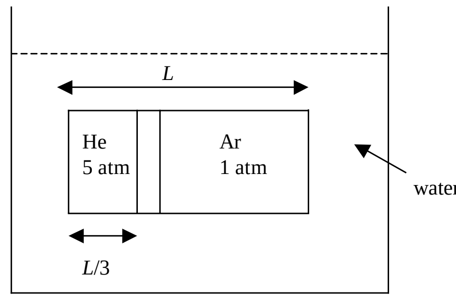
University of Illinois at Chicago
Department of Physics

Thermodynamics & Statistical Mechanics
Qualifying Examination

January 8, 2008
9.00 am – 12:00 pm

Full credit can be achieved from completely correct answers to <u>4 questions</u>. If the student attempts all 5 questions, all of the answers will be graded, and the <u>top 4 scores</u> will be counted toward the exam's total score.

Problem 1: A cylindrical container of length *L* is separated into two compartments by a thin piston, originally clamped at a position *L*/3 from the left end. The left compartment is filled with 1 mole of helium gas at 5 atm of pressure; the right compartment is filled with argon gas at 1 atm of pressure. These gases may be considered ideal. The cylinder is submerged in 1 liter of water, and the entire system is initially at the uniform temperature of 25°C, and thermally isolated from the surroundings. The heat capacities of the cylinder and the piston may be neglected. When the piston is unclamped, the system ultimately reaches a new equilibrium situation.



(a) What is the change in the temperature of the water?

(b) How far from the left end of the cylinder will the piston come to rest?

(c) Starting from $dS = \left(\frac{\partial S}{\partial V}\right)_T dV + \left(\frac{\partial S}{\partial T}\right)_V dT$, find the total increase in the entropy of the system.

(d) Now consider a slightly different situation, in which the left side of the cylinder contains 5 moles of real (not ideal) gas, with attractive intermolecular interactions. The right side still contains 1 mole of an ideal gas. As before, the piston is initially clamped at a position *L*/3 from the left end. When the piston is unclamped and released, does the temperature of the water increase, decrease, or stay the same? Does the internal energy of the gas increase, decrease, or remain the same? Explain your reasoning.

Problem 2: A copper block is cooled from T_B to T_A using a Carnot engine operating in reverse between a reservoir at T_C and the copper block. The copper block is then heated back up to T_B by placing it in thermal contact with another reservoir at T_B. ($T_C > T_B > T_A$)

(a) What is the limiting value of the heat capacity per mole for the copper block at high temperatures?

(b) Find the total entropy change of the universe in the cyclic process $B \rightarrow A \rightarrow B$ and show that it is greater than zero?

(c) How much work is done on the system, consisting of the copper block and the Carnot engine?

(d) For the cyclic path $B \rightarrow A \rightarrow B$, does the system absorb heat from the reservoirs or reject heat?

Problem 3: Two magnetic spin systems with N_1 = 500 spins and N_2 = 1000 spins are placed in an external magnetic field H. They are initially thermally isolated from one another and are prepared with spin excess values of m_1 = +20 and m_2 = +250, where $m = N_\uparrow - N_\downarrow$. The magnetic moment of each spin is denoted by μ_m. Assume that one can use the Gaussian approximation for the number of states of each system with energies between E and E + dE:

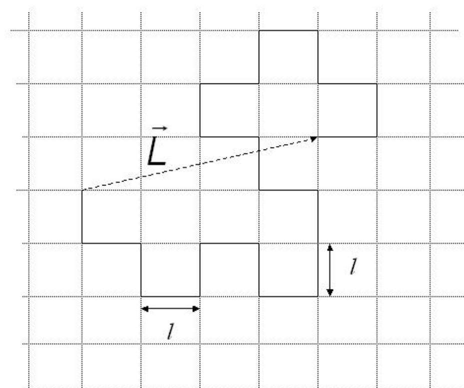
$$\Omega(N,E) = \frac{2^N}{\sqrt{2\pi N \mu_m^2 H^2}} \exp\left(-\frac{E^2}{2N\mu_m^2 H^2}\right) dE$$

(a) What is the total energy in each system (in units of $\mu_m H$) and the initial temperature of each system (in units of $\mu_m H / k$)?

(b) The two systems are brought into thermal contact. What are the spin excess values m_1^{eq} and m_2^{eq} and the final temperature, after they reach equilibrium?

(c) What is ΔS, the total change in the entropy of the combined system (in units of k), and what is the probability of finding the system in the initial configuration relative to the probability of finding the system in the equilibrium configuration?

Problem 4: Consider a 2-dimensional polymer, consisting of N links, each of length l. Each link has four allowed orientations, pointing in the $+x$ or $-x$ direction, or in the $+y$ or $-y$ direction.



(a) Show that the average end-to-end distance squared for this polymer is given by $< \vec{L} \bullet \vec{L} > = < L^2 > = Nl^2$

(b) Now consider a force f that extends the length of the polymer in the x-direction. In this simplified two-dimensional picture, the three allowed energy levels of each link are (i) $\varepsilon = -fl$, if the link is oriented in the direction of the applied force, $\varepsilon = +fl$, if the link is oriented opposite to the direction of the applied force, and (iii) $\varepsilon = 0$, if the link is oriented perpendicular to the direction of the applied force. Find the average extension $< L_x >$ in the x-direction as a function of the applied force, and show that, at low forces ($fl << k_B T$), the polymer behaves like a Hookean spring.

(c) The polymer is stretched quasistatically and isothermally such that the average extension in the x-direction is 5% of its unperturbed size $L = \sqrt{N}l$? Assume that the polymer still behaves as a Hookean spring. What is the change in the Helmholtz free energy of the polymer?

(d) Now consider that the polymer is stretched quasistatically and adiabatically. Will the temperature of the polymer increase or decrease in this process?

Problem 5: Consider a system consisting of impurity atoms in a semiconductor. Suppose that the impurity atom has one "extra" electron (with two degenerate spin states), compared to the neighboring atoms (e.g. a phosphorus atom occupying a lattice site in a silicon crystal). The extra electron is easily removed, contributing to conduction electrons, and leaving behind a positively charged ion.

(a) What is the probability that a single donor atom is ionized? Express your result in terms of the ionization energy I, and the chemical potential of the "gas" of ionized electrons.

(b) If every conduction electron comes from an ionized donor, and the conduction electrons behave like an ideal gas, write down an expression that relates the number of conduction electrons N_c and the number of donor atoms N_d, in terms of the volume V of the sample, the temperature T and fundamental constants.

(c) Show that in the limit of low $(kT << I)$ and high $(kT >> I)$ temperatures, the ratio N_c / N_d has the expected values.

(d) Write down an expression for the Gibbs free energy of the conduction electrons in terms of N_c, T and V and show that it is an extensive quantity.

Equations and constants:

$k_B = 1.381\times10^{-23}$ J/K; $N_A = 6.022\times10^{23}$; $R = 8.315$ J/mol/K;   1 atm = 1.013×10^5 N/m^2

Hyperbolic functions

$$\sinh x = \frac{e^x - e^{-x}}{2} \qquad \cosh x = \frac{e^x + e^{-x}}{2} \qquad \tanh x = \frac{\sinh x}{\cosh x}$$

Inequality

$$\ln(y) \le y - 1$$

Maxwell's relations

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V; \qquad \left(\frac{\partial T}{\partial V}\right)_P = -\left(\frac{\partial P}{\partial S}\right)_T; \qquad \left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P; \qquad \left(\frac{\partial T}{\partial P}\right)_V = \left(\frac{\partial V}{\partial S}\right)_T$$

Ideal gas

$$\mu = -k_B T \ln\left(\frac{V Z_{\text{int}}}{N v_q}\right); \qquad v_q = \left(\frac{h^2}{2\pi m k_B T}\right)^{3/2}$$