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</u> <u>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.
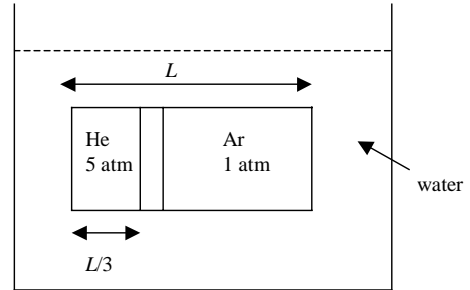
(a) What is the change in the temperature of the water?

For the system consisting of the cylinder, the piston and the gases,
$$\Delta U = Q + W = Q$$
The expanding gas on the left side of the cylinder does work on the right side of the cylinder, with net work done on the system $W = 0$.

If $\Delta U > 0 \Rightarrow Q > 0$, i.e. the system will absorb heat from the water. The temperature of the gases in the cylinder will increase, while the temperature of the water will decrease, in violation of the second law of thermodynamics. Similarly, if $\Delta U < 0 \Rightarrow Q < 0$, while would result in a decrease in the temperature of the gases and an increase in the temperature of water, again in violation of the second law. The only situation possible is $\Delta U = Q = 0$. No heat is absorbed or rejected by the system, and the temperature of the water, and the gases, remains unchanged.

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

The initial situation, before the piston is unclamped, gives

$$P_L V_L = n_L RT \text{ and } P_R V_R = n_R RT \Rightarrow \frac{P_L V_L}{P_R V_R} = \frac{n_L}{n_R} = \frac{5V/3}{2V/3} = 5/2$$

The number of moles of gas on the right side $n_R = \frac{2}{5} n_L = 2/5$

When the piston is unclamped, the pressure on both sides is equal

$$P_f = \frac{n_L RT}{V_{Lf}} = \frac{n_R RT}{V_{Rf}} \Rightarrow \frac{V_{Lf}}{V_{Rf}} = \frac{n_L}{n_R} = 5/2$$

The piston will move to a distance $5L/7$ from the left side of the cylinder.

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

$$dS = \left(\frac{\partial S}{\partial V}\right)_T dV + \left(\frac{\partial S}{\partial T}\right)_V dT = \left(\frac{\partial S}{\partial V}\right)_T dV \ \text{ since } \ dT = 0$$

Use the Maxwell relation $\left(\dfrac{\partial S}{\partial V}\right)_T = \left(\dfrac{\partial P}{\partial T}\right)_V$ to get $dS = \left(\dfrac{\partial P}{\partial T}\right)_V dV = nR\dfrac{dV}{V}$ for an ideal gas.

The total entropy change of the system is then given by

$$\Delta S = \Delta S_L + \Delta S_R = n_L R \ln\left(\frac{V_{Lf}}{V_{Li}}\right) + n_R R \ln\left(\frac{V_{Rf}}{V_{Ri}}\right) = R\ln\left(\frac{5V/7}{V/3}\right) + \frac{2}{5}R\ln\left(\frac{2V/7}{2V/3}\right) = R\ln(15/7) + \frac{2}{5}R\ln(3/7)$$

$\Delta S = 3.52$ Joules/K

(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.

We still have $\Delta U = Q$, as in part (a), since $W = 0$.

If the system was thermally isolated from the surroundings, we would have had $\Delta U = Q = 0$.

For a real gas, U is a function of volume and temperature. An increase in volume increases the intermolecular distance between the gas molecules, thus increasing the potential energy contribution to the internal energy. Therefore, if the system was thermally isolated, an increase in the potential energy of the gas would be compensated by a decrease in the kinetic energy, to maintain $\Delta U = 0$, and the gas would cool. Since our system is in thermal contact with water, the cooling gas will absorb heat from the water, and the water will cool. The water and the gas will equilibrate to a temperature lower than the initial temperature of 25°C. From $\Delta U = Q$ we can see that the total internal energy of the gas will increase.

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?

From the equipartition theorem $U = f/2kT$ where $f \approx 6N$ are the quadratic degrees of freedom corresponding to 3N vibrational modes in the solid. Therefore $U = 3NkT = 3nRT$ and the heat capacity $C = 3nR$, which gives heat capacity per mole of ≈ 25 J/K.

(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?

For the reversible path $B \rightarrow A$

$$\Delta S_{system}^{B \rightarrow A} = \int_{T_B}^{T_A} \frac{C}{T} dT = C \ln\left(\frac{T_A}{T_B}\right) < 0$$

$$\Delta S_{reservoir}^{B \rightarrow A} = -\Delta S_{system}^{B \rightarrow A} = C \ln\left(\frac{T_B}{T_A}\right) > 0$$

For the irreversible path $A \rightarrow B$

$$\Delta S_{system}^{A \rightarrow B} = -\Delta S_{system}^{B \rightarrow A} = C \ln\left(\frac{T_B}{T_A}\right) > 0$$

$$\Delta S_{reservoir}^{A \rightarrow B} = \frac{Q_R}{T_R} = \frac{-Q_{system}}{T_B} = \frac{-\int_{T_A}^{T_B} C dT}{T_B} = C \frac{T_A - T_B}{T_B} < 0$$

$$\Delta S_{cycle} = C \ln\left(\frac{T_B}{T_A}\right) - C\left(1 - \frac{T_A}{T_B}\right)$$

Use the inequality $\ln(y) \leq y - 1$ or $\ln\left(\frac{1}{y}\right) \geq 1 - y$ to get $\ln\left(\frac{T_B}{T_A}\right) \geq 1 - \frac{T_A}{T_B} \Rightarrow \Delta S_{cycle} \geq 0$

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

The work is done along the path $B \rightarrow A$ when the block is cooled. In this process, work is done on the Carnot engine, which is run in reverse, as a refrigerator. In each Carnot cycle, an amount of heat dQ_2 is extracted from the copper block and a larger amount of heat $dQ_1 = dQ_2 + dW$ is transferred to the reservoir at T_c, where dW is the work done on the refrigerator.

Also, from the thermodynamic definition of temperature $\dfrac{dQ_1}{T_C} = \dfrac{dQ_2}{T}$

where T is the instantaneous temperature of the copper block.

The infinitesimal work done in each cycle is given by

$$dW = dQ_1 - dQ_2 = dQ_2\left(\dfrac{T_C}{T} - 1\right) = -CdT\left(\dfrac{T_C}{T} - 1\right)$$

where we have written $dQ_2 = -CdT$ is the heat rejected by the system in each cycle.

Net work done is $W = -C\displaystyle\int_{T_B}^{T_A}\left(\dfrac{T_C}{T} - 1\right)dT = CT_C\ln\left(\dfrac{T_B}{T_A}\right) - C(T_B - T_A)$

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

In the cyclic path, there is no change in the state functions. Therefore, $\Delta U = 0$

From the first law, $\Delta U = Q + W$
From the result of part (c), you can show that $W > 0$, using the same inequality as in part (b) and since $T_C > T_B$
Therefore $W > 0 \Rightarrow Q < 0 \Rightarrow$ net heat is rejected by the system to the reservoirs.
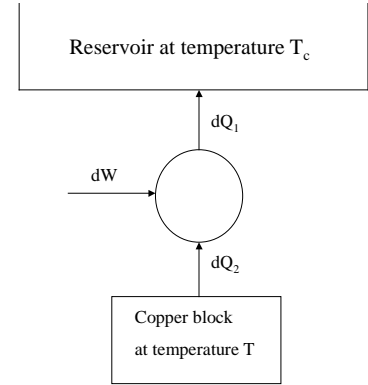
Problem 3

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 $E + dE$:

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

(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 $\mu_m H / k$)?

$$\dfrac{1}{T} = \left(\dfrac{\partial S}{\partial E}\right)_{N,H} = k\left(\dfrac{\partial \ln\Omega}{\partial E}\right) = -k\dfrac{E}{N\mu_m^2 H^2} \Rightarrow T = -\dfrac{N\mu_m^2 H^2}{Ek}$$

But $E = -m\mu_m H \Rightarrow T = \dfrac{N}{m}\dfrac{\mu_m H}{k}$

Therefore, $T_1^{initial} = 25\dfrac{\mu_m H}{k}$ and $T_2^{initial} = 4\dfrac{\mu_m H}{k}$

$E_1^{initial} = -20\mu_m H$ and $E_2^{initial} = -250\mu_m H$

(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?

At equilibrium $T_1^{eq} = T_2^{eq} \Rightarrow \dfrac{N_1}{m_1^{eq}} = \dfrac{N_2}{m_2^{eq}} \Rightarrow \dfrac{m_2^{eq}}{m_1^{eq}} = \dfrac{N_2}{N_1} = 2$

Also, the total energy of the combined system is a constant

$E_1^{initial} + E_2^{initial} = E_1^{eq} + E_2^{eq} \Rightarrow m_1^{initial} + m_2^{initial} = m_1^{eq} + m_2^{eq} = 270$

$\Rightarrow m_1^{eq} + 2m_1^{eq} = 270 \Rightarrow m_1^{eq} = 90$ and $m_2^{eq} = 180$

$T_1^{eq} = T_2^{eq} = 5.55\dfrac{\mu_m H}{k}$

(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?

$$\Delta S = S_f - S_i = k\ln\left(\dfrac{\Omega_f}{\Omega_i}\right) = k\ln\left(\dfrac{\Omega_1^{final}\Omega_2^{final}}{\Omega_1^{initial}\Omega_2^{initial}}\right) = k\ln\left(\dfrac{\exp\left[-\dfrac{1}{2\mu_m^2 H^2}\left(\dfrac{E_1^{eq^2}}{N_1} + \dfrac{E_2^{eq^2}}{N_2}\right)\right]}{\exp\left[-\dfrac{1}{2\mu_m^2 H^2}\left(\dfrac{\left(E_1^{initial}\right)^2}{N_1} + \dfrac{\left(E_2^{initial}\right)^2}{N_2}\right)\right]}\right)$$

Simplify to get

$$\Delta S = \dfrac{k}{2\mu_m^2 H^2}\left[-\dfrac{E_1^{eq^2}}{N_1} - \dfrac{E_2^{eq^2}}{N_2} + \dfrac{\left(E_1^{initial}\right)^2}{N_1} + \dfrac{\left(E_2^{initial}\right)^2}{N_2}\right] = \dfrac{k}{2}\left[\dfrac{\left(m_1^{initial}\right)^2 - m_1^{eq^2}}{N_1} + \dfrac{\left(m_2^{initial}\right)^2 - m_2^{eq^2}}{N_2}\right]$$

$\Delta S = 7.35k$ which is greater than zero, as expected for an irreversible process.

$\dfrac{p^{initial}}{p^{eq}} = \dfrac{\Omega^{initial}}{\Omega^{eq}} = \exp(-\Delta S/k) = \exp(-7.35) \approx 6.4 \times 10^{-4}$

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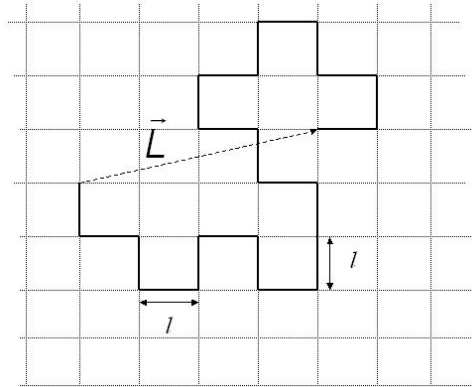
(a) Show that the average end-to-end distance squared for this polymer is given by $< \vec{L} \bullet \vec{L} >=< L^2 >= Nl^2$

$$< L^2 >=< L_x^2 > + < L_y^2 >= N < l_x^2 > +N < l_y^2 >$$

Since each link has four allowed orientations, with equal energy, which we can set equal to zero, the statistical weight of each orientation is 1 and the partition function for a single link is $Z_1 = 4$

We can write $< l_x^2 >= \dfrac{l^2(1) + l^2(1) + 0 + 0}{4} = l^2 / 2$

Similarly, $< l_y^2 >= \dfrac{l^2(1) + l^2(1) + 0 + 0}{4} = l^2 / 2$

Therefore, $< L^2 >= Nl^2 / 2 + Nl^2 / 2 = Nl^2$

(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 ($fl \ll k_{\mathrm{B}}T$), the polymer behaves like a Hookean spring.

The average projection of each link in the x-direction is given by

$$< l_x >= \dfrac{- l\exp(-\varepsilon_- / kT) + l\exp(-\varepsilon_+ / kT) + 0(\exp(-\varepsilon_0 / kT) + 0(\exp(-\varepsilon_0 / kT)}{\exp(-\varepsilon_- / kT) + \exp(-\varepsilon_+ / kT) + (\exp(-\varepsilon_0 / kT) + (\exp(-\varepsilon_0 / kT)}$$

$$< l_x >= \dfrac{- l\exp(-fl / kT) + l\exp(fl / kT)}{\exp(-fl / kT) + \exp(fl / kT) + 2} = l\dfrac{\sinh(fl / kT)}{\cosh(fl / kT) + 1}$$

Average extension in the x-direction is

$$< L_x >= N < l_x >= Nl\dfrac{\sinh(fl / kT)}{\cosh(fl / kT) + 1}$$

In the limit $fl \ll kT$, $\sinh(x) \approx x$ and $\cosh(x) \approx 1$, where $x = fl/kT$

$$< L_x > = Nl\frac{(fl/kT)}{2} = \frac{Nfl^2}{2kT}$$

Rewrite as $f = \frac{2kT}{Nl^2} < L_x >$

The polymer behaves like an entropic spring, with a spring constant $k_{sp} = \frac{2kT}{Nl^2}$

(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?

For a quasistatic process at constant temperature, $\Delta F = W$

The work done to stretch the polymer is $W = \frac{1}{2}k_{sp}(\Delta L)^2 = \frac{1}{2}\left(\frac{2kT}{Nl^2}\right)\left(0.05\sqrt{N}l\right)^2 = 0.05kT$

Therefore $\Delta F = 0.05kT$

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

When the polymer is stretched, the configuration of the polymer goes from more random to less random, which tends to decrease the configurational entropy. However, in a reversible, adiabatic process, the total entropy of the system does not change (isoentropic process). Therefore, the temperature of the polymer must increase to compensate for the loss of configurational entropy.

More formally, consider $S(T,L)$

$$dS = \left(\frac{\partial S}{\partial T}\right)_L dT + \left(\frac{\partial S}{\partial L}\right)_T dL = 0$$

or $\left(\frac{\partial T}{\partial L}\right)_S = -\left(\frac{\partial S}{\partial L}\right)_T\left(\frac{\partial T}{\partial S}\right)_L$

The first term on the right is negative, since the entropy of the chain decreases as the length increases at constant temperature. The second term on the right is related to the inverse of the heat capacity, and is positive.

Therefore $\left(\frac{\partial T}{\partial L}\right)_S > 0$.

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.

Taking the system to be a single donor atom, there are three possible states: one ionized state with no electron, and two un-ionized states (with one electron present, either spin-up or spin-down).

The energies and Gibbs factors of these states are:

ionized: $\varepsilon = 0, \ n = 0$,   Gibbs factor $= \exp(0) = 1$
unionized: $\varepsilon = -I, \ n = 1$,   Gibbs factor $= \exp(-(-I - \mu)/kT) = \exp((I + \mu)/kT)$

The grand partition function can be written as
$$\Xi = 1 + 2\exp((I + \mu)/kT)$$
and the probability that the donor atom is ionized is
$$P(ionized) = \frac{1}{1 + 2\exp((I + \mu)/kT)}$$

(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.

$$P(ionized) = \frac{N_c}{N_d}$$

Also, for an ideal gas of conduction electrons with two spin states per particle, the chemical potential is $\mu = -kT\ln\left(\frac{VZ_{int}}{N_c v_q}\right) = kT\ln\left(\frac{N_c v_q}{2V}\right)$

where $Z_{int} = 2$ for the two spin orientations, and $v_q = \left(\frac{h^2}{2\pi mkT}\right)^{3/2}$ is the quantum volume.

Therefore, we can write

$$\frac{N_c}{N_d} = \frac{1}{1 + 2\left(\frac{N_c v_q}{2V}\right)\exp(I/kT)} = \frac{1}{1 + (N_c/V)v_q \exp(I/kT)}$$

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To solve for N_c rewrite the equation in terms of dimensionless quantities:

$$x = \frac{1}{1+xy} \text{ where } x = N_c / N_d \text{ and } y = (N_d / V) v_q \exp(I/kT)$$

or $x^2 y + x - 1 = 0 \Rightarrow x = \dfrac{-1 \pm \sqrt{1+4y}}{2y}$

Since x is a positive quantity, retain the solution with the plus sign to get:

$$N_c = \frac{V}{2v_q \exp(I/kT)} \left(\sqrt{1 + 4(N_d/V) v_q \exp(I/kT)} - 1 \right)$$

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

You can start with $\dfrac{N_c}{N_d} = \dfrac{1}{1 + (N_c/V) v_q \exp(I/kT)}$

to show that, in the limit $T \to 0$, $\exp(I/kT) \gg 1$ and $v_q \gg V/N_c$

$$\Rightarrow \frac{N_c}{N_d} = \frac{V}{N_c v_q \exp(I/kT)} \Rightarrow N_c^2 = \frac{N_d V}{v_q} \exp(-I/kT) \Rightarrow N_c = \sqrt{\frac{N_d V}{v_q}} \exp(-I/2kT)$$

In the limit $T \to 0$, $N_c / N_d \to 0$

In the high T limit, $\exp(I/kT) \to 1$ and $v_q \to 0 \Rightarrow N_c / N_d \to 1$ as expected, with all the donor atoms ionized.

(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.

Gibbs free energy $G = \mu N_c = kTN_c \ln\left(\dfrac{N_c v_q}{2V} \right)$

If the size of the system doubles, $V \to 2V$ and $N_c \to 2N_c$ while N_c/V, v_q and T remain unchanged.

The Gibbs free energy doubles, as expected for an extensive quantity.

Equations and constants:

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

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