.\qquad(\gamma=2\mu_B/\hbar) \tag{7}$$

Here $\boldsymbol{H}^\pm{}_{\text{eff}}$ is the sum of $\boldsymbol{H}'$ and the anisotropic Weiss molecular field for a fictive + or − spin with a scalar g equal to 2.

Gorter confined himself to absolute zero, but he has derived a very interesting result. This is that, when the external field is in the ac-plane, there exists a hyperbola, with H_x and H_z as coordinate axes, of such a property that, if the field is inside it, the spin axis is in the neighbourhood of the a-axis, but if the field comes outside it, the spin axis turns and comes to coincide with the b-axis. We can derive this critical hyperbola for an arbitrary temperature in a very simple way as follows. We shall denote the direction cosines of the spin axis as α, β, γ and those of the applied field as α_H, β_H, γ_H. In order to find the equilibrium direction of the spin axis, we construct the free energy:

$$\begin{aligned}&-\frac{1}{2}\chi_\parallel H'^2(\alpha\alpha_H+\beta\beta_H+\gamma\gamma_H)^2\\&-\frac{1}{2}\chi_\perp H'^2\,[1-(\alpha\alpha_H+\beta\beta_H+\gamma\gamma_H)^2]+K_1\beta^2+K_2\gamma^2,\end{aligned} \tag{8}$$

where K_1 and K_2 are the anisotropy constants which are in a certain relation with a's and c's of (2). The equilibrium direction can be found by looking for the minimum of this free energy under a supplementary condition $\alpha^2+\beta^2+\gamma^2=1$. This is a typical eigenvalue problem, and the result for the critical hyperbola is

$$\frac{H_x'^2}{2K_1}-\frac{H_z'^2}{2(K_2-K_1)}=\frac{1}{\chi_\perp-\chi_\parallel}. \tag{9}$$

Now, the resonance frequency can be obtained by solving (7) in the neighbourhood of the equilibrium position. The major part of this has been done by Yosida, but I have found an additional result that the resonance occurs for a certain range of temperature at the critical field strength. At the critical field, the spin system turns in the ab-plane, and there is an orientation at which resonance takes place. All the main features of Ubbink's experiment can be explained in this way. Details of the comparison between theory and experiment will be reported in the conference, together with our another additional little calculation of the change of the Curie point with the strength of the applied field.

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Problems of Anisotropy energy of Antiferromagnetics and of Ferrites

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Sources of the anisotropy energy of antiferromagnetic substances can be considered to consist of the following three parts. The first part is the anisotropy of the crystalline electric field around magnetic ions, the second is the magnetic dipole interaction between magnetic ions and the third is the anisotropic exchange interaction between them. Which is the most predominant among these three sources depends not only upon the species of the magnetic ions and the crystal structure but also upon the superstructure due to the spin orientation. For instance, Keffer[1] has shown that in MnF_2 with a crystal structure of a rutile type, the anisotropy energy is mainly reigned over by the magnetic dipole interaction which makes the direction of spins parallel to the c-axis. However, in the case of MnO_2[2] which has the same crystal structure as MnF_2 this interaction makes the spins point in the plane perpendicular to the c-axis on account of the difference in the magnetic superstructure. Moreover, in CoF_2 with the same structure, the measurements of the anisotropy of the susceptibility by Stout and Matarrese[3] seem to suggest that the anisotropy of the crystalline field makes a considerable contribution. On the other hand, Van Vleck and Kittel[4] have recently pointed out that the anisotropic exchange interaction which is considered to be a main origin of the anisotropy energy of the ferromagnetic metals would become important also in the antiferromagnetic substances. Such circumstances would be the case for the anisotropy energy of the ferrites.

We shall here report the results calculated about the anisotropy energy of $CuCl_2 2H_2O$ on which the systematic experiments have been made by Gorter and his collaborators, and the results of the theoretical work made by Kotani on the anisotropy of the ferrites, especially the anisotropy of the g-factor.

a) *The origin of the anisotropy energy in* $CuCl_2 2H_2O$.

Since the crystal structure of $CuCl_2 2H_2O$ is orthorhombic, its anisotropy energy may be expressed by the following form:

$$f_{an.}=\kappa_1\beta^2+\kappa_2\gamma^2, \tag{1}$$

where β and γ are the direction cosines of the common axis of + and − spins with respect to the a- and b-axes. From the experimental results of the antiferromagnetic resonance absorption studies on $CuCl_2 2H_2O$ by Gorter and his collaborators[5] can be deduced the values of κ_1 and κ_2 per one Cu^{2+} ion as follows:

$$\kappa_1=0.8\times10^{-2}\mathrm{cm}^{-1},\quad \kappa_2=2.6\times10^{-2}\mathrm{cm}^{-1}. \tag{2}$$

In this substance the anisotropy energy from the anisotropy of the crystalline field does not appear because the magnitude of the spin of a Cu^{2+} ion is equal to $^1/_2$. The anisotropy constants arising from the magnetic dipole interaction can be calculated by the Ewald-Kornfeld method as Keffer[1] has done for MnF_2. Basing on the superstructure inferred by Poulis and Hardeman[6] from the analysis of the proton resonance absorption experiments, and assuming the isotropic g-value equal to 2, we obtain the following results:

$$\kappa_1=-0.027\times10^{-2}\mathrm{cm}^{-1},\quad \kappa_2=2.91\times10^{-2}\mathrm{cm}^{-1}. \tag{3}$$

As seen from the comparison of these results with (2), κ_2 is of the same order of magnitude as the experimental value but κ_1 is too small and opposite in sign and so the remaining anisotropy or that from the anisotropic exchange interaction would play an important role in the anisotropy in the ab-plane.

A free Cu^{2+} ion is in ^2D state but in the crystal the five-fold degeneracy of ^2D is lifted by the crystalline field and the Cu^{2+} ion in this substance is considered to be in its lowest energy state which is still doubly degenerate due to its spin. The perturbation energy consisting of the L-S coupling and the exchange interaction gives rise to, in the third order approximation, the following anisotropic exchange interaction between two Cu^{2+} ions which are in these lowest states:

$$V=\frac{1}{3}\sum_i\frac{J_{ig}\lambda^2}{(E_i-E_g)^2}\sum_{\substack{x,y,z\\ \mathrm{cyclic}}}\{(|l_{1x}|^2+|l_{1y}|^2+|l_{1z}|^2-3|l_{1x}|^2)s_{1x}\cdot s_{2x}-3l_{1x}l_{1y}(s_{1x}s_{2y}+s_{1y}s_{2x})\} \tag{4}$$

where J_{ig} is the exchange integral between two Cu^{2+} ions one being in the ground state and the other in the excited state corresponding to the higher energy by E_i-E_g. λ is the coefficient of the L-S coupling and l_{1x}, l_{1y},… mean the matrix element of the orbital angular momentum between the excited state and the ground state. The anisotropic exchange interaction expressed by (4) does not essentially differ from that derived by Van Vleck[4].

It would be difficult to calculate precisely the part of the anisotropy energy arising from (4). Therefore, for only an order estimation, we assume a Cu^{2+} ion to be subjected by the crystalline field which has an orthorhombic symmetry whose principal axes lie in the direction joining a Cu^{2+} ion and its nearest Cl^- ion, the direction of the b-axis and that perpendicular to them (this direction nearly coincides with the direction joining a Cu^{2+} ion and its next nearest Cl^- ion), and estimate the values of the energy differences E_i-E_g from the experimental g-value at room temperature obtained by Itoh and his collaborators.[7] Then we obtain the following values of κ_1 and κ_2:

$$\kappa_1=-0.027\times10^{-2}\,\mathrm{cm}^{-1},\quad \kappa_2=2.91\times10^{-2}\,\mathrm{cm}^{-1}. \tag{5}$$

The sum of (5) and (4) has the same order of magnitude as the experimental values. Thus it may be concluded that in $CuCl_2 2H_2O$, the anisotropy in the ab-plane arises mainly from the anisotropic exchange interaction and that in the ac-plane mainly from the magnetic dipole interaction.

b) *A contribution of the orbital angular momentum to the magnetization of the ferrites.*

Since the studies made by Néel[8], it has been considered that in the ferrites $Fe_2O_3\cdot MO$ (M=Mn, Fe, Co, Ni, Cu) having a so-called inverse spinel structure, a half of Fe^{3+} ions are situated on the 8f site and the other half of them and M^{2+} ions are on the 16c site, and the spins of the 16c site point antiferromagnetically in the opposite direction to those of the 8f site, and therefore the spontaneous magnetization of ferrites arises from the magnetization of M^{2+} ions which is the difference between the magnetization of the 16c site and that of the 8f site. According to the measurements by the several authors[9], the magnitude of the magnetization corresponds to the value arising from only spins for Mn-ferrite but for Fe-, Co-, Ni-, Cu-ferrites it is a little larger than that value. This is because in these ferrites, the orbital angular momentum of an M^{2+} which is in a non-S state makes more or less contribution to its magnetization, as has been pointed out by Néel[9].

Kotani has applied a general method developed by himself to this problem of treating a contribution of the orbital moment to the magnetization of ferrites. He has first made a reasonable assumption that the most important exchange interaction in ferrites is that between an M^{2+} ion and its next nearest Fe^{3+} ion situated on the 8f site because its nearest magnetic ions exist along the perpendicular direction with respect to the position of an intermediary O^{2-} ion. Then we have only to take into consideration the system including an M^{2+} ion and its next nearest six Fe^{3+} ions which have no orbital moment. At sufficiently low temperatures we can consider the spins of Fe^{3+} ions to align in the easy direction and so our seven ion problem would be reduced to one ion problem. Thus we can discuss the magnetic moment of ferrites by solving the Hamiltonian of one M^{2+} ion consisting of the crystalline field, the

L-S coupling, and the exchange interactions with six Fe^{3+} ions. As the simplest case, the value of the g-factor of Cu-ferrite has been calculated.

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Resonance Absorption Experiments in Ferrites

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Using four microwave frequencies from 9,450 *Mc/sec* to 47,000 *Mc/sec* at room temperature and at the temperature of liquid nitrogen, the microwave resonance in Ni ferrite and Mn ferrite was observed with polycrystalline spherical specimens, and it was found that the frequency and temperature dependence of the apparent g factor could be explained in relation to the internal field in the material.

Many spherical specimens whose diameters varied from about 3 *mm* to 0.2 *mm* were polished from sintered blocks, and after studying the size effect on the g factor at each frequency, the resonance fields H_z were determined by extrapolating to zero diameter.

The results obtained at room temperature are shown in Table I. The g factor at each frequency, designated by g^* in the table, was calculated by Kittel's formula

$$\nu=\gamma^*/2\pi\ H_z, \tag{1}$$

where $\gamma^*=g^*e/2\,mc$. The g factor obtained was found to depend on the frequency, that is, it approached the value of $g^*=2$ at shorter wave length.

Table I. g^* factor at room temperature calculated by Kittel's formula $\nu=\gamma^*/2\pi\ H_z$.

Material	*Frequency* ν *(Mc/sec)*	*Resonance Field* H_z *(oersteds)*	g^*
$NiOFe_2O_3$	9,450	2,780	2.43
	18,400	5,930	2.22
	23,500	7,660	2.19
	47,000	15,870	2.12
$MnOFe_2O_3$	9,450	3,120	2.16
	18,400	6,320	2.08
	23,500	8,190	2.05
	47,000	16,620	2.02

As the spectrosplitting factor is a materially constant factor, it should have the same value at any frequency.

To eliminate the frequency dependence of the apparent g factor, it may easily be seen from the data in the table that the relation between frequency and the resonance field should be formulated

$$\nu=\gamma/2\pi\ (H_z+H_i) \tag{2}$$

where $\gamma=ge/2\,mc$. The most probable values of H_i were found from the resonance data to be 507 O*e* for Ni ferrite and 278 O*e* for Mn ferrite. Substituting these values in Eq. (2), we obtained the g values for both ferrites as shown in Table II.

Table II. g factor calculated by $\nu=\gamma/2\pi\ (H_z+H_i)$.

Material	*Frequency* ν *(Mc/sec)*	g
$NiOFe_3O_3$	9,450	2.05
	18,400	2.04
	23,500	2.06
	47,000	2.05
$MnOFe_2O_3$	9,450	1.99
	18,400	1.99
	23,500	1.98
	47,000	1.99

These g values are independent of the frequency and agree satisfactorily with one another within experimental errors.

The same experiments were further made at the temperature of liquid nitrogen, and the apparent g factor at lower temperature was found to be greater than that obtained at room temperature. But by using the Eq. (2), the temperature dependence of the apparent g factor is reduced to the temperature change of H_i. The results are listed in Table III, where H_i of both ferrites were found to be 601 O*e* for Ni ferrite and 504 O*e* for Mn ferrite.

Table III. Resonance data at the temperature of liquid nitrogen.

Material	*Frequency* ν *(Mc/sec)*	*Resonance Field* H_z *(0e)*	g^* *calculated by* $\nu=\gamma^*/2\pi\ H_z$	g *calculated by* $\nu=(\gamma/2\pi)(H_z+H_i)$
$NiOFe_2O_3$	9,450	2,640	2.56	2.08
	18,400	5,780	2.27	2.06
	47,000	15,620	2.15	2.06
$MnOFe_2O_3$	9,450	2,750	2.45	2.07
	18,400	6,100	2.15	1.99
	23,500	7,950	2.11	1.99
	47,000	16,390	2.05	1.99

As illustrated in the table, the g factor was found to be independent of both frequency and temperature. In the table the results obtained at longest wave length show some discrepancy in comparison with the results obtained at shorter wave length: they seem to be due to the unsaturated magnetization at low temperature which resulted from the increased magnetic anisotropy.

Though still lacking in theoretical background, the present experiment shows that the Eq. (2) should be used in the determination of the true g value of ferrite.

Lastly, eliminating the frequency shift and the size effect, the half line widths of absorption lines of nickel and manganese ferrites, and the g values in nickel-zinc and manganese-zinc binary ferrites were also determined.

A Prepared Discussion

T. Nagata

(The title is not known, Aug. 28).

The Temperature Dependency of Susceptibilities of Ferrites on the Basis of the Theory of Ferrimagnetism

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As a test case for the theory of ferrimagnetism developed by Néel, the temperature dependency of magnetization of various mixed ferrites has been analysed on the basis of that theory, and qualitative agreement between theory and experiment was found, assuming appropriate parameter values included in the theory. A similar analysis of the magnetization vs. composition was also made by Néel himself at almost the same time as the author has done, and the major part of the results of his analysis was naturally in accord with the author's. Some points, however, were at variance with ours:

1) Néel's analysis started from the data of susceptibilities above the Curie point of various mixed ferrites (Ni—Zn ferrites), and gave increasing values of interaction constants n and $|\alpha|$ ($8f$—$16c$, and $8f$—$8f$ interactions, respectively) with increasing Zn content. If one extrapolates these values to the composition of Zn-ferrite, he

will find that they are fairly large ($n > 600$, $|\alpha| > 6$). As an interpretation of these parameter values, Néel assumed that a strong superexchange coupling existed between the ions in the $8f$ position with the type Fe-Zn-Fe. On account of the minor fraction of the Fe ions in that position present, this assumption is very doubtful.

2) If one analyses Serres' data of the susceptibilities of Zn-ferrite following Néel's procedure of evaluation of the interaction parameters, he finds that the experimental points do not fit with Néel's theoretical curve. This suggests that Néel's analysis is not adequate for the explanation of the data.

The author, on the other hand, has assumed that the values of α were nearly constant, say -0.4, over the whole range of the compositions of the mixed ferrites. The theoretical curves of the spontaneous magnetizations and the Curie points are not so much affected by the α values: the results would be essentially the same if we used Néel's large values. The results of the calculated χ (susceptibilities) vs. temperature curve is indeed affected by them, and is therefore in disaccordance with experimental curve, giving lower χ values than experiment. However, the inclination of the $1/\chi - T$ curve is in rough agreement with experiment. The author believes that these facts are probably caused by the following two effects:

1) Contamination by Fe^{2+} ions. The ferrous ions will be introduced by the high temperature heat treatment of the sample or might have been included in the raw material (α-Fe_2O_3). This will have an effect of raising the Curie temperature as well as the χ values near the Curie temperature, and hence of increasing the inclination of the $1/\chi - T$ curve.

2) Zn-ferrite is not a completely normal ferrite. The parameter λ (which is the measure of the number of Fe^{3+} ions migrated into the $8f$-position) is not zero, but is equal to some small finite value. The increase of λ results in increase of the high temperature susceptibilities and hence in decrease of the inclination of the $1/\chi - T$ curve.

So the observed $1/\chi - T$ curve of Zn-ferrite may be interpreted as the combined result of the two effects just mentioned. The same effects will, of course, affect the $1/\chi - T$ curve of ferrites of other compositions.

Magnetic Relaxation in Solids

N. Bloembergen

The interations and the establishment of thermal equilibrium in electronic and nuclear spin systems are discussed. The history of theory and experiment is outlined briefly. The early non-resonant absorption and dispersion experiments of Gorter determine spin-lattice and spin-spin relaxation times, which can now also be obtained from resonance experiments. The complete theoretical interpretation of the relaxation times in paramagnetic salts is impeded by the crystalline field and exchange interactions. If the spin levels are unequally spaced, more than one characteristic time is necessary to describe the relaxation.

The nuclear spin systems are simpler as the magnetic dipolar interaction is the only important one. As far as the nuclear spin-lattice relaxation time is concerned, three classes of solids can be distinguished: metals, solids with internal motion, and crystals in which lattice vibrations constitute the only type of thermal motion. In the latter, relaxation occurs either by spin diffusion to paramagnetic impurities or by quadrupole interaction. The anisotropy of the relaxation and the contact between two systems of different spins is discussed. The concept of spin temperature, and in particular the negative spin temperature, is analyzed. Non-resonant experiments with nuclear spin systems may provide an interesting and better check on the theories of spin-spin relaxation than the experiments with paramagnetic salts. The simultaneous flip-flop of electron and nuclear spins in a metal is the basis for a method proposed by Overhauser to achieve nuclear polarization.

Finally the spin system with a large exchange interaction is discussed. The equivalence of the random modulation of the dipolar interaction by exchange and by thermal motion is stressed. Experimental evidence is given that the exchange interaction acts as a thermal reservoir for the spins which have absorbed magnetic energy. Thus the absorbed quanta in a magnetic resonance experiment are first transformed into exchange energy before they are dissipated to the lattice. Although somewhat similar relations seem to hold below the Curie point, many problems in ferromagnetic relaxation have not yet been solved. A phenomenological description of the damping in ferromagnetic materials can be given, which includes shape-dependent effects. Certainly a distinction must be made between the "magnetic part" and the "exchange part" of the spin system. The first spin system consists of the spin waves of zero wave number, the second system with a much larger heat capacity contains all other spin waves. Imperfections may play an important role in establishing thermal contact between these two systems. Characteristic experimental times are of the order of 10^{-8} sec. The transition to paramagnetic relaxation with exchange above the Curie point is continuous.

Broadening in Nuclear Magnetic Resonance Absorption

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The purpose of this paper is to develope the quantum-mechanical Fourier-integral method for computing line contours of resonance absorption and to apply it to the discussion of nuclear magnetic resonance absorption.

As several authors have already noticed, the intensity distribution of resonance absorption is related to the auto-correlation $<M(t+\tau)M(t)>$ of the dipole moment M, which represents the interaction of the system with the radiation field. The dipole moment operator $M(t)$ in the Heisenberg representation develops in course of time following the equation of motion characterized by the Hamiltonian $H=H_0+H'$, where the unperturbed Hamiltonian H_0 is assumed such that will give sharp resonance lines if the natural broadening is neglected and the perturbation H' is supposed to be mainly responsible for the observed broadening. The explict solution of the time-dependence of $M(t)$, with the initial condition $M(0)=M$, is conveniently expressed as

$$M(t)=M_t^{(0)}+M_t^{(1)}+M_t^{(2)}+\cdots\cdots$$

where

$$M_t^{(0)}=e^{-iH_0t}Me^{iH_0t}$$

$$M_t^{(n)}=\int_0^t idt_1\int_0^{t_1} idt\cdots\cdots\int_0^{t_{n-1}} idt_n[\cdots[M_t^0, H(t_1)], H'(t_2)]\cdots\cdots[H'(t_n)]$$

with

$$H'(t)=e^{-iH_0t}H'e^{iH_0t}.$$

We assume the canonical distribution for the initial distribution of the system, so that the average in the definition of auto-correlation is the quantum-mechanical average with the density matrix $e^{-\beta H}/Tr\,e^{-\beta H}$. Computing the traces, $Tr\{e^{-\beta H}M_t^{(n)}M\}$, we obtain the characteristic function of the intensity distribution, which is an expansion in powers of the coupling parameter involved in the perturbation. A complete calculation is usually impossible, but we can obtain useful informations about the line shape even if we terminate the series at a certain stage. Thus, for example, from the second order approximation, we can guess an approximate characteristic function valid in the second order of the coupling parameter, which can be transformed into the required intensity distribution. The nature of this procedure is similar to that of the method employed by P. W. Anderson and P. R. Weiss for the exchange narrowing in paramagnetic resonance, although mathematical forms are different.

As an illustrative example, we apply the method to the dipolar broadening of the nuclear magnetic resonance absorption, in which the narrowing is due to the motion of nuclei. Since we confine ourselves to the second order of the dipolar coupling constant, the extreme case of rigid lattice corresponds to a Gaussian form of intensity distribution. It is seen that, when the narrowing mechanism is in act, the intensity distribution is always of Cauchy's type (damped oscillator type) around the center of the absorption line, but falls off more rapidly in the wings. This is very much similar to the case of exchange narrowing discussed by Anderson and Weiss. In the case of strong narrowing, the exact expression for the breadth of the Cauchy distribution, which is $1/T_2$ by usual terminology, is easily given in terms of the correlation functions of nuclear coordinates. The final results are almost equivalent to those given by Bloembergen, Purcell and Pound, but there are some minor corrections. One can remove, in this form of the theory, some of the ambiguities in the former theories and also see the general features of the narrowing, either by diffusion process or by molecular rotation.

In particular, we propose a typical function to describe the diffusion narrowing;

$$f(\omega)=\frac{e^{\gamma^2}}{\pi\omega_1}\sum_{n=0}^{\infty}\frac{(-)^n}{n!}\gamma^{2n}\frac{(\gamma+n/\gamma)}{(\gamma+n/\gamma)^2+(\omega/\omega_1)^2},$$

where ω_1 stands for the breadth in the limit of rigid lattice, and $\gamma=\omega_1\tau_0$, τ_0 being the relaxation time. This function goes to be Gaussian as $\gamma\to\infty$ and to be of Cauchy's type for very small γ.

Other applications of the theory, especially those to the narrowing due to molecular rotation, will also be discussed.

Resonance Absorption Experiments of Paramagnetic Salts

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(1) Frequency Dependence of Resonance Line Shapes by Two Dissimilar Cu^{++} Ions Under Exchange Coupling

Line shapes of paramagnetic resonance absorption are determined by dipolar and exchange coupling between magnetic ions, and they depend upon the frequency of microwaves used in the resonance absorption. When we have two dissimilar ions in unit cell, for instance $CuSO_4\cdot 5H_2O$ or $CuK_2Cl_4\cdot 2H_2O$, the crystalline fields of two kinds of ions are different, and their g-tensors have different orientations. Then, in general direction of applied static magnetic field, we can expect two absorption lines corresponding to two different g-values, g_1 and g_2. But, in some cases, these two lines unify to one by the effect of exchange coupling, the g-value of the unified line being about the mean of g_1 and g_2. In this case, we can expect remarkable frequency dependence of line shapes. The unification of two lines may occur when

$$2J\geqq|g_1-g_2|\beta H$$

where $2J$ is the exchange energy, β the Bohr magneton and H the applied magnetic field. When we use higher frequency of microwave, the magnetic field at resonance increases and finally $|g_1-g_2|\beta H$ becomes comparable with or larger than $2J$. In this case, the unified two lines are separated to original ones. These sorts of separation of absorption lines in $CuSO_4\cdot 5H_2O$ has been already observed at $\lambda=0.8$ cm by Bagguley and Griffiths[1].

We have observed resonance lines in $CuK_2Cl_4\cdot 2H_2O$ at wave lengths of 6.5, 3.2, 1.6, 1.1, 0.78 and 0.54 cm. From the results of X-ray analysis of this salt, it is expected that g_1 and g_2 are most separated when the static magnetic field is normal to (110) plane. Two resonance lines in this direction unify to one when we use wave lengths longer than 1.1 cm, though the half widths of resonance lines get broader with decreasing wave length. At $\lambda=0.78$ cm, the resonance line seems to be composed of two lines, and we can observe clearly two lines at $\lambda=0.54$ cm.

When we assume that $2J=|g_1-g_2|\beta H$ at $\lambda=0.78$ cm, and substitute the values of g_1 and g_2 obtained by two peaks at $\lambda=0.54$ cm, we have $2J\geqq 0.09\ \mathrm{cm}^{-1}$.

g_1 and g_2 coincide in the c-axis, in which direction, the resonance lines are sharpest, and the widths in this direction "decrease" when the wave length is reduced. The possibility of this phenomena was pointed out by Anderson and Weiss[2] and is called "10/3 effect" by them, as the widths at sufficiently long wave length will be about 10/3 times larger than that at sufficiently short wave length. The width observed in our experiment at longest wave length is three or four times of that at shortest wave length.

(2) Anomalous Resonance Absorption of Cu^{++} Ion in Copper Acetate and Copper Propionate

Bleaney[3] and we[4)5] have observed anomalous absorption of Cu^{++} in copper acetate, in which two Cu^{++} ions (each $S=1/2$) are strongly coupled by exchange coupling to form an equivalent spin of $S=1$. We have recently observed similar anomaly in copper propionate.

(3) Paramagnetic Relaxation Time of Cu^{++}.

We have observed line widths of resonance lines of diluted salts of Cu^{++} ions $((Cu+Mg)(NH_4)_2(SO_4)_2\cdot 6H_2O$, $(Cu+Zn)SO_4\cdot 7H_2O)$ from room temperature to 100°K. The relaxation time deduced from these data are plotted against T. Most of observed points scatter about a curve $\propto T^{-2}$, whereas the data of Cu^{++} by Bagguley and Griffiths[6] lie on a curve $\propto T^{-1}$. Results of Van Vleck's calculation[7] of Cr^{+++} and Ti^{+++} are compatible with our data. But we must take into account that the crystal lattice contracts at lower temperature and, in some cases, the crystalline field changes with temperature.

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On the Spin-Lattice Relaxation in the Nuclear Magnetic Absorption in Solids

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—Attempt to search for any possible mechanism for spin-lattice relaxation in solids which have no trace of the residual paramagnetic ions involved—

According to Bloembergen, the paramagnetic impurities involved artificially or naturally within the crystal are supposed to play a decisive role in the nuclear spin-lattice relaxation phenomena. Although Bloembergen's idea is really ingenious one, still the following questions seem to remain unsettled so far.

(1) Whether all the crystals artificially purified as possible involve always the amount of residual paramagnetic impurity sufficiently responsible for the experimental data of spin-lattice relaxation time or not?

(2) How long is the spin-lattice relaxation time of the ideally purified crystal? The question seems to me very important both theoretically or experimentally in view of Bloembergen's idea being unable to be completely settled at present.

With the above questions in mind, we have attempted to search for any possible mechanism for spin-lattice relaxation except for Waller's one, and proposed a few years ago a new mechanism which is the second or third order effect due to the dipolar interaction between electronic and nuclear spins (δH_{eN}) and to the electronic interaction with lattice vibrations (δH_{eL}), being taken to become a quite natural extension of the same phenomena in metals.

As in the mentioned relaxation in metal and in the similar phenomena of the optical dispersion in insulator (electronic transitions participate in the virtual process only), we have adopted, for simplicity, "one electron approximation" for working out the above mentioned transition process, allowing for the Fermi's factor of electron distribution over the energy bands, as usual in the theory of electronic conduction.

Stimulated by Bloembergen through his correspondence to us, we have endeavoured to improve our former theory on the basis of many electron problem. The Slater's determinantal wave functions and the corresponding energies of both ground and excited states of the electronic system can be computed approximately along a similar way to the method of Roothaan in the molecular structure. Once the electronic wave functions have been set up in Slater's sence, the following computation of the transition matrix components are quite straightforward according to the previous mechanism mentioned above. The detailed computation, however, shows that the non-vanishing matrix components of δH_{eN} are always connected with the vanishing ones of δH_{eL} and vice versa, which results into the vanishing transition probability, quite different from the previous results of one electron approximation.

In view of the above situation, we are, instead of δH_{eL}, forced to take into consideration the $\vec{u}$ dependent part of the spin-orbit interaction of crystal electrons, namely,

$$\delta H_{s0}=\frac{e^2\hbar^2}{4m^2c^2}\,\frac{Z^*}{i}\sum_{s,j}\left\{-\frac{[\vec{u}_s\times grad_j]}{|\vec{r}_j-\vec{R}_s|^3}+3\frac{(\vec{r}_j-\vec{R}_s)\cdot\vec{u}_s}{|\vec{r}_j-\vec{R}_s|^5}[(\vec{r}_j-\vec{R}_s)\times grad_j]\right\}\vec{\sigma}_{ej}\,,$$

together with δH_{eN} for the effective interactions responsible for the spin-lattice relaxation. The derived transition probability for the "direct process", W_d, becomes of the following form for the case of polycrystal.

$$W_d=(2T_1)^{-1}=\frac{9}{20}\,\frac{Z^{*2}}{\pi}\mu_N{}^2\mu_e{}^6\frac{a^5}{M\hbar^4}\,\frac{1}{u_1{}^5}\,\frac{(2\mu_N H)^3}{(\Delta E_1)^4}\,\frac{\exp(2\mu_N H/kT)}{\exp(2\mu_N H/kT)-1}\cdot(\gamma_2 K+\beta_1 J)^2(A+A')^2\cdot$$

$$\left\{(1+4\delta_1{}^5)\left[\frac{32}{35}-\frac{16}{21}\left(\frac{\Delta E_1}{\Delta E_3}\right)^2+\frac{512}{315}\left(\frac{\Delta E_1}{\Delta E_3}\right)^4\right]-(1-\delta_1{}^5)\left[-\frac{8}{35}+\frac{6}{7}\left(\frac{\Delta E_1}{\Delta E_3}\right)^2-\frac{548}{315}\left(\frac{\Delta E_1}{\Delta E_3}\right)^4\right]\right\},$$

$$A=\int_0^\infty dR_s/dr\cdot R_p/r\cdot dr,\quad A'=\int_0^\infty (dR_p/dr\cdot R_s/r+2R_pR_s/r-3R_pR_s/r^2)\,dr.$$

ΔE_1 and ΔE_3 represent the mean energy distances of the excited singlet and triplet bands from the ground state and the remaining quantities have the same meaning as in the previous paper.

The above result becomes considerably small although Waller's theory gives still far smaller value for W_d and, moreover, is understood to give a lower limit for W_d and an upper limit for the relaxation time, since both contributions from the excitation levels lying just below the continuum of the excited band and from the Raman process have not been involved in the above transition probability. If the ratio of the relaxation times for the direct and Raman processes, computed by the previous method of one electron approximation, were supposed to be still valid in our case of many electron treatment, the relaxation times of the Raman process might be estimated to become $10^4\sim10^7$ times of that of the direct one ($T\gtrsim 10°K$).

As seen in the above mentioned discussions, we are unable to reach a final conclusion as yet, and the nuclear spin-lattice relaxation in solids is still an open problem unless the Raman process and the contribution of the excitation levels to the direct process are actually worked out; which computations are now in progress.

Dependence of Paramagnetic Resonance on Frequency and Crystalline Anisotropy

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The dependence of the line shape on resonance frequency in $CuK_2Cl_4\cdot 2H_2O$ will be discussed by K. Tomita taking the fourth moment into account.

Under the assumption that there is no change in line shape the dependence of line width on the crystalline anisotropy in copper ammonium Tutton salt will be discussed by S. Koide using tensor *g*-factor and the second moment.

Electrons in Dielectrics

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The energy levels of an electron moving in a periodic potential field have the well known band structure as first shown by F. Bloch[1]. In applying this result to electrons in solids the assumption is usually made that the interaction of an electron with the other electrons can be described in terms of a periodic field of force. In metals, or in the filled bands of insulators, it has not been possible, as yet, to justify this hypothesis. For single electrons in the conduction band of insulators, however, there is little doubt that the assumption holds as long as the atoms of the lattice are considered as fixed rigidly to the lattice points. On this assumption slow electrons in the conduction band can be considered as free provided the electronic mass is replaced by an effective mass m. The main purpose of the present discussion is to find the influence of the displacement of atoms from their respective lattice points on the motion of an electron. Such a displacement arises either through thermal vibration or through the interaction with the electron. The former essentially leads to a scattering of the electron while the latter can be expressed in terms of a change of the effective mass.

The interaction between the lattice displacements and an electron is particularly strong in the case of ionic crystals, and the present discussion is restricted to the following simple model: The crystal is described[2] by its polarization P considered as a superposition of the optical polarisation P_0 (due to displacement of bound electrons of the lattice) and the infra-red polarisation P_{ir}. The latter has a single resonance frequency $\omega/2\pi$ in the infra-red. For sufficiently slow electrons the optical polarisation can always be considered as inequilibrium, described by a high frequency dielectric constant ε_∞. Also P_{ir} can be regarded as a continuous function in space (and time). The whole system consisting of the lattice and a single electron is then described by a Hamiltonian

$$H=H_{el}+H_f+H_{int} \tag{1}$$

consisting of the contributions of the electron (H_{el}) the lattice field (H_f) and the interaction (H_{int}). By introducing $\hbar\omega$ as unit of energy, and

$$1/u=(\hbar/2m\omega)^{\frac{1}{2}} \tag{2}$$

as unit of length, a reduced, dimensionless Hamiltonian $H/\hbar\omega$ can be introduced which contains a single parameter α,

$$\alpha=\frac{1}{2}\left(\frac{1}{\varepsilon_\infty}-\frac{1}{\varepsilon}\right)\frac{e^2u}{\hbar\omega} \tag{3}$$

where ε is the static dielectric constant (e=electronic charge).

The problem as presented here is essentially one of field theory. The field in question has a single frequency $\omega/2\pi$ independent of the wave length, a fact which greatly simplifies the solution. If the interaction parameter α satisfies $\alpha<1$, then perturbation theory can be applied[3] to calculate the lowest energy level E_0,

$$E_0=-\alpha\hbar\omega \tag{4}$$

For many materials α is larger than unity. Thus for NaCl e.g., $\alpha\simeq6$ if the electronic mass is used for the value of m. To deal with this case a new method was developed by Gurari[4], and independently by Lee, Low and Pines[5] (cf. also[6]). This method is closely related to Tomonaga's[7] method of intermediate coupling. For the ground state the result (4) is found to hold, even outside the range of validity of perturbation theory. The wave functions used in this method differ, however, considerably from those of perturbation theory if $\alpha>1$.

Another result of perturbation theory[3] holds, however, for $\alpha>1$: The expectation value of the polarisation as function of the distance r from the electron is the same as in the case of a classical point charge if $r\gg1/u$. It deviates from it, however, if $r<1/u$, roughly as if the electron were smeared out over a sphere of radius $1/u$. An electron thus carries a certain polarisation with it; the whole system is often referred to as a polaron. The effective mass of a polaron is found to be[4,5]

$$m^*=m(1+\alpha/6) \tag{5}$$

i.e. it differs little from m for $\alpha=6$.

In the case of very strong coupling, i.e. very large α another approach can be made essentially due to Landau[8] and Pekar[9]. In this approach the dynamic properties of the lattice are neglected. On this assumption a polarisation of the lattice due to the electron exists which can be maintained in a self consistent way. It leads to an energy

$$E_L=-\frac{25}{256}\alpha^2\hbar\omega \tag{6}$$

Both results, (4) and (6) can be derived by variational methods, but (6) involves the additional assumption that the kinetic energy of the lattice is negligible. Clearly (4) is certain to be the more reliable result so long as $|E_0|>E_L$, i.e. $\alpha<10$. Values of $\alpha>10^{10}$ would either require extremely small values of the frequency ω (corresponding to wave lengths of the order of 10^{-1}cm.) or large effective electron mass m (as distinct from the polaron mass m^*) at least of the order of ten electron masses. In this case equation (5) for m^* will also be invalid, and a larger ratio m^*/m should be expected.

The above considerations hold essentially for the ground state of the system and for excited states less than $\hbar\omega$ above it. Higher energy states lead to the possibility of "free" quanta of the lattice. In equilibrium, at any temperature T different from zero, the number of free quanta is also different from zero and proportional to the volume. The energy of the system is then very much higher than $\hbar\omega$.

One should expect, however, that the system can then be considered as composed of a polaron and of free quanta, provided that their density is very low, and that $kT \ll \hbar\omega$. In this case the mean free path, or the relaxation time τ of a polaron required in the calculation of electric conductivity can be obtained in the usual manner. If perturbation theory holds, then[3)]

$$\tau = \frac{(3)}{2\alpha\omega}\left(e^{\hbar\omega/kT}-1\right) \tag{7}$$

Here the factor (3) should probably be removed for reasons indicated at the end of reference[3)]*.

The case $\alpha > 1$ where perturbation theory does not hold has been considered by Low and Pines[11)], and leads to a very similar result. The case in which $kT > \hbar\omega$ creates difficulties, however, which have not yet been overcome.

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* The calculation, due to Zienau[10)] contains a numerical error by a factor 2/3 which has been corrected by C. Herring (private communication).

The Quantum Theory of Dielectrics

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The dielectric properties of matters are usually described by the Clausius-Mosotti equation. Surely it holds very well for gases at moderate pressure, but with liquids or ionic crystals there are noticeable deviations from it. In the case of liquids the origin of the deviation is mainly ascribed to the fluctuations in the arrangement of molecular dipoles in it. Using the statistical mechanics Kirkwood and others have succeeded in deriving the formulas which give a good agreement with experiments. In the case of ionic crystals the above mentioned effect is supposed to be negligible. In solids, on the other hand, each constituent ion overlaps appreciably with its nearest neighbouring ions, then, as pointed out by Mott and others, the assumption of the point dipole is by no means a good approximation. As well known, the overlap of the electronic charge brings about the exchange interaction between ions, these circumstances lead us necessarily to use the quantum mechanical procedures.

In quantum mechanical computation of the dielectric constant it is convenient to use the relation between the dielectric constant κ (in static field) or κ_0 (in high frequency field) and the energy change of the total system ΔE under the influence of a homogenious external field F; $\Delta E = -1/2\chi F^2$ and $\kappa - 1 = 4\pi N\chi$. The energy change ΔE consists of two parts; ΔE_0 and ΔE_1, where ΔE_0 is the energy change of the constituent ions in free state, ΔE_1 is the change of the inter-ionic energy, which consists of the electrostatic energy and the exchange energy and S- energy between ions, under the influence of the external field. In order to compute the energy change ΔE by the Heitler-London approximation we shall here make use of the method of Slater-Kirkwood and adopt the method of Landshoff-Löwdin for evaluating the exchange integrals among the non-orthogonal wave functions. In the following we shall compute the dielectric constant of LiF and MgO, in which case the perturbed wave function for 2p-electron of a negative ion is assumed as follows:

$$\psi(\vec{r}) = \psi_0(\vec{r})\,(1+\lambda r\cos\theta),$$

where $\psi_0(\vec{r})$ is the unperturbed wave function and λ is the variational parameter. The deformation of the positive ion is neglected. Under these assumptions the energy change is expressed as follows:

$$\Delta E = -p_e F - \frac{1}{2}\,\frac{4\pi N}{3}\,p_e^2 + 3\lambda^2 + A\lambda^2 - p_x F - \frac{1}{2}\,\frac{4\pi N}{3}\,p_x^2 + Cx^2 - \frac{4\pi N}{3}\,p_x p_e + Bx\lambda,$$

where p_x $(=2ex)$ is the electric dipole due to ion displacement, p_e $(=4\overline{r^2}e\lambda)$ is that due to the charge deformation of a negative ion. The second term means the mutual interaction energy of the dipoles p_e, the sixth term that of p_x, the eighth term that between p_x and p_e, the third term means the change of the kinetic energy of a negative ion. Besides these it contains further three terms Cx^2, $Bx\lambda$ and $A\lambda^2$, which are caused by the change of the degree of charge-overlap due to the displacement or deformation of ions. Cx^2 is the usual repulsive potential in ionic crystals, and when the repulsive force is assumed to be effective only among the nearest neighbouring ions, C is given by $12a/\beta$: (β, compressibility; a, inter-ionic distance). It must be noticed that the linear terms of x and λ are canceled out by symmetry, but the term $Bx\lambda$ is not canceled out. The parameters x and λ are to be determined so as to minimize the energy change of the total system. In the case of high frequency field is to be assumed as zero. After elementary but rather laborious numerical calculations of A and B and using the observed value for C we have obtained the values of the dielectric constant as follows: κ_0 for LiF$=2.33$, that for MgO$=4.56$ and κ for FiF$=10.1$. The observed values are 1.92, 2.95 and 9.3 respectively. Also we have found out that the energy contribution from the Lorentz energies $-4\pi N p_e^2/6$ and $-4\pi N p_x p_e/3$ is almost canceled out by that from $A\lambda^2$ and $Bx\lambda$. Thus we find that the deviation from the Clausius-Mosotti equation is caused mainly by the above reasons.

As for the ionic crystal its dielectric constant has been considered to be nearly independent of temperature. The precise observation, however, has shown that the dielectric constant of the alkali-halide crystals increases actually with increasing temperature. Now, in order to work the effect of temperature upon the dielectric constant we must determine the wave functions so as to minimize the change of the total free energy in each temperature. The constants A, B and C depend upon temperature through the change of inter-ionic distance. When inter-ionic distance increases, the values of the constants become smaller, whose effect is usually larger than that of the decrease of the density. After some computations the temperature change of the dielectric constant of NaCl $(d\kappa/\kappa dT)$ becomes 3.2×10^{-4}, while the observed value is 3.75×10^{-4}.

From the theoretical consideration above it may be right for us to suppose that the energy change due to the electric field is well expressed by the quadratic form of two quantities p_x and p_e with three constants A, B and C. As it is a rather laborious task to determine these constants for each material theoretically, the more conventional method may be to determine them phenomenologically with experimental values of κ_0, κ and β. Then we shall have a energy formula for each dielectrics containing no arbitrary constant. According to these procedures we have found that the Lorentz energy $-4\pi Np_xp_e/3$ is almost completely canceled out by the term $Bx\lambda$ in NaCl crystals. Next using the above formula let us compute the "Reststrahlen-frequenz" of NaCl and compare it with the observed value. The computed value of the frequency of the transverse wave (ω_t) is 3.08×10^{13}sec.$^{-1}$, while the observed value is about 3.0×10^{13}sec.$^{-1}$ The good agreement may suggest the correctness of our procedures. Also the frequency of the longitudinal wave (ω_l) is computed as 4.79×10^{13}sec.$^{-1}$, with which the value of $(\omega_l/\omega_t)^2$ becomes 2.42, which is again nearly equal to the observed value $(\kappa/\kappa_0)=2.49$.

As for the static dielectric constant κ of MgO the above procedure has not succeeded in obtaining reasonable values for B and C. Then we have used another method, that is, we have determined these constants by using the three observed quantities κ_0, κ and ω_t instead of β. Then we have found out that so determined C value is about twice larger than that determined from the compressibility. This interesting fact may suggest that the nature of oxide crystals is in general not so simple as that of alkali-halide crystals.

Finally we further notice that from the above quadratic formula we can easily derive many useful formulas as written down in the book of Fröhlich.

Polarization Field in Ionic Crystals

K. S. KRISHNAN

(Abstract is not yet received, Aug. 28)

Ferroelectricity and Antiferroelectricity

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We consider a flat plate of an ionic crystal with electrodes on its both faces. The crystal may be decomposed into a suitable set of sublattices i, j,$\cdots$etc. Let the charge and electronic dipole moment of an ion which belongs to the i-th sublattice be denoted by e_i and p_i respectively, and the mean displacement of the i-th ions be denoted by z_i.

The free energy F of the system can be expressed as a sum of the following four terms: (1) the electrostatic energy U_e of all the mutual interactions among the ions with charges and moments at displaced positions and the surface charges distributed on the electrodes, (2) the work V necessary to polarize the ions.

$$V=\sum_i \frac{1}{v_i}\frac{\gamma_i}{2}p_i^2,$$

where $1/v_i$ is the number per unit volume of the i-th ions, and γ_i is a certain constant proportional to the rigidity of the electron cloud of the ions, (3) the mechanical energy W necessary to set up lattice strains on account of the relative displacements among the sublattices, namely

$$W=\sum_{i,j}[\lambda_{ij}(z_i-z_j)^2+\mu_{ij}(z_i-z_j)^4],$$

where the constants λ's and μ's can be given by the knowledge of the interaction energy of the ion pairs, and (4) the free energy Z due to thermal oscillation of the ions,

$$Z=\sum_{i,x}\frac{kT}{v_i}\log\frac{h\nu_{ix}}{kT}.$$

The ions are oscillating about the mean positions which are displaced from the lattice points, and the frequencies are functions of the relative displacements.

Any increase in the free energy of the total system must be equal to the work done from the outside. Hence, if it were assumed that p's and z's are independent of each other, we get

$$\partial F/\partial p_i=E\ \partial D/\partial p_i$$
$$\partial F/\partial z_i=E\ \partial D/\partial z_i$$

or

$$\gamma_i p_i=E+\sum_j(1/\varepsilon_0 v_j)\{p_j+e_j(z_j-z_i)\}f_{ij}, \tag{1}$$

$$\left.\begin{aligned}&v_i[\sum_j\{2\lambda_{ij}(z_i-z_j)+4\mu_{ij}(z_i-z_j)^3\}+\sum_{j,x}(kT/v_j)(\partial\log\nu_{jx}/\partial z_i)]\\&=e_i[E+\sum_j{}'(1/\varepsilon_0 v_j)\{p_j+e_j(z_j-z_i)\}f_{ij}]-p_i\sum_j{}'(1/\varepsilon_0 v_j)e_jf_{ij},\end{aligned}\right\}(2)$$

where f_{ij}, the coefficient of the local field, is to be calculated from the undisplaced lattice.

Eq. (1) shows that the electronic moment induced on the i-ion is proportional to the strength of the local field at the displaced site.[1] The left hand side of Eq. (2) is the restoring force due to W and Z, while the right hand side is the driving force due to electrostatic origins U_e and E.D. It must be noted that the term due to the i-th lattice itself drops from the summations in the right hand side; the driving force is therefore not the same as the local field even if the last term, moment multiplied by the field gradient, were neglected. But in such simple crystals as alkalihalides the right hand sides of Eqs. (1) and (2) turn out to agree on account of the conditions $f_{11}=f_{22}=f_{12}$ and $e_1+e_2=0$.

Solving these fundamental equations, we can in principle calculate all the dielectric properties of the given system. To start with, for the sake of simplicity, we have investigated an ionic crystal of the CsCl type.

Main features of the results obtained are as follows: (1) if both kinds of ions are poorly polarizable, the crystal turns out to be of normal properties; (2) if, on the other hand, one kind of ions happens to be highly polarizable, the other kind of ions becomes spontaneously displaced in an antiferroeletric Z_5 configuration[2] at sufficiently low temperatures; (3) if the derivative $\partial v/\partial z$ is positive, the above displacement decreases with increasing temperature and disappear at a certain critical point; and (4) if both kinds of ions are highly polarizable, one kind becomes displaced in antiparallel Z_6 configuration while the other kind in an antiparallel Y_7 configuration.[2]

Thus a CsCl type crystal never becomes ferroelectric, so long as p_i is assumed to be entirely determined through the local field F_i as shown in Eq. (1). The situation becomes greatly modified, however, if we assume that some part of p depends directly upon the lattice strains regardless of the intensity of the local field. The conditions for the appearance of ferroelectricity have been investigated.

Whether such an effect of short range nature is indispensable to explain the ferroelectricity of barium titanate or not[3] is now being investigated. The results will be reported at the conference.

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On the Electric Conduction of Dielectrics under Strong Electric Field

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Free electrons in a dielectric under a strong electric field are multiplied due to the ionizations by collisions, and finally destroy the lattice of the dielectric,(1),(2) if the number of electrons becomes so large. We can take into account two typical cases of the electron multiplication. The first case is that the resistivity of the dielectric is so high and the crystal structure is so perfect that the chance for the collisions between electrons, for the electron-hole recombinations and for the trappings of electrons are very few. In this case an electron which is put into the dielectric at the cathode is multiplied to be $\exp(d/\lambda)$ at the anode, where d is the thickness of the dielectric while λ the mean range for generating a secondary electron. Because such electron avalanche is extremely localized ($<10^{-6}\,\mathrm{cm}^3$), the dielectric can be destroyed by the energy dissipation due to the drift of the avalanche. On the other hand if the situations are reversed compared to the first case, the avalanche cannot grow up independent of the other electrons, but the electrons are multiplied as the whole intimately coupling one another. Fröhlich(3) has described this situation in terms of the rise of electron temperature.

Experimentally, the two typical cases are distinguished either by the behaviors at the dielectric breakdown or by the prebreakdown current. For the former case the breakdown strength decreases as the temperature is lowered because of the increased mean free path of the electrons. This is the case for almost all the crystalline dielectrics at the temperatures lower than the room temperature. On the other hand, the amorphous dielectrics such as glass or plastics show a reversed change of dielectric strength v.s. temperature, which fact is explained by Frölich(3) under the assumption that the interactions between electrons themselves are more dominant than those between electrons and phonons. If the disruption occurs by a single avalanche, the phenomena must have extremely large statistical fluctuations. We have observed(4) that the statistical time lag of the breakdown of mica is as large as 10^{-3} sec. at 10 percent overvoltage, though the formative time lag is as small as 10^{-8} sec., and therefore the disruption occurs only after repeated applications of the voltage pulses of several hundredths of a microsecond.(5) This is contrasted to the case of glass where the disruption is brought about by a single voltage pulse of $10^{-8}\sim10^{-7}$ sec. The large electron avalanches which grow up freely from the hindrances due to the trappings, recombinations or collisions between the electrons will constitute an extremely noisy current at the prebreakdown region. For mica, we have measured(4) the size of the electron avalanche just before the disruption from the noise pulse and found that it is sufficient to cause the breakdown. The noise pulse was observed also by Suita(6) and his collaborators for KCl and sulphur. It has also been observed that the increased number of electrons hinder the growth of avalanche. Thus it is expected that in the case of glass, where the picture of electron temperature is applicable, the prebreakdown current ought to be fairly noiseless. According to the experiment by Haworth and Bozorth(7), however, there is an evidence that this is not the case.

In conclusion we expect the appearance of a reasonable treatment on the interactions between electrons and between electrons and holes, while in the experiment the separation of the fluctuation inherent to the phenomena from the experimental errors is a difficulty that must be overcome.

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Theory of Color Centers in the Alkali Halides

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The extensive experiments on the coloration of the alkali halides which has been carried out since 1946 make it possible to advance our understanding another step. None of this experimental work makes it seem necessary to introduce any radical changes in viewpoint concerning the nature of the *F*-center or of centers derived from *F*-centers by coagulation. The model of the *F*-center proposed by de Boer has withstood the test of time and remains an anchor-point.

Important new information on *V*-centers has become available. It now seems highly likely that the V_1-center is the counterpart, or antimorph, of the *F*-center. The V_2-, V_3- and V_4-bands are probably associated with coagulates of vacancies and holes analogous to the *R*- and *M*-bands. It is suggested that the V_3-center consists of two positive-ion vacancies and a single hole, being therefore negatively charged. This charge will account for its great stability under conditions in which free electrons are produced in the lattice.

Although we still do not possess all the critical experimental information on the factors which determine the darkenability of the alkali halides when exposed to X-rays, it seems possible to approach somewhat nearer to the solution of this problem. Most important for this aspect of the subject are the experiments which demonstrate that the halogen ions next to halogen-ion vacancies and *F*-centers possess characteristic absorption bands (the α- and β-bands). The writer has proposed that the extensive darkening which can be induced at temperatures at and below liquid nitrogen temperature, involves the production of vacancies from jogs at dislocations by thermal 'spikes' which occur at the dislocations when excitons or electron-hole pairs die near them. *F*-centers are formed when the halogen-ion vacancies 'evaporated' from dislocations in this way capture electrons either by trapping free electrons or decomposing excitons which wander near by. V_1-centers are formed in a similar way when positive-ion vacancies capture free holes.

It is possible that the great sensitivity of the darkening process to traces of impurities, particularly the halides of divalent metals which enhance darkenability, rests on secondary processes, such as the ability of the positive-ion vacancies associated with divalent ions to help transport negative-ion vacancies away from the region where they are produced.

Crystals darkened at helium-like temperature are, on the whole, much like those darkened at nitrogen temperatures. There is strong evidence, however, that the *F*-type and *V*-type imperfections are very densely packed in localized regions, attaining concentrations near 10^{21} centers per cc. Such regions should cluster mainly about the surfaces swept out by the dislocations which climb as vacancies evaporate.

Recent Experiments on Colour Centres

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§1. On the two electron-surplus centres in the ultra violet region

An electron-surplus centre made its appearance strongly when electronic currents were passed through NaCl crystals from a pointed cathode at 450°*C* or below. In our laboratory this was called the *K*-centre. Irradiation of *K*-centre with *K*-light excites luminescence simultaneously with photo-current.

In the electric field *K*-centres drift toward the anode. By continuing the irradiation at room temperature its absorption coefficient gradually decreases, and *F*-centres are formed ($\sim 10^{16}/cc$). After complete transformation of *K* (principally into *F*), if the crystal is warmed up to 400°*C*, the *K*-band recovers its initial absorption coefficient.

At room temperature the density of negative ion vacancy will be very small, therefore it may be considered that negative ion vavancies are produced through the destruction of *K*-centres.

These results are well explained assuming that the structure of *K* consists of a negative ion vacancy and an *F*-centre, i.e., F_2^+, but to a conclusive determination more experiments must be carried out, because of the fact that F_2^+ centre is already assigned to R_1 or R_2 band by Seitz.

Another electron-surplus centre, called *K'*, was found automatically accompanied with the *K*-centre. These two centres (*K* and *K*′) are transferred into each other optically.

§2. On the M-centre

The structure of the *M*-centre consisting of a pair of positive and negative ion vacancies and an *F*-centre as proposed by Seitz had been accepted experimentally by our method of bleaching with polarized lights.

M-centres were generated in KCl crystal from additively coloured *F*-centres by irradiation of *F*-light. Then they were bleached with the polarized light, its electric vector being orientated along [011] direction of the crystal. At different stages of bleaching, absorption curves of *M* were measured with each of two lights polarized mutually perpendicular.

Measurements showed that *M*-centres have several orientations in some of which they are destroyed by the [011] light and others are not. Then if we adopt the above model having the symmetry of C_{2v}, after a sufficiently long irradiation with one of the two polarized lights, the density of surviving *M*-centres, which are to be in turn destroyed with the other polarized light, must be 1/6 of the initial value. That prediction was verified in this experiment.

Thus our results, in concert with the calculation of energy levels by Inui, Uemura and Toyozawa, strongly support Seitz's model.

§3. On the V-centre

Hitherto, most of the investigations on *V*-centres of alkali halides have been carried out on the samples coloured by *X*-ray irradiation. In such cases, since the *V*-centres are inevitably accompanied by the *F*-centre, causing the thermal instabilities of both centres, the interpretation of experimental facts becomes considerably difficult. Recently we have studied the thermally stable *V*-centres produced either by heating KI and NaI in iodine vapour or by pushing the positive holes into the crystal from a pointed anode (see below). In Fig. 1, the full curve shows the *V*-absorption of KI coloured in iodine vapour. Measurements were carried out at room temperature. Mollwo's data, the broken line, is also shown for comparison. There are some evidences that the discrepancies appearing between these two curves can be attributed to some impurities in the case of Mollwo. The full curve of Fig. 1 may be resolved into three bands I, II, and III, absorption maxima and half breadths of which are shown in the following table:

	Peak		Half Breadth
	mμ	*e.v.*	*e.v.*
Band I	365	3.40	0.72
Band II	298	4.16	0.70
Band III	~260	~4.77	~0.50

Band III does not appear in the case of point anode colouring and it is rather obscure to attribute it to V-centres.

The following facts were found (1) The heights of Band I and II are proportional to the pressure of iodine vapour. (2) Band I and II show a nearly constant ratio (~0.5) in their maximum absorption coefficients, independent of the crystal temperature and the iodine vapour pressure at which the *V*-centres were produced. (3) This constancy in ratio is maintained during the course of the thermal bleaching. All these facts suggest that both bands issue from a single kind of centre. (4) By irradiation of a near ultra violet light, Band I and II are bleached as shown in Fig. 2. However, when they vanish completely, a stable broad band ranging from near u.v. to the long wave length side of the fundamental absorption band appears. So in this case, the constant ratio between Band I and II is not maintained. (5) After this broad band appears in its fullness, if the crystal is heated up to 250°C, it disappears and Band I and II recover their original shapes to a great extent.

Similar facts were also found in NaI crystals (Fig. 3).

It is generally accepted that the *V*-centres are electron-deficient and the positive holes generated in the crystal might play an important role. A strong support to this speculation has been given by our experiment in which the *V*-centres were pushed into the KI crystal at an elevated temperature from a pointed anode, just as *F*-centres were from a pointed cathode. Considering the nature and mechanism of the formation of *V*-centres, it may be concluded that positive holes can be injected into alkali halide crystals.

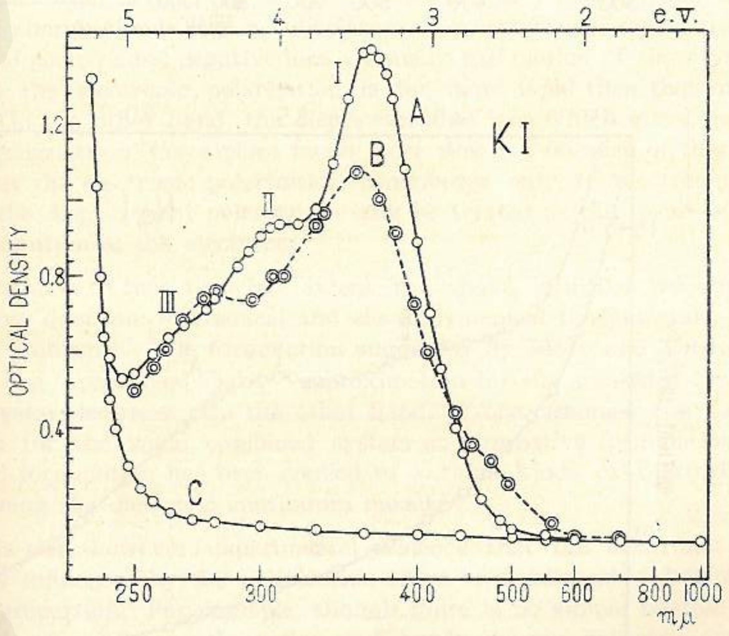

Fig. 1. Absorption curves of KI crystal containing excess iodine.
A: colouring at 530°C in iodine vapour of ~1.3 atm. pressure,
B: after Mollwo,
C: original blank KI crystal.

Correcting the curve A by the curve C, it can be resolved into three bell-shaped component bands designated as I, II, and III.

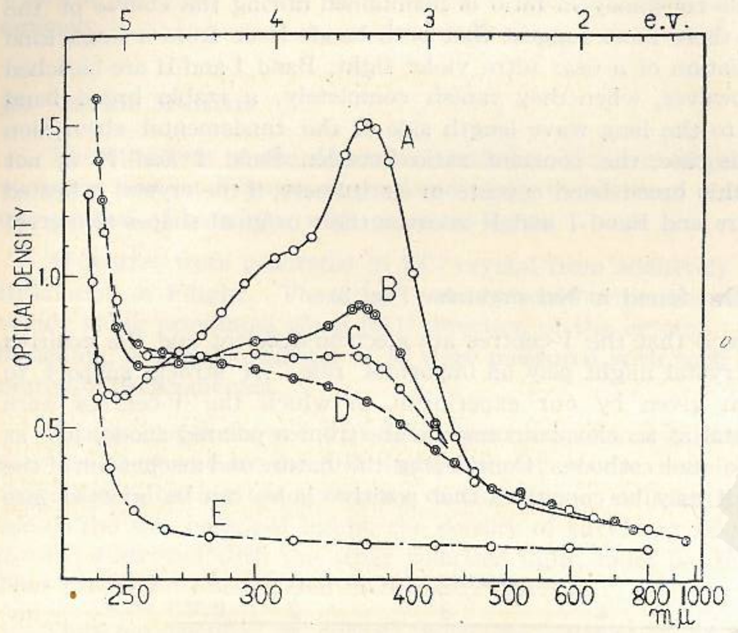

Fig. 2.

Light bleaching of additively coloured V-centre in KI irradiated by 310- and 365-$m\mu$ light from Hg-arc at room temperature.

A: initial state,
B: after the irrad. of 4 hrs.,
C: after the further irrad. of 6 hrs.,
D: after the further irrad. of 10 hrs.,
E: original blank crystal.

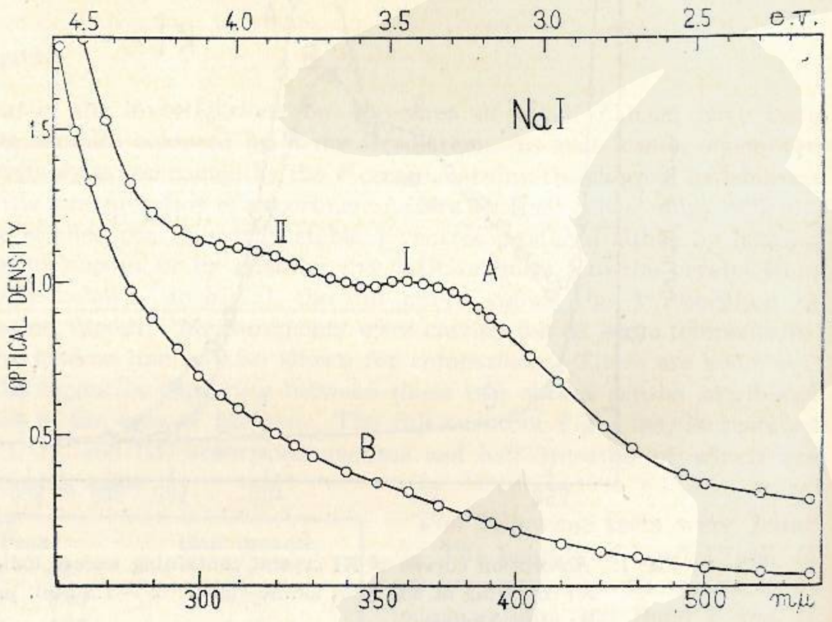

Fig. 3. Absorption curve of NaI crystal containing excess iodine.
A: colouring at 530°C in iodine vapour of ∼3.5 atm. pressure,
B: original blank NaI crystal,

The scale of the optical density is arbitrary, and can not be common for two curves.

The Electronic Structure of Color Centers

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The main purpose of this report is to give a survey of theoretical work on color centers carried out recently in Japan. Neither a historical survey nor a systematic discussion will be given of many important topics[1]; we will rather speak mainly about the "electronic structure" of color centers. The problems of thermal and photo-chemical processes will also be touched briefly.

In discussing color centers, which are "combined systems" consisting of trapped electrons (or holes) and trapping centers (any types of ion vacancies in the crystal lattice), we encounter two important effects. The first is the polarization caused by the vacancies in the crystal lattice and by the introduction of trapped particles around them. The second is the effect of the surrounding field.

The polarization is made up of an "electronic polarization" due to the redistribution of charge clouds plus a "displacement polarization" due to the relative displacements of positive and negative ions. Usually the motion of the crystal electrons that causes the electronic polarization is far more rapid than that of the trapped electrons. On the other hand, the displacement of ions which gives rise to the displacement polarization takes place much more slowly. Because of this it is usually assumed that the electronic polarization contributes only to electrostatic shielding effect and the displacement polarization may be treated as the result of the average charge distribution of the electrons.

It is desirable to test to what extent the above intuitive treatment is valid. Starting from quantum mechanical and electrodynamical fundamentals, we have discussed this problem.[2] The formulation suggested by Mott and Gurney results if one applies the "pseudo-adiabatic" approximation for the combined systems of additive and crystal electrons. On the other hand, if one assumes the "Hartree" approximation for the same combined system an alternative formulation is obtained. This second formulation has been applied to various kinds of thermal and optical processes using the dielectric continuum model.[2]

There is also, however, experimental evidence that the electronic structure is not strongly influenced by the polarization effect in certain cases, but rather depends on lattitce properties. For example, though there is no simple relation between the wave length of maximum absorption of F bands and the dielectric constant of the bulk crystals, Mollwo and Ivey have found a simple empirical relationship between the peak wave length and the interionic distance.[3] Nagamiya has interpreted this in a simple way using classical quantum theory.[4]

We have calculated the electronic energy states of F, M and V centers of several alkali halides using the so-called LCAO-MO method instead of the usual treatment

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which assumes the color center is a simple attractive center in a dielectric continuum.[5)6)7)] The result obtained in the case of *F*-centers provides a means for explaining the Mollwo-Ivey rule. As for the *M*-center in LiCl the NaCl, we have calculated the wave lengths of the *A*—*B* transitions, employing the *L*-shape model of Seitz.[8)] The results are in good agreement with observations.[6)] Ueta's experiment on the bleaching effect of *M*-centers by polarized light seems provides evidence for the proposed model.[9)]

Very recently, a powerful micro wave tecnique has been applied to the study of electronic structure of color centers by Kittel and collaborators.[10)] They analyze very carefully the width of the electron spin resonance absorption line associated with *F*-centers in colored crystals of alkali halides and suggest that the width of the resonance line is not caused by interactions between the *F*-centers but by the interactions of *F*-center electrons with their immediate environment in the *F*-centers. They further show that the LCAO-MO model gives a natural explanation of the shape while the ordinary continuum model fails.

Let us now consider two electronic processes briefly, absorption of light and thermal ionization. In crystals these processes are strongly coupled with the vibration of the lattice and therefore we must treat them as many phonons processes. The shape of *F*-bands and its temperature dependence have been explained semi-empirically by us and later by Nagamiya using the Frank-Condon principle, invoking the thermal expansion of the lattice.[4)5)6)]

Some time ago, Muto proposed a general method to treat light absorption quantum mechanically and Huang and Rhys then succeeded in calculating suitably the probability of light-absorption coupled with many phonons.[11)] More recently, Kubo and Lax developed a general method for treating the same problem in which they used the method of moments derived from generating functions.[12)] Kubo has also discussed the thermal ionization of the trapped electron from the same point of view.[13)]

Finally we would like to mention Kojima's suggestion[14)] concerning the photo-chemical processes observed by Petroff.[15)] He concluded that there are probably no paired vacancies in the virgin crystals prepared by Petroff and inferred from the appearance of the new bands such as *A*, *B* etc. that there are close relations between the crystal dislocations and the corresponding centers.

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Application of the Wigner-Seitz Method to the F-Centre

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The electronic wave functions and the energy levels of an *F*-center in NaCl are calculated by use of the cellular method. The whole crystal is divided into cells such that the ratio of the volumes of Na^+ and Cl^- polyhedra is equal to the ratio of the cube of the respective ionic radii. In each cell the Schrödinger equation is solved numerically and the obtained wave functions are joined at the cell boundaries.

The potential function in each cell is taken as

$$V=-\frac{\alpha e^2}{d}+\frac{e^2}{R}\left(1-\frac{1}{K_0}\right) \qquad (R=0.95\,d)^{1)} \qquad \text{in the (000) vacancy,}$$

$$V=+\frac{\alpha e^2}{d}-\frac{e^2}{d}+\frac{e^2}{d}\left(1-\frac{1}{K_0}\right) + (\text{Na}^+\text{ potential}) \qquad \text{in the (100) Na}^+\text{ cell,}$$

$$V=-\frac{\alpha e^2}{d}-\frac{e^2}{\sqrt{2}\,d}+\frac{e^2}{\sqrt{2}\,d}\left(1-\frac{1}{K_0}\right)+(\text{Cl}^-\text{ potential}) \qquad \text{in the (110) Cl}^-\text{ cell,}$$

etc.,

where d is the lattice constant and K_0 is the optical dielectric constant of NaCl. The first terms, $\pm\alpha e^2/d$, are the Madelung potential, the second and third terms the potential due to the vacancy neglecting the displacement of the ions. They are assumed to be constant in each cell in order to make it easy to solve the equations. The remaining terms enclosed in parenthesis are the Hartree-Fock potential of the Na^+ or Cl^- ions, in which the exchange potential is included in the Slater's free electron approximation.[2)]

The following sets of spherical harmonics are used to construct the ground state wave function:

s and *g* functions in the (000) vacancy,
s and *p* functions in the (100) Na^+ cell,
s, *p*, *d* and *d′* functions in the (110) Cl^- cell,
s, *p* and *d* functions in the (200) Cl^- cell,
s and *p* functions in the (111) Na^+ cell.

The wave functions for different cells are joined so as to be continuous together with their normal derivatives at the center of

the boundary plane between (000) cell and (100) cell,
,, (100) cell and (200) cell,
,, (000) cell and (110) cell,

and continuous at the center of

the boundary plane between (100) cell and (110) cell,
,, (110) cell and (200) cell,
,, (110) cell and (111) cell.

The continuity requirements of the normal and the tangential derivatives at the last three points are approximately satisfied in the meaning of the least square method by using only two undetermined coefficients. Among two remaining coefficients, the one is determined by the normalization, the other coefficients and the eigenvalue are determined by the condition that the wave function vanishes at the infinity along the [100] and [110] directions. Beyond the (200) or (110) cell, only s and p functions are used in each cell to join along the (100) and (110) directions.

Our result shows that the wave function localizes to a considerable extent at the ions near the vacancy and is rather flat in the vacancy unlike the Tibbs' calculation.[3] This result may be compared with that obtained by Kittel[4] from the magnetic resonance experiment.

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Introductory Talk

L. Onsager

(Abstract is not yet received, Aug. 28)

Some Recent Data on Liquid Helium

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Some data on liquid helium recently obtained in Leiden will be reviewed and discussed.

Measurements of the viscosity of helium I at different pressures, carried out by *Tjerkstra* have confirmed that the λ-transformation announces itself a few tenths of a degree above the λ-point by a dip in the viscosity. At higher temperatures and low constant density the viscosity increases while at densities above 0.17 it decreases as a function of temperature. By suitable adjustment of the temperature dependence of the radius of the hard spheres in *Enskog*'s theory these data can be described satisfactorily.

The adsorption of helium on a surface at pressures slightly below the saturated vapour pressure is a controversial subject during some time already. Early Leiden observations about adsorption on a glass surface and certain observations on powders could be interpreted as indications of the adsorption of thick layers comparable to the well-known *Rollin-Simon* film; this would seem to be corroborated by high heat transport along surfaces even considerably below the saturated vapour pressure. On the other hand it was not clear why those phenomena disappear at precisely the λ-temperature of the bulk liquid. Repetition by *Tjerkstra* of the experiments on the glass surface mentioned did not confirm the early interpretation and recent investigations carried out in Oxford and Chicago also appear to exclude anomalously high adsorptions. The increase in adsorption, setting in well above 90% of the saturated vapour pressure, may lead in a natural way to the *Rollin-Simon* film at pressures which differ by 10^{-4} or less from the saturated vapour pressure if one accepts the existence of a negative term in the surface energy which is inversely proportional to the square of the layer thickness. Superfluid transport of helium atoms may give the film an unusual stability below the λ-temperature.

The phenomena of liquid helium between 1.1°K and the λ-point are commonly described by the two fluid model of *Tisza* and *Landau* and there is no difference of opinion about the equations of motion of the fluids as long as the velocities are small. In the description of the heat transport and flow phenomena in capillaries and not too narrow slits, the assumption of a mutual friction between the fluids, proportional to a power higher than one of the relative velocity, is quite successful. However, the data collected by *Winkel* show that in slits of the order of a few microns this description breaks down, the coefficient of mutual function apparently growing at the expense of the viscosity of the normal fluid. It is not yet clear whether introduction of critical velocities, in analogy to *Mendelssohn*'s critical velocity in the film, is required to describe the many complicated data. In connection with certain anomalies occurring in apparatus of much larger dimensions too, it may be mentioned that the condition, so often proposed by theoreticians, that the rotation of the superfluid velocity should be zero has not yet been used in the quantitative discussion of the data.

In the two fluid model the so-called diffusion force drives the fluids in opposite directions as soon as there is a gradient of the relative concentration x of the normal fluid. The magnitude of this force determines the fountain effect and the mechano-caloric effect, which according to *De Groot* are interconnected by the laws of irreversible thermodynamics.

H. London proposed for the fountain effect $dp/dT=\rho S$, where S is the specific entropy and ρ the density and for the mechano-caloric effect $Q^*=ST$, while certain Japanese and Netherlands thermodynamicians prefer to replace S in these expressions by $x(\partial S/\partial x)_T$. Whilst the latter formulation cannot easily be proved or disproved since $(\partial S/\partial x)_T$ cannot be measured directly, it may be stated that the experimental data available above 1.1°*K* are in reasonable agreement with *H. London*'s formulae. Below 1.4°*K* the fountain effect is a few percent higher than expected while above 1.7°*K* the rather uncertain fountain effects are considerably lower. *Kapitza*'s data on the mechano-caloric effect, on the other hand, are generally about 10% higher than is expected from *H. London*'s formula.

Quite recently *Bots* has carried out an investigation on the fountain effect below 1°*K*. The integrated fountain effect was measured keeping one side of a powder packed tube at a constant temperature of about 1.1°*K* while the other side was in contact with a paramagnetic powder which slowly warmed up from about 0.2°*K*. Up to 0.5°*K* no decrease of the integral fountain effect was observed, though *H. London*'s formula predicted a decrease of 1.3 *cm*. With increasing temperature *H. London*'s formula was approached when the cold side was about 1.0°*K*. Taking the experimental accuracy of a few millimeters helium pressure into account the results were identical for various tubes if only the powder was packed tightly. Specific heat data of *Kramers* indicate that below 0.5°*K* the only surviving excitations are the phonons and the sound pressure due to them is the only fountain effect for which *H. London*'s formula can be rigourously derived. It seems mysterious why just in this case no fountain effect is observed.

Feebly damped heat waves have only been observed in liquid helium II and the picture in which the two fluids oscillate with respect to each other, in such a way that one has kinetic energy and inertia effects without net mass motions, satisfactorily describes this second sound. From the accurate measurements of the second sound velocity one may conclude that when T varies x is approximately proportional to the entropy S, a conclusion which at the higher temperatures is confirmed by direct determination of x by *Andronikashvili*'s method.

Landau suggested in 1941 the normal fluid to consist of two kinds of excitation which he called phonons and rotons and he expected that below 1°*K* the rotons would rapidly die out. On the basis of this picture he predicted the second sound velocity to rise below 1°*K* from a relatively low value to $V_I/\sqrt{3}$ where V_I denotes the velocity of normal sound. Though early investigations seemed to confirm this prediction, recent researches carried out in different laboratories lead to other results.

Using the pulse technique and tubes of different lengths *Kramers* has found that at temperatures below 0.2°*K* the front of the heat pulse travels with the velocity V_I of normal sound. This indicates that at those temperatures the phonon mean free path is at least several centimeters though it is not evident which are the frequencies associated with those phonons. At somewhat higher temperatures the front is less well defined, its velocity becoming smaller and dependent on the length of the tube; there is then some analogy with any heat conductor into which a heat pulse is introduced. At about 0.8°*K* the well known phenomena of second sound appear, though the damping is considerable. This high damping has disappeared at 1.1°*K*. It seems appropriate to reserve the term second sound for the waves travelling at the higher temperatures where long free paths of the phonons have not yet led to strong damping or even have changed the whole character of the phenomenon.

Taconis and his group are carrying out observations on dilute solutions of ^{3}He in ^{4}He, which we shall not discuss in any detail. In general the dynamical and thermodynamical behaviour of these solutions seems to be in agreement with the hypothesis that the ^{3}He atoms join the normal fluid. The results do not all agree with those obtained elsewhere. The statement made by *Taconis* and *Beenakker* that the line giving the concentration of ^{3}He in the vapour as a function of T has a knick at the λ-point may be corroborated by a general thermodynamical argument. Experiments in this field are greatly complicated by concentration gradients and extra temperature jumps at walls set up by even small heat currents and by filtering action of the *Rollin-Simon* film creeping out of the mixture.

Review of the Recent Works in Japan on the Two Fluid Theory of Liquid Helium

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Since 1949, we have developed the two fluid theory to obtain a consistent description of various experimental facts on the dynamic properties of liquid helium II. The theory has been formulated mainly by Usui and applied to various phenomena by many authors. Some of our recent studies will be reported here.

1° By applying the general method of thermodynamics of irreversible processes, Usui formulated the two fluid theory, including the relaxation of the reaction between the normal and superfluid components. In order to estimate the relaxation time, he derived the expressions for the Kapitza heat resistance in bulk liquid and dispersion and attenuation of first and second sounds. Unfortunately the lack of the detailed data prevents us from drawing a definite conclusion about the relaxation time, though he obtained a value ~10^{-6} sec. from the data on the attenuation of second sound. He found also that the effects of the viscosity and thermal conduction are additive in δ^2, δ being the thickness of the boundary layer in which the Kapitza heat resistance exists.

2° The two fluid theory was applied by Kasuya[1] to the surface flow. He found that the damping of the oscillation of the surface film is caused by the temperature difference between the inside and outside of the vessel, which is due to the Kapitza heat resistance existing in bulk liquid. He concluded thus that the surface flow is, in itself, perfectly frictionless, if the velocity does not exceed a critical value.

Above a certain critical velocity, he assumed that the superfluid is subject to the frictional forces exerted by the boundary wall as well as by the normal fluid:

$$\left.\begin{array}{l} f=-A\rho_s\rho_n(v_s-v_n)^3-(B_3/d)\,\rho_s v_s^3, \\ A=0 \quad \text{if} \quad |v_n-v_s|<v_c, \quad B=0 \quad \text{if} \quad |v_s|<v_c, \end{array}\right\} \qquad (1)$$

where d is the thickness of the surface film (or the width of the slit). He succeeded in explaining the saturation of the surface flow rate, and also various phenomena connected with the mass flow through slits, in particular, the experiment of Bower and Mendelssohn[2]. The first term of (1) is the well-known friction introduced by Gorter and Mellink[3] and the second is suggested by Hung et al.[4] (without the critical velocity). The origin of the critical velocity and mutual friction is, however, not clear.

For the slit narrower than 1 μ, Inoue assumed the slip of the normal fluid at the boundary wall:

$$\frac{dv_n}{dx}=-\frac{B\rho_n\rho}{\eta_n}v_n, \quad \frac{B}{d}\sim 10^5\,\mathrm{g^{-1}\,cm^3\,sec^{-1}},$$

by which he could account for the observed heat flow without assuming any anomalous value[3] of viscosity η_n. He also introduced the mutual friction proportional (v_n-v_s). Though this can be expected from the general formalism, its existence is rather doubtful as pointed out by Takahashi et al.

3° Second sound below 1°K was discussed by Usui from the phenomenological points of view, and by Kasuya, Shimizu, Morita, and Nakajima from the kinetic theory of the phonon gas. All of them assumed the local equilibrium of the phonon system. The recent experiment, however, indicates that the mean free path of a phonon increases so rapidly below 0.6°K that we can hardly assume the local equilibrium. Shimizu has shown that the observed shape of the received heat pulse can be explained by regarding the phonon system as a rarefied gas of Knudsen type.

4° The two fluid theory was first applied by Koide and Usui[5] to the He^3+He^4 mixtures. They accounted for the observed increase of the second sound velocity and decrease of the thermal Rayleigh disc torque on the two assumptions: i) the Gibbs free energy is given by the model of de Boer and Gorter[6] and ii) the He^3 component follows the barycentric motion.

Recently Mikura has shown that the second sound in the mixture can also be explained on the assumptions: i′) the free energy is given by the model of Daunt and Heer[7] and ii′) the He^3 component moves with the normal component of He^4. The second assumption agrees with the observed fact in the stationary heat flow of the mixture.

As for the formulation of the two fluid theory of the mixture, Usui has criticized the theory of Mazur and Prigogine[8]; their assumption on the thermostatic relation of the free energy can not be satisfied by the observed values of various quantities. Avoiding this difficulty, Nakajima has reformulated the theory by applying the fundamental Gibbs relation only to the barycentric motion. On the basis of it, Kasuya has criticized previous works. In particular, he pointed out that the theory of Mikura fails to explain the observed decrease of the Rayleigh disc torque and that, in order to improve this point, we necessitate a new model of the free energy which is intermediary between the above-mentioned two models with respect to the mixing entropy.

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Atomic Theory of Liquid Helium

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Liquid helium II is studied from first principles. We show how the central features of the two fluid model arise.

In previous work[1] the λ-transition was interpreted as the Bose-Einstein condensation of a non-ideal gas. We are concerned here with lower temperatures. The ground state wave function and the types of excited states available at low temperatures are studied.

The wave function φ, of the ground state is visualized qualitatively. The helium atoms are nearly hard spheres. The wave function is everywhere real and positive and is symmetric for interchange of the atoms. It is described by giving the amplitude for various configurations of the atoms. If atoms are in contact or overlapping the function vanishes, and it is largest when they are well separated from one another. Thus the atoms tend to stay apart and to produce a kind of local structure similar in density distribution to that of a classical liquid.

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An increase of mean density over a large volume represents an energy increase because of the rise of zero-point energy occasioned by the decrease of free volume. Long wave sound can therefore be carried by the liquid, and there are density fluctuations corresponding to the zero-point oscillations of this sound field.

Keeping the mean separations of the atoms fixed, and the mean density fixed, there are still configurations which differ from one another, but just in the sense that one can be "stirred" into the other. Since the structure is fairly open in the liquid, there is no effective barrier to such stirrings, and the lowest state corresponds to equal amplitude for all such configurations.

What are the character and energy of the lowest excited states of the system? First, there are excitations of the long compressional waves, phonons of energy $\hbar KC$ for wave number K, where C is the sound velocity. The specific heat variation as T^3 (below 0.7^0K) shows there are no other states of low energy. Why this is so is seen as follows.

The wave function must not be altered by any change which simply interchanges the atoms. Yet the excited state must be orthogonal to the ground state. Starting at any configuration A, and supposing the amplitude to be positive, one must find a new configuration B to which we can assign a negative amplitude, and which differs from the old configuration A by just a stirring of the atoms without change of mean density (to omit phonon states). It is clear that every such configuration is close to the original one, albeit with some atoms interchanged. So it is hard to find a configuration to give a negative amplitude which is sufficiently far (in configuration space) from the original one of positive amplitude to result in a low gradient of amplitude and thus a low energy. The lowest state will have B differ as much as possible from A.

Configuration B is furthest from A if all of the atoms in B are between the sites occupied in A. The transition from positive amplitude for A to equal negative amplitude for B is as smooth as possible if the amplitude for other intermediate configurations is simply proportional to the number of atoms on A sites minus the number on B sites. Density fluctuations and overlapping atoms must be avoided just as in the ground state. It is therefore deduced that the wave function of the excited states will, to a good approximation, be of the form

$$\psi=\Sigma_i f(R_i)\varphi \tag{1}$$

where φ is the ground state function and $f(R)$ is $+1$ if R is at an A site and -1 if at a B site, and the sum is taken over all the atoms, coordinates R_i.

Other chains of reasoning starting from other viewpoints concur in the conclusion that (1) is a good approximation to the wave function with $f(R)$ some function with variations predominately of wave length equal to the atomic spacing.

Knowing that (1) is the form of the function, we turn to a mathematical argument to obtain a detailed evaluation of the best choices for $f(R)$ and the energies to which they belong. We shall compute the fraction

$$E=\langle\psi^*, H\psi\rangle/\langle\psi^*, \psi\rangle \tag{2}$$

in terms of f and find the f's which make it stationary. Measuring energies above E_0, the ground state energy, the hamiltonian is

$$H=-(\hbar/2m)\,\Sigma_i\nabla_i^2+V-E_0 \tag{3}$$

From (1) and (3), using $H\varphi=0$, we find

$$H\psi=-(\hbar/2m)\,\Sigma_i(\varphi\nabla_i^2 f(R_i)+2\nabla_i\varphi\cdot\nabla_i f(R_i))$$

Substituting into (2), noting that φ is real and that $2\varphi\nabla\varphi=\nabla\varphi^2$ and integrating by parts, one gets

$$E=(\hbar^2/2m)\left(\Sigma_i\int\varphi^2\nabla_i f^*(R_i)\cdot\nabla_i f(R_i)\,d^NV\right)\Big/\left(\Sigma_i\Sigma_j\int\varphi^2 f^*(R_i)f(R_j)\,d^NV\right) \tag{4}$$

The integral d^NV is over all configurations of all the atoms. In the denominator we can first integrate φ^2 over all variables except i, j. This gives a result proportional to the correlation function $p(R_i-R_j)$ for the ground state (that is, $p(R-R')$ is the probability per unit volume of finding an atom at R' if one is known to be at R). Similarly the numerator is integrated first over all variables but R_i, giving the chance to find an atom at R_i, which is constant. Thus (4) reduces to

$$E=(\hbar^2/2m)\int\nabla f^*(R)\cdot\nabla f(R)\,d^3R\Big/\iint p(R-R')f^*(R)f(R')\,d^3R\,d^3R'$$

This is stationary if f satisfies

$$-(\hbar^2/2m)\nabla^2 f(R)=E\int p(R-R')f(R')\,d^3R'$$

which has the solution $f(R)=\exp(iK\cdot R)$ with energy

$$E_K=\hbar^2K^2/2mS(K) \tag{5}$$

where $S(K)$ is the liquid form factor for He at absolute zero, the fourier transform of the correlation function;

$$S(K)=\int p(R)\exp(iK\cdot R)\,d^3R.$$

The function $S(K)$ can be obtained directly from X-ray or neutron scattering experiments. The behaviour for small K can be obtained theoretically from its relation to the zero point density fluctuations of the sound field. One gets $S(K)=\hbar K/2mC$, so that $E_K=\hbar KC$, the energy of a phonon. This must check, because the form (1) for low K is also exactly the form of the wave function for the first excited state of the sound field.

For very high K, $S(K)$ approaches 1 because $p(R)$ contains a delta function at the origin. For intermediate K, $S(K)$ rises to a maximum and falls away, with perhaps other subsidiary oscillations, as a result of the local order occasioned by the tendency of the atoms to stay apart. This maximum makes a ring in the x-ray scattering corresponding to a value of K of order $2\pi/a$.

Therefore, E_K rises first linearly with K, but then falls to a minimum and rises again. The states available at low temperatures are therefore either phonons, or else excitations near the minimum of the curve (where it has the parabolic form $\Delta+(\hbar^2/2\mu)(K-K_0)^2$. Landau has shown that this is just the kind of an energy curve which will qualitatively and quantitatively describe the properties of helium II. The kinetic aspects of the two fluid model are also readily understood starting from this point.

On the Theory of Sound Waves Applied to Energy Spectra of Helium II

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When one aims to get the statistical properties of Helium II at very low temperatures, one meets with mathematical difficulties in solving the eigenvalue problem of many boson assembly. We apply the theory of sound waves devised by Bloch and Tomonaga[1] to the many boson problem and examine if this theory bears to obtain energy spectra of interacting Bose particles in the scheme of second quantization.

By expressing the Hamiltonian in terms of the density operator and the velocity operator $v(\boldsymbol{k})$ one obtains the eigenfrequency of phonons and the energy of the ground state,[2] which are shifted due to effect of unharmonic terms.

Up to third order terms the total Hamiltonian reads

$$H=H_0+H'+\frac{1}{2}G(0)N^2-\frac{1}{2}G_0N-\frac{\hbar^2}{4m}\sum k^2 \tag{1}$$

$$H_0=\frac{mN}{2}\sum_{k\neq0}v(k)v(-k)+\frac{m}{2N}\sum_{k\neq0}\frac{\omega_0(k)^2}{|k|^2}\rho(k)\rho(-k), \tag{2}$$

$$H'=\frac{m}{2}\sum_{k\neq l}v(k)v(-l)\rho(l-k)-\frac{\hbar^2}{16mN^2}\sum_{k\neq l}(k\cdot l)\rho(k)\rho(-l)\rho(l-k), \tag{3}$$

where $$v(k)=ik\Phi(-k)/m,\quad [\rho(k),\Phi(l)]=i\hbar\delta_{kl}, \tag{4}$$

$$\omega_0(k)=|k|\left[\frac{\hbar^2k^2}{4m^2}+\frac{N}{m}G(k)\right]^{1/2},\quad G(k)=\frac{1}{V}\int G(x)\exp(-ikx)\,dx, \tag{5}$$

and $G(x)$ is the interaction energy. Introducing the creation operator $\boldsymbol{b}^*(\boldsymbol{k})$ and annihilation operator $\boldsymbol{b}(\boldsymbol{k})$ the second order terms become

$$H_0=\hbar\sum_k\omega_0(k)\left[b^*(k)b(k)+\frac{1}{2}\right], \tag{6}$$

where $\omega_0(k)$ is called "phonon energy". Regarding the unharmonic terms as perturbation energy one gets the energy shift of phonons:

$$\hbar\omega'(k)=|k|(3mC^2/2\rho-\hbar^2k_0|k|/8m\rho-o(|k|^3)/2\pi, \tag{7}$$

by evaluating the second order perturbation energy:

$$\Delta E=-\frac{i}{2\hbar}\left\langle\left[H'(0),\int_{-\infty}^{0}H'(t)\,dt\right]\right\rangle_{AV.}, \tag{8}$$

and the ground state energy becomes

$$E_0=\frac{1}{2}G(0)N^2-\frac{1}{2}G_0N-\frac{L}{2\pi}\left(\frac{\hbar^2K_0^3}{6m}-\frac{\hbar^2K_0^4}{48m\rho}+\cdots\cdots\right). \tag{9}$$

$G_0=\frac{1}{L}\int G(x)\,dx$, K: cut-off number L: length of one dimensional "box".

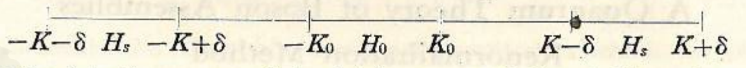
These unharmonic terms show effects of the individual particle motion since they come from the Hamiltonian of free particles. If the excitation energy is very small the phonon excitation is the unique one, however as the excitation energy becomes larger the individual particle motion becomes predominant. In spite of dealing with the unharmonic term directly we wish to give a model-like interpretation of effects of the random particle motion giving rise to the energy shift of phonon.

We assume that excited particles are distributed in two regions of the momentum space. For simplicity we restrict ourselves to the one dimensional case. One of them has two boundaries $\hbar k=\pm\hbar K_0$, $K_0>0$ and the other has four boundaries $\hbar k=\hbar(\pm K\pm\delta)$, $K>\delta>0$. If the propagation number K is sufficiently larger than K_0 and δ is a small quantity, the total Hamiltonian splits into three parts as follows:

$$H=H_0+H'+H_s, \tag{10}$$

$$H_s=K_s+\frac{1}{2}\sum_k G(k)\rho_s(k)\rho_s(-k), \tag{11}$$

$$H'=\sum_k G(k)\rho_s(k)\rho(-k) \tag{12}$$



where K_s is the kinetic energy of the high energy shell and H_0 is that of the lower energy region which is expressed by the phonon energy (2) with sufficient accuracy. $\rho_s(k)$ appearing in the interaction energy H' is given by wave functions $\boldsymbol{a}^*$ and $\boldsymbol{a}$ as follows:

$$\rho_s(k)=\sum_{K'}a^*\left(K'-\frac{k}{2}\right)a\left(K'+\frac{k}{2}\right), \tag{13}$$

where the summation with respect to K' is restricted at the neighborhood of K. Since $[H_0, H_s]=[H_0, \rho_s]=[\rho, H_s]=0$, the problem is reduced to the interaction of phonons with particles. By virtue of a canonical transformation of the form

$$U=\exp\left(\left[\frac{i}{\hbar}\rho_s(k)\Phi(k)+\frac{m}{\hbar k\alpha}J_s(-k)\rho(k)\right]a(k)\right), \tag{14}$$

$$[\rho_s, U]=a\rho,\quad [\rho, U]=-a\rho_s, \tag{15}$$

$$a(k)=-\left[\left(\frac{\hbar K}{m}\right)^2+\frac{\alpha-N}{m}G(k)\right.$$
$$\left.+\left[\left\{\left(\frac{\hbar K}{m}\right)^2+\frac{\alpha-N}{m}G(k)\right\}^2+\frac{dN}{m^2}G(k)^2\right]^{1/2}\right]\frac{\sqrt{\alpha N}}{m}G(k), \tag{16}$$

$$J_s(k)=\frac{\hbar}{m}\sum_l la^*\left(l-\frac{k}{2}\right)a\left(l+\frac{k}{2}\right), \tag{17}$$

one can successively rewrite the kinetic energy K in terms of the density operator $\rho_s(k)$ and the current operator $J_s(k)$. As for the energy shell the excitation energy is approximately given by $\hbar K\left[\left(\frac{\hbar K}{m}\right)^2+\frac{\alpha}{m}G(k)\right]^{1/2}$ which has the same form with Tomonaga's phonon. Hence the problem is reduced to the interaction between this phonon and that of the lower energy part. We find the normal frequencies of the form

$$\omega(k)=\frac{|k|}{\sqrt{2}}\left[\left(\frac{\hbar K}{m}\right)^2+\frac{\alpha+N}{m}G(k)\pm\left[\left\{\left(\frac{\hbar K}{m}\right)^2+\frac{\alpha-N}{m}G(k)\right\}^2+\frac{4\alpha N}{m^2}G(k)^2\right]^{1/2}\right]^{1/2}, \tag{18}$$

where α is the number of excited particles.

We shall make some discussions on the relationship of the results (7) and (18) to Landau's energy spectrum of Helium II. Kamiya has obtained more or less similar results with ours making use of some renormalization processes.

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A Quantum Theory of Boson Assemblies
—Renormalization Method—

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Résumé: The author will show a suggestion of the general applicability of the renormalization process which is familiar to the theory of the elementary particle, to the many-body problem. The reduced Hamiltonian includes the results obtained by Prof. Tomonaga and Nishiyama who both have treated the problem from the viewpoint of Bloch's theory of sound wave. Applying this method to one dimensional case, we shall conclude that all bosons are not perfectly degenerate to the zero-state of momentum space in the ground state under the influence of the mutual interaction.

1 The Renormalized Hamiltonian of Boson Assemblies

The Hamiltonian of boson assemblies is described as

$$H=\sum_q a_q^* a_q E_q+\sum_k \frac{G(k)}{2}\rho_k\rho_{-k}-\frac{\rho_0}{2}G(0) \tag{1·1}$$

We transform the above Hamiltonian with an unitary matrix $U=\exp iS/\hbar$. S is determined by

$$[\sum_q a_q^* a_q E_q, S]=i\hbar\{H^0{}_{ph}-\sum_{H_0'} M_{H_0'}H^0{}_{ph}M_{H_0'}\}$$
$$H^0{}_{ph}=\sum_k\{A(k)\Phi_k\Phi_{-k}+B(k)\rho_k\rho_{-k}\},\quad [\rho_k, \Phi_{-k'}]_-=i\hbar\delta_{kk'} \tag{1·2}$$

where $M_{H_0'}$ is the projection operator belonging to the proper value H_0' of $\sum_q a_q^* a_q E_q$ and both $A(k)$ and $B(k)$ are to be determined by the renormalization process.

The transformed Hamiltonian becomes

$$H'=U^{-1}HU=\sum_q a_q^* a_q E_q+\sum_k\{A(k)\Phi_k\Phi_{-k}+B(k)\rho_k\rho_{-k}\}+\sum_k\frac{G(k)}{2}\rho_k\rho_{-k}$$

$$-\frac{\rho_0}{2}G(0)-\sum_{H_0'} M_{H_0'}\sum_k\{A(k)\Phi_k\Phi_{-k}+B(k)\rho_k\rho_{-k}\}M_{H_0'}$$
$$+\sum_{n=1}^{\infty}(-i\hbar)^{-n}\left\{\frac{r_n}{n!}+\frac{(f_n-g_n)}{(n+1)!}\right\} \tag{1·3}$$

$$r_1=\Big[\sum_k\frac{G(k)}{2}\rho_k\rho_{-k}, S\Big]_-\quad r_{k+1}=[r_k, S]_-,\quad f_1=[H_{ph}{}^0, S]_-\quad f_{k+1}=[f_k, S]_-$$
$$g_1=[\sum_{H_0'} M_{H_0'}H_{ph}{}^0M_{H_0'}, S]_-\quad g_{k+1}=[g_k, S]_- \tag{1·3'}$$

In the Hamiltonian (1.3), we perform such renormalization as

$$\sum_q a_q^* a_q E_q-\sum_{H_0'} M_{H_0'}\sum_k\{A(k)\Phi_k\Phi_{-k}+B(k)\rho_k\rho_{-k}\}M_{H_0'}$$
$$-\sum_{n=1}^{\infty}(-i\hbar)^{-n}g_n/(n+1)!=-\beta \tag{1·4}$$

where β is a constant.
Inserting (1·4) in (1·3), we obtain the renormalized Hamiltonian H_r' of (1·3)

$$H_r'=H_{ph}{}^0+\sum_k\frac{G(k)}{2}\rho_k\rho_{-k}-\frac{\rho_0}{2}G(0)+\sum_{n=1}^{\infty}(-i\hbar)^{-n}\left\{\frac{r_n}{n!}+\frac{f_n}{(n+1)!}\right\}-\beta. \tag{1·5}$$

Then, let H_r denote the renormalized original Hamiltonian which we obtain by renormalization of (1·1) with (1·4)

$$H_r=UH_r'U^{-1}=\sum_k\Big[A(k)\Phi_k\Phi_{-k}+\Big\{B(k)+\frac{G(k)}{2}\Big\}\rho_k\rho_{-k}\Big]-\Big[\frac{\rho_0}{2}G(0)+\beta\Big]$$
$$+[V_r+\sum_{n=1}^{\infty}(i\hbar)^{-n}F_n/n!] \tag{1·6}$$

$$V_r=\sum_{n=1}^{\infty}\frac{f_n}{(-i\hbar)^n}\left\{\frac{1}{(n+1)!}-\frac{1}{n!}\right\},\quad F_1=[V_r, S]_-\quad F_{k+1}=[F_k, S]_- \tag{1·6'}$$

Explaining the above Hamiltonian (1·6), the first term will represent the sound wave and the third term is probably due to anharmonicity.

2 One Dimensional Case

We define

$$\rho_k=\rho_k{}^+ + \rho_k{}^- =\sum_{q\geq 0} a_q^*{}_{-k/2}a_{q+k/2}+\sum_{q<0} a_q^*{}_{-k/2}a_{q+k/2} \tag{2·1}$$

When all bosons are almost degenerate to the so-called zero-state in the momentum space where their momentum vanishes, we can obtain approximately the following relation on bosons,

$$[\rho_k{}^+, \rho_{k'}{}^+]_-=N_+(k)\delta_{k,-k'}\quad [\rho_k{}^-, \rho_{k'}{}^-]_-=N_-(k)\delta_{k,-k'}\quad [\rho_k{}^-, \rho_k'{}^+]_-=0 \tag{2·2}$$

where we put

$$N_+(k)=\sum_{q\geq 0}(n_{q-k/2}-n_{q+k/2}),\quad N_-(k)=\sum_{q<0}(n_{q-k/2}-n_{q+k/2})$$

n_q is the number of bosons occupied by the q-th state.
In this simple case, we can determine Φ_k in the explicit form.

$$\Phi_{-k}=\frac{-i\hbar}{2}\{\rho_k{}^+/N_+(k)+\rho_k{}^-/N_-(k)\} \tag{2·3}$$

Then we obtain

$$H_{ph}{}^0=\sum_k\hbar^2A(k)\{1/N_+(k)-1/N_-(k)\}\{\rho_k{}^+\rho_{-k}{}^+/N_+(k)-\rho_k{}^-\rho_{-k}{}^-/N_-(k)\} \tag{2·4}$$

where we have assumed

$$B(k)+\hbar^2 A(k)/N_+(k)N_-(k)=0 \tag{2·4'}$$

We neglect the higher order terms of (1·6) and (1·4) so that

$$H_r=H_{ph}{}^0+\frac{(i\hbar)^{-1}}{2}[H_{ph}{}^0, S]_-+\sum_{\kappa}\frac{G(k)}{2}\rho_k\rho_{-k}-\left(\frac{\rho_0 G(0)}{2}+\beta\right) \tag{2·5}$$

$$\sum_q\frac{\hbar^2 q^2}{2m}a_q{}^*a_q-\sum_{H_0'}M_{H_0'}H_{ph}{}^0 M_{H_0'}=-\beta \tag{2·6}$$

Using (2·6), (2·4), we can determine $A(k)$, $B(k)$ and β as

$$A(k)=\frac{k^2\rho_0}{2m},\quad B(k)=-\hbar^2k^2\rho_0/2m\,N_+(k)N_-(k),\quad \beta=\sum_\kappa\frac{\hbar^2k^2}{4m} \tag{2·7}$$

The explicit form of H_r of (2·5) will be shown in the example.

3 Ground State of Boson Assemblies

We shall apply the obtained results in section 2 to the case, in which all bosons are nearly degenerate to the zero-state in the momentum space and only α bosons are in a q_1-th state, i.e. $n_0=\rho_0-\alpha$; $n_{q_1}=\alpha$; $n_q=0$ except $q=0$ and q_1, where $\alpha\ll\rho_0$. From (2·5), the Hamiltonian of the system becomes

$$\begin{aligned}H_{q_1}=&\sum_{\substack{k>2|q_1|\\k<-2|q_1|}}\left\{b^*(k)b(k)+\frac{1}{2}\right\}\hbar\omega_0(k)+\sum_{k>2|q_1|}\frac{\alpha k^3\hbar^2}{2m\rho_0}\{b^*(k)b(k)-b^*(-k)b(-k)\}\\&+\sum_{-2|q_1|<k<2|q_1|}\begin{cases}\left\{b^*(k)b(k)+\frac{1}{2}\right\}\hbar\omega_1{}^-(k)+\dfrac{\alpha\hbar^2k^4\rho_0{}^2\{1+b^*(-k)b(-k)-b^*(k)b(k)\}}{16m(\rho_0-\alpha)^3q_1(q_1-k)} & \text{for}\quad q_1>0\\ \left\{b^*(k)b(k)+\frac{1}{2}\right\}\hbar\omega_1{}^+(k)-\dfrac{\alpha\hbar^2k^4\rho_0{}^2\{1+b^*(-k)b(-k)-b^*(k)b(k)\}}{16m(\rho_0-\alpha)^3q_1(q_1+k)} & \text{for}\quad q_1<0\end{cases}\\&+\frac{G(0)}{2}\rho_0(\rho_0-1)-\sum_k\frac{\hbar^2k^2}{4m}\end{aligned} \tag{3·1}$$

where

$$\omega_0(k)=\left\{\frac{\hbar^2k^4}{4m^2}+\frac{\rho_0}{m}k^2G(k)\right\}^{1/2}$$

$$\omega_1{}^\pm(k)=\omega_0(k)+\frac{\alpha k^2}{8(\rho_0-\alpha)}\left\{\frac{\omega_0(k)\rho_0}{q_1(q_1\pm k)(\rho_0-\alpha)}+\frac{2\hbar^2k^2}{m^2\omega_0(k)}\right\}$$

Now we compare the ground energy $E_{q_1}(\alpha)$ of the above case (3·1) with the ground energy E_0 of the case, in which all bosons are perfectly degenerate to the zero-state, i.e. $\alpha=0$.
We have

$$E_{q_1}(\alpha)-E_0\simeq\frac{\alpha\hbar}{16\rho_0 m}\sum_{-2|q_1|<k<2|q_1|}\left[k^2\left\{\frac{w_0(k)m}{q_1(q_1\mp k)}+\frac{2\hbar^2k^2}{m\omega_0(k)}\right\}\pm\frac{\hbar k^4}{q_1(q_1\mp k)}\right] \tag{3·2}$$

Concerning $\omega_0(k)$, we use such approximation as

$$\omega_0(k)\simeq|k|\left\{\frac{\rho_0}{m}G(0)\right\}^{1/2}=C|k| \tag{3·3}$$

which is resonable in the limit $|k|\leq\frac{2m}{\hbar}C$

$$E_{q_1}(\alpha)-E_0\simeq\frac{\hbar\alpha}{32m\pi N_0}\left\{(\log 3-4)Cq_1{}^2m+\frac{16\hbar^2q_1{}^4}{mC}+\left(\log 3-4-\frac{16}{3}\right)\hbar|q_1|^3\right\} \tag{3·4}$$

where N_0 is the number of bosons per unit length.
From (3·4), we can show easily that

$$E_{q_1}(\alpha)-E_0\leq 0 \tag{3·5}$$

in the limit $|q_1|\leq\frac{0.78}{\hbar}mC$, $0\leq\alpha\leq\alpha_0\ll\rho_0$ and the value of $(E_{q_1}(\alpha)-E_0)$ becomes minimum at $|q_1|=\frac{0.56}{\hbar}mC$

$$<E_{q_1}(\alpha)-E_0>_{\min}=-\frac{0.73\,m^2C^3}{16hN_0}\alpha$$

For Helium, its numerical value is $-1\times10^{-16}\alpha$ erg. From (3·5), we conclude that all bosons are not perfectly degenerate to the zero-state of momentum space in the ground state of boson assemblies of which the particles interact mutually.

Uncertainty Relations and Ground States of Liquid Helium

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Remarks on the Theory of Superconductivity

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The electron theory of metals in its conventional form is based on the hypothesis that in an idealised lattice (with ions rigidly fixed to lattice points) the electrons can be considered as moving independently of each other, (free electron hypothesis). The whole interaction of an electron with all the others is then described in terms of a periodic potential only. On the basis of this hypothesis, F. Bloch[1] has shown that the displacement of ions from their lattice points leads to an additional interaction with the electrons which can be described in terms of absorption or emission of vibrational quanta. Some time ago it occurred to me[2] that this represents one aspect of a field theory in which the electrons are the sources of the field describing the lattice displacements. In another aspect this field must lead to an interaction energy between electrons. The calculation of this interaction energy involves very great difficulties which have not been overcome as yet[3]. Very strong reasons can be given, however, to support the assumption that it is this interaction which is responsible for superconductivity.

To show this consider the Hamiltonian

$$H=H_{el}+H_f+H_{int} \tag{1}$$

in which H_{el} and H_f are the Hamiltonians of the electrons and the lattice field respectively and H_{int} refers to the interaction between the two; the latter has matrix elements corresponding to emission and absorption of field quanta connected with the corresponding electronic transitions. To discuss the order of magnitude of the energies involved, assume one free electron per atom and let $\zeta\simeq1$ e-volt be of the order of magnitude of the Fermi energy of the electrons. Further let $\sigma'/K\sim10^{-2}$–10^{-3} be the ratio of the velocity of sound (in the absence of H_{int}) to the average velocity of a free electron. Then per atom, $\zeta\sigma'/K$ gives the order of the zero point vibrational energy, due to H_f. The main part of the interaction energy is rather uninteresting. It can be estimated by assuming that the electrons follow the lattice vibrations adiabatically, leading to a magnitude $-F'\zeta\sigma'/K$ per atom where F' is a numerical constant. It has been pointed out by Wentzel[4] that $F'<1$ is required to keep the lattice stable. This part of the interaction can also be treated in terms of a canonical transformation[5] which essentially leads to a renormalization of the velocity of sound to a value which must be equated to the measured one. This transformation takes account of the interaction of the bulk of the electrons with the vibrational field. Transitions in which energy is very nearly conserved cannot be treated, however, in this way. After carrying out canonical transformation, therefore, a Hamiltonian results which still contains an interaction term which, however, is restricted so as to lead only to transitions in which energy is nearly conserved, i.e. involving electrons in a narrow region near the Fermi surface only. It is this term which is of principal interest here. The difficulty of treating it is largely due to the high degeneracy of the system of very many electrons interacting through the vibrational field.

Certain features of this interaction can, however, be considered without having a complete solution. Assume – as is likely – that the remaining interaction matrix elements referring to emission or absorption of a quantum with frequency ν conserve energy within a range less than $h\nu$. Then in the absence of free quanta a distribution of N electrons in which all the N lowest levels are occupied does not give rise to any contribution to the remainig interaction. An electron removed from this contribution to higher energries will, however, make a contribution which can be calculated easily on the assumption that other electrons do not get involved except through the Pauli principle. The energy gained in this way must be compared with the increase in zero order electronic energy. It is found then that the original distribution is unstable if a certain parameter F is larger than unity; also $F=F'\sigma'/\sigma$ where $F'<1$ has been introduced above, and $\sigma'/\sigma=1/(1-F')>1$ is the ratio of the velocities of sound before and after taking account of the interaction with the bulk of the electrons. The value of the parameter F can be obtained semiempirically from the ordinary resistivity ρ_T at a high temperature T at which ρ_T/T is temperature independent – together with the empirical value ζ of the velocity of sound. It is found then that for nearly all normal metals $F<1$ whereas for most superconductors $F>1$. The order of magnitude of the energy ζ which can be gained in the case $F>1$ by assuming at $T=0$ (in zere order) an electron distribution different from the Fermi distribution can be estimated to be about $\zeta\simeq(F-1)\zeta\sigma^2/K^2$ per atom. Thus ζ is seen to be about σ/K ($\sim10^{-2}$–10^{-3}) times smaller than the main part of the interaction energy and hence should have only a very weak influence on the velocity of sound.

The hypothesis that $F>1$ defines a superconductor not only leads to a division of metals into normal and superconductive metals, in fair agreement with the experimental evidence, but it also has led to the prediction of the isotope effect[2]. From the above, ζ should be (per atom) the energy difference between the normal and the superconductive state of a metal. This energy is of a reasonable order of magnitude. Moreover it is inversely proportional to the isotopic mass M a relation which has been confirmed experimentally[6]. This isotope effect, proving that $\zeta\propto1/M$, is a very large effect; several orders of magnitude less would be expected from the influence of the isotopic mass on other types of interaction. It seems, therefore, that the isotope effect represents a most direct confirmation for the hypothesis advanced above.

Bardeen[7] starting from a knowledge of the isotope effect has also advanced the above hypothesis and has arrived at a similar criterion for superconductivity.

As mentioned before, a satisfactory detailed treatment of the electrons interacting through the vibrational field is still outstanding, and it has, therefore, not been possible to deal theoretically with the questions of electromagnetic and thermal properties. From a study of various methods I have come to the conclusion that any treatment related to methods of perturbation theory would have to go practically to infinite order. Also I think that if in the correct solution, say for the ground state, the interaction parameter is put equal to zero, the result would not be describable in terms of a singe electron distribution (in momentum space) but rather in terms of a superposition of many distributions. I feel, therefore, that it is profitable to look for new representations already in the case of the free electron gas.

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On the Phase Transition of the Electron-Lattice Vibration System

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In Fröhlich's theory[1] of the superconductivity, it has been shown that a peculiar distribution with a shell has a lower energy than the usual Fermi one, when the interaction constant between electrons and lattice vibrations exceeds a certain value. Such a distribution with single or multiple shells has been considered as identical with the superconducting state. However, the appropriateness of this identification is questionable. In some cases, the distribution may undergo a deformation gradually with the rise of the temperature and lose its characteristic shell structure, approaching to the usual one. In this case, we cannot expect the occurrence of the transition between the superconducting and the normal state. Recently, Zimmermann[2] discussed the thermodynamical properties of the electron-lattice vibration system somewhat in details, but he did not clarify the mechanism of the transition, thus the identification did not become an object of discussion. The aim of the present work is to study the phase transition of the system in some details. As the result of this work, it has been concluded that a) the transition does not occur unless the distribution with odd number of shells is most stable at absolute zero, b) the transition is of the first kind, and c) the dependence of the trasition temperature on the isotopic mass M is not expressed as proportional to $M^{-1/2}$. With regards to these results, it may be difficult to attribute the phase transition of the electron-lattice vibration system to that between the superconducting and the normal state.

Now the distribution function is determined as a solution of the following equations:

$$\left.\begin{aligned} \varepsilon(\boldsymbol{k}) &= \frac{\hbar^2}{2m}k^2 - \frac{V}{(2\pi)^3}\int \frac{8F\zeta}{3nV}\,\psi(\boldsymbol{k},\boldsymbol{k}')f_{\boldsymbol{k}'}d\boldsymbol{k}', \\ f_{\boldsymbol{k}} &= \frac{1}{e^{\frac{\varepsilon(\boldsymbol{k})-\zeta(T)}{KT}}+1}, \end{aligned}\right\} \tag{1}$$

or

$$2f(x)\pm 1 = \mathrm{th}\,\frac{1}{KT}\left[\frac{4F\zeta\sigma_0}{k_0}\left\{\int \overline{\psi}(x,y)f(y)\frac{dy}{\sigma}+L(x)\right\}-\frac{\zeta}{k_0}x\right] \qquad (x \lesseqgtr 0), \tag{1'}$$

where Fröhlich's notations are used. At very high temperatures the above equation (1′) can be treated approximately as a linear integral equation, which has only one solution for a given interaction constant. While, below a certain temperature there exist generally three solutions, if the interaction is strong enough. This circumstance is somewhat similar to that in Weiss' theory of the ferromagnetism, where the equation from which the magnetization can be obtained has three solutions below the Curie temperature. The weak interaction in the present problem corresponds to the strong applied field in the problem of magnetism, and there exists only one solution in both cases. If the free energy for one of the three distributions is the lowest below a certain temperature, while that for another is the lowest above that temperature, we may be able to infer a phase transition at that temperature. Thus we see that it is essential for the occurence of the phase transition that (1′) has more than one solution.

At absolute zero the integral equation (1′) can be reduced to the following form:

$$\left.\begin{aligned} f(x) &= \begin{matrix}1,\\0,\end{matrix} \quad \text{for} \quad \varphi(x) = \frac{4F\zeta\sigma_0}{k_0}\left\{\int \overline{\psi}(x,y)f(y)\frac{dy}{\sigma}+L(x)-\frac{\zeta}{k_0}x \gtrless 0 \right. && (x>0), \\ f(x) &= \begin{matrix}-1,\\0,\end{matrix} \quad \text{for} \quad \varphi(x) \lesseqgtr 0 && (x<0). \end{aligned}\right\} \tag{2}$$

From (2) the distributions at 0°K can be easily obtained by simple numerical calculations, and further also the energies for these distributions. Fig. 1 shows the energy *vs.* interaction constant curves, taking the energy for the Fermi distribution as standard.

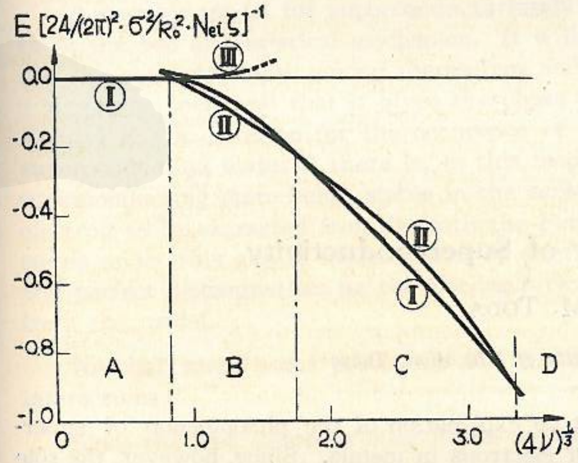

Fig. 1

Curves I and II represent the energies for the distribution functions with none or even number and odd number of shells respectively, and curve III is the same as curve II with reference to the parity of the number of shells. As for the curves at higher temperatures, II and III will be deformed and displaced to the right, leaving I alone. Suppose that the interaction constant lies in one of the ranges B, D, ..., then the distribution II which is refer to the curve II is most stable at absolute zero, while with increasing temperature the distribution will change from type II into type I which is only one allowed to exist at high temperatures. On the contrary, when the interaction constant lies in one of the ranges A, C, ..., the distribution of type I is most stable at absolute zero as well as at very high temperatures. Accordingly, the distribution may change its form gradually through the temperature range without any abrupt change, and the phase transition will not occur in this case. Thus, we see that the criterion for the occurence of the transition is not that the interaction constant exceeds a certain value, but that the distribution with odd number of shells is most stable at absolute zero.

We shall next consider the case in which the transition occurs at very low temperature. In this case, the free energies for each distributions are given as follows:

$$\left.\begin{aligned} F_{\mathrm{I}}(T) &= E_{\mathrm{I}}(0)-\gamma_{\mathrm{I}}T^2, \\ F_{\mathrm{II}}(T) &= E_{\mathrm{II}}(0)-\gamma_{\mathrm{II}}T^2, \end{aligned}\right\} \tag{3}$$

where
$$\gamma_i = \frac{\pi^2 K^2}{6} \sum_{X} \frac{1}{|\varphi_i'(X)|} \qquad (X:\ \text{roots of } \varphi_i(x)=0)$$
is the temperature coefficient of the specific heat. From (3) the transition temperature T_c and the latent heat L can be obtained. We have

$$\left.\begin{aligned} T_c &= \sqrt{\frac{E_{\mathrm{I}}(0)-E_{\mathrm{II}}(0)}{\gamma_{\mathrm{I}}-\gamma_{\mathrm{II}}}}, \\ L &= 2\,[E_{\mathrm{I}}(0)-E_{\mathrm{II}}(0)]. \end{aligned}\right\} \tag{4}$$

Since the energy difference $E_{\mathrm{I}}(0)-E_{\mathrm{II}}(0)$ is evidently not proportional to the interaction parameter F which has M^{-1} as a factor, the $M^{-1/2}$ law of the isotope effect will not hold. Even in other cases, we shall arrive at the same conclusions.

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On the Theory of Superconductivity

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It has seemed very difficult to get an explanation of the phenomenon of superconductivity in terms of the theory of electrons in metals. Since, however, the rôle of the interaction between electrons and lattice waves was clarified and emphasized by Fröhlich, it has become hopeful to overcome the difficulties. In our country many researchers are devoting themselves to extend and to complete the calculation concerning the electron-lattice interaction. Among these we may cite Kitano, Y. who computed the interaction more precisely and found that there may happen many shells above the Fermi-surface. He also took the effect of magnetic field into account and is going on to the problem of the phase transitions in superconductors. (Lecture). Nakajima, S., Nakano, F., Kitano, Y. and Hayakawa, S. examined the interaction more closely using the renormalization method and achieved nearly the same results as Fröhlich himself published last year.

Nishiyama, T. two years ago extended the treatment, by Tomonaga, S., of many Fermion-system to three dimentional case. He aimed to include the static interaction between electrons. This was the problem enunciated by Wentzel, G. Recently Nakajima, S. made efforts to renormalize the Hamiltonian including both electron-lattice and electron-electron interactions.

On the other hand Ichimura, H. has long been attacking the problem by statistical mechanics to gain an explanation as to the phase transitions in superconductors. After the Fröhlich's first paper appeared Ichimura replaced the interaction between electrons he assumed by the electron-lattice interaction. He assumed the condition for second order transition, but instead, it seems rather likely that the phase transition of first order will be more natural in his treatment. He has also stressed that coulomb interaction is of the same order of magnitude as the Fröhlich's interaction and must not be negrected.

Heisenberg's theory of superconductivity published several years ago attributed the phenomena entirely to the coulomb interaction between electrons. We are rather sceptical about his argument. But neverthless it is undoubtedly the next step to take the coulomb interaction into consideration. In spite of the simplicity of the functional form of the interaction computation seems more difficult for the coulomb interaction rather than the Fröhlich's term, because there is no clear cut between the term giving rise to the cohesive energy and the excess term with which the electrons interact each other.

A possible model for superconductors will be given. This model is made so as to fit the use of statistical mechanics. It will be shown this model includes both the electron interaction among themselves and the coupling with lattice phonons in a simple manner, and that it gives the phase transition, transition temperature being about 1°K. A criterion for the occurence of superconductivity will be given. In superconducting material there is, in this model, a energy gap for electronic levels, superconducting state being stable in the sense that a finite energy is needed for an electron to be extracted from beneath the Fermi-surface, and the majority of the states under this gap is characterized by electronic supercurrent. Thus supercurrent and perfect diamagnetism or the London's two fundamental equations will be derived from the model.

We shall make some postulates for the model with regard to the mechanism of interactions.

Since the free electrons obey Fermi statistics, they fill approximately a sphere in momentum space, whose radius is determined by the density of the electrons. Momentum space is the aggregate of the quantum states for the entirely free electrons. It is therefore convenient to express the interactions in terms of the electron occupying a state and the vacancy or the hole, that is to say the state which is not occupied by an electron.

A Comment on Fröhlich's Theory

—On the Divergence in the Perturbational Calculation—

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Recently Fröhlich[1] has pointed that the difficulty of the divergence in the calculation of the interactions between electrons and lattice vibrations can be avoided, by leaving the intermediate states almost degenerating to the initial state. We shall here atempt to show that a straightforward calculation which is regardless of the above difficulty gives a reasonable result, contrary to the expectation,

For simplicity we shall take a system whose Hamiltonian is given by

$$\left.\begin{aligned} &H=H_0+H_1+H_2,\\ &\quad H_0=\textstyle\sum_i (P_i^*P_i+\Omega_i^2Q_i^*Q_i)+(p^*p+\omega'^2q^*q),\\ &\quad H_1=\textstyle\sum_i C_i(Q_i^*q+Q_iq^*),\\ &\quad H_2=(\omega^2-\omega'^2)q^*q. \end{aligned}\right\} \tag{1}$$

By thel canonical transformation

$$U=e^{iS}=\exp\left[i\sum_i \frac{C_i}{\Omega_i^2-\omega'^2}\{P_i'q'+P_i'^*q'^*-Q_i'p'-Q_i'^*p'^*\}\right], \tag{2}$$

the above Hamiltonian passes into the following form:

$$\left.\begin{aligned} &H=H_0'+H_2'+H_3'+H_4'+\cdots\cdots,\\ &\quad H_0'=\textstyle\sum_i (P_i'^*P_i'+\Omega_i^2Q_i'^*Q_i')+(p'^*p'+\omega'^2q'^*q'),\\ &\quad H_2'=\frac{1}{2}\sum_{i,j}\frac{C_iC_j}{\Omega_i^2-\omega'^2}(Q_i'^*Q_j'+Q_i'Q_j'^*),\\ &\quad H_3'=-\frac{1}{3}\left\{\sum_j\frac{C_j^2}{(\Omega_j^2-\omega'^2)^2}\right\}\sum_i C_i(Q_i'^*q'+Q_i'q'^*),\\ &\quad H_4'=\frac{1}{8}\left\{\sum_k\frac{C_k^2}{\Omega_k^2-\omega'^2}\right\}\sum_{i,j}\frac{C_iC_j}{(\Omega_i^2-\omega'^2)(\Omega_j^2-\omega'^2)}(Q_i'^*Q_j'+Q_i'Q_j'^*)\\ &\qquad\quad -\frac{1}{8}\left\{\sum_k\frac{C_k^2}{(\Omega_k^2-\omega'^2)^2}\right\}\sum_{i,j}\frac{C_iC_j}{\Omega_i^2-\omega'^2}(Q_i'^*Q_j'+Q_i'Q_j'^*),\\ &\quad\cdots\cdots\cdots\cdots\cdots\cdots. \end{aligned}\right\} \tag{3}$$

where ω'^2 is chosen so as to satisfy the equation

$$\omega^2-\omega'^2=\sum_i\frac{C_i^2}{\Omega_i^2-\omega'^2}. \tag{4}$$

It should be noticed that none of the solutions obtained from (4) is equal to any Ω_i^2, and there appears no term where denominator vanishes in the present calculations. If we take a proper ω'^2, the summation $\sum_i \frac{F_i}{\Omega_i^2-\omega'^2}$ may be replaced

by the principal value of the integral $\int\frac{F_i}{\Omega_i^2-\omega'^2}dj(\Omega_i^2)$, without excluding any term. However, as pointed out by Fröhlich, the expansion (3) does not converge, owing to terms as $\sum_j\frac{C_j^2}{(\Omega_j^2-\omega'^2)^2}$ so far as the terms with small denominator are not excluded. Here, it will be shown that the energy correction calculated by the purterbational method from (3) does converge. For instance, the energy of the ground state is obtained as

$$\left.\begin{aligned} &E=E_0+E_2+E_4+\cdots\cdots,\\ &\quad E_0=\textstyle\sum_i\Omega_i+\omega',\\ &\quad E_2=\frac{C_i^2}{2\Omega_i(\Omega_i^2-\omega'^2)},\\ &\quad E_4=-\frac{C_i^2C_j^2}{4\Omega_i\Omega_j(\Omega_i+\Omega_j)(\Omega_i^2-\omega'^2)(\Omega_j^2-\omega'^2)},\\ &\quad\cdots\cdots\cdots\cdots\cdots\cdots. \end{aligned}\right\} \tag{5}$$

Though the contribution from the diagonal part of H_4' to E_4 is extremely large, it is compensated by that from the nondiagonal part of H_2'. Perhaps, the same may fit to the higher order correction. Also in the problem of the electron-lattice vibration system we may arrive at the similar conclusion. By a rough estimation we get

$$\frac{E_4}{E_2}\approx(4\pi^2\nu F)\left(\frac{\sigma_0}{k_0}\right)^2$$

from which it can be seen that E_4 is sufficiently small to be neglected.

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Statistical Mechanics of Electron-Lattice System

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Basing on Prof. Fröhlich's idea for the interaction of electrons and lattice phonons, we have calculated the free energy of the system of conduction electrons by a method which has been proposed by the author. In this model the Hamiltonian can be written as

$$\left.\begin{aligned} &H=\sum n_k\varepsilon_k+\sum N_g\hbar\omega_g+\Gamma N\\ &N=-i\sum_q\sum_k\sqrt{q}\,(b_qa_{k+q}^*a_k-b_q^*a_{k-q}^*a_k),\quad \Gamma=\left(\frac{2}{3}\frac{\hbar}{N_a}\mu_0c_0F\right)^{1/2} \end{aligned}\right\} \tag{1}$$

where $\boldsymbol{q}, \boldsymbol{k}$ are the wave number vectors; a, a^* (for electron) b, b^* (for phonon) are the operators which usually appear in the number representation; N_a is the number of the atoms in the lattice of volume V; c_0 is the velocity of sound; $F=c^2/3Mc_0^2\mu_0$ as in Fröhlich's paper; $\mu_0=h^2(3N/8\pi V)^{2/3}/2m$ (N: the number of electrons in V, m is the effective mass). With this Hamiltonian we can define the grand partition function Z for our system as

$$Z=Sp\,(\lambda^{\Sigma n_\kappa}\lambda_L{}^{\Sigma N_q}e^{-\beta H}),\quad \beta=\frac{1}{\kappa T} \tag{2}$$

where λ is the absolute activity for the electron and $\lambda=\exp(\beta\mu)$ (μ is the chemical potential); λ_L is that of the phonon and is taken to be equal to 1 afterwards. Sp means to take the trace of the operator in the bracket and if we use the number representation it is equivalent to the multiple summation

$$\sum_{n_1=0}^{1}\sum_{n_2=0}^{1}\cdots\cdots\sum_{N_1=0}^{\infty}\sum_{N_2=0}^{\infty}\cdots\cdots$$

Using the expansion technique invented by Prof. Feynman, we can calculate Z in the expanded form in powers of Γ and obtain

$$\left.\begin{aligned}
&Z=\prod_{k}(1+\lambda e^{-\beta\varepsilon_k})\prod_{q}(1-\lambda_L e^{-\beta\hbar\omega_q})^{-1}\exp[\Gamma^2(<A_1>+<A_2>)+0(\Gamma^4)]\\
&\Gamma^2<A_1>=B\sum_{q}\sum_{k}q\left\{\frac{1}{\boldsymbol{k}'^2-\boldsymbol{k}^2+\sigma_0'q}\frac{1}{1-e^{-\beta\hbar\omega_q}}+\frac{1}{\boldsymbol{k}'^2-\boldsymbol{k}^2-\sigma_0'q}\frac{e^{-\beta\hbar\omega_q}}{1-e^{-\beta\hbar\omega_q}}\right\}f_k\\
&\Gamma^2<A_2>=B\sum_{q}\sum_{k}\frac{q^2}{(\boldsymbol{k}'^2-\boldsymbol{k}^2)^2-\sigma_0'^2q^2}f_kf_{k'}\\
&f_k=\frac{\lambda e^{-\beta\varepsilon_k}}{1+\lambda e^{-\beta\varepsilon_k}},\quad \sigma_0'=\frac{2mc_0}{\hbar},\quad B=\frac{2\beta\sigma_0'\mu_0F}{3N_a}
\end{aligned}\right\} \tag{3}$$

We can determine λ from the equation

$$N=\lambda\frac{\partial}{\partial\lambda}\log Z=\sum_{k}\frac{\lambda e^{-\beta\varepsilon_k}}{1+\lambda e^{-\beta\varepsilon_k}}+\lambda\frac{\partial}{\partial\lambda}(\Gamma^2<A_1>+\Gamma^2<A_2>) \tag{4}$$

Assuming the second term in the left is small, we get

$$\mu=\mu_0-\frac{\pi^2}{12}\frac{(\kappa T)^2}{\mu_0}-(\xi_1+\xi_2),\quad \xi_i=\frac{2\mu_0}{3N}\lambda\frac{\partial}{\partial\lambda}(\Gamma^2<A_i>) \tag{5}$$

ξ_1 becomes approximately

$$\xi_1=\frac{\mu_0\nu F}{6}\left(\frac{\sigma_0'}{k_0}\right)\left(1+4\pi^2\left(\frac{\kappa T}{\hbar c_0k_0}\right)^2+\cdots\cdots\right),\quad \mu_0=\frac{\hbar^2}{2m}k_0^2,\quad \nu=\frac{N}{N_a},$$

The term ξ_2 has special characters and we can proceed as follows. If we rewrite the equation for ξ_2 as

$$\xi_2=\xi_2^0+\xi,\quad \xi_2^0=-2\mu_0\nu F\left(\frac{\sigma_0'}{k_0}\right)^2Q \tag{6}$$

(Q is a constant of order 1), we have

$$\xi=G(\xi)=G_1\xi+G_2\xi^2+\cdots\cdots\qquad(\text{near } \xi=0) \tag{7}$$

Eq. (7) have solutions $\xi\equiv0$ and another one $\xi\neq0$, if we stop with ξ^2. From these results we can calculate the free energy ϕ of the electrons as

$$\phi_n=\frac{3}{5}\mu_0-\frac{\pi^2}{4}\frac{(\kappa T)^2}{\mu_0}-\xi_1'-\xi_2^{0\prime}$$

$$\phi_s=\phi_n-\xi';\quad \xi'=\frac{3\mu_0}{16\nu FQ_2}\left(\frac{k_0}{\sigma_0'}\right)^2\left(\frac{\kappa T}{\mu_0}\right)^2\left\{\frac{2}{3}(1-z_m)F-1-\frac{2}{3}I\left(\frac{k_0}{\sigma_0'}\right)^2\left(\frac{\kappa T}{\mu_0}\right)^2\right\}$$

where Q_1, Q_2, z_m and I are the numerical constants. ϕ_s corresponds to non-zero ξ. With these two equations we can discuss the transition between two branches. If the interaction parameter F satisfies the relation $\frac{2}{3}(1-z_m)\nu F>1$, ϕ_s branch is more stable at low temperatures and transition point appears. This transition is the first order phase change.

A Note on the Electron-Phonon Interaction

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The self-consistent field method was first applied by Bardeen to the theory of conductivity and then by Toya to that of lattice vibrations. As we shall see, the theory of these authors can be compactly formulated in terms of the renormalization theory. Our method seems somewhat more general, since we do not necessitate the adiabatic treatment, and will be useful to elucidate the basis of Fröhlich's theory of superconductivity.

The hamiltonian of the system consisting of electrons and ions is given by

$$H=\int\psi^*(x)\left(-\frac{1}{2}\nabla^2\right)\psi(x)\,dx+\frac{1}{2}\iint\frac{\rho(x)\rho(x')}{|x-x'|}dxdx'+\int\rho(x)V^i(x,X)\,dx+H_i. \tag{1}$$

$\psi(x)$: the quantized electron wave (without spin), $\rho(x)=\psi^*(x)\psi(x)$: the density operator, V^i: the Coulomb potential between electrons and ions, H_i=the kinetic energy of ions+the Coulomb repulsion between ions.

The ordinary Bloch function u_k satisfies

$$\left(-\frac{1}{2}\nabla^2+V^i(x,X^0)+\int\frac{\rho_0(x')}{|x-x'|}dx'\right)u_k(x)=\varepsilon_ku_k(x),$$

where X^0 represents the equilibrium configuration of ions and is the diagonal part of $\rho(x)$. In the case of monovalent metals, $u_k(x)\cong e^{ikx}U(x)\cong e^{ikx}$ so that ρ_0 may be regarded as independent of the electron configuration.

We make the usual expansion $\psi(x)=\sum a_ku_k(x)$. Expanding also the potentials into the powers of $(X-X^0)$ and introducing the suitable normal coordinates q and p, we have

$$H=\sum\varepsilon_ka_k^*a_k+\sum\left(\frac{1}{2M}p_\kappa{}^2+\frac{1}{2}\Omega_\kappa{}^2q_\kappa{}^2\right)+\sum V_\kappa{}^i\rho_{-\kappa}q_\kappa+\sum\frac{2\pi}{\kappa^2}\rho_{-\kappa}\rho_\kappa, \tag{2}$$

where Ω_κ is the fictitious normal frequency, which we would have if ions were vibrating in the fixed charge density ρ_0, V_κ^l the Fourier transform of $(\partial V^l/\partial X^0)$, and the last term the Coulomb repulsion between the non-diagonal parts of $\rho(x)$. According to the renormalization theory, the hamiltonian (2) is rewritten as

$$H=\sum \varepsilon_k a_k{}^* a_k+\sum\left(\frac{1}{2M}p_\kappa{}^2+\frac{1}{2}\omega_\kappa{}^2 q_\kappa{}^2\right)+\sum V_\kappa{}^p \rho_{-\kappa} q_\kappa$$
$$+\sum\frac{2\pi}{\kappa^2}\rho_{-\kappa}\rho_\kappa+\sum(V_\kappa{}^l-V_\kappa{}^p)\rho_{-\kappa}q_\kappa+\frac{1}{2}\sum(\Omega_\kappa{}^2-\omega_\kappa{}^2)q_\kappa{}^2, \tag{3}$$

where ω_κ is the observed frequency and $V_\kappa{}^p$ the observed interaction matrix element between electrons and phonons. We make the canonical transformation to eliminate the third term of (3) and, in the transformed hamiltonian, cancel out the terms having the forms of the electron-phonon interaction and of the phonon self-energy. This condition determines the values of $V_\kappa{}^p$ and ω_κ. Up to the second order of $V_\kappa{}^p$, we have

$$\left.\begin{aligned} V_\kappa{}^p&=V_\kappa{}^l-\frac{4\pi}{\kappa^2}\sum\frac{V_\kappa{}^p(n_k-n_{k-\kappa})}{\varepsilon_{k-\kappa}-\varepsilon_k+h\omega_\kappa},\\ \frac{\Omega_\kappa{}^2-\omega_\kappa{}^2}{\omega_\kappa}&=\sum\left(\frac{h}{2M\omega_\kappa}\right)\frac{(V_\kappa{}^{p*}V_\kappa{}^l+V_\kappa{}^p V_\kappa{}^{l*})}{\varepsilon_{k-\kappa}-\varepsilon_k+h\omega_\kappa}(n_{k-\kappa}-n_k).\end{aligned}\right\} \tag{4}$$

These results agree with those obtained by Bardeen and Toya if we neglect ω_κ in the energy denominators. Our renormalized frequency does not agree with Fröhlich's value, because he did not make the correction for estimating doubly the Coulomb interaction between electrons by the self-consistent field method.

On the Renormalization Calculation of the Interaction between Electrons and Lattice Waves

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The Hamiltonian of the system of electrons and lattice waves in the metal can be expressed,

$$\left.\begin{aligned} H&=H_0+H_1+H_2,\\ H_0&=\frac{\hbar^2}{2m}\sum_\kappa \kappa^2 a_\kappa{}^* a_\kappa+\hbar\sum_k\omega_k\left(b_k{}^*b_k+\frac{1}{2}\right),\\ H_1&=\alpha(v)\sum_{\kappa,k}k^{1/2}(a^*_{\kappa+k}a_\kappa b_k+a_\kappa{}^*a_{\kappa+k}b_k{}^*),\\ H_2&=\sum_k\frac{\Omega_k{}^2-\omega_k{}^2}{4\omega_k}(b_k{}^*b_k+b_kb_k{}^*+b_kb_{-k}+b_k{}^*b_{-k}{}^*).\end{aligned}\right\} \tag{1}$$

The meaning of the notation is the following.

$\alpha(v)$: the coupling constant, a function of the sound velocity, v.

$\Omega(k)$, $\omega(k)$: the virtual and actual angular frequency of the sound with the wave number k, and therefore $\omega_k=2\pi vk$. The renormalization calculation once carried out by us[1] can be detected in the viewpoint of the scattering matrix in the field theory. We can discuss the problem of the transitions among the stationary states of H_0 by H_1 by making use of the so-called scattering matrix, viz.,

$$U_+(t)=1-i\hbar\int_{-\infty}^{t}d\tau H_1(\tau)e^{-\gamma|\tau|}U_+(\tau),$$
$$U_-(t)=1+i\hbar\int_{t}^{\infty}d\tau H_1(\tau)e^{-\gamma|\tau|}U_-(\tau),$$

where
$$H_1(\tau)=\exp(iH_0\tau)H_1\exp(-iH_0\tau),$$

and γ is the adiabatic factor. Then the transformation matrix used in I is constructed from the above matrices, as follows,

$$U=\frac{1}{2}\lim_{\gamma\to 0}[U_+(0)+U_-(0)] \tag{2}$$

The limiting process $\gamma\to 0$ is justified by the condition that the perturbing potential H_1 become extremely small before and after the scattering. In the present problem, however, as electrons moves in the metal always interacting with the lattice phonons, this condition is not fulfilled, and γ cannot be made tend to zero. If the adiabatic factor is assumed $\gamma(k)$ for the collision process with the phonon k, the transformation matrix becomes

$$\left.\begin{aligned} U&=\exp(S),\\ S&=\alpha(v)\sum_{\kappa,k}k^{1/2}\frac{\varphi(\kappa,k)}{\varphi(\kappa,k)^2+\gamma(k)^2}(a_{\kappa+k}{}^*a_\kappa b_k+a_\kappa{}^*a_{\kappa+k}b_k{}^*),\\ \varphi(\kappa,k)&=\frac{\hbar^2}{2m}(\kappa+k)^2-\frac{\hbar^2}{2m}\kappa^2-\hbar\omega_k,\end{aligned}\right\} \tag{3}$$

which reduces to (2) with vanishing $\gamma(k)$.

The Hamiltonian transposed by means of this matrix is

$$H'=\exp(S)H\exp(-S),$$
$$=H_0'+H_1'+H_2'+H_3'+\cdots\cdots$$

in the ascending powers of $\alpha(v)$. The same treatment may be done as in I in regard to the terms H_2', and then the final form of H' is effectively

$$H'\simeq H_d+H_{nd},$$
$$H_d=\frac{\hbar^2}{2m}\sum_\kappa\kappa^2a_\kappa{}^*a_\kappa+\hbar\sum_k\omega_k\left(b_k{}^*b_k+\frac{1}{2}\right)$$
$$+\frac{\alpha(v)^2}{2}\sum_{\kappa,k}\frac{k}{\varphi(\kappa,k)}(a_\kappa{}^*a_\kappa+a_{\kappa+k}{}^*a_{\kappa+k}-2a_\kappa{}^*a_\kappa a_{\kappa+k}{}^*a_{\kappa+k}),$$
$$H_{nd}=H_1'=\alpha(v)\sum_{\kappa,k}\frac{\gamma(k)^2}{\varphi(\kappa,k)^2+\gamma(k)^2}(a_{\kappa+k}{}^*a_\kappa b_k+a_\kappa{}^*a_{\kappa+k}b_k{}^*).$$

In order that this might be the principal of H', the adiabatic factor $\gamma(k)$ should fulfill the condition, $|\Omega_k{}^2-\omega_k{}^2|\ll\gamma(k)^2\ll\varphi(\kappa,k)$, except in the very small regions of which is also the condition that the collision terms in H_3' with the same form as H_1' might be ignored in comparison with H_1'. The collision term H_{nd} gives no influence on the distribution of thermal equilibrium. If the external electric field disturbs this distribution, H_{nd} decides the collision of electrons with phonons, and the usual theory of electric resistance can be developed. The character of this calculation is almost the same as that of Fröhlich's.[2]

References

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2) H. Fröhlich, Proc. Roy. Soc., **A215**, 291, (1952).

A Remark on Electron-Phonon Interactions

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Concerning the interpretation of the superconducting state, it is of essential importance to realize that both electron and phonon do not exist independently but interact with each other everywhere in a crystal, as pointed out by a number of authors in terms of the renormalization of phonon velocity. The eigen function of the electron-phonon system in an equilibrium state is not of the free Hamiltonian but of the Hamiltonian involving the self-energy, H_∞. When an electric field is applied, the eigen function Φ is so modified as to describe the momentum flow

$$\Lambda\Phi=(1-\xi(E-H_\infty)Z)\Phi, \tag{1}$$

where $\xi(x)=P(1/x)-i\pi\delta(x)$ and Z is a complex diagonal matrix. This wave may further be distorted due to the interaction as

$$\Psi=\Lambda\Phi+\xi(E-H_\infty)H'\Psi \tag{2}$$

with $H=H_\infty+H'$ (total Hamiltonian). Ψ expresses a decaying state as Φ does, so that

$$(E-H)\Psi=(E-H_\infty-Z)\Phi$$

Hence the outgoing part of Ψ involves a part $\xi(E-H_\infty)Z\Phi$ and a non-diagonal part that describes the scattering of electrons as

$$\Psi=\Lambda\Phi+\xi(E-H_\infty)(Z+U)\Phi=(1+\xi(E-H_\infty)U)\Phi. \tag{3}$$

This is nothing but the formalism proposed by Arnous[1]

Introducing the self-energy H_s

$$H_\infty=H_0-H_s,\quad H'=H_1+H_s, \tag{4}$$

where H_0 and H_1 are free and interaction Hamiltonians respectively, we have

$$Z=H_s+D(H_1\xi(E-H_\infty)U), \tag{5a}$$

$$U=ND(H_1+(H_1+H_s)\xi(E-H_\infty)U). \tag{5b}$$

Here we have made use of that H_1 has no diagonal part.

Z is decomposed into level shift and level width as

$$Z=\Delta+\frac{i}{2}\Gamma. \tag{6}$$

Δ should be taken to vanish. In the lowest order perturbation theory,

$$U=ND(H_1),\quad \Delta=H_s+H_1P(E-H_\infty)H_1. \tag{7}$$

This is what has been worked out by a number of authors.

In order to obtain the transition amplitude, we have only to take the coefficient of $\Lambda\Phi$ in Ψ. Then the transition probability is given by

$$w_{ba}(E)\,dE_a=\sum_{E_a}\frac{|<b|U|a>|^2}{(E-E_a)^2+\frac{1}{4}\Gamma_a{}^2}\,dE_a \tag{8}$$

where subscript a indicates the quantities in the initial state. For vanishing Γ,

$$w_{ba}(E)\,dE_a\cong2\pi\sum_{E_a}|<b|U|a>|^2\,\delta(E_b-E_a)=\Gamma_a. \tag{9}$$

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Methods of Approximation in the Theory of Electronic Structure of Molecules

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1. Results of calculations of configuration interaction in simple molecles LiH, Li_2, CH, CH_2, C_2H_2 (π electrons only taken into account explicitly) etc. will be reported, which have been carried out by the author's co-workers in Univ. of Tokyo, Univ. of Kyoto and Tokyo Inst. of Technology. On the basis of these and related results, discussions will be given (1) on the comparison of HL and MO methods, (2) on the possibility of simple approximations, (3) on the degree of importance of ionic structures, (4) on the structure of the triple bond, etc.

2. The applicability of the VB method has been considerably extended by the introduction of hybridized orbitals, and usually the choice of orbitals is made so as to minimize the interatomic energy. However, the interatomic or promotional energy is very important, so that the actual situation is a compromise between these two. In this respect the relative importance of s^2p^2, sp^3 and p^4 configurations of the carbon atom in molecules is a very interesting problem. Semi-emprirical calculations have been made for the cases of CH_3 and CH_4, the results of which suggest that lower atomic states contribute to the valence state much more than is anticipated from the so-called sp^2 (trigonal) and sp^3 (tetrahedral) hybridization. The non-planar pyramidal configurations of CH_3 have also been studied, and the choice of the best set of hybridized orbitals is determined in dependence on the vertex angle of the pyramid. The examination of this problem by taking non-orthogonality duly into account seems to be very desirable.

3. The quantum theory of molecules has made a remarkable progress, especially through systematic use of MO method. Still, we could hardly say that the quantum theory of molecules has reached as satisfactory stage. For instance, one of the basic facts of the molecular-structure, that each "bond" in a molecule has its proper "individuality" and is fairly independent of the others in the same molecule, appears rather puzzling to the theory. Prof. Stater's recent approach to this problem is very important from this point of view. The VB type theory used with the neglection of non-orthogonality looks rather suitable to formulate this individuality of bonds, but is open to serious objection. However, in the history of the theory of molecules we have so many instances of "good" results, which prove to be unsound in the next stage of approximation, and hence whose agreement with observation is regarded as more or less fortuitous. This situation seems to suggest that the "crude" theory is not always really so crude and sometimes at least partial justification might be possible by proceeding to still higher approximations. Along this line of thought, a quite tentative trial will be discussed to avoid the higher order permutation difficulty by deforming the wave-functions of bonding orbitals.

Equation of State by Fast Computing Machines

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The development of electoronic computing machines capable of performing a thousand multiplications per second has made it feasible to solve many statistical mechanical problems numerically by the Monte Carlo method.

In order to calculate the properties of a substance by the Monte Carlo method we consider it to be composed of many identical cells, each containing several hundred molecules. We then confine our attention to one of these cells. First, the molecules are assigned arbitrary initial positions in the cell. They are then moved successively according to the following prescription: A molecule is moved a random distance in a random direction. If the move leads to a decrease in the energy of the system the move is allowed. If it leads to an increase in energy of the system it is allowed with a probability $exp(-\Delta E/kT)$. It can easily be shown⁽¹⁾ that this prescription leads to a sampling of points in the configuration space of the system with a relative probability $exp(-E/kT)$. Thus by averaging any desired property of the system over the configurations reached one obtains its canonical average. In practice it seems sufficient in most cases to move each molecule about one hundred times in order to reach equilibrium, and obtain good statistical accuracy.

The system of two-dimensional molecules with Lennard-Jones intermolecular potential has been calculated and the qualitative features of the liquid-gas phase transition were observed. However, large fluctuations in the neighborhood of the transition region made accurate quantitative results difficult to obtain.

The system of two-dimensional rigid spheres was studied and is discussed in reference (1).

In the case of three-dimensional rigid spheres an equation of state has been obtained which is believed to be accurate to about 5% at all densities. It agrees at low densities with the virial expansion, while at high densities (greater than one-half the close-packed density) it is in fair agreement with the free-volume equation of state⁽²⁾ and gives considerably higher pressures than the superposition theory of Kirkwood and Born-Green⁽³⁾.

The radial distribution function at high densities is of a crystalline nature, showing the various layers of neighbors smeared out around their lattice positions. At low densities one obtains a smoothly oscillating radial distribution function of

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(1) N. Metropolis, A. Rosenbluth, M. Rosenbluth, A. Teller and E. Teller, J. Chem. Phys., **21**, 1087, 1953.

(2) W. W. Wood, J. Chem. Phys., **20**, 1334, (1952).

(3) J. Kirkwood, E. Maun, and B. Alder, J. Chem. Phys., **18**, 1040, (1950).

the type observed in liquids. The transition between these types of distribution function occurs at about two-thirds the close packed density. The equation of state does not indicate a phase transition, but a transition involving a small change of density, or a higher order transition, could easily have been smeared out.

The Monte Carlo method appears of wide applicability in calculating the equilibrium properties of substances obeying classical statistics. Further, by following the detailed molecular motions it should be possible to study non-equilibrium phenomena. The authors are now working on an extension of the method so as to treat Bose-Einstein substances at absolute zero.

The authors would like to point out that the possible application of computing machines to statistical mechanical problems has long been considered by many persons, and would like in particular to acknowledge their debt to Professor Edward Teller whose collaboration in the inception and carrying out of this work has been essential. We would also like to thank the Los Alamos MANIAC Group for their kind cooperation.

A New Approach to the Theory of Electrons in Solids

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The most familiar method for treating the electrons in a solid is the tight-binding approximation due to Bloch, and developed by Mott and others. This is essentially the same as the molecular-orbital treatment in molecules. It regards the solid as composed of a large number of atoms arranged in a regular lattice. But, although this is the account which is natural to a *physicist*, it is not the account which is natural to a *chemist*. For the chemist is interested in bonds, and he thinks of a solid as an aggregate of bonds. Bonds have characteristic bond properties, such as length, polarity, force constant, etc., and for this reason Pauling has developed a theory starting with bonds, and allowing resonance.

It is possible to combine these two approaches in a variant of the tight-binding approximation. Studies with molecules, both of saturated type (e.g. the paraffins) and unsaturated type (e. g. the aromatic molecules such as benzene) have shown that a molecular-orbital may be constructed from bond orbitals, and not, as usual, from atomic orbitals. These bond orbitals are directly related to the chemist's bond. A similar approach is possible for solids, and has been commenced.

This new method yields the $N(E)$ curve for the distribution of energy levels as a function of the energy E; and it also gives the bond orders, and hence the interatomic distances. It may be used both for valence solids, such as diamond, and for metals. It is related to the method of equivalent orbitals introduced by Lennard-Jones and to the localised Wannier functions developed in the U. S. A.

It is interesting to notice that in many cases, e.g. a single graphite layer, the predicted shape of the $N(E)$ curve is identical with that obtained by the older tight-binding approximation. But in some others, e.g. the simple cubic, it somewhat generalises the older distribution function.

It should be possible to introduce varying amounts of hybridisation; but the work here is not yet complete. When it is, a link with Pauling's scheme should be obtained.

At this stage it does not seem likely that the method will be directly useful for the absolute calculation of binding energies.

Appendix

Researches in Japan
on
Chemical Physics

This is a list of main papers on chemical physics in Japan. Brief introductions are also given, since some of the papers have been written in Japanese and hence their currency is limited.

CONTENTS

Crystal Plasticity and Dislocation

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The early stage of researches on crystal plasticity in Japan goes back to 1928, when late *Yamaguchi* (1928, 1929) published the world-known pioneering works on slip bands of aluminum single crystals. Japanese researchers, however, had been rather indifferent to the problems of crystal plasticity until 1941. Stimulated by the review paper on dislocation theory by *Seitz* and *Read* (1941), Japanese investigators began to be interested in this subject. But the outbreak of the World War II (1941) prevented the undertaking of extensive fundamental researches, although not a few papers of metallurgical importance were published during the War.

The real first step towards active researches was taken when the War was ended (1945). In early postwar period, the researches were chiefly conducted by three groups, i.e. Sendai, Tokyo and Kyoto groups. At present, however, more than a hundred investigators, including solid state physicists and physical metallurgists, are actively engaged in the researches.

Now a brief summary of some of the recent papers will be given here. The readers are also referred to the appended list of papers published since January 1951 and works read before various conferences since January last year.

(1) **Theory of Dislocation.** Purely theoretical works are rather scarce, reflecting the infancy of this branch of science in this country. But it should not be overlooked that *H. Suzuki* published excellent works on the interaction between solute atoms and extended dislocation (H. Suzuki, 1952) and on a detailed consideration of dislocation networks (H. Suzuki, 1953). *Ookawa* (1953) explained the fine structure of slip bands considering dislocation loops crossing screw dislocations. *Hasiguti* and *Doyama* (1953) made some calculations on dislocations from the point of view of elasticity.

(2) **Deformation of Single Crystals.** It is not easy to summarize in a few lines the researches on the deformation of single crystals, because so many papers have been published on the subject. The readers are referred to the appended bibliography. But attention is called to the beautiful works by *Nishimura* and *Takamura* (1951, 1952, 1953) on the study of slip bands by means of electron microscope and X-ray. The present writer would like to point out that late *Yamaguchi's* tradition is still alive in this field.

(3) **Recovery and Recrystallization.** This is one of the favorite items of Japanese investigators. A vast number of papers of metallurgical importance have

been published, which are not included in the appended list. *Kanzaki* (1951), *Kanzaki* and *Tani* (1951) and *Tani* and *Kanzaki* (1953) made some experiments of recovery and explained it in terms of dislocation theory.

(4) **Grain Boundary and Sub-boundary.** *H. Suzuki* (1951) made an interesting study of boundary migration induced by temperature gradient.

(5) **Microplasticity.** *T. Suzuki* and *Yamamoto* (1952, 1953) and *T. Suzuki* (1953) made an extensive research on microplasticity and related it to atomic diffusion.

(6) **Internal Friction and Anelasticity.** *Hasiguti* and *Hirai* (1951) found a maximum of internal friction of copper single crystals measured as a function of cold working. *Tani* and *Oosawa* (read, 1951) also obtained the same results. According to *Takahashi* (1952), a zinc single crystal shows an interesting non-elastic behavior when it is under vibration, *Kunitomi* (1952, 1953) and *Kunitomi* and his co-workers (1952, 1953) made extensive anelastic measurements of recovery, precipitation and diffusion.

(7) **Bubble Raft Model.** Dynamical behaviors of grain boundaries of bubble raft model crystals were observed by *Fukushima* and *Ookawa* (1953).

The following list of papers and works is by no means a complete one. The writer is responsible for the selection of them.

Abbreviations

J. P. S. J.:	Journal of the Physical Society of Japan. (In English)
J. J. I. M.:	Journal of the Japan Institute of Metals. (In Japanese with English abstract unless otherwise noted)
J. A. P. J.:	Journal of Applied Physics, Japan. (In Japanese)
D. C. P.:	Read before the Divisional Conference of Crystal Plasticity of the Physical Society of Japan.
C. M.:	Read before Conference of the Japan Institute of Metals.
C. A. P.:	Read before the Conference of the Society of Applied Physics, Japan.

Introduction

Seitz, F. & Read, T. A. 1941, J. Appl. Phys. **12**, 100, 170, 470, 538.

Yamaguchi, K. 1928, Sci. Pap. Inst. Phys. Chem. Res. Tokyo, **8**, 289.

Yamaguchi, K. 1929, Sci. Pap. Inst. Phys. Chem. Res. Tokyo, **11**, 223.

1. Theory of Dislocation

Hasiguti, R. R. & Doyama, M. 1952, C. M. Nov., Core energy.

Hasiguti, R. R. & Doyama, M. 1953, D. C. P. May, Core energy.

Hasiguti, R. R. & Doyama, M. 1953, D. C. P. May, Polygonization.

Hasiguti, R. R. & Doyama, M. 1953, D. C. P. May, Half dislocation.

Hasiguti, R. R. & Doyama, M. 1953, D. C. P. May, Sessile dislocation.

Hirone, T. & Adachi, K. 1951, Sci. Rep. Res. Inst. Tohoku Uuiv. **3**, 454, Electrical properties, (In English).

Nakamura, T. 1953, Divisional Conf. Phys. Soc. April, Domain wall of Rochelle salt and screw dislocation.

Ookawa, A. 1953, D. C. P. May, Dislocation loop crossing screw dislocation.

Suzuki, H. 1952, Sci. Rep. Res. Inst. Tohoku Univ. **4**, 455, Solute atoms and dislocations, (In English).

Suzuki, H. 1953, D. C. P. May, Slip mechanism.

Suzuki, H. 1953, D. C. P. May, Dislocation network.

Takeuchi S. & Suzuki, H. 1953, C. M. April, Martensite formation.

Yokobori, T. 1952, Phys. Rev. **88**, 1423, Yielding of iron.

2. Deformation of Single Crystals

Fujiwara, T. & Ogura, I. 1952, J. Sci. Hiroshima Univ. A, **16**, 107, Electron micrograph, Al, (In English).

Fujiwara, T. & Ogura, I. 1953, D. C. P. May, Slip band, Al.

Fujita, E., Suzuki, T. & Yamamoto, M. 1952, C. M. Nov., Slip band structure and work hardening.

Fujita, E., Suzuki, T. & Yamamoto, M. 1953, D. C. P. May, Slip band.

Gokyu, I., Abe, H. & Kohara, S. 1952, J. J. I. M. **16**, 529, Lattice distortion, Al.

Hasiguti, R. R. & Hattori, T. 1952, C. M. April, Deformation band, slip cluster, Al.

Hasiguti, R. R., Hattori, T. & Doyama, M. 1952, C. M. Nov., Bending, Al.

Hasiguti, R. R., Hattori, T. & Kamoshita, G. 1952, C. M. Nov., Shape of slip bands.

Hasiguti, R. R., Namiki, C. & Takagi, K. 1953, C. M. April, Zn crystal in mercury.

Hasiguti, R. R., & Matsuura, E. 1953, D. C. P. May, Creep, Al.

Hasiguti, R. R. & Kamoshita, G. 1953, D. C. P. May, Slip cluster.

Igarashi, I. & Okada, K. 1951, J. J. I. M. **15**, 354, Al-Cu alloy.

Igarashi, I. Okada, K. & Hirakata, T. 1952, J. J. I. M. **16**, 425, Deformation band, Al.

Igarashi, I., Okada, K. & Hirakata, T. 1952, C. M. April, Deformation band.

Igarashi, I., Okada, K. & Kawashima, N. 1953, C. M. April, X-ray, Al.

Isshiki, S. & Kimura, H. 1953, C. M. April, Compression, α-brass.

Ito, M., Onoe, T. & Shinoda, G. 1953, C. M. April, Deformation by high speed rotation.

Kaieda, H. & Oda, T. 1952, C. M. Nov., Deformation band.

Kanzaki, H. 1951, J. P. S. J. **6**, 454, Two stages of deformation, Cu.

Kanzaki, H. 1953, D. C. P. May, Pure glide.

Kawada, T. 1951, J. P. S. J. **6**, 485, Zn bicrystal.

Kawada, T. 1952, J. P. S. J. **7**, 240, Discontinuous elongation.

Nishimura, H. & Takamura, J. 1951, Memoirs Faculty Engng. Kyoto Univ. **13**, 1, Effect of strain rate, Al, (In English).

Nishimura, H. & Takamura, J. 1952, Tech. Rep. Engng. Res. Inst. Kyoto Univ. **2**, 139, Deformation band, (In English).

Nishimura, H. & Takamura, J. 1953, C. M. April, Effect of surface film.

Oda, T. 1952, C. M. Nov., Region between slip bands.

Ogura, I. 1953, J. Sci. Hiroshima Univ. A, **16**, 535, Electron micrograph, Al, (In English).

Oono, K. 1952, C. M. Nov., Al.

Oono, K. 1953, C. M. April, Al.

Senda, T. & Suzuki, M. 1952, C. M. April X-ray pattern.

Shinoda, G. & Amano, Y. 1952, J. A. P. J. **21**, 363, Divergent X-ray, Al.

Shinoda, G. & Amano, Y. 1952, C. A. P. April, Al.

Sonoike, S., Ninomiya, T. & Gunji, T. 1953, C. A. P. April, Silver chloride.

Suzuki, T. & Sakata, S. 1953, D. C. P. May, Stress annealing and stress-strain curve.

Takeuchi, S., Suzuki, H. & Ikeda, S. 1952, C. M. Nov., Stress-strain curve, α-brass.

Takeuchi, S. & Suzuki H. 1953, C. M. April, Stress-strain curve of F. C. C. crystal.

Tani, Y. & Kanzaki, H. 1952, Conf. Phys. Soc., Short range order, α-brass.

Yamamoto, M. & Nishiyama, Z. 1952, C. M. Nov., X-ray diffraction microscopy.

Yanagisawa, M. 1952, J. A. P. J. **21**, 161, Ionic crystal.

Yoshioka, S. & Imura, T. 1951, J. J. I. M. **15,** 4; **15,** 244, Internal strain.
Yoshioka, S. & Imura, T. 1952, J. J. I. M. **16,** 77, Internal strain.

3. Recovery and Recrystallization

Fujiwara, T. & Tohi, S. 1953, J. Sci. Hiroshima Univ. **16,** 545, Recrystallization, Al single crystal, (In English).
Gokyu, I. & Abe, H. 1953, J. J. I. M. **17,** 101, Recrystallization texture, Cu, (In English).
Kanzaki, H. 1951, J. P. S. J. **6,** 90, Recovery.
Kanzaki, H. 1951, J. P. S. J. **6,** 456, Recovery and dislocation.
Kanzaki, H. 1951, J. A. P. J. **20,** 29, Recovery.
Kanzaki, H. & Tani, Y. 1951, Rep. Div. Conf. Japan Inst. Met. No. 6, 30, Recovery (In Japanese).
Kanzaki, H. 1953, D. C. P. May, Activation energy of recovery.
Okamoto, T. & Suzuki, M. 1952, C. M. April, Recovery, Al.
Shimba, H. & Kitajima, T. 1951, J. J. I. M. **15,** 407, Recovery, Al.
Shimba, H. & Kitajima, T. 1952, C. M. Nov., Polygonization and recrystallization.
Shimba, H., Kitajima, T. & Wakabayashi, A. 1953, C. M. April, Recovery and recrystallization.
Suzuki, H. & Ikeda, S. 1952, J. J. I. M. **16,** 584, Rate of growth, Al.
Tani, Y. & Kanzaki, H. 1953, C. A. P. April, Recovery and energy of dislocations.
Yokobori T. 1951, J. P. S. J. **6,** 404, Rate of nucleation.

4. Grain Boundary and Sub-boundary

Iwamura, H. & Shiota, N. 1951, J. P. S. J. **6,** 227, Sub-boundary, Al.
Nishimura, H. & Takamura, J. 1951, Tech. Rep. Engng. Res. Inst. Kyoto Univ. **1,** 19, Substructure, (In English).
Suzuki, H. 1951, J. P. S. J. **6,** 522, Boundary migration induced by temperature gradient.

5. Microplasticity

Ookawa, A. 1951, Bulletin Kobayashi Inst. Phys. Res. **1,** 255, Creep and diffusion, (In Japanese).
Suzuki, T. & Yamamoto, M. 1952, C. M. Nov., Viscosity and diffusion.
Suzuki, T. & Yamamoto, M. 1953, C. M. April, Diffusion and transformation.
Suzuki, T. 1953, D. C. P. May, Diffusion and microplasticity.

6. Internal Friction and Anelasticity

Hasiguti, R. R. & Hirai, T. 1951, J. Appl. Phys. **22,** 1084, Internal friction, cold-worked Cu.
Hasiguti, R. R. 1952, C. M. April, Internal friction due to vacancies.
Hasiguti, R. R., Hirai, T. & Kamoshita, G. 1953, D. C. P. May Cold-work and internal friction, Al.
Hasiguti, R. R. 1953, D. C. P. May, Internal friction due to vacancies.
Hirone, T., Kunitomi, N. & Sato, K. 1952, C. M. Nov. Precipitation and, anelastic anelasticity.
Hirone, T., Kunitomi, N. & Sato, K. 1953, D. C. P. May, Precipitation and internal friction.
Hori, Y. & Kamisawa, I. 1952, C. M. Nov., Internal friction, Cu.
Kunitomi, N. & Ogura, T. 1952, J. J. I. M. **16,** 365, Recovery and internal friction, Al.
Kunitomi, N. 1952, Sci. Rep. Res. Inst. Tohoku Univ. **4,** 386, Recovery and anelasticity, (In English).
Kunitomi, N. 1953, D. C. P. May, Diffusion and anelasticity.

Mima, G. & Imoto, S. 1952, C. M. April, Internal friction, Zn.
Takahashi, S. 1952, J. Appl. Phys, **22,** 866 Anelasticity, Zn.
Takahashi, S. & Imai, H. 1953, C. M. April, Internal friction and elastic modulus, Cu alloy.

7. Rubble Raft Model

Fukushima, E. & Ookawa, A. 1953, J. P. S. J. **8,** 129, Grain boundary.
Fukushima, E. & Ookawa, A. 1953, J. P. S. J. **8,** 280, Dynamical behavior of grain boundary.
Fukushima, E. & Ookawa, A. 1953, D. C. P. May, Grain boundary movement.
Shiota, N. 1953, C. M. April, Grain boundary.

Polymers

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I. Statistical Mechanics of Chain Molecules and Rubber Elasticity

Since 1940, various attempts in this field have been made by *Oka* (1942), *Sakai* (1943), *Kubo* (1947) and *Ochi* (1947). *Kubo* proposed a method of eigenvalue problems. Afterwards, *Y.* and *K. Suzuki* (1947, 1949) carried out the similar investigations, taking account of the interaction between adjacent elements, and *Isihara* (1951, 1952) calculated the distribution of segments of linear polymer about its center of gravity and also the probable distribution under the shear force of laminar flow. The excluded volume effect was studied by *Teramoto* and *Yamamoto* (1951, 1952), leading to the result that the correction to the mean square of end-to-end distance is proportional to $N^{3/2}$ (N: the number of elements), and *Saitô* (1953) confirmed this result by the method of coupling paramenter. And now this feature of the volume effect is being tested with square-lattice-chains by the stochastic experiments using cards by *Teramoto* and others.

As for the theory of rubber elasticity, *Sakai* put forward a pioneering work in Japan in 1943, criticizing *Kuhn's* original theory. *Kubo* (1943) also developed a theory based on his general theory of linear polymers. *Sakai* and *Isihara* (1946,

1948) extended the investigation to the elasticity of chain network systems and to the effect of crystallization. Recently, taking into account of the non-Gaussian character and the non-linear connectivity of the network, *Isihara* (1952) developed a theory, and succeeded in explaining an experimental anomaly revealed by *Treloar*. Theory of wool-like elasticity based on the molecular structure of keratin was also presented by *Sakai* and extended by *Miyake* (1950, 1951). *Hayasi* (1951) investigated the effect of crystallization on the rubber elasticity. *Satô* (1952) developed a theory on the elasticity of liquid silk.

II. Theories of Thermodynamical Properties of Solutions

As early as 1944 *Huzisiro* gave a thermodynamical theory of polymer solutions using lattice model, and later *Oosawa* (1947) and *Oyama* (1947) extended and refined it considerably. Theories of gas-like model of polymer molecule solutions were developed by *Isihara* (1950, 1951), following the theories of McMillan-Mayer-Zimm, yielding rigorous expressions for the second osmotic coefficients of solutions of ovaloids and of dumbbell molecules; they were applied by *Isihara* and *Toda* (1951) to pearl-necklace molecules, and by *Isihara* and *Kihara* (1951, 1952) to anisotropic colloidal solutions to explain the appearance of anisotropic phase in tobacco mosaic virus or bentonite solutions. *Ichimura* (1952) and *Yamamoto* (1952) made new attempts to take account of interactions between polymer molecules, and *Kurata* and *Watari* (1952) presented an improved lattice-model theory applicable to dilute solutions of flexible chains with sufficient accuracy. The equation of state of surface films and the surface tension were discussed, using a lattice-model by *Saitô* (1950) and by *Kurata* (1952), and a nature of coacervation, especially the stabilization of coacervates of the intermediate size by salt ions, was studied by *Oosawa* (1951, 1953).

Angular distribution of intensity of light scattered by solutions of particles with various shape was calculated by *Saitô* and *Ikeda* (1951, 1952). A relation between osmometry and turbidimetry in multicomponent systems, and the turbidity of electrolytic solutions were studied by *Shoogenji* and *Okajima* (1953). In parallel with these theoretical investigations, experiments were carried out by photographical (*Shoogenji* and *Okajima*, 1951), visual (*Inagaki*, 1951), and photoelectrical (*Yamada*, 1952) means of photometry.

III. Viscosity and Viscoelasticity

Many efforts have been done for the investigation of the non-Newtonian character of polymer solutions. The effect of the Brownian motions on the intrinsic viscosity was considered and the calculation for ellipsoids and other models were performed by *Saitô*. His theory was reconsidered from thermodynamical point of view (*Saitô* and *Sugita* (1952)), and moreover was confirmed by experiments on virus (*Wada* (1952)). Theories on the concentrated solutions were presented by *Yamamoto* (1952) and *Mizutani* (1951, 1952) taking into account of the network structure of polymer solution.

The inter-relation between the theories of Debye-Bueche and that of Kirkwood-Riseman was shown by *Isihara* and *Toda* (1952). Recently *Amemiya* (1953) investigated the similar problem. Current theories on the concentration dependence of the viscosity were criticized by *Saitô* (1952) and the diversity of the results obtained hitherto was elucidated.

The visco-elastic behaviors of polymer solutions and solids have been studied, since about 1949, mainly by the measurements of creep (*Fukada*, *Iwayanagi*), of dynamic loss (*Tokita*, *Hidesima*, *Tohara*) and of ultrasonics (*Furuiti*, *Kaneko*, *Ooi*, and others). New methods of the measurements of dynamic properties of polymer solids have been devised by *Kawai* (1951—). Theoretical contributions, concerning the change of loss factor with elongation, to the study of viscoelasticity were given by *Miyake* (1952). The rheological behaviors accompanied by thermal stress were discussed by *Takizawa* (1952).

IV. Charged and Polar Polymers

For polyelectrolytes *Oosawa* and *Imai* (1951) succeeded in giving exact solutions of Poisson-Boltzmonn equations, suggesting the strong condensation of counter-ions in the vicinity of macro-ions, which is rigid-spherical, rod-like or coiled, in solutions with and without salts. Theoretical investigation of mechano-chemical systems were also made by *Asakura* (1953), in parallel with the experimental work by *Noguchi* (1953).

For the polydisperse polar polymers the relaxation time distribution and the loss factor are calculated by *Oka* and *Nakada* (1950), according to the theory of Kirkwood and Fuoss. *Kataoka* (1953) also extended this theory to the case involving hindered internal rotation. *Miyake* (1951) investigated theoretically the change in dielectric constant of solid polymers with water content. Experimental attacks on the molecular state of water in solid polymers were carried out with dielectric constant measurements by *Kawai* and *Kurosaki* (1951) and with measurements of infra-red spectra by *Kawai* and *Tuboi* (1951).

V. Miscellaneous

Besides the researches mentioned above following investigations were also carried out recently in Japan.

i) The theory of cylindrical viscometer, in which a consideration was taken on the feature of viscoelastic materials, was accomplished by *Oka* and *Takami* (1952, 1953). *Hotta* (1952) also investigated the method of analysis of viscosity measurement.

ii) Theoretical researches on colloids were initiated by *Oka* (1940) in this country, and in recent years statistical mechanics of charged colloidal systems was discussed by *Ikeda* (1952).

iii) Crystallization and second order transition phenomena of high polymers as rate processes were investigated by *Sakai* (1946), *Isihara* (1946, 1948, 1953), *Kikuchi* (1947) and *Ookawa* (1951).

iv) Several methods of approximate solution of non-linear diffusion equation were developed, one of which was successfully applied to high-polymeric systems (*Yamada* (1950), *Fujita* et. al. (1951, 1952)).

v) Theoretical studies on biophysics were also carried out by several authors. Thermodynamical analysis of the biochemical reaction concerning the synthesis and the destruction was studied by *Sugita* (1949). He introduced an idea of the metabolic turnover of the negative entropy. Electronic state in proteins was investigated by *Oomori* (1951), and interaction between long conjugated double bond systems was discussed by *Oshida* (1953).

vi) There remain many interesting researches not mentioned above in the intermediate field between physics and technology of high polymers, among which may be included, for example, the research on spinnability of high polymer solutions by *Inagaki* and *Yamamoto* (1953).

List of Papers in Japan
1941——1950

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Statistical Mechanics of Liquid

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Researches in the field of the theory of liquid began, in Japan, in the latter part of nineteen-thirties after the theories by Prof. *Kirkwood* (Statistical Mechanics of Fluid Mixtures) 1935 and Prof. *Eyring* (Hole Theory of Liquid) 1936, and Profs. *Lennard-Jones* and *Devonshire* (Free-volume Theory of Liquid) 1937, 1938 appeared. In earlier papers which were published in this country liquids were treated mainly by the method of assuming some models, and they were not strictly correct from the statistical mechanical point of view. But some relations were obtained by these elementary theories. Among the relations obtained the following may be mentioned: a) Relation between the change of volume and the heat of fusion of metals at the melting points: $\Delta V/V=\frac{3}{2}Q/L$ (*Harasima* 1938) where ΔV is the change of volume at the melting point, Q the heat of fusion and L is the heat of sublimation. b) Formula for heat conductivity of liquids: $K=3.1\times10^{-3}\frac{T_m{}^{1/2}}{M^{1/2}V^{2/3}}$ cal/cm deg (*Osida* 1939), where K is the heat conductivity, M the molecular weight and V is the molar volume.

Attempts to improve the well-known papers by Lennard-Jones and Devonshire concerning the liquid state and the phenomenon of melting were made by Prof. *Ochiai* 1942 and Prof. *Toda* 1941 who was then one of many distinguished pupils of Prof. *Ochiai*.

Soon after the end of the World War II Prof. *Toda* 1947 published two books, one with the title "Theory of the Structure of Liquids" and the other with the title "Theory of Liquid". The manuscripts for these books had been prepared by Prof. *Toda* as early as 1944, but the publication had been delayed owing to the war circumstances. It may be noted that such books as concerning the theory of liquid were published in this country in the period of confusion after the war.

Researches in the field of the theory of liquid were not completely suspended by the war. Some progress was made in the theory of surface energy and surface tension. Attempts to improve the theories of Prof. *Margenau* 1931, Drs. *Kassel* and *Muskat* 1932 were made by *Harasima* 1940. Assuming quasicrystalline structure he calculated the surface energies of some simple liquids and obtained results which were in good agreement with the observed ones. Further the relation between the surface energy and the heat of vaporization was derived. The result was

$$\frac{Q+\frac{1}{2}RT}{UV^{/3}}=2.3\times10^{9}$$

Q: Heat of vaporization in *ergs/mol.*
U: Surface energy in *ergs/cm²*
V: Molar volume in *cm³*

which could be considered as a version of Stefan's law.

The theory was later improved by Prof. *Ono* 1947 on the basis of the lattice theory. He determined the hole-molecule ratio on each layer parallel to the interface by the condition of minimization of the free energy.

On the other hand considerable improvements in the lattice theory of liquid were achieved in the papers of Prof. *Ono* 1947 and Prof. *Toda* 1947. They introduced the free volume notion in the theory of Profs. *Cernushi* and *Eyring* and assumed that the free volume for each molecule depends on the hole-molecule ratio in a comparatively simple way. Thus they could obtain good agreement with experiment in the calculation of the equation of state and the properties at the critical temperatures of many liquids.

In the theory of atomic distribution function of liquid some calculations were made by *Harasima* 1943 on the basis of free volume theory and temperature dependence of the first peak of the radial distribution function was derived and compared with experiments on liquid mercury by Drs. *Boyd* and *Wakeham* 1939. It was shown that the height of the first peak of the function $Rg(R)$ is proportional to the square root of the absolute temperature. An attempt to solve the integral equation of Prof. *Kirkwood* was made by Prof. *Ono* 1948 who assumed that the radial distribution function $g(R,\xi)$ for any value of the coupling parameter ξ is proportional to the value $g(R)$ for full coupling and solved by numerical calculations.

As is well known, the statistical mechanical basis of the free volume theory of liquid was established by Prof. *Kirkwood* 1950 and recent investigations by Prof. *Prigogine* et al 1942, 1948 are of great importance. Moreover the work by Profs. *Mayer* and *Careri* 1952 has made a great contribution by showing how to secure self consistency in the theory. Now attempts to introduce correlations of the positions of molecules which are in neighboring cells are being made by Harasima and some attempts to improve the statistical mechanical theory of surface tension are being made by *Harasima* and by Drs. *Teramoto* and *Segawa*.

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Statistical Mechanics of Transport Phenomena and Thermodynamics of Irreversible Processes

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1. Statistical Mechanics of Transport Phenomena

In 1942, *M. Kotani* carried out an extensive calculation of the transport coefficients of gases at low density for the case of the intermolecular potential of Sutherland's type, and determined the diffusion ratio of gaseous mixture of isotopes, by means of Enskog and Chapman's solution of the Maxwell-Boltzmann equation. And then, in 1943, he and *T. Kihara* performed the similar calculation for the case of the Lennard-Jones potential. This work preceded the papers of *J. de Boer* and *J. von Kranendonk* and the one by *J. O. Hirschfelder, R. B. Bird,* and *E. L. Spotz,* both published in 1948, on the determination of the constants in the Lennard-Jones potential between gas molecules from the transport coefficients of rarefied gases.

Since 1949, *T. Koga* and *N. Taketa* have tried to establish a new method to treat the systems considerably departing from thermal equilibrium, to which the ordinary Maxwell-Boltzmann method may not be applicable, but they have not yet succeeded in obtaining concrete results.

A. Isihara (1950) calculated the viscosity of a degenerate gas according to the Uehling-Uhlenbeck equation. Recently *S. Ono* and *H. Mori* (1952) derived analytically the Uehling-Uhlenbeck equation, which is a quantal modification of the Maxwell-Boltzmann equation from the Irving-Zwanzig equation, which determines the temporal variation of the phase-space distribution function of Wigner. Then, having generalized the notion of the phase-space distribution function, *Mori* (1952) succeeded in analytical derivation of the Bloch equation in the electron theory of metals, from the quantal Liouville equation for the density matrix. And he applied this method to the theory of light absorption in solid. And *Ono* (1953) refined the method for deriving the Uehling-Uhlenbeck equation, by adopting a suitable orthonormal set of functions instead of a set of plane waves. And he (1953) tried to obtain a quantal modification of Kirkwood's generalized Fokker-Planck equation, and showed that Eisenschitz's derivation of the quantal Fokker-Planck equation is not quite correct.

H. Sato (1953) derived the transport equation for phonons in crystal lattices, by means of an adequate averaging procedure, but he did not use the time-averaging process of any kind. *M. Toda* (1953) presented a method for treating transport phenomena, by considering the change in the distribution as the diffusion process in the momentum space.

2. Statistical Mechanics of Irreversible Processes

N. Hashitsume (1950) derived the equation of entropy transport in a simple gas and a free electron gas in metals (1951), by adopting Boltzmann's *H*-function as the definition of entropy. Then he obtained the expression for the rate of irreversible production of entropy in agreement with that given by Tolman and Fine and others from purely phenomenological consideration. And he (1951) extended the above method to the gaseous mixture of reacting molecules. Recently *T. Murakami* (1953) proposed far simpler method for the same problem, and obtained the linear phenomenological coefficients in the galvano-magnetic phenomena, by using Gans's solution for the free-electron theory. Having made use of Gibbs's canonical ensemble in classical statistical mechanics, *M. Shimoji* (1951) obtained the same expressions that furnished by the phenomenological thermodynamics of irreversible processes for the case of the chemical reactions.

T. Yamamoto (1952) obtained successfully M. S. Green's Fokker-Planck equation for the gross variables directly from the Liouville equation, without the assumption that the grossly observable variables are represented by a Markoff random process, while this assumption of Markoff process is essential in M. S. Green's theory of time-dependent phenomena. *Yamamoto* believed, however, that this equation is confined to the change in gross variables, but it is suggested by *Ono* (1953) that Yamamoto's derivation of the equation is applicable not only to the case of gross variables but also to the one of the microvariables such as the positional coordinates of a single molecules, and that Kirkwood's method of derivation of the generalized Fokker-Planck equation is essentially equivalent to Yamamoto's method of derivation of Green's equation. And *Mori* (1953) obtained the expressions for the so-called transition probabilities from the formal solution of the Liouville equation, proved that these transition probabilities obey Smolouchowski's equation, and obtained the equation formerly obtained by Green and Yamamoto. And he also derived the generalized Langevin equation for the mechanical variables of rather general types. *Ono* (1953) proposed an alternative method for deriving Smolouchowski's equation, using the coarse-grained transition probabilities of Callen. This method simplifies the process of derivation of M. S. Green's equation.

3. Statistical Theory of Thermal Fluctuations

In 1942, *H. Takahasi* extended Nyquist's formula on the thermal noise in electrical circuits to a multipole. And he (1952) recently developed a general theory of thermal fluctuation in a system in thermal equilibrium on the basis of Gibbs's classical statistical mechanincs. Having introduced the after-effect function for a phase-function responding to a unit change of an external parameter, he obtained the formula giving the cross-correlation function for the phase-function and the generalized force associated with external parameter. And he also generalized Onsager's reciprocity relation to a system with after effect.

Hashitsume (1952) generalized the Fokker-Planck equation and Langevin equation to systems such that treated by the phenomenological thermodynamics of irreversible processes, based on the transition probability for two states occuring at different times proposed by Onsager. His results are in complete agreement with those obtained By Yamamoto, Ono and Mori on the basis of the statistical mechanics of an isolated system. Hashitsume applied this theory to the problem of the Brownian motion in a colloidal particle and obtained the results coinciding with the usual one. For the problem of one dimensional heat-conduction, he obtained, however, the result which contradicts with Ornstein and Milatz's one.

H. Sato (1952) obtained the expression for the transition probability in open system in equilibrium, based on the assumption that the stochastic processes under consideration are all Markoffian.

4. Phenomenological Thermodynamics of Irreversible Processes

In 1950, *M. Sugita* published a monograph entitled "Thermodynamics of Transient Phenomena," which covers the fields of the kinetics of phase-transition and thermodynamic processes in living systems as well as such field of the irreversible thermodynamics as developed in de Groot's book. He (1950, 1953) gave the further consideration on the application of the thermodynamics of transient phenomena to the biological processes. And he and *N. Saito* (1952) investigated the diffusion of ideal gases, sedimentation of dilute colloidal solution, dielectric anomalies of polar solutions, and intrinsic viscosity of non-spherical macro-molecules from the above stand-point of view. And they obtained the relation between the energy dissipation or entropy production and the probability current of molecules in dilute systems.

S. Yomosa (1953) presented some consideration on the biological processes from thermodynamical and statistical-mechanical stand-points. But there are some persons who have some objections to his conclusion.

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General Theories in Statistical Mechanics

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In the field of statistical mechanics there were few workers before 1940. Among these, Prof. *Husimi, K.*[1] of the Osaka Univ. worked out the elaborate paper on the properties of the density matrix of canonical assemblies (1940), which is still having its proper reputation. Prof. *Harasima, A.*[2], now in the Tokyo Institute of Technology, contributed very much to the theory of liquids from its early stages (1939). He had a small circle for the study of the statistical mechanics, especially of liquids. Among the members of the circle were Dr. *Oka, S.*, one of the noted researchers of high-polymers, Prof. *Nagamiya, T.*[3] (Osaka Univ.) and Dr. *Oshida* (Kobayashi Institute of Science). These promoted the application of statistical mechanics, guided the young workers and drew down to our country the present prosperity in the research works on the atomic theory of the properties of matter in bulk or more shortly of what is called "Busseiron" in Japanese. It is quite true that workers in this field are in some connections with the these pioneers, directly or indirectly. Professors in the Tokyo University, *Yamanouchi, T.*, *Kotani, M.*, *Ochiai, K.*, *Sakai, T.*, and *Muto, Y.*, guided and encouraged all of these workers with helpful suggestions and comments.

We should like to cite some important papers concerning the general theory in statistical mechanics which, partly due to the ill conditions during the war, have not been known so widely to foreign countries. Some of the papers were written in Japanese and had not been published in current languages. We have here an example of the evil influence of drawing curtains between countries.

Prof. *Takahashi, H.*[4] in 1942 showed that one dimensional system can have no phase transition at all. The proof was one of the most beautiful use of the grand partition function. Prof. *Toda, M.*5) proved the validity of the virial theorem in quantum mechanics as well as in quantum statistical mechanics with applications. Prof. *Kubo, R.*6) invented the matrix method for the order-disorder problem, which was quite equal to but preceded the famous paper of *Kramers* and *Wannier*. Prof. *Takagi Y.*7) developed a theory of order-disorder seeking for a kind of the self-consistent solution for the probability of atomic arrangements. It was shown that his method lead to nearly the same results to the Bethe's method, but was very convenient for practical applications.

Nowadays we have several hundreds workers who are skilled in statistical mechanics and are engaged in the research problems concerning the atomic theories of the properties of matter in bulk. Remembering that the famous texts in these fields had been scarecely published before 1949, we can safely say that the theoretical physicists in our country have done so much in these fields, and we believe that it is not accidental that their contributions are increasing with years.

Following is a list of papers published in these several years in the field of the general methods in statistical mechanics, mainly the papers concerning the problems of order-disorder and of condensation.

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,, 1951, J. Chem. Phys. **19**, 1320 Thermodynamic Pressure
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,, **6**, 1025 Plasma Like Oscilation
,, **6**, 1 Algebraic Theory of Density Matrix
,, **7**, 417 Velocity Operator in Quantum Mechanics
,, **8**, 655 Quantum Theory of Boson Assemblies
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Liquid Helium

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A theoretical work of *Nagamiya* on the zero-point motion in solid helium appeared early in 1939, although there was no helium liquifier in Japan until 1952 and our experimental researches on very low temperature phenomena have just started. Soon after the war, *Nagamiya* wrote a concise book on liquid helium, which was a critical review of previous works and was very stimulative for younger theoretists. Many important theoretical contributions have followed it in spite of deficience in the experimental side, and the theory of liquid helium is now one of the most actively investigated subjects in Japan.

After the war, we first took up the two fluid theory to accomplish a consistent phenomenological description of various facts, on which the molecular theory should be constructed. In 1949, *Nakajima*, *Tomita*, and *Usui* formulated the two fluid theory by means of the thermodynamic method. Extension and generalization were done mainly by *Usui* and we now have the theory in a completed form, in which the recent powerful method of thermodynamics of irreversible processes is fully utilized. The theory has been applied to the analyses of various phenomena (second sound, dispersion and attenuation of sounds, thermal Rayleigh discs, heat transfer, surface flows, isotopic mixtures) by many authors (see the list of papers).

On the basis of and in parallel with these phenomonological works, the molecular theoretical considerations have been developed. In 1949, *Toda* proposed a model, in which the statistical correlation between atoms is taken into account by assuming a sort of molecular formation. This model was also applied to the isotopic mixture of He^3–He^4 by *Toda* and *Isihara*. *Harasima* treated the isotopic mixture by considering it as a mixture of the modified Bose gas and the Fermi gas. The orthodox method of quantum statistics has been developed by *Matsubara*, who applied the Hartree-Fock approximation to the Bose condensation of the interacting assembly. He also succeeded in formulating the Bose condensation of the ideal gas in the same form with Mayer's theory of ordinary condensation; generalizing it to the interacting boson assembly, he tried to replace Toda's "molecule" by the more resonable concept of cluster, which is formed by helium atoms on account of the statistical correlation.

As for theroetical approach to the solid, the earlier work of *Nagamiya* on the zero-point energy was extended by *Murayama* and *Ueda*. *Kubo* has proposed a hole theory of quantum liquid; he supposed liquid helium as a sort of solid, in which "plastic" flows occur on account of the quantum mechanical resonance effect, but not of thermal agitation.

There are a few works on the transport phenomena, though they are rather preliminary ones. The gas kinetic theories of the ideal Bose gas and of the phonon gas have been discussed by several authors.

It should also be mentioned that quantum hydrodynamics is one of our main subjects. *Nishiyama* has developed quantum hydrodynamics on the basis of second quantization formalism not only to justify Landau's rather crude theory, but also to establish a new method of approach to the quantum mechanical many body problems. On the other hand, *Ito* formulated the variation principle of classical hydrodynamics by the Clebsch transformation in 1951 and has recently quantized it.

List of Papers

Note: B. K. is the abreviation for *Busseiron-Kenkyu* (Japanese Journal of Chemical Physics)

I. Two Fluid Theory

Harasima,A. 1951, B. K. **37,** 63 (Hamilton's principle for the equations of motion of He II)
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Research Works on the Electronic Theory of Solids in Japan

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As is well known, the electronic theory of solids has a history of about twenty-five years since the famous work of Bloch and its development covers at present a very wide range of the field. In our country, too, various kinds of the research works concerning this field have been published. Their subject matters, however, seem to be taken up in rather divergent ways and have never been concentrated on some specified problems in that field. As a matter of course, it is hard at present to find where the stress is especially placed in our research works.

Roughly speaking, however, they may be classified into two main tendencies; the study of the electronic structure of solids and that of the interaction between electrons and lattice vibrations. In the former, the main subjects worked out so far are as follows; the electronic structure of silicon (*Morita*, 1949 a), and bismuth (*Morita*, 1949 b) by the method of the tightly bound approximation, of silicon by the method of Lage-Bethe's cell method (*Yamaka* and *Sugita*, 1953), the cohesive energy of LiF crystals by Heitler-London approximation (*Yamashita* and *Kojima* 1952), and electronic state of O^{--} ions in MgO crystals (*Yamashita*, 1952) and so on. In the latter, the following works have been done; the improved treatments of the electrical conductivity of alkali-metals and transition metals (*Toya*, 1953 a, b), the theory of the mobility of electrons of semiconductors in strong electrostatic field (*Yamashita* and *Watanabe*, 1952), the temperature effect of electronic energy bands in crystals (*Muto* and *Oyama* 1950, 1951) and so on. Further it must be noticed that the above research works are not isolated, but are connected to the study of the behaviour of electrons in dielectrics, the electronic structure of colour centres in alkali-halide crystals or the theory of the super-conductivity.

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Yamashita J. (1952 b) Jour. Phys. Soc. Jap. **7**, 284 Quantum Mechanical Computation of the Lattice Energy and the Lattice Constant of LiF Crystals

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Antiferromagnetism and Ferrimagnetism

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The investigation of magnetic properties of matter in Japan has a very early origin. In the later years of the last century *J. A. Ewing* visited Japan and stayed at the University of Tokyo. He and his pupils *H. Nagaoka* and *K. Honda* carried out a number of pioneer experiments of ferromagnetism. Thus, as early as 1888, *Nagaoka* made an experiment of the magnetostriction in Ni wire, measuring the intensity of magnetization as a function of torsion. Later works by himself and his collaborator *Honda* on the magnetostriction in Fe, Ni, Co, Fe–Ni alloys constituted the earliest precise measurements of that sort we ever had. Subsequent numerous works by *Honda* and his pupils in the earlier half of this century are widely known. Among them are *S. Kaya's* precise measurements of the magnetization curves for the single crystals of Fe, Ni, Co, which you may find in any textbook of ferromagnetism.

In last decade, it seems that a keen interest has been generally directed to the magnetic properties of ferrites and other compounds, especially with the development of high frequency technic and of neutron diffraction technic. In this region, investigations in Japan are not inactive.

We shall first describe the theoretical development of antiferromagnetism in Japan. A number of more or less interesting papers, published or unpublished, appeared on this subject during and just after the war, of which we shall mention the names of the authors only: *S. Miyahara*, *Y. Takagi*, *T. Nagamiya*, *S. Nakajima* and *M. Shimizu*. When a paramagnetic resonance experiment by *Trounson* and others with Cr_2O_3 appeared in Phys. Rev. (1950), *Nakajima* and *Shimizu* tried to explain its results by combining Kittel's theory of ferromagnetic resonance and Van Vleck's theory of the susceptibility of antiferromagnetics which is based on the approximation of Weiss molecular field, but this trial failed. Then *Nagamiya* (1951) took the anisotropy energy explicitly into the theory, as it was already done by Néel in 1936, and computed expression for the susceptibility as well as resonance formula. This constitutes the earliest general theory of antiferromagnetic resonance. In the same year and in the following early years, *Yosida* extended this theory to the case of spins of a finite magnitude (because *Nagamiya* confined himself to the classical spin), and applied his theory to MnF_2 and $CuCl_2 \cdot 2H_2O$. As regards the latter substance, experiments of particular interst have been carried out at Leiden under Prof. *Gorter*, and Gorter himself worked out in 1952 an apparently more general theory of the antiferromagnetism of this substance for the special case of absolute zero. *Nagamiya* has now shown, however, that Gorter's theory and the subsequent extention of it by *Ubbink* to the resonance problem are equivalent to his and Yosida's theory as regards formalism, and could explain all the main features of Ubbink's resonance experiment to a good approximation not only for absolute zero but also for elevated temperature. Other problems of $CuCl_2 \cdot 2H_2O$, such as the theory of the change of Néel point with the strength of applied field and quantum theory of computing numerical values of the anisotropy constants, have just been done by *Yosida* and his collaborators (1953).

Spin wave theory of antiferromagnetism and other approximational methods higher than the approximation of Weiss field have been developed by *R. Kubo* and *T. Nakamura*. *Kubo* (1952–53) extended Anderson's (1951–52) spin-wave treatment to a higher approximation and to an arbitrary temperature. His method of employing a variational principle (1953, Rev. Mod. Phys.), which in some sense is a Hartree-Fock method, may be estimated as an interesting mathematical technic. *Nakamura* (1952) calculated the resonance frequency for an electromagnetic field by spin-wave method and obtained a result which agreed with Nagamiya's for absolute zero and for the field parallel to the easy axis of the spin system. *Shoji* (1951), treated a one-dimensional antiferromagnetic system of spins of 1/2 by a method somewhat

similar to that of spin-wave and calculated the ground energy level and the partition function. Other methods have been developed by *Kubo* and his collaborators (1951–53) and *Nakamura* (1953), but have not been very successful.

A band theoretical treatment of antiferromagnetism has also been developed by *T. Matsubara* (1952–53) along the line of the idea put forward by *Slater* (1951). Super-exchange has been discussed, too, by *M. Shimizu* (1953).

A very brief survey of the experimental and theoretical investigations of the magnetic properties of ferrites and other compounds in Japan will now be given.

A research group at Tohoku University under Prof. *Honda* was working before the war with magnetite, pyrrhotite, and CrS, measuring their magnetization, electrical conductivity, Hall effect, thermal properties and X-ray patterns, with both natural and synthetic materials. *T. Okamura*, *T. Hirone* and *S. Miyahara* were mainly responsible for these experiments. *Miyahara* (1939–40) and later *Hirone* and *Miyahara* (1942–43) developed a theory of the ferromagnetism of these substances under an assumption that these substances might be a semi-conductor of Wilson type with exchange interaction between electrons. After the war, microwave technic was introduced into Japan, and a great number of ferrites have been investigated by the resonance method, by *T. Okamura* and *Y. Torizuka*, and by *T. Hirone*, *H. Watanabe*, and *N. Tsuya* during the past few years. Néel's theory of ferrimagnetism has been highly appreciated in this country, and a number of measurements of this phenomenon have been done by Watanabe, the group under *Okamura*, *S. Iida* (Tokyo), *E. Uchida* and *H. Kondo* (Osaka), *I. Sugiura* (Nagoya), *Y. Takagi* and *F. Sawaguchi* (Tokyo), *H. Takagi* (Kyoto), etc. At present, an association of research groups of ferrites and other compounds has been formed and is managed by Prof. *Kaya* of Tokyo University. This includes theoretical groups and, at the same time, is in contact with those who are interested in practical applications.

Of special interest might be the properties of pyrrhotite and magnetite. A number of measurements have been done with pyrrhotite by *Miyahara* (1940 and onward), *Hirone*, *Watanabe*, and *Tsuya* (1950), *S. Nagasaki* (1950, specific heat), *R. Ueda* (1951, lattice constant and specific heat), *Y. Torizuka* (1952, resonance, but no definite result yet). A theory has been published by *Yosida* (1951), and also by *Tsuya* (1951), as an extention of Néels theory of ferrimagnetism, which though inconsistent with Bertaut's (1952, France) superstructure determination of Fe_7S_8, might contain something true. *Yosida* (1951, Physica) extended his theory to hematite and others.

Magnetite has also been studied from various sides. A theory of double-peak resonance observed by Bickford (U.S.A.) at low temperatures has been published by *Nagamiya* (1953).

Before concluding this short survey, we might refer briefly to *T. Nagata's* very interesting investigations of the self-reversal of themoremanent magnetism of igneous rocks. This means that some rocks have a permanent magnetization reversed to the direction of the earth's magnetic field. This gave an impetus to Néel for this interpretation of this phenomenon. He has shown (1953) among others that the rocks contained two kinds of magnetic substances with different Curie temperature, giving thus a support to Néels theory.

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Research Works on the Magnetic Resonance Absorption in Japan

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The world-wide developments of the new field of research on the magnetic resonance absorption and microwave spectroscopy have aroused much concern among Japanese physicists just after the war, and stimulated by the important and hopeful aspects of such new development, the research works in that field have been started with fresh activities by Japanese researchers both experimental and theoretical despite of the severe situations of the various kinds of shortage in both research materials and living conditions. Now, the contributions in the mentioned field, published or unpublished, have been accumulated to a considerable amount in such short interval. Moreover, the subjects of the research works performed so far cover a wide range of the field, i.e., nuclear-para-and ferro-magnetic resonance absorption of the various kinds of substances in liquid and solid states, as seen in the accompanying list. Unfortunately in Japan the low temperature instruments to produce liquid helium are not available at present except for the Institute for the Studies of Metals, Tohoku University. Such unfavourable situation seems to hinder for all the magnetic resonance experiments in our country to be extended to the most interesting region of extremely low temperatures. The brief outline of the present situation of the main laboratories and the research problems persued therein shall be described here.

Okamura's Lab. of Tohoku University.
Ferromagnetic resonance absorption in the various kinds of ferrites at high and low temperatures.

Tsuya's Lab. of Tohoku University,
Mechanism of spin-lattice relaxation in the ferromagnetic resonance.

Kotani's Lab. of Tokyo University,
Theory of spin-spin relaxation in the paramagnetic ions within the crystalline solids.

Muto's Lab. of Tokyo University,
Theory of the nuclear-spin lattice relaxation in the crystalline solids and the dynamical aspects of the behaviour of proton in the hydrogen bond.

Kumagaya's Lab. of Tokyo University,
Paramagnetic resonance absorption of some metallic ions within the crystalline paramagnetic salts.

Kakiuchi's Lab. of Tokyo University,
Structure-determination by nuclear magnetic resonance method of some hydrogen containing compounds in liquid and solid states and the structure of hydrogen bonds.

Murakawa's Lab. of Tokyo University,
Experimental measurements of both nuclear spins and electric quadrupole moments of the various kinds of nuclei by means of the nuclear resonance absorption.

Ariyama's Lab. of Nagoya University,
Ferromagnetic resonance absorption and its relaxation.

Nagamiya's Lab. of Osaka University,
Theory of the antiferromagnetic resonance absorption and the related problems.

Ito's Lab. of Osaka University,
Structural analysis of the organic crystals by both nuclear and para-magnetic resonance absorptions.

Tomita's Lab. of Kyoto University,
Theoretical studies of the states of both solid methane and hydrogen by means of nuclear magnetic resonance absorption.

Kanda's Lab. of Kobe University,
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In addition to the above mentioned laboratories, a lot of young and active physicists in the other Universities and Institutes have been working with the common problems in the magnetic resonance absorption.

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Researches on Colour Centres in Japan

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This is a brief survey of research works in Japan on the colouring of alkali-halides and related subjects in the field of semi-conductors. It was after the war that our physicists started intensive studies in this field, although there had been several contributions before that time.

During the war, extensive experimental works were carried out on the thermo- and photo-cathodes materials at *Mazda Research Lab., Tokyo-Shibaura Elec. Co.* (Nishibori and Kawamura 1940, Kawamura and Shinohara 1942, Kawamura 1943, 1946, and 1948, Nishibori, Kawamura and Hirano 1941, Sayama and Asami 1944, Sayama 1947) and on luminescent materials by *Makishima* (Makishima 1944). In 1944, *Nagamiya* made an attempt to calculate the activation energies of electrons trapped at vacancies in BaO and SrO (Nagamiya 1944) and *Kubo* presented a theory on the coupling of electronic motions and the polarization of ionic lattice (Kubo 1948, 1949a and 1949b). Theoretical calculations were given by *Muto* and *Yamashita* on the external photo-electric effect and the thermo-electricity of semi-conductors (Muto 1947a, Yamashita 1949).

Immediately after the war, *Uchida* started experimental studies on coloured alkali-halides, and he found with his collaborators a new band, the "K-band" by his designation, in NaCl and KCl (Uchida, Ueda and Nakai 1949, and 1951, Ueda 1950). They studied the transformations $K \rightleftarrows F$, the luminescence and the photo-conduction due to this K-centre. *Uchida* has also examined in detail the structure of absorption band between F and M (Uchida and Yagi 1953). A very interesting experiment has recently been done by one of his group, *Ueda*, on the bleaching of M-band using polarized light to prove the structural symmetry of the model proposed by Seitz (Ueda 1951, 1952). The F-absorption in KCl–KBr mixture has been observed by *Kondo* and *Matsumoto* (Kondo and Matsumoto 1953). They showed that the peak of the absorption shifts linearly with concentration ratio. *Yokota* reported his observation of the colouring phenomena in quartz and fused quartz (Yokota 1952a, 1952b). Absorption spectrum of Cu_2O has been observed by *Hayashi* and *Katsui* (Hayashi and Katsui, 1950 and 1952). There are other experiments such as the abnormal dispersion and the dielectric breakdown in alkali-halides (Okada 1949, Kondo and Suita 1950, Okazaki and Suita 1951, Suita 1951, Yamanaka and Suita 1951).

Theoretical activities were very much excited after the war. Quite a number of works have appeared in hope to calculate energy levels of various types of colour centres, and, if possible, to decide theoretically between various models. The molecular orbital method, first used by *Muto* for F-centre (Muto 1949a, 1949b), has been extensively applied to quantitative calculations of various centres by *Inui* and his collaborators (Inui and Uemura 1949, 1950a, Inui, Uemura and Toyosawa

1951, 1952). Although, at the present stage, exact calculations seem almost impossible, especially because of the effect of ionic displacement, they could obtain many valuable results. *Nagamiya* and *Kojima* have been trying to apply the Wigner-Seitz method to the electronic state localized at imperfections. Some others tried to give rough estimations of relative magnitudes of excitation energies using, for instance, the continuum model like that of Tibbs, or the self-consistent method proposed by *Kubo* (Kubo 1948), which is very much the same as Simpson discussed. (Nagamiya and Tatsuma 1951, Shimizu and Shogenji 1951, Shimizu 1951). *Inui* and others recently criticized this method and tried some generalizations (Toyosawa, Inui and Uemura 1951). The effect of ionic displacement on the electronic states was discussed dynamically by *Kubo* and *Morita* (Kubo 1949c, Morita 1950). Recently *Yokota* applied a variational method to polaron states (which was independently done also by Lee, Low and Pines) and discussed the possibility of self-trapping of conduction electrons. (Yokota, T. 1953). The concept of polaron states was extended by *Toyosawa* to conduction electrons moving under the influence of polarizable core electrons (Toyosawa 1953).

The broadening and shift, that is the temperature effect of the shape, of the F-band was discussed by *Muto* and by *Inui* and *Uemura* (Muto 1949a, Inui and Uemura 1949, 1950b). An interpretation of Mollwo's relation was given by *Nagamiya* using a very simple model. He also discussed the nature of the V-centres (Nagamiya 1950a, 1950b. 1952a and 1952b). *Toyosawa* has recently pointed out that the degeneracy of p-state would be of some importance for the broadening of F-band.

Theoretical works were also done on some electronic processes related to coloured crystals. *Muto* extended his former theory of external photoeffect to coloured crystals, for which the external photoeffect had been observed by Asmus (Muto 1947b). *Kojima* discussed photochemical reactions in alkali-halides (Kojima 1952). *Kubo* gave a simple theory of multiphonon process involved in thermal ionization of trapped electrons (Kubo 1952). *Kubo* and *Takano* have also discussed the probability of the production of excitons by impacting particles (Kubo and Takano 1951).

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Superconduction

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Theoretical studies of superconduction in Japan were commenced alike as those of liquid helium precedingly experimental researches, which have just now started with the helium liquifier, that has been equipped in Tohoku University in 1952. Earliest theoretical works are those of *Mikura* (1940) and of *Ariyama* (1941), the former raising an objection against the generally accepted opinion of perfect diamagnetism and the latter being a supplement to Welker's proposal of exchange magnetic interaction. Besides they both wrote concise review articles on superconduction respectively. After the war just as interest of younger theoretists in the theory of superconduction was charged up, appeared papers of *Heisenberg* and of *Fröhlich*, and moreover *Tomonaga's* Fermion theory. Comparatively many notable theoretical works followed hereafter, and theory of superconduction is now one of the most exciting subjects in Japan.

Theoretical works after the war in Japan may be classified roughly as follows: (I) Phenomenological theory, (II) Statistical mechanical theory, (III) Electron-phonon interaction theory, and (IV) Miscellanea.

Of these (III) is the most actively investigated. Starting with criticism of *Fröhlich's* theory, particularly concerning lattice vibration frequency, applications of adiabatic theorem, Bohm-Pines transformation and Tomonaga's self-consistent subtraction method by *Kitano*, *Nakano*, *Nakajima* and *Hayakawa* have clarified the situation of Fröhlich's theory. Expectation of reconstruction of Fröhlich's theory by introducing Coulomb interaction energy has been disputed by *Nishiyama*. Improvements of the theory, involving temperature effect or magnetic effect, or rather assuming Hamiltonian from more general point of view are now in progress.

It should be mentioned that *Kitano* has shown that in spite of imcompleteness of treatment, Macke's calculations give correct correlation energies and correlation functions of electron gases, and further that *Mase* has pointed out that pressure effect of transition temperature is favourable for Heisenberg-Koppe theory, but fairly possibly not for Fröhlich's theory in its present form.

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Note: B.K. is the abbreviation for *Busseiron-Kenkyu* (in Japanese)

Pre-war

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Nakano, H. 1950 B. K. **28**, 14 (Phenomenological theory and variation principle).
Nakano, H. 1950 B. K. **30**, 10 (Energy momentum tensor)

II. Statistical Mechanical Theory

Ichimura, H. 1949 J. Phys. Soc. Japan **4**, 265 (Statistical mechanical treatment of conduction electron).
Ichimura, H. 1951 Phys. Rev. **84**, 375 (Statistical thermodynamics).
Ichimura, H. 1952 J. Phys. Soc. Japan **7**, 233 (Statistical thermodynamics).

III. Electron-Phonon Interaction Theory

Kitano, Y. & Nakano, H. 1952 B. K. **53**, 67 (Electron-phonon interaction)
Nakajima, S., Ogawa, S. & Yamada, E. 1952 B. K. **57**, 32 (Lattice vibration)
Nishiyama, T. 1951 Prog. Theor. Phys. **6**, 897 (Interaction of the lattice vibrations with the conduction electrons).

Kanazawa, H., Koide, S. & Noguchi, T. 1953 B. K. **58,** 17 (Lattice vibration and effective mass of electrons).
Mikoshiba, N. 1953 B. K. **62,** 106 (Electron-phonon interaction and low temperature specific heat of non-superconducting metals).

IV. Miscellanea
Nishiyama, T. 1951 B. K. **34,** 83 (Correlation function of many electrons).
Kitano, Y. 1951 B. K. **46,** 33 (Mutual interactions of electron gas).
Mase, S. 1952 B. K. **53,** 10 (Pressure effect of transition temperature).
Mase, S. 1952 B. K. **53,** 16 (Thermoelectromotive force)

Domain Theory and Process of Magnetization of Ferromagnet

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The researches in this field were commenced by *Nagaoka* and *Honda* fifty years ago in this country. The results of researches will be classified conveniently into following three sub-groups, domain structure, magnetization process and accompanying phenomena with magnetization.

In 1946, *Kaya* made a discussion on the influence of the "stray field" due to the free magnetism of domain boundary in ferromagnet. After *Williams* and *Shockley* established their method of observation of the domain boundary pattern, both *Yamamoto* and *Sugiura* made observations of domain patterns of various ferromagnetic substances by the said method, making discussions on their domain structure and crystallographic symmetry. *Chikazumi* made an observation of the changes of "maze pattern" due to electrolytic polishing of the surface of ferromagnet and concluded that the maze pattern will be a sort of closure domains produced by the mechanical polishing. *Tatsumoto* is now making a precise determination of domain structures of iron-silicon crystals by the same method. On the other hand *Murakawa*, *Okamura-Hirone-Miyahara*, and *Sawada*(26)(27)(8) made their observations respectively of the Barkhausen jump in the course of magnetization on various kinds of ferromagnet and determined the velocity of domain boundary displacement. After, *Muto*'s calculation of spin reversal probability in ferromagnet, *Katayama* proposed a formula of the displacement velocity of domain boundary by calculating the probability of spin reversal at domain boundaries. *Hirone*, *Watanabe* and their collaborators proposed a pipe domain model of the stressed perminvar wire based on their observation of the Barkhausen jump of the same ferromagnet.

The research on magnetization process began from *Honda-Masumoto-Kaya*'s, and especially *Kaya*'s investigation on the behavior of ferromagnetic single crystal. *Kaya*'s formula of the domain distribution at the remanent point of demagnetization was the basis for the recent investigation by *Takaki* on the magnetic behavior of iron-silicon single crystal. *Kaya* and his collaborators made a series of researches on the origin of high permeability of Ni$_3$Fe (Permalloy). His results have been developed by *Chikazumi*,(2) *Iida*,(9) *Sato*(25) and others, the former proposing an idea of "directional order" formation of Ni–Fe alloys. *Iida* made a phenomenological survey of ferromagnetic anisotropy energy with a special reference to the high permeability problem of field-cooled ferromagnet. Recently *Miyahara* discussed the influence on the permeability due to the anisotropic form of the precipitated particles in field-cooled ferromagnet. *Sato*(25) also made elaborate investigation on the ferromagnetic behavior of the various kinds of superlattice alloys.

Those researches of magnetization process provoked inventions of various kinds of magnetic materials mainly by physicists in this country. For example, Permanent Magnet by *Honda-Masumoto-Shirakawa*, by *Mishima* and by *Takei*, high permeable alloy by *Nishina* and by *Masumoto*, Magnetostrictive Alloy by *Masumoto* etc.

Katayama(12) made an evaluation of the strained ferromagnetic lattice and reproduced theoretically *Takaki*'s result of measurement on the temperature change of magnetostriction of the crystals of iron. After *Masiyama*'s elaborated works on magnetostriction on the polycrystals of various kinds of ferromagnetic alloys, *Tatsumoto* made a measurement of magnetostriction of silicon-iron crystals. *Funatogawa*(3) completed his measurement of magneto-thermoelectric effect of iron and nickel crystals and, on the basis of his result, he made a discussion with the electronic structure of these metals. In connection with *Shirakawa*'s research on the change of resistance due to magnetization of various ferromagnet and *Yamamoto*'s investigation on so-called ΔE effect, some domain-theoretical discussions are made by these authors. *Kimura* is now studying the inverse Wiedeman effect with a special reference to the domain structure of ferromagnet. Lastly *Tomono*(29)(30) developed *Snoek*'s idea of magnetic after-effect and basing on it he is now making an observation on the retardation of magnetization in steels of low carbon contents. On the other hand *Taoka* found a long period variation of magnetization in ordered Ni$_3$Mn. *Maeda*(13)(14)(15)(22) proposed a theory of magnetic after-effect by assuming a simple model of domain boundary displacement, the results agreeing with his results of observation of the magnetic after-effect in the irreversible course of magnetization of the ferromagnet.

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20) H. Masumoto, H. Saito, ditto A4 (1952), 321 (Fe–Al).
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26) H, Sawada J. Phys. Soc. Japan, 7 (1952), 564 (Barkhausen effect).
27) H. Sawada, ditto **7** (1952), 571. (Barkhausen effect).
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30) Y. Tomono, ditto **7** (1952), 180. (Magnetic after effect).
31) M. Yamamoto, and T. Iwata, Phys. Rev. **81** (1951), 887 L (Domain pattern).
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Molecules

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The electronic structure of simple molecules have been studied by *M. Kotani G. Araki*, *K. Niira*, *K. Tomita*, *E. Ishiguro* and their collaborators. The molecules studied so far include LiH, Li_2, CH, CH_2 CH_3, C_2H_2, C_2, O_2 F_2, and the comparison of various methods of approximation (MO, VB, LCAOSCF,…), configuration interaction, competition between intra-atomic and interatomic energies, etc. have been discussed on some of these molecules. *G. Araki* and *I. Osida* studied π-electron systems; absorption spectra of cartenoids, intermolecular force between long molecules with conjugated double bonds, reactivity of aromatic molecules, solvent effect of absorption spectra etc. have been their main subjects of interest.

As the basis of these calculations a large number of so-called "molecular integrals" are required and the project of tabulation of those integrals have been continued since 1938 by *M. Kotani*, *A. Amemiya*, recently collaborated by *E. Ishiguro* and others. *G. Araki's* group has also published several tables of molecular integrals.

Electromagetic properties (polarizability, diamagnetic susceptibility, chemical shift of proton resonance, etc.) of the hydrogen molecule have been studied with the use of the variational method by *E. Ishiguro*, *T. Arai* and *S. Koide*.

M. Mizushima studied various problems of molecules, including life-time of metastable states of benzene, pressure broadening of spectral lines, the hfs in the rotational spectra of XYZ_3 type molecules, etc. *K. Takayanagi* has been interested in collision between molecules, and applied the results to the theory of dispersion of supersonic in the hydrogen gas. *Y. Kakiuchi* proved the existence of the oxonium ion H_3O^+ with the use of nuclear resonance absorption, and determined the shape of this ion. In the microwave region *K. Shimoda* measured the microwave spectrum of methylamine molecule, while *S. Kojima* measured and analysed the spectrum of bromoform. *K. Tomita* discussed the state of methane and hydrogen molecules in the solide state, utilizing the recent data of nuclear resonance absorption. All these authors belong to a research group of molecular structure, and this group is publishing its "Progress Report" semi-annually.

Besides members of this group, *S. Nagakura*, *K. Nukazawa* and other members of chemistry departments, have made series of investigations on π-electron systems. The internal rotation of molecules is the subject in which Prof. *S. Mizushima* and his co-workers have been particularly interested, and the work done in his laboratory will be summarized in his recent treatise "Internal Rotation".

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7) W. Watari: Electronic States of F_2- and O_2-molecules. Prog. Theor. Phys. **8** (1953) 524.
8) G. Araki, Tutihasi S. and W. Watari: Electronic States of C_2-molecule I, II, III. Prog. Theor. Phys. **6** (1951) 135, 945, 961.
9) M. Mizushima: Tentative Discussions on the Electronic Structure of Benzene by the two-Electron Approximation. Busseiron-kenkyu **37** (1951) 142 (in Japanese).
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Recent Studies of Dielectrics in Japan

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Stimulated by Slater's brilliant theory on the phase transition in KH_2PO_4 (J. Chem. Phys. **9** (1941) 16), numerous papers have appeared concerning the same material. *Takahasi*, paying attention to the existence of the chains of hydrogen bonds, each penetrating the crystal with a definite sense and being free from source or sink in the interior of the crystal, could prove that the perfect flatness of the free energy curve at the Curie point is not an accidental result due to approximate nature of the treatment but a rigorous conclusion to be derived from the model conceived. *Takagi* reformulated Slater's combinatory formula and made it easy to investigate more general cases in which some of the restrictions imposed upon the configurations of the hydrogen bonds around PO_4-groups or on bonding lines were loosened or entirely given up. *Nagamiya* and *Yomosa* took into acount the effect of crystal strain and of local field; they arrived at a satisfactory theory to explain quantitatively nearly all the experimental properties observed by Mason (Phys. Rev. **69** (1946) 173).

In January 1944, a little later than Wainer and Salomon, but of course independently, *Ogawa* came to notice the high dielectric constant of ceramic $BaTiO_3$, and found the λ-type peak at a temperature near 120°C. This discovery has attracted much attention of the physicists in this field. Soon, *Miyake* and *Ueda* confirmed that the material has a perowskite structure, which is cubic about the Curie point while slightly tetragonal below it. Exhaustive experimental researches of barium titanate itself and the related materials of similar structure such as $SrTiO_3$, $PbTiO_3$, $PbZrO_3$, etc. as well as various solid solutions composed of them were carried out by *Hori* and *Waku*, *Sawada*, *Ueda*, *Shirane* and others. *Takahasi* proposed a theory, in which he attributed the origin of ferroelectricity of $BaTiO_3$ to the Lorentz field exerted on Ti ions which is considerably enhanced by the oxigen ions in the same line with them; this idea was the same as was developed independently by Slater (Phys. Rev., **78** (1950) 748). Besides, he pointed out another possibility that in some crystals there may be also an antiparallel arrangement of dipoles, and thus inspired a notion of antiferroelectricity into the mind of experimental physicists. Through accumulation of several date essentially conflicting with well established characteristics of typical ferroelectric crystals, *Sawaguchi*, *Shirane* and *Takagi* were lead to the conclusion that $PbZrO_3$ must be an example of the antiferroelectric crystals, though it seems as if it were ferroelectric because of its high peak value of the dielectric constant. *Sawaguchi* examined the crystal structure of the material and proved that it really consists of the ions displaced in antiparallel directions to each other. The question why such an crystal can show a high peak value of the dielectric constant, was partly answered by *Takagi* using a rather simplified model containing rotatable polar molecules. The structure of $NH_4H_2PO_4$ suggested by *Nagamiya* after his elaborate theoretical analysis of the experimental data was another example of antiferroelectric crystals.

In 1946 *Nagasawa* discovered that WO_3 behaves like a ferroelectric. The detailed investigations were at once commenced by *Sawada, Ueda, Hirakawa* and others yielding ample results which may be of value for future theories. *Sawada* found numerous transition points distributed over wide temperature range from low to very high temperatures, −20°, 330°, 740°, 910° and 1230°C, and *Ueda* determined the crystal structure which is different from that reported by Braekken.

As early as 1941, *Miyake* conclusively demonstrated by means of x-ray measurements that Rochelle salt crystal must split into tiny domains. Then several efforts were paid to get more concrete knowledge about the details of the domain patterns. *Kojima* and *Kato* have detected the Barkhausen effect at the steep portion of the hysteresis loop. At last *Mitsui* and *Furuichi* succeeded to observe through the polarization microscope very beautiful domain patterns of sliced Rochelle salt crystals and KH_2PO_4 crystals (Figs. 1 and 2 after Mitsui and Furuichi). They also succeeded to follow the movement of the domain boundaries under the influence of applied field. They developed a theory concerning the boundaries and thus could estimate the amount of energy associated with these boundaries. Yet, the origin of the low frequency dispersion at about 10 cycles per second found by *Kawai* and *Marutake* remaing still unexplained. *Sawaguchi* proposed a new theory and attributed the origin of ferroelectricity to the breakdown of balance between two antiparallel rows of polarized cells. The model may be called a kind of *ferrielectricity*. The theory seems to be prosperous because it explains a rather complicated behaviour shown by the crystal when it contains some part of ammonium Rochelle salt.

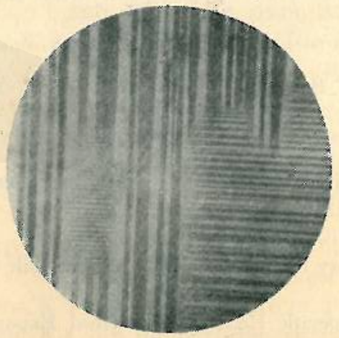

Fig 1. Domain Structure of Rochelle Salt

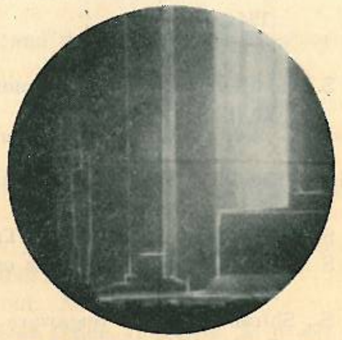

Fig 2. Domain Structure of KH_2PO_4

As for the quantum mechanical treatment of the normal dielectrics such as alkali halides, *Yamashita* and *Kurosawa* tried with notable success to settle down the dispute concerning the effect of overlapping upon the local field coefficients. They succeeded to get a consistent theory to explain numerous properties known for these materials.

With respect to the theory of dielectric properties of the polar liquids as well as the system of dipoles there were rather a few works if compared with those of solids, among them, however the papers due to *Tanaka* and other may especially be noted.

The dipole moments of polar molecules have been actively investigated mainly by chemists; the most eminent contributions have come from *Mizushima* and his collaborators.

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