First consider the case of finding the specific set of particles 1 through K and no others in the region ΔX. The N dimensional volume available to such a state is given by

$$V = \int_{-\frac{\Delta x}{2}}^{\frac{\Delta x}{2}} dx_1 \int_{-\frac{\Delta x}{2}}^{\frac{\Delta x}{2}} dx_2 \ldots \int_{-\frac{\Delta x}{2}}^{\frac{\Delta x}{2}} dx_k \int_{\substack{-\frac{\Delta x}{2} \\ -L/2}}^{\substack{L/2 \\ \frac{\Delta x}{2}}} dx_{k+1} \cdots \int_{\substack{-\frac{\Delta x}{2} \\ -\frac{L}{2}}}^{\substack{L/2 \\ \frac{\Delta x}{2}}} dx_N = \Delta x^k \, (L - \Delta x)^{N-k} \tag{311}$$

where $\int_{\substack{-\frac{\Delta x}{2} \\ L/2}}^{\substack{L/2 \\ \Delta x/2}}$ means the integral is to go from $-\Delta x/2$ to $-L/2$ and from $\Delta x/2$ to $L/2$.

This volume is a series of N dimensional rectangles. Examples are shown in the figures for two and three dimensions.

FIGURES

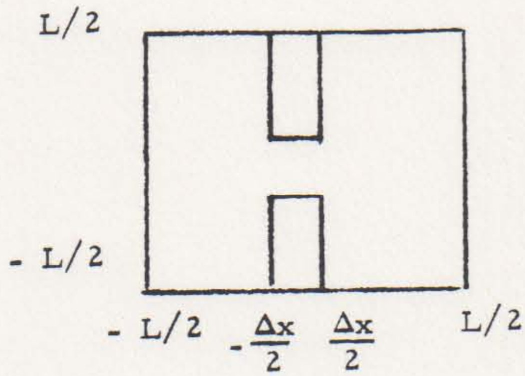


Fig. I.

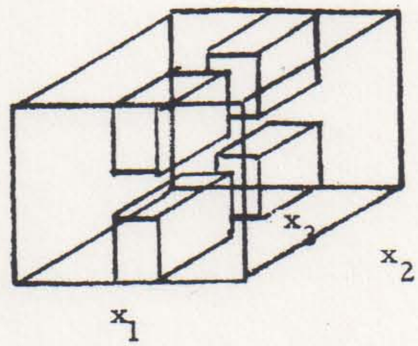


Fig. II.

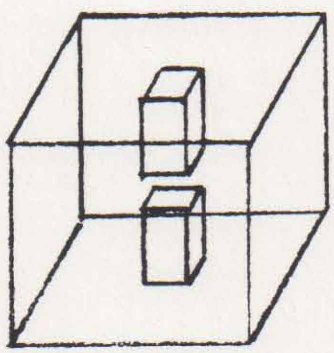


Fig. III.

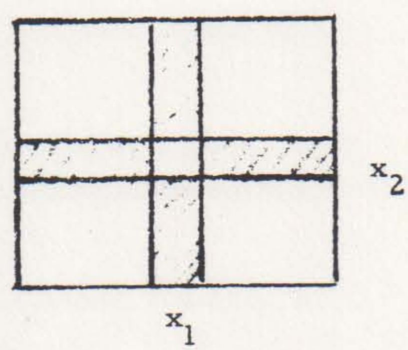


Fig. IV.

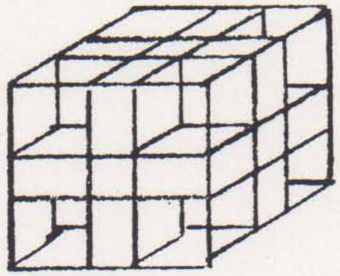


Fig. V.

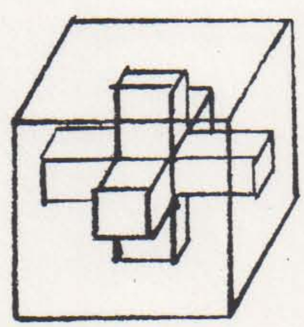


Fig. VI.

In the first figure, we have two particles, particle 1 is in and 2 is outside. In the second figure, we have three particles and particle 1 is in Δx and 2 and 3 are outside. In figure 3, we have three particles and particles 1 and 2 are in Δx and 3 is outside. We could find the surface area of these figures by taking the derivative of the volume with respect to the limits of integration. However, let us first consider what happens when we relax the condition that we find a given set of K particles in Δx and allow any set of K to be in Δx .

The volume is obtained by multiplying (311) by the number of ways the K particles can be chosen, $N_0! / (N-K)_0! K_0!$.

$$V = \frac{N_0! \, \Delta x^K}{(N-K)_0! \, K_0!} (L - \Delta x)^{N-K} \tag{312}$$

are shown in Figures IV-VI. We observe that the region where more than K particles are present in Δx is inaccessible from the region where less that K particles are in Δx because the system must pass through the state of having just K particles in it to reach this state. Likewise, the state of having less than K particles in Δx is inaccessible from regions having more than K particles in Δx . One or the other of these regions contains the most volume depending on whether or not K is greater or less than the average number of particles contained in Δx (we shall prove this shortly). Most of the systems are contained in the larger region and diffusion out of this region into the desired state will determine the time we must wait to find the desired state. We need consider diffusion only across the surfaces bounding the larger region. Now the regions between $-\Delta x/2$ and $\Delta x/2$ for integrals of this type $\int_{-L/2}^{L/2}\int_{-\Delta x/2}^{\Delta x/2}$ are the regions which allow more than K particles in Δx, while the regions $-\frac{L}{2} \le x \le \frac{\Delta x}{2}$ and $\frac{\Delta x}{2} \le x \le \frac{L}{2}$ in the integrals $\int_{-\Delta x/2}^{\Delta x/2}$ are the regions where there are less than K particles in Δx. For the case when the larger volume corresponds to less than K particles, the surface area is obtained by taking derivatives with respect to the upper and lower limits of the integrals $\int_{-\Delta x/2}^{\Delta x/2}$ while for the case when the larger volume corresponds to more than K particles in Δx the appropriate surface area is determined by taking derivatives of the volume with respect to the middle limits in the integrals

$$\int_{-L/2}^{L/2}\int_{-\Delta x/2}^{\Delta x/2}$$

Taking the appropriate derivatives of (311) [actually (312)] we find:

I. Most volume in region with less than K in Δx

$$A_{<K}(\Delta x) = \frac{2N!}{(N-K)!\,(K-1)!}\,\Delta x^{K-1}(L-\Delta x)^{N-K} \tag{313}$$

II. Most volume in region with more than K in Δx

$$A_{K>}(\Delta x) = \frac{2N!}{(N-K-1)!\,K!}\,\Delta x^{K}(L-\Delta x)^{N-K-1} \tag{314}$$

These expressions can be approximated by writing $L = Na_o$ where a_o is the mean interparticle spacing and by making use of Stirling's approximation, $N! = \sqrt{2\pi N}\left(\frac{N}{e}\right)^N$

and

$$\left(1 - \frac{\Delta x}{Na}\right)^N \xrightarrow[N \to \infty]{} e^{-\frac{\Delta x}{a}}$$

Thus the two areas become

$$A_{<K}(\Delta x) = \frac{1}{\sqrt{2\pi K}} \frac{2L^N}{K^{K-1}} \frac{\Delta x^{K-1}}{a_c^K} e^{-\frac{\Delta x}{a_o} + K} \tag{315}$$

$$A_{>K}(\Delta x) = \frac{1}{\sqrt{2\pi K}} \frac{2L^N}{K^K} \frac{\Delta x^K}{a_o^{K+1}} e^{-\frac{\Delta x}{a_o} + K} \,. \tag{316}$$

Also applying the same approximations to the volume given by (312) gives

$$V = \frac{1}{\sqrt{2\pi K}} \frac{L^N}{e} \left(\frac{\Delta x}{a_c K}\right)^K e^{-\frac{\Delta x}{a_o} + K} \,. \tag{317}$$

We see from expression (317) that if $K = \frac{\Delta x}{a_c}$, the expected number of particles, then the volume V is nearly equal to the total volume available, but it decreases rapidly for K either greater or less than this value. Thus if K is larger than the average number most of the excluded volume will be in the region corresponding to less than K particles in Δx and we should use (315); while if K is less than the average K, most of the volume is in the region for more than K particles in Δx and Eq. (313) should be used.

Now to find the rate at which systems are diffusing across these bounding surfaces, we assume that the density of systems is constant on the surfaces $\Delta x = \ell$ = constant. The flux F across each such surface must be the same so we have

$$D\, e_n \cdot \nabla P\, A = F = \text{constant}$$

or
$$D \frac{dP}{d\ell} A(\ell) = F \tag{318}$$

or
$$\frac{dP(\ell)}{d\ell} = \frac{F/D}{A(\ell)} \tag{319}$$

For K > K average, we have from (319)

$$\frac{dP}{d\ell} = C \frac{e^{+\ell/a_0}}{\ell^{K-1}}$$

$$P = C \int_{\Delta x}^{\ell} \frac{e^{\ell/a_0}}{\ell^{K-1}}\, d\ell$$

$$P = C \left[-\frac{1}{K} \frac{e^{\ell/a_0}}{\ell^{K-2}} \Big|_{\Delta x}^{\ell} + \int \frac{e^{\ell/a_0}\, d\ell}{K a_0 \ell^{K-2}} \right] \tag{320}$$

Since Ka_o is larger than ℓ (for ℓ near Δx) we ignore the second integral, and we have

$$P \approx \frac{C\, e^{\frac{\Delta x}{a_0}}}{K \cdot \Delta x^{K-2}} \left[1 - e^{\frac{\ell - \Delta x}{a_0}} \left(\frac{\Delta x}{\ell}\right)^{K-2} \right] \tag{321}$$

Since P is a probability its integral over the whole volume must be 1 . We thus choose C so that

$$P(\ell) = \frac{1}{L^N}\left\{1 - e^{\frac{\ell - \Delta x}{a_0}}\left(\frac{\Delta x}{\ell}\right)^{K-2}\right\} \tag{322}$$

where $\ell > \Delta x$

(This expression only holds for ℓ not too large compared to Δx . We could actually take $P(\ell)$ to be given by (322) out to the point where $dP(\ell)/d\ell$ is zero and then take $P(\ell)$ constant after that. If $K > \bar{K}$, then $P(\ell)$ increases rapidly to 1 as ℓ becomes bigger than Δx, and P will be nearly 1 at the point where P' vanishes. This can all be done more rigorously by using a function of the form (322) out to the $P''(\ell) = 0$ point and P = constant for the rest of the volume in the variational principal developed earlier.)

We now compute the flux.

$$F = D\,A(\Delta x)\left(\frac{dP}{d\ell}\right)_{\Delta x} = \frac{2D}{\sqrt{2\pi K}}\,\frac{K(K-2)}{K^K}\,\frac{\Delta x^{K-2}}{a_0^{K}}\,e^{K - \frac{\Delta x}{a}} \tag{323}$$

(Keeping only the largest term, the derivative with respect to $1/\ell$.)

Equating $F\tau = 1$ gives

$$\tau_K = \frac{\sqrt{2\pi K}}{2D}\left(\frac{a_0 K}{\Delta x}\right)^K \frac{\Delta x^2}{K(K-1)}\, e^{\frac{\Delta x}{a_0} - K} \tag{324}$$

We can expand τ_K about the K for which it has its smallest value. We then find

$$\tau \simeq \tau_{min}\, e^{\frac{(K-\bar{K})^2}{2\bar{K}}} \tag{325}$$

where $\bar{K} = \Delta x / a_o$

and

$$\tau_{min} = \frac{a_o^2}{2D} \sqrt{2\pi\, \Delta x / a_o} \tag{326}$$

Proceeding in the same way for the case when $K < \bar{K}$, we find

$$P(\ell) = \frac{1}{L^N} \left[1 - e^{\frac{\ell - \Delta x}{a_o}} \left(\frac{\Delta x}{\ell} \right)^K \right] \quad \ell < \Delta x \tag{327}$$

$$F = \frac{2D}{\sqrt{2\pi K}} \left(\frac{\Delta x}{K a_o} \right)^K \frac{1}{a_o^2}\, e^{-\frac{\Delta x}{a_o} + K} \tag{328}$$

and for τ

$$\tau = \frac{\sqrt{2\pi K}}{2D}\, a_o^2 \left(\frac{K a_o}{\Delta x} \right)^K e^{\frac{\Delta x}{a_o} - K} \tag{329}$$

This can also be expanded about the K for which τ is a minimum, and we again find approximately

$$\tau = \tau_{min}\, e^{\frac{(K-\bar{K})^2}{2\bar{K}}} \tag{330}$$

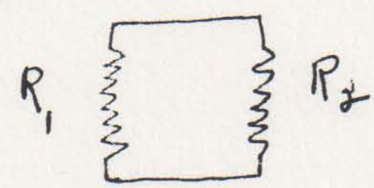
with τ_{min} again given by (326).

PLEASE NOTE: Equations (331-333) has been deleted.

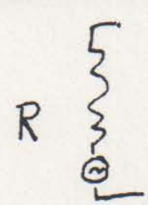
Nyquist's Theorem

For the problem of Brownian motion we saw that there was a relation between the systematic drag on a particle and the random fluctuations it experiences. Thus the fluctuations were related to the dissipation. Another example of a fluctuation dissipation theorem is Nyquist's theorem relating the thermal voltage fluctuations across a resistor to its resistance.

Consider a circuit consisting of two resistors connected by perfectly conducting wires.



Because of the random thermal motion of the electrons in the resistors, there will be a fluctuating voltage across the resistors. We may view each as being a generator with a certain internal resistance



Each resistor will generate all frequencies because the random motion of the electrons will contain all frequencies at least up to some very high frequency where quantum effects become important. Let the voltage generated by generator 1 be E_1 and that developed by 2 by E_2.

The current produced by E_1 is

$$I_1 = \frac{E_1}{R_I + R_2} , \tag{336}$$

while that produced by E_2 is

$$I_2 = \frac{E_2}{R_I + R_2} . \tag{337}$$

Here we have assumed that the circuit has no inductance or capacitance.

The rate of dissipation of energy in resistor 2 due to the current generated by 1 is

$$R_2 I_I^2 = \frac{E_1^2 R_2}{(R_I + R_2)^2} . \tag{338}$$

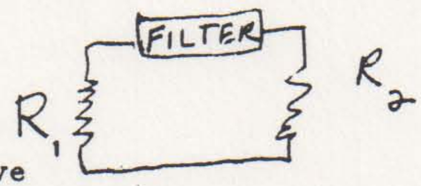
Likewise the rate of dissipation of energy is resistor 1 due to the current generated by 2 is

$$R_1 I_2^2 = \frac{E_2^2 R_1}{(R_1 + R_2)^2} . \tag{339}$$

Now the first of these expressions is the rate at which 1 is delivering energy to 2 while the second of these expressions is the rate at which 2 is giving energy to 1 . If the two resistors are at the same temperature, then these two rates must be the same on the average for otherwise one of the resistors would heat up while the other cools down which would violate the second law of thermodynamics. Thus we have

$$\frac{\overline{E_1^2}\,R_2}{(R_I + R_2)^2} = \frac{\overline{E_2^2}\;R_1}{(R_1 + R_2)^2} \quad . \tag{340}$$

This relation must hold not only for total power, but also for every frequency interval since we could put a filter between the two resistors that allows current to flow only in a very narrow frequency range.



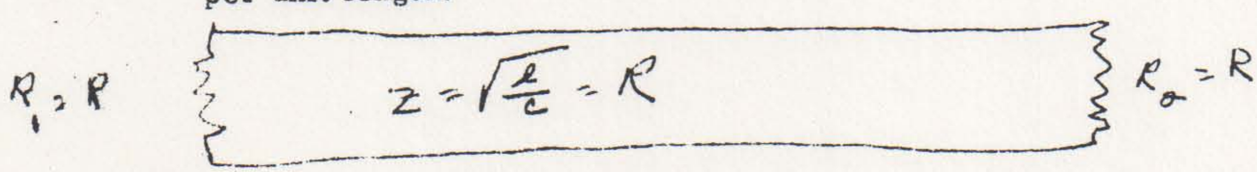
Thus we have

$$\frac{\overline{E_1^2(f)\,R_2\,\Delta f}}{(R_1 + R_2)^2} = \frac{E_2^2(f)\,R_1\,\Delta f}{(R_1 + R_2)^2} \;\text{ or }\; G_1(f)R_2 = G_2(f)R_1 \quad . \tag{341}$$

Let us take R_1 equal to R_2 and let us connect the two resistors by means of a transmission line whose characteristic impedance is also R_1

$$Z = \sqrt{\frac{\ell}{c}} = R = R_1 = R_2 \tag{342}$$

where ℓ is the inductance per unit length and c is the capacitance per unit length.



A transmission line with characteristic impedance $z = R$ which is terminated in a resistor with resistance R is aid to be terminated in a matched load. Any disturbance arriving at the resistor is completely absorbed by the resistor and no power is reflected. Thus for the transmission line connecting resistors 1 and 2 above all waves traveling to the right are absorbed by R_2 while all waves traveling to the left are absorbed by R_1 .

Now suppose that at a certain time we were to short out the ends of the line just in front of the resistors. The waves that were on the line would now be perfectly reflected from the shorts and the energy would bounce back and forth forever between the ends of the line. The field on the shorted line may be Fourier analyzed to obtain normal modes. The boundary conditions require that an integral number of half wave lengths fit on the wire. Thus

$$\frac{n\lambda}{2} = L \quad . \tag{343}$$

The frequency corresponding to λ is given by

$$f = \frac{v}{\lambda} = \frac{nv}{2L} \quad . \tag{344}$$

The number of modes in the frequency interval df is the number of n's which correspond to df .

$$dn = \frac{2L}{v}\, df \quad . \tag{345}$$

Now each mode behaves like a harmonic oscillator. During the time the line is terminated by the resistors these oscillators come to thermal equilibrium with the resistors. Thus they have energy kT , $kT/2$ electrical energy and $kT/2$ magnetic energy. The energy on the line is the frequency interval df is thus

$$kT\ dn = \frac{2k\ Tl}{v}\ df \quad , \tag{346}$$

and the energy density (energy per unit length of the line in df) is

$$\frac{kT\ dn}{L} = \frac{2kT}{v}\ df \ . \tag{347}$$

If the shorts are now removed energy will flow from the line into the resistors. Half the energy flows to the right at velocity v while the other half flows to the left with velocity v . The rate of absorption of energy by either resistor in the frequency interval df is

$$P_f = kT\ df \ . \tag{348}$$

Now the line looks like a resistor of resistance R to either resistors, and thus each one supplies power to the line in accordance with equation (340).

$$\frac{\overline{E^2(f, df)}}{4R} = kT\ df \tag{349}$$

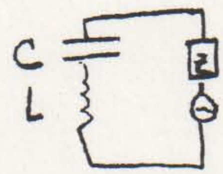
$$\overline{E^2(f, df)} = 4kTR\ df \ . \tag{350}$$

The power spectrum for $\overline{E^2}(f)$ is

$$\overline{E^2(f, df)}/df = 4kTR = G(f) \ . \tag{351}$$

An Alternate Derivation of Nyquists' Theorem

Rather than take our resistor to be hooked into a transmission line let us hook it into an oscillator. Let us further generalize the resistor to be an arbitrary impedance



Again we imagine that we can divide the impedance into a pure impedance and a generator. When the oscillator comes to equilibrium with the impedance it will have energy kT, $\frac{1}{2}kT$ energy in the inductance (magnetic energy) and $\frac{1}{2}kT$ energy in the capacitance (electrical energy). Now the equations governing the above circuits are

$$E_C = Q/C \tag{352}$$

E_C is the voltage across the capacitor, Q is the charge on the capacitor and C is its capacitance.

$$E_L = L\,\frac{dJ}{dt} \tag{353}$$

E_L is the voltage across the inductance, J is the current in the circuit

$$\frac{dQ}{dt} = J \tag{354}$$

E_Z is the voltage drop across the impedance

E_g is the voltage produced by the generator

The total voltage around the circuit must add up to zero so we have

$$E_C + E_L + E_Z = E_g \tag{355}$$

Equations (352)-(355) may be combined to yield

$$\frac{Q}{C} + L\frac{dJ}{dt} + E_Z = E_g \tag{356}$$

or taking time derivative

$$L\frac{d^2J}{dt^2} + \frac{dE_z}{dt} + \frac{J}{C} = \frac{dE_g}{dt} \tag{357}$$

We may Fourier analyze (357). As before, we imagine that the process goes on for a long but finite time T. We have

$$E_q = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} E_q(\omega) e^{i\omega t} d\omega \tag{358}$$

$$J = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} J(\omega) e^{i\omega t} d\omega \tag{359}$$

$$E_z = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} E_z(\omega) e^{i\omega t} d\omega = \int_{-\infty}^{\infty} z(\omega) J(\omega) e^{i\omega t} d\omega \tag{360}$$

The condition that all quantities be real for all times requires

$A(-\omega) = A^*(\omega)$ where A is any one of the quantities,

E_q, J, E_q, or Z. Upon substitution of these relations into Eq. (357) we find,

$$L\left(-\omega^2 + \omega_0^2 + \frac{i\omega z(\omega)}{L}\right) J(\omega) = i\omega E_q(\omega) \tag{365}$$

or

$$J(\omega) = \frac{i\omega E_q(\omega)}{L\left(\omega_0^2 - \omega^2 + \frac{i\omega z(\omega)}{L}\right)} \tag{366}$$

Here $\omega_0^2 = \frac{1}{LC}$.

Now the instantaneous energy in the inductance is

$$W_J = \frac{1}{2} L J^2 = -\frac{L}{4\pi} \int_{-\infty}^{\infty}\int_{-\infty}^{\infty} \frac{\omega\omega' E_q(\omega) E^*(\omega) e^{i(\omega+\omega')t} d\omega\, d\omega'}{L^2\left(\omega_0^2 - \omega^2 + \frac{i\omega z(\omega)}{L}\right)\left(\omega_0^2 - \omega'^2 - \frac{i\omega' z^*(\omega')}{L}\right)} . \tag{368}$$

Taking the time average of W_J gives

$$
\begin{aligned}
W_J &= \frac{1}{T}\int_{-\frac{T}{2}}^{+\frac{T}{2}} \tfrac{1}{2} L J^2 \, dt \\
&= \frac{1}{2TL}\int_{-\infty}^{+\infty} \frac{\omega^2 \, |E_q(\omega)|^2 \, d\omega}{\left[\omega_o^2-\omega^2+\frac{i\omega Z(\omega)}{L}\right]\left[\omega_o^2-\omega^2-\frac{i\omega Z^*(\omega)}{L}\right]}
\end{aligned}
\tag{369}
$$

Taking the ensemble average

$$
\overline{W_J} = \frac{1}{4L}\int_{-\infty}^{+\infty} \frac{\omega^2 \, G_q(\omega) \, d\omega}{\left[\omega_o^2-\omega^2+\frac{i\omega Z(\omega)}{L}\right]\left[\omega_o^2-\omega^2-\frac{i\omega Z^*(\omega)}{L}\right]}
\tag{370}
$$

$$G_q(\omega) = 2\,\overline{|E_q(\omega)|^2}/T$$

Now let us consider the case when L is very large and C is small, i.e.,

$$
\begin{aligned}
L &\to \infty \\
C &\to 0
\end{aligned}
\qquad \omega_o^2 = \frac{1}{LC} = \text{Constant}
$$

Let us also write $Z(\omega)$ as

$$
\begin{aligned}
Z(\omega) &= R(\omega) + i\,X(\omega) \\
Z(-\omega) &= R(\omega) - i\,X(\omega)
\end{aligned}
\tag{371}
$$

We may factor the denominator. We have in the limit of large L

$$
\begin{aligned}
\left(\omega^2-\omega_o^2+\frac{i\omega Z}{L}\right) &\simeq \left(\omega-\omega_o+\frac{iZ}{2L}\right)\left(\omega+\omega_o+\frac{iZ}{2L}\right) \\
&= \left(\omega-\omega_o-\frac{(X-iR)}{2L}\right)\left(\omega+\omega_o-\frac{(X-iR)}{2L}\right)
\end{aligned}
\tag{372}
$$

$$
\left(\omega^2-\omega_o^2-\frac{i\omega Z^*}{L}\right) \simeq \left(\omega-\omega_o-\frac{(X+iR)}{2L}\right)\left(\omega+\omega_o-\frac{(X+iR)}{2L}\right)
\tag{373}
$$