The Phonon Gas

• *The system:* A solid with N atoms occupying a volume V, in thermal equilibrium at temperature T. The atoms are kept in place by their mutual interactions, represented by a potential energy $U(\mathbf{r}_1, ..., \mathbf{r}_N)$ with a minimum at equilibrium positions $\mathbf{r}^0_1, ..., \mathbf{r}^0_N$ forming a lattice. At any $T > 0$, the positions of the atoms are subject to fluctuations which propagate as waves throughout the solid. The Fourier components of these (discrete) waves can be considered as pseudoparticles called phonons. A gas of phonons differs from a gas of photons in that: (i) Since there are a total of $3N$ degrees of freedom, there are only finitely many modes, and (ii) There are both transverse and longitudinal modes, in general propagating at different speeds.

• *Hamiltonian:* If the atoms are close to their equilibrium positions, the Hamiltonian can be written as

$$H = \sum_{i=1}^{N} \frac{\mathbf{p}_i^2}{2m} + U(\mathbf{r}_1, ..., \mathbf{r}_N) = \sum_{I=1}^{3N} \frac{p_I^2}{2m} + U_0 + \tfrac{1}{2} \sum_{I,J=1}^{3N} \Delta r_I\, K_{IJ}\, \Delta r_J + \text{h.o.t.}\,,$$

where $\Delta r_I := r_I - r^0_I$ $(I = 1, ..., 3N)$, $U_0 = U(\mathbf{r}^0_1, ..., \mathbf{r}^0_N)$, $K_{IJ} := \partial^2 U/\partial r_I \partial r_J|_{\mathbf{r}=\mathbf{r}^0}$, and at low temperatures we can just keep those terms in the Taylor series expansion of U. If we diagonalize the symmetric matrix K_{IJ} and call $\mathbf{q}_I$ its eigenvectors, each of which identifies one of the normal modes of the system, then $K\,\mathbf{q}_I = \kappa_I \mathbf{q}_I$ and we can write H in the decoupled form

$$H = \sum_{I=1}^{3N} \frac{p_I^2}{2m} + U_0 + \tfrac{1}{2} \sum_{I=1}^{3N} \kappa_I q_I^2 = U_0 + \sum_{I=1}^{3N} \left(\frac{p_I^2}{2m} + \tfrac{1}{2}\, \kappa_I q_I^2 \right).$$

• *Quantum states:* For small deviations from equilibrium, every normal mode contributes a degree of freedom that behaves like a simple harmonic oscillator with frequency $\omega_I = \sqrt{\kappa_I/m}$, so the eigenvalue of the total Hamiltonian operator corresponding to the state $|\alpha\rangle = |n_1, ..., n_{3N}\rangle$ is

$$E_\alpha = E_0 + \sum_{I=1}^{3N} n_I\, \hbar\omega_I\,, \qquad \text{where} \qquad E_0 = U_0 + \tfrac{1}{2} \sum_{I=1}^{3N} \hbar\omega_I \qquad \text{and} \qquad \omega_I := \sqrt{\kappa_I/m}.$$

A convenient labeling of states is to specify their wave vector and polarization (one longitudinal or acoustic mode, governed by the bulk modulus, and two transverse modes, governed by the shear modulus), $I = (\mathbf{k}, \gamma)$.

• *Goal:* Treating this system from the point of view of thermodynamics, we would like to obtain the energy equation of state, and the contribution to the specific heat of the solid from lattice excitations—to be added to that of the electron gas (if any) and the one from the internal degrees of freedom of the atoms. Experimentally, the value found at high temperatures is $C_V = 3Nk_\text{B}$ for all solids (Dulong-Petit law—universality), but for low T it goes to zero as $C_V \propto T^3$ (Debye's law), consistently with the third law.

Canonical Ensemble

• *Partition function:* As for all bosons, and similarly to what we saw for the gas of photons, we find that after summing over values of the occupation numbers $n_{\mathbf{k},\gamma}$ the partition function becomes

$$Z = \mathrm{e}^{-\beta E_0} \prod\nolimits_{\mathbf{k},\gamma} \frac{1}{1 - \mathrm{e}^{-\beta\epsilon_{\mathbf{k},\gamma}}}\,,$$

where the wave vector $\mathbf{k}$ and polarization γ label the single-particle states, with energies $\epsilon_{\mathbf{k},\gamma} = \hbar\omega_{\mathbf{k},\gamma}$.

• *Density of States:* In this case we don't know the form of $\omega_{\mathbf{k},\gamma}$, but in general we can say that $g(\omega)$ can also be directly defined as a sum over the $3N$ values of $(\mathbf{k}, \gamma)$, $g(\omega) = \sum_{\mathbf{k},\gamma} \delta(\omega - \omega_{\mathbf{k},\gamma})$. The main difficulty in the calculation of the lattice heat capacity for a solid lies in writing down the right $g(\omega)$. One often uses approximations, like the two we will see next.

• *Free energy:* From the partition function above,

$$\beta F = -\ln Z = \beta E_0 + \sum_{\mathbf{k},\gamma} \ln(1 - \mathrm{e}^{-\beta\hbar\omega_{\mathbf{k},\gamma}}) = \beta E_0 + \int_0^\infty \mathrm{d}\omega\, g(\omega) \ln(1 - \mathrm{e}^{-\beta\hbar\omega})\,.$$

The Einstein Model

• *Idea:* A model for a solid in which all atoms are considered to be harmonic oscillators with the same frequency ω_0, so only one "phonon" energy level $\epsilon_0 = \hbar\omega_0$ is occupied. This may be expected to be a reasonable approximation at low temperatures, where we can assume that all oscillators are in their ground state and have the same frequency. The density of states becomes of the form $g(\omega) = 3N\,\delta(\omega-\omega_0)$.

• *Specific heat:* In this model, $\beta F = \beta E_0 + 3N\ln(1-\mathrm{e}^{-\beta\hbar\omega_0})$ and

$$\bar E = \frac{\partial(\beta F)}{\partial\beta} = E_0 + 3N\frac{\hbar\omega_0}{\mathrm{e}^{\beta\hbar\omega_0}-1}\;, \qquad C_V = -k_{\rm B}\beta^2\,\frac{\partial\bar E}{\partial\beta} = 3N\,k_{\rm B}\beta^2\,(\hbar\omega_0)^2\,\frac{\mathrm{e}^{\beta\hbar\omega_0}}{(\mathrm{e}^{\beta\hbar\omega_0}-1)^2}\;,$$

which at high temperatures satisfies the principle of equipartition ($\bar E = 3Nk_{\rm B}T$) and the Dulong-Petit law ($C_V = 3Nk_{\rm B}$). It also vanishes as $T\to 0$, which was very significant historically, but it does so exponentially and not at the observed rate, because it does not properly take into account the dispersion relation $\omega(k)$.

The Debye Theory

• *Idea:* Assume that for all wave vectors and all polarizations the phase velocity $c = \omega/k$ is the same, or $\omega_{\mathbf{k},\gamma} = ck$, independent of $\hat{\mathbf{k}}$ and γ (this relationship holds up to the maximum value of k, which is of the order of the inverse lattice spacing). This amounts to treating the solid as if it was an elastic medium or fluid, rather than a collection of discrete particles, except for the existence of a maximum k, which is a good approximation for long wavelengths and gives better results than the Einstein model at low temperatures.

• *Density of states:* If $\omega = ck$, where c is a constant speed of sound (the same dispersion relation as for photons, but different c), we get that $\mathrm{d}\omega/\mathrm{d}k = c$ and, for a general $f(\omega)$ and using the fact that here $\nu = 3$,

$$\sum_{\mathbf{k},\gamma} f(\omega_{\mathbf{k},\gamma}) \approx \frac{3\,V}{(2\pi)^3}\int_0^{\omega_{\rm D}} \frac{4\pi\,\omega^2\mathrm{d}\omega}{c^3}\,f(\omega)\;, \qquad \text{or} \qquad g(\omega) = \frac{3\,V}{2\pi^2\,c^3}\,\omega^2\;,$$

where the Debye frequency $\omega_{\rm D}$ corresponds to the maximum value of k. Using the fact that the total number of degrees of freedom is $\sum_{\mathbf{k},\gamma} 1 = 3N$, we find $\omega_{\rm D} = c\,(6\pi^2\,N/V)^{1/3}$, typically an infrared frequency.

• *Free energy:* Then, from the general expression for the lattice free energy derived above,

$$\beta F = \beta E_0 + \int_0^\infty \mathrm{d}\omega\,g(\omega)\ln(1-\mathrm{e}^{-\beta\hbar\omega}) = \beta E_0 + \frac{3\,V}{2\pi^2\,c^3}\int_0^{\omega_{\rm D}}\mathrm{d}\omega\,\omega^2\ln(1-\mathrm{e}^{-\beta\hbar\omega})\;.$$

(Recall that for massless bosons the mean number of particles in mode $\mathbf{k}$ was $\bar N_{\mathbf{k}} = 1/(\mathrm{e}^{\beta\hbar\omega}-1)$.)

• *Heat capacity:* The general expression for the mean energy in the Debye theory is

$$\bar E = \frac{\partial(\beta F)}{\partial\beta} = E_0 + \int_0^\infty \mathrm{d}\omega\,g(\omega)\,\frac{\hbar\omega}{\mathrm{e}^{\beta\hbar\omega}-1} = E_0 + \frac{3\,V}{2\pi^2\,c^3}\int_0^{\omega_{\rm D}}\mathrm{d}\omega\,\frac{\hbar\omega^3}{\mathrm{e}^{\beta\hbar\omega}-1}\;.$$

Since we don't know how to evaluate this expression exactly, we will consider just the small-T and large-T approximations. More precisely, if we introduce $\theta_{\rm D} := \hbar\omega_{\rm D}/k_{\rm B}$, and the dimensionless $x := \beta\hbar\omega$, then

$$C_V = \frac{\partial\bar E}{\partial T} = k_{\rm B}\,\frac{3V}{2\pi^2(c\beta\hbar)^3}\int_0^{\beta\hbar\omega_{\rm D}}\frac{x^4\,\mathrm{e}^x}{(\mathrm{e}^x-1)^2}\,\mathrm{d}x\;.$$

(Some $\theta_{\rm D}$ values used are: 428 K for Al, 470 K for Fe, 170 K for Au and 645 K for Si.) Limiting behavior:
<u>$T\to 0$</u>: For $T \ll \theta_{\rm D}$ the range of integration can be extended to infinity and we get $C_V \propto T^3$ (Debye's law).
<u>$T\to\infty$</u>: For $T \gg \theta_{\rm D}$, to leading order

$$\frac{1}{\mathrm{e}^{\beta\hbar\omega}-1} \approx \frac{k_{\rm B}T}{\hbar\omega}\;,$$

so we get that $\bar E = E_0 + 3\,Nk_{\rm B}T$, and we recover $C_V \approx 3\,Nk_{\rm B}$ (the Dulong-Petit law).

Reading

• *Course textbook:* Kennett, § 4.7.2 (Einstein model) and § 9.4.
• *Other books:* Plischke & Bergersen, —; Chandler, § 4.3; Mattis & Swendsen, § 5.6;
Pathria & Beale, §§ 7.4 and 7.5; Reif, §§ 10.1–10.2; Schwabl, § 4.6.