

## Vibrational heat capacities of solids [tln57]

The interaction between atoms is attractive at long distances and repulsive at short distances. The lowest-energy configuration of a macroscopic system of  $N$  atoms is a perfect lattice. This is the equilibrium state at  $T = 0$ . It has zero entropy. Heat input  $\delta Q = C dT$  causes lattice vibrations. In the following we study vibrational heat capacities in successively improved approximations.

### Atoms bound to rigid lattice by harmonic force (classical model):

The theory of Dulong and Petit considers an array of  $N$  classical 3D harmonic oscillators with identical frequencies. The resulting vibrational heat capacity,  $C = 3Nk_B$ , is  $T$ -independent and is calculated in exercise [tex74] for a microcanonical ensemble and in exercise [tex78] for a canonical ensemble.

The main insufficiency of the Dulong-Petit result is that  $C$  does not approach zero in the low-temperature limit, in violation of the third law.

### Atoms bound to rigid lattice by harmonic force (quantum model):

The theory of Einstein considers an array of  $N$  quantum 3D harmonic oscillators with identical angular frequencies  $\omega$ . The resulting vibrational heat capacity,

$$C = \left(\frac{\Theta_E}{T}\right)^2 \frac{3Nk_B e^{\Theta_E/T}}{(e^{\Theta_E/T} - 1)^2}, \quad k_B \Theta_E = \hbar \omega,$$

goes to zero exponentially in the low- $T$  limit,  $C \sim e^{-\Theta_E/T}$ , and approaches the Dulong-Petit result,  $C = 3Nk_B$ , at high  $T$ . Einstein's result is derived in exercise [tex75] for the microcanonical ensemble and in exercise [tex82] for the canonical ensemble.

The main insufficiency of Einstein's result is that it contradicts experimental evidence, which suggests  $C \sim T^3$  at low  $T$ .

### Atoms interacting via harmonic force:

$$H = \sum_{i=1}^{3N} \frac{p_i^2}{2m} + \sum_{ij} A_{ij} q_i q_j = \sum_{i=1}^{3N} \left[ \frac{p_i^2}{2m} + \frac{1}{2} m \omega_i^2 Q_i^2 \right].$$

Here  $\{A_{ij}\}$  is the dynamical matrix. The second equation results from a transformation to normal-mode coordinates. In the present context the normal modes are sound waves (phonons).

Quantum mechanically, this system is an array of  $3N$  independent harmonic oscillators with normal mode frequencies  $\omega_i$ :

$$H = \sum_{i=1}^{3N} \hbar \omega_i \left( n_i + \frac{1}{2} \right), \quad n_i = 0, 1, 2, \dots$$

The resulting Helmholtz free energy (in generalization to the result derived in [tex82]) reads:

$$A = \frac{1}{2} \sum_{i=1}^{3N} \hbar \omega_i + k_B T \sum_{i=1}^{3N} \ln (1 - e^{-\beta \hbar \omega_i}).$$

In Debye's theory, the normal modes, which, in general, consist of multiple branches of acoustic and optical phonons, are replaced by a single branch of sound waves with linear dispersion  $\omega = ck$  as is expected in a continuous isotropic elastic medium.

Total number of modes:  $3N$  (same as in original lattice model).

Density of modes in  $k$ -space:  $V/(2\pi)^3$ .

Number of polarizations: 3 (2 transverse, 1 longitudinal).

Number of modes in  $d\omega$ :  $n(\omega)d\omega = \frac{V}{8\pi^3}(3)(4\pi) \frac{\omega^2}{c^2} \frac{d\omega}{c} = \frac{3V}{2\pi^2 c^3} \omega^2 d\omega$ .

Debye frequency:  $\frac{3V}{2\pi^2 c^3} \int_0^{\omega_D} d\omega \omega^2 = 3N \Rightarrow \omega_D^3 = \frac{6N\pi^2 c^3}{V}$ .

Density of modes:  $n(\omega) = \frac{9N}{\omega_D^3} \omega^2$ .

The resulting vibrational heat capacity is calculated in exercise [tex83] and does show the experimentally observed  $\sim T^3$  behavior as  $T \rightarrow 0$ :

$$C = 9Nk_B \left( \frac{T}{\Theta_D} \right)^3 \int_0^{\Theta_D/T} dx \frac{x^4 e^x}{(e^x - 1)^2}, \quad \Theta_D = \hbar \omega_D / k_B.$$