

5.6: The Ideal Bose Gas

Crystalline solids support propagating waves called *phonons*, which are quantized vibrations of the lattice. Recall that the quantum mechanical Hamiltonian for a single harmonic oscillator, $\hat{H} = \frac{p^2}{2m} + \frac{1}{2}m\omega_0^2 q^2$, may be written as $\hat{H} = \hbar\omega_0(a^\dagger a + \frac{1}{2})$, where a and a^\dagger are 'ladder operators' satisfying commutation relations $[a, a^\dagger] = 1$.

One-dimensional chain

Consider the linear chain of masses and springs depicted in Figure [lchain]. We assume that our system consists of N mass points on a large ring of circumference L . In equilibrium, the masses are spaced evenly by a distance $b = L/N$. That is, $x_n^0 = nb$ is the equilibrium position of particle n . We define $u_n = x_n - x_n^0$ to be the difference between the position of mass n and The Hamiltonian is then

$$\begin{aligned}\hat{H} &= \sum_n \left[\frac{p_n^2}{2m} + \frac{1}{2}\kappa (x_{n+1} - x_n - a)^2 \right] \\ &= \sum_n \left[\frac{p_n^2}{2m} + \frac{1}{2}\kappa (u_{n+1} - u_n)^2 \right] + \frac{1}{2}N\kappa(b-a)^2,\end{aligned}$$

where a is the unstretched length of each spring, m is the mass of each mass point, κ is the force constant of each spring, and N is the total number of mass points. If $b \neq a$ the springs are under tension in equilibrium, but as we see this only leads to an additive constant in the Hamiltonian, and hence does not enter the equations of motion.

The classical equations of motion are

$$\begin{aligned}\dot{u}_n &= \frac{\partial \hat{H}}{\partial p_n} = \frac{p_n}{m} \\ \dot{p}_n &= -\frac{\partial \hat{H}}{\partial u_n} = \kappa (u_{n+1} + u_{n-1} - 2u_n).\end{aligned}$$

Taking the time derivative of the first equation and substituting into the second yields

$$\ddot{u}_n = \frac{\kappa}{m} (u_{n+1} + u_{n-1} - 2u_n). \quad (5.6.1)$$

We now write

$$u_n = \frac{1}{\sqrt{N}} \sum_k \tilde{u}_k e^{ikna}, \quad (5.6.2)$$

where periodicity $u_{N+n} = u_n$ requires that the k values are quantized so that $e^{ikNa} = 1$, $k = 2\pi j/Na$ where $j \in \{0, 1, \dots, N-1\}$. The inverse of this discrete Fourier transform is

$$\tilde{u}_k = \frac{1}{\sqrt{N}} \sum_n u_n e^{-ikna}. \quad (5.6.3)$$

Note that \tilde{u}_k is in general complex, but that $\tilde{u}_k^* = \tilde{u}_{-k}$. In terms of the \tilde{u}_k , the equations of motion take the form

$$\ddot{\tilde{u}}_k = -\frac{2\kappa}{m} (1 - \cos(ka)) \tilde{u}_k \equiv -\omega_k^2 \tilde{u}_k. \quad (5.6.4)$$


Thus, each \tilde{u}_k is a normal mode, and the normal mode frequencies are

$$\omega_k = 2\sqrt{\frac{\kappa}{m}} \left| \sin\left(\frac{1}{2}ka\right) \right|. \quad (5.6.5)$$

The density of states for this band of phonon excitations is

$$\begin{aligned}g(\varepsilon) &= \int_{-\pi/a}^{\pi/a} \frac{dk}{2\pi} \delta(\varepsilon - \hbar\omega_k) \\ &= \frac{2}{\pi a} (J^2 - \varepsilon^2)^{-1/2} \Theta(\varepsilon) \Theta(J - \varepsilon),\end{aligned}$$

where $J = 2\hbar\sqrt{\kappa/m}$ is the phonon bandwidth. The step functions require $0 \leq \varepsilon \leq J$; outside this range there are no phonon energy levels and the density of states accordingly vanishes.

 [lchain] A linear chain of masses and springs. The black circles represent the equilibrium positions of the masses. The displacement of mass n relative to its equilibrium value is u_n .

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The entire theory can be quantized, taking $[p_n, u_{n'}] = -i\hbar\delta_{nn'}$. We then define

$$p_n = \frac{1}{\sqrt{N}} \sum_k \tilde{p}_k e^{ikna}, \quad \tilde{p}_k = \frac{1}{\sqrt{N}} \sum_n p_n e^{-ikna}, \quad (5.6.6)$$

in which case $[\tilde{p}_k, \tilde{u}_{k'}] = -i\hbar\delta_{kk'}$. Note that $\tilde{u}_k^\dagger = \tilde{u}_{-k}$ and $\tilde{p}_k^\dagger = \tilde{p}_{-k}$. We then define the ladder operator

$$a_k = \left(\frac{1}{2m\hbar\omega_k} \right)^{1/2} \tilde{p}_k - i \left(\frac{m\omega_k}{2\hbar} \right)^{1/2} \tilde{u}_k \quad (5.6.7)$$

and its Hermitian conjugate a_k^\dagger , in terms of which the Hamiltonian is

$$\hat{H} = \sum_k \hbar\omega_k \left(a_k^\dagger a_k + \frac{1}{2} \right), \quad (5.6.8)$$

which is a sum over independent harmonic oscillator modes. Note that the sum over k is restricted to an interval of width 2π , $k \in [-\frac{\pi}{a}, \frac{\pi}{a}]$, which is the *first Brillouin zone* for the one-dimensional chain structure. The state at wavevector $k + \frac{2\pi}{a}$ is identical to that at k , as we see from Equation [uFT].

General theory of lattice vibrations

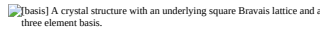
The most general model of a harmonic solid is described by a Hamiltonian of the form

$$\hat{H} = \sum_{\mathbf{R}, i} \frac{\mathbf{p}_i^2(\mathbf{R})}{2M_i} + \frac{1}{2} \sum_{i,j} \sum_{\alpha,\beta} \sum_{\mathbf{R}, \mathbf{R}'} u_i^\alpha(\mathbf{R}) \Phi_{ij}^{\alpha\beta}(\mathbf{R} - \mathbf{R}') u_j^\beta(\mathbf{R}'), \quad (5.6.9)$$

where the *dynamical matrix* is

$$\Phi_{ij}^{\alpha\beta}(\mathbf{R}-\mathbf{R}') = \frac{\partial^2 U}{\partial u_i^\alpha(\mathbf{R}) \partial u_j^\beta(\mathbf{R}')}, \quad (5.6.10)$$

where U is the potential energy of interaction among all the atoms. Here we have simply expanded the potential to second order in the local displacements $u_i^\alpha(\mathbf{R})$. The lattice sites \mathbf{R} are elements of a Bravais lattice. The indices i and j specify *basis elements* with respect to this lattice, and the indices α and β range over $\{1, \dots, d\}$, the number of possible directions in space. The subject of crystallography is beyond the scope of these notes, but, very briefly, a Bravais lattice in d dimensions is specified by a set of d linearly independent *primitive direct lattice vectors* \mathbf{a}_i , such that any point in the Bravais lattice may be written as a sum over the primitive vectors with integer coefficients: $\mathbf{R} = \sum_{i=1}^d n_i \mathbf{a}_i$. The set of all such vectors $\{\mathbf{R}\}$ is called the *direct lattice*. The direct lattice is closed under the operation of vector addition: if \mathbf{R} and \mathbf{R}' are points in a Bravais lattice, then so is $\mathbf{R} + \mathbf{R}'$.



[basis] A crystal structure with an underlying square Bravais lattice and a three element basis.

A crystal is a periodic arrangement of lattice sites. The fundamental repeating unit is called the *unit cell*. Not every crystal is a Bravais lattice, however. Indeed, Bravais lattices are special crystals in which there is only one atom per unit cell. Consider, for example, the structure in Figure [basis]. The blue dots form a square Bravais lattice with primitive direct lattice vectors $\mathbf{a}_1 = a \hat{\mathbf{x}}$ and $\mathbf{a}_2 = a \hat{\mathbf{y}}$, where a is the *lattice constant*, which is the distance between any neighboring pair of blue dots. The red squares and green triangles, along with the blue dots, form a *basis* for the crystal structure which label each *sublattice*. Our crystal in Figure [basis] is formally classified as a *square Bravais lattice with a three element basis*. To specify an arbitrary site in the crystal, we must specify both a direct lattice vector \mathbf{R} as well as a basis index $j \in \{1, \dots, r\}$, so that the location is $\mathbf{R} + \boldsymbol{\eta}_j$. The vectors $\{\boldsymbol{\eta}_j\}$ are the *basis vectors* for our crystal structure. We see that a general crystal structure consists of a repeating unit, known as a *unit cell*. The centers (or corners, if one prefers) of the unit cells form a Bravais lattice. Within a given unit cell, the individual sublattice sites are located at positions $\boldsymbol{\eta}_j$ with respect to the unit cell position \mathbf{R} .

Upon diagonalization, the Hamiltonian of Equation [Hcrystal] takes the form

$$\hat{H} = \sum_{\mathbf{k}, a} \hbar \omega_a(\mathbf{k}) \left(A_a^\dagger(\mathbf{k}) A_a(\mathbf{k}) + \frac{1}{2} \right), \quad (5.6.11)$$

where

$$[A_a(\mathbf{k}), A_b^\dagger(\mathbf{k}')] = \delta_{ab} \delta_{\mathbf{k}\mathbf{k}'}. \quad (5.6.12)$$

The eigenfrequencies are solutions to the eigenvalue equation

$$\sum_{j, \beta} \Phi_{ij}^{\alpha\beta}(\mathbf{k}) \mathbf{e}_{j\beta}^{(a)}(\mathbf{k}) = M_i \omega_a^2(\mathbf{k}) \mathbf{e}_{i\alpha}^{(a)}(\mathbf{k}), \quad (5.6.13)$$

where

$$\tilde{\Phi}_{ij}^{\alpha\beta}(\mathbf{k}) = \sum_{\mathbf{R}} \Phi_{ij}^{\alpha\beta}(\mathbf{R}) e^{-i\mathbf{k} \cdot \mathbf{R}}. \quad (5.6.14)$$

Here, \mathbf{k} lies within the first *Brillouin zone*, which is the unit cell of the *reciprocal lattice* of points \mathbf{G} satisfying $e^{i\mathbf{G} \cdot \mathbf{R}} = 1$ for all \mathbf{G} and \mathbf{R} . The reciprocal lattice is also a Bravais lattice, with primitive reciprocal lattice vectors \mathbf{b}_i , such that any point on the reciprocal lattice may be written $\mathbf{G} = \sum_{i=1}^d m_i \mathbf{b}_i$. One also has that $\mathbf{a}_i \cdot \mathbf{b}_j = 2\pi \delta_{ij}$. The index a ranges from 1 to $d \cdot r$ and labels the *mode* of oscillation at wavevector \mathbf{k} . The vector $\mathbf{e}_{i\alpha}^{(a)}(\mathbf{k})$ is the *polarization vector* for the \mathbf{a}^{th} phonon branch. In solids of high symmetry, phonon modes can be classified as longitudinal or transverse excitations.

For a crystalline lattice with an r -element basis, there are then $d \cdot r$ phonon modes for each wavevector \mathbf{k} lying in the first Brillouin zone. If we impose periodic boundary conditions, then the \mathbf{k} points within the first Brillouin zone are themselves quantized, as in the $d = 1$ case where we found $k = 2\pi n/L$. There are N distinct \mathbf{k} points in the first Brillouin zone – one for every direct lattice site. The total number of modes is then $d \cdot r \cdot N$, which is the total number of translational degrees of freedom in our system: rN total atoms (N unit cells each with an r atom basis) each free to vibrate in d dimensions. Of the $d \cdot r$ branches of phonon excitations, d of them will be *acoustic modes* whose frequency vanishes as $\mathbf{k} \rightarrow 0$. The remaining $d(r - 1)$ branches are *optical modes* and oscillate at finite frequencies. Basically, in an acoustic mode, for \mathbf{k} close to the (Brillouin) zone center $\mathbf{k} = 0$, all the atoms in each unit cell move together in the same direction at any moment of time. In an optical mode, the different basis atoms move in different directions.

There is no number conservation law for phonons – they may be freely created or destroyed in anharmonic processes, where two photons with wavevectors \mathbf{k} and \mathbf{q} can combine into a single phonon with wavevector $\mathbf{k} + \mathbf{q}$, and *vice versa*. Therefore the chemical potential for phonons is $\mu = 0$. We define the density of states $g_a(\omega)$ for the \mathbf{a}^{th} phonon mode as

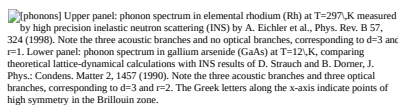
$$g_a(\omega) = \frac{1}{N} \sum_{\mathbf{k}} \delta(\omega - \omega_a(\mathbf{k})) = \mathcal{V}_0 \int_{BZ} \frac{d^d k}{(2\pi)^d} \delta(\omega - \omega_a(\mathbf{k})), \quad (5.6.15)$$

where N is the number of unit cells, \mathcal{V}_0 is the unit cell volume of the direct lattice, and the \mathbf{k} sum and integral are over the first Brillouin zone only. Note that ω here has dimensions of frequency. The functions $g_a(\omega)$ is normalized to unity:

$$\int_0^\infty d\omega g_a(\omega) = 1. \quad (5.6.16)$$

The total phonon density of states per unit cell is given by³

$$g(\omega) = \sum_{a=1}^{dr} g_a(\omega). \quad (5.6.17)$$



[phonons] Upper panel: phonon spectrum in elemental rhodium (Rh) at $T = 297$ K measured by high precision inelastic neutron scattering (INS) by A. Eichler *et al.*, *Phys. Rev. B* 57, 324 (1998). Note the three acoustic branches and no optical branches, corresponding to $d=3$ and $r=1$. Lower panel: phonon spectrum in gallium arsenide (GaAs) at $T = 12$ K, comparing theoretical lattice-dynamical calculations with INS results of D. Strauch and B. Dorner, *J. Phys.: Condens. Matter* 2, 1457 (1990). Note the three acoustic branches and three optical branches, corresponding to $d=3$ and $r=2$. The Greek letters along the x-axis indicate points of high symmetry in the Brillouin zone.

The grand potential for the phonon gas is

$$\begin{aligned} \Omega(T, V) &= -k_B T \ln \prod_{\mathbf{k}, a} \sum_{n_a(\mathbf{k})=0}^{\infty} e^{-\beta \hbar \omega_a(\mathbf{k}) \left(n_a(\mathbf{k}) + \frac{1}{2} \right)} \\ &= k_B T \sum_{\mathbf{k}, a} \ln \left[2 \sinh \left(\frac{\hbar \omega_a(\mathbf{k})}{2k_B T} \right) \right] \\ &= N k_B T \int_0^\infty d\omega g(\omega) \ln \left[2 \sinh \left(\frac{\hbar \omega}{2k_B T} \right) \right]. \end{aligned}$$

Note that $V = NV_0$ since there are N unit cells, each of volume V_0 . The entropy is given by $S = -\left(\frac{\partial \Omega}{\partial T}\right)_V$ and thus the heat capacity is

$$C_V = -T \frac{\partial^2 \Omega}{\partial T^2} = Nk_B \int_0^\infty d\omega g(\omega) \left(\frac{\hbar\omega}{2k_B T} \right)^2 \text{csch}^2 \left(\frac{\hbar\omega}{2k_B T} \right) \quad (5.6.18)$$

Note that as $T \rightarrow \infty$ we have $\text{csch} \left(\frac{\hbar\omega}{2k_B T} \right) \rightarrow \frac{2k_B T}{\hbar\omega}$, and therefore

$$\lim_{T \rightarrow \infty} C_V(T) = Nk_B \int_0^\infty d\omega g(\omega) = r d N k_B. \quad (5.6.19)$$

This is the classical Dulong-Petit limit of $\frac{1}{2}k_B$ per quadratic degree of freedom; there are rN atoms moving in d dimensions, hence $d \cdot rN$ positions and an equal number of momenta, resulting in a high temperature limit of $C_V = r d N k_B$.

Einstein and Debye models

Historically, two models of lattice vibrations have received wide attention. First is the so-called *Einstein model*, in which there is no dispersion to the individual phonon modes. We approximate $g_a(\omega) \approx \delta(\omega - \omega_a)$, in which case

$$C_V(T) = Nk_B \sum_a \left(\frac{\hbar\omega_a}{2k_B T} \right)^2 \text{csch}^2 \left(\frac{\hbar\omega_a}{2k_B T} \right). \quad (5.6.20)$$

At low temperatures, the contribution from each branch vanishes exponentially, since $\text{csch}^2 \left(\frac{\hbar\omega_a}{2k_B T} \right) \simeq 4 e^{-\hbar\omega_a/k_B T} \rightarrow 0$. Real solids don't behave this way.

A more realistic model, due to Debye, accounts for the low-lying acoustic phonon branches. Since the acoustic phonon dispersion vanishes linearly with $|\mathbf{k}|$ as $\mathbf{k} \rightarrow 0$, there is no temperature at which the acoustic phonons 'freeze out' exponentially, as in the case of Einstein phonons. Indeed, the Einstein model is appropriate in describing the $d(r-1)$ optical phonon branches, though it fails miserably for the acoustic branches.

In the vicinity of the zone center $\mathbf{k} = 0$ (also called Γ in crystallographic notation) the d acoustic modes obey a linear dispersion, with $\omega_a(\mathbf{k}) = c_a(\hat{\mathbf{k}})k$. This results in an acoustic phonon density of states in $d = 3$ dimensions of

where \bar{c} is an average acoustic phonon velocity (speed of sound) defined by

$$\frac{3}{\bar{c}^3} = \sum_a \int \frac{d\mathbf{k}}{4\pi} \frac{1}{c_a^3(\mathbf{k})} \quad (5.6.21)$$

and ω_{D} is a cutoff known as the *Debye frequency*. The cutoff is necessary because the phonon branch does not extend forever, but only to the boundaries of the Brillouin zone. Thus, ω_{D} should roughly be equal to the energy of a zone boundary phonon. Alternatively, we can define ω_{D} by the normalization condition

$$\int_0^{\omega_{\text{D}}} d\omega g(\omega) = 3 \quad \text{or} \quad \omega_{\text{D}} = \left(\frac{6\pi^2}{CV} \right)^{1/3} \bar{c}.$$

This allows us to write

The specific heat due to the acoustic phonons is then

$$C_{V,T} = 9Nk_B \left(\frac{T}{\Theta_D} \right)^3 \int_0^{\Theta_D/T} dx x^3 \text{csch}^2 x \quad (5.6.22)$$

where $\Theta_D = \hbar\omega_{\text{D}}/k_B$ is the *Debye temperature* and

$$\phi(x) = \int_0^x dt t^4 \text{csch}^2 t = \begin{cases} \frac{1}{3}x^3 & x \rightarrow 0 \\ \frac{\pi^4}{30} & x \rightarrow \infty. \end{cases} \quad (5.6.22)$$

Therefore,

$$C_V(T) = \begin{cases} \frac{12\pi^4}{5} Nk_B \left(\frac{T}{\Theta_D} \right)^3 & T \ll \Theta_D \\ 3Nk_B & T \gg \Theta_D. \end{cases} \quad (5.6.23)$$

Thus, the heat capacity due to acoustic phonons obeys the Dulong-Petit rule in that $C_V(T \rightarrow \infty) = 3Nk_B$, corresponding to the three acoustic degrees of freedom per unit cell. The remaining contribution of $3(r-1)Nk_B$ to the high temperature heat capacity comes from the optical modes not considered in the Debye model. The low temperature T^3 behavior of the heat capacity of crystalline solids is a generic feature, and its detailed description is a triumph of the Debye model.

Melting and the Lindemann criterion

Atomic fluctuations in a crystal

For the one-dimensional chain, Equation [5.6.18] gives

$$\tilde{u}_k = i \left(\frac{\hbar}{2m\omega_k} \right)^{1/2} (a_k - a_k^\dagger). \quad (5.6.24)$$

Therefore the RMS fluctuations at each site are given by

$$\begin{aligned} \langle u_n^2 \rangle &= \frac{1}{N} \sum_k \langle \tilde{u}_k \tilde{u}_{-k} \rangle \\ &= \frac{1}{N} \sum_k \frac{\hbar}{m\omega_k} \left(n(k) + \frac{1}{2} \right), \end{aligned}$$

where $n(k, T) = [\exp(\hbar\omega_k/k_B T) - 1]^{-1}$ is the Bose occupancy function.

[debiab] Debye temperatures (at $T = 0$) and melting points for some common elements (carbon is assumed to be diamond and not graphite). (Source: the internet!)

Element	Ag	Al	Au	C	Cd	Cr	Cu	Fe	Mn
Θ_D (K)	227	433	162	2250	210	606	347	477	409
T_{melt} (K)	962	660	1064	3500	321	1857	1083	1535	1245

Element	Ag	Al	Au	C	Cd	Cr	Cu	Fe	Mn
Element	Ni	Pb	Pt	Si	Sn	Ta	Ti	W	Zn
$\Theta_{\text{ssr}}(\text{D})$ (K)	477	105	237	645	199	246	420	383	329
T_{melt} (K)	1453	327	1772	1410	232	2996	1660	3410	420

Let us now generalize this expression to the case of a d -dimensional solid. The appropriate expression for the RMS position fluctuations of the i^{th} basis atom in each unit cell is

$$\langle \mathbf{u}_i^2(\mathbf{R}) \rangle = \frac{1}{N} \sum_{\mathbf{k}} \sum_{a=1}^{dr} \frac{\hbar}{M_{ia}(\mathbf{k}) \omega_a(\mathbf{k})} \left(n_a(\mathbf{k}) + \frac{1}{2} \right). \quad (5.6.25)$$

Here we sum over all wavevectors \mathbf{k} in the first Brillouin zone, and over all normal modes a . There are dr normal modes per unit cell d branches of the phonon dispersion $\omega_a(\mathbf{k})$. (For the one-dimensional chain with $d = 1$ and $r = 1$ there was only one such branch to consider). Note also the quantity $M_{ia}(\mathbf{k})$, which has units of mass and is defined in terms of the polarization vectors $\mathbf{e}_{i\alpha}^{(a)}(\mathbf{k})$ as

$$\frac{1}{M_{ia}(\mathbf{k})} = \sum_{\mu=1}^d |\mathbf{e}_{i\mu}^{(a)}(\mathbf{k})|^2. \quad (5.6.26)$$

The dimensions of the polarization vector are $[mass]^{-1/2}$, since the generalized orthonormality condition on the normal modes is

$$\sum_{i,\mu} M_i \mathbf{e}_{i\mu}^{(a)*}(\mathbf{k}) \mathbf{e}_{i\mu}^{(b)}(\mathbf{k}) = \delta^{ab}, \quad (5.6.27)$$

where M_i is the mass of the atom of species i within the unit cell ($i \in \{1, \dots, r\}$). For our purposes we can replace $M_{ia}(\mathbf{k})$ by an appropriately averaged quantity which we call M_i ; this 'effective mass' is then independent of the mode index a as well as the wavevector \mathbf{k} . We may then write

$$\langle \mathbf{u}_i^2 \rangle \approx \int_0^\infty d\omega g(\omega) \frac{\hbar}{M_i \omega} \cdot \left\{ \frac{1}{e^{\hbar\omega/k_B T} - 1} + \frac{1}{2} \right\}, \quad (5.6.28)$$

where we have dropped the site label \mathbf{R} since translational invariance guarantees that the fluctuations are the same from one unit cell to the next. Note that the fluctuations $\langle \mathbf{u}_i^2 \rangle$ can be divided into a temperature-dependent part $\langle \mathbf{u}_i^2 \rangle_{th}$ and a temperature-independent quantum contribution $\langle \mathbf{u}_i^2 \rangle_{qu}$, where

$$\begin{aligned} \langle \mathbf{u}_i^2 \rangle_{th} &= \frac{\hbar}{M_i} \int_0^\infty d\omega \frac{g(\omega)}{\omega} \cdot \frac{1}{e^{\hbar\omega/k_B T} - 1} \\ \langle \mathbf{u}_i^2 \rangle_{qu} &= \frac{\hbar}{2M_i} \int_0^\infty d\omega \frac{g(\omega)}{\omega}. \end{aligned}$$

Let's evaluate these contributions within the Debye model, where we replace $g(\omega)$ by

$$g(\omega) = \frac{d^3 \Omega}{(2\pi)^3} \frac{4\pi \omega^2}{v} \frac{1}{\omega} = \frac{d^3 \Omega}{(2\pi)^3} \frac{4\pi \omega}{v} \quad (5.6.29)$$

We then find

$$\langle \mathbf{u}_i^2 \rangle_{th} = \frac{\hbar}{M_i} \int_0^\infty d\omega \frac{g(\omega)}{\omega} \frac{1}{e^{\hbar\omega/k_B T} - 1} = \frac{\hbar}{M_i} \frac{d^3 \Omega}{(2\pi)^3} \frac{4\pi}{v} \int_0^\infty d\omega \frac{\omega}{e^{\hbar\omega/k_B T} - 1}$$

where

$$F_d(x) = \int_0^x ds \frac{s^{d-2}}{e^s - 1} = \begin{cases} \frac{x^{d-2}}{d-2} & x \rightarrow 0 \\ \zeta(d-1) & x \rightarrow \infty \end{cases}. \quad (5.6.29)$$

We can now extract from these expressions several important conclusions:

- The $T = 0$ contribution to the fluctuations, $\langle \mathbf{u}_i^2 \rangle_{qu}$, diverges in $d = 1$ dimensions. *Therefore there are no one-dimensional quantum solids.*
- The thermal contribution to the fluctuations, $\langle \mathbf{u}_i^2 \rangle_{th}$, diverges for any $T > 0$ whenever $d \leq 2$. This is because the integrand of $F_d(x)$ goes as s^{d-3} as $s \rightarrow 0$. *Therefore, there are no two-dimensional classical solids.*
- Both the above conclusions are valid in the thermodynamic limit. Finite size imposes a cutoff on the frequency integrals, because there is a smallest wavevector $k_{\min} \sim 2\pi/L$, where L is the (finite) linear dimension of the system. This leads to a low frequency cutoff $\omega_{\min} = 2\pi\bar{c}/L$, where \bar{c} is the appropriately averaged acoustic phonon velocity from Equation (5.6.29), which mitigates any divergences.

Lindemann melting criterion

An old phenomenological theory of melting due to Lindemann says that a crystalline solid melts when the RMS fluctuations in the atomic positions exceeds a certain fraction η of the lattice constant a . We therefore define the ratios

$$x_i^2 = \frac{\langle \mathbf{u}_i^2 \rangle}{a^2} = \frac{\langle \mathbf{u}_i^2 \rangle_{th} + \langle \mathbf{u}_i^2 \rangle_{qu}}{a^2} = \frac{\langle \mathbf{u}_i^2 \rangle_{th}}{a^2} + \frac{\langle \mathbf{u}_i^2 \rangle_{qu}}{a^2} \quad (5.6.30)$$

with $x_i = \sqrt{x_{i,th}^2 + x_{i,qu}^2} = \sqrt{\langle \mathbf{u}_i^2 \rangle} / a$.

Let's now work through an example of a three-dimensional solid. We'll assume a single element basis ($r = 1$). We have that

$$\frac{9\hbar^2/4k_B}{1 \text{ amu } \text{\AA}^2} = 109 \text{ K}. \quad (5.6.30)$$

According to table (5.6.25), the melting temperature always exceeds the Debye temperature, and often by a great amount. We therefore assume $T \gg \Theta_{\text{ssr}}(\text{D})$, which puts us in the small x limit of $F_d(x)$. We then find

$$x_{qu}^2 = \frac{\langle \mathbf{u}_i^2 \rangle_{qu}}{a^2} = \frac{\hbar}{2M_i} \frac{d^3 \Omega}{(2\pi)^3} \frac{4\pi}{v} \int_0^\infty d\omega \frac{1}{\omega} = \frac{\hbar}{2M_i} \frac{d^3 \Omega}{(2\pi)^3} \frac{4\pi}{v} \frac{1}{\omega_{\min}} \quad (5.6.31)$$

where

$$\Theta^* = \frac{109 \text{ K}}{M_i^{1/3} \cdot (a/\text{\AA})^2}. \quad (5.6.31)$$

The total position fluctuation is of course the sum $x^2 = x_{i,th}^2 + x_{i,qu}^2$. Consider for example the case of copper, with $M = 56$ amu and $a = 2.87$ Å. The Debye temperature is $\Theta_{\text{D}} = 347$ K. From this we find $x_{qu} = 0.026$, which says that at $T = 0$ the RMS fluctuations of the atomic positions are not quite three percent of the lattice spacing (the distance between neighboring copper atoms). At room temperature, $T = 293$ K, one finds $x_{th} = 0.048$, which is about twice as large as the quantum contribution. How big are the atomic position fluctuations at the melting point? According to our table, $T_{\text{melt}} = 1083$ K for copper, and from our formulae we obtain $x_{\text{melt}} = 0.096$. The Lindemann criterion says that solids melt when $x(T) \approx 0.1$.

We were very lucky to hit the magic number $x_{\text{melt}} = 0.1$ with copper. Let's try another example. Lead has $M = 208$ amu and $a = 4.95$ Å. The Debye temperature is $\Theta_{\text{D}} = 105$ K ('soft phonons'), and the melting point is $T_{\text{melt}} = 327$ K. From these data we obtain $x(T = 0) = 0.014$, $x(293 \text{ K}) = 0.050$ and $x(T = 327 \text{ K}) = 0.053$. Same ballpark.

We can turn the analysis around and predict a melting temperature based on the Lindemann criterion $x(T_{\text{melt}}) = \eta$, where $\eta \approx 0.1$. We obtain

$$T_{\text{melt}} = \frac{1}{\eta^2} \left(\frac{\Theta_{\text{D}}}{\Theta_{\text{D}}^*} \right)^2 \Theta_{\text{D}}^2$$

We call T_{melt} the *Lindemann temperature*. Most treatments of the Lindemann criterion ignore the quantum correction, which gives the -1 contribution inside the above parentheses. But if we are more careful and include it, we see that it may be possible to have $T_{\text{melt}} < 0$. This occurs for any crystal where $\Theta_{\text{D}} < \Theta_{\text{D}}^*$.

Consider for example the case of ^4He , which at atmospheric pressure condenses into a liquid at $T_c = 4.2$ K and remains in the liquid state down to absolute zero. At $p = 1$ atm, it never solidifies! Why? The number density of liquid ^4He at $p = 1$ atm and $T = 0$ K is $2.2 \times 10^{22} \text{ cm}^{-3}$. Let's say the Helium atoms want to form a crystalline lattice. We don't know *a priori* what the lattice structure will be, so let's for the sake of simplicity assume a simple cubic lattice. From the number density we obtain a lattice spacing of $a = 3.57$ Å. OK now what do we take for the Debye temperature? Theoretically this should depend on the microscopic force constants which enter the small oscillations problem (the spring constants between pairs of Helium atoms in equilibrium). We'll use the expression we derived for the Debye frequency, $\omega_{\text{D}} = \sqrt{\frac{6\pi^2}{CV} \frac{1}{\rho}}$, where V_0 is the unit cell volume. We'll take $\bar{c} = 238$ m/s, which is the speed of sound in liquid Helium at $T = 0$. This gives $\Theta_{\text{D}} = 19.8$ K. We find $\Theta^* = 2.13$ K, and if we take $\eta = 0.1$ this gives $\Theta^*/\eta^2 = 213$ K, which significantly exceeds Θ_{D} . Thus, the solid should melt because the RMS fluctuations in the atomic positions at absolute zero are huge: $x_{\text{qu}} = (\Theta_{\text{D}}^*/\Theta_{\text{D}})^{1/2} = 0.33$. By applying pressure, one can get ^4He to crystallize above $p_c = 25$ atm (at absolute zero). Under pressure, the unit cell volume V_0 decreases and the phonon velocity \bar{c} increases, so the Debye temperature itself increases.

It is important to recognize that the Lindemann criterion does not provide us with a theory of melting *per se*. Rather it provides us with a heuristic which allows us to predict roughly when a solid should melt.

Goldstone bosons

The vanishing of the acoustic phonon dispersion at $\mathbf{k} = 0$ is a consequence of *Goldstone's theorem* which says that associated with every *broken generator* of a *continuous symmetry* there is an associated bosonic gapless excitation (one whose frequency ω vanishes in the long wavelength limit). In the case of phonons, the 'broken generators' are the symmetries under spatial translation in the x , y , and z directions. The crystal selects a particular location for its center-of-mass, which breaks this symmetry. There are, accordingly, three gapless acoustic phonons.

Magnetic materials support another branch of elementary excitations known as spin waves, or *magnons*. In *isotropic magnets*, there is a global symmetry associated with rotations in internal spin space, described by the group $SU(2)$. If the system spontaneously magnetizes, meaning there is long-ranged ferromagnetic order ($\uparrow\uparrow\uparrow \dots$), or long-ranged antiferromagnetic order ($\uparrow\downarrow\uparrow \dots$), then global spin rotation symmetry is broken. Typically a particular direction is chosen for the magnetic moment (or staggered moment, in the case of an antiferromagnet). Symmetry under rotations about this axis is then preserved, but rotations which do not preserve the selected axis are 'broken'. In the most straightforward case, that of the antiferromagnet, there are two such rotations for $SU(2)$, and concomitantly two gapless magnon branches, with linearly vanishing dispersions $\omega_a(\mathbf{k})$. The situation is more subtle in the case of ferromagnets, because the total magnetization is conserved by the dynamics (unlike the total staggered magnetization in the case of antiferromagnets). Another wrinkle arises if there are long-ranged interactions present.

For our purposes, we can safely ignore the deep physical reasons underlying the gaplessness of Goldstone bosons and simply posit a gapless dispersion relation of the form $\omega(\mathbf{k}) = A|\mathbf{k}|^\sigma$. The density of states for this excitation branch is then

$$g(\omega) = C \omega^{\frac{d}{\sigma}-1} \Theta(\omega_c - \omega), \quad (5.6.32)$$

where C is a constant and ω_c is the cutoff, which is the bandwidth for this excitation branch.⁴ Normalizing the density of states for this branch results in the identification $\omega_c = (d/\sigma C)^{\sigma/d}$.

The heat capacity is then found to be

$$\begin{aligned} C_V &= N k_B C \int_0^{\omega_c} d\omega \omega^{\frac{d}{\sigma}-1} \left(\frac{\hbar\omega}{k_B T} \right)^2 \text{csch}^2 \left(\frac{\hbar\omega}{2k_B T} \right) \\ &= \frac{d}{\sigma} N k_B \left(\frac{2T}{\Theta} \right)^{d/\sigma} \phi(\Theta/2T), \end{aligned}$$

where $\Theta = \hbar\omega_c/k_B$ and

$$\phi(x) = \int_0^x dt t^{\frac{d}{\sigma}-1} \text{csch}^2 t = \begin{cases} \frac{\sigma}{d} x^{d/\sigma} & x \rightarrow 0 \\ 2^{-d/\sigma} \Gamma(2 + \frac{d}{\sigma}) \zeta(2 + \frac{d}{\sigma}) & x \rightarrow \infty, \end{cases} \quad (5.6.33)$$

which is a generalization of our earlier results. Once again, we recover Dulong-Petit for $k_B T \gg \hbar\omega_c$, with $C_V(T \gg \hbar\omega_c/k_B) = N k_B$.

In an isotropic ferromagnet, a ferromagnetic material where there is full $SU(2)$ symmetry in internal 'spin' space, the magnons have a k^2 dispersion. Thus, a bulk three-dimensional isotropic ferromagnet will exhibit a heat capacity due to spin waves which behaves as $T^{3/2}$ at low temperatures. For sufficiently low temperatures this will overwhelm the phonon contribution, which behaves as T^3 .

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