

1 Condensed matter

1.1 Materials properties

The equilibrium state is determined by the balance between the electrostatic attraction and quantum repulsion. The last is characterised by the confinement energy

$$\epsilon_q \sim \frac{p^2}{m_e} \sim \frac{\hbar^2}{m_e a^2}, \quad (1.1)$$

where a is the interatomic distance. Note that the Fermi momentum of the degenerate electron gas, defined by the relation

$$2 \frac{(4/3)\pi p_F^3}{(2\pi\hbar)^3} = n, \quad (1.2)$$

where n is the electron number density, may be presented as $p_F = \hbar(3\pi^2 n)^{1/3} \approx 3\hbar a^{-1}$, so that the average electron wavelength is of the order of their separation distance.

In the cases of ionic, covalent and metallic bonds, the Coulomb attraction is characterised by the potential energy

$$\epsilon_p \sim -\frac{e^2}{a}. \quad (1.3)$$

The minimum of the total energy, $\epsilon_q + \epsilon_p$, occurs at $\epsilon_q \sim \epsilon_p$, the corresponding size is roughly

$$a \sim a_B = \frac{\hbar^2}{e^2 m_e} = 0.5 \text{ \AA}. \quad (1.4)$$

Typical sizes of atoms, and therefore the interatomic distance, is a few times larger. As a typical value, one can take the diameter of atoms and the interatomic distance to be $a = 3\text{ \AA}$. Then a quite good estimate for the density of many substances is just

$$\rho \simeq \frac{Am_p}{a^3} = \frac{A}{15} \text{ g} \cdot \text{cm}^{-3}. \quad (1.5)$$

The cohesive energy is now estimated as

$$\epsilon_c \sim \frac{e^2}{a} = \frac{2a_B}{a} \text{ Ry} \approx 5 \text{ eV} \approx 100 \text{ kcal} \cdot \text{mole}^{-1}. \quad (1.6)$$

In order to estimate Young's modulus, consider dependence of the total energy of the atom in the lattice, $E = E_q + E_p$, on a small shift, x , from the equilibrium state: $E = \epsilon_c + (1/2)E''x^2$. Then the force on the atom is $f = E''x$ and Young's modulus is found as

$$Y = \frac{f}{a^2} : \frac{x}{a} = \frac{E''}{a}. \quad (1.7)$$

Substituting the estimate $E'' \sim \epsilon_c/a^2$, one gets

$$Y \sim \frac{\epsilon_c}{a^3} \sim \frac{e^2}{a^4} = 2.5 \cdot 10^{11} \text{ erg} \cdot \text{cm}^{-3} = 25 \text{ GPa} \quad (1.8)$$

The typical Young's modulus of strong solids is $\sim 100 \text{ GPa}$.

The sound velocity is

$$v_s = \sqrt{\frac{Y}{\rho}} \sim \sqrt{\frac{e^2}{Ma}}, \quad (1.9)$$

where $M = Am_p$ is the atomic mass. Now one gets

$$v_s \sim \sqrt{\frac{2m_e a_B}{Am_p a}} \alpha c \approx \frac{10^{-2}}{\sqrt{A}} \alpha c \approx \frac{20}{\sqrt{A}} \text{ km} \cdot \text{s}^{-1}. \quad (1.10)$$

In this simple model, the atom in the lattice is considered as an oscillator with the elastic constant $k = E'' \sim \varepsilon_c/a^2$. The frequency of this oscillator is

$$\omega_v = \sqrt{\frac{k}{M}} = \sqrt{\frac{\varepsilon_c}{a^2 M}}. \quad (1.11)$$

Note that the same estimate is applicable to a single molecule. In this case, ω_v is the vibrational frequency of the molecule. The corresponding energy is estimated, taking into account eq. (1.1) and the fact that at the equilibrium, $\epsilon_q \sim \epsilon_p \sim \epsilon_c$, as

$$\epsilon_v = \hbar\omega_v \sim \sim \sqrt{\frac{m_e}{M}} \epsilon_c. \quad (1.12)$$

In solids, one can conveniently use the Debye temperature, $k_B T_D = \epsilon_v$, instead of the vibrational energy.

The thermal expansion occurs because the potential well for atoms in the lattice is not symmetric, $U(x) = U(0) + \frac{1}{2}U''(0)x^2 + \frac{1}{6}U'''(0)x^3$. One can roughly expect that $U'''(0) \sim \varepsilon_c/a^2$ etc. In this case, heating by $k_B T \sim \varepsilon_c$ should formally lead to doubling the interatomic distance. Then one gets an estimate for the thermal expansion coefficient, $\alpha \equiv \Delta l/l$:

$$\alpha \sim \frac{k_B}{\varepsilon_c} \sim 2 \cdot 10^{-5} \text{ K}^{-1}. \quad (1.13)$$

1.2 Competition between the energy and the entropy: melting, evaporation, ionization

One can assume that the lattice melts when the amplitude of thermal oscillations of atoms, δ , reaches a significant fraction of the interatomic distance, $\delta = \zeta a$, where $\zeta < 1$. The oscillation amplitude is found from the equipartition theorem, $k_B T = k\delta^2$ therefore one can present an estimate for the melting temperature as

$$k_B T_m = \zeta^2 Y a^3 \sim \zeta^2 \varepsilon_c. \quad (1.14)$$

Taking into account that typically $\varepsilon_c \approx 5 \text{ eV} = 60000 \text{ K}$ whereas the melting temperatures are typically $1000 - 2000 \text{ K}$, one sees that crystals melt already at $\zeta \approx 0.15 - 0.2$. With the same assumption, one can find a relation between the melting and the Debye temperatures:

$$k_B T_m = M\omega^2 \delta^2 = M \frac{k_B^2 T_D^2}{\hbar^2} \zeta^2 a^2, \quad (1.15)$$

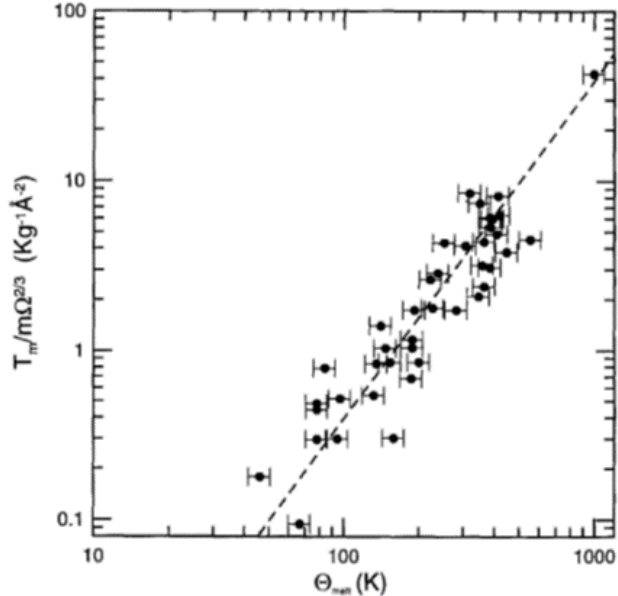


Figure 1: The reduced melting point vs the Debye temperature at the melting point, Θ_{melt} , for 41 elements. Here T_m is the melting point, M the atomic mass, Ω the atomic volume.

which could be written as a relation between experimentally measured quantities (known as the **Lindemann melting criterion**)

$$T_m = C\mu T_D^2 V^{2/3} \quad (1.16)$$

where μ is the molecular weight, $V = N_A a^3$ the molar volume. Empirically, $C = (3 - 7) \cdot 10^{-5} \text{ cm}^{-2} \text{ grad}^{-1}$.

The equilibrium at a given temperature is determined by the minimum of the free energy, $F = E - TS$ ¹. At a high enough temperature, the increasing in the energy may be compensated by the entropy increasing; then a phase transition occurs. The temperature of the phase transition is determined by the condition that the free energies of two phases are equal. Taking into account

¹Since the transition typically occurs at a constant pressure, not volume, one has to seek for the minimum of the Gibbs free energy, $G = H - TS$, where $H = E + pV$ is the enthalpy. However, the contribution of the term pV is small. This is evident for melting because in this case, the density of the substance does not change much. For evaporation this follows from the fact that for vapour, $pV = RT$, and, as it will be explained later in this subsection, RT is much less than the heat of vaporization even at the boiling temperature.

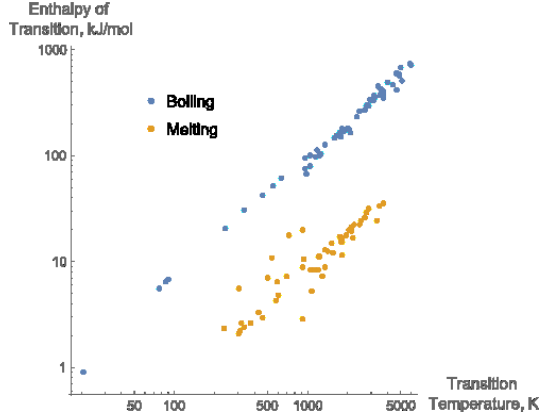


Figure 2: The transition enthalpy vs the transition temperature for melting and boiling

that $S = k_B \ln \Omega$, where Ω is the number of states of the system, one finds the relation between the latent heat of the transition and the transition temperature:

$$\Delta E = k_B T_{\text{tr}} \ln \frac{\Omega_2}{\Omega_1} \quad (1.17)$$

Taking into account that $\Omega \propto \omega^N$, where ω is the number of states per single atom/molecule, N the total number of atoms/molecules in the system, one sees that the latent heat of transition between the states 1 and 2 per atom/molecule may be related to the transition temperature as

$$\Delta \varepsilon = k_B T_{\text{tr}} \ln \frac{\omega_2}{\omega_1}. \quad (1.18)$$

When the lattice is melted, the density does not vary significantly, and the number of states does not increase significantly, $\omega_2/\omega_1 \sim \text{few}$. Therefore $\ln \omega_2/\omega_1 \sim 1$, which means that typically the melting temperature is close, in the energy units, to the heat of fusion per atom/molecule.

The vapour density is typically significantly smaller than the density of the condensed matter so that in this case, $\omega_2/\omega_1 \gg 1$, and one can roughly take $\ln \omega_2/\omega_1 \sim 10$. Therefore the boiling temperature is typically an order of magnitude less than the heat of vaporization. This justifies an empirical **Trouton's rule**: at the normal pressure,

$$\Delta H_{\text{evap}} = 10.5 R T_b, \quad (1.19)$$

where ΔH_{evap} is the molar heat of vaporization (enthalpy of vaporization), R the universal gas constant, T_b the boiling temperature.

The same consideration is applied to ionization. Inasmuch as the number of electronic states in the continuum is much larger than the number of states within the atom, ionization typically occurs at temperatures, an order of magnitude less than the ionization energy. For example, the ionization energy of hydrogen is $I_H = \text{Ry} = 13.6 \text{ eV} = (160,000 \text{ K}) \cdot k_B$ however, hydrogen in the Universe is ionized already at $T \sim 10,000 \text{ K}$.