

PHYSICS 715

Problem Set 9

Due Friday, April 7, 2006

HOURLY EXAM IN CLASS ON WEDNESDAY, APRIL 12

Reading: Landau and Lifshitz, Secs. 53–57, 85–88, 94

LD 29: Frenkel defects in crystalline solids: the density of defects and the equilibrium between holes and interstitial atoms (Frenkel pairs).

Consider a crystalline solid with N lattice sites per unit volume and M interstitial sites per unit volume. There are N atoms per unit volume in the solid. An atom displaced from a normal lattice site to an interstitial site (a Frenkel defect) has an energy $+\epsilon$ relative to the energy it would have at a lattice site. (That is, its *binding energy* is smaller by ϵ .)

- Determine the equilibrium density of defects by minimizing the Helmholtz free energy F_m for m defects, or equivalently, by maximizing Z_m with respect to m . The relation $N!/(N-n)! \approx N^n$, $N \gg n$, will be useful. M and N are comparable and have a fixed ratio which depends on the geometry of the lattice. The number of defects m must be much smaller than M (or N) for the physical picture to be useful.
- Recalculate the density of defects by finding the equilibrium configuration for a “gas” of n holes (unoccupied lattice sites) mixed with a second “gas” of m interstitial atoms. The binding energy of an atom at a lattice site is ϵ_ℓ ; the binding energy at an interstitial site is ϵ_{int} . $\epsilon_{\text{int}} = \epsilon_\ell - \epsilon$. [Hint: calculate the grand partition function for the system with the interstitial atoms and the holes treated as independent, and then use the constraint $\bar{n} = \bar{m}$ to determine the condition for equilibrium.]
- Calculate the contribution of the defects to the entropy and specific heat of the system. $C_X = T(\frac{\partial S}{\partial T})_X$. M and N are fixed; m is not.

LD 30: Thermal dissociation of H_2 as a source for a beam of monatomic hydrogen

- Suppose you wish to form a thermal beam of neutral hydrogen atoms (atomic beam) by dissociating molecular hydrogen in a tungsten oven and allowing the dissociated atoms to escape through a small opening. Derive the “chemical” relation which connects the equilibrium partial pressures of H_2 and H in the oven to T and P directly, that is, without using the stoichiometric coefficients, by minimizing the Gibbs free energy $G(T, P, N_{H_2}, N_H) = \mu_{H_2}N_{H_2} + \mu_H N_H$ at fixed

T and P subject to the constraint that the number of hydrogen atoms remains constant, $N_H + 2N_{H_2} = 2N_{H_2}^0$. [Hint: Start with the expressions for the chemical potentials for the two component gases expressed in terms of T , P , N_H , and N_{H_2} , eliminate V and N_H , and minimize with respect to N_{H_2} . Do not forget to include the dissociation or binding energy of H_2 .]

- (b) Determine the temperature at which you must operate the oven to have 90% dissociation of the H_2 molecules, $N_{H_2} = 0.1 N_{H_2}^0$, for $P = 10^{-3}$ atm. Include the effects of rotation and vibration of the H_2 molecule. Treat the rotation as classical, but include any relevant spin and symmetry effects. The melting point of tungsten is 3680 K. [Hint: Solve the equation which determines T by numerical iteration. It is useful to measure T in units of 10^3 K, *i.e.*, $T \equiv 10^3 T_3$.]

Calculate the fractional occupation of the lowest five vibrational levels in H_2 . Why is the unexpectedly low occupation of the higher excited levels consistent with nearly total dissociation of the H_2 ?

Useful information: binding energy of $H_2 = 4.48$ eV, mean separation of the nuclei in the ground state of $H_2 = 0.75$ Å, spacing of lowest vibrational levels $\Delta E = 0.5$ eV, electronic spin of $H_2 = 0$ ($^1\Sigma_g$ ground state), lowest excited electronic states at 11.37 eV ($^1\Sigma_u$) and 12.40 eV ($^1\Pi_u$, rotation about the symmetry axis). See G. Herzberg, *Molecular Structure and Molecular spectra*, Vol. I, *Spectra of Diatomic Molecules*, pp. 339, 349). For a classic Noble Prize experiment using this method, see W.E. Lamb and R.C. Retherford, Phys. Rev. **79**, 549 (1950) (the measurement of the “Lamb shift” splitting of the $2S_{1/2}$ and $2P_{1/2}$ energies in the hydrogen spectrum).

LD 31: The virial expansion for ideal quantum gases.

The virial expansion of the equation of state for a gas is

$$PV = NkT \left(1 + \frac{B(T)}{V} + \dots \right),$$

where $B(T)$ is the second virial coefficient. Calculate the first quantum correction to the classical expression for $\ln \mathcal{Z}$ for the ideal nonrelativistic Bose-Einstein and Fermi-Dirac gases with spin degeneracy g , and the corrected expressions for N and PV . Solve for $e^{\mu\beta}$ by iteration, and calculate the second virial coefficient for the quantum gases. How do the results reflect the fact that “fermions repel” and “bosons attract”? [Hint: be consistent in the orders of $e^{\mu\beta}$ kept in all expansions!]