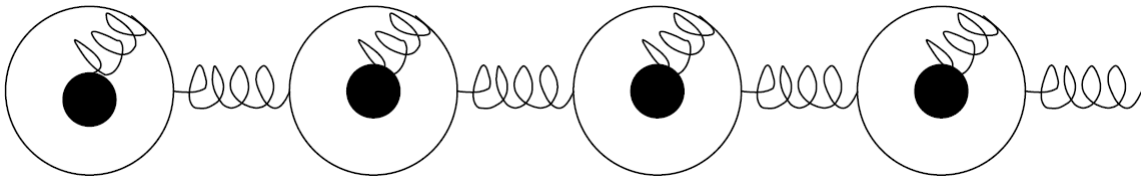


Due Fri. Sept. 21

Note: Ziman starts Ch. 2 with a brief mention of “Van der Waals forces.” The $1/R^6$ attractive force between neutral spherical atoms was briefly derived in class. A good discussion is in the classic book *Dynamical Theory of Crystal Lattices* by Born & Huang.

1. The “shell model” is a way of enlarging the classical point mass model of lattice dynamics to include an internal degree of freedom which is intended to capture some of the reality of the true quantum picture with rich electronic internal degrees of freedom. Just as in the quantum picture, the classical shell model ends up treating the shell as a variable which follows nuclear displacements adiabatically. The figure below illustrates it in 1d. [The most common 3d implementations assign negative and positive charges to the shell and nucleus, and include Coulomb interactions, which are omitted here.]



The Hamiltonian for this is

$$H = \sum_{\ell} \left[\frac{P_{\ell}^2}{2M} + \frac{p_{\ell}^2}{2m} + \frac{K(s_{\ell} - s_{\ell+1})^2}{2} + \frac{k(s_{\ell} - u_{\ell})^2}{2} \right]$$

where P_{ℓ} and p_{ℓ} are the nuclear and shell momenta, M and m are the nuclear and shell masses, and u_{ℓ} and s_{ℓ} are the nuclear and shell displacements. As usual, the system repeats periodically after N units.

- a. Write the Newtonian equations for $M\ddot{u}_{\ell}$ and $m\ddot{s}_{\ell}$. Choose the Bloch properties $u_{\ell} = u_Q \exp(iQ\ell)$ and $s_{\ell} = s_Q \exp(iQ\ell)$. Eliminate the variable s_Q by using the adiabatic approximation $m\ddot{s}_{\ell} = 0$ (or $m=0$).
 - b. Find the eigenfrequency ω_Q , and plot ω_Q versus Q for the cases (i) $k \rightarrow \infty$, and (ii) $k=2K$.
2. Density of state is defined by $D(\omega) = (1/N) \sum_{\lambda} \delta(\omega - \omega_{\lambda})$ (for phonons). The sum is over all normal modes, and the $1/N$ is a convenient normalization. For the one-dimensional chain with nearest neighbor springs, the quantum number λ is Q and the frequency is $\omega_Q = 2\sqrt{K/M} |\sin(Qa/2)|$. Find the formula for $D(\omega)$.
 3. Diatomic molecules have an effective one-particle Hamiltonian $P^2/2\mu + Kx^2/2$, (in harmonic approximation) where μ is reduced mass.
 - a. If the effective potential has the Lennard-Jones form $\epsilon[(\sigma/x)^{12} - 2(\sigma/x)^6]$, then there is a predicted relation between oscillation frequency ω , binding

energy ε , reduced mass μ , and internuclear “equilibrium” separation σ . Derive this relation.

- b. For molecular Cl_2 , in vacuum, the measured values are $\sigma=1.99$ Angstrom, $\omega=560 \text{ cm}^{-1}$, and $\varepsilon=2.48 \text{ eV}$. How well do these agree with the Lennard-Jones prediction? Note that energy measured in cm^{-1} (“wavenumbers”) has to be converted to ω in rad/s, or some other appropriate conversion.
- c. For Cl_2 , what is the amplitude of zero point oscillations? What is the expected mean thermal energy level $\langle n \rangle$ at 300K? 600K? What is the classical value of the *rms* amplitude of oscillation at 300K? 600K?