Physics 127a: Class Notes

Lecture 16: Photons and Phonons

The thermodynamics of electromagnetic radiation in a cavity or of the vibrational motion of a crystal can be treated in two equivalent ways:

1. an assembly of harmonic oscillators with quantized energy levels $(n + \frac{1}{2})\hbar\omega_s$, with ω_s, $s = 1, 2, \ldots$ the frequencies of the normal modes of the cavity or crystal;

2. an ideal gas of identical, indistinguishable quanta (photons or phonons) with the energy of a single quanta for the mode s equal to $\hbar\omega_s$, so that for n quanta the contribution to the energy is $n\hbar\omega_s$. The *vacuum state* with no quanta present has the zero point energy $\frac{1}{2}\hbar\omega_s$ for each mode. The quanta are Bosons, but with chemical potential $\mu = 0$, since their number is not conserved.

The equivalence is fundamental in the quantum mechanics of these systems (wave-particle duality), but can easily be seen from the consistency of the statistical mechanical description of the two approaches:

$$Q = \mathcal{Q} = \prod_s \sum_{n_s} e^{-\beta\hbar\omega_s} = \prod_s \frac{1}{1 - e^{-\beta\hbar\omega_s}}, \tag{1}$$

$$A = \Omega = kT \sum_s \ln\left(1 - e^{-\beta\hbar\omega_s}\right). \tag{2}$$

Note that the canonical description of the first approach, and the grand canonical description of the second approach with $\mu = 0$ are identical, and formulas based on either approach may be used. In these expressions, and from now on, I have left out the zero point energy, since it is not relevant to the thermodynamics. (It is also infinite for the e.m. case!)

Photons

For a cavity of sides L with periodic boundary conditions the modes are labelled by the wave vector $\mathbf{k} = \frac{2\pi}{L}(l, m, n)$ and one of 2 polarizations. The spectrum is $\omega_{\mathbf{k}} = ck$, with c the speed of light. As usual, for L large we replace the sum over discrete wave vectors by an integral over a continuum, which for integrands that only depend on ω or $|\mathbf{k}|$ is

$$2\sum_{\mathbf{k}} \cdots \rightarrow 2\frac{V}{(2\pi)^3} \int_0^\infty 4\pi k^2 \cdots dk = V \int_0^\infty g(\omega) \cdots d\omega \tag{3}$$

with the density of states (no of states per unit frequency integral) for unit volume

$$g(\omega) = \frac{\omega^2}{\pi^2 c^3}. \tag{4}$$

The energy per volume is

$$u = \frac{U}{V} = \int_0^\infty g(\omega)\hbar\omega\, n_B(\omega)\, d\omega \tag{5}$$

with $n_B(\omega) = (e^{\beta\hbar\omega} - 1)^{-1}$ the Bose function. The energy spectrum $\varepsilon(\omega) = g(\omega)\hbar\omega\, n_B(\omega)$ such that $u = \int \varepsilon(\omega)\, d\omega$ is

$$\varepsilon(\omega) = \frac{\hbar}{\pi^2 c^3}\frac{\omega^3}{e^{\beta\hbar\omega} - 1} \tag{6}$$

is known as the Planck distribution. Notice that without the quantum effects (e.g. expand at low frequencies, or high T) $\varepsilon(\omega) = (\pi^2 c^3)^{-1} kT \, \omega^2$ which leads to a divergent total energy—one of the paradoxes of classical mechanics that led to the quantum theory.

The total energy per volume is

$$u = \left(\frac{8\pi}{h^3 c^3}\right) (kT)^4 \int_0^\infty dx \frac{x^3}{e^x - 1}. \tag{7}$$

The integral evaluates to $\pi^4/15$. The energy flux p from a nonreflecting surface at temperature T must balance the energy incident from the radiation giving

$$p = \frac{1}{4} uc = \sigma T^4 \tag{8}$$

yielding an expression for Stefan's constant σ.

The photons also exert a pressure on a bounding container. From the general arguments we know for the spectrum $\varepsilon_k \propto k$ the pressure is

$$P = \frac{1}{3} u. \tag{9}$$

This can also be derived using $PV = \ln \mathcal{Q}$, and integrating the resulting integral by parts.

Phonons

The *Debye model* for the vibrational degrees of freedom of a crystal is very similar, except we must recognize that there are only a finite number of degrees of freedom in the crystal, so there is a maximum wave vector cutoff to the sums.

In the Debye model the dispersion relation of the modes is *approximated* by the small wave vector expressions, which are linear—the longitudinal sound (speed c_l, one polarization) and transverse sound (speed c_t, two polarizations) that can be derived using the equations of macroscopic elasticity theory. The density of states, in analogy with Eq. (4) is

$$g(\omega) = \frac{\omega^2}{2\pi^2} \left(\frac{1}{c_l^3} + \frac{2}{c_t^3}\right) = \frac{3\omega^2}{2\pi^2 \bar{c}^3} \tag{10}$$

where $\bar{c}$ is an average speed *defined* by this expression.

In the sum over modes we define a cutoff at a the *Debye frequency* ω_D

$$\sum_s \cdots \rightarrow V \int_0^{\omega_D} d\omega \, g(\omega) \cdots \tag{11}$$

with ω_D defined such that the total number of modes is the number of dynamical degrees of freedom $3N$

$$\int_0^{\omega_D} d\omega \, g(\omega) = \frac{\omega_D^3}{2\pi^2 \bar{c}^3} = \frac{3N}{V}. \tag{12}$$

This gives the result

$$\omega_D = (6\pi^2 N/V)^{1/2} \bar{c}. \tag{13}$$

This corresponds to a wave vector of order the inverse atomic spacing. The temperature $\theta_D = \hbar\omega_D/k$ is called the Debye temperature. For many solids θ_D is comparable to room temperature (e.g diamond, 1850K; aluminum, 398K; lead, 88K).
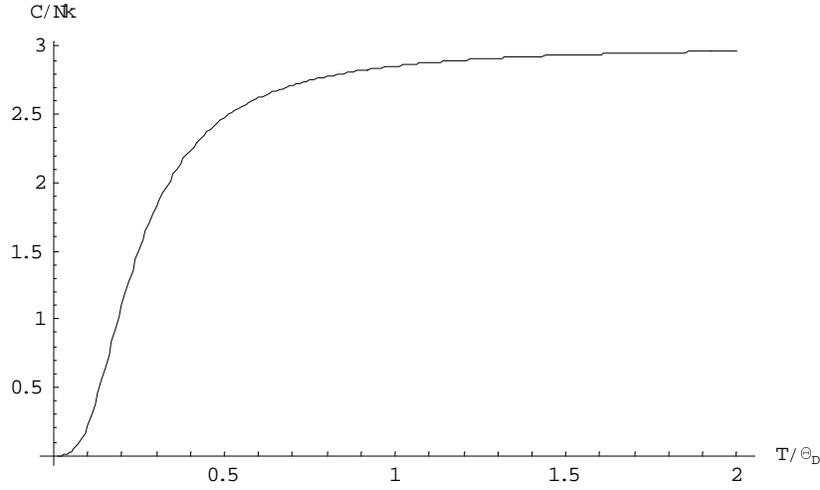
Figure 1: Debye specific heat C/Nk as a function of T/θ_D.

The energy U and specific heat $C = dU/dT$ are now readily calculated. Scaling the integration variable gives

$$C(T) = 3Nk \left(\frac{3}{x_0^3}\right) \int_0^{x_0} \frac{x^4 e^x}{(e^x - 1)^2} dx \tag{14}$$

with $x_0 = \hbar\omega_D/kT$. This is the *Debye formula* for the specific heat of a crystal. Notice that the result only depends on T/θ_D. At small T the upper limit of the integration may be replaced by ∞, when the integral evaluates to $4\pi^4/15$, so that

$$C(T \to 0) = 3Nk \left(\frac{3}{x_0^3}\right) \int_0^{\infty} \frac{x^4 e^x}{(e^x - 1)^2} dx = Nk \frac{12\pi^4}{5} \left(\frac{T}{\theta_D}\right)^3. \tag{15}$$

For large T, i.e. $kT \gg \hbar\theta_D$ we get (expand the exponentials in the integrand) the classical equipartition result $C \to 3Nk$. The T^3 low temperature expression is only a good approximation for *very* low temperatures, e.g. better than 3% below $0.1\theta_D$.

Counting States in a Periodic System

We are often interested in periodic systems such as a crystal. The periodicity is defined by the *lattice* which is the set of points (lattice vectors) formed from the *primitive lattice vectors* $\mathbf{a}$, $\mathbf{b}$, $\mathbf{c}$

$$\mathbf{x}_{l,m,n} = l\mathbf{a} + m\mathbf{b} + n\mathbf{c}, \qquad l, m, m \text{ integers.} \tag{16}$$

The vectors $\mathbf{a}$, $\mathbf{b}$, $\mathbf{c}$ define a parallelepiped called the *primitive unit cell*, that is the smallest repeat unit of the structure (the red region in the figure). The volume of the primitive unit cell is $\mathbf{a} \cdot \mathbf{b} \times \mathbf{c}$. The periodic structure is formed by copying the contents of this parallelepiped to every lattice point. The states (phonons, electron eigenstates, vibrational modes etc.) in a periodic system such as a crystal are no longer simple plane waves. However *Bloch's theorem* tells us that the states are still labelled by a wave vector $\mathbf{k}$. The displacement of the ith atom in the unit cell at $\mathbf{x}_{l,m,n}$ in a vibrational mode, for example, in the state labelled by $\mathbf{k}$ takes the form

$$\mathbf{u}_{\mathbf{k}}^{(i)}(l, m, n) = e^{i\mathbf{k}\cdot(l\mathbf{a}+m\mathbf{b}+n\mathbf{c})}\mathbf{e}^{(i)} \tag{17}$$
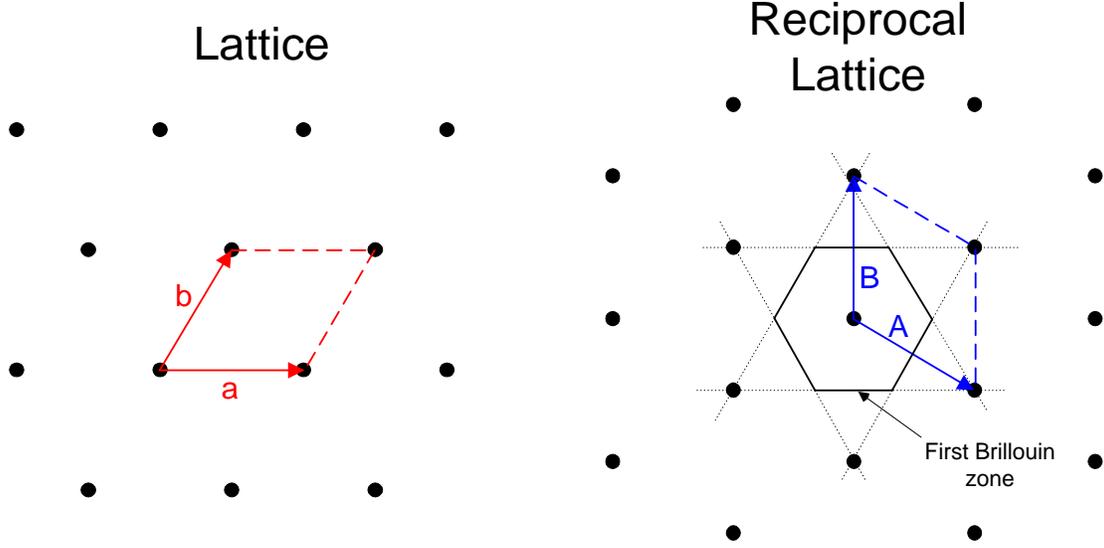
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Figure 2: Lattice and reciprocal lattice for hexagonal crystal.

and an electron wavefunction at the point $\mathbf{x} = \mathbf{x}_{l,m,n} + \Delta\mathbf{x}$ in the unit cell at $\mathbf{x}_{l,m,n}$ can be written

$$\psi_{\mathbf{k}}(\mathbf{x}) = e^{i\mathbf{k}\cdot(l\mathbf{a}+m\mathbf{b}+n\mathbf{c})}\phi(\Delta\mathbf{x}). \tag{18}$$

In each case the wave vector $\mathbf{k}$ tells us the phase change of the state on moving through a distance equal to a lattice vector i.e. a displacement that leaves the periodic structure unchanged.

It is useful to define the *reciprocal lattice* in the space of wave vectors. The primitive lattice vectors of the reciprocal lattice are defined as

$$\mathbf{A} = \frac{2\pi\mathbf{b}\times\mathbf{c}}{\mathbf{a}\cdot\mathbf{b}\times\mathbf{c}}, \ \ \mathbf{B} = \frac{2\pi\mathbf{c}\times\mathbf{a}}{\mathbf{a}\cdot\mathbf{b}\times\mathbf{c}}, \ \ \mathbf{C} = \frac{2\pi\mathbf{a}\times\mathbf{b}}{\mathbf{a}\cdot\mathbf{b}\times\mathbf{c}}, \tag{19}$$

and $\mathbf{A}$, $\mathbf{B}$, $\mathbf{C}$ define a parallelepiped which is the unit cell of the reciprocal lattice (the blue region in the figure). Any vector in the lattice

$$\mathbf{G} = l'\mathbf{A} + m'\mathbf{B} + n'\mathbf{C}, \qquad l', m', n' \text{ integers.} \tag{20}$$

is a *reciprocal lattice vector*.

The importance of the reciprocal lattice vector is that wave vectors differing by any $\mathbf{G}$ (i.e. $\mathbf{k}$ and $\mathbf{k}' = \mathbf{k} + \mathbf{G}$) define the *same* state via Eqs. (17) and (18) since $\mathbf{G}\cdot\mathbf{x}_{l,m,n} = 2\pi \times$ integer. This means that in counting the states we must restrict the $\mathbf{k}$ to lie *within a single unit cell of the reciprocal lattice*. The volume of the reciprocal lattice unit cell is $8\pi^3/\mathbf{a}\cdot\mathbf{b}\times\mathbf{c}$ and the volume of k-space per state is $8\pi^3/V$ (take periodic boundary conditions over a volume V). Thus the number of wave vectors corresponding to distinct states is $V/\mathbf{a}\cdot\mathbf{b}\times\mathbf{c}$ *i.e. the number of unit cells in the crystal*. Rather than the unit cell of the reciprocal lattice delineated by $\mathbf{A}$, $\mathbf{B}$, $\mathbf{C}$ is is convenient to use the *first Brillouin zone* which retains the rotational symmetry of the crystal. This unit cell may be defined as the region such that each point is *nearer to the origin than to any other reciprocal lattice point* $\mathbf{G}$ (see Fig. (2). It is easily constructed by the *perpendicular plane* construction: draw planes that bisect each reciprocal lattice vector $\mathbf{G}$ perpendicularly, and then the first Brillouiin zone is the smallest volume entirely enclosed by the planes.

The thermodynamics is giving by summing over state of given frequency ω or energy ε. We therefore need to calculate the density of states. e.g. $g(\omega)$. Since $g(\omega)d\omega$ gives the number of states between ω and

$\omega + d\omega$, this may be calculated as the volume in k-space between frequency surfaces ω and $\omega + d\omega$ divided by the volume of k-space per state:

$$\sum_{\mathbf{k}} \rightarrow \int d\omega \, g(\omega) \tag{21}$$

with

$$g(\omega) = \frac{1}{8\pi^3} \int \frac{dS_\omega}{v_G}. \tag{22}$$

Here v_G is the group speed $d\omega/dk$ (which gives us the distance dk between surfaces separated by $d\omega$), and the integral is the surface integral over the constant ω surface.