Quantum Fluctuations Affect the Critical Properties of Noble Gases [*]

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Interacting argon atoms are simulated with a recently developed quantum Langevin transport treatment that takes approximate account of the quantum fluctuations inherent in microscopic many-body descriptions based on wave packets. The mass distribution of the atomic clusters is affected significantly near the critical temperature and thus it may be important to take account of quantum fluctuations in molecular-dynamics simulations of cluster formation processes.

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Molecular dynamics presents a powerful tool for elucidating the features of mesoscopic systems [1]. The present communication draws attention to the possible importance of quantum fluctuations in such treatments. To illustrate this issue, we focus on the cluster mass distribution for argon atoms in thermal equilibrium.

Entities interacting via van der Waals forces, such as atoms of noble gases, form clusters exhibiting enhancements at magic mass numbers associated with especially compact geometric configurations [2]. Several studies based on molecular dynamics have been devoted to the exploration of the mass spectrum of argon clusters in various scenarios (see for example [3–7]). However, the detailed formation process of the clusters, and their observed relative abundance, is not yet fully understood and may well depend on the specific experimental conditions. Because of this delicacy, we examine here the possible role of quantum fluctuations. Such fluctuations are in principle present in the the classical description because it is based on the assumption that the many-body wave function can be regarded as a product of single-particle wave packets, which are not energy eigenstates.

Specifically, our discussion invokes a recently developed treatment in which this inherent effect is emulated by a quantal Langevin force augmenting the usual classical molecular-dynamics equations of motion [8,9]. That treatment was developed in the context of nuclear fragmentation processes and we first briefly describe its adaptation to atomic systems. Subsequently we use the model to calculate the cluster mass spectrum for thermal ensembles of argon atoms and discuss how the results compare with the usual classical simulation.

The interaction between two atoms i and j is described by the usual Lennard-Jones potential,

$$V_{ij} = 4\epsilon \left((\frac{\sigma}{r_{ij}})^{12} - (\frac{\sigma}{r_{ij}})^6 \right) , \tag{1}$$

where the values $\sigma = 3.405$ rA and $\epsilon = 119.8$ K are appropriate for argon atoms and they provide convenient scales for distance and energy, respectively. (For numerical convenience, the potential is truncated at $r_{ij} = 6\sigma$ which has no effect on the results.) The minimum in the potential occurs at an interatomic separation of $r_0 = 2^{1/6}\sigma \approx 1.1225$ σ. Furthermore, the strength of the interaction is characterized by the parameter ϵ which equals the magnitude of the potential at its minimum, $V_0 = -\epsilon$, and provides a convenient energy unit.

The simulation of a classical fluid in thermal equilibrium can be accomplished by augmenting the molecular-dynamics equations of motion by a stochastic term representing the coupling to a thermal reservoir,

$$\dot{r} = \frac{1}{m}p , \tag{2}$$

$$\dot{p} = f - \nu M^2 \cdot p + \sqrt{\nu T} M \cdot \zeta . \tag{3}$$

Here $f_i = -\sum_j \nabla V_{ij}$ is the force exerted on the atom i by all the other atoms $j \neq i$ via the employed Lennard-Jones potential (1). Furthermore, the Langevin force ζ emulating the coupling to the reservoir is a standard white noise with the correlation function

$$\prec \zeta_i(t)\zeta_j(t') \succ = 2\delta_{ij} I \delta(t - t') , \tag{4}$$

where I is the 3×3 unit matrix. The rate ν determines the strength of the coupling and should be chosen to be sufficiently small that its value does not affect the results. Finally, the matrix M has the elements $M_{ij} = (\delta_{ij} - 1/N)I$, and so the Langevin force does not affect the overall momentum $P = \sum_i p_i$.

When the equations of motion are propagated by a simple leap-frog method, the increment in the atomic momenta can be calculated as $p_i \rightarrow p_i + \Delta p_i$ with

$$\Delta p_i = f_i \Delta t - \nu \Delta t p_i + \sqrt{\nu \Delta t T} \chi_i$$
$$+ \frac{1}{N}(\nu \Delta t \sum_j p_j - \sqrt{\nu \Delta t T} \sum_j \chi_j) , \tag{5}$$

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where $\boldsymbol{\chi}_i$ are a random vectors whose components have a normal distribution, $\prec \boldsymbol{\chi}_i \succ = \boldsymbol{0}$ and $\prec \boldsymbol{\chi}_i \boldsymbol{\chi}_j \succ = 2\delta_{ij}\boldsymbol{I}$.

In the quantal treatment, each individual atom is described by a Gaussian wave packet with a spatial variance equal to $\Delta r^2 = \hbar/2m\omega$, where m is the atomic mass and the frequency ω is determined by from the relation $\omega^2 = V_0''/m$. The corresponding "level spacing" is

$$ D \equiv \hbar\omega = \hbar c \left(\frac{V_0''}{mc^2} \right)^{\frac{1}{2}} \approx 0.2265 \, \epsilon \; . \tag{6} $$

The inclusion of the quantum Langevin force effectively modifies the drift term for the intrinsic cluster motion by a factor given by [9,10]

$$ \alpha = \frac{T}{D} \left(1 - \mathrm{e}^{-D/T} \right) < 1 \; . \tag{7} $$

In terms of this reduction factor α, the quantal Langevin equation can be written as follows.

$$ \dot{\boldsymbol{p}} = \boldsymbol{f} - \nu\boldsymbol{M}^2 \cdot [\alpha(\boldsymbol{p} - m\boldsymbol{V}) + m\boldsymbol{V}] + \sqrt{\nu T}\boldsymbol{M} \cdot \boldsymbol{\zeta} \; , \tag{8} $$

where $\boldsymbol{V}$ is the velocity of the cluster to which the atom belongs. The only complication arises from the requirement that the center-of-mass motion of each individual cluster retain a classical character. Thus, in order to determine $\boldsymbol{V}$, it is necessary to perform a cluster analysis of the N-body system at each time step. This task can be easily accomplished by considering two atoms as belonging to the same cluster if (and only if) their separation is less than a certain critical value, taken to be equal to 2σ. When the drift term is modified correspondingly, the expression (5) for the momentum increment is being replaced by

$$ \Delta\boldsymbol{p}_i = \boldsymbol{f}_i\Delta t - \nu\Delta t[\alpha(\boldsymbol{p}_i - m\boldsymbol{V}_n) + m\boldsymbol{V}_n] + \sqrt{\nu\Delta t T}\boldsymbol{\chi}_i $$
$$ + \frac{1}{N}(\nu\Delta t \sum_j \boldsymbol{p}_j - \sqrt{\nu\Delta t T} \sum_j \boldsymbol{\chi}_j) \; , \tag{9} $$

where $\boldsymbol{V}_n$ is the velocity of the cluster n containing i.

The occurrence of the quantum Langevin force is a consequence of the fact that the wave packets are not energy eigenstates. That same feature causes another complication, namely the need for taking account of the thermal distortion of the intrinsic structure of each wave packet (the relative weight of each energy component of the wave packet is temperature dependent). This feature can be taken into account by subjecting the dynamical state of the system to a cooling process before making the observation [9,10]. In the present case, this amounts to integrating the equation

$$ \frac{\partial\boldsymbol{p}_i}{\partial\tau} = -\frac{2\Delta p^2}{\hbar}(\boldsymbol{p}_i - m\boldsymbol{V}_n) \; , \; \frac{\partial\boldsymbol{r}_i}{\partial\tau} = \frac{2\Delta r^2}{\hbar}\boldsymbol{f}_i \tag{10} $$

from $\tau = 0$ to $\tau = \hbar/2T$, thereby distorting the current dynamical values $(\boldsymbol{r}(t), \boldsymbol{p}(t))$ into $(\boldsymbol{r}'(t), \boldsymbol{p}'(t))$. As a result of this cooling process, the atoms change their

positions and so the cluster structure may be modified. While this is a significant effect in the case of nuclear fragmentation [10], the effect is unimportant for atomic systems, since the width of the wave packet Δr is quite small (less than 5% of σ in the case of argon).
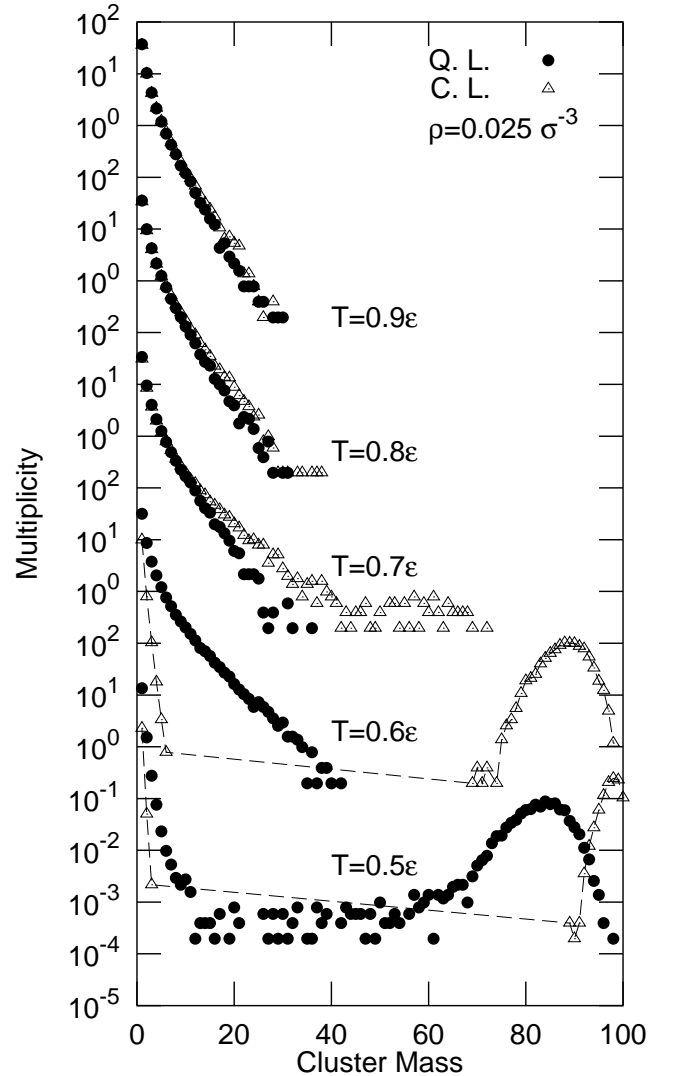

FIG. 1. The mass distribution of argon clusters calculated either *with* (solid circle) or *without* (open triangle) the quantum Langevin force emulating the quantum fluctuations inherent in wave-packet dynamics. The temperatures are indicated in units of ϵ and the atomic density is $\rho = 0.025 \, \sigma^{-3}$.

In order to illustrate the effect of the energy fluctuations caused by the use of wave packets, we show in Fig. 1 the cluster mass distributions obtained for a system of argon atoms held at a specified temperature T. These calculations consider 100 atoms confined within a cubic box and subjected to periodic boundary conditions. The temperatures considered range from well above to below critical. At high temperatures the cluster mass distribution falls off rapidly, whereas there is a preference for condensation into large clusters at low

temperatures. When the classical Langevin equation (3) is employed, the critical temperature associated with this gas-liquid phase transition is approximately $T^{cl} \approx 0.6\epsilon$, as can be seen from the figure. The inclusion of the quantum Langevin force, Eq. (8), produces a steeper slope in the mass distribution at high temperatures and the phase transition occurs at a lower temperature, $T^{qu} \approx 0.5\epsilon$, as might then be expected.

The change of the critical temperature can be understood quantitatively by noting that it is possible to extract an effective classical temperature from the quantal Langevin equation (8). The effective temperature can be estimated by means of the Einstein relation as the square of the diffusion coefficient divided by the drift coefficient,

$$ T_{\text{eff}} = \frac{\nu T}{\alpha \nu} = \frac{T}{\alpha} = D/(1 - e^{-D/T}) > T \; . \qquad (11) $$

This estimate ignores the correction terms arising from the cluster center-of-mass motion, as is justified when we are interested in the cluster mass distribution, because this observable depends mainly on the intrinsic degrees of freedom of the cluster. In addition, the cluster mass distribution is not affected much by the cooling process, as already mentioned. Thus, it is expected that a calculation with the classical Langevin model at the effective temperature, T_{eff}, will yield results that are similar to those obtained with the quantal Langevin model at the real temperature, T.
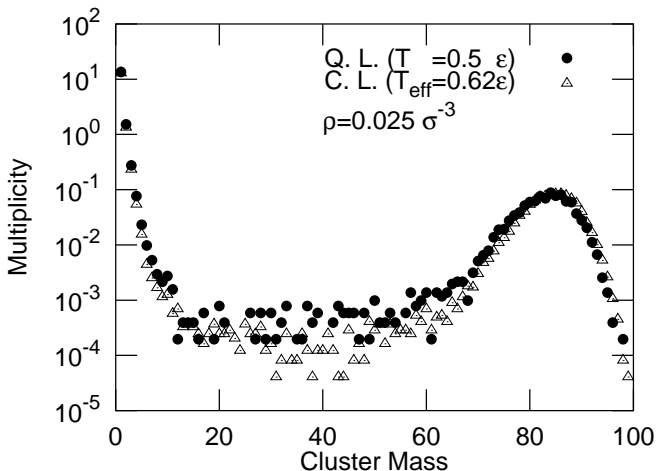

FIG. 2. The cluster mass distribution obtained with either the quantal Langevin model at $T = 0.5\epsilon$ (solid circles) or the classical Langevin model at the corresponding effective temperature $T_{\text{eff}} = 0.62\epsilon$ (open triangles), at the density $\rho = 0.025 \; \sigma^{-3}$.

This expectation is indeed borne out, as shown in Fig. 2 where we compare the cluster mass distribution obtained with the quantal model at $T = 0.5\epsilon$ to the result of the classical treatment carried out at the corresponding effective temperature $T_{\text{eff}} = 0.62\epsilon$. The quantitative similarity between the two distributions is remarkable and supports the above discussion.

The temperature shift depends the system under consideration and the specific observables extracted. For example, the temperature shift is in the opposite direction for particles in a harmonic oscillator potential [9,11] and for nuclear fragmentation [10]. This is because the cooling process affects the observables as well as the modification of the drift term for these systems. In order to illustrate this feature, we consider here the evolution of the distorted momentum (i.e. the solution to Eq. (10)) which is given by

$$ \boldsymbol{p}_i'(t) \equiv \boldsymbol{p}_i(t, \tau = \frac{\hbar}{2T}) = e^{-D/2T} \boldsymbol{p}_i(t) \; . \qquad (12) $$

Thus, in the rest frame of the cluster, the distorted momenta of the constituent atoms are governed by a modified Langevin equation,

$$ \dot{\boldsymbol{p}}' = e^{-D/2T} \boldsymbol{f} - \alpha \nu \boldsymbol{M}^2 \cdot \boldsymbol{p}' + e^{-D/2T} \sqrt{\nu T} \boldsymbol{M} \cdot \boldsymbol{\zeta} \; . \qquad (13) $$

Since this equation of motion has a classical form (c.f. Eq. (3)), we can again invoke the Einstein relation and extract an effective temperature for the intrinsic cluster motion,

$$ T_{\text{eff}}' = \frac{e^{-D/T} \nu T}{\alpha \nu} = D/(e^{D/T} - 1) < T \; . \qquad (14) $$

It has been shown that calculations with classical molecular dynamics at this equivalent temperature T_{eff}' yields results that are very similar to the exact quantal results for the real temperature T, for non-interacting particles in a harmonic potential [9,11–13]. It is to be expected that this feature holds as well for the distribution of intrinsic excitation energies of atomic clusters. Therefore, it would be interesting to measure the atomic cluster mass distribution simultaneously with the intrinsic excitation energy distribution, since the associated temperature shifts are predicted to be of opposite sign (and thus they could not be mocked up by a simple readjustment of the classical temperature).

The present treatment takes account of the fact that the intrinsic atomic motion in a cluster and its center-of-mass motion are of different character. While the latter can be considered as classical, the quantal features of the former may be significant and lead to modifications of the Einstein relation, as we have discussed in the framework of wave-packet dynamics. This important point was already noted by Ikeshoji et al. [7] in their recent study of magic-cluster formation and it might thus be interesting to apply the present treatment to the cluster formation process in an expanding and cooling noble gas.

In the present paper we have adapted a recently developed quantal Langevin treatment to a system of argon atoms in thermal equilibrium. The method was developed in the context of nuclear dynamics and takes approximate account of the energy fluctuations that are necessarily present when wave packets are used to describe the system. The presence of these quantum fluctuations changes the character of the specific heat from

classical to quantal and their inclusion by the developed method leads to a significant improvement of the statistical properties in a number of simple test cases that can be subjected to exact analysis [9,11] as well as for finite nuclei [8,9]. When incorporated into microscopic dynamical simulations of nuclear collisions, it leads to a significant improvement of the calculated fragment mass distribution [10]. For atomic systems, the effect of quantum fluctuations is generally expected to be small, due to the relatively large mass of the "particles". Nevertheless, as we have shown above, the inherent quantum fluctuations may also play a role in atomic physics. Certainly, as our study brings out, it appears that the critical properties of noble gases are affected significantly. The quantum fluctuations may therefore also affect the formation process and might affect the outcome of dynamical simulations aimed at understanding the observed mass distributions.

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