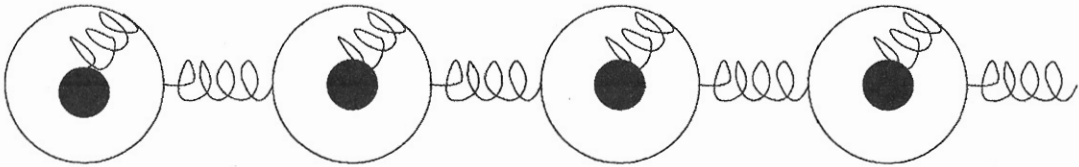


Physics 555 Fall 2007 HW#2
answers

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

$$H = \sum_i \left[\frac{P_i^2}{2M} + \frac{p_i^2}{2m} + K(s_i - s_{i+1})^2 / 2 + k(s_i - u_i)^2 / 2 \right]$$

where P_i and p_i are the nuclear and shell momenta, M and m are the nuclear and shell masses, and u_i and s_i are the nuclear and shell displacements. As usual, the system repeats periodically after N units.

- Write the Newtonian equations for $M\ddot{u}_i$ and $m\ddot{s}_i$. Choose the Bloch properties $u_i = u_0 \exp(iQ\ell)$ and $s_i = s_0 \exp(iQ\ell)$. Eliminate the variable s_0 by using the adiabatic approximation $m\ddot{s}_i = 0$ (or $m=0$).
- Find the eigenfrequency ω_Q , and plot ω_Q versus Q for the cases (i) $k \rightarrow \infty$, and (ii) $k=2K$.

$$M\ddot{u}_i = -\frac{\partial H}{\partial u_i} = k(s_i - u_i) \rightarrow -M\omega^2 u_i$$

$$m\ddot{s}_i = -\frac{\partial H}{\partial s_i} = K(s_{i+1} + s_{i-1} - 2s_i) + k(u_i - s_i) \rightarrow -m\omega^2 s_i$$

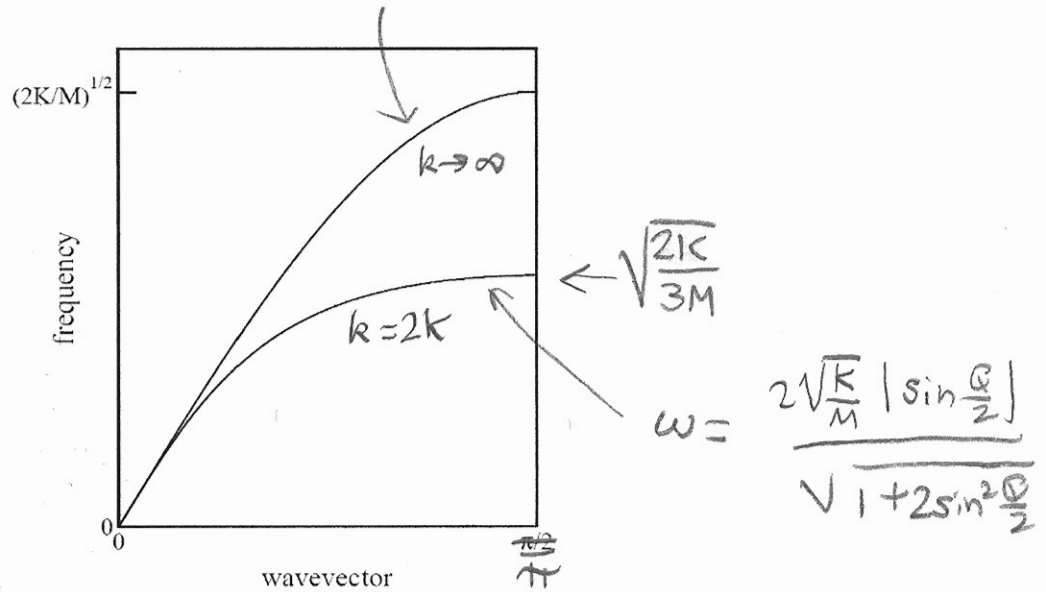
$$M\omega^2 u_i = k(u_i - s_i)$$

$$m\omega^2 s_i = K(2 - 2\cos Q\ell) s_i + k(s_i - u_i)$$

if $m\omega^2 s_i \rightarrow 0$ then $s_i = u_i / \left[1 + \frac{K}{k} (2 - 2\cos Q\ell) \right]$
 then $M\omega^2 u_i = k \left[1 - \frac{K/k}{k/k + 4 \sin^2 Q\ell/2} \right] u_i$

$$\omega_Q^2 = \frac{4K}{M} \left[\frac{\sin^2 Q\ell/2}{1 + 4 \frac{K}{k} \sin^2 Q\ell/2} \right]$$

$$\omega = 2\sqrt{\frac{K}{M}} \left| \sin \frac{Q}{2} \right|$$



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 $D(\omega)$.

$$\text{In } d=1, \quad \frac{1}{N} \sum_{\lambda} \rightarrow \frac{a}{2\pi} \int_{-\pi/a}^{\pi/a} dQ$$

$$\text{So } D(\omega) = \frac{a}{2\pi} \int_{-\pi/a}^{\pi/a} dQ \delta(\omega - \omega_M |\sin(Qa/2)|)$$

$$= \frac{2a}{2\pi} \int_0^{\pi/a} dQ \delta(\omega - \omega_M \sin \frac{Qa}{2}) = \frac{2}{\pi} \int_0^{\pi/2} dx \delta(\omega - \omega_M \sin x)$$

$$= \frac{2}{\pi} \left. \frac{1}{\omega_M |\cos x|} \right]_{x = \sin^{-1}(\frac{\omega}{\omega_M})}$$

$$\cos(\sin^{-1} \theta) = \sqrt{1 - \sin^2 \theta} \quad \text{so}$$

$$D(\omega) = \frac{2}{\pi} \frac{1}{\omega_M \sqrt{1 - (\frac{\omega}{\omega_M})^2}} = \frac{2/\pi}{\sqrt{\omega_M^2 - \omega^2}}$$

if $0 \leq \omega \leq \omega_M$ (otherwise $D(\omega) = 0$)

3. Diatomic molecules have an effective one-particle Hamiltonian $P^2/2\mu + Kx^2/2$, (in harmonic approximation) where μ is reduced mass.

- 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.
- For molecular Cl_2 , in vacuum, the measured values are $\sigma = 1.99$ Angstrom, $\omega = 560 \text{ cm}^{-1}$, and $\epsilon = 2.48 \text{ eV}$. 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.
- 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?

$$(a) \quad \frac{V}{\epsilon} = \frac{1}{y^{12}} - 2 \frac{1}{y^6} \quad y = \frac{x}{\sigma}$$

$$\frac{d}{dy} \left(\frac{V}{\epsilon} \right) = -12 \left(\frac{1}{y^{13}} - \frac{1}{y^7} \right) = 0 \quad \text{when } y=1 \Rightarrow V \text{ is minimum when } x = \sigma$$

$$\frac{d^2}{dy^2} \left(\frac{V}{\epsilon} \right) = 12 \left(\frac{13}{y^{14}} - \frac{7}{y^8} \right) = 72 \quad \text{when } y=1 \Rightarrow V_{\min} = -1$$

$$V(x) \sim \epsilon \left[-1 + \frac{72}{2} \left(\frac{x-\sigma}{\sigma} \right)^2 + \dots \right]$$

Spring constant $K = \frac{72\epsilon}{\sigma^2}$

$$\mu = M/2 \quad M = 35.45 \text{ amu (Cl atom)}$$

$$\omega = \sqrt{K/\mu} = \frac{12}{\sigma} \sqrt{\frac{\epsilon}{M}}$$

$$(b) \quad \omega = \left(\frac{12}{1.99 \times 10^{-10} \text{ m}} \right) \left(\frac{2.48 \text{ eV} \times 1.602 \times 10^{-19} \text{ J/eV}}{35.45 \text{ amu} \times 1.67 \times 10^{-27} \text{ kg/amu}} \right)^{1/2}$$

$$\omega = 1.56 \times 10^{14} \text{ s}^{-1} \quad \text{predicted} = \frac{2\pi c}{\lambda}$$

$$\frac{1}{\lambda} = \frac{1.56 \times 10^{14} \text{ s}^{-1}}{2\pi \cdot 3 \times 10^{10} \text{ cm/s}} = 828 \text{ cm}^{-1} \quad (\text{predicted}) \text{ vs } 560 \text{ cm}^{-1} \text{ measured.}$$

LJ force constant K is too large by 2.2

$$(c) \quad \langle u^2 \rangle = \frac{\hbar}{\mu \omega} \left(n + \frac{1}{2} \right) \rightarrow \frac{1.054 \times 10^{-34} \text{ Js}}{2 \left(\frac{35.54 \text{ amu}}{2} \right) (1.67 \times 10^{-27} \text{ kg/amu}) (1.055 \times 10^{14} \text{ rad/s})}$$

$$\langle u^2 \rangle^{1/2} = 4.1 \times 10^{-12} \text{ m}$$

at 300K

$$\left. \begin{aligned} \omega &= 560 \text{ cm}^{-1} = 69. \text{ meV} \\ RT &= .025 \text{ eV} = 25 \text{ meV} \end{aligned} \right\} \frac{\hbar\omega}{RT} = 2.76$$

$$h = \frac{1}{e^{2.76} - 1} = 0.068$$

at 600K, $\frac{\hbar\omega}{RT} = 1.38$, $n = 0.34$

Quantum $\langle u^2 \rangle^{1/2} = (4.1 \times 10^{-12} \text{ m}) \sqrt{2n+1} = \begin{cases} 4.4 \times 10^{-12} \text{ m} & (300\text{K}) \\ 5.3 \times 10^{-12} \text{ m} & (600\text{K}) \end{cases}$

Classical $\langle u^2 \rangle = (4.1 \times 10^{-12} \text{ m}) \left(\frac{2kT}{\hbar\omega} \right) = \begin{cases} 3.5 \times 10^{-12} \text{ m} & (300\text{K}) \\ 4.9 \times 10^{-12} \text{ m} & (600\text{K}) \end{cases}$