1 Introduction: Time Dependent Phenomena and Transport in Condensed Matter

The study of time dependent phenomena in condensed matter systems is important in a broad range of contexts, and correspondingly, the approaches to them involve several different concepts. In the simplest instance, one may consider the time dependent course of the establishment of thermodynamic equilibrium in a system which is slightly displaced from equilibrium, either by spontaneous fluctuations, or because of applied external fields. An example could be the change by a tiny amount of the applied magnetic field on a magnet. The time course of the response of the system can be understood in reference to the equilibrium fluctuations and their time correlations at the initial thermodynamic state. Such an analysis extends to the time domain the study of susceptibilities of a system in equilibrium to applied fields. One can easily extend this to the study of the response of the system to time dependent fields, which is important for both understanding the outcome of many experimental measurements, as well as of intrinsic interest since many external perturbations one may impose on a system are time dependent, such as electromagnetic radiation. One also typically has, as part of the response of the system, the transport of some quantity across the system. The propagation of sound waves when external pressure is applied is an example. In this category of situations, the response of the system to external perturbation is linear in the applied perturbation. For most of the course, we will be interested in such, near equilibrium, linear, regimes. Beyond this regime, one may have highly non-linear response, such as the phase transformation of a system by, e. g. nucleation, upon a small change in temperature. Such phenomena may still be analyzed and described by reference to the equilibrium thermodynamics of the system, but requiring new concepts. Finally, one may be interested in systems that are driven out of equilibrium perpetually by strong external driving. We will hopefully touch upon such cases briefly towards the end of the course. For the most part, we will focus on the linear response regime. A characteristic feature of most contexts we will consider is that the response of the system to perturbations will be dissipative, with, e. g. energy put into a small number of degrees of freedom being distributed over time into the others, owing to interactions between degrees of freedom that can be treated as stochastic. Historically, many of the key concepts described above are illustrated by the classic problem of Brownian motion, which therefore offers a good starting point for the discussion of the statistical mechanics of time dependent phenomena.

In covering material in this course, I will largely try to follow the book by Zwanzig. Other texts that may be consulted can be found in the list of reference books.

2 Brownian Motion

Brownian motion is the motion of mesoscale particles immersed in a liquid, typically considered without the presence of external forces. For macroscopic particles, in the absence of external forces, the end state is one of
zero velocity, even if the particle starts out with an initial velocity. This is because of the frictional force that is exerted by the fluid. Thus, if we write the equation of motion in general (but considering only one spatial dimension for simplicity) as:

\[
m \frac{dv}{dt} = F_{total}(t),
\]

for a macroscopic particle we have

\[
m \frac{dv}{dt} = -\zeta v
\]

with the solution

\[
v(t) = \exp(-\zeta t/m) \; v(0).
\]

This would predict the long time velocity to be zero. This cannot be strictly true for a particle in equilibrium with the fluid at a given temperature \( T \). Equipartition requires \(< v^2 >_{eq} = k_B T/m \). Here the average indicated by \(< \ldots >_{eq} \) is over the equilibrium thermodynamic ensemble of the liquid-particle system, and we will usually drop the subscript \( eq \). Further, when we consider Brownian particles now, which are sufficiently small/light, the observation is that such particle appear to perform random looking zig-zag motion. The modification suggested by such “Browninan” motion is that the surrounding fluid exerts forces on the Brownian particle, which, in addition to the “systematic” part that is included in the frictional force term above, has a “random” or “fluctuating” component. Including such forces, we can write the equation of motion as

\[
m \frac{dv}{dt} = -\zeta v + \delta F(t).
\]

This is the *Langevin equation* for this problem, and we will consider the general case later. If the full microscopic dynamics of the fluid atoms were known, the fluctuating force will be a deterministic, time varying force, but here we make an assumption of randomness of these forces and proceed. As a basic description of the forces, we need to specify the first two moments of the distribution of their values (and implicitly assume a Gaussian distribution, which is fully described by these two moments), but in addition we need to say something about the relationship between forces at different times. We assume that forces at different times are fully decorrelated. Thus, we assume

\[
< \delta F(t) > = 0; \quad < \delta F(t) \delta F(t') > = 2B \delta(t-t'),
\]

where the average is over the realization of the fluctuating forces. We can treat it as equivalent to an ensemble average by considering the equivalence of time averages and ensemble averages.

Since we assume that the Brownian particle is in equilibrium with \(< v^2 >_{eq} = k_B T/m \), we expect that the strength of the fluctuating force, \( B \) and the friction coefficient, \( \zeta \), are related. In order to determine that relation, we solve for \( v(t) \) by writing first

\[
v(t) = \exp(-\zeta t/m) \; \phi(t).
\]

Using the equation of motion, we get
\[ v(t) = \exp(-\zeta t/m) \, v(0) + \int_0^t dt' \exp[-\zeta(t-t')] \, \delta F(t')/m. \] (7)

We use this solution to write down the expression for \( <v^2(t)> \). The product has four terms, of which two vanish since they will involve \( \langle \delta F \rangle = 0 \). Of the other two, the first is simply \( \exp(-2\zeta t/m) \, v(0)^2 \). The last term is the integral

\[ \int_0^t dt' \exp[-\zeta(t-t')] \int_0^t dt'' \exp[-\zeta(t-t'')] \, \langle \delta F(t') \delta F(t'') \rangle /m^2 > \] (8)

which simplifies to

\[ \int_0^t dt' \exp[-\zeta(t-t')] \int_0^t dt'' \exp[-\zeta(t-t'')] \, 2B \delta(t'-t'')/m^2. \] (9)

The solution is thus

\[ <v^2(t)> = \exp(-2\zeta t/m) \, v(0)^2 + \frac{B}{\zeta m} \, [1 - \exp(-2\zeta t/m)]. \] (10)

In the long time limit, the exponentials decay to zero and we are left with \( B/\zeta m \), and the left hand side equates to \( k_B T/m \). Thus we have

\[ B = \zeta k_B T. \] (11)

This relation tells us that the fluctuating and the dissipative parts of the forces are related, in equilibrium. This is a particular realization of the fluctuation-dissipation theorem for the case of Brownian motion.

We discussed earlier how the initial velocity of a Brownian particle may decay. A more precise way to do this is to consider a time correlation function of the quantity of interest. Instead of calculating \( <v(t)v(0)> \) as we just did, we could compute \( <v(t)v(t')> \). We get, simply,

\[ <v(t)v(0)> = \exp(-\zeta t/m) \, v(0)^2 = \exp(-\zeta t/m)k_B T/m. \] (12)

Here, we have considered the average over the initial ensemble of velocities in writing \( <v(0)^2> = k_B T/m \). More generally, we wish to compute and study the properties of \( <v(t)v(t')> \). To do this, let us consider times \( t \) and \( t' \) which are sufficiently removed from the initial time (which can be treated at negative infinity) that only the second term in Eq. 5 remains. Thus we write, with a change of variables

\[ v(t) = \int_0^\infty \exp(-\zeta u/m) \delta F(t-u) du/m. \] (13)

The correlation function, averaged over noise is

\[ <v(t)v(t')> = \int_0^\infty \exp(-\zeta u_1/m) \int_0^\infty \exp(-\zeta u_2/m) \, \delta F(t-u_1) \delta F(t'-u_2) > du_1 du_2 /m^2. \] (14)
From the property of the fluctuating force
\[ <v(t)v(t')> = (2B/m^2) \int_0^\infty \exp(-\zeta u_1/m) \int_0^\infty \exp(-\zeta u_2/m) \delta(t - u_1 - t' + u_2) du_1 du_2 \]  
(15)

This double integral can be written as the sum over two half-planes defined by conditions \( u_2 > u_1 \) and \( u_2 < u_1 \). Correspondingly, we can define variables \( s_1 = u_1 - u_2 \), and \( s_2 = u_2 - u_1 \), and write
\[ \int_0^\infty \exp(-\zeta u_1/m) \int_0^\infty \exp(-\zeta u_2/m) \delta(t - u_1 - t' + u_2) du_1 du_2 = I_1 + I_2, \]  
(16)

with
\[ I_1 = \int_0^\infty du_2 \int_0^\infty ds_1 \exp(-\zeta (s_1 + 2u_2)/m) \delta((t - t') - s_1) \]  
(17)

and
\[ I_2 = \int_0^\infty du_1 \int_0^\infty ds_2 \exp(-\zeta (s_2 + 2u_1)/m) \delta((t - t') + s_2). \]  
(18)

Clearly, depending on the sign of \( t - t' \) only one of \( I_1 \) and \( I_2 \) will be finite, with the integral being the same in both cases, and the solution for the velocity correlation can be written as
\[ <v(t)v(t')> = (2B/m^2) \exp(-\zeta |t - t'|/m) \frac{m}{2\zeta}. \]  
(19)

Using \( B = \zeta k_B T \), we get the expected result
\[ <v(t)v(t')> = (k_B T/m) \exp(-\zeta |t - t'|/m). \]  
(20)

Note however that this expression is an improvement over the earlier form we had for \( <v(t)v(0)> \) in being symmetric in the time difference \( t - t' \). This also means that the function is singular at \( t - t' = 0 \), which is associated with the assumption of delta correlation for the noise. In reality, for very small differences, we should expect smoother behavior in both cases.

We next consider the relationship of this correlation function to the long time properties of Brownian motion. As we will discuss more explicitly later, a Brownian particle will exhibit *diffusive* motion, which is characterized by a diffusion coefficient, \( D \). If one considers the mean squared displacement of a diffusing particle (starting at \( x = 0 \) at \( t = 0 \), for simplicity), it increases linearly with time at long times, as
\[ <x(t)^2> = 2Dt \]  
(21)

or
\[ \frac{\partial <x(t)^2>}{\partial t} = 2D. \]  
(22)

The mean squared displacement can be written using
\[ x(t) = \int_0^t ds v(s) \]  
(23)
we have

\[ < \chi^2(t) > = \int_0^t ds_1 \int_0^t ds_2 < v(s_1)v(s_2) > \]  

Taking the derivative with respect to time,

\[ \frac{\partial < \chi^2 >}{\partial t} = 2 \int_0^t ds < v(t)v(s) > . \]  

We can do a variable transform, and take the limit of \( t \to \infty \), to obtain

\[ D = \int_0^\infty dt < v(t)v(0) > . \]  

This equation relates the diffusion coefficient, a transport coefficient, to the time integral of a correlation function, the velocity auto correlation function. It is an example of Green-Kubo relations, which provide expressions for transport coefficients in terms of time integrated correlation functions.

Instead of using the definition of the diffusion coefficient in terms of the assumed long time limit of \( < \chi^2(t) > \), we can consider the solution for \( v(t) \) and evaluate \( < \chi^2(t) > \). The result of such a calculation is

\[ < \chi^2(t) > = 2k_B T \left[ t - \frac{m}{\zeta} + \frac{m}{\zeta} \exp(-\zeta t/m) \right] . \]  

In the long time limit, this yields

\[ < \chi^2(t) > = 2k_B T \zeta t . \]  

Comparing with the earlier expression for \( < \chi^2(t) > \) for diffusion, we have

\[ D = \frac{k_B T}{\zeta} . \]  

This is the Einstein formula for the diffusion coefficient of a Brownian particle. Using the Stokes formula for the frictional coefficient of a particle in a liquid, \( \zeta = \frac{6\pi \eta a}{\zeta} \), where \( \eta \) is the viscosity and \( a \) is the radius of the Brownian (spherical) particle, we have the Stokes-Einstein formula

\[ D = \frac{k_B T}{6\pi \eta a} . \]  

### 3 Langevin Equation

We will now consider writing the Langevin equation in more general contexts. We consider first the generalization of the above description to an arbitrary (and unspecified) set of variables, which we assume satisfy the same kind of equations as the velocity of the Brownian particle. For such a set of dynamical variables \([a_1, a_2, \ldots]\), we can then write the Langevin equation

\[ \frac{\partial a_j}{\partial t} = \sum_k \Theta_{jk} a_k + \delta F_j(t) \]
which we can write in matrix form as
\[ \frac{\partial \mathbf{a}}{\partial t} = \mathbf{\Theta}.\mathbf{a} + \delta \mathbf{F}(t). \] (32)

Since the system approaches equilibrium at long times, we assume that elements of \( \mathbf{\Theta} \) will have real negative parts, but make no other assumptions right now. The strength of the noise is given by
\[ <\delta F_j(t)\delta F_k(t)> = 2B_{jk}\delta(t-t'). \] (33)

Note that \( \mathbf{B} \) is by definition a symmetric matrix. As before we can write the solution for \( \mathbf{a}(t) \) as
\[ \mathbf{a}(t) = \int_0^t ds \exp[(t-s)\mathbf{\Theta}].\delta \mathbf{F}(s) \] (34)

where we have assumed that the first term depending on initial values of \( \mathbf{a} \) can be set to zero. We now construct the matrix \( <\mathbf{a}(t)\mathbf{a}(t)^T> \)
\[ <\mathbf{a}(t)\mathbf{a}(t)^T> = 2 \int_0^\infty dt \exp[t\mathbf{\Theta}].\mathbf{B}.\exp[t\mathbf{\Theta}^T]. \] (35)

The correlation of the forces can be expressed in terms of \( \mathbf{B} \)
\[ <\mathbf{a}(t)\mathbf{a}(t)^T> = 2 \int_0^\infty dt \exp[t\mathbf{\Theta}].\mathbf{B}.\exp[t\mathbf{\Theta}^T]. \] (36)

For long times, once again we demand that the above correlation reaches the equilibrium value, which we represent as \( \mathbf{M} \). Thus
\[ <\mathbf{a}\mathbf{a}^T>_{eq} = \mathbf{M} = 2 \int_0^\infty dt \exp[t\mathbf{\Theta}].\mathbf{B}.\exp[t\mathbf{\Theta}^T]. \] (37)

\( \mathbf{M} \) is symmetric by definition, like \( \mathbf{B} \) but \( \mathbf{\Theta} \) is not. To proceed further, we construct a symmetrized quantity \( \mathbf{\Theta} \mathbf{M} + \mathbf{M} \mathbf{\Theta}^T \) and evaluate it from the expression above. Thus
\[ \mathbf{\Theta} \mathbf{M} + \mathbf{M} \mathbf{\Theta}^T = 2 \int_0^\infty dt \frac{d}{dt} \exp[t\mathbf{\Theta}].\mathbf{B}.\exp[t\mathbf{\Theta}^T] + 2 \int_0^\infty dt \exp[t\mathbf{\Theta}].\mathbf{B}.\exp[t\mathbf{\Theta}^T].\mathbf{\Theta}^T \]
\[ = 2 \int_0^\infty dt \frac{d}{dt} \exp[t\mathbf{\Theta}].\mathbf{B}.\exp[t\mathbf{\Theta}^T] \]
\[ = 2(\exp[t\mathbf{\Theta}].\mathbf{B}.\exp[t\mathbf{\Theta}^T])_{t=\infty} - 2\mathbf{B}. \] (38)

The first term vanishes since \( \mathbf{\Theta} \) components have real negative parts, and we get the general form of the fluctuation-dissipation relation
\[ \mathbf{\Theta} \mathbf{M} + \mathbf{M} \mathbf{\Theta}^T = -2\mathbf{B}. \] (39)

Since \( \mathbf{B} \) and \( \mathbf{M} \) are symmetric, the above equation can be realized for \( \mathbf{\Theta} \) having a symmetric part and an antisymmetric part, written as:
\[ \mathbf{\Theta} = i\mathbf{\Omega} - \mathbf{K}. \] (40)

Thus,
\[ \mathbf{B} = \mathbf{K} \mathbf{M} = \mathbf{M} \mathbf{K}^T \] (41)
and
\[ i\Omega M = -M i\Omega^T \] (42)

As an illustration, we consider a one dimensional harmonic oscillator but write the equations for both position and momentum:

\[ \frac{dx}{dt} = \frac{p}{m} \]
\[ \frac{dp}{dt} = -m\omega^2 x - \zeta \frac{p}{m} + \delta F_p(t). \] (43)

For this case,

\[ a = \begin{pmatrix} x \\ p \end{pmatrix} \]

\[ F = \begin{pmatrix} 0 \\ \delta F_p(t) \end{pmatrix} \]

\[ M = \begin{pmatrix} <x^2> & 0 \\ 0 & <p^2> \end{pmatrix} \]

or

\[ M = \begin{pmatrix} k_B T & 0 \\ \frac{m\omega^2}{k_B T} & m k_B T \end{pmatrix} \]

\[ i\Omega = \begin{pmatrix} 0 & 1/m \\ -m\omega^2 & 0 \end{pmatrix} \]

and

\[ K = \begin{pmatrix} 0 & 0 \\ 0 & \zeta/m \end{pmatrix} \]

We next discuss the generalization of the Langevin equation to cases where the friction and fluctuating forces at a given time do not only contribute to the instantaneous change in the variable of concern, but can contribute to the time derivative at future times. In other words, we will consider “non-Markovian” cases.

To motivate the general form of the Langevin equation in such a case, consider again the harmonic oscillator example:

\[ \frac{dx}{dt} = \frac{p}{m} \]
\[ \frac{dp}{dt} = -m\omega^2 x - \zeta \frac{p}{m} + \delta F_p(t). \] (44)

We can write the solution for the momentum as
\[ p(t) = \int_{-\infty}^{t} ds \exp(-\zeta(t-s)/m)(-m\omega^2x(s) + \delta F_p(s)) \]
\[ = \int_{0}^{\infty} ds \exp(-\zeta(s/m)(-m\omega^2x(t-s) + \delta F_p(t-s))). \quad (45) \]

Here, we have assumed the \textit{initial} time to be \(-\infty\) so that the first term in the general solution is strictly zero. We can put this back in the equation for the position, and write it as

\[ \frac{dx}{dt} = -\int_{0}^{\infty} ds K(s)x(t-s) + \delta F_x(t). \quad (46) \]

We have

\[ K(t) = \omega^2 \exp(-\zeta|t|/m) \]

and

\[ \delta F_x(t) = \frac{1}{m} \int_{0}^{\infty} ds \exp(-\zeta s/m) \delta F_p(t-s). \quad (48) \]

In equilibrium we have

\[ <x^2>_{eq} = \frac{k_B T}{m\omega^2} \]

and we can easily get

\[ <\delta F_x(t)\delta F_x(t')>_T = <x^2>_{eq} K(|t-t'|). \quad (50) \]

Thus, by eliminating the variable \( p \), we got a description where the friction and fluctuating forces have finite time correlations, and the \textit{memory function} \( K \) is not a delta function. On the other hand, if we consider dynamics over very long time scales, we can approximate the memory function as a delta function and recover a Langevin equation that is Markovian.

Based on the above discussion, the general form of the Langevin equation can be written as

\[ \frac{da(t)}{dt} = i\Omega a(t) - \int_{0}^{\infty} ds K(s)a(t-s) + \delta F(t), \quad (51) \]

with

\[ <\delta F(t)\delta F(t')>_T = K(t-t'). <aa^T>_{eq} \quad (52) \]

\textit{Brownian motion in a Harmonic Oscillator Heat Bath:}

In our description of Brownian motion, our statements about the origin of the fluctuating force have been qualitative, and we have had to assume the nature of correlations of such forces. As we saw above, even with the assumption of delta correlated fluctuating forces, correlations emerge when we integrate out variables. To see more microscopically how these features arise, it is useful to consider a concrete example where a Langevin description may be obtained starting with a “microscopic description”. For this, we consider a Brownian particle or “solute” couple to a bath that is composed of harmonic oscillators. The Hamiltonian of the system...
\[ H = H_s + H_B, \]  

where

\[ H_s = \frac{p^2}{2m} + U(x) \]  
is the Hamiltonian involving the coordinate and momentum of the Brownian particle, and

\[ H_B = \sum_j \left[ \frac{p_j^2}{2} + \frac{1}{2}\omega_j^2 \left( q_j - \frac{\gamma_j}{\omega_j^2}x \right)^2 \right] \]  

where the sum is over the harmonic oscillators. The strength of the coupling is controlled by the variables \( \gamma_j \).

The equations of motion corresponding to this Hamiltonian are:

\[ \frac{dx}{dt} = \frac{p}{m}, \quad \frac{dp}{dt} = -U'(x) + \sum_j \gamma_j \left( q_j - \frac{\gamma_j}{\omega_j^2}x \right), \]  

\[ \frac{dq_j}{dt} = p_j, \quad \frac{dp_j}{dt} = -\omega_j^2 q_j + \gamma_j x. \]  

If we assume that the time dependence of \( x(t) \) is known, we can write the solution for \( q_j \) treating \( x(t) \) as an external force. This can be done by obtaining the Green’s function for the applied force and writing the general solution in terms of the solution to the homogeneous equation for \( q \) without the force and the extra part coming from the presence of the forces. The Green’s function for this problem is \( \sin(\omega_j t)/\omega_j \) for \( q_j \), and the full solution is

\[ q_j(t) = q_j(0)\cos(\omega_j t) + p_j(0)\frac{\sin(\omega_j t)}{\omega_j} + \gamma_j \int_0^t dsx(s)\frac{\sin(\omega_j(t-s))}{\omega_j}. \]  

This can be reorganized by integration by parts to

\[ \left[ q_j(t) - \frac{\gamma_j}{\omega_j^2}x(t) \right] = \left[ q_j(0) - \frac{\gamma_j}{\omega_j^2}x(0) \right]\cos(\omega_j t) + p_j(0)\frac{\sin(\omega_j t)}{\omega_j} - \gamma_j \int_0^t ds \frac{p(s)}{m} \frac{\cos(\omega_j(t-s))}{\omega_j^2}. \]  

We now insert this into the equation for \( \frac{dp}{dt} \) and write the result as

\[ \frac{dp}{dt} = -U'(x) - \int_0^t dsK(s)\frac{p(t-s)}{m} + F_p(t), \]  

and from a comparison with the explicit expression, we have

\[ K(t) = \sum_j \frac{\gamma_j^2}{\omega_j^2}\cos(\omega_j t), \]  

and

\[ F_p(t) = \sum_j \gamma_j \left[ q_j(0) - \frac{\gamma_j}{\omega_j^2}x(0) \right]\cos(\omega_j t) + \sum_j \gamma_j p_j(0)\frac{\sin(\omega_j t)}{\omega_j}. \]
Now, we have not said anything about the actual frequencies. Thus a given choice of frequencies will lead to a particular type of memory function. If the set of frequencies were to be continuous, we could write

\[ K(t) = \int d\omega g(\omega) \frac{\gamma^2(\omega)}{\omega^2} \cos(\omega t), \]  

(63)

where \( g(\omega) \) is the density of states. If we choose \( g(\omega) \) to be proportional to \( \omega^2 \) (as in the Debye spectrum), and \( \gamma \) to be constant, we get \( K(t) \propto \delta(t) \), which means that the Langevin equation is Markovian.

We next consider the relation between the memory function and the fluctuating force. For this, we consider that the harmonic oscillator coordinates are distributed according to the Boltzmann weight associated with \( H_B \), or

\[ f_{eq}(p, q) \propto \exp(-H_B/k_B T). \]  

(64)

Then, we have

\[ < [q_j(0) - \frac{\gamma_j}{\omega_j^2} x(0)] > = 0; < p_j(0) > = 0, \]  

(65)

and

\[ < [q_j(0) - \frac{\gamma_j}{\omega_j^2} x(0)]^2 > = \frac{k_B T}{\omega_j^2}; < p_j^2(0) > = k_B T. \]  

(66)

Since we have no cross-correlations, either between different oscillators or between coordinates and momenta, we can evaluate the noise correlation easily and verify

\[ < F_p(t) F_p(t') > = k_B T K(t - t') \]  

verifying the fluctuation-dissipation theorem for this model. Thus, this simple model allows one to explicitly realize all the assumptions made in writing the Langevin equation for the Brownian particle and gives us an idea of the microscopic origin of special cases that we may wish to consider.

## 4 Classical Dynamics

In subsequent descriptions of dynamics, starting with writing the Fokker-Planck equation, we shift our attention from trying to write an equation of motion, \( e.g. \), for the variable that is undergoing “Brownian” dynamics to writing an equation that describes the time evolution of the distribution function for the variable. Since this approach can also be more generally undertaken to describe the time evolution of a many body system, we first start by a discussion of the latter.

In classical mechanics, we have the motion of the system in phase space governed by Hamilton’s equations,

\[ \frac{dq}{dt} = \frac{\partial H}{\partial p}, \quad \frac{dp}{dt} = -\frac{\partial H}{\partial q}. \]  

(68)
where $H$ is the Hamiltonian of the system whose coordinates and momenta are represented by vectors $\mathbf{q}$ and $\mathbf{p}$. Both coordinates and momenta together will be represented (later) by vector $\mathbf{X}$. In terms of these variables, in the context of statistical mechanics, we can define a distribution function $f(\mathbf{q}, \mathbf{p}, t)$ or $f(\mathbf{X}, t)$, which defines the probability density of the system at a given time $t$. The total probability is conserved at all times:

$$\int d\mathbf{X} f(\mathbf{X}, t) = 1.$$  \hspace{1cm} (69)

The local version of this statement gives us the continuity equation

$$\frac{\partial f}{\partial t} = -\frac{\partial}{\partial \mathbf{X}} (f(\mathbf{X}, t) \mathbf{V})$$  \hspace{1cm} (70)

where $\mathbf{V} = \frac{d\mathbf{X}}{dt}$. The Liouville equation for the probability distribution can be written in terms of the Liouville operator

$$L = \frac{\partial H}{\partial \mathbf{p}} \frac{\partial}{\partial \mathbf{q}} - \frac{\partial H}{\partial \mathbf{q}} \frac{\partial}{\partial \mathbf{p}}$$  \hspace{1cm} (71)

as

$$\frac{\partial f}{\partial t} = -Lf.$$  \hspace{1cm} (72)

The formal solution of this can be written as

$$f(\mathbf{X}, t) = \exp(-tL)f(\mathbf{X}, 0).$$  \hspace{1cm} (73)

Note that the same operator can be used to write the equation motion for any function of coordinates and momenta $A$ (which we assume has no explicit time dependence) as

$$\frac{dA}{dt} = LA.$$  \hspace{1cm} (74)

The formal solution of this can be written as

$$A(\mathbf{X}, t) = \exp(tL)A(\mathbf{X}, 0).$$  \hspace{1cm} (75)

The Liouville operator as defined is anti-self-adjoint. This can be seen by considering the average of quantity $A$ over the phase space, with $L$ operating on it:

$$\int d\mathbf{X} LAf = -\int d\mathbf{X} \frac{d}{d\mathbf{X}} (\mathbf{V}Af) = -\oint_{\text{Surface}} d\mathbf{S} (\mathbf{V}Af).$$  \hspace{1cm} (76)

We normally need to assume that fluxes and probabilities vanish at the boundary of the system’s phase space, which leads to the above integral vanishing. Then, using $L(Af) = (LA)f + A(Lf)$, we get

$$\int d\mathbf{X} A(Lf) = -\int d\mathbf{X} (LA)f.$$  \hspace{1cm} (77)
Likewise, considering the time average $\langle A(t) \rangle$ which can be written as an integral of $A(X)$ over the time evolved $f$ or vice versa, we see that their equivalence corresponds to the operator $L$ being anti-self-adjoint:

$$< A(t) > = \int dX A(X) f(X, t) = \int dX A(X) \exp(-tL) f(X, 0)$$

and

$$< A(t) > = \int dX A(X, t) f(X) = \int dX (\exp(tL)A(X)) f(X, 0).$$

In terms of these, we can write a time correlation function between two variables $A$ and $B$ as

$$C_{AB}(t) = \int dX A(X, t) B(X) f_{eq}(X)$$

which equals

$$C_{AB}(t) = \int dX (\exp(tL)A(X, 0)) B(X) f_{eq}(X) = \int dX A(X, 0)(\exp(-tL)B(X) f_{eq}(X))$$

leading to

$$C_{AB}(t) = C_{BA}(-t).$$

5 Fokker-Planck Equation

In order to obtain the Fokker-Planck equation, we first start with a system described by the Langevin equation

$$\frac{da}{dt} = v(a) + F(t)$$

where $v$ is some unspecified set of functions. We assume the noise to be Gaussian and delta correlated as before:

$$\langle F(t)F(t') \rangle = 2B \delta(t - t').$$

We now try to use these to write the equation for a distribution function $f$, which is conserved. Thus:

$$\frac{\partial f}{\partial t} + \frac{\partial}{\partial a} \left( \frac{da}{dt} f \right) = 0.$$ 

Substituting for the time evolution of $a$, we have

$$\frac{\partial f}{\partial t} = -\frac{\partial}{\partial a} (v(a)f + F(t)f).$$

We define a Liouville-like operator

$$LA = \frac{\partial}{\partial a} (v(a)A),$$

in terms of which the deterministic part of the above equation can be written as

$$\frac{\partial f}{\partial t} = -Lf$$

leading to

$$C_{AB}(t) = C_{BA}(-t).$$
whose formal solution can be written as

$$f(a, t) = \exp(-tL)f(a, 0).$$  \hfill (89)

The full equation with the noise term is

$$\frac{\partial f}{\partial t} = -Lf - \frac{\partial}{\partial a} \langle F(t) f \rangle. \hfill (90)$$

This equation can be integrated to give

$$f(a, t) = \exp(-tL)f(a, 0) - \int_0^t ds \exp(-(t-s)L) \frac{\partial}{\partial a} \langle F(s) f(a, s) \rangle. \hfill (91)$$

We insert this solution into the earlier equation, and take the average over the noise. Thus,

$$\frac{\partial f}{\partial t} = -Lf - \frac{\partial}{\partial a} \langle F(t) \exp(-tL)f(a, 0) \rangle + \frac{\partial}{\partial a} \langle F(t) \int_0^t ds \exp(-(t-s)L) \frac{\partial}{\partial a} \langle F(s) f(a, s) \rangle \rangle, \hfill (92)$$

after the averaging leads to

$$\frac{\partial \langle f(a, t) \rangle}{\partial t} = -\frac{\partial}{\partial a} \langle v(a) \langle f(a, t) \rangle \rangle + \frac{\partial}{\partial a} \langle B \frac{\partial}{\partial a} \langle f(a, t) \rangle \rangle. \hfill (93)$$

This is the Fokker-Planck equation. Note that the average is over the noise at all times leading up to time $t$. A simple way to think through this clearly is to discretize time, and average over the noise at each of these times, and then work back to the continuum limit. A few points to keep in mind. The only term that has survived is the average $\langle F(t) \rangle < F(s) >$, although $f(a, s)$ in principle contains additional $F$ terms. But these have to be at earlier times than $s < s'$ and thus do not contribute. In other words we are considering $t > s > s'$. Also, the limit of integration on $s$ is $t$ and thus after we write $\langle F(t) \rangle < F(s) >= 2B \delta(t - s)$, and integrate over $s$ instead of the delta function leaving us with a factor of $2B$, we have only $B$. We can verify this by considering a sequence of functions approximating the delta function and taking the limit.

In this Fokker-Planck equation, we have not yet imposed any fluctuation-dissipation condition, and thus do not a priori know whether stationary solutions can be found.

We will next consider some simple examples to illustrate this equation. The first is the Brownian motion of a particle inside a potential $U(x)$. The Langevin equations for this system are

$$\frac{dx}{dt} = \frac{p}{m}$$

$$\frac{dp}{dt} = -U'(x) - \frac{\zeta p}{m} + \delta F_p(t). \hfill (94)$$

And we have

$$\langle F_p(t) F_p(t') \rangle = 2\zeta k_B T \delta(t - t'). \hfill (95)$$

The quantities that we need for the Fokker-Planck equation are

$$a = \begin{pmatrix} x \\ p \end{pmatrix}$$
\[ v = \left( \begin{array}{c} \frac{p}{m} \\ -U'(x) - \zeta \frac{p}{m} \end{array} \right) \]

\[ F = \left( \begin{array}{c} 0 \\ F_p(t) \end{array} \right) \]

and

\[ B = \left( \begin{array}{cc} 0 & 0 \\ 0 & \zeta k_B T \end{array} \right) \]

The Fokker-Planck equation is

\[ \frac{\partial f}{\partial t} = -\frac{\partial}{\partial x} \left( \frac{dx}{dt} f \right) - \frac{\partial}{\partial p} \left( \frac{dp}{dt} f \right) + \zeta k_B T \frac{\partial^2}{\partial p^2} f. \]  

(96)

This equals

\[ \frac{\partial f}{\partial t} = -\frac{\partial}{\partial x} \left( \frac{p}{m} f \right) - \frac{\partial}{\partial p} \left( (-U'(x) - \zeta p/m) f \right) + \zeta k_B T \frac{\partial^2}{\partial p^2} f. \]  

(97)

This is the one dimensional version of the Kramers equation. Without the terms arising from noise and friction, this reduces to the Liouville equation for the Hamiltonian,

\[ H = \frac{p^2}{2m} + U(x). \]  

(98)

We may therefore expect that the Fokker-Planck equation describes, in the steady state, the equilibrium, Boltzmann distribution

\[ f_{eq}(x,p) = \frac{1}{Q} \exp\left( -\frac{H}{k_B T} \right). \]  

(99)

We can verify this by setting \( f(x,p) = f(H) \), \( \frac{\partial f}{\partial t} = 0 \), and solving the Fokker-Planck equation with the terms noise and friction.

We now consider the case where the external potential is zero. In this case, we can simply start with the Langevin equation for the velocity and proceed to write the corresponding Fokker-Planck equation.

\[ \frac{\partial f}{\partial t} = \zeta \frac{\partial}{\partial p} ((p/m)f) + \zeta k_B T \frac{\partial^2}{\partial p^2} f. \]  

(100)

This equation is called Rayleigh’s equation. The corresponding Langevin equation is of course what we studied at the outset.

\[ \frac{dp}{dt} = -\zeta \frac{p}{m} + \delta F_p(t). \]  

(101)

or

\[ m \frac{dv}{dt} = -\zeta v + \delta F_p(t). \]  

(102)
We had the solution for this

\[ v(t) = \exp(-\zeta t/m) v(0) + \int_0^t dt' \exp[-\zeta(t-t')]m \delta F(t')/m. \]  \hfill (103)

\[ <v^2(t)> = \exp(-2\zeta t/m) v(0)^2 + \frac{k_BT}{m} [1 - \exp(-2\zeta t/m)]. \]  \hfill (104)

Which we could write also as

\[ <v^2(t)> - <v(t)>^2 = \frac{k_BT}{m} [1 - \exp(-2\zeta t/m)]. \]  \hfill (105)

with

\[ <v(t)> = \exp(-\zeta t/m) v(0) \]  \hfill (106)

With these, if we assume that the resulting distribution \( f \) is Gaussian, we can write it in terms of the mean and variance we have just written down, as

\[ f(v, t|v_0) = \left[ \frac{m}{2\pi k_BT(1 - \exp(-2\zeta t/m))} \right]^{1/2} \exp \left[ -\frac{(v - v(0) \exp(-\zeta t/m))^2}{2 \frac{k_BT}{m} [1 - \exp(-2\zeta t/m)]} \right]. \]  \hfill (107)

This is called the Ornstein-Uhlenbeck distribution, which clearly goes to the Maxwell distribution if we wait long enough:

\[ f_{eq}(v) = \left[ \frac{m}{2\pi k_BT} \right]^{1/2} \exp \left[ -\frac{mv^2}{2k_BT} \right]. \]  \hfill (108)

\textbf{Smoluchowski Equation:}

We next consider the general case of the Langevin equation of a Brownian particle moving in an external potential.

\[ \frac{m}{\zeta} \frac{d^2x}{dt^2} = -U'(x) - \frac{dx}{dt} + F(t). \]  \hfill (109)

When the time constant defined by \( m/\zeta \) is large (the high friction limit), this equation reduces to

\[ \frac{dx}{dt} = -\frac{1}{\zeta} U'(x) + \frac{1}{\zeta} F(t). \]  \hfill (110)

We can get this more systematically by considering a new time variable \( s = t/(\zeta/m) \). With this, we will have

\[ \frac{m^2}{\zeta} \frac{d^2x}{ds^2} = -\frac{1}{m} U'(x) - \frac{dx}{ds} + \frac{1}{m} F(t). \]  \hfill (111)

If we take the limit \( \zeta \to \infty \) and \( t \to \infty \) such that \( s \) remains finite, the inertial term drops out, and get the above equation. This is a little confusing since we had the time constant for the velocity autocorrelation as \( \frac{m}{\zeta} \), but
when the friction or the viscosity (using the Stokes formula) is high, the dynamics gets slower, and the scaling we used therefore is appropriate.

Now we write the corresponding Fokker-Planck equation, noting that the time derivative of $x$ is given by $-\frac{1}{\zeta} U'(x)$ and the noise average will give us

$$\frac{1}{\zeta^2} < F(t) F'(t') > = 2 \frac{k_B T}{\zeta}. \quad (112)$$

Thus, we have

$$\frac{df}{dt} = \frac{1}{\zeta} \frac{\partial}{\partial x} (U'(x)f) + \frac{k_B T}{\zeta} \frac{\partial^2 f}{\partial x^2}. \quad (113)$$

We can write, with the notation $D = \frac{k_B T}{\zeta}$, as

$$\frac{df}{dt} = D \frac{\partial}{\partial x} \exp\left(-\frac{U(x)}{k_B T}\right) \frac{\partial}{\partial x} \left[ \exp\left(\frac{U(x)}{k_B T}\right) f \right]. \quad (114)$$

This is called the Smoluchowski equation, which describes diffusion in an external potential. Note that $D$ is the diffusion coefficient as given by the Einstein formula, and when the external potential is turned off, we get the diffusion equation.

When the potential is not zero, but we ask instead for a time invariant solution, it is easy to verify that

$$f_{eq}(x) = C \exp\left(-\frac{U(x)}{k_B T}\right) \quad (115)$$

will satisfy the Smoluchowski equation with the time derivative equal to zero.

However, we can write this in a little different fashion that will be of use later. The Smoluchowski equation can be written in the form of a continuity equation, by introducing a current density $j$, as

$$\frac{df}{dt} + \frac{\partial j}{\partial x} = 0. \quad (116)$$

The current density is defined by

$$j(x,t) = -\frac{1}{\zeta} (U'(x)f) - \frac{k_B T}{\zeta} \frac{\partial f}{\partial x}. \quad (117)$$

The condition for equilibrium can be stated by saying that the current density has to be a constant, $j(x,t) = j^{st}$. The solution for this, as can easily be verified is,

$$f_{eq}(x) = \left[ C - \frac{j^{st}}{k_B T} \int dx \exp\left(\frac{U(x)}{k_B T}\right) \right] \exp\left(-\frac{U(x)}{k_B T}\right) \quad (118)$$

Before we move on, we write the Smoluchowski equation when the potential is simple harmonic, i.e. $U(x) = \frac{m\omega^2 x^2}{2}$, and $U'(x) = m\omega^2 x$.

$$\frac{df}{dt} = \frac{1}{\zeta} \frac{\partial}{\partial x} \left( m\omega^2 x \, f \right) + \frac{k_B T}{\zeta} \frac{\partial^2 f}{\partial x^2}. \quad (119)$$

This has the same form as Rayleigh’s equation for the velocities, and will thus have the same form of the solution.
Kramer’s escape rate formula: Now we consider a case where the motion in an external field will correspond to crossing a potential energy barrier. This is schematically shown in Figure 1. We can think of this representing the energy surface for a chemical reaction, or some other activated process. We consider a region \((a,b)\) around \(x_0\) as the initial state, and would like to consider the rate at which the system escapes across the barrier at \(x_1\) to some point like \(x_2\). The escape rate can be defined as

\[
\lambda_{\text{esc}} = \frac{\text{flux at } x_2}{\text{probability of being around } x_0}
\]

(120)

To calculate this, we first compute the probability of being around \(x_0\) by integrating the probability around \(x_0\). For convenience, we write

\[
f_{\text{eq}}(x) = f_{\text{eq}}(x_0) \exp \left[ \frac{U(x_0) - U(x)}{k_B T} \right].
\]

(121)

The integral of \(f_{\text{eq}}(x)\) can be performed by noting that this can be done using a Gaussian approximation. So

\[
\int_a^b dx f_{\text{eq}}(x) = f_{\text{eq}}(x_0) \int_a^b \exp \left[ \frac{U(x_0) - U(x)}{k_B T} \right] \approx f_{\text{eq}}(x_0) \left( \frac{2\pi k_B T}{U''(x_0)} \right)^{1/2}
\]

(122)

Now we consider the expression for the steady state current density, which can be rewritten as

\[
j_{\text{st}} = -\frac{k_B T}{\zeta} \exp(-U(x)/k_B T) \frac{\partial}{\partial x} \exp(U(x)/k_B T)f_{\text{eq}}(x)
\]

(123)

We take the \(\exp(-U(x)/k_B T)\) to the left hand side, and integrate both sides from \(x_0\) to \(x_2\). Thus

\[
j_{\text{st}} \int_{x_0}^{x_2} dx \exp(U(x)/k_B T) = \frac{k_B T}{\zeta} \left[ \exp(U(x_0)/k_B T)f_{\text{eq}}(x_0) - \exp(U(x_2)/k_B T)f_{\text{eq}}(x_2) \right].
\]

(124)

If we make the same Gaussian approximation for the left side, and assume that the equilibrium probability is low at \(x_2\) and hence neglect the term, we will have

\[
\int_{x_0}^{x_2} dx \exp(U(x)/k_B T) \approx \exp(U(x_1)/k_B T) \left( \frac{2\pi k_B T}{|U''(x_1)|} \right)^{1/2}
\]

(125)

\[
j_{\text{st}} = \frac{k_B T}{\zeta} \left( \frac{2\pi k_B T}{|U''(x_1)|} \right)^{-1/2} f_{\text{eq}}(x_0) \exp(-\Delta U/k_B T)
\]

(126)

Taking the ratio of \(j_{\text{st}}\) with the integrated probability around \(x_0\) will give us the escape rate,

\[
\lambda_{\text{esc}} = \left[ \frac{U''(x_0)|U''(x_1)|}{2\pi \zeta} \right]^{1/2} \exp(-\Delta U/k_B T).
\]

(127)

The escape rate therefore depends exponentially on the barrier height, and also on the curvature of the potential at the minimum and maximum respectively.
6 Quantum Dynamics

In many subsequent sections, we would like to present in parallel both classical and quantum treatments of important results. In order to do so, we summarize the manner in which dynamics of a quantum system will be described. This will consist of two parts. The first is standard quantum mechanical equations in the Schrödinger and Heisenberg representations. The second is the manner in which quantum statistical mechanical averages are taken. In what follows we consider states that may be represented in terms of a complete basis made up of discrete states.

In quantum mechanics, the state of the system is described in terms of the occupancy of quantum states, which form a Hilbert space. The dynamics of the system may either be described by the evolution of the wave function, or time dependent operators. In taking equilibrium averages with respect to some statistical mechanical ensemble, the equivalent of the phase space distribution function will be the quantum mechanical density matrix.

Without bothering about how the Hamiltonian is represented, the time independent solution of a system consists of solving the eigenvalue problem

\[ H\phi_j(q) = E_j\phi_j(q) \]  \hspace{1cm} (128)

where \( q \) system coordinates, and \( \phi_j \) are the wave functions corresponding to the representation of the eigen states. We have the usual orthonormalization condition:

\[ \int dq \phi_j^*(q)\phi_k(q) = \delta_{jk}. \]  \hspace{1cm} (129)

The expectation value of some operator with respect to the \( j^{th} \) state is

\[ <A> = \int dq \phi_j^*(q)A\phi_j(q). \]  \hspace{1cm} (130)

The probability that in thermal equilibrium the system is in the \( j^{th} \) state is

\[ \rho_{j(eq)} = \frac{1}{Q}\exp(-\beta E_j); Q = \sum_j \exp(-\beta E_j) \]  \hspace{1cm} (131)

where \( \beta = 1/k_BT \). The equilibrium average of \( A \) is given by its expectation value averaged over all eigenstates, weighted by the probability:

\[ <A>_{(eq)} = \sum_j \rho_{j(eq)} <A> \]  \hspace{1cm} (132)

In general, it is not necessary, and often not feasible to first find the orthonormal basis in which the Hamiltonian is diagonal, in order to compute equilibrium averages. In order to obtain the corresponding expressions, we consider a complete orthonormal basis \( f_k(q) \) with

\[ \int dq f_j^*(q)f_k(q) = \delta_{jk}. \]  \hspace{1cm} (133)

An arbitrary state (say, energy eigen states that also form a complete basis) can be represented by
\[ \phi_j(q) = \sum_k S_{jk} f_k(q). \] (134)

The matrix of coefficients is
\[ S_{jk} = \int dq \phi_j^*(q)f_k(q). \] (135)

We can easily see that the inverse transformation is given by
\[ f_j(q) = \sum_k S_{kj}^* \phi_k(q). \] (136)

Thus, the transformation matrix \( S \) is unitary, with
\[ (S^{-1})_{lk} = S_{kl}^* \] (137)
and
\[ \sum_l S_{jl} S_{lk} = \delta_{jk}. \] (138)

This property will cause some confusion in terms of the ordering of indices in summations, which can be sorted out by recalling the unitarity property above.

In the arbitrarily chosen basis \( f \), the Hamiltonian will not be diagonal, but instead, will be represented by a matrix, which can be written as:
\[ H_{jk} = \int dq f_j^*(q)Hf_k(q) = \sum_m S_{mj} E_m S_{mk}^*. \] (139)

by in turn expressing \( f_j, f_k \) in terms of energy eigenfunctions.

The density matrix may be written by evaluating the matrix representation of the operator \( \exp(-\beta H) \):
\[ \rho_{jk(eq)} = \sum_m S_{mj} \rho_{m(eq)} S_{mk}^*. \] (140)

Similarly, the expectation value of an operator \( A \) in eigen state \( j \) can be written as
\[ <A>_j = \sum_m \sum_n S_{jm}^* A_{mn} S_{jn}. \] (141)

The equilibrium average then is
\[ <A>_{(eq)} = \sum_j \rho_{j(eq)} <A>_j = \sum_j \rho_{j(eq)} \sum_m \sum_n S_{jm}^* A_{mn} S_{jn}. \] (142)

This looks messy but can be rewritten as
\[ <A>_{(eq)} = \sum_m \sum_n \rho_{mn(eq)} A_{mn} = \text{Trace} (\rho_{eq}) \cdot A. \] (143)
All of this simply states that (a) the equilibrium average of $A$ is the trace of the product $\rho A$ and (b) that the trace is invariant with respect to a change of basis.

Comparing the classical and quantum expressions for the equilibrium averages,

$$<A>_{\text{classical}}^{(eq)} = \int dX A(X) f_{eq}(X)$$

(144)

and the quantum expression above, we see that they are very similar indeed, with the distribution function $f$ and the density matrix $\rho$ correspond to each other.

**Time Dependence:** We next consider how we describe time dependence in quantum mechanics. This is done with the time dependent Schrödinger equation (and we assume for the time being a time independent Hamiltonian):

$$i\hbar \frac{\partial \phi_j}{\partial t} = H \phi_j,$$

(145)

with the solution

$$\phi_j(q, t) = \exp(-itH/\hbar)\phi_j(q, 0).$$

(146)

The time dependent expectation value of a variable $A$ at time $t$ can be written as

$$<A, t> = \int dq \phi_j^*(q, t) A \phi_j(q, t).$$

(147)

Using the solution for $\phi(q, t)$ above, we can write this as

$$<A, t> = \int dq \phi_j^*(q, 0)(\exp(itH/\hbar)A \exp(-itH/\hbar))\phi_j(q, 0).$$

(148)

This allows us to write the time dependent Heisenberg operator

$$A(t) = \exp(itH/\hbar)A \exp(-itH/\hbar).$$

(149)

In the Heisenberg picture, the time dependence is contained in the time dependent operators, and the expectation values are obtained over time independent basis functions. We can write the time evolution equation for this, which is the Heisenberg equation:

$$\frac{dA(t)}{dt} = \frac{i}{\hbar} [H, A].$$

(150)

Defining a quantum Liouville operator $L$ by

$$LA = \frac{i}{\hbar} [H, A]$$

(151)

and comparing with the classical equation for the time evolution of a variable, we have the correspondence:
\[ L_{\text{classical}} = \frac{\partial H}{\partial p} \frac{\partial}{\partial q} - \frac{\partial H}{\partial q} \frac{\partial}{\partial p} \leftrightarrow L_{\text{quantum}} = \frac{i}{\hbar} [H, \cdot] \]  

(152)

The equation of motion is then

\[ \frac{dA(t)}{dt} = LA \]  

(153)

with the formal solution

\[ A(t) = \exp(tL)A(0). \]  

(154)

Like in classical mechanics, this operator is anti-self adjoint, and we have

\[ \text{Trace } A \exp(tL)B = \text{Trace } B \exp(-tL)A \]  

(155)

In the same fashion that we define a time dependent operator \( A(t) \), we can define a time dependent density matrix \( \rho(t) \), and using

\[ <A,t> = \text{Trace } (A(t)\rho(0)) = \text{Trace } A \exp(-tL)\rho(0) = \text{Trace } A\rho(t). \]  

(156)

Thus the equation for the time dependence of \( \rho \) is

\[ \frac{\partial \rho(t)}{\partial t} = -L\rho(t) = -\frac{i}{\hbar} [H, \rho(t)]. \]  

(157)

Equations of Motion: The Heisenberg picture allows one to make classical - quantum correspondences simpler. To illustrate this, and for use later, we write down the equations of motion, assuming a general Hamiltonian of the form:

\[ H = \frac{p^2}{2m} + U(x) \]  

(158)

where the different quantities are now understood to be operators. Using the commutator relations

\[ [x, p] = i\hbar \]  

(159)

and


(160)

one can obtain, for some general functions \( F(p) \) and \( G(x) \),

\[ [x, F(p)] = i\hbar \frac{\partial F}{\partial p} \]  

(161)

and
\[ [p, G(x)] = -\hbar \frac{\partial G}{\partial x}. \] (162)

With this, for the Hamiltonian above, we can write

\[ \frac{dx}{dt} = \frac{p}{m} \] \hspace{1cm} (163)

and

\[ \frac{dp}{dt} = -\frac{\partial}{\partial x} U(x). \] \hspace{1cm} (164)

There are exactly the same equations of motion as one would obtain from classical Hamiltonian dynamics, with the caveat that since \( x, p \) etc are now operators, (a) one must take care of their commutation properties, and (b) expectation values have to be evaluated in addition to averages over ensembles through the density matrix. In considering time dependent operators, one must be careful that the usual commutation relations that apply for (implicitly) equal time operators will not carry over to distinct-time commutators. For example, \( [x(0)x(t)] \neq 0 \), since \( x(t) \) will involve \( p \) which does not commute with \( x \).

**Golden Rule:** In further discussions of quantum dynamics, we will need to describe transitions between quantum states, and the rates of such transitions, when a perturbation is added to a Hamiltonian, is obtained at the level of first order perturbation theory from Fermi’s Golden rule, which we now discuss. We also use the bracket notation to make the algebra more transparent.

Consider an unperturbed Hamiltonian \( H \), with

\[ H |j> = E_j |j>. \] \hspace{1cm} (165)

We add a time dependent perturbation \( V(t) \) with

\[ V_{jk}(t) = <j|V(t)|k>. \] \hspace{1cm} (166)

The time dependent Schrödinger’s equation is

\[ \frac{\partial |\Psi(t)>}{\partial t} = -\frac{i}{\hbar} [H + V(t)] |\Psi(t)> \] \hspace{1cm} (167)

We consider that we start with an eigen state \( |n> \),

\[ |\Psi(0)> = |n>. \] \hspace{1cm} (168)

The time dependent solution can be written as

\[ \Psi(t) = \sum_j a_j(t) |j>. \] \hspace{1cm} (169)

We can then write the equation of motion for the coefficients:
\frac{\partial a_j(t)}{\partial t} = -\frac{i}{\hbar} E_j a_j(t) - \frac{i}{\hbar} \sum_k V_{jk}(t)a_k(t). \quad (170)

The initial condition is \( a_j(0) = \delta_{jn} \). In similar fashion to earlier calculations, we can write the solution

\[ a_j(t) = \exp(-iE_j t/\hbar)\delta_{jn} - \frac{i}{\hbar} \sum_k \int_0^t ds \exp(-iE_j(t-s)/\hbar)V_{jk}(s)a_k(s), \quad (171) \]

and to find the solution to first order in perturbation, substitute the zeroth order solution in the integral:

\[ a_j(t) = \exp(-iE_j t/\hbar)\delta_{jn} - \frac{i}{\hbar} \sum_k \int_0^t ds \exp(-iE_j(t-s)/\hbar)V_{jk}(s)\exp(-iE_k s/\hbar)\delta_{kn} + \ldots \quad (172) \]

The amplitude of the \( m \)th state \( m \neq n \), is given as

\[ a_m(t) = -\frac{i}{\hbar} \int_0^t ds \exp(-iE_m(t-s)/\hbar)V_{mn}(s)\exp(-iE_n s/\hbar) + \ldots \quad (173) \]

When the perturbation is time independent, writing

\[ \frac{E_m - E_n}{\hbar} = \omega_{mn} \quad (174) \]

we have

\[ a_m(t) = -\frac{1}{\hbar} \exp(-iE_m t/\hbar)V_{mn} \frac{\exp(i\omega_{mn} t) - 1}{\omega_{mn}} + \ldots \quad (175) \]

The probability of finding the system in the \( m \)th state is

\[ P_m(t) = |a_m(t)|^2 + \ldots = \frac{1}{\hbar^2} |V_{mn}|^2 \Delta(t) + \ldots \quad (176) \]

where

\[ \Delta(t) = \frac{\exp(i\omega_{mn} t) - 1}{\omega_{mn}} \frac{\exp(-i\omega_{mn} t) - 1}{\omega_{mn}} = \frac{4\sin^2(\omega_{mn} t/2)}{\omega_{mn}^2}. \quad (177) \]

\( \Delta(t) \) is a peaked function which becomes more sharply peaked as time goes on, with the height increasing as \( t^2 \) and width decreasing as \( 1/t \), and the area under it increasing linearly in \( t \). It can be written, in the limit of large time, as

\[ \Delta(t) = 2\pi t\delta(\omega_{mn}) = 2\pi\hbar t\delta(E_m - E_n). \quad (178) \]

Thus, at large times,

\[ P_m(t) = \frac{2\pi}{\hbar} t|V_{mn}|^2\delta(E_m - E_n). \quad (179) \]

Defining a transition rate as the rate of increase of this probability, we have
$$w_{mn}(t) = \frac{2\pi}{\hbar} |V_{mn}|^2 \delta(E_m - E_n).$$  \hspace{1cm} (180)

This result for the transition rate is the Golden Rule.

When the perturbation is periodic,

$$V(t) = V \cos(\omega t),$$  \hspace{1cm} (181)

the same calculations carry through with small changes:

$$a_m(t) = -\frac{1}{2\hbar} \exp(-iE_m t/\hbar) V_{mn} \left( \frac{\exp(i(\omega_{mn} + \omega)t) - 1}{\omega_{mn} + \omega} \right) + \ldots$$  \hspace{1cm} (182)

The time dependent factor $\Delta(t)$ will be

$$\Delta(t) = \left| \frac{\exp(i(\omega_{mn} + \omega)t/\hbar) - 1}{\omega_{mn} + \omega} + \frac{\exp(i(\omega_{mn} - \omega)t/\hbar) - 1}{\omega_{mn} - \omega} \right|^2.$$  \hspace{1cm} (183)

The corresponding transition probability will be

$$w_{mn}(t) = \frac{\pi}{2\hbar} |V_{mn}|^2 \left( \delta(E_m - E_n + \hbar\omega) + \delta(E_m - E_n - \hbar\omega) \right).$$  \hspace{1cm} (184)

In the limit $\omega$ goes to zero, the two rates differ by a factor of 2, which arises from interference effects which we have neglected in taking the large time limit first and then the $\omega \to 0$ limit.

**Example – Electron Transfer Kinetics:** We consider the problem of describing the transition of an electron from one state to another, in a molecule that is surrounded by a medium, which could be a polar liquid like water. The charge fluctuations involved in changes in coordinates of the charges in the molecule couple to dielectric fluctuations in the medium. In such a system described quantum mechanically, one could have tunneling between states in the presence of a perturbing field. We describe how coupling to a heat bath affects such tunneling. The model we consider is the one we considered earlier, where the system of interest (here, an electron in a molecule) is coupled to a bath of harmonic oscillators:

$$H_s = \frac{p^2}{2m} + U(x)$$  \hspace{1cm} (185)

is the Hamiltonian involving the coordinate and momentum of the electron, and

$$H_B = \sum_j \left[ \frac{p_j^2}{2} + \frac{1}{2} \omega_j^2 \left( q_j - \frac{\gamma_j}{\omega_j^2} x \right)^2 \right]$$  \hspace{1cm} (186)

where the sum is over the harmonic oscillators. The strength of the coupling is controlled by the variables $\gamma_j$.

The first problem to consider is how the dynamical equations of this system will be affected, along the lines that we followed to write down the Langevin equation for the Brownian particle, where the friction and fluctuating force terms were related to the heat bath degrees of freedom. At the first level, this proves to be an entirely straight forward exercise. In the Heisenberg representation, the equations of motion and the solutions carry over entirely. The only non-trivial part of this exercise will be (before we get to the Langevin equation...
for the variables $x$ and $p$) the evaluation of the average values needed for evaluating the mean and variance of the bath variables. This is left as an exercise.

We now consider the problem with the potential $U(x)$ describing a two level system, which is the simplest case where we will be interested in the corresponding solution. Thus, we imagine that we have “left” and “right” states, which are eigenstates of the unperturbed Hamiltonian, and represent the Hamiltonian in this basis by a $2 \times 2$ matrix:

$$H_s = \begin{pmatrix} E_L & V \\ V & E_R \end{pmatrix}$$

The system coordinate in the same representation will be

$$x = \begin{pmatrix} x_L \\ 0 \\ 0 \\ x_R \end{pmatrix}$$

This is a bit puzzling at first, but effectively we are only considering the ground states in each of the wells, and the coordinate $x$ has only two values. In the same representation, we can write the whole Hamiltonian as

$$H = \begin{pmatrix} E_L + H_L & V \\ V & E_R + H_R \end{pmatrix}$$

where $H_L$ and $H_R$ are the heat bath Hamiltonians with $x$ taking values $x_L$ or $x_R$:

$$H_{L/R} = \sum_j \left[ \frac{p_j^2}{2} + \frac{1}{2} \omega_j^2 \left( q_j - \frac{\gamma_j}{\omega_j^2} x_{L/R} \right)^2 \right].$$

Correspondingly we have eigen value equations:

$$H_L |\mu_L> = \epsilon_{\mu_L} |\mu_L>$$

and

$$H_R |\nu_R> = \epsilon_{\nu_R} |\nu_R>$$

Now, the transitions between the states are caused by the perturbation

$$H' = \begin{pmatrix} 0 & V \\ V & 0 \end{pmatrix}$$

We can thus write the Golden rule formula for the transitions between these states:

$$w(\mu_L \rightarrow \nu_R) = \frac{2\pi}{\hbar} |\mu_L| V |\nu_R> |^2 \delta(\epsilon_{\mu_L} - \epsilon_{\nu_R})$$

Now we consider the total transition probability by summing over all the initial heat bath states weighted by the density matrix, and summing over all the final heat bath states:
\begin{align*}
w(L \rightarrow R) &= \frac{2\pi}{\hbar} |V|^2 \sum_{\mu} \rho_{\mu L} \sum_{\nu} \langle \mu L | \nu R \rangle |^2 \delta(\epsilon_{\mu L} - \epsilon_{\nu R} + E_L - E_R). \quad (191)
\end{align*}

We can write the delta function as an integral, conveniently chosen as:

\begin{align*}
\delta(E) &= \frac{1}{2\pi \hbar} \int_{-\infty}^{\infty} dt \exp(itE/\hbar) \quad (192)
\end{align*}

Using this, we write

\begin{align*}
w(L \rightarrow R) &= \frac{1}{\hbar^2} |V|^2 \int_{-\infty}^{\infty} dt \exp(it(E_L - E_R)/\hbar) \sum_{\mu} \rho_{\mu L} \exp(it\epsilon_{\mu L}/\hbar) \sum_{\nu} \langle \mu L | \nu R \rangle |^2 \exp(-ite_{\nu R}/\hbar) \quad (193)
\end{align*}

We note that

\begin{align*}
\sum_{\nu} | \langle \mu L | \nu R \rangle |^2 \exp(-ite_{\nu R}/\hbar) &= \sum_{\nu} < \mu L | \exp(-ite_{\nu R}/\hbar) \nu R | \mu L > \quad (194)
\end{align*}

which simplifies to

\begin{align*}
\sum_{\nu} | \langle \mu L | \nu R \rangle |^2 \exp(-ite_{\nu R}/\hbar) &= \langle \mu L | \exp(-ite_{H_R}/\hbar) | \mu L >
\end{align*}

Similarly we can reorganize the rest of the expression, leading to

\begin{align*}
\sum_{\mu} \rho_{\mu L} \exp(it\epsilon_{\mu L}/\hbar) \sum_{\nu} | \langle \mu L | \nu R \rangle |^2 \exp(-ite_{\nu R}/\hbar) &= \sum_{\mu} \rho_{\mu L} < \mu L | \exp(itH_L/\hbar) \exp(-itH_R/\hbar) | \mu L > \\
&= < \exp(itH_L/\hbar) \exp(-itH_R/\hbar) >_L \quad (195)
\end{align*}

Thus,

\begin{align*}
w(L \rightarrow R) &= \frac{1}{\hbar^2} |V|^2 \int_{-\infty}^{\infty} dt \exp(it(E_L - E_R)/\hbar) < \exp(itH_L/\hbar) \exp(-itH_R/\hbar) >_L. \quad (196)
\end{align*}

At this stage, we are going to make the approximation that the heat bath degrees of freedom are classical. This allows us to (a) treat the corresponding operators as commuting, and (b) use the classical values for various averages. Thus,

\begin{align*}
< \exp(itH_L/\hbar) \exp(-itH_R/\hbar) >_L &= < \exp(it(H_L - H_R)/\hbar) >_L \quad (197)
\end{align*}

where

\begin{align*}
(H_L - H_R) &= - \sum_j \gamma_j q_j (x_L - x_R) + (K/2)(x_L^2 - x_R^2) \quad (198)
\end{align*}
with $K = \sum_j \frac{\gamma_j^2}{\omega_j^2}$ and using

$$< q_j >_L = \frac{\gamma_j}{\omega_j} x_L; < (q_j - < q_j >)^2 >_L = \frac{k_B T}{\omega_j}$$

we can write

$$< (H_R - H_L) >_L = (K/2)(x_L - x_R)^2 \equiv \lambda$$

(200)

where $\lambda$ is called the Marcus reorganization energy. We can now write

$$< \exp(it(H_L - H_R)/\hbar) >_L = \exp(-itK(x_R^2 - x_L^2)/(2\hbar)) < \exp(-it\sum_j \gamma_j q_j (x_L - x_R)/\hbar) >_L .$$

(201)

Using the averages mentioned above, and noting that $q$ have a Gaussian distribution with the mentioned mean and variances, we can evaluate the average over $L$ by completing squares,

$$< \exp[it(H_L - H_R)/\hbar] >_L = \exp(-itK(x_R - x_L)^2/2\hbar) \exp(-\frac{t^2}{2\hbar^2}(x_L - x_R)^2/k_B T K)$$

(202)

The transition probability then can be written as

$$w(L \rightarrow R) = \frac{1}{\hbar^2} |V|^2 \int_{-\infty}^{\infty} dt \exp(it(E_L - E_R)/\hbar) \exp(-it\lambda/\hbar) \exp(-\frac{\lambda^2 k_B T}{\hbar^2})$$

(203)

By performing the integration over $t$ we get

$$w(L \rightarrow R) = \frac{|V|^2}{\hbar} \sqrt{\frac{\pi}{\lambda k_B T}} \exp\left(-\frac{1}{\lambda k_B T} \frac{(E_R - E_L + \lambda)^2}{4\lambda}\right).$$

(204)

This is the Marcus theory result for electron transfer rates.

7 Master Equations

Master equations describe the dynamics of probabilities of occupation of states and are written in terms of transition rates between states, and are linear in the probabilities and rates. For a quantum mechanical system with a Hamiltonian $H_0$ whose eigen states are known, and labeled by indices $m$ (when the states form a discrete set, which we consider here), we can write

$$H_0|m> = E_m|m> .$$

(205)

We consider adding a perturbation $\lambda V$ where $\lambda$ controls the strength of the perturbation, so that the total Hamiltonian is now

$$H = H_0 + \lambda V .$$

(206)
Based on the earlier discussion of the Golden Rule, we can write the master equation for the probability that the $m^{th}$ state is occupied, $P_m(t)$ as

$$\frac{dP_m(t)}{dt} = \sum_n W_{mn} P_n(t) - \sum_n W_{nm} P_m(t)$$

(207)

where

$$W_{mn} = \frac{2\pi}{\hbar} \chi^2 |V_{mn}|^2 \delta(E_n - E_m).$$

(208)

This is called the Pauli master equation, and the transition rates involved only allow transitions between states of equal energy, and is ‘microcanonical’. Further, we have

$$W_{mn} = W_{nm}$$

(209)

Under suitable conditions (determined by the matrix elements $V_{mn}$, this equation may be expected to generate an equilibrium distribution where all the $P_m$ are equal.

**Heat Bath Master Equation:** In general we are interested in systems which are coupled to a heat bath, and we would like to be able to consider Hamiltonians of the form

$$H = H_s + H_b + \lambda V.$$ 

(210)

Let us consider eigen states of $H_s$ and $H_b$,

$$H_s|m\rangle = E_m|m\rangle; H_b|\alpha\rangle = \epsilon_\alpha|\alpha\rangle.$$ 

(211)

The unperturbed system will have product states that obey

$$(H_s + H_b)|m\alpha\rangle = (E_m + \epsilon_\alpha)|m\alpha\rangle.$$ 

(212)

The master equation for the combined system can be written as

$$\frac{dP_{m\alpha}(t)}{dt} = \sum_{n\beta} W_{m\alpha n\beta} P_{n\beta}(t) - \sum_{n\beta} W_{n\beta m\alpha} P_{m\alpha}(t)$$

(213)

The Golden Rule rates for transition are

$$W_{m\alpha n\beta} = \frac{2\pi}{\hbar} \chi^2 |\langle V|n\beta\rangle|^2 \delta(E_n + \epsilon_\beta - E_m - \epsilon_\alpha).$$

(214)

We now assume that the state of the bath remains in thermal equilibrium, regardless of what happens to the system. Thus,

$$P_{m\alpha}(t) = P_m(t) \rho_\alpha$$

(215)
Putting this into the master equation and summing over \( \alpha \), we have

\[
\frac{dP_m(t)}{dt} = \sum_{n\alpha\beta} W_{m\alpha n\beta} \rho_\beta P_n(t) - \sum_{n\alpha\beta} W_{n\beta m\alpha} \rho_\alpha P_m(t)
\]

which can be written as

\[
\frac{dP_m(t)}{dt} = \sum_n w_{mn} P_n(t) - \sum_n w_{nm} P_m(t)
\]

with

\[
w_{mn} = \sum_{\alpha\beta} W_{m\alpha n\beta} \rho_\beta; \quad w_{nm} = \sum_{\alpha\beta} W_{n\beta m\alpha} \rho_\alpha.
\]

In this case, the \( w \)'s are not symmetrical, but are related. Taking \( \rho_\alpha \propto \exp(-\epsilon_\alpha/k_BT) \), since the full system has energy conservation, we can obtain

\[
w_{mn} \exp(-E_n/k_BT) = w_{nm} \exp(-E_m/k_BT),
\]

which is called the “principle of detailed balance”.

Many perturbation Hamiltonians have the form of a system degree of freedom coupling to a field (magnetic moment times magnetic field, for example). We will accordingly consider this as a general example:

\[
V = F \cdot G
\]

where \( F \) is a system degree of freedom and \( G \) is a function of bath variables (and we take \( \lambda = 1 \)). We have

\[
V_{m\alpha n\beta} = F_{mn} G_{\alpha\beta}.
\]

The rates of transition, \( w_{mn} \), can be expressed as

\[
w_{mn} = \frac{2\pi}{\hbar} |F_{mn}|^2 \sum_{\alpha,\beta} \delta(E_m - E_n + \epsilon_\alpha - \epsilon_\beta) |G_{\alpha\beta}|^2 \rho_\beta.
\]

Replacing the delta function by its integral representation,

\[
w_{mn} = \frac{1}{\hbar^2} |F_{mn}|^2 \int_{-\infty}^{\infty} dt \exp(i\omega_{mn} t) \sum_{\alpha,\beta} \exp(it\epsilon_\alpha/\hbar) G_{\alpha\beta} \exp(-it\epsilon_\beta/\hbar) G_{\beta\alpha} \rho_\beta
\]

where \( \omega_{mn} = (E_m - E_n)/\hbar \). Using the Heisenberg representation, we can write

\[
G(t)_{\alpha\beta} = \exp(it\epsilon_\alpha/\hbar) G_{\alpha\beta} \exp(-it\epsilon_\beta/\hbar)
\]

and thus
\[ w_{mn} = \frac{1}{\hbar^2} |F_{mn}|^2 \int_{-\infty}^{\infty} dt \exp(i\omega_{mn} t) < G(t)G(0) >_{eq}. \] (225)

The transition rate is thus given in terms of the spectral density of the time correlation function of the heat bath variable \( G \).

We consider again the harmonic oscillator bath.

\[ H_s = \frac{p^2}{2m} + U(x) \] (226)

and

\[ H_B = \sum_j \left[ \frac{p_j^2}{2} + \frac{1}{2} \omega_j^2 \left( q_j - \frac{\gamma_j}{\omega_j^2} x \right)^2 \right] \] (227)

Here,

\[ F = x; G = -\sum \gamma_j q_j \] (228)

The time correlation of \( G \) is straightforwardly given by

\[ < G(0)G(t) >_{eq} = \sum_j \gamma_j^2 \cos(\omega_j t) < q_j^2 >_{eq} + \sum_j \frac{\gamma_j^2}{\omega_j} \sin(\omega_j t) < p_j q_j >_{eq}. \] (229)

Considering classical averages,

\[ < G(0)G(t) >_{eq} = k_B T \sum_j \frac{\gamma_j^2}{\omega_j^2} \cos(\omega_j t) = k_B T K(t) \] (230)

where \( K(t) \) is the memory function described earlier. If we have a Markovian friction \( K(t) = 2\zeta \delta(t) \), then we get

\[ w_{mn} = \frac{k_B T \zeta}{\hbar^2} |F_{mn}|^2. \] (231)

### 7.1 Master equations in other contexts

We have dealt with specific instances where a master equation may be written for describing the dynamics of a system. This type of equation can however be arrived at from a broad range of considerations and are used extensively in many studies of nonequilibrium statistical mechanics. We will not discuss them further here.

### 8 Linear Response Theory and the Fluctuation Dissipation Theorem

In linear response theory, one considers the influence of a small external field on a system that is initially in thermal equilibrium. With the application of such a small perturbation, the system will come to a new equilibrium eventually, and one may wish to ask what the nature of that new equilibrium is. This is a question of static response which could be discussed within the framework of equilibrium statistical mechanics. One
could also, however, be interested in the time dependent response of the system. As a special case, the applied perturbation may be periodic in time, with a specified frequency. Hence in this case, one is interested in the frequency dependent response of the system. We will address these questions in turn, treating the problems both classically and quantum mechanically.

### 8.1 Static linear response: Classical Treatment

Here and later discussion, we consider an unperturbed Hamiltonian $H(X)$ where $X$ stands for all the system coordinates, and consider a perturbation Hamiltonian that linearly couples an external field $E$ to some function of system coordinates $M(X)$. For concreteness, one can keep in mind the application of an electric field which will couple to the electric dipole moment. The perturbed Hamiltonian is thus $H(X, E) = H(X) - M(X)E$.

To compute the response classically, we consider the unperturbed distribution function

$$f(X) = \frac{1}{Q} \exp(-\beta H(X)); Q = \int dX \exp(-\beta H(X))$$

(232)

where $Q$ is the partition function.

The corresponding perturbed distribution and partition functions are

$$f(X; E) = \frac{1}{Q(E)} \exp(-\beta H(X) + \beta ME)$$

(233)

and

$$Q(E) = \int dX \exp(-\beta H(X) + \beta ME)$$

(234)

We can write the perturbed distribution function and partition function, to leading order in $E$, using

$$\exp(-\beta H(X) + \beta ME) \approx (1 + \beta ME) \exp(-\beta H(X))$$

(235)

and

$$Q(E) \approx Q(1 + \beta <M>E)$$

(236)

where $<M>$ refer to the average over the unperturbed partition function. Thus, we can write

$$f(X; E) = (1 + \beta [M(X) - <M>]E)f(X) + O(E^2).$$

(237)

We restrict discussion below to the case where $<M> = 0$ for simplicity. We can now write the average value of any property $A$ based on the above, as

$$<A; E> = <A> + \chi_{AM}E + O(E^2),$$

(238)

which defines a susceptibility $\chi_{AM}$, which can be evaluated using the discussion above as

$$\chi_{AM} = \beta <AM>.$$
In particular, for $A = M$, we have

$$
\chi_{MM} = \beta < MM > .
$$
(240)

The equilibrium average (in the unperturbed state) of $M^2$ thus determines the linear response of $M$.

## 8.2 Dynamic Linear Response: Classical Treatment

In order to consider time dependent response, we consider a perturbing Hamiltonian $-M(X)E(t)$ where $E(t)$ is a time dependent external field. We wish to evaluate the time dependent distribution function $f(X; t)$ with the initial condition $f(X; 0)$ being the equilibrium distribution of the unperturbed Hamiltonian.

The time dependent distribution function obeys the Liouville equation,

$$
\frac{\partial f}{\partial t} = -Lf = -L_0 f - L_1 E(t)f
$$
(241)

where $L_0$ is the unperturbed Liouville operator

$$
L_0 = \frac{\partial H}{\partial p} \frac{\partial}{\partial q} - \frac{\partial H}{\partial q} \frac{\partial}{\partial p}
$$
(242)

and $L_1 f$ is the Poisson bracket of $-M$ and $f$, or

$$
L_1 = -\frac{\partial M}{\partial p} \frac{\partial}{\partial q} - \frac{\partial M}{\partial q} \frac{\partial}{\partial p}.
$$
(243)

Now we consider writing the solution $f$ in a series in powers of $E$, and we are interested only in terms up to linear order. Thus

$$
f = f_0 + f_1 + O(E^2).
$$
(244)

Collecting terms of the same order in $E$, we have

$$
\frac{\partial f_0}{\partial t} = -L_0 f_0
$$
(245)

and

$$
\frac{\partial f_1}{\partial t} = -L_0 f_1 - L_1 E(t)f_0
$$
(246)

We are starting with the initial conditions:

$$
f_0(0) = f_{eq}; f_1(0) = 0.
$$
(247)

We have, for all time,

$$
f_0(t) = f_{eq}
$$
(248)
since the time derivative of the equilibrium distribution is zero. The second equation is an inhomogeneous first order equation, and since the initial value vanishes, we have the solution

$$f_1(t) = - \int_0^t ds \exp \left( -(t-s)L_0 \right)L_1 E(s)f_0(s)$$

(249)

where \(f_0(s)\) can be replaced by \(f_{eq}\). We have

$$L_1 f_{eq} = - \left[ \frac{\partial M}{\partial p} \frac{\partial f_{eq}}{\partial q} - \frac{\partial M}{\partial q} \frac{\partial f_{eq}}{\partial p} \right].$$

(250)

Using the known expression \(f_{eq} = \exp \left[ - \beta H \right]/\mathcal{Q} \), this transforms to

$$L_1 f_{eq} = + \beta f_{eq} \left[ \frac{\partial M}{\partial p} \frac{\partial H}{\partial q} - \frac{\partial M}{\partial q} \frac{\partial H}{\partial p} \right].$$

(251)

But the Poisson bracket is the negative of the time derivative of \(M\). Thus,

$$L_1 E(s)f_{eq} = - \beta E(s) \dot{M} f_{eq}$$

(252)

The perturbation to \(f\) then is

$$f_1(t) = \int_0^t ds \beta E(s) \exp \left( -(t-s)L_0 \right) \dot{M} f_{eq}.$$  

(253)

Using this distribution function, we may now find the time dependent average of some quantity \(A\):

$$\langle A; t \rangle = \langle A \rangle_{eq} + \beta \int_0^t ds E(s) \int dX A(X) \exp \left( -(t-s)L_0 \right) \dot{M} f_{eq}.$$  

(254)

We assume that equilibrium averages of \(A\) and \(M\) are zero, which we can easily arrange by suitable choice of variables. The Liouville operator can operate on \(A\), leading to

$$\langle A; t \rangle = \beta \int_0^t ds E(s) \langle A(t-s) \dot{M}(0) \rangle_{eq} + \ldots$$  

(255)

We define a time dependent analog of the static susceptibility, the response function

$$\phi_{AM}(t) = \beta \langle A(t) \dot{M}(0) \rangle_{eq}.$$  

(256)

By a change of variables from \(s\) to \(t-s\), we arrive at the standard form of the linear response formula:

$$\langle A; t \rangle = \beta \int_0^t ds \phi_{AM}(s) E(t-s) + \mathcal{O}(E^2).$$  

(257)

If we consider the time dependent field to be constant for \(t > 0\), and consider the value of \(A\) as \(t \to \infty\), we are back to the static linear response problem:

$$\langle A; \infty \rangle = \chi_{AM} E.$$  

(258)
which expresses the susceptibility $\chi$ in terms of $\phi$ as

$$\chi_{AM} = \int_0^\infty dt \phi_{AM}(t).$$  \hspace{1cm} (259)$$

To see the connection of this expression with what we derived earlier, we note that the time derivative can be moved from $M$ to $A$, with a change of sign, and the time derivative of $A$ can be integrated, to obtain $A(\infty) - A(0)$. Since the correlation $<A(\infty)M(0)>$ is zero, we are left with

$$\chi_{AM} = \beta <A(0)M(0)>_{eq}$$ \hspace{1cm} (260)

which is the result we obtained previously.

**Frequency Dependent Response:** A typical problem which we will encounter is one where the time dependent applied field is a periodic function of time. As before we consider that the applied field $E(t) = 0$ for $t < 0$ and that the quantity $A$ also has zero average value for $t < 0$. We write the Fourier transforms of $E$ and $<A;t>$:

$$E_\omega = \frac{1}{2\pi} \int_{-\infty}^{\infty} dt \exp(i\omega t) E(t) = \frac{1}{2\pi} \int_0^{\infty} dt \exp(i\omega t) E(t)$$ \hspace{1cm} (261)

and

$$<A>_{\omega} = \frac{1}{2\pi} \int_{-\infty}^{\infty} dt \exp(i\omega t) <A;t> = \frac{1}{2\pi} \int_0^{\infty} dt \exp(i\omega t) <A;t>.$$ \hspace{1cm} (262)

These are in fact Laplace transforms with $s = i\omega$. Now we also Fourier transform the linear response equation

$$<A;t> = \int_0^t ds \phi_{AM}(s)E(t-s) + O(E^2).$$ \hspace{1cm} (263)

We have

$$\int_0^\infty dt \exp(i\omega t) \int_0^t ds \phi_{AM}(s)E(t-s) = \int_0^\infty ds \exp(i\omega s) \phi_{AM}(s) \times \int_0^\infty dt \exp(i\omega t) E(t)$$ \hspace{1cm} (264)

since the expression we are transforming is a convolution. We can thus write

$$<A>_{\omega} = \chi_{AM}(\omega)E_\omega$$ \hspace{1cm} (265)

where

$$\chi_{AM}(\omega) = \int_0^{\infty} dt \exp(i\omega t) \phi_{AM}(t)$$ \hspace{1cm} (266)

We have defined $\chi_{AM}(\omega)$ as a one sided transform, which will have both real and imaginary parts. Unlike $E$ and $A$, $\phi_{AM}(t)$ is not zero for $t < 0$. The real and imaginary parts are not independent and satisfy the Kramers-Kronig relation, which we will discuss in detail later.
8.3 Static Response: Quantum Mechanical Treatment

In the quantum mechanical treatment, in addition to all the considerations earlier, we must pay attention to commutation properties of operators we will encounter. In order to discuss this, we will focus on the density matrix of the perturbed system. We obtain the Laplace transform of this operator first:

$$\int_0^\infty d\beta \exp[-\beta z] \exp[-\beta(H - ME)] = \frac{1}{z + H - ME}.$$

(267)

The transform obeys the operator identity

$$S = R - R(S^{-1} - R^{-1})S$$

(268)

to

$$\frac{1}{z + H - ME} = \frac{1}{z + H} + \frac{1}{z + H} ME \frac{1}{z + H - ME} + O(E^2).$$

(269)

We can iterate this by substituting the left hand side into the last term on the right hand side, and keeping terms to leading order in $E$ we have

$$\frac{1}{z + H - ME} = \frac{1}{z + H} + \frac{1}{z + H} ME \frac{1}{z + H} + O(E^2).$$

(270)

We now invert the Laplace transform, noting that the second term has the form of a convolution. Thus,

$$\exp[-\beta(H - ME)] = \exp[-\beta H] + \int_0^\beta d\lambda \exp(-\lambda H) ME \exp[-(\beta - \lambda)H] + O(E^2).$$

(271)

Now, considering the time evolution of an operator in the Heisenberg picture, we see the second term containing a time evolved variable $M$ but with an imaginary time $i\hbar\lambda$:

$$\exp(-\lambda H)M \exp(\lambda H) = M(i\hbar\lambda).$$

(272)

We have then

$$\exp[-\beta(H - ME)] = \exp[-\beta H] + \int_0^\beta d\lambda M(i\hbar\lambda) E \exp(-\beta H) + O(E^2).$$

(273)

We further define a transform called the Kubo transform, to simplify notation:

$$\tilde{M} = \frac{1}{\beta} \int_0^\infty d\lambda M(i\hbar\lambda)$$

(274)

which, in the classical limit, will reduce to $M$. Using the above results, we can write the susceptibility as

$$\chi_{AM} = \beta <\tilde{A}\tilde{M}>.$$  

(275)

This differs from the classical result in that the variable $M$ is replaced by its Kubo transform.
8.3 Static Response: Quantum Mechanical Treatment

In order to discuss time dependent response quantum mechanically, we note the differences in treating the time dependent problem quantum mechanically. First,

Thus

\[
< A >_{\text{Classical}}^{(eq)} = \int dX A(X) f_{eq}(X)
\]

becomes

\[
< A >_{\text{Quantum}}^{(eq)} = \text{Trace} \left( \rho_{(eq)} A \right).
\]

Second, the classical Liouville operator

\[
L_{\text{Classical}} = \frac{\partial H}{\partial p} \frac{\partial}{\partial q} - \frac{\partial H}{\partial q} \frac{\partial}{\partial p} = \{H, \} \text{ PoissonBracket}
\]

goes over to

\[
L_{\text{Quantum}} = \frac{i}{\hbar} [H].
\]

Third, instead of the time evolution equation

\[
\frac{\partial f}{\partial t} = -L_{\text{Classical}} f
\]

we consider the equation for the density matrix

\[
\frac{\partial \rho}{\partial t} = -L_{\text{Quantum}} \rho
\]

With these changes, much of the treatment earlier goes through as before. We start with the Hamiltonian, written slightly differently as

\[
H(t) = H_0 + H_1 E(t)
\]

and write the corresponding Liouville operator as

\[
L(t) = L_0 + L_1 E(t).
\]

We expand the density matrix in orders of \(E\) as before:

\[
\rho(t) = \rho_0 + \rho_1(t) + \mathcal{O}(E^2).
\]

We have initial conditions:

\[
\rho_0(t = 0) = \rho_{eq}; \rho_1(t = 0) = 0.
\]

Considering terms of the same order in \(E\), we have equations
\[ \frac{\partial \rho_0}{\partial t} = -L_0 \rho_0 \] (286)

and

\[ \frac{\partial \rho_1}{\partial t} = -L_0 \rho_1 - L_1 E(t) \rho_0. \] (287)

As before we have

\[ \rho_0(t) = \rho_{eq} \quad \text{for all } t. \] (288)

and the formal solution to the equation for \( \rho_1(t) \) is

\[ \rho_1(t) = -\int_0^t ds \exp[-(t-s)L_0]L_1 E(s)\rho_{eq}. \] (289)

The average of some variable \( A \) at time \( t \) is therefore

\[ <A; t> = \int_0^t \phi(t-s)E(s)ds \] (290)

with the response function \( \phi \) defined as

\[ \phi(t) = -\text{Trace}[A \exp(-tL_0)L_1 \rho_{eq}] = -\text{Trace}[A(t)L_1 \rho_{eq}] \] (291)

Up to here, the equations look the same in the quantum mechanical treatment, but in evaluating \( \phi \) further, we need to take note of the commutation relations that apply. To do so, we write the commutator form of the operator \( L_1 \):

\[ \phi(t) = -\text{Trace}[A(t)L_1 \rho_{eq}] = -\text{Trace}[A(t)\frac{i}{\hbar}[H_1, \rho_{eq}]]. \] (292)

We next use the invariance of the trace to a cyclic permutation, to write

\[ \phi(t) = -\text{Trace}[\rho_{eq} \frac{i}{\hbar}[A, H_1]] = <L_1 A(t)>_{eq}. \] (293)

This is a compact form but does not look like the expression for the classical case, in terms of a correlation function. To obtain an expression that is closer in form we define

\[ \Phi = [H_1, \exp(-\beta H_0)] \exp(\beta H_0) = (L_1 \rho_{eq}) \exp(\beta H_0) \] (294)

which vanishes for \( \beta = 0 \), and we can write a differential equation for it from the definition,

\[ \frac{\partial \Phi}{\partial \beta} = \exp(-\beta H_0)[H_0, H_1] \exp(\beta H_0) \] (295)

and correspondingly write the solution
We have already stated the fluctuation dissipation theorem earlier, in particular in the context of linear response theory. Here we present a slightly more elaborate discussion of the fluctuation-dissipation theorem, expressing it in a different form that arises commonly in literature. The linear response, to linear order in the applied field, was written earlier as

\[
<A; t> = \int_0^t ds \phi_{AM}(s) E(t - s)
\]

with

\[
\phi_{AM}(t) = \beta <A(t) \dot{M}(0)>_{eq}.
\]

For the sake of illustration, we consider the case that \( A = M \) and we have a constant field \( E \) for \( t \geq 0 \). As before, we choose \( A \) to have a zero equilibrium value. Then, we can define a time dependent susceptibility function \( \chi_{AA}(t) \) to be

\[
\chi_{AA}(t) = \frac{<A; t>}{E}
\]

and clearly, this is related to the response function \( \phi_{AA}(t) \) by
\[ \frac{\partial \chi_{AA}(t)}{\partial t} = \phi_{AA}(t). \]  \hspace{1cm} (304)

In turn, from the definition of \( \phi_{AA}(t) \) (and by moving the time derivative over to \( A(t) \), i.e. using \(< A(t)\dot{A}(0)>_{eq} = -< \dot{A}(t)A(0)>_{eq} \) ) we have

\[ \frac{\partial \chi_{AA}(t)}{\partial t} = \phi_{AA}(t) = -\frac{1}{k_B T} \frac{\partial C_{AA}(t)}{\partial t}, \]  \hspace{1cm} (305)

where \( C_{AA}(t) = < A(t)A(0) >_{eq} \) is the correlation function of \( A \). This form of a relation between the susceptibility and correlation function is often seen in the literature, for example on aging glassy systems (but in that case without assuming time translation invariance). In the integrated form, this relation is

\[ C_{AA}(t) = k_B T [\chi_{AAeq} - \chi_{AA}(t)] = C_{AA}(0) (1 - \chi_{AA}(t)/\chi_{AAeq}) \equiv C_{AA}(0) \psi(t) \]  \hspace{1cm} (306)

which defines a "relaxation function" \( \psi \) which describes how the integrated response of the system reaches the equilibrium susceptibility (and we have defined a quantity that correspondingly goes to zero). We have \( C_{AA}(0) = k_B T \chi_{AAeq} \) which defines the static response relationship for the system that we have encountered before. If one plots \[ \chi_{AA}(t) \] against \( C_{AA}(t) \), the slope in equilibrium is the negative of the inverse temperature. In out of equilibrium situations, this equality will not hold.

We will discuss the Fluctuation Dissipation relation in the frequency domain in the following section.

9 Time Correlation and Response Functions

We have introduced the formulation of time dependent linear response of a system subjected to an external perturbation in the previous discussion. This discussion has involved correlation functions, functions describing the time (and frequency) dependent response of the system, and the susceptibility, which we have so far only discussed in the static case. In the following, we will consider these in more detail.

**Fourier and Laplace Transforms:** Before we proceed, we attempt to set a common notation for the Fourier and Laplace transforms that will be used, since there are many different conventions used in literature.

When considering a “space” Fourier transform, we will use the convention

\[ g(k) = \int d\mathbf{r} \exp(-i\mathbf{k}.\mathbf{r})g(\mathbf{r}) \]  \hspace{1cm} (307)

and the inverse transform will be

\[ g(\mathbf{r}) = \frac{1}{(2\pi)^d} \int d\mathbf{k} \exp(i\mathbf{k}.\mathbf{r})g(\mathbf{k}) \]  \hspace{1cm} (308)

for spatial dimension \( d = 3 \) (which we will restrict our attention to unless otherwise stated).

A “time” Fourier transform will be defined by

\[ f(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} dt \exp(i\omega t)f(t). \]  \hspace{1cm} (309)
and the inverse transform

\[ f(t) = \int_{-\infty}^{\infty} d\omega \exp(-i\omega t) f(\omega). \] (310)

The Laplace transform of \( f(t) \) with respect to variable \( z \) will be designated by \( \tilde{f}(z) \) or \( \mathcal{L}\{f(t), z\} \):

\[ \tilde{f}(z) = \int_{0}^{\infty} dt \exp(-zt) f(t) = \mathcal{L}\{f(t), z\} \] (311)

and the inverse transform

\[ \mathcal{L}^{-1}\{\tilde{f}(z), t\} = \frac{1}{2\pi i} \int_{c-i\infty}^{c+i\infty} dz \exp(zt) \tilde{f}(z) \] (312)

where \( c \) indicates a shift along the positive real axis such that the integration is parallel to the y-axis along a line that is to the right of all singularities of \( \tilde{f}(z) \). We will not have occasion to evaluate the inverse transforms explicitly but the following common transforms (and implied inverse transforms) will be useful:

\[ \tilde{\dot{f}}(z) = \int_{0}^{\infty} dt \frac{df(t)}{dt} = \frac{z}{2} \tilde{f}(z) - f(0). \] (313)

Similarly

\[ \tilde{\ddot{f}}(z) = \int_{0}^{\infty} dt \frac{d^2f(t)}{dt^2} = \frac{z^2}{2} \tilde{f}(z) - zf(0) - \dot{f}(0). \] (314)

Other useful Laplace transforms are

\[ \mathcal{L}\{\exp(-at), z\} = \frac{1}{z + a} \] (315)

\[ \mathcal{L}\{\exp(-at)f(t), z\} = \tilde{f}(z + a) \] (316)

\[ \mathcal{L}\{t^n, z\} = \frac{n!}{z^{n+1}} \] (317)

\[ \mathcal{L}\{\cos(\omega t), z\} = \frac{z}{z^2 + \omega^2} \] (318)

\[ \mathcal{L}\{\sin(\omega t), z\} = \frac{\omega}{z^2 + \omega^2} \] (319)

An important relationship between Laplace and Fourier transforms is

\[ \tilde{C}(z) = i \int_{-\infty}^{\infty} d\omega \frac{C(\omega)}{(iz - \omega)}. \] (320)
**Time Correlation Functions:** Here we discuss some general properties of time correlation functions, and also typical correlation functions that are of interest in studying interacting particle systems which are near equilibrium. We will generally be interested in dynamical variables that won’t have explicit time dependence, but depend on time through coordinates and momenta of (for concreteness) the $N$ structureless particles that the system is composed of.

Thus,

\[ A(t) = A[p^N(t), p^N(t)]. \] (321)

We will be defining correlation functions between two such quantities $A$ and $B$, as

\[ C_{AB}(t', t'') = < A(t') B(t'') > \] (322)

where $< .. >$ indicates an equilibrium average. If the system is in equilibrium, the properties of the system are time translation invariant. Thus we can simply write

\[ C_{AB}(t) = < A(t) B(0) > = < A(t) B > \] (323)

where $B$ without an argument will by convention mean at $t = 0$. Similarly, we will use the convention (where it matters) of having the variable at $t = 0$ to the right of that at time $t$. Finally, if $A$ and $B$ are complex, the generalization of the correlation function will be

\[ C_{AB}(t) = < A(t) B^*(0) > . \] (324)

We can derive a number of useful properties about correlation functions from general considerations of the nature of the equilibrium and of microscopic dynamics. Considering

\[ C_{AB}(t) = < A(t) B(0) > = < A(t + s) B(s) > \] (325)

and that because of stationarity

\[ \frac{d < A(t + s) B(s) >}{ds} = 0 = < \dot{A}(t + s) B(s) > + < A(t + s) \dot{B}(s) > \] (326)

we have

\[ < \dot{A}(t) B > = - < A(t) \dot{B} > \] (327)

In particular,

\[ < \dot{A} A > = 0 \] (328)

where, of course, the absence of arguments means that $A$ and $\dot{A}$ are at $t = 0$. 

The above formula is useful in various manipulations. Considering the second derivative of the time correlation function $C$, and using the above relation, we have

$$\frac{d^2}{dt^2} <A(t)B> = <\ddot{A}(t)B> = <A(t)\dot{B}>.$$  

(329)

Consider Taylor expanding the correlation function $C_{AA}$:

$$C_{AA}(t) = \sum_{n=0}^{\infty} \frac{t^{2n}}{(2n)!} C_{AA}^{(2n)}(0) = \sum_{n=0}^{\infty} \frac{t^{2n}}{(2n)!} <A^{(2n)}A(0)^*>.$$  

(330)

where the coefficients $C_{AA}^{(2n)}(0)$ refer to $2n^{th}$ derivatives and the odd derivatives are zero by time reversal symmetry. This can be rewritten as

$$C_{AA}(t) = \sum_{n=0}^{\infty} \frac{t^{2n}}{(2n)!} (-1)^n <A^{(n)}A^{(n)}*>.$$  

(331)

We can also consider an expansion of the inverse Fourier transform of $C(\omega)$ which will lead us to define moments

$$<w^{2n}>_{AA} = \int_{-\infty}^{\infty} w^{2n} C_{AA}(\omega) d\omega = (-1)^n C_{AA}^{(2n)}(0).$$  

(332)

This relation can be used to compute the short time explanation of a correlation function in terms of static averages. We will see soon how that can be useful.

Let us consider the time reversal transformation and let us assume each variable has a different signature with respect to it, $\epsilon_A$, etc. Then, we have

$$C_{AB}(t) = \epsilon_A \epsilon_B C_{AB}(-t) = \epsilon_A \epsilon_B C_{BA}(t)$$  

(333)

where we obtain the second equality by time translation invariance. This means in particular, that autocorrelation functions $C_{AA}(t)$ are symmetric to time reversal. Using this property, it is also easy to see that $C_{AA}(t)$ is a real function for all times.

We have limits for the correlation functions

$$lt \to 0 C_{AB}(t) = <AB*>; lt \to \infty C_{AB}(t) = <A><B*>.$$  

(334)

In order to define a correlation function that goes to zero at long times, it is conventional to define

$$C_{AB}(t) = <[A(t) - <A>][B^* - <B*>]>.$$  

(335)

and often, also to normalize by the $t = 0$ value.

Using the Schwarz inequality, we have

$$|<A(t)B^*>| \leq [<AA^*> <BB^*>]^{1/2}.$$  

(336)
where we have used the equality of equal-time correlations for any time \( t \). Considering autocorrelation functions, we then have

\[
C_{AA}(t) \leq< AA^\ast > = C_{AA}(0). \tag{337}
\]

Thus, the autocorrelation function at any time \( t > 0 \) is always smaller than the value at \( t = 0 \). Though this may appear obvious, this is not true in general but only for autocorrelations.

Considering the Fourier transforms of autocorrelation functions, we have

\[
C_{AA}(\omega) = < A(\omega)A^\ast(\omega) > \tag{338}
\]

which is therefore always positive.

We now consider some commonly encountered correlation functions. Given a system of \( N \) particles, one can define a variable \( A \) as a function of space and time as follows:

\[
A(r, t) = \sum_{i=1}^{N} a_i(t) \delta(r - r_i(t)). \tag{339}
\]

The variable \( a_i \) decides which particular quantity we are discussing, and can be the mass, velocity etc of the particle \( i \). In general, we can define the space Fourier components,

\[
A_k(t) = \int A(r, t) \exp(-i\mathbf{k.r}) dr = \sum_{i=1}^{N} a_i(t) \exp(-i\mathbf{k.r}_i(t)). \tag{340}
\]

Two such quantities of interest are the number density \( \rho \) and the particle current \( j \):

\[
\rho(r, t) = \sum_{i=1}^{N} \delta(r - r_i(t)) \tag{341}
\]

and the particle current

\[
j(r, t) = \sum_{i=1}^{N} u_i(t) \delta(r - r_i(t)). \tag{342}
\]

Correspondingly, the Fourier transforms are:

\[
\rho_k(t) = \sum_{i=1}^{N} \exp(-i\mathbf{k.r}_i(t)) \tag{343}
\]

and

\[
j_k(t) \sum_{i=1}^{N} u_i(t) \exp(-i\mathbf{k.r}_i(t)) \tag{344}
\]

Now, a time correlation function of the density is defined commonly with the symbol \( G \) as
\[ G(r', r, t) = \frac{1}{N} \langle \rho(r' + r, t) \rho(r', 0) \rangle. \] (345)

We can integrate out the dependence of the choice of origin by integrating over \( r' \) and we get the time dependent \textit{van Hove} correlation function

\[ G(r, t) = \frac{1}{N} \sum_{i=1}^{N} \sum_{j=1}^{N} \delta[r + r_i(0) - r_j(t)]. \] (346)

This is usually separated into a “self” and “distinct” part, as

\[ G_s(r, t) = \frac{1}{N} \sum_{i=1}^{N} \delta[r + r_i(0) - r_i(t)] \] (347)

and

\[ G_d(r, t) = \frac{1}{N} \sum_{i=1}^{N} \sum_{j \neq i} \delta[r + r_i(0) - r_j(t)]. \] (348)

The initial value of this function can be written as

\[ G(r, 0) = \delta(r) + \frac{1}{N} \sum_{i=1}^{N} \sum_{j \neq i} \delta[r + r_i(0) - r_j(0)] = \delta(r) + \rho g(r) \] (349)

where \( g \) is the pair correlation function.

Based on the earlier discussion of the Fourier transforms, we can define a time correlation function of the density, written as

\[ F(k, t) = \frac{1}{N} \langle \rho_k(t) \rho_{-k} \rangle = \int G(r, t) \exp(-i k \cdot r) \, dr. \] (350)

This function is called the intermediate scattering function.

The time Fourier transform of \( F(k, t) \) defined as

\[ S(k, \omega) = \frac{1}{2\pi} \int F(k, t) \exp(i \omega t) \, dt \] (351)

is called the dynamic structure factor. The inverse Fourier transform, for \( t = 0 \) will give

\[ \int S(k, \omega) \, d\omega = F(k, 0) = S(k) \] (352)

where \( S(k) \) is the static structure factor.

The reason for the nomenclature is to be found in the role of these quantities have in the scattering cross sections in scattering experiments. For example, in inelastic neutron scattering, the differential cross section is given by
\[ \frac{d^2 \sigma}{d \Omega d \omega} = \hbar^2 \left( \frac{k_2}{k_1} \right) NS(k, \omega) \]  
(353)

where \( b \) is the scattering length of the atoms, \( k_1 \) and \( k_2 \) are the incoming and outgoing wavevectors related to \( k \) by

\[ \hbar k = \hbar k_1 - \hbar k_2 \]  
(354)

and the frequency \( \omega \) is related to the incoming and outgoing energies by

\[ \hbar \omega = E_2 - E_1. \]  
(355)

Response Functions:

We write again the linear response relation for the time evolution of a variable \( A \) subject to a time varying perturbation Hamiltonian \(-M(X)E(t)\).

\[ < A; t > = \int_0^t ds \phi_{AM}(s)E(t - s) \]  
(356)

with

\[ \phi_{AM}(t) = \beta < A(t)\dot{M}(0) >_{eq}. \]  
(357)

Earlier, we wrote the frequency dependent response equation as

\[ < A >_\omega = \chi_{AM}(\omega)E_\omega \]  
(358)

where

\[ \chi_{AM}(\omega) = \int_0^\infty dt \exp(i\omega t)\phi_{AM}(t) \]  
(359)

is the complex dynamical susceptibility or response function. We can write

\[ \chi_{AM}(\omega) = \chi'_{AM}(\omega) + i\chi''_{AM}(\omega) \]  
(360)

\[ \chi_{AM}(\omega) = \int_0^\infty dt \exp(i\omega t)\phi_{AM}(t) \]  
(361)

In other words, we can write

\[ \chi_{AM}(\omega) = \mathcal{L}(\phi_{AM}(t); -i\omega). \]  
(362)

\[ \mathcal{L}(\phi_{AM}(t); -i\omega) = \mathcal{L}(\beta < A(t)\dot{M}(0) >; -i\omega) = -\mathcal{L}(\beta < \dot{A}(t)M(0) >; -i\omega). \]  
(363)
We can write this as
\[
\mathcal{L}(\phi_{AM}(t); -i\omega) = \beta (i\omega \tilde{C}_{AM}(-i\omega) + C_{AM}(0)).
\] (364)

Now
\[
\tilde{C}_{AM}(s = -i\omega) = i \int_{-\infty}^{\infty} d\omega \frac{C(\omega)}{(is - \omega)}.
\] (365)

Using
\[
l_{t} \rightarrow 0 \quad \frac{1}{x - i\epsilon} = P \frac{1}{x - i\epsilon} + i\pi \delta(x)
\] (366)

we have
\[
\tilde{C}_{AM}(s = -i\omega) = i \left[ P \int_{-\infty}^{\infty} d\omega \frac{C(\omega)}{(is - \omega)} - i\pi C(is) \right].
\] (367)

Thus,
\[
Re[\tilde{C}_{AM}(s = -i\omega)] = \pi C_{AM}(is = \omega).
\] (368)

If we now consider \( M = A \), we know that \( C_{AA}(\omega) \) is real. Thus, we get
\[
C_{AA}(\omega) = \frac{k_{B}T}{\pi\omega} \chi_{AA}(\omega).
\] (369)

This is a particular form of the fluctuation dissipation theorem that makes the relation between “fluctuation” (spectrum of the autocorrelation function) and “dissipation” (imaginary part of the dynamical susceptibility or response) apparent.

10 Transport Coefficients and Green-Kubo Relations

We next discuss briefly the relationship between time correlations and transport coefficients, which are important in quantifying transport processes in many contexts, including fluids. We have already encountered one of them, namely the diffusion coefficient and the related mobility, and we illustrate the Green Kubo relation for this case.

Let us consider the perturbing Hamiltonian to be \( H_1 = -F x \theta(t) \) where \( x \) is the coordinate of some “Brownian” particle. Let us consider the variable of interest to be the \( x \) velocity of the same particle. Then, the application of the linear response relation is
\[
< u_x; t > = \beta F \int_{0}^{t} < u_x(t') \dot{x} > dt' = \beta F \int_{0}^{t} < u_x(t') u_x > dt'.
\] (370)

In the steady state, the velocity is proportional to the force \( F \), and the proportionality is the mobility \( \mu \):
\[
\mu = \beta \int_{0}^{\infty} < u_x(t') u_x > dt' = \frac{D}{k_{B}T}.
\] (371)
A somewhat related, time dependent version is the calculation of the electrical conductivity in the presence of an applied electric field, which can be oscillatory. The time dependent Hamiltonian is

\[ H_1(t) = -\sum_{i=1}^{N} z_i e \mathbf{r}_i \cdot \mathbf{E}(t). \] (372)

We define the charge current as

\[ e \mathbf{j}(t) = \sum_{i=1}^{N} z_i e \mathbf{\dot{r}}_i(t) \] (373)

If the electrical field is oscillatory, along the \( x \) axis, with \( E_x = Re E_0 \exp(-i\omega t) \), we have (with choice \( A = ej_x \))

\[ e < j_x(t) > = Re \sigma(\omega) E_0 \exp(-i\omega t) \] (374)

with electrical conductivity per unit volume given by

\[ \sigma(\omega) = \frac{\beta e}{V} \int_0^\infty < j_x(t) > \sum_{i=1}^{N} z_i e \mathbf{\dot{r}}_i(t) \exp(i\omega t) dt \] (375)

which simplifies to

\[ \sigma(\omega) = \frac{\beta e^2}{V} \int_0^\infty < j_x(t) > \exp(i\omega t) dt. \] (376)

The static conductivity is defined as

\[ \sigma = lt_{\omega \to 0} \sigma(\omega) \] (377)

which will then have the Green-Kubo form, similar to the mobility earlier.

## 11 Hydrodynamics and Kinetic Theory

Hydrodynamics is concerned with the dynamics of a fluid at large wavelengths and correspondingly long time scales, compared to atomic dimensions and processes. In a liquid, the short range structural order persists typically over a few atomic diameters. If one were to be concerned with gas dynamics, it is conventional to consider a “mean free path” \( l \) as the characteristic length scale, and a “collision time” \( \tau \) as the characteristic time scale. With these, we can define the domain of hydrodynamics as \( kl << 1 \), and \( \omega \tau << 1 \), where \( k \) and \( \omega \) are the wave number and frequencies of interest. Hydrodynamics in the usual treatment describes the fluctuations of a set of hydrodynamic variables, which correspond to the conserved quantities, mass, momentum and energy. The relevant conservation equations are expressed in the form of continuity equations (see below) and the currents that appear in the continuity equations are related to local gradients through constitutive laws or relations that involve phenomenological transport coefficients. Fick’s law for diffusion is an example.

In terms of the microscopic fields \( \rho(\mathbf{r}, t) \) etc., that we defined earlier, we now define “coarse grained” variables, by integrating over some small volume. Thus,
\[ \dot{\rho}(\mathbf{r}, t) = \frac{1}{v} \int_\mathbf{r} \rho(\mathbf{r}' - \mathbf{r}, t) d\mathbf{r}' \]  

(378)

where \( v \) is imagined to be large enough that one could speak of a well defined thermodynamic state within the volume, with a mean density, temperature, etc, and in discussing fluctuations, we are only concerned about fluctuations across such small volumes in the system. With these coarse grained variables, one can also define the corresponding Fourier components, correlation functions, etc as before, and we assume that in the long wave length limit, the microscopic and coarse grained correlated functions are the same:

\[ \text{lt}_{kl} \ll 1; t/\tau \gg 1 \]

\[ \langle \rho_k(t) \rho_{-k} \rangle = \langle \bar{\rho}_k(t) \bar{\rho}_{-k} \rangle. \]  

(379)

Self motion: In the earlier discussion on the van Hove correlation function, we divided it into self and distinct components. The self part describes dynamics that is not affected by the motion of particles, of course affected by the surrounding particles, but in a limit that interactions between the population that is being explicitly described can be ignored. This is a little tricky to discuss in this way, so we introduce a notion that is in fact what is used in experiments, namely tracer or tagged particles. Imagine that a very small fraction of the particles are somehow tagged (e.g. that they are radioactive, or fluoresce), and otherwise they behave like all other particles in the system. Because their concentration is very low, the tagged particles do not interact with each other, while they interact with other particles. If we were to follow the motion of one of the tagged particles, it would not be different from the motion of any other particle, so one can deduce properties such as “self diffusion” from studying tracer particles. If we denote by \( \rho^{(s)}(t) \) and \( \mathbf{j}^{(s)}(t) \) the density and currents associated with the tracer particles, we can write a continuity equation of the form:

\[ \frac{\partial \rho^{(s)}(\mathbf{r}, t)}{\partial t} + \nabla \cdot \mathbf{j}^{(s)}(\mathbf{r}, t) = 0. \]  

(380)

The constitutive equation that relates the current \( \mathbf{j}^{(s)}(\mathbf{r}, t) \) to gradients in the density field is known as Fick’s law:

\[ \mathbf{j}^{(s)}(\mathbf{r}, t) = -D \nabla \rho^{(s)}(\mathbf{r}, t), \]  

(381)

where \( D \) is the self diffusion coefficient. Combining the two, we get the usual diffusion equation:

\[ \frac{\partial \rho^{(s)}(\mathbf{r}, t)}{\partial t} = D \nabla^2 \rho^{(s)}(\mathbf{r}, t) \]  

(382)

which we can write in reciprocal space as

\[ \dot{\rho}_k(t) = -Dk^2\rho_k(t). \]  

(383)

The solution for this equation can easily be written down as

\[ \rho_k(t) = \rho_k \exp(-Dk^2t) \]  

(384)

where \( \rho_k \) as before denotes the \( t = 0 \) value of the tagged particle density. The correlation function can readily be written as

\[ \frac{1}{n} < \rho_k(t) \rho_{-k} > = \exp(-Dk^2t) \]  

(385)

where \( n \) is the number of tagged particles (the reader/student can, and should, derive this from treating the tagged particles as an ideal gas, and convince oneself that this is the correct thing to do). The correlation
function we have written is the self intermediate scattering function we defined earlier. A key feature to note is that as \( k \to 0 \), the time constant for this decaying function diverges. One can understand this from the need to transport mass over larger and larger distances as \( k \) gets smaller.

By Fourier transforming, we can thus write the self van Hove function as

\[
G_s(r, t) = \frac{1}{(4\pi Dt)^{3/2}} \exp(-r^2/4Dt)
\]

(386)

The corresponding self dynamic structure factor is

\[
S_s(k, \omega) = \frac{1}{\pi} \frac{Dk^2}{\omega^2 + (Dk^2)^2}.
\]

(387)

From this expression, we can see that the diffusion coefficient can be obtained from the self dynamic structure factor through

\[
D = \lim_{\omega \to 0} \lim_{k \to 0} \frac{\omega^2}{k^2 \pi S_s(k, \omega)}.
\]

(388)

Since \( D \) is related to the velocity auto correlation function, this implies that the corresponding spectrum is related to \( S_s(k, \omega) \). We return shortly to this point.

From considering the initial velocity distribution, one can derive the short time van Hove distribution function to be a Gaussian, but with a variance that goes as \( t^2 \) (in the notation below, \( \alpha(t) = \beta m/t^2 \) which the reader/student is encouraged to verify), and in the long time limit as well, we have a Gaussian form (with \( \alpha(t) = 1/4Dt \)). Thus, we can ask if a generalized Gaussian form

\[
G_s(r, t) = \left( \frac{\alpha(t)}{\pi} \right)^{3/2} \exp(-\alpha(t) r^2)
\]

(389)

can be written for all times. If this can be done, using the property of the Gaussian, one can show that

\[
<r^2(t)> = \frac{3}{2\alpha(t)}
\]

(390)

and from this, we can obtain \( F_s(k, t) \) to be

\[
F_s(k, t) = \exp(-\frac{1}{6} k^2 <r^2(t)>).
\]

(391)

This Gaussian approximation is indeed good at very short and very long times, but at intermediate times the width of the distribution is larger than expected for a Gaussian. One can make an expansion of \( F_s(k, t) \) in terms of cumulants, and show the leading order correction to read:

\[
F_s(k, t) = \exp(-\frac{1}{6} k^2 <r^2(t)>) \times \left[ 1 + \frac{1}{2} \left( \frac{3 <r^4(t)>}{5<r^2(t)>^2} - 1 \right) \left( \frac{1}{6} k^2 <r^2(t)>)^2 \ldots \right]
\]

(392)

The quantity

\[
\alpha_2(t) \equiv \left( \frac{3 <r^4(t)}> \frac{5 <r^2(t)>^2} - 1 \right)
\]

(393)

is called the non-Gaussian parameter, and is studied intensely in the context of understanding heterogeneous dynamics.
Considering now the currents, we can define the current for a tagged particle as
\[ j_{ki}(t) = u_i(t) \exp(-i k \cdot r_i(t)). \] (394)

The self longitudinal current correlation is defined as
\[ C_s(t) = \langle k \cdot j_{ki}(t) k \cdot j_{-ki} \rangle. \] (395)

Defining the velocity autocorrelation function
\[ Z(t) = \langle u_{iz}(t) u_{iz} \rangle \] (396)
(where \( z \) is taken to be the direction of \( k \)) we have
\[ Z(t) = lt_{k \rightarrow 0} \frac{1}{k^2} C_s(t) = - lt_{k \rightarrow 0} \frac{1}{k^2} \frac{d^2}{dt^2} F_s(k, t). \] (397)

Taking the Fourier transform on either side, and simplifying, we have
\[ Z(\omega) = \omega^2 lt_{k \rightarrow 0} \frac{1}{k^2} S_s(k, \omega). \] (398)

The Green-Kubo relation for the diffusion coefficient can be stated as \( D = lt_{\omega \rightarrow 0} \). The corresponding relation is
\[ D = lt_{\omega \rightarrow 0} lt_{k \rightarrow 0} \frac{\omega^2}{k^2} S_s(k, \omega), \] (399)
which is the same as what we wrote earlier.

### 11.1 Hydrodynamic modes

We now consider the conventional hydrodynamic description of the density, momentum and energy fields and derive from it equations for hydrodynamic modes. We have already defined the coarse grained density \( \bar{\rho}(\mathbf{r}, t) \) (we will omit the over bar from here on). Correspondingly, we can define a current or equivalently momentum fields as
\[ \mathbf{p}(\mathbf{r}, t) = m \rho(\mathbf{r}, t) \mathbf{u}(\mathbf{r}, t) = m \mathbf{j}(\mathbf{r}, t). \] (400)

The conservation equation for the density can be written as
\[ \frac{\partial \rho}{\partial t} + \frac{1}{m} \nabla \cdot \mathbf{p}(\mathbf{r}, t) = 0 \] (401)

We will now first discuss the Euler and Navier-Stokes equations for the momentum (equivalently the velocity) field. If we consider a fluid element of volume \( v \), the net force acting on it is equal to the negative of the surface integral of the pressure. We can thus write
\[ \frac{\rho}{\text{d}t} \frac{\text{d}u}{\text{d}t} = -\nabla P \]  
\hfill (403)

where \( P \) is the pressure. The total derivative of the velocity can be written as

\[ \rho \frac{\text{d}u}{\text{d}t} = \frac{\partial u}{\partial t} + (u \cdot \nabla) u \]  
\hfill (404)

by taking account of the changes in the velocity field in space. This leads to Euler’s equation

\[ \rho \frac{\partial u}{\partial t} + (u \cdot \nabla) u = -\nabla P. \]  
\hfill (405)

Now, if we consider the partial time derivative of the current (we write for one component for convenience), we have

\[ \frac{\partial (\rho u_i)}{\partial t} = \rho \frac{\partial u_i}{\partial t} + \frac{\partial \rho}{\partial t} u_i. \]  
\hfill (406)

From the continuity equation, we can write

\[ \frac{\partial \rho}{\partial t} = -\nabla \cdot (\rho u) = - \frac{\partial (\rho u_k)}{\partial x_k}. \]  
\hfill (407)

where \( x_k \) is one of the coordinates and we sum over the repeated index \( k \). The Euler equation can be written as

\[ \frac{\partial u_i}{\partial t} = -u_k \frac{\partial u_i}{\partial x_k} - \frac{1}{\rho} \frac{\partial P}{\partial x_i} \]  
\hfill (408)

to obtain

\[ \frac{\partial (\rho u_i)}{\partial t} = -\rho u_k \frac{\partial u_i}{\partial x_k} - \frac{\partial P}{\partial x_i} - u_i \frac{\partial (\rho u_k)}{\partial x_k}. \]  
\hfill (409)

which can be written as

\[ \frac{\partial (\rho u_i)}{\partial t} = -\delta_{ik} \frac{\partial P}{\partial x_k} - \frac{\partial (\rho u_i u_k)}{\partial x_k}. \]  
\hfill (410)

Defining the tensor as

\[ \Pi_{ik} = P \delta_{ik} + \rho u_i u_k = \sigma_{ik} + \rho u_i u_k \]  
\hfill (411)

we have

\[ \frac{\partial (\rho u_i)}{\partial t} = -\frac{\partial \Pi_{ik}}{\partial x_k}. \]  
\hfill (412)

Above, \( \sigma_{ik} \) is the stress tensor that arises from the pressure. When we have in addition viscous forces, which dissipate the velocity, we must alter the stress tensor to include viscous forces. Such forces will arise when we have different parts of the fluid moving at different velocities, and thus the viscous stress \( \sigma'_{ik} \) should be proportional to the spatial derivative of the velocities, or shear rates. The viscous stress is written in the general form

\[ \sigma'_{\alpha\beta}(r, t) = -\eta \left( \frac{\partial u_{\alpha}(r, t)}{\partial r_\beta} + \frac{\partial u_{\beta}(r, t)}{\partial r_\alpha} \right) - \frac{2}{3} \delta_{\alpha\beta} \nabla \cdot u(r, t) - \delta_{\alpha\beta} \zeta \nabla \cdot u(r, t) \]  
\hfill (413)

\[ \sigma'_{\alpha\beta}(r, t) = -\eta \left( \frac{\partial u_{\alpha}(r, t)}{\partial r_\beta} + \frac{\partial u_{\beta}(r, t)}{\partial r_\alpha} \right) - \frac{2}{3} \delta_{\alpha\beta} \nabla \cdot u(r, t) - \delta_{\alpha\beta} \zeta \nabla \cdot u(r, t) \]  
\hfill (414)
where we have introduced the shear viscosity $\eta$ and the bulk viscosity $\zeta$ in the above, constitutive, relation. The total stress is

$$\sigma^{\alpha\beta}(r,t) = \delta_{\alpha\beta} P(r,t) - \eta \left( \frac{\partial u_\alpha(r,t)}{\partial r_\beta} + \frac{\partial u_\beta(r,t)}{\partial r_\alpha} \right) + \delta_{\alpha\beta}(2\eta/3 - \zeta) \nabla \cdot \mathbf{u}(r,t) \quad (415)$$

Using this total stress in place of the pressure in the Euler equation, one gets the Navier-Stokes equation

$$\rho \left[ \frac{\partial \mathbf{u}}{\partial t} + (\mathbf{u} \cdot \nabla) \mathbf{u} \right] = -\nabla P + \eta \nabla^2 \mathbf{u}(r,t) + \left( \frac{\eta}{3} + \zeta \right) \nabla \cdot \mathbf{u}(r,t) = 0 \quad (417)$$

Ignoring the advection term, as we will do in what follows, will lead to a linearized form

$$\rho_m \frac{\partial \mathbf{u}}{\partial t} + \nabla P(r,t) - \eta \nabla^2 \mathbf{u}(r,t) + \left( \frac{\eta}{3} + \zeta \right) \nabla \cdot \mathbf{u}(r,t) = 0 \quad (418)$$

The conservation law for the momentum can be written as

$$\frac{\partial P}{\partial t}(r,t) + \nabla \cdot \sigma(r,t) = 0 \quad (420)$$

where we must understand the resulting partial derivatives of the velocity field to include the advection term. As we shall ignore that contribution here, this will not matter to us.

Finally, we can write the conservation equation for the energy as follows:

$$\frac{\partial e}{\partial t}(r,t) + \nabla \cdot \mathbf{J}^e(r,t) = 0 \quad (422)$$

where $e$ is the energy density, and $\mathbf{J}^e$ is the energy current. Physically, the energy current arises from the transport of fluid volumes with a given energy density, and from diffusive transport because of thermal gradients.

First let us consider as above the case where dissipation is absent. The energy can be written as

$$e = \rho \left( \frac{u^2}{2m} + \epsilon \right) \quad (424)$$

where $\epsilon$ is the internal energy per unit mass. The time derivative of the energy can be written by considering the time derivatives of the two terms.

$$\frac{\partial \rho \left( \frac{u^2}{2m} \right)}{\partial t} = \left( \frac{u^2}{2m} \right) \frac{\partial \rho}{\partial t} + \rho \mathbf{u} \cdot \frac{\partial \mathbf{u}}{\partial t}. \quad (425)$$
Using the equation of continuity and Euler’s equation we have

\[
\frac{\partial \rho (u^2/2m)}{\partial t} = -\left(\frac{u^2}{2m}\right) \nabla \cdot (\rho \textbf{u}) - \textbf{u} \cdot \nabla P - \rho \textbf{u} \cdot (\textbf{u} \cdot \nabla) \textbf{u}. \tag{426}
\]

Now, we can write

\[
\rho \textbf{u} \cdot (\textbf{u} \cdot \nabla) \textbf{u} = \frac{1}{2} \textbf{u} \cdot \nabla u^2 \tag{427}
\]

and we can write \( \textbf{u} \cdot \nabla P \) using the thermodynamic relation

\[
dh_m = T ds + \frac{1}{\rho} \frac{dP}{dt}. \tag{428}
\]

where \( h_m \) is the enthalpy per unit mass and \( s \) is the entropy per unit mass, as

\[
\nabla P = \rho \nabla h_m - \rho T \nabla s \tag{429}
\]

resulting in

\[
\frac{\partial \rho (u^2/2m)}{\partial t} = -\left(\frac{u^2}{2m}\right) \nabla \cdot (\rho \textbf{u}) - \rho \textbf{u} \cdot \nabla ((u^2/2m) + h_m) + \rho T (\textbf{u} \cdot \nabla) s. \tag{430}
\]

In order to write

Thus we write \( \frac{\partial \rho}{\partial t} \) we use the thermodynamic identity

\[
d\epsilon = T ds - PdV = T ds + (P/\rho^2)d\rho. \tag{431}
\]

Since \( \epsilon + P/\rho \) is the enthalpy per unit mass \( h_m \), we have

\[
d(\rho \epsilon) = \epsilon d\rho + \rho d\epsilon = h_m d\rho + \rho T ds \tag{432}
\]

and

\[
\frac{\partial \rho \epsilon}{\partial t} = h_m \frac{\partial \rho}{\partial t} + \rho T \frac{\partial s}{\partial t}. \tag{433}
\]

We consider the continuity equation for density and the corresponding equation for entropy, under adiabatic conditions, as

\[
\frac{\partial s}{\partial t} + \textbf{u} \cdot \nabla s = 0. \tag{434}
\]

Using these, we have

\[
\frac{\partial [\rho (u^2/2m) + \rho \epsilon]}{\partial t} = -[(u^2/2m) + h_m] \nabla \cdot (\rho \textbf{u}) - \rho \textbf{u} \cdot \nabla ((u^2/2m) + h_m) \tag{435}
\]

and finally

\[
\frac{\partial [\rho (u^2/2m) + \rho \epsilon]}{\partial t} = -\nabla [\rho \textbf{u} ((u^2/2m) + h_m)] \tag{436}
\]

Thus, the quantity

\[
\textbf{J}^0 \epsilon = (\rho \textbf{u}) ((u^2/2m) + h_m) \tag{437}
\]
defines the energy flux density, and we can rewrite this as
\[ J_e^0 = uh = u(e + P) \] (438)

where \( h = e + P \) is the enthalpy density (per unit volume) including the bulk kinetic energy term.

When we have in addition viscous processes, the energy flux density also has a component that arises from heat diffusion. This term is included in the form of a constitutive relation describing heat diffusion, to write
\[ J_e^0(r, t) = hu(r, t) - \lambda \nabla T(r, t) \] (439)
(440)

where \( T(r, t) \) is the local temperature and \( \lambda \) is the thermal conductivity.

Using the energy and density continuity equations, we get
\[ \frac{\partial}{\partial t} \left[ e(r, t) - \frac{e + P}{\rho} \rho(r, t) \right] - \lambda \nabla^2 T(r, t) = 0 \] (441)

We can write this as
\[ \dot{Q}(r, t) - \lambda \nabla^2 T(r, t) = 0 \] (442)
(443)

where
\[ Q(r, t) = e(r, t) - \frac{e + P}{\rho} \rho(r, t) \] (444)
(445)

which we identify as the heat density. This identification can be seen to be valid from considering the thermodynamic relation:
\[ TdS = dU + PdV \] (446)
\[ = d(eV) + PdV \] (447)
\[ = V de - eV \frac{d\rho}{\rho} - PV \frac{d\rho}{\rho} \] (448)
\[ \frac{T}{V}dS = de - \frac{e + P}{\rho} d\rho \] (449)
\[ = dQ \] (450)
(451)

Now we have a set of five equations for mass, momentum and energy densities, that involve mass density, momentum density, energy density as well as pressure and heat density. We wish to write self-contained equations for the mass, momentum and energy densities (we make the choice of replacing this with the temperature
field), and in order to do so, we make an assumption of local thermodynamic equilibrium, and write expressions for the deviations of $P$ and $Q$ from the equilibrium values in terms of the corresponding deviations of density and temperature. Thus, with $\delta P(r,t) = P(r,t) - \bar{P}$, $\delta Q(r,t) = Q(r,t) - \bar{Q}$, $\delta \rho(r,t) = \rho(r,t) - \bar{\rho}$, and $\delta T(r,t) = T(r,t) - \bar{T}$, we write

\[
\delta P(r,t) = \left( \frac{\partial P}{\partial \rho} \right)_T \delta \rho(r,t) + \left( \frac{\partial P}{\partial T} \right)_\rho \delta T(r,t) \tag{452}
\]

\[
\delta Q(r,t) = T \left( \frac{\partial S}{\partial \rho} \right)_T \delta \rho(r,t) + \frac{T}{V} \left( \frac{\partial S}{\partial T} \right)_\rho \delta T(r,t) \tag{453}
\]

\[
= \rho T \left( \frac{\partial(S/N)}{\partial \rho} \right) \delta \rho(r,t) + \rho c_V \delta T(r,t) \tag{454}
\]

where $c_V$ is the constant volume heat capacity. By making use of the thermodynamic identity

\[
\left( \frac{\partial(S/N)}{\partial \rho} \right) = -\frac{1}{\rho^2} \left( \frac{\partial P}{\partial T} \right)_\rho \tag{455}
\]

and inserting the above expressions for $P$ and $Q$, we get a closed set of linear equations

\[
\frac{\partial \delta \rho(r,t)}{\partial t} + \nabla \cdot \mathbf{j}(r,t) = 0 \tag{457}
\]

\[
\left( \frac{\partial}{\partial t} - a \nabla^2 \right) \delta T(r,t) - \frac{T}{\rho^2 c_V} \left( \frac{\partial P}{\partial T} \right)_\rho \frac{\partial}{\partial t} \delta \rho(r,t) = 0 \tag{458}
\]

\[
\left( \frac{\partial}{\partial t} - \frac{\eta}{\rho m} \nabla^2 - \frac{\eta}{\rho m} \nabla \cdot \nabla \right) \mathbf{j}(r,t) + \left( \frac{\partial P}{\partial \rho} \right)_T \nabla \delta \rho(r,t) + \left( \frac{\partial P}{\partial T} \right)_\rho \nabla \delta T(r,t) = 0 \tag{459}
\]

where

\[
a = \frac{\lambda}{\rho c_V} \tag{460}
\]

We can solve these equations by consider space Fourier and time Laplace transforms, defined for example, by

\[
\rho_k(s) = \int_0^\infty dt \exp(-st) \int \delta \rho(r,T) \exp(-ik \cdot r) dr. \tag{461}
\]

We have

\[
s \rho_k(s) + ik \cdot j_k(s) = \rho_k \tag{462}
\]
(s + ak^2)T_k(s) + \frac{i}{\rho^2c_V} \left( \frac{\partial P}{\partial T} \right)_\rho k_jk(s) = T_k \tag{464}

(s + \eta k^2 + \eta/3 + \zeta) j_k(s) + ik \left( \frac{\partial P}{\partial T} \right)_\rho \rho_k(s) + \frac{ik}{m} \left( \frac{\partial P}{\partial T} \right)_\rho T_k(s) = j_k \tag{465}

Choosing \( k \) along the \( z \) axis, we can write these as

\[(s + bk^2)j_z^z(s) + \frac{ik}{m} \left( \frac{\partial P}{\partial T} \right)_\rho T_k(s) + \frac{ik}{m} \left( \frac{\partial P}{\partial \rho} \right)_\rho T_k(s) = j_z \tag{466}\]

for the \( z \) component, and for \( \alpha = x, y \)

\[(s + \nu k^2)j_\alpha^\alpha(s) = j_\alpha \tag{467}\]

where

\[b = \frac{4\eta + \zeta}{\rho m} \tag{469}\]
\[\nu = \frac{\eta}{\rho m} \tag{470}\]

We can write the full set of equations in matrix form as

\[
\begin{pmatrix}
    s & 0 & 0 & ik \left( \frac{\partial P}{\partial T} \right)_\rho & 0 & 0 \\
    0 & s + ak^2 & ik \left( \frac{\partial P}{\partial T} \right)_\rho & 0 & 0 \\
    \frac{ik}{m} \left( \frac{\partial P}{\partial \rho} \right)_\rho & \frac{ik}{m} \left( \frac{\partial P}{\partial T} \right)_\rho & s + bk^2 & 0 & 0 \\
    0 & 0 & 0 & s + \nu k^2 & 0 \\
    0 & 0 & 0 & 0 & s + \nu k^2 \\
\end{pmatrix}
\begin{pmatrix}
    \rho_k(s) \\
    T_k(s) \\
    j_z^z(s) \\
    j_x^\alpha(s) \\
    j_y^\alpha(s) \\
\end{pmatrix}
= \begin{pmatrix}
    \rho_k \\
    T_k \\
    j_z^z \\
    j_x^\alpha \\
    j_y^\alpha \\
\end{pmatrix} \tag{471}
\]

The above hydrodynamic matrix is block diagonal, correspondingly, the determinant of the matrix can be written as

\[D(k,s) = D_l(k,s)D_t(k,s) \tag{472}\]

where

\[D_l(k,s) = s(s + ak^2)(s + bk^2) + (s + ak^2) \left( \frac{\partial P}{\partial \rho} \right)_\rho + s \frac{k^2T}{\rho^2c_V} \left( \frac{\partial P}{\partial T} \right)_\rho \tag{473}\]

and
\[ D_t(k, s) = (s + \nu k^2)^2. \tag{474} \]

Since we can formally write the solution of the above equation in terms of the hydrodynamic matrix, the dispersion relation for the collective modes are given by the poles of the inverse of \( D(k, s) \), and can be obtained by solving

\[ D(k, s) = 0. \tag{475} \]

For the transverse modes, these are simply the double root

\[ s = -\nu k^2. \tag{476} \]

From inspection we see that these correspond to a “diffusive” solution. For the longitudinal component, we have the cubic equation

\[ s^3 + s^2(a + b)k^2 + s(abk^2 + c_s^2)k^2 + (a/\gamma)c_s^2k^4 = 0 \tag{477} \]

where \( \gamma = c_p/c_v \), and the adiabatic speed of sound \( c_s \) is given by

\[ c_s^2 = \frac{\gamma}{m} \left( \frac{\partial P}{\partial \rho} \right)_T \tag{478} \]

and the thermodynamic relation \( \left[ \left( \frac{\partial P}{\partial \rho} \right)_T \right]^2 = \frac{c_s^2}{T}(c_p - c_v) \left( \frac{\partial P}{\partial \rho} \right)_T \) (478)

has been used.

We obtain finally the solutions

\[ s_0 = -D_T k^2 \tag{479} \]

\[ s\pm = \pm ic_s k - \Gamma k^2 \tag{482} \]

which corresponds to mass thermal diffusion, with thermal diffusivity given by

\[ D_T = \frac{a}{\gamma} = \frac{\lambda}{\rho c_p}. \tag{481} \]

Finally we have two propagating damped modes,
where

\[ \Gamma = \frac{1}{2}[a(\gamma - 1)/(\gamma + b)]. \]  \hspace{1cm} (484)

**Transverse Current Correlations:** The equation for the transverse current

\[ (s + \nu k^2)j_k^\alpha(s) = j_k^\alpha, \quad \alpha = x, y \]  \hspace{1cm} (485)

we wrote earlier corresponds to a simple differential equation in the time domain

\[ \frac{\partial j_k^\alpha(t)}{\partial t} + \nu k^2 j_k^\alpha(t) = 0. \]  \hspace{1cm} (486)

This has the same form as the diffusion equation. As in the case of diffusion, it is useful to consider the time correlation function corresponding to the transverse current, which is

\[ C_t(k, t) = \frac{k^2}{N} < j_k^\alpha(t)j_{-k}^\alpha >, \quad \alpha = x, y \]  \hspace{1cm} (487)

The multiplication by \( k^2 \) makes this correlator have the same dimensions as the density correlation function. We can more generally write the current correlation function in terms of its components as

\[ C_{\alpha\beta} = \frac{k^2}{N} < j_k^\alpha(t)j_{-k}^\beta > = \frac{k^2}{N}\hat{k}_\alpha\hat{k}_\beta C_t(k, t) + (\delta_{\alpha\beta} - \hat{k}_\alpha\hat{k}_\beta)C_t(k, t). \]  \hspace{1cm} (488)

Taking the wave vector along the z direction as before, we obtain the form of the transverse correlation function given, for \( \alpha = x, y \). The equation for \( C_t \) becomes

\[ \frac{\partial C_t(k, t)}{\partial t} + \nu k^2 C_t(k, t) = 0 \]  \hspace{1cm} (489)

with the solution

\[ C_t(k, t) = C_t(k, 0) \exp(-\nu k^2 t) \equiv \omega_0^2 \exp(-\nu k^2 t) \]  \hspace{1cm} (490)

and of course this is the solution for small wave numbers and long times. It can be easily seen from the definition that

\[ C_t(k, 0) = \omega_0^2 = k^2 \left( \frac{k_B T}{m} \right). \]  \hspace{1cm} (491)

The Laplace transform is given by

\[ \tilde{C}_t(k, s) = \frac{\omega_0^2}{s + \nu k^2} \]  \hspace{1cm} (492)

Considering \( s = -i\omega \), and in the limit of small \( k \), we can write,

\[ \tilde{C}_t(k, s = -i\omega) = \frac{\omega_0^2}{-i\omega} \left( 1 - \frac{\nu k^2}{i\omega} \right)^{-1} \approx \frac{\omega_0^2}{-i\omega} \left( 1 + \frac{\nu k^2}{i\omega} \right) \]  \hspace{1cm} (493)
By noting that the hydrodynamic limit also corresponds to the limit of $\omega \to 0$ and using the relation we wrote earlier

$$\text{Re}[\tilde{C}_{AB}(s = -i\omega)] = \pi C_{AB}(is = \omega).$$  \hspace{1cm} (494)

we can write the viscosity as

$$\eta = \beta \rho m^2 \lim_{\omega \to 0} \frac{\omega^2}{k^4} \text{Re} \tilde{C}_1(k, s = -i\omega) = \pi \beta \rho m^2 \lim_{\omega \to 0} \frac{\omega^2}{k^4} \text{Re} C_1(k, \omega).$$ \hspace{1cm} (495)

where $C_1(k, \omega)$ is the Fourier transform. In terms of the definition of the correlator, we can write this as

$$\beta \rho m^2 \lim_{\omega \to 0} \int_0^\infty \frac{1}{k^4} \frac{\omega^2}{k^4} \text{Re} \tilde{C}_1(k, s = -i\omega)$$ \hspace{1cm} (496)

Now, we consider the integral

$$\int_0^\infty \frac{k^2}{N} \langle j_k^x(t) j_k^z \rangle \exp(i\omega t) dt$$ \hspace{1cm} (497)

which we can write as

$$- \int_0^\infty \frac{d^2}{dt^2} C_1(k, t) \exp(i\omega t) dt = \omega^2 \tilde{C}_1(k, s = -i\omega) - i\omega \omega_0^2$$ \hspace{1cm} (498)

from the property of Laplace transforms. Taking the real part of it, and comparing with the above expression for $\eta$ we can write

$$\eta = \beta \rho m^2 \lim_{\omega \to 0} \int_0^\infty \frac{1}{Nk^2} \langle j_k^x(t) j_k^z \rangle \exp(i\omega t) dt.$$ \hspace{1cm} (499)

From the conservation law for momentum, we have

$$\dot{j}_k^x(t) + \frac{ik}{m} \sigma_{k}^{zx}(t) = 0$$ \hspace{1cm} (500)

where we have the momentum vector along the $z$ direction. This leads to the expression for $\eta$ which, taking the limits, reads

$$\eta = \frac{\beta}{V} \int_0^\infty \lim_{k \to 0} \langle \sigma_k^{zx}(t) \sigma_{-k}^{zx} \rangle dt \equiv \int_0^\infty \eta(t) dt$$ \hspace{1cm} (501)

where

$$\eta(t) = \frac{\beta}{V} \lim_{k \to 0} \langle \sigma_k^{zx}(t) \sigma_{-k}^{zx} \rangle.$$ \hspace{1cm} (502)

### 12 Generalized Hydrodynamics

Results from the hydrodynamic limit are not expected to hold for wavelengths comparable to atomic dimensions, and corresponding time scales. Indeed, the correct short time or large frequency limits are not obtained from the
hydrodynamic results. A simple example to see this would be to consider free particle limit for particle motion. The corresponding self dynamic structure would be a Gaussian in frequency, whereas the earlier discussion of self motion would indicate that we would obtain a Lorentzian. Thus, on smaller length and time scales, modifications have to be considered for the hydrodynamic description. We consider two examples where such modifications are seen to be needed.

Transverse Current Correlations: Transverse current correlations, as we have seen above, are predicted to decay exponentially. However, early computer simulations showed the decay was not described by a simple exponential, and indeed, the decay was non-monotonic, exhibiting oscillatory behavior. A physical explanation of oscillatory behavior could be given in terms of the fact that at short times, particles respond in an elastic manner, and the corresponding relation between stress and strain is

$$\sigma_{xz} = -G_\infty \left( \frac{\partial r_x}{\partial z} + \frac{\partial r_z}{\partial x} \right)$$

(503)

Thus, our constitutive relation

$$\sigma_{xz} = -\eta \frac{\partial}{\partial t} \left( \frac{\partial r_x}{\partial z} + \frac{\partial r_z}{\partial x} \right)$$

(504)

has to be modified. We can write the modified equation for stress as

$$\left( \frac{1}{\eta} + \frac{1}{G_\infty \frac{\partial}{\partial t}} \right) \sigma_{xz} = -\frac{\partial}{\partial t} \left( \frac{\partial r_x}{\partial z} + \frac{\partial r_z}{\partial x} \right).$$

(505)

This is equivalent to replacing the viscosity in the original constitutive relation by a frequency dependent viscosity

$$\eta(\omega) = \eta \frac{1}{1 - i\omega \tau_M}$$

(506)

where

$$\tau_M = \eta / G_\infty$$

(507)

which is called the Maxwell relaxation time. When $\omega \tau_M \ll 1$ we obtain the viscous limit, whereas $\omega \tau_M \gg 1$ leads to elastic response. Such elastic response will be applicable to short length scales as well. A general way of writing the generalization of the hydrodynamic limit of the equation for transverse currents is to write it in terms of a memory function:

$$\frac{\partial}{\partial t} C_t(k, t) + k^2 \int_0^t \nu(k, t - s) C_t(k, s) ds = 0.$$  

(508)

We require, for the hydrodynamic limit,

$$lt_\omega \to 0 \quad lt_k \to 0 \nu(k, \omega) = \nu$$

(509)

and in the other limit of short times,

$$\nu(k, t = 0) = \frac{\omega^2}{\tau_M^2} / k^2 = G_\infty(k) / \rho m$$

(510)
where $\omega_1^2$ describes the behavior of leading order time dependence of the transverse current correlation function

$$C_t(k, t) = \omega_0^2 \left( 1 - \omega_1^2 \frac{t^2}{2} + \ldots \right)$$

and thus

$$\omega_1^2 = -\frac{d^2}{dt^2} C_t(k, t)|_{t=0}$$

and we have $\omega_0^2 = k^2 \left( \frac{k_B T}{m} \right)$ from before. $\omega_1^2$ in turn is given as an equilibrium average, in terms of the pair correlation function and the second derivative of the interaction potential (for two-body interactions).

Velocity Autocorrelation Function: Similar to the transverse current correlation function, the velocity autocorrelation function [VACF] decays exponentially in the treatments we have seen before. However, from early computer simulations, it was found that this function had a “long time tail”, with a decay of $\sim t^{-d/2}$ where $d$ is the spatial dimension. An intuitive argument (Pomeau and Resibois, 1975) to understand this is as follows: Consider that at time $t = 0$, a particle $i$ has a given velocity along the $x$ axis $u_{ix}(0)$. For simplicity, the surrounding particles are considered, on average, to be at rest. After some elapsed time $\tau$, the velocity of the particle $i$ gets distributed among its surrounding neighbors, and one can estimate their number as $\rho V_x$ where $V_x$ is the volume that will be affected. This volume can be estimated from the range over which the transverse current would propagate in such a time, and from this we obtain $V_x \sim (\nu t)^{-3/2}$. From this, it immediately follows that $Z(t) \sim (\nu t)^{-3/2}$. If one now also considers that the particle $i$ moves around, the range should be estimated as $[(D + \nu)t]^{1/2}$. This yields

$$Z(t) \sim [(D + \nu)t]^{-3/2}.$$

A more detailed discussion considers rewriting the VACF as

$$Z(t) = \langle u_{ix}(t)u_{ix} \rangle = \int d\mathbf{r}_0 d\mathbf{u}_0 u_{ix} < u_{ix}(t)\delta(\mathbf{u}_i - \mathbf{u}_0)\delta(\mathbf{r}_i - \mathbf{r}_0) > .$$

In turn

$$< u_{ix}(t)\delta(\mathbf{u}_i - \mathbf{u}_0)\delta(\mathbf{r}_i - \mathbf{r}_0) > = \frac{< u_{ix}(t)\delta(\mathbf{u}_i - \mathbf{u}_0)\delta(\mathbf{r}_i - \mathbf{r}_0) >}{\delta(\mathbf{u}_i - \mathbf{u}_0)\delta(\mathbf{r}_i - \mathbf{r}_0)}$$

where $\phi_0(\mathbf{u}_0)$ is the equilibrium Maxwell distribution of velocities. We can write the average $< u_{ix}(t) >$ as

$$< u_{ix}(t) >_{n.e.} = \int d\mathbf{r}\rho^{(s)}(\mathbf{r}, t) u_{ix}(\mathbf{r}, t)$$

where $\rho^{(s)}(\mathbf{r}, t)$ is the density of tagged particles. Using a Fourier transform of this integral, we can write

$$Z(t) = \frac{1}{3V} \int d\mathbf{r}_0 \int d\mathbf{u}_0 \phi_0(\mathbf{u}_0) \frac{1}{V} \sum_k \rho^{(s)}(t) \mathbf{u}_k(t).\mathbf{u}_0$$

Once again, we assume that the velocity and position correlations decay as exponentials given by $D$ and $\eta$ respectively. Then, with some simplification, we can write
\[
Z(t) = \frac{2k_B T}{(2\pi)^3 \hbar m} \int dk e^{x \left[ -(D + \nu)k^2 t \right]} \tag{518}
\]

However, the limit of the \(k\) integral is given by \(k \sim (D + \nu |t|)^{-1/2}\) which leads to
\[
Z(t) \sim [(D + \nu |t|)^{-3/2} \tag{519}
\]
as before. This calculation forms an example of a coupling between modes, which we will discuss in more detail later.

*Kinetic Theory:* From the discussion of the Liouville equation earlier, we recall that we can write the equation for the time evolution of the \(N\)-body distribution function \(f\) as
\[
\frac{\partial f^{(N)}}{\partial t} + Lf^{(N)} = 0. \tag{520}
\]
with
\[
L = \frac{\partial H}{\partial p} \frac{\partial}{\partial q} - \frac{\partial H}{\partial q} \frac{\partial}{\partial p}. \tag{521}
\]

We can separate the forces that appear in the second term into external and internal forces. We can define a hierarchy of \(n\)-body distribution functions \(f^{(n)}\), the equations for which can be written by integrating the above equation over the remaining degrees of freedom. The resulting equation for \(f^{(n)}\) depends on the distribution function \(f^{(n+1)}\), in a hierarchy known as the BBGKY hierarchy. In particular, the 1-body distribution function will depend on the pair distribution function. In a dilute gas, one can express the corresponding term as one that leads to a change in the single particle distribution function due to interactions or “collisions” between particles, and write
\[
\frac{\partial f}{\partial t} + \mathbf{v} \cdot \nabla f + \frac{1}{m} \mathbf{F}(\mathbf{r}) \cdot \nabla \mathbf{v} f = \frac{\partial f}{\partial t}_{\text{collision}}. \tag{522}
\]

This is the Boltzmann equation, which was considered by Boltzmann with a specific form for the collision term, expressed in terms of binary collisions. This constitutes a particular kinetic model. Such kinetic models have been studied for a variety of reasons, starting with the proof of the H-theorem by Boltzmann, to obtaining hydrodynamic equations, to building detailed models of liquid state dynamics. We will not discuss this in detail, but consider a particular kinetic model, known as the BGK model (Bhatnagar, Gross and Krook, 1954), to give a flavor of these types of analyses, and use it to obtain a derivation of the H-theorem.

We define the function \(f(\mathbf{V}, \mathbf{r}, t)\) as the mass, rather than probability, density in terms of phase space coordinates. This difference is only in the normalization. Correspondingly, the density will be multiplied by \(m\), so that \(\rho(\mathbf{r}, t) = mn(\mathbf{r}, t)\) where \(n(\mathbf{r}, t)\) is the number density. The momentum density is \(\rho(\mathbf{r}, t)\mathbf{v}(\mathbf{r}, t)\) and we define \(T(\mathbf{r}, t)\) as the other hydrodynamic variable.

We have
\[
\rho(\mathbf{r}, t) = \int f(\mathbf{V}, \mathbf{r}, t) d\mathbf{V} \tag{523}
\]
and
\[ \rho(r, t)v(r, t) = \int V f(V, r, t) dV. \]  (524)
The “molecular velocity” relative to bulk motion of the fluid is
\[ C(r, t) = V - v(r, t). \]  (525)
The internal energy density and the temperature are defined as
\[ \rho(r, t)e(r, t) = \frac{3}{2} n(r, t) k_B T(r, t) = \frac{1}{2} |C(r, t)|^2 f(V, r, t) dV. \]  (526)
Now we define a velocity average of some quantity A as
\[ < A > = \int dV A \frac{f(V, r, t)}{\rho(r, t)} \]  (527)
Then,
\[ v(r, t) = < V > \]  (528)
and
\[ e(r, t) = < \frac{1}{2} |C(r, t)|^2 > \]  (529)
which also defined \( T(r, t) \) correspondingly. The BGK kinetic model (a) defines a local equilibrium distribution \( f_{loc} \) and (b) makes the assumption that the consequence of collisions is to drive \( f \) towards \( f_{loc} \), and correspondingly writes a form of the collision term.

The BGK local distribution function is
\[ f_{loc}(V, r, t) = \rho(r, t) \left( \frac{m}{2 \pi k_B T(r, t)} \right)^{3/2} \exp \left( \frac{m}{2 k_B T(r, t)} (V - v(r, t))^2 \right). \]  (530)
This involves all the five hydrodynamic variables, and leads to
\[ < V > = < V >_{loc} \]  (531)
\[ < (V - v(r, t))^2 > = < (V - v(r, t))^2 >_{loc} \]  (532)
and consequently
\[ \int dV f \ln f_{loc} = \int dV f_{loc} \ln f_{loc}. \]  (533)
The BGK form for the collision term is
\[ \frac{\partial f}{\partial t \text{ collision}} = -\lambda (f - f_{loc}). \]  (534)
Ignoring external forces, the BGK equation is then

$$\frac{\partial f}{\partial t} + \mathbf{V} \cdot \nabla f = -\lambda (f - f_{loc}).$$  \hspace{1cm} (535)

The Boltzmann $H$ function is defined as

$$H = \int \int d\mathbf{r} d\mathbf{V} f(\mathbf{V}, \mathbf{r}, t) \ln f(\mathbf{V}, \mathbf{r}, t)$$  \hspace{1cm} (536)

The rate of change of $H$ is

$$\frac{dH}{dt} = \int \int d\mathbf{r} d\mathbf{V} \frac{\partial f}{\partial t} (1 + \ln f)$$  \hspace{1cm} (537)

which can be written using the BGK equation as

$$\frac{dH}{dt} = \int \int d\mathbf{r} d\mathbf{V} \left[\frac{\partial f}{\partial t} \left( -\mathbf{V} \cdot \nabla f - \lambda (f - f_{loc}) \right) \right] (1 + \ln f).$$  \hspace{1cm} (538)

The first of these terms vanishes upon partial integration, the integrals over $f$ and $f_{loc}$ equal unity, and we have

$$\frac{dH}{dt} = \int \int d\mathbf{r} d\mathbf{V} \left[ -\lambda (f - f_{loc}) \right] \ln f.$$  \hspace{1cm} (539)

Using the equality above for integrals of $f \ln f$ and $f \ln f_{loc}$, we can write this as

$$\frac{dH}{dt} = \int \int d\mathbf{r} d\mathbf{V} \left[ -\lambda (f - f_{loc}) \right] \frac{f}{f_{loc}}.$$  \hspace{1cm} (540)

Using the inequality

$$(x - y) \ln \frac{x}{y} \geq 0$$  \hspace{1cm} (541)

we have

$$\frac{dH}{dt} \leq 0,$$  \hspace{1cm} (542)

which is the statement of the H-theorem.

### 13 Projection Operator Formalism

We have discussed in various contexts the idea of separating the dynamics in to a “slow” set of variables, and writing dynamical equations for them. A general approach, starting with the Liouville equations of motion, to obtaining a generalized Langevin equation description is through the use of projection operators, which we describe now.

Let $A_{\nu}$ be any operator that depends on the coordinates and momenta of a many body classical system specified by a Hamiltonian $H$. The time evolution of $A_{\nu}$ is given by

$$\frac{dA_{\nu}}{dt} = \{A_{\nu}, H\} \equiv LA_{\nu} = \sum_i \left( \frac{\partial H}{\partial p_i} \frac{\partial}{\partial r_i} - \frac{\partial H}{\partial r_i} \frac{\partial}{\partial p_i} \right) A.$$  \hspace{1cm} (543)
where $L$ is the Liouville operator), whose symbolic solution is

$$A_{\nu}(t) = e^{Lt}A_{\nu}(0).$$  \hfill (544)

We consider in general a set of operators $A = \{A_1, ..., A_N\}$.

We define a projection operator $\hat{P}$ into the subspace defined by these operators, as

$$\hat{P}B = \langle A \mid B \rangle \cdot \langle A \mid A \rangle^{-1} A$$  \hfill (545)

or more explicitly

$$\hat{P}B \equiv \sum_{n,m} |A_n\rangle \langle A_m| B \rangle \langle A| A \rangle_{nm}^{-1}$$  \hfill (546)

The scalar product $\langle A \mid B \rangle$ is defined to be the ensemble average $\langle BA^*_i \rangle_{eq}$. We have $\hat{P}A = A$. In defining the set of operators $A$ one has in mind that these constitute a set of slow degrees of freedom, or modes, and the remaining degrees of freedom are fast, and act as a “bath” to these modes. It is instructive to keep in mind the simple example of a Brownian particle in a liquid where the degrees of freedom corresponding to the Brownian particle are the slow degrees of freedom, and the liquid degrees of freedom are the fast degrees of freedom. In this case, it is clear that the liquid degrees of freedom are the origin of the friction and the random forces to which a Brownian particle is subject.

Considering the time evolution of $A$, we can write,

$$\frac{dA}{dt} = e^{Lt}[\hat{P} + (1 - \hat{P})]LA(0)$$  \hfill (547)

$$= e^{Lt} \hat{PL}A(0) + e^{Lt}(1 - \hat{P})LA(0)$$  \hfill (548)

$$= i\vec{\Omega}.\vec{A}(t) + e^{Lt}(1 - \hat{P})LA(0)$$  \hfill (549)

where

$$i\vec{\Omega} = \langle A \mid LA \rangle \cdot \langle A \mid A \rangle^{-1}.$$  \hfill (550)

Defining $G(t) \equiv e^{Lt}$ and $S(t)$ by

$$e^{Lt} = e^{Lt}S(t) + e^{(1-\hat{P})Lt}$$  \hfill (551)

and taking the Laplace transform on both sides, we get

$$G(s) = \frac{1}{s - L}$$  \hfill (552)

$$= \frac{1}{s - (\hat{P} + \hat{Q})L}$$  \hfill (553)

$$= \frac{1}{s - \hat{Q}L} + \frac{1}{s - L} \hat{PL} \frac{1}{s - QL}$$  \hfill (554)

where $\hat{Q} = 1 - \hat{P}$. This can be obtained also with the operator identity

$$S = R - S(S^{-1} - R^{-1})R.$$  \hfill (555)
Taking inverse Laplace transform on both sides, we have

\[ G(t) = e^{QLt} + \int_0^t d\tau e^{L(t-\tau)} \hat{P}Le^{QL\tau}, \]

and hence

\[ S(t) = e^{-Lt} \int_0^t d\tau e^{L(t-\tau)} \hat{P}Le^{QL\tau} \]

\[ = \int_0^t d\tau e^{-L\tau} \hat{P}Le^{QL\tau}. \]

We have,

\[ e^{Lt}(1 - \hat{P})LA = [e^{Lt} \int_0^t d\tau e^{-L\tau} \hat{P}Le^{QL\tau} + e^{(1-\hat{P})Lt}](1 - \hat{P})LA \]

\[ = \int_0^t d\tau e^{L(t-\tau)} \hat{P}Lf(\tau) + f(t) \]

where the second line defines \( f(t) \) as

\[ f(t) = e^{(1-\hat{P})Lt}(1 - \hat{P})LA(0) \]

\[ = e^{(1-\hat{P})Lt} f(0) \]

We consider

\[ \hat{P}Lf(\tau) = \langle A|Lf(\tau)\rangle \langle A|A\rangle^{-1}.A \]

Since \( f(t) \) is always orthogonal to \( A \) that is \( (A,f(t)) = 0 \), we have

\[ \langle A|Lf(\tau)\rangle = -\langle LA|f(\tau)\rangle = \langle \hat{Q}LA|f(\tau)\rangle = -(f(0),f(\tau)). \]

We now define

\[ K(t) \equiv \langle f(0)|f(t)\rangle \langle A|A\rangle^{-1} \]

With these relations, the equation for \( A \) becomes a generalized Langevin-like equation with \( f(t) \) taking the place of the “random” or fluctuation force.

\[ \frac{dA}{dt} = i\vec{\Omega}.\vec{A} - \int_0^t d\tau K(\tau)A(t - \tau) + f(t) \]

If \( A \) is a time correlation function \( C \) then

\[ \frac{dC}{dt} = i\vec{\Omega}.\vec{C} - \int_0^t d\tau K(\tau)C(t - \tau). \]

A formal solution for this equation can be written by Laplace transforming it as

\[ \tilde{C}(s) = \frac{1}{s - i\Omega + K(s)} C(0). \]

In turn, one could write a memory equation for the memory function \( K \), with a solution

\[ \tilde{K}(s) = \frac{1}{s - i\Omega_1 + K_1(s)} K(0) \]
and inserting it to
\[
\tilde{C}(s) = \frac{1}{s - i\Omega + \frac{1}{s - \tilde{\alpha}_1 + K_1(s)}}K(0).C(0).
\] (570)

This leads to a continued fraction expansion of the memory equation, with a series of coefficients \(\tilde{\alpha}_i\) and \(K_i(0)\) which can in principle be evaluated as equilibrium averages. This is formally exact, but also can be practically useful, since one can choose the level of the expansion at which one makes a termination of the continued fraction with a harmless or physically meaningful approximation.

14 Mode coupling theory

The generalized Langevin equation derived in the previous section is formally exact, and linear in structure. However, an assumption of separation into slow and fast variables has been made, which needs to be justified. In many cases, in addition to the nominal slow modes chosen, products of such modes arise naturally as variables that are coupled to slowly decaying modes. In other words, the projection operator includes only a projection into the subspace that is linear in operators \(A\) we have chosen, but the possibility remains that products of these modes are contained in the projected out subspace of “fast” modes. These need to be taken into account in developing an accurate description of dynamics.

In the simplest version, such “mode coupling” theories attempt to approximate the memory function by considering its projection into a second set of slow variables composed of products of slow variables. Considering the leading order, we can then define a projection operator \(\hat{P}_2\) such that
\[
\hat{P}_2g = \langle AA|g\rangle \cdot (AA|AA)^{-1}AA.
\] (571)

Considering
\[
K(t) = \langle f(0)|f(t)\rangle \langle A|A\rangle^{-1} = \langle f(0)|e^{(1-\hat{P})Lt}f(0)\rangle \langle A|A\rangle^{-1}
\] (572)
the mode coupling approximation to \(K\) is written as
\[
K_{MC}(t) = \langle \hat{P}_2f(0)|e^{(1-\hat{P})Lt}\hat{P}_2f(0)\rangle \langle A|A\rangle^{-1}
\] (573)

This in turn can be written as
\[
K_{MC}(t) = |\langle AA|f(0)\rangle|^2 \cdot (AA|AA)^{-1} \cdot (AA|AA)^{-1} \cdot \langle AA|e^{(1-\hat{P})Lt}AA\rangle \langle A|A\rangle^{-1}.
\] (574)
This is simplified by making two approximations, namely (i) approximation of the fourth order correlation by the product of second order correlations:
\[
\langle AA|AA\rangle \approx |\langle A|A\rangle|^2
\] (575)

and (ii) approximating the projected dynamics by the normal time evolution:
\[ \langle AA \rangle e^{(1-P)Lt} |AA\rangle \approx |A \rangle e^{Lt} |A\rangle^2. \] (576)

With these approximations, we will have

\[ K_{MC}(t) = |V(AA,f)|^2 \langle A | A(t) \rangle \cdot \langle A | A(t) \rangle. \] (577)

The “vertex” V contains all the time independent terms arising from the above manipulations.

We illustrate the “mode coupling” approach, by considering the mode coupling theory for structural relaxation in glass forming liquids.

Let us consider the set A of slow variables to be the set of operators for density fluctuations and longitudinal current in Fourier space.

\[ A = \left( \begin{array}{c} \delta \rho_q \\ j_q^L \end{array} \right) \]

And the correlation function are given by the matrix elements

\[ C = \langle A^*(0)A(t) \rangle \]

Explicitly, we have,

\[ \delta \rho_q = \sum e^{i\vec{q} \cdot \vec{r}_i} - (2\pi)^3 \rho \delta(\vec{q}) \] (578)

\[ j_q^L = \frac{1}{m} \sum_i \vec{q} \vec{p}_i e^{i\vec{q} \cdot \vec{r}_i} \] (579)

\[ C(t) = \left( \begin{array}{cc} \langle \delta \rho_{-\vec{q}}(0) \delta \rho_q(t) \rangle & \langle \delta \rho_{-\vec{q}}(0) j_q^L(t) \rangle \\ \langle j_{-\vec{q}}^L(0) \delta \rho_q(t) \rangle & \langle j_{-\vec{q}}^L(0) j_q^L(t) \rangle \end{array} \right) \] (580)

\[ C(0) = \left( \begin{array}{cc} NS(\vec{q}) & 0 \\ 0 & \frac{Nk_B T}{m} \end{array} \right) \] (581)

Here, \( S(\vec{q}) = F(0) \), the structure factor. We note for use below that the lower left hand corner element of the time derivative of C is \( \frac{Nk_B T}{m} \frac{dF}{d\vec{q}} \) \( (F \) being the intermediate scattering function), and will evaluate the same element of the matrix on the right hand side. We evaluate \( \Omega \) by considering time \( t = 0 \),

\[ i\Omega = \langle A^* A(0) \rangle \langle A, A \rangle^{-1} \] (582)

\[ = \left( \begin{array}{cc} 0 & i\frac{Nk_B T}{m} \\ i\frac{Nk_B T}{m} & 0 \end{array} \right) \left( \begin{array}{cc} 1/NS(\vec{q}) & 0 \\ 0 & \frac{m}{Nk_B T} \end{array} \right) \] (583)

\[ = \left( \begin{array}{cc} 0 & i\frac{k_B T}{mS(\vec{q})} \\ i\frac{k_B T}{mS(\vec{q})} & 0 \end{array} \right) \] (584)

From this, the lower left hand corner element of \( i\Omega C(t) \) is \( i\frac{k_B T}{mS(\vec{q})} F \). Similarly, the fluctuating force at time
where the last step defines $R_q$. The correlation matrix of $f$ is

$$K(t) = \begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix} (A, A)^{-1}$$

Therefore, the product of $K$ with $C$ appearing in the memory term is

$$K(t)C(t - \tau) = \begin{pmatrix} 0 & 0 \\ 0 & m\langle R_{-q}R_q(t) \rangle \end{pmatrix} \begin{pmatrix} (\delta \rho_{-q}(0)\delta \rho_q(t)) \\ (j_{p-q}^L(0)\delta \rho_q(t)) \end{pmatrix}$$

Considering the lower left matrix element, we get the equation for $F(q, t)$, in the form

$$\frac{d^2 F}{dt^2} + \frac{q^2 k_BT}{mS(q)} F(q, t) + \frac{m}{Nk_B T} \int_0^t d\tau \langle R_{-q}R_q(t) \rangle \frac{dF}{dt} = 0$$

This equation is approximated in order to obtain the mode coupling equation. In the above equation, the quantity $\langle R_{-q}R_q(t) \rangle$ needs to be evaluated.

An analysis of $R_q$ reveals that it contains products of density operators in its expression, and therefore, contrary to expectation at the outset, the fluctuating force contains contributions from the slow modes, which leads to the coupling of modes in the final equation for $F$. Taking only the product of two densities as an approximation to $R_q$ leads to a product of correlation functions $F$ multiplying $\frac{dF}{dt}$ in the equation above.

The approximation for $\langle R_{-q}R_q(t) \rangle$ used in mode coupling theory is

$$\langle R_{-q}R_q(t) \rangle = \frac{\rho^2(k_BT)^2}{2m^2} \sum_k |\tilde{V}_{q-k,k}|^2 F(k, t) F(|q-k|, t)$$

where

$$\tilde{V}_{q-k,k} = \frac{ik_BT}{2mN} \left\{ \frac{\hat{q}_k}{S(k)} + \frac{\hat{q}_k(q-k)}{S(|k-q|)} - q \hat{q} \right\}$$
which is in line with the general description we gave above.

**Schematic mode coupling theory** The mode coupling equation above has been studied in a schematic version, obtained by considering a single q-independent time correlation function, by various authors. We follow here the treatment in Leutheusser, E., *Phys. Rev. A* **29**, 2765 - 2773, (1984).

Considering a single time correlation function \( \Phi(t) \) we write the schematic mode coupling equation for this function as

\[
\frac{d^2 \Phi}{dt^2} + \gamma \dot{\Phi}(t) + \Omega_0^2 \Phi(t) + 4 \lambda \Omega_0^2 \int_0^t d\tau \Phi^2(\tau) \dot{\Phi}(t - \tau) = 0.
\]

Here, the parameter \( \lambda \) represents the strength of the mode coupling term, which one may expect to change as temperature in a supercooled liquid is varied. A Laplace transform of this equation\(^1\) can be written as

\[
\Phi(z) = \frac{1}{z - \Omega_0^2 z + D(z)}
\]

where

\[
D(z) = i \gamma + 4 \lambda \Omega_0^2 \mathcal{L}\{\Phi^2(t)\}.
\]

Normally, the correlation function \( \Phi(t) \) should decay to zero at long times. If the above equation were to describe a dynamical transition leading to structural arrest, however, one expects that the long time limit of \( \Phi(t) \) will be non-zero. Writing an *ansatz* for \( \Phi(t) \) based on this expectation as

\[
\Phi(z) = -f/z + (1 - f) \Phi_v(z),
\]

where \( \Phi_v(t) \) has an initial \((t = 0)\) value of 1 and decays to zero at long time. \( D(z) \) can be evaluated from this, and has the form

\[
D(z) = -4 \lambda f^2/z + D_v(z)
\]

\(^1\)The Laplace transform here, is defined to be \( \phi(z) = i \int_0^\infty dt \exp(it)\phi(t) \) related to the more common \( \phi(s) = \int_0^{\infty} dt \exp(-st)\phi(t) \) by \( s = iz \), and \( \phi(s) = i\phi(z) \).
Inserting this in the original expression for $\Phi(z)$ and comparing with the ansatz, one gets an expression for $f$ as

$$f = \frac{1}{2}(1 + \sqrt{1 - 1/\lambda}).$$  \hspace{1cm} (602)

For $\lambda > \lambda_c = 1$, this expression admits real solutions, and therefore, one has a non-decaying solution to $\Phi(t)$, as seen in Figure 1 which shows numerical solutions for $\Phi$ using the above equations.
REFERENCES

References


