8.044 Lecture Notes
Chapter 7: Thermal Radiation

Lecturer: McGreevy
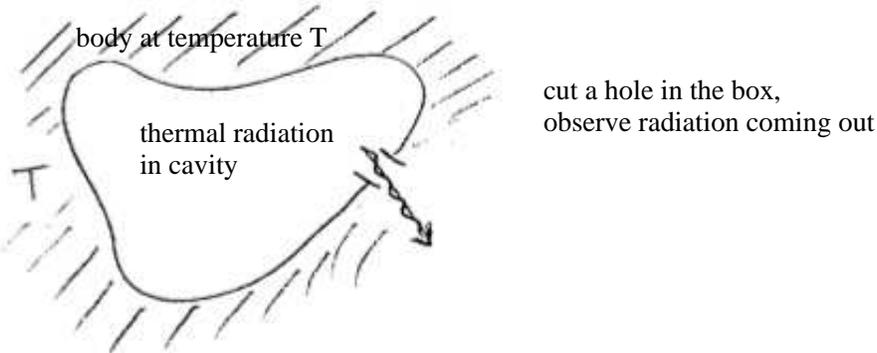
Reading: Baierlein, Chapters 4.1 and 6.

Thermal radiation (a.k.a "blackbody" radiation) is the answer to the following simple question:

What is the state of the electromagnetic (EM) field in equilibrium with its surroundings at temperature T?

It is what happens when you heat up empty space.

3 (equivalent) viewpoints:

1. As a particular thermodynamic system (This is §7.1).

2. Via normal mode solutions to Maxwell's equations in the cavity are standing EM waves. In §7.2, we will do stat mech from this starting point.

3. As a gas of photons (subsequently, and in Chapter 9 this will be our viewpoint).

We're going to try to figure out:

$$u(\nu, T)d\nu \equiv \frac{\text{energy of thermal radiation with } \nu \leq \text{frequency} \leq \nu + d\nu}{\text{unit volume}}$$

in thermal equilibrium at temperature T. Here ν ('nu') indicates the frequency of the EM radiation. u is called the "spectral energy density".

$$[u] = \frac{\text{energy}}{\text{vol} \cdot \text{frequency}}$$

To begin, here are some observed facts about thermal radiation (which we'll come to understand):

- $u(\nu, T)$ is independent of the cavity shape and the wall material. The walls of the cavity play the role of the heat bath, keeping the EM field at temperature T.

- The radiation is isotropic and unpolarized.

- The shape of $u(\nu, T)$ looks like this:
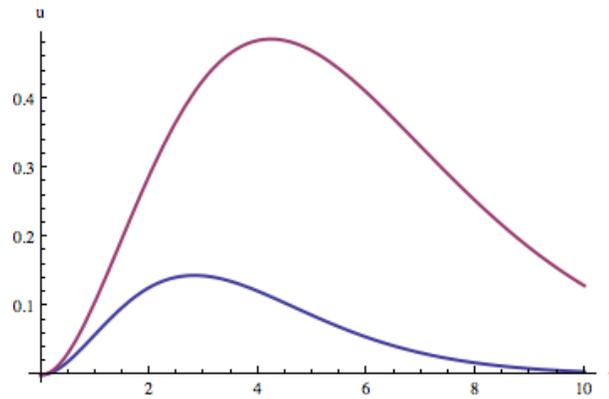
Shown are $T = 1$ and $T = 1.5$. [1]

At $T = T_{\text{Room}}$, $\nu_{\text{peak}} \sim 10^{13}$Hz ($\lambda_{\text{peak}} \sim 50\mu$m) is in the IR (not visible).
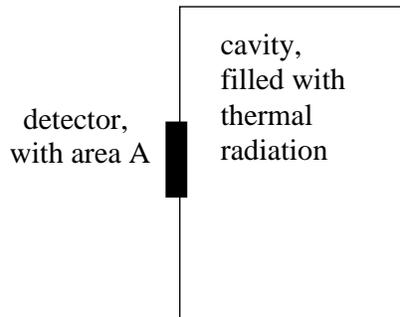
[End of Lecture 18.]

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[1] in some units with $\hbar = 1 = c$; the energy density and the frequency are both measured in units of the temperature.

7.1   Thermodynamics of blackbody (thermal) radiation

First: How far can we go with just macroscopic (*i.e.* thermodynamic) arguments?

Relate energy density u to energy flux.

cavity, filled with thermal radiation

detector, with area A

$\Delta E \equiv$ energy that hits the detector in time Δt

$$\text{energy flux} \equiv \frac{\Delta E}{A \Delta t} = \text{power incident on detector} \equiv \text{intensity}$$

Calculate ΔE: consider just the radiation with frequency ν and given momentum direction. ($|\vec{p}| = h\nu/c$ always.)

In time Δt all the radiation in this cylinder that is moving in this direction will hit the detector:
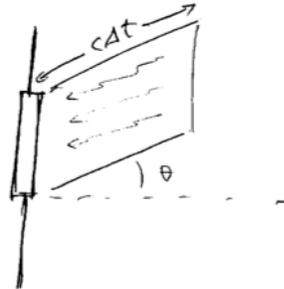
Integrate over directions (θ and φ):

$$\Delta E = \underbrace{\int_0^{\pi/2}}_{\text{if } \theta > \pi/2, \text{ we're outside}} d\theta \int_0^{2\pi} d\varphi \quad \text{(energy in cylinder)} \qquad \underbrace{p(\theta, \varphi)}_{\text{prob that radiation is going in the right dir}}$$

$$= \int_0^{\pi/2} d\theta \int_0^{2\pi} d\varphi \left(u \cdot \underbrace{A\cos\theta}_{\text{area of slice} \perp \text{ to } \vec{p}} \cdot c\Delta t \right) \underbrace{\frac{\sin\theta}{4\pi}}_{\text{isotropic radiation}}$$

$$= \frac{cuA\Delta t}{4\pi} \underbrace{\int_0^{\pi/2} d\theta \cos\theta \sin\theta}_{=1/2} \underbrace{\int_0^{2\pi} d\varphi}_{=2\pi} .$$

$$\implies \boxed{\text{energy flux per unit freq} = \frac{1}{4}cu(\nu, T)}$$

On the LHS is the energy per unit volume per unit frequency, so the units work out.

Next let's calculate the
Radiation pressure

$$\text{pressure} = \frac{\text{force}}{\text{area}} = \frac{\Delta p / \Delta t}{\text{area}}$$
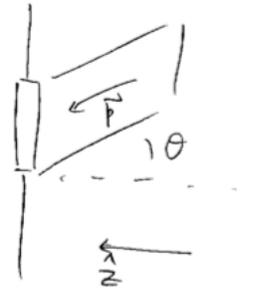
$p_z = |\vec{p}| \cdot \cos\theta$

Recall: for a chunk of EM radiation, $|\vec{p}| = \text{energy}/c$

For definiteness, assume reflecting walls (doesn't affect answers).

The change in momentum of the radiation that *reflects* off the wall in time Δt:

$$\equiv \Delta p_z = \int_0^{\pi/2} d\theta \int_0^{2\pi} \underbrace{(\text{energy in cylinder}) \cdot \frac{\cos\theta}{c}}_{\text{momentum normal to wall} = \frac{\cos\theta}{c} \times \text{energy}} \cdot \underbrace{2}_{\text{reflects}} \cdot \underbrace{p(\theta, \varphi)}_{\text{as before}} \quad .$$

$$= \frac{cuA\Delta t}{4\pi} \frac{2}{c} \underbrace{\int_0^{\pi/2} d\theta \cos^2\theta \sin\theta}_{=1/3} \underbrace{\int_0^{2\pi} d\varphi}_{=2\pi} \; .$$

$$\implies \boxed{\text{pressure exerted by radiation with freq } \nu = \frac{\Delta p_z}{A\Delta t} = \frac{1}{3} u(\nu, T)} \; .$$

Thermodynamics

That was for *each* frequency. Now let's integrate over ν.

$$\underbrace{P}_{\text{the familiar thermodynamic pressure}} = \frac{1}{3} \int_0^\infty d\nu \ u(\nu, T)$$

$$\underbrace{U/V}_{U \text{ is the familiar thermodynamic energy}} = \int_0^\infty d\nu \ u(\nu, T) \equiv u(T)$$

i.e. $U = Vu(T)$, and this is the only V-dependence in u – it's extensive.[2]

So, thermal radiation satisfies:

$$\boxed{P = \frac{1}{3}\frac{U}{V}}$$

(Compare to results on pset for ultra-relativistic gas.)

Thermal radiation is described by $P, V, T, U, S...$ – it is a hydrostatic system.

Remarkably, we can go most of the way toward finding $u(T)$.

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[2]Actually, the fact that the energy density is independent of V is not clear from what we have said so far. A simple argument for it relies on the *scale invariance* of Maxwell's equations – there is no quantity with the dimensions of length appearing in Maxwell's equations. Therefore, when you heat up a patch of empty space, the only quantity with units of length is the size of the patch of empty space. The energy per unit volume must be independent of the volume.

$$dU = TdS - PdV$$

$$\Longrightarrow \underbrace{\left(\frac{\partial U}{\partial V}\right)_T}_{=u(T),\text{ since } U=Vu} = T \underbrace{\left(\frac{\partial S}{\partial V}\right)_T}_{=\left(\frac{\partial P}{\partial T}\right)_V \text{ by Maxwell reln}} - P$$

$$\Longrightarrow \quad u(T) \;=\; T\left(\frac{\partial P}{\partial T}\right)_V - P$$

$$=\; T\left(\frac{1}{3}\frac{du(T)}{dT}\right) - \frac{1}{3}u(T)$$

$$\Longrightarrow \; \frac{4}{3}u(T) = \frac{T}{3}\frac{du(T)}{dT}$$

$$\Longrightarrow \; \frac{du}{dT} = 4\frac{u}{T} \;\Longrightarrow\; \boxed{u(T) = bT^4}$$

for some constant b. b cannot depend on T or V, or the properties of the cavity. It must be some constant of nature.

$$\boxed{U = bVT^4} \quad \boxed{P = \frac{b}{3}T^4}$$

$$\text{energy flux, out of a hole in the cavity} = \frac{cb}{4}T^4.$$

We've determined the pressure and the energy density (*i.e.* all the thermodynamics) of thermal radiation, in terms of one constant b. Conventionally:

$$\frac{1}{4}cb \equiv \sigma, \quad \text{Stefan-Boltzmann constant}$$

Next we'll show that :

$$\sigma = \frac{2\pi^5 k_B^4}{15h^3 c^2} = \frac{\pi^2}{60}\underbrace{\overbrace{k_B^4}^{\text{stat mech}}}_{}\underbrace{\frac{1}{\hbar^3}}_{\text{QM}}\underbrace{\frac{1}{c^2}}_{\text{EM, SR}} = 10^{-8}\cdot 5.67\frac{W}{m^2 K^4}.$$

Why thermal radiation = "blackbody radiation"?

A *body* (*i.e.* a thing of finite size, *i.e.* a thing) can be characterized by $\alpha(\nu, T), e(\nu, T)$:

$$\text{Absorptivity} \equiv \alpha(\nu, T) \quad = \quad \frac{\text{energy absorbed}}{\text{energy incident}}$$

$$\text{Emissivity} \equiv e(\nu, T) \quad = \quad \frac{\text{energy radiated}}{\text{unit time} \cdot \text{unit area} \cdot \text{unit freq}}$$

both defined when the body has temperature T.

Thought experiment: put the body in the cavity we discussed before. Wait long enough that the cavity, radiation and body are in equilibrium.

In equilibrium, the body emits and absorbs *the same* amount of radiation, *at each frequency*. Else, if the body were emitting radiation in some frequency more than it absorbed, the radiation would not be in equilibrium – the state of the radiation field would be changing. This is called "detailed balance".
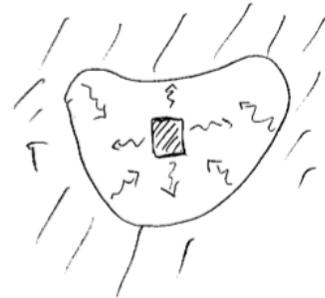
$$(\star): \quad E_{\text{emitted}}(\nu) \quad = \quad E_{\text{absorbed}}(\nu)$$

$$e(\nu, T) \cdot \underbrace{A}_{\text{surface area of body}} \cdot \Delta t \quad = \quad \alpha(\nu, T) \cdot \underbrace{(\text{energy flux hitting body})}_{\frac{1}{4} c u(\nu, T)} \cdot A \cdot \Delta t.$$

$$\implies \quad \boxed{\frac{e(\nu, T)}{\alpha(\nu, T)} = \frac{1}{4} c u(\nu, T)} \quad \text{"Kirchoff's Law"}$$

This is an amazing fact: the LHS has two material properties, each of which varies wildly with material. The RHS is independent of the material, of the shape, of anything. [3]

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[3] There is a notational issue with Baierlein's chapter 6: Baierlein uses a nonstandard definition of emissivity, in his (6.33). What Baierlein has done instead is to define:

$$e_{\text{Baierlein}}(\nu, T) = e_{\text{Standard}}(\nu, T) \frac{1}{[u(\nu, T)c/4]}$$

which means that for Baierlein, Kirchhoff's Law (which he states in words right after (6.33)) is:

$$e_{\text{Baierlein}}(\nu, T) = \alpha(\nu, T).$$

You need to be aware of Baierlein's nonstandard definition if you compare any equation that has emissivity in it between Baierlein's version and the version in my lecture notes.

Conclusion: a good absorber (at freq ν) is a good emitter (at freq ν).

A *perfect* absorber $\equiv$ "black body" is a body with $\alpha(\nu, T) = 1$ for all ν, T. Such a body emits radiation with an emitted flux

$$\boxed{e(\nu, T) = \frac{1}{4}cu(\nu, T)} \quad \text{for a blackbody.}$$

But this is the flux out of a little hole in the cavity $\rightarrow$

(Note: if the hole is small enough, waves incident from outside the little hole go in and never come out: so this is consistent with the statement that the *hole* has $\alpha_{\text{hole}} = 1$.)
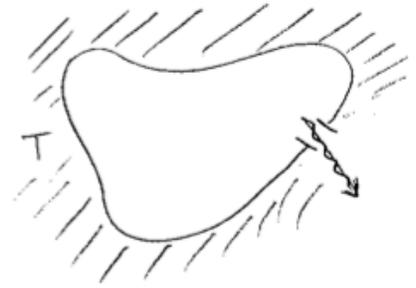
So: thermal radiation *is* blackbody radiation.

This proves that the size, shape, reflectivity of the cavity don't affect the spectrum.

We have determined the $\frac{\text{energy radiated}}{\text{unit area}\cdot\text{unit time}}$ for *any* blackbody, in terms of one unknown constant b. To find b, we need stat mech, next.

7.2 Statistical treatment of thermal radiation

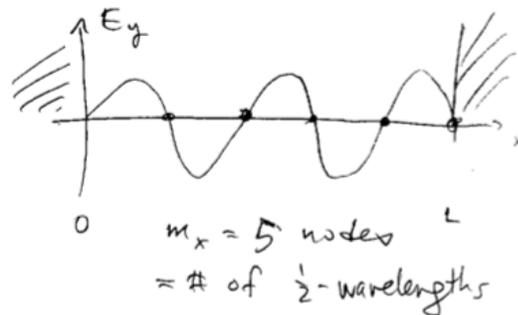For some of you, this will be your first exposure to quantum field theory.

We want to calculate $u(\nu, T)$ and $u(T) = \int d\nu \ u(\nu, T)$.

Consider a cubic cavity. We will build up the answer mode by mode (not point by point).

EM facts [8.02 or 8.03]:
Maxwell's equations in a cavity have standing wave solutions, *e.g.*:

$$E_y(\vec{r}, t) = \sin k_x x \times E(t), \qquad k_x = \frac{m_x \pi}{L}$$

Maxwell's equations include:

$$\vec{\nabla} \times \vec{B} = \frac{1}{c}\partial_t \vec{E} \implies B_z(\vec{r}, t) = \frac{1}{k_x c} \underbrace{\dot{E}(t)}_{\text{so far unknown}} \cos(k_x x)$$

$$\text{energy density}, u = \frac{1}{8\pi}\left(\vec{E}^2 + \vec{B}^2\right) = \frac{1}{8\pi}\left(E^2 \sin^2 k_x x + \frac{\dot{E}^2}{(k_x c)^2}\cos^2 k_x x\right)$$

$$H_{\text{one mode}} = \int_{\text{vol of cavity}} u = \underbrace{\frac{1}{2}V}_{\int \sin^2 = \frac{1}{2}V = \int \cos^2} \frac{1}{8\pi}\left(\frac{\dot{E}(t)^2}{(k_x c)^2} + E^2(t)\right)$$

The EM dynamics of each mode E is an SHO! $H_{SHO} = \frac{1}{2}m\dot{x}^2 + \frac{1}{2}\kappa x^2$ with $\omega^2 = \kappa/m$; we have $\omega^2 = (k_x c)^2$. Pick a mode number, m_x, this gives $k_x = \frac{m_x \pi}{L}$ which gives $\omega_m = k_x c = \frac{m_x \pi c}{L}$.

The solutions for the time evolution are $E(t) = a\sin(\omega_m t + \varphi)$ where a, φ are integration constants determined by initial conditions.

But we know how to do stat mech for SHOs!

Comments:

- Rather than springs at each point in space, these oscillators that we just found are each modes which *fill* the box – they are distinguished by their

$$\text{wavenumber} \quad \vec{k} = (k_x, k_y, k_z) = \frac{\pi}{L}(m_x, m_y, m_z),$$

  not by their location.

- Crucial point: Maxwell's equations are linear. This means that to find the general solution, we can just add up solutions for each mode:

$$\vec{E} = \sum_k \vec{E}_k$$

  and further

$$H = \sum_k (\text{energy of each mode})$$

  so in the canonical ensemble, the modes will be statistically independent – the partition function will factorize.

- Claim: boundary conditions are not important for determining the thermal spectrum. They affect at most a few modes and their contribution becomes negligible in the thermodynamic limit of a large enough box (compared to the length scale set by T). (You can (and will in recitation) redo the following analysis with *e.g.* periodic boundary conditions.)

Outline of calculation of thermal radiation spectrum

The calculation of the thermal radiation spectrum takes two steps:

1. Count modes to get $D(\omega)$, the density of states:

$$D(\omega)d\omega = \# \text{ of modes with } \omega \leq \text{freq} < \omega + d\omega$$

2. Calculate $\langle \epsilon(\omega) \rangle$, the mean energy in the mode with frequency ω, in thermal equilibrium.

Then the things we want are:

$$\boxed{U = \int d\omega \langle \epsilon(\omega) \rangle D(\omega)}$$

$$\boxed{u(\omega, T) = \underbrace{\langle \epsilon(\omega) \rangle D(\omega)}_{\text{energy in modes with freq } \omega} \frac{1}{V}}$$

Note that I am using the angular frequency ω and the ordinary frequency ν interchangeably. They differ by a factor of 2π.

Step 1: Counting modes

Modes are labelled by $\vec{k} = \left(\frac{m_x \pi}{L}, \frac{m_y \pi}{L}, \frac{m_z \pi}{L}\right)$ with $m_x = 1, 2...; m_y = 1, 2...; m_z = 1, 2....$ [4] For each choice of (m_x, m_y, m_z), there are two modes, because there are two polarizations of the EM field. In the example above, we had k_x, E_y, B_z nonzero; the other polarization state with wavenumber along k_x has nonzero E_z, B_y.

ω depends on $\vec{k}$, *i.e.* is different for different modes, as we determined above:

$$\omega^2 = c^2 \left(k_x^2 + k_y^2 + k_z^2\right) = \frac{c^2 \pi^2}{L^2} \left(m_x^2 + m_y^2 + m_z^2\right)$$

This is called the *dispersion relation*. The allowed $\vec{k}$s for a given box, make a 3d grid (a lattice). Here is what this grid would look like for a 2-dimensional box:

(The 3d version is on the next page.)
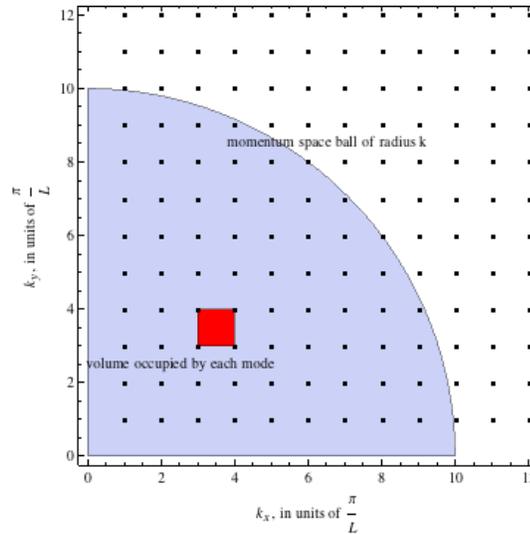
Cumulative number of states:

$$N(k) \equiv \text{\# of modes with } |\vec{k}| \leq k$$

$$= \underbrace{2}_{\text{polarization}} \times \underbrace{\frac{\frac{1}{8} \times \frac{4}{3}\pi k^3}{\left(\frac{\pi}{L}\right)^3}}_{\text{\# of lattice points}} \qquad \begin{array}{l} \longleftarrow \text{vol of one octant of sphere with radius } k \\ \longleftarrow \text{vol in } \vec{k}\text{-space around each lattice point} \end{array}$$

$$= \frac{1}{3} \frac{L^3 k^3}{\pi^2}$$

Convert to $N(\omega)$ using the dispersion relation $\omega^2 = c^2 \left(k_x^2 + k_y^2 + k_z^2\right)$, *i.e.* $\omega = ck$: $N(\omega) = \frac{1}{3}\frac{L^3 \omega^3}{\pi^2 c^3}$ The density (of states) is obtained from the cumulative number (of states) in the usual way:

$$D(\omega) = \frac{d}{d\omega}N(\omega) \qquad \Longrightarrow \qquad \boxed{D(\omega) = \frac{L^3}{\pi^2 c^3}\omega^2} \, .$$

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[4]The example in the picture above had $m_x = 5$ and didn't say what m_y and m_z were. With hard-wall boundary conditions (the parallel component of the electric field vanishes at the walls), each of the three modenumbers have to be nonzero in order to have a mode with nonzero amplitude ($\sin(0) = 0$). Actually, the normal component of the electric field need not vanish in general – so there can be *e.g.* a mode of E_y with $(m_x \neq 0, m_y = 0, m_z \neq 0)$ – but this depends on the polarizability of the walls. This kind of thing is the subject of 8.03, I'm told. As you'll see in recitation, this difference of one mode is not important for thermodynamics.
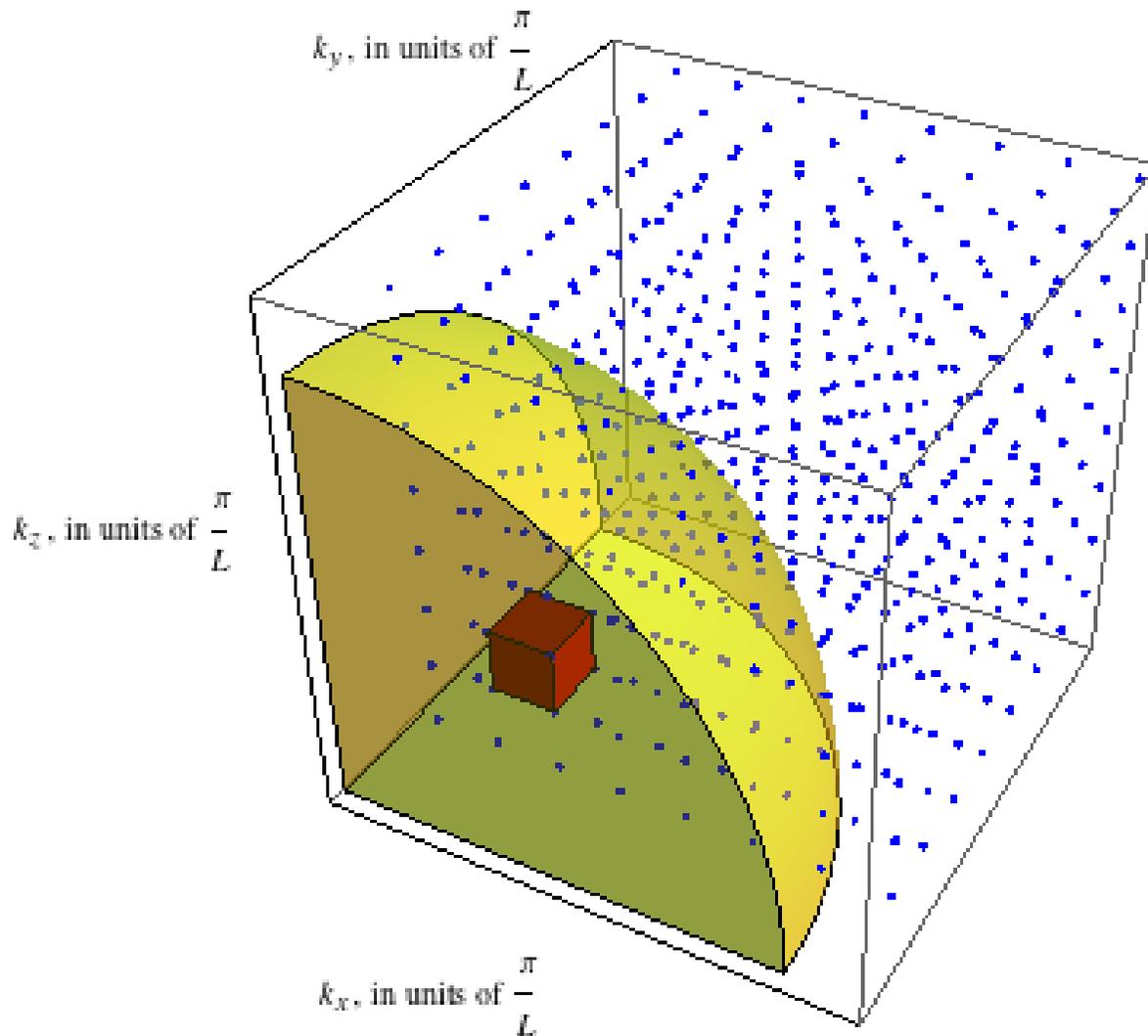
Here I have drawn (told Mathematica to draw) :

- a blue dot for each mode of a 3d box,

- the region of k space with $|\vec{k}| \leq 7$ (shaded yellow) – its volume is the numerator in the DoS,

- the region of k space occupied by a single dot (red cube), in particular the one at $(k_x, k_y, k_z) = \frac{\pi}{L}(2, 1, 2)$ – its volume is the denominator in the DoS.

## Step 2: Computing the energy in each mode (classical version)

Before the advent of QM, we would have said

$$\langle \epsilon(\omega) \rangle = k_B T \quad \text{classical equipartition for a classical oscillator}$$

$$\implies u(\omega, T) = \frac{D(\omega)\langle \epsilon(\omega) \rangle}{V} = \frac{L^3}{\pi^2 c^3} \omega^2 k_B T \frac{1}{L^3} = \frac{\omega^2 k_B T}{\pi^2 c^3}$$

$$\implies u(T) = \int_0^\infty d\omega \, u(\omega, T) = \frac{k_B T}{\pi^2 c^3} \frac{\omega^3}{3}\Big|_0^\infty = \infty.$$

Oops. In a classical world, an empty cavity at any nonzero temperature contains an infinite energy per unit volume. Each little patch would have an infinite energy. It's not just an infinite constant that you could subtract off either, because it depends on the temperature. This seems to be in conflict with observation. This was rightly called "the Ultraviolet Catastrophe".
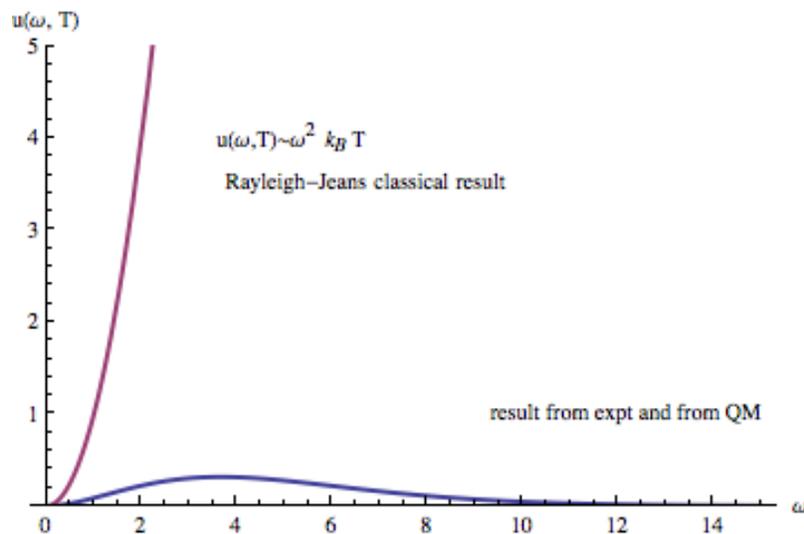
This is the problem that Planck solved in 1895, by an inspired guess which began the understanding by humans of quantum mechanics.

Next: the correct quantum treatment, which is already clear to you from the fact that the EM field in box is just a bunch of quantum harmonic oscillators.

Step 2: Computing the energy in each mode (quantum version)

The allowed energy levels are $\epsilon_n = \hbar\omega\left(n + \frac{1}{2}\right), n = 0, 1, 2....$

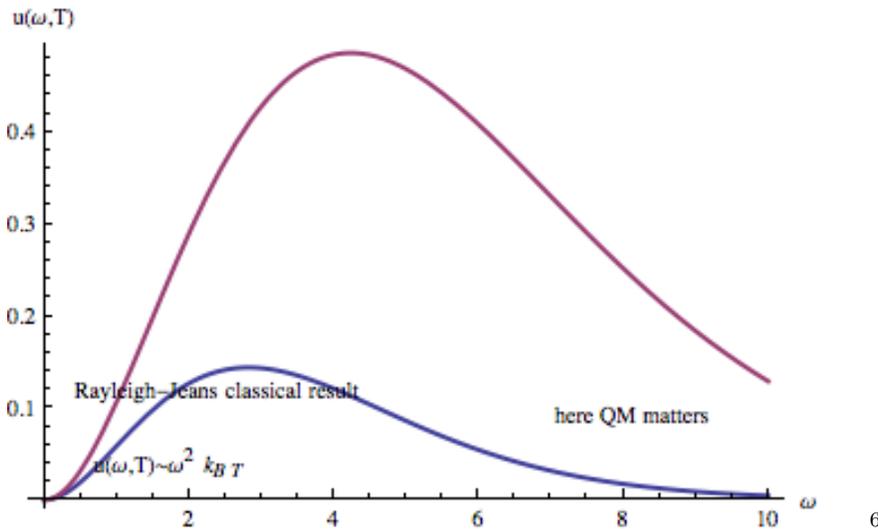$$\langle\epsilon(\omega)\rangle = \langle\epsilon_n\rangle = \hbar\omega\left(\langle n\rangle + \frac{1}{2}\right)$$

$$= \frac{\hbar\omega}{e^{\beta\hbar\omega} - 1} + \underbrace{\frac{1}{2}\hbar\omega}_{\text{"zero point energy"}}$$

We drop the zero point energy. In the integral over ω, it gives an infinite constant. We can safely drop this by choosing the zero of energy, as long as we're not worrying about its gravitational effects.[5]

$$u(\omega, T) = \langle\epsilon(\omega)\rangle D(\omega)\frac{1}{L^3}$$

$$\boxed{u(\omega, T) = \frac{\hbar}{\pi^2 c^3}\frac{\omega^3}{e^{\frac{\hbar\omega}{k_B T}} - 1}}$$ the Planck distribution

[End of Lecture 19.]

On the right: For $\hbar\omega \gg k_B T$, the oscillator at frequency ω is likely to be in its groundstate, is rarely excited; therefore it contributes $\ll k_B T$ worth of energy.
On the left: for $\hbar\omega \ll k_B T$, these modes have classical occupation numbers, contribute $k_B T$ per mode.

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[5] (Trust me that you don't want to worry about its gravitational effects right now.) This process of taking advantage of an ambiguity in the definition of the microscopic model (adding an (infinite) constant to the energy of every state) is an example of a procedure called "renormalization" which is crucial in studying systems with lots of degrees of freedom distributed over space, like a quantum field theory.

Location of maximum: $0 = \frac{du}{d\omega} \implies \frac{\hbar\omega_{\text{max u}}}{k_B T} \simeq 2.82$. At T_{room}, $\lambda_{\text{max }u} \simeq 10^{-5} \cdot 4.6$ m which is 100 times lower freq (and 100 times longer wavelength) than visible light.

Energy density:

$$u(T) = \frac{U}{V} = \int_0^\infty d\omega\; u(\omega, T) = \frac{\hbar}{\pi^2 c^3} \int_0^\infty \frac{d\omega\; \omega^3}{e^{\beta\hbar\omega} - 1}$$

$$= \frac{\hbar}{\pi^2 c^3} \left(\frac{k_B T}{\hbar}\right)^4 \underbrace{\int_0^\infty \frac{dx\; x^3}{e^x - 1}}_{=\pi^4/15}.$$

$$\boxed{\frac{U}{V} = \underbrace{\frac{\pi^2}{15}\frac{k_B^4}{\hbar^3 c^3}}_{=4\sigma/c,\text{ Stefan-Boltzmann const}} T^4}$$

as promised. We can also find all the other thermodynamic quantities (Z, F, P, S). Since H is a sum of the energies of each mode,

$$Z = \prod_{\text{all modes}} Z_i \implies F = -k_B T \ln Z = -k_B T \sum_\omega \text{degeneracy}(\omega) \ln Z(\omega)$$

$$F = -k_B T \int_0^\infty d\omega\; D(\omega) \ln Z(\omega)$$

$$= -k_B T \int_0^\infty d\omega \frac{L^3}{\pi^2 c^3} \omega^2 \ln\left(\frac{1}{1 - e^{-\hbar\omega/k_B T}}\right)$$

$$= \frac{k_B T L^3}{\pi^2 c^3} \left(\frac{k_B T}{\hbar}\right)^3 \underbrace{\int_0^\infty dx\; x^2 \ln\left(1 - e^{-x}\right)}_{=-\pi^4/45}.$$

$$\implies \boxed{F = -\frac{1}{45}\frac{\pi^2 k_B^4}{c^3 \hbar^3} T^4 V}.$$

Negative F means $TS > E$.

$$P = -\left(\frac{\partial F}{\partial V}\right)_T = \frac{1}{45}\frac{\pi^2 k_B^4}{\hbar^3 c^3} T^4$$

$$S = -\left(\frac{\partial F}{\partial T}\right)_V = \frac{4}{45}\frac{\pi^2 k_B^4}{\hbar^3 c^3} T^3 V$$

$$U = F + TS = \left(-\frac{1}{45} + \frac{4}{45}\right)\frac{\pi^2 k_B^4}{\hbar^3 c^3} T^4 V = \frac{1}{15}\frac{\pi^2 k_B^4}{\hbar^3 c^3} T^4 V$$

as before.

$$P = \frac{1}{3}\frac{U}{V}$$

as before, and

$$\sigma = \frac{\pi^2}{60}\frac{k_B^4}{c^2 \hbar^3}.$$

Compare to experiment

The best known blackbody is the universe as a whole. At some time in the recent past (13 billion years ago) there was a hot big bang, and all the stuff was in thermal equilibrium at a very high temperature; since then it's been expanding and cooling. The universe is filled with thermal radiation at $T_{\mathrm{CMB}} = 2.726$ K, whose peak is in the microwave frequency range[7].

A lot has been learned about the early universe by studying the fluctuations in the temperature from different directions, which have a size of order $\frac{\delta\rho}{\rho} \sim 10^{-5}$.

The same spectrum also applies to gluons at $t_{\mathrm{universe}} \sim$ microseconds (the presence of quarks leads to corrections at the 10-20% level; we'll learn to include them in Chapter 9).
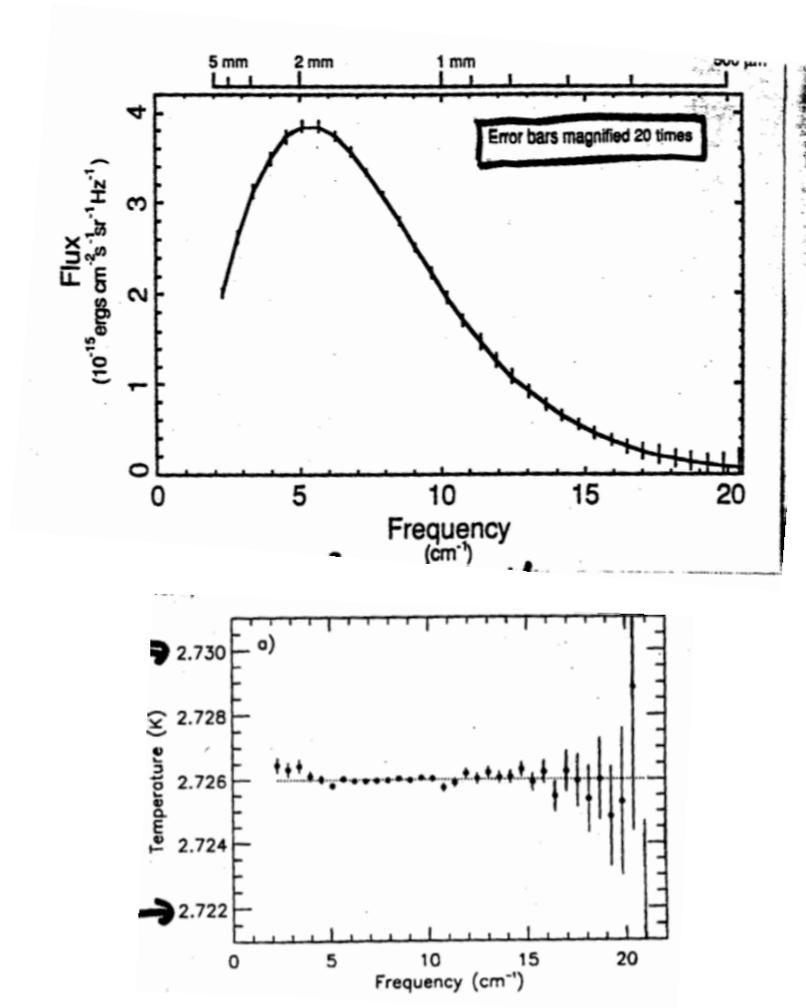

It's a really good blackbody.

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[7]This value T_{CMB} comes from the temperature above which electrons and protons decide to no longer form neutral atoms (this a chemistry energy, of order a few eV $= 10^4$K. This then gets divided by a factor of 1000 to account for the redshift due to the expansion of the universe since the time when the temperature was so high.

7.3 Phonons in a solid

Soundwaves in a crystal are a lot like lightwaves in a cavity.

- c_{sound} replaces c. So the dispersion relation is $\omega = c_{\text{sound}}|\vec{k}|$.

- In counting modes for each wavenumber, for light there were two (transverse) polar-izations. For sound, there are three – two transverse and one longitudinal. (In a gas, only the longitudinal mode is present.)

- There is one more distinction which will be important below, which is that (the quan-tum version of) Maxwell's equations are valid down to as short a wavelength as we usually care about. On the other hand, soundwaves only are well-described as such if their wavelength is much longer than the spacing between the atoms of the solid.
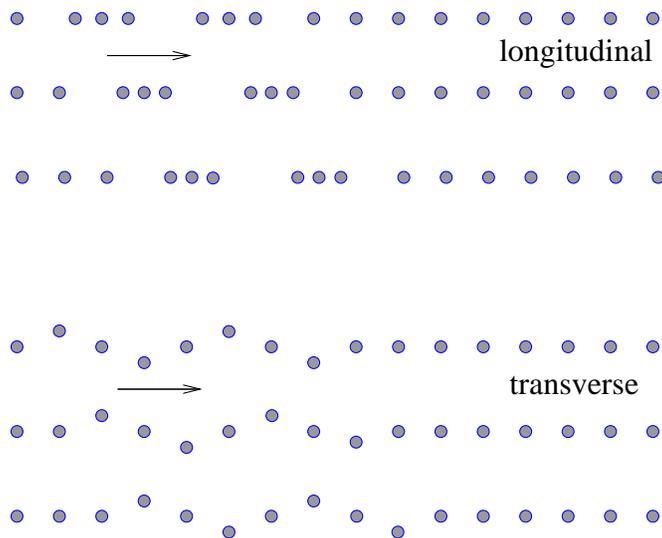
With these replacements, we can immediately write down the density of states:

$$D(\omega) = \frac{3}{2} \cdot \frac{V}{\pi^2 c_{\text{sound}}^3} \cdot \omega^2$$

for the range of frequencies ω where the soundmodes exist as such. A simple way to see that this formula can't persist up to $\omega = \infty$ is that these are modes of vibration of the positions of N atoms; these positions are specified by $3N$ coordinates. There are therefore exactly $3N$ modes! [Recall from 8.03 that there are two useful perspectives (*i.e.* bases) here: the vibrations of each atom, or the Fourier basis of normal modes which diagonalize the energy.]

Debye model of solid

Debye suggested a reasonable approximate way to take this into account:

$$3N = \int_0^{\omega_D} d\omega \; D(\omega)$$

this defines ω_D, the Debye frequency, which then serves as a high-frequency cutoff on all the integrals, a "UV cutoff". This gives

$$3N = \frac{V}{2\pi^2 c_s^3}\omega_D^3 \quad \Longrightarrow \quad \omega_D = \left(6\pi^2\right)^{1/3} c_s/a$$

where $a \equiv \left(\frac{V}{N}\right)^{1/3}$ is the average interatomic spacing.

ω_D defines a temperature Θ_D, the Debye temperature,

$$\hbar\omega_D \equiv k_B\Theta_D, \quad i.e. \;\; \Theta_D = \left(6\pi^2\right)^{1/3}\frac{\hbar}{k_B}c_s/a$$

This approximation does a good job if we ask the right questions: it makes an error at the high-frequency end of the ω integrals; but the large-ω physics is suppressed by the Boltzmann factor, as long as $T \ll \Theta_D$. A more correct answer depends on details of the crystal structure – *e.g.* is it a cubic lattice, is it a diamond lattice, is it a pyrochlore lattice.

Following our previous analysis of light in thermal equilibrium, the energy density in atomic vibrations ('phonons') in the Debye model is:

$$\frac{U}{V} = \int_0^{\omega_D} d\omega \; D(\omega)\langle\epsilon(\omega)\rangle = \frac{3}{2}\frac{\hbar}{\pi^2 c_s^3}\int_0^{\omega_D}\frac{d\omega\;\omega^3}{e^{\hbar\omega/k_BT} - 1}$$

Numerically, this gives a heat capacity which looks like this:
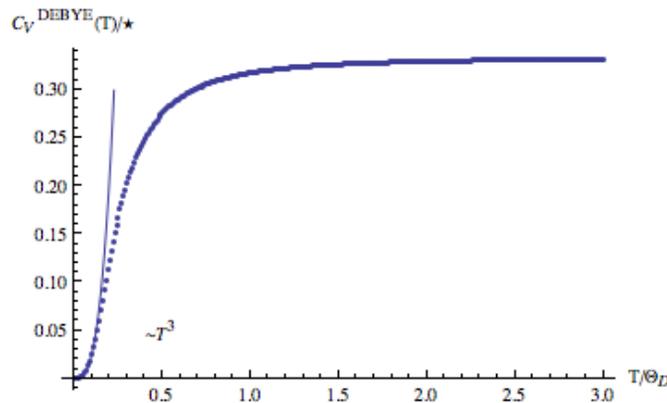
(the quantity $\star$ which sets the units on the vertical axis is $V\frac{3}{2}\frac{\hbar}{\pi^2 c_s^3}\left(\frac{k_B}{\hbar}\right)^4$.) To get some intuition for this answer, we consider ...

Limits

This problem is a little more complicated than the EM problem – there are two energy scales involved: T and Θ_D.

$\boxed{\text{High } T : T \gg \Theta_D}$

(This regime is less interesting since it's where we know the model is wrong.) In this regime, we can Taylor expand the Boltzmann factor $e^{-\beta\hbar\omega} \sim 1 - \beta\hbar\omega...$:

$$\frac{U}{V} = \frac{3}{2}\frac{\hbar}{\pi^2 c_s^3}\int_0^{\omega_D}\frac{d\omega\,\omega^3}{\hbar\omega/k_B T} = \frac{3}{2}\frac{\hbar}{\pi^2 c_s^3}\frac{k_B T}{\hbar}\frac{\omega_D^3}{3}$$

The $\hbar$s cancel!

$$= \frac{3}{2}\frac{k_B T}{\pi^2 c_s^3}\frac{1}{3}(6\pi^2)\frac{c_s^3}{V}N = \frac{3}{2}k_B T\frac{N}{V}$$

$$U = \frac{3}{2}Nk_B T, \qquad C_V = \frac{3}{2}Nk_B \qquad \text{classical equipartition of } 3N \text{ oscillators}$$

$\boxed{\text{Low } T : T \ll \Theta_D}$

At low enough temperatures, the Debye cutoff doesn't matter, so the model does a good job.

$$\frac{U}{V} = \frac{3}{2}\frac{\hbar}{\pi^2 c_s^3}\left(\frac{k_B T}{\hbar}\right)^4 \underbrace{\int_0^{\omega_D/T\to\infty}\frac{dx\,x^3}{e^x - 1}}_{=\pi^4/15 \text{ again}} = \frac{3}{2}\frac{\pi^2}{15}\frac{k_B^4 T^4}{\hbar^3 c_s^3}$$

$$\boxed{C_V = V\frac{6\pi^2}{15}\frac{k_B^4}{\hbar^3 c_s^3}T^3}$$

The answer is the same as blackbody radiation with $c \to c_s$ and a factor of $3/2$ to account for the longitudinal polarization.

Translating this using the def of Θ_D ($\frac{Vk_B^3}{\hbar^3 c_s^3} = \frac{6\pi^2 N}{\Theta_D^3}$)

$$\boxed{C_V = \frac{12\pi^4}{5}Nk_B\left(\frac{T}{\Theta_D}\right)^3} \qquad \text{for } T \ll \Theta_D$$

This is the dominant contribution to the heat capacity at low temperatures of solids which are not conductors. (As we'll see in Chapter 9, conduction electrons contribute $C_V \propto T$ at low temperatures. This is larger.)

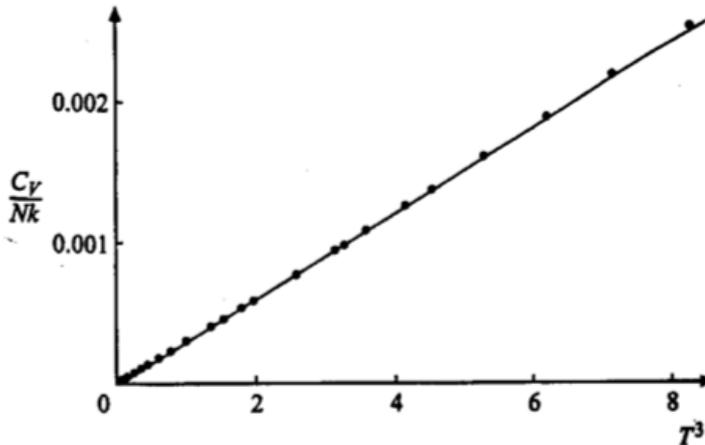**Compare to experiment** (Figures from Baierlein)

Figure 6.7 The heat capacity of solid argon at low temperatures: 0.44 K to 2.02 K. The slope of the C_V versus T^3 line is well fit with $\theta_D = 92$ K. Then the upper end of the temperature range corresponds to $T/\theta_D = 2/92 = 0.022$, and so the Debye approximation should be excellent, as indeed it is. [*Source*: Leonard Finegold and Norman E. Phillips, *Phys. Rev.* 177, 1383–91 (1969).]

The slope determines Θ_D.

Table 6.2 *Some elements and their experimental Debye tempera-tures, taken from experiments in the range where the T^3 law holds. Most of the experiments were done at liquid helium temperatures and below: 4.2 K and lower.*

	θ_D (K)		θ_D (K)
Neon	75	Carbon (diamond)	2,230
Argon	93	Iron	467
Lithium	344	Cobalt	445
Sodium	158	Copper	343
Potassium	91	Zinc	327
Rubidium	56	Silver	225
Cesium	38	Gold	165
Silicon	640	Boron	1,250

Source: AIP Handbook, 3rd edn, edited by D. E. Gray (McGraw-Hill, New York, 1972).

$\omega_D \sim \Theta_D \sim \frac{c_S}{a}$. More rigid solids give bigger c_s and hence bigger Θ_D. Notice diamond.
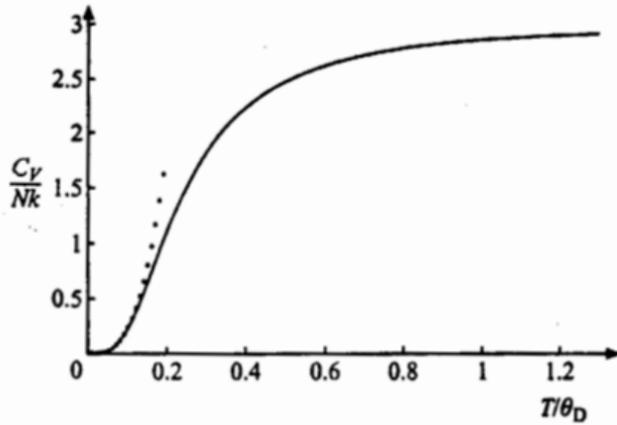
Figure 6.8 The full run of the Debye theory's heat capacity as a function of temperature. The dotted curve is a strictly T^3 curve whose third derivative at the origin agrees with the Debye theory's third derivative. Evidently the T^3 behavior is restricted to temperatures below $T \cong 0.1\theta_D$. Indeed, when $T \leqslant 0.1\theta_D$, the T^3 form differs from the exact value by 1 percent or less. At the other limit, the heat capacity has reached 95 percent of its asymptotic value when $T/\theta_D = 1$, specifically, $C_V/Nk = (0.952) \times 3$ at $T = \theta_D$.
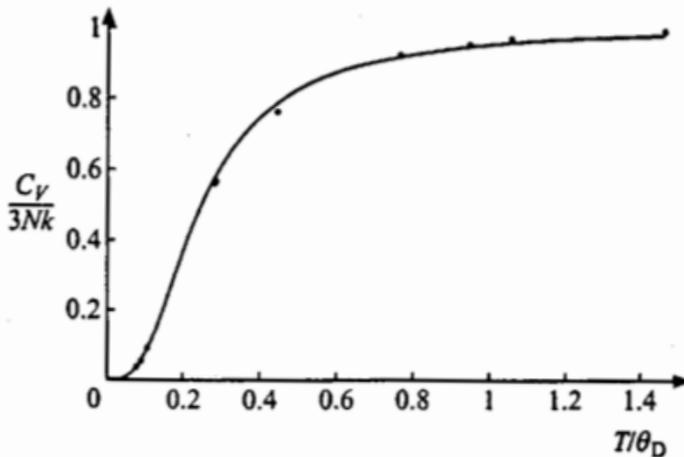

Figure 6.9 The ratio $C_V/3Nk$ versus T/θ_D for copper, as presented by Debye, who chose $\theta_D = 309$ K. The experiments provided C_P; Debye corrected to C_V before plotting. (The maximum correction was 3.6 percent.) [*Source:* Peter Debye, *Ann. Phys. (Leipzig)* 39, 789–839 (1912).]

The Debye model does a lovely job of parametrizing our ignorance of the microscopic physics in terms of just one parameter, which can then be measured. This is a nice example of an *effective field theory*: it describes the long-wavelength physics of a system in terms of a continuum of modes; we know this description breaks down at some *UV cutoff scale* (here the Debye frequency); dependence on the physics at such short wavelengths is parametrized in terms of a few parameters (here, *e.g.* the sound speed). Other examples of such theories include the Standard Model of particle physics.