

UVA PHYSICS DEPARTMENT PHD QUALIFYING EXAM PROBLEM FILE
STATISTICAL MECHANICS & THERMODYNAMICS

UPDATED: OCTOBER 2008

1. (a) For a gas of free electrons in d dimensions, compute the isothermal compressibility, $\kappa_T(0)$ at zero temperature, in terms of the mean number of particles per unit volume, $n = \langle N \rangle / V$ and the Fermi energy, ϵ_F . Give the answer to an overall numerical constant C_d .
- (b) Estimate numerically the Fermi temperature of metallic copper by treating the electrons as a gas of free particles in 3-dimensions. The density of copper is 8920 kg.m^{-3} , its atomic weight is 63.5 and it may be assumed that there is one conduction electron per atom.

$$\text{(hint: } \kappa_T^{-1} = -V \left(\frac{\partial P}{\partial V} \right)_{N,T=0} \text{)}.$$

2. N atoms of spin $1/2$ and mass m are confined to a volume V . The atoms can form bound pairs of spin zero and binding energy $-u_0$ per pair, where $u_0 > 0$. The atoms and bound pairs are otherwise non-interacting particles. The chemical potential of the atom is μ_1 and that of the bound pair is μ_2 .
- (a) Using the free energy approach, derive a relation that expresses μ_2 in terms of μ_1 when the system is in thermal equilibrium. (*Note:* No credit will be awarded if you fail to present a derivation based on free energy consideration.)
- (b) What is the number of bound pairs at $T = 0$? Why? (You may assume that N is very large.)
- (c) What must μ_1 be if the pairs undergo a Bose-Einstein condensation (BEC)? Why?
- (d) Find the atomic density N/V for the pairs to undergo a BEC at the transition temperature T_c , assuming $k_B T_c \ll u_0$. [If the expression you obtain contains an integral that does not depend on any physical constant or parameter, you may let the integral be equal to a number called γ .]
- (e) Identify the phases (i.e., atoms, pairs, etc) that exist at (i) $T = 0$; (ii) $T_c > T > 0$; and (iii) $T > T_c$. Justify your answer.

3. A vessel of volume V_1 contains N molecules of a classical ideal gas held at temperature T and pressure P_1 . The energy of a molecule may be written in the form

$$E_j(p_x, p_y, p_z) = \frac{p_x^2}{2m} + \frac{p_y^2}{2m} + \frac{p_z^2}{2m} + \varepsilon_j$$

where ε_j denotes the energy levels corresponding to the internal states j of the molecules of the gas.

- (a) Evaluate the free energy, F . Explicitly display the dependence on the volume V_1 , leaving your answer in terms of the internal free energy

Now consider another vessel of volume V_2 , also at temperature T , containing the same number of molecules of identical gas held at pressure P_2 .

- (b) Give an expression for the total entropy of the two gases in terms of P_1 , P_2 , T and N .
- (c) The vessels are then connected to permit the gases to mix without doing work. Evaluate explicitly the change in entropy of the system. Does your answer make sense? Check it by considering the special case $V_1 = V_2$ ($P_1 = P_2$).

4. Consider a large regular lattice of magnetic atoms in an external field, \vec{B} . The spin-dependent part of the Hamiltonian is approximately

$$-\frac{1}{2}J \sum_{i,j} \vec{S}_i \cdot \vec{S}_j - \mu \sum_i \vec{S}_i \cdot \vec{B},$$

where the double sum is restricted to the q nearest neighbors of each atom. For simplicity you can assume spin $1/2$ and that the external magnetic field is along the z -direction.

- (a) Which sign of J leads to ferromagnetism? Choose this sign for the rest of the problem.
- (b) Using mean field theory (the Weiss molecular-field approximation), find the self-consistent equation for the mean value of each spin, or equivalently for the magnetization, when the atomic density is $n = N/V$ atoms per unit volume.
- (c) Find the Curie temperature T_c in terms of J and q .
- (d) For $T < T_c$, the onset of magnetization is proportional to $(T_c - T)^\beta$. Calculate the value of β in the mean field theory.

5. (a) For a classical system with the Hamiltonian

$$H(q, p) = \sum_{i=1}^N \frac{p_i^2}{2m_i} + \sum_{i=1}^N \frac{k_i}{2} q_i^2$$

at a temperature τ , show that

$$\left\langle \frac{p_i^2}{2m_i} \right\rangle = \frac{\tau}{2} \quad \frac{k_i}{2} \langle q_i^2 \rangle = \frac{\tau}{2}$$

- (b) Consider a system of a large number of classical particles and assume a general dependence of the energy of each particle on the generalized coordinate or momentum component q given by $\varepsilon(q)$, where

$$\lim_{q \rightarrow \pm\infty} \varepsilon(q) = +\infty.$$

Show that in thermal equilibrium, the generalized equipartition theorem holds:

$$\left\langle q \frac{\partial \varepsilon}{\partial q} \right\rangle = \tau.$$

6. In a uniform magnetic field, B , applied along the z -direction, the orbital motion of the electron projected on the xy -plane makes a circular motion with angular frequency, $\omega_c = eB/mc$ (also known as the cyclotron frequency) due to the Lorentz force. The circular motion can be regarded as a quantized harmonic oscillation. The energy levels of this electron are given by the following expression:

$$E = \hbar\omega_c \left(n + \frac{1}{2} \right) + p_z^2 / 2m$$

- (a) Provide an expression for the grand partition function. Ignore the electron spin contribution. Assume that each Landau level has degeneracy g , and consider it to be $g = eB/\hbar c L_x L_y$, where L is the length. Leave your answer in the form of an integral.
- (b) Evaluate the grand partition function in the high temperature limit. Assume the fugacity $f = e^{\mu/kT}$ satisfies $f \ll 1$ in this limit.
- (c) Evaluate the magnetization, M , in this high temperature limit. Simply stating the definition of M is not sufficient.

7. An electron in a magnetic field H has energy $\varepsilon \mp \mu_B H$, depending on whether the spin magnetic moment is aligned, respectively, parallel or anti-parallel to the field. Here ε is the electron kinetic energy and μ_B is the Bohr magneton. Assume that an electron gas with a fixed number N of electrons in a volume V is nearly degenerate; N and V are large enough so that the thermodynamic limit applies. The gas is neutral due to a background charge—in this problem we'll be concerned only with the electrons. Ignoring any electron orbital motion, evaluate the following quantities at low temperatures:

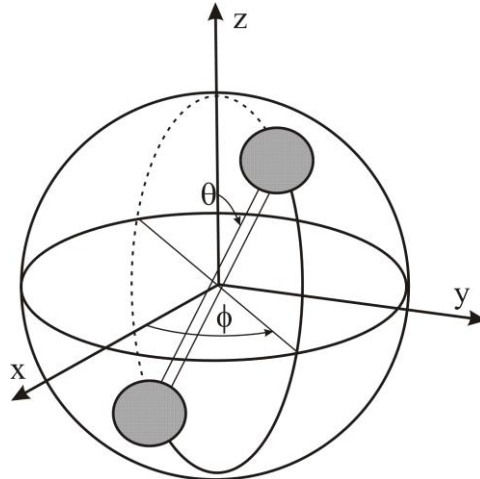
- The density of states, $g(\varepsilon)$, associated with translational motion of the electrons in the container.
- The average number of particles having their spins parallel or anti-parallel to the field. (Use the grand canonical ensemble).
- The average magnetization $\langle M \rangle \equiv -\mu_B (\langle N_+ \rangle - \langle N_- \rangle)$, where $\langle N_+ \rangle$ is the number of particles with their spins parallel to the magnetic field and $\langle N_- \rangle$ is the number of particles with their spins anti-parallel. Evaluate this quantity at low temperatures, by which we mean that you can assume (here the quantity μ is the chemical potential) that $(\mu \pm \mu_B H)/\tau \gg 1$, where $\tau \equiv kT$. If we call $x \equiv (\mu \pm \mu_B H)/\tau$, you may therefore want the following large- x approximation:

$$\text{if } I_{1/2} x \equiv \int_0^\infty \frac{\sqrt{u}}{e^{u-x} + 1} du, \quad \text{then } I_{1/2} x \cong \frac{2}{3} x^{3/2} + \frac{\pi^2}{12} x^{-1/2} + \dots$$

- The *zero-field* spin paramagnetic susceptibility, χ , of the electron gas at low temperatures. (This quantity is defined in the limit as $H \rightarrow 0$ of $\partial \langle M \rangle / \partial H$). Your answer should include the first correction to the low-temperature leading term. You can leave your answer without explicit evaluation of μ .

8. The rotational motion of a classical two-atom molecule about its center of mass is described by two angular variables ϕ and θ (see the figure) and the corresponding canonical momenta p_ϕ and p_θ . The kinetic energy of the classical rotational motion has the form

$$E^{rot} = \frac{1}{2I} p_\theta^2 + \frac{1}{2I \sin^2 \theta} p_\phi^2.$$



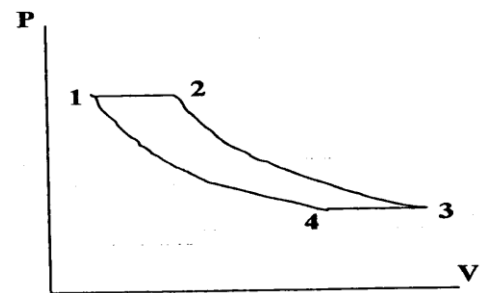
Problem #8

Consider an ideal gas of such two-atom molecules and

1. Calculate the partition function of the classical rotational motion.
 2. Find the entropy and the heat capacity of the rotational motion. Can the result for the heat capacity be understood without calculations?
9. The energy of a gas of photons at temperature T in a volume V is known to be $U = \alpha VT^4$, where α is a constant that can ultimately be expressed in terms of fundamental constants.

- (a) Determine the entropy S of this gas.
- (b) Determine the equation of state of the photon gas.

A certain engine uses the photon gas as its working material. The engine cycle is shown as a (reversible) pV diagram in the figure, following the path $1 \rightarrow 2 \rightarrow 3 \rightarrow 4 \rightarrow 1$, where paths 12 and 34 are isobaric and paths 23 and 41 are adiabatic.



Problem #9

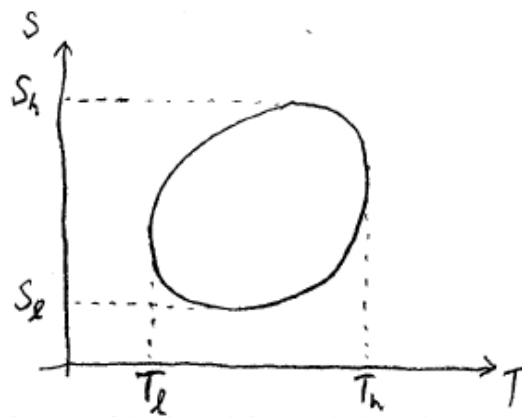
- (c) Draw the cycle shown as an ST diagram, identifying the (S, T) coordinates that correspond to the (p, V) points 1, 2, 3, and 4. Use an arrow to indicate the direction of the cycle as you have drawn it on the ST diagram, and describe the shape of the cycle on the ST diagram.
- (d) Use your ST plot (NOT the pV plot) to determine the efficiency of the engine. As always, explain your reasoning.

10. The double helix of a DNA molecule may be modeled as two strands connected by N links. For DNA replication, the two strands must first disconnect (“unzip”) from each other to produce two parental strands. This is achieved by opening the connecting links. Each link has energy 0 when it is connected and energy $\varepsilon_0 (> 0)$ when it is unzipped. Picture now a DNA molecule depicted along a horizontal line. Assume that the strands can only unzip from the right side, and that the s th link can only unzip if all the links to its right are already unzipped. Furthermore, since the two sides of each unzipped link can have different orientations with each other, each link is assumed to have a g -fold degeneracy.
- Assuming $N \gg 1$, derive the partition function Z and the Helmholtz free energy F of the DNA molecule at temperature T .
 - Find the chemical potential μ . Sketch μ as a function of T .
 - Determine if there is a phase transition for the DNA molecule in the limit of arbitrarily large N . (No credit will be given for unsupported answers!)
11. The partition function for an ideal gas of N buckyball molecules (C_{60} , i.e., each molecule is made up of 60 carbon atoms) in a volume V at temperature T can be written in the form

$$Z = \frac{z^N}{N!}.$$

- If z in turn can be written in the form $z = V^\theta \zeta$, on what variables (i.e., p , V , N , μ , T , ...) does ζ depend? What is θ ? Explain your answers!
- Derive the equation of state for the C_{60} -buckyball gas.
When N_l buckyballs condense to form a liquid, the crudest approximation one can make is to treat these molecules as if they still form a gas, with the additional provisos that (i) each C_{60} molecule is assumed to have a potential energy $-\varepsilon_0$ due to interactions with the rest of the molecules, and (ii) each molecule is free to move in a volume of $N_l v_0$, where v_0 is a constant.
- Based on the above information, find the partition function for a buckyball liquid consisting of N_l buckyballs in terms of the function ζ and relevant parameters given in this problem. (You may want to use the approximation $\ln N! \cong N \ln N - N$.)
- Find an expression for the vapor pressure of an ideal C_{60} gas in equilibrium with its liquid phase.

12. The entropy-temperature (S - T) cycle of a “nameless” reversible engine is shown in the figure. The highest and lowest temperatures T_h and T_l as well as the highest and lowest entropies S_h and S_l are marked on the figure. The area of the loop in the ST -plane is A in some units. Clearly $S(T)$ as well as the inverse $T(S)$ are double-valued functions except at the extremes T_h , T_l , S_h , and S_l . Accordingly, these functions are more properly written as $S(T) = f_{\pm}(T)$ and $T(S) = g_{\pm}(S)$, where the two signs $+$ and $-$ denote the upper and lower branches of these double-valued functions, respectively.



Problem #13

For parts (b)-(d) of this problem express your answers in terms of the above-defined variables and functions.

- Using an arrow, indicate on the figure the direction of the S - T path traversed by the engine cycle when it does work in each cycle. Explain this result.
 - What is (i) the work done by the engine in one cycle and (ii) the heat input to the engine over one cycle?
 - Suppose now that you have a Carnot engine that operates between the same temperature extremes T_h and T_l as our “nameless” engine. Draw a representation on the ST -plot above, or on your own reproduction of it, of this Carnot cycle, including the direction of the path, assuming that the Carnot engine does the same amount of work per cycle as the “nameless” engine. Describe and quantify your plot.
 - Is the “nameless” engine more efficient than, equal in efficiency to, or less efficient than the Carnot cycle you described in part (c)? Prove this result.
13. Here are two facts about a substance:
- The entropy is the following function of T and V :
- $$S = R \frac{V_0}{V} \left(\frac{T}{T_0} \right)^{\alpha-1}$$
- At constant temperature T_0 the work the substance does on its surroundings as it expands from V_0 to V is

$$W|_{T_0} = RT_0 \ln \frac{V}{V_0}.$$

- (a) Find the Helmholtz free energy F , assuming that it is zero at the state values specified by the subscript 0.
- (b) Find the equation of state of this stuff. Is there a point in parameter space where it is ideal?
- (c) For this part we'll simplify the algebra by assuming that $\ln(V/V_0) = 1$ and also $\alpha = 1$. At what temperature T' would the system do twice as much work in going from V_0 to V as it does at $T = T_0$?
14. You are interested in learning about the p - V - T (pressure-temperature-volume) relation as well as the energy U of a system. [Feel free to use $\beta = 1/kT$ if you like.] You have been able to calculate the grand canonical partition function \mathbb{Z} of your system.
- (a) On what variables does \mathbb{Z} depend?
- (b) How can you express the pressure and the energy in terms of \mathbb{Z} ?
- (c) What is \mathbb{Z} for a gas of N noninteracting bosons, expressed as an appropriate product (i.e., your system is in a small box and the energies are discrete). As a second part to this, express $\ln \mathbb{Z}$ as a discrete sum.
- (d) Your system has some peculiar features: The box is a μ -dimensional cube with sides of length L , and the energy-momentum relation is $\varepsilon = \alpha p^s$, where α is a proportionality constant. Using these facts, allow the box to get large and convert the sum over allowed energies to an integral over a continuum of energies; express $\ln \mathbb{Z}$ as an integral.
- (e) Show that $pV = (s/\mu)U$.
15. (a) Find the Bose-Einstein condensation temperature TBEC for a large number, N , of non-interacting atoms of mass M confined to a volume V . Assume the atoms have spin 0, or have integer spin but the spin degeneracy is lifted by an applied magnetic field. A derivation of the full result is required (8 points), but you can get partial credit by just answering such questions as: What is the momentum of an atom in the condensate? What is the value of the chemical potential for $T \leq \text{TBEC}$? What can be said about the value of TBEC by dimensional analysis alone?

- (b) How can one create, in practice, such a BE condensate? (1 point)
- (c) Estimate the number density N/V necessary to obtain TBEC = 1 μ K if the atoms are Na23 (1 point).

Useful integral:

$$\int_0^{\infty} dx \frac{\sqrt{x}}{e^x - 1} = \frac{\sqrt{\pi}}{2} \zeta(3/2) \cong 2.3152.$$

16. A set of N electrons are confined to a restricted area A of a plane but can move freely within those constraints. When a magnetic field \vec{B} is applied perpendicular to the plane, the Landau quantization of the electron orbits produces energy levels

$$E_{\ell} = \hbar\omega_c \left(\ell + \frac{1}{2} \right), \text{ where } \ell = 0, 1, 2, \dots$$

and $\omega_c = eB/mc$ is the cyclotron frequency. The degeneracy of the ℓ^{th} quantum level is

$$\xi = 2eBA/(hc) = \Phi/\Phi_0, \text{ (independent of } \ell \text{)}$$

where $\Phi = BA$ is the magnetic flux passing through the area A and $\Phi_0 = hc/2e$ is the magnetic flux quantum. In what follows ignore (i) interactions between the electrons, and (ii) interactions of electron spin with the magnetic field, i.e., imagine that the electrons have no magnetic dipole moment.

- (a) Calculate the magnetic field dependence of the Fermi energy E_F . (You can assume that the temperature is at absolute zero.)
- (b) Sketch the Fermi energy as a function of magnetic field in the range $0.8B_0 < B < 1.2B_0$, where $B_0 = \Phi_0 N/A$.
- (c) Explain the physical origin of the Fermi energy change when the field is close to B_0 .
- (d) Electrons of density $\rho = 10^{19} \text{ cm}^{-3}$ are confined to a 1 nm-thick layer. Estimate the strength of the magnetic field that will produce the shift in Fermi energy near B_0 .
- (e) Estimate the temperature at which the Fermi energy effect of part (c) can be observed in the laboratory.

Some possibly useful quantities:

$$\Phi_0 = hc/2e = 2.068 \times 10^{-11} \text{ Tesla-cm}^2$$

$$\frac{e\hbar}{mc} = 1.16 \times 10^{-4} \text{ eV/Tesla}$$

$$\text{The Boltzmann constant } k_B = 8.62 \times 10^{-5} \text{ eV/K}$$

17. Consider the Stirling cycle, consisting of the following:
- Isothermal compression from volume V_a to volume V_b at temperature T_1 ,
 - Heating from temperature T_1 to temperature T_2 at fixed volume V_b ,
 - Isothermal expansion from V_b to V_a at temperature T_2 , and
 - Cooling back to temperature T_1 at fixed volume V_a .

What is the efficiency of the Stirling cycle? ($\eta_{\text{Stirling}} \equiv$ work done divided by total heat intake in steps (ii) and (iii)). Assume that the cycle is carried out with an ideal classical gas with a temperature independent heat capacity C_V at fixed volume. Compare this result with the efficiency of a Carnot engine operating between the same two temperatures. By writing an explicit formula for the ratio $\eta_{\text{Carnot}}/\eta_{\text{Stirling}}$, show that this ratio is always > 1 .

18. Distinguishable particles of spin $1/2$ with magnetic moment μ_B are placed in an external magnetic field H (i.e. the energy of each particle is $-S_z \mu_B H$ and its magnetization is $S_z \mu_B$). The number of particles is not fixed.
- Find the grand canonical partition function at chemical potential μ and temperature T (with $\mu < -(kT + \mu_B |H|)$).
 - Find the magnetization from the grand canonical partition function.
19. Consider an ideal gas of massless bosons in thermal equilibrium, where the number N of particles is a conserved quantity.
- Derive an expression for the number of thermally excited particles N_{ex} (i.e. particles with momenta $\vec{p} \neq 0$).

- (b) If the number-density is $\rho = \frac{N}{V} = 10^{20} \text{ cm}^{-3}$, find the critical temperature, below which $N_{ex} < N$. Why does this critical temperature not occur in a photon gas?
- Useful information: $\zeta(2) = 1.645\dots$, $\zeta(3) = 1.202\dots$, $\zeta(4) = 1.082\dots$

20. Consider a system consisting of a liquid and a gas in phase equilibrium. Assume that the gas phase can be approximated by an ideal gas and that the volume occupied by the liquid phase is negligible.

- (a) Derive the Clausius-Clapeyron equation, the equation which determines the slope of the phase boundary in the pV -plane. The equation is

$$\frac{dp}{dT} = \frac{q}{T\Delta v},$$

where q is the latent heat of vaporization per molecule and Δv is the change in volume when one molecule is transferred from the liquid to the gas.

- (b) Determine dv/dT , the change in volume per particle of the gas per unit change of temperature along the phase equilibrium curve. Express your answer in terms of p , q , and kT .
- (c) Determine the specific heat per molecule c_{curve} of the gas along the phase equilibrium curve. This quantity is defined as

$$c_{curve} = \left(\frac{\partial q_g}{\partial T} \right)_{curve},$$

where q_g is the amount of heat per molecule added to the gas per unit change in the temperature, with the restriction that as the temperature is varied, the pressure and volume are varied to keep the system along the coexistence curve. (Thus, do not include any latent heat of transformation). Express your answer in terms of q and c_p .

- (d) Find an expression for the temperature dependence of the phase coexistence boundary $p(T)$ at low temperatures, assuming q is independent of temperature in that region.

21. (a) A gas does work when it expands adiabatically. What is the energy source for this work? Consider an adiabatic curve plotted for a gas on a P - V diagram. Give a general argument, either physical or mathematical, to prove that the

adiabatic curve must always be steeper than the isothermal one where they cross.

- (b) Forty-four grams of CO_2 taken to be an ideal gas, are used to operate a Carnot heat engine between the isotherms $T_1 = 273\text{K}$ and $T_2 = 373\text{K}$, and the adiabatics $S_1 = 198 \text{ Joules/K}$ and $S_2 = 222 \text{ Joules/K}$. In one cycle, how much work does the engine do, and what is its efficiency? By what factor does the volume change during either isothermal segment of the cycle.

22. Consider a system of N distinguishable non-interacting spins in a magnetic field B . Each spin has a magnetic moment of size μ , and each can point either parallel or antiparallel to the field. Thus, the energy of a particular state is

$$\sum_{i=1}^N (-n_i \mu B) \quad n_i = \pm 1$$

- (a) Determine the thermodynamically defined internal energy U of this system as a function of $\beta = 1/kT$, B , and N by employing an ensemble characterized by these variables.
- (b) Determine the entropy S of this system as a function of β , B , and N .
- (c) Determine the behavior of the energy U and the entropy S for this system in the limit $T \rightarrow 0$.
23. (a) Correct the following Kelvin statement of the Second Law: "No process exists which converts all of a given amount of heat into work".
- (b) The following process appears to violate the above incorrect statement:
A cylinder of gas is at a pressure p , a temperature T and volume V . Heat ΔQ is added at constant volume thus increasing the pressure to $p + \Delta p$ and the temperature to $T + \Delta T$. The gas is now allowed to expand adiabatically and reversibly doing an amount of work equal to ΔQ and thus converting the heat added into useful work.
- Plot the p-V phase diagram.
- Integrate the combined First and Second Laws and show that $\Delta S > 0$ for the process starting at the initial point and ending at the final point.

24. An ideal monatomic gas is contained in a thermally insulated cylinder. The gas is compressed by a piston moving with a uniform velocity u , which is small compared to the average molecular speed. Using kinetic theory, compute the rate of change of the pressure with time. Hence compute dP/dV and show that the result is consistent with the adiabatic equation of state $PV^{5/3} = \text{constant}$. Use the following standard symbols:

P, V, T = pressure, volume, temperature

A = area of piston

m = mass of molecule

n = number of molecules per unit volume

v_z = component of molecular velocity normal to the piston

25. (a) What is the molar specific heat at constant volume of a perfect diatomic gas at room temperature?

A rough estimate is sufficient. The presence of molecular vibrations can usually be neglected.

Explain why this is correct.

- (b) What is the specific heat at constant pressure of the same gas?

26. The surface temperature of the sun is T_0 ($=5500\text{K}$); its radius is R_0 ($=7 \times 10^{10}$ cm); the radius of the moon is R ; the mean distance between sun and moon is L ($=1.5 \times 10^{13}$ cm). Assume that both the sun and the moon absorb all electromagnetic radiation incident upon them.

- (a) What is the total flux of energy from the sun? It is sufficient to indicate how this depends on R_0 and T_0 .

- (b) What is the incident flux of energy on an element of the lunar surface, as a function of a properly defined angle θ ? What is the flux of energy radiated by the same element?

- (c) Neglecting the thermal conductivity of the lunar soil, compute the temperature distribution on the lunar surface.

27. A thin-walled vessel of volume V , kept at constant temperature, contains a gas which slowly leaks out through a small hole of area A . The outside pressure is very low compared to the pressure in the vessel.

- (a) Relate the flow of molecules through the hole to the density and some average velocity of the gas molecules in the vessel. It is not necessary to compute explicitly numerical factors of order unity.

- (b) Find the time required for the pressure (or density) in the vessel to decrease to $1/e$ of its initial value.

28. A neutron star consists mainly of neutrons, but it also contains protons and electrons in thermal equilibrium through the reactions



(The antineutrino or neutrino on the right side of these equations escapes the star, and hence do not reach equilibrium with the other particles; their chemical potentials can be set to zero.) In the model of the neutron star to be considered here, the neutrons, protons, and electrons are all taken to be ultrarelativistic, $E = \hbar c |\vec{k}|$. (Real life is more complicated.) The star is electrically neutral.

- (a) Obtain an expression for the Fermi energy E_F as a function of the number density N/V for an ultrarelativistic gas of identical fermions.
- (b) Find the thermal equilibrium relation between E_F^n, E_F^p , and E_F^e for the neutron star, where the superscripts on E_F label particle types.
- (c) Using the results of the first part of the problem, find in our model the relative numbers of neutrons, protons, and electrons.
29. A sample of weight W_0 hangs from an elastic thread of cross-section A_0 and length L_0 (at equilibrium). For a small change of the weight, ΔW , the length of the thread changes by an amount ΔL proportional to ΔW , $\Delta L = C \Delta W$.
- (a) How do you expect C to depend on A_0 and L_0 ?
- (b) Write a “free energy” which is a function of ΔW and a “free energy” which is a function of ΔL . Make an explicit analogy to the usual F and G functions.
- (c) Write an expression for the root mean square fluctuation in the position of the sample. Exhibit the dependence on temperature and on the geometrical factors A_0 and L_0 ?
30. A solution of heavy molecules in water is put in a centrifuge (a cylinder of radius R) and spun about its symmetry axis with constant angular velocity ω . Let the mass of a molecule be M and the mass of an equivalent volume of water be m , with $M > m$. Suppose that the initial concentration of the solution is c_0 . Find the equilibrium concentration in the spinning centrifuge as a function of the radial coordinate r ($r < R$). Assume that the molecules in the solution do not interact with each other.

31. Consider a dilute gas of identical molecules, each having (in addition to very tightly bound electrons) one loosely bound electron with binding energy $-E_b$. As a function of temperature and of the volume per molecule what fraction of the molecules are ionized?
32. A closed cylinder is divided by partitions into 3 equal compartments of volume V which each contain one mole of a different inert ideal gas. The gases are at the same temperature. Calculate the change in entropy which occurs when the partitions are removed allowing the three gases to diffuse isothermally to a uniform mixture. Use either macroscopic thermodynamics or statistical thermodynamics.
33. (a) Derive an expression for the Joule-Thompson coefficient $\mu \equiv (\partial T / \partial p)_H$ for a general gas in terms of c_p and α .
- (b) Prove that no cooling of an ideal gas will result when it is forced through a porous plug.
34. A system maintained at constant temperature T is compressed from pressure P_1 to pressure P_2 . Find a) the change in entropy and b) the change in internal energy.
35. (a) Explain briefly the theorem of equipartition of energy.
- (b) The lattice translational and rotational modes for diatomic molecules in solids and liquids have frequencies of the order of 10^{12} Hz while stretching modes have frequencies of the order of 10^{13} Hz. On the basis of these numbers, estimate the numerical value of the specific heat of liquid N_2 around 100°K .

$$(h = 6.6 \times 10^{-27} \text{ erg}, k = 1.38 \times 10^{-16} \text{ ergs/}^\circ\text{K})$$

37. Prove that the maximum work which can be extracted from an arbitrary system held at constant volume by cooling it from a temperature T_1 to a temperature T_0 is

$$W = NC_v \left[T_1 - T_0 - T_0 \ln T_1 / T_0 \right]$$

38. Consider a closed composite system made up of two sub-systems separated by a rigid, impermeable, adiabatic partition. System A on one side has N_A particles of a *monatomic* ideal gas with entropy S_A , internal energy U_A and volume V_A . System B on the other side

has M_B particles of a *diatomic* gas with corresponding properties S_B , U_B , V_B . Initially the temperature T_A is greater than T_B . The partition is now made diathermic.

- (a) Prove that when the systems achieve equilibrium, the final temperatures are equal.
 - (b) Prove that the net flow of heat has occurred from A to B .
 - (c) If $V_A = V_B$, and numerically $N_A = M_B$, will the final pressures be equal? Give a reason for your answer.
39. The thermodynamic quantity C_p is measured as a function of temperature under constant pressure conditions, yielding the experimental curve C_p vs T . You wish to make a detailed comparison of this curve with theory; but all you can find is a curve C_v vs T , derived theoretically under the assumption of constant volume. You elect to convert your experimental curve C_p vs T to constant-volume conditions.
- (a) Derive the relation between C_p and C_v at any particular temperature.
 - (b) Interpret physically any derivatives appearing in your answer to a), and suggest what companion experimental measurements must be made before conversion can be carried out.
 - (c) At what point is $C_p(T) = C_v(T)$?
 - (d) Outline the steps you would follow to convert the C_p vs T to an experimental C_v vs T curve.

40. The fundamental relation in the entropy representation for black body radiation is

$$S = \frac{4}{3} 4\sigma V U^3 / c^{1/4}$$

where σ is the Stefan-Boltzmann constant.

- (a) Find the equations of state for black body radiation (one for U in terms of V , T ; one for P in terms of V , T).
- (b) Evaluate C_p , C_v and C_p / C_v for black body radiation.
- (c) Show that the Gibbs free energy, G , and hence the chemical potential μ are zero for black body radiation and explain why.
- (d) Show that $PV^{4/3} = \text{constant}$ in adiabatic expansion of black body radiation.