Preliminary Examination: Thermodynamics and Stat. Mech.

Department of Physics and Astronomy
University of New Mexico

Fall 2004

Instructions:

- The exam consists two parts: 5 short answers (6 points each) and your pick of 2 out 3 long answer problems (35 points each).
- Where possible, show all work, partial credit will be given.
- Personal notes on two sides of a 8X11 page are allowed.
- Total time: 3 hours

Good luck!

Short Answers:

S1. Describe the microscopic mechanism by which evaporation cools a cup of hot coffee?

S2. A molecule of oxygen is composed of two oxygen atoms, each having a mass of 2.7×10^{-26} kg, separated from one another by a fixed distance of 1.24×10^{-10} m. Below what characteristic temperature will the rotational degrees of freedom of O_2 gas be effectively "frozen out"? Sketch a graph of the heat capacity at constant volume as a function of temperature for one mole of dilute O_2 gas, over a range which includes this characteristic temperature.

S3. The fermi level of a certain metal is 5.25 eV at room temperature. What is the probability that a state which is 0.10 eV above the fermi level is occupied by an electron?

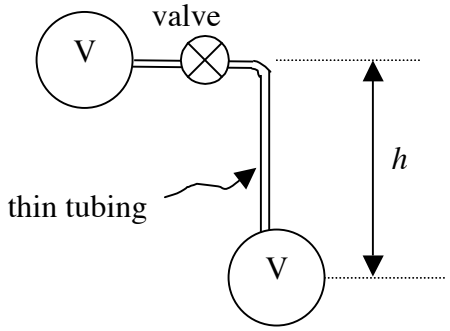
S4. To model the process by which gas is adsorbed on the surface of a metal, the metal surface can be described as a corregated muffin-tin potential, as shown in the figure. Gas atoms can lower their energy by sitting in the potential minima on the surface, which serve as a set of identical adhesion sites. Interactions between the gas atoms can be ignored, except for the fact that each site may be occupied no more than one atom.

Consider a thermodynamic system consisting of a metal surface with M adhesion sites which are occupied by N indistinguishable gas atoms ($N<M$). What is the change in the entropy of this system if one more gas atom is added to the surface?

S5. A narrow potential well consists of only two bound states, a ground state and a first excited state. The potential well is occupied by exactly two noninteracting indistinguishable particles, which are bosons. The energy to place a particle in the excited state is higher than the energy to place a particle in the ground state by Δ. What is the probability that both particles are in the excited state at a temperature T.

Long Answers: Pick two out of three problems below

L1. A glass bulb of volume V containing N atoms of ideal gas each with mass m is connected by a long thin tube to a second bulb of volume V, which is evacuated. The first bulb is located at a height h above the second bulb, as shown in the figure below, and initially the tube is closed off by a valve. The entire system is in contact with the surroundings at a temperature T. When the stopcock is opened, the gas expands to fill both bulbs. The volume of gas residing in the connecting tube is negligible.



(a) The partition function for an ensemble describing an ideal gas having N atoms which is in equilibrium at constant T and V in a vessel which is at an elevation h is given by

$$\frac{V^N}{N!}\left(\frac{mkT}{2\pi\hbar^2}\right)^{3N/2}\exp\left[-\frac{Nmgh}{kT}\right]$$

What is the Helmholtz free energy of the gas before the stopcock is opened?
Show how to derive the equation of state from the Helmholtz free energy.

(b) After the expansion, what is the gas pressure in the upper bulb? What is the gas pressure in the lower bulb?

(c) How much heat is absorbed by the gas from the surroundings in the expansion?

L2. A crystalline solid contains N similar, immobile, statistically independent defects. Each defect has 5 possible states with energies, $\varepsilon_1 = \varepsilon_2 = 0$, $\varepsilon_3 = \varepsilon_4 = \varepsilon_5 = \Delta$.

(a) Find the partition function of the system.

(b) Find the defect contribution to the entropy of the crystal as a function of Δ and the temperature T.

(c) Without doing a detailed calculation, find the contribution to the internal energy due to the defects, in the high temperature limit $kT >> \Delta$.

L3. A cylinder containing n moles of ideal gas is positioned vertically as shown in the figure below. The ambient pressure and temperature are P_{ext} and T respectively, and the heat capacity of the gas at constant volume is $(5/2)nR$ where R is the ideal gas constant. The cylinder is closed by a piston which has a mass M and surface area A, and slides with no friction on the walls of the cylinder. In equilibrium, the total downward force $P_{ext}A + Mg$ on the piston is equal to the upward force PA exerted by the gas. When the piston is depressed slightly and released, it oscillates with a frequency

$$\omega = \sqrt{\frac{A^2}{M}\left(-\frac{\partial P}{\partial V}\right)}.$$

(a) Assuming that the oscillation frequency is slow enough so that the gas compressions are nearly isothermal, show that

$$\omega = \sqrt{\frac{\left(P_{\text{ext}}A + Mg\right)^2}{nRTM}}$$

(b) Alternatively, obtain an expression for ω as a function of T and P_{ext} for the case that the compressions may be considered to be adiabatic. Compare this result to the result from part (a) and discuss the physical origin of the difference.

Preliminary Examination: Thermodynamics and Statistical Mechanics

Department of Physics and Astronomy
University of New Mexico

Fall 2005

Instructions:

•The exam consists of two parts: Complete 5 short answer problems (6 points each) and your choice of 2 of 3 long answer problems (35 points each).

•Where possible, show all work; partial credit will be given.

•Personal notes on two sides of an 8×11 page are allowed.

•Total time: 3 hours.

Short Answers:

S1. A heat pump is used to heat a house in Albuquerque in the winter. The pump can maintain an inside temperature of 21° C when the outside temperature is 0° C. Assuming optimal efficiency, how many kJ of electrical energy must be expended to operate the pump for every kJ of heat that is deposited in the house?

S2. The work to place a charge Q on a capacitor at constant temperature T is given by the change in Helmoholtz free energy,

$$\Delta A = \frac{Q^2}{2C},$$

where C is the capacitance. If the capacitance $C = \lambda/T$ is inversely proportional to temperature, where λ is a constant, how does the capacitor's internal energy U depend on the charge Q?

S3. The free energy of a system containing N identical particles at a temperature T is given by

$$A = NkT\left(\ln\frac{N}{N_0} - 1\right) + N\varepsilon_0,$$

where the number N_0 and the energy ε_0 are constants. What is the value of N in equilibrium if the system is placed in contact with a particle reservoir having a chemical potential μ?

S4. The Hamiltonian for an *anharmonic* oscillator in one dimension is given by

$$H = \frac{p^2}{2m} + \frac{1}{4}kx^4.$$

The oscillator is in contact with a heat reservoir at a temperature T which is high enough so that classical mechanics is applicable. According to the law of equipartition, the average kinetic energy of a particle in thermal equilibrium is $kT/2$ per degree of freedom. Use the law of equipartition together with the virial theorem,

$$\left\langle p\frac{\partial H}{\partial p} \right\rangle = \left\langle x\frac{\partial H}{\partial x} \right\rangle,$$

to determine the average energy of the oscillator.

S5. The vibrational motion of a solid containing N atoms is sometimes modeled as a collection of $3N$ independent harmonic oscillators, each having the same natural frequency ω_0. Obtain an expression for the heat capacity of such a system, and graph the heat capacity versus temperature for $kT \ll \hbar\omega_0$ to $kT \gg \hbar\omega_0$.

Long Answers: Choose 2 out of 3 problems below.

L1. A system in equilibrium at room temperature consists of a dilute noninteracting gas of N molecules which are confined to a vessel having a volume V. Each molecule has a permanent dipole moment $\vec{p}_0$ and a mass m. A uniform electric field of strength E is maintained inside the vessel.

(a) Enumerate the states semiclassically and calculate the partition function associated with this system. You may neglect the rotational kinetic energy.

(b) Obtain an expression for the polarizability $\vec{\pi} = \frac{N}{V} \langle \vec{p}_0 \rangle$, and deduce from this the linear susceptibility χ.

(c) Suppose that the same gas is maintained at a constant pressure $P_{\rm ext}$ and field $E = 0$ in the environment external to the vessel. If a small hole is drilled in the vessel to allow gaseous exchange with the environment, how will the pressure P in the vessel differ from $P_{\rm ext}$ in equilibrium?

L2. Many of the electronic properties of a metal may be understood though a simple model in which the mobile electrons in the conduction band are treated as a gas of noninteracting particles having spin 1/2 and mass m. For a typical metal, the conduction band electron density is $n \simeq 30 \times 10^{27}$ m^{-3}, and $m \simeq 0.51$ MeV/c^2 (9.1×10^{-31} kg). For these material parameters, carry out the following calculations in the low temperature ($T = 0$) limit:

(a) Calculate the chemical potential μ for the electron gas (in eV).

(b) Derive an expression for the distribution of particle speeds $v = |\vec{v}|$.

(c) Use the distribution of particle speeds together with arguments from kinetic theory to determine the electron gas pressure in atmospheres (1 atm $\simeq 10^5$ N/m^2). If you would prefer to find the pressure in some other manner, you may do so, but be sure to elucidate your method.

L3. A solid is composed of atoms whose nuclei have spin one. Because the nuclear charge distribution is not spherically symmetrical, the energy ε of the nucleus of each atom depends on its azimuthal quantum number m. Assume that this orientation energy is $\varepsilon = \varepsilon_0$ for $m = 1$ and $m = -1$, and $\varepsilon = 0$ for $m = 0$.

(a) Find the contribution of the nuclear orientation energy to the molar energy of the crystal as a function of temperature.

(b) Find the corresponding entropy.

(c) Sketch the temperature dependence of the nuclear contribution to the molar specific heat. Give a physical explanation for the behavior at low and high temperatures.

Preliminary Examination: Thermodynamics and Statistical Mechanics

Department of Physics and Astronomy
University of New Mexico

Fall 2006

Instructions:

•The exam consists of 10 problems (10 points each).

•Personal notes on two sides of an 8×11 page are allowed.

•You will be graded on your work, so be sure to show it; display all of the steps in your derivations and include explanations if necessary. Partial credit will not be awarded for haphazard expressions, nor for writing down results that have been worked out elsewhere and/or previously.

•Total time: 3 hours.

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

P	:	Pressure
T	:	Absolute Temperature
k	:	Boltzmann's constant
$\hbar$	:	Planck's constant divided by 2π
β	:	$(kT)^{-1}$
S	:	Entropy
V	:	Volume

Useful Integrals and Sums:

$$\int_{-\infty}^{\infty} dx e^{-ax^2} e^{bx} = e^{\frac{b^2}{4a}} \sqrt{\frac{\pi}{a}};\ \mathrm{Re}\, a > 0$$

$$\sum_{m=0}^{\infty} x^m = \frac{1}{1-x}\ ;\ |x| < 1.$$

P1. It can be shown using the first and second laws of thermodynamics that the heat capacity at constant pressure C_p is greater than the heat capacity at constant volume C_V for any physical substance. Suppose that the equation of state for n moles of a particular fluid is given by $PV = nRT$, while its internal energy is given by $U = \frac{7}{2}nRT$, where R is a constant. Prove that, in such a case, $C_p - C_V = nR$.

P2. According to Planck, the internal energy of a blackbody with volume V is given by the integral expression

$$U = \frac{V}{\pi^2 c^3} \int_0^\infty d\omega \frac{\hbar \omega^3}{e^{\beta \hbar \omega} - 1},$$

where c is the speed of light. Given this expression for U, show that the energy for a blackbody is proportional to T^4.

P3. The Helmholz free energy of a gas of N noninteracting electrons in a volume V at low temperatures is given by

$$A = \frac{(3N)^{5/3}}{V^{2/3}} \left(\frac{\pi^{4/3}\hbar^2}{10m} \right).$$

where m is the electron mass. Use this expression for A to obtain an expression for the chemical potential (fermi energy).

P4. Consider a system in thermal equilibrium consisting of two point-particles, each having mass m, moving in three dimensions, their locations with respect to a fixed origin specified by position vectors $\vec{r}_1$ and $\vec{r}_2$ respectively. The particles are harmonically attracted to the origin, and to each other, such that the potential energy $V(\vec{r}_1, \vec{r}_2)$ is as follows:

$$V(\vec{r}_1, \vec{r}_2) = \frac{1}{2}\zeta \left|\vec{r}_1 - \vec{r}_2\right|^2 + \frac{1}{2}\eta \left|\vec{r}_1\right|^2 + \frac{1}{2}\eta \left|\vec{r}_2\right|^2 .$$

Here, ζ and η are positive constants. Find the heat capacity of this system for high temperatures.

P5. A system consists a mass m moving in one dimension, and attached to a rigid wall by a spring having stiffness constant K, as shown in Figure 1. The mass is subjected to a constant force F, and it is in equilibrium with the surroundings at a temperature T. Assuming that the system states may be enumerated semiclassically, calculate the partition function and show that it is given by

$$Z = \frac{\exp\left(\frac{\beta F^2}{2K}\right)}{\hbar\beta\sqrt{K/m}}.$$

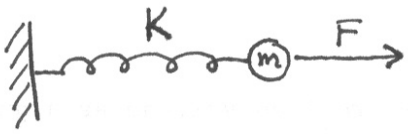


Figure 1

P6. The Gibbs free energy for the oscillator depicted in Figure 1 is given by $G = -kT \ln Z$. Using the expression provided in P5 for Z, and the relation

$$dG = -SdT - XdF,$$

where X is the average displacement of the spring from its unstretched length,

(a) derive the equation of state,

$$F = KX.$$

(b) Use the relation $G = U - TS - FX$ to obtain an expression for the internal energy,

$$U = \frac{1}{2}KX^2 + kT.$$

P7. The harmonic oscillator depicted in Fig. 1 is in thermal equilibrium under a constant force F. As discussed above, the equation of state relating F to the oscillator's displacement X is given by $F = KX$, and the internal energy is given by $U = \frac{1}{2}KX^2 + kT$, where K is a positive constant.

Consider the process in which F is increased slowly by a factor of two, so that the mass moves reversibly to a new equilibrium at force $2F$ and temperature T.

(a) Calculate the heat that is transferred to the system from the surroundings for this process.

(b) Calculate the heat added to the system for the same displacement if, instead, F is suddenly increased to $2F$. Discuss the difference with your result for (a).

P8. A container having a constant volume V initially contains N atoms of a dilute gas in thermal equilibrium with the surroundings at a temperature T. After some time, a number of these atoms adhere to the walls of the container, each occupying one of N_0 available surface states having binding energy Δ. When M atoms are adsorbed on the surface and $N - M$ atoms remain in the gas, the partition function for the system is given by

$$Z = \frac{q^{(N-M)} \left(N_0 e^{\Delta/kT}\right)^M}{(N-M)!M!},$$

where the single particle partition function for translational motion $q = q(T, V)$ is a function of T and V. Determine the fraction of the total atoms that will be adsorbed when material equilibrium is ultimately reached between the gas and the surface. Assume $N, M \gg 1$.

P9. A vessel with fixed volume V contains a fluid with N noninteracting *distinguishable* particles, each labeled by an index i, and each having a unique mass m_i. The system is in equilibrium at a temperature T. Calculate the partition function Z, and use your expression for Z to obtain the equation of state. What becomes of Z and the equation of state change if the particles are instead taken to be *indistinguishable*?

P10. The motion of a collection of particles that are tightly bound to one another is described by the Hamiltonian

$$\hat{H} = \sum_{i=1}^{N} \left(\hat{n}_i + \frac{1}{2} \right) \hbar \omega_i .$$

Here N is the number of normal modes of vibration, and $\hat{n}_i$ is the operator giving the number of excitations of the ith normal mode, having a frequency ω_i. Derive an expression for the average number of excitations in the system when it is in equilibrium at a temperature T.

Preliminary Examination: Thermodynamics and Statistical Mechanics

Department of Physics and Astronomy
University of New Mexico

Fall 2007

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
R	=	8.314 J/mole/K: gas constant
k	=	$\dfrac{R}{6.02 \times 10^{23}}$: Boltzmann's constant
$\hbar$	:	Planck's constant divided by 2π
β	:	$(kT)^{-1}$
S	:	Entropy
V	:	Volume

Useful Relations:

$$\begin{aligned}
\int_{-\infty}^{\infty} dx e^{-\alpha x^2} &= \sqrt{\frac{\pi}{\alpha}};\ \mathrm{Re}\,\alpha > 0 \\
\int_0^{\infty} dx x^{\nu} e^{-\beta x} &= \frac{\Gamma(\nu+1)}{\beta^{\nu+1}} \\
\Gamma(\nu+1) &= \nu\Gamma(\nu) \\
\sum_{m=0}^{\infty} x^m &= \frac{1}{1-x}\ ;\ |x| < 1. \\
\ln N! &\sim N\ln N - N
\end{aligned}$$

P1. The partition function for a system of N independent spins in a uniform magnetic field B in equilibrium with the surroundings at a temperature T is

$$Z = (2\cosh\beta\mu B)^N$$

where μ is the spin magnetic moment. Calculate the entropy $S(T, B, N)$ and explain its limiting behavior for high and low T.

P2. The Helmholtz free energy for an ideal gas consisting of N diatomic molecules of each of mass m and moment of intertia I in a volume V at a temperature T is

$$A = -kT \ln\left(V \cdot \left(\frac{mkT}{2\pi\hbar^2}\right)^{3/2} \cdot \left(\frac{2IkT}{\hbar^2}\right)\right)^N /N!$$

If the gas is initially in equilibrium at a temperature T_1 and is put in contact with the surroundings at a temperature T_2, how much heat will be transferred to the gas from the surroundings to bring it to equilibrium at T_2, assuming that V is held constant?

P3. The partition function Z for a dilute gas of N atoms confined to a volume V in equilibrium with the surroundings at a temperature T can be written as an integral over the energy E,

$$Z = \frac{\left((2m\pi)^{3/2}\, V\right)^N}{N!\;\Gamma\left(\frac{3N}{2}\right)} \int_0^\infty E^{3N/2-1} \exp\left(-\beta E\right) dE.$$

Determine the system's average energy, and also its most probable energy, and compare the two.

P4. An ideal gas of helium atoms, each having a mass of 25×10^{-27} kg, is confined to a cube having a volume 1000 cm^3, and is in equilibrium at a temperature of 25 degrees celcius, and at a pressure of 10^5 $\mathrm{N/m}^2$. If one face of the cube is suddenly opened to release the helium, estimate the initial escape rate, i.e. calculate the number of helium atoms that will leave the cube per second.

P5. A system contains N independent harmonic oscillators, each having the same frequency ω_0, in equilibrium with the surroundings at a temperature T. Calculate the partition function and derive an expression for the internal energy,

$$U = N\hbar\omega_0/2 + \frac{\hbar\omega_0}{e^{\beta\hbar\omega_0} - 1}$$

P6. You may recall from quantum mechanics that the energy eigenvalues for a particle in a box, that is, a particle in a three dimensional infinite square well potential, depend on three positive integers, n_x, n_y, n_z, such that,

$$\varepsilon_{n_x,n_y,n_z} = \frac{1}{3}\left(n_x^2 + n_y^2 + n_z^2\right)\Delta_0,$$

where $\varepsilon_{1,1,1} = \Delta_0$ is the ground state energy. Suppose that a large number of noninteracting indistinguishable particles are confined to a square well in thermal equilibrium at a temperature T, and the particles are bosons. If M_0 particles are in the ground state, how many particles M_1 are in the first excited state?

P7. In some crystals, vacancies are formed when atoms migrate from the interior and take up positions on the surface. This rearrangement leads to a small increase in volume. The Gibbs free energy for a crystal of N atoms in equilibrium at constant T and P is given by

$$G(P,T,N) = \frac{NP}{\rho_0} - NkT\ln\left(1 + e^{-\beta P/\rho_0}e^{-\beta\Delta}\right)$$

where Δ is the energy to create a vacancy, and ρ_0 is the density of a perfect crystal. What is the equation of state relating P, T, and the volume V?

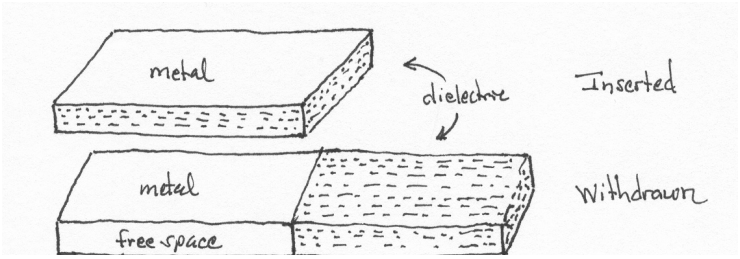
P8. A system consists of a charged parallel plate capacitor together with a removeable dielectric, as shown in the figure below. When the dielectric is fully inserted, the free energy at constant q and T is

$$A_1 = \frac{q^2}{2C_0\kappa(T)} + cT\,(1 - \ln T)$$

where C_0 is the free space capacitance, c is the heat capacity which is constant, and the dielectric constant $\kappa = T_0/T$ of the spacer is inversely proportional to T with proportionality constant T_0. On the other hand, when the dielectric is completely withdrawn, the free energy is

$$A_2 = \frac{q^2}{2C_0} + cT\,(1 - \ln T)$$

Calculate the entropies, S_1 and S_2, corresponding to A_1 and A_2. If the system is initially at a temperature T_i and insulated from the surroundings, and the dielectric is withdrawn reversibly while q remains constant, what will be the final temperature T_f? Is the change in T in the direction you would anticipate? Explain.



P9. The pressure P for a fluid of N particles confined to a volume V in equilibrium at a temperature T is given by

$$P = \frac{\alpha k T}{e^{\alpha V/N} - 1},$$

where α is a positive constant. The following relations are also known:

$$\begin{aligned} \left(\frac{\partial U}{\partial T}\right)_V &= \frac{3}{2} N k; \\ \left(\frac{\partial U}{\partial V}\right)_T &= 0 \end{aligned}$$

Prove that the heat capacity at constant pressure is

$$C_p = \frac{3}{2} N k + \frac{N k}{\left(\frac{\alpha k T}{P} + 1\right)}.$$

P10.

A vessel of volume V contains dilute gas consisting of N hydrogen atoms in equilibrium at a temperature T. A number of the atoms combine to form diatomic hydrogen. If the number of single atoms is M_a and the number of diatomic molecules is M_b, the free energy for the system is

$$\begin{aligned} A &= -M_a k T \ln\left(V/v_a\right) + k T \ln\left(M_a!\right) \\ &\quad -M_b k T \ln\left(V/v_b\right) + k T \ln\left(M_b!\right) - M_b E_b \end{aligned}$$

where v_a and v_b are known functions of temperature, and E_b is the binding energy of the H_2 molecule. Obtain the relationship between the concentrations (number densities) of the two species H and H_2 in equilibrium.

Department of Physics and Astronomy, University of New Mexico

Thermodynamics and Statistical Mechanics Preliminary Examination

Fall 2008

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 $8\frac{1}{2}'' \times 11''$ page are allowed.
- Total time: 3 hours.

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

P: Pressure

T: Absolute Temperature

R: gas constant; $R = 8.314$ J . mole^{-1}1 . Kelvin $^{-1}$

k: Boltzmann's constant; $k = \frac{R}{6.02 \times 10^{23}}$

$\beta = (kT)^{-1}$

S: Entropy

V: Volume

U: Internal energy

N: Number of particles (Assume $N \gg 1$)

$\hbar = \frac{h}{2\pi}$ ($h = 6.626 \times 10^{-34}$ Js is Planck's constant)

1− An ideal monatomic gas occupies a volume of 2 m^3 at a pressure of 4 atm (1 atm $\approx 10^5$ Pa) and a temperature of 293 K. The gas is compressed to a final pressure of 8 atm.

Compute the final volume, the work done on the gas, the heat released to the surrounding, and the change in the internal energy for a reversible isothermal compression.

2− Two identical objects A and B, are thermally and mechanically isolated from the rest of the world. Their initial temperatures are $T_A > T_B$. Each object has heat capacity C (the same for both objects) which is independent of temperature.

Suppose the objects are used as the high and low temperature heat reservoirs of a heat engine. The engine extracts heat from object A (lowering its temperature), does work on the outside world, and dumps heat to object B (raising its temperature). When the temperatures of A and B are the same, and the heat engine is in the same state as it started, the process is finished. Suppose this heat engine performs the maximum work possible. What are the final temperatures of the objects? How much work does the engine do in this process?

3− The Gibbs free energy of N molecules of a certain gas at temperature T and pressure P is

$$G = NkT\ \mathrm{ln}P + A + BP + \frac{CP^2}{2} + \frac{DP^3}{3}, \tag{1}$$

where $A,\ B,\ C$, and D are constants. Find the equation of state of the gas.

4− A box with volume V, which is isolated from the rest of the world, is divided into two equal parts by the means of a partition. Initially the left half of the box contains n moles of an ideal gas at temperature T, while the right half is empty.

Suppose that the partition is suddenly lifted. After a sufficiently long time the gas will occupy all of the box. Find the change in the temperature and entropy for this process.

5− For an ideal gas consisting of diatomic molecules the equation os state and the internal energy are given by

$$PV = nRT\,,$$
$$U = \frac{5}{2}nRT\,,$$

respectively (n is the number of moles). Find the specific heat capacity at constant volume c_V and specific heat capacity at constant pressure c_P for this gas.

6− Consider a line of 3 spins. A spin can point up or down. Suppose that when two adjacent spins point in the same direction, they contribute $-\epsilon$ to the energy of the system and when they point in the opposite directions, their contribution is $+\epsilon > 0$. Non-adjacent spins have no interaction.

(a) What are the possible energies of this system and how many states are there with each energy?

(b) If the system is in thermal equilibrium with a heat bath at temperature T, the probability that it has energy E, among the possible values found in part (a), is given by $A\, e^{-E/kT}$ (where A is a constant). Find A in terms of ϵ, k, and T.

7− Consider a noninteracting Fermi gas consisting of electrons. In such a gas the energy states are occupied according to the following distribution function

$$f(\vec{p}) = \frac{1}{e^{(E-E_F)/kT} + 1}\,,$$

where E_F is the Fermi energy, $E = \sqrt{(pc)^2 + (m_e c^2)^2}$ is the energy, $\vec{p}$ is the momentum, $p \equiv |\vec{p}|$ is the magnitude of the momentum, and m_e is the mass of the electron.

(a) Draw f as a function of E in the limit that $T \to 0$.

(b) The total number density of electrons in the gas is given by

$$n = \frac{4\pi}{h^3} \int_0^\infty f(\vec{p}) p^2 dp\,,$$

where h is the Planck's constant. Find n in terms of E_F and h for $T = 0$.

8− Consider a particles of mass m in a box of volume V that is in equilibrium with the surrounding at a temperature T.

(a) Determine the partition function of the particle in terms of β, m, V, and h. Hint: helpful expression:

$$\frac{1}{\sqrt{2\pi}} \int_0^\infty x^2 e^{-x^2/2} dx = 1\,.$$

(b) Use the partition function and find the average energy of the particle at temperature T.

9− Consider a system of N noninteracting identical bosons of mass m confined to a vessel of fixed volume, in equilibrium with the surroundings at a temperature T. In the limit that $T \to 0$, all particles will go to the ground state whose energy is $E_0 = mc^2$.

(a) Find the entropy of this system at $T = 0$.

(b) We add one more particle to the system at zero temperature. What is the resultant change in the energy and entropy? Use this to find the chemical potential μ of this system at $T = 0$.

10− Blackbody radiation is a gas consisting of photons at a temperature T. The energy density of photon gas ρ is given by

$$\rho = \frac{1}{\pi^2 c^3} \int_0^\infty \frac{\hbar\omega^3 d\omega}{e^{\hbar\omega/kT} - 1}\,, \tag{2}$$

(a) Given this expression, show that ρ is proportional to T^4.

(b) Photon wavelength λ is given by $\lambda = 2\pi c/\omega$. Show that in the limit that $\lambda \gg (hc/kT)$ the spectral density (energy per volume per wavelength) is proportional to λ^{-4}, i.e. the classical limit known as Rayleigh's law is recovered.

Preliminary Examination: Statistical Mechanics

Department of Physics and Astronomy
University of New Mexico

Fall 2009

Instructions:

- You should attempt all 10 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.

P1. State the partition function of a quantum mechanical gas of N noninteracting free distinguishable particles in a cube of length L at temperature T. How is it related to a ratio of L to the thermal deBroglie wavelength of each particle? Comment on the significance of the largeness or smallness of that ratio for the corresponding system of indistinguishable particles.

P2. Comment on the relation, if any, between the Pauli exclusion principle on the one hand and the Fermi-Dirac and Bose-Einstein distribution functions on the other. Give two examples each of particles that obey these two distribution functions.

P3. Consider the average magnetization M of a large number N of non-interacting spins each of magnetic moment μ at temperature T and subjected to a magnetic field B. Present two sketches and label any important quantities on the sketches: M as a function of T at fixed B, and M as a function of B at fixed T. Now let $B = 0$ and indicate what change you expect in the $M - T$ plot if the spins interact among themselves as to align cooperatively.

P4. Draw sketches to show how the pressure P of an ideal gas varies with its volume V at constant temperature T and also with T at constant V. Combining these and additional observations if necessary, write down an equation of state for the gas. Generalize the equation of state for nonideal gases in which the constituent molecules exert repulsive forces on each other. Explain your reasoning. Finally, incorporate intermolecular interactions which are attractive if the molecules are within a short enough distance with respect to each other. This final generalization is what is known as Van der Waals equation of state. Draw $P - V$ curves at several constant temperatures T corresponding to this last equation of state.

P5. By writing the energy of a 1-d harmonic oscillator of frequency ω as $E_n = (n+1/2)\hbar\omega$, and performing a geometric sum (show your work explicitly), show that the partition function is given by

$$Z = \sum_n e^{-\beta(n+1/2)\hbar\omega} = \frac{1}{2\sinh(\beta\hbar\omega/2)}.$$

From this expression calculate the temperature dependence of the heat capacity of a 1-d insulating solid. Explain what feature(s) of this dependence agrees and does not agree with experiment and indicate this on the sketch.

P6. Give an estimate of the following quantities in terms of a number and units where required:

- chemical potential of a collection of photons in a black body cavity of volume $10cm^3$ at temperature $4K$.
- the factor by which the Fermi energy of electrons in a normal metal at room temperature would go up if the electron number density goes up by a factor of 27. You may treat the electrons as 3-d free particles with an energy density of states that is proportional to the square root of the energy.

P7. Calculate as a function of temperature the entropy of a collection of N noninteracting distinguishable two-level systems (for instance atoms), the energy difference between the two levels being Δ.

P8. You are given no other information about a system in equilibrium at temperature T except that its energy can have any value in the continuum between 0 and ∞ and that its energy density of states is a constant C (independent of the energy). Calculate the T- dependence of the free energy of this system.

P9. What kind of systems would exhibit heat capacities that tend to (i) zero at zero temperature, (ii) zero at very large temperatures? Explain your reasoning.

P10. Estimate the critical temperature for Bose-Einstein condensation in a system of 10^{20} free bosons in a 2-dimensional box of size 1 cm on the side.

Preliminary Examination: Thermodynamics and Statistical Mechanics

Department of Physics and Astronomy
University of New Mexico

Fall 2010

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
$\hbar$	:	Planck's constant divided by 2π
β	:	$(kT)^{-1}$
S	:	Entropy
V	:	Volume

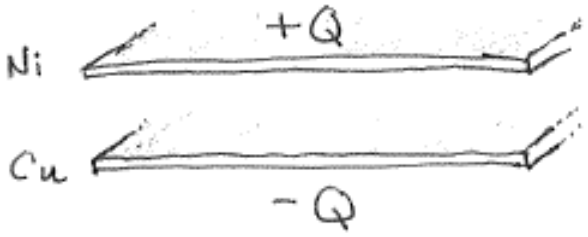
Useful Relations:

$$\begin{aligned}
\int_{-\infty}^{\infty} dx e^{-\alpha x^2} e^{\beta x} &= \sqrt{\frac{\pi}{\alpha}} \exp(\frac{\beta^2}{4\alpha});\ \mathrm{Re}\,\alpha > 0 \\
\int_0^{\infty} dx x^{\nu} e^{-\beta x} &= \frac{\Gamma(\nu+1)}{\beta^{\nu+1}} \\
\Gamma(\nu+1) &= \nu\Gamma(\nu) \\
\sum_{m=0}^{N} x^m &= \frac{1-x^{N+1}}{1-x}\ ;\ |x|<1. \\
\ln N! &\sim N\ln N - N \\
\frac{d}{dx}\tanh(x) &= \cosh(x)^{-2}
\end{aligned}$$

P1. An isolated capacitor with capacitance C is comprised of two metal plates, one of nickel having a chemical potential μ_{Ni}, and the other of copper having a chemical potential μ_{Cu}. When the capacitor is given a charge Q (nickel side $+Q$, copper side $-Q$) the free energy is

$$F = \frac{Q^2}{2C} - \frac{Q}{e}\left(\mu_{\mathrm{Cu}} - \mu_{\mathrm{Ni}}\right).$$

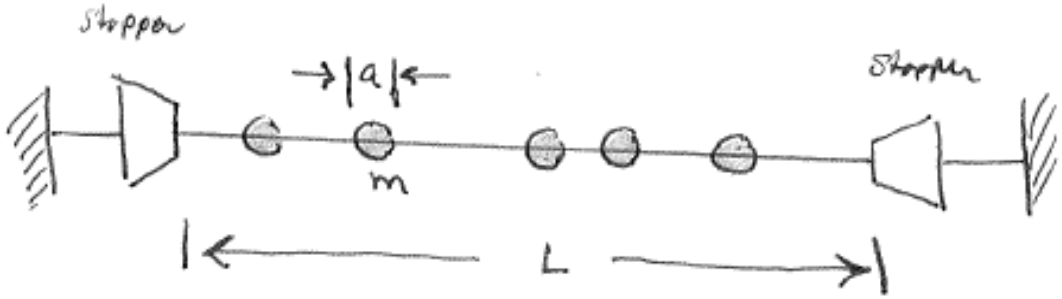
Assuming that the capacitor has a slow leak so that charge can move between the plates, what is the charge Q on the capacitor when it comes to equilibrium? (The dependence of the chemical potential difference on Q is negligible.)



P2. A system consists of N beads in equilibrium with the surroundings at a temperature T. The beads slide on a frictionless wire stretched along the x axis.Each bead has a mass m and length a, and they are are confined to a segment of wire of length L by two stoppers, as shown in the figure. The partition function is

$$Z = \left(\sqrt{\frac{2\pi mkT}{h^2}}\right)^N \frac{(L - Na)^N}{N!}$$

Calculate the average force F exerted on either of the stoppers by the beads, and show that it is an intensive quantity. Explain the behavior of the force as $Na \to L$.



P3. The potential energy V for aligning the magnetic moment $\vec{m}$ of an electron in a magnetic field $\vec{B} = B_0\hat{z}$ is given by

$$V = -\vec{m} \cdot \vec{B} = \pm\mu_{\rm B} B_0,$$

with the $\pm$ depending on whether the electron spin is aligned or anti-aligned with the z axis; here $\mu_{\rm B}$ is the Bohr magneton. Consider a solid containing n noninteracting electron spins per unit volume. What is the magnetization at a temperature T if the magnetic field in the solid is uniform, with magnitude B_0?

P4. The partition function for a fluid consisting of N molecules in a fixed volume V, in equilibrium at a temperature T, is given by

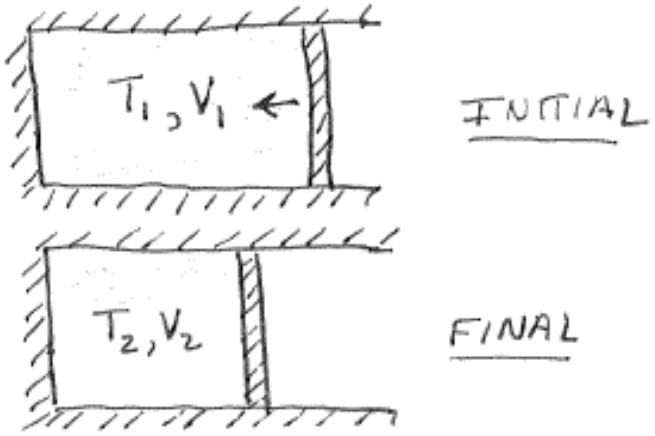
$$Z = \frac{\left[\eta \left(\frac{kT}{\hbar^2}\right)^{5/2} V\right]^N}{N!},$$

where η is a molecular constant. If the fluid, initially at a temperature T_1, comes to equilibrium with the surroundings at a lower temperature T_2, what is the heat transferred to the surroundings?

P5. The partition function at constant T and V for a non-ideal gas of N atoms each having mass m is given by

$$Z = \left(\sqrt{\frac{2\pi mkT}{h^2}}\right)^{3N} \frac{V^N \left(1 - \frac{N\alpha}{V}\right)^N}{N!}$$

where α is a constant.



The gas is confined to an insulated cylinder fitted with a piston at an initial volume V_1 and initial temperature T_1. If adiabatically and reversibly compressed to a volume V_2, what will be the final temperature T_2?

P6. The Hamiltonian for two harmonic oscillators is given by

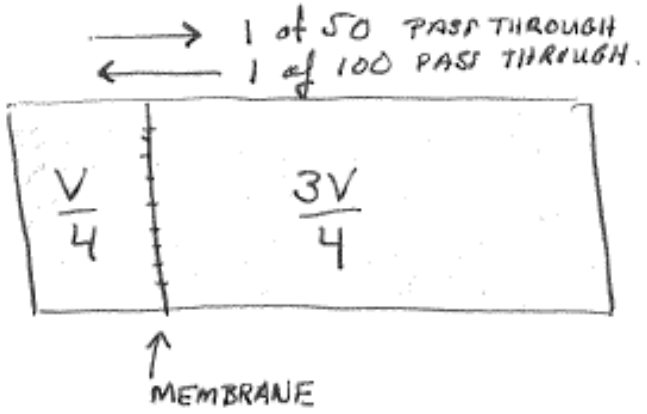
$$H = \frac{p_1^2}{2m} + \frac{1}{2}Kx_1^2 + \frac{p_2^2}{2m} + \frac{1}{2}Kx_2^2 + \eta x_1 x_2$$

The oscillators are coupled together with an interaction term $\eta x_1 x_2$. The configurational integral is given by

$$Z = \int_{-\infty}^{\infty} dx_1 \int_{-\infty}^{\infty} dx_2 \exp\left[-\beta\left(\frac{1}{2}Kx_1^2 + \frac{1}{2}Kx_2^2 + \eta x_1 x_2\right)\right].$$

What the average of the interaction energy $\langle \eta x_1 x_2 \rangle$ at a temperature T? Assume that $|\eta| < K$.

P7. Consider an ideal gas of N atoms confined to a cylinder having a volume V, in equilibrium with the surroundings at a temperature T. The cylinder is partitioned into two parts by a semi-permeable membrane, as shown in the figure. The volume on the left is $V/4$, and the volume on the right is $3V/4$. Atoms colliding with the membrane when moving from left to right will penetrate the membrane and emerge on the right hand side in 1 out of every 50 collisions. Molecules colliding with the membrane when moving from right to left penetrate and emerge on the left hand side in 1 out of every 100 collisions. In equilibrium, how many molecules will be on the left, and how many will be on the right?

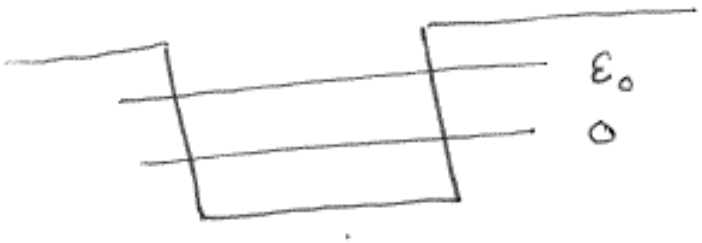


P8. The possible energies for a quantum mechanical harmonic oscillator are given by

$$H = \hbar\omega_0 \left(n + \frac{1}{2} \right)$$

where n is an integer and ω_0 is the natural frequency. Derive an expression for the entropy of a system containing N such oscillators in equilibrium at a temperature T, and show that your result agrees with the third law of thermodynamics.

P9. A system consists of N indistinguishable and noninteracting bosons, confined to a one dimensional square well and in equilibrium at a temperature T. Consider excitations of the system in which only the ground and first excited particle-in-a-box states are occupied, having single-particle energies 0 and ε_0, respectively. Write down an expression for the partition function.



P10. The equation of state for a gas of N weakly interacting particles is given by

$$P = \frac{NkT}{V} - a\frac{N^2}{V^2},$$

where a is the second virial coefficient. Initially the gas has a volume V, and is in equilibrium with the surroundings at a temperature T. If the gas undergoes an isothermal compression, such that the volume is suddenly reduced by a factor of 2, what will be the change in internal energy?

Preliminary Examination: Thermodynamics and Statistical Mechanics

Department of Physics and Astronomy
University of New Mexico

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.

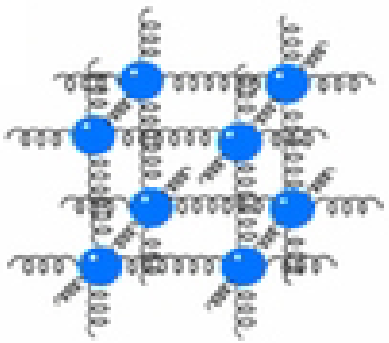
Unless otherwise noted, commonly used symbols are defined as follows:

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:

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

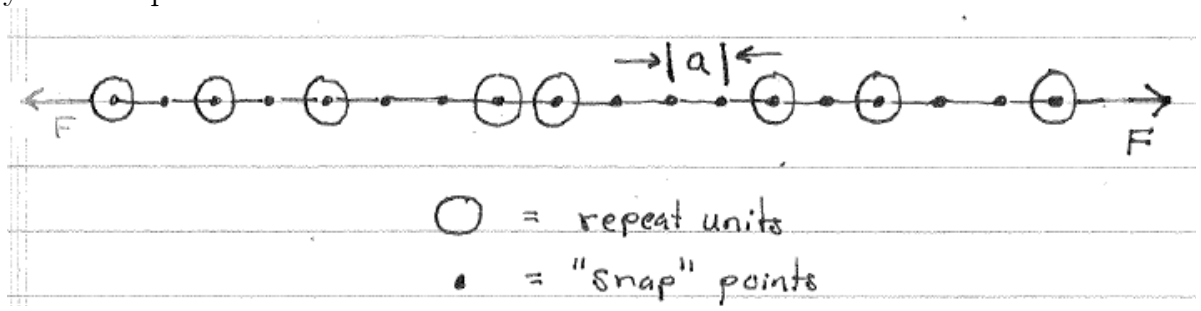
P1: A macroscopic crystalline solid consists of N atoms connected to one another by Hooke's law interactions. What is its heat capacity at high temperatures? How does this depend on the dimensionality of the solid?



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 $m_i = 0, 1, 2, ...$ is an integer associated with the ith 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 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.

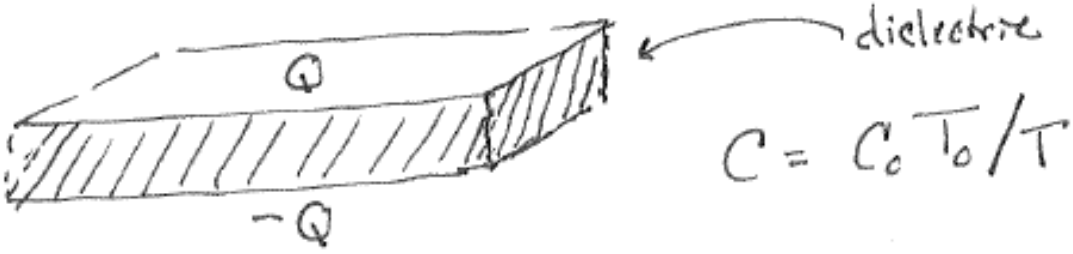
P4: An ideal gas of N particles fills a vessel of volume V, in equilibrium at a temperature T. If the particles each have a mass m, at what rate do the particles collide with the walls of the container, per unit area?

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?

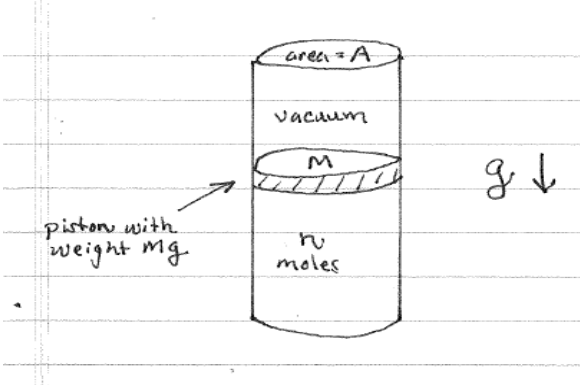
P6. A parallel plate capacitor has a capacitance varying inversely with temperature, $C(T) = C_0 \frac{T_0}{T}$, where C_0 and T_0 are constants. The heat capacity κ of the uncharged capacitor is a constant. Both of these quantities appear in an expression for the free energy,

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

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.)



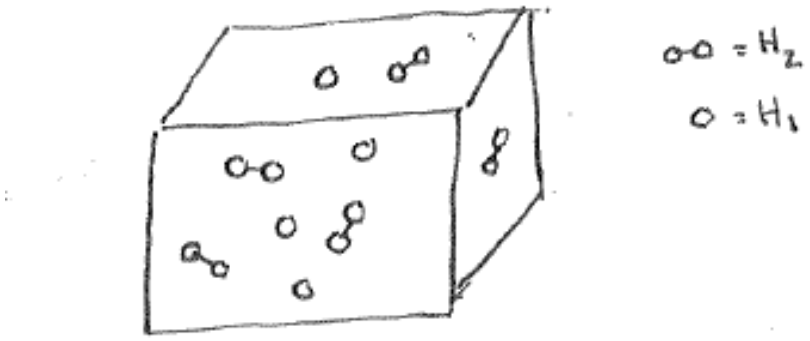
P8. The free energy for a noninteracting gas of monatomic hydrogen H_1, in thermal equilibrium at a temperature T and volume V, is given by

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

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 ($T \to 0$) limit. Show that

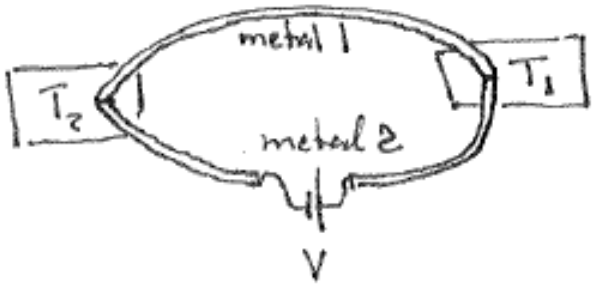
$$U = \frac{8\pi V}{10mh^3} (2m\mu)^{5/2},$$

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 $T_1 = 0$ °C, and $T_2 = 21$ °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?



Preliminary Examination: Thermodynamics and Statistical Mechanics

Department of Physics and Astronomy
University of New Mexico

Fall 2012

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.

P1: The ideal gas law $PV = nRT$ states the relationship between the pressure P exerted by a gas on the walls of the container of volume V to the temperature T of the gas, n being the number of moles and R the universal gas constant. Consider collisions of the gas molecules with the walls of the container and derive under reasonable assumptions the relationship

$$\frac{1}{2}mv^2 = \frac{3}{2}k_B T$$

between the translational kinetic energy of a molecule of the gas and the temperature of the gas. Carefully explain the assumptions you make during the derivation and show what the connection is between the Boltzmann constant k_B and the gas constant R.

P2: Develop a quantitative model of linear thermal expansion by assuming that atoms in a solid are confined in one direction by a one-dimensional potential energy function, that one may analyze the problem as involving a set of single particles each with a small displacement x from equilibrium, the confining potential being of the form $V(x) = ax^2 - bx^3 + \ldots$, b being small (in some appropriate sense), and using the Maxwell-Boltzmann distribution function to derive an expression for $\langle x \rangle$. Show that the expansion of the solid is linearly proportional to the temperature and to the anharmonicity coefficient b. You might find of use the integral

$$\int_{-\infty}^{\infty} e^{-mx^2} dx = \sqrt{\pi/m}.$$

P3: Evaluate the partition function of a free particle of mass m confined to, and in equilibrium with, a 3-dimensional container of volume V at temperature T and express it as the ratio of the container volume V to another volume V_c characteristic of the particle. State clearly the physical significance of V_c and comment on its dependence on the mass of the particle and the temperature. *Hints*: One method of evaluation is classical in approach and involves an integration over the coordinate x and momentum p, followed by the introduction of a factor $1/h^3$, where h is Planck's constant, to make the partition function dimensionless. Another method is quantum mechanical and involves a summation over the free particle states, approximating the summation by an integration. Choose whichever you prefer. The characteristic volume V_c is often called the thermal de Broglie volume of the particle. The Gaussian integral in problem P2 may be of use to you here.

P4: A gas of $N \sim 10^{23}$ non-interacting spin-1/2 fermions of mass m and temperature $T = 0$ is confined to a cubic region of edge length L and volume $V = L^3$. Find an expression for the largest occupied single particle energy ε_f (the Fermi energy) and express it as a function of the gas particle density $\rho = N/V$. Compute the total internal energy U of the gas, and use this to compute the pressure exerted by the gas on the container that holds it.

P5: Consider a 3-dimensional system of classical spins that do not interact among themselves but interact with a magnetic field B. If the angle θ between the moment and the field is *larger than* 45 *degrees* the energy U of a spin (magnetic moment μ) is zero. If the angle is *smaller than* 45 *degrees*, the energy is given by

$$U = -\mu B \cos\theta.$$

Calculate the partition function. Use it to calculate and sketch the B-dependence of the magnetization.

P6: Einstein's theory of the specific heat of an insulator relies on envisaging the solid as a collection of identical independent oscillators each of frequency ω and computing the average energy of each oscillator to be given by

$$\bar{\epsilon} = \left(\bar{n} + \frac{1}{2}\right)\hbar\omega$$

where $\bar{n} = \left(e^{\hbar\omega/k_BT} - 1\right)^{-1}$. Consider a similar situation with the difference that each oscillator is replaced by a two-level system, the energy difference between the two levels being Δ. Calculate the specific heat, and show how its behavior at low and high temperatures would differ from that of the Einstein model. Indicate also what you mean by high and low (temperature.)

P7: State the Fermi-Dirac distribution, the Bose-Einstein distribution, and the Maxwell-Boltzmann distribution describing the occupation number of a fixed number N of particles each with a given energy ϵ in terms of the chemical potential μ and temperature T. The crucial ratio in these expressions is $(\epsilon - \mu)/k_BT$. Consider the argument that the ratio goes to zero as the temperature becomes very large and that consequently the Fermi-Dirac distribution becomes classical in the *small* rather than large temperature limit? What is wrong in this argument? Explain.

P8: The underlying equations of mechanics are reversible in time. Yet every day behavior we observe is irreversible. Briefly explain how you understand the resolution of this paradox.

P9: Which of the two statements (if either) is correct and under what physical conditions? If neither is correct, write a corrected version of each and if the statements or slight modifications are valid under other physical conditions point it out carefully. A legalistic answer will not give you credit. Treat this question as an opportunity to show the examiners that you understand the relevant physics:

Statement 1: In thermal equilibrium, a large enough system occupies its energy states of energy E with equal probability.

Statement 2: In thermal equilibrium, a large enough system occupies its energy states of energy E with probability proportional to the factor $\exp(-E/k_BT)$ where T is the temperature.

P10: Planck's radiation law states that the average energy density per unit volume E_ν in a black body at frequency ν is given by

$$\frac{8\pi h(\nu/c)^3}{e^{h\nu/k_BT}-1}.$$

For 0.75 of the credit of this problem, state (with clear explanation) how this expression would be modified in Flatland (2-dimensional universe.) For full credit derive an expression for that case.

Preliminary Examination: Thermodynamics and Statistical Mechanics

Department of Physics and Astronomy
University of New Mexico

Fall 2013

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 for this test: 3 hours.

Information that could be useful:

- 1 joule = 6.2×10^{18} eV.
- kT at room temperature is approximately equal to 0.025 eV.
- $$\int_{-\infty}^{\infty} e^{-ax^2} dx = \sqrt{\pi/a}.$$

P1: A cup of hot coffee at 80 C is mixed together with two cups of cold coffee at 40 C at constant pressure in an insulated container. The specific heat for coffee at constant pressure is known to be 4.2 J/g/deg at room temperature and 1 atmosphere. Determine the resultant temperature of the mixture. Make, and state clearly, any reasonable approximations you need to obtain your result.

P2: The non-interacting Fermi gas is a useful model for understanding the electronic properties of a metal. Suppose that the chemical potential for electrons in the conduction band of a certain metal is 4 eV at room temperature. Sketch a graph of the corresponding Fermi-Dirac distribution function at room temperature ($T \approx 300$ K) as a function of energy lying between 3.9 eV and 4.1 eV. Also show on your graph, for comparison, the shape of the distribution function at T = 0 K and T=100000 K.

P3: State the Fermi-Dirac distribution, the Bose-Einstein distribution, and the Maxwell-Boltzmann distribution describing the occupation number of a fixed number N of particles each with a given energy ϵ in terms of the chemical potential μ and temperature T. The crucial ratio in these expressions is $(\epsilon - \mu)/k_B T$. Consider the argument that the ratio goes to zero as the temperature becomes very large and that consequently the Fermi-Dirac distribution becomes classical in the *small* temperature limit. What is wrong in this argument? (Remember that it is usually said that the classical limit is the *large* temperature limit. Explain.

P4: The ideal gas law $PV = nRT$ states the relationship between the pressure P exerted by a gas on the walls of the container of volume V to the temperature T of the gas, n being the number of moles and R the universal gas constant. Consider collisions of the gas molecules with the walls of the container and derive under reasonable assumptions the relationship $\frac{1}{2}mv^2 = \frac{3}{2}k_B T$ between the translational kinetic energy of a molecule of the gas and the temperature of the gas. Carefully explain the assumptions you make during the derivation and show what the connection is between the Boltzmann constant k_B and the gas constant R.

P5: The underlying equations of mechanics are reversible in time. Yet every day behavior we observe is irreversible. Briefly explain how you understand the resolution of this paradox.

P6: Which of the two statements below (if either) is correct and under what physical conditions? If neither is correct, write a corrected version of each and if the statements or slight modifications are valid under other physical conditions point it out carefully. A legalistic answer will not give you credit. Treat this question as an opportunity to show the examiners that you understand the relevant physics:

Statement 1: In thermal equilibrium, a large enough system occupies its energy states of energy E with equal probability.

Statement 2: In thermal equilibrium, a large enough system occupies its energy states of energy E with probability proportional to the factor $\exp(-E/k_B T)$ where T is the temperature.

P7: You are required to calculate the classical partition function of a free particle of mass m confined to a 3-dimensional container of volume V at temperature T. Noticing that this calculation involves an integration over coordinates x and momenta p and that the product of x and p has the dimensions of Planck's constant h, introduce a multiplicative factor $1/h^3$ to make the partition function dimensionless. Now show that the result so obtained for the partition function has the suggestive form of the ratio of the container volume V to another volume characteristic of the particle. Comment on this and state clearly the physical significance of the other volume. *Hint*: The other volume sometimes goes under the name of the thermal de Broglie volume of the particle at temperature T, and involves h, the temperature, and the mass of the particle.

P8: Planck's radiation law states that the spectral energy density E_ν in a black body at frequency ν is given by

$$\frac{8\pi h(\nu/c)^3}{e^{h\nu/k_BT}-1}.$$

For 0.75 of the credit of this problem, state (with clear explanation) how this expression would be modified in Flatland (2-dimensional universe.) For full credit derive an expression for that case.

P9: Einstein's theory of the specific heat of an insulator relies on envisaging the solid as a collection of identical independent oscillators each of frequency ω and computing the average energy of each oscillator to be given by

$$\bar{\epsilon} = \left(\bar{n} + \frac{1}{2}\right)\hbar\omega$$

where $\bar{n} = \left(e^{\hbar\omega/k_BT} - 1\right)^{-1}$. Consider a similar situation with the difference that each oscillator is replaced by a two-level system, the energy difference between the two levels being Δ. Calculate the specific heat, and show how its behavior at low and high temperatures would differ from that of the Einstein model. Indicate also what you mean by high and low (temperature.)

P10: A gas of $N \sim 10^{23}$ non-interacting spin-1/2 fermions of mass m and temperature $T = 0$ is confined to a cubic region of edge length L and volume $V = L^3$. Find an expression for the largest occupied single particle energy ε_f (the Fermi energy) and express it as a function of the gas particle density $\rho = N/V$. Compute the total internal energy U of the gas, and use this to compute the pressure exerted by the gas on the container that holds it.

Preliminary Examination: Thermodynamics and Statistical Mechanics

Department of Physics and Astronomy
University of New Mexico

Fall 2014

Instructions:

- The exam consists of 10 problems worth 10 points each; total time: 3 hours.
- Where possible, show all work; partial credit will be given if merited.
- NO cheat sheets of any kind are allowed.
- Under standard conditions water boils at 212 degrees F or at 100 degrees C and freezes at 32 degrees F or 0 degrees C.
- If G is a positive integer and $x < 1$, the geometric sum $\sum_{r=0}^{r=G-1} x^r$ equals $\frac{1-x^G}{1-x}$.
- In standard notation, the Hamiltonian of a free particle is $p^2/2m$, and $p = \hbar k$.

P1: Consider a collection of a large non-interacting number N of a peculiar kind of anharmonic oscillators whose energy spectrum is similar to that of the harmonic oscillator but differs in that it has a maximum energy which is finite and starts out with a gap near the ground state. Thus, given that n is a non-negative integer smaller than an integer R, the energy E_n of the oscillator takes the values:

$$0 \text{ for } n = 0,$$
$$\Delta + n\epsilon \text{ for } R > n > 0.$$

Calculate and sketch the temperature dependence of the specific heat of the system and compare with that a similar collection of normal harmonic oscillators. Comment, with a sketch, on the respective limits of small and large ϵ/Δ.

P2: Consider a system of 3 spins along a straight line. Each spin can only point up or down: no translations or other rotations are possible. Non-adjacent spins have no interaction. When two adjacent spins point in the same direction, they contribute $-\epsilon$ to the energy of the system and when they point in opposite directions, their contribution is $+\epsilon > 0$.
(a) What are the possible energies of this system and how many states are there with each energy?
(b) If the system is in thermal equilibrium with a heat bath at temperature T, the probability that it has energy E, among the possible values found in part (a), is given by Ae^{-E/k_BT} where k_B is the Boltzmann constant. Evaluate A in terms of ϵ, k_B and T.

P3. In the above problem, the factor e^{-E/k_BT} has made its appearance. Comment as completely as you can on whether that factor comes from a law of nature independent of other laws, whether it is a mathematical conclusion drawn from other laws, whether it incorporates a mysterious spiritual belief, or something else.

P4: Calculate the energy density of states for a free quantum particle in 1 dimension (the particle is constrained to lie within a segment of length L). From your expression comment on whether the density of states increases, decreases or remains constant as the energy varies, and whether that behavior is the same as in higher dimensions.

P5: How is the partition function of a system in equilibrium related to the energy state density of the system? How can you calculate the free energy of the system knowing the partition function? A simplified model of a gas of noninteracting classical particles at volume V and temperature T results in the following expression for the free energy A :

$$A + Nk_BT\ln(V-b) + \frac{a}{V} = 0$$

Work out an expression for the pressure exerted by the gas as a function of N, T, V, and comment on what physical meaning N, a, b might have in this model.

P6: Briefly explain in *any three* of the following cases the term and its relevance in practical physics:
(i) Brownian motion, (ii) Ising model, (iii) Poincare recurrence, (iv) ergodic hypothesis, (v) Bose-Einstein condensation.

P7: A cup of cold tea at 70 degrees F is mixed with two cups of hot tea at 150 degrees F at constant pressure in an insulated container. The specific heat for tea at constant pressure is $4.2\,J/g$ per degree Kelvin at room temperature and one atmosphere. Determine the resultant temperature of the mixture in degrees F. Make any reasonable approximations you need to obtain your result but state those approximations clearly.

P8: For an ideal gas consisting of N noninteracting diatomic molecules, the equation of state and the internal energy are given in standard notation by $PV = nRT$ and $U = (5/2)nRT$ respectively, where n is the number of moles of the gas. Derive the specific heat at constant volume and the specific heat at constant pressure for this gas.

P9. The specific heat of a metal has a sizable part that varies at room temperature in a power law form as T^n. So does that of an insulating solid at high T and also at low T. The values of n are different in these three cases: 0, 1, and 3, NOT necessarily in that order. Explain what physical characteristics of the systems lead to these three power law dependences and why n has the particular value for each system. Justify your answer on the basis of analytic expressions and clear arguments.

P10. Blackbody radiation may be considered as a 3-dimensional gas of photons in equilibrium at a temperature T. Deduce that the energy density of this radiation is proportional to T^4. Show all your derivations or arguments quantitatively.

Preliminary Examination: Thermodynamics and Statistical Mechanics

Department of Physics and Astronomy
University of New Mexico

Fall 2015

Instructions:

• The exam consists of 10 problems worth 10 points each; total time: 3 hours.

• Where possible, show all work; partial credit will be given if merited.

• NO cheat sheets of any kind are allowed. You have been provided with all the information you need within the statement of the problems.

• Under standard conditions water boils at 212 degrees F or at 100 degrees C and freezes at 32 degrees F or 0 degrees C.

P1: In a two-dimensional world, the ideal gas law is $PA = nRT$ where P is the pressure exerted by a gas on the walls of a container of area A, T is the temperature of the gas, n is the number of moles of the gas, and R is a certain universal constant. Consider collisions of the gas molecules with the walls of the container in this two-dimensional world and derive, under reasonable assumptions (make them clear!), the relationship

$$mv^2/2 = sk_BT$$

between the translational kinetic energy of a molecule of the gas and the temperature of the gas. State the value of s and explain why, and also what the connection is between the Boltzmann constant k_B and R.

P2: Consider a system of 4 spins along a straight line. Each spin can only point up or down: no translations or other rotations are possible. Non-adjacent spins have no interaction. When two adjacent spins point in the same direction, they contribute $-\epsilon$ to the energy of the system and when they point in opposite directions, their contribution is $+\epsilon > 0$.

(a) What are the possible energies of this system and how many states are there with each energy?

(b) If the system is in thermal equilibrium with a heat bath at temperature T, the probability that it has energy E, among the possible values found in part (a), is given by Ae^{-E/k_BT}. Evaluate A in terms of ϵ, k_B and T.

P3. Derive an expression for the entropy of a system of N noninteracting quantum mechanical harmonic oscillators of frequency ω which are in equilibrium at temperature T. You are reminded that $H = \hbar\omega(n + 1/2)$ describes each of these oscillators–the symbols have their usual meanings.

P4: Calculate the energy density of states for a free quantum particle in 2 dimensions, constrained to lie within a square of side L. From your result comment on whether the density of states increases, decreases or remains constant as the energy varies, and whether that behavior is the same as in 1- and 3- dimensions. If it is not the same, state without calculation what it is in each of those cases.

P5: Consider a two-level system, Δ being the energy difference of the two levels. A collection of N such noninteracting systems is in equilibrium with a heat bath at temperature T. Calculate their specific heat. Comment carefully on how the specific heat of this system differs at both high and low temperatures relative to what it does in Einstein's model of an insulator. (That model treats the system as consisting of N noninteracting harmonic oscillators.) Specify clearly what you mean in both systems by high and low temperatures.

P6: How is the partition function of a system in equilibrium related to the energy state density of the system? How can you calculate the free energy of the system knowing the partition function? A simplified model of a gas of noninteracting classical particles at volume V and temperature T results in the following expression for the free energy A :

$$A + Nk_BT\ln(V - b) + \frac{a}{V} = 0$$

Work out an expression for the pressure exerted by the gas as a function of N, T, V, and comment on what physical meaning N, a, b might have in this model.

P7: Briefly explain in *any three* of the following cases the term and its relevance in practical physics:
(i) Poincare recurrence, (ii) ergodic hypothesis, (iii) Bose-Einstein condensation, (iv) Brownian motion, (v) Ising model.

P8: A cup of cold tea at a certain temperature T degrees F is mixed with two cups of hot tea at 120 degrees F at constant pressure in an insulated container. The specific heat for tea at constant pressure is $4.2\,J/g$ per degree Kelvin at room temperature and one atmosphere. The resultant temperature of the mixture is 80 degrees F. Determine the original temperature T of the cup of cold tea. Make any reasonable approximations you need to obtain your result but state those approximations clearly.

P9: For an ideal gas consisting of N noninteracting diatomic molecules, the equation of state and the internal energy are given in standard notation by $PV = nRT$ and $U = (5/2)nRT$ respectively, where n is the number of moles of the gas. Derive the specific heat at constant volume and the specific heat at constant pressure for this gas.

P10. Blackbody radiation may be considered as a 3-dimensional gas of photons in equilibrium at a temperature T. Deduce that the energy density of this radiation is proportional to T^r and determine r. Show all your derivations or arguments quantitatively.

Preliminary Examination: Thermodynamics and Statistical Mechanics

Department of Physics and Astronomy
University of New Mexico

Spring 2005

Instructions:

•The exam consists of two parts: Complete 5 short answer problems (6 points each) and your choice of 2 of 3 long answer problems (35 points each).

•Where possible, show all work; partial credit will be given.

•Personal notes on two sides of an 8×11 page are allowed.

•Total time: 3 hours.

Short Answers:

S1. It can be shown that the efficiency of a Carnot heat engine in which the working fluid is an ideal gas only depends on the temperatures of the hot and cold reserviors. Assuming the validity of the second law of thermodynamics, prove that the Carnot efficiency must be independent of the working fluid.

S2. An insulated piston contains n moles of ideal gas at a temperature of 300 K. The heat capacity of the gas at constant pressure is $\frac{5}{2}nR$ where R is the gas constant. What is the change in the entropy of the gas when it is heated to 400 K at constant pressure?

S3. A narrow potential well consists of only two bound states, a ground state and a first excited state. The potential well is occupied by exactly N noninteracting *distinguishable* particles. The ground and excited state energies are the same for all particles, and the energy to place a particle in the excited state is higher than the energy of the ground state by Δ. Obtain an expression for the average number of particles in the excited state as a function of temperature.

S4. The energy per unit volume u and the pressure P for electromagnetic waves in a cavity are related through the Maxwell stress tensor, such that $u = 3P$. On the other hand, u and P are also related through thermodynamics, for $u = -\frac{T^2}{V}\frac{\partial}{\partial T}(A/T)_V$ and $P = -T\frac{\partial}{\partial V}(A/T)_T$ can both be obtained from derivatives of the Helmholtz free energy A. Assuming that, in

thermal equilibrium, the energy density u is independent of volume, derive the Stefan-Boltzmann relation, $u \propto T^4$.

S5. Assuming that the average kinetic energy for a particle moving in d dimensions at a temperature T is given by $\frac{d}{2}kT$, use arguments from the kinetic theory of gases to derive the equation of state for a one dimensional gas of noninteracting particles which undergo elastic collisions with the ends of a closed "container" of length L.

Long Answers: Choose 2 out of 3 problems below.

L1. A system consists of an electrically isolated parallel plate capacitor which is immersed in a liquid dielectric having a temperature-dependent dielectric constant $\kappa = T_0/T$ obeying Curie's law, where T_0 is a constant. The capacitor is given a charge q, and the system is placed in contact with the surroundings at a temperature T. The Hemholtz free energy is given by

$$A(q,T) = \frac{1}{2}\frac{q^2}{C},$$

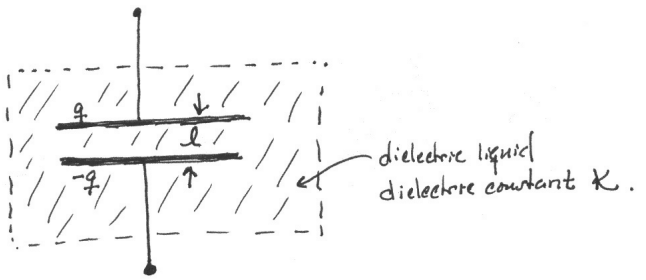
where the capacitance is $C = \kappa C_0$, where $C_0 = \epsilon_0 a/\ell$ is the capacitance in free space; a is the plate area, ℓ is the plate separation, and ϵ_0 is the free-space permittivity.

(a) Obtain an expression for the force between the plates at constant charge. Is this force attractive or repulsive? How does the force depend on temperature?

Suppose that, instead, the capacitor is electrically connected in series with a battery having a fixed voltage $V = q/C$.

(b) Find the Gibbs free energy $G(T,V)$ and obtain an expression for the force between the plates in this case.

(c) Compare the direction, magnitude, and temperature dependencies of the forces found in parts (a) and (b) above.



L2. The core of a long solenoid is filled with a paramagnetic salt which may be described as a uniform density n of independent atoms, each with spin-1/2 due to an unpaired electron. The magnetic moment of each atom is $\vec{\mu} = \frac{-2\mu_B}{\hbar}\vec{S}$, where μ_B is the Bohr magneton and $\vec{S}$ is the electron spin.

(a) Show that the average magnetic moment of an atom in the direction of a uniform magnetic field of strength B is given by

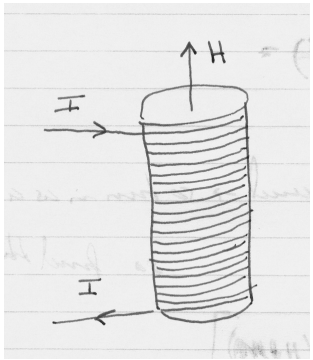
$$\langle \mu \rangle = \mu_B \tanh\left(\frac{\mu_B B}{kT}\right),$$

where μ_B is the Bohr magneton. This implies a magnetization per unit volume, $M = n\langle \mu \rangle$.

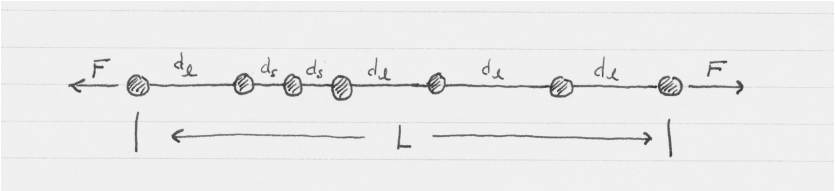
Recall now that the field B is related to the magnetic intensity H such that $B = \mu_0(H + M)$ where μ_0 is the permeability of free space. The magnetic intensity $H = \eta I$ is directed along the solenoid axis, and is proportional to the current I in the windings, where η is the number of windings per unit length.

(b) Obtain an expression for the magnetic susceptibility $\chi = M/H$ as a function of temperature at high temperatures.

(c) Find the critical temperature below which there will be (spontaneous) magnetization for $I = 0$.



L3. A linear molecule consists of $N >> 1$ atoms connected to each other in a chain in one dimension. There are two possible lengths for each bond, a short length d_s, and a long length, d_ℓ. The energy of a short bond is higher than the energy of a long bond by Δ. The molecule is held at a fixed length L, and is in equilibrium with the surroundings at a temperature T.



(a) What is the partition function for constant T and constant L?

(b) Use the partition function to find the equation of state, i.e., find the force F required to hold the molecule at a length L. For what value of L will F be zero?

Preliminary Examination: Thermodynamics and Statistical Mechanics

Department of Physics and Astronomy
University of New Mexico

Spring 2006

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.

P1. A system containing N particles confined to a container with volume V is in equilibrium at a temperature T. The partition function is given by

$$Z = \left(\alpha V T^{\frac{7}{2}}\right)^N$$

where α is a constant. Use this information to determine the pressure exerted on the walls of the container as a function of N, T, and V. Comment on how your result differs, if it does, from the corresponding result for an ideal gas. If you see no difference, comment on whether this means that the system under consideration is an ideal gas.

P2. A cup of hot coffee at 80 °C is mixed together with two cups of cold coffee at 40 °C at constant pressure in an insulated container. The specific heat for coffee at constant pressure is known to be 4.2 J-g^{-1}-deg^{-1} at room temperature and one atmosphere. Determine the resultant temperature of the mixture. Make any reasonable approximations you need to obtain your result.

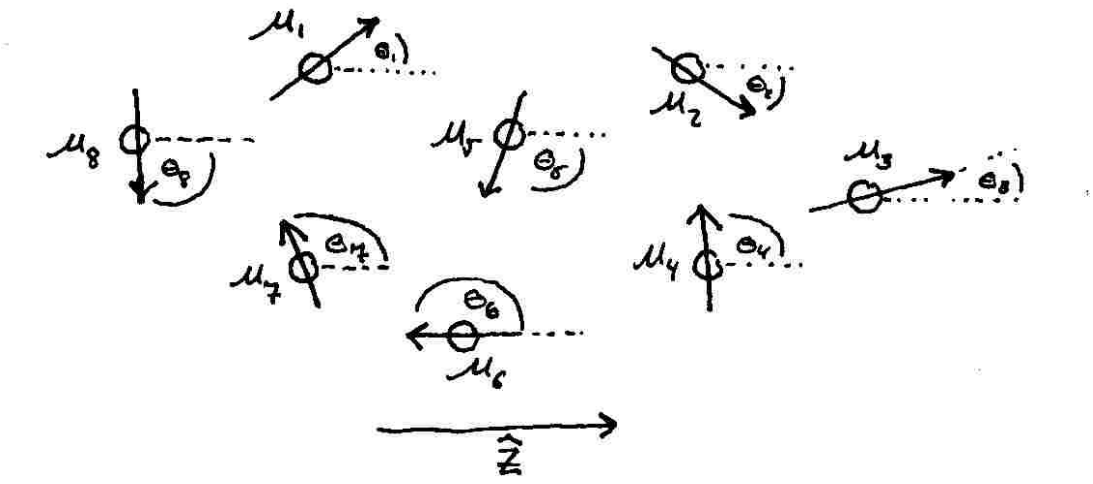
P3. The non-interacting fermi gas is a useful model for understanding the electronic properties of a metal. Suppose that the chemical potential (fermi energy) for electrons in the conduction band of a certain metal is 4.000 eV at room temperature. Sketch a graph of the corresponding fermi-dirac distribution function at room temperature ($T \simeq 300$ K) as a function of energy ε, from 3.900 eV $< \varepsilon <$ 4.100 eV. Also show on your graph, for comparison, the shape of the distribution function at $T = 0$ K.

P4. The partition function for a system of N distinguishable, noninteracting, freely orientable classical magnetic dipoles, each having a magnetic moment μ, in the presence of a constant uniform magnetic field $\vec{B} = B_0\hat{z}$, is given by

$$Z = \sum_{\theta_1,\theta_2,\theta_3,\ldots\theta_N} e^{\beta\mu B_0(\cos\theta_1+\cos\theta_2+\cos\theta_3+\ldots\cos\theta_N)}$$

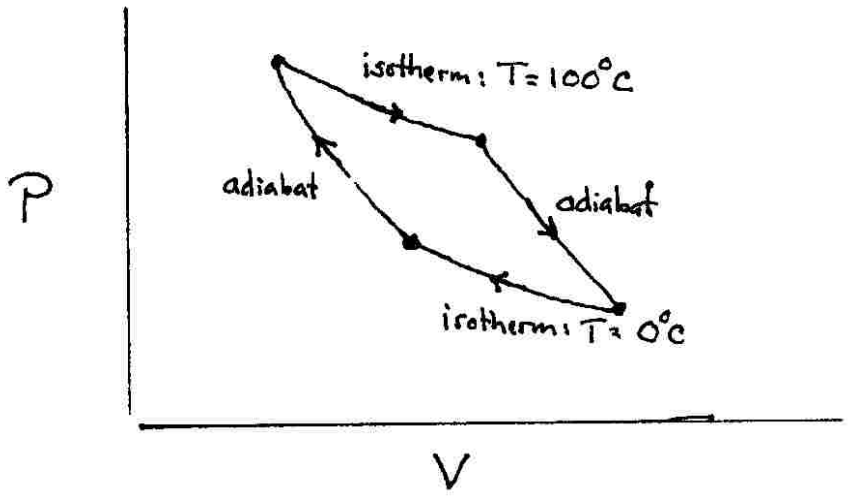
where θ_i is the angle that the i^{th} magnetic dipole makes with the z axis and $\beta = (kT)^{-1}$. We are neglecting the effect of the induced magnetic field. Obtain an expression for the average magnetic moment of the system. Sketch the magnetization as a function of temperature.

Useful integral: $\int_0^{2\pi} d\phi \int_0^{\pi} d\theta \sin\theta \exp(\beta\mu B_0 \cos\theta) = 4\pi \frac{\sinh(\beta\mu B_0)}{\beta\mu B_0}$.



P5. Hidden away in a government laboratory in Albuquerque NM is a cylinder containing the last existing sample of an experimental fluid manufactured in the late 1950s and code-named "fluid-X". The cylinder is fitted with a frictionless piston so that fluid-X can be expanded and contracted over a cycle that consists of two reversible isotherms alternating with two reversible adiabats, as shown in the figure below. The temperatures of the isotherms are 0 °C and 100 °C, respectively. After one complete cycle, it is found that the ratio of the net work performed on the surroundings to the heat absorbed during the expansion at 100 °C is given by $\eta = 0.27$. An Albuquerque newspaper has recently reported that one of the laboratory's objectives at their new nanofabrication facility is to use modern techniques in computational chemistry and self-assembly to design and manufacture a fluid for which this ratio is higher than 0.27, for exactly the same cycle.

What is the significance of η? Is it thermodynamically possible to make a fluid for which η is higher than that of fluid-X for the same cycle? Is it possible to make a fluid for which η is lower? Discuss the reasons why or why not for both cases.



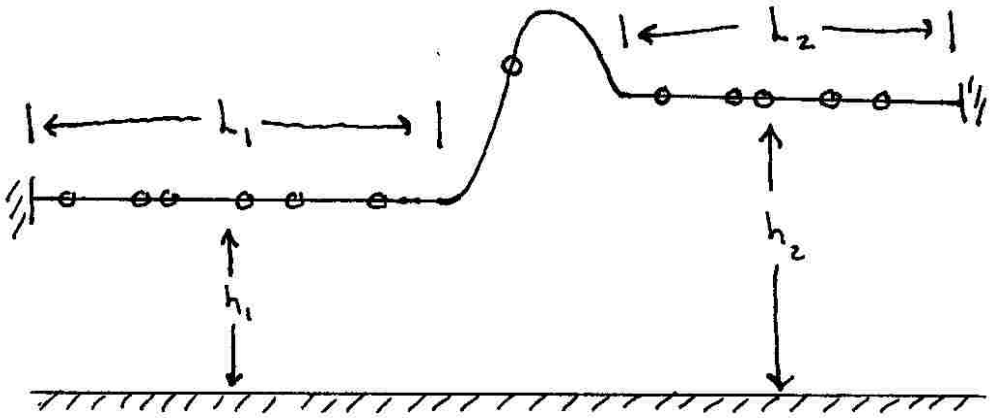
P6. A system consists of N very small beads each having a mass m that are free to slide on a stiff horizontal wire of length L. Collisions of the beads with one another and with the ends of the wire bring the system into equilibrium with the surroundings at a temperature T. When the wire is at an elevation h, the partition function Z and its associated free energy A are as follows:

$$\begin{aligned} Z &= \frac{\left(\sqrt{mkT/2\pi\hbar^2}Le^{-\beta mgh}\right)^N}{N!}; \\ A &\sim Nmgh - kT\left(N\ln\frac{L}{N}+N\right) - \frac{N}{2}kT\ln\left(mkT/2\pi\hbar^2\right). \end{aligned}$$

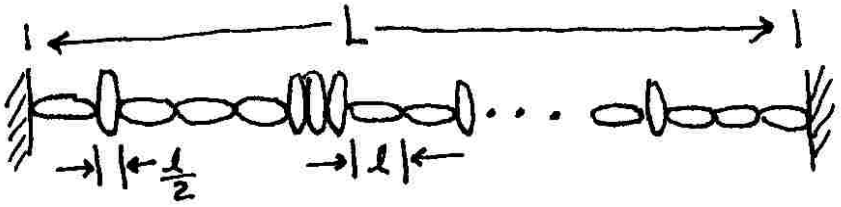
Here g is the acceleration of gravity and $\beta = (kT)^{-1}$. Stirling's approximation for $\ln(N!)$ was employed in obtaining A from Z above. (a) What is the chemical potential of the system?

Suppose that the wire is bent so that a horizontal segment of length L_1 at an elevation h_1 is separated from a horizontal segment of length L_2 at an elevation h_2 by a barrier, as shown in the figure below. It is possible for the beads to slide over the barrier, but they don't often make it over the top. (b) When

equilibrium is reached, what will be the ratio of the bead concentration $n_1 = N_1/L_1$ in segment 1 to the concentration $n_2 = N_2/L_2$ in segment 2?



P7. A single strand of polymer is composed of $N \gg 1$ cigar-shaped molecules that are aligned, end-to-end, in a chain, as shown in the figure below. The polymer is confined to one dimension, and is in equilibrium with the surroundings at a temperature T. The individual molecules may be oriented in one of two distinct positions; either horizontally, or vertically, as shown. When oriented horizontally, each molecule contributes a length ℓ to the overall length of the strand, but when oriented vertically, this contribution is only $\ell/2$. The polymer strand is under tension so as to remain a fixed length L. The energy does not depend on molecular orientation, to a very good approximation.What is the partition function for the polymer strand? What will be the equilibrium length when the tensile force is set to zero?



P8. According to the Debye model for the heat capacity of a solid, the vibrational internal energy is given by the integral expression,

$$U = \frac{9V}{8\pi^2 c^3} \int_0^{\omega_0} d\omega \frac{\hbar\omega^3}{e^{\beta\hbar\omega} - 1}$$

where c is the speed of sound, $\beta = (kT)^{-1}$, V is the volume, and the upper limit $\omega_0 = 2c\left(\pi^2 n\right)^{1/3}$ on the integral is determined by the cube root of the number of atoms per unit volume, n. Show that the vibrational contribution to the heat capacity at low-temperatures is proportional to T^3, and discuss precisely what is meant by a "low" temperature in this system.

P9. A dilute gas containing N molecules of oxygen O_2 is confined to a volume V and is in equilibrium with the surroundings at a reasonably high temperature T . The partition function is given by

$$Z = \frac{\left(q_{\text{trans}} q_{\text{rot}} q_{\text{vib}}\right)^N}{N!}$$

where $q_{\text{trans}} = V\left(mkT/2\pi\hbar^2\right)^{3/2}$ is the single-particle partition function for the translational motion of particles having mass m, and $q_{\text{rot}} = 2kTI/\hbar^2$ and $q_{\text{vib}} = kT/\hbar\omega$ are the single-particle partition functions for the rotational and vibrational degrees of freedom of the O_2 molecule, respectively, where I is the molecular moment of inertia and ω is the vibrational frequency. The electronic degrees of freedom are frozen out. Write down an expression for the Helmholtz free energy and use this to determine the heat capacity at constant volume.

P10. A system consisting of a dilute monoatomic gas that is confined to a volume V contains N neutral atoms of mass m. The system is in equilibrium with the surroundings at a temperature T. The electronic ground state of each atom is three-fold degenerate. The free energy A for this system is given by

$$A = -kT \ln \frac{(3q)^N}{N!}$$

where $q = V\left(mkT/2\pi\hbar^2\right)^{3/2}$ is the single-particle partition function for translational motion. Suppose now that the gas is subjected to a uniform electric field which doesn't affect the translational motion but has the effect of splitting the ground state of each atom into a triplet, having the energies $E = 0, \pm\varepsilon$, respectively. How must the expression for A be modified so that it gives the free energy of the final equilibrium state that obtains after thermal relaxation at constant volume, temperature, and electric field?

Preliminary Examination: Thermodynamics and Statistical Mechanics

Department of Physics and Astronomy
University of New Mexico

Spring 2007

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
$\hbar$	:	Planck's constant divided by 2π
β	:	$(kT)^{-1}$
S	:	Entropy
V	:	Volume
μ	:	Chemical potential

Useful Integrals and Sums:

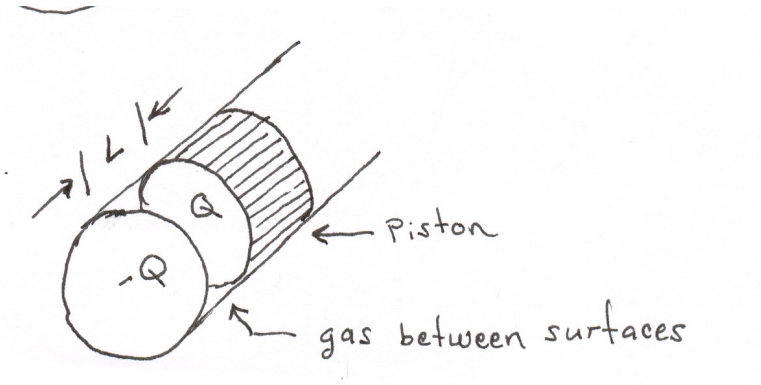
$$\begin{aligned} \int_{-\infty}^{\infty} dx e^{-\alpha x^2} &= \sqrt{\frac{\pi}{\alpha}};\ \mathrm{Re}\,\alpha > 0 \\ \int dx e^{-x} &= -e^{-x} + C \\ \sum_{m=0}^{\infty} x^m &= \frac{1}{1-x}\ ;\ |x| < 1. \end{aligned}$$

P1. An isolated system consisting of N noninteracting, distinguishable, spin-1/2 particles is in equilibrium in a uniform magnetic field of strength B. Of these, exactly N_1 spins are aligned with the field and $N - N_1$ spins are aligned against the field, so that the total energy $E = -N_1\mu B + (N - N_1)\,\mu B$, where μ is the magnetic moment of each particle. Obtain an expression for the temperature of the system as a function of N, N_1, and B. Are there any restrictions on N_1?

P2. A dilute gas having N atoms of mass m is confined to a cylinder with radius r and length L and in equilibrium at a temperature T. The length is controlled by a piston which is held in place by a couple of pins. The bottom face of the cylinder and the head of the piston comprise the two electrodes of a parallel plate capacitor. These surfaces are given the charges Q and $-Q$ respectively, and their mutual attraction that compresses the gas in the cylinder. (See figure.) The free energy for constant Q, L, T and N is given by

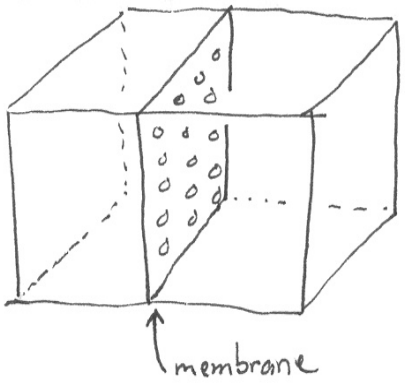
$$F = -NkT \ln\left(\frac{\pi r^2 L}{N}\right) - \frac{3}{2}NkT \ln\left(\frac{mkT}{2\pi\hbar^2}\right) + \frac{1}{2}\left(\frac{L}{\epsilon_0 \pi r^2}\right) Q^2.$$

where ϵ_0 is the permittivity of free space. If the pins are removed and the piston is allowed to slide freely, what will be the value of L when the system reaches equilibrium?



P3. A gas of N noninteracting ions (ideal gas) is in thermal equilibrium at a temperature T in a vessel of volume V . The vessel is divided in half by a rigid membrane, but there are small channels in the membrane through which the ions can pass. (See figure.) Within a channel, an ion experiences an accelerating electric field such that the energy to be on one side of membrane is higher than the energy to be on the other side by an amount Δ. Show that the difference in pressure δP across the membrane is given by

$$\delta P = \frac{2NkT}{V} \tanh\left(\Delta/2kT\right).$$

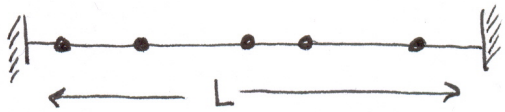


P4. Many of the electronic properties of a metal may be understood through a model in which the mobile electrons in the conduction band are treated as a gas of noninteracting indistinguishable particles having spin 1/2 and mass m. For a typical metal, the conduction band electron density is $n = 30 \times 10^{27}$ m^{-3}, and $m = 0.51$ MeV/c^2 (9.1×10^{-31} Kg). For these material parameters, find the speed (in m/s) of the fastest conducton electrons in the low temperature ($T \to 0$) limit.

P5. Consider a one-dimensional gas of N point-particles, each having mass m, confined to a line of length L. (See figure.) The particles move freely except when in contact with each other, and then their potential energy is infinite; this prevents them from changing places on the line. The leftmost and rightmost particles recoil elastically from the end stops, which are at fixed positions. By integrating over (classical) phase space, show that the canonical partition function is

$$Z = \left(\sqrt{mkT/2\pi\hbar^2}\right)^N \frac{L^N}{N!}.$$

Find the average force f on the end stops, as a function of L and T.



P6. The fundamental equation for the thermodynamic properties of a rubber band is given by

$$S = S_0 + cL_0 \ln \frac{U}{U_0} - \frac{b(L - L_0)^2}{2\,(L_1 - L_0)},$$

where S is the entropy, U is the internal energy, and L is the length of the rubber band, and c, b, U_0, and S_0 are positive constants. The unstretched length is L_0, and the length at the elastic limit is L_1. Suppose that a rubber band in equilibrium at a temperature T is allowed to contract isothermally and reversibly, from $L = L_1$ to $L = L_0$. How much heat will be absorbed from the surroundings during this process?

P7. A system at constant volume is in equilibrium with a particle reservoir at a temperature T. The energy of the system is proportional to the number of particles; when the system contains n particles, the system's energy $E = n\Delta$, where the incremental energy $\Delta = 2.5$ meV. The chemical potential of the reservoir is 1.25 meV. Evaluate the grand canonical partition function

$$Z = \sum_i e^{-\beta E_i} e^{\beta \mu N_i}$$

and show that $\langle n \rangle = 200$ when $T = 300$ K.

P8. A system contains N noninteracting particles, each of which can be in one of two states having energies $\varepsilon = 0$ and $\varepsilon = \Delta$ respectively. The system is in equilibrium with the surroundings at a temperature T. Calculate the energy average, $\langle E \rangle$, and the rms deviation, $\delta E = \sqrt{\langle E^2 \rangle - \langle E \rangle^2}$. How does the ratio $\delta E / \langle E \rangle$ depend on the size of the system, and what is its significance to thermodynamics?

P9. If the temperature of the atmosphere is $5°C$ on a winter day and if 1 kg of water at $90°C$ is available, what is the maximum amount of work that can be extracted (assuming that one is clever enough to figure out a way to do so) as the water is cooled to the ambient temperature? Assume that the volume of water is constant, and assume that the molar heat capacity at constant volume is 4.17 kJ $\text{kg}^{-1}\text{K}^{-1}$ and is independent of temperature.

P10. For audible frequencies, the speed of sound in air is given by $v = \sqrt{B_S/\rho}$ where ρ is the mass density and

$$B_S = -V \left(\partial P / \partial V\right)_S$$

is the adiabatic bulk modulus. Assuming ideal gas behavior ($PV = nRT$), with a molar heat capacity at constant volume $\bar{C}_V = \frac{5}{2}RT$, calculate the adiabatic bulk modulus and show that

$$v = \sqrt{\frac{7RT}{5A}},$$

where A is the average molecular weight (grams/mole) of an air molecule.

Preliminary Examination: Thermodynamics and Statistical Mechanics

Department of Physics and Astronomy
University of New Mexico

Spring 2008

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 $8\frac{1}{2}$"$\times$11" page are allowed.
- Total time: 3 hours.

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

P	:	Pressure
T	:	Absolute Temperature
R	:	gas constant; $R = 8.314\ \mathrm{J}\cdot\mathrm{mole}^{-1}\cdot\mathrm{Kelvin}^{-1}$
k	:	Boltzmann's constant; $k = \dfrac{R}{6.02\times 10^{23}}$
$\hbar$	:	Planck's constant divided by 2π
β	:	$(kT)^{-1}$
S	:	Entropy
V	:	Volume
N	:	Number of particles (Assume $N >> 1$)

Useful Relations and Constants:

$$\begin{aligned}
\sum_{m=0}^{\infty} x^m &= \frac{1}{1-x}\ ;\ |x|<1. \\
\ln N! &\sim N\ln N - N \\
(1+x)^{\nu} &\simeq 1+\nu x;\ \ |x|\ll 1 \\
h &= 6.626\times 10^{-34}\ \mathrm{Js} \\
m_e &= 9.1\times 10^{-31}\ \mathrm{kg}
\end{aligned}$$

P1. A vessel of fixed volume V contains a noninteracting gas of N diatomic molecules having mass m and rotational inertia I in equilibrium with the surroundings at a temperature T. The partition function is given by

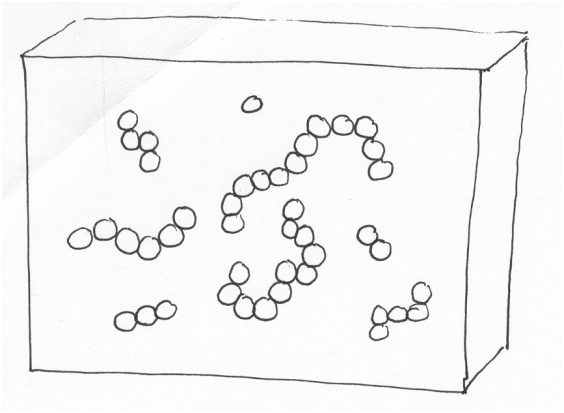
$$Z = \frac{\left[V\left(\frac{mkT}{2\pi\hbar^2}\right)^{3/2}\left(\frac{2IkT}{\hbar^2}\right)\right]^N}{N!}$$

Intramolecular vibrations are frozen out. What is the heat capacity at constant volume?

P2. A system consists of N molecules in a solution of volume V and at a temperature T. It is energetically favorable for the molecules to bond to one another end-to-end, forming polymers. It has been proposed by some investigators that, as a function of T, V, and N, the internal energy U is adequately described by the function

$$U = -N\Delta\left(\frac{\sqrt{V + 4NV_0e^{\beta\Delta}} - \sqrt{V}}{\sqrt{V + 4NV_0e^{\beta\Delta}} + \sqrt{V}}\right),$$

where V_0 is the volume of a single molecule and Δ is the binding energy per bond. If this proposal has any merit, U must be extensive. Show that it is, or show that it is not.



P3. The allowed energy levels of a harmonic oscillator are given by

$$E_n = \hbar\omega\left(n + \frac{1}{2}\right)$$

where $n = 0, 1, 2, ...$ is a positive integer. Suppose that the harmonic oscillator is in thermal equilibrium at a temperature T. Calculate the partition function and obtain from this an expression for the entropy S. Show that your result is in agreement with the third law of thermodynamics.

P4. The partition function for a system of N atoms of mass m in a volume V in equilibrium at a temperature T is

$$Z = \frac{\left(\frac{V}{\lambda^3}\right)^N}{N!}$$

where $\lambda = h/\sqrt{2\pi mkT}$. What is the Helmholtz free energy? What is the maximum amount of work that can be performed on the surroundings by the system if it is allowed to expand at constant temperature to twice its original volume?

P5. To first approximation, the conduction electrons in a metal are modeled as a noninteracting gas of spin-1/2 fermions, each having a charge $-e$ and an effective mass m. The electron density $n = 10^{29}\mathrm{m}^{-3}$ is large enough that the fermi gas is highly degenerate at room temperature, meaning that the states below the fermi surface are largely occupied; as a function of energy the fermi distribution function may be approximated by a step-function. Using the property that the chemical potential μ is related to the number N of conduction electrons through an integral over single particle phase space,

$$N = \frac{2}{(2\pi\hbar)^3}\int d^3x d^3p \frac{1}{e^{-\beta\mu}e^{\beta\frac{p^2}{2m}} + 1},$$

show that the electrons at the fermi surface are moving with a speed

$$v \simeq \frac{\hbar}{m}\left(3\pi^2 n\right)^{1/3} = 1.7 \times 10^6 \mathrm{m/s}$$

that is an order of magnitude higher than what one would expect from equipartition at room temperature.

P6. A cup of water initially at a temperature of 100 degrees Celsius is placed in contact with the environment at 25 degrees C and a constant pressure of 1 atm. Left alone, the water spontaneously cools to 25 C. If the cup contains 100 g of water and the heat capacity at constant pressure $C_p = 4.186$ J/g/deg is approximately constant, independent of temperature, what is the change in entropy of the water for this process? Explain how your result is consistent with the second law of thermodynamics.

P7. As a function of S and T, the internal energy U of a system containing N particles is given by

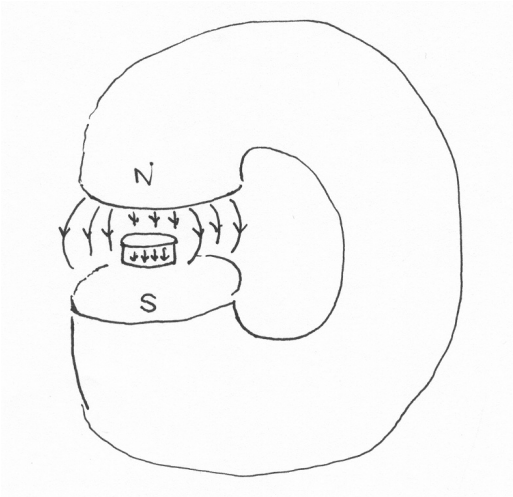
$$U = aN^{5/3}\left(V - bN\right)^{-2/3} \exp\left(\frac{2S}{3Nk}\right)$$

where a and b are constants. Using the combined statement of the first and second laws,

$$dU = TdS - PdV,$$

find an equation for the pressure P as a function of T and V.

P8. An insulating solid with volume V contains N spin-1/2 atoms, each having a magnetic moment $\vec{\mu} = -2\frac{\mu_0}{\hbar}\vec{S}$ where μ_0 is the Bohr magneton and $\vec{S}$ is the spin. When the solid is placed between the poles of magnet, the magnetic field within the solid is uniform with strength B. Assuming that the spins are noninteracting, determine the partition function for the system at constant T and B, and obtain from this an expression for the magnetization M. Sketch a graph showing M as a function of B.



P9. The entropy of a system of N spins in a magnetic field of strength B is given by

$$S = Nk\left[\ln 2 - \frac{(\beta\mu_0 B)^2}{2}\right]$$

in the temperature range of interest. Here μ_0 is the Bohr magneton. Suppose that the system is thermally insulated from the surroundings and the magnetic field is slowly (reversibly) reduced from an initial value of B_1 to a final value B_2. If the temperature is initially T_1, what will be the final temperature T_2?

P10. Consider the system spin in **P9**. If the magnetic field is held constant, how much heat must be added to raise the temperature from an initial temperature T_1 to a final temperature T_2 ?

Preliminary Examination: Thermodynamics and Statistical Mechanics

Department of Physics and Astronomy
University of New Mexico

Spring 2009

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
$\hbar$	:	Planck's constant divided by 2π
β	:	$(kT)^{-1}$
S	:	Entropy
V	:	Volume
g	:	9.8 m/s^2

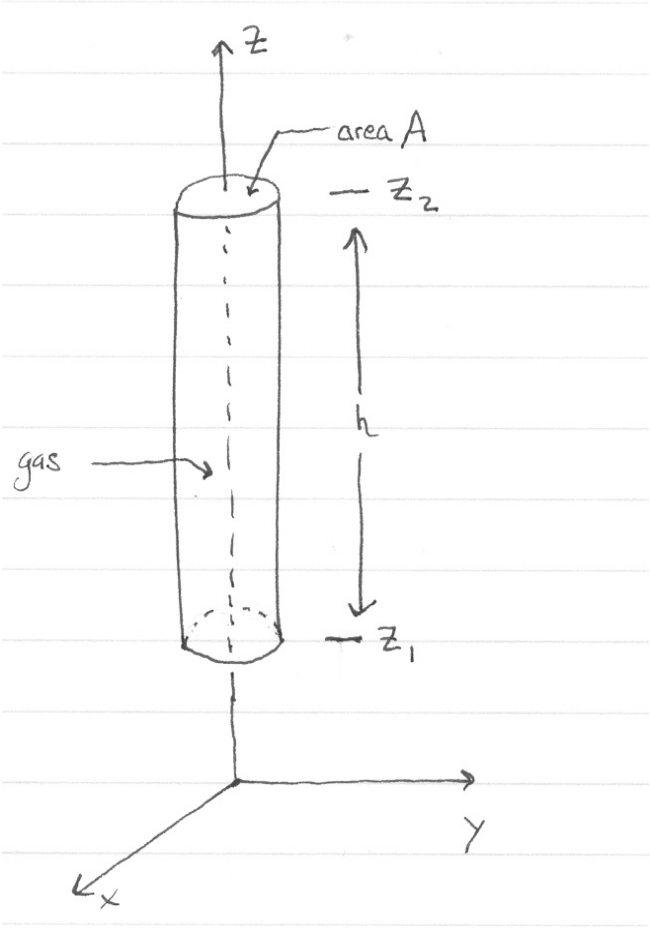
Useful Relations:

$$\begin{aligned}
\int_{-\infty}^{\infty} dx e^{-\alpha x^2} &= \sqrt{\frac{\pi}{\alpha}};\ \mathrm{Re}\,\alpha > 0 \\
\int_0^{\infty} dx x^{\nu} e^{-\beta x} &= \frac{\Gamma(\nu+1)}{\beta^{\nu+1}} \\
\Gamma(\nu+1) &= \nu\Gamma(\nu) \\
\sum_{m=0}^{N} x^m &= \frac{1-x^{(N+1)}}{1-x}\ ;\ |x|<1. \\
\ln N! &\sim N\ln N - N
\end{aligned}$$

The partition function for a gas of N noninteracting indistinguishable free particles of mass m in a vessel of fixed volume V and temperature T is given by

$$\mathbb{Z}_0 = \frac{1}{N!}\left[\frac{1}{(2\pi\hbar^3)}\int dp_x dp_y dp_z \int dx dy dz \, \exp\left(-\beta\frac{p^2}{2m}\right)\right]^N = \frac{V^N}{N!}\left(\frac{mkT}{2\pi\hbar^2}\right)^{3N/2}.$$

Suppose now that the vessel is a tall vertical column with area A and height h, so that $V = Ah$. For the following three problems, consider the case that h is large enough that gravitational effects are important.



P1. Show that when gravity is included, the partition function for the noninteracting gas,

$$\mathbb{Z}(z_1, z_2) = \left(\frac{\exp(-\beta m g z_1) - \exp(-\beta m g z_2)}{\beta m g h} \right)^N \mathbb{Z}_0,$$

is modified so that $\mathbb{Z}_0$ is multiplied by an additional factor having to do with the gravitational potential energy. Here z_1 is the elevation of the bottom of the column, and $z_2 = z_1 + h$ is the location of the top of the column.

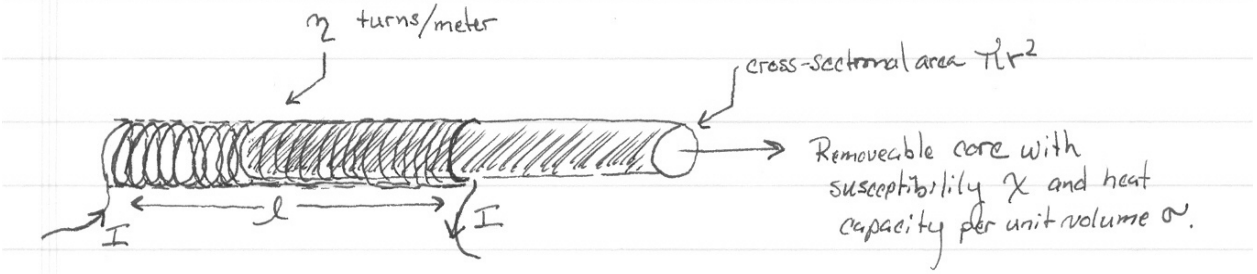
P2. Starting with $\mathbb{Z}(z_1, z_2)$ above, derive expressions for the gas pressure at the bottom and the top of the column respectively. If the gas under consideration is Xe, and the pressure at the bottom of the column is 1.00 atm, what is the pressure at the top of the column at an elevation $h = 3000$ m, assuming ideal gas behavior at room temperature? The molecular weight of Xe is 54 g/mole.

P3. Derive an expression for the heat capacity at constant volume in the two limiting cases; $h << kT/mg$, and $h >> kT/mg$.

A solenoid of length ℓ, and radius r, with a winding density (number of turns per unit length) η, carries a current I. The core of the solenoid is comprised of a solid having a permeability μ that is greater than the permeability of free space μ_0. The free energy at constant I and T is given by

$$\mathcal{F} = -\left(\frac{1}{2}\mu\eta^2 I^2 + \sigma T \ln\tfrac{T}{T_0}\right) V$$

where the constant σ is the heat capacity per unit volume of the core, T_0 is a constant, and $V = \pi r^2 \ell$ is the volume.



P4. The core can be withdrawn from the solenoid by sliding it along the cylindrical axis. What is the minimum work that must be performed to completely withdraw the core at constant I and T?

P5. The permeability $\mu = \mu_0\,(1+\chi)$ is determined by a linear susceptibility

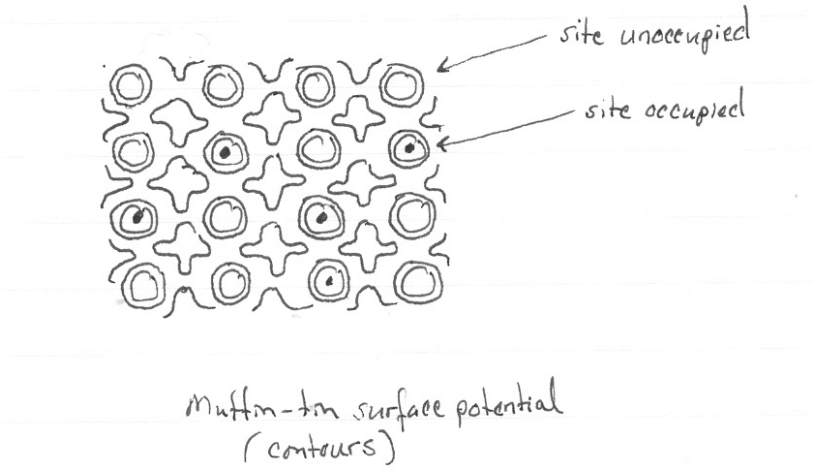
$$\chi = \frac{C}{T}$$

that is inversely proportional to temperature with a Curie constant C. Show that the entropy of the solenoid/core system is given by

$$S = V\left[\sigma\left(1 + \ln\tfrac{T}{T_0}\right) - \left\{\begin{array}{cc} \frac{1}{2}\frac{\mu_0\chi\eta^2 I^2}{T} & \text{(core within solenoid)} \\ 0 & \text{(core withdrawn)} \end{array}\right\}\right]$$

P6. Suppose that the core is withdrawn adiabatically and reversibly, while the current I is held constant. If the initial temperature of the core is T_1, what is the final temperature T_2 after it has been withdrawn?

One model for the adsorption of gas atoms on a metal surface considers the surface to be a corrugated muffin-tin potential, as shown in the figure. Gas atoms can lower their energy by sitting in the potential minima, which serve as a set of identical adhesion sites, each with a binding energy Δ. Interactions between the adsorbed atoms can be ignored, except for the constraint that each site may be occupied by only one atom.



P7. Show that the entropy of a metal surface with M adhesion sites and N adsorbed atoms in equilibrium at a temperature T is given by

$$S = k\left[M \ln\left(\frac{M}{M-N}\right) - N \ln\left(\frac{N}{M-N}\right)\right].$$

Assume that N, M, and $M-N$, are each much larger than 1.

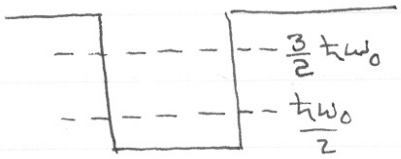
P8. Show that the chemical potential of a metal surface with M adhesion sites and N adsorbed atoms in equilibrium at a temperature T is given by

$$\mu = -\Delta - kT \ln\left(\frac{M-N}{N}\right)$$

P9. Now consider a metal surface in which the M adhesion sites are comprised of equal populations of sites of two different types, A and B, having binding energies Δ_A and Δ_B, respectively. If the total number of adsorbed atoms is one half of the total number of sites, i.e. $N = \frac{1}{2}M$, what is the occupation of each type of site as a function of the temperature T and the difference in binding energy $\delta = \Delta_A - \Delta_B$?

P10. A potential well admits of only two bound states, a ground state having energy $\varepsilon_0 = \frac{1}{2}\hbar\omega_0$ and an excited state with energy $\varepsilon_1 = \frac{3}{2}\hbar\omega_0$. The potential well is occupied by exactly N noninteracting indistinguishable bosons, and is in equilibrium with the surroundings at a temperature T. Show that for large enough N, the energy of the system is given by

$$U \sim \frac{1}{2}N\hbar\omega_0 + \frac{\hbar\omega_0}{e^{\beta\hbar\omega_0} - 1}$$



Preliminary Examination: Statistical Mechanics

Department of Physics and Astronomy
University of New Mexico

Spring 2010

Instructions:

•You should attempt all 10 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.

It may help you to remember that

- if n is an integer that runs from n_1 to n_2, the geometrical sum

$$S = \sum_{n_1}^{n_2} x^n = \frac{x^{n_1} - x^{n_2+1}}{1-x};$$

- room temperature is about $0.025eV$.

P1. A system is in thermal equilibrium with a heat bath at temperature T. The ground state of the system has angular momentum 0 and linear momentum 0. A certain state ξ of the system energetically higher than the ground state by an amount E has angular momentum L units and linear momentum p units. What is the relative occupation of state ξ relative to that of the ground state? How does the principle of equal a priori probability conflict or not conflict with your answer? State in a few sentences (say 4) your reasoning, making clear how your answer may be justified.

P2. A system of N noninteracting particles is in equilibrium at temperature T. The single-particle energy, i.e., the energy that any of the particles can possess, varies from 0 to ∞. Sketch the dependence of the number of particles in a (single-particle) state of a given energy versus that energy for the three cases when the statistics are: (i) Maxwell-Boltzmann, (ii) Fermi-Dirac, and (iii) Bose-Einstein. Explain under what physical conditions any of these may be approximated by any other(s).

P3. Draw sketches to show how the pressure P of an ideal gas varies with its volume V at constant temperature T and also with T at constant V. Combining these and additional observations if necessary, write down an equation of state for the gas. Generalize the equation of state for nonideal gases in which the constituent molecules exert repulsive forces on each other. Explain your reasoning. Finally, incorporate intermolecular interactions which are attractive if the molecules are within a short enough distance with respect to each other. This final generalization is what is known as Van der Waals equation of state. Draw $P - V$ curves at several constant temperatures T corresponding to this last equation of state.

P4. Consider a system of noninteracting particles each of which has energy $E_n = n\Delta$ where n varies through integer values from 0 to a finite number N. Calculate the heat capacity of this system and SKETCH it (important!) indicating characteristic values if possible.

P5. An electron in in thermal equilibrium in a metal at room temperature. Calculate the probability that it occupies a state $0.01eV$ higher than the Fermi energy. State also whether you expect the chemical potential of the electron to vary (increase or decrease?) appreciably or remain essentially constant as the temperature is varied by (i) 10 deg. C (ii) 1000 deg. C.

P6. The magnetic moment of a system of N noninteracting classical spins subjected to a magnetic field B at temperature T increases with increasing field and saturates at large fields. Derive an expression for the moment considering the system is 1-dimensional (which means that the spins are either aligned or anti-aligned with B). What qualitative and/or quantitative differences would appear for a 2-d and 3-d counterpart of the system?

P7. Would the measurement of the heat capacity of a substance have different values if performed under constant pressure versus constant volume conditions? If your answer is yes, express quantitatively their difference in case the system is a perfect gas. Derive the expression you show.

P8. The specific heat of an insulating solid plunges to zero at low temperatures and saturates to a constant value at high temperatures. Does the dependence of the specific heat on temperature at either of these ends follow an approximate power law? If so, does the exponent in the power law depend on any universal characteristic or on the specifics of the solid? Justify your answer on the basis of an analytic expression.

P9. The mixing paradox of Gibbs appears to represent a serious failure of statistical mechanics. Briefly explain the paradox and mention how it may be 'resolved'. Comment on the 'resolution' and express your opinion on whether this has anything to do with Quantum Mechanics.

P10. The Gibbs free energy of N molecules of a given gas at pressure P and temperature T is $NkTlnP + f(P)$ where $f(P) = a + bP + cP^2 + dP^3$, a, b, c and d being constants. Determine the equation of state of the gas.

Department of Physics and Astronomy, University of New Mexico

Thermodynamics and Statistical Mechanics Preliminary Examination

Spring 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 $8\frac{1}{2}'' \times 11''$ 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

$\beta = (kT)^{-1}$ (k is Boltzmann constant)

S: Entropy

V: Volume

U: Internal energy

μ: Chemical potential

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

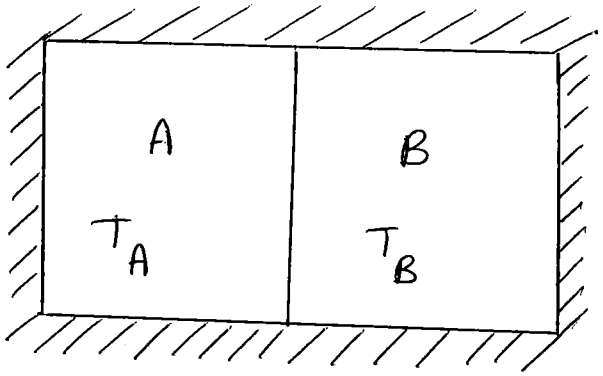
$\sigma = 5.670 \times 10^{-8}$ W m^{-2} K^{-4}; Stefan-Boltzmann constant

1– An ideal diatomic gas occupies a volume of 2 m^3 at a pressure of 5 atm (1 atm $\approx 10^5$ Pa) and a temperature of 293 K. The gas is compressed reversibly and adiabatically to a final pressure of 10 atm.

Compute the final volume, the work done on the gas, the heat released to the surrounding, and the change in the internal energy.

2– Two objects A and B, mechanically and thermally isolated form the surrounding, have initial temperatures $T_A > T_B$. Each object has heat capacity C_V, the same for both objects, which is independent of temperature.

The objects are brought into contact until equilibrium is reached. Assuming the volumes of A and B remain constant, find the final temperatures of the objects. How much has the entropy of the system $A + B$ changed?



3– The Helmholtz free energy of N molecules of a certain gas at temperature T and volume V is given by

$$F = -NkT \ln(V - b) - \frac{a}{V}, \tag{1}$$

where $a < 0$ and $b > 0$ are constants.

Find the equation of state of the gas. What is the minimum volume for this gas? Give a physical interpretation for your answer.

4– The conduction electrons in a monomolecular sheet of graphene can be modeled, to first approximation, as a system of N noninteracting fermions freely moving in a two-dimensional space having area $A = L^2$. In the limit of zero temperature, obtain an expression for the chemical potential as a function of the electron density $\sigma = N/A$.

5– The temperature T_s at the surface of a star can be obtained by fitting the spectrum to a blackbody curve. For $T_s \simeq 6000$ K and a luminosity $L \cong 4 \times 10^{26}$ W, estimate the radius of the star.

6– A particle with mass m is constrained to move freely on the surface of a sphere with radius R, as shown in the figure. Its motion is described by the Hamiltonian

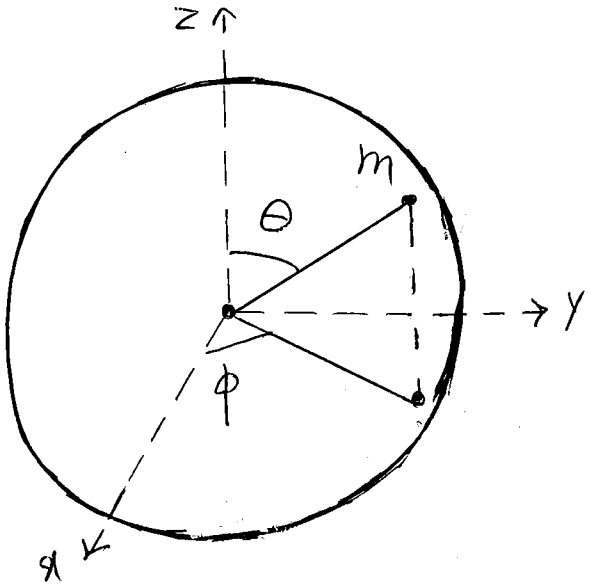
$$H = \frac{P_\theta^2}{2mR^2} + \frac{P_\phi^2}{2mR^2\sin^2\theta},$$

where θ and ϕ are the azimuthal and polar angles, and P_θ and P_ϕ are their conjugate momenta, respectively.

Calculate the canonical partition function for the single particle at a temperature T. Using this partition function, find the average energy and show that it has the value you expect. Assume that m is large enough when integrating over phase space. (Useful information: the number of states in a differential element of phase space is given by $dP_\theta dP_\phi \sin\theta d\theta d\phi/h^2$. Do the momentum integrals first. You may use the following expression for a Gaussian integral

$$\int_{-\infty}^{+\infty} e^{-ax^2} dx = \sqrt{\frac{\pi}{a}} \qquad a > 0,$$

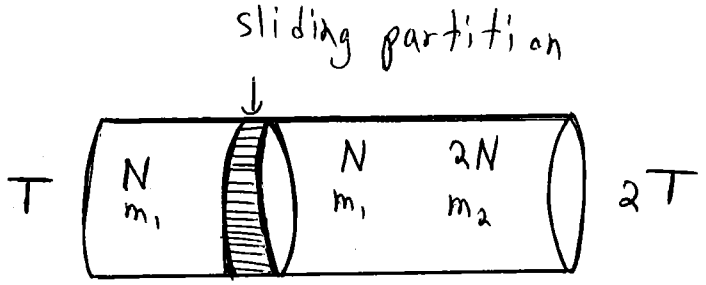
without proof.)



7– Estimate the critical temperature below which a Bose-Einstein condensate starts to form for ^{87}Rb atoms with a density $n \approx 10^{12}$ cm^{-3}. (Mass of ^{87}Rb atom is $m \approx 1.46 \times 10^{-25}$ Kg.)

8– A cylinder with total volume V is partitioned into two parts as shown in the figure. The left-hand part is filled with an ideal gas consisting of N particles of mass m_1. The right-hand part contains an ideal gas that is an admixture of N particles of mass m_1 and $2N$ particles of mass m_2. The left- and right-hand parts of the cylinder are in contact with reservoirs at temperature T and $2T$ respectively. There is no heat transfer between the two parts through the partition.

Assuming that the partition can slide freely, where will it be located when equilibrium is reached?



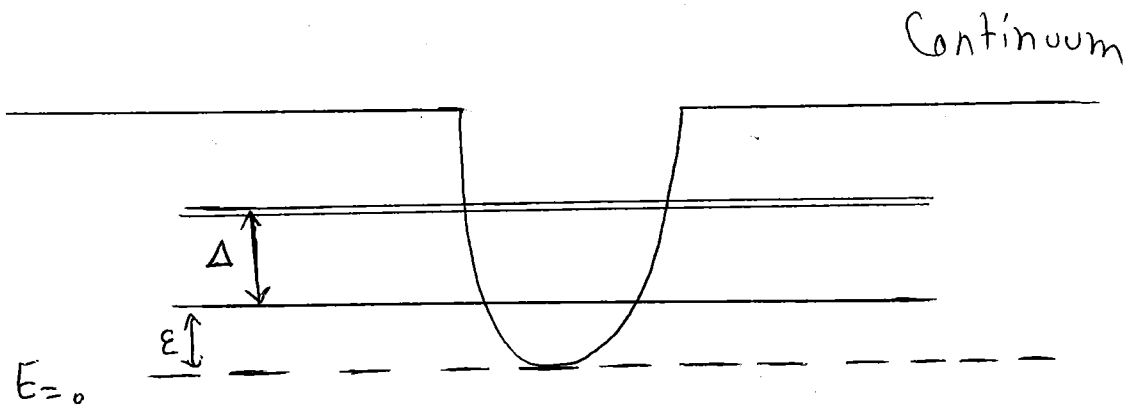
9– Consider a system of N indistinguishable and non-interacting bosons confined to a potential in three dimensions. The potential allows two bound states for a single particle: the ground state with energy ϵ and the first excited state, which is doubly degenerate, and has energy $\epsilon + \Delta$. The system is in equilibrium at a temperature T. Show that in the limit $N\beta\Delta \gg 1$ the partition function for this system is:

$$Z = \frac{e^{-\beta N\epsilon}}{(1 - e^{\beta\Delta})^2}\,.$$

(Hint: You may use the following identity

$$\sum_{n=0}^{+\infty} (n+1)a^n = \frac{1}{(1-a)^2} \qquad 0 < a < 1\,,$$

without proof.)



10– A vessel with volume V in contact with the surroundings at a temperature T is initially filled with N atoms of helium gas. After some time, it is found that N_1 of the atoms remain in the gas phase, and $N_2 = N - N_1$ atoms adhere to the surface of the vessel. The partition function for the gas phase is

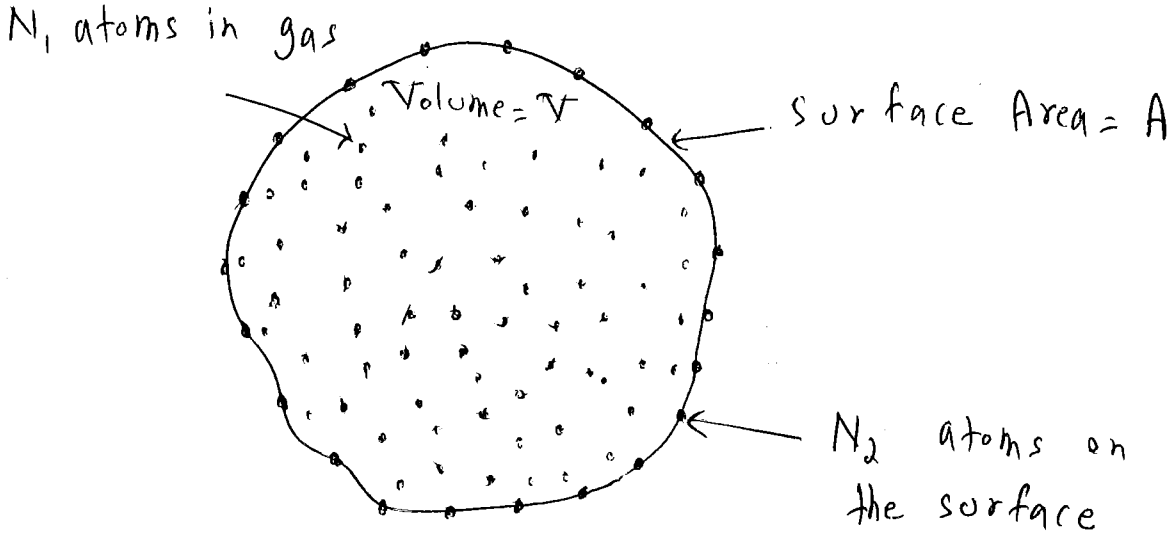
$$Z_1 = \frac{1}{N_1!}\left(\frac{V}{\lambda^3}\right)^{N_1},$$

and the partition function for the surface atoms

$$Z_2 = \frac{e^{\beta N_2 \Delta}}{N_2!}\left(\frac{A}{\lambda^2}\right)^{N_2}.$$

Here $\lambda = (2\pi\hbar^2/mkT)^{1/2}$ is the thermal de Broglie wavelength for an atom having mass m, A is the surface area of the vessel and $\Delta > 0$ is the surface binding energy.

What are the chemical potentials μ_1 and μ_2 for the two subsystems, respectively? When equilibrium is reached, what will be the ratio N_2/N_1?



Preliminary Examination: Thermodynamics and Statistical Mechanics

Department of Physics and Astronomy
University of New Mexico

Spring 2012

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.

P1: The application of statistical mechanics results in an expression for the average magnetic moment of an atom in the direction of a uniform applied magnetic field of strength B in certain common physical systems at temperature T, which is of the form

$$\mu = const \cdot f(B,T).$$

where the limit of $f(B,T)$ as T tends to 0 or B tends to ∞ is 1. What is the physical meaning of the factor *const*? Give the explicit form of the function $f(B,T)$ for two different physical systems (indicate which is which and explain symbols) and point out what the expected qualitative behavior of $f(B,T)$ is, in both examples you give, as T and B are varied.

P2: Calculate the energy density of states for free noninteracting quantum particles in 2 dimensions and answer from your expression whether it increases, decreases or remains constant as the energy varies.

P3: The Hamiltonian for an extreme classical anharmonic oscillator in 1-dimension is given by

$$H = \frac{p^2}{2m} + \frac{1}{10}kx^{10}.$$

The oscillator is in contact with a heat reservoir at temperature T. The equipartition law states that the average kinetic energy of a particle in thermal equilibrium is $k_B T/2$ per degree of freedom. Using that law together with the virial theorem,

$$\langle p\frac{\partial H}{\partial p}\rangle = \langle x\frac{\partial H}{\partial x}\rangle,$$

determine the average energy of the oscillator.

P4: How is the partition function of a system in equilibrium related to the energy state density of the system? How can you calculate the free energy of the system knowing the partition function? A simplified model of a gas at volume V and temperature T results in the following expression for the free energy A :

$$A + Nk_BT\ln(V-b) + \frac{a}{V} = 0$$

Work out an expression for the pressure exerted by the gas as a function of N, T, V, and comment on what physical meaning N, a, b might have in this model.

P5: Consider a *charmonic* oscillator whose energy levels are given by $E_n = n\epsilon$ where n is a non-negative integer smaller or equal to a finite number N. Calculate the specific heat of a collection of noninteracting *charmonic* oscillators and specify clearly the difference relative to a collection of *harmonic* oscillators , each with the same energy spacing ϵ but with a nonvanishing zero-point energy and infinite N. Make plots of the two specific heats and indicate on the plot the effects of the difference in N and in the zero-point energy.

P6. Consider a gas of N atoms which can be considered to be non-interacting bosons the energy spectrum of each comprising only of two states of energies E_1 and E_2. The gas is in thermal equilibrium at temperature T. Calculate the average energy as a function of N, T, E_1 and E_2 and sketch as a function of T.

P7. Briefly explain in *any three* of the following cases the term and its relevance:
(i) Gibbs mixing paradox, (ii) self-avoiding random walker, (iii) Poincare recurrence, (iv) ergodic hypothesis, (vi) Fermi energy.

P8. A system of N identical noninteracting particles is in equilibrium at temperature T. The single-particle energy, i.e., the energy that any of the particles can possess, varies from 0 to ∞. Sketch the dependence of the average number of particles in a (single-particle) state of a given energy versus that energy for the three cases when the statistics are: (i) Maxwell-Boltzmann, (ii) Fermi-Dirac, and (iii) Bose-Einstein. Explain under what physical conditions any of these may be approximated by any other(s).

P9. Explain the origin of the Boltzmann factor $\exp(-E/k_BT)$ where E is the energy and T the temperature? Is it a law of nature, a postulate
of mathematics, a mysterious religious belief or something else?

P10. The specific heat of a metal has an important part that varies strongly as T^n. So does that of an insulating solid at high T and also at low T. The values of n are different in these three cases: 0, 1, and 3, NOT necessarily in that order. Explain what physical characteristics of the systems lead to these three power law dependences and why n has the particular value for each system. Justify your answer on the basis of analytic expressions and clear arguments.

Preliminary Examination: Thermodynamics and Statistical Mechanics

Department of Physics and Astronomy
University of New Mexico

Spring 2013

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.

P1: Consider a collection of a large non-interacting number N of a certain kind of anharmonic oscillators (CAO) whose energy spectrum is similar to that of the harmonic oscillator but starts out with a gap near the ground state. Specifically, the energy E_n of the CAO equals 0 for $n = 0$ and $\Delta + (n-1)\epsilon$ for $n > 0$, where n is an integer. Calculate the partition function and compare with that of the harmonic oscillator. With or without calculation, sketch the temperature dependence of the specific heat of the CAO system showing differences, if any, from that for the harmonic oscillator. Comment on three cases: $\epsilon/\Delta = 1, >> 1, << 1$.

P2. Einstein's theory of the specific heat of an insulating solid assumes the solid to be composed of noninteracting harmonic oscillators. What observed feature of the temperature dependence of the specific heat is incompatible with Einstein's prediction? How would you extend Einstein's theory to address this incompatibility? How would your extension show (present clear analytic arguments with expressions) that the temperature dependence of the specific heat depends on the dimensionality d of the solid (d=1,2,3)?

P3: What are micro-canonical, canonical and grand canonical ensembles and how would you choose which of them to use, in a given situation, for calculations in equilibrium statistical mechanics? Explain if there are any conditions under which they give the same results for thermodynamic quantities and explain why.

P4: Consider an ideal 3-dimensional classical gas of a large number N of free noninteracting particles in equilibrium at temperature T. Each particle has energy proportional to the magnitude of its momentum. Find the free energy of the gas and comment on the difference between its temperature dependence and that of its normal counterpart in which the particle energy is proportional to the square of the momentum.

P5. A random walker has its probability density $P(x, y, z, t)$ of being at position (x,y,z) at time t governed by the equation

$$\frac{\partial P(x, y, z, t)}{\partial t} = D\nabla^2 P(x, y, z, t)$$

where D is a constant that describes how fast the walker walks. Place the walker at the origin at the initial time. Multiply the probability density by the square of the distance of the walker from the origin and integrate over all space. Call the square root of the value of the integral the average distance of the walker from the origin at time t. By making some reasonable assumptions about the behavior of P at infinite distances, show that the average distance varies as $K\sqrt{t}$ where K is a constant. What is the precise dependence of K on D? How would K differ if the random walker were to move on a flat surface instead of in 3-dimensional space?

P6. Explain the origin of the Boltzmann factor $\exp(-E/k_BT)$ where E is the energy and T the temperature. Is it a law of nature, a postulate of mathematics, a mysterious religious belief or something else?

P7. Recall that the classical partition function of a single particle in a box of volume V is $z = V/\lambda^3$ with λ as the thermal de Broglie wavelength of the particle. Surely then, the partition function of two identical counterparts of the particle noninteracting with each other should be z^2 and that of N noninteracting particles all together in a system should be z^N. Show that this argument leads to the violation of the expectation that thermodynamic quantities such as the free energy of the gas are extensive.

P8. Explain a "correction" argument based on the supposed indistinguishability of the N particles that might be used to fix the problem discussed in P7 above. Comment on whether, and why, you find the argument acceptable or unacceptable. If you do not find it acceptable, explain how you reconcile yourself to this unsatisfactory situation in statistical mechanics.

P9. Calculate the dependence (at zero temperature) of the energy of a d-dimensional gas of noninteracting free fermions on the density of the gas for d=1,2,3.

P10. Sketch without calculation the following. Show as much detail indicating characteristic values of relevant quantities as you can.

a. The Maxwell-Boltzmann distribution as a function of velocities.

b. The energy density of states of a free particle in a box as a function of the energy.

c. The allowed frequencies in the Debye theory of the specific heat of an insulating solid as a function of the wavenumber.

Preliminary Examination: Statistical Mechanics

Department of Physics and Astronomy
University of New Mexico

Spring 2014

Instructions:

•You should attempt all 10 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. This sheet must be attached to your answers and submitted.

•Total time: 3 hours.

It may help you to remember that

- if n is an integer that runs from n_1 to n_2, the geometrical sum

$$S = \sum_{n_1}^{n_2} x^n = \frac{x^{n_1} - x^{n_2+1}}{1-x};$$

- room temperature is about $0.025eV$.
- Boltzmann's constant k_B in MKS units is $1.38 \times 10^{-23} J/K$.

P1. Electronic properties of many metals may be understood through a model in which the mobile electrons in the conduction band are treated as a gas of noninteracting indistinguishable particles of spin 1/2 and mass $9.1 \times 10^{-31} kg$. Consider a typical metal for which the conduction band electron density is $5 \times 10^{28} m^{-3}$. Calculate the average speed (in m/s) of the fastest conduction electrons at room temperature. State why this may be considered as a low temperature limit.

P2. An isolated 1-dimensional system consisting of N noninteracting distinguishable spin 1/2 particles is in equilibrium in a uniform magnetic field of strength B. Of these, N_1 spins are aligned with the field and the remaining against the field so that the total energy $E = -N_1\mu B + (N - N_1)\mu B$, where μ is the magnetic moment of each particle. Obtain an expression for the temperature of the system as a function of N, N_1 and B. State any restrictions on N_1 that are necessary for your argument.

P3. What kind of systems would exhibit heat capacities that tend to (i) zero at zero temperature, (ii) zero at very large temperatures? Explain your reasoning.

P4. Calculate the temperature dependence of the entropy of a collection of a large number N of noninteracting distinguishable two-level systems (for instance atoms), the energy difference between the two levels being Δ.

P5. The Helmholtz free energy of N molecules of a certain gas at temperature T and volume V is given by

$$F = -Nk_BT \ln(V - b) - \frac{a}{V},$$

where a and b are constants. Find the equation of state of the gas. Give a clear physical interpretation to the constants a and b.

P6. Recall that the energy of a 1−d harmonic oscillator of frequency ω is $E_n = (n + 1/2)\hbar\omega$ where $n = 0, 1, 2, ...$ Show that the partition function of the system is

$$Z = \frac{1}{2\sinh(\hbar\omega/2k_BT)}.$$

From this expression calculate the temperature dependence of the heat capacity of a 1−d insulating solid. Explain with the help of a sketch what feature(s) of this dependence does not agree with experiment.

P7. Comment on the relation, if any, between the Pauli exclusion principle on the one hand and the Fermi-Dirac and Bose-Einstein distribution functions on the other. Give two examples of particles that obey the Fermi-Dirac distribution and two of particles that obey the Bose-Einstein distribution.

P8. The mixing paradox of Gibbs appears to represent a serious failure of statistical mechanics. Briefly explain the paradox and mention how it may be 'resolved'. Comment on the 'resolution' and express your opinion on whether this has anything to do with Quantum Mechanics.

P9. Consider the Hamiltonian for an anharmonic oscillator in $1-$dimension

$$H = \frac{p^2}{2m} + \frac{kx^4}{4}.$$

The oscillator is in contact with a heat reservoir at temperature T which is high enough so that classical mechanics is applicable. Use the equipartition theorem and the virial theorem in combination to determine the average energy of the anharmonic oscillator. The former states that the average kinetic energy of a particle in thermal equilibrium is $k_B T/2$ per degree of freedom. The latter states that

$$\langle p\frac{\partial H}{\partial p}\rangle = \langle x\frac{\partial H}{\partial x}\rangle$$

where the angular brackets denote averages.

P10. A system consisting of N noninteracting particles, each of which can be in one of two states having energies $\epsilon = 0$ and $\epsilon = \Delta$, is in thermal equilibrium at temperature T. Calculate the average energy $\langle E\rangle$ and the root mean square deviation $\delta E = \sqrt{\langle E^2\rangle - \langle E\rangle^2}$. How does the ratio $\delta E/E$ depend on the size of the system and what is its significance to thermodynamics?

Preliminary Examination: Thermodynamics and Statistical Mechanics

Department of Physics and Astronomy
University of New Mexico

Spring 2015

Instructions:

- **No notes or cheat sheets of any kind are allowed.**
- Attempt all 10 questions (for 10 points each).
- Where possible, show all work; partial credit will be given if merited.
- Total time for the test: 3 hours.

Information that may or may not be useful in this exam:

- 1 joule $= 6.2 \times 10^{18}$ eV.
- $k_B T$ at room temperature is approximately equal to 0.025 eV.
- Equation of state of an ideal gas is $PV = nRT$ in usual notation.
- $$\int_{-\infty}^{\infty} e^{-ax^2} dx = \sqrt{\pi/a}.$$

P1: A cubic box, each side being 1 meter long, isolated from the rest of the universe, is divided into two equal parts by the means of a partition. Initially, one half of the box contains 4 moles of an ideal gas at room temperature, while the other half is empty. Suppose that the partition is suddenly lifted. After a sufficiently long time the gas will occupy the entire box. Find the final temperature in degrees Celsius, and the change in entropy (in appropriate units) for this process. Assume any information that you feel you need but have not been given.

P2: The internal energy of an ideal diatomic gas is (5/2)nRT where T is the absolute temperature, R is the universal gas constant, and n is the number of moles. Calculate the specific heat capacity for this gas: at constant volume on the one hand and at constant pressure on the other .

P3: Consider electrons in a metal at room temperature as non-interacting fermions. (a) Write an expression for their distribution function as a function of energy, explaining the symbols you use. Sketch the distribution function for zero, intermediate and high temperature (define appropriately the words intermediate and high in this context). (b) Calculate the number density of the electrons at *room temperature* in terms of its Fermi energy by using *zero temperature* analysis. Justify your use of the zero temperature analysis for room temperature calculations.

P4: The vibrational motion of a solid containing N atoms is sometimes modeled as that of a collection of $3N$ independent harmonic oscillators, each having the same natural frequency ω_0. Obtain an expression for the heat capacity of such a system and graph it versus temperature for small and large temperatures. Specify what you mean by small and large. What physical properties of the solid are NOT explained by this model?

P5: The underlying equations of mechanics are reversible in time. Yet every day behavior we observe is irreversible. Briefly explain how you understand the resolution of this paradox.

P6: The heat capacity of certain systems tends to zero at very small temperatures. Explain carefully what physical features of the systems would lead to such behavior and what 'very small' temperatures could mean. Now consider, instead, certain other systems whose heat capacity tends to zero at very large temperatures. Explain what physical features would result in this behavior and explain 'very large'. Is it possible for the same system to exhibit both behaviors? Explain your reasoning.

P7: According to the Debye model for the heat capacity of an insulating solid, the vibrational internal energy is proportional to

$$\int_0^{\omega_0} d\omega \frac{\omega^3}{e^{\beta\hbar\omega} - 1}$$

where the proportionality constant depends on the volume of the solid and the speed of sound in the solid, β being $1/k_B T$. State what the dependence on the volume is. Show that the vibrational contribution to the heat capacity is proportional to the cube of the temperature T at low temperature and explain what 'low' means here.

P8: Consider a system of N distinguishable, noninteracting, freely orientable (in 3-dimensions), classical magnetic dipoles, each of magnetic moment μ, in a constant magnetic field of strength B pointing in a fixed direction in space. (a) Write down the partition function for this system. (b) Calculate the magnetic moment for this system at a temperature T and sketch how it varies with respect to T and B.

P9: An ideal classical gas of N particles fills a cubic vessel of volume V in equilibrium at temperature T. If the particles each have a mass m, at what rate do the particles collide with the walls of the container?

P10: State the Fermi-Dirac distribution, the Bose-Einstein distribution and the Maxwell-Boltzmann distribution describing the occupation number of a fixed number N of particles each with a given energy ϵ in terms of the chemical potential μ and the temperature T. The crucial ratio in these expressions is $(\epsilon - \mu)/k_B T$. Doesn't this ratio become large as the temperature becomes very small? Shouldn't therefore the Fermi-Dirac distribution tend to the classical distribution for *small* T rather than for *large* T as is always claimed? Explain what is wrong with the reasoning.

Preliminary Examination: Thermodynamics and Statistical Mechanics

Department of Physics and Astronomy
University of New Mexico

Winter 2016

Instructions:

- The exam consists of 10 problems (10 points each).
- Where possible, show all work; partial credit will be given if merited.
- Useful formulae are provided below; crib sheets are not allowed.
- Total time: 3 hours

Useful Information:

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

P	:	Pressure
T	:	Absolute Temperature
k	:	Boltzmann's constant
R	:	gas constant
$\hbar$	:	Planck's constant divided by 2π
β	:	$(kT)^{-1}$
S	:	Entropy
V	:	Volume

Useful Relations:

$$\int_{-\infty}^{\infty} dx e^{-\alpha x^2} e^{\beta x} = \sqrt{\frac{\pi}{\alpha}} \exp(\frac{\beta^2}{4\alpha}); \ \mathrm{Re}\,\alpha > 0$$

$$\int_0^{\infty} dx x^{\nu} e^{-\beta x} = \frac{\Gamma(\nu+1)}{\beta^{\nu+1}}$$

$$\Gamma(\nu+1) = \nu\Gamma(\nu)$$

$$\sum_{m=0}^{N} x^m = \frac{1-x^{N+1}}{1-x} \ ; \ |x| < 1.$$

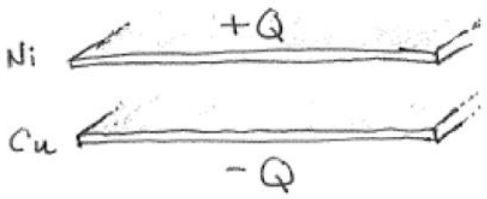
$$\ln N! \sim N \ln N - N$$

$$\frac{d}{dx}\tanh(x) = \cosh(x)^{-2}$$

P1. A leaky parallel plate capacitor with plate area A and plate separation x and permittivity ε having capacitance $C = \varepsilon A / x$ is comprised of two metal plates, one of nickel having chemical potential μ_{Ni} and the other of copper having chemical potential μ_{Cu}. The free energy F governing the transfer of charge Q from the copper plate to the nickel plate is given by

$$F = \frac{Q^2 x}{2\varepsilon A} - \frac{Q}{e}\left(\mu_{Cu} - \mu_{Ni}\right).$$

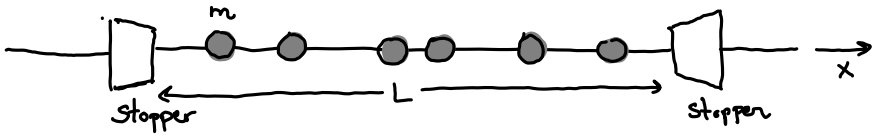
Show that in equilibrium the force of attraction between the plates varies inversely with the square of the plate separation. (The dependence of the chemical potential difference on Q is negligible.)



P2. A one-dimensional gas consists of N beads in equilibrium with the surroundings at a temperature T. The beads slide on a frictionless wire stretched along the x axis. Each bead has a mass m and negligible length, and they are confined to a segment of wire of length L by two stoppers, as shown in the figure. The partition function is

$$Z = \left(\sqrt{\frac{2\pi mkT}{h^2}}\right)^N \frac{L^N}{N!}$$

Suppose that the system is insulated from the surroundings and the stoppers are slowly (reversibly) separated, increasing the length of the segment by a factor of 3. What will be the new temperature?



P3. A fluid of interacting particles is observed to obey the physical equation of state,

$$P = \frac{a}{\bar{V}^2} + \frac{kT}{\bar{V} - b}\ .$$

Here $\bar{V}$ is the molar volume and a and b are constants. Use this, together with the second law of thermodynamics $dU = TdS - PdV$ (or an equivalent statement of the second law), to determine an expression for the fluid's internal energy $U(T,V)$ as a function of T and V, up to an unspecified function of only T. Assume n moles.

P4. Consider a one-dimensional square well that admits only two bound states, a ground state having energy ε_0 and an excited state having energy $\varepsilon_0 + \Delta$. Suppose that the square well occupied by *exactly* N non-interacting indistinguishable bosons. The system is in equilibrium with the surroundings at a temperature T. Show that the partition function Z for an ensemble of such systems given by

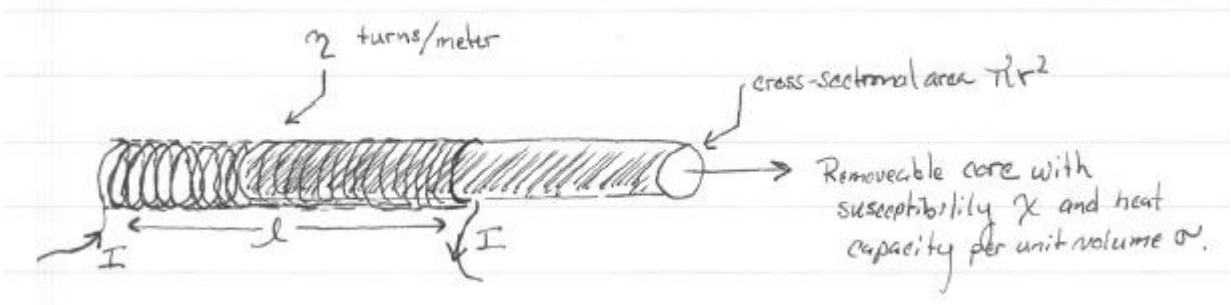
$$Z = e^{-\beta N \varepsilon_0} \left(\frac{e^{\beta\Delta} - e^{-\beta N \Delta}}{e^{\beta\Delta} - 1} \right),$$

and deduce that the probability to find all of the particles in the ground state is finite and equal to $1 - e^{-\beta\Delta}$ for sufficiently large N. Show that the heat capacity $C = k \dfrac{(\beta\Delta/2)^2}{\sinh^2(\beta\Delta/2)}$ is independent of N in this limit.

A long solenoid of length ℓ and radius r, with a winding density (number of turns per unit length) η, carries a current I. The core of the solenoid is comprised of a solid having a permeability μ that is greater than the permeability of free space μ_0. The free energy at constant I and T is given by

$$F = -\left(\frac{1}{2} \mu \eta^2 I^2 + \sigma T \ln \frac{T}{T_0} \right) V,$$

where the constant σ is the heat capacity per unit volume of the core, T_0 is a constant, and $V = \pi r^2 \ell$ is the volume.



P5. Suppose that the permeability $\mu = \mu_0 (1+\chi)$ of the core is enhanced by a linear susceptibility $\chi = \frac{C}{T}$ that is inversely proportional to the temperature with a curie constant C. Show that the entropy of the solenoid/core system is given by

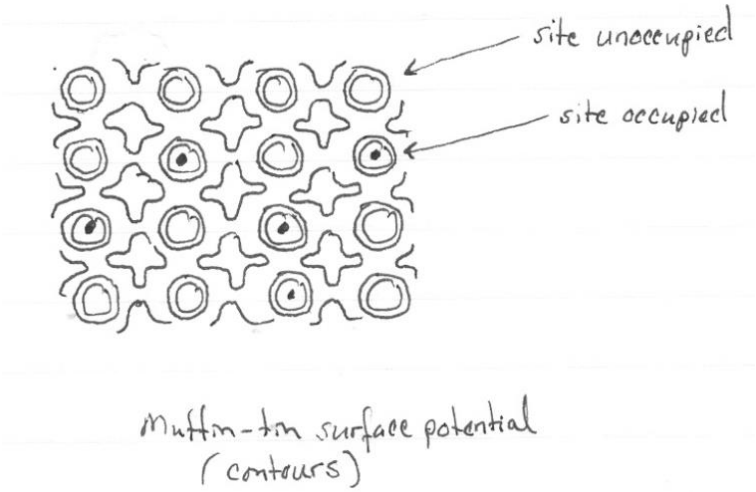
$$S = V\left[\sigma\left(1+\ln\frac{T}{T_0}\right) - \left\{\begin{array}{l}\frac{1}{2}\left(\frac{C\mu_0\eta^2 I^2}{T^2}\right); \text{ (core within solenoid)} \\ 0; \text{ (core withdrawn from solenoid)}\end{array}\right\}\right]$$

P6. In adiabatic demagnetization refrigeration, a solenoid at initial temperature T and carrying an initial current I is thermally insulated from the surroundings. Subsequent reduction of the current causes a decrease of the temperature of the solenoid's core. Show that, for the system above, if the current is adiabatically and reversibly reduced to zero, the final temperature,

$$T_{final} = T\exp\left(-\frac{C\mu_0\eta^2 I^2}{\sigma T^2}\right),$$

will be smaller than the initial temperature by an exponential factor depending on the initial current-to-temperature ratio.

One model for the adsorption of gas atoms on a metal surface considers the surface to be a corregated muffin-tin potential, as shown in the figure. Gas atoms can lower their energy by sitting in the potential minima, which serve as a set of identical adhesion sites, each with a binding energy Δ . Interactions between the absorbed atoms can be ignored, except for the constraint that each site may be occupied by only one atom.



P7. Show that the free energy of a metal surface with M adhesion sites and N absorbed atoms in equilibrium at a temperature T is given by

$$F = -N\Delta + MkT\left[(1-x)\ln(1-x) + x\ln x\right]$$

where $x = N/M$ is the fraction of occupied sites. Assume that N, M, and $M-N$, are each much geater than 1.

P8. If the surface atoms described above come to equilibrium with gas-phase atoms at temperature T and pressure P, what fraction of the adhesion sites will be filled? The chemical potential for surface atoms is given by

$$\mu_{surface} = \left(\frac{\partial F}{\partial N}\right)_T$$

where F is given in P7, while the chemical potential for gas phase atoms is given by

$$\mu_{gas} = -kT\ln\left(\frac{(2\pi mkT)^{3/2}}{h^3}\frac{kT}{P}\right).$$

Here m is the mass of an atom.

P9. A vessel of fixed volume V contains a non-interacting gas of N diatomic molecules having a mass m and a rotational inertia I and a vibrational frequency ω_0 in equilibrium with the surroundings at a high temperature T. The partition function is given by

$$Z = \frac{\left[V\left(\frac{mkT}{2\pi\hbar^2}\right)^{3/2}\left(\frac{2IkT}{\hbar^2}\right)\left(\frac{kT}{\hbar\omega_0}\right)\right]^N}{N!}$$

What is the heat capacity at constant volume?

P10. A cup of water initially at a temperature of 100 degrees C is placed in contact with the environment at 25 degrees C and a constant ambient pressure of 0.83 atm. Left alone, the water spontaneously cools to 25 degrees C. If the cup contains 100 g of water and the heat capacity at constant pressure $C_p = 4.186$ is nearly independent of temperature in this range, what is the change in the entropy of the universe (system *plus* surroundings) for the process? What is the maximum work that could be extracted from the process were one so inclined?