INSERT III.4

k_{jn} . We normalize the eigen vectors by requiring

$$\sum_j k_{jn} k_{jn} = 0 \ . \qquad \text{III. 22}$$

The eigen vectors are orthogonal.

PROOF:

Let λ_n and λ_m and $\underset{\sim}{k}_n$ and $\underset{\sim}{k}_m$ be two eigen values and the associated eigen vectors. Then from III. 21 we have

$$\sum_j \overline{r_i r_j} k_{jn} = \lambda_n k_{in} \qquad \text{III. 23}$$

$$\sum_j \overline{r_i r_j} k_{jm} = \lambda_m k_{im} \ . \qquad \text{III. 24}$$

Multiplying III. 23 by k_{im} and III. 24 by k_{in} and summing over i gives

$$\sum_{ij} \overline{r_i r_j} \ k_{im} k_{jm} = \lambda_n \sum_i k_{in} k_{im} = \lambda_m \sum_i k_{in} k_{im} \qquad \text{III. 25}$$

$$(\lambda_n - \lambda_m) \sum_i k_{in} k_{im} = 0 \ . \qquad \text{III. 26}$$

If $\lambda_n \neq \lambda_m$ then

$$\sum_i k_{in} k_{im} = 0 \ . \qquad \text{III. 27}$$

Thus

$$\sum_i k_{in} k_{im} = \delta_{nm} \ .$$

INSERT III. 5

We may expand any vector $\underset{\sim}{K}$ in terms of these eigen vectors.

For the $\underline{i}$th component

$$K_i = \sum_n \tilde{K}_n k_{in} \quad . \tag{III. 28}$$

Multiplying by k_{im} and summing over i gives

$$\tilde{K}_m = \sum_i K_i k_{im} \quad . \tag{III. 29}$$

Expanding $\underset{\sim}{k}$ in terms of $\underset{\sim}{k}_n$ the exponent in Equation (14) becomes

$$e^{-\underset{\sim}{k} \cdot \frac{\overline{\underset{\sim}{r}\underset{\sim}{r}}}{2} \cdot \underset{\sim}{k} N + i\underset{\sim}{k} \cdot \underset{\sim}{s}} = e^{-N \sum_m \lambda_m K_m^2 + i \sum_m s_m K_m} \quad . \tag{III. 30}$$

Complete the square

$$\exp\left\{ -\sum_m \left[N\lambda_m \left(K_m + \frac{is_m}{2n\lambda_m} \right)^2 + \frac{s_m^2}{4N\lambda_m} \right] \right\} \quad . \tag{III. 31}$$

Integrating over K_m gives

$$\prod_{m=1}^{N} \frac{1}{\sqrt{4\pi n \lambda_m}} \exp\left\{ -\frac{s_m^2}{4N\lambda_m} \right\} \quad . \tag{III. 32}$$

We may now convert back to the original set of coordinate axes by using III. 29

$$s_m = \sum_i s_i k_{im} \quad .$$

INSERT III. 6

Thus

$$P(\underset{\sim}{s}) = \prod_{m=1}^{N} \frac{1}{\sqrt{4\pi n \lambda_m}} \exp\left\{ - \frac{\sum_{ij} s_i s_j k_{im} k_{jm}}{4N \lambda_m} \right\} . \qquad \text{III. 33}$$

INSERT IV.1

Alternate Derivation of the Fokker Planck Equation

Let $P(x,t)$ be the probability of finding x in dx centered at x at time t and let $P(x \mid \xi, \Delta t)$ be the probability that x changes by ξ in time Δt (we assume it is independent of t). Then $P(x, t+\Delta t)$, Δt small, is given by

$$P(x, t+\Delta t) = \int_{-\infty}^{\infty} P(x-\xi, t)\, P(x-\xi \mid \xi, \Delta t)\, d\xi \quad . \qquad \text{(IV.1)}$$

Since Δt is to be small the probability of ξ being large compared to the scale (width in x) of P should be vanishingly small. We shall also assume that $P(x \mid \xi, \Delta t)$ is a slowly varying function of x compared to its variation with ξ. We can then expand (IV.1) and thus obtain

$$P(x, t+\Delta t) = \int_{-\infty}^{\infty} \Big[P(x,t)\, P(x \mid \xi, \Delta t) - \xi \frac{\partial}{\partial x} P(x,t)\, P(x \mid \xi, \Delta t) + \frac{\xi^2}{2} \frac{\partial^2}{\partial x^2} P(x,t)\, P(x \mid \xi, \Delta t) \Big]\, d\xi \qquad \text{(IV.2)}$$

We may take the x derivatives outside the integral to obtain

$$P(x, t+\Delta t) = P(x,t) - \frac{\partial}{\partial x} \overline{\xi(x, \Delta t)}\, P(x,t) + \frac{1}{2}\frac{\partial^2}{\partial x^2} \overline{\xi^2(x, \Delta t)}\, P(x,t) \qquad \text{(IV.3)}$$

where

$$\overline{\xi(x, \Delta t)} = \int \xi\, P(x \mid \xi, \Delta t)\, d\xi \qquad \text{(IV.4)}$$

and

$$\overline{\xi^2(x, \Delta t)} = \int \xi^2 P(x \mid \xi, \Delta t)\, d\xi \quad . \qquad \text{(IV.5)}$$

INSERT IV. 2

Now $\overline{\xi(x,\Delta t)}$ is the mean change in x during the time Δt. We shall take it to be proportional to Δt and write

$$\overline{\xi(x,\Delta t)} = A(x)\Delta t \; . \qquad \text{(IV. 6)}$$

Likewise, $\overline{\xi^2(x,\Delta t)}$ is the mean square of the spread in x after Δt. If we have a diffusion like behavior then this will also be proportional to Δt. Thus we write

$$\overline{\xi^2(x,\Delta t)} = B(x)\Delta t \; . \qquad \text{(IV. 7)}$$

Equation (IV. 3) then becomes

$$\frac{P(x,t+\Delta t) - P(x,t)}{\Delta t} = -\frac{\partial}{\partial x} A(x)\, P(x,t) + \frac{1}{2}\frac{\partial^2}{\partial x^2} B(x)\, P(x,t) \; . \qquad \text{(IV. 8)}$$

Taking Δt to be small (ideally passing to the limit of Δt equals zero) we write equation (IV. 8) in the form

$$\frac{\partial P(x,t)}{\partial t} + \frac{\partial}{\partial x} A(x)\, P(x,t) - \frac{1}{2}\frac{\partial^2}{\partial x^2} B(x)\, P(x,t) = 0 \; . \qquad \text{(IV. 9)}$$

The above derivation may be generalized to the case of x being a vector with components $x_1, x_2, \ldots, x_n$. In this case we find

$$\frac{\partial P(\underset{\sim}{x},t)}{\partial t} + \sum_i \frac{\partial}{\partial x_i} A_i(\underset{\sim}{x}) P(\underset{\sim}{x},t) - \frac{1}{2}\sum_{ij} \frac{\partial}{\partial x_i}\frac{\partial}{\partial x_j} B_{ij}(\underset{\sim}{x})\, P(\underset{\sim}{x},t) = 0 \qquad \text{(IV. 10)}$$

where

$$A_i(\underset{\sim}{x})\Delta t = \int \xi_i \, p(\underset{\sim}{x} \,|\, \underset{\sim}{\xi}, \Delta t)\, d\underset{\sim}{\xi} \qquad \text{(IV. 11)}$$

INSERT IV.3

$$B_{ij}(\underset{\sim}{x})\Delta t = \iint \xi_i \xi_j p(\underset{\sim}{x} | \underset{\sim}{\xi}, \Delta t)\, d\underset{\sim}{\xi} \quad . \tag{IV.12}$$

Here i and j refer to the ith and jth components of the vector x .

INSERT VI.1

Generalized Nyquist Theorem

We have just derived Nyquist theorem for voltage fluctuations in a resistor and a continuous conductor. We will now obtain a generalized version of this theorem for an arbitrary system and an arbitrary fluctuating quantity. Let us consider that we have a system whose Hamiltonian is given by H_o . Consider a quantity A which is a function of the position and momentia of the system. For example, it might be the dipole moment of the system, the current flowing in the system, the amplitude of the kth Fourier decomposition of the density or the current or any one of a number of other things. We assume the average value of A in thermal equilibrium is zero. Next, let us imagine that we have a harmonic oscillator of frequency ω_o whose Hamiltonian is given by H_{os}

$$H_{os} = \frac{P^2}{2M} + \frac{K r^2}{2} , \quad \omega_o^2 = \frac{K}{M} \tag{1}$$

where M is the oscillator's mass, K is the spring constant, P is the momentum associated with the oscillator, and r is the position or q coordinate. We now further imagine that we weakly couple the oscillator to the system under investigation through the quantity A and that the interaction Hamiltonian is given by ($A(q_1, \cdots q_N)$, q's are the coordinates of the particles in the system of interest, the p's could also be involved)

$$H_1 = A r \tag{2}$$

The Hamiltonian for the combined system is

$$H = H_o + H_{os} + A r = H_o + \frac{P^2}{2M} + \frac{K r^2}{2} + A r \tag{3}$$

INSERT VI. 2

The equations of motion of the oscillator are

$$\dot{r} = \frac{\partial H}{\partial p} = \frac{p}{M} \tag{4}$$

$$-\dot{p} = \frac{\partial H}{\partial r} = kr + A \tag{5}$$

or

$$M\ddot{r} = -kr - A \tag{6}$$

Now since the coupling of the oscillator to the system is to be weak, we assume that the system makes a systematic linear response to the motion of the oscillator

$$A(\omega) = \chi(\omega)\, r(\omega) \tag{7}$$

(In the end, we shall let the mass of the oscillator and its spring constant go to ∞ so as to keep ω_0 fixed; then its amplitude will go to zero, $\overline{r^2} = \overline{\frac{kT}{k}}$, and hence the coupling Ar will go to zero.) Finally, we assume that A is also driven by the random motion of the particles of the system, and we represent this by adding a random generator force to (7) to find the actual

$$A(\omega) = \chi(\omega)\, r(\omega) + a_g(\omega) \tag{8}$$

From equation (6), we have

$$M(\omega^2 - \omega_0^2)\, r(\omega) = A(\omega) \tag{9}$$

Substituting into (8) gives

$$M\left[(\omega^2 - \omega_0^2) - \frac{\chi(\omega)}{M}\right] r(\omega) = a_g(\omega) \tag{10}$$

INSERT VI.3

or

$$M\, r(\omega) = \frac{a_g(\omega)}{\left[(\omega^2 - \omega_0^2) - \frac{\chi(\omega)}{M}\right]} \tag{11}$$

The mean kinetic energy of the oscillator is given by

$$\langle K.E.\rangle = -\frac{M}{2\times 2\pi T}\int_{-T/2}^{T/2} dt \int_{-\infty}^{\infty}\int_{-\infty}^{\infty} \omega\omega'\, r(\omega)\, r(\omega')\, e^{i(\omega+\omega')t}\, d\omega\, d\omega'$$

$$= \frac{2\pi M}{2\times 2\pi T}\int_{-\infty}^{\infty} \omega^2\, |r(\omega)|^2\, d\omega$$

$$= \frac{1}{2TM}\int_{-\infty}^{\infty} \frac{\omega^2\, |a_g(\omega)|^2\, d\omega}{\left[(\omega-\omega_0)(\omega+\omega_0) - \frac{\chi(\omega)}{M}\right]\left[(\omega-\omega_0)(\omega+\omega_0) - \frac{\chi^*(\omega)}{M}\right]} \tag{12}$$

Now the only important part of χ is its imaginary part; the real part simply shifts the frequency slightly off of $\pm\omega_0$. Let the imaginary part of χ be χ_i. We may approximate (12) by

$$\langle K.E.\rangle = \frac{1}{2TM}\int_{-\infty}^{\infty} \frac{\omega^2\, |a_g(\omega)|^2\, d\omega}{\left[\omega-\omega_0 - \frac{i\chi_i}{2\omega_0 M}\right]\left[\omega+\omega_0 + \frac{i\chi_i}{2\omega_0 M}\right]\left[\omega-\omega_0 + \frac{i\chi_i}{2\omega_0 M}\right]\left[\omega+\omega_0 - \frac{i\chi_i}{2\omega_0}\right]}$$

$$= \frac{1}{2TM}\, \omega_0^2\, |a_g(\omega_0)|^2\, 2\pi i \left[\frac{2}{\frac{8 i \chi_i \omega_0^2}{2\omega_0 M}}\right]$$

$$= \frac{\pi}{2T}\, \frac{\omega_0\, |a_g(\omega_0)|^2}{\chi_i} = \frac{\Theta}{2} \tag{13}$$

INSERT VI.4

or $$G_{a_g}(\omega) = \frac{2\Theta}{\pi} \, \frac{\operatorname{Im} X(\omega)}{\omega}$$

If the system is uncoupled from the oscillator, then by (8) we have

$$A(\omega) = a_g(\omega)$$

or

$$G_A(\omega) = \frac{2}{T} \overline{|A(\omega)|^2} = \frac{2\Theta}{\pi} \, \frac{\operatorname{Im} X(\omega)}{\omega} \tag{14}$$

If we wish to take account of spatial fluctuations as well as time fluctuations, we must Fourier analyze in both time and space. We may proceed as we did for the case of the voltage fluctuations in a continuous conductor. In that case, we consider the system in a large cubical box of size L^3, consider each Fourier mode as a degree of freedom, and proceed as before. We then obtain

$$G_A(\underline{k}, \omega)\, d^3k \, d\omega = \frac{4\Theta}{(2\pi)^4} \, \frac{\operatorname{Im}}{\omega} [X(\underline{k}, \omega)] \quad d^3k \, d\omega \tag{15}$$

Review of Formula for Longitudinal Fields

$$G_E(\underline{k}, \omega) = \frac{4\Theta}{(2\pi)^4} \left(\frac{4\pi}{\omega} \operatorname{Im} \frac{1}{\epsilon} \right) = \frac{4\Theta}{(2\pi)^4} \, \frac{4\pi}{\omega} \, \frac{\operatorname{Im} \epsilon}{\epsilon \epsilon^*}$$

$$G_{E_g}(\underline{k}, \omega) = \frac{\omega^2 |Z|^2}{(4\pi)^2} G_E$$

with $\quad \Theta = kT$

and $\quad \epsilon = \frac{1}{1 + 4\pi i/\omega Z(k, \omega)} \qquad \operatorname{Im} \frac{1}{\epsilon} = \frac{4\pi \operatorname{Re} Z}{\omega Z Z^*}$

$$G_{J_r}(\underline{k},\omega) = \frac{\omega^2}{(4\pi)^2} |\epsilon|^2 G_E(\underline{k},\omega) = \frac{|\epsilon|^2}{|Z|^2} G_{E_g}(\underline{k},\omega)$$

$$G_J(\underline{k},\omega) = \frac{G_{J_r}(\underline{k},\omega)}{|\epsilon|^2}$$

$$\frac{\partial E_r}{\partial t} + 4\pi \bar{J}_r = 0$$

$$i\omega E_r + 4\pi \bar{J}_r = 0$$

$$G_E(\underline{k},\omega) = G_{E_1} / |\epsilon|^2$$

For the General Case

$$H_1 = A r$$

$$\bar{A} = X r$$

$$G_A(\omega) = \frac{4\Theta}{2\pi\omega} \operatorname{Im} X(\omega)$$

For Space and Time Fluctuations

$$G_A(\underline{k},\omega)\, d^3k\, d\omega = \frac{4\Theta}{(2\pi)^4 \omega} \operatorname{Im}\left[X(\underline{k},\omega)\right] d^3k\, d\omega .$$

Occurrence of Fluctuations and Recurrence Times

Among the more interesting problems of statistical mechanics are those involved with how long we should have to wait to observe a fluctuation of a certain size. We can find the answer to such questions for some simple cases from the Fokker Planck equation.

To begin with, consider the following simple example. Suppose we have an ensemble of systems which are all one-dimensional of length $2L$ and each of which contains one Brownian ~~Browman~~ particle. Suppose initially the particles are distributed uniformly at random between 0 and $2L$, e.g.,

$$P(x)dx = \frac{dx}{2L} \quad . \tag{257}$$

Let us ask how long must we wait on the average before we find the particle for the first time in a little element of volume Δx at the center of the system. The method of finding this time is the following. We remove a system from the ensemble the instant its Brownian particle enters the observed volume and record the time. We continue doing this until there are no more systems in the ensemble (this of course takes an infinite length of time) and find the average time at which the system left the ensemble.

Now $P(x)dx$ tells us the fraction of the systems which have their Brownian particle in dx at x . Further the Fokker Planck equation governs the time evolution of $P(x)$. In this case it is just the

the Diffusion equation since we are asking no questions about the velocity and we neglect microtime effects.

$$\frac{\partial}{\partial t} P(x,t) - \frac{1}{2} D \frac{\partial^2}{\partial x^2} P(x,t) = 0 \tag{258}$$

The initial conditions require that initially $P(x,0)$ is $1/2L$ for all x. Every time a particle enters the little volume Δx we remove its system from the ensemble. Thus P is 0 for x in Δx. This gives the boundary condition that $P = 0$ at $x = \pm \Delta x/2$. If Δx is very small we can essentially replace this with the boundary condition $P = 0$ at $x = 0$. Further by symmetry we need only consider the half of the system from 0 to L. Finally, we do not allow particles to cross the point $x = L$ so that $P(x) = 0$ for $x > L$. No systems are added or removed with particles at $x = L$ so that we have the boundary condition

$$\left.\frac{\partial P}{\partial x}\right|_{x=L} = 0 \tag{259}$$

The Diffusion equation separates and we may write

$$P(x,t) = T(t)\, X(x) \tag{260}$$

Substituting in (258) gives

$$\frac{T'}{T} - \frac{D}{2} \frac{X''}{X} = 0 \tag{261}$$

from which we find

$$X'' = -k^2 X \tag{262}$$

$$X = X_k \begin{Bmatrix} \sin & kx \\ \cos & kx \end{Bmatrix} \tag{263}$$

$$T' = -\frac{D k^2}{2} T \tag{264}$$

$$T = \exp\left\{-\frac{Dk^2}{2} t\right\} . \tag{265}$$

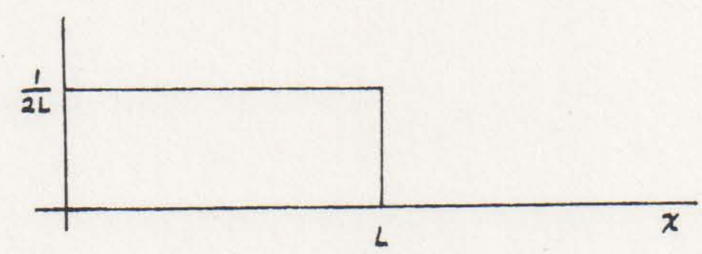
The boundary conditions $P = 0$ at $x = 0$ means we take only the sin solution while the boundary condition $\frac{\partial P}{\partial x} = 0$ at $x = L$ restricts k to the values

$$L k = (n + 1/2)\pi . \tag{266}$$

Thus

$$P(x,t) = X_n \sin\left(\frac{2n+1}{2L}\right)\pi x \exp\left\{-\frac{D(2n+1)^2 t}{8L^2}\right\} \tag{267}$$

Initially P has the form



Solving for x_n we have

$$X_n = \frac{2}{L}\int_0^L \frac{1}{2L} \sin\left(\frac{2n+1}{2L}\right)\pi x \; dx \tag{268}$$

$$= \frac{1}{L^2} \frac{2L}{(2n+1)\pi} = \frac{1}{L} \frac{2}{(2n+1)\pi}$$

$$P(x,t) = \sum_{n=0}^{\infty} \frac{2}{L(2n+1)\pi} \sin \frac{(2n+1)}{2}\frac{x\pi}{L} \exp\left\{\frac{-D(2n+1)^2\pi^2 t}{8L^2}\right\} \tag{269}$$

The fraction of systems left at time t is

$$f = 2\int P(x,t)dx = \sum_{n=0}^{\infty} \frac{8}{(2n+1)^2\pi^2} \exp\left\{-\frac{D\pi^2(2n+1)^2 t}{8L^2}\right\} \tag{270}$$

For finite t the terms of this series decrease rapidly with n so that we can approximate the series by the first term.

$$f(t) \cong \frac{8}{\pi^2} \exp\left\{\frac{-D\pi^2}{8L^2} t\right\} \tag{271}$$

The fraction of the systems having in dt is

$$df = \frac{D}{L^2} \exp\left\{-\frac{D\pi^2}{8L^2} t\right\} dt \tag{272}$$

The average time of leaving is

$$\bar{t} = \int t\, df = \int_0^{\infty} \frac{Dt}{L^2} \exp\left\{\frac{-D\pi^2}{8L^2} t\right\} dt$$

$$= \frac{D}{L^2}\left\{-\frac{d}{d\beta}\int_0^{\infty} e^{-\beta t}\, dt\right\} \quad ; \quad \beta = \frac{D\pi^2}{8L^2} \tag{273}$$

$$= \frac{D}{L^2}\frac{1}{\beta^2} = \frac{64 L^2}{\pi^4 D}$$

$\bar{t}$ is essentially the time it takes for a particle to diffuse the length of the system.

The mean square time of leaving is

$$\overline{t^2} = \int t^2 dt = \frac{D}{L^2} \frac{d^2}{d\beta^2} \int e^{-\beta t} dt \tag{274}$$

$$\overline{t^2} = \frac{D}{L^2} \frac{2}{\beta^3} = \frac{2D}{L^2} \frac{\delta^3 L^6}{\pi^6 D^3} = \frac{2\times\delta^3}{\pi^6} \frac{L^4}{D^2} \tag{275}$$

$$\overline{t^2} - \bar{t}^2 = \frac{L^4}{D^2}\left\{\frac{2\times\delta^3}{\pi^6} - \frac{\delta^4}{\pi^8}\right\} = \frac{\delta^3 L^4}{\pi^6 D^2}\left\{2 - \frac{\delta}{\pi^2}\right\}. \tag{276}$$

We see from this that the deviations from the mean are of the order of the mean. This is a reflection of the fact that there is no peak in the time of leaving. We can make no accurate prediction about when a system will leave the ensemble. The error in the predicted time will be of the order of the predicted time. Thus we can make no accurate prediction about when the particle will enter the little volume.

Fluctuations in Systems Containing Many Brownian Particles

We now consider the problem of N one-dimensional Brownian particles. We imagine they are all independent of each other. We wish to know how long we must wait to find them all in a little element of volume Δx at the center of the system.

The state of any member of an ensemble of systems is given by giving the positions of all N particles in it, $x_1, \cdots, x_N$. This is a point in an N dimensional space. Let $P(x_1, \cdots, x_N, t)$ be the fractional number of systems lying in $dx_1 \, dx_2, \ldots, dx_N$ at time t . P satisfies a Fokker Planck equation which is simply a diffusion equation in N dimensions since the particles are independent.

$$\frac{\partial P}{\partial t}(x_1,\ldots,x_n,t) - \frac{D}{2}\sum_i \frac{\partial^2}{\partial x_i^2} P(x_1,\ldots,x_n,t) = 0 \tag{277}$$

We may again separate variables. We write

$$P = T(t)\, X(x_1,\ldots,x_n) \tag{278}$$

We have

$$\frac{T^1}{T} = \frac{D}{2}\frac{\nabla_n^2 X}{X} \tag{279}$$

$$T = e^{-t/\tau} \tag{280}$$

$$\frac{D}{2}\nabla_n^2 X + \frac{X}{\tau} = 0 \tag{281}$$

Again all systems are removed from the ensemble when they enter the little N dimensional cube of size Δx at the origin. Thus we must solve this equation subject to the boundary conditions

$$X = 0$$

on the surface of an N dimensional cube of dimensions Δx-centered at the origin and $\nabla X = 0$ on the surface of an N dimensional cube with side L centered at the origin. These boundary conditions make this problem very difficult to solve. However, we are not so interested in an exact solution as we are in the general behavior of the solution. We shall therefore employ a variational technique to obtain an approximate solution. First we will give a short derivation of the variational equation.

Let X_1, τ_1 and X_2, τ_2 be two solutions and the associated τ's to (281). Then

$$\int X_1 X_2 \, d^n x = 0 \qquad 1 \neq 2 \tag{282}$$

Proof

Multiplying the X_1 equation by X_2 and the X_2 equation by X_1 and subtracting gives

$$\frac{D}{2}\left(X_2 \nabla_n^2 X_1 - X_1 \nabla_n^2 X_2\right) + \left(\frac{1}{\tau_1} - \frac{1}{\tau_2}\right) X_1 X_2 = 0 \tag{283}$$

Integrating over all x space we have

$$\begin{aligned}\left(\frac{1}{\tau_1} - \frac{1}{\tau_2}\right)\int X_1 X_2 d^N x &= -\frac{D}{2}\int \left(X_2 \nabla_n^2 X_1 - X_1 \nabla_n^2 X_2\right) d^N x \\ &= -\frac{D}{2}\int \nabla_N \left(X_2 \nabla_N X_1 - X_1 \nabla_N X_2\right) d^N x = -\frac{D}{2}\int \vec{n} \cdot \left(X_2 \nabla_N X_1 - X_1 \nabla_N X_2\right) d^N x \\ &= 0.\end{aligned} \tag{284}$$

Here $\vec{n}$ is the normal to the surface and either X or ∇X vanish on the boundary surface. Thus if $\tau_1 \neq \tau_2$

$$\int X_1 X_2 d^N x = 0 \tag{285}$$

We will normalize X so that

$$\int X^2 d^N x = 1 \tag{286}$$

It is possible for $\tau_1 = \tau_2$ and X_1 not to be identical with X_2. Then one has degeneracy. We will assume this does not happen or that the X's can be chosen so as to satisfy these equations anyway.

Now let X be an arbitrary function of the x's which satisfies the boundary conditions. We assume that the functions which satisfy (281) form a complete set and we can expand X in terms of them.

$$X = \sum_i A_i X_i \tag{287}$$

We have from (281)

$$\frac{D}{2} \nabla_N^2 X = \sum_i \frac{A_i X_i}{-\tau_i} \tag{288}$$

Multiplying by X

$$\frac{D}{2} X \nabla_N^2 X = -\sum_{ij} \frac{A_i A_j X_i X_j}{\tau_i} \tag{289}$$

Integrating over all x's gives

$$\frac{D}{2}\int X \nabla_N^2 X d^N x = \frac{D}{2}\left\{\int \nabla_N (X \nabla_N X) d^N x - \int (\nabla_N X)^2 d^N x\right\}$$

$$= -\frac{D}{2}\int (\nabla_N X)^2 d^N_x = -\sum_i \frac{Ai^2}{\tau i} \tag{290}$$

$$\sum_i \frac{Ai^2}{\tau i} \geq \frac{1}{\tau_{max}} \sum_i A_i^2 = \frac{1}{\tau_{max}} \int X^2 d^N x \tag{291}$$

Thus

$$\frac{1}{\tau_{max}} \leq -\frac{\frac{D}{2}\int (\nabla X)^2 d^N_x}{\int x^2 \, d^N_x} = \frac{1}{\tau} \tag{292}$$

By choosing a trial function X with a number of adjustable parameters and adjusting them so as to minimize τ^{-1} we can obtain an approximation to τ_{max}. We are primarily interested in τ_{max} since it gives the slowest decaying mode and will primarily determine the length of time a system will remain in the ensemble.

For our problem we will choose for a trial function a function which is constant on the surface of concentric and parallel N dimensional cubes. The function we choose is

$$X = \left[1 - \left(\frac{\Delta x}{\ell}\right)^S\right] + \epsilon\left(1 - \left(\frac{\ell}{\Delta x}\right)\right) \tag{293}$$

where ℓ is the length of the side of the cube and S and ϵ are adjustable parameters. The reason for choosing the first term is that for a spherically symmetric problem with a sink at the origin imbedded in an ∞ medium the solution to the diffusion equation is of the form

$$1 - \left(\frac{r_o}{r}\right)^{N-2} \tag{294}$$

The last term is added so as to satisfy boundary conditions at ℓ equals L. ϵ will turn out to be very small

Taking the gradient of X gives

$$\nabla_N X = \vec{n}\,\frac{dX}{d\ell} = \left\{S\,\frac{\Delta x^S}{\ell^{S+1}} - \frac{\epsilon}{\Delta x}\right\}\vec{n} \tag{295}$$

Requiring $\nabla_N X = 0$ at $\ell = L$ gives

$$\epsilon = S \left(\frac{\Delta x}{L}\right)^{S+1} \quad . \tag{296}$$

Substituting in the equation for τ gives

$$\frac{1}{\tau} = \frac{D}{2} \frac{\int \left\{ S \frac{\Delta x^S}{\ell^{S+1}} - S \frac{\Delta x^S}{L^{S+1}} \right\} \cancel{N\ell}\ \ell^{N-1} d\ell}{\int \left\{ \left[1 - \left(\frac{\Delta x}{\ell}\right) \right]^S + S \left(\frac{\Delta x}{L}\right)^{S+1} \left[1 - \frac{\ell}{\Delta x} \right] \right\}^2 \cancel{N\ell}\ \ell^{N-1} d\ell} \tag{297}$$

$$\int_{\Delta x}^{L} S^2 \Delta x^{2S} \ell^{N-1-2S-2} - 2 S^2 \Delta x^{2D} \ell^{N-Z-S} L^{-S-1} + S^2 \Delta x^{2S} L^{-S-1} \ell^{N-1} \quad d\ell \tag{298}$$

$$\cong \frac{S^2 \Delta x^{2S}}{N-2S-2} \quad \Delta x^{N-2S-2}$$

Since if S is large as we will find it to be $L^S \gg \ell^S$ for almost all ℓ and Δx should be much smaller than L. The denominator approximately integrates to L^N/N

$$\frac{1}{\tau} \cong - \frac{DNS^2 \Delta x^{N-2}}{2 (N-2S-2) L^N} \tag{299}$$

$$\frac{d^1/\tau}{dS} = \frac{-D}{2} \frac{N \Delta x^{N-2}}{L^N} \left\{ \frac{2S}{N-2S-2} + \frac{2S^2}{(N-2S-2)^2} \right\} = 0 \tag{300}$$

$$S + N - 2S - 2 = 0 \tag{301}$$

$$S = N - 2 \tag{302}$$

$$\frac{1}{\tau_{max}} \cong \frac{D}{2} \frac{N(N-2)}{\Delta x^2} \left(\frac{\Delta x}{L}\right)^N \tag{303}$$

or

$$\tau_{max} \cong \left(\frac{L}{\Delta x}\right)^{N} \frac{2}{N(N-2)} \frac{\Delta x^2}{D} \tag{304}$$

This result has a simple interpretation. The surface area of the n-dimensional cube of side Δx is

$$= n\Delta x^{n-1} \tag{305}$$

The flow of systems across a surface is equal to the diffusion constant $D/2$ times the gradient of the density of systems times the area of the surface. The flux through the surface of a cube is

$$F = \frac{DdP}{2d\ell} N\ell^{N-1} \tag{306}$$

In order to have a quasi steady state in the vicinity of the cube the flux of systems across all surface must be the same so

$$\frac{dP}{d\ell} = C \frac{1}{\ell^{N-1}} \tag{307}$$

Integrating gives P

$$P = P\left(1 - \left(\frac{\Delta x}{\ell}\right)^{N-2}\right) \tag{308}$$

The Flux of systems into the little cube Δx is

$$F = \frac{D}{2} P(N-2)N \Delta x^{N-2} \tag{309}$$

The total number of systems is $N = P L^N$. We have

$$\frac{dN}{d\tau} = \frac{dP}{d\tau} L^N = -F = -\frac{D}{2} N(N-2)\Delta x^{N-2} P \qquad (310)$$

From this we find the same τ as before.

There is a second simple physical interpretation. The probability of finding all the particles in Δx is $(\Delta x/L)^N$. Now if all the particles are in Δx, then their density is $N/\Delta x$, and on the average there is a particle within $\Delta x/N$ of the boundary of the region of interest. A particle will diffuse out of the volume in roughly the time $(\Delta x/N)^2 \, 1/D$. When a particle leaves the little volume, then the state of having all the particles in the volume is destroyed. But for an equilibrium ensemble the number of systems entering a state must be equal to the number leaving. Thus the fraction of the number of systems entering the state with all the particles in Δx per unit time must be

$$\left(\frac{\Delta x}{L}\right)^N D\left(\frac{N}{\Delta x}\right)^2$$

or the time for one system to enter this state is

$$\left(\frac{L}{\Delta x}\right)^N \frac{1}{D}\left(\frac{\Delta x}{N}\right)^2$$

which agrees with what we just found.

Now let us ask how long do we have to wait to find K of the N particles in Δx. We shall use the idea just developed and compute the flux of systems into the volume specified by computing the surface area and the gradient.