# Che 210B: Homework 5. Due February 15, 2005.

1. *Vapor pressure of a Debye Crystal.* Calculate the vapor pressure of a Debye crystal in the limiting case of low temperature. You may assume that the gas phase is ideal.

2. *Frequency Distribution in a Continuous 1D Solid.* In class we learned that the key assumption in the Debye approximation is setting the frequency distribution in the crystal to that of a continuous elastic solid.

   In 1D, consider the crystal to be a solid where movement is allowed only along the *x*-axis. The crystal has $N$ units with spacing $a$ for a total length $L = Na$. During the propagation of the wave, the mass at point $x$ is displaced to position $x + u(x,t)$. The equation of motion for a wave of velocity $v$ is:

$$\frac{\partial^2 u}{\partial x^2} = \frac{1}{v^2}\frac{\partial^2 u}{\partial t^2} \tag{1}$$

   The general solution to this partial differential equation is:

$$u = Ae^{2\pi i(\omega t - \alpha x)} \tag{2}$$

   (a) Determine the values of $\alpha$ that satisfy (1) with the functional form of (2).

   (b) What is the wavelength $\lambda$ for each value of $\alpha$?

   The form of (2) is that of a *traveling* wave. The normal modes of vibration in a crystal are *standing* waves, which may be formed by taking linear combinations of the sin and cos parts of the solutions (2). In this case, there are four such types of standing waves.

   (c) What are the functional forms of these four waves? Express your answers in terms of $\omega$, $t$, $x$, and $\lambda$.

   For a large crystal, we can pick any set of boundary conditions (because the 2 ends are such a small contribution with respect to the N-2 remaining particles). Assume then that the solid is fixed at the ends, so $u(0) = u(L) = 0$.

   (d) Which of the standing waves in part (c) satisfy these boundary conditions? What are the allowed wavelengths? What are the allowed frequencies?

(e) Since there are only $N$ degrees of freedom, what is the largest frequency?

(f) What is g(ω) for the 1D continuous solid? *Hint*: Define a function F(ω) that counts the number of allowed frequencies in the interval $0 \le \omega_n \le \omega$. Then what operation should you perform on F(ω) to get g(ω) = { # of frequencies between w and ω + dω } ?

3. *Frequency Distribution in a Continuous 3D Solid*. In class we derived $\omega_D$ for a 3D crystal by using the result $g(\omega) = \alpha\,\omega^2$. The coefficient α, which drops out of the expression for $\omega_D$, comes from the same treatment in Problem 2 applied to the 3D case. Here, a wave has three possible directions of propagation, and two different velocities. The first is the longitudinal wave with velocity $v_L$, and two transverse waves that propagate perpendicular to the longitudinal wave. The equations of motion are now:

$$\nabla^2 u_L = \frac{1}{v_L{}^2}\frac{\partial^2 u}{\partial t^2} \tag{3}$$

$$\nabla^2 u_T = \frac{1}{v_T{}^2}\frac{\partial^2 u}{\partial t^2} \tag{4}$$

The solutions to (3) and (4) have an analogous form to (2):

$$u = Ae^{2\pi i(\omega t - \boldsymbol{\alpha}\cdot\mathbf{x})} = Ae^{2\pi i\left(\omega t - \left(\alpha_x x + \alpha_y y + \alpha_z z\right)\right)} \tag{5}$$

(a) Derive a relationship between $\boldsymbol{\alpha}$, ω, and $v$, where here $v$ is either $v_L$ or $v_T$.

(b) What is the wavelength λ?

(c) Define the vector **l** as the unit vector corresponding to $\boldsymbol{\alpha}$, i.e. $l_i = \alpha_i/|\boldsymbol{\alpha}|$. Re-express (5) using $l_i$ and λ instead of $\alpha_i$ to express the dot product $\boldsymbol{\alpha}\cdot\mathbf{x}$. How many wave equations are there which satisfy the relationship you derived in (a)?

(d) There are a number of standing waves that could be formed from the sin and cos parts of the wave equations you enumerated in (c). Only two forms will satisfy the boundary conditions analogous to those that we used in Problem 2, namely

$$u = 0 \text{ for } \begin{Bmatrix} x = 0 & x = L_x \\ y = 0 & y = L_y \\ z = 0 & z = L_z \end{Bmatrix} \tag{6}$$

What constrains do these boundary conditions impose upon the relationship between $l_i$, $L_i$, and $\lambda$? *Hint*: All of the sin terms need to be zero at the boundaries, so their arguments have to be an integral multiple of $2\pi$. Call this factor $n_i$, where i indexes *x*, *y*, or *z*.

(e) Use the fact that **l** is a unit vector and the three relationships you derived in part (d) to express the frequency $\omega$ in terms of *v*, $L_i$, and the $n_i$.

(f) Use your result from (e) to define the function $F(\omega)$ that counts the number of frequencies between 0 and $\omega$. *Hint*: Each point $(n_x,n_y,n_z)$ in the positive octant of $(n_x,n_y,n_z)$ gives a possible frequency of $\omega(n_x,n_y,n_z)$. There is one such point per unit volume of space. What is this volume?

(g) Use your result from (f) to calculate $g(\omega)$ in terms of the wave velocities. *Remember, there are three waves with velocities $v_T$ and $v_L$. Each contributes equally to $g(\omega)$.*

4. *Adsorption of p-xylene in silicalite:* The zeolite silicalite is a nanoporous crystal that can adsorb small molecules such as xylene at specific binding sites within the crystal's unit cell. Each cell contains two types of sites, type 1 and type 2, and there are 4 sites of each type per cell. Assume that molecules in different sites do not interact with each other (which actually is a pretty big assumption) and that both sites have a simple harmonic oscillator potential :

$$\begin{aligned} U(r) &= \varepsilon_i + f_i r^2 \\ \varepsilon_1 &= -46\frac{\text{kJ}}{\text{mol}};\ f_1 = 0.2\frac{\text{kJ}}{\text{mol Å}^2} \\ \varepsilon_2 &= -5\frac{\text{kJ}}{\text{mol}};\ f_2 = 1.0\frac{\text{kJ}}{\text{mol Å}^2} \end{aligned} \tag{7}$$

Plot the average number of xylene molecules adsorbed per unit cell at T = 300 K as a function of $\log_{10}(p)$, where p is the pressure in an ideal xylene gas in equilibrium with the silicalite. Use classical statistical mechanics.