Physical Principles of Solids

Hilary 2018

Due: 5pm Thursday Week 5

1. **Free Electron Theory**
   Given that the bcc unit cell of Na has a cell length of 0.423 nm, use Free Electron Theory to calculate for Na the valence electron concentration, the Fermi energy, the Fermi temperature, and the Fermi velocity.

2. **Fermi Radius**
   Show that the wavefunctions and energy levels of a 2-dimensional electron gas comprising N electrons constrained to a quantum well of dimensions $L \times L$ can be written in the form,

   $$\psi(\mathbf{r}; \mathbf{k}) = A \exp\left[i\mathbf{k} \cdot \mathbf{r}\right] = A \exp\left[i\left(k_x x + k_y y\right)\right], \tag{1}$$

   where,

   $$k_x = \frac{2\pi n}{L}; \quad k_y = \frac{2\pi m}{L}; \quad n \in \mathbb{Z}, \tag{2}$$

   with the corresponding energy,

   $$E(\mathbf{k}) = \frac{\hbar^2}{2m} |\mathbf{k}|^2. \tag{3}$$

   These solutions can be represented by a grid of points in k-space and the Fermi energy by a circle of radius k_f. By evaluating the area occupied by one grid point and the area of the Fermi circle, show that,

   $$N = 2\pi k_f^2 \left(\frac{L}{2\pi}\right)^2, \tag{4}$$

   and hence that,

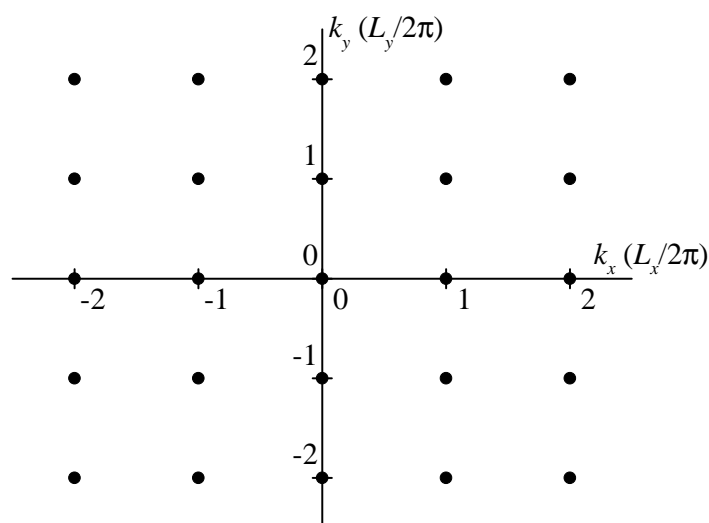 $$k_f = (2\pi n)^{\frac{1}{2}}, \tag{5}$$

   where n is the electron concentration per unit area.

3. **Free Electron Theory II**
   Describe the extent to which the heat capacity and magnetic properties of conduction electrons in simple metals can be understood using Free Electron Theory.

4. **Harmonic Oscillator Model**
   The mean thermal energy U_T in a simple harmonic oscillator of frequency ν can be

expressed by the equation,

$$U_T - U_0 = \frac{h\nu}{\exp\left(\frac{h\nu}{k_B T} - 1\right)}. \tag{6}$$

Describe how this expression is derived and how it can be exploited in models to explain the heat capacity of solid-state compounds. Comment on the successes and failures of such models in explaining experimental data.

5. **Einstein Model**

The Einstein model for the specific heat c_v of a monoatomic solid predicts that this is described by the equation:

$$c_v = \frac{3R(\Theta_E/T)^2}{[\exp(\Theta_E/T) - 1]^2} \exp(\Theta_E/T). \tag{7}$$

(a) Deduce the limits of the heat capacity as $T \to 0$ and $T \to \infty$.

(b) The heat capacity of diamond is 6.1 J K^{-1} mol^{-1} at $T = 298$ K. By using a method of 'trial substitution' or otherwise, deduce the Einstein temperature for diamond.

(c) For an ideal gas the difference $c_p - c_v = R$. What would it be for (i) an Einstein solid; (ii) a 'real' solid?

6. **Debye Theory**

c_v for solid Ar has been measured for $T < 2$ K and the data is presented in the table below.

T (K)	1.10	1.39	1.59	1.75	1.88
c_v (mJ mol^{-1} K^{-1})	3.3	6.7	10	13	16.5

(a) Show that the data is consistent with the low temperature prediction of Debye's theory, and calculate the Debye temperature.

(b) Calculate the entropy of solid Ar at 5 K.

(c) Potassium has the same Debye temperature as Ar, but the heat capacity at 0.5 K is 1.4 mJ mol^{-1} K^{-1}. Explain the difference between the values for K and Ar, and use the data to estimate the Fermi temperature of potassium.

7. **Point Defects**
Probability theory shows that the number of ways W of distributing n identical objects at random over N distinguishable sites, each of which can contain only one objects, is,
$$W = \frac{N!}{(N - n)!n!}.$$

(a) Why does this relationship play an important role in the calculation of the equilibrium concentration of point defects in a crystal?

(b) Use the relationship given above to show that the entropy of an ionic crystal comprising N anionic sites and N cationic sites, with n cation vacancies and n anion vacancies, is given by,

$$S = 2k_B(N \ln N - n \ln n - (N - n) \ln(N - n)).$$

[You may use Stirling's approximation, which is $\ln x! \approx x \ln x - x$.]

(c) Calculate the entropy per mole of a crystal when $n/N = 0.026$.

8. **Adsorption entropy**
The expression for W given in question 7 can also be used to calculate the configurational entropy of molecules adsorbed on a solid surface. For N_A sites, calculate this entropy when adsorption sites are 50% occupied.
This calculation is based on random occupancy of the available surface sites. Why might this be an unreliable assumption?

9. **Ammonia Adsorption**
Ammonia adsorbs on charcoal at 273 K and the following data has been reported.

P / mbar	50	100	200	400	600
x	0.056	0.084	0.111	0.134	0.143

x refers to the mass in kg of ammonia adsorbed per unit mass of charcoal. Show that the data obey the Langmuir adsorption isotherm and calculate the surface area per kg of charcoal, given that the are occupied by one ammonia molecule is 1.3×10^{-19} m^2. Why are the predictions of the Langmuir equation not always followed exactly?

10. **Physisorbtion**

Nitrogen physisorbs on charcoal black at low temperatures and the ratios of the pressures at 77 K and 90 K required to yield a particular surface coverage, Θ, have been measured.

Θ	0.5	0.9	1.5
$p(90 \text{ K})/p(77 \text{ K})$	9.1	10.4	4.2

Calculate the heats of adsorption at the different coverages and explain the results you obtain (latent heat of condensation of nitrogen is 5.7 J K^{-1} mol^{-1}). Explain what differences would arise in the adsorption characteristics if the molecule chemisorbed instead.

11. **Competitive Adsorption**

According to the Langmuir model, competitive adsorption of two gases A and B on the same surface yields equilibrium surface coverages of the form,

$$\Theta_A = \frac{K_A p_A}{(1 + K_A p_A + K_B p_B)},$$

$$\Theta_B = \frac{K_B p_B}{(1 + K_A p_A + K_B p_B)}.$$

A heterogenous catalyst catalyses the formation of CO_2 from CO and O_2. Measurement of the kinetics shows that the rate of production of CO_2 is proportional to the gas pressure of CO, inversely proportional to the gas pressure of O_2 and independent of the gas pressure of CO_2. Suggest why this is observed.

12. **[Based on PART IB 2014]**

(a) The second virial coefficient is given by

$$B_2(T) = -2\pi \int_0^\infty \left[\exp\left(-\beta\phi(r)\right) - 1 \right] r^2 \mathrm{d}r,$$

where $\phi(r)$ is the intermolecular pair potential as a function of the separation, r, and $\beta = 1/(k_b T)$. Consider the square well interaction potential:

$$\phi(r) = \begin{cases} \infty, & r < \sigma, \\ -\varepsilon, & \sigma \le r \le \lambda\sigma, \\ 0, & r > \lambda\sigma. \end{cases}$$

   i. Sketch the potential, clearly labelling $\lambda\sigma$, σ, and ε on your diagram. **[4]**
   ii. Find an expression for the second virial coefficient for this potential. **[6]**
   iii. The properties of nitrogen gas can be described using the above square well potential with $\sigma = 3.277$ Å, $\lambda = 1.58$, and $\varepsilon/k_B = 95.2$ K. Calculate the predicted value of the Boyle temperature. **[5]**

(b) The classical molecular partition function is given by,

$$q_{\text{class}} = \frac{1}{h^3} \int \dots \int \exp\left[-\beta H(p,\tau)\right] \mathrm{d}p\mathrm{d}\tau,$$

where $H(p,\tau)$ is the classical Hamiltonian, which depends on the momenta and position coordinates p and τ, respectively. Note that $\mathrm{d}p = \mathrm{d}p_x\mathrm{d}p_y\mathrm{d}p_z$ and $\mathrm{d}\tau = \mathrm{d}\tau_x\mathrm{d}\tau_y\mathrm{d}\tau_z$.

Consider a perfect gas of molecules with a permanent electric dipole moment μ in an electric field $\mathbf{E}$. Neglecting the polarisability, the potential energy is $u = -\mu E \cos\theta$, where θ is the angle between μ and $\mathbf{E}$.

  i. Give the expression for the classical single-particle Hamiltonian $H(p,\tau)$. [2]

  ii. Calculate the classical molecular partition function, q_{class}, for this system, assuming that $\theta = 0°$. [4]

  iii. Calculate the additional effect of the electric field E in the internal energy U. [4]

Note that

$$\int_{-\infty}^{\infty} e^{-\alpha x^2} \mathrm{d}x = \frac{\pi}{\alpha},$$

and

$$U = k_B T^2 \left(\frac{\partial \ln Q}{\partial T}\right)_{N,V}.$$

13. **[Based on PART IB 2015]**

(a) Describe the principal assumptions wich underlie the free electron theory of metals. According to this theory, the number N of free electrons states with energy less than or equal to E_{f} in a metal of volume V is given by,

$$N = \frac{V}{2\pi^2} \left(\frac{2m_{\text{e}}}{\hbar^2}\right)^{3/2} \int_0^{E_{\text{f}}} \sqrt{E}\mathrm{d}E.$$

Using this expression or otherwise, show that the Fermi energy is,

$$E_{\text{f}} = \frac{\hbar^2}{2m_{\text{e}}} \left(3\pi^2 n\right)^{3/2},$$

where $n = N/V$. Na has a bcc unit cell with a lattice parameter of 0.423 nm. Calculate its Fermi Temperature $T_{\text{f}} = E_{\text{f}}/k_B$, and explain why the electronic heat capacity for Na is far smaller than the result expected from equipartition theory.

(b) The internal energy or a mole of independent simple harmonic oscillators with frequency ν is,

$$U(T) - U(0) = \frac{N_{\text{A}} h\nu}{e^{h\nu/k_B T} - 1}.$$

Show that this leads to a molar heat capacity of,

$$C_V(T) = R\left(\frac{h\nu}{k_BT}\right)^2 \frac{\mathrm{e}^{h\nu/k_BT}}{\left(\mathrm{e}^{h\nu/k_BT} - 1\right)^2},$$

and describe the extent to which this equation can be used to explain the following observations:

(i) The room temperature constant volume heat capacity of many elemental solids is approximately 25 J K^{-1} mol^{-1}, although the value for diamond is significantly below this.

(ii) The low temperature heat capacity of many solids displays a T^3 dependence.

(iii) Cu expands when heated and has a constant pressure heat capacity in excess of 28 J K^{-1} mol^{-1} at a temperature of 900 K.

(c) There are n K$^+$ vacancies and the same number of Cl$^-$ vacancies in a crystal of KCl. Use Stirling's approximation ($\ln N! \approx N\ln N - N$) to show that the entropy change in a crystal associated with the creation of these vacancies is,

$$\Delta S = 2k_B\left[N\ln N - (N-n)\ln(N-n) - n\ln n\right],$$

where N is the number of K$^+$ lattice sites.

How would you expect the enthalpy of the crystal to vary with n? Assuming that $N \gg n$, show that the equilibrium value of n is,

$$n = N\mathrm{e}^{-\Delta H/2RT},$$

where T is the temperature of the crystal and ΔH is the enthalpy change to create a mole of vacancy pairs. Given that $\Delta H = 260$ kJ mol^{-1}, calculate the temperature at which the crystal at thermal equilibrium contains 1 ppm of vacancy pairs.

(d) Explain the assumptions used in the derivation of the Langmuir isotherm, and discuss the origins of deviations from the isotherm which are often observed. Two gases, A and B, adsorb competitively on a surface. Show that within the Langmuir model the fractional coverage of gas A can be expressed in the form,

$$\theta_A = \frac{B_A p_A}{1 + B_A p_A + B_B p_B},$$

where p_A and p_B are the partial pressures of the two gases.

The rate of formation of ammonia from nitrogen and hydrogen on an iron catalyst is found to be proportional to the partial pressure of nitrogen and inversely proportional to the square root of the partial pressure of hydrogen. Show how this can be understood using the Langmuir model.