University of Illinois at Chicago
Department of Physics

Thermodynamics & Statistical Mechanics
Qualifying Examination

January 9, 2009
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 vertical cylinder contains n moles of an ideal gas, and is closed off by a piston of mass M and area A. The acceleration due to gravity is g. The molar specific heat Cv (at constant volume) of the gas is a constant independent of temperature. The heat capacities of the piston and the cylinder are negligibly small, and any frictional forces between the piston and the cylinder walls can be neglected. The whole system is thermally isolated. Initially the piston is clamped in position so that the gas has a volume V_o and a temperature T_o. The piston is now released and, after some oscillations, comes to rest in a final equilibrium state corresponding to a larger volume of the gas. Assume that the external air pressure is negligible.

(a) Does the temperature of the gas increase, decrease, or stay the same. Explain your answer.

(b) Does the entropy of the gas increase, decrease, or remain the same? Explain your answer.

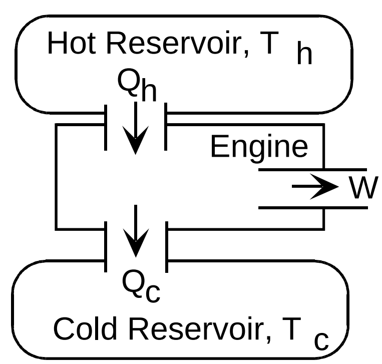
(c) Express the ratio T_f/V_f in terms of M, g, A, n and the gas constant R, where T_f and V_f are the final temperature and volume, respectively, of the gas.

(d) What is the net work done by the gas in this process? Express your answer in terms of V_o, V_f, M, g, and A.

(e) What is the final temperature T_f? Express your answer in terms of T_o, V_o, M, g, A, C_v, n and R.

Problem 2

The diagram shows the energy flow in a heat engine.



(a) State the definition of the efficiency of this heat engine in terms of the heat Q_h absorbed from the hot reservoir, and the heat Q_c rejected to the cold reservoir. Do not assume that the engine is reversible.

(b) Based upon entropy considerations, derive an inequality between the efficiency of the engine, and the temperatures of the reservoirs.

For parts (c)-(e), replace the reservoirs by two identical but finite bodies, each characterized by a heat capacity at constant pressure C, which is independent of temperature. The bodies remain at constant pressure and undergo no change of phase. Initially, their temperatures are T_1 and T_2, respectively; finally, as a result of the operation of the heat engine, the bodies will attain a common final temperature T_f.

(c) What is the total amount of work W done by the engine? Do not assume that the engine is operated reversibly. Express your answer in terms of C, T_1, T_2, and T_f.

(d) As in part (b), use entropy considerations to derive an inequality relating T_f to the initial temperatures T_1 and T_2.

(e) For given initial temperatures T_1 and T_2, what is the maximum amount of work obtainable by operating an engine between these two bodies?

Problem 3

Consider a paramagnetic material consisting of N non-interacting spin-1 particles (with magnetic dipole moment $\vec{\mu} = \frac{\mu}{\hbar}\vec{S}$, $S_z = m\hbar$, $m = 0, \pm 1$). Suppose that these spins reside in (and are in thermal equilibrium with) a crystal lattice, which is in good thermal contact with a reservoir at temperature T. We apply a magnetic field of magnitude B in the z-direction.

(a) Write the partition function of the paramagnetic system in terms of $k_B T$ and μB.

(b) How does the average energy of the N spins vary with temperature T?

(c) Calculate the spin contribution to the entropy of the crystal and show that it is only a function of $\mu B / k_B T$.

(d) What are the limiting values of the entropy as $T \to 0$ and as $T \to \infty$? How would your results change if the system consisted of spin-1/2 particles?

(e) The crystal is initially in contact with a reservoir at $T = T_1$ and the magnetic field has a magnitude B_1. The crystal is now thermally isolated, and the magnetic field strength is slowly turned down to a value B_2. Calculate the final temperature T_2 of the spins (and therefore the temperature of the crystal lattice).

Problem 4

(a) Consider a spinless quantum mechanical particle of mass m in a simple harmonic oscillator potential in one dimension of frequency ν and at temperature T. The energy levels for this particle are given by $E_n = (n + 1/2)h\nu$. Write down the partition function, Z_1, of a single such particle in the oscillator. Express your result in terms of the dimensionless quantity $\alpha = h\nu / k_B T$

(b) Consider N spinless, distinguishable particles placed in this oscillator. Write down the partition function Z_N for N such particles.

(c) Now consider two identical spinless particles placed in this oscillator. Write down the partition function Z_2 for the two particles at temperature T as an expansion in $\xi = e^{-\alpha}$ up to and including order ξ^4.

(d) Repeat part (c) for two identical Fermi particles, of spin 1/2, put in such an oscillator, one with spin up and the other with spin down.

(e) How does the partition function from part (d) change if the two fermions are both in spin-up states in the oscillator.

Problem 5

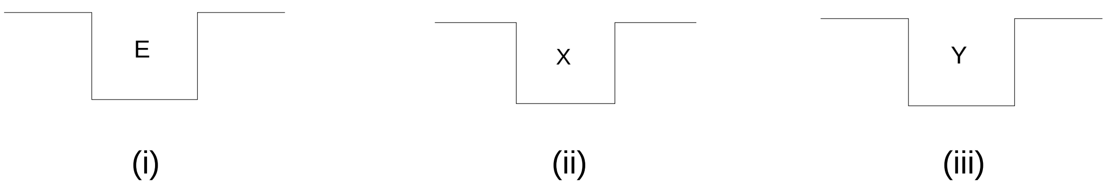
The internal energy U and entropy S of an ideal monatomic gas at temperature T are, respectively:

$$U = 3Nk_B T/2; \qquad\qquad S = Nk_B\left[\ln(n_o/n) + 5/2\right]$$

Here k_B is the Boltzmann constant, N is the number of atoms, $n = N/V$ is the average concentration, and $n_o = \left(Mk_B T/2\pi\hbar^2\right)^{3/2}$, with M the atomic mass.

(a) Show that the chemical potential μ of the gas is related to the pressure P of the gas by $\mu = -k_B T \ln\left(n_o k_B T/P\right)$.

Two such gases, X and Y, are in equilibrium with surface sites at which the gases bind to a metal surface. In the presence of X and Y simultaneously there are just three possible configurations of each surface site: (i) the surface site is empty (denoted by E below); (ii) the surface site is occupied by one X atom, with energy ε_x relative to the empty site; (iii) the surface site is occupied by one Y atom, with energy ε_y relative to the empty site. Excited configurations at the site are not bound, and multiple occupancy is forbidden.



(b) The metal surface is at equilibrium with gases X and Y simultaneously at temperature T. In terms of the parameters defined above, and chemical potentials μ_x and μ_y, write down the grand partition function for the configurations of one site.

(c) Calculate the probability that the site is (i) empty, (ii) occupied by X, (iii) occupied by Y.

(d) At room temperature, and fixed partial pressures of $P_x = P_y = 0.5$ atm, the sites are occupied in the ratio n_E:n_X:n_Y = 1:1:2. What is the energy difference $\Delta\varepsilon = \varepsilon_X - \varepsilon_Y$? Ignore any differences in the atomic masses M_x and M_Y. Express your answer in units of $k_B T$.

(e) The partial pressures are now doubled to 1 atm each. What is the new value of the ratio n_E:n_X:n_Y?

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

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

Maxwell's relations

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