8.044 Lecture Notes
Chapter 6: Statistical Mechanics at Fixed Temperature
(Canonical Ensemble)

Lecturer: McGreevy

Reading: Greytak, Notes on the Canonical Ensemble;
Baierlein, Chapters 5, 13, 14.

Optional Reading for §6.6: Greytak, Notes on (Raman Spectroscopy of) Diatomic Molecules.

6.1 Derivation of the Canonical Ensemble

In Chapter 4, we studied the statistical mechanics of an *isolated* system. This meant fixed E, V, N.

From some fundamental principles (really, postulates), we developed an algorithm for calculating (which turns out not to be so practical, as you'll have seen *e.g.* if you thought about the random 2-state systems on pset 6):

1. Model the system

2. Count microstates for given E: $\Omega(E, V, N)$.

3. from Ω, derive thermodynamics by $S = k_B \ln \Omega$.

4. from Ω, derive microscopic information by $p(X) = \frac{\Omega'(X)}{\Omega}$.

The fixed-energy constraint makes the counting difficult, in all but the simplest problems (the ones we've done). Fixing the temperature happens to

Consider a system $\boxed{1}$ which is not isolated, but rather is in thermal contact with a heat bath $\boxed{2}$, and therefore held at fixed temperature T equal to that of the bath. An ensemble of such systems is called the "canonical ensemble". I don't know why.

The fact that T is fixed means E is not: energy can be exchanged between the system in question and the reservoir.

heat bath, T
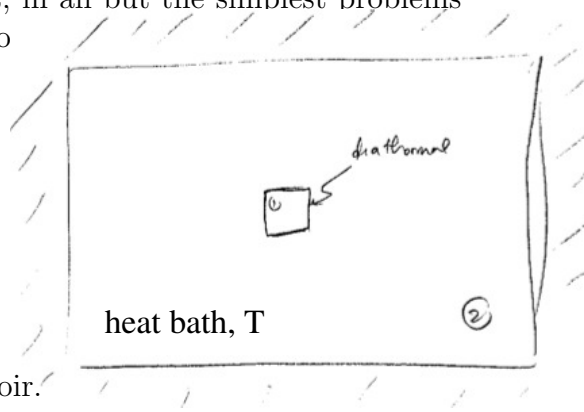
Assume that $\boxed{1} + \boxed{2}$ together are isolated, with fixed energy $E_{\text{total}} = E_1 + E_2$. Then we can apply the microcanonical ensemble to $\boxed{1} + \boxed{2}$. Note that $\boxed{1}$ could be itself macroscopic (it just has to have a much smaller C_V than $\boxed{2}$), in which case we can learn about its thermodynamics. Alternatively, $\boxed{1}$ could be microscopic, with just a few degrees of freedom (like one square of a grid of 2-state systems, in which case we can ask for the probability that it is ON).

Consider a specific microstate A of $\boxed{1}$ with energy E_1.

Q: What the equilibrium probability that system $\boxed{1}$ is in state A? We can apply the method of Chapter 4 to $\boxed{1} + \boxed{2}$:

$$\text{Prob(system } \boxed{1} \text{ is in state A)} = p(\underbrace{\{p_1, q_1\}}_{\text{specific values for all vars of system 1 in state A}}) = \frac{\Omega'_{1+2}(A)}{\Omega_{1+2}(E_{\text{total}})}$$

$$= \frac{\text{\# of microstates of system } \boxed{2} \text{ with energy } E_{\text{total}} - E_1}{\text{total \# of microstates of } \boxed{1} + \boxed{2} \text{ with energy } E_{\text{total}} = E_1 + E_2, \text{ fixed}}$$

$$\implies \quad p(\{p_1, q_1\}) = \frac{\Omega_2(E_{\text{total}} - E_1)}{\Omega_{1+2}(E_{\text{total}})}$$

Take logs for smoother variation:

$$k_B \ln p(\{p_1, q_1\}) = S_2(\underbrace{E_{\text{total}} - E_1}_{E_2}) - S_{1+2}(E_{\text{total}})$$

So far, what we've done would be valid even if systems $\boxed{1}$ and $\boxed{2}$ were of the same size. But now let's use the fact that $\boxed{2}$ is a reservoir by recognizing that $E_1 \ll E_{\text{total}}$. We should Taylor expand in small E_1:

$$k_B \ln p(\{p_1, q_1\}) \simeq \left(S_2(E_{\text{total}}) - E_1 \underbrace{\frac{\partial}{\partial E_2} S_2(E_2)|_{E_2 = E_{\text{total}}}}_{\frac{1}{T_2}} + \mathcal{O}(E_1^2) \right) - S_{1+2}(E_{\text{total}})$$

$$\frac{\partial S_2}{\partial E_2} = \frac{1}{T_2} = \frac{1}{T}$$

where T is the temperature of the bath $\boxed{2}$. (Here we are using the fact that $\boxed{2}$ is a reservoir in saying that its temperature remains T even if we ignore the contribution of E_1 to E_{total}.)

$$k_B \ln p(\{p_1, q_1\}) = -\frac{E_1}{T} + \underbrace{S_2(E_{\text{total}}) - S_{1+2}(E_{\text{total}})}_{\text{independent of microstate of } \boxed{1}} + \mathcal{O}(E_1^2)$$

$$= -\frac{H_1(\{p_1, q_1\})}{T} + \ldots$$

H_1 here is the energy of system $\boxed{1}$ in the specified microstate A.[1]

$$p(\{p_1, q_1\}) = \underbrace{e^{-\frac{H_1(\{p_1, q_1\})}{k_B T}}}_{\text{Boltzmann factor}} \underbrace{e^{\frac{S_2(E_{\text{total}}) - S_{\text{total}}(E_{\text{total}})}{k_B}}}_{C, \text{ indep of microstate of } \boxed{1}} \tag{1}$$

[End of Lecture 14.]

---

[1] H is for Hamiltonian. It's not the enthalpy.

Q: why can we ignore the $\mathcal{O}(E_1^2)$ terms in the Taylor expansion?

A: because they become small very rapidly as we make the reservoir larger, and we can make the reservoir as large as we want. In particular, the next term of the Taylor expansion of $S_2(E_{\text{total}} - E_1)$ is:

$$\frac{1}{2}E_1^2 \frac{\partial^2 S_2}{\partial E^2}$$

What's this last term?

$$\frac{\partial^2 S}{\partial E^2} \overset{\text{take one derivative}}{=} \frac{\partial}{\partial E}\left(\frac{1}{T}\right) \overset{\text{chain rule}}{=} -\frac{1}{T^2}\frac{\partial T}{\partial E} \overset{\text{def of } C_V}{=} -\frac{1}{T^2}\frac{1}{C_V}$$

This C_V is the heat capacity of the reservoir – the defining property of the reservoir is the hugeness of its heat capacity. So the biggest term we are ignoring is of magnitude

$$\frac{E_1^2}{T^2}\frac{1}{C_V(\boxed{2})}$$

and we should compare this to the last term we keep, which is $\frac{E_1}{T}$. The term we are ignoring becomes smaller and smaller as we add degrees of freedom to the reservoir (*e.g.* it would go like $1/N$ if it were comprised of N ideal gas atoms), whereas E_1/T does not.

Boltzmann factor

In particular,

$$p(\{p_1, q_1\}) \propto e^{-\frac{H_1(\{p_1, q_1\})}{T}}$$

- Energy scale is set by $k_B T$.

- Recall that in the ensemble with fixed energy, we didn't ever compare microstates with different energies.

- Microstates with high/low energy are less/more probable.

- This last statement is NOT the same as "higher energy is less probable": Suppose there is some set of microstates of $\boxed{1}$ with the same energy E_1. Then:

$$p(\boxed{1} \text{ is in some state with energy } E_1) \propto e^{-\frac{E_1}{k_B T}} \times \left(\underbrace{\text{degeneracy}}_{\text{\# of microstates with energy } E_1} \right)$$

This last factor, called the 'density of states' can contain a lot of physics. It is the number of microstates of system $\boxed{1}$ with energy E_1, also known as

$$\Omega_1(E_1) = e^{S_1(E_1)/k_B} \ .$$

Notice that it depends on E_1.

Partition function

Missing: the normalization of the probability distribution:

$$1 \stackrel{!}{=} \int_{\text{all microstates of system } \boxed{1}} \{dp_1 dq_1\} \, p\left(\{p_1, q_1\}\right)$$

$$= \int \{dp_1 dq_1\} e^{-H_1(\{p_1,q_1\})/(k_B T)} \times \underbrace{C}_{\text{the thing above, determined by this equation}}$$

$$\implies \quad p\left(\{p_1, q_1\}\right) = \frac{e^{-H_1(\{p_1,q_1\})/(k_B T)}}{Z} = \frac{e^{-H_1(\{p_1,q_1\})/(k_B T)}}{\int \{dp_1 dq_1\} e^{-H_1(\{p_1,q_1\})/(k_B T)}} \, .$$

This quantity which enters our consciousness as a normalization factor,

$$\boxed{Z \equiv \int \{dp_1 dq_1\} e^{-H_1(\{p_1,q_1\})/(k_B T)}} \qquad \text{partition function}$$

is called the *partition function*, and it is the central object in the canonical ensemble. ('Z' is for *Zustandssumme*, German for 'state sum'.)

To recap, our answer for the equilibrium probability distribution at fixed temperature is:

$$\boxed{p\left(\{p_1, q_1\}\right) = \frac{1}{Z} e^{-H_1(\{p_1,q_1\})/(k_B T)}} \qquad \text{Boltzmann distribution}$$

This is the probability that system $\boxed{1}$ is in the microstate labelled by $\{p_1, q_1\}$ when it is in contact with a heat bath at temperature T (and in equilibrium). We derived this by applying the microcanonical ensemble to system $\boxed{1}$ *plus* the heat bath.

Fixed E_1: (microcanonical, chapter 4)
Constrained integral that counts microstates with fixed E_1.
Integrand $= 1$
Limits of integration: tricky.

Fixed T: (canonical, chapter 6)
Suitably weighted integral over *all* microstates of $\boxed{1}$.
Integrand is $e^{-\beta H}$, not 1 (not just counting).
Limits of integration: straightforward. Integrate over everything (including some very unlikely states).

Note: for a system with discrete states labelled $i = 1, 2...$:

$$p(\text{system } \boxed{1} \text{ is in a specific microstate } \psi_i) = \frac{1}{Z} e^{-\frac{E_i}{k_B T}}$$

$$\text{with} \quad Z \equiv \sum_{i,\text{all states of the system}} e^{-\frac{E_i}{k_B T}}$$

Thermodynamics from the partition function

So we already have the microscopic info: we've found $p(\text{microstate})$ at fixed T. We haven't yet assumed that $\boxed{1}$ is thermodynamically large. Next: **suppose $\boxed{1}$ is also macroscopic**, and let's learn to extract its thermodynamics from the partition function Z.

Compare expressions for $\frac{1}{Z}$ from (1):

$$\frac{1}{Z} = e^{(S_2(E_\text{total}) - S_{1+2}(E_\text{total}))/k_B}$$

Does the RHS really depend on system $\boxed{2}$?

$$S_{1+2}(E_\text{total}) = S_1(\underbrace{\langle E_1 \rangle}_{\text{mean } E_1 \text{ in equilibrium}}) + S_2(\underbrace{\langle E_2 \rangle}_{\text{mean } E_2 \text{ in equilibrium}})$$

$$S_2(E_\text{total}) \;\simeq\; S_2\left(\underbrace{E_\text{total} - \langle E_1 \rangle}_{\langle E_2 \rangle}\right) + \langle E_1 \rangle \frac{\partial S_2}{\partial E_2}\Big|_{E_2 = \langle E_2 \rangle} + \dots$$

$$= \; S_2(\langle E_2 \rangle) + \frac{\langle E_1 \rangle}{T}$$

$$\implies \quad \frac{1}{Z} = e^{\frac{1}{k_B}\left(-S_1(\langle E_1 \rangle) + \frac{\langle E_1 \rangle}{T}\right)}$$

Everything having to do with $\boxed{2}$ has disappeared, and we've written the answer in terms of thermodynamic variables of $\boxed{1}$. So we have two true expressions for Z:

$$Z = \int_{\text{microstates of } \boxed{1}} e^{-H_1/(k_B T)} \qquad \text{and} \qquad Z = e^{-\frac{1}{k_B}\left(-S_1(\langle E_1 \rangle) + \frac{\langle E_1 \rangle}{T}\right)}$$

the left one involving only microscopic information about $\boxed{1}$ and the right one involving only thermodynamics.

Bridge between thermodynamics and canonical ensemble

We can now drop the notational baggage we've been carrying around (the subscripts and the $\langle .. \rangle$s), since everything refers to system $\boxed{1}$ in thermal equilibrium. We've written Z in terms of the thermodynamic variables of the system of interest ($\boxed{1}$):

$$\boxed{Z = e^{-\frac{1}{k_B T}(E - TS)} = e^{-\frac{F}{k_B T}}}$$

where I remind you that $F(T, V, N) = E - TS$ is the Helmholtz free energy,

$$dF = -SdT - PdV \quad . \tag{2}$$

This is the bridge between microscopic stuff (Z) and thermodynamics (F) in the canonical ensemble:

$$F = -k_B T \ln Z(T, V, N)$$

All of thermodynamics follows from this.
Previously (ch 4): count, find Ω, find $S = k_B \ln \Omega$, take derivatives.
Now (ch 6): compute Z, find $F = -k_B T \ln Z$, then from (2), we have:

$$S = -\left(\frac{\partial F}{\partial T}\right)_V, \quad P = -\left(\frac{\partial F}{\partial V}\right)_T, \ldots$$

$$E = F + TS, H = E + PV, G = H - TS.$$

A simpler way to get E:

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

$$= -T^2 \partial_T|_V \left(-k_B \ln Z\right) = -\partial_\beta \ln Z|_V$$

with $\beta \equiv \frac{1}{k_B T}$.

This concludes the derivation of the canonical ensemble. The canonical ensemble is the primary tool of the practicing statistical mechanic. What to remember from Chapter 4, *i.e.* the most important application of the microcanonical ensemble: how to derive the canonical ensemble.

Next: a warning about a common misconception, then an important special case. Then many examples – the rest of 8.044.

Probability for a fixed microstate *vs* probability for a fixed energy

For a system in equilibrium at fixed temperature T, we have:

$$p(\text{system is in microstate A}) = Z^{-1}e^{-E_A/(k_B T)}$$

However, the probability distribution for the energy of the system,

$$p(E) \text{ is NOT proportional to } e^{-E/(k_B T)} \ .$$

Rather, the dependence of this quantity on the energy must also include a degeneracy factor:

$$p(E) = Z^{-1}e^{-E/(k_B T)}(\text{degeneracy}) \ .$$

For a discrete system, the quantity in brackets is the number of microstates with energy E, the degeneracy. This depends on E. Because of this factor $p(E)$ can have a completely different dependence on E.

If E is continuous, then
$$p(E) = Z^{-1}e^{-E/(k_B T)}D(E) \tag{3}$$
where
$$p(E)dE = \text{prob}(E \leq \text{energy} \leq E + dE)$$
$$D(E)dE = \text{ the number of states with } E \leq \text{energy} \leq E + dE \ .$$

$D(E)$ is called the 'density of states'. Our first example below will be the ideal gas, which will illustrate this nicely.

Putting things on top of other things

Suppose the system separates into parts, with independent degrees of freedom:

$$\{q, p\} = \{q_a, p_a\} \times \{q_b, p_b\}$$

(that is: to specify a state of the system, we have to specify a state of part a *and* a state of part b) and

$$H\left(\{q, p\}\right) = H_a\left(\{q_a, p_a\}\right) + H_b\left(\{q_b, p_b\}\right)$$

so that there are no interactions between the parts. Then the Boltzmann factor is a product:

$$e^{-H(\{q,p\})/(k_B T)} = e^{-H_a(\{q_a, p_a\})/(k_B T)} e^{-H_b(\{q_b, p_b\})/(k_B T)}$$

$$\implies p\left(\{q, p\}\right) = p\left(\{q_a, p_a\}\right) p\left(\{q_b, p_b\}\right)$$

The variables $\{q_a, p_a\}$ are statistically independent of $\{q_b, p_b\}$. In this circumstance

$$Z = \int \{dq_a dp_a\} e^{-H_a(\{q_a, p_a\})/(k_B T)} \int \{dq_b, dp_b\} e^{-H_b(\{q_b, p_b\})/(k_B T)}$$

$$= Z_a Z_b$$

$$\implies F = -k_B T \ln Z = -k_B T \left(\ln Z_a + \ln Z_b\right) = F_a + F_b$$

$$\implies S = -\left(\frac{\partial F}{\partial T}\right)_V = S_a + S_b$$

As a result, all the thermodynamic variables that are extensive add.

Next, two special cases.

N identical but distinguishable non-interacting systems:

e.g. N atoms in a crystal, distinguishable by their locations
or *e.g. N* 2-state systems, distinguishable by their locations. To specify the state of the
whole system, we must specify the state of *each* atom. If they don't interact,

$$H = H_1 + H_2 + ... + H_N$$

$$\implies \quad Z = Z_1 Z_2 ... Z_N$$

But since the systems are identical, all the Hs are the same function of their respective
coordinates. So therefore are all the Z-integrals.

$$\implies \quad Z = (Z_1)^N$$

This is an expression for the partition function of a (potentially ginormous) collection of N
non-interacting systems, in terms of the partition function for just one (microscopic) system.
It follows that

$$F = NF_1, \quad S = NS_1 \quad \text{are extensive.}$$

N indistinguishable, non-interacting subsystems:

e.g. N atoms in an ideal gas.

Claim: here the consequence of indistinguishablity is

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

where Z_1 = partition function for one subsystem. A direct canonical-ensemble derivation of
this statement requires more QM than we want to use here. Let's check that it is the same
prescription we derived microcanonically in Chapter 4:

$$Z = \frac{(Z_1)^N}{N!} \implies F = -NkT \ln Z_1 + kT \ln N!$$

$$\implies S = -\left(\frac{\partial F}{\partial T}\right)_V = (S \text{ we would get without the } 1/N!) - k_B \ln N!$$

$$\implies \Omega = e^{S/k_B} = \frac{(\Omega \text{ we would get without the } 1/N!)}{N!}$$

So this is the same prescription as we gave in Chapter 4.

6.2 Monatomic, classical, ideal gas, at fixed T

Consider N non-interacting atoms in a volume V. We're going to treat them classically.

Your further progress in statistical mechanics will be marked by a steady modification of the adjectives from this phrase: 'monatomic' means we ignore internal degrees of freedom of the particles – we'll fix that in Chapter 6.6; 'classical' means the wavefunctions of the particles don't overlap much – we'll fix that in Chapter 9; 'ideal' means the particles don't interact with each other – that's a job for 8.08 or 8.333.

$$H\left(\{q,p\}\right) = H\left(x_1, y_1, z_1, x_2, y_2, z_2, ...p_{x1}, p_{y1}, p_{z1}, p_{x2}, p_{y2}, p_{z2}, ...\right)$$

$$= \sum_{i=1}^{N} \frac{1}{2m}|\vec{p}_i|^2 = \sum_{i=1}^{N} H_i(p_i)$$

$$\implies Z = Z_1^N/N!$$

In treating the system classically, we are assuming that the quantum wave functions of the particles do not overlap much. Much more on this assumption, and what happens when it breaks down, in Chapter 9.

Let's find Z_1:
$$H_1 = \frac{p_x^2 + p_y^2 + p_z^2}{2m}$$

$$Z_1 = \int \frac{dx\,dp_x}{h} \frac{dy\,dp_y}{h} \frac{dz\,dp_z}{h} e^{-\frac{p_x^2+p_y^2+p_z^2}{2mk_BT}}$$

The factors of h make the integral dimensionless. This constant doesn't affect the thermodynamics, and it cancels out of probabilities. The factor will return in our later discussion of the breakdown of the classical treatment. At that time, we'll show that this is the right factor when the classical system arises from the classical limit of a quantum system.

$$Z_1 = \frac{1}{h^3} L_x L_y L_z \left(\int dp\ e^{-\frac{p^2}{2mkT}} \right)^3 = \frac{V}{h^3} \left(2\pi mkT\right)^{3/2} \ .$$

$$\underbrace{Z_1}_{\text{dimensionless}} = \underbrace{V}_{\text{volume}} \underbrace{\left(\frac{2\pi mkT}{h^2}\right)^{3/2}}_{1/\text{length}^3}$$

Check:
$$\text{length}^{-2} \overset{?}{=} [\frac{mk_BT}{h^2}] = \frac{\text{mass} \cdot \text{energy}}{\text{energy}^2 \cdot \text{time}^2} = \frac{\text{mass/time}^2}{\text{energy}} \quad \checkmark$$

This length is

$$\boxed{\lambda_D \equiv \sqrt{\frac{h^2}{2\pi m k_B T}}} = \frac{h}{\sqrt{2\pi m k_B T}} \sim \frac{h}{\sqrt{2m E_{\text{thermal}}}} = \frac{h}{\text{momentum}_{\text{thermal}}}$$

the "thermal de Broglie wavelength". In terms of which:

$$Z_1 = \frac{V}{\lambda_D^3}.$$

$$Z = \frac{Z_1^N}{N!} = \frac{V^N}{N!}\lambda_D^{-3N} = \frac{V^N}{N!}\left(\frac{2\pi m k T}{h^2}\right)^{3N/2}.$$

Thermodynamics from Z

$$F = -k_B T \ln Z$$

$$= -k_B T \left(-N \ln N + N + N \ln V + \frac{3N}{2} \ln \left(\frac{2\pi m k_B T}{h^2} \right) \right)$$

$$= -N k_B T \left(\ln \frac{V}{N} + \frac{3}{2} \ln T + 1 + \frac{3}{2} \ln \left(\frac{2\pi m k_B}{h^2} \right) \right)$$

Recall: $dF = -SdT - PdV$.

$$\implies \quad P = -\left(\frac{\partial F}{\partial V} \right)_T = \frac{N k_B T}{V}, \qquad PV = N k_B T \quad \checkmark$$

$$\implies \quad S = -\left(\frac{\partial F}{\partial T} \right)_V = N k_B \left(\ln \frac{V}{N} + \frac{3}{2} \ln T + 1 + \frac{3}{2} \ln \left(\frac{2\pi m k_B}{h^2} \right) \right) + \frac{3}{2} N k_B$$

$$= N k_B \left(\ln \frac{V}{N} + \frac{3}{2} \ln T + \frac{5}{2} + \frac{3}{2} \ln \left(\frac{2\pi m k_B}{h^2} \right) \right) \quad \checkmark$$

and

$$E = F + TS = \frac{3}{2} N k_B T \quad \checkmark$$

Success: we've reproduced all the thermodynamics of the ideal gas.

The hardest thing we had to do here was a Gaussian integral over one p variable. This is easier than the microcanonical ensemble where I had to quote some formula for volumes of balls.

[End of Lecture 15.]

Fixed-T equilibrium distributions of microscopic vars. in ideal gas

Think of system $\boxed{1}$ as a single atom, with location $\vec{r} = (x, y, z)$ and momentum $\vec{p} = (p_x, p_y, p_z)$. At fixed temperature T, the distribution for these variables is the Boltmann distribution:

$$p_B(\vec{r}, \vec{p}) = \frac{1}{Z_1} e^{-\frac{p_x^2 + p_y^2 + p_z^2}{2mk_B T}}$$

$$= \frac{1}{V} \left(\frac{h^2}{2\pi m k_B T} \right)^{3/2} e^{-\vec{p}^2/(2mk_B T)} \quad .$$

One small annoyance: Note the normalization

$$1 = \int \frac{d^3 r \, d^3 p}{h^3} p_B(\vec{r}, \vec{p})$$

So this p_B is actually dimensionless. To get the usual normalization for the probability distribution, remove the h^3:

$$p(\vec{r}, \vec{p}) = \frac{p_B}{h^3} = \frac{1}{V} \left(\frac{1}{2\pi m k_B T} \right)^{3/2} e^{-\vec{p}^2/(2mk_B T)} \quad .$$

What's the momentum distribution? Squash the probability mountain in $\vec{r}$:

$$p(\vec{p}) = \int_V d^3 r \, p(\vec{r}, \vec{p}) = \left(\frac{1}{2\pi m k_B T} \right)^{3/2} e^{-\vec{p}^2/(2mk_B T)} \qquad \checkmark$$

This was what we got from the microcanonical ensemble.

Distributions for speeds and energies

From this you can work out the distributions for various related random variables using the 'functions of a random variable' technology. For example, the distribution for the velocity $\vec{v} \equiv \vec{p}/m$ is

$$p(\vec{v}) = \left(\frac{m}{2\pi k_B T}\right)^{3/2} e^{-\frac{1}{2}m\vec{v}^2/(k_B T)}$$

The velocity distribution is gaussian and isotropic.

The distribution for the energy $E_1 = \frac{1}{2}m(v_x^2 + v_y^2 + v_z^2)$ (as you worked out on Pset 4) is

$$p(E_1) = \frac{2}{(k_B T)^{3/2}} \sqrt{\frac{E_1}{\pi}} e^{\frac{-E_1}{k_B T}}$$

Compare this with our expression (3) above for the probability that system $\boxed{1}$ has a given energy. This comparison implies that the density of states for this system is

$$D(E) \propto \sqrt{E}.$$

Note that there are more states with larger energy. More on this later.

Finally, the speed distribution $v \equiv |\vec{v}|$ is

$$p(v) = \int_{\theta,\varphi} p(\vec{v})v^2 \sin\theta d\theta d\varphi = 4\pi v^2 p(\vec{v}) = 4\pi v^2 \left(\frac{m}{2\pi k_B T}\right)^{3/2} e^{-\frac{1}{2}mv^2/(k_B T)}.$$

This is called the Maxwell speed distribution. The scale in this distribution is set by making a velocity out of T and m: $v_{\text{interesting}} \sim \sqrt{\frac{kT}{m}}$. The numerical prefactor depends on which question we ask.

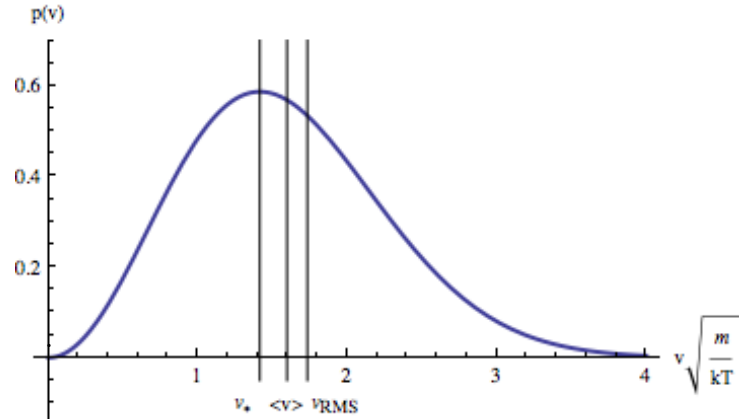The most probable speed (the value with the maximum $p(v)$) is

$$v_\star = \sqrt{2}\sqrt{\frac{kT}{m}}$$

The mean speed is

$$\langle v \rangle = \int_0^\infty v p(v) dv = \sqrt{\frac{8}{\pi}}\sqrt{\frac{kT}{m}}.$$

The root-mean-square speed is

$$v_{\text{RMS}} = \langle v^2 \rangle^{1/2} = \sqrt{3}\sqrt{\frac{kT}{m}} \simeq 511\text{m/s for } N_2 \text{ at room temp.}$$

For more on this see Baierlein Chapter 13.

6.3 Two-level systems, re-revisited

Let's consider a model of impurity atoms in a solid; it's a small elaboration of the model with the pink and white squares from Chapter 1.

[This problem is treatable by the microcanonical ensemble. Try it. This method is easier, though.]

The model is: each impurity is a $g+1$-state system. The groundstate (called ψ_0) we think of as an empty site; then there are g degenerate states $\psi_i, i = 1...g$ with energy ε, which represent some extra particle living at the site in one of g possible ways (if you like chemistry, imagine an electron which has to choose between some degenerate orbitals).
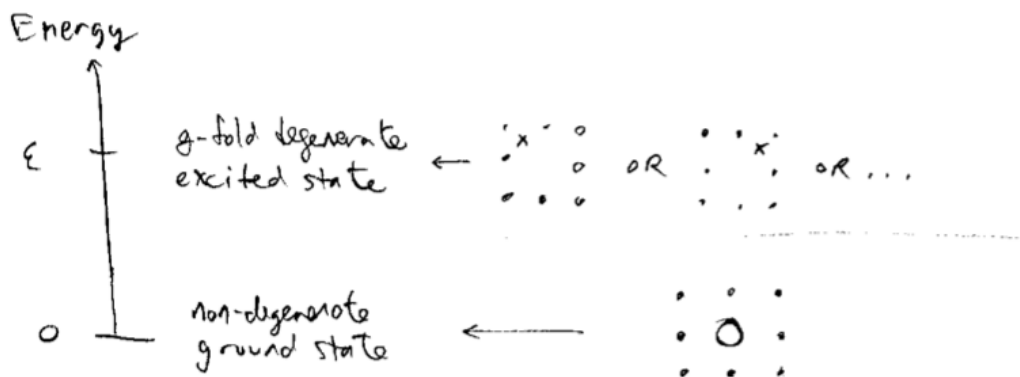
States: $\underbrace{\psi_0}_{E=0}$ and $\underbrace{\psi_1, \psi_2...\psi_g}_{E=\varepsilon}$

The partition function for *one* impurity is:

$$Z_1 = \sum_{\text{all states of one impurity}} e^{-E_{\text{state}}/(k_B T)} = e^{-0} \times 1 + e^{-\varepsilon/(k_B T)}g = 1 + ge^{-\varepsilon/(k_B T)}$$

End of arduous calculation. All of the information is in this expression; next we practice getting it out.

The impurities are distinguishable by their locations (and we will assume they don't interact), but each has the same Z_1, so if there are N impurities:

$$Z = Z_1^N \ .$$

Microscopic information

$$p(\text{state of one impurity}) = e^{-E_{\text{state}}/(k_B T)}\frac{1}{Z_1}$$

$$p(\psi_0) = \frac{1}{Z_1} = \frac{1}{1 + ge^{-\varepsilon/k_B T}}, \quad p(\psi_i, i = 1 \text{ or } 2 \text{ or } ... \text{ or } g) = \frac{e^{-\varepsilon/k_B T}}{Z_1} = \frac{e^{-\varepsilon/k_B T}}{1 + ge^{-\varepsilon/k_B T}}$$
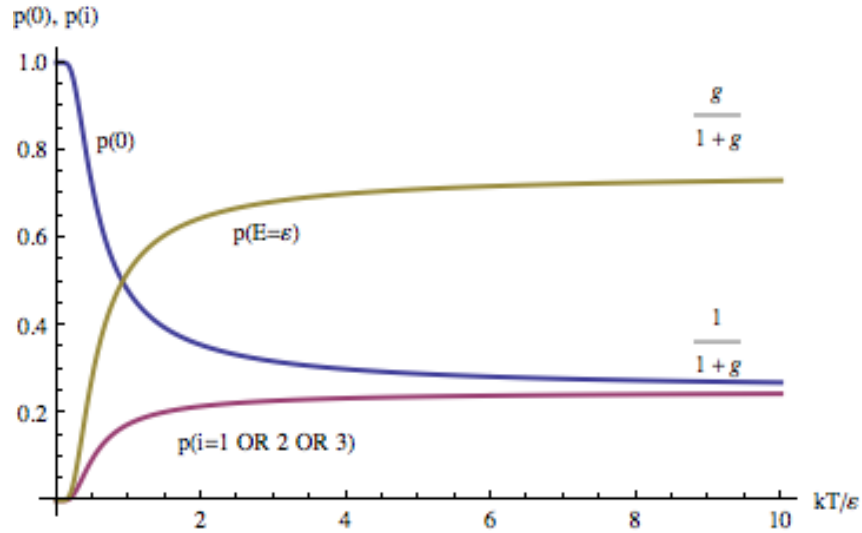
The picture is for $g = 3$.

low temperature $T \to 0$: $e^{-\varepsilon/k_B T} \to 0$, lowest-energy state wins.

high temperature $T \to \infty$: $e^{-\varepsilon/k_B T} \to 1$, all states equally likely.

Check: $g = 1$ is the two-state system. $\frac{g}{1+g} = \frac{1}{2}$.

Thermodynamics

A small elaboration of the model, which makes for more interesting thermodynamics: Let $\varepsilon = \varepsilon(V)$, where V is the volume. The idea is : squeezing the crystal reduces the volume; this squeezes the cage in which the impurity sits, and increases the energy cost ε.

To pick a concrete model, let:

$$\varepsilon(V) = \epsilon_0 \left(\frac{V}{V_0} \right)^{-\alpha}$$

where $\epsilon_0, V_0, \alpha > 0$ are parameters (α is called the 'Gruneisen Parameter').

This doesn't change our answers so far:

$$Z = Z(T, V, N) = \left(1 + g e^{-\varepsilon(V)/k_B T} \right)^N$$

$$F = F(T, V, N) = -k_B T \ln Z = -N k_B T \ln \left(1 + g e^{-\varepsilon(V)/k_B T} \right)$$

$$S = - \underbrace{\left(\frac{\partial F}{\partial T} \right)_V}_{i.e.\ \text{fixed } \varepsilon} = +N k_B \ln (...) + \frac{N g \varepsilon}{T} e^{-\varepsilon/k_B T} \frac{1}{1 + g e^{-\varepsilon(V)/k_B T}}$$

$$E = F + TS = \frac{N g \varepsilon e^{-\varepsilon/k_B T}}{1 + g e^{-\varepsilon(V)/k_B T}}$$

Check 0: Redo microcanonically and get the same answer. This is left as an exercise.

Check 1: We could also get E from:

$$E = k_B T^2 \left(\frac{\partial}{\partial T} \right)_V \ln Z = N k_B T^2 \left(\frac{\partial}{\partial T} \right)_V \ln \left(1 + g e^{-\varepsilon(V)/k_B T} \right) = \text{as above.}$$

Check 2: We could also also get E from $E = N \langle E_1 \rangle$ with the average energy of one impurity

$$\langle E_1 \rangle = \underbrace{\sum_{i=0...g}}_{\text{states of one impurity}} E_1(\psi_i) p(\psi_i) = \frac{1}{Z_1} \sum_{i=0...g} E_1(\psi_i) e^{-E_1(\psi_i)/k_B T} = k_B T^2 \frac{\partial}{\partial T} \ln Z_1$$

The last step is the formula we get by applying the canonical ensemble to one impurity – it works! Note that $E = N \langle E_1 \rangle$ depends on the constituents of the system being non-interacting.

Thermodynamics of two-level systems, cont'd

To evaluate the pressure, we make (copious!) use of the chain rule of calculus:

$$P = -\left(\frac{\partial F}{\partial V}\right)_T = -\left(\frac{\partial F}{\partial \varepsilon}\right)_T \cdot \frac{\partial \varepsilon}{\partial V}$$

$$= +\frac{Nk_BT}{1 + ge^{-\varepsilon(V)/k_BT}}\left(\frac{-g}{k_BT}\right)e^{-\varepsilon/k_BT} \cdot \epsilon_0\left(\frac{V}{V_0}\right)^{-\alpha}\left(\frac{-\alpha}{V}\right)$$

$$= +\frac{\alpha Ng\varepsilon}{V}\frac{e^{-\varepsilon/k_BT}}{1 + ge^{-\varepsilon(V)/k_BT}} = \frac{\alpha E}{V}.$$

This last formula is the equation of state.

Another simple generalization of the collection of two-state systems we solved in chapter 4.4 is to make the energy spacings of each of the two-state systems different: the energy difference between ON and OFF for the ith site is ε_i. This problem (which appeared in the extra credit on Pset 6) is *hard* to solve using the microcanonical ensemble, but quite easy with the canonical ensemble. Try it. The only difference from the problem above is that since the sites are not identical, we can no longer simply take the Nth power of the 1-site partition function. Rather we must retreat to the result $Z = Z_1Z_2...Z_N$.

6.4 Classical harmonic oscillators and equipartition of energy

Next, we're going to replace our 2-level systems with simple harmonic oscillator (SHO), first classical then quantum. So consider N non-interacting classical SHOs in equilibrium at temperature T. Each one has two degrees of freedom (x, p), and hamiltonian

$$H_1 = H_1(x, p) = \frac{p^2}{2m} + \frac{1}{2}\kappa x^2 = \frac{p^2}{2m} + \frac{1}{2}m\omega^2 x^2 \ ,$$

where m is the mass and κ is the spring constant; in the second expression, $\omega \equiv \sqrt{\kappa/m}$ is the natural frequency. Assume their locations are fixed so they are distinguishable, although identical. Then $Z = Z_1^N$ where Z_1 is the partition function of one of them:

$$Z_1 = \frac{1}{h} \int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dp \ e^{-\frac{p^2}{2mk_BT}} e^{-\frac{x^2}{2k_BT/\kappa}}$$

Notice that we let the displacement of the spring go all the way to ∞ in the integral here. This is a specification of the toy model we are studying; happily, the effects of this choice are negligible because the contributions of these configurations are suppressed by the Boltzmann factor.

This is two Gaussian integrals:

$$Z_1 = \frac{1}{h}\sqrt{2\pi m k_B T}\sqrt{2\pi k_B T/\kappa} = \frac{2\pi}{h}\sqrt{\frac{m}{\kappa}}k_B T = \frac{k_B T}{\hbar\omega} \ .$$

In the last step, we re-wrote the answer in terms of the natural frequency of the oscillator. (Note that this is a ratio of energies.)

Now consider many oscillators (like positions of atoms in a crystal), and let's extract the thermodynamics:

$$Z = Z_1^N \quad \Longrightarrow \quad F = -Nk_B T \ln Z_1 = -N \underbrace{k_B T}_{1/\beta} \ln \left(\underbrace{k_B T}_{1/\beta}/(\hbar\omega) \right)$$

$$E = -\frac{\partial}{\partial\beta} \ln Z = -\frac{\partial}{\partial\beta} \ln \frac{1}{\beta\hbar\omega} = +\frac{N}{\beta} = Nk_B T$$

$$\boxed{\frac{E}{N} = k_B T}$$

$\frac{E}{N}$ is the energy per oscillator. Since our oscillators don't interact, the energy per oscillator is the same as $\langle E_1 \rangle$, the energy of a single oscillator. To evaluate this, we could instead have directly computed

$$\langle E_1 \rangle = -\frac{\partial}{\partial\beta} \ln Z_1 = -\frac{\partial}{\partial\beta} \ln \frac{1}{\beta\hbar\omega} = \frac{1}{\beta} = k_B T.$$

This is an example of the ...

Equipartition Theorem

Assume:

1. Classical system. This a statement about classical statistical mechanics. We will see next that this assumption means

$$k_B T \gg \text{ the spacing between quantum energy levels.}$$

2. Somewhere in the problem is an SHO:

$$H(q_1...q_N, p_1...p_N) = ay^2 + H(\text{all other variables besides } y)$$

where y is a q or a p, and $a > 0$ is a constant. That is: there is some variable y that only appears in H via the quadratic term ay^2.

THEN:

$$\langle ay^2 \rangle = \frac{1}{2} k_B T$$

This is the mean value of the contribution of the variable y to the energy of the system when it is in thermal equilibrium at temperature T. Notice that it is independent of a, as long as $a > 0$.

Proof:

$$\langle ay^2 \rangle = \frac{\int \{dpdq\} e^{-\beta H(\{p,q\})} ay^2}{\int \{dpdq\} e^{-\beta H(\{p,q\})}}$$

note that y is one of the ps or qs

$$= \frac{\int_{-\infty}^{\infty} dy \ ay^2 e^{-\beta ay^2} \int d(\text{other vars}) \ e^{-\beta H_{\text{other}}}}{\int_{-\infty}^{\infty} dy \ e^{-\beta ay^2} \int d(\text{other vars}) \ e^{-\beta H_{\text{other}}}}$$

$$= \frac{-\partial_\beta \left(\sqrt{\frac{\pi}{\beta a}} \right)}{\sqrt{\frac{\pi}{\beta a}}} = \frac{\frac{1}{2}\beta^{-3/2}}{\beta^{-1/2}} = \frac{1}{2\beta} = \frac{1}{2} k_B T$$

QED.

In thermal equilibrium, each such 'quadratic variable', *i.e.* each variable appearing only quadratically in the Hamiltonian, contributes $\frac{k_B T}{2}$ to the energy.

Some sample consequences:

- *e.g.* $E = N k_B T$ for N harmonic oscillators each with $H_1 = \frac{1}{2m} p^2 + \frac{1}{2}\kappa x^2$, two quadratic variables apiece, therefore $2N$ quadratic variables altogether.

- *e.g.* $E = \frac{3}{2}Nk_BT$ for a monatomic ideal gas with $H_1 = \frac{1}{2m}p_x^2 + \frac{1}{2m}p_y^2 + \frac{1}{2m}p_z^2$ for each atom – three quadratic variables per atom, therefore $3N/2$ altogether.

- Basically every system that we understand is made up of lots of SHOs, plus non-quadratic terms in H that we treat as perturbations – think of the quadratic term as the first non-trivial term in a Taylor expansion of H about an equilibrium configuration where the force $\frac{\partial H}{\partial y}\big|_{\text{equilibrium}} = 0$. Equipartition gives the leading-order result for thermodynamics of any such classical system.

- Here is an example of a physical conclusion that we can draw from this theorem: Air is made up of various different kinds of molecules: N_2, O_2. Approximate it is an ideal gas with these various constituents (not too bad a thing to do), and assume we are at temperatures at which we can ignore the internal degrees of freedom. Equipartition tells us that each molecule contributes $\frac{3}{2}k_BT$ to the average energy. But the energy of a given molecule is then $\langle \frac{|\vec{p}|^2}{2m} \rangle = \frac{3}{2}k_BT$. We conclude that heavier ones carry less momentum:

$$v_{RMS} \equiv \frac{1}{m}\sqrt{\langle |\vec{p}|^2 \rangle} = \sqrt{\frac{3k_BT}{m}} \ .$$

[End of Lecture 16.]

6-22

6.5 Quantum harmonic oscillators

Consider a single *quantum* harmonic oscillator in thermal equilibrium with a heat bath. H is the same as in the last subsection, now with hats:
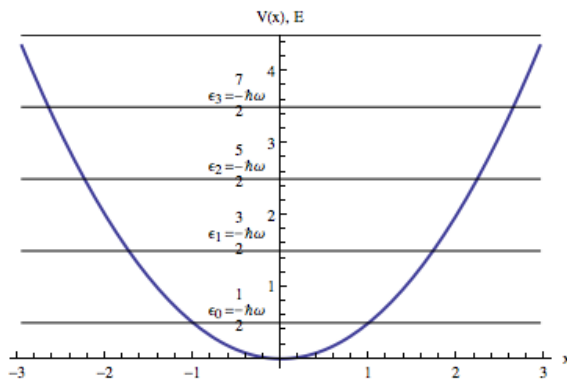
$$\hat{H} = \frac{1}{2m}\hat{p}^2 + \frac{1}{2}\kappa\hat{x}^2$$

The hats remind us that $\hat{p}, \hat{x}$ are quantum mechanical operators, as is the Hamiltonian operator $\hat{H}$. Acting on wavefunctions, the momentum operator acts as $\hat{p} = -i\frac{d}{dx}$. The eigenstates of the Hamiltonian satisfy (the time-independent Schrödinger equation)

$$\hat{H}\psi_n = \epsilon_n\psi_n \ .$$

The nth energy eigenvalue is

$$\epsilon_n = \hbar\omega\left(n + \frac{1}{2}\right), \qquad n = 0, 1, 2...\infty$$

A measurement of the energy of the oscillator always results in an element from this list. (The wavefunctions $\psi_n(x)$ are known but not needed here. (!))

A general state of the oscillator is a *superposition* of energy eigenstates

$$\psi_{\text{general}} = c_0\psi_0 + c_1\psi_1 + c_2\psi_2 + ...$$

where the c_n are complex numbers; in this state the (quantum) probability that when measuring the energy you measure ϵ_n is $|c_n|^2$.

A full treatment of *quantum* statistical mechanics therefore has two sources of uncertainty.

We will largely dodge this issue by the following restriction: We suppose the system is in an energy eigenstate, and we avoid measuring things other than the energy (more precisely, we'll avoid measuring expectation values of operators which do not commute with the Hamiltonian, which would take us out of an energy eigenstate). We are hereby limiting the scope of our ambitions, and ignoring effects of superposition. We will still be able to understand equilibrium thermodynamics of simple quantum systems, and we will be able to ask many (though not all) microscopic questions. Everything we do will be correct.

Partition function of quantum harmonic oscillator

$$Z_1 \equiv Z(\text{one oscillator}) = \sum_{\text{states},n=0,1,2...} e^{-\beta \epsilon_n}$$

$$= e^{-\frac{1}{2}\frac{\hbar\omega}{k_B T}} \sum_{n=0}^{\infty} \left(e^{-\frac{\hbar\omega}{k_B T}}\right)^n \overset{\text{geometric series}}{=} e^{-\frac{1}{2}\frac{\hbar\omega}{k_B T}} \frac{1}{1 - e^{-\frac{\hbar\omega}{k_B T}}}.$$

Microscopic information: What's the probability that the oscillator is in the state ψ_n with energy ϵ_n:

$$p(n) = \frac{1}{Z_1} e^{-\left(n+\frac{1}{2}\right)\frac{\hbar\omega}{k_B T}}$$

$$p(n) = e^{-n\frac{\hbar\omega}{k_B T}} \left(1 - e^{-\frac{\hbar\omega}{k_B T}}\right) = a^n(1-a) \text{ with } a \equiv e^{-\frac{\hbar\omega}{k_B T}}, 0 < a < 1$$

Note that $a = e^{-\beta\hbar\omega} \rightarrow 1$ at $T \rightarrow \infty$ and $a \rightarrow 0$ at $T \rightarrow 0$. This is the "Geometric" or "Bose-Einstein" probability distribution we encountered in Chapter 2.

$$\langle n \rangle = \sum_{n=0}^{\infty} n p(n) = (1-a)\sum_{n=0}^{\infty} n a^n = (1-a)a\frac{d}{da}\underbrace{\sum_{n=0}^{\infty} a^n}_{\frac{1}{1-a}}$$

$$= \frac{(1-a)a}{(1-a)^2} = \frac{a}{1-a} = \frac{e^{-\frac{\hbar\omega}{kT}}}{1 - e^{-\frac{\hbar\omega}{kT}}}$$

$$\langle n \rangle = \frac{e^{-\frac{\hbar\omega}{kT}}}{1 - e^{-\frac{\hbar\omega}{kT}}} \qquad \boxed{\langle n \rangle = \frac{1}{e^{\frac{\hbar\omega}{kT}} - 1}}$$
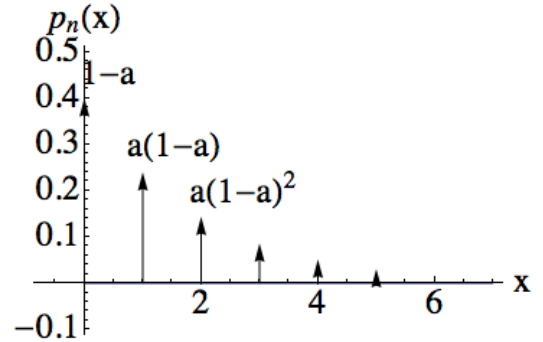
If I knew how to put more boxes around a formula in TeX, I would do it for this one. This formula for the mean occupation number of a quantum SHO will get heavy use in the rest of 8.044 – it will come up in our discussions of *e.g.*. photons, phonons, Bose-Einstein condensates, and many other things as well.

Mean energy of one oscillator (Baierlein calls this $\langle \varepsilon \rangle$, and I have occasionally called it $\langle E_1 \rangle$):

$$\langle \epsilon \rangle = \langle \hbar\omega \left(n + \frac{1}{2}\right)\rangle = \hbar\omega \left(\langle n \rangle + \frac{1}{2}\right) = \hbar\omega \left(\frac{1}{e^{\frac{\hbar\omega}{kT}} - 1} + \frac{1}{2}\right)$$

Limits of high and low temperature, compared to the oscillator frequency:

Low T: $k_B T \ll \hbar\omega$, much smaller than the level spacing. Then $e^{\beta\hbar\omega} \gg 1$ and

$$\langle n \rangle \simeq e^{-\frac{\hbar\omega}{k_B T}},$$

$\langle n \rangle$ is between 0 and 1, close to zero: $p(0) \gg p(1) \gg p(2) \gg ...$

$$\langle \epsilon \rangle \simeq \underbrace{\frac{1}{2}\hbar\omega}_{\text{ground state energy}} + \underbrace{\hbar\omega e^{-\frac{\hbar\omega}{k_B T}}}_{\text{very small correction}}$$

At low temperatures, most of the ensemble of oscillators are in the groundstate. The small correction to the energy comes from rare excitations to the first excited state (with energy $\hbar\omega\left(\frac{1}{2}+1\right)$) which occur with probability $\propto e^{-\beta\hbar\omega}$.
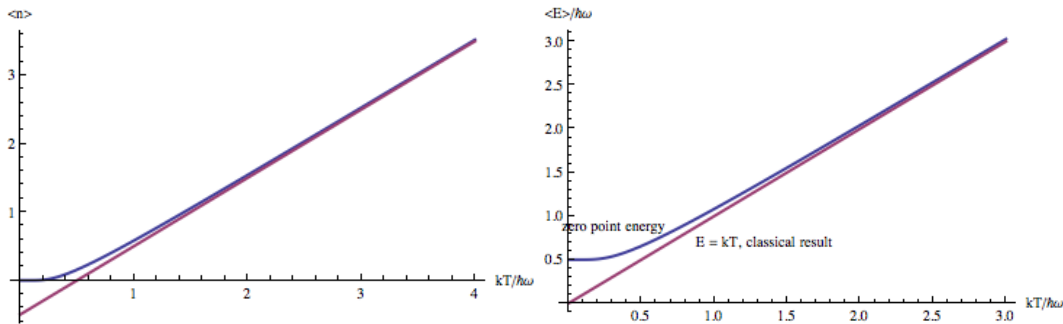
High T: $k_B T \gg \hbar\omega$. In this limit we can Taylor expand the Boltzmann factor:
$e^{-x} \overset{x\ll 1}{\simeq} 1 - x + \frac{1}{2}x^2 - ...$

$$\langle n \rangle = \frac{1}{1 + \frac{\hbar\omega}{k_B T} + \frac{1}{2}\left(\frac{\hbar\omega}{k_B T}\right)^2 + ... - 1}$$

$$\simeq \frac{k_B T}{\hbar\omega} \cdot \frac{1}{1 + \frac{1}{2}\left(\frac{\hbar\omega}{k_B T}\right)} \simeq \frac{k_B T}{\hbar\omega}\left(1 - \frac{1}{2}\frac{\hbar\omega}{k_B T}\right) = \frac{k_B T}{\hbar\omega} - \frac{1}{2} + \mathcal{O}\left(\frac{\hbar\omega}{k_B T}\right)$$

And

$$\langle \epsilon \rangle = \hbar\omega\left(\langle n \rangle + \frac{1}{2}\right) = k_B T + \mathcal{O}\left(\frac{\hbar\omega}{k_B T}\right)$$

This, not coincidentally, agrees with the classical result (that is, the equipartition theorem) when $k_B T \gg \hbar\omega$ = the spacing between quantum levels.

Interlude about quantum uncertainty in statistical mechanics

The following discussion is "not examinable" and is meant to flag an omission in our discussion, so that you are prepared to correct this omission later in your education.

I want to explain why our expression for the partition function of the quantum SHO is the right thing to do, given that the general state is a *superposition* $\psi = \sum_n c_n \psi_n$ of energy eigenstates, not just an energy eigenstate.

The general formula for the thermal partition function of a quantum system with Hamiltonian $\hat{H}$ is the following expression, which we will not derive:

$$Z = \text{Tr } e^{-\beta \hat{H}}$$

('Tr' is short for 'trace')

$$\equiv \underbrace{\sum_n}_{\substack{any \text{ orthonormal} \\ \text{basis of states}}} \int dx\, \phi_n^\star(x) \underbrace{e^{-\beta \hat{H}}}_{=1 - \beta\hat{H} + \frac{1}{2}\beta^2 \hat{H}^2 + \dots} \phi_n(x) \tag{4}$$

The set of all eigenstates $\psi_n(x)$ of the hamiltonian is one good choice for a complete orthonormal basis of states. Any other orthonormal basis is made from linear combinations of the ψ_n and would work just as well. It is a (simple) math fact (proved in linear algebra and in 8.05) that the trace operation Tr defined above is independent of basis choice – *i.e.* it's the same in any basis.

So we can evaluate the fancy general expression (4) for Z using the energy eigenstate basis:

$$\begin{aligned} Z &= \sum_n \int dx\, \psi_n^\star(x) e^{-\beta \hat{H}} \psi_n(x) \\ &= \sum_n e^{-\beta E_n} \underbrace{\int dx\, \psi_n^\star \psi_n}_{=1} \\ &= \sum_n e^{-\beta E_n} \end{aligned}$$

which is the expression we used for the SHO. This last expression is all we will need for 8.044.

A question you can ask, though, is: what is $p(\phi)$, the probability that the system (in thermal equilibrium) is found in some state ϕ other than an energy eigenstate? The answer is:

$$p(\phi) = \frac{1}{Z} \int dx\, \phi^\star(x) e^{-\beta \hat{H}} \phi(x). \tag{5}$$

6-26

Notice that in the special case that ϕ is an energy eigenstate ψ_n, this expression (5) reduces to

$$p(\psi_n) = \frac{1}{Z} e^{-\beta E_n}$$

which we used above. On the other hand, suppose $\phi = c_0 \psi_0 + c_1 \psi_1$ is a superposition of two energy eigenstates; then

$$p(\phi) = \frac{1}{Z} \left(|c_0|^2 e^{-\beta E_0} + |c_1|^2 e^{-\beta E_1} \right).$$

This formula has both quantum mechanics uncertainty and statistical mechanics uncertainty. We're not going to think more about these issues further in 8.044.

This is the end of the unexaminable interlude.

[End of Lecture 17.]

Thermodynamics of N (distinguishable) quantum oscillators

Suppose we have N quantum SHOs, distinguishable, *e.g.* by their locations.

$$Z = Z_1^N$$

$$F = -Nk_BT \ln Z_1 = -\frac{N}{\beta} \ln \left(\frac{e^{-\frac{1}{2}\beta\hbar\omega}}{1 - e^{-\beta\hbar\omega}} \right)$$

$$E = -\partial_\beta \ln Z = -N\partial_\beta \ln \left(\frac{e^{-\frac{1}{2}\beta\hbar\omega}}{1 - e^{-\beta\hbar\omega}} \right)$$

$$= -N\frac{\left(1 - e^{-\beta\hbar\omega}\right)}{e^{-\frac{1}{2}\beta\hbar\omega}} \left(\frac{-\frac{1}{2}\hbar\omega e^{-\frac{1}{2}\beta\hbar\omega}}{1 - e^{-\beta\hbar\omega}} - \frac{\hbar\omega e^{-\frac{1}{2}\beta\hbar\omega}e^{-\beta\hbar\omega}}{(1 - e^{-\beta\hbar\omega})^2} \right)$$

$$= N \left(\frac{1}{2}\hbar\omega + \hbar\omega \frac{e^{-\beta\hbar\omega}}{1 - e^{-\beta\hbar\omega}} \right)$$

$$= N \left(\frac{1}{2}\hbar\omega + \hbar\omega \frac{1}{e^{\beta\hbar\omega} - 1} \right)$$

$$= N\langle E_1 \rangle = N\langle \epsilon \rangle$$

which we could have expected.

Next, heat capacity. No work done means ω is fixed as we add heat.

$$C_V = \frac{\partial E}{\partial T} = N\partial_T \langle \epsilon \rangle = N \left(-\frac{1}{k_BT^2} \right) \left(\frac{-(\hbar\omega)^2 e^{\beta\hbar\omega}}{(e^{\beta\hbar\omega} - 1)^2} \right)$$

There is no notion of volume of a harmonic oscillator, but 'C_V' generally indicates that the heat is added without doing work.

$$\boxed{C_V = Nk_B \left(\frac{\hbar\omega}{k_BT} \right)^2 \frac{e^{\frac{\hbar\omega}{k_BT}}}{(e^{\beta\hbar\omega} - 1)^2}}$$

$\boxed{\text{Low T:}}\ k_BT \ll \hbar\omega$

$$C_V \sim Nk_B \left(\frac{\hbar\omega}{k_BT} \right)^2 e^{-\frac{\hbar\omega}{k_BT}}$$

Same as the 2-state system with $\varepsilon = \hbar\omega$.

$\boxed{\text{High T:}}\ k_BT \gg \hbar\omega$

$$C_V \sim Nk_B \left(\frac{\hbar\omega}{k_BT} \right)^2 \frac{1}{\left(1 + \frac{\hbar\omega}{k_BT} + ... - 1 \right)^2} = Nk_B \left(1 + \mathcal{O} \left(\frac{\hbar\omega}{k_BT} \right) \right)$$

which is the classical equipartition answer.

As we raise the temperature of a 2-state system, the C_V falls off once half of the spins are up and half are down, and $\langle E \rangle$ approaches a constant. For the SHO, the levels just don't stop, so as we raise the temperature, we keep populating new levels (at a uniform rate, because of the uniform level spacing). $\langle E \rangle$ keeps rising, and C_V approaches a constant.
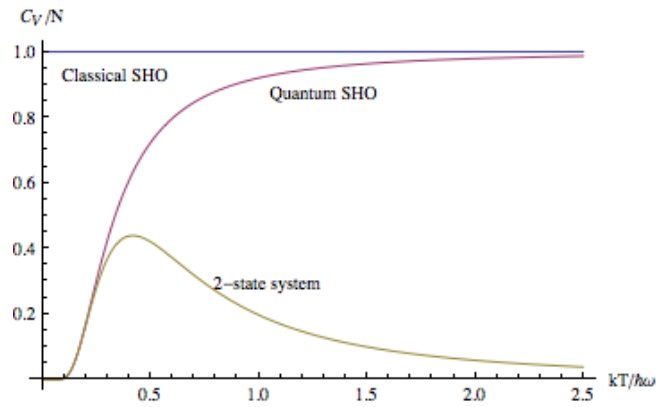
6.6 Heat capacity of a diatomic ideal gas

Consider an ideal gas made from complex, polyatomic molecules.

Assume the gas is dilute, so that we can neglect interactions between the molecules. This means that $PV = Nk_BT$ still.

We will still assume that the molecules are identical and indistinguishable. So:

$$Z = Z_1^N/N!$$

where Z_1 is the partition function of one molecule:

$$Z_1 = \sum_{\text{all states of 1 molecule}} e^{-\beta E_{\text{state}}} \quad .$$

The new twist is that now the energy of a state of the molecule has more terms in it

$$E_{\text{state}} = \underbrace{E_{\text{CM}}}_{\text{energy of motion of center of mass}} + E_{\text{rotation}} + E_{\text{vibration}} + E_{\text{excitations of electrons in the atoms}}$$

Here E_{CM} is the kinetic energy of the center of mass motion of the molecule; this is what we have analyzed so far in the monatomic case.

$$E_{\text{excitations of electrons in the atoms}} \equiv E_{\text{atomic excited state}} - E_{\text{atomic groundstate}}$$

is typically of order of a few eV. Recall : $\frac{1\text{eV}}{k_BT} = 1$ for $T \sim 10000K$. (actually $T = 11605K$).

As long as $T \ll$ this temperature, it's exponentially improbable ($p \propto e^{-1\text{eV}/k_BT}$) that any of the atoms are in a state other than the groundstate. So we can safely ignore this energy scale.

[Actually: before we reach temperatures that are so large as to make us worry about this approximation, the molecules will have fallen apart. It's the same physics and hence the same energy scales that are involved in the binding energies of the molecules.]

$E_{\text{vibration}}$: is the energy associated with distortions of the shape of the molecule. The simplest case, and the only one we will discuss is the case of a diatomic molecule, like H_2, O_2, N_2.... which we think of as balls attached by a (quantum) spring. The reason it is safe to treat it as a SHO is that deviations from the quadratic potential can be neglected if the vibrations are not too big. (These can be treated, but we will not do it.)
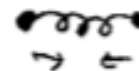
E_{rotation}: is the energy of rotation (angular kinetic energy) associated with rotation of the molecule, which is now not spherically symmetric.

For a *classical* monatomic gas with $E = E_{\text{CM}}$,
$E_{\text{total}} = \frac{3}{2}Nk_BT$, by classical equipartition with 3 quadratic variables, p_x, p_y, p_z. Therefore $C_V = \frac{3}{2}Nk_B, C_P = \frac{5}{2}Nk_B$.

Why was it OK (e.g. at room temperature) for us to treat these gases classically? The quantum center of mass motion is a particle in a box. A big box means small level spacing. $k_BT_{\text{room}} \gg$ level spacing. We'll return to the case of low temperatures (or small rooms) where this is not the case.

For a diatomic molecule, the terms in the hamiltonian add, and involve different variables. This means the partition function factorizes:

$$Z_1 = \underbrace{(Z_1)_{\text{CM}}}_{\text{contributes } C_V = \frac{3}{2}Nk_B} \underbrace{(Z_1)_{\text{VIB}}}_{\text{quantum oscillator}} (Z_1)_{\text{ROT}}$$

So we've already done the VIB case, we just need to know the frequency. Letting $\Theta_V \equiv \frac{\hbar\omega}{k_B}$ be the temperature that we can make out of the frequency, we have

$$C_V = Nk_B \left(\frac{\Theta_V}{T}\right)^2 \frac{e^{\Theta_V/T}}{\left(e^{\Theta_V/T} - 1\right)^2}$$

molecule	Θ_V
H_2	6215 K
N_2	3374 K
O_2	2256 K
Cl_2	808 K
I_2	308 K

Looking at the values of this quantity for various diatomic gases, we see that we definitely need the quantum formula, and can't just use the equipartition high-temperature answer.

e.g. for O_2 at 300K, $C_V^{\text{VIB}} = 0.031 Nk_B$.

$$C_V^{\text{VIB}} \ll Nk_B \text{ for } T \ll \Theta_V$$

$$C_V^{\text{VIB}} \simeq Nk_B \text{ for } T \geq \Theta_V$$

Rotational excitations of diatomic molecules

Next: $(Z_1)_{\mathrm{ROT}}$

$$\hat{H}_{\mathrm{rotation}} = \frac{1}{2I}\hat{L}^2$$

I = moment of inertia, $\hat{L}$ = quantum mechanical angular momentum operator.
$I = \frac{1}{2}M_{\mathrm{atom}}R^2$ for 'homonuclear' diatomic molecules (that is, two of the same kind of atom) like $H_2, Cl_2, O_2...$, where R is the mean separation between the two atoms.

So: energy eigenstates are eigenstates of $\hat{L}^2$. I am told that this has been discussed in 8.04. The result is:

$$\hat{L}^2\psi_{\ell,m} = \hbar^2\ell(\ell+1)\psi_{\ell,m}$$

with $\ell = 0, 1, 2, ...$
and: for each ℓ there are $2\ell+1$ values of m (the eigenvalue of $\hat{L}_z$, $\hat{L}_z\psi_{\ell,m} = m\psi_{\ell,m}$) given by $m = -\ell, -\ell+1.... -1, 0, 1, ...\ell-1, \ell$.

$$\epsilon_\ell = \frac{\hbar^2}{2I}\ell(\ell+1)$$

$$(Z_1)_{\mathrm{rotation}} = \sum_{\ell=0,1,2,...}\sum_{m=-\ell}^{\ell} e^{-\beta\epsilon_\ell}$$

$$= \sum_{\ell=0}^{\infty} \underbrace{(2\ell+1)}_{\text{degeneracy factor}} e^{-\beta\frac{\hbar^2}{2I}\ell(\ell+1)}$$

$$\text{let } \Theta_R \equiv \frac{\hbar^2}{2Ik_B}$$

$$= \sum_{\ell=0}^{\infty}(2\ell+1)e^{-\ell(\ell+1)\frac{\Theta_R}{T}}$$
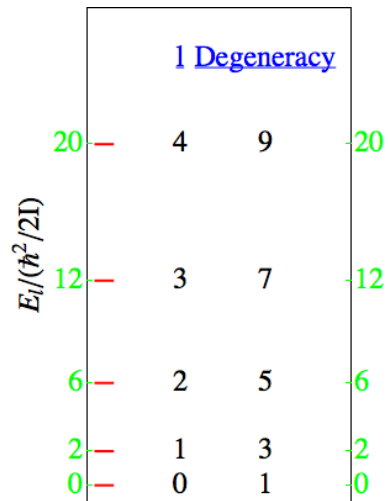
molecule	Θ_R
H_2	85 K
N_2	2.9 K
O_2	2.1 K
Cl_2	0.35 K
I_2	0.05 K

For all of these except H_2, it's a good approximation to take $T \gg \Theta_R$, in which case the classical accounting will work.

1 Degeneracy

$E_{ll}/(\hbar^2/2I)$

20	—	4	9	20
12	—	3	7	12
6	—	2	5	6
2	—	1	3	2
0	—	0	1	0

Let's think about the low temperature limit first, since it's eaiser:

$\boxed{T \ll \Theta_R}$:

$$(Z_1)_{\text{rotation}} \overset{k_B T \ll \Theta_R}{\simeq} 1 + 3e^{-2\Theta_R/T} = 1 + 3e^{-2k_B\Theta_R\beta}$$

$$\langle \epsilon \rangle = -\frac{\partial}{\partial \beta} \ln Z \simeq \frac{1}{Z} 6k_B\Theta_R e^{-2k_B\Theta_R\beta} \simeq 6k_B\Theta_R e^{-2\Theta_R/T}$$

$$C_V^{\text{ROT}} \overset{k_B T \ll \Theta_R}{\simeq} N\frac{\partial \langle \epsilon \rangle}{\partial T} \simeq 6k_B\Theta_R \frac{2\Theta_R}{T^2} e^{-2\Theta_R/T} = 12Nk_B \left(\frac{\Theta_R}{T}\right)^2 e^{-2\Theta_R/T}.$$

Just like 2-state system and SHO, we find exponential 'thermally activated' behavior at low temperature. Actually, this is a hypothetical result, because at $T = 2K$, the gas is frozen.

$\boxed{T \gg \Theta_R}$: At high temperature (more relevant at common earthling temperatures), we can convert the sum to an integral:

$$(Z_1)_{\text{rotation}} \overset{k_B T \gg \Theta_R}{\simeq} \int d\ell (2\ell + 1) e^{-\ell(\ell+1)\Theta_R/T}$$

Let $x \equiv \ell(\ell+1)\Theta_R/T$ so: $dx = d\ell(2\ell + 1)\Theta_R/T$

$$(Z_1)_{\text{rotation}} \simeq \frac{T}{\Theta_R} \int_0^\infty dx\, e^{-x} = \frac{T}{\Theta_R}$$

$\left(= \frac{1}{k_B\Theta_R\beta}. \right)$

$$\langle \epsilon \rangle = -\frac{\partial}{\partial \beta} \ln Z = +\frac{1}{\beta} = k_B T$$

$$C_V^{\text{ROT}} \overset{k_B T \gg \Theta_R}{\simeq} k_B.$$

This is another example of classical equipartition: two angular degrees of freedom (no restoring force, just kinetic energy) of a particle moving on a sphere; its coordinates can be taken to be θ, φ. This means two quadratic variables, which contribute $C_V = 2 \cdot \frac{1}{2}k_B T$.

An evaluation of C_V^{ROT} at arbitrary temperatures gives the picture at right: (this is not so easy! I did the sums numerically by just leaving out $\ell > 500$.) Note that the answer is a bit different from the SHO, since the rotor has a different level spacing. It actually overshoots the equipartition answer – this is a sign that its density of states is larger than the equal-spacing of the SHO.
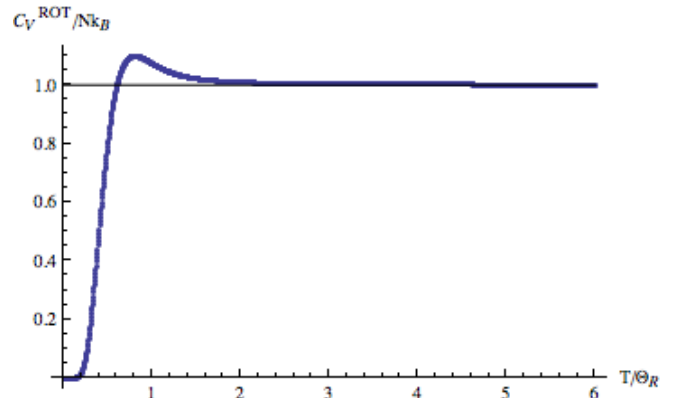
For $T \gg \Theta_R$ and $T \gg \Theta_V$, both rotational and vibrational degrees of freedom are classical and we can use equipartition:

$$C_V = \underbrace{\frac{3}{2}Nk_B}_{\text{translation}} + \underbrace{\frac{2}{2}Nk_B}_{\text{vibration}} + \underbrace{\frac{2}{2}Nk_B}_{\text{rotation}}$$

translation	vibration	rotation
p_x, p_y, p_z	one mode – one x one p	2 angular vars, no restoring force
$H \propto p_x^2 + p_y^2 + p_z^2$	with a restoring force	$H \sim L^2$
no restoring force	$H \sim p^2 + x^2$	ind of angles
3 quadratic vars	2 quadratic vars	2 quadratic vars

Putting it all together:
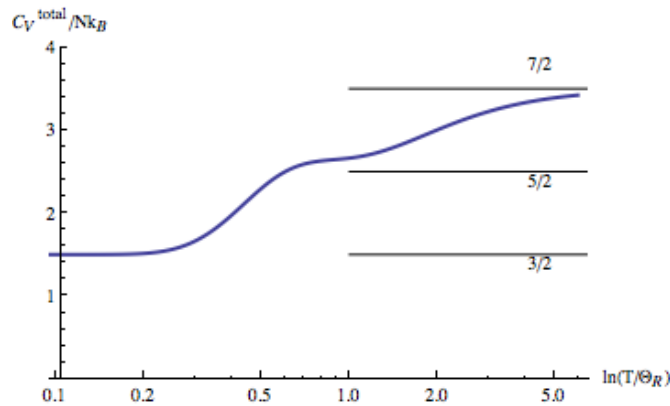
There is more interesting physics in the rotational degrees of freedom. We can ask more detailed questions than just C_V and C_P. See Prof. Greytak's notes on (Raman Spectroscopy of) Diatomic Molecules. They involve a bit more quantum mechanics than I can require of everybody, so this is an optional reading assignment.

6.7   Paramagnetism

Consider a solid made of a collection of atoms in fixed positions. The atoms are distinguishable by their positions.

Assume each atom has total angular momentum quantum number J.

At low temperatures, we can and will ignore vibrations of the positions of the atoms (we'll talk about phonons later).

The simplest nontrivial case is when the atoms have $J = \frac{1}{2}$. This will happen if there is a single electron in the outermost orbital of the atom. In this simple case all the spin and orbital motion of the inner electrons cancel out and can be ignored.

More generally, J could be $\frac{1}{2}, 1, \frac{3}{2}, 2, \frac{5}{2}, ...$, which arises from some combination of spin and orbital angular momentum in a way which is a subject for 8.05 and 8.06.

An atom with angular momentum J has $2J + 1$ degenerate ground states, labelled by

$$m_J \in \{-J, -J+1, ...J-1, J\}$$

$$e.g. \qquad J = \frac{1}{2}: \qquad m_J \in \{-\frac{1}{2}, \frac{1}{2}\}$$

which two states are usually called spin down and spin up respectively.

An atom with $J \neq 0$ can have a nonzero magnetic moment. This means that if we put the atom in a magnetic field $\vec{H} = H\hat{z}$, we split the $2J + 1$ degeneracy – the energy of each state depends on its m_J:

$$\underbrace{\epsilon}_{\text{energy of one atom due to its magnetic moment}} = - \underbrace{\mu}_{\text{the magnetic moment, a constant}} H m_J$$

This fact is called the Zeeman effect.[2]

---

[2](A cultural remark which will not matter for us: when the spin comes from an unpaired electron, the magnetic moment can be written as $\mu = g\mu_B$ where g is the "gyromagnetic ratio", a dimensionless number which is close to $g = 2$ for electrons, and $\mu_B = \frac{3e\hbar}{2m_e}$ is called the "Bohr magneton".)

For $J = 5/2$ the energies as a function of H look like this:
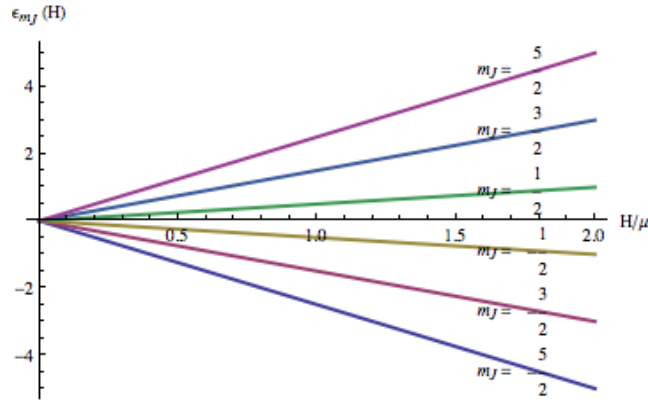
Now consider N atoms with such magnetic moments in thermal equilibrium with a heat bath at temperature T. Assume the moments do not interact with each other – so their energies are affected by an applied field, but not by the m_J of the other atoms.

The fact that they are identical but distinguishable by their locations means that

$$Z = Z_1^N$$

where the partition function for one atom is

$$Z_1 = \sum_{m_J=-J}^{J} e^{-\beta(-\mu H m_J)}$$

$$= \sum_{m_J=-J}^{J} e^{x m_J} \qquad \text{with } x \equiv \beta\mu H = \frac{\text{level spacing}}{k_B T}$$

$$= \sum_{m_J=-J}^{\infty} e^{x m_J} - \sum_{m_J=J+1}^{\infty} e^{x m_J}$$

$$= \frac{e^{-xJ}}{1-e^x} - \frac{e^{x(J+1)}}{1-e^x} = \frac{e^{-x\left(J+\frac{1}{2}\right)} - e^{x\left(J+\frac{1}{2}\right)}}{e^{-x/2} - e^{x/2}}$$

$$Z_1 = \frac{\sinh\left(x\left(J+\frac{1}{2}\right)\right)}{\sinh\left(\frac{x}{2}\right)}$$

A few things to note: Z depends on T and H, not T and M, even though M is the extensive variable.
Z depends only on the ratio H/T.

Something funny is going on with the thermodynamics. You'll come back to this on problem set 9. Note though, that the magnetization curves that you compute from this Z (which are called 'the Brillouin equation' in the caption below) compare favorably to actual data on paramagnets:
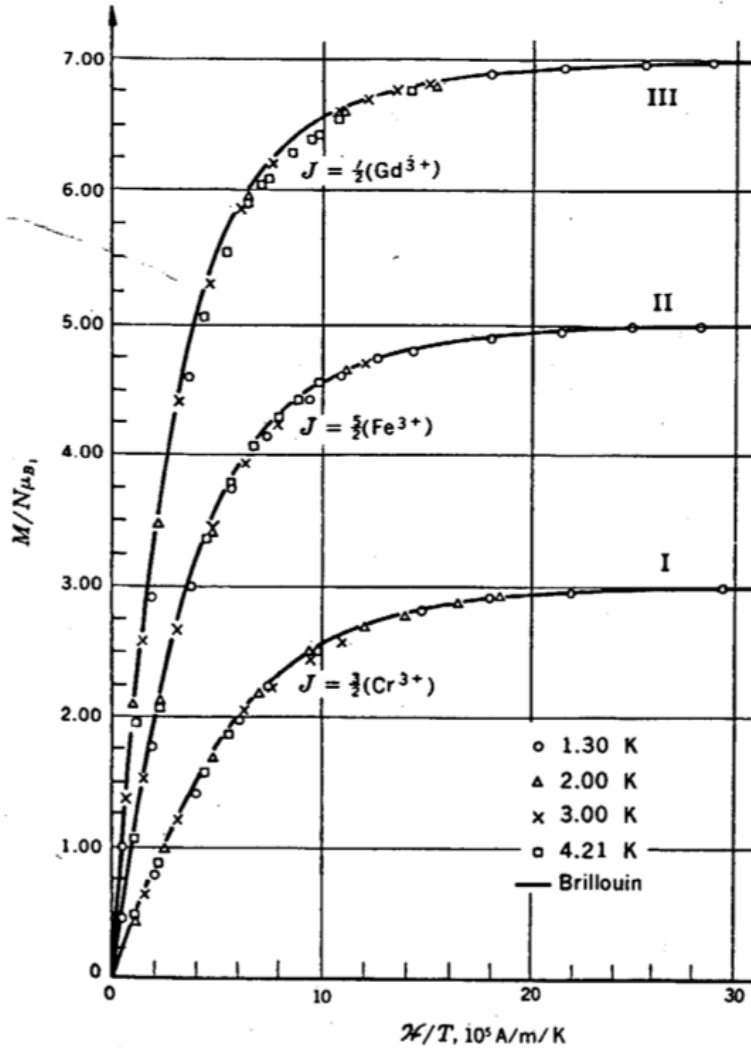

Figure 18-3 The magnetization divided by the number of Bohr magnetons plotted against $\mathcal{H}/T$ for (I) chromium potassium alum ($J = \frac{3}{2}$); (II) iron ammonium alum ($J = \frac{5}{2}$); and (III) gadolinium sulfate ($J = \frac{7}{2}$). (*The points are experimental results of W. E. Henry (1952), and the solid curves are graphs of the Brillouin equation.*)

Microscopic info:

What is the probability that the atom is a state with a given m_J:

$$p(m_J) = \frac{1}{Z_1}e^{-\beta\epsilon m_J} = \frac{1}{Z_1}e^{\beta\mu H m_J} = \frac{e^{xm_J}\sinh\left(\frac{x}{2}\right)}{\sinh\left(x\left(J+\frac{1}{2}\right)\right)}$$
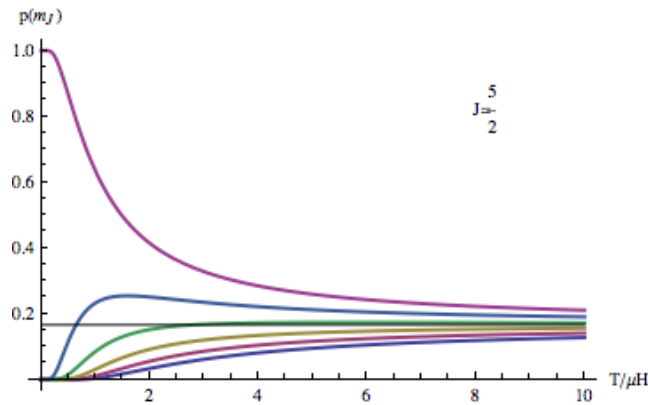
Consider $J = 1/2$, where there are two choices for $m_J = \pm\frac{1}{2}$.
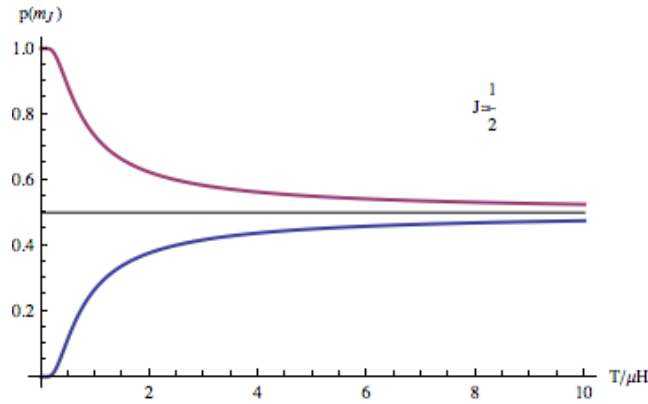
This is the familiar answer for the two-state system. To make this explicit:

$$p\left(-\frac{1}{2}\right) = \frac{e^{-x/2}\sinh\left(x/2\right)}{\sinh x} = \frac{e^{-x/2}\left(e^{x/2} - e^{-x/2}\right)}{e^x - e^{-x}} = \frac{1 - e^{-x}}{e^x - e^{-x}} = \frac{1 - e^{-x}}{\left(1 - e^{-x}\right)\left(1 + e^x\right)} = \frac{1}{1 + e^x}$$

For $J = 5/2$:

The line is at $p = \frac{1}{2J+1}$ in each case, which is the high-temperature limit of each of these curves.

## 6.7.1 Cooling by adiabatic demagnetization

The funny thermodynamics of a paramagnet allows the following great refrigerator.

1920s: temperatures as low as 1K had were routinely achievable by starting with liquid Helium at 4K, and pumping off vapor.

1930s: leap by a factor of 10^{-3} (milliKelvin) as follows.
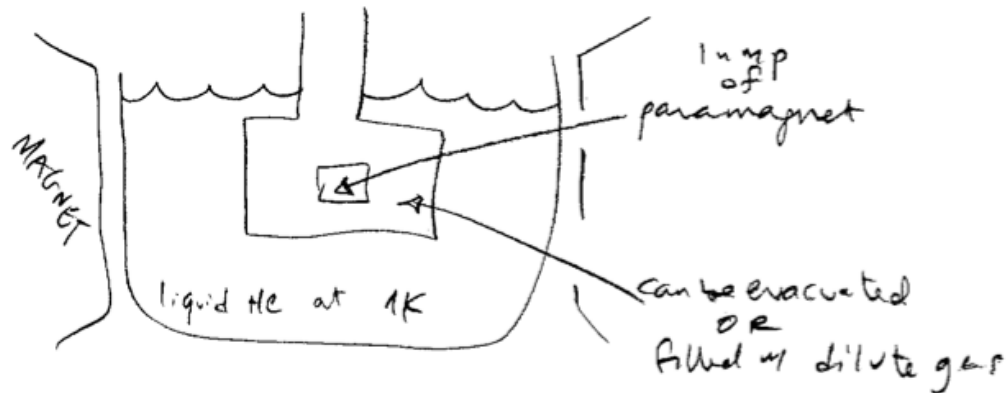
As you'll show on the problem set, the entropy curve as a function of temperature (for two values of H) looks like this:
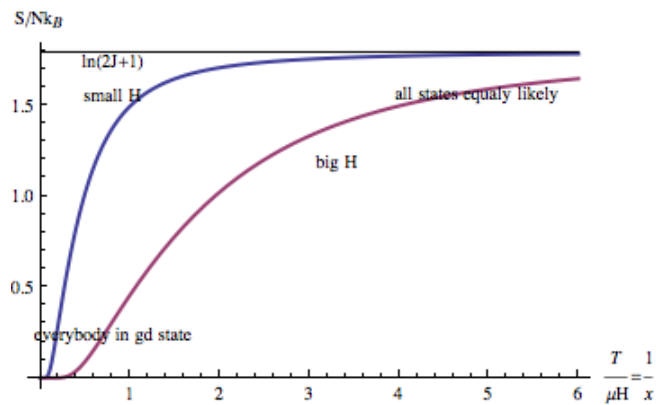
Recall that S depends only on the ratio H/T.

Protocol:

- $\boxed{A \to B}$: Put gas in the chamber and isothermally increase H. (The role of the gas in the chamber is to keep the paramagnet at fixed temperature). Looking at the curve, we see that this drives down the entropy, so heat must leave the paramagnet, through the gas.

- $\boxed{\text{At } B}$: Evacuate chamber: now the physics is adiabatic. That means that if we do things quasistatically, S is fixed.

- $\boxed{B \to C}$: Reduce H, **at fixed** S. Looking at the entropy curve, this means that T drops in a way proportional to H.
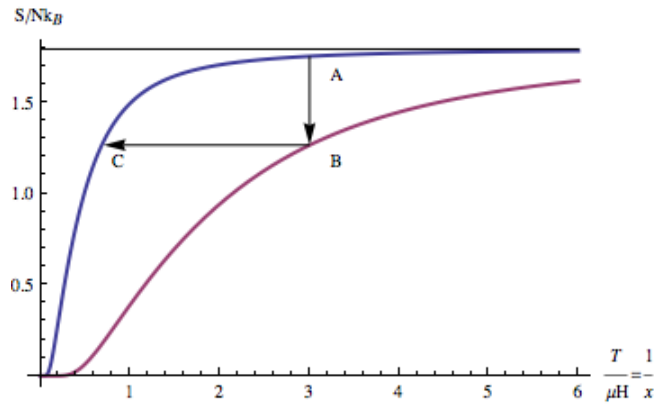

Can be used to get as low as $T \sim 0.002K$ (Cerium Magnesium Nitrate).

If you could turn off the field completely, you could get to $T = 0$. The limit on T_f is set by the following: Even if you turn off the applied field, there's always a small field seen by each spin from its neighbors. (Engineering conclusion: to get good refrigerators, we want material whose spins are far apart, so they don't interact much.)
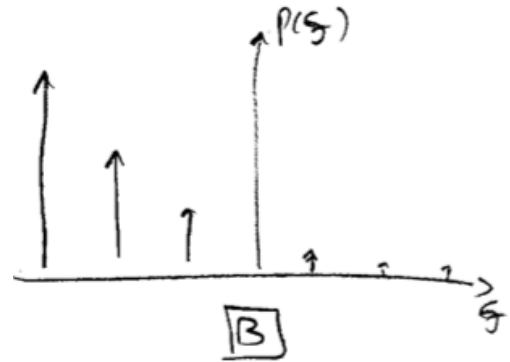
Microscopically:

$\boxed{A}$: H small $\implies$ ϵ_Js close together. [3]
$T = T_i \gg H\mu$ $\implies$ all levels equally likely.
S large.
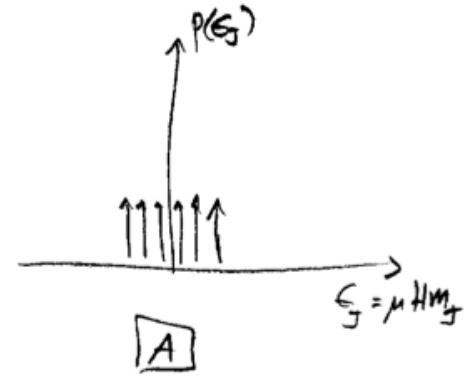
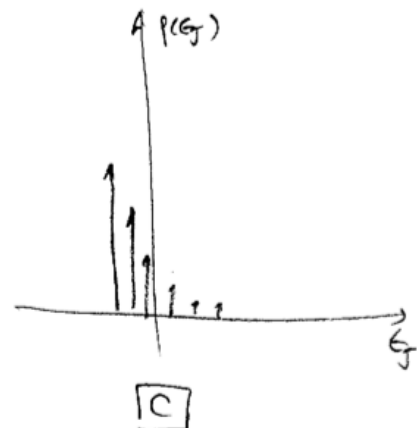$\boxed{A \to B}$: work done, heat leaves, S decreases

$\downarrow$

$\boxed{B}$: H large $\implies$ ϵ_Js far apart
$T = T_i \ll H\mu$ $\implies$ lowest ϵ_J most likely.
S smaller.

$\boxed{B \to C}$: adiabatic, H decreases, no heat loss.

$\downarrow$

$\boxed{C}$: H small $\implies$ ϵ_Js close together.
S as in $\boxed{B}$ $\implies$ lowest ϵ_J still most likely.

---

[3]On this page, I have used ϵ_J as a (not great) shorthand for ϵ_{m_J}.

6.8 The Third Law of Thermodynamics

Three equivalent statements:

- $T = 0$ cannot be achieved by any finite sequence of processes.

- As $T \to 0$, the entropy of a substance approaches a constant value, independent of other thermodynamic variables:
$$\lim_{T \to 0} S = S_0.$$

  This is a consequence of quantum mechanics:

$$S_0 = k_B \ln \left(\text{degeneracy of ground state} \right)$$

  Often: $S_0 = k_B \ln 1 = 0$.

- The entropy change in any isothermal process goes to zero as $T \to 0$.

An illustration of all three statements from the paramagnet: