Thermal & Statistical Physics
Study Questions for the Spring 2021 Department Exam
November 24, 2020

1. a. Obtain the Van der Waals equation of state

$$\left(p + N^2 a / V^2\right)\left(V - Nb\right) = N\, kT$$

   by making the following two corrections to the ideal gas: (i) use an "effective volume," instead of the usual volume, (ii) include interactions in a mean field form. State clearly where the mean field assumption comes in.

   b. What is the work done by the gas if it expands isothermally from V_1 to V_2 at some temperature T.

2. a. Define the chemical potential μ. Show that two systems are in diffusive equilibrium if $\mu_1 = \mu_2$. You may start with $F = F_1 + F_2$ (free energy) and use the fact that $\mu_1 = \mu_2$ should minimize F.

   b. Now consider a 1-d gas of length L and number of distinguishable and non-interacting particles N. Assume that temperature T is high enough that we are in the classical regime. Find the chemical potential μ in terms of T and other parameters of the problem.

   c. Now find the free energy F and the specific heat at constant volume C_V.

3. A sample of helium gas inside a cylinder terminated with a piston doubles its volume from $Vi = 1m^3$ to $Vf = 2m^3$. During this process the pressure and volume are related by $PV^{6/5} = A = $ constant.

   Assume that the product PV always equals $\frac{2}{3}U$, where U is the internal energy.

   a. What is the change in energy of the gas?
   b. What is the change in entropy of the gas?
   c. How much heat was added to or removed from the gas?

4. You have a gaseous mixture of 50% helium-4 and 50% molecular hydrogen (by weight) in equilibrium at 300 K and 1.0 atm pressure. The universal gas constant is R=8.31 J/mol·k. Determine

   a. the rms speed of the helium atoms.
   b. the rms speed of the hydrogen molecules.
   c. the partial pressure due to the hydrogen molecules.

5. Consider 3-d lattice of N atoms arranged in a box of side L.

   a. Briefly explain why there are only 3N independent phonon modes and show that ω_{max} (Debye frequency) is given by

   $$\omega_m = \left(\frac{\pi c}{L}\right)\left(\frac{6N}{\pi}\right)^{1/3}.$$

   b. Show that at high temperatures the internal energy $U = 3Nk_BT$ and that at low temperatures it is proportional to T^4. You can use the Bose-Einstein distribution to determine the occupation number of the states.

6. Consider two single-particle states and two particles. Find the entropy of this system when the following statistics apply:

   a. Maxwell-Boltzmann (classical)
   b. Fermi-Dirac
   c. Bose-Einstein
   d. Derive an approximate condition relating temperature and density to determine when or when not quantum statistics must be used.

7. Calculate the magnetic susceptibility $\left(\frac{\partial M}{\partial H}\bigg|_{H=0} = X\right.$ where M is the magnetic moment of the sample and H is the applied field) as a function of T of a gas of N permanent dipoles each of moment μ,

   a. if any direction is allowed (classical spines).
   b. if the dipole is only allowed to assume 2 directions, parallel and opposite to the applied field (Ising spins).

8. In a mono-atomic crystalline solid each atom can occupy either a regular lattice site or an interstitial site. The energy of an atom at an interstitial site exceeds the energy of an atom at a lattice site by ε. Assume that the number of atoms, lattice sites, and interstitial sites are all equal in number.

   a. Calculate the entropy of the crystal in the state where exactly n of the N atoms are at interstitial sites.
   b. What is the temperature of the crystal in this state, if the crystal is at thermal equilibrium?
   c. If $\varepsilon = 0.5$ eV and the temperature of the crystal is 273 K, what is the fraction of atoms at interstitial sites?

   Hint: You have *two* choices to make in this problem – which atoms to put in interstitial sites, and which interstitial sites to put them in.

9. a. Write down the Boltzmann equation for a gas. Explain the meaning of each of the quantities appearing in it. Make sure you write the right-hand-side (collision integral) in its general form as an integration over distribution functions.

    b. What assumptions have gone into this equation? Quantify them if you can. When would you expect these assumptions to be valid? Indicate where these assumptions are used in the derivation of the Boltzmann equation.

    c. Consider a dilute gas in a steady state with a concentration gradient $(\partial n(x)/\partial s)$. Show that within the relaxation time τ and to first order, the particle flux may be written

    $$J_x = n\vec{V}x = -D\frac{\partial n(x)}{\partial x}; \quad D = \frac{kT\tau}{m}$$

    where $\vec{V}_x$ is the average value of vx. Assume that locally the particles follow a Maxwell-Boltzmann distribution

    $$f_o(v,x) = n(x)\frac{m}{(2\pi kT)^{3/2}}\exp(-mv^2/2kT).$$

10. A thin-walled vessel of volume V is kept at a constant temperature T. A gas leaks slowly out of the vessel through a small hole of area A into surrounding vacuum. Find the time required for the pressure in the vessel to drop to half of its original value.

11. A <u>classical</u> monatomic ideal gas of N particles (each of mass m) is confined to a cylinder of radius r and infinite height. A gravitation field points along the axis of the cylinder downwards.

    a. Determine the Helmholtz energy A.
    b. Find the internal energy U and the specific heat C_v.
    c. Why is $C_v \neq 3/2\, Nk$?

12. Consider a 1-dimensional ideal electron gas, length $L(\equiv V)$ and temperature T.

    a. Show that the energy for 1 electron may be written

    $$\varepsilon_1 = (\hbar^2/2m)\left(\frac{\pi}{L}\right)^2 n^2 \quad (n = 1,2,3,...)$$

    b. Find the partition function for N electrons and hence show that PV = NRT.

13. Consider a large reservoir energy $U_o - \varepsilon$ in thermal contact with a system with energy ε.

    a. Give an argument based on the multiplicity (number of distinguishable ways a state with given energy may be obtained) which leads to the result

$$P(\varepsilon) \sim \exp(-\varepsilon/kT)$$

    where $P(\varepsilon)$ is the probability of finding the system in a particular state with energy ε.
    Hint: recall that the entropy $S = k \log$ (multiplicity).

    b. A system of N magnetic moments $(\overline{\mu})$ may orient themselves parallel or antiparallel to an

    applied field. Deduce from (a) the total magnetization $\overline{M} \equiv \Sigma_1 \overline{\mu}_i$ as a function of H and T.

14. Consider an ideal gas of diatomic molecules. The rotational motion is quantized according to
$\varepsilon_j = j\,(j+1)\varepsilon_o$, $j = 0, 1, 2, \ldots$ The multiplicity of each rotational level is $g_j = 2j+1$.

    a. Find the rotational part of the partition function Z for one molecule.
    b. Convert the sum (for Z) to an integral and evaluate the integral for $kT \ll \varepsilon_o$. From this find an
    expression for the specific heat capacity at constant volume at low temperatures.

15. Consider a Fermi gas of N extremely relativistic electrons, with energies $\varepsilon \gg mc^2$, in a cube of
volume $V=L^3$. The energy levels are $\varepsilon = pc$ where p is the momentum.

    a. Determine the Fermi energy (T=0) in terms of the electron density n=N/V.
    b. Find the total energy of this gas in the ground state.

16. Consider a container of volume V with N_g monoatomic ideal gas molecules at pressure P and
temperature T in contact with a surface of area A with N_s molecules adsorbed where the adsorption
energy is ϕ per molecule. The adsorbed molecules are free to move about on the two-dimensional
surface.

    a. Show that the partition function for the gas molecules in the container is

$$Z_g = \left[V \left(2\pi mkT/h^2 \right)^{3/2} \right]^{N_g} / N_g!$$

    where m is the molecular mass, k is Boltmann's constant and h is Planck's constant.
    b. Show that the partition function for the adsorbed molecules is

$$Z_s = \left[\left(2\pi AmkT/h^2 \right) \exp\left(\phi/kT \right) \right]^{N_s} / N_s!$$

    c. Show that at equilibrium the number of adsorbed molecules per unit area is

$$n = \left(hP/kT \right) \left(2\pi mkT \right)^{-1/2} \exp\left(\phi/kT \right).$$

Note: $\int_0^\infty dx\ \exp\left(-a^2 x^2 \right) = \pi^{1/2}/(2a)$.

17. In a temperature range near absolute temperature T, the tension force F of a stretched plastic rod is related to its length L by the expression

$$F = aT^2(L - L_o)$$

where a and Lo are positive constants, Lo being the unstretched length of the rod. When $L = L_o$, the heat capacity CL of the rod (measured at constant length) is given by the relation CL = bT, where b is a constant.

a. Write down the fundamental thermodynamic relation for this system, expressing dS in terms of dE and dL.
b. The entropy S(T,L) of the rod is a function of T and L. Compute $(\partial S / \partial L)_T$.
c. Knowing S(To,Lo), find S(T,L) at any other temperature T and length L. (It is most convenient to calculate first the change of entropy with temperature at the length Lo where the heat capacity is known.)
d. If the rod is thermally insulated but stretched a small distance δL from equilibrium, find the change in T.
e. Calculate the heat capacity CL (L,T) of the rod when its length is L instead of Lo.

18. A lead bullet with mass m=10 grams, leaves a gun with speed v=500m/s and a temperature of 150°C. It is shot into a large body of water at 25°C. The specific heat of lead is 128 J/kg·K, and for water it is 4190 J/kg·K.

a. Describe briefly what time-dependent temperature changes might occur in the bullet and in the water near it.
b. Estimate the energy transferred to the water.
c. Estimate the total entropy change after the bullet has cooled to the water temperature.

19. Consider a paramagnetic substance with the equation of state M = AH/(T-T$_0$). Here M is the magnetization, H is the applied magnetic field, A and T$_0$ are constants, and T is the temperature. The equation of state is valid only for T>T$_0$. Show that C$_M$, the heat capacity at constant magnetization, is independent of M.

20. a. Consider the liquid-gas co-existence curve (called the vapor-pressure curve or the condensation curve) in the P-T plane of a single component system. In order for equilibrium between phases, we need the chemical potentials of the two phases to be equal, i.e., all along the condensation curve $\mu_L(P,T) = \mu_G(P,T)$. Starting from this basic information, obtain an expression for the slope of the co-existence curve in terms of the latent heat of vaporization L, the temperature T and the difference in the molar volumes of the liquid and the gas phase. This is the so-called Clausius-Clapeyron equation.

[Hint: It may be useful to recall that the chemical potential μ is related to the Gibbs potential as $G(T,P) = N\mu(T,P)$.]

b. Consider the vapor pressure of cesium in equilibrium with liquid cesium. Cesium vapor pressure is so low that cesium vapor is approximately an ideal gas. Also, the molar volume of the vapor is much larger than the molar volume of the liquid; and the latent heat of vaporization varies with temperature approximately as $L = a(T_c-T)^2$. Start from the Clausius-Clapeyron equation and use the above information to obtain an expression for the vapor pressure of cesium at a temperature T.

21. A zipper has N links; each link has a state in which it is closed with energy 0 and a state in which it is open with energy ε. We require, however, that the zipper can only unzip from the left end, and that the link number s can only open if all links to the left (1, 2, ----, s - 1) are already open.

a. Show that the partition function can be summed in the form:

$$Q_N = \frac{1-\exp[-(N+1)\beta\varepsilon]}{1-\exp[-\beta\varepsilon]}.$$

b. In the limit $\varepsilon \gg kT$, find the average number of open links.

The above model is a very simplified model of the unwinding of two-stranded DNA molecules.

22. Consider diatomic molecules adsorbed on a flat surface at temperature T. The molecules are free to move on the surface and to rotate within the plane of the surface – this is a non-interacting 2D gas with rotational motion about one axis. The rotational state of the molecules is given by a single quantum number m (m=0, ±1, ±2, ±3…) and the rotational energy is given by $\varepsilon_m = \left(\hbar^2 / 2I\right)m^2$, where I is the moment of inertia of the molecule.

a. Find an expression for the rotational partition function of a single molecule. You need not evaluate the infinite series.

b. Find the ratio of the probabilities of finding a molecule in states m=3 and m=2.

c. Find the probability that m=1 given that $\varepsilon \le \left(\hbar^2 / 2I\right)$.

d. Find the rotational contribution to the internal energy of the gas (N molecules) in the high temperature limit, where $kT \gg \hbar^2 / 2I$.

23. Similar to the van der Waals equation of state is the Dieterici equation of state.

$$p(V - b) = RTe^{-a/RTV}$$

Find the critical constants pc, Vc and Tc in this model of a weakly interacting gas. This equation of state was proposed to account for the interaction of gas atoms with walls.

24. The surface temperature of the sun is T_o (= 5800°K); its radius is R (= 7×10^8 m) while the radius of the earth is r (= 6.37×10^6 m). The mean distance between the sun and the earth is L (= 1.5×10^{13} m). In first approximation one can assume that both the sun and the earth absorb all electromagnetic radiation incident upon them.

Assume the earth has reached a steady state at some temperature T.

a. Find an approximate expression for the temperature T of the earth in terms of the astronomical parameters mentioned above.
b. Calculate the temperature T numerically.

25. An ideal diatomic gas has rotational energy levels given by $\varepsilon_j = \dfrac{h^2}{8\pi^2 I} j(j+1)$, with degeneracies $g_j = 2j+1$.

a. For oxygen, with $\theta_{rot} = \dfrac{h^2}{8\pi^2 I k_B} = 2K$, what fraction of the molecules is in the lowest rotational energy state at T=50K?
b. Repeat for hydrogen, with $\theta_{rot} = 85K$.

26. a. Compare the 4 level systems below. More than one particle may occupy a level. Which system has

   highest temperature _____   lowest temperature _____
   lowest specific heat _____   highest entropy_____

(i) (ii) (iii) (iv)
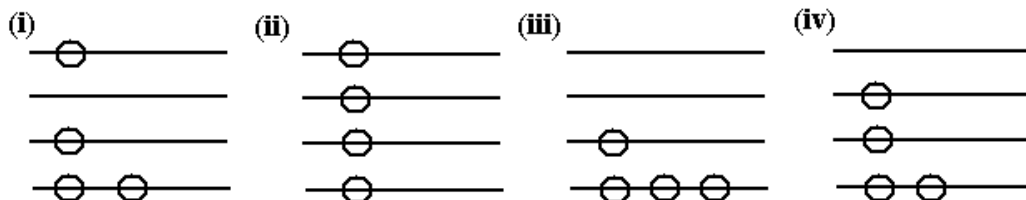
   b. Consider the system below. Explain why it can be thought of as having a <u>negative</u> temperature. (Hint: Consider the Boltzmann factor $e^{-E/kT}$).
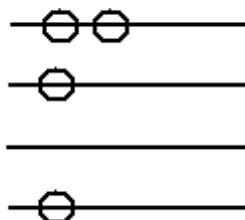
   c. If this system (of part (b)) is brought into contact with a large reservoir at temperature TR (positive) draw a graph indicating how its temperature will change as a function of time as it comes to equilibrium with the reservoir. (Take the initial temperature of the system to be TS a negative number).
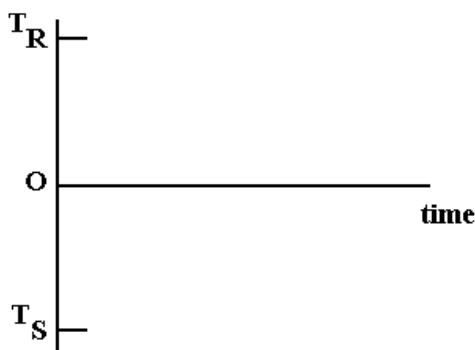
   d. Explain why no problems with the third law are encountered in part (c).

27. A 1.00 gram drop of water is supercooled to -5.00°C (remains in liquid state). Then suddenly and irreversibly it freezes and becomes solid ice at the temperature of the surrounding air, -5.00°C. The specific heat of ice is 2.220 J/g·K, of water is 4.186 J/g·K, and the heat of fusion of water is 333 J/g.

   a. How much heat leaves the drop as it freezes?
   b. What is the change in entropy of the drop as it freezes?

28. A certain solid contains N identical nuclei. Each nucleus can be in any one of three spin states labeled by the quantum number m, where m =1, 0, or -1. Each nucleus has zero energy in the m = 0 state, and has energy ε in both the m = 1 and the m = −1 states.

a. Find an expression, as a function of temperature T, for the nuclear contribution to the average energy <E> of the solid. Assume that the N identical nuclei are located in distinct positions in the solid where the fields are identical.

b. Find an expression, as a function of T, of the contribution of these N nuclei to the entropy S of the solid.

c. By considering the total number of accessible states, calculate the nuclear contribution to the entropy of the solid in the   limit. Compare this with your answer in part (b).

d. Calculate the nuclear contribution to the heat capacity CV of the solid.

29. Consider a three dimensional cubic lattice of N atoms arranged in a box of side L. The modes of this system are called phonons.

   a. What is the total number of modes of this system? What would the total number have been if we were thinking of photons in a 3D box?
   b. What is the maximum frequency that the phonons can have in the Debye model?
   c. Calculate the total thermal energy of the phonons in the Debye model. Your answer may involve an integral.

$$\int_0^{x_D} dx \, \frac{x^3}{e^x - 1}$$

   d. Calculate the low temperature heat capacity of the lattice in the Debye model.

30. Consider a system made out of one single classical oscillator in contact with a heat reservoir at a temperature T. The potential energy of this *one-dimensional* oscillator is $V(x) = \varepsilon_0 |x/a|^n$ where ε_0 and a are constants. What is the thermal energy of the oscillator?

   (Note: Don't get scared by the integral that you will face; only powers of kT in the partition function would contribute to the thermal energy.)

31. Equipartition. A classical harmonic oscillator

$$H = \frac{p^2}{2m} + \frac{Kq^2}{2}$$

is in thermal contact with a heat bath at temperature T. Calculate the partition function for the oscillator in the canonical ensemble and show explicitly that

$$\langle E \rangle = k_B T, \text{ and}$$

$$\left\langle (E - \langle E \rangle)^2 \right\rangle = (k_B T)^2.$$

32. For a gas of molecules with diameter d, number density n and at a temperature T, find
    a. the mean free path,
    b. their average speed, and
    c. the pressure of the gas using kinetic arguments.

33. A sample of ideal gas is taken through the cyclic process *abca* shown in the figure. At point *a*, T = *300 K*.

    a. What are the temperatures of the gas at points *b* and *c*?
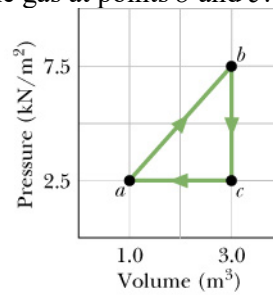
    b. Complete the table by inserting the correct numerical value in each indicated cell. Note that Q is positive when heat is absorbed by the gas and W is positive when work is done by the gas. ΔE is the change in internal energy of the gas.

	Q	W	ΔE
$a \rightarrow b$			
$b \rightarrow c$			
$c \rightarrow a$			