

1. **molecular solids** The Lennard-Jones potential between pairs of atoms is

$$U(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right]$$

When considering the cohesive energy in a solid, we must sum up this interaction energy over all of the atoms. For a monoatomic fcc structure in which each atom has 12 nearest neighbors, the corresponding cohesive energy for a molecular solid with N atoms (neglecting the KE)

$$U = \frac{1}{2} N 4\epsilon \left[12.13188 \left(\frac{\sigma}{R} \right)^{12} - 14.45392 \left(\frac{\sigma}{R} \right)^6 \right]$$

where R is the nearest neighbor distance and the $1/2$ ensures that we count each atom only once.

- What is the origin of the attractive and repulsive terms in the LJ potential?
- Find the nearest neighbor separation in terms of the parameter σ (hint, this occurs when the energy is minimized).
- for Ne, $\epsilon = 0.0031 \text{ eV}$ and $\sigma = 2.74 \text{ \AA}$ (this is obtained by measurements in the gas phase). For solid Ne what is the theoretical cohesive energy per atom? what is the theoretical nearest neighbor separation? The experimental values are 3.13 \AA and 0.02 eV respectively. The slight departure is due to quantum mechanical zero point motion of the Ne atoms. Do you expect the agreement to be better or worse as one moves down the periodic table (Ar, Kr, Xe)?

2. **Ionic crystals** The interaction in ionic crystals is a combination of long range electrostatic potentials and a short range repulsive interaction. For two atoms i and j , the energy is

$$U_{ij} = \lambda e^{-r_{ij}/\rho} \pm \frac{q^2}{r_{ij}}$$

where we use cgs units (as in Kittel), q is the charge of the ions, r_{ij} is the distance between the two ions, and we choose (+) or (-) depending on whether we are considering like ions (repulsive) or unlike ions (attractive) and λ and ρ are parameters to be extracted from the experimental data.

- Typically ρ is on order of 10% of the nearest neighbor separation. Thus, show that the exponential term can be neglected past nearest neighbors such that the total cohesive energy may be written for N pairs of positive and negative ions as

$$U = N \left(z \lambda e^{-R/\rho} - \frac{\alpha q^2}{R} \right)$$

where z is the number of nearest neighbors, and R is the nearest neighbor separation negative ions, and α is the Madelung constant:

$$\alpha = \sum_j \frac{(\pm)}{p_{ij}}$$

where $r_{ij} = p_{ij} R$.

- The Madelung constant depends only on the structure. For the sodium chloride structure it is 1.747565, for the cesium chloride structure it is 1.762675 and for the zinc-blende structure it is 1.6381. Calculate the lattice energy of KCl in the zinc-blende, sodium chloride and zinc-blende structure. Compare with the experimental value of the lattice energy which is 7.17 eV per molecular unit. (See figure 3.10 in Kittel for a plot of the energy per KCl pair showing the Madelung and

repulsive contributions).

The experimentally determined values of R , ρ and $z\lambda$ for KCl are:

	R	ρ	$z\lambda$
KCl	3.147 Å	0.326 Å	2.05×10^{-8} erg

3. **Possibility of an ionic crystal $\mathbf{R^+R^-}$.** Imagine a crystal that exploits for its bonding the coulomb attraction of the positive and negative ions of the same atom or molecule R. This is believed to occur with certain organic molecules, but is not found when R is a single atom.

Evaluate the stability of such a form of Na (assuming the NaCl structure) relative to normal metallic sodium (cohesive energy = 1.112 eV/atom) by calculating the cohesive energy of the Na^+Na^- crystal assuming the same interatomic distance as in pure sodium, 3.66 Å. Take the electron affinity of Na = 0.55eV (energy gained by accepting one electron), the ionization potential of Na = 5.14 eV (energy cost to give up one electron) and $\rho = 0.31$ Å. You don't need to know λ , why?

4. Calculate the phonon density of states (energy) for a linear monoatomic chain containing N atoms connected by nearest neighbor interactions (and constrained to move in only one dimension). Show that there is a singularity at the Brillouin zone boundary.
5. Consider a linear diatomic chain as series of masses M_1 and M_2 and lattice spacing a . with the masses attached by identical springs of spring constant C constrained to move in only one dimension.
- Calculate the dispersion relationship for the two phonon branches in terms of the quantities given above assuming $M_1 > M_2$. Show that there is an energy gap between the acoustic and optical phonon branches at the edge of the Brillouin zone. How does the gap depend on the difference between the masses? Sketch the dispersion relation.
 - Show that in the limit that $M_1 = M_2$ that the gap closes and the dispersion relation is equivalent to that of a monoatomic crystal with lattice spacing $a/2$.
6. Consider a 3 dimensional monoatomic crystal in the Debye approximation for the phonon dispersion.

- Derive the general form of the lattice contribution to the specific heat:

$$C_V = 9Nk_B \left(\frac{T}{\Theta_D} \right)^3 \int_0^{\Theta_D/T} \frac{x^4 e^x}{(e^x - 1)^2} dx$$

where $\Theta_D = \hbar\omega_D/k_B$, is the Debye Temperature. You may assume that all three phonon branches have the same speed of sound v .

- Show that at sufficiently low temperatures the specific heat is proportional to T^3 and that at very high temperatures the specific heat approaches the classical limit $3Nk_B$. hint: You may find the following integral useful:

$$\int_0^\infty \frac{x^3}{e^x - 1} dx = \sum_{n=1}^\infty \int_0^\infty x^3 e^{-nx} dx = 6 \sum_{n=1}^\infty \frac{1}{n^4} = \frac{\pi^4}{15}$$

- Derive an expression with the thermal energy density $u = U/N$ for a crystal in the low temperature limit. Compare your result to the Stefan-Boltzmann law for black body radiation

$$u_{EM} = \frac{\pi^2 (k_B T)^4}{15 (\hbar c)^3}$$

and comment on the significance of the similarities and differences.