The microcanonical ensemble

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Canonical Ensemble (Gibbs formula, $p = \frac{e^{-\beta E}}{Z}$):

↳ Your system can have any size, but it is always coupled to a very large heat bath.

Microcanonical Ensemble ($S = \ln \Omega$)

↳ Your system itself is very large and it is completely isolated

The microcanonical ensemble is valuable from a conceptual point of view: it will help us have a deeper interpretation of thermal phenomena. However, it is terrible for solving problems.

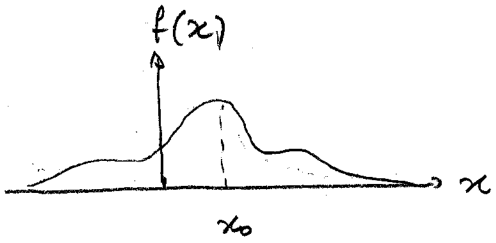
References:

- Salinas, chapters 2 and 4
- Landau, chapter 1.

Laplace's asymptotic method

Before we begin I want to show you a method to approximate integrals of the form

$$I = \int_{-\infty}^{\infty} dx \; e^{Nf(x)} \qquad (1)$$



Here f(x) is an arbitrary function which has a maximum somewhere at x_0. Moreover, N is a very large integer (maybe 10^{23}).

The whole point of this integral is that when you exponentiate $Nf(x)$ you exacerbate the maximum. And when N is large, you exacerbate it a lot (see example in the next page). the position of the maximum remains the same, but it becomes much much sharper.

The idea is then to expand f(x) in a Taylor series around its maximum:

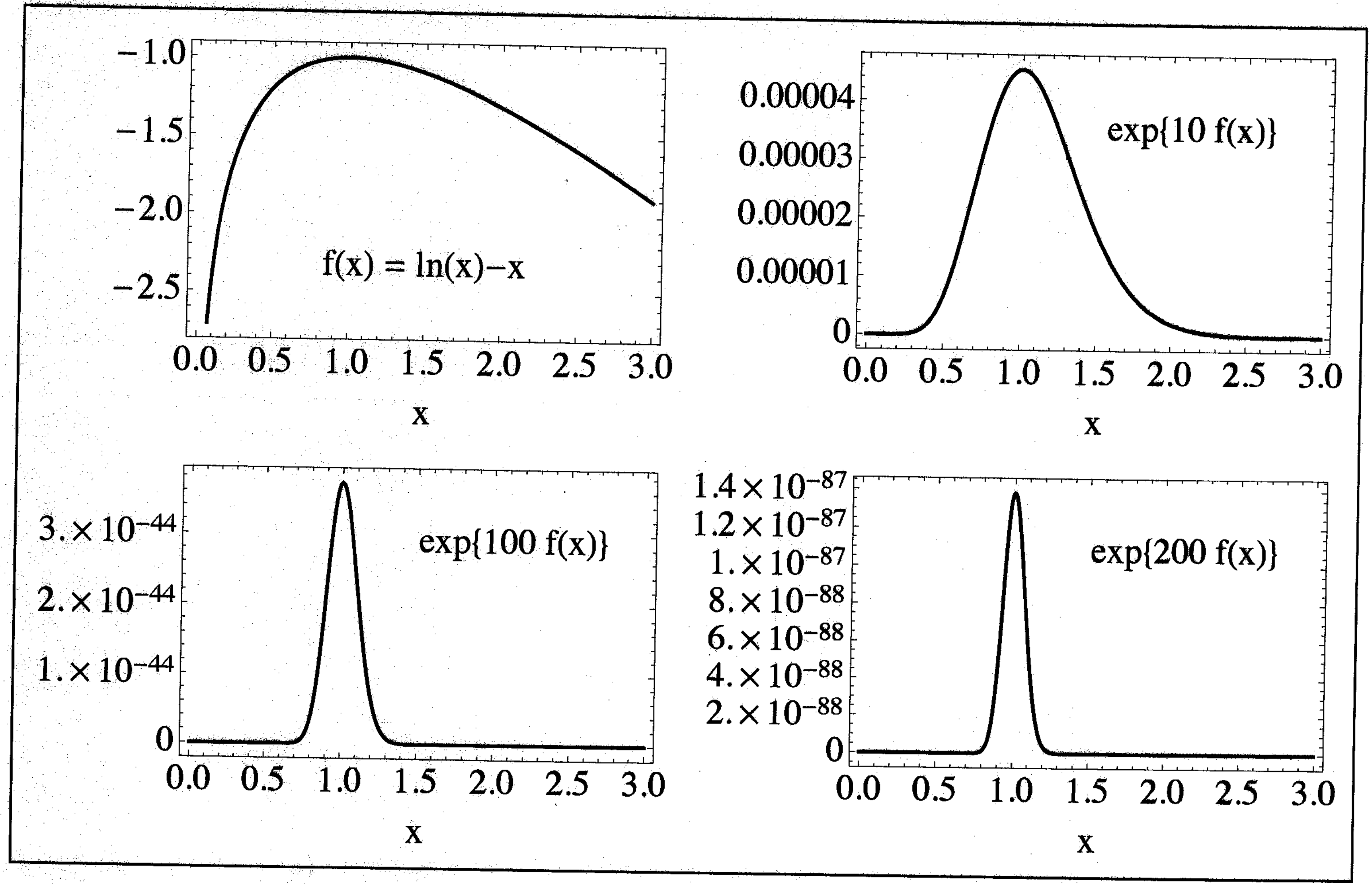
$$f(x) \simeq f(x_0) + \underbrace{f'(x_0)(x-x_0)}_{\substack{=0 \text{ for a} \\ \text{maximum}}} + \frac{f''(x_0)}{2!}(x-x_0)^2 + \dots \qquad (2)$$

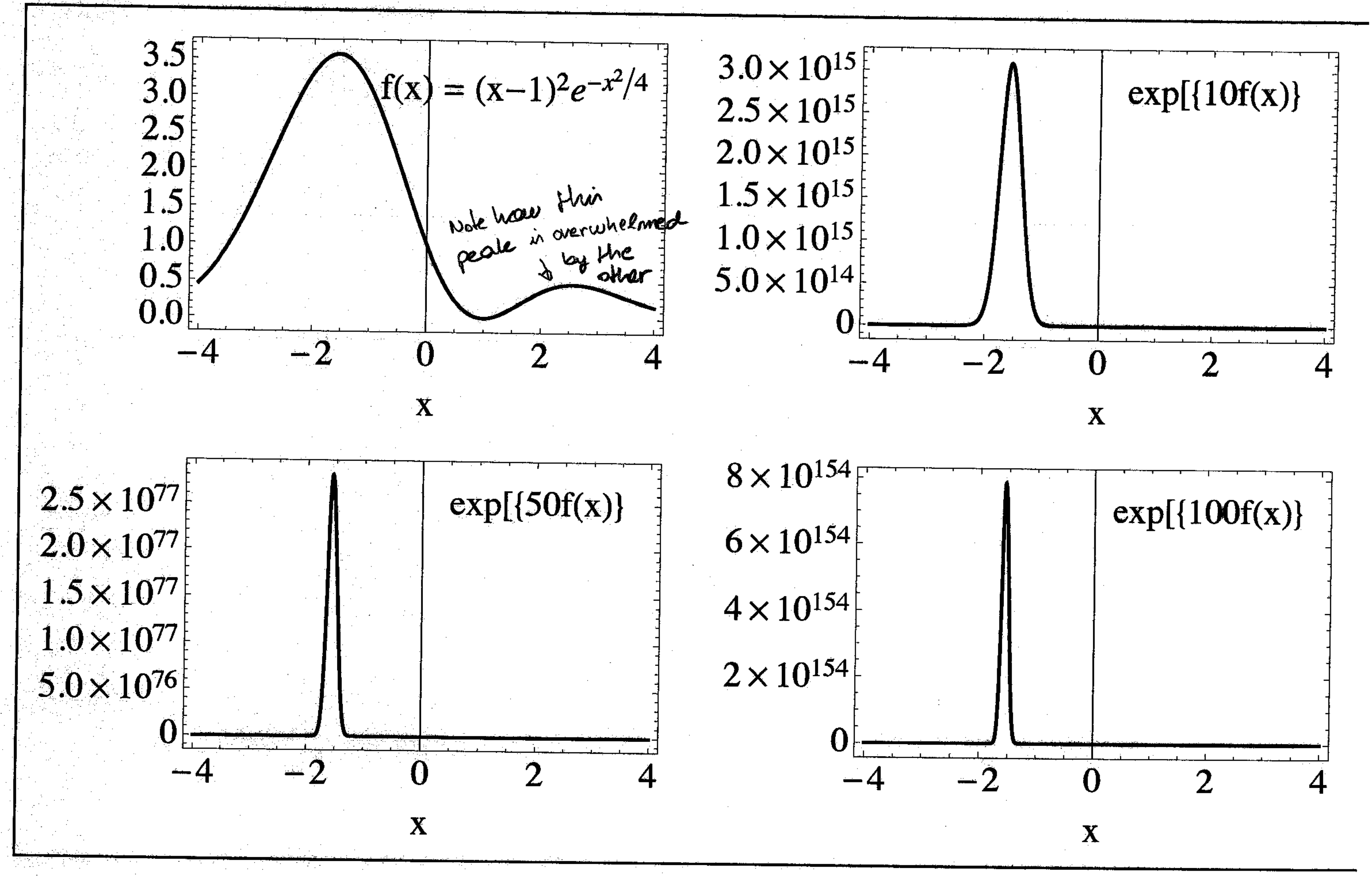
Since we are talking about a maximum $f'(x_0) = 0$ and $f''(x_0) < 0$.

Eq (1) then becomes

$$I \simeq \int_{-\infty}^{\infty} dx \, \exp\left\{ N \left[f(x_0) - \frac{|f''(x_0)|^2}{2!}(x-x_0)^2 \right\}\right.$$

$$= e^{Nf(x_0)} \int_{-\infty}^{\infty} dx \, e^{-a(x-x_0)^2} \qquad a = \frac{N|f''(x_0)|}{2}$$





Note how this peak is overwhelmed by the other this is a Gaussian integral. thus we get

$$I \simeq e^{Nf(x_0)} \sqrt{\frac{\pi}{a}} = e^{Nf(x_0)} \sqrt{\frac{2\pi}{N|f''(x_0)|}}$$

thus, we finally arrive at Laplace's method:

$$\boxed{\int_{-\infty}^{\infty} e^{Nf(x)}\,dx \simeq e^{Nf(x_0)} \sqrt{\frac{2\pi}{N|f''(x_0)|}}} \qquad (3)$$

<u>Remarks</u>:

- the integral does not have to be from $-\infty$ to ∞. All you need is that the interval of integration encompasses the maximum.
- If $f(x)$ has many local maxima, then usually the global maximum will dominate.
- If $f(x)$ has two or more maxima with the same height, then you should consider the contribution of both
- the important part of (3) is the exponential. the pre-factor is just a tiny correction. thus, if you are in a hurry, you may simply use

$$\boxed{\int_{-\infty}^{\infty} dx\, e^{Nf(x)} \simeq e^{Nf(x_0)}} \qquad (4)$$

- this method can also be extended to integrals in the complex plane. then it's called the <u>Saddle point method</u>
- there is also another method for complex integration, which is called the <u>Stationary phase method</u>. the idea is similar but the principles are different.

Example: Stirling's formula for $\ln N!$

We may write $N!$ in terms of the Gamma function

$$N! = \int_0^\infty dx\, x^N e^{-x} = \int_0^\infty dx\, e^{-x + N\ln x} \tag{5}$$

$$= \int_0^\infty dx\, \exp\{N(\ln x - x/N)\} \tag{6}$$

This is the form (3) with $f(x) = \ln x - x/N$. This function will have a maximum at

$$0 = f'(x) = \frac{1}{x} - \frac{1}{N} \quad \rightsquigarrow \quad x_0 = N$$

Thus, applying (3) we get $f(x_0) = \ln N - 1$, $|f''(x_0)| = 1/N^2$

$$\boxed{N! \simeq (2\pi N)^{1/2} e^{N(\ln N - 1)}} \tag{7}$$

or

$$\boxed{\ln N! \simeq N\ln N - N + \frac{1}{2}\ln(2\pi N)} \tag{8}$$

The last term is $\mathcal{O}(\ln N)$ so for large N it becomes completely irrelevant. Eq (8) is Stirling's formula.

Multiplicity

We will now consider an isolated system. For instance, we could have a gas in a cylinder. There is no bath. Just the system. We also assume that the system is macroscopically large and sufficiently chaotic in order to ensure that it is ergodic (Any gas will behave like this since hard-sphere collisions are highly chaotic).

The central quantity for this type of system is the multiplicity

$$\boxed{\text{Multiplicity} = \Omega(E) = \text{number of microstates corresponding to a given macrostate}} \tag{9}$$

The "macrostate" here means a given energy E.

Example: two-state system

Suppose you have N particles that can either have energy $E_0 = 0$ or $E_1 = \epsilon$. How many ways are there to configure the system so that the total energy is E? That is $\Omega(E)$.

Now, let N_1 be the number of particles with energy $E_1 = \epsilon$ and $N_0 = N - N_1$ the number of particles with energy $E_0 = 0$. Then the only allowed energies E of the system will be multiples of ϵ since

$$E = N_0 E_0 + N_1 E_1 = N_1 \epsilon \tag{10}$$

So to have energy E we must have $N_1 = E/\epsilon$ particles in the excited state

We have therefore reduced the problem to a combinatorial question: how many ways are there to choose N_1 out of N particles? The answer is

$$\Omega(E) = \binom{N}{N_1} = \frac{N!}{N_1!\,(N-N_1)!} \tag{11}$$

or,

$$\Omega(E) = \frac{N!}{\left(\frac{E}{\epsilon}\right)!\,\left(N-\frac{E}{\epsilon}\right)!} \tag{12}$$

this is the multiplicity of the energy E: the number of microstates whose energy is E.

The fundamental postulate of statistical mechanics

There is one postulate which permeates all of equilibrium statistical mechanics: the postulate of equal a priori probabilities

In thermal equilibrium all states with the same energy are equally likely (13)

We used it before when we derived the Gibbs formula. Now we will use it again

In the present context, our system is isolated. So if we prepare it in a way that its total energy is E, this energy will not change in time (we are not performing work so energy is conserved).

Thus, if the energy is E and the system is in equilibrium, all states with energy E must be equally likely. This is where the multiplicity enters: since they are all equally likely, by normalization their probabilities must be $1/\Omega(E)$. Thus

$$\rho_m = \begin{cases} \dfrac{1}{\Omega(E)} & \text{if } E_m = E \\ 0 & \text{otherwise} \end{cases} \qquad (14)$$

this result is valid for each energy E that you put the system on

The entropy of the system will be

$$S = -k_B \sum_m P_m \ln P_m$$

$$= -k_B \sum_{\substack{m \text{ with} \\ E_m = E}} \frac{1}{\Omega} \ln (1/\Omega)$$

← there are Ω terms

$$= k_B \frac{1}{\Omega} \ln \Omega \sum_{\substack{m \text{ with} \\ E_m = E}} 1$$

∴

$$\boxed{S = k_B \ln \Omega} \qquad (15)$$

The entropy is directly related to the multiplicity! This is Boltzmann's formula. It is engraved in his tombstone in Vienna. Note that here $S = S(E)$ and not T. Temperature haven't yet entered the game.

<u>Ex</u>: <u>two-state system</u> [Eqs (11) or (12)]

$$S = k_B \ln N! - k_B \ln N_1! - k_B \ln (N - N_1)!$$

$$\approx k_B \{ N \ln N - N \} - k_B \{ N_1 \ln N_1 - N_1 \} - k_B \{ (N-N_1) \ln (N-N_1) + - (N-N_1) \}$$

$$= k_B \{ N \ln N - N_1 \ln N_1 - (N - N_1) \ln (N - N_1) \}$$

$$= k_B \left\{ N \ln \left(\frac{N}{N-N_1} \right) - N_1 \ln \left(\frac{N_1}{N-N_1} \right) \right\}$$

or

$$\boxed{S(E,N) = k_B \left\{ N \ln \left(\frac{N}{N - E/\epsilon} \right) - \frac{E}{\epsilon} \ln \left(\frac{E/\epsilon}{N - E/\epsilon} \right) \right\}} \qquad (16)$$

Note how S/N is a function only of E/N :

$$\frac{S}{N} = k_B \ln\left(\frac{1}{1 - E/\epsilon N}\right) - \frac{E}{\epsilon N} \ln\left(\frac{E/\epsilon N}{1 - E/\epsilon N}\right)$$

If we let $u = E/\epsilon N$ then we get

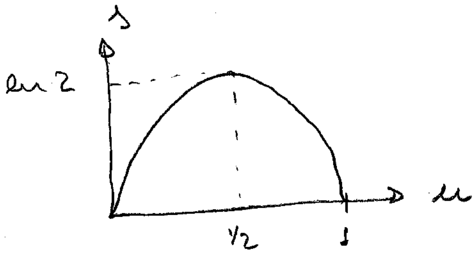
$$\boxed{s = \frac{S}{N} = -k_B \ln(1-u) - u \ln\left(\frac{u}{1-u}\right)} \qquad (17)$$

The entropy is therefore an extensive quantity.

The quantity u may vary in the interval

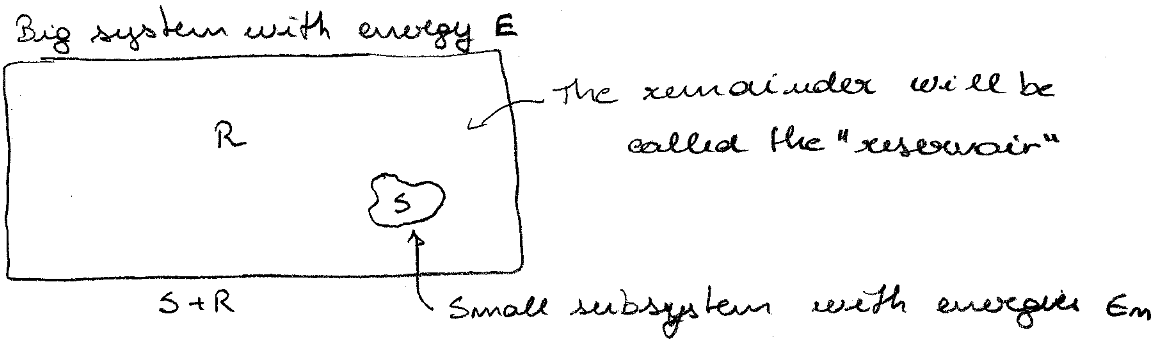
$$\text{All particles in the ground state}\left\{\begin{array}{c} 0 \leq u \leq 1 \\ 0 \leq E \leq N\epsilon \end{array}\right\}\text{All particles in the excited state.} \qquad (18)$$

Eq (17) looks like this



Alternative derivation of the Gibbs formula

Now I want to show you how we may derive the Gibbs formula from Eq (13). Suppose we look at a small part of our big system



We now ask for the probability P_m that the small subsystem has energy ϵ_m. Since S is very tiny, we may assume that S and R are statistically independent. that is

$$\underset{\substack{\uparrow \\ \frac{1}{\Omega(E)}}}{P_{S+R}} \approx \underset{\substack{\uparrow \\ \frac{1}{\Omega_R(E-\epsilon_m)}}}{P_R} P_S \leftarrow P_m$$

Since the total energy is E, and since we are asking about S having energy ϵ_m, the reservoir energy must be $E - \epsilon_m$. So its probability will be proportional to $\Omega_R(E-\epsilon_m)$, where Ω_R is the multiplicity of the reservoir.

Thus

$$P_m = \frac{\Omega_R(E-\epsilon_m)}{\Omega(E)} \qquad (19)$$

The subsystem S is tiny compared with the reservoir, so we may as well write $\Omega_R = c\,\Omega$, where c is some constant.

We now have

$$P_m = c\,\frac{\Omega(E-\epsilon_m)}{\Omega(E)} = c\exp\left\{ \ln\Omega(E-\epsilon_m) - \ln\Omega(E) \right\}$$

$$= c\exp\left\{ \frac{S(E-\epsilon_m) - S(E)}{k_B} \right\}$$

To finish, we expand $S(E-\epsilon_m)$ in a Taylor series as $\epsilon_m << E$.

We then get

$$S(E-\epsilon_m) \simeq S(E) - \frac{\partial S}{\partial E}\epsilon_m$$

Thus

$$\boxed{P_m = c\exp\left\{ -\frac{1}{k_B}\left(\frac{\partial S}{\partial E}\right)\epsilon_m \right\}} \qquad (20)$$

this has the structure of the Gibbs formula with

$$\boxed{\beta := \frac{1}{k_B}\frac{\partial S}{\partial E}} \qquad (21)$$

the constant c is simply the normalization $1/Z$, so we conclude that

$$P_m = \frac{e^{-\beta\epsilon_m}}{Z}. \qquad (22)$$

which is the Gibbs formula

Eq (21) establishes β as being a property of the bath. It therefore defines microscopically what is the temperature of the bath

$$\boxed{\frac{1}{T} = \frac{\partial S}{\partial E} = k_B \frac{\partial}{\partial E} \ln \Omega(E)} \tag{23}$$

Thus, T is proportional to the slope (or sensitivity) of $\Omega(E)$ to changes in E. This gives a purely microscopic interpretation of temperature.

Example: 2-state system

In (17) we found that

$$s = \frac{S}{N} = -k_B \ln(1-u) - k_B u \ln\left(\frac{u}{1-u}\right)$$

where $u = E/N\epsilon$. Now:

$$\frac{\partial S}{\partial E} = \frac{\partial(S/N)}{\partial(E/N)} = \frac{1}{\epsilon}\frac{\partial s}{\partial u}$$

$$= -\frac{k_B}{\epsilon}\frac{\partial}{\partial u}\ln(1-u) - \frac{k_B}{\epsilon}\frac{\partial}{\partial u}\left[u \ln\left(\frac{u}{1-u}\right)\right]$$

$$= -\frac{k_B}{\epsilon}\left[\frac{-1}{1-u}\right] - \frac{k_B u}{\epsilon}\underbrace{\left[\frac{1}{u} - \frac{(-1)}{1-u}\right]}_{\frac{1-u+u}{u(1-u)} = \frac{1}{u(1-u)}} - \frac{k_B}{\epsilon}\ln\left(\frac{u}{1-u}\right)$$

Thus

$$\frac{\partial S}{\partial E} = -\frac{k_B}{\epsilon}\ln\left(\frac{u}{1-u}\right) = \frac{1}{T}$$

This gives

$$\frac{u}{1-u} = e^{-\epsilon/k_B T}$$

or

$$u\left(1 + e^{-\beta\epsilon}\right) = e^{-\beta\epsilon}$$

thus

$$\frac{E}{N\epsilon} = \frac{e^{-\beta\epsilon}}{1+e^{-\beta\epsilon}} = \frac{1}{e^{\beta\epsilon}+1}$$

$$\Rightarrow \boxed{\frac{E}{N} = \frac{\epsilon}{e^{\beta\epsilon}+1}}$$

this is the same result we get using the Gibbs formula:

$$Z_1 = \sum_{m=0,1} e^{-\beta E_m} = e^{-\beta E_0} + e^{-\beta E_1} = 1 + e^{-\beta \epsilon}$$

$$U_1 = -\frac{\partial}{\partial \beta} \ln Z_1 = - \frac{1}{1 + e^{-\beta \epsilon}} \left(-\epsilon e^{-\beta \epsilon} \right)$$

$$= \frac{\epsilon}{e^{\beta \epsilon} + 1}$$

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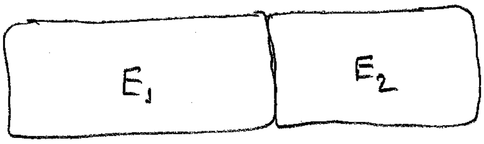
The 2^{nd} law of thermodynamics

When we have an isolated system, the 2^{nd} law may be formulated as

2^{nd} law: when a system is allowed to evolve in isolation, it will tend to the macrostate having the highest multiplicity (which is the same as highest entropy) (24)

To understand how this works, consider two systems separated by walls that allow them to exchange heat



Let $E = E_1 + E_2$. The composite system is isolated, but the individual parts will exchange heat with each other until they reach thermal equilibrium. According to the 2^{nd} law, the equilibrium state will be that which maximizes the multiplicity

$$\Omega(E, E_1) = \Omega_1(E_1)\,\Omega_2(E - E_1) \tag{25}$$

Here I noted that E is fixed (because the system is isolated) so Ω will actually only depend on E_1 and we may write $E_2 = E - E_1$.

Since $\ln(x)$ is a monotonically increasing function, we may as well maximize

$$
\begin{aligned}
S(E, E_1) &= k_B \ln \Omega(E, E_1) \\
&= S_1(E_1) + S_2(E - E_1) \\
&= k_B \ln \Omega_1(E_1) + k_B \ln \Omega_2(E - E_1) \qquad (26)
\end{aligned}
$$

To find the maximum we differentiate S w/r to E_1:

$$
\begin{aligned}
\frac{\partial S}{\partial E_1} &= \frac{\partial S_1}{\partial E_1} + \frac{\partial S_2(E - E_1)}{\partial E_1} \\
&= \frac{\partial S_1}{\partial E} + \underbrace{\frac{\partial (E - E_1)}{\partial E_1}}_{-1} \frac{\partial S_2}{\partial E_2} \qquad (E_2 = E - E_1)
\end{aligned}
$$

Thus, the maximum will occur when

$$\frac{\partial S_1}{\partial E_1} - \frac{\partial S_2}{\partial E_2} = 0 \qquad (27)$$

But from (23) this is the same as

$$\frac{1}{T_1} - \frac{1}{T_2} = 0$$

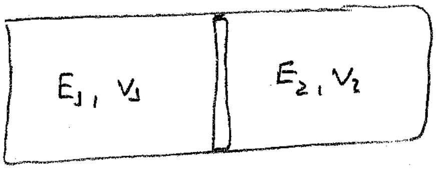
or

$$\boxed{T_1 = T_2} \qquad (28)$$

We therefore conclude that, when the two systems equilibrate, the most likely configuration will be that in which both systems have the same temperature. According to the 2nd law, this is the state the system will tend to.

Thermal and mechanical interaction

Now consider the same setup, but suppose that the wall sepparating the two systems is movable:



$$\left.\begin{aligned} E &= E_1 + E_2 \\ V &= V_1 + V_2 \end{aligned}\right\} \text{fixed}$$

Now we will have

$$S = S_1(E_1, V_1) + S_2(E_2, V_2)$$
$$= S_1(E_1, V_1) + S_2(E - E_1, V - V_1)$$

According to the 2nd law, the equilibrium configuration will be that which maximizes S. Thus we should set

$$\frac{\partial S}{\partial E_1} = 0 \qquad \frac{\partial S}{\partial V_1} = 0$$

We then get

$$\frac{\partial S}{\partial E_1} = \frac{\partial S_1}{\partial E_1} + \frac{\partial S_2}{\partial E_1} = \frac{\partial S_1}{\partial E_1} - \frac{\partial S_2}{\partial E_2} = 0$$

which gives, as before

$$\frac{\partial S_1}{\partial E_1} = \frac{1}{T_1} = \frac{1}{T_2} = \frac{\partial S_2}{\partial E_2}$$

Now we do the same for V_1 :

$$\frac{\partial S}{\partial V_1} = \frac{\partial S_1}{\partial V_1} + \frac{\partial S_2}{\partial V_1} = \frac{\partial S_1}{\partial V_1} - \frac{\partial S_2}{\partial V_2} = 0$$

If we now recall the 2nd law

$$dE = TdS - pdV$$

so
$$dS = \frac{dE}{T} + \frac{p}{T}dV$$

we therefore conclude that

$$\frac{\partial S_i}{\partial V_i} = \frac{P_i}{T_i}$$

so the 2nd law gives

$$\frac{P_1}{T_1} = \frac{P_2}{T_2}$$

But since $T_1 = T_2$ this is the same as saying that

$$\boxed{P_1 = P_2.}$$

Whence, when two gases are placed in contact with a movable wall, they will reach equilibrium exactly when $P_1 = P_2$: the pressure on both sides is the same (this makes sense!)

Ensemble equivalence

Now I want to show you that, when you are dealing with a macroscopic system, you get the same results using the canonical or the microcanonical ensembles.

In the canonical ensemble we compute Z as

$$Z = \int d^3r_1\, d^3p_1 \ldots d^3r_N\, d^3p_N\, e^{-\beta H} \tag{29a}$$

or

$$Z = \sum_{n_1,\ldots,n_N} e^{-\beta E_{n_1,\ldots,n_N}} \tag{29b}$$

where n_i represents all quantum numbers of particle i. Now, in either case we may try to transform to an integral over the total energy E of the system. Even in the quantum case, there are so many energy levels that E varies practically continuously. ($N \sim 10^{23}$).

If we convert to an integral over E we will get a coefficient in front. This is similar to the density of states (DOS), except that now E is the energy of N particles, not one.

The coefficient that appears in this transformation must be the multiplicity:

$$\boxed{Z = c\int dE\, \Omega(E)\, e^{-\beta E}} \tag{30}$$

where c is some constant (which is not important)

Eq (30) is called a <u>Laplace</u> <u>transform</u>. It is similar to the Fourier transform, but with $is \to -\beta$. We now see therefore, that Z and Ω contain the same information.

In general, however, computing (30) exactly is quite difficult. Luckly, we don't need to. We may instead use Laplace's formula to find an approximate expression that becomes practically exact when N is large.

We start by writting (30) as

$$Z = c \int dE \exp\left\{ \frac{S(E)}{k_B} - \beta E \right\} \tag{31}$$

Now, both S and E are extensive. So this has the form

$$\frac{S}{k_B} - \beta E = N\left(\frac{s}{k_B} - \beta \epsilon\right)$$

which falls precisely onto the framework of Laplace's method.

The 1st step is therefore to maximize $S(E) - \beta E$ with respect to E:

$$\frac{\partial}{\partial E}\left[\frac{S(E)}{k_B} - \beta E\right] = \frac{1}{k_B}\frac{\partial S}{\partial E} - \beta = 0$$

this therefore defines an energy E^*, which maximizes $S - \beta E$. This energy will be a function of β: $E^*(\beta)$.

$$\boxed{\begin{array}{c} \left.\dfrac{1}{k_B}\dfrac{\partial S}{\partial E}\right|_{E=E^*} = \beta \\ \text{Defines } E^*(\beta) \end{array}} \tag{32}$$

According to Eq (4) we will now have

$$\boxed{Z \simeq c \exp\left\{\frac{S(E^*)}{k_B} - \beta E^*\right\}} \qquad (33)$$

Before we proceed, let us compute the internal energy U in the canonical ensemble:

$$U = -\frac{\partial}{\partial \beta} \ln Z = -\frac{\partial}{\partial \beta}\left\{\frac{S(E^*(\beta))}{k_B} - \beta E^*(\beta)\right\}$$

$$= -\frac{\partial E^*}{\partial \beta} \underbrace{\frac{\partial S}{\partial E^*}\frac{1}{k_B}}_{\beta} + E^* + \beta \frac{\partial E^*}{\partial \beta}$$

$$= E^*$$

thus

$$\boxed{U = E^*} \qquad (34)$$

the average energy U, computed using the canonical ensemble, is precisely the energy E^* which maximizes $S - \beta E$.

Finally we write

$$F = -k_B T \ln Z = -k_B T\left(\frac{S}{k_B} - \beta U\right) - k_B T \ln c$$

The last term is a little weird. But it is just a constant. So if we consider the free energy per particle $f = F/N$, this last term will vanish when N is large. We then get

$$\boxed{F = U - TS} \qquad (35)$$

which is a formula we already knew.

Example: the ideal gas

The ideal gas is characterized by the Hamiltonian

$$H = \sum_{i=1}^{N} \frac{p_i^2}{2m} = \sum_{i=1}^{N} \frac{(p_{ix}^2 + p_{iy}^2 + p_{iz}^2)}{2m} \qquad (36)$$

Now we need to find $\Omega(E)$. This is the number of microstates with a given energy E. But here the states vary continuously so what we can look for is the fraction of phase space having energy E. This can be written as

$$\Omega(E) = \int_{H=E} d^3\mathbf{r}_1 \ldots d^3\mathbf{r}_N \, d^3\mathbf{p}_1 \ldots d^3\mathbf{p}_N \qquad (37)$$

We integrate over phase space and get only that small part for which H = E. Since H does not depend on $\mathbf{r}_i$, we may integrate over $\mathbf{r}_1 \ldots \mathbf{r}_N$. Each integral gives V so we get

$$\Omega(E) = V^N \int_{\sum_i p_i^2 = 2mE} d^3\mathbf{p}_1 \ldots d^3\mathbf{p}_N \qquad (38)$$

This remaining integral is the surface area of a 3N dimensional sphere. For instance, the surface area of a 3-dimensional sphere would be

$$\int_{x_1^2 + x_2^2 + x_3^2 = R^2} dx_1 \, dx_2 \, dx_3$$

Eq (38) is the same idea, but in 3N dimensions and with radius $R = \sqrt{2mE}$

Now: the surface area of a n-dimensional sphere is

$$S_n = \frac{2\pi^{n/2}}{\Gamma(\frac{n}{2})} R^{n-1} \tag{39}$$

Let us check to see if this makes sense:

$n=3$: (sphere) $\rightarrow$ $\Gamma(3/2) = \frac{\sqrt{\pi}}{2}$ $\rightsquigarrow$ $S_3 = \frac{2\pi^{3/2}}{\sqrt{\pi}/2} R^2 = 4\pi R^2$

$n=2$: (circle) $\rightarrow$ $\Gamma(1) = 1$ $\rightsquigarrow$ $S_2 = 2\pi R$

(the surface area of a circle is the perimeter).

In our case we therefore get

$$\Omega(E) = V^N \frac{2\pi^{3N/2}}{\Gamma(\frac{3N}{2})} (2mE)^{\frac{3N-1}{2}} \tag{40}$$

Since N is very large we may approximate $(2mE)^{\frac{3N-1}{2}} \sim (2mE)^{3N/2}$.

Moreover:

$$\Gamma\left(\frac{3N}{2}\right) = \left(\frac{3N}{2}-1\right)! \simeq \left(\frac{3N}{2}\right)!$$

We now use Stirling's formula

$$\ln N! \simeq N\ln N - N \rightsquigarrow N! = e^{N(\ln N-1)} = e^{N\ln(N/e)}$$
$$= \left(\frac{N}{e}\right)^N$$

Thus we get

$$\Gamma\left(\frac{3N}{2}\right) \simeq \left(\frac{3N}{2e}\right)^{\frac{3N}{2}} \tag{41}$$

Eq (40) then finally becomes

$$\Omega(E) = V^N \, 2 \left[\frac{2\pi m E}{(3N/2e)} \right]^{\frac{3N}{2}}$$

$$\boxed{\Omega(E) = V^N \, 2 \left(\frac{4\pi m e E}{3N} \right)^{\frac{3N}{2}}} \qquad (42)$$

The entropy will then be

$$S = k_B \ln \Omega = k_B \ln 2 + N k_B \ln \left[V \left(\frac{4\pi m e E}{3N} \right)^{3/2} \right] \qquad (43)$$

Notice how the entropy is not extensive. We also found this in the canonical ensemble, where it could be fixed by dividing Z by N!.

Here in the microcanonical ensemble this actually makes sense: $\Omega(E)$ counts the number of microstates. Thus, since the particles are identical, two states that differ only by the permutation of the particles are not different. We are over counting the number of states by a factor N! We should therefore divide (42) by N! writing $N! \simeq \left(\frac{N}{e}\right)^N$ we then get

$$\Omega(E) = \left(\frac{Ve}{N}\right)^N 2 \left(\frac{4\pi m e E}{3N} \right)^{\frac{3N}{2}} \qquad (44)$$

so

$$\boxed{S(E,V,N) = k_B \ln 2 + k_B N \ln \left[\frac{Ve}{N} \left(\frac{4\pi m e E}{3N} \right)^{3/2} \right]} \qquad (45)$$

Now S is extensive because it depends only on V/N and E/N.

Spin 1/2 paramagnetism revisited

Let us consider once again the problem of spin 1/2 paramagnetism. We N particles, each described by a variable $\sigma_i = \pm 1$, $i = 1, \dots, N$. The total energy of interaction between the spins and a magnetic field B is

$$E = -\mu B \sum_{i=1}^{N} \sigma_i \tag{46}$$

the energy therefore depends on N quantum numbers σ_i.

Let us first review how to solve this problem in the canonical ensemble. We start with

$$Z = \sum_{\sigma_1, \dots, \sigma_N} e^{-\beta E} \tag{47}$$

this sum has 2^N terms. But since the spins do not interact, we may factor Z into the product of N sums.

$$Z = \sum_{\sigma_1 \dots \sigma_N} e^{\beta \mu B \sigma_1} e^{\beta \mu B \sigma_2} \dots e^{\beta \mu B \sigma_N}$$

$$= \sum_{\sigma_1} e^{\beta \mu B \sigma_1} \sum_{\sigma_2} e^{\beta \mu B \sigma_2} \dots \sum_{\sigma_N} e^{\beta \mu B \sigma_N}$$

the sums are all identical ...

$$Z_1 = \sum_{\sigma} e^{\beta \mu B \sigma} = e^{\beta \mu B} + e^{-\beta \mu B}$$

$$= 2 \cosh(\beta \mu B)$$

Thus

$$\boxed{Z = Z_1^N = (2\cosh\beta\mu B)^N} \tag{48}$$

The fact that Z factors out for non-interacting systems is the biggest advantage of the canonical ensemble over the microcanonical.

Now that we have Z, we just run the usual script

$$U = -\frac{\partial}{\partial\beta}\ln Z = -\frac{\partial}{\partial\beta}\ln\left[(2\cosh(\beta\mu B))^N\right]$$

$$= -N\,\frac{2\mu B\sinh(\beta\mu B)}{2\cosh(\beta\mu B)}$$

or

$$U = -N\mu B\tanh(\beta\mu B) \tag{49}$$

Next:

$$F = -k_BT\ln Z = -Nk_BT\ln\left[2\cosh(\beta\mu B)\right] \tag{50}$$

so the entropy will be

$$S = \frac{U-F}{T} = -\frac{N\mu B}{T}\tanh(\beta\mu B) + Nk_B\ln\left[2\cosh(\beta\mu B)\right]$$

or

$$\boxed{\frac{S}{Nk_B} = -\beta\mu B\tanh(\beta\mu B) + \ln\left[2\cosh(\beta\mu B)\right]} \tag{51}$$

Eq (51) expresses S as a function of T. We could also express it as a function of U. To do that we define

$$\epsilon = \frac{U}{N\mu B} \tag{52}$$

Since μB has units of energy, ϵ will be dimensionless. Eq (49) then becomes

$$\tanh(\beta\mu B) = -\epsilon \tag{53}$$

We now substitute this in Eq (51). To do that it is convenient to know that

$$\beta\mu B = \operatorname{arctanh}(-\epsilon) = \frac{1}{2}\ln\left(\frac{1-\epsilon}{1+\epsilon}\right) \tag{54}$$

Moreover

$$\cosh\beta\mu B = \cosh\left[\ln\left(\frac{1-\epsilon}{1+\epsilon}\right)^{1/2}\right] = \frac{e^{\ln\left(\frac{1-\epsilon}{1+\epsilon}\right)^{1/2}} + e^{-\ln\left(\frac{1-\epsilon}{1+\epsilon}\right)^{1/2}}}{2}$$

$$= \frac{\left(\frac{1-\epsilon}{1+\epsilon}\right)^{1/2} + \left(\frac{1+\epsilon}{1-\epsilon}\right)^{1/2}}{2} = \frac{1}{2}\,\frac{1-\epsilon+1+\epsilon}{(1-\epsilon^2)^{1/2}}$$

Thus

$$\cosh\beta\mu B = \frac{1}{\sqrt{1-\epsilon^2}} \tag{55}$$

We then get

$$\boxed{s = \frac{S}{Nk_B} = \frac{\epsilon}{2}\ln\left(\frac{1-\epsilon}{1+\epsilon}\right) + \ln 2 - \frac{1}{2}\ln(1-\epsilon^2)} \tag{56}$$

We will now show how to get the same result in the microcanonical ensemble

In the microcanonical ensemble we cannot work with the individual spins. Instead we must look at the total energy

$$E = -\mu B \sum_{i=1}^{N} \sigma_i$$

There are 2^N possible configurations of the σ_i, but the number of distinct energy levels is not so high.

In fact, if we let N_+ be the number of particles with spin up and N_- the number of particles with spin down, then we may write

$$E = -\mu B N_+ + \mu B N_- \qquad (57)$$

But $N_+ + N_- = N$ so the energy depends only on N_+ (or N_-):

$$E = -\mu B N_+ + \mu B (N - N_+)$$

$$= \mu B N - 2\mu B N_+ \qquad (58)$$

the problem of finding Ω is now identical to the two-state system: we need to figure out the number of ways of arranging N_+ out of N particles in the + state. Thus

$$\Omega(E) = \binom{N}{N_+} = \frac{N!}{N_+!(N-N_+)!}$$

But from (58)

$$N_+ = \frac{1}{2}\left(N - \frac{E}{\mu B}\right)$$

$$= \frac{N}{2}\left(1 - \frac{E}{N\mu B}\right)$$

$$= \frac{N}{2}(1 - \epsilon) \quad \leftarrow \text{see (52)} \qquad (59)$$

the entropy will be

$$S = k_B \ln \Omega = k_B \left\{ \ln N! - \ln N_+! - \ln (N-N_+)! \right\}$$

$$\simeq k_B \left\{ N \ln N - N_+ \ln N_+ - (N-N_+) \ln (N-N_+) \right\}$$

$$= k_B \left\{ N \ln \left(\frac{N}{N-N_+} \right) - N_+ \ln \left(\frac{N_+}{N-N_+} \right) \right\}$$

Now :

$$\frac{N}{N-N_+} = \frac{N}{N - \frac{N}{2}(1-\epsilon)} = \frac{1}{\frac{1}{2}(1+\epsilon)} = \frac{2}{1+\epsilon}$$

$$\frac{N_+}{N-N_+} = \frac{\frac{N}{2}(1-\epsilon)}{\frac{N}{2}(1+\epsilon)} = \frac{1-\epsilon}{1+\epsilon}$$

Thus

$$s = \frac{S}{N k_B} = \ln 2 - \ln(1+\epsilon) - \frac{1}{2}(1-\epsilon) \ln \left(\frac{1-\epsilon}{1+\epsilon} \right)$$

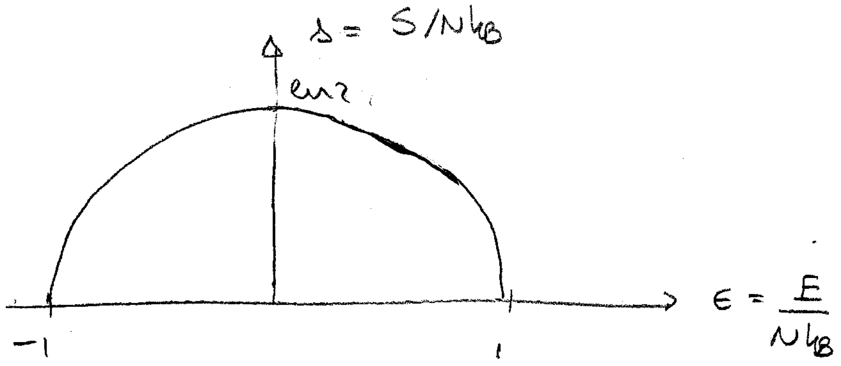
$$= \frac{\epsilon}{2} \ln \left(\frac{1-\epsilon}{1+\epsilon} \right) + \ln 2 \underbrace{- \ln(1+\epsilon) - \frac{1}{2} \ln \left(\frac{1-\epsilon}{1+\epsilon} \right)}_{-\frac{1}{2} \ln (1-\epsilon^2)}$$

we therefore get precisely (56)

$$\boxed{s = \frac{S}{N k_B} = \ln 2 + \frac{\epsilon}{2} \ln \left(\frac{1-\epsilon}{1+\epsilon} \right) - \frac{1}{2} \ln (1-\epsilon^2)} \qquad (60)$$

Negative temperatures revisited

A plot of Eq (60) gives



The temperature of the system is

$$\frac{1}{T} = \frac{\partial S}{\partial E} = \frac{k_B}{\mu B}\frac{\partial s}{\partial \epsilon}$$

Now: we don't need to compute $\partial s/\partial \epsilon$. We already did it in the canonical case [Eq (54)]:

$$\frac{\mu B}{k_B T} = \frac{1}{2}\ln\left(\frac{1-\epsilon}{1+\epsilon}\right)$$

$$\rightsquigarrow \quad \frac{k_B T}{\mu B} = \frac{2}{\ln\left(\frac{1-\epsilon}{1+\epsilon}\right)}$$

This plot looks like this