Gene F. Mazenko

Nonequilibrium Statistical Mechanics

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Contents

Nonequilibrium Statistical Mechanics. Gene F. Mazenko

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Preface

This is the third volume in a series of graduate level texts on statistical mechanics. Volume 1, *Equilibrium Statistical Mechanics* (ESM), is a first year graduate text treating the fundamentals of statistical mechanics. Volume 2, *Fluctuations, Order and Defects* (FOD), treats ordering, phase transitions, broken symmetry, long-range spatial correlations and topological defects. This includes the development of modern renormalization group methods for treating critical phenomena. The mathematical level of both texts is typically at the level of mean-field theory.

In this third volume, *Nonequilibrium Statistical Mechanics* (NESM), I treat nonequilibrium phenomena. The book is divided into three main sections. The first, Chapters 1–4, discusses the connection, via linear response theory, between experiment and theory in systems near equilibrium. Thus I develop the interpretation of scattering and transport experiments in terms of equilibrium-averaged time-correlation functions. The second part of the book, Chapters 5–8, develops the ideas of linear hydrodynamics and the generalized Langevin equation approach. This is also known as the memory-function method. The theory is applied, in detail, to spin diffusion and normal fluids. In these applications the Green–Kubo equations connecting transport coefficients and time integrals over current–current time-correlation functions are established. It is then demonstrated that this memory-function approach is very useful beyond the hydrodynamic regime. It is shown in Chapter 7 how these ideas can be used to develop modern kinetic theory. In Chapter 8 the generalized Langevin equation approach is used to develop the conventional theory of dynamic critical phenomena and linearized hydrodynamics in systems with broken continuous symmetry and traveling Nambu–Goldstone modes.

The third part of the book is devoted to nonlinear processes. In Chapter 9 the generalized Langevin approach is used to derive the generalized Fokker–Planck equation governing the dynamics of the reduced probability distribution for a set of slow variables. These dynamic equations lead to the nonlinear Langevin equations that serve as the basis for the theory of dynamic critical phenomena and the theory of the kinetics of first-order phase transitions.

Nonequilibrium Statistical Mechanics. Gene F. Mazenko

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Analytic methods of treatment of these nonlinear equations are discussed in Chapters 9–11. In particular the methods of Ma and Mazenko for carrying out the dynamic renormalization group are introduced in Chapter 10 in the important cases of the relaxational time-dependent Ginzburg–Landau (TDGL) model and the case of the isotropic ferromagnet. In Chapter 11 we discuss the strongly nonequilibrium behavior associated with phase-ordering systems.

This text is compatible with one of the central themes in FOD. In FOD we developed the idea of coarse-grained effective Hamiltonians governing the long-distance equilibrium correlations for a variety of systems: magnets, superfluids, superconductors, liquid crystals, etc. Here I indicate how one generates a coarse-grained dynamics consistent with these effective Hamiltonians.

The methods of attack on the nonlinear models discussed in Chapters 9 and 10 are very useful for treating systems at the lowest order in perturbation theory. There exist less physical and mathematically more powerful methods for handling higher order calculations. These methods will be discussed in the final volume of this series.

I thank my sister Debbie for crucial help and my wife Judy for her support.

Gene Mazenko
Chicago, July 2006

Abbreviations

COP	Conserved order parameter
ESM	Equilibrium Statistical Mechanics (Volume 1)
FOD	Fluctuations, Order and Defects (Volume 2)
FTMCM	Field Theory Methods in Condensed Matter Physics (Volume 4)
FDT	Fluctuation-dissipation theorem
GCE	Grand canonical ensemble
LGW	Landau–Ginzburg–Wilson
NCOP	Nonconserved order parameter
NG	Nambu–Goldstone
RG	Renormalization group
TDGL	Time-dependent Ginzburg–Landau

Nonequilibrium Statistical Mechanics. Gene F. Mazenko

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1
Systems Out of Equilibrium

1.1
Problems of Interest

The field of nonequilibrium statistical mechanics is wide and far- reaching. Using the broadest interpretation it includes the dynamics of all macroscopic systems. This definition is far too inclusive for our purposes here, and certainly beyond what is generally understood. Rather than discussing matters in abstract generality, let us introduce some examples of nonequilibrium phenomena of interest:

- A very familiar example of time-dependent phenomena is the propagation of sound through air from the speaker's mouth to the listener's ears. If the intensity of the sound is not too great, then the velocity of sound and its attenuation are properties of the medium propagating the sound. This is a very important point since it says that *sound* has significance independent of the mouth and ears generating and receiving it. A question of interest to us is: how can we relate the sound speed and attenuation to the microscopic properties of the air propagating the sound?

- Next, consider a thermally insulated bar of some homogeneous material at a temperature T_0. (See Fig. 1.1). We bring one end of this bar into contact at time t_0 with a heat bath at a temperature $T_1 > T_0$. For times $t >$

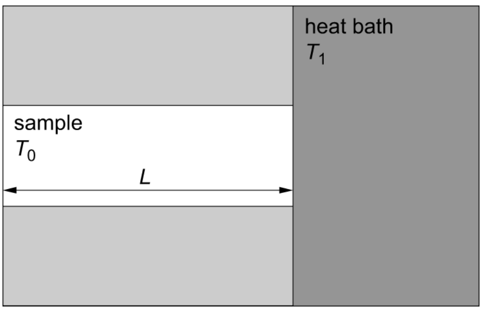

Fig. 1.1 Thermal conductivity experiment. See text for discussion.

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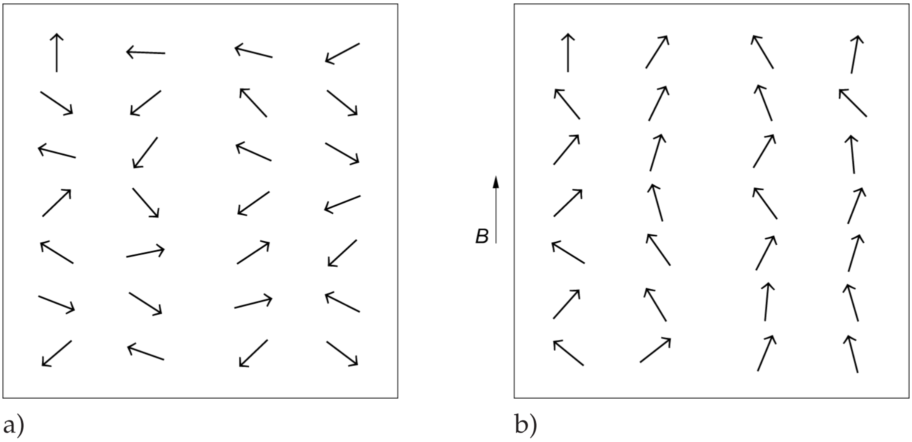

Fig. 1.2 Configurations for a set of paramagnetic spins. **a** Zero external magnetic field. **b** Subject to an external magnetic field along the direction shown.

t_0 heat will flow toward the cold end of the bar and eventually the bar will equilibrate at the new temperature T_1. We know from elementary courses in partial differential equations that this heat flow process is governed by Fourier's law [1] , which tells us that the heat current **J** is proportional to the gradient of the temperature:

$$\mathbf{J} = -\lambda\vec{\nabla}T \tag{1}$$

with the thermal conductivity λ being the proportionality constant. Combining this constitutive relation with the continuity equation reflecting conservation of energy leads to a description (see Problem 1.1) in terms of the heat equation. The thermal conductivity is a property of the type of bar used in the experiment. A key question for us is: How does one determine the thermal conductivity for a material? From a theoretical point of view this requires a careful analysis establishing Fourier's law.

- A paramagnet is a magnetic system with no net magnetization in zero applied external field. In Fig. 1.2a we represent the paramagnet as a set of moments (or spins) $\vec{\mu}(\mathbf{R})$ localized on a periodic lattice at sites **R**. At high enough temperatures, in zero externally applied magnetic field, the system is in a disordered state where the average magnetization vanishes,

$$\langle \mathbf{M} \rangle = \left\langle \sum_{\mathbf{R}} \vec{\mu}(\mathbf{R}) \right\rangle = 0 \quad , \tag{2}$$

due to symmetry. Each magnetic moment is equally likely to point in any direction. If one applies an external magnetic field **B** to a paramagnet the magnetic moments, on average, line up along the field:

$$\mathbf{M} \approx \mathbf{B} \quad . \tag{3}$$

As shown in Fig. 1.2b, the spins deviate in detail from the *up* orientation along **B** because of thermal fluctuations (for nonzero temperatures). When we turn off **B** at time t_0, the spins relax to the original disordered equilibrium state, where $\langle \mathbf{M} \rangle = 0$, via thermal agitation. How can we quantitatively describe this relaxation process? As we discuss in Chapter 5, this process is analogous to heat diffusion.

- Suppose we fill a bowl with water and put it in a freezer. Clearly, over time, the water freezes. How do we describe the time evolution of this process? What does this process depend upon? In this case we have a dynamic process that connects thermodynamic states across a phase (liquid–solid) boundary.

The common elements in these situations is that we have externally disturbed the system by:

1. Mechanically pushing the air out of ones mouth;
2. Putting heat into a bar;
3. Turning off a magnetic field;
4. Drawing heat out of a system.

For the most part in this text we will focus on situations, such as examples 1–3, which can be understood in terms of the *intrinsic* dynamical properties of the condensed-matter system probed and do not depend in an essential way on *how* the system is probed. Such processes are part of a very important class of experiments that do not strongly disturb the thermodynamic state of the system. Thus, when one talks in a room one does not expect to change the temperature and pressure in the room. We expect the sound velocity and attenuation to depend on the well-defined thermodynamic state of the room.

In cases 1–3 we have applied an external force that has shifted the system from thermal equilibrium. If we remove the applied external force the system will return to the original equilibrium state. These intrinsic properties, which are connected to the return to equilibrium, turn out to be independent of the probe causing the nonequilibrium disturbance. Thus the speed of sound and its attenuation in air, the thermal conductivity of a bar and the paramagnetic relaxation rates are all properties of the underlying many-body systems.

We need to distinguish *weak*, linear or intrinsic response of a system from *strong* or nonlinear response of a system. Linear response, as we shall discuss

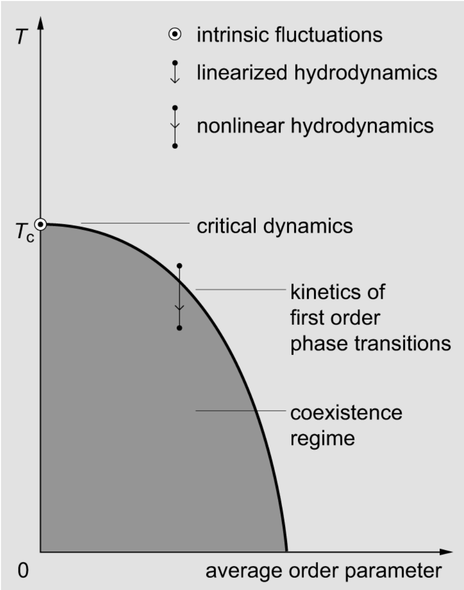

Fig. 1.3 Schematic of the type of dynamic processes studied in terms of movement on a generic phase diagram.

in detail, corresponds to those situations where a system remains near thermal equilibrium during the time-dependent process. In strongly nonlinear processes one applies strong forces to a system that fundamentally change the state of the system. The freezing of the bowl of water falls into this second category. Other nonlinear processes include:

- Nucleation where we rapidly flip the applied magnetic field such that a system becomes metastable. The system wants to follow but has a barrier to climb.
- Spinodal decomposition, where we quench the temperature of a fluid across a phase boundary into an unstable portion of the phase diagram.
- Material deposition where one builds [2] up a film layer by layer.
- Turbulence where we continuously drive a fluid by stirring.

In these examples an understanding of the dynamics depends critically on how, how hard and when we hit a system.

In organizing dynamical processes we can think of two classes of processes. The first set, which will be the primary concern in this text, are processes that connect points on the equilibrium phase diagram. The second set of processes involves driven systems that are sustained in intrinsically nonequilibrium states. The first set of processes can be roughly summarized as shown in Fig. 1.3 where five basic situations are shown:

1. intrinsic fluctuations in equilibrium;
2. linear response (perturbations that change the state of the system infinitesimally;
3. nonlinear hydrodynamics – substantial jumps in the phase diagram within a thermodynamic phase;
4. critical dynamics – dynamic processes near the critical point.
5. kinetics of first-order phase transitions – jumps across phase boundaries.

It is shown in Chapter 2 that processes in categories 1 and 2 are related by the fluctuation-dissipation theorem. Nonlinear hydrodynamics is developed and explored in Chapters 9, 10 and 11. Critical dynamics is treated in Chapters 8, 9, and 10. Finally the kinetics of first-order phase transitions is treated in Chapter 11.

In the second set of processes, like turbulence and interfacial growth [2], systems are maintained in states well out of equilibrium. In a Rayleigh–Benard experiment [3] (Fig. 1.4) where we maintain a temperature gradient across a sample, we can generate states with rolls, defects, chaos and turbulence, which are not associated with any equilibrium state. These more complicated sets of problems, such as driven steady-state nonequilibrium problems [4], will not be treated here.

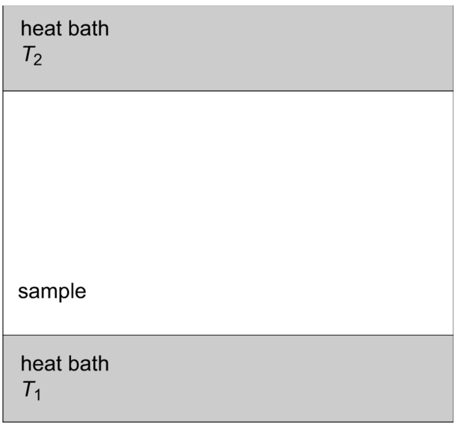

Fig. 1.4 Schematic of the Rayleigh–Benard experiment. A fluid sample is between two plates held at different temperatures $T_2 > T_1$. As the temperature difference increases a sequence of nonequilibrium behaviors occurs, including convection, rolls and turbulence.

1.2
Brownian Motion

1.2.1
Fluctuations in Equilibrium

Before we begin to look at the formal structure of the theory for systems evolving near equilibrium, it is useful to look at the historically important problem of Brownian motion [5]. It will turn out that many intuitive notions about the dynamics of large systems that evolve out of this analysis are supported by the full microscopic development. Indeed this discussion suggests a general approach to such problems.

Consider Fig. 1.5, showing the process of Brownian motion as taken from the work of Jean Perrin [6] near the turn of the previous century. Brownian motion corresponds to the irregular motion of *large* particles suspended in fluids. The general character of this motion was established by Robert Brown [7] in 1828. He showed that a wide variety of organic and inorganic particles showed the same type of behavior. The first quantitative theory of Brownian motion was due to Einstein [8] in 1905. Einstein understood that one needed an underlying atomic bath to provide the necessary fluctuations to account for the erratic motion of the large suspended particle. He realized that many random collisions, which produce no net effect on average, give rise to the observed *random walk* behavior [9].

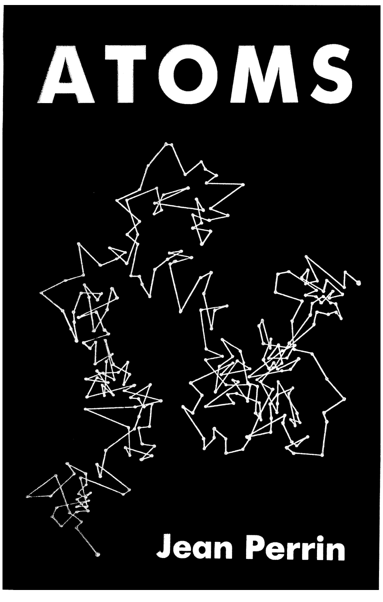

Fig. 1.5 Brownian motion path from cover of Ref. [6].

Let us consider a very large particle, with mass M and velocity $V(t)$ at time t, which is embedded in a fluid of relatively small particles. For simplicity let us work in one dimension. Assume the particle has velocity V_0 at time t_0. We are interested in the velocity of the particle for times $t > t_0$. In the simplest theory the basic assumption is that the force on the large particle can be decomposed into two parts. The first part is a frictional force F_1 opposing the persistent velocity V of the particle and is proportional to the velocity of the large particle:

$$F_1 = -M\gamma V \quad , \tag{4}$$

where γ is the friction constant [10]. The second contribution to the force, representing the random buffeting the particle suffers from the small particles, is given by:

$$F_2 = M\eta \quad , \tag{5}$$

where η is called the noise. Newton's law then takes the form:

$$M\dot{V} = -M\gamma V + M\eta \quad . \tag{6}$$

This is in the form of the simplest *Langevin equation* [11]:

$$\dot{V} = -\gamma V + \eta \quad . \tag{7}$$

Next we need to solve this equation. The first step is to write:

$$V(t) = \mathrm{e}^{-\gamma t}\phi(t) \quad . \tag{8}$$

Taking the time derivative of this equation gives:

$$\dot{V} = -\gamma V + \mathrm{e}^{-\gamma t}\dot{\phi} \quad . \tag{9}$$

Substituting this result back into the Langevin equation we obtain:

$$\mathrm{e}^{-\gamma t}\dot{\phi}(t) = \eta(t) \quad . \tag{10}$$

Clearly we can integrate this equation using the initial value for $V(t)$ to obtain:

$$\phi(t) = \mathrm{e}^{\gamma t_0} V_0 + \int_{t_0}^{t} \mathrm{d}\tau \mathrm{e}^{\gamma\tau}\eta(\tau) \tag{11}$$

or in terms of the velocity:

$$V(t) = \mathrm{e}^{-\gamma(t-t_0)} V_0 + \int_{t_0}^{t} \mathrm{d}\tau \mathrm{e}^{-\gamma(t-\tau)}\eta(\tau) \quad . \tag{12}$$

The physical interpretation seems clear. The velocity of the particle loses *memory* of the initial value V_0 exponentially with time. $V(t)$ is determined by the sequence of bumps with the noise for $t \gg t_0$.

To go further we must make some simple assumptions about the properties of the noise. We will assume that the noise is a random variable described by its statistical properties. The first assumption is that the noise produces no net force:

$$\langle \eta(t_1) \rangle = 0 \quad . \tag{13}$$

Next we need to specify the variance $\langle \eta(t_1)\eta(t_2) \rangle$. Physically we expect that the kicks due to the small particles will be of very short-time duration and noise at different times will be uncorrelated. Thus it is reasonable to assume that we have *white noise*:

$$\langle \eta(t_1)\eta(t_2) \rangle = A\delta(t_1 - t_2) \quad , \tag{14}$$

where we will need to consider the proper choice for the value of the constant A. The other important consideration is causality. The velocity of the large particle can not depend on the noise at some later time:

$$\langle \eta(t_1)V(t_2) \rangle = 0 \quad \text{if} \quad t_1 > t_2 \quad . \tag{15}$$

We can now investigate the statistical properties of the velocity. The average velocity is given by:

$$\langle V(t) \rangle = \mathrm{e}^{-\gamma(t-t_0)} \langle V_0 \rangle + \int_{t_0}^{t} \mathrm{d}\tau \mathrm{e}^{-\gamma(t-\tau)} \langle \eta(\tau) \rangle \quad . \tag{16}$$

Since the average of the noise is zero, the average of the velocity is proportional to the average over the initial conditions. If the initial directions of the velocity of the pollen are randomly distributed (as in the case where the system – particle plus fluid – is in thermal equilibrium, then $\langle V_0 \rangle = 0$ and the average velocity is zero:

$$\langle V(t) \rangle = 0 \quad . \tag{17}$$

Thus if the system is in equilibrium we expect no net motion for a collection of Brownian particles. If the pollen molecules are introduced with a net average velocity, the system will lose memory of this as time evolves.

We turn next to the velocity autocorrelation function defined by the average:

$$\psi(t, t') = \langle V(t)V(t') \rangle \quad . \tag{18}$$

If we multiply the solution for $V(t)$, given by Eq. (12), by that for $V(t')$ and average we see that the cross terms vanish since:

$$\langle \eta(t)V_0 \rangle = 0 \qquad \text{for} \quad t > t_0 \tag{19}$$

and we have:

$$\psi(t,t') = \int_{t_0}^{t} d\tau \int_{t_0}^{t'} d\tau' e^{-\gamma(t-\tau)} e^{-\gamma(t'-\tau')} \langle \eta(\tau)\eta(\tau')\rangle + e^{-\gamma(t+t'-2t_0)} \langle V_0^2 \rangle \quad . \tag{20}$$

Using the statistical properties of the noise, Eq. (14), gives:

$$\psi(t,t') = \int_{t_0}^{t} d\tau \int_{t_0}^{t'} d\tau' e^{-\gamma(t-\tau)} e^{-\gamma(t'-\tau')} A\delta(\tau-\tau') + e^{-\gamma(t+t'-2t_0)} \psi(t_0,t_0) \quad . \tag{21}$$

It is left as a problem (Problem 1.2) to show that after performing the τ and τ' integrations one obtains the result:

$$\psi(t,t') = \frac{A}{2\gamma} e^{-\gamma|t-t'|} + \left[\psi(t_0,t_0) - \frac{A}{2\gamma}\right] e^{-\gamma(t+t'-2t_0)} \quad . \tag{22}$$

Notice that the initial condition is properly maintained.

Suppose the system is initially in equilibrium at temperature T_0. This allows us to determine the value of:

$$\psi(t_0,t_0) = \langle V_0^2 \rangle \quad . \tag{23}$$

This is because in equilibrium we can assume that the velocity of the particle satisfies Maxwell–Boltzmann statistics:

$$P[V_0] \approx e^{-\beta_0 \frac{M}{2} V_0^2} \quad , \tag{24}$$

where $\beta_0^{-1} = k_B T_0$, where k_B is the Boltzmann constant. One can then evaluate the average velocity squared as:

$$\langle V_0^2 \rangle = \frac{\int dV_0\, V_0^2 e^{-\beta_0 \frac{M}{2} V_0^2}}{\int dV_0\, e^{-\beta_0 \frac{M}{2} V_0^2}} \quad . \tag{25}$$

It is easy enough to evaluate these Gaussian integrals and obtain:

$$\langle V_0^2 \rangle = \frac{kT_0}{M} \quad , \tag{26}$$

which is just a form of the equipartition theorem:

$$\frac{M}{2} \langle V_0^2 \rangle = \frac{kT_0}{2} \quad . \tag{27}$$

Let us put this back into our expression for the velocity correlation function and concentrate on the case of equal times $t = t'$ where we have:

$$\psi(t,t) = \frac{A}{2\gamma} + \left[\frac{kT_0}{M} - \frac{A}{2\gamma}\right] e^{-\frac{2\gamma}{M}(t-t_0)} \quad . \tag{28}$$

If the system is in equilibrium, then there is nothing special about the time t_0. Unless we disturb the system from equilibrium it is in equilibrium at all times t and we expect $\psi(t,t)$ to be time independent and equal to $\frac{kT_0}{M}$. For this to be true we require:

$$\frac{kT_0}{M} - \frac{A}{2\gamma} = 0 \quad , \tag{29}$$

which allows us to determine:

$$A = 2\gamma\frac{k_B T_0}{M} \quad . \tag{30}$$

This means that we have determined that the autocorrelation for the noise is given by:

$$\langle \eta(t)\eta(t')\rangle = 2\frac{k_B T_0}{M}\gamma\delta(t-t') \quad . \tag{31}$$

Thus the level of the noise increases with temperature as expected. Note also that the noise is related to the friction coefficient. In this particular problem, because we know that the velocity has a Gaussian (Maxwell–Boltzmann) distribution, we can infer (see Problem 1.9) that the noise must also have a Gaussian distribution.

Inserting this result for A into Eq. (22) for the velocity autocorrelation function we now obtain, for an arbitrary initial condition,

$$\psi(t,t') = \frac{kT_0}{M}e^{-\gamma|t-t'|} + \left[\psi(t_0,t_0) - \frac{kT_0}{M}\right]e^{-\gamma(t+t'-2t_0)} \quad . \tag{32}$$

The assumption here is that the background fluid is at some temperature T_0 and we can insert a set of Brownian particles at some time t_0 with a velocity correlation $\psi(t_0,t_0)$ without disturbing the equilibrium of the fluid in any significant way. Then, as time evolves and t and t' become large, the system loses memory of the initial condition and:

$$\psi(t,t') = \frac{kT_0}{M}\chi_V(t-t') \quad , \tag{33}$$

where the normalized equilibrium-averaged velocity autocorrelation function is given by:

$$\chi_V(t-t') = e^{-\gamma|t-t'|} \quad . \tag{34}$$

This is interpretated as the velocity decorrelating with itself exponentially with time. There is little correlation between the velocity at time t and that at t' if the times are well separated. Note that our result is symmetric in $t \leftrightarrow t'$, as we require. Note also that it depends only on the time difference, which reflects the time-translational invariance of the system in equilibrium.

Since the velocity of the large particle is related to its position by:

$$V(t) = \frac{dx(t)}{dt} \quad , \tag{35}$$

we can also investigate the root-mean-square displacement of the particle performing Brownian motion. Thus we need to integrate:

$$\frac{d}{dt}\frac{d}{dt'}\langle x(t)x(t')\rangle = \frac{kT_0}{M}e^{-\gamma|t-t'|} \quad . \tag{36}$$

These integrations are tedious (see Problem 1.6) and lead to the final result:

$$\langle (x(t)-x(t_0))(x(t')-x(t_0))\rangle = \frac{kT_0}{M}\int_{t_0}^{t} d\tau \int_{t_0}^{t'} d\tau' e^{-\gamma|\tau-\tau'|} \tag{37}$$

$$= \frac{kT_0}{M\gamma}\left[t+t'-|t-t'|-2t_0+\frac{1}{\gamma}\left[e^{-\gamma(t-t_0)}+e^{-\gamma(t'-t_0)}-1-e^{-\gamma|t-t'|}\right]\right]. \tag{38}$$

This is of particular interest for equal times where:

$$\langle [x(t)-x(t_0)]^2\rangle = 2\frac{kT_0}{M\gamma}\left[t-t_0-\frac{1}{\gamma}\left(1-e^{-\gamma(t-t_0)}\right)\right] \quad . \tag{39}$$

For long times we see that the averaged squared displacement is linear with time. If we have free particle or ballistic motion (see Problem 1.4), the displacement of the particle is linear in time. The random forcing of the noise causes the average displacement to go as the square root of time.

It is worth stopping to connect up this development to the behavior of density fluctuations for large particles moving in a fluid background. If $n(x,t)$ is the density of the Brownian particles, then because the number of Brownian particles is conserved, we have the continuity equation:

$$\frac{\partial n}{\partial t} = -\frac{\partial J}{\partial x} \quad , \tag{40}$$

where J is the particle current. Since the Brownian particles share momentum with the background fluid, the current J is not, as in a simple fluid, itself conserved. Instead, for macroscopic processes, J satisfies Fick's law [12]:

$$J = -D\frac{\partial n}{\partial x} \quad , \tag{41}$$

where D is the diffusion coefficient. Clearly Fick's law is similar to Fourier's law, but for particle transport rather than heat transport. We discuss such constitutive relations in detail in Chapter 5. Putting Eq. (41) back into Eq. (40)

one finds that on the longest length and time scales the density, $n(x,t)$, satisfies the diffusion equation:

$$\frac{\partial n}{\partial t} = D\frac{\partial^2 n}{\partial x^2} \quad . \tag{42}$$

It is shown in Problem 1.7, for initial conditions where the density fluctuation is well localized in space, near $x(t_0)$, so that we can define:

$$\langle [x(t) - x(t_0)]^2 \rangle = \frac{1}{N}\int \mathrm{d}x\, x^2 n(x,t) \tag{43}$$

and:

$$N = \int \mathrm{d}x\, n(x,t) \quad , \tag{44}$$

then:

$$\langle [x(t) - x(t_0)]^2 \rangle = 2Dt \tag{45}$$

for long times. Comparing with Eq. (39) we find that the diffusion constant is related to the friction coefficient by:

$$D = \frac{k_B T_0}{M\gamma} \quad . \tag{46}$$

It was well known at the time of Einstein's work [13], starting from the equations of hydrodynamics, that the drag on a sphere of radius a in a flowing liquid with viscosity ν is given by the Stoke's law result:

$$M\gamma = 6\pi\nu a \quad . \tag{47}$$

If we put this back into the equation for the diffusion coefficient we obtain the *Stokes–Einstein* relation [13]:

$$D = \frac{k_B T}{6\pi\nu a} \quad . \tag{48}$$

If we know the viscosity and temperature of the liquid and measure the diffusion coefficient D through an observation of the Brownian motion, then we can determine a. If a is known, then this offers a method for determining Avogadro?s number: $N_A = R/k_B$ where R is the gas constant. Solving Eq. (48) for Boltzmann's constant and using Eq. (45) we find:

$$N_A = \frac{R}{k_B} = \frac{t}{\langle(\delta x)^2\rangle}\frac{RT}{3\pi a\nu} \quad . \tag{49}$$

Perrin found, for example for gamboge grains, that $a \approx 0.5$ μm and $N_A \approx 80 \times 10^{22}$.

1.2.2
Response to Applied Forces

Suppose now that we apply an external force, $F(t)$, to our particle. Clearly our equation of motion, Eq. (6), is then modified to read:

$$M\dot{V}(t) = -M\gamma V(t) + M\eta(t) + F(t) \quad . \tag{50}$$

Now the average velocity of the particle is nonzero since the average of the external force is nonzero. Since the average over the noise is assumed to remain zero (suppose the background particles are neutral while the large particles are charged) we have, on averaging the equation of motion:

$$M\langle\dot{V}(t)\rangle = -M\gamma\langle V(t)\rangle + F(t) \quad . \tag{51}$$

We assume that the force is weak, such that γ can be assumed to be independent of F. We can solve Eq. (51) again using an integrating factor, to obtain:

$$\langle V(t)\rangle = \mathrm{e}^{-\gamma(t-t_0)}\langle V(t_0)\rangle + \frac{1}{M}\int_{t_0}^{t} \mathrm{d}\tau \mathrm{e}^{-\gamma(t-\tau)}F(\tau) \quad . \tag{52}$$

For $t \gg t_0$ the average loses memory of the initial condition and:

$$M\langle V(t)\rangle = \int_{t_0}^{t} \mathrm{d}\tau \mathrm{e}^{-\gamma(t-\tau)}F(\tau) \quad . \tag{53}$$

Notice that the response to the force can be written as a product of terms:

$$M\langle V(t)\rangle = \int_{t_0}^{t} \mathrm{d}\tau \chi_V(t-\tau)F(\tau) \quad . \tag{54}$$

It can be written as a product of an internal equilibrium response of the system times a term that tells how hard we are forcing the system.

The conclusions we can draw from this simple example have a surprisingly large range of validity.

- Friction coefficients like γ, which are intrinsic properties of the system, govern the evolution of almost all nonequilibrium systems near equilibrium.

- Thermal noise like η is essential to keep the system in thermal equilibrium. Indeed for a given γ we require:

  $$\langle\eta(t)\eta(t')\rangle = 2\gamma\frac{k_B T_0}{M}\delta(t-t') \quad . \tag{55}$$

  So there is a connection between the friction coefficient and the statistics of the noise. Clearly the noise amplitude squared is proportional to the temperature.

- The response of the system to an external force can be written as a product of a part that depends on how the system is driven and a part that depends only on the fluctuations of the system in equilibrium.

One of the major unanswered questions in this formulation is: how do we determine γ? A strategy, which turns out to be general, is to relate the kinetic coefficient back to the velocity correlation function, which is microscopically defined. Notice that we have the integral:

$$\int_0^\infty \mathrm{d}t\, \chi_V(t) = \int_0^\infty \mathrm{d}t\, \mathrm{e}^{-\gamma t} = \frac{1}{\gamma} = D\frac{M}{kT_0} \quad . \tag{56}$$

This can be rewritten in the form:

$$D = \frac{kT_0}{M}\int_0^\infty \mathrm{d}t\, \chi_V(t) = \int_0^\infty \mathrm{d}t\, \psi(t,0). \tag{57}$$

Thus if we can evaluate the velocity–time correlation function we can determine D.

You may find it odd that we start with a discussion of such an apparently complex situation as pollen performing a random walk in a dense liquid. Historically, nonequilibrium statistical mechanics was built on the *Boltzmann paradigm* [14] where there are N spherical particles in an isolated enclosed box, allowed to evolve in time according to Newton's laws. Out of this dynamical process comes the mixing and irreversible behavior from which we can extract all of the dynamical properties of the system: viscosities, thermal conductivities and speeds of sound. This situation appears cleaner and more appealing to a physicist than the *Langevin paradigm* [15] , where the system of interest is embedded in a *bath* of other particles. The appeal of the Boltzmann paradigm is somewhat illusory once one takes it seriously, since it leads to the difficult questions posed by ergodic theory [16] and whether certain isolated systems decay to equilibrium. We will assume that irreversibility is a physical reality. A system will remain [17] out of equilibrium only if we act to keep the system out of equilibrium. While the Langevin paradigm appears less universal, we shall see that this is also something of an illusion. In the Langevin description there is the unknown parameter γ. However, if we can connect this parameter back to the equilibrium fluctuations as in Eq. (56), then we have a complete picture. To do this we must develop a microscopic theory including the background fluid degrees of freedom to determine $\chi_V(t)$ as a function of time. Then we can extract $1/\gamma$ as an integral over a very short time period. The Langevin equation then controls the behavior on the longer time scales of particle diffusion.

The notion of a set of rapid degrees of freedom driving the evolution of slower degrees of freedom is a vital and robust idea. The separation of time scales in the case of Brownian motion comes about because of the larger mass