

Preliminary Examination: Thermodynamics and Statistical Mechanics

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Fall 2011

Instructions:

- The exam consists of 10 short-answer problems (10 points each).
- Where possible, show all work; partial credit will be given if merited.
- Personal notes on two sides of an 8×11 page are allowed.
- Total time: 3 hours.

Unless otherwise noted, commonly used symbols are defined as follows:

P : Pressure

T : Absolute Temperature

k : Boltzmann's constant

R : Gas constant

β : $(kT)^{-1}$

S : Entropy

V : Volume

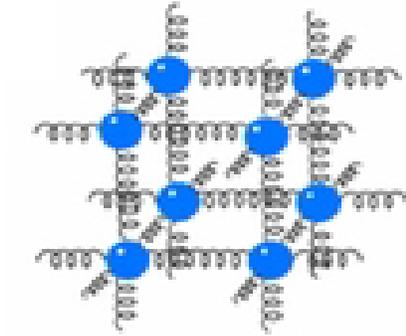
μ : Chemical potential

$\hbar = \frac{h}{2\pi} = 1.05 \times 10^{-34}$ Js; Planck's constant

Useful Integral:

$$\int_{-\infty}^{\infty} dx x^{2p} \exp(-\alpha x^2) = (-1)^p \frac{d^p}{d\alpha^p} \left(\sqrt{\pi/\alpha} \right)$$

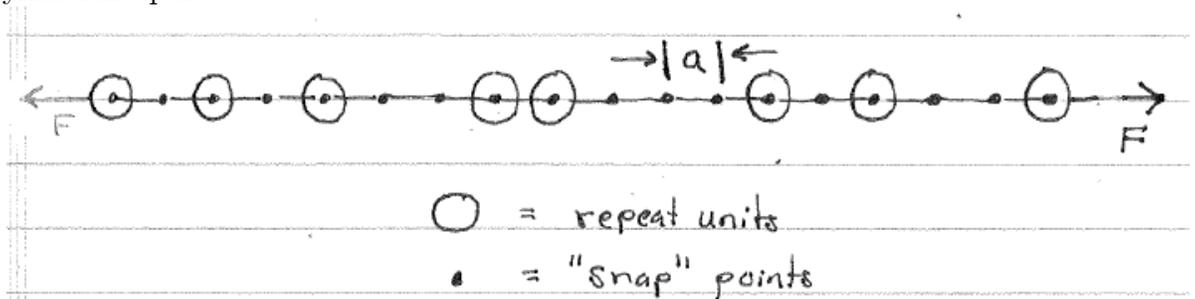
P1: A macroscopic crystalline solid consists of N atoms connected to one another by Hooke's law interactions. What is its heat capacity at high temperatures? How does this depend on the dimensionality of the solid?



P2: Consider a model for a polymer chain that is reminiscent of a child's snap-bead toy. The repeat units are aligned in one dimension, with allowed bond lengths that are discrete multiples of the lattice constant a , as though they "snap" into certain locations, as shown in the figure. The total length of the polymer is $\sum_{i=1}^N (m_i + 1) a$, where $m_i = 0, 1, 2, \dots$ is an integer associated with the i th bond having any value between 0 and ∞ , and N is the total number of bonds in the chain. Longer bonds have proportionally higher energy, in multiples of $\hbar\omega_0$. When placed under a constant tensile force F , the system Hamiltonian is given by

$$H = \sum_{i=1}^N (\hbar\omega_0 - Fa) (m_i + 1)$$

The polymer is in thermal equilibrium at a temperature T . Calculate the partition function for the polymer strand. Obtain an expression for the average length as a function of T and F . At what maximum force F will the polymer fall apart?



P3: A paramagnetic solid consists of a N atoms in a volume V , each having spin $S = 1$ and magnetic moment $\vec{\mu} = \frac{\mu_0}{\hbar} \vec{S}$. Assuming that the magnetic moments respond independently in an applied magnetic field, derive an expression for the magnetic susceptibility at high temperatures.

P4: An ideal gas of N particles fills a vessel of volume V , in equilibrium at a temperature T . If the particles each have a mass m , at what rate do the particles collide with the walls of the container, per unit area?

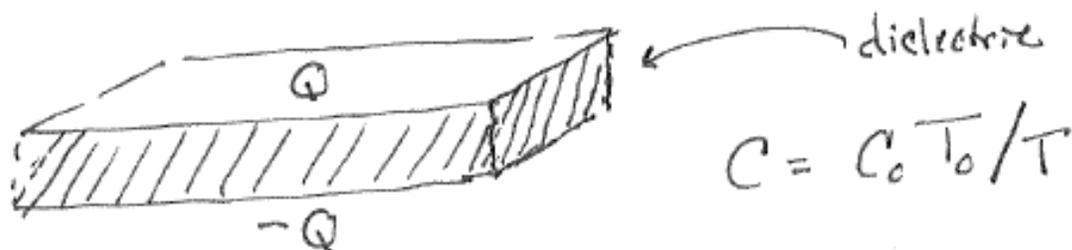
P5: When a crystal surface is exposed to helium gas, a fraction of the atoms will come out of the gas phase and adhere to interstitial sites located on the surface. Consider a surface consisting of M adhesion sites, which can be thought of as depressions in a "muffin tin" potential. (See sketch below.) If each site can be occupied by either zero or one helium atom, what is the surface entropy when N helium atoms are adsorbed? For what value of N will the entropy be a maximum?



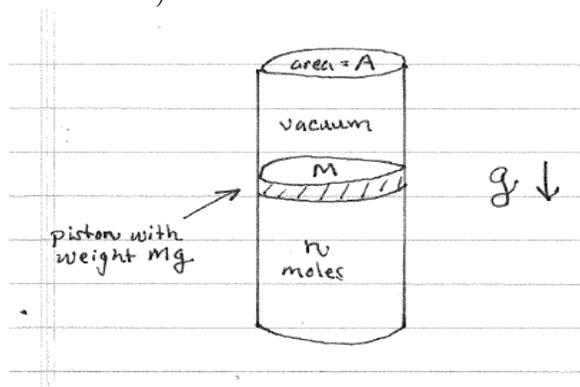
P6. A parallel plate capacitor has a capacitance varying inversely with temperature, $C(T) = C_0 \frac{T_0}{T}$, where C_0 and T_0 are constants. The heat capacity κ of the uncharged capacitor is a constant. Both of these quantities appear in an expression for the free energy,

$$F = \frac{Q^2}{2C(T)} + \kappa T \left(1 - \ln \frac{T}{T_0} \right),$$

where Q is the charge. Suppose that the capacitor is initially given a charge Q_0 at a temperature T_1 , and that it is thermally, mechanically, and electrically isolated from the surroundings. After some time it discharges due to a small leak in the dielectric spacer. What is the final temperature T_2 ? What is the change in entropy for this spontaneous process?



P7. A vertical cylinder with cross sectional area A is sealed at both ends, and divided into two chambers by a frictionless piston with mass M , as shown in the figure. The upper chamber is evacuated. The lower half contains 1 mole of a monatomic ideal gas, in equilibrium at a temperature T_1 , and is compressed by the weight of the piston. If the cylinder is placed in contact with the surroundings at a higher temperature $T_2 = 2.718 T_1$, how much heat will be transferred to the gas? What is the change in entropy of the system? What is the change in entropy of the surroundings? Show that the change in entropy of the universe is positive. (Neglect the weight of the gas molecules.)



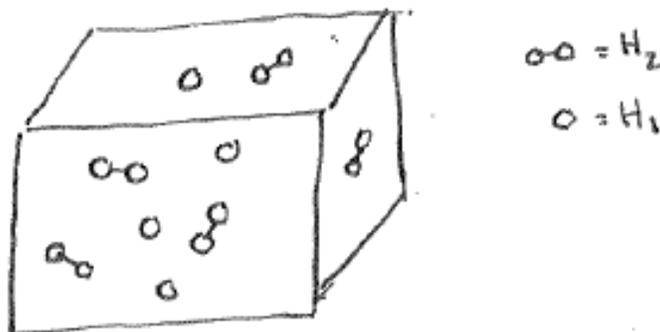
P8. The free energy for a noninteracting gas of monatomic hydrogen H_1 , in thermal equilibrium at a temperature T and volume V , is given by

$$A_1 = -N_1 kT \left[\ln \left(\alpha_1 \frac{VT^{3/2}}{N_1} \right) + 1 \right]$$

Here N_1 is the number of atoms, and α_1 is a constant. Similarly, the free energy for N_2 molecules of diatomic hydrogen H_2 is given by

$$A_2 = -N_2 kT \left[\ln \left(\alpha_2 \frac{VT^{5/2}}{N_2} \right) + 1 \right] - N_2 \Delta$$

Here α_2 is a different constant, and Δ is their binding energy. When chemical equilibrium between H_1 and H_2 is established in a closed vessel at temperature T , the ratio $\kappa = (C_1)^2 / (C_2)$ will be a function of only temperature. Here $C_1 = N_1/V$ and $C_2 = N_2/V$. Derive an expression for κ and show that this is the case.



P9. To first approximation, the conduction band in a metal may be modeled as a noninteracting electron gas. The number of conduction electrons N in metal of volume V at a temperature T is given by an integral over phase space,

$$N = \frac{2}{h^3} \int \frac{d^3x d^3p}{e^{-\beta\mu} e^{\beta \frac{p^2}{2m}} + 1}.$$

Weighting the integrand by $p^2/2m$ gives an expression for the internal energy,

$$U = \frac{2}{h^3} \int d^3x d^3p \left(\frac{p^2/2m}{e^{-\beta\mu} e^{\beta \frac{p^2}{2m}} + 1} \right).$$

(a) Perform these integrals in the degenerate ($T \rightarrow 0$) limit. Show that

$$U = \frac{8\pi V}{10mh^3} (2m\mu)^{5/2},$$

and show that

$$\mu = \frac{1}{2m} \left(\frac{3Nh^3}{8\pi V} \right)^{2/3}.$$

(b) Using the results from part (a), together with the third law, show that $U = \frac{3}{2}PV$.

P10. A thermocouple is comprised of a wire loop of two different metals, as shown in the figure. One junction is immersed in a cold reservoir at a temperature T_1 , and the other junction is immersed in a hot reservoir at a temperature T_2 . The difference in temperature at the two junctions produces an emf that induces an electrical current in the closed loop. The flow can be reversed by inserting a battery in series opposition. In such a case, the device will behave as a thermoelectric refrigerator; the flow of charge will be accompanied by a transfer of heat from the cold reservoir to the hot reservoir. Assuming that $T_1 = 0\text{ }^\circ\text{C}$, and $T_2 = 21\text{ }^\circ\text{C}$, what is the maximum heat that can be transferred from the cold reservoir to the hot reservoir for each Joule of electrical work performed by the battery?

