Diffusion-Controlled Processes

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Goals

• Give a flavor of non-equilibrium statistical physics: Not so much the study of specific subjects, but rather a collection of ideas and tools that work for an incredibly wide range of problems.

• Exemplify key insights that have emerged from the analysis of far-from-equilibrium behaviors.

• Diffusion-reaction systems (major lessons, a couple of long-standing challenges).
Aimed at graduate students, this book explores some of the core phenomena in non-equilibrium statistical physics. It focuses on the development and application of theoretical methods to help students develop their problem-solving skills.

The book begins with microscopic transport processes: diffusion, collision-driven phenomena, and exclusion. It then presents the kinetics of aggregation, fragmentation, and adsorption, where basic phenomenology and solution techniques are emphasized. The following chapters cover kinetic spin systems, by developing both a discrete and a continuum formulation, the role of disorder in non-equilibrium processes, and hysteresis from the non-equilibrium perspective. The concluding chapters address population dynamics, chemical reactions, and a kinetic perspective on complex networks. The book contains more than 200 exercises to test students’ understanding of the subject. A link to a website hosted by the authors, containing an up-to-date list of errata and solutions to some of the exercises, can be found at www.cambridge.org/9780521851039.

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A Kinetic View of

STATISTICAL PHYSICS

Pavel L. Krapivsky
Sidney Redner
Eli Ben-Naim

1. Aperitifs
2. Diffusion
3. Collisions
4. Exclusion
5. Aggregation
6. Fragmentation
7. Adsorption
8. Spin Dynamics
9. Coarsening
10. Disorder
11. Hysteresis
12. Population Dynamics
13. Diffusive Reactions
14. Complex Networks

+ >200 problems & soln manual
Simplified Reactions

- Coalescence: $A + A => A$
- Single-Species Annihilation: $A + A => 0$
- Two-Species Annihilation: $A + B => 0$
Single-Species Annihilation
Single-Species Annihilation
Hydrodynamic description

\[ \frac{dn}{dt} = -Kn^2, \quad n = \frac{n_0}{1 + n_0Kt} \approx \frac{1}{Kt} \]

\( n \)  particle density

\( K \)  reaction rate
Hydrodynamic description

\( n \) particle density

\( K \) reaction rate

\[
\frac{dn}{dt} = -Kn^2, \quad n = \frac{n_0}{1 + n_0Kt} \approx \frac{1}{Kt}
\]

\( n(t) \sim \begin{cases} 
  t^{-1/2} & d = 1 \\
  t^{-1} \ln t & d = 2 \\
  t^{-1} & d > 2 
\end{cases} \)
Dimensional analysis

\[ K = K(D, R) \sim DR^{d-2} \]

\[ n \sim \frac{1}{DR^{d-2} t} \]

\[ n = n(D, t) \sim \frac{1}{\sqrt{Dt}} \quad \text{when} \quad d = 1 \]
Polya Theorem

If you need more than five lines to prove something, then you are on the wrong track. *Anonymous.*

\[
\#(\text{sites visited by RW}) \sim \begin{cases} 
\sqrt{t} & d = 1 \\
\frac{t}{\ln t} & d = 2 \\
t & d \geq 3
\end{cases}
\]

Polya theorem ‘explains’ the asymptotic behavior in the single-species annihilation process.
Lessons

There is a critical dimension $d_c$ that separates different kinetic behaviors. (For single-species annihilation, $d_c = 2$.)

Above $d_c$, the rate equation description is OK.

Below $d_c$, it is wrong.

At $d_c$, at most logarithmically wrong.
Coalescence in 1D

$V_n$: density of voids of length $n$.

Evolution of $V_3$ is exemplified.
Coalescence in 1D: Equations

\[
\frac{dV_n}{dt} = V_{n+1} - 2V_n + V_{n-1}
\]

\[V_n(0) = \delta_{n,0} \quad \text{fully occupied lattice}\]
Coalescence in 1D: Equations and Solutions

\[
\frac{dV_n}{dt} = V_{n+1} - 2V_n + V_{n-1}
\]

\[
V_n(t) = e^{-2t} \left[ I_n(2t) - I_{n+2}(2t) \right]
\]

\[
c(t) = \sum_{n \geq 0} V_n(t) = e^{-2t} \left[ I_0(2t) + I_1(2t) \right]
\]

\(c(t)\): Density of particles

\(I_n(2t)\): Modified Bessel function
In non-equilibrium statistical physics the Diffusion Equation plays a role of the Harmonic Oscillator. One must express some characteristics of a strongly interacting many-particle system via the diffusion equation.
Annihilation process with impurity: Unsolved

What is the survival probability $S(t)$ of the impurity particle?

$D_{\text{bulk}} = 1 \quad D_{\text{impurity}} = D$

$S \sim t^{-\theta(D)}, \quad \theta(1) = \frac{1}{2}, \quad \theta(0) = \frac{3}{8}, \quad \theta(D) \approx \sqrt{\frac{1 + D}{8}}$
The survival probability $S_n(t)$ is the probability that the $n^{th}$ particle is alive at time $t$. How $S_n(t)$ decays?
\[ S_1 \sim t^{-\alpha}, \quad \alpha \approx 0.225 \]

\[ S_2 \sim t^{-\beta}, \quad \beta \approx 0.865 \]
$S_1 \sim t^{-\alpha}$, $\alpha \approx 0.225$

$S_2 \sim t^{-\beta}$, $\beta \approx 0.865$

Just two (non-trivial!) exponents.

$S_{77} \sim t^{-0.225}$, $S_{666} \sim t^{-0.865}$

Never $t^{-1/2}$
Average Density

\[ c(x, t) = \frac{1}{\sqrt{2\pi Dt}} C(X), \quad X = \frac{x}{\sqrt{2Dt}} \]

\[ C(X) = \frac{1}{2} \text{Erfc}(X) + \frac{1}{\sqrt{8}} e^{-X^2/2} \text{Erfc}\left(-\frac{X}{\sqrt{2}}\right) \]
Number of particles in the initially empty half-line

\[ \langle N \rangle_c = \frac{3}{8} + \frac{1}{2\pi} = 0.53415494309 \ldots \]

\[ \langle N \rangle_a = \frac{1}{2} \langle N \rangle_c = \frac{3}{16} + \frac{1}{4\pi} = 0.2670774715 \ldots \]

\( \langle N \rangle \) is finite, so we need the full distribution \( P(N) \).
Number of particles in the initially empty half-line

\[ P_c(0) = \frac{1}{2} \quad \text{(elementary)} \]

\[ P_a(0) \approx 0.74 \quad \text{(unknown)} \]

\[ P_a(0) + P_a(2) + P_a(4) + \ldots = \frac{3}{4} \quad \text{(duality)} \]

\[ P_c(1) = 0.4660959764\ldots \quad \text{(very involved derivation)} \]

\[ P_c(1) = \frac{11\pi - 4}{16\pi} + \frac{1}{2\pi} \left[ \arctan\left(\frac{1}{\sqrt{8}}\right) - 2 \arctan\left(\frac{1}{\sqrt{2}}\right) \right] \]
Localized Input

\[ \frac{\partial n}{\partial t} = D \nabla^2 n - K n^2 + J \delta(r) \]

\[ n \sim \begin{cases} 
\frac{1}{r^{d-2}} & d > 4 \\
\frac{1}{r^2 \ln r} & d = 4 \\
\frac{1}{r^2} & 4 > d > 2 \\
\frac{\ln r}{r^2} & d = 2 \\
\frac{1}{r^d} & 2 > d 
\end{cases} \]

\[ N \sim \begin{cases} 
\frac{t}{\ln t} & d > 4 \\
\sqrt{t} & d = 4 \\
(ln t)^2 & d = 3 \\
\ln t & d = 2 \\
\ln t & d = 1 
\end{cases} \]

\[ N \sim \int \sqrt{t} \, dr \, r^{d-1} \, n(r) \]
The specialist knows more and more about less and less and finally knows everything about nothing.  

Konrad Lorenz

\[ c_1 \sim r^{-(\sqrt{17}+1)/2} \quad \text{in} \quad 3d \]

\[ n \sim \begin{cases} 
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\[ N \sim \begin{cases} 
\frac{t}{\ln t} & d = 4 \\
\sqrt{t} & d = 3 \\
(\ln t)^2 & d = 2 \\
\ln t & d = 1 
\end{cases} \]

\[ N \sim \int_{0}^{\sqrt{t}} dr \, r^{d-1} \, n(r) \]
Reaction

$K_{ij}$
Two-Species Annihilation
Two-Species Annihilation
Rate Equation

Description

Suppose densities are equal: \( n_A = n_B = n \)

\[
\frac{dn}{dt} = -Kn^2, \quad n \sim t^{-1}
\]
Suppose densities are equal:  \( n_A = n_B = n \)

\[
\frac{dn}{dt} = -Kn^2, \quad n \sim t^{-1}
\]

Correct answer: \( n \sim \begin{cases} 
  t^{-1/4} & d = 1 \\
  t^{-1/2} & d = 2 \\
  t^{-3/4} & d = 3 \\
  t^{-1} & d \geq 4
\end{cases} \)
Asymptotic Spatial Arrangement

\[
L \sim t^{1/2} \quad \text{domain size}
\]
\[
 \ell_{AA} = \ell_{BB} \sim t^{1/4} \quad \text{inter-particle spacing}
\]
\[
\ell_{AB} \sim t^{3/8} \quad \text{depletion zone}
\]
Heuristic Derivation

In physics, your solution should convince a reasonable person. In math, you have to convince a person who’s trying to make trouble.  

Frank Wilczek

\[ L \sim (Dt)^{1/2} \quad \text{typical mixing scale} \]

\[ \#(A \text{ particles}) = n_0 L + \sqrt{n_0 L} \]

\[ \#(B \text{ particles}) = n_0 L - \sqrt{n_0 L} \]

\[ n_A \sim \frac{\#(A) - \#(B)}{L} \sim \sqrt{n_0} (Dt)^{-1/4} \]

\[ \frac{dn}{dt} \sim \frac{\Delta n}{\Delta t} \sim -\frac{(Dt)^{-1/2}}{\ell_{AB}^2/D} \quad \text{leads to} \quad \ell_{AB} \sim t^{3/8} \]

\[ \text{In } d \text{ dimensions} \quad n \sim \frac{\sqrt{n_0 L^d}}{L^d} \sim L^{-d/2} \sim t^{-d/4} \]
Lessons

(1) $d_c = 4$ for two-species annihilation
(2) Three characteristic length scales
(3) Exact solution is lacking even in one dimension
(4) The $t^{-3/4}$ asymptotic in $d = 3$ is beyond the reach in simulations (but maybe not in Nature)
(5) No log-correction at $d = d_c = 4$
Trapping Reaction

(1) Stationary traps absorb particles
(2) Diffusing non-interacting particles
Trapping Reaction

(1) Stationary traps absorb particles
(2) Diffusing non-interacting particles
Mean-Field and Exact Descriptions

\[ \frac{dn}{dt} = -K \rho n, \quad n \sim e^{-K \rho t} \]

The mean-field description is \textbf{wrong} in all dimensions:

\[ n \sim \exp \left[ -A_d \rho^{2/(d+2)} (Dt)^{d/(d+2)} \right] \]
Higher Dimensions
Higher Dimensions

Premature optimization is the root of all evil.  
*Donald E. Knuth*

(1) The best chance to survive is to be in a large void.

(2) The competition between increasing the survival probability and decreasing the existence probability of a void by increasing its size selects the optimal void.

(3) One can posit the adsorption BC on the ‘boundary’ of a void.

(4) Asymptotically the density in such a void \( \sim \exp(-\Lambda_1^2 Dt) \) \((\Lambda_1^2\) is the smallest eigenvalue of the Laplacian).

(5) Overall \( n \sim \int \exp\left(-\lambda_1^2 Dt/V^2/d - \rho V\right) \rho dV \)

(6) Minimal \( \lambda_1 \) corresponds to the spherical void.  
(Rayleigh-Faber-Krahn theorem.)
Quantum Reactions is a Challenge

The only success (up to now) is with the trapping reaction. The key is it is essentially a single-particle problem. One associates an imaginary potential energy $-i\Gamma$ with each trap.

The density decays as $\exp(-A_d t^{d/(d+3)})$.

Recall that in the classical case the decay is $\exp(-B_d t^{d/(d+2)})$. 
Annihilation in Quantum Regime

(1) An ultracold Fermi gas like $^6$Li is a two-component Fermi gas.

(2) When two atoms with opposite spin collide, they can form a molecule.

(3) The energy and momentum conservation makes $A + A \rightarrow A_2$ impossible.

(4) The three-body process $A + A + A \rightarrow A_2 + A$ is possible.

(5) The energies of the products are so large that they overcome a trapping potential and leave the system.

(6) Thus essentially $A + A + A \rightarrow \emptyset$
Classical vs. Quantum
Particle on a lattice

\[ p_n(t), |\psi_n(t)|^2 \]

- Classical
- Quantum
Infinite chain with a single trap

\[ i \frac{d\psi_n}{dt} = \psi_{n-1} + \psi_{n+1} - i\gamma \delta_{n,0} \psi_0, \quad \psi_n(t = 0) = \delta_{n,a} \]
Particle on a finite ring with a single trap

**Classical:** survival prob decays as \( \exp\left(-\frac{\pi^2 t}{N^2}\right) \)

**Quantum:** survives with prob \( \frac{1}{2} \)
except when it starts at \( a = 0 \) or \( a = N/2 \)

Why? Thanks to avoiding modes.
Summary

(1) Non-equilibrium statistical physics has traditionally dealt with small deviations from equilibrium.

(2) Far-from-equilibrium systems do not have an underlying master equation, there are no analogs e.g. to the Boltzmann factor or the partition function of equilibrium statistical physics.

(3) Still far-from-equilibrium systems often have simple collective behaviors.

(4) Various tools efficiently work in numerous problems.
The End