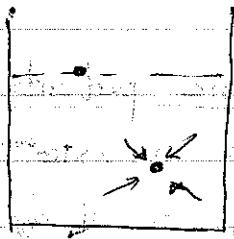# MEAM 663

ENTROPIC FORCES IN BIOMECHANICS

Spring 2007

Ref: Selected papers on noise and stochastic processes
Edited by Nelson Wax.

MOTIVATION FOR ENTROPIC FORCES

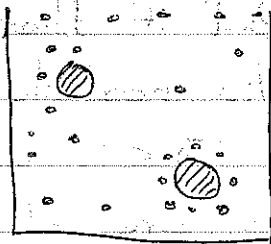~~Suppose we have~~ Entropic forces are those that have their origin in fluctuations around equilibrium. There are many examples of systems where such forces are present, many of which we are already familiar with. I recount some examples here.
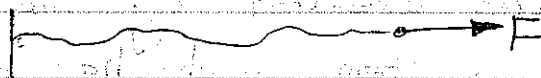
A) <u>Brownian motion</u> : In Brownian motion a small pollen grain or colloidal particle is bombarded from all sides by the ~~atoms~~ water molecules. The average position of the particle does not change by the mean squared position changes.

B) <u>Depletion interaction</u> : Suppose there are two large particles surrounded by a sea of small particles. The small particles constantly bombard the large particle and the situation is the same as a single colloidal particle. But if the two large particles are too close then what happens. Imagine two large round tables kept in the middle of a dance floor. If they are two close that the people cannot get in between them then they will be pushed closer. There is a short-ranged attractive force. It is entropic in origin.

c) <u>Force-elongation of polymers</u> : Imagine a rope which has just been pulled taut. Now suppose

a strong wind blows which causes the rope to flutter like a flag. In order to hold the rope straight one now has to apply a larger force. The force goes into straightening out fluctuations around the straight shape. Exactly the same type of mechanics is applicable to membranes as well. Their elasticity is entropic in ▪ nature.

D) Directed motion due to asymmetric potential.

Imagine a particle on a track in one dimension. It is being randomly kicked by small molecules from

both directions. If it was equally difficult to slide in either direction then the average position of the particle will not change. But if there is asymmetry then the position of the particle will change — it will move in one direction. This is another situation where random ▪▪ forces are at ▪ work.

A) ▪ Langevin dynamics

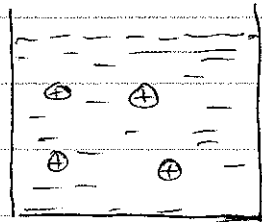osmotic press▪ B) Entropy of an ideal gas — Sakur Tetrode formula

C) Worm-like chain model and the freely jointed chain model for entropic elasticity

D) Fokker-Planck equation and Smoluchowski's equation.

The WLC model is an example of a system where ▪▪▪ the bending mechanics of a rod is coupled with the random forces exerted by the environment. Another example of a system which has deterministic

and random forces working in tandem is when we consider electrostatics in solution. So for example if we had charged plate in solution then the opposite charges are dispersed closed to it and there is charge in concentration of

the ions as one moves away from the plate. The behavior is described by the Poisson-Boltzmann equation and we will do a bit of this as well.

Finally, we will spend some time trying to understand Kramer's rate theory which was developed for understanding the rates of reactions.

$$\frac{\partial H}{\partial p_i} = \dot{q}_i \qquad -\frac{\partial H}{\partial q_i} = \dot{p}_i \qquad H = \sum_i \frac{p_i^2}{2m} + V(q_i).$$

BASIC THERMODYNAMICS

In this course, as in most natural (biological) phenomena we are concerned with the behavior of a system of a large number of atoms and molecules or particles. In order to describe the behavior of such a system of many particles one could start by describing a single particle in terms of Newtonian or Hamiltonian mechanics and then integrate forward in time to get the state of the particle at another time. For example state of a single particle is described by the variables $\{q_i, p_i\}$ ($i = 1, 2, 3$). The energy levels of this particle are

$$\varepsilon_{q,p} = \frac{\hbar^2 |p|^2}{2m}$$

and $\underline{p} = \{p_x, p_y, p_z\} = \{(\frac{2\pi}{L})\ell_x, (\frac{2\pi}{L})\ell_y, (\frac{2\pi}{L})\ell_z\}$ with ℓ_x, ℓ_y, ℓ_z being the three quantum numbers. If we give the three positions q_x, q_y, q_z and the three quantum numbers ℓ_x, ℓ_y, ℓ_z then we have all the information needed to determine the state of the particle at another instant. But this same exercise cannot be repeated for a system of N ($\sim 10^{23}$) particles. We really need some other method to extract relevant information from a system of a large number of particles. ~~The~~ This is where thermodynamics comes in. Obviously, we will need to make some simplifying assumptions. These are:

(A) ~~If~~ we wait long enough, the initial conditions become irrelevant. In other words the particles exchange energy and momentum so many times that all memory of the initial conditions is washed away.

When a system reaches this condition, it is said to be in __equilibrium__.

(B) For a system in equilibrium, all possible quantum states are equally likely. In other words any particular kind of state is not preferred.

Given these two assumptions and the fact that we know how to count quantum states of a many particle systems we will be able to extract a lot of useful information about the system. The business of counting quantum states of systems is the job of __statistical mechanics__.

To make a beginning let us assume that there are N particles in a box of volume $V = L^3$ and that the total energy of all the particles is E. Assume also that this system of particles in the box is isolated. Suppose we know that there are Γ possible states of this system then the __entropy__ is __defined__ as

$$S = k_B \log \Gamma$$

where k_B is Boltzmann's constant. S is a function of E, N and V. Or,

$$S = S(E, N, V).$$

Further S is a way of expressing the number of choices (of quantum states) that the system has and therefore S will increase as E increases since the system will have more ways of dividing the energy. Since S is monotonic in E we can invert the relation above to get

$$E = E(S, N, V).$$

Or, $dE = \left(\frac{\partial E}{\partial S}\right)_{N,V} dS + \left(\frac{\partial E}{\partial N}\right)_{S,V} dN + \left(\frac{\partial E}{\partial V}\right)_{S,N} dV$.

In the above we define,

$\left(\frac{\partial E}{\partial S}\right)_{N,V} = T$ temperature

$\left(\frac{\partial E}{\partial V}\right)_{S,N} = -P$ pressure

$\left(\frac{\partial E}{\partial N}\right)_{S,V} = \mu$ chemical potential.

The quantities E, S, N, V scale with the size of the system and are called extensive variables but the quantities T, P, μ do not depend on the size of the system and are called intensive. Let us rewrite the definition above :

$$dE = T dS - P dV + \mu dN$$

for an isolated system.

The subject of thermodynamics starts with these definitions and is built upon four fundamental laws.

Zeroth Law   If A and B are in thermal equilibrium and B and C are in thermal equilibrium then A and C are in thermal equilibrium.

First Law   This is the law of conservation of energy. For an isolated system the change in energy is given

$$dE = dQ + dW$$

where Q is heat and W is work. For example for a gas compressed in a cylinder with a piston $dW = -P dV$. This is one way of increasing the energy of the system. But the energy can also be increased at constant V and N

by adding heat. Since volume is constant no work is
done, so, $dE = dQ = dE)_{N,V} = TdS$.

In other words for a fixed number of particles, in
equilibrium we can write the first law as

$$dE = TdS - PdV$$

The <u>second law</u> states that the entropy of an
isolated system out of equilibrium will tend to increase.
Therefore at equilibrium the entropy is a maximum.

The <u>Third law</u> states that at the absolute zero
of temperature the entropy is zero. The third law
informs us that thermodynamic arguments must really
be restricted only to non-zero temperatures.

Now if we know the energy of system with
constant N in terms of S and V, or $E(s,v)$ then
we can obtain $T = \dfrac{\partial E}{\partial S}\Big)_V$ and $P = -\dfrac{\partial E}{\partial V}\Big)_S$. In
general $T = T(v,s)$ and $P = P(v,s)$ and this will give
us $T(P,V)$ while $T(v,s)$ can be inverted to get $s(v,T)$
If on the other hand we knew E as $E(T,V)$
then we will not be able to get the entropy s
by integrating $T = \dfrac{\partial E}{\partial S}\Big)_V$. For this reason S and V
are called the <u>proper variables</u> of E. But $E(s,v)$
is rarely given to us, insted we have measurements
of T, P and V of a system. We will therefore need
some other energy-like functions whose proper
variables are more convenient. These energy-like
functions are:

(a) <u>Helmholtz free energy</u> : $F = E - TS$
$$dF = dE - TdS - SdT = -SdT - PdV$$

Hence, $\quad S = -\dfrac{\partial F}{\partial T}\bigg)_V \quad$ and $\quad P = -\dfrac{\partial F}{\partial V}\bigg)_T$

Hence the proper variables for F are T and V, $F = F(T,V)$
At constant temperature $\quad dF\big) _T = -PdV\big)_T \quad$ so that
changes in the Helmholtz free energy at a given temp
is equal to the mechanical work done on the system.

(b) $\underline{\text{Gibbs free energy}}$: $\quad \Phi = F + PV = E - TS + PV$

Hence, $\quad d\Phi = -SdT + VdP$

or, $\quad S = -\dfrac{\partial \Phi}{\partial T}\bigg)_P \quad$ and $\quad V = \dfrac{\partial \Phi}{\partial P}\bigg)_T$

so that $\Phi = \Phi(T,P)$ in terms of proper variables.
Since T and P are both intensive (do not depend on the
size of the system) the Gibbs free energy is useful
when the size of the system is of no importance.

(c) $\underline{\text{Enthalpy}}$: $\quad H = \Phi + TS = E + PV$

so that, $\quad dH = TdS + VdP$

and, $\quad T = \dfrac{\partial H}{\partial S}\bigg)_P \quad$ and $\quad V = \dfrac{\partial H}{\partial P}\bigg)_S$

Note that for a constant pressure process $dH\big)_P = TdS\big)_P$
$= dQ$. This fact is used in chemical reactions that
occur under constant pressure (atmospheric) to measure
the enthalpies of various species. Now consider the
following derivative:

$$\frac{\partial P}{\partial T}\bigg)_V = \frac{\partial}{\partial T}\left(-\frac{\partial F}{\partial V}\right)\bigg)_{T/V} = -\frac{\partial}{\partial V}\left(-\frac{\partial F}{\partial T}\right)\bigg)_{V/T} = \frac{\partial S}{\partial V}\bigg)_T$$

Similarly we can derive other such relations.

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V, \quad \left(\frac{\partial V}{\partial S}\right)_P = \left(\frac{\partial T}{\partial P}\right)_S \quad \text{and} \quad \left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$$

These relations are also known as <u>Maxwell relations</u>
and they tell us that for a system of constant number
of particles, everything is determined if we know
any two variables that are not conjugate to each
other and we know that the system is in eqbm.
    If the number of particles in a system is allowed
to change then,

$$dE = TdS - PdV + \mu dN \quad\quad \longrightarrow \quad \textcircled{1}$$

and then the definitions of F, Φ, H etc are:

$$dF = -SdT - PdV + \mu dN$$
$$d\Phi = -SdT + VdP + \mu dN$$
$$dH = TdS + VdP + \mu dN$$

μ is an intensive variable and is conjugate to N.
Now if we had a chunk of matter for which eqn $\textcircled{1}$
is valid then for the same material but a λ times
bigger chunk we will want to obey,

$$d(\lambda E) = Td(\lambda s) - Pd(\lambda V) + \mu d(\lambda N)$$

Or, $\lambda dE + Ed\lambda = \lambda(TdS - PdV + \mu dN) + (TS - PV + \mu N)d\lambda$

Or, $\quad E = TS - PV + \mu N \quad$ since λ is arbitrary.

So in fact we find $\Phi = E - TS + PV = \mu N$

For a system to be in equilibrium T, P and μ should
have no gradients. Finally, a useful potential for mass
transfer is the Landau potential

$$\Omega = F - \mu N \quad\quad\quad (\text{Note } \Omega = -PV)$$

so that $\quad d\Omega = -SdT - PdV - Nd\mu$

Hence the proper variables of Ω are T, V and μ.

VARIATIONAL PRINCIPLES IN THERMODYNAMICS

Really there is only one variational principle in thermodynamics and it is the second law – "For an isolated system in equilibrium the entropy is a maximum." But more often than not we work with systems which are in a constant temperature bath and can exchange heat and work with it, meaning they are not isolated. How do we address the equilibrium behaviour of such a system. To do this we consider the system of interest, the temperature bath and the work source as an isolated system. We assume that the bath is always in internal equilibrium. Its energy E' and entropy S' are connected by

$$dE' = T dS'$$

We have assumed that no work can be done on it. Next we imagine a work source that is thermally isolated from the sample and the bath so that its changes in energy are simply δR_0.

$$\delta R_0 - P \delta V = 0$$

Now since the sample, bath and work source are an isolated system we have

$$\delta(E' + E + R_0) = 0$$

Or, $\quad T dS' + \delta E - P \delta V = 0$

Also for this isolated system the entropy should be a maximum and hence

$$\delta S + \delta S' \geq 0$$

$$\text{Or, } \delta E \leq T \delta S - P \delta V$$

If the sample is in equilibrium then equality holds. If changes take place at fixed T and fixed V then we must have $\quad \delta E - \delta TS \leq 0 \quad$ or $\quad \delta(E - TS) \leq 0$

Which means that Helmholtz free energy will only decrease during the process and when eqbm is reached then F will be a minimum. If changes occur at constant T and P then $\delta(E - TS + PV) \leq 0$ which means that at equilibrium Φ (Gibbs free energy) will be a minimum. Note that if no work is done (V = const) then we minimise F and if work is done then we minimise Φ. More generally, if no work is done then we minimise F; if work is done, we subtract it off and minimise what is left. The general variational principle therefore is,

$$\delta E \leq T\delta S + H \delta \int M dV - P \delta V + \mu \delta N + \ldots$$

For example if T, V and μ are fixed and N varies then we minimise $\Omega = F - \mu N$.

Next we will consider thermodynamic inequlities, but first some definitions. The specific heat at constant volume and at constant pressure respectively are defined as,

$$C_V = T \left(\frac{\partial S}{\partial T} \right)_V$$

$$C_P = T \left(\frac{\partial S}{\partial T} \right)_P$$

These are heat capacities and they can be measured by adding heat to a substance under specified conditions. They give us a way to measure changes in entropy indirectly. Remembering that

$$\delta E = T\delta S - P\delta V$$

for a system in equilibrium we may see that,

$$C_V = \left(\frac{\partial E}{\partial T} \right)_V$$

$$f(x,y,z) = 0 \quad \left(\text{like } \frac{PV}{nRT} - 1 = 0\right)$$

$$df = 0 = \frac{\partial f}{\partial x} dx + \frac{\partial f}{\partial y} dy + \frac{\partial f}{\partial z} dz.$$

Now. if, $dz = 0$ then $\frac{\partial y}{\partial x} = \frac{-\partial f/\partial x}{\partial f/\partial y}$ etc.

Use this to show that
$$\frac{\partial y}{\partial x}\Big|_z \frac{\partial x}{\partial z}\Big|_y \frac{\partial z}{\partial y}\Big|_x = -1.$$

In other words C_V is the total change in energy of a system when no work is done on it. We can also see that

$$C_V = -T\left(\frac{\partial^2 F}{\partial T^2}\right)_V$$

$$C_p = -T\left(\frac{\partial^2 \Phi}{\partial T^2}\right)_P$$

These are second derivatives of the potentials F and Φ. There are similarly other second derivatives. In particular the _isothermal_ compressibility and the _adiabatic_ compressibility are defined as

$$K_T = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T = -\frac{1}{V}\left(\frac{\partial^2 \Phi}{\partial P^2}\right)_T$$

$$K_S = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_S = \frac{1}{V}\left[\left(\frac{\partial^2 E}{\partial V^2}\right)_S\right]^{-1}$$

Now there are definite relations between these quantities. We can derive them through many alternate means. For example, we know that $S = S(P, T)$.

$$dS = \left(\frac{\partial S}{\partial P}\right)_T dP + \left(\frac{\partial S}{\partial T}\right)_P dT$$

Or, $\dfrac{C_V}{T} = \left(\dfrac{\partial S}{\partial T}\right)_V = \left(\dfrac{\partial S}{\partial P}\right)_T \left(\dfrac{\partial P}{\partial T}\right)_V + \dfrac{C_p}{T}$

Now, $\left(\dfrac{\partial S}{\partial P}\right)_T = -\left(\dfrac{\partial V}{\partial T}\right)_P$ so we can eliminate it and get,
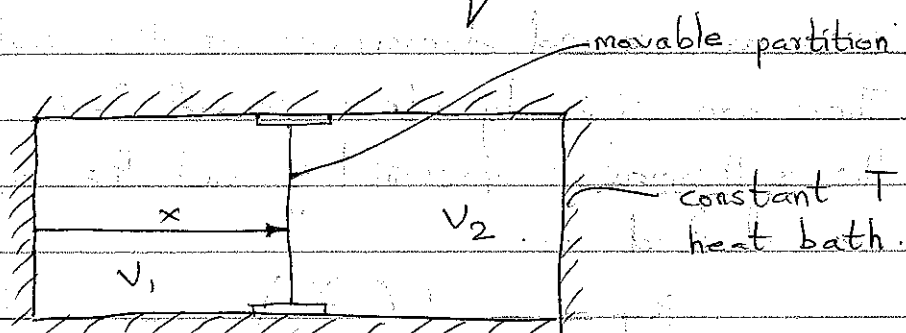
$$\frac{C_p - C_V}{T} = \left(\frac{\partial V}{\partial T}\right)_P \left(\frac{\partial P}{\partial T}\right)_V$$

We observe that $\left(\dfrac{\partial V}{\partial T}\right)_P \left(\dfrac{\partial T}{\partial P}\right)_V \left(\dfrac{\partial P}{\partial V}\right)_T = -1$ so that,

$$C_p - C_V = -T\left(\frac{\partial V}{\partial P}\right)_T \left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial P}{\partial T}\right)_V = TV K_T \left[\left(\frac{\partial P}{\partial T}\right)_V\right]^2$$

$$C_p - C_v = \frac{T}{VK_T}\left[\left(\frac{\partial V}{\partial T}\right)_P\right]^2.$$

The heat capacities and compressibilities are also called response functions. They are always positive. We can show this by using the variational principle like F must be a minimum at equilibrium.

The material on both sides of the partition is the same and it will find its equilibrium position by minimising F with respect to its position x or equivalently with respect to V_1, subject to the condition that

$$dV_1 + dV_2 = dV = 0.$$

$$\frac{\partial F}{\partial V_1} = \frac{\partial}{\partial V_1}(F_1 + F_2) = \frac{\partial F_1}{\partial V_1} - \frac{\partial F_2}{\partial V_2} = 0$$

These are derivatives at constant T, meaning $\frac{\partial F}{\partial V}\big)_T = -P$ and we have determined that the equilibrium position of the partition will be such as $P_1 = P_2$. Now F is not only stationary with respect to variations in V_1 it is actually a minimum, meaning $\frac{\partial^2 F}{\partial V_1^2} > 0$ at eqbm.

$$\frac{\partial^2 F}{\partial V_1^2} = \frac{\partial}{\partial V_1}(P_2 - P_1) = -\frac{\partial P_2}{\partial V_2} - \frac{\partial P_1}{\partial V_1} = \frac{1}{V_1 K_{T_1}} + \frac{1}{V_2 K_{T_2}} > 0$$

But V_1 and V_2 contain the same material so that $K_{T_1} = K_{T_2} = K_T$. So we get $K_T > 0$.

We will show by an analogous argument that $C_V > 0$. For this assume an isolated system of the same type as before but this time it is such that its energy and volume are constant. We will now maximise entropy, subject to $E_1 + E_2 = E$

$$\frac{\partial S}{\partial E_1} = \frac{\partial S_1}{\partial E_1} - \frac{\partial S_2}{\partial E_2} \Rightarrow \frac{1}{T_1} - \frac{1}{T_2} = 0$$

Meaning at equilibrium $T_1 = T_2$. Now with the second derivative

$$\frac{\partial^2 S}{\partial E_1^2} = \frac{\partial}{\partial E_1}\left(\frac{1}{T_1}\right)_V + \frac{\partial}{\partial E_2}\left(\frac{1}{T_2}\right)_V$$

$$= -\frac{1}{T_1^2}\frac{\partial T_1}{\partial E_1} - \frac{1}{T_2^2}\frac{\partial T_2}{\partial E_2}$$

$$= -\frac{1}{T_1^2 C_{V_1}} - \frac{1}{T_2^2 C_{V_2}} \leq 0$$

But $T_1 = T_2$ and if we choose the two volumes equal then we immediately see that $C_V \geq 0$. Remember,

$$C_p - C_V = \frac{T}{V K_T}\left[\left(\frac{\partial V}{\partial T}\right)_p\right]^2$$

Since $K_T \geq 0 \Rightarrow C_p > 0$. The conditions we have derived $K_T > 0$ and $C_V > 0$ are really physically quite reasonable. There is another more mathematical way of deriving the same conditions. Consider a body in a bath at constant T_0 and P_0. Then at eqbm its Gibbs free energy is a minimum hence any arbitrary fluctuation causes

$$\delta E - T_0 \delta S + P_0 \delta V > 0 \qquad \longrightarrow \textcircled{A}$$

We will now expand δE in a series around the eqbm values.

$$\delta E = \frac{\partial E}{\partial S}\delta S + \frac{\partial E}{\partial V}\delta V + \frac{1}{2}\left[\frac{\partial^2 E}{\partial S^2}(\delta S)^2 + 2\frac{\partial^2 E}{\partial S \partial V}\delta S \delta V + \frac{\partial^2 E}{\partial V^2}(\delta V)^2\right]$$

But $\frac{\partial E}{\partial S} = T$ and $\frac{\partial E}{\partial V} = -P$ and so the first order terms cancel when we substitute for δE into Ⓐ. We are left with

$$\frac{\partial^2 E}{\partial S^2}(\delta S)^2 + 2\frac{\partial^2 E}{\partial S \partial V}\delta S \delta V + \frac{\partial^2 E}{\partial V^2}(\delta V)^2 > 0$$

This must hold for all values of δS and δV. This implies that

$$\frac{\partial^2 E}{\partial S^2} > 0$$

and

$$\frac{\partial^2 E}{\partial S^2}\frac{\partial^2 E}{\partial V^2} - \left(\frac{\partial^2 E}{\partial S \partial V}\right)^2 > 0$$

Since $\frac{\partial^2 E}{\partial S^2} = \left(\frac{\partial T}{\partial S}\right)_V = \frac{T}{C_V}$ we obtain $C_V > 0$. We can use this in the second condition and end up with $K_T > 0$.

— — — — — — — — — — — — — —

$$P = P(V,T) \qquad dP = \frac{\partial P}{\partial V}\bigg)_T dV + \frac{\partial P}{\partial T}\bigg)_V dT$$

$$\Rightarrow dP = dT\left(\frac{\partial P}{\partial V}\bigg)_T \frac{\partial V}{\partial T} + \frac{\partial P}{\partial T}\bigg)_V\right)$$

If we want $\frac{\partial V}{\partial T}\big)_P$ we must set $dP = 0$ then,

$$0 = \frac{\partial P}{\partial V}\bigg)_T \frac{\partial V}{\partial T}\bigg)_P + \frac{\partial P}{\partial T}\bigg)_V$$

$$\Rightarrow \frac{\partial P}{\partial V}\bigg)_T \frac{\partial V}{\partial T}\bigg)_P \frac{\partial T}{\partial P}\bigg)_V = -1$$

DERIVATION OF THE PARTITION FUNCTION

With this really quick review of thermodynamics we now want to review the methods of statistical mechanics. Remember that we started with the assumption that $S = k_B \log \Gamma$ where Γ was the number of states of an isolated system with energy E, volume V and number of particles N. The business of statistical mechanics is to count states so as to obtain Γ; more precisely stat mech teaches us how to avoid counting states! Now given a body with certain V and N, we generally want to know thermodynamic properties as a function of the temperature T and not the energy E. We want F(T,V,N) or $\Omega(T, V, \mu)$ and not so much E(S,V,N). For this purpose we will assume that the body of interest to us is embedded in a very large medium whose temperature T and chemical potential μ is not affected by what our body is doing. We therefore imagine that the body of interest to us is a <u>subsystem</u> embedded in a <u>medium</u> which is very large and they both together constitute a system which is isolated. The energy of the system, medium and body are:

<u>System</u> $\longrightarrow$ $E_0, V_0, S_0, \Gamma_0, N_0$. (At eqbm $S_0 = k_B \log \Gamma_0$)

<u>Medium</u> $\longrightarrow$ E', S', V', N', Γ'

<u>Body</u> $\longrightarrow$ E, S, N, V, Γ

The medium is always thought to be in equilibrium internally
$$dE' = T dS' - P dV' + \mu dN'$$
Note that E', S', V' and N' all depend on what the body is doing but T, P and μ of the medium are fixed. We will <u>assume</u> that the body has a fixed volume

but it can exchange energy and particles with the medium. We will also assume that for each possible quantum state of the body which we call α,

$$E_\alpha \ll E_0 \quad \text{and} \quad N_\alpha \ll N_0.$$

Since $E_\alpha \ll E_0$ and $N_\alpha \ll N_0$, S', E' and N' change very little and we will assume safely that,

$$\frac{\partial E'}{\partial S'} = T \quad \text{and} \quad \frac{\partial E'}{\partial N'} = \mu.$$

Now under any specified set of conditions in which the subsystem has Γ choices and the ~~body~~ medium Γ' the total system will have choices given by

$$\Gamma_t = \Gamma \Gamma'$$

and, $$S_t = S + S'.$$

In equilibrium $S_t = S_0$ and the propbability of any particular quantum state of the system is

$$W_{eq} = \frac{1}{\Gamma_0}.$$

not the body

Suppose we imagine that the system (body + medium) is not in equilibrium, rather the body is in state α characterise by E_α and N_α and the medium now as Γ'_α choices. The probability that the body is in state α with energy is

$$W_\alpha = \frac{\Gamma'_\alpha}{\Gamma_0}.$$

W_α clearly depends on α, for example if E_α is big then E' is small and the medium will have smaller number of states Γ'_α and so W_α will be low. The quantity W_α is of great importance. If f is a property of the body then,

$$\bar{f} = \sum_{\alpha} f_\alpha W_\alpha$$

where $\quad 1 = \sum_{\alpha} W_\alpha$.

$\bar{f}$ is an average value of the property f.

If the body is in state α, then the medium has entropy S'_α. In fact,

$$S'_\alpha = k_B \log \Gamma'_\alpha$$

and also $S' = S'(E', N') = S'(E_0 - E_\alpha, N_0 - N_\alpha)$. Clearly,

$$S_0 - S'_\alpha = - k_B \log \frac{\Gamma'}{\Gamma_0} = - k_B \log W_\alpha \longrightarrow Ⓐ$$

The quantity $S_0 - S'_\alpha$ is __not__ the entropy of the body, since we know that the body is in state α. By averaging S'_α over all possible states of the body we will get the equilibrium entropy S of the body and also that of the medium.

$$S = \overline{S_0 - S'_\alpha} = \sum_{\alpha} W_\alpha (- k_B \log W_\alpha).$$

Now from eqn Ⓐ we see that

$$W_\alpha = \exp\left(- \frac{S_0 - S'_\alpha}{k_B}\right) = A \exp\left(\frac{S'_\alpha}{k_B}\right)$$

Also, $\quad S'_\alpha = S'(E_0 - E_\alpha, N_0 - N_\alpha)$

$$= S'(E_0, N_0) - \left(\frac{\partial S'}{\partial E'}\right)_{V', N'} E_\alpha - \left(\frac{\partial S'}{\partial N'}\right)_{V', E'} N_\alpha$$

why? see at the end.

$$= \text{const} - \frac{E_\alpha}{T} \oplus \frac{\mu N_\alpha}{T}$$

The const is the $S'(E_0, N_0)$ which is the entropy the medium would have if all the particles and all the energy were in the medium. This does not depend on α.

Hence,

$$W_\alpha = B \exp\left(- \frac{E_\alpha - \mu N_\alpha}{k_B T}\right)$$

$$\sum_{\alpha} W_{\alpha} = 1 \implies B = \frac{1}{\sum_{\alpha} \exp\left(-\frac{(E_{\alpha} - \mu N_{\alpha})}{k_B T}\right)}$$

For our body which can exchange both energy and particles with the medium

$$\overline{N} = \frac{\sum_{\alpha} N_{\alpha} \exp\left[-(E_{\alpha} - \mu N_{\alpha})/k_B T\right]}{\sum_{\alpha} \exp\left[-(E_{\alpha} - \mu N_{\alpha})/k_B T\right]}$$

and

$$\overline{E} = \frac{\sum_{\alpha} E_{\alpha} \exp\left[-(E_{\alpha} - \mu N_{\alpha})/k_B T\right]}{\sum_{\alpha} \exp\left[-(E_{\alpha} - \mu N_{\alpha})/k_B T\right]}$$

Also,

$$S = -k_B \sum_{\alpha} W_{\alpha} \log W_{\alpha}$$

$$= -k_B \log B \sum_{\alpha} W_{\alpha} + \frac{1}{T} \sum_{\alpha} W_{\alpha} E_{\alpha} - \frac{\mu}{T} \sum_{\alpha} W_{\alpha} N_{\alpha}$$

$$= -k_B \log B + \frac{\overline{E} - \mu \overline{N}}{T}$$

Or,

$$k_B T \log B = \overline{E} - T S - \mu \overline{N} = F - \mu \overline{N} = \Omega$$

Hence, we have found that,

$$\Omega = -k_B T \log \sum_{\alpha} \exp\left(-\frac{E_{\alpha} - \mu N_{\alpha}}{k_B T}\right)$$

We have thus obtained $\Omega = \Omega(T, V, \mu)$ since V was fixed and T and μ are given. We assumed all along that E and N could vary for the subsystem but V was fixed and T was fixed. Instead if we want N to be fixed as well then we will set $N_{\alpha} = N$ for all α. Then,

$$\Omega = -k_B T \log\left[\exp\left(\frac{\mu N}{k_B T}\right) \sum_{\alpha} \exp\left(-\frac{E_{\alpha}}{k_B T}\right)\right]$$

$$= -\mu N - k_B T \log \sum_{\alpha} \exp\left(-\frac{E_{\alpha}}{k_B T}\right)$$

We know that $F = \Omega + \mu N$ so that

$$F = -kT \log \sum_\alpha' \exp\left(-\frac{E_\alpha}{k_B T}\right)$$

$$Z = \sum_\alpha' \exp\left(-\frac{E_\alpha}{k_B T}\right) \qquad \text{partition function.}$$

$$\mathcal{L} = \sum_\alpha' \exp\left(-\frac{E_\alpha - \mu N_\alpha}{k_B T}\right) \qquad \text{grand partition function.}$$

These functions form the core of statistical mechanics.

- -

$$S_\alpha' = S'(E_0, N_0) - \left(\frac{\partial S'}{\partial E'}\right)_{V', N'} E_\alpha - \left(\frac{\partial S'}{\partial N'}\right)_{V', E} N_\alpha.$$

Now, $\left.\dfrac{\partial S'}{\partial N'}\right)_{E'} = -\left.\dfrac{\partial S'}{\partial E'}\right)_{N'} \left.\dfrac{\partial E'}{\partial N'}\right)_{S'} = -\dfrac{\mu}{T}$

Hence, $S_\alpha' = S'(E_0, N_0) - \dfrac{E_\alpha}{T} + \dfrac{\mu N_\alpha}{T}$

Note that we could be careless and write

$$\frac{\partial S'}{\partial N'} = \frac{\partial S'}{\partial E'} \frac{\partial E'}{\partial N'}.$$

where we have missed a $-$ sign.

DENSITY OF STATES

In the previous derivation we considered the probability of a single state α whose energy is E_α, and we called that probability W_α. But there are many states with energy E_α, in fact as E_α increases the number of states with energy E_α also increases and each of these states has the same probability. Hence, if ρ_{E_α} is the number of states with energy E_α then

$$W(E_\alpha) = \rho_{E_\alpha} W_\alpha$$

where $W(E_\alpha)$ is the probability of a state having energy E_α. Now if a state has energy E_α then the medium has Γ'_α number of states. The probability of a state having energy E_α is therefore given by;

$$W(E_\alpha) = \frac{\rho_{E_\alpha} \Gamma'_\alpha}{\Gamma_0}$$

All we have learnt is that $W_\alpha = \Gamma'_\alpha / \Gamma_0$, as we had assumed before. ρ_{E_α} is the <u>density of states</u> in a discrete sense and the partition function can be written in terms of it by summing over states with energy E_α rather than the states individually.

$$Z = \sum_{E_\alpha} \rho_{E_\alpha} \exp\left(-\frac{E_\alpha}{k_B T}\right)$$

$$W(E_\alpha) = \frac{1}{Z} \rho_{E_\alpha} \exp\left(-\frac{E_\alpha}{k_B T}\right)$$

Notice that W_α reduces as E_α goes up but ρ_{E_α} increases rapidly as E_α goes up. Hence $W(E_\alpha)$ has a maximum close to E which is the average energy of the body. For macroscopic bodies the energy levels E_α are very closely spaced and we can treat the energy spectrum as being continuous. $W(\mathcal{E})$ is then the probability density function which tells us the probability

the subsystem will have energy between $\mathcal{E}$ and $\mathcal{E}+d\mathcal{E}$.
Normalization demands that

$$\int_0^\infty w(\mathcal{E}) \, d\mathcal{E} = 1$$

Also we see by analogy with the discrete case that

$$w(\mathcal{E}) = \frac{\rho(\mathcal{E})}{Z} \exp\left(-\frac{\mathcal{E}}{k_B T}\right)$$

and, $\quad Z = \int_0^\infty \rho(\mathcal{E}) \exp\left(-\frac{\mathcal{E}}{k_B T}\right) d\mathcal{E}$

$\rho(\mathcal{E})$ is the density of states function and a lot of statistical mechanics deals with getting this guy. With $\mathcal{E}$ written as a continuous variable

$$F = -kT \log \int_0^\infty \rho(\mathcal{E}) \exp\left(-\frac{\mathcal{E}}{k_B T}\right) d\mathcal{E}$$

We have learnt so far how to calculate the partition function. Once we have it we can use it to calculate all other quantities. However, one important comment is in order. Under any conditions the entropy of the system as a whole (subsystem + medium + work source) is simply

$$S_t = k_B \log \Gamma_t$$

If the subsystem has energy E_α then,

$$S_t(E_\alpha) = k_B \log \rho_{E_\alpha} \Gamma_\alpha'$$

and $S_0 - S_t(E_\alpha) = -k_B \log \dfrac{\rho_{E_\alpha} \Gamma_\alpha'}{\Gamma_0} = -k_B \log w(E_\alpha)$

Hence, we arrive at the equation

$$w(E_\alpha) = A \exp\left[\frac{S_t(E_\alpha)}{k_B}\right]$$

Hence the probability that the subsystem has energy E_α is written in terms of the <u>entropy of the total system</u> when

we specify that the subsystem has energy E_α. But we could have followed the same argument through any other variable x which affects the medium. In particular,

$$S'_x = S'_{\bar{x}} - \frac{\partial S'}{\partial x}(x - \bar{x})$$

where $\bar{x}$ is the average value of x, where x is some property of the subsystem. We note that

$$w(x) = A \exp\left[\frac{S_t(x)}{k_B}\right]$$

Now, we already know that $\bar{x}$ is characterised by equilibrium

$$\left(\frac{\partial S_t}{\partial x}\right)_{x=\bar{x}} = 0 \quad \text{and} \quad \left(\frac{\partial^2 S_t}{\partial x^2}\right)_{x=\bar{x}} < 0$$

which is saying that entropy is a maximum at equilibrium if the energy and number of particles of the <u>whole system</u> is held constant. Remember S_t is the entropy of the whole system! By a Taylor series expansion we get,

$$S_t(x) = S_t(\bar{x}) - \frac{1}{2}\beta(x - \bar{x})^2$$

where $\beta > 0$ is. This immediately implies,

$$w(x) = D \exp\left[-\frac{\beta(x - \bar{x})^2}{2 k_B}\right]$$

and
$$\int_{-\infty}^{\infty} w(x) = 1 = D\sqrt{\frac{2\pi k_B}{\beta}}$$

This is a Gaussian form with most of the contribution to $w(x)$ coming from $x = \bar{x}$. We have made what is called the 'quadratic approximation' and this was first derived by Einstein in 1904.

Going back to the usefulness of the partition function let us use it to derive some simple results.

$$E = F + TS \qquad \text{(average energy)}$$

But, $\quad S = -\dfrac{\partial F}{\partial T} = k_B \log Z + \dfrac{k_B T}{Z} \dfrac{\partial Z}{\partial T}$

Or, $\quad E = \cancel{-k_B T \log Z} + \cancel{k_B T \log Z} + \dfrac{k_B T^2}{Z} \dfrac{\partial Z}{\partial T}$

Or, $\quad E = \dfrac{k_B T^2}{Z} \left(\dfrac{\partial Z}{\partial T} \right)_{V,N}$.

Remember, $\dfrac{\partial Z}{\partial T} = \dfrac{1}{k_B T^2} \sum_{\alpha} E_{\alpha} \exp\left(-\dfrac{E_{\alpha}}{k_B T} \right)$

So that, $\quad E = \dfrac{1}{Z} \sum_{\alpha} E_{\alpha} \exp\left(-\dfrac{E_{\alpha}}{k_B T} \right)$

which is entirely expected. As another example,

$$p = -\frac{\partial F}{\partial V} = \frac{k_B T}{Z} \frac{\partial Z}{\partial V} = -\frac{1}{Z} \sum_{\alpha} \frac{dE_{\alpha}}{dV} \exp\left(-\frac{E_{\alpha}}{k_B T} \right)$$

PARTITION FUNCTION OF THE IDEAL GAS

Imagine a bunch of particles in a box of fixed volume V. The number of particles is fixed at N. The particles do not interact with each other and the probability of occupation by multiple particles of a single-particle state is negligible. This last statement amounts to what we call an _ideal gas_. The particles could ~~be~~ be non-interacting but multiple particles could occupy a single particle state. Then the gas would be perfect but non-ideal.

For one particle of the ideal gas,

$$Z_1 = \sum_{q} \exp\left(-\frac{\varepsilon_q}{k_B T} \right)$$

where ε_q is the energy of a particle which is in state $\underline{q} = \{ q_x, q_y, q_z \}$ etc. The particles are considered indisting

-uishable and so the many-body partition function will be

$$Z = \frac{1}{\lfloor N} (Z_1)^N$$

where we divide by $\lfloor N$ since the particles cannot be distinguished from each other. Think of an array of N states each to be filled up by one particle and get this result from permutations.

$$F = -k_B T \log Z = -N k_B T \log Z_1 + k_B T \log \lfloor N .$$

$$P(V,T) = -\frac{\partial F}{\partial V}\Big)_T = \frac{N k_B T}{Z_1} \frac{\partial Z_1}{\partial V} \longrightarrow \text{(A)}$$

Now remember that $\varepsilon_q = \frac{\hbar^2 q^2}{2m} = \frac{\hbar^2 (q_x^2 + q_y^2 + q_z^2)}{2m}$

where $q_x = \left(\frac{2\pi}{L}\right) l_x$ etc $l_x = 0, \pm 1, \pm 2, \pm 3, \dots$

Therefore, since $L^3 = V$ we have

$$\frac{\partial Z_1}{\partial V} = -\frac{1}{k_B T} \sum_q \frac{\partial \varepsilon_q}{\partial V} \exp\left(-\frac{\varepsilon_q}{k_B T}\right) = \frac{2/3}{V k_B T} \sum_q \varepsilon_q \exp\left(\frac{-\varepsilon_q}{k_B T}\right)$$

Plugging this back in (A) we find

$$P = \frac{2}{3} \frac{N}{V} \bar{\varepsilon} = \frac{2}{3} \frac{E}{V}$$

where $\bar{\varepsilon} = \frac{1}{Z_1} \sum_q \varepsilon_q \exp\left(-\frac{\varepsilon_q}{k_B T}\right)$. In terms of density of states we have

$$\bar{\varepsilon} = \frac{\int \varepsilon \rho(\varepsilon) e^{-\varepsilon/k_B T} d\varepsilon}{\int \rho(\varepsilon) e^{-\varepsilon/k_B T} d\varepsilon}.$$

For a single particle, the number of ~~particles~~ states in a region $d^3p \, d^3r$ of its phase space is

$$\frac{d^3p \, d^3r}{(2\pi\hbar)^3} \qquad \left(\hbar = \frac{h}{2\pi} \text{ is Planck's const}\right)$$

where $d^3p = dp_x \, dp_y \, dp_z$ etc. The volume of a single

unit of phase-space is $(2\pi\hbar)^3$ since we cannot specify the momentum and position of a particle any more accurately than saying $\Delta p_k \Delta r_k = 2\pi\hbar$. Now for a perfect gas nothing depends on r and the problem is isotropic so that the number of states between $p+dp$ and p is

$$\frac{4\pi V}{(2\pi\hbar)^3} p^2 dp$$

The number of states per unit range of energy is,

$$\rho(\varepsilon)d\varepsilon = \frac{4\pi V}{(2\pi\hbar)^3} p^2 \frac{dp}{d\varepsilon} d\varepsilon$$

For classical particles $\varepsilon = \frac{p^2}{2m}$ and hence;

$$\rho(\varepsilon)d\varepsilon = \frac{4\pi\sqrt{2} \, V \, m^{3/2}}{(2\pi\hbar)^3} \varepsilon^{1/2} d\varepsilon$$

Once we have arrived at the density of states we can use it to calculate the partition function, the average energy etc. For example,

$$\overline{\varepsilon} = \frac{\int \varepsilon\rho(\varepsilon) e^{-\varepsilon/k_B T} d\varepsilon}{\int \rho(\varepsilon) e^{-\varepsilon/k_B T} d\varepsilon} = \frac{\int \varepsilon^{3/2} e^{-\varepsilon/k_B T} d\varepsilon}{\int \varepsilon^{1/2} e^{-\varepsilon/k_B T} d\varepsilon}$$

We know $\Gamma(n+1) = \int_0^\infty x^n e^{-x} dx$ are generalised factorials with the property $\frac{\Gamma(n+1)}{\Gamma(n)} = n$. $(\Gamma(n) = \underline{n-1})$

Hence $\overline{\varepsilon} = k_B T \dfrac{\int_0^\infty x^{3/2} e^{-x} dx}{\int_0^\infty x^{1/2} e^{-x} dx} = \frac{3}{2} k_B T.$

This when taken together with $PV = \frac{2}{3} N\overline{\varepsilon}$ gives

$$PV = N k_B T$$

which is the well known result. Electrons in a metal, phonons in a crystal, electron pairs in superconductors, and

spin waves in ferromagnetic materials can all be treated using the methods used for perfect gases. That is the reason why it is useful to derive the partition function of an ideal gas.

SAKUR-TETRODE FORMULA

Let us try to compute the entropy of an ideal gas confined to a volume V with fixed E and N.

$$E = \frac{1}{2m} \sum_{i=1}^{N} p_i^2 \quad (=) \quad \frac{1}{2m} \sum_{i=1}^{N} \sum_{j=1}^{3} p_{i,j}^2$$

Clearly the locus of allowed values of the momenta is the surface of a hypersphere of radius $r = \sqrt{2mE}$ in 3N dimensional space. The surface area of this sphere is proportional to r^{3N-1}. The microstate of a particle can be specified completely if we supply both the momentum and position of the particle. Each particle can be located anywhere in the volume V so a factor V^N will enter into the number of states. The area of the hypersphere in 3N dimensions is,

$$\left(\frac{2\pi^{3N/2}}{\lfloor \frac{3N}{2} - 1} \right) (2mE)^{\frac{3N-1}{2}} \qquad \qquad \Gamma\left(\frac{3N}{2}\right)$$

Hence the total number of available states is:

$$\frac{1}{\lfloor N} \frac{2\pi^{3N/2}}{\lfloor \left(\frac{3N}{2} - 1\right)} \frac{(2mE)^{\frac{3N-1}{2}} V^N}{(2\pi\hbar)^{3N}}$$

The $\lfloor N$ in the front appears because the particles are indistinguishable.

Sakur-Tetrode formula.

$$S = k_B \log\left[\frac{2\pi^{\frac{3N}{2}}}{\lfloor \frac{3N}{2} - 1} (2mE)^{\frac{3N-1}{2}} V^N \frac{1}{\lfloor N} \frac{1}{(2\pi\hbar)^{3N}} \right]$$

$$= N k_B \log\left[V E^{3/2} \right] + \text{const.} \qquad (\text{extensive when N is large} \sim 10^{23})$$

$$\rho(\mathcal{E})d\mathcal{E} \propto \frac{\partial V^*}{\partial \mathcal{E}} d\mathcal{E} \quad \text{where } V^* \text{ is the } \sout{\text{distinguishable}} \text{ volume}$$

in momentum space of N indistinguishable particles. Remember $p^* = \sqrt{2m\mathcal{E}}$.

$$V^* \propto p^{*\, 3N} \underset{\text{No!}}{\cancel{(-1)}} \Rightarrow \frac{\partial V^*}{\partial \mathcal{E}} = p^{*\, 3N-1} \frac{\partial p^*}{\partial \mathcal{E}} \propto (\mathcal{E}^{1/2})^{3N-1} \mathcal{E}^{-1/2}$$

Let us now go back to the case where we have a fixed volume V containing ideal gas at constant temperature T. The probability of finding the gas with total energy $\mathcal{E}$ is simply

$$W(\mathcal{E}) = C_N \, \mathcal{E}^{\frac{3N}{2}-1} \exp\left(-\frac{\mathcal{E}}{k_B T}\right).$$

We enforce $\int_0^\infty W(\mathcal{E})\, d\mathcal{E} = 1$

or, $\frac{1}{C_N} = (k_B T)^{\frac{3N}{2}} \int_0^\infty x^{\frac{3N}{2}-1} e^{-x}\, dx \quad \left(\because x = \frac{\mathcal{E}}{k_B T}\right)$

$$= \Gamma\left(\frac{3N}{2}\right) (k_B T)^{\frac{3N}{2}}$$

This means that the probability of finding the gas with energy between $\mathcal{E}$ and $\mathcal{E}+d\mathcal{E}$ is

$$W(\mathcal{E}) = \frac{1}{\Gamma\left(\frac{3N}{2}\right)} \left(\frac{\mathcal{E}}{k_B T}\right)^{\frac{3N}{2}-1} \frac{1}{k_B T} e^{-\frac{\mathcal{E}}{k_B T}}$$

For a single particle this reduces to

$$W(\mathcal{E}) = \frac{1}{\Gamma\left(\frac{3}{2}\right) (k_B T)^{3/2}} \mathcal{E}^{1/2} e^{-\mathcal{E}/k_B T}$$

The product initially rises with energy $\mathcal{E}$ (near zero) and then reaches a maximum and then drops with the energy $\mathcal{E}$ since the exponential $\exp\left(-\frac{\mathcal{E}}{k_B T}\right)$ goes to zero faster than any power of $\mathcal{E}$ increases. Most importantly there is a maximum in $W(\mathcal{E})$ which will tell us the most likely state. If the maximum in $W(\mathcal{E})$ is extremely sharp then the most probable energy will also be the average energy. The most probable energy is obtained by setting

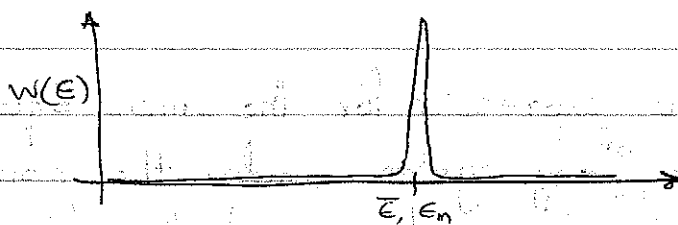$$\frac{dW}{d\mathcal{E}} = 0 \Rightarrow \mathcal{E}_m = \left(\frac{3N}{2} - 1\right) k_B T$$

The average energy is obtained by $\overline{\mathcal{E}} = \int \mathcal{E} W(\mathcal{E})\, d\mathcal{E}$.

$$\bar{\mathcal{E}} = C_N \int \mathcal{E}^{\frac{3N}{2}} e^{-\mathcal{E}/k_B T} \, d\mathcal{E}$$

$$= C_N (k_B T)^{\frac{3N}{2}+1} \int x^{\frac{3N}{2}} e^{-x} \, dx \qquad \left(x = \frac{\mathcal{E}}{k_B T} \right)$$

$$= C_N (k_B T)^{\frac{3N}{2}+1} \; \Gamma \left(\frac{3N}{2} + 1 \right)$$

$$= \frac{3N}{2} k_B T$$

We see that $\mathcal{E}_m$ and $\bar{\mathcal{E}}$ are nearly equal only if N is extremely large. For a single particle

$$\bar{\mathcal{E}} = \frac{3}{2} k_B T \quad \text{and} \quad \mathcal{E}_m = \frac{1}{2} k_B T$$

which immediately tells us that the distribution is not very sharply peaked. For many particles the result is almost a delta function.

We will now look at fluctuations which will give us some idea about the ~~a~~ width of the distribution.

FLUCTUATIONS

In a constant temperature ensemble the energy of the sub-system can fluctuate about the average value.

$$\Delta E = \mathcal{E} - E \qquad \left(E = \bar{\mathcal{E}} \; \text{\st{ }} = \int \mathcal{E} W(\mathcal{E}) \, d\mathcal{E} \right)$$

Clearly $\overline{\Delta E} = 0$. Now let us square the fluctuations before averageing.

$$\overline{(\Delta E)^2} = \overline{(\mathcal{E} - E)^2} = \overline{(\mathcal{E}^2 - 2\mathcal{E}E + E^2)} = \overline{\mathcal{E}^2} - 2\bar{\mathcal{E}}E + E^2$$

$$\Rightarrow \overline{(\Delta E)^2} = \overline{\mathcal{E}^2} - E^2$$

$$= \int \mathcal{E}^2 W(\mathcal{E}) \, d\mathcal{E} - E^2$$

We can use a trick to compute this quantity directly from the partition function. We remember that

$$Z = \int \rho(\mathcal{E}) e^{-\mathcal{E}/k_B T} d\mathcal{E}$$

and $\quad F = -k_B T \log Z$

Now let us calculate $\dfrac{\partial^2 F}{\partial T^2} = -\dfrac{\partial^2}{\partial T^2}\left(-k_B T \log Z\right)$

$$\frac{\partial^2 F}{\partial T^2} = \frac{1}{k_B T^3}\left[\frac{\left(\int \mathcal{E}\rho(\mathcal{E}) e^{-\mathcal{E}/k_B T} d\mathcal{E}\right)^2}{Z^2} - \frac{1}{Z}\int \mathcal{E}^2 \rho(\mathcal{E}) e^{-\mathcal{E}/k_B T} d\mathcal{E}\right]$$

$$= \frac{E^2 - \overline{\mathcal{E}^2}}{k_B T^3}$$

Hence, $\quad \overline{(\Delta E)^2} = \overline{\mathcal{E}^2} - E^2 = -k_B T^3 \dfrac{\partial^2 F}{\partial T^2} = k_B T^2 C_V$

This is the expression for the mean square fluctuations in the energy of any system under the constraint that it is at constant temperature and the fluctuations occur at constant volume. In case of an ideal gas

$$E = \overline{\mathcal{E}} = \frac{3}{2} N k_B T$$

$$C_V = \frac{\partial E}{\partial T}\bigg) = \frac{3}{2} N k_B$$

$$\frac{\sqrt{\overline{(\Delta E)^2}}}{E} = \frac{\sqrt{k_B T^2 \frac{3}{2} N k_B}}{\frac{3}{2} N k_B T} = \frac{1}{\sqrt{\frac{3}{2}}} \frac{1}{\sqrt{N}} \sim \frac{1}{\sqrt{N}}$$

The relative fluctuations in the energy are of order $\frac{1}{\sqrt{N}}$. One can similarly show that when V and T are held fixed but N is allowed to vary that

$$\frac{\overline{(\Delta N)^2}}{N^2} = \frac{k_B T}{V} K_T$$

For an ideal gas $\quad PV = Nk_BT$

$$K_T = -\frac{1}{V}\frac{\partial}{\partial P}\left(\frac{Nk_BT}{P}\right) = \frac{Nk_BT}{P^2V} = \frac{1}{P}$$

$$\frac{\sqrt{\overline{(\Delta N)^2}}}{N} = \frac{\sqrt{k_BT/PV}}{N} = \frac{1}{\sqrt{N}}$$

Now these results depend on the values of C_v and K_T for an ideal gas but for any other type of material C_v and K_T are not too different. Hence the _relative_ RMS fluctuations are always of order $N^{-1/2}$.

Once we know the mean square energy fluctuation we can determine the fluctuation in other quantities. For example, if we have a situation where V and N are constant then,

$$\Delta T = \left(\frac{\partial T}{\partial E}\right)_{V,N}\Delta E = \frac{\Delta E}{C_v}$$

$$\overline{(\Delta T)^2} = \frac{1}{C_v^2}\overline{(\Delta E)^2} = \frac{kT^2}{C_v}$$

In order to calculate mean square fluctuations of various thermodynamic quantities in a general way we make use of the Gaussian approximation of Einstein. Suppose we take $\bar{x} = 0$, so that x is itself departure from equilibrium of a quantity. Then

$$\overline{x^2} = \sqrt{\frac{\beta}{2\pi}}\int_{-\infty}^{\infty} x^2 \exp\left(-\frac{1}{2}\beta x^2\right)dx$$

$$= \frac{1}{\beta}$$

x could be temperature ΔT or pressure or any quantity we like.

Often we have a sub-system immersed in a bath at constant T and P and both S and V of the subsystem can fluctuate. How can we get a joint probability distribution for these fluctuations. Remember that

$$w(x) \propto \exp\left(\frac{\Delta S_t}{k_B}\right)$$

where, $\Delta S_t = S_t(x) - S_t(0)$

S_t being the entropy of the sub-system + medium combined. $S_t = S + S'$ where S' is the entropy of the sub-system. The medium is always in eqbm.

$$\Delta S' = \frac{\Delta E' + P\Delta V'}{T} = \frac{-\Delta E - P\Delta V}{T}$$

where we use $V' + V = $ const and $E' + E = $ const. Hence,

$$w \propto \exp\left(-\frac{\Delta E - T\Delta S + P\Delta V}{k_B T}\right)$$

where all quantities now refer to the sub-system alone. Now at equilibrium the argument of the exponential is zero to leading order (Gibbs free energy is minimum) so we expand to second order in fluctuations assuming that the fluctuations are small in comparison to the size of the medium.

$$\Delta E = \frac{\partial E}{\partial S}\Delta S + \frac{\partial E}{\partial V}\Delta V + \frac{1}{2}\left[\frac{\partial^2 E}{\partial S^2}(\Delta S)^2 + 2\frac{\partial^2 E}{\partial S \partial V}\Delta S \Delta V + \frac{\partial^2 E}{\partial V^2}(\Delta V)^2\right]$$

But $\left.\frac{\partial E}{\partial S}\right)_V = T$ and $\left.\frac{\partial E}{\partial V}\right)_S = -P$ and hence we find

$$w \propto \exp\left(-\frac{1}{2k_B T}\left(\frac{\partial^2 E}{\partial S^2}(\Delta S)^2 + 2\frac{\partial^2 E}{\partial S \partial V}\Delta S \Delta V + \frac{\partial^2 E}{\partial V^2}(\Delta V)^2\right)\right)$$

$$\left(\frac{\partial^2 E}{\partial S^2}\Delta S + \frac{\partial^2 E}{\partial S \partial V}\Delta V\right)\Delta S + \left(\frac{\partial^2 E}{\partial S \partial V}\Delta S + \frac{\partial^2 E}{\partial V^2}\Delta V\right)\Delta V$$

$$= \Delta S \, \Delta\left(\frac{\partial E}{\partial S}\right) + \Delta V \, \Delta\left(\frac{\partial E}{\partial V}\right) = \Delta S \Delta T - \Delta V \Delta P$$

So, $\quad w \propto \exp\left(-\dfrac{\Delta T \, \Delta S - \Delta P \, \Delta V}{2 k_B T}\right)$

How are temperature and pressure fluctuations going on? The <u>medium</u> is at const temp and pressure. The body is fluctuating about this temp and pressure. A bit more simplification makes this prob ~~dist~~ density function more transparent. Suppose $S = S(T,V)$ then

$$\Delta S = \left.\frac{\partial S}{\partial T}\right)_V \Delta T + \left.\frac{\partial S}{\partial V}\right)_T \Delta V = \frac{C_V}{T}\Delta T + \left.\frac{\partial P}{\partial T}\right)_V \Delta V$$

$$\Delta P = \left.\frac{\partial P}{\partial T}\right)_V \Delta T + \left.\frac{\partial P}{\partial V}\right)_T \Delta V = \left.\frac{\partial P}{\partial T}\right)_V \Delta T - \frac{1}{V K_T}\Delta V$$

$$\Delta T \, \Delta S - \Delta P \, \Delta V = \frac{C_V}{T}(\Delta T)^2 - \frac{1}{V K_T}(\Delta V)^2$$

$$w(\Delta T, \Delta V) \propto \exp\left(-\frac{C_V (\Delta T)^2}{2 k_B T^2} \oplus \frac{(\Delta V)^2}{2 k_B T K_T}\right)$$

Gaussian distribution in two variables. Note that $\overline{\Delta T \, \Delta V} = 0$, they are uncorrelated.