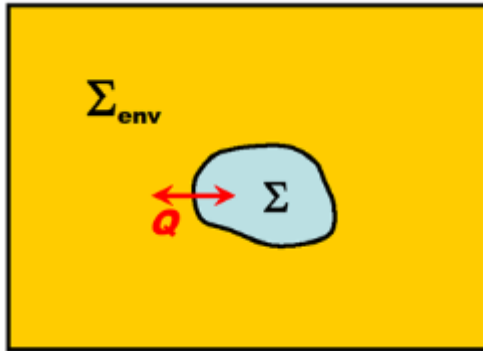
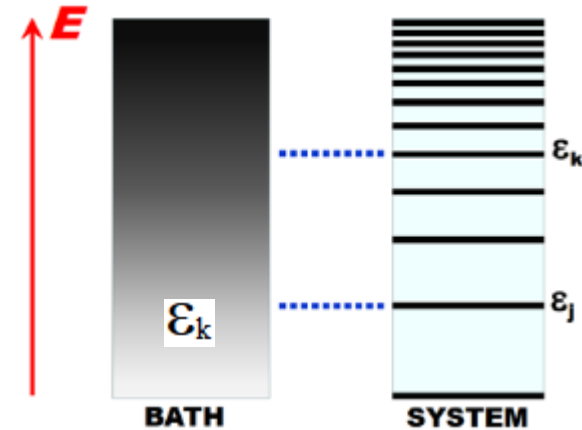


The CANONICAL DISTRIBUTION



We now go to the more physically relevant case where the system is coupled to a heat bath, which defines the temperature. Suppose the eigenenergies of system & bath are ϵ_j & ϵ_k respectively. Then we have $E_0 = \epsilon_k + \epsilon_j = \text{const}$

Because the bath is huge, we also know that $\epsilon_j/E_0 \ll 1$



Let's now count the microstates of the total. Holding the total energy E_0 constant, we then have

$$\Omega_0(\epsilon_k, \epsilon_j) = \Omega(\epsilon_j) \Omega_{\text{env}}(\epsilon_k) \delta(E_0 - (\epsilon_j + \epsilon_k))$$

which has a maximum for some value of the bath energy E & the system energy $\epsilon = E_0 - E$. However the environment is much bigger than the system, so its density of states at any energy is MUCH larger, and increases FAR faster with energy. So Ω is maximized when $E = E_0$, and $\epsilon = 0$!! How does it vary with E ? We have

$$\begin{aligned} \ln \Omega_{\text{env}}(E) &= \ln \Omega_{\text{env}}(E_0) + \left. \frac{d \ln \Omega_{\text{env}}}{d E} \right|_{E=E_0} (E_0 - E) + \dots \\ &= \ln \Omega_{\text{env}}(E_0) - \beta \epsilon + \dots \quad \text{where } \beta = 1/k_B T, \end{aligned}$$

The probability $P(\epsilon)$ for the system to have energy ϵ is thus proportional to $e^{-\beta \epsilon}$. In fact we can write

$$P(\epsilon_j) = \exp[-\beta \epsilon_j] / Z \quad \text{where} \quad Z(\beta) = \sum_j \exp[-\beta \epsilon_j]$$

The all-important PARTITION FUNCTION

CANONICAL DISTRIBUTION - SOME KEY RESULTS

THERMODYNAMIC QUANTITIES: The 1st & obvious thing to do is calculate the thermodynamic quantities. We assume energy eigenvalues E_i

Energy: We have $U = \langle E \rangle = \sum p_i E_i = Z^{-1} \sum_i E_i \exp[-\beta E_i] = -Z^{-1} \frac{\partial Z}{\partial \beta} = -\frac{\partial \ln Z}{\partial \beta}$

We then get: $U = -\left(\frac{\partial \ln Z}{\partial \beta}\right)_V = k_B T^2 \frac{\partial \ln Z}{\partial T}$

Free Energy & Entropy: We now calculate both F & S together; this will lead to some nice results. We first note that

$U = \left(\frac{\partial(\beta F)}{\partial \beta}\right)_V$ Integrating this gives $\beta F = -[\ln Z + c]$, so that $F = -k_B T [\ln Z + c]$

and so that $S = -\left(\frac{\partial F}{\partial T}\right)_V = k_B \left[T \frac{\partial \ln Z}{\partial T} + \ln Z + c \right] = k_B \left[-\beta \frac{\partial \ln Z}{\partial \beta} + \ln Z + c \right]$

How do we find the constant c ? Well, let's go to $T=0$ where only the ground state is occupied, so that

$Z \rightarrow \Omega_0 \exp[-E_0/k_B T]$, implying $S = k_B (E_0/k_B T + \ln \Omega_0 - E_0/k_B T + c)$

However we know that at $T=0$, we must have $S = k_B \ln \Omega_0$, so we arrive at 2 key results:

$F = -k_B T \ln Z$ and $S = k_B \left[-\beta \frac{\partial \ln Z}{\partial \beta} + \ln Z \right]$

More on Entropy: We can get another very illuminating expression for S , in which the entropy is just a weighted sum over all the states of the quantity $\ln P_i$ for each state (ie., over the "entropy for each state"). Let's prove this - we have

$$\sum_i P_i \ln P_i = \sum_i Z^{-1} \exp[-\beta E_i] [-\beta E_i - \ln Z] \rightarrow -\beta Z^{-1} \left(\sum_i E_i \exp[-\beta E_i] \right) - Z^{-1} \ln Z \sum_i \exp[-\beta E_i]$$

But this is just the same as

$$\sum_i P_i \ln P_i = \beta Z^{-1} \frac{\partial Z}{\partial \beta} - \ln Z = \beta \frac{\partial \ln Z}{\partial \beta} - \ln Z \quad \& \text{ so cf. last page): } \boxed{S = -k_B \sum_i P_i \ln P_i}$$

NB: for the microcanonical ensemble, for which $P_i = 1/\Omega$, where Ω is the total number of microstates, we then get

$$S = -k_B \sum_i \frac{1}{\Omega} \ln \frac{1}{\Omega} = k_B \Omega^{-1} \ln \Omega \sum_i 1 = k_B \ln \Omega \quad \text{which we already found before}$$

FLUCTUATIONS in THERMODYNAMIC QUANTITIES: This is a big step beyond thermodynamics. Let's first look at energy fluctuations. We have

$$\text{Mean energy: } \langle E \rangle = U \quad \text{Mean square fluctuation: } \langle \Delta E^2 \rangle = \langle E^2 \rangle - \langle E \rangle^2$$

Working these out we have

$$\langle E \rangle = \sum_i p_i E_i = Z^{-1} \sum_i E_i \exp[-\beta E_i] = -Z^{-1} \frac{\partial Z}{\partial \beta}$$

Hence

$$\langle \Delta E^2 \rangle = Z^{-1} \frac{\partial^2 Z}{\partial \beta^2} - Z^{-2} \left[\frac{\partial Z}{\partial \beta} \right]^2 = -\frac{\partial \langle E \rangle}{\partial \beta}$$

which we can also write as

$$\langle \Delta E^2 \rangle = k_B T^2 C_V(T)$$

$$\langle E^2 \rangle = \sum_i p_i E_i^2 = Z^{-1} \sum_i E_i^2 \exp[-\beta E_i] = Z^{-1} \frac{\partial^2 Z}{\partial \beta^2}$$

MULTIPLE SYSTEMS: We now come to a simple but fundamental result.

Suppose we combine 2 systems A and B which are not interacting with each other (but can have lots of internal interactions). Then we can write

$$Z_A Z_B = \sum_j \exp[-\beta E_j] \sum_\alpha \exp[-\beta \mathcal{E}_\alpha] \rightarrow \sum_{j,\alpha} \exp[-\beta(E_j + \mathcal{E}_\alpha)] = Z_{A+B}$$

so that partition functions multiply, just like state multiplicities. This argument clearly extends to N different systems, and if they are all identical, we have

$$Z_N = Z_1^N$$

Then, for an extensive quantity like energy, we have

$$U = \langle E_{tot} \rangle = -\frac{\partial \ln Z_{tot}}{\partial \beta} = -N \frac{\partial \ln Z_1}{\partial \beta} \rightarrow N \langle E_1 \rangle$$

and indeed any extensive quantity will be proportional to a sum over the logarithms of the partition functions for each sub-system

SUMMARY – Basic Ideas of Canonical Distribution

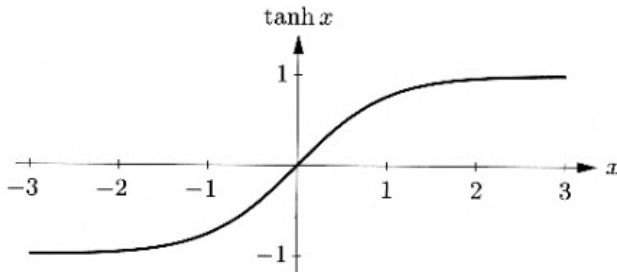
1. In the canonical ensemble, the probability of occupying a state is NOT the same for all states, but falls exponentially with the energy of the state.
2. Extensive quantities are proportional to $\ln Z$ (log of the partition function)
3. Fluctuations about the mean are also simple functions of Z .

EXAMPLES

EXAMPLE 1: N-QUBIT SYSTEM: We go to our tried and trusted set of N non-interacting spin-1/2 systems. The energy of each spin takes values $E_+ = \mu B$, $E_- = -\mu B$, so that the single spin partition function is just

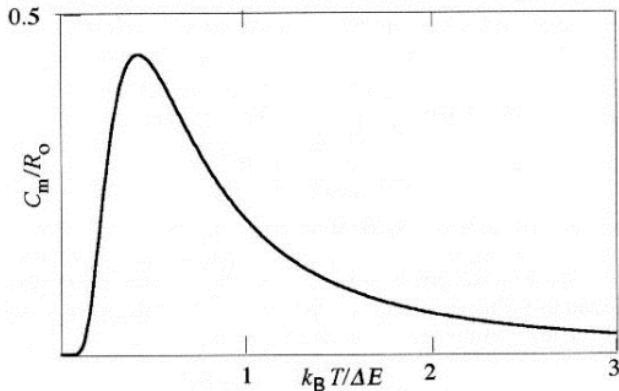
$$Z_1 = \exp[\beta\mu B] + \exp[-\beta\mu B] \quad \text{and hence} \quad Z_N = Z_1^N$$

Energy: We have $U = -NZ_1^{-1} \frac{\partial Z_1}{\partial \beta} = -N\mu B \frac{\exp[\beta\mu B] - \exp[-\beta\mu B]}{\exp[\beta\mu B] + \exp[-\beta\mu B]} = -N\mu B \tanh(\beta\mu B)$



High-T limit: $U \cong -N\beta(\mu B)^2 = -N \frac{(\mu B)^2}{k_B T}$ $k_B T \gg \mu B$

Low-T limit: $U \approx -N\mu B$ $k_B T \ll \mu B$



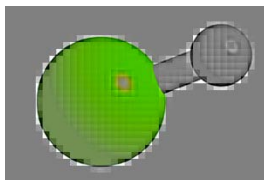
Specific Heat: This is just

$$C(T) = \left(\frac{\partial U}{\partial T} \right)_B = -k_B \beta^2 \left(\frac{\partial U}{\partial \beta} \right)_B = k_B N (\mu B \beta)^2 \operatorname{sech}^2(\beta \mu B)$$

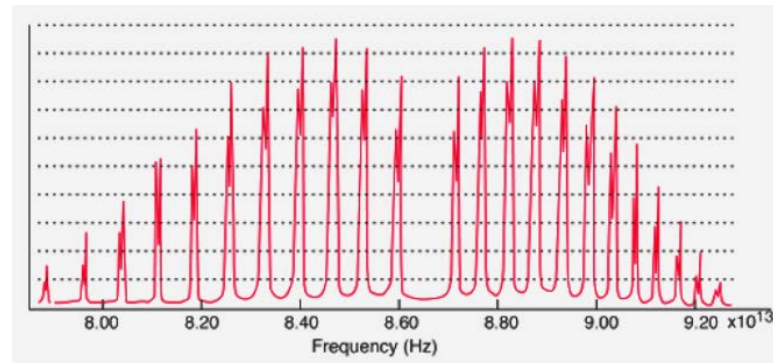
This takes the characteristic “Schottky” form, shown at left as a function of T . It is usually very obvious in low- T experiments - other modes (phonons, electrons, etc.) give v. different form.

EXAMPLE 2: VIBRONS/OPTICAL "EINSTEIN" PHONONS: These exist in most solids, & in all molecules - they are vibrational modes.

(a) Molecules

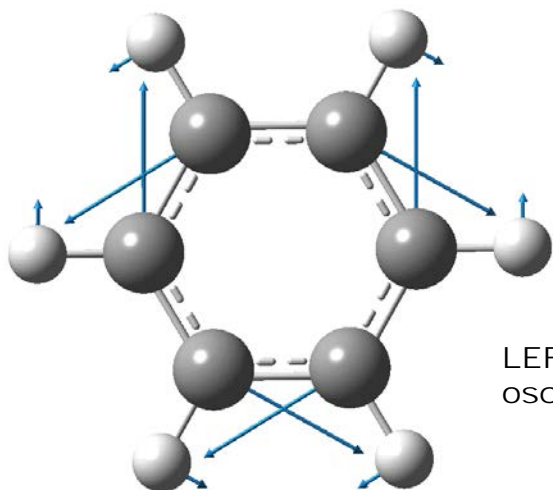


Consider the HCl molecule, shown schematically. The only possible vibron mode describes oscillations in the distance between the H & Cl ions. We thus get a set of absorption lines which are those of a simple oscillator.

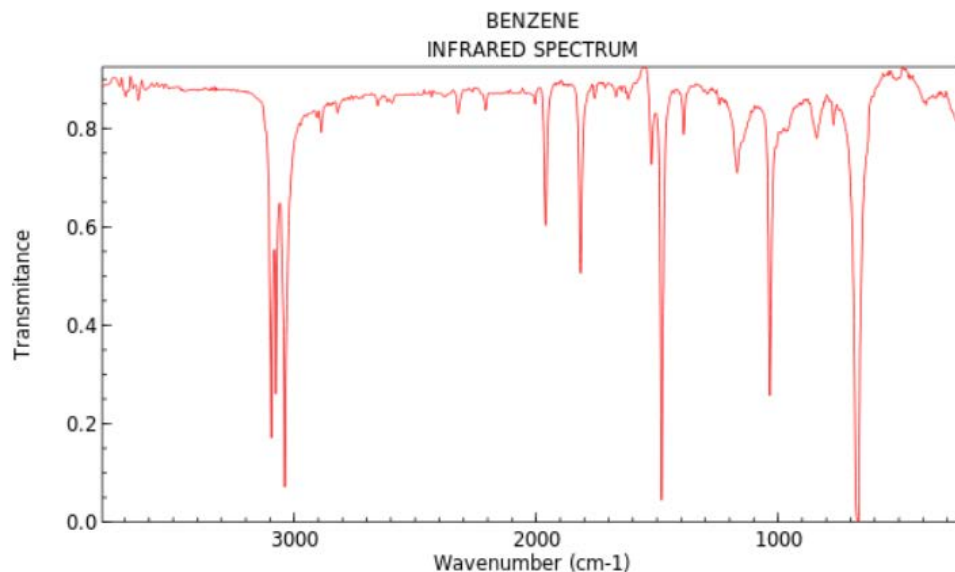


IR absorption lines of HCl molecule

More interesting is the spectrum of benzene (C_6H_6), where one can have compressional, flexural (twisting) and 'wiggling' modes. Many of these are degenerate because of the symmetry, and they interact weakly ('hybridize') with each other, behaving as weakly coupled oscillators of different frequencies.



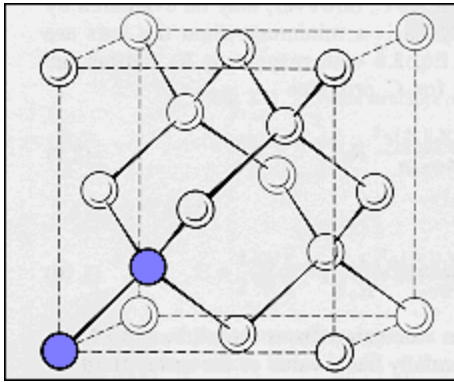
LEFT: Benzene oscillations



RIGHT: Benzene spectrum

(b) Phonons in crystals In any periodic system we have quantized vibrations propagating freely through the system as waves – these are acoustic phonons, with energy $\omega(k) = ck$ at long wavelengths (ie. for small k), where c is the sound velocity.

If there is more than one ion per unit cell, then we can also have relative oscillations between these ions, which may be strongly localized in each cell, and look like molecular vibrons. Weak coupling between neighbouring vibrons allows them to propagate slowly as waves across the crystal.

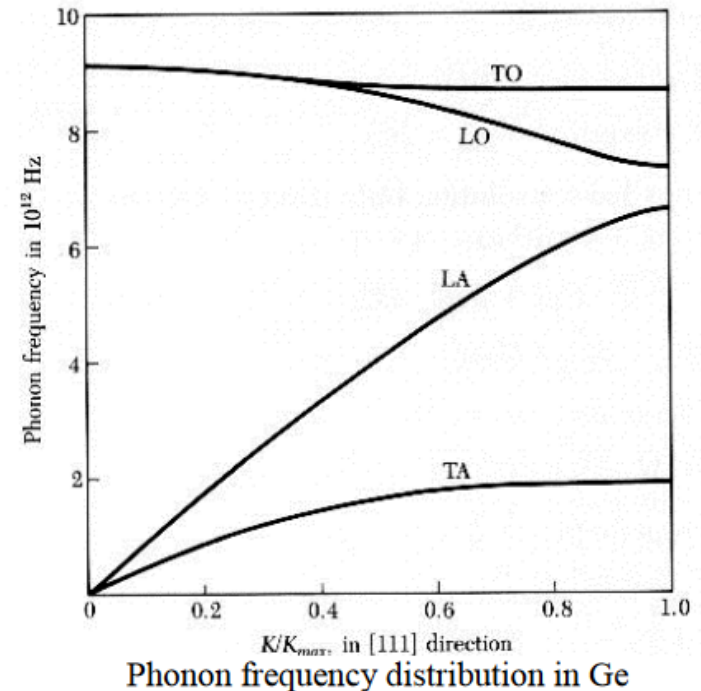


Position of ions in a Ge crystal

A very interesting case is the semiconductor Ge, where the 2 Ge atoms in each unit cell are in different surroundings (different crystal electric fields). There are thus also finite frequency vibron modes, which when they couple together across the crystal give rise to “optical modes”. The crystal thus has both acoustic and optical modes

In a crude approximation we can just ignore the coupling between the local Ge vibrons, & then we have the “Einstein model” of N different 3-d oscillators, each with the same frequency.

In a 3-d system the oscillations can be divided into longitudinal L modes (compressional) and transverse T modes.



Statistical Mechanics of Einstein Model: We can now work this out, by starting with the results for a single oscillator.

Recall that for a single oscillator we have energies: $E_n = (n + 1/2)h\nu$
The 1-oscillator partition function is then:

$$\begin{aligned} Z_1(T) &= \sum \exp[-\beta E_n] = \exp[-\beta h\nu/2] \sum (\exp[-\beta h\nu])^n \\ &= \exp[-\beta h\nu/2] \sum (\exp[-\beta h\nu])^n \\ &= \frac{1}{2} \operatorname{cosech}(h\nu/2k_B T) \end{aligned}$$

Now recall that $U = \left(\frac{\partial(\beta F)}{\partial \beta} \right)_V = - \left(\frac{\partial \ln Z}{\partial \beta} \right)_V$

The T-dependent 1-oscillator energy expectation value, and 1-oscillator specific heat, are then

$$U_1(T) = \frac{1}{2} h\nu \operatorname{coth}(h\nu/2k_B T) \quad \text{and} \quad C_V(T) = k_B (h\nu/2k_B T)^2 \operatorname{cosech}^2(h\nu/2k_B T)$$

What now of the N-oscillator system? Clearly, since the partition functions Z_j multiply and the $\ln Z_j$ add over the different oscillators labelled by j , then we must have

$$Z(\beta) = \prod_{j=1}^N Z_j(\beta) \quad \text{and} \quad \ln Z(\beta) = \sum_{j=1}^N \ln Z_j(\beta)$$

where the individual partition functions are just given by the functions above, with different frequencies ν_j for the different oscillators

EXAMPLE 3: N DISTINGUISHABLE PARTICLES in a BOX: Let us imagine a d-dimensional box with sides L & volume $V=L^d$; we will let L be macroscopic, so that the density of states can be approximated by a continuous function.

Recall that the N-particle density of states has the form

$$\mathcal{N}(E) = \sum_n \Omega(N, n) \delta(E - E_n^{(N)})$$

which for a 1-particle system we write as $g(E) = \sum_n g(N, n) \delta(E - E_n^{(N)}) |_{N=1}$ where $g(1, n)$ is the degeneracy of the n-th level. The number of states in an energy interval dE around E is then $g(E) dE$. Since our particles in the present case are non-interacting, we can do everything for the 1-particle case, just as we did for spins and oscillators above; ie., we find Z for the 1-particle system, and then sum over $\ln Z$ for each particle to get the result for the N-particle system.

Continuous density of States: Let the probability for the 1-particle system to have an energy E be $P(E)$, so that in the canonical ensemble we must have, for a system of volume V , that

$$p(E)dE = Z^{-1}Vg(E)\exp[-\beta E]dE \quad (\text{note key Boltzmann factor})$$

with a partition function

$$Z = \sum_i g_i \exp[-\beta E_i] \rightarrow V \int_0^{\infty} g(E) \exp[-\beta E] dE$$

$$\text{so that } p(E) = \frac{\int_0^{\infty} g(E) \exp[-\beta E] dE}{\int_0^{\infty} g(E) \exp[-\beta E] dE}$$

so now we have to find $g(E)$ for different d

1-dimensional box: The density of states is easy to find here. First recall that the quantized momenta are $k_n = \pi n/L$, with non-relativistic energies given by

$$E_n = \frac{(\hbar k_n)^2}{2m} = \frac{\pi^2 \hbar^2}{2mL^2} n^2$$

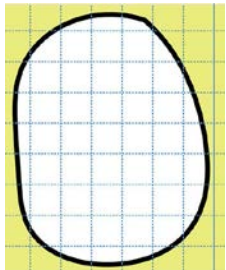
The interval between states is then $\Delta k = \pi/L$, so that the density of states $g(k)$ in k -space is $g(k) = L/\pi$.

We want to rewrite this in energy space, ie., to change variables. Going over to a continuous density of states, we use

$$k = \frac{(2mE)^{1/2}}{\hbar}$$

Now $g(k) = dN/dk = dN/dE (dE/dk) = g(E) (dE/dk)$; so $g_{1D}(E) = 2\pi (m/2E)^{1/2} / \pi \hbar$
(per unit volume)

2-dimensional box: Now we have to count discrete states in the 2-d k -plane, & convert to a continuous density of states. Each state occupies a k -space area of π^2/L^2 ; inside a circle in k -space with radius k we then have a total



$$N(k) = \frac{\pi k^2}{4} \frac{L^2}{\pi^2} = \frac{2mE}{\hbar^2} \frac{L^2}{4\pi} \quad \text{different states}$$

The possible energies are

$$E_{nm} = \frac{\hbar^2 (\kappa_x^2 + \kappa_y^2)}{2m} = \frac{(\pi \hbar)^2}{2mL^2} (n^2 + l^2)$$

and, going over to continuous energy, we get after changing variables as above that, per unit volume

$$g_{2D}(E) = \frac{m}{2\pi \hbar^2} \quad \text{(2-d density of states is a constant)}$$

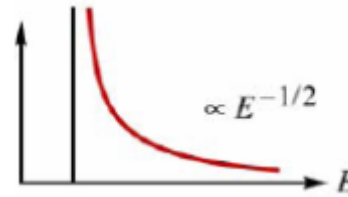
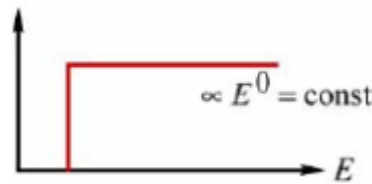
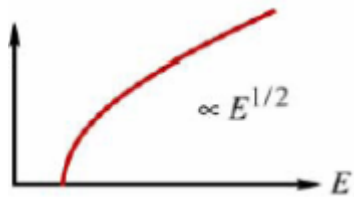
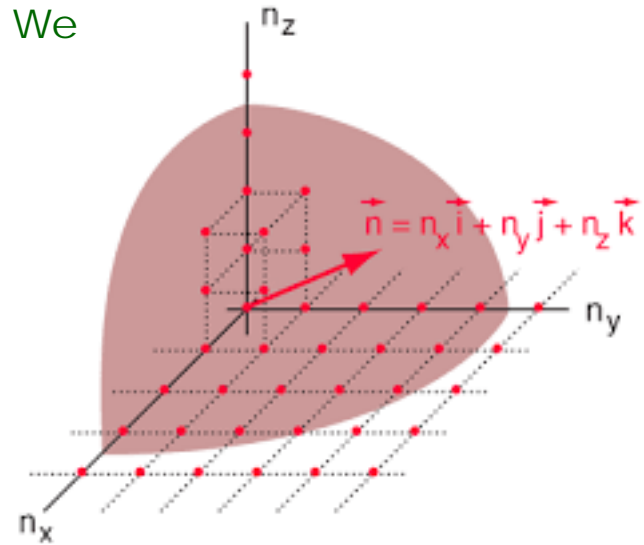
3-dimensional box: Here I will not go through the derivation – it is an obvious generalization of what we have already been doing. We have to deal with a 3-d spherical region in k-space, as shown.

We then get a total number of

$$N(k) = k^3/6\pi^2$$

states per unit volume, and a density of states per unit volume given by

$$g_{3D}(E) = \frac{1}{4\pi^2} \left(\frac{2m}{\hbar^2} \right)^{3/2} E^{1/2}$$



The final results are as shown for 1-d, 2-d, & 3-d

More on the 3-d Gas: Suppose we now write the partition function. For a single particle we now have:

$$\begin{aligned} Z_1 &= V \int_0^{\infty} g_{3D}(E) \exp[-\beta E] dE = \frac{V}{4\pi^2} \left(\frac{2m}{\hbar^2} \right)^{3/2} \int_0^{\infty} E^{1/2} \exp[-\beta E] dE \\ &= \frac{V}{4\pi^2} \left(\frac{2m}{\beta \hbar^2} \right)^{3/2} \int_0^{\infty} x^{1/2} \exp[-x] dx \end{aligned}$$

This integral is easily found – see next page

The integral on the last page gives:

$$Z_1 = \frac{V}{4\pi^2} \left(\frac{2m}{\beta\hbar^2} \right)^{3/2} \frac{\pi^{1/2}}{2} = V \left(\frac{m}{2\pi\beta\hbar^2} \right)^{3/2} = V \left(\frac{m}{2\pi\hbar^2} \right)^{3/2} \beta^{-3/2} \rightarrow V/V_q = V\rho_q$$

where

$$V_q \equiv \left(\frac{2\pi\beta\hbar^2}{m} \right)^{3/2} \sim (0.7 \lambda)^3 \quad \text{and} \quad \lambda = \frac{h}{(3mk_B T)^{1/2}} \quad (\text{thermal de Broglie wavelength})$$

This means we count roughly 1 state per cube of size $V_q \sim \lambda^3$

There is a paradox here – isn't the partition function suppose to increase exponentially with volume V , so that the free energy is proportional to volume? Here we have

$$F = -Nk_B T [3/2 \ln \rho_q - \ln V]$$

To answer this, note that we still have $Z_N = Z_1^N$, so that F is proportional to N . However, if, eg., we keep N constant and double V , we are not actually "doubling the system"; rather we are putting the same N particles & eigenstates into a larger V , although the energies decrease (and their density in energy increases). To check, note that the thermodynamics is still fine – we have

$$p = - \left(\frac{\partial F}{\partial V} \right)_T \rightarrow \left(\frac{Nk_B T}{V} \right) \quad (\text{ie., the usual ideal gas law } pV = RT, \text{ with } R = Nk_B)$$

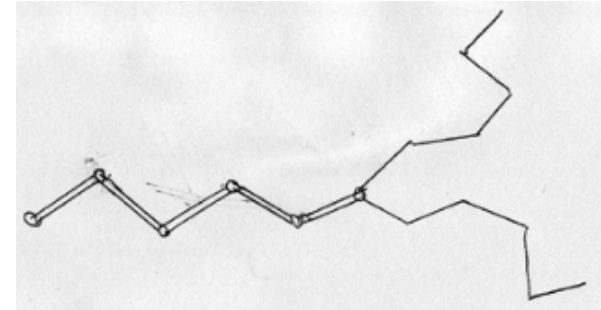
$$\text{and the energy per particle is } \langle E \rangle = -Z^{-1} \frac{\partial Z}{\partial \beta} = \frac{3}{2\beta} = \frac{3}{2} k_B T$$

Equipartition
theorem

$$\text{giving a total energy } U = \frac{3}{2} N k_B T \quad \& \quad \text{specific heat } C_V = \frac{3}{2} N k_B$$

CUTE CASE 1: DNA ZIPPER MODEL: DNA molecules are made of 2 intertwined helical strands, easily pulled apart. To set up a toy model, let's suppose that:

- (i) There are g_0 ways of opening a link; each costs energy E_0 ; a closed zipper has $E=0$
- (ii) The # of microstates for a closed zipper is $\Omega_0^{(N)} = f(N)$; & for a zipper with r open links is $\Omega_r^{(N)} = f(N-r) g_0^r$. Assume $NE_0 \gg k_B T$.
- (iii) We will assume that $f(N-r) = f(N)$ for all r .



The 3rd assumption is debatable - we'll discuss it in class.

Then
$$Z = \sum_{r=0}^N g_0^r \exp[-r\beta E_0] = \sum_{r=0}^N [g_0 \exp(-\beta E_0)]^r = \frac{1 - g_0^{N+1} \exp[-(N+1)\beta E_0]}{1 - g_0 \exp[-\beta E_0]}$$

- (1) Let $g_0 = 1$: unzipped chain has same Ω but higher E than zipped chain.

Then $Z \cong \frac{1}{\beta E_0}$ & $\ln Z \cong -\ln \beta - \ln E_0$ so that $\langle E \rangle = \langle r \rangle E_0 = -\frac{\partial \ln Z}{\partial \beta} = k_B T$ & $\langle r \rangle = k_B T / E_0$

- (2) Now let $g_0 > 1$: unzipped chain has higher Ω & higher E than zipped chain.

- (i) Suppose $g_0 \exp[-\beta E_0] < 1$. Then analysis is same as above.

- (ii) Suppose $g_0 \exp[-\beta E_0] > 1$. Then $p(r) = Z^{-1} g_0^r \exp[-r\beta E_0]$ diverges with r .
We deduce that equilibrium value of r is infinite.

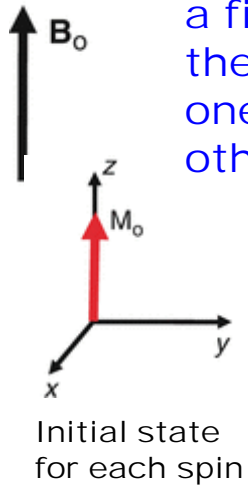
- (iii) Suppose $g_0 \exp[-E_0/k_B T_c] = 1$ so that $k_B T_c = E_0 / \ln g_0$

Then T_c is "unzipping transition temperature"

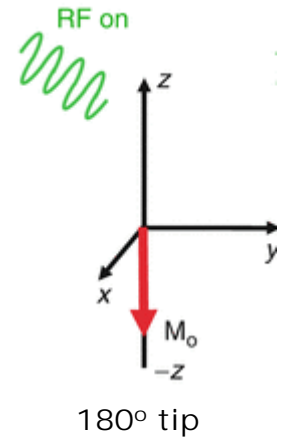
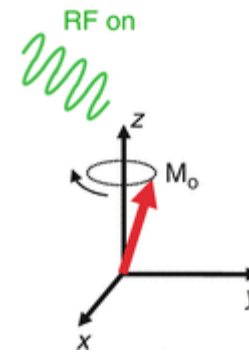
Note the competition between TS & U in $F = U - TS$.

CUTE CASE 2: NEGATIVE SPIN TEMPERATURES: This case was discussed in the notes in Ch 3, in the microcanonical ensemble. Now let's discuss this in realistic (canonical ensemble) terms, and in terms of a concrete experiment.

We apply a field B_0 along $+z$; the spins are initially at $T=0$ and so oriented along z , in their lowest energy state. Then we can do the following - apply a field pulse perpendicular to B_0 , to tip the spin. Two examples are shown - in one, the spin is partially tipped, in the other, tipped by 180° .

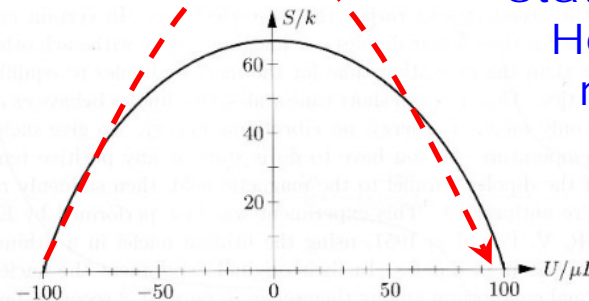
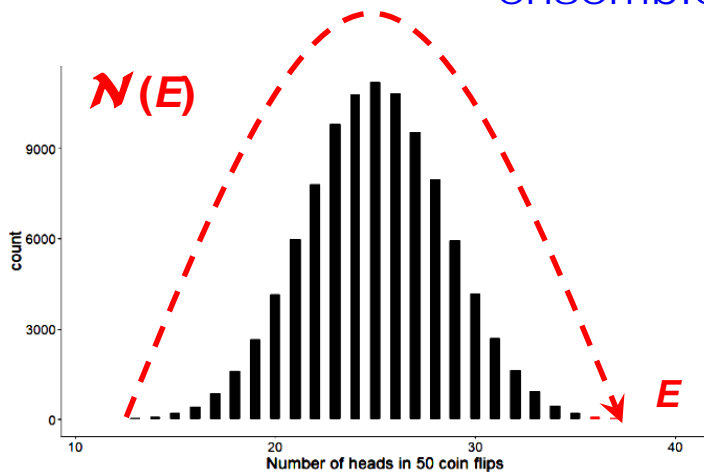


So now, tip all spins down. The system is now in its highest energy state! Note we can get the same effect by just reversing the external field, again leaving the system with all spins antiparallel to the field.



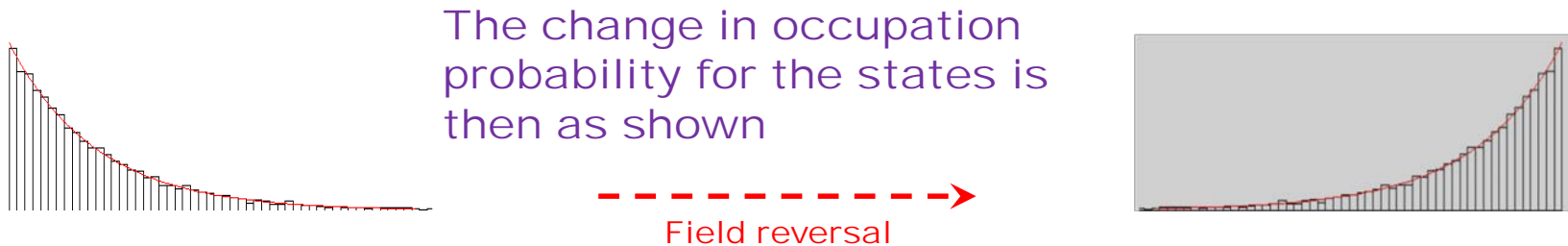
If we are at $T=0$, we can discuss this in the microcanonical ensemble, since the system is not in some probabilistic distribution of states - it simply jumps from one state to another.

However we have the mysterious result that $dS/dU = 1/T$ has changed sign; what does this mean?



Spin Reversal at Finite T: Now suppose we do the reversal at finite T . An ensemble of systems has the states occupied with a probability decaying exponentially with energy, proportional to $\exp[-E/k_B T]$; thus only states with polarization strongly aligned with the field are significantly occupied (the lowest energy states).

However when the field flips relative to the spins – but leaving the spins in the ensemble untouched – we see the opposite is now true – the probability is now proportional to $\exp[+E/k_B T]$; the spins now preferentially occupy high E states!



Clearly this final state is NOT an equilibrium state – eventually it will relax back to the low energy state, again with the spins pointing parallel to the field. But the mechanism for this works slowly – it requires the energy to be carried off by photons or phonons, & the matrix elements for this may be very small. Thus this high energy metastable state lasts a long time. For much shorter times we can treat it as approximately a thermodynamic state.

In a question I will assign, you will be able to show that this metastable states has a negative temperature.