8.044 Lecture Notes
Chapter 9: Quantum Ideal Gases

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Reading: Baierlein, Chapters 8 and 9.

9.1 Range of validity of classical ideal gas

For a classical ideal gas, we derived the partition function

$$Z = \frac{Z_1^N}{N!}, \qquad Z_1 = \frac{V}{\lambda_{\text{th}}^3} = V\left(\frac{2\pi m k_B T}{h^2}\right)^{3/2} ,$$

where the length scale $\lambda_{\text{th}} \equiv \frac{h}{2\pi m k_B T}$ is determined by the particle mass and the temperature.

When does this break down?

1. If 'idealness' fails, *i.e.* if interactions become important. This is interesting and important but out of bounds for 8.044. We'll still assume non-interacting particles.

2. If 'classicalness' fails. Even with no interactions, at low enough temperatures, or high enough densities, quantum effects modify Z.

An argument that classicalness must fail comes by thinking harder about λ_{th}, the "thermal de Broglie wavelength". Why is it called that? Recall from 8.04 that the de Broglie wavelength for a particle with momentum p is $\lambda_{\text{dB}} = \frac{h}{p}$. For a classical ideal gas, we know the RMS momentum from equipartition

$$\langle\frac{\vec{p}^2}{2m}\rangle = \frac{3}{2}k_B T \implies p_{\text{RMS}} \equiv \sqrt{\langle\vec{p}^2\rangle} = \sqrt{3m k_B T} .$$

We could have defined

$$\tilde{\lambda}_{\text{th}} \equiv \frac{h}{p_{\text{RMS}}} = \frac{h}{\sqrt{3m k_B T}} ;$$

there's no significance to the numerical prefactor of $\frac{1}{\sqrt{2\pi}}$ instead of $\frac{1}{\sqrt{3}}$.

Now recall the significance of λ_{dB} in QM:

$$\lambda_{\text{dB}} = \frac{h}{p} \sim \text{ minimum } \textbf{size} \text{ of a wavepacket with momentum } p .$$

So we can infer that

$\lambda_{\text{th}} \sim$ minimum **size** of quantum wavepackets describing atoms in a quantum ideal gas .

The classical picture of atoms as billiard balls with well-defined trajectories only makes sense if

$$\lambda_{\text{th}} \ll \text{typical spacing between particles} = \left(\frac{V}{N}\right)^{1/3}$$

And this inequality $\lambda_{\text{th}} \sim \frac{1}{\sqrt{T}} \ll \left(\frac{V}{N}\right)^{1/3}$ is violated at low T or high density. The above inequality is the condition for validity of the classical treatment.

System	T	$\left(\frac{V}{N}\right)^{1/3}/\lambda_{\text{th}}$	conclusion
air	300K	180	classical
Liquid ^{4}He	4 K	0.86	not classical
Conduction e^- in Cu	300 K	0.053	not classical

A second derivation of the same criterion, this time in momentum space:

Consider solutions to the Schrödinger equation in an $L \times L \times L$ box. The energy eigenstates of one particle are

$$\phi_{\vec{m}}(\vec{x}) = \sin(k_x x)\sin(k_y y)\sin(k_z z) \qquad \text{with } k_x = \frac{\pi}{L}m_x, \quad \text{and } m_x = 1,2,3...$$
$$\substack{y \\ z} \qquad \substack{y \\ z} \qquad \substack{y \\ z}$$

with energy eigenvalues

$$\epsilon = \frac{\hbar^2}{2m}\left(k_x^2 + k_y^2 + k_z^2\right)$$

Let's ask under what circumstances we can ignore the QM.

The mean energy per particle in a classical ideal gas is $\frac{3}{2}k_B T$. How many 1-particle states with energies like this are there to put our N particles into? The number of states with $\epsilon \leq \frac{3}{2}k_B T$ is

$$N(\epsilon) = \frac{\frac{1}{8}\left(\frac{4}{3}\pi\left(\frac{2m\frac{3}{2}k_B T}{\hbar^2}\right)^{3/2}\right)}{(\pi/L)^3} = \frac{\text{volume of octant of sphere in } \vec{k}\text{-space with radius } \left(\frac{2mE}{\hbar^2}\right)^{1/2}}{\text{volume in } \vec{k}\text{-space per allowed grid point}}$$

$$= V\left(\sqrt{\frac{mk_B T}{h}}\right)^3 \times 4\sqrt{3}\pi = \frac{V}{\lambda_{\text{th}}^3} \times \frac{\sqrt{3\cdot 2}}{\sqrt{\pi}}$$

So: when $N \gg \frac{V}{\lambda_{\text{th}}^3}$, the number of particles is big compared to the number of possible one-particle states for the particles to sit in. So we need to worry about things like the Pauli Exclusion principle, which prevents us from putting more than one particle in each state. For $N \ll \frac{V}{\lambda_{\text{th}}^3}$, the classical analysis is fine – we needn't worry about the particles needing to occupy the same 1-particle state.

9.2 Quantum systems with many indistinguishable particles

[This section is about quantum mechanics. You've already encountered some of these ideas in 8.04, and will discuss this further in 8.05. We'll come back in subsection 9.4 and think about when this business reduces to classical mechanics.]

Consider two particles. Their state can be described by a wavefunction $\psi(x_1, x_2)$. (We won't worry right now about how many coordinates of each particle (*e.g.* how many dimensions) we have to specify.) If the particles are *indistinguishable*, then

$$|\psi(x_1, x_2)|^2 = \text{Prob}\left(\text{finding a particle at } x_1 \text{ and a particle at } x_2\right)$$

Note that we make no specification of which particle is where. Indistinguishability requires:

$$|\psi(x_1, x_2)|^2 = |\psi(x_2, x_1)|^2$$

Swapping the arguments twice should give back the same ψ, not just the same $|\psi|^2$:

$$\psi(x_1, x_2) = \pm\psi(x_2, x_1)$$

Two choices:

Bosons

- particles for which $\psi(x_1, x_2) = +\psi(x_2, x_1)$.

- *i.e.*, the wavefunction is *symmetric*.

- It is a fact (observed experimentally, understood via quantum field theory) that they have integer spin.

- *e.g.*: hydrogen atoms, ^{4}He, photons, phonons, magnons, gluons, Higgs bosons (?).

- The stat mech of a gas of them was developed by Bose and Einstein, so in the context of stat mech, these are called "Bose-Einstein statistics".

Fermions

- particles for which $\psi(x_1, x_2) = -\psi(x_2, x_1)$.

- *i.e.*, the wavefunction is *antisymmetric*.

- It is a fact (observed experimentally, understood via quantum field theory) that they have half-integer spin $(1/2, 3/2...)$

- *e.g.*: electron, proton, neutron, ^{3}He, ^{7}Li.

- The stat mech of a gas of them was developed by Fermi and Dirac, hence "Fermi-Dirac statistics".

For **non-interacting** Bose or Fermi particles (we will always assume this):
energy eigenstates are always (symmetric or antisymmetric) linear combinations of products of single-particle energy eigenstates.

[Recall: there is more to QM than energy eigenstates, but they are enough to construct the partition function.]

Wavefunctions of several bosons or fermions

Consider for example two indistinguishable quantum particles in a box. Label the possible states of *one* quantum particle in the box by a fancy label α which is a shorthand for all its quantum numbers, *e.g.*, the wavenumbers (m_x, m_y, m_z) of its wavefunction.

If they are bosons, the wavefunction must be of the form

$$\Psi(x_1, x_2) = \underbrace{\phi_\alpha(x_1)}_{\substack{\text{an energy eigenstate} \\ \text{of one particle}}} \cdot \underbrace{\phi_\beta(x_2)}_{\substack{\text{another energy eigenstate} \\ \text{for one particle}}} \underbrace{+}_{\substack{\text{makes it symmetric} \\ \text{OK state of bosons}}} \phi_\beta(x_1)\phi_\alpha(x_2).$$

$$\underbrace{}_{\substack{\text{not sym or antisym} \\ \text{hence not allowed}}}$$

For fermions:

$$\Psi(x_1, x_2) = \phi_\alpha(x_1)\phi_\beta(x_2) \underbrace{-}_{\substack{\text{makes it antisymmetric} \\ \text{OK state of fermions}}} \phi_\beta(x_1)\phi_\alpha(x_2).$$

Working our way up to 3 indistinguishable particles:

$$
\begin{aligned}
\Psi(x_1, x_2, x_3) \;=\; & \phi_\alpha(x_1)\phi_\beta(x_2)\phi_\gamma(x_3) \pm \phi_\alpha(x_1)\phi_\gamma(x_2)\phi_\beta(x_3) \\[2mm]
& \phi_\beta(x_1)\phi_\gamma(x_2)\phi_\alpha(x_3) \pm \phi_\beta(x_1)\phi_\alpha(x_2)\phi_\gamma(x_3) \\[2mm]
& \phi_\gamma(x_1)\phi_\alpha(x_2)\phi_\beta(x_3) \pm \phi_\gamma(x_1)\phi_\beta(x_2)\phi_\gamma(x_3)
\end{aligned}
$$

with $+$ for bosons and $-$ for fermions.

This time we count 1, 2, 3, many:

N indistinguishable particles:

1. Pick N single particle states α, β, γ....

2. There is exactly *one* symmetric combination. This is an energy eigenstate for N bosons.

3. **IF** α, β, γ.... are **ALL DIFFERENT** then there is exactly one antisymmetric combination. This is an energy eigenstate for N fermions.

- This fact that "Fermions must all be in different single particle eigenstates" is the Pauli Exclusion Principle.

- Many bosons can be in the same single-particle energy eigenstate.

- If the particles were distinguishable, there would be $N!$ states for each choice of α, β, γ.....

- If the particles are indistinguishable, there is (at most) one such state.

Occupation number representation of the many-particle state

For either bosons or fermions, the state $\Psi(x_1, x_2...x_N)$ is fully specified by indicating

1. Which 1-particle states are occupied?

2. If bosons, how many particles are in each 1-particle state? (For fermions, this number can only be 0 or 1.)

Label the 1-particle states α (*e.g.* m_x, m_y, m_z for ideal gas, or n, ℓ, m for Hydrogen atoms) So: the state Ψ is specified by a set of *integers* called **OCCUPATION NUMBERS**:

$$n_\alpha(\Psi) \equiv \# \text{ of particles in 1-particle state } \alpha$$

when the many-particle state is Ψ.

$$\text{Fermions: } n_\alpha \in \{0, 1\} \qquad \text{Bosons: } n_\alpha \in \{0, 1, 2, 3...\}$$

These numbers also specify $N, E, ...$, as follows.

$$\text{total \# of particles in state } \Psi: \qquad N = \sum_\alpha n_\alpha(\Psi)$$

The sum here is over all possible states in which one of the particles could be; many of them will be unoccupied. This is *not* a sum over particles.

Similarly, if

$$\epsilon_\alpha = \text{ the energy eigenvalue of the 1-particle energy eigenstate } \alpha$$

then the total energy in the many-particle state Ψ is

$$\text{total energy in state } \Psi: \qquad E(\Psi) = \sum_\alpha n_\alpha(\Psi)\epsilon_\alpha$$

9.3 Statistical mechanics of N non-interacting (indistinguishable) bosons or fermions

We'll use the canonical ensemble: an ensemble of copies of the system, all with the same N, T (hence, E varies amongst the copies in the ensemble), in contact with a heat bath at temperature T.

$$\langle E \rangle = \sum_{i \in \text{ensemble}} \underbrace{E_i}_{\substack{\text{total energy} \\ \text{of } N \text{ particles}}} \cdot \underbrace{p(\Psi_i)}_{\substack{\text{prob of finding} \\ \text{the } N\text{-particle state} \\ \Psi_i \text{ in the ensemble}}}$$

$$= \sum_i \left(\sum_\alpha n_\alpha(\Psi_i)\epsilon_\alpha \right) \cdot p(\Psi_i)$$

$$= \sum_\alpha \epsilon_\alpha \cdot \underbrace{\left(\sum_i n_\alpha(\Psi_i)p(\Psi_i) \right)}_{\substack{\equiv \langle n_\alpha \rangle \\ \text{mean value of the occupation number} \\ \text{of the 1-particle state } \alpha \\ \text{in the ensemble of } N\text{-particle states}}}$$

So: if we know $\langle n_\alpha \rangle \equiv \sum_i n_\alpha(\Psi_i)p(\Psi_i)$, then we know

$$\boxed{\langle E \rangle = \sum_\alpha \epsilon_\alpha \langle n_\alpha \rangle} \quad .$$

A check on this formalism:

$$\sum_\alpha \langle n_\alpha \rangle = \sum_\alpha \sum_i n_\alpha(\Psi_i)p(\Psi_i) = \sum_i \underbrace{\left(\sum_\alpha n_\alpha(\Psi_i) \right)}_{=N} p(\Psi_i) = N \sum_i p(\Psi_i) = N$$

So: how do we calculate the average occupation numbers $\langle n_\alpha \rangle$?

$\langle n_\alpha \rangle$ for fermions

$$\langle n_\alpha \rangle = \sum_{\text{all } N\text{-particle states } \Psi_i} n_\alpha(\Psi_i) p(\Psi_i) \qquad \boxed{p(\Psi) = Z(N)^{-1} e^{-\beta E(\Psi)}}$$

$$= \frac{1}{Z(N)} \sum_i n_\alpha(\Psi_i) e^{-\beta E_i}$$

$$= \frac{1}{Z(N)} \underbrace{\sum_{n_1=0}^{1} \sum_{n_2=0}^{1} \sum_{n_3=0}^{1} \ldots}_{\text{subject to the constraint } n_1 + n_2 + \ldots = N} \quad n_\alpha \; e^{-\beta(n_1\epsilon_1 + n_2\epsilon_2 + \ldots)}$$

We just sum over all occupation numbers, consistent with the fact that there are N particles altogether. One of these sums is special, so let's write the two terms $n_\alpha = 0$ and $n_\alpha = 1$ explicitly:

$$\langle n_\alpha \rangle = \underbrace{0}_{n_\alpha=0} + \frac{1}{Z(N)} e^{-\beta\epsilon_\alpha} \underbrace{\sum_{n_1=0}^{1} \sum_{n_2=0}^{1} \sum_{n_3=0}^{1} \ldots}_{\substack{\text{doesn't include } n_\alpha \\ \text{which is 1} \\ \text{so the rest are} \\ \text{subject to the constraint} \\ n_1 + n_2 + \ldots = N - 1}} \underbrace{e^{-\beta(n_1\epsilon_1 + n_2\epsilon_2 + \ldots)}}_{\text{excluding } n_\alpha \epsilon_\alpha}$$

Repackage in a sneaky way which takes advantage of $n_\alpha = 0$ or 1:

$$\langle n_\alpha \rangle = \frac{1}{Z(N)} e^{-\beta\epsilon_\alpha} \underbrace{\sum_{n_1=0}^{1} \sum_{n_2=0}^{1} \sum_{n_3=0}^{1} \ldots}_{\substack{\text{includes } n_\alpha \\ \text{subject to the constraint} \\ n_1 + n_2 + \ldots = N - 1}} (1 - n_\alpha) \underbrace{e^{-\beta(n_1\epsilon_1 + n_2\epsilon_2 + \ldots)}}_{\text{includes } n_\alpha \epsilon_\alpha}$$

Notice that the $n_\alpha = 1$ term in the summation gives zero; this means it doesn't matter if we include it in the Boltzmann factor. The $n_\alpha = 0$ term in the summation gives what we had before.

$$\langle n_\alpha \rangle = \frac{1}{Z(N)} e^{-\beta\epsilon_\alpha} \left(Z(N-1) - \langle n_\alpha \rangle_{\text{for } N-1 \text{ particles}} Z(N-1) \right)$$

$$= \frac{Z(N-1)}{Z(N)} e^{-\beta\epsilon_\alpha} \left(1 - \langle n_\alpha \rangle_{\text{for } N-1 \text{ particles}} \right) \tag{1}$$

The Fermi-Dirac distribution

We want to rewrite our expression for $\langle n_\alpha \rangle_{\text{fermions}}$ as a function of T, μ.

To do this, recall that

$$\mu \equiv F(T, V, N) - F(T, V, N-1) = -k_B T \left(\ln Z(N) - \ln Z(N-1) \right)$$

$$\implies \boxed{\frac{Z(N-1)}{Z(N)} = e^{\mu/k_B T}} \ .$$

Now, in a box with three particles, $\langle n_\alpha \rangle_{N=3} \neq \langle n_\alpha \rangle_{N-1=2}$. But for $N \sim 10^{25}$,

$$\langle n_\alpha \rangle_N \approx \langle n_\alpha \rangle_{N-1} \quad \text{for } N \ggg 1.$$

$$\implies \langle n_\alpha \rangle = e^{\mu/k_B T} e^{-\epsilon_\alpha/k_B T} \cdot (1 - \langle n_\alpha \rangle)$$

solve this for $\langle n_\alpha \rangle$: $\langle n_\alpha \rangle (1 + e^x) = e^x$, with $x \equiv \beta(\mu - \epsilon_\alpha)$:

$$\implies \boxed{\langle n_\alpha \rangle = \frac{e^x}{1 + e^x} = \frac{1}{e^{\beta(\epsilon_\alpha - \mu)} + 1}} \quad \text{for FERMIONS}$$

What's μ? It's determined from the relation between μ and N:

$$N = \sum_\alpha \langle n_\alpha \rangle = \sum_\alpha \frac{1}{e^{\beta(\epsilon_\alpha - \mu)} + 1}$$

Notice: each $\langle n_\alpha \rangle \in [0, 1]$, since $e^{-x} \in [0, \infty]$ for real x. This is the Pauli Principle in action. The extremes are realized in the $T \to \infty, 0$ limits, if we hold μ fixed. More on this below.

$\langle n_\alpha \rangle$ **for Bosons** (the Bose-Einstein distribution)

$$\langle n_\alpha \rangle \;=\; \frac{1}{Z(N)} \underbrace{\sum_{n_1=0}^{\infty} \sum_{n_2=0}^{\infty} \sum_{n_3=0}^{\infty} \cdots}_{\text{with } n_1 + n_2 + \ldots = N} n_\alpha \; e^{-\beta(n_1\epsilon_1 + n_2\epsilon_2 + \ldots)}$$

$$\text{one special sum: } \sum_{n_\alpha=0}^{\infty} n_\alpha e^{-\beta n_\alpha \epsilon_\alpha}$$

No contribution from $n_\alpha = 0$. Tricky step: let $n'_\alpha \equiv n_\alpha - 1$

$$= \;\frac{1}{Z(N)} \underbrace{\sum_{n_1=0}^{\infty} \sum_{n_2=0}^{\infty} \sum_{n_3=0}^{\infty} \cdots}_{\text{with } n_1 + n_2 + \ldots + n'_\alpha + \ldots = N-1} (n'_\alpha + 1)\, e^{-\beta\epsilon_\alpha(1+n'_\alpha) - \beta(n_1\epsilon_1 + \ldots)}$$

$N - 1$ in all states including ϕ_α, at least one particle in ϕ_α.

$$= \;\frac{e^{-\beta\epsilon_\alpha}}{Z(N)} \left(Z(N-1) + \langle n_\alpha \rangle_{\text{for } N-1 \text{ particles}} \cdot Z(N-1) \right)$$

The only difference from fermions is the red plus sign. Making the same steps following equation (1)

$$\implies \boxed{\langle n_\alpha \rangle = \frac{1}{e^{(\epsilon_\alpha - \mu)/k_B T} - 1}} \qquad \text{for BOSONS.}$$

Notice that the minus sign in the denominator is very significant: with this sign, the denominator can become small, and so $\langle n_\alpha \rangle_{\text{BOSONS}}$ can be larger than unity.

Again μ is determined from the relation between μ and N:

$$N = \sum_\alpha \langle n_\alpha \rangle = \sum_\alpha \frac{1}{e^{\beta(\epsilon_\alpha - \mu)} - 1}$$

Summary:

$$\sum_\alpha \langle n_\alpha \rangle \;=\; N$$

$$\sum_\alpha \langle n_\alpha \rangle \epsilon_\alpha \;=\; \langle E \rangle$$

$$\langle n_\alpha \rangle_{\text{FERMIONS}} \;=\; \frac{1}{e^{(\epsilon_\alpha - \mu)/k_B T} + 1} \qquad \text{is between 0 and 1.}$$

$$\langle n_\alpha \rangle_{\text{BOSONS}} \;=\; \frac{1}{e^{(\epsilon_\alpha - \mu)/k_B T} - 1} \qquad \text{is between 0 and } N.$$

9.4 Classical ideal gas limit of quantum ideal gas

The rest of 8.044 will be decoding the physics in the expressions on the previous page (and there is a **lot** of physics in them). First let's check that we can recover our previous classical results in the right limit.

If $e^{(\epsilon_\alpha - \mu)/k_B T} \gg 1$ then

$$\langle n_\alpha \rangle_{\text{fermions}} = \langle n_\alpha \rangle_{\text{bosons}} \approx e^{-(\epsilon_\alpha - \mu)/k_B T} \equiv \langle n_\alpha \rangle_{\text{Boltzmann}} \ll 1$$

This factor gives the occupation numbers for "Boltzmann statistics".

Claim: this is the classical limit. A weak check on this claim is the fact that the B and F distributions reduce to the same expression in this limit. To show: $\langle n_\alpha \rangle_{\text{Boltzmann}}$ are the classical occupation numbers in thermal equilibrium.

[End of Lecture 21.]

1. Classical when $e^{-\mu/k_B T} \gg 1 \implies e^{+\mu/k_B T} \ll 1$. We saw in the previous chapter that a classical ideal gas has

$$-\frac{\mu}{k_B T} = \ln \left(\frac{V}{N} \frac{1}{\lambda_{\text{th}}^3} \right)$$

So

$$e^{-\mu/k_B T} \ll 1 \implies \frac{V}{N} \frac{1}{\lambda_{\text{th}}^3} \gg 1$$

which is our classicality criterion from before (subsection 9.1).

2. Now that we know we're in the right limit, let's examine the Boltzmann occupation number, and show that it's the classical expectation.

$$\langle n_\alpha \rangle_{\text{Boltzmann}} = e^{(\mu - \epsilon_\alpha)/k_B T}$$

Previously we wrote everything in terms of N, so let's do that now:

$$N = \sum_\alpha \langle n_\alpha \rangle = e^{\mu/k_B T} \underbrace{\sum_\alpha e^{-\beta \epsilon_\alpha}}_{=Z_1}$$

$$\implies \boxed{e^{\mu/k_B T} = \frac{N}{Z_1}} \quad \text{for Boltzmann statistics}$$

$$\mu = -k_B T \ln \frac{Z_1}{N}$$

This is the familiar classical ideal gas result, if we can show that Z_1 is indeed the classical ideal gas 1-particle partition function. We also have

$$\langle n_\alpha \rangle_{\text{Boltzmann}} = \frac{N}{Z_1} e^{-\epsilon_\alpha/k_B T}$$

which is a familiar fact from the canonical ensemble. That is, it is equivalent to the happy statement

$$\text{prob}\,(1 \text{ atom is in state } \alpha) = p(\alpha) = \frac{e^{-\beta\epsilon_\alpha}}{Z_1} = \frac{\langle n_\alpha \rangle_{\text{Boltzmann}}}{N}$$

Also, we saw earlier in Chapter 8 that in general, from the definition of chemical potential,

$$Z(N) = e^{-\mu/k_B T} Z(N-1)$$

For the particular case of Boltzmann statistics:

$$
\begin{aligned}
Z(N) &= \frac{Z_1}{N} Z(N-1) \qquad \text{this becomes a recursion relation!} \\
&= \frac{Z_1}{N}\frac{Z_1}{N-1} Z(N-2) = \frac{Z_1}{N}\frac{Z_1}{N-1}\frac{Z_1}{N-2} Z(N-3) = ... \\
Z(N) &= \frac{(Z_1)^N}{N!}
\end{aligned}
$$

We have now derived this result from the classical limit of the quantum result.

Finally, we evaluate Z_1:

$$
\begin{aligned}
Z_1 &= \sum_\alpha e^{-\beta\epsilon_\alpha} \qquad \text{where } \alpha \text{ is a label on single-particle energy eigenstates} \\
&= \sum_{k_x}\sum_{k_y}\sum_{k_z} e^{-\frac{\hbar^2}{2mk_B T}\left(k_x^2 + k_y^2 + k_z^2\right)} \\
&= \left(\sum_{k_x} e^{-\frac{\hbar^2}{2mk_B T}k_x^2}\right)^3 \qquad\qquad \text{with } k_x = m_x \frac{\pi}{L}, \quad m_x = 1,2,3...
\end{aligned}
$$

In the high temperature or low-density limit, the steps in k_x are negligible and we can approximate the sum as an integral.

$$
\begin{aligned}
Z_1 &= \left(\int_0^\infty dk_x \frac{L}{\pi} e^{-\frac{\hbar^2}{2mk_B T}k_x^2}\right)^3 = \left(\int_{-\infty}^\infty dk_x \frac{L}{2\pi} e^{-\frac{\hbar^2}{2mk_B T}k_x^2}\right)^3 \\
&= \left(\frac{L}{2\pi}\left(\frac{2\pi m k_B T}{\hbar^2}\right)^{1/2}\right)^3 = V\left(\frac{2\pi m k_B T}{\hbar^2}\right)^{3/2} \\
&= \frac{V}{\lambda_{\text{th}}^3} \;.
\end{aligned}
$$

Finally, this is the fulfillment of the promise that the factor of $\frac{1}{\hbar^3}$ that we apparently arbitrarily used to normalize our classical phase space integrals would come from QM, *i.e.* it's what we get when we start with the correct QM answer and take the classical limit.

9.5 Ultra-high temperature ($k_B T \gg mc^2$ and $k_B T \gg \mu$) limit

Let's evaluate the average energy $\langle E \rangle$ for an ultrarelativistic gas of fermions or bosons at high temperature, in particular at temperature bigger than any other energy scale: $kT \gg mc^2, kT \gg \mu$.

$$\langle E \rangle = \sum_\alpha \epsilon_\alpha \langle n_\alpha \rangle = \int_0^\infty \frac{\frac{1}{8} 4\pi k^2 dk}{(\pi/L)^3} \epsilon(k) \langle n_k \rangle$$

where [8.033]

$$\epsilon(k) = \sqrt{p^2 c^2 + m^2 c^4} = \sqrt{\hbar^2 c^2 k^2 + m^2 c^4} \approx \hbar c k$$

– this last approximation will be valid in the high-temperature regime –

$$\text{and } \langle n_k \rangle = \frac{1}{e^{(\epsilon(k) - \mu)/k_B T} \pm 1} \qquad \begin{array}{l} + : \text{fermions} \\ - : \text{bosons} \end{array} \quad .$$

So:

$$\frac{\langle E \rangle}{V} = \frac{\hbar c}{2\pi^2} \int_0^\infty \frac{dk\, k^3}{e^{(\hbar c k - \mu)/k_B T} \pm 1}$$

For $k_B T \gg \mu$, we can ignore the contribution from μ. Then we can non-dimensionalize the integral by introducing $x \equiv \frac{\hbar c k}{k_B T}$, in terms of which

$$\frac{\langle E \rangle}{V} = \frac{(k_B T)^4}{2\pi^2 (\hbar c)^3} \underbrace{\int_0^\infty \frac{dx\, x^3}{e^x \pm 1}}$$

$$= \begin{cases} \frac{7\pi^4}{15}, & \text{for fermions} \\ \frac{8\pi^4}{15}, & \text{for bosons} \end{cases}$$

$$\implies \quad \frac{\langle E \rangle}{V} = \frac{\pi^2 (k_B T)^4}{30 (\hbar c)^3} \times \begin{cases} 1, \text{ for bosons} \\ \frac{7}{8}, \text{ for fermions} \end{cases}$$

Observation: the blackbody radiation answer is obtained from this formula with two species of massless bosons with $\mu = 0$.

Reinterpretation: $\langle n \rangle$ for the harmonic oscillator modes of EM field $\equiv$ the occupation number for $\vec{k}$-space modes of these bosons.

- These bosons are called **photons**.

- There are two species because of the two polarizations.

- They are massless because the dispersion relation for EM waves is $\omega = ck$; there is no parameter with dimensions of mass in Maxwell's equations. This a deep fact. A mass term in the energy density of the EM field would look something like $m^2 A_\mu A^\mu$; but this is not invariant under gauge transformations.

- Unlike the number of atoms in a box, the number of photons is not a conserved quantity. This forces the chemical potential to be zero – there's no need for a constraint fixing N, and hence no need for the Lagrange multiplier μ

  Relatedly, $\mu = 0$ says there is no free energy cost to adding one more photon. The fact that they are massless means we can add photons with $\vec{k} = 0$ at zero energy cost, since $\epsilon(k = 0) = 0$. (The fact that they are bosons means we can keep doing this over and over, even if the mode already has nonzero occupation number.)

  As T grows, the total number of photons $= \sum_\alpha \langle n_\alpha \rangle$ also grows. This is distinct from the case of $e.g.$ Helium atoms, where the chemical potential $\mu(T)$ must adjust to keep the number of atoms fixed.

Where can we find an example of a ultra-relativistic gas of fermions? Cosmology.

Generally, heating something up by an extreme amount is a good way to figure out what are its constituents. Conveniently for particle physicists, the whole universe somehow got heated up quite a bit in the past. The early universe is a great source of examples of ultrarelativistic bosons and fermions at high temperature. For example, at $k_B T = 4 \times 10^8 eV = 400 MeV$ ($i.e.$ $T \sim 10^{12} \cdot 5$ K), which was the situation at about 1 microsecond after the Big Bang, an accounting of the energy density begins by thinking about a gas of photons, electrons, positrons, quarks, antiquarks, gluons. If we treat them as ultra-relativistic and non-interacting (not necessarily a good idea), we get:

$$\frac{\langle E \rangle}{V} = \frac{\pi^2}{30} \frac{(k_B T)^4}{(\hbar c)^3} \times \left(\underbrace{(\text{\# of bosons})}_{\underbrace{2}_{\text{photons}} + \underbrace{2 \times 8}_{\text{gluons}}} \times 1 + \underbrace{(\text{\# of fermions})}_{\underbrace{2 \times 2}_{\substack{\text{2 spins of } q \text{ and } \bar{q}}} \times \underbrace{3 \times 3}_{\substack{\text{of 3 colors and 3 flavors}}} + \underbrace{2 \times 2 \times 5}_{\substack{\text{2 spins of } e, \bar{e}, \mu, \bar{\mu} \text{ and } \nu, \bar{\nu} \times 3}}} \times \frac{7}{8} \right)$$

People have recently recreated similar conditions by colliding heavy ions at very high speeds (initially at RHIC on Long Island, NY and more recently at the LHC at CERN). They have created a new state of matter called Quark-Gluon Plasma, which turns out to be a liquid at the temperatures and densities that have been studied so far.

Statistical mechanics flowchart

Identical particles in Volume V, at temp T.

Do they interact with each other? → **YES** → POST-8.044

↓ **No**

Are they localized? → **YES** →

$$Z = Z_1^N, \quad Z_1 = \sum_\alpha e^{-\epsilon_\alpha/k_B T}$$

$$\langle n_\alpha \rangle = \frac{N}{Z_1} e^{-\epsilon_\alpha/k_B T}, \text{ Boltzmann distribution}$$

↓ **No**

IS $V/N \gg \lambda_{th}^3$? → **YES** →

CLASSICAL STATISTICS:
$$Z = Z_1^N/N!$$
Z_1, $\langle n_\alpha \rangle$ as above

Ch. 4 & 6

↓ **NO**

FERMIONS? → **YES** →

$$\langle n_\alpha \rangle = \frac{1}{e^{\beta(\epsilon_\alpha - \mu)} + 1} \equiv f_{FD}(\epsilon_\alpha)$$

(Fermi-Dirac statistics)

$$\langle G \rangle = \int d\epsilon \, f_{FD}(\epsilon) \, D(\epsilon) \, G(\epsilon)$$

§9.6, next

↓ **No**

BOSONS!

↓

Is the number fixed? → **YES** →

$$\langle n_\alpha \rangle = \frac{1}{e^{\beta(\epsilon_\alpha - \mu)} - 1} \equiv f_{BE}(\epsilon_\alpha)$$

(Bose-Einstein statistics)

$$\langle G \rangle = \int d\epsilon \, f_{BE}(\epsilon) \, D(\epsilon) \, G(\epsilon)$$

§9.7

↓ **No**

$$\langle n_\alpha \rangle = \frac{1}{e^{\beta\epsilon_\alpha} - 1}$$

(Planck distribution)

← Phonons + photons Ch. 7

9.6 Fermions at low temperatures

So far we've discussed high temperatures. Low temperatures is where quantum statistics –
the differences between boson, fermions, and 'Boltzmons' – are most dramatic.

  For fermions in thermal equilibrium, the occupation number of the single-particle state α
is

$$\langle n_\alpha \rangle = \frac{1}{e^{(\epsilon_\alpha - \mu)/k_B T} + 1}.$$

The only property of the single-particle state that enters is its energy, so we may relabel this
(as is conventional) as

$$f(\epsilon) \equiv \frac{1}{e^{(\epsilon - \mu)/k_B T} + 1}, \quad \text{the Fermi distribution function.}$$

This one function contains the physics of metals, semiconductors, white dwarves, neutron
stars...

  Consider first the extreme $T \to 0$ limit of this function.
It looks like this: $\longrightarrow \longrightarrow \longrightarrow \longrightarrow \longrightarrow$
A useful fact: $f(\epsilon = \mu) = \frac{1}{2}$ at any temperature.

f(ε) at T=0

f(ε=μ)=1/2

f(ε<μ)=1   f(ε>μ)=0

  How do we understand this answer for the distribution
of occupied states at $T = 0$? At $T = 0$ the system is in
its groundstate. The groundstate of N free fermions is
constructed by filling the N lowest-energy single-particle
states. The highest energy level that's filled is called ϵ_F,
the Fermi energy. (Note that this is a single-particle en-
ergy level, not an energy of all N particles.) The answer
we've found for f says that, at $T = 0$, all states below the
chemical potential are filled ($f = 1$) and all states above the chemical potential are empty
($f = 0$). So:

$$\boxed{\epsilon_F = \mu(T = 0)}.$$
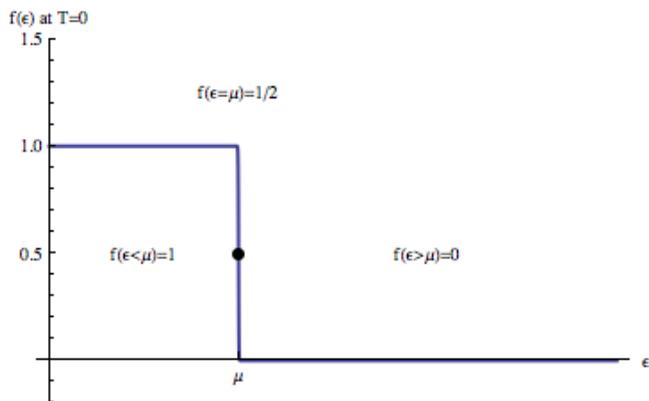
Note that μ will be T-dependent.

  The value of ϵ_F is determined by N:

$$
\begin{aligned}
N = \sum_\alpha \langle n_\alpha \rangle \;&=\; \int_0^\infty d\epsilon\, D(\epsilon) f(\epsilon) && \text{at any } T \\
&=\; \int_0^{\epsilon_F = \mu(T=0)} d\epsilon\, D(\epsilon) && \text{at } T = 0
\end{aligned}
$$

$D(\epsilon)$
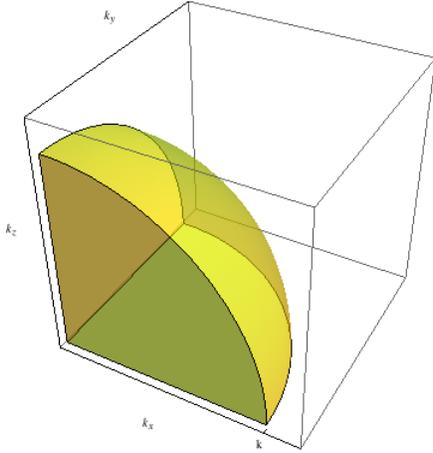
$D(\epsilon)$ is the same kind of object that we considered earlier in the context of blackbody radiation. The counting of momentum states is the same as in Chapter 7:

$$N(k) = \text{\# of states with } |\vec{k}| < k = \underbrace{2}_{\text{spin-}\frac{1}{2} \text{ fermions}} \frac{\frac{1}{8}\frac{4}{3}\pi k^3}{(\pi/L)^3} \ .$$

For spin-$\frac{1}{2}$ fermions, there are two spin states ('up' and 'down') for each wavenumber.

The only difference is that now we will consider *non-relativistic* fermions, which have a dispersion relation

$$\epsilon = \frac{\vec{p}^2}{2m} = \frac{\hbar^2}{2m}\vec{k}^2.$$

So

$$N(\epsilon) = \frac{V}{3\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\epsilon^{3/2}$$

$$D(\epsilon) = \frac{d}{d\epsilon}N(\epsilon) = V\underbrace{\frac{1}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}}_{\equiv a}\epsilon^{1/2}$$

$$N = N(\epsilon_F) = \int_0^{\epsilon_F} D(\epsilon)d\epsilon = \frac{2}{3}aV\epsilon_F^{3/2} = \frac{2}{3}aV\mu_0^{3/2} \tag{2}$$

(here I wrote $\mu_0 \equiv \mu(T=0)$ for aesthetic reasons).

This gives the relationship between N and $\mu(T=0)$:

$$\boxed{\mu(T=0) = \epsilon_F = \left(\frac{N}{V}\frac{3}{2a}\right)^{2/3}.}$$

The following formula will be useful below:

$$D(\epsilon_F) = \frac{3}{2}\frac{N}{\epsilon_F}. \tag{3}$$

Another useful quantity to define is the *Fermi momentum* (or Fermi wavenumber)

$$k_F \equiv \sqrt{2m\epsilon_F}/\hbar^2$$

in terms of which

$$N = 2\frac{\frac{1}{8}\frac{4}{3}\pi k_F^3}{(\pi/L)^3}$$

and so

$$k_F = \left(3\pi^2\frac{N}{V}\right)^{1/3}.$$

At $T = 0$, all states with $k < k_F$ (and hence $\epsilon < \epsilon_F$) are filled. All states with $k > k_F$ (and hence $\epsilon > \epsilon_F$) are empty. The locus $\{\vec{k}$ such that $|\vec{k}| = k_F\}$ is called the *Fermi surface*. The stuff inside is called the *Fermi sea*.

Now: what's the total energy E of the N fermions in thermal equilibrium?

$$E = \sum_\alpha \epsilon_\alpha \langle n_\alpha \rangle \quad \overset{\text{any } T}{=} \quad \int_0^\infty d\epsilon \quad \underbrace{\epsilon}_{\text{what are we averaging}} \quad \cdot \quad \underbrace{D(\epsilon)}_{\text{how many states have this energy?}} \quad \cdot \quad \underbrace{f(\epsilon)}_{\text{how many are occupied?}}$$

$$\overset{\text{at } T = 0}{=} \quad \int_0^{\epsilon_F} d\epsilon\, \epsilon D(\epsilon) = \int_0^{\epsilon_F} d\epsilon\, \epsilon V a \epsilon^{1/2}$$

$$\implies \quad E = \frac{2}{5}aV\epsilon_F^{5/2}.$$

Using the expression (2) to eliminate a :

$$\boxed{E = \frac{3}{5}N\epsilon_F \propto N\left(\frac{N}{V}\right)^{2/3}}$$

Notice how completely different this is from a classical ideal gas. In particular, the internal energy depends on the volume. This is because the wavefunctions of the fermions are spread over the container, so they care how big it is.

Electrons in a metal

How big is ϵ_F for the conduction electrons in Copper?

$$\frac{N}{V} = \frac{1 \ e^- \ \text{per Cu atom}}{1 \ \text{Cu atom per unit cell of crystal}} = 10^{22} \cdot 8.45 \frac{e^-}{cm^3}$$

$$\implies k_F = \left(3\pi^2 \frac{N}{V}\right)^{1/3} = 10^8 \cdot 1.36 cm^{-1}$$

$$\implies \epsilon_F = \frac{\hbar^2 k_F^2}{2m_e} \approx 7eV.$$

If we define the *Fermi velocity* v_F by

$$\epsilon_F = \frac{1}{2}mv_F^2 \qquad \implies v_F = 10^8 \frac{cm}{s} \approx \frac{c}{200}$$

which is much bigger than the few hundred meters per second of classical ideal gas at T_{ROOM} (though they are still reliably non-relativistic). Even though $T = 0$ here, some of the electrons have lots of kinetic energy. This shows in dramatic fashion that in general you cannot think of temperature as "average kinetic energy" like you can for a *classical* ideal gas.

We can also define a *Fermi temperature* by $k_F T_F = \epsilon_F$, which comes out to $T_F \approx 80,000K$. What's this? It's the temperature that the conduction electrons consider *high*. Notice that it's bigger than the melting temperature of the solid; actually, it's even bigger than the temperature at which the solid vaporizes. So it's very high. This means that it's a good idea to treat the conduction electrons in a metal as if they are at low temperature for most purposes.

Nonzero (but low) temperature
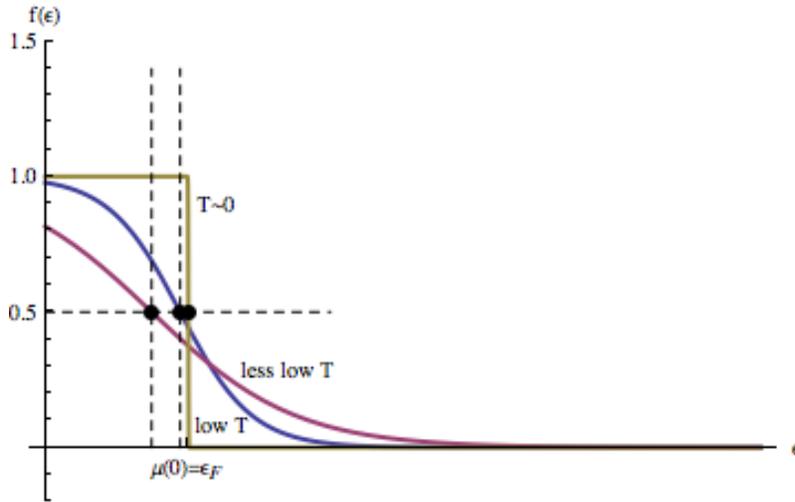
Shown here is the Fermi-Dirac distribution

$$f(\epsilon) = \frac{1}{e^{(\epsilon - \mu(T))/k_B T} + 1}$$

for three values of T, *at the same N* [1]. Recall that $f(\epsilon = \mu(T)) = \frac{1}{2}$ for any T; the three black dots show the values of $\epsilon = \mu(T)$ where this occurs at each T. μ is a decreasing function of T. Why is that?

At T increases, we fill some states above μ_0 and empty some states below μ_0.
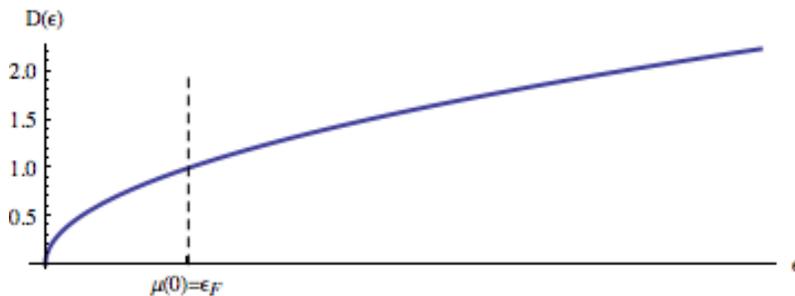
But since $D(\epsilon)$ is an increasing function of ϵ, μ must decrease in order to keep N fixed.[2]

---

[1]The values of T are $T = 0, \mu_0/4$ and $\mu_0/2$ – if I showed lower temperatures you wouldn't be able to see $\mu(T)$ changing.

[2]Cultural remark: The actual dependence of μ on T is not so easy to extract

$$N = aVT^{3/2} \int_0^\infty \frac{\sqrt{x}dx}{e^{x - \mu(T)/kT} + 1} = aVT^{3/2} \left(-\frac{\sqrt{\pi}}{2} Li_{3/2}\left(-e^{\mu(T)/kT}\right)\right)$$

– it involves the inverse of a PolyLog, which is not an elementary function.

Semi-quantitative account of specific heat

The actual calculation of the energy and specific heat involves some horrible integrals which you can do in your spare time or when you take a more advanced stat mech course. For $0 < T \ll T_F$ (*e.g.* electrons in a metal at room temp), we can approximate $f(\epsilon)$ as a ramp:
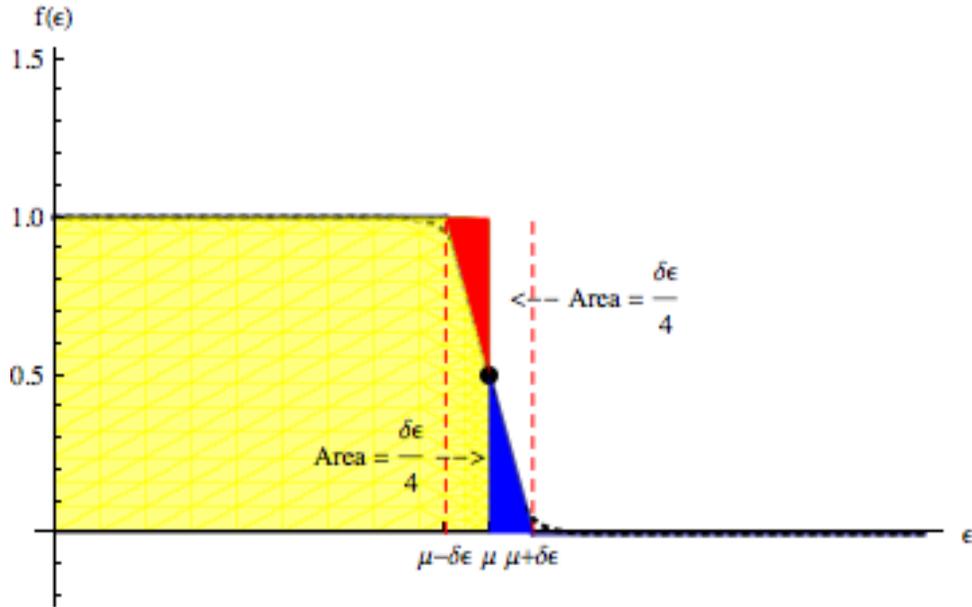
interpolating linearly between 1 and 0 at $\epsilon = \mu$ over a range $\delta\epsilon$ which depends (linearly) on T ($\delta\epsilon = 3k_B T$ is a good numerical value). In this plot is also the actual F-D distribution (dotted curve), with $T = \delta\epsilon/3k_B$, but you can barely see it – this is not such a bad approximation. The number of fermions is then:

$$N \approx \underbrace{\int_0^{\mu(T)} D(\epsilon)d\epsilon}_{\text{yellow rectangle}} - \underbrace{D(\epsilon - \tfrac{1}{2}\delta\epsilon)\tfrac{1}{4}\delta\epsilon}_{\text{red triangle}} + \underbrace{D(\epsilon + \tfrac{1}{2}\delta\epsilon)\tfrac{1}{4}\delta\epsilon}_{\text{blue triangle}}$$

We know from $T = 0$ that

$$N = \int_0^{\epsilon_F} D(\epsilon)d\epsilon \qquad \epsilon_F = \mu_0$$

Subtracting the previous two expressions gives

$$0 \approx (\mu - \epsilon_F)D(\epsilon_F) + \frac{1}{4}(\delta\epsilon)^2 D'(\epsilon_F)$$

$$\implies \mu \approx \epsilon_F - \frac{1}{4}\frac{D'(\epsilon_F)}{D(\epsilon_F)}(\delta\epsilon)^2$$

On the other hand

$$D(\epsilon) \propto \epsilon^{1/2} \implies \frac{D'(\epsilon_F)}{D(\epsilon_F)} = \frac{1}{2\epsilon_F}$$

If we take $\delta\epsilon \approx 3k_BT$, the result is

$$\mu(T) \approx \epsilon_F - \frac{9}{8}\frac{(k_BT)^2}{\epsilon_F}$$

The actual correct answer [8.08] is

$$\mu(T) = \epsilon_F - \frac{\pi^2}{12}\frac{(k_BT)^2}{\epsilon_F} + \dots = \epsilon_F\left(1 - \frac{\pi^2}{12}\left(\frac{T}{T_F}\right)^2 + \mathcal{O}\left(\frac{T}{T_F}\right)^4\right)$$

This is a small shift, especially given that for Cu at room temp $\frac{T}{T_F} = \frac{k_BT_{\text{ROOM}}}{\epsilon_F} = \frac{293}{81,000}$.

3

[End of Lecture 22.]

---

[3]Why is the deviation of the chemical potential from μ_0 quadratic in the temperature? (Thanks to Mustafa Amin for asking for some physical explanation of this.) One answer to this question is the following: The statement that $\mu(T \sim 0) \sim \mu_0 - aT^2$ says that $\left(\frac{\partial\mu}{\partial T}\right)_{N,V}|_{T=0} = 0$. But this quantity participates in a Maxwell relation

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

(which comes from demanding that F is a state variable, $dF = -SdT + \mu dN$). The quantity on the RHS vanishes at $T = 0$ for a simple reason: the groundstate of free fermions is unique for any N. Hence $S(T = 0, N) = 0$ is independent of N.

Energy, in this 'ramp' approximation

$$E \approx E(T=0) - \underbrace{(\epsilon_F - \mu)D(\epsilon_F)\epsilon_F}_{\substack{\text{change because } f(\epsilon) = 1/2 \\ \text{is at } \epsilon = \mu < \epsilon_F}} + \underbrace{\frac{1}{4}(\delta\epsilon)^2 D(\epsilon_F)}_{\substack{\text{change because we shift} \\ \frac{1}{4}\delta\epsilon D(\epsilon_F) \text{ particles} \\ \text{upwards in } E \text{ by } \delta\epsilon}}$$

$$
\begin{aligned}
\implies E &\simeq E(T=0) - \frac{1}{8}\frac{(\delta\epsilon)^2}{\epsilon_F}D(\epsilon_F)\epsilon_F + \frac{1}{4}\frac{(\delta\epsilon)^2}{\epsilon_F}D(\epsilon_F)\epsilon_F \\
&= E(T=0) + \frac{1}{8}\frac{(\delta\epsilon)^2}{\epsilon_F}D(\epsilon_F)\epsilon_F \\
&= E(T=0) + \frac{9}{8}(k_B T)^2 D(\epsilon_F) .
\end{aligned}
$$

The useful rough summary of this formula is

$$E \approx E(T=0) + (\text{number of fermions shifted}) \cdot (\text{by how much their energy shifts}) .$$

The reason the change in energy goes like $(\delta\epsilon)^2 \sim T^2$ is that the amount of particles that change energy is of order $\delta\epsilon$, and the amount by which each one changes energy is of order $\delta\epsilon$.

The actual answer from the exact $f(\epsilon)$ is:

$$
\begin{aligned}
E &= E(T=0) + \frac{\pi^2}{6}(k_B T)^2 D(\epsilon_F) + \mathcal{O}\left(T^4\right) \\
&= E(T=0) + \frac{\pi^2}{4}N\frac{(k_B T)^2}{\epsilon_F} + \mathcal{O}\left(T^4\right)
\end{aligned}
$$

(we used (3) in the second step) which gives

$$C_V = \frac{\pi^2}{2}N k_B \frac{k_B T}{\epsilon_F} = \frac{\pi^2}{2}N k_B \frac{T}{T_F} \ll N k_B$$
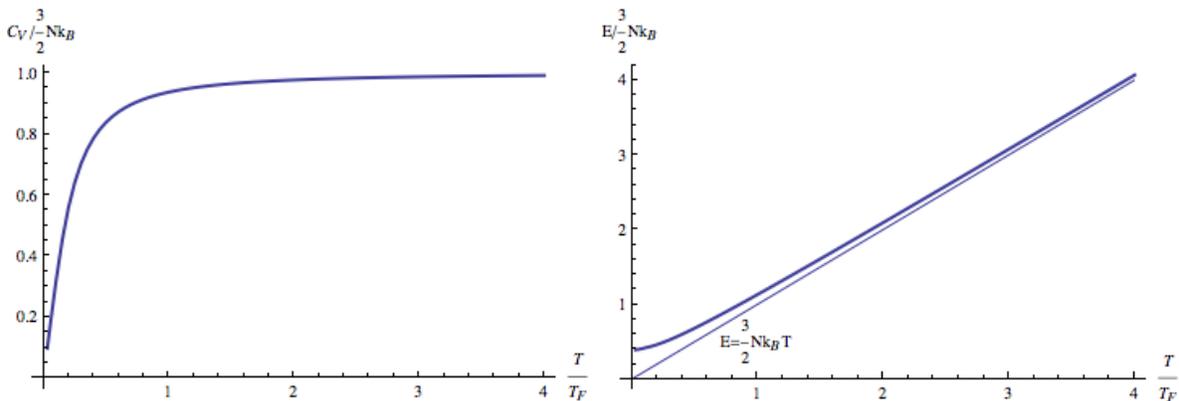
For conduction electrons in a metal, we can't actually reach $T = T_F$ because the metal melts (even vaporizes) first.

Basic theory of metal

We've calculated here the contribution from the conduction electrons to the heat capacity of a metal. Previously in §7.3 we calculated the contribution from phonons – soundwaves made from vibrations of the ions in the crystal. Putting these together (adding them requires that we ignore interactions between the electrons and the phonons, which is a very good first approximation) gives: for a metal with $T < \Theta_D$ and $T \ll T_F$

$$\frac{C_V}{Nk_B} = \underbrace{\frac{\pi^2}{2}\left(\frac{T}{T_F}\right)}_{\substack{\text{fermion contribution} \\ \text{(conduction electrons)}}} + \underbrace{\frac{12\pi^4}{5}\left(\frac{T}{\Theta_D}\right)^3}_{\substack{\text{boson contribution} \\ \text{(phonons)}}}$$

For $T \gg \Theta_D$, the phonon contribution approaches the equipartition value, $3Nk_B$.

$$\frac{C_V}{Nk_B} = \gamma T + AT^3 \quad \Longrightarrow \quad \frac{C_V}{Nk_B T} = \gamma + AT^2$$

should be linear with an intercept $\propto 1/T_F$ (telling us the density of conduction electrons) and a slope $\propto \Theta_D^{-3}$ (telling us about the rigidity of the crystal):

Figure 9.4 The heat capacity of copper at low temperature. The literal temperature range is $1.1 \le T \le 4.2$ K. The upper limit is approximately 1 percent of the Debye temperature: $\theta_D = 343$ K. Experimentally, the intercept as $T^2 \to 0$ is 8.27×10^{-5} K^{-1}, accurate to within 1 percent. Equation (9.20) and table 9.1 predict an intercept of $\pi^2/(2T_F) = 6.05 \times 10^{-5}$ K^{-1}. [Source: William S. Corak et al., Phys. Rev. **98**, 1699–707 (1955).]

Bookmarks for a better theory of solids

This is a pretty good accounting of the basic excitations of a metal. Full disclosure: there's more to metals than this. The two main important things we've ignored (which one learns more about in a class on the Theory of Solids (aka Condensed Matter Physics)) are

- crystal lattice – the detailed structure of the crystal, ignored by the Debye model.

  - changes the value of Θ_D
  - changes the **shape** of the Fermi surface. not round.
  - changes the value of T_F

- interactions between electrons

  - often, these effects can be accommodated by a simple "renormalization" of coupling parameters (m_e, Θ_D, T_F). The fermion excitation is an electron plus its cloud of influence on its companions that it must drag along with itself. This changes, *e.g.*, its effective mass.
  - the result is called Landau Fermi Liquid Theory.
  - sometimes this fails: "non-Fermi liquid". This is an open problem.

Fermi (degeneracy) pressure and white dwarf stars

A rather spectacular consequence of our previous analysis is that a Fermi gas has a nonzero pressure, even at $T = 0$.

$$E = \frac{3}{5} N \left(\frac{N}{V} \frac{3}{2a} \right)^{2/3} \qquad a = \frac{1}{2\pi^2} \left(\frac{2m}{\hbar^2} \right)^{3/2}$$

(In terms of the Fermi energy, this is $E = \frac{3}{5} N \epsilon_F$. It would be $1 \cdot N \epsilon_F$ if all states were at the Fermi energy.)

$$dE = \underbrace{T}_{=0} dS - P dV \implies P(T = 0) = -\frac{dE}{dV} = +\frac{2}{3} \frac{E}{V} .$$

This is totally because of Pauli exclusion: if you squeeze the box, it reduces the volume, and the energy of the lowest N states goes up.

This is an important component in the compressibility of a metal. There Coulomb repulsion – *i.e.* interactions – between the electrons also plays a role.

An example where Fermi pressure is dominant is in white dwarf stars. Why doesn't a star collapse under its own weight? Because some internal pressure balances gravity. In an ordinary star, this comes from the pressure of some hot gas, kept hot by some nuclear fusion reactions. What happens when the nuclear fuel runs out?

When the fuel (He) runs out, the star collapses, until it's (maybe, if it's not too heavy, as we'll see) supported by the degeneracy pressure of the electrons. This is a white dwarf.

Model:

1. What's left when the nuclear fuel of not-too-big stars like our sun (H, He) runs out is carbon and oxygen. (Only very heavy stars can burn these in nuclear reactions.) Let's ignore the oxygen, and suppose for simplicity that what's left is ^{13}C, which is a fermion.[4] There are 6 e^- for each ^{13}C, so that the net electric charge is zero.

2. We will suppose the star is a uniform-density ball. To get exactly correct answers, one must include a density profile which depends on the distance from the center. We are going to make an *estimate*; we'll get the right dependence on the radius, but the numerical prefactors will be wrong. Solving the correct equations (a differential equation for the density profile) is not too hard with a computer.

---

[4]This is not exactly right – ^{12}C is more stable – but it's not wrong in an important way for our purposes.

A white dwarf glows white because its temperature is something like $T \sim 10000K$. But from the point of view of the electrons, this is *cold*! This temperature is much less than T_F – the thing is very dense.

The total kinetic energy of all the particles in the star is

$$\text{KE} \quad \simeq \quad \frac{3}{5} N_e \underbrace{\epsilon_F}_{\epsilon_F \text{ of electrons}} + \frac{3}{5} N_C \underbrace{\epsilon_F^C}_{\epsilon_F \text{ of Carbon} \ll \epsilon_F \, :\propto \frac{1}{m_C}}$$

Kinetic energy of electrons dominates over that of carbon.

$$= \quad \frac{3}{5} N_e \frac{\hbar^2}{2m_e} \left(3\pi^2 \frac{N_e}{V} \right)^{2/3}$$

$$= \quad \frac{3}{5} N_e \frac{\hbar^2}{2m_e} \left(\frac{9\pi}{4} \frac{N_e}{R^3} \right)^{2/3}$$

The mass of the star is $M = N_C m_C = \frac{N_e}{6} m_C$ where m_C = mass of Carbon nucleus, so $N_e = 6M/m_C$.

$$\text{KE} \approx M^{5/3} \cdot \frac{1}{R^2} \cdot c_1 \qquad c_1 = \frac{3\hbar^2}{10m_e} \left(\frac{6}{m_c} \right)^{5/3} \left(\frac{9\pi}{4} \right)^{2/3}$$

Reducing R increases the energy: voila, Fermi pressure.

Gravity
Without gravity, the star would explode.

$$\text{Gravitational potential energy} = - \underbrace{\frac{3}{5}}_{\text{uniform density sphere}} G_N \frac{M^2}{R}.$$

$$E_{\text{total}} = c_1 \frac{M^{5/3}}{R^2} - \frac{3}{5} G_N \frac{M^2}{R} \ .$$
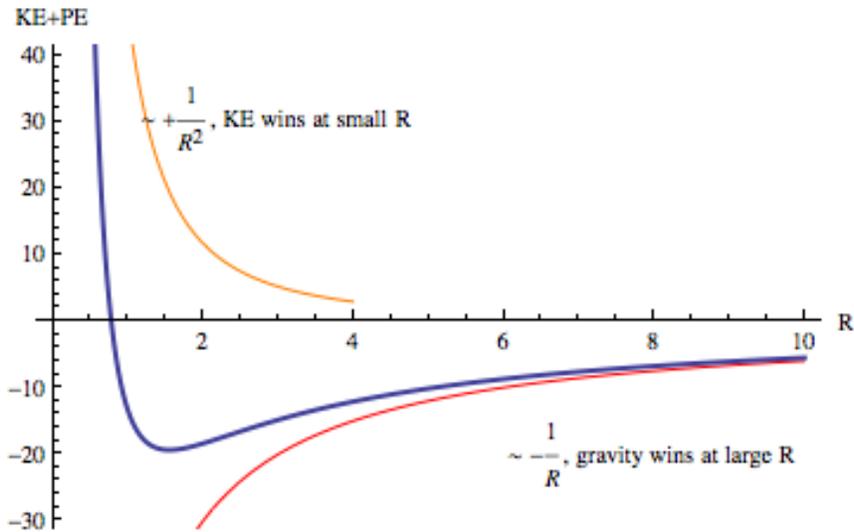
The minimum of the potential – the preferred radius of the white dwarf star – occurs when

$$0 = \frac{\partial}{\partial R}E_{\text{total}}|_{R=R_\star} \implies M_\star R_\star^3 = \left(\frac{10c_1}{3G_N}\right)^3 = 2 \cdot 3^9 \cdot \pi^2 \frac{\hbar^6}{G_N^3 m_e^3 m_C^5}$$

that is, when $R_\star \propto \frac{1}{M_\star^{1/3}}$. Heavier ones are *smaller* – this is different from most stuff in our common experience. You can see from the plot of $E_{\text{total}}(R)$ that this is a stable minimum.

Numerically[5] :

$$\left(\frac{M}{M_{\text{sun}}}\right)\left(\frac{R}{7260km}\right)^3 = 1$$

Observations:
Sirius B: $M = 1.05 M_{\text{sun}}, R = 5100km$ (the above result predicts 11000km).
40 Eri B: $M = 0.447 M_{\text{sun}}, R = 9000km$ (the above result predicts 14000km).

This is pretty good! Why isn't it perfect? Also: what happens if we keep adding mass? The formula predicts that the thing gets smaller and smaller. Clearly that cannot go on forever (at some point we'd have to include nuclear physics and general relativity and quantum gravity...).

---

[5]The more correct calculation which includes a nontrivial density profile gives

$$\left(\frac{M}{M_{\text{sun}}}\right)\left(\frac{R}{11,000km}\right)^3 = 1 \ .$$

Let's compute the kinetic energy of these electrons.

$$\epsilon_F = \left(\underbrace{\frac{N_e}{V}}_{\frac{6M/m_C}{\frac{4}{3}\pi R^3}} \right)^{2/3} \left(\frac{3}{2} 2\pi^2 \right)^{2/3} \frac{\hbar^2}{2m_e} \simeq 0.1 m_e c^2.$$

The density is

$$\frac{N_e}{V} = \frac{6M/m_C}{\frac{4}{3}\pi R^3} = 10^{29} \cdot 3.7 cm^{-3} \text{ for } M = M_{\text{sun}}, R = 10^3 km$$

(ridiculously huge!). So $v_F/c \simeq \sqrt{0.2} = 0.44$ in our model. The actual (smaller) radius makes it even closer to the speed of light.

So: $\epsilon_F \approx 0.1 m_e c^2$ is a large fraction of the rest energy of an electron – we should be very nervous about using the non-relativistic dispersion relation $\epsilon = \hbar^2 k^2/2m$. On Pset 11 you'll have the chance to "bracket the truth from the other side" and consider the other extreme – the ultra-relativistic case, where $\epsilon = \hbar c k$; this is valid for $\epsilon_F \gg m_e c^2$, where we can ignore the mass completely. Here's what you should find:

Ultra-relativistic fermi gas:

$$KE = \frac{3}{4} N_e \epsilon_F \text{ with } \epsilon_F = (3\pi^2)^{1/3} \hbar c \left(\frac{N}{V} \right)^{1/3}$$

$$= c_2 \frac{M^{4/3}}{R} \text{ with } c_2 = \frac{3}{4} \hbar c \left(\frac{9\pi}{4} \right)^{1/3} \left(\frac{6}{m_C} \right)^{4/3}.$$

$$\implies E_{\text{total}} = \left(c_2 M^{4/3} - \frac{3}{5} G_N M^2 \right) \frac{1}{R}.$$

So you'll find that in this case, both terms go like $1/R$. This means that no minimum of the potential exists in the ultra-relativistic regime. There's a critical value of the mass

$$0 = c_2 M_{\text{crit}}^{4/3} - \frac{3}{5} G_N M_{\text{crit}}^2 \implies M_{\text{crit}} = \left(\frac{5 c_2}{3 G_N} \right)^{3/2}$$

which divides two extremely different cases. For $M < M_{\text{crit}}$, the radius will increase until it gets to the non-relativistic regime (recall that big R means less relativistic, since lower density means lower ϵ_F).
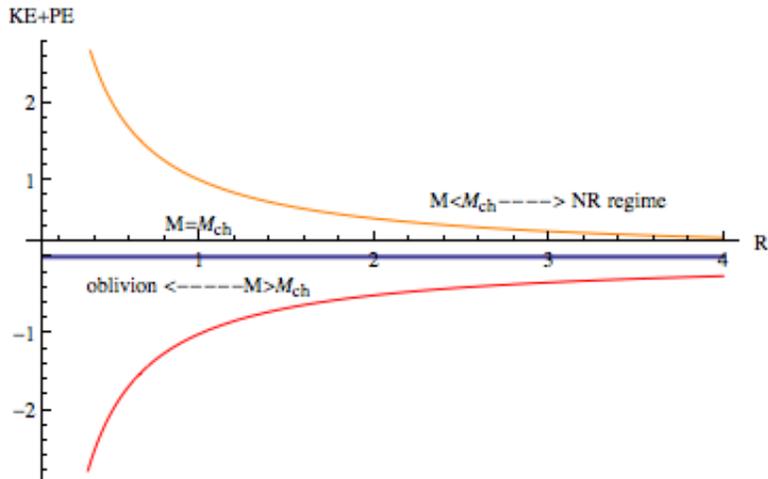
For $M > M_{\rm crit}$, the density just can't get big enough for the electron degeneracy pressure to stop the collapse: there is a **maximum mass** (called the Chandrasekhar mass), beyond which no stable white dwarf stars exist. Its value from the more correct analysis with the density profile is:

$$M_{\rm Chandra} = \left(\frac{\hbar c}{G_N} \right)^{3/2} \frac{1}{m_{\rm proton}^2} 0.77$$

(the analysis above gives 0.92 instead of 0.77 if we use $m_C = 12 m_{\rm proton}$).

$$M_{\rm Planck} \equiv \left(\frac{\hbar c}{G_N} \right)^{1/2} \quad \text{is a mass}$$

– it's a mass scale intrinsic to gravity. Remarkably,

$$M_{\rm Chandra} = m_{\rm proton} \left(\frac{M_{\rm Planck}}{m_{\rm proton}} \right)^3 0.77 \quad = m_{\rm proton} \left(10^{19} \cdot 1.3 \right)^3 0.77 = 1.42 M_{\rm sun}.$$

This seems to be a bit of a numerical coincidence, but we can't be too surprised, since the physics that determines the size of the sun also involves $\hbar, c, G_N, m_{\rm proton}$ and a balance of gravitational energies against energies having to do with $m_{\rm proton}$.

So: our sun will become a white dwarf when it runs out of nuclear fuel a few billion years from now.

What if it were heavier by a factor of $3/2$ or more? Beyond this critical mass: neutron degeneracy pressure can also hold up the star. There is an analogous limit to neutron star masses, $M_{\rm Chandra}^{\rm neutrons} \sim M_{\rm sun} \times$ a few. The value is uncertain because neutron-neutron interactions matter.

For masses beyond even that: black holes are the only known possibility.

9.7   Bosons at low temperatures

Here will think about N bosonic particles, maybe ^{4}He or sodium or hydrogen or rubidium atoms. We will suppose that N is fixed. (Recall that this is not the case for *e.g.* photons whose number is not conserved in general.)
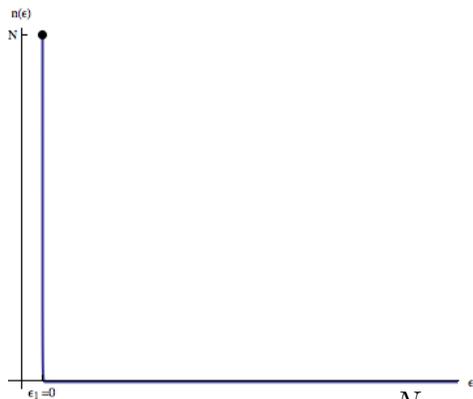
Start at $T = 0$. This is easy: all the N particles are in the 1-particle groundstate!

$$E(T = 0) = N\epsilon_1$$

For an $L \times L \times L$ box with hard walls,

$$\epsilon_1 = \frac{\hbar^2}{2m}\frac{\pi^2}{L^2}\left(1^2 + 1^2 + 1^2\right) = \frac{3\pi^2\hbar^2}{2m}\frac{1}{V^{2/3}}$$

$$\implies E(T = 0) \propto \frac{N}{V^{2/3}} \implies P = -\left(\frac{\partial E(T=0)}{\partial V}\right)_S \propto -\frac{1}{V^{5/3}} \overset{V\to\infty}{\to} 0$$

There is no "Bose pressure" at $T = 0$. Very different from fermions at $T = 0$.

Bosons at $T > 0$

We might expect based on classical intuition that as soon as $k_B T > \epsilon_2 - \epsilon_1$, (where ϵ_2 is the energy of the first excited state, $\epsilon_2 = \frac{\hbar^2}{2m}\frac{\pi^2}{L^2}\left(2^2 + 1^2 + 1^2\right) = \frac{5}{3}\epsilon_1$) there will be nothing special about the groundstate, that the other low-lying 1-particle states will be occupied nearly as much. (*e.g.* for ^{4}He in $(1\text{cm})^3$, this is $\Delta\epsilon/k_B \sim 10^{-14}K$.)

This classical expectation is dramatically wrong. We must remember that $\mu(T)$ is determined from N by

$$N = \sum_\alpha \langle n_\alpha \rangle = \sum_\alpha \frac{1}{e^{(\epsilon_\alpha - \mu)/k_B T} - 1}.$$

What's the chemical potential at $T = 0$? At $T = 0$,

$$N = \lim_{T\to 0}\langle n_1 \rangle = \lim_{T\to 0}\frac{1}{e^{(\epsilon_1 - \mu)/k_B T} - 1}.$$

Getting a big answer (like N) from the RHS requires $e^{(\epsilon_1 - \mu)/k_B T} \sim 1$; this means we can Taylor expand the exponential. In particular, it requires

$$\frac{1}{N} \overset{!}{=} e^{(\epsilon_1 - \mu)/k_B T} - 1 \approx 1 + \frac{(\epsilon_1 - \mu)}{k_B T} - 1 \qquad \implies (\epsilon_1 - \mu)/k_B T = \frac{1}{N} + \dots$$

$$\implies \mu(T \to 0) = \epsilon_1 - \underbrace{\frac{k_B T}{N}}_{\text{small!}}.$$

The chemical potential for bosons at zero temperature is just infinitesimally below the energy of the lowest single-particle level.

$$
\begin{aligned}
N &= \langle n_1 \rangle + \sum_{\alpha \geq 2} \langle n_\alpha \rangle \\
&= \langle n_1 \rangle + \int_{\epsilon_2 \approx 0}^{\infty} d\epsilon\, D(\epsilon) \frac{1}{e^{(\epsilon-\mu)/k_B T} - 1} \quad .
\end{aligned}
$$

We need to talk about the lower limit of the integral here: really the lower limit should be ϵ_2. But $\epsilon_2 \sim \frac{1}{L^2} \to 0$ as the box becomes large. Also, you may find comfort in the fact that (in 3 dimensions) $D(\epsilon = 0) = 0$. Actually, it only matters that $D(\epsilon \to 0)$ is finite: even if we do let the integral go all the way to zero, the one point $\epsilon = 0$ contributes with zero measure to the integral. If the classical intuition were correct, we wouldn't need to do this, but ... we do need to do it, as Einstein was the first to realize.

Suppose (guess and check):

$$
\langle n_1 \rangle = \frac{N}{b} \qquad \text{a fraction of } N, \text{ finite as } N \to \infty
$$

The important part here is that b is independent of N.

What is μ?

$$
\lim_{T \to 0} \langle n_1 \rangle = N \implies \mu = \epsilon_1 - \frac{k_B T}{N/b} \sim 0
$$

This means we can set $\mu = 0$ in the integral over states, and *do* the integral:

$$
N = \int_0^{\infty} d\epsilon \underbrace{D(\epsilon)}_{= V a \epsilon^{1/2}} \frac{1}{e^{\beta \epsilon} - 1} + \frac{N}{b}
$$

$$
a = \frac{1}{4\pi} \left(\frac{2m}{\hbar} \right)^{3/2} = \frac{1}{2} \text{ that of spin-}\frac{1}{2} \text{ fermions; these are spin 0 bosons}
$$

$$
= V a \int_0^{\infty} \frac{\sqrt{\epsilon}\, d\epsilon}{e^{\beta \epsilon} - 1} + \frac{N}{b}
$$

$$
= V a \underbrace{(k_B T)^{3/2}}_{T \to 0 \ \checkmark} \underbrace{\int_0^{\infty} \frac{\sqrt{x}\, dx}{e^x - 1}}_{=1.306\sqrt{\pi} = \frac{1}{2}\zeta\left(\frac{3}{2}\right)\sqrt{\pi}} + \frac{N}{b}
$$

$$
\boxed{\text{With our guess, we have} \qquad N = \langle n_1 \rangle + \underbrace{2.612 V \left(\frac{m k_B T}{2\pi \hbar^2} \right)^{3/2}}_{<N?}}
$$

Does the guess make sense? Yes, as long as the second term is less than N, in particular, it has to be $(1 - 1/b)N$. If not, then the guess is wrong. This is a condition on T.

$n_1 (T)/N$

Fraction of particles in condensate

$T = T_B$

$\mu(T)$

$T = T_B$
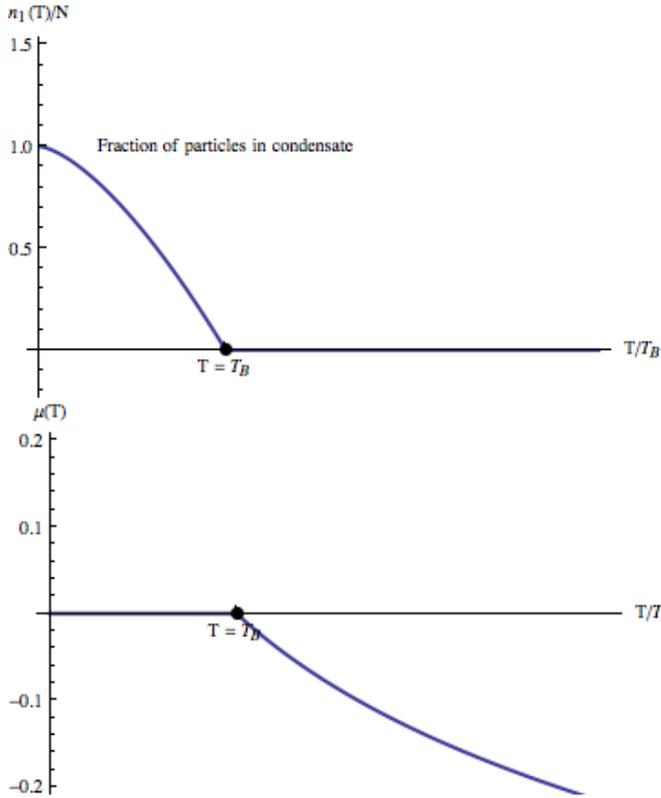
Def: $T_B \equiv T$ such that $\displaystyle\sum_{\alpha \geq 2} \langle n_\alpha \rangle = N$

$$\implies \quad T_B = \left(\frac{2\pi\hbar^2}{mk_B}\right)\left(\frac{N}{2.612V}\right)^{2/3}.$$

For $T < T_B$, the 'Bose temperature', the guess is self-consistent, and $\mu = 0$.

For $T > T_B$, $\mu < 0$, and we have to redo the integral. (A useful characterization of T_B starting from high temperature is the temperature where $\mu \to 0$.)

For $T < T_B$: $\qquad \langle n_1 \rangle + \left(\dfrac{T}{T_B}\right)^{3/2} N = N$

$$\implies \quad \boxed{\langle n_1 \rangle = N\left(1 - \left(\frac{T}{T_B}\right)^{3/2}\right).}$$

The word 'condensate' here denotes a macroscopic number of particles in the same quantum state.

For $T < T_B$, a finite fraction of the particles are in the 1-particle groundstate. The rest are distributed according to the Bose-Einstein distribution.

Where have we seen T_B before? Notice that

$$\text{at } T = T_B = \frac{h^2}{2\pi m k_B}\left(\frac{N}{2.612V}\right)^{2/3},$$

$$\lambda_{\text{th}} = \frac{h}{\sqrt{2\pi m k_B T}} = 2.612^{1/3}\left(\frac{V}{N}\right)^{1/3}$$

$T < T_B$ is the criterion for the failure of classicality (up to the same order-one uncertainty as earlier).
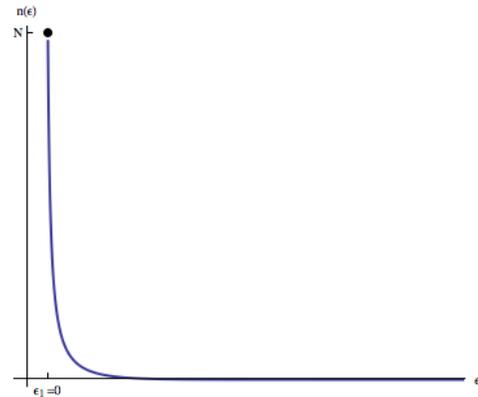
Energy and specific heat

For $T < T_B$:
$$E = \underbrace{\epsilon_1}_{=0} + \int_0^\infty \frac{d\epsilon\, D(\epsilon)\epsilon}{e^{\epsilon/k_B T} - 1} \sim T^{5/2}$$

by the same kind of scaling analysis that you are good at by now (let $x \equiv \epsilon/k_B T$...). More precisely,

$$E \simeq 0.770 \left(\frac{T}{T_B}\right)^{3/2} Nk_B T \qquad \ll \frac{3}{2} Nk_B T \text{ (the classical answer).}$$

Note that therefore at high T, E must approach $E_{\text{classical}} = \frac{3}{2} Nk_B T$ from *below*. That means that C_V decreases to the classical value – it approaches $\frac{3}{2} Nk_B$ from *above*.
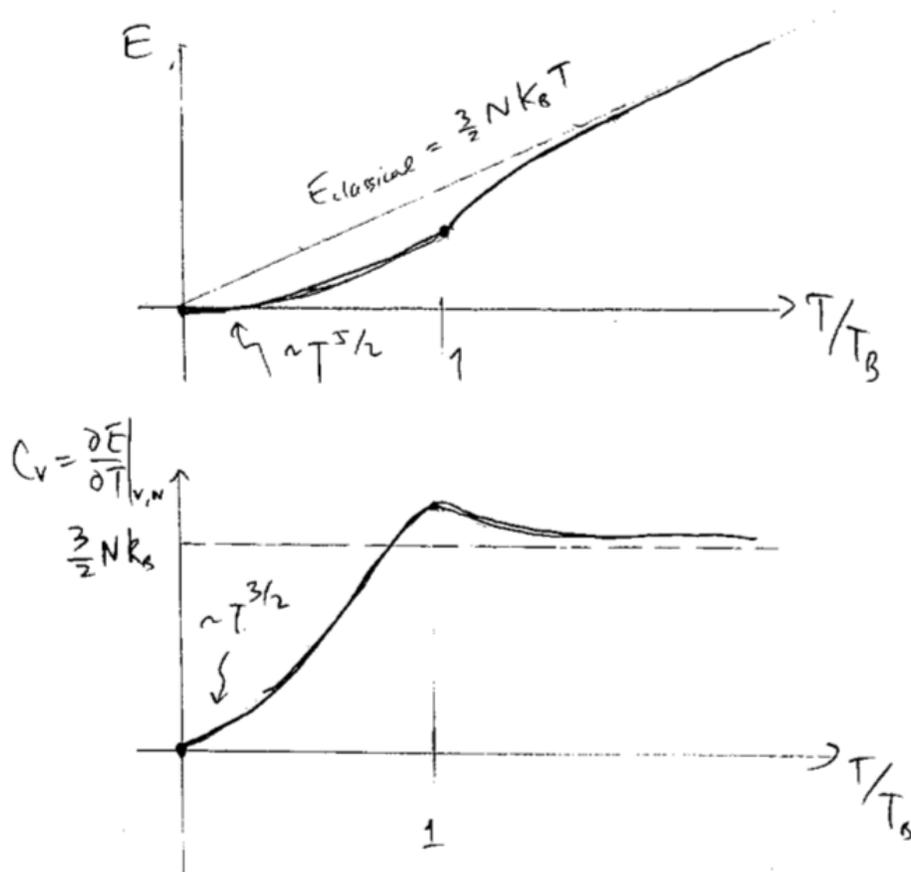
Note that there **are** sharp bends in these curves at $T = T_B$ – "non-analyticities" where the derivative (or some higher derivative) blows up. It is therefore called a (continuous) *phase transition.*

Comments about Bose-Einstein condensation

- An important fact about it that I can't explain well in terms of things we've learned so far: the resulting state is a *superfluid*. Roughly, this means that even when the stuff moves, there is no dissipation of energy by the fraction of the atoms sitting in the groundstate, no friction; the only source of friction is from changing the state.

- This condensation phenomenon was predicted by Einstein in 1924 as a result of his role as the editor, referee and translator (from English into German) of a paper by S. Bose describing blackbody radiation by counting states of non-interacting bosons. He published his results with those of Bose as 'a note from the translator'.

- In 1937, superfluidity in liquid ^{4}He was observed:
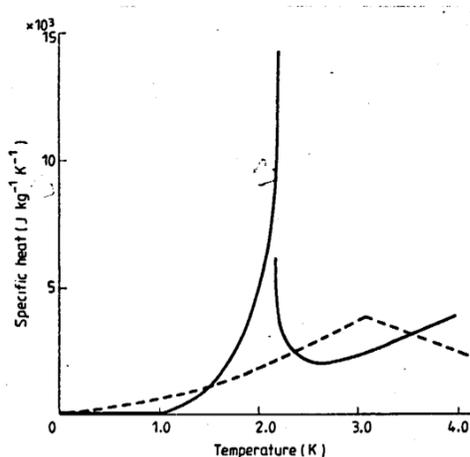
Figure 1.4 Specific heat of liquid ^{4}He (after Atkins 1959). Broken line shows specific heat of ideal Bose–Einstein gas having same density as liquid ^{4}He.

(This is called the 'λ-transition' because of the shape of this curve.) The dashed line is the ideal bose gas result discussed above – it predicts $T_B = 3.15K$ at the relevant density, using $m_{^4\text{He}}$. Interactions matter (hence 'liquid' not 'gas').

- Efforts to cool bosonic atoms to temperatures below their T_B are problematized by the fact that many collections of atoms aren't *gases* at such low temperatures and high enough densities. The fact that $T_B \propto \frac{1}{m}$ led people to try hydrogen for a long time (since the 1970s) – the relevant number turned out (in 1998) to be $T_B \sim 50\mu K$. This led people (many of them at MIT) to invent clever new cooling techniques. Other kinds of atoms (Rb, Na) turned out to be easier to cool (by laser cooling), and they condensed first, in 1995, at a couple of μK.

- How do they tell that the bosons condense? This takes advantage of the fact that their bosons are not particles-in-a-box, but are trapped in a (approximately) harmonic potential made from lasers. Turning off the laser trap lets the particles propagate freely. Shining light on them, they cast a shadow. The lowest-energy state of the well

has small momentum and the particles occupying it, when released, don't travel far, and therefore cast a dark shadow in the center of the cloud. The picture on the cover of Baierlein is a 3d plot of the darkness of the shadow (from the Colorado group).
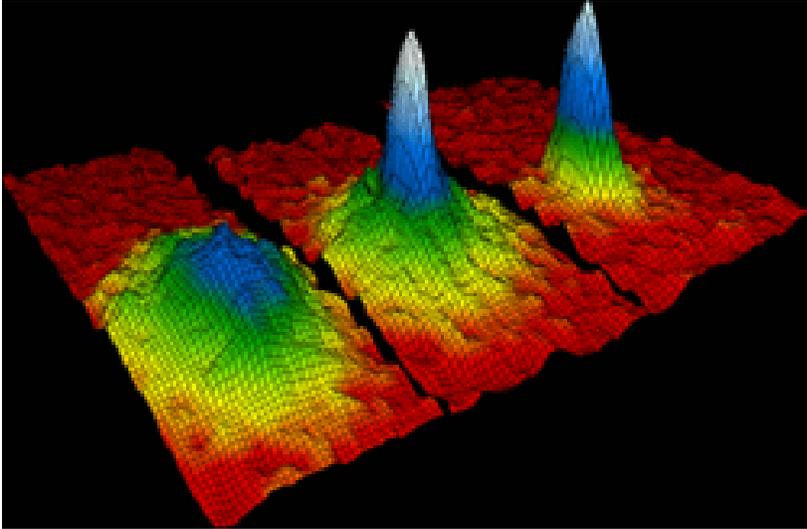
The last page.

This is the end of 8.044.

The next topics demanding to be studied are the grand canonical ensemble (what happens if we fix μ instead of N?) and the theory of phase transitions.

Surely you agree now that many particles can do things that a few particles cannot do (more is indeed different). The kinds of connections we've made between macroscopic phenomena and microscopic models, and the techniques we've developed for doing so are useful in every kind of physics and in lots of other subjects, too.

Special thanks to those of you who brought typos to my attention or asked questions that helped improve the notes.