5. NONEQUILIBRIUM THEORIES

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The theories for nonequilibrium phenomena are reasonably well established now. For systems close to equilibrium and evolving towards equilibrium, we have good agreement between theory and experiment. Equilibrium theories which can now handle quite complex systems relate the system properties to the microscopic Hamiltonian of the interacting system. In nonequilibrium theories, there are two distinct approaches. One approach starts with the system Hamiltonian and deals with equations for the reduced distribution functions or other correlation functions by averaging over the "other" or "remaining" degrees of freedom. In an alternative approach, one includes a stochastic force term at the very beginning which is not derivable from the microscopic Hamiltonian. The stochastic or the random force term represents in an average and uncorrelated manner how the medium surrounding a given molecule affects the motion of this molecule under consideration. Since the random force at one moment is uncorrelated to its value at a later moment, the time displacements can not be arbitrarily small. Implicit in the stochastic models is a relaxation time, such as the momentum relaxation time of the medium (which could be of the order of femtoseconds) and the theories can not predict anything within the time required for this relaxation process. We will label the former methods as the Hamiltonian approaches and the latter as the stochastic methods.

We will begin this chapter with the Liouville equation, followed by correlation functions theory and linear response theory. Expressions for transport properties will be derived. Additional details of linear response theory and applications will be given in a later chapter. The random walk problem has already been dealt with in Chapter 2. In the stochastic methods, we start with a differential equation (the diffusion equation) for the random walk problem and then consider the Langevin equation. This is followed by the Smoluchowsky equation, the Fokker Planck equation and the Chandrasekhar equation. Selected chemical applications will be given for each of these methods

5.1 Liouville Equation

The time dependence of a system of N particles can be described in terms of the time evolution of the positions and momenta of these particles. The space of 6N variables (3N coordinates and 3N momenta) is referred to as phase space or Γ (gamma space). Each point in phase space corresponds to a set of values of $\underset{\sim}{r}^N \equiv (\vec{q}_1, \vec{q}_2, ...\vec{q}_N)$ for positions in a generalized system of coordinates and momenta $\underset{\sim}{p}^N \equiv (\vec{p}_1, \vec{p}_2, ...\vec{p}_N)$.

The time dependence of a general function $C(\Gamma_N, t) = C(\underset{\sim}{r}^N, \underset{\sim}{p}^N, t)$ is given by

$$\frac{d\,C(\Gamma_N,t)}{d\,t} = \frac{\partial C(\Gamma_N,t)}{\partial t} + \sum_{i=1}^{3N}\left[\frac{\partial C(\Gamma_N,t)}{\partial q_i}\dot{q}_i + \frac{\partial C(\Gamma_N,t)}{\partial p_i}\dot{p}_i\right] \tag{5.00}$$

A dynamical variable B such as energy, or momentum depends only on the values of $(\underset{\sim}{r}^N, \underset{\sim}{p}^N)$. For a dynamical variable, the partial derivative of B with time is zero and therefore

$$\frac{dB}{dt} = \sum_{i=1}^{3N}\left[\frac{\partial B}{\partial q_i}\dot{q}_i + \frac{\partial B}{\partial p_i}\dot{p}_i\right] = \sum_{i=1}^{3N}\left[\frac{\partial B}{\partial q_i}\frac{\partial H}{\partial p_i} - \frac{\partial B}{\partial p_i}\frac{\partial H}{\partial q_i}\right] = [B, H] \qquad (5.00)$$

Where we have used the Hamilton's equations [Eq. (1.15)] and the Poisson bracket [Eq. (1.17)]. The solution to this equation can be formally written as

$$B(t) = e^{iLt}\, B(0), \quad L = i\sum_{i=1}^{3N}\left[\frac{\partial H}{\partial q_i}\frac{\partial}{\partial p_i} - \frac{\partial H}{\partial p_i}\frac{\partial}{\partial q_i}\right] \qquad (5.00)$$

The equation also defines the Liouville operator L.

Let us consider a canonical ensemble of $\mathbb{N}$ members. Each member is represented by a point in phase space and as time evolves, these points also move in phase space. The phase space probability density is represented by $f(\Gamma, t)$. The number of members of the ensemble in a volume element of phase space $d\Gamma$ at Γ is given by $d\mathbb{N} = \mathbb{N}\, f(\Gamma, t)\, d\Gamma$. These points are shown in fig. (5.1)

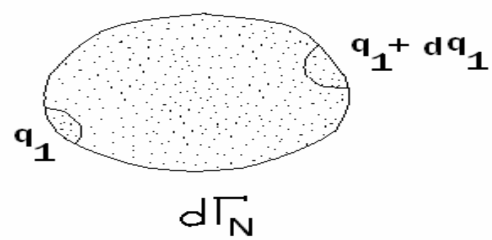

Figure 5.1 A volume element in phase space. Two faces "perpendicular" to the q_1 axis are shown.

The net flux of the points entering the volume along the face q_1 (the number of points present in the area multiplied by the velocity of points at the area and leaving at the face $q_1 + dq_1$ is given by

$$\begin{aligned}&\mathbb{N}\, f(q_1,....p_{3N})\, dq_2 dq_3..dp_N\, \dot{q}_1(q_1,....p_{3N}) \\ &\quad - \mathbb{N}\, f(q_1+dq_1,....p_{3N})\, dq_2 dq_3..dp_N\, \dot{q}_1(q_1+dq_1,....p_{3N})\end{aligned} \qquad (5.00)$$

where the values of f and $\dot{q}_1$ in the second term are evaluated at $q_1 + dq_1$. Expanding the second term by a Taylor series, we get

$$\mathbb{N}\left[f\,\dot{q}_1 - (f + \frac{\partial f}{\partial q_1}dq_1)(\dot{q}_1 + \frac{\partial \dot{q}_1}{\partial q_1}dq_1)\right]dq_2 dq_3...dp_{3N} \qquad (5.00)$$

Keeping only the terms linear in dq_1 and summing over all the *6N* faces, we get

$$-\mathbb{N}\sum_{i=1}^{3N}\left[\frac{\partial f}{\partial q_i}\dot{q}_i + f\frac{\partial \dot{q}_i}{\partial q_i} + \frac{\partial f}{\partial p_i}\dot{p}_i + f\frac{\partial \dot{p}_i}{\partial p_i}\right] \quad (5.00)$$

The second term and the fourth term cancel because $\frac{\partial \dot{q}_i}{\partial q_i} = \frac{\partial^2 H}{\partial q_i \partial p_i} = \frac{\partial^2 H}{\partial p_i \partial q_i} = -\frac{\partial \dot{p}_i}{\partial p_i}$.

The expression in Eq. (5.00) is the net change of *f* in time *dt* at the phase point Γ in the volume element $d\Gamma$,

$$\left[\frac{\partial[\mathbb{N} f(\Gamma,t)]}{\partial t}\right]_\Gamma \quad (5.00)$$

Equating the above two equations, we get the Liouville equation

$$\frac{\partial f(\Gamma,t)}{\partial t} = -[f,H] = -iLf, \quad or \quad \frac{df}{dt} = 0 \quad (5.00)$$

This is the equation of conservation of density in phase space. This implies that as time evolves, the volume element of phase space representing the members of the ensemble will move to another point without a change in density, ie., the shape of the volume element may change but not the density.

The function $f(\Gamma, t)$ is a function of 6N variables (which is an extremely large number for N of the order of Avogadro number) and is not useful in practice. Reduced distribution functions, which depend on a *6n* variables for small values of *n* are far more manageable and useful. The reduced distribution functions are defined by (in analogy to the functions used in equilibrium theory)

$$f^{(n)}(\underset{\sim}{r}^n, \underset{\sim}{p}^n, t) = \frac{N!}{(N-n)!}\int\int\int f(\underset{\sim}{r}^N, \underset{\sim}{p}^N, t)\; d\underset{\sim}{r}_{n+1}..d\underset{\sim}{r}_N\; d\underset{\sim}{p}_{n+1}..dp_N \quad (5.00)$$

Taking the partial derivative with respect to time on both sides and substituting the Liouville equation on the r.h.s. and taking all the terms in the summation from 1 to n to the left side, we get the equation of the BBGKY hierarchy which his discussed in greater detail in chapter 12 on linear response theory. These equations connect $f^{(n)}$ to $f^{(n+1)}$ and an additional "closure" relation between the two functions is needed to solve it. The simplest way is to write $f^{(n+1)}$ as a product of $f^{(n)}$ and $f^{(1)}$. The BBGKY equation is

$$\left\{\frac{\partial}{\partial t} + \sum_{i=1}^{n}\left[\frac{\underset{\sim}{p}_i}{m}\frac{\partial}{\partial \underset{\sim}{r}_i} + \left(\underset{\sim}{X}_i + \sum_{j\neq i}^{n}\underset{\sim}{F}_{ij}\right)\cdot\frac{\partial}{\partial \underset{\sim}{p}_i}\right]\right\} f^{(n)}(\underset{\sim}{r}^n, \underset{\sim}{p}^n, t)$$

$$= -\sum_{i=1}^{n}\int\int d\underset{\sim}{r}_{n+1} d\underset{\sim}{p}_{n+1}\underset{\sim}{F}_{i,n+1}\cdot\frac{\partial}{\partial \underset{\sim}{p}_i} f^{(n+1)}(\underset{\sim}{r}^{n+1}, \underset{\sim}{p}^{n+1}, t) \quad (5.00)$$

It should be noted that the above equations (5.00), (5.00) and (5.00) are all reversible in time. What this means is that if the system evolves from point A to point B in time t and if after time t, the direction of time is reversed, then the system will return to state A after another interval of time t. This is true of systems which are governed by Hamiltonian dynamics. In systems driven by stochastic dynamics, time reversibility is lost at the very outset due to the presence of random or stochastic terms. One such example is the Boltzmann equation for $f^{(1)}(\underset{\sim}{r}, \underset{\sim}{p}, t)$, which includes a collision term on the r.h.s.

5.2 The Random Walk Problem and the Diffusion Equation

In chapter 2, the one dimensional walk problem has been discussed in detail. In the one dimensional problem, the random walker (or the object undergoing the walk) can either go to the left or to the right by a displacement Δ. We may assume that the time required to take each step is τ.

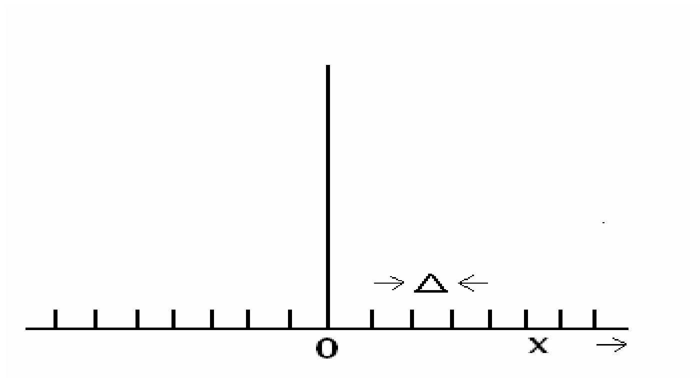

Figure 5.1 Random Walk in One dimension

It was shown there that the probability of the walker lying at n_l after N steps is

$$W(n_l) = (2\pi Npq)^{-\frac{1}{2}} \exp\left[\frac{-(n_l - Np)^2}{2Npq}\right] \tag{5. 00}$$

where p and q are the probabilities of talking a step to the right and left respectively and n_l and n_2 are the number of steps to the right and left respectively. The net displacement is $m = n_l - n_2$. If p = q = ½, then,

$$W(m) = (2/\pi N)^{\frac{1}{2}} \exp(-m^2/2N) \tag{5.00}$$

See Eqs. (2.1) to (2.5) for details. To go into a description in terms of continuous variables, let $x = m\Delta$ be the net displacement from the starting point of x = 0.If dx is much larger than Δ, then the probability that the particle is at x in an interval dx is given by

$$W(x,N)\,dx = W(m,N)(dx/2\Delta) \tag{5.00}$$

The division by 2 on the right hand side is due to the fact that m is even or odd depending on whether N is even or odd. Simplifying the r.h.s. of the above equation,

$$W(x,N) = (2\pi N\Delta^2)^{-1/2}\, e^{-x^2/(2N\Delta^2)} \tag{5.00}$$

Let us now convert N into a continuous variable. If the particle undergoes j displacements per unit time, then, the probability that the particle will be found between x and x + dx is

$$W(x,t)\,dx = 2(\pi Dt)^{-1/2}\, e^{-x^2/(4Dt)}\, dx;\;\; D = \tfrac{1}{2}\, j\,\Delta^2 \qquad (5.\ )$$

This is a solution of the problem of random walk in one dimension. It is straight forward to extend the solution to the cases wherein there are absorbing and reflecting barriers, using the method of images.

A differential equation for W can be derived by the arguments proposed by Kac. Consider the conditional probability $P(n\,|\,m,s)$ that the particle is at m at time t if it were at n at time 0. It should be actually written as $P(n,0\,|\,m,s)$, but we drop the zero. $P(n\,|\,m,s)$ satisfies the following difference equation.

$$P(n\,|\,m,s+1) = \tfrac{1}{2}P(n\,|\,m-1,s) + \tfrac{1}{2}P(n\,|\,m+1,s) \qquad (5.00)$$

This is because the particle can come to the location m at s + 1 only if it was at either at m - 1 or m + 1 at time s. Since n → n Δ, m→ m Δ and s → s τ, where Δ is the displacement per step and τ is the time per step, we get

$$\frac{P(n\Delta\,|\,m\Delta,(s+1)\tau) - P(n\Delta\,|\,m\Delta,s\tau)}{\tau} = \frac{\Delta^2}{2\tau}\left\{\frac{P(n\Delta\,|\,(m+1)\Delta,s\tau) - 2P(n\Delta\,|\,m\Delta,s\tau) + P(n\Delta\,|\,(m-1)\Delta,s\tau)}{\Delta^2}\right\} \qquad (5.00)$$

In the l.h.s., positions are fixed, while on the r.h.s., time is fixed. The l.h.s can be taken as $(\partial P/\partial t)_x$ while the r.h.s. is the second derivative of P with respect to x, i.e., $(\partial^2 P/\partial x^2)_t$. The quantity $\Delta^2/2\tau$ may be replaced by D (in analogy with the result to be shown later that the diffusion coefficient in one dimension is given by $D = \langle x^2 \rangle/(2t)$. It should be specifically noted that in this model, the limit of Δ/τ goes to ∞ as $\tau \to 0$. As mentioned in the introduction, these derivatives have a meaning only beyond a characteristic time such as the momentum relaxation time of the medium. The Eq. (5.00) becomes

$$\frac{\partial P}{\partial t} = D\frac{\partial^2 P}{\partial x^2} \qquad (5.00)$$

This is the diffusion equation in one dimension and it is readily verified that the function W(x,t) of Eq. (5.00) satisfies the diffusion equation. In three dimensions, this can be readily generalized to

$$\frac{\partial P}{\partial t} = D\nabla^2 P \qquad (5.00)$$

The diffusion equation can be derived starting from a more general equation,

$$W(\underset{\sim}{R}, t+\Delta t) = \int_{-\infty}^{\infty} \psi(\Delta\underset{\sim}{R}, \Delta t)\, W(\underset{\sim}{R} - \Delta\underset{\sim}{R}, t)\, d(\Delta\underset{\sim}{R}) \qquad (5.00)$$

The above equation is a generalization of Eq. (5.). $\psi(\Delta\underset{\sim}{R}, \Delta t)$ is the transition probability, i.e., the probability that the particle suffers a displacement of $\Delta\underset{\sim}{R}$ in time Δt. In the case of Eq. (5.), $\psi(\Delta\underset{\sim}{R}, \Delta t)$ was ½ and it connected only adjacent points in the Figure 5.1 In Eq. (5.00), there can be displacements of different magnitude $\Delta\underset{\sim}{R}$ in time

Δt. Note that $\psi(\Delta \underset{\sim}{R}, \Delta t)$ is independent of time and only depends on Δt. Processes in which a variable at time $t + \Delta t$ depends only on the present time t and not on its past history is called a Markov process. The equation (5.00) is called the Chapman-Kolmogorov equation and is a general characteristic of a Markov process. A very useful model for the transition probability is given by the formula

$$\psi(\Delta \underset{\sim}{R}, \Delta t) = (4\pi D \Delta t)^{-1/2} e^{-\frac{|\Delta \underset{\sim}{R}|^2}{4D\Delta t}} \tag{5.00}$$

By expanding $\psi(\Delta \underset{\sim}{R}, \Delta t)$, $W(\underset{\sim}{R} - \Delta \underset{\sim}{R}, t)$ and $W(\underset{\sim}{R}, t + \Delta t)$ in Taylor series in $\underset{\sim}{R}$ and t we can obtain the diffusion equation. We can also obtain the diffusion equation from the continuity equation by using the Fick's law for the particle flux..

$$\frac{\partial \rho(\underset{\sim}{R}, t)}{\partial t} + \underset{\sim}{\nabla} \cdot \underset{\sim}{j}(\underset{\sim}{R}, t) = 0; \quad \underset{\sim}{j}(\underset{\sim}{R}, t) = -D \underset{\sim}{\nabla} \rho(\underset{\sim}{R}, t) \tag{5.00}$$

Here, $\rho(\underset{\sim}{R}, t)$ is the density of particles at point $\underset{\sim}{R}$ at time t and $\underset{\sim}{j}(\underset{\sim}{R}, t)$ is the flux of the particles. It is rather satisfying that a given equation can be derived in so many different ways.

5.3 Langevin Equation

The Lanegvin equation represents an excellent example of an exactly solvable model of a stochastic process and has a number of applications in chemistry as it includes the frictional forces as well as random forces which are intrinsic properties of the behaviour of fluids. It also leads to a number of useful relations that relate the fluctuations in a medium to dissipative forces. The equation has been generalized to include time dependent friction. A generalized Langevin equation can also be arrived at starting with the Liouiville equation. The Langevin equation is given by

$$\dot{\underset{\sim}{p}}(t) = \frac{d\underset{\sim}{p}(t)}{dt} = -\xi \underset{\sim}{p}(t) + \underset{\sim}{R}(t) + \underset{\sim}{X}(t) \tag{5.00}$$

where $\underset{\sim}{p}(t) = m\underset{\sim}{u}(t)$ is the momentum of the particle, m its mass and $\underset{\sim}{u}(t)$ its velocity. The friction coefficient is denoted by ξ. As a particle moves in a given direction in a liquid, the particles in its path have to eventually occupy the space vacated by the particle during its forward motion, thereby causing the drag. The random force and the external force are represented by $\underset{\sim}{R}(t)$ and $\underset{\sim}{X}(t)$ respectively. The random forces are a result of incessant bombardment of any given particle by the particles surrounding it. The equation describes very well the motion of colloidal or other large particles in a solvent medium. It is less accurate in describing the motion of water molecules in liquid water because the friction experienced by the molecules is not instantaneous. This is a stochastic differential equation and the solution to this equation is naturally probabilistic. A solution to the equation should yield $W(\underset{\sim}{p}(t), t; \underset{\sim}{p}_0)$, the probability that the particle has a momentum $\underset{\sim}{p}(t)$ at time t if it had a momentum $\underset{\sim}{p}_0$ at time 0. We also expect that at long times, the particle's velocity would conform to the equilibrium Maxwellian form. These statements can be expressed as

$$W(\underset{\sim}{p}(t),t;\underset{\sim}{p}_0)=\delta(p_x-p_{x0})\,\delta(p_y-p_{y0})\,\delta(p_z-p_{z0}),\;\; as\;\; t\to 0 \qquad (5.00)$$

$$=(2\pi m k_B T)^{-3/2}\; e^{-p^2/2m k_B T},\;\; as\;\; t\to\infty. \qquad (5.00)$$

A formal solution to the Langevin equation is given by

$$\underset{\sim}{p}(t)=e^{-\xi t}\underset{\sim}{p}(0)\; + e^{-\xi t}\int_0^t e^{\xi s} R(s)\,ds \qquad (5.00)$$

It can be readily verified that this satisfies the Langevin equation. Kubo considered a situation wherein the random forces possess the following properties.

$$<\underset{\sim}{R}(t)>_{eq}\; = 0 \qquad (5.00)$$

$$<\underset{\sim}{R}(t)\cdot \underset{\sim}{p}(0)> \,= 0,\;\; t>0 \qquad (5.00)$$

$$<\underset{\sim}{R}(t)\cdot \underset{\sim}{R}(0)> \,= 2\pi R_0\,\delta(t) \qquad (5.00)$$

The physical meanings are: The mean value of the random force is zero at equilibrium. The values of the random forces are uncorrelated to the initial momentum at all later times and that the power spectrum (the Fourier transform) of the random force is a constant. This means that the random forces have constant contributions from all frequency components. This is called white noise.

$$R_0=(2\pi)^{-1}\int_{-\infty}^{\infty} e^{i\omega t}\, <\underset{\sim}{R}(t)\cdot \underset{\sim}{R}(0)>\, dt \qquad (5.00)$$

Consider a stationary process represented by the Langevin equation when the external force is a constant. Examples are charged colloidal particles subjected to a constant electric field. Then taking the average of the Langevin equation, we get

$$\left\langle \dot{\underset{\sim}{p}}(t)\right\rangle = -\xi\left\langle \underset{\sim}{p}(t)\right\rangle+\left\langle \underset{\sim}{R}(t)\right\rangle+\left\langle \underset{\sim}{X}(t)\right\rangle$$

$$-\xi\left\langle \underset{\sim}{p}(t)\right\rangle+\left\langle \underset{\sim}{X}(t)\right\rangle,\quad or\;\; \underset{\sim}{p}_{av}=\underset{\sim}{X}/\xi=\tau \underset{\sim}{X}$$

In a stationary process, $\underset{\sim}{p}_{av}$ takes on a steady value (such as the mobility of the colloidal particles in an electric field) and the mobility $\underset{\sim}{p}_{av}/m$ (velocity in a unit external field) is given by τ/m. Associated with this transport process there is a dissipation of energy and the energy loss per unit time equals $X\,p_{av}/m=(\tau/m)X^2$. This is called the first *fluctuation dissipation theorem* and relates the fluctuations (governed by random forces) to dissipation (caused by frictional forces).

Let us now consider the fluctuations in the equilibrium ensemble in the absence of an external field. Multiply the Langevin equation and take the expectation value. We have denoted $\underset{\sim}{p}(0)$ by $\underset{\sim}{p}$.

$$\left\langle \dot{\underset{\sim}{p}}(t)\cdot \underset{\sim}{p}\right\rangle = -\xi\left\langle \underset{\sim}{p}(t)\cdot \underset{\sim}{p}\right\rangle+\left\langle \underset{\sim}{R}(t)\cdot \underset{\sim}{p}\right\rangle$$

The second term is zero from Eq. (5.00) and writing in terms of the correlation functions, $\dot{c}_{pp}(t) = -c_{pp}/\tau$.
Integrating,
$$\tau = \int_0^\infty \frac{c_{pp}(t)}{c_{pp}(0)}\,dt$$
This is a general definition of a correlation time. For the Langevin equation, the correlation function decays exponentially and only for systems obeying Langevin equation, we can get the correlation time by plotting $\ln\,[c_{pp}(t)/c_{pp}(0)]$ versus t.

We now will obtain the second fluctuation dissipation theorem. This relates the cooling of the brownon (a particle undergoing Brownian motion) to its heating by the noise (or random forces. This is referred to as the Nyquist theorem when the random term is the fluctuating voltage across a resistance.

$$\left\langle \underset{\sim}{p}^2(t)\right\rangle = e^{-2t/\tau}\left[\underset{\sim}{p}(0)^2 + 2\int_0^t e^{s/\tau}\left\langle \underset{\sim}{R}(s)\cdot \underset{\sim}{p}(0)\right\rangle ds + \int_0^t ds\, e^{s/\tau}\int_0^t du\, e^{u/\tau}\left\langle \underset{\sim}{R}(s)\cdot \underset{\sim}{R}(u)\right\rangle\right] \quad (5.33)$$

The second term in the square brackets is zero from Eq. (5.00) and substituting Eq. (5.00) the integral over *du* in the last term becomes $e^{s/\tau}2\pi R_0$. We now have

$$\int_0^t ds\, e^{2s/\tau}\, 2\pi R_0 = \pi R_0 \tau[e^{2t/\tau}-1]$$

$$\left\langle \underset{\sim}{p}^2(t)\right\rangle - \left\langle \underset{\sim}{p}^2(0)\right\rangle e^{-2t/\tau} = \pi R_0\tau[1-e^{-2t/\tau}]$$

At equilibrium, $\left\langle \underset{\sim}{p}^2(t)\right\rangle = \left\langle \underset{\sim}{p}^2(0)\right\rangle = 3\,m\,k_B T$ and at large times, $e^{-2t/\tau} \to 0$ and we have

$$\xi = \frac{1}{\tau} = \frac{\pi R_0}{3\,m\,k_B T} = \frac{\beta}{3\,m}\int_0^\infty < \underset{\sim}{R}(t)\cdot \underset{\sim}{R}(0) > dt$$

This is the statement of the second <u>*fluctuation dissipation theorem*</u> and relates the friction coefficient to the strength of $< R(t)^2 >$ at $t = 0$.

Now consider the mean square displacement of a brownon obeying Langevin equation at time *t* if it starts at the origin at time 0. Writing $\underset{\sim}{p}(t)$ as $m\,\underset{\sim}{u}(t)$,

$$m\,\underset{\sim}{r}(t)\cdot \dot{\underset{\sim}{u}}(t) = -\xi\, m\, \underset{\sim}{r}(t)\cdot \underset{\sim}{u}(t) + \underset{\sim}{r}(t)\cdot \underset{\sim}{R}(t)$$
Using

$\underset{\sim}{r} \cdot \underset{\sim}{u} = \underset{\sim}{r} \cdot \dot{\underset{\sim}{r}} = \frac{1}{2}\frac{d}{dt} r^2; \; \underset{\sim}{r} \cdot \dot{\underset{\sim}{u}} = \underset{\sim}{r} \cdot \ddot{\underset{\sim}{r}} = \frac{1}{2}\frac{d^2}{dt^2} r^2 - |\underset{\sim}{u}|^2$

Equation (5.00) can be written as

$\frac{1}{2} m \frac{d^2}{dt^2} |\underset{\sim}{r}(t)|^2 + \frac{1}{2} \xi m \frac{d}{dt} |\underset{\sim}{r}(t)|^2 = m |\underset{\sim}{u}(t)|^2 + \underset{\sim}{r}(t) \cdot \underset{\sim}{R}(t)$

Taking averages and using the equipartition theorem,

$\frac{d^2}{dt^2}\left\langle |\underset{\sim}{r}(t)|^2 \right\rangle + \xi \frac{d}{dt}\left\langle |\underset{\sim}{r}(t)|^2 \right\rangle = 6 k_B T / m$

The general solution to this second order differential equation is

$\left\langle |r(t)|^2 \right\rangle = 6 k_B T\, t / m + C_1 + C_2 e^{-\xi t}$

Using the boundary conditions $\left\langle |\underset{\sim}{r}(0)|^2 \right\rangle = 0$ and $\frac{d}{dt}\left\langle |\underset{\sim}{r}(0)|^2 \right\rangle = 2\left\langle \underset{\sim}{r}(0) \cdot \underset{\sim}{u}(0) \right\rangle = 0$, we have

$\left\langle |\underset{\sim}{r}(t)|^2 \right\rangle = 6 k_B T / m (1 + \frac{1}{\xi} + \frac{1}{\xi} e^{-\xi t})$

For short times, $\xi t << 1$ and the solution becomes

$\left\langle |\underset{\sim}{r}(t)|^2 \right\rangle \approx 3 k_B T / m \; t^2 = \left\langle \underset{\sim}{u}^2 \right\rangle t^2$

This is like the behaviour of a free particle or a newton (newtonian particle)

For large times, $\xi t >> 1$ and

$\left\langle |\underset{\sim}{r}(t)|^2 \right\rangle \approx (6 k_B T / \xi m)\; t = 6Dt$

$D = k_B T / \xi$

This is diffusive behaviour, with the mean square displacement being proportional to t.

5.3.1 Diffusion coefficient

Consider the velocity autocorrelation function Z(t) defined as

$Z(t) = <u_x(t)\, u_x(0)> = 1/3 <\vec{u}(t) \cdot \vec{u}(0)>$

At t = 0, its value is u^2 averaged, which by equipartition theorem equals $3k_BT/m$. At $t \to \infty$, the value of u at a later time is uncorrelated with its value at initial tiem and Z(t) is expected to go to zero. At intermediate times, the extent of correlation is measured by the average of the projection of u(t) on its initial value u(0).We already know that the Einstein's relation can be derived from the Langevin equation

$D = \lim_{t \to \infty} \frac{1}{6t} <|\vec{r}(t) - \vec{r}(0)|^2>$

Let us obtain this in terms of Z(t). First express r(t) – r(0) in terms of velocities.

$$\vec{r}(t) - \vec{r}(0) = \int_0^t \vec{u}(t')\, dt'$$

Squaring and averaging this over the initial conditions, we have

$$<|\vec{r}(t)-\vec{r}(0)|^2>=\int_0^t dt' \int_0^t <\vec{u}(t'')\cdot\vec{u}(t')>dt''$$

The average on the right hand side is invariant under time reversal as well as the origin of time. It can therefore written in terms of the velocity autocorrelation function.

$$<|\vec{r}(t)-\vec{r}(0)|^2>=6Dt=2t\int_0^t d\tau\left(1-\frac{\tau}{t}\right)<\vec{u}(0)\cdot\vec{u}(\tau)>$$

where the integration over t' is carried out as the integral is independent over one variable t' and the substitution is made by setting τ = t''- t'. We finally get, by taking the large t limit,

$$D=\int_0^\infty Z(s)\,ds$$

5.4 The Chandrasekhar Equation

The Chapmann Kolmogorov equation when the transition probability depends on both $\Delta\vec{r}$ and $\Delta\vec{p}$ is given by

$$W(\vec{r},\vec{u},t+\Delta t)=\iint W(\vec{r}-\Delta\vec{r},\vec{u}-\Delta\vec{u},t)\ \psi(\vec{r}-\Delta\vec{r},\vec{u}-\Delta\vec{u};\Delta\vec{r},\Delta\vec{u})\ d(\Delta\vec{r})\ d(\Delta\vec{u})\ (5.111)$$

This is the basic equation for a Markov process in phase space. According to this, the value of W at rime $\vec{r},\vec{u},\ t+\Delta t$ is determined by its value at $\vec{r}-\Delta\vec{r},\vec{u}-\Delta\vec{u},t$ and the transition probability that depends only on $\Delta\vec{r}$ and $\Delta\vec{u}$. There is no dependence on times earlier that *t*, i.e., all the earlier memory of events has no role to play. There is only minimal dependence on the events at time t. The other extremes are the fully random processes like tossing a coin (which has no dependence on any past events) and a fully deterministic process such as the classical planetary motion which is completely determined by the initial conditions at the most distant past. To obtain a differential equation, let us expand W and ψ in Taylor series.

One integration in the above equation can be reduced by noting (from the Langevin equation) that

$\Delta\vec{r}=\vec{u}\,\Delta t,\ \Delta\vec{u}=-(\xi\,\vec{u}-\vec{K})\ \Delta t+\vec{A}\,\Delta t$

Where K is the external force per unit mass and A is the random force per unit mass (in place of X and R) taken from the Langevin equation. The transition probability can therefore be written as

$$\psi(\vec{r},\,\vec{u};\,\Delta\vec{r},\,\Delta\vec{u})\ =\ \psi(\vec{r},\,\vec{u};\,\Delta\vec{u})\ \ \delta(\Delta\vec{r}-\vec{u}\ \Delta t)$$

The integration over $\Delta\vec{r}$ can be easily using the above delta function to get

$$W(\vec{r}+\vec{u}\Delta t,\,\vec{u},t+\Delta t)=\iint W(\vec{r},\,\vec{u}-\Delta\vec{u},t)\ \ \psi(\vec{r},\,\vec{u}-\Delta\vec{u};\,\Delta\vec{u})\ \ d(\Delta\vec{u})$$

$$W(\vec{r}+\vec{u}\,\Delta t,\vec{u},t+\Delta t)=W(\vec{r},\vec{u},t)+\left[\ \frac{\partial W}{\partial t}+\vec{u}\cdot\nabla_{\vec{r}}W\ \right]\Delta t+O(\Delta t^2)=$$

$$\int d(\Delta\vec{u}) \ \left[W(\vec{r},\vec{u},t) - \sum_j \frac{\partial W}{\partial u_j}\Delta u_j + \frac{1}{2}\sum_j \frac{\partial^2 W}{\partial u_j^2}\Delta u_j^2 + \sum_{i<j}\frac{\partial^2 W}{\partial u_i \partial u_j}\Delta u_i \ \Delta u_j \ldots \ \right]$$

$$\times \left[\psi(\vec{u},\Delta\vec{u}) - \sum_i \frac{\partial \psi}{\partial u_i}\Delta u_i + \frac{1}{2}\sum_i \frac{\partial^2 \psi}{\partial u_i^2}\Delta u_i^2 + \sum_{i<j}\frac{\partial^2 \psi}{\partial u_i \partial u_j}\Delta u_i \ \Delta u_j \ldots \ \right]$$

The two terms in the brackets on the right hand side can be multiplied through and the terms involving the Δu_j s can be averaged over the transition probability ψ as follows.

$$\left[\ \frac{\partial W}{\partial t} + \vec{u}\cdot\nabla_{\vec{r}} W \ \right]\Delta t + O(\Delta t^2) =$$

$$\sum_j \frac{\partial}{\partial u_j}(W < \Delta u_j >) \ + \ \frac{1}{2}\sum_j \frac{\partial^2}{\partial u_j^2}(W < \Delta u_j^2 >) \ + \ \sum_{i<j}\frac{\partial^2}{\partial u_i \partial u_j}(W < \Delta u_i \ \Delta u_j >) \ldots \ ]$$

Here the averages are defined as

$$< \Delta u_i > = \int_{-\infty}^{\infty} \Delta u_i \ \ \psi(\vec{u};\, \Delta\vec{u})\, d(\Delta\vec{u})$$

$$< \Delta u_i^2 > = \int_{-\infty}^{\infty} \Delta u_i^2 \ \ \psi(\vec{u};\, \Delta\vec{u})\, d(\Delta\vec{u})$$

$$< \Delta u_i \, \Delta u_j > = \int_{-\infty}^{\infty} \Delta u_i \, \Delta u_j \ \ \psi(\vec{u};\, \Delta\vec{u})\, d(\Delta\vec{u})$$

These averages can be easily worked out to obtain

$$< \Delta u_j > = -(\ \xi u_j - K_j)\Delta t + \ldots \qquad < \Delta u_j^2 > = \frac{2\ \xi\, KT}{m}\Delta t + \ldots$$

$< \Delta u_i \, \Delta u_j > = 0$; when $i \neq j$

The last equation follows from the requirement that different components the random force are uncorrelated. Substituting the above, we get the Chandrasekhar equation

$$\frac{\partial W}{\partial t} + \vec{u}\cdot\nabla_{\vec{r}} W + \vec{K}\cdot\nabla_{\vec{u}} W = \xi\, \nabla_{\vec{u}}\cdot\left(W\vec{u}\right) + \frac{\xi\, kT}{m}\nabla_{\vec{u}}^2 W$$

The left hand side is the same as that of the Liouville or the Boltzmann equations. The right hand side is a stochastic representation of terms in phase space obtained through the Langevin equation. Alternatively, they can be obtained by suitable forms for the transition probability. When the $\nabla_{\vec{r}}$ and the $\vec{K}$ terms are not present, this reduces to the Fokker Planck equation which is the equivalent of the diffusion equation in momentum space.

We shall consider an important application of the Chandrasekhar equation to the calculation of the rate of escape of a particle over a large harmonic barrier. This was forst considered by Kramers.
The Chandrasekhar equation may be rewritten as

$$\frac{\partial W}{\partial t} = \xi(\nabla_{\vec{u}} - \frac{1}{\xi}\nabla_{\vec{r}})\cdot(W\vec{u} + \frac{kT}{m}\nabla_{\vec{u}} W - \frac{\vec{K}}{\xi}W + \frac{kT}{m\xi}\nabla_{\vec{r}} W) + \nabla_{\vec{r}}\cdot(\frac{kT}{\xi m}\nabla_{\vec{r}} W - \frac{\vec{K}}{\xi}W) \quad (5.222)$$

This equation may be integrated along a straight line on which $\vec{r} - \vec{u}/\xi = \vec{r}_0 =$ constant. The integral over the first term on the right is zero because of the first term in the parenthesis. We get

$$\frac{\partial}{\partial t}\int_{\vec{r}-\vec{u}/\xi=\vec{r}_0} W\, d\vec{u} = \int_{\vec{r}-\vec{u}/\xi=\vec{r}_0} \nabla_{\vec{r}}\cdot(\frac{kT}{\xi m}\nabla_{\vec{r}} W - \frac{\vec{K}}{\xi}W)\, d\vec{u}$$

If $\vec{K}(\vec{r})$ does not change appreciably over distances of the order $(kT/m\xi^2)^{1/2}$, $W(\vec{r},\vec{u},t)$ may be written as a Maxwellian for t $t \gg 1/\xi$ as

$$W(\vec{r},\vec{u},t) = [\ \frac{m}{2\pi kT})\ ]^{3/2}\ e^{-m|u^2|/2kT}\ w(\vec{r},t)$$

Substituting this in the above equation and carrying out the integration on the left hand side,

$$\frac{\partial w}{\partial t} = \nabla_{\vec{r}_0}\cdot\{\frac{kT}{\xi m}\nabla_{\vec{r}_0} w(\vec{r}_0) - \frac{\vec{K}(\vec{r}_0)}{\xi} w(\vec{r}_0)\}$$

The dominant contribution to the integral is from the range when $|u| \le (kT/m)^{1/2}$. The variation in $\vec{r} \sim \vec{u}/\xi \sim (kT/m\xi^2)^{1/2}$ in this range is small such that $\vec{K}$ and w are nearly unchanged and thus we can write

$$\frac{\partial w(\vec{r},t)}{\partial t} = \nabla_{\vec{r}}\cdot\{\frac{kT}{\xi m}\nabla_{\vec{r}} w(\vec{r},t) - \frac{\vec{K}(\vec{r})}{\xi} w(\vec{r},t)\} = -\nabla_{\vec{r}}\cdot\vec{j}$$

This is the well known Smoluchowsky equation written in terms of the diffusion current

$$\vec{j} = -\{\ \frac{kT}{\xi m}\nabla_{\vec{r}} w(\vec{r},t) - \frac{\vec{K}(\vec{r})}{\xi} w(\vec{r},t)\ \}$$

If the force term is derivable from a potential U as in $\vec{K} = -\nabla U$, then $\vec{j}$ can be written as

$$\vec{j} = -\frac{kT}{\xi m} e^{-\frac{mU}{kT}} \nabla_{\vec{r}}\{w(\vec{r},t)\, e^{\frac{mU}{kT}}\}$$

Integrating the current between any two points A and B, we get

$$\vec{j}\cdot\int_A^B e^{\frac{mU}{kT}}\, d\vec{s} = -\frac{kT}{m} w(\vec{r},t)\, e^{\frac{mU}{kT}}\ \Big|_A^B$$

This was first derived by Kramers. This formalism can be used to calculate the rate of escape of a particle over a barrier.

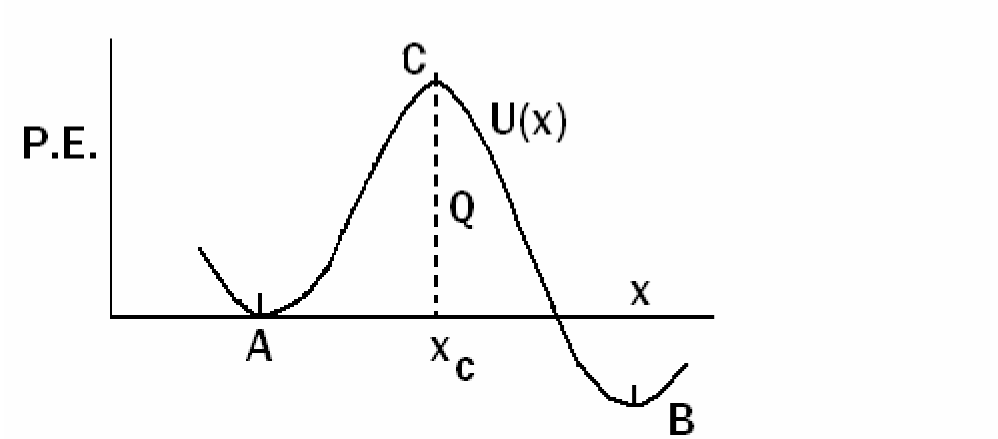

Figure 5.2 One dimensional potential energy barrier. The transition state corresponds to point C. The wells at A and at C are assumed to be harmonic. The height of the barrier is much larger that *kT*.

Consider the escape of a particle over a barrier U(x) in one dimension as shown in Fig. 5.2. Initially the particle is at A. The escape over the barrier is due to Brownian motion. Assume that mQ is much greater than kT. Maxwell Boltzmann distribution for the particle density as a function of x is accurate near A but not for all x, especially for values beyond point C. At C there will be no density initially, but it will frow at C due t o diffusion. For $t \gg \xi^{-1}$ and for constant value of ξ the above equation can be expressed as

$$j = \frac{kT}{m\xi} \frac{w(\vec{r},t)\, e^{\frac{mU}{kT}} \Big|_B^A}{\int_A^B e^{\frac{mU}{kT}}\, ds}$$

Assuming quasi stationary conditions, the number of particles near A is given by

$$d\nu_A = w_A e^{-mU/kT} dx$$

Assume that the potential is parabolic near A, i.e., $U(x) = \frac{1}{2}\omega_A^2 x^2$ near x = A = 0. Then,

$$\nu_A = w_A \int_{-\infty}^{\infty} e^{-m\omega_A^2 x^2/2kT} dx$$

Since most of contribution to the integral initially comes from x near zero, we get

$$\nu_A = \frac{w_A}{\omega_A}\left(\frac{2\pi kT}{m}\right)^{1/2}$$

Assuming the density at B to be initially small, *j* can be written as

$$j = \frac{kT}{m\xi} \frac{w_A}{\int_A^B e^{\frac{mU}{kT}}\, dx}$$

The rate of escape of a particle initially caught in the well A (over the barrier) is

$$P = \frac{j}{\nu_A} = \frac{\frac{w_A}{\xi}\left(\frac{kT}{2\pi m}\right)^{1/2}}{\int_A^B e^{\frac{mU}{kT}}\, dx}$$

Since we have $mQ \gg kT$, the main contribution to the integral above will come from U(x) near C. Assuming *U(x)* to have the following form (inverted parabola) near C,
$U(x) = Q - \frac{1}{2}\, \omega_C^2 (x - x_C)^2$
With ω_C as a constant referred to as the barrier frequency, we have

$$\int_A^B e^{\frac{mU}{kT}}\, dx \cong e^{mQ/kT} \int_A^B e^{\frac{-m\omega_C^2 (x-x_C)^2}{kT}}\, dx = e^{mQ/kT} \left(\frac{2\pi kT}{m\,\omega_C^2}\right)^{1/2}$$

The rate is now given by

$$P = \frac{\omega_A \omega_C}{2\pi\xi} e^{-mQ/kT}$$

Since $t \gg \xi^{-1}$, this relation is valid in the large friction limit. The above result is an improvement over Eyring's activated complex theory as there is no assumption of an equilibrium between the particles at A and at C and an explicit dynamical calculation is made.

For small values of friction, Kramers considered the one dimensional diffusion equation in phase space (the Chandrasekhar equation) which is

$$\frac{\partial W}{\partial t} + u\frac{\partial W}{\partial x} + K\frac{\partial W}{\partial u} = \xi u \frac{\partial W}{\partial u} + \xi W + \frac{\xi kT}{m}\frac{\partial^2 W}{\partial u^2}$$

where, $K = -\partial U / \partial x$.
To solve the above equation for *W*, Kramers wrote a trial solution of the form
$W(x,u) = C\, F(x,u)\, e^{-mu^2/2kT} e^{-mQ/kT}$
For *F(x,u)* = 1, the above *W* satisfies the diffusion equation for a constant C.
Since *F* is nearly equal to 1 near 0 and goes to zero for *x* much greater x_C, we require that
$F(x,u) = 1, \quad x = 0$
$F(x,u) = 0, \quad x \gg x_C$
We need to obtain an equation for *F* and finally obtain *j*, ν_A, and finally *P*. *F* is obtained at C by treating U as an inverted parabola as above. Kramers result for P is

$$P = e^{-mQ/kT} \frac{\omega_A}{2\pi\omega_C}[\,(\xi^2/4 + \omega_C^2)^{1/2} - \xi/2\,]$$

Note that as $\xi \to 0$, P reduces to the transition state theory result of $P = \frac{\omega_A}{2\pi} e^{-mQ/kT}$

Kramers result as well more recent results for rate as a function of friction are shown in the following graph. Kramers theory gives $k/k_{TST} = 1$ at zero friction whereas the recent theories give a value of $k/k_{TST} = 0$ even at zero friction. This has been rationalized by considering the diffusion of energy of the reactant in the product state. At zero friction, the product state is not stabilized and returns to the reactant state thereby reducing the rate constant.

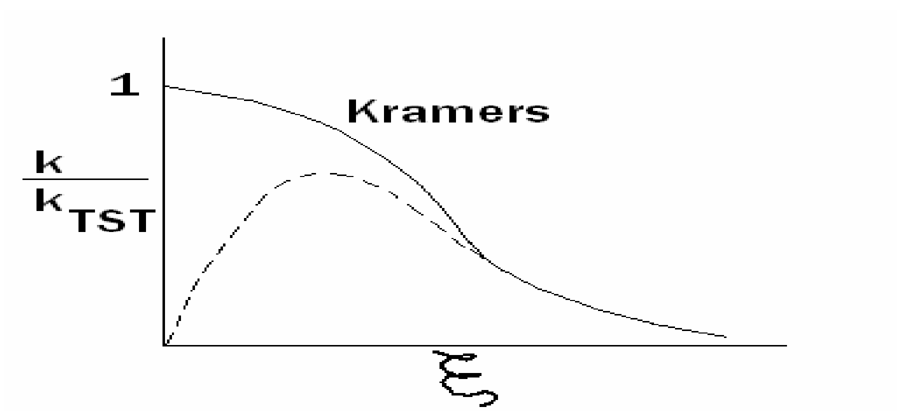

Figure 5.3 *k/k*$_{TST}$ versus the friction coefficient ξ. Thick line is the Kramers result and the dashed line is the more recent work.

5.5 Linear response Theory

It has been found that the early response of a system to weak fields is described very well by linear response theory. In fact, this response can be calculated in terms of the tiem correlation functions that describe the equilibrium system. Let the unperturbed hamiltonian be H_0 and H' be the perturbation which is switched at a given time.

$H = H_0 + H'$

A general way to describe the interaction is in terms of the coupling of the system to an external field $F(\vec{r},t)$ through coupling parameter A (for example, if F is an electric field, then A is the dipole moment)

$$H' = -\int A(\vec{r})F(\vec{r},t)\,d\vec{r}$$

If $F(\vec{r},t)$ is a single plane wave represented by $F_k\, e^{(i\vec{k}\cdot\vec{r}-\omega t)}$

$$H' = -A_k\, F_k e^{-i\omega t}$$

Where A_k is the Fourier transform of $A(\vec{r})$. For the present we consider a spatially homogeneous perturbation and the k or r dependence can be included later. To ensure that F(t) goes to zero as t → ∞, we include a -ε t in the exponent and set ε to zero at the end of the calculations. The perturbation now becomes,

$$H' = -A F_0 e^{-i(\omega + i\varepsilon)t}$$

To find out how a dynamical variable changes due to the perturbation, we find out the change in the phase space distribution function Δf and calculate the averages using this change. The change in *f* is given by the Liouville equation.

$$\frac{\partial f^N(t)}{\partial t} = -i L f^N(t) = \{H_0 + H', f^N(t)\} = \{H_0 - AF(t),\ f^N(t)\}$$
$$= -i L_0 f^N(t) - \{A, f^N(t)\} F(t)$$

Here, L_0 is the Liouville operator for the unperturbed Hamiltonian.
The initial state is the unperturbed state whose distribution function is given by

$$f^N(-\infty) = f_0^N(\vec{r}^N, \vec{p}^N) = \frac{1}{N!h^{3N}} \frac{e^{-\beta H_N(\vec{r}^N, \vec{p}^N)}}{Q_N(V,T)}$$

On the application of a weak field, the distribution function may be written as

$$f^N(t) = f_0^N + \Delta f^N(t)$$

Substituting this in the Liouville equation and retaining only the linear terms in the perturbation, we get,

$$\frac{\partial \Delta f^N(t)}{\partial t} = -i L_0 \Delta f^N(t) - \{A,\ f_0^N\} F(t)$$

The following solution to the above equation can be readily verified by differentiation.

$$\Delta f^N(t) = \int_{-\infty}^{t} e^{-i(t-s)L_0} \{A,\ f_0^N\} F(s)\, ds$$

This $\Delta f^N(t)$ can now be used to evaluate the changes in dynamical variables at time t.

$$< \Delta B(t) > = \iint \Delta f^N(t) B(\vec{r}^N, \vec{p}^N)\, d\vec{r}^N d\vec{p}^N$$

Substituting for $\Delta f^N(t)$, we get

$$= \iint d\vec{r}^N d\vec{p}^N \int_{-\infty}^{t} e^{-i(t-s)L_0} \{A,\ f_0^N\}\, B F(s)\, ds$$

$$= \iint d\vec{r}^N d\vec{p}^N \int_{-\infty}^{t} \{A,\ f_0^N\} e^{i(t-s)L_0} B F(s)\, ds$$

$$= \iint d\vec{r}^N d\vec{p}^N \int_{-\infty}^{t} \{A,\ f_0^N\}\, B(t-s) F(s)\, ds$$

Where we have used $B(t) = B(\vec{r}^N(t), \vec{p}^N(t)) = e^{-i L_0 t} B(\vec{r}^N, \vec{p}^N)$. We have also used the hermitian property of the product of operators.
Defining an after-effect function as

$$\Phi_{BA}(t) = -\iint \{A, f_0^N\}\, B(t)\, d\,\vec{r}^{\,N} d\,\vec{p}^{\,N}$$

the change in B is given by

$$< \Delta B(t) > = \int_{-\infty}^{t} \Phi_{BA}(t-s)\, F(s)\, ds$$

$\Phi_{BA}(t)$ is referred to as the after effect function. The change in B at time t is a superposition of the contributions of F(s) at all the earlier times. The after effect function is the response at time t to a delta function force applied at the initial time.
It is straight forward to show by using $\partial f_0^N / \partial \vec{p}_i = -\beta(\partial H_0^N / \partial \vec{p}_i) f_0^N$ that

$$\{A, f_0^N\} = -\beta(iL_0^N A) f_0^N = -\beta \dot{A} f_0^N$$

$$\Phi_{BA}(t) = \beta < B(t)\dot{A} > = -\beta < \dot{B}(t) A > = - < \{B(t), A\} >$$

This is the central result of linear response theory. In the quantum mechanical case, the Poisson bracket is replaced by $(-i/\hbar)[B(t), A]$
If the external field is frequency dependent as in $F_0\, e^{-i\omega t}$, then the response is given by

$$< \Delta B(t) > = \int_{-\infty}^{t} \Phi_{BA}(t-s)\, F_0\, e^{-i(\omega + i\varepsilon)s}\, ds$$

$$= F_0 e^{-i(\omega + i\varepsilon)t} \int_{-\infty}^{t} \Phi_{BA}(t-s)\; e^{-i(\omega + i\varepsilon)(s-t)}\, ds$$

$$= F_0 e^{-i(\omega + i\varepsilon)t} \int_{0}^{\infty} \Phi_{BA}(t)\; e^{i(\omega + i\varepsilon)t}\; dt$$

Now, taking the limit $\varepsilon \to 0+$, we get

$$< \Delta B(t) > = \chi_{BA}(\omega)\, F_0 e^{-i(\omega + i\varepsilon)t}$$

where, the complex dynamic susceptibility $\chi_{BA}(\omega)$ is defined as

$$\chi_{BA}(\omega) = \chi'_{BA}(\omega) + i\; \chi''_{BA}(\omega) = \lim_{\varepsilon \to 0+} \int_{0}^{\infty} \Phi_{BA}(t)\; e^{i(\omega + i\varepsilon)t}\; dt$$

The above response function can also be treated as Laplace transform of in the upper half of the complex plane (Im z > 0), i.e.,

$$\chi_{BA}(z) = \int_{0}^{\infty} \Phi_{BA}(t)\; e^{izt}\; dt$$

The details of linear response theory are taken up in chapter 12. Here, we give an elementary application of linear response theory to the calculation of a transport coefficient. If the external force is acting on a tagged particle 1, the force on this particle is F and the perturbation Hamiltonian is $H' = Fx_1\theta(t)$, where the step function $\theta(t)$ is equal to 1 only for positive times and zero for all negative times. This means that the force is applied at time 0. The average change in this particle's velocity is given by linear response theory as

$$< \Delta u_{1x}(t) > = \beta \int_{-\infty}^{t} < u_{1x}(t') \dot{x}_1 > F\, \theta(t')\, dt' = \beta F \int_{0}^{t} < u_{1x}(t')\, u_{1x}(t) > dt'$$

This immediately leads to the Einstein's relation for the mobility μ as follows.

$$\mu = \frac{D}{kT} = \lim_{t\to\infty} \beta \int_{0}^{t} < u_{1x}(t')\, u_{1x}(t) > dt'$$

This relates the fluctuation in the medium represented by D to the mobility which is the response of the system to a unit external field and this can be related to the dissipation in the system.

When a time dependent electric field $E(t)$ is applied to a system of N charged particles, the resulting charge current $e\,\vec{j}^{z}(t)$ ($z_i\, e$ is the charge on particle i) is given by

$$e\,\vec{j}^{z}(t) = \sum_{i=1}^{N} z_i\, e\, \dot{\vec{r}}_i(t)$$

The perturbation hamiltonian is given by

$$H'(t) = \sum_{i=1}^{N} z_i\, e\, \vec{r}_i(t) \cdot \vec{E}(t)$$

If the system is isotropic and the external field is applied in the x direction, then on averaging, only the x component of the current will survive. From the above expression in the linear response theory for a time dependent field is given by

$$e < j_x^{z}(t) > = \mathrm{Re}\ \sigma(\omega)\ E_0 e^{-i\omega t}$$

The frequency dependent electrical conductivity per unit volume is given by

$$\sigma(\omega) = \frac{\beta e}{V} \int_{0}^{\infty} < j_x^{z}(t) \sum_{i=1}^{N} z_i\, e\, \dot{x}_i(t) > e^{i\omega t}\, dt = \frac{\beta e^2}{V} \int_{0}^{\infty} < j_x^{z}(t)\, j_x^{z} > e^{i\omega t}\, dt$$

The term that is averaged is the total weighted (with the charge magnitudes) velocity autocorrelation function in the absence of the external field. This is a feature of linear response theory, that the transport coefficients are determined by the equilibrium autocorrelation functions. The zero frequency or the static electrical conductivity is given by

$$\sigma = \lim_{\omega\to 0} \sigma(\omega)$$

5.6 Space time Correlation functions

5.7 Projection Operator methods and Mode Coupling theories

5.8 Systems far from Equilibrium

5.9 Summary

In this chapter, the different techniques of statistical mechanics useful for studying nonequilibrium phenomena are outlined. Specific details are given in section 2 of this book. When detailed intermolecular forces are not known adequately, stochastic equations, beginning with the Langevin equation are very useful. With a good knowledge of intermolecular forces, linear response theory offers a good starting point. Currently, extensive progress is being made in studying problems wherein, the starting point of a system is far from equilibrium and linear response theory is not appropriate

Problems

1) Verify the steps of the Langevin equation.
2) Verify the integral for D in terms of the velocity autocorrelation function.
3) Use appropriate forms for ψ to derive the Chandrasekhar equation and the Diffusion equation.
4) Study in detail the solution for the passage over an activation provided first by Kramers.