PC5202 Advanced Statistical Mechanics

Midterm test, closed book, 10:00-12:00 Friday 8 March 2019

1. Callen thermodynamics.
    a. State the Callen postulate II, which is about the entropy of a composite system.
    b. Consider ideal gas in two equal volume V and V. Initially all the molecules are in the first volume with total number of particle N and energy U (and volume V). And the second volume has no particle and zero energy U. Entropy of such a constrained equilibrium state is given by the Sackur-Tetrode formula, $S(N,U,V) = k_B N \ln\left(VU^{\frac{3}{2}}\right) + \frac{5}{2} k_B N\,(1 - \ln N) + \text{const.}$ If we connect the two volumes with a diathermal and permeable wall such that atom number N and energy U can be partitioned freely in the two volumes, what is the final equilibrium values of energy U_1 and U_2 and particle numbers N_1 and N_2 in the two volumes. Answer this question using the Callen's postulates.
    c. What is the total entropy in the final state?

    $N_1 = N_2 = N/2$, $U_1 = U_2 = N/2$, entropy increases by $k_B N \ln 2$.

2. Consider *N* non-interacting atoms, each atom has three energy levels with energy $-\epsilon$, 0, and $+\epsilon$.
    a. Determine the partition function Z of a canonical ensemble, and derived the associated entropy of the system S_1.
    b. Now work in micro-canonical ensemble. Work out a formula for the count $\Omega(E)$, which is the number of states with a total energy E of N atoms. Since energy is discrete in units of $\epsilon > 0$, the total energy E should be a multiple of ϵ. From the Boltzmann principle, determine the entropy S_2.
    c. Show that the two entropies S_1 and S_2 calculated in the canonical and micro-canonical ensembles are equal in the thermodynamic limit.

    The partition function is $Z = z^N$, $z = e^{\beta\epsilon} + 1 + e^{-\beta\epsilon}$. Entropy S_1 is from $-\partial F/\partial T$. The number of states in b is sum of $N!/(N_+!N_0!N_-!)$ consistent with $N_+ + N_0 + N_- = N$, and $N_+ - N_- = E/\epsilon$. To show the equivalence, we note that only one term in the sum dominates in the thermodynamic limit (N becomes very large).

3. Consider the van der Waals equation

    $$p = \frac{Nk_BT}{V-Nb} - a\left(\frac{N}{V}\right)^2.$$

    a. We introduce the density variable $\rho = N/V$ and making so-called virial expansion. Find the first two terms of the power series expansion in ρ of the pressure p. That is, let us write this expansion as $p = c_1\rho + c_2\rho^2 + O(\rho^3)$, give the explicit expressions for c_1 and c_2 in terms of the original parameters of the van der Waals equation, T, a, b.
    b. As the c_1 term linear in ρ is just the same as the ideal gas law, we focus on the second term c_2. If the potential energy between two molecules (treated as point particles) is

$V(r)$ where r is the distance between the two molecules, derive an expression relating this potential to the second virial coefficient c_2. [Hint, better use grand-canonical ensemble].

c₁=k_bT, c₂ = k_BTb – a. The formula in b is $c_2 = -\frac{k_BT}{2V}\int_0^\infty \left(e^{-\beta V(r)} - 1\right) 4\pi r^2 dr$*, a result of cluster expansion for the equation of state.*

4. A generalized Ising model defined on a triangular lattice takes the form $H(\sigma) = -J\sum_{<ij>} \sigma_i\, \sigma_j + g\sum_{<ijk>} \sigma_i \sigma_j \sigma_k$.

   Here the summation of the first term $< ij >$ is over the nearest neighbors of the spins summed once, each site has six neighbors. The triple $< ijk >$ denotes the three sites of a triangle and the summation is over all the triangles.

   a. Use the Feynman-Jensen-Bogoliubov inequality, with $H_0(\sigma) = -h\sum_i \sigma_i$, and $H'(\sigma) = H(\sigma) - H_0(\sigma)$, derive a mean-field approximation for the Helmholtz free energy F, from it, derive the mean-field equation.
   b. Discuss qualitatively, what sort of phase transition, if any, the system may have.

The inequality is $F \le F_0 + < (H - H_0) >_0 = \Psi$. *The function is* $\Psi(m, h) = -k_BTN \ln(e^{\beta h} + e^{-\beta h}) - 3JNm^2 + 2gNm^3 + hNm$. *Making partial derivatives with respect to m and h obtained a pair of mean-field equations. For b, the system has a first order phase transition as the free energy is an odd function of the order parameter m.*

PC5202 Advanced Statistical Mechanics

Midterm Test, Wednesday 7 March 2018

1. The Stefan-Boltzmann thermal radiation law says the radiative energy (thermal photon gas energy) per unit volume is $\frac{U}{V} = aT^4$, here a is some universal constant, and the pressure produced by the photon gas is $p = \frac{U}{3V}$. From these equations of state, determine the entropy S of photon gas, as a function of temperature T and volume V.

2. Consider a collection of N classical ideal rotators, each characterized by an angle $0 \leq \theta_j < 2\pi$ and the moment of inertia I_j such that the Hamiltonian is $H = \sum_{j=1}^{N} \frac{L_j^2}{2I_j}$, here L_j is the angular momentum canonically conjugating to the angle θ_j.
    a. Give the associated Hamilton's equations of motion, and also solve them. Discuss the physical meaning of your solution [Note the canonical pair is (θ_j, L_j)].
    b. Consider the micro-canonical ensemble, determine the phase space volume constrained with $H \leq U$. You can use the formula that the volume of a hypersphere in n dimensions is $\pi^n/(n/2)!$.
    c. Based on the result in b, determine the thermodynamic entropy S. Make a sketch of the curve entropy S vs energy U. How does the answer differ from the ideal gas of the Sackur-Tetrode formula?
    d. Show that the equal-partition theorem is valid, i.e., $\langle \frac{L_j^2}{2I_j} \rangle = k_B T/2$. Explain the meaning of the average $\langle \cdots \rangle$ you are using.

3. We can turn the above question 2 as a quantum problem.
    a. Focusing on one single rotator, with angle θ and angular momentum operator $\hat{L}$, what commutation relation should we give for $[\theta, \hat{L}]$? Choose a differential operator for $\hat{L}$ that fulfill this quantization requirement.
    b. Solve the time-independent Schrödinger equation to find the energy eigenvalues the rotator. What determined the discreteness of the eigenvalues?
    c. Using canonical ensemble, determine the partition function z of a single rotator. What is the partition of N rotators?
    d. Give an expression for the entropy S. Try to simply it, and see if you can reduce it to be in agreement with the classical result in 2c. in some limit (when temperature is high or equivalently when $\hbar$ is negligible).

4. What is a Jensen inequality? What is the Feynman-Jensen-Bogoliubov inequality?

PC5202 Advanced Statistical Mechanics

Midterm test, closed book, 1 March 2017

1. Answer briefly the short questions below. Explain your symbols.
    a. What is the Boltzmann principle?
    b. Give a quick derivation of the Gibbs-Duhem relation.
    c. What is the von Neumann equation?
    d. What is a convex function?

a.the Boltzmann principle gives the quantitative relation between entropy in micro-canonical ensemble to the number of microscopic states by $S = k_b \ln \Omega$*. b. Derive the Euler equation U=TS-pV+μN first using the fact that S is a homogeneous function of degree 1 of U,V,N. Then combine with fundamental thermodynamics relation, dU = TdS – pdV + μdN, given SdT-Vdp + Ndμ=0. c. the equation for the density matrix,* $i\hbar \frac{d\rho}{dt} = [H, \rho]$ *. d.* $f(\lambda x_1 + (1-\lambda) x_2) \leq \lambda f(x_1) + (1-\lambda) f(x_2)$*, for any* $0 \leq \lambda \leq 1$*.*

2. Thermal radiation or photons can be described by equilibrium thermal dynamics. The pressure due to thermal photons is given by $p = U/(3V)$, where U is internal energy, V is volume. It is also known that the energy density $u = U/V$ is a function of the temperature T only. There is no particle number N as a variable as photon numbers are not conserved quantity. Based on the information given, derive the entropy $S = S(U,V)$ of thermal radiation. [Note the basic thermodynamic equation $dU = TdS - pdV$ and the Maxwell relation due to $\frac{\partial^2 S}{\partial U \partial V} = \frac{\partial^2 S}{\partial V \partial U}$].

The tricky part is to be sure what is varying and what is fixed. Since we assume S is a function of U and V, everything else depends on U and V only. Most importantly, u(T) = U/V, so T is a function of U and V by the combination U/V only. With that, one can use the Maxwell equation to find the u=u(T) dependence to be $u = a T^4$*. Then S is proportional to* VT^3 *proportional to* $V^{1/4} U^{3/4}$*. This is exactly what Boltzmann did in 1884, now known as Stephan-Boltzmann law.*

3. Consider a collection of quantum harmonic oscillators of Hamiltonian $H = \sum_{j=1}^{N} \hbar \omega_j \hat{a}_j^\dagger \hat{a}_j$ with eigenvalues $\varepsilon_j = \hbar \omega_j n_j$ for each mode j. Here n_j takes nonnegative integers 0, 1, 2, ….
    a. Compute the entropy s_j of the mode j (using canonical ensemble).
    b. If the number of modes are very large ($N \to \infty$), and the frequencies ω_j become a continuum, we can change the sum $\sum_j s_j$ to an integral $\int_0^\infty s(\omega) D(\omega) d\omega$. If the density of states in frequency is $D(\omega) = b\omega^2 V$ where b is a constant and V is the

volume, show that the total entropy S of the system agrees with the thermodynamic result in Prob. 2.

a.Fixing on one oscillator of mode j, the energy spectrum is $\epsilon_n = \hbar\omega_j n$*. The partition function is* $Z_j = \sum_{n=0}^{\infty} e^{-\beta\hbar\omega_j n} = \frac{1}{1-e^{-\beta\hbar\omega_j}}$*. Entropy is* $s_j = -\frac{\partial F_j}{\partial T} = k_B[-\ln(1-e^{-x}) + x/(e^x-1)]$ *, here we have use the short-hand notation* $x = \beta\hbar\omega_j$*. b do the integral with density of state D(ω), and do a change of variable to x, we find* $S \propto VT^3$*, same as in question 2.*

4. Consider the nearest neighbor Ising model with each site having z neighbors, and total of N spins. The Hamiltonian is of the standard form: $H = -J\sum_{\langle i,j\rangle}\sigma_i\sigma_j - h\sum_{i=1}^{N}\sigma_i$.
    a. Focusing on one particular site, derive the mean-field equation for the average magnetization $m = \langle\sigma_i\rangle$.
    b. Based on the solution in a, give expression for the zero-field ($h=0$) heat capacity, $C = d\langle H\rangle / dT$. Discussion the three cases of asymptotic behavior of the heat capacity when temperature T is low, close to T_c , and high. Also draw a graph to illustrate your results.

a.focusing on one spin, the effective Hamilton for one spin is $H = -Jzm\sigma - h\sigma$*. Find average value of the spin, we get* $\langle\sigma\rangle = m = \tanh[\beta(Jzm + h)]$*. This is the mean-field equation. b. setting h=0, energy is* $\langle H\rangle = -NJzm^2/2$ *if* $T>T_c$*, m = 0, so heat capacity C = 0. If T goes to 0, m goes to 1, so C decrease exponentially with T. Near Tc, m goes* $(T_c-T)^{1/2}$*, C goes to a constant.*

PC5202, Advanced Statistical Mechanics

Midterm Test, 12:00 noon Wed 2 March 2016

1. (a) Three variables, x, y, z, are related through a function $f(x, y, z) = 0$. Prove that $\frac{\partial x}{\partial y}\frac{\partial y}{\partial z}\frac{\partial z}{\partial x} = -1$.

(b) Consider a magnetic system with the following thermodynamic variables, internal energy E, entropy S, and magnetic field h, as such a triplet of variables satisfying a constraint. Use the result 1(a) to show that $T\left(\frac{\partial S}{\partial h}\right)_E = -\left(\frac{\partial E}{\partial h}\right)_S$, where T is the thermodynamic temperature.

(c) Discuss in what condition $\left(\frac{\partial E}{\partial h}\right)_S = \langle\frac{\partial \hat{H}}{\partial h}\rangle$, where the angular brackets denote some kind of ensemble average, and $\hat{H}$ is the Hamiltonian (quantum or classical).

2. Consider a collection of N classical harmonic oscillators, with the Hamiltonian

$$H = \sum_{i=1}^{N} \frac{1}{2}(p_i^2 + \omega^2 q_i^2).$$

(a) Compute the phase space volume less than a given energy E. You may need the formula for the volume of a unit hyper-sphere in d dimensions, which is given by $\pi^{\frac{d}{2}}/(d/2)!$

(b) Based on result in 2(a), compute the Gibbs volume entropy, S_G, and Boltzmann entropy, S_B, as a function of energy, E.

(c) Show that the two entropies in (b) are equal in the thermodynamic limit.

3. Consider photon as particle having energy $\hbar\omega$ and chemical potential μ so that n such photons have energy $n\hbar\omega$. (a) Using the grand-canonical ensemble, compute the grand partition function Ξ, grand potential ψ, entropy S, and average number of photons $\langle N\rangle$.

(b) In fact, the chemical potential μ of photon is 0. Give an argument as to why this is so.

(c) Consider a collection of different modes (frequencies) of photons $\omega_k = c2\pi k/L$, where $k = 1,2,3,\ldots$, takes all the natural numbers, and c is the speed of light, and L is the length of a one-dimensional line on which the photons are constrained. Determine the (total) energy per unit length, u, of the thermal photons or black-body radiation, as a function of temperature T. You may assume that L is sufficiently large such that the summation can be turned into an integral.

4. Superconductor/superfluid or magnetic spins with a planar rotation symmetry can be thought as systems with a two-dimensional vector $\vec{M} = (M_x, M_y)$ as the order parameter. Construct a Landau theory out of it, i.e., make a proposal of the Landau free energy as a function of the vector $\vec{M}$, considering the symmetries of the problem (that is, how the component of the order parameter enters into the free energy), then work out its consequences. For example, how the order parameter changes with temperatures in the ordered phase. This is a completely open-ended question. You may propose to calculate other quantities, within the framework of Landau theory for phase transitions.

[WJS]

-- The end --

PC5202 Advanced Statistical Mechanics

Midterm Test (closed book), 4 March 2015

1. This question is on the fundamentals of thermodynamics.
    a. State the Postulate II and III of Callen on thermodynamics.
    b. Using the postulates, show that they imply that if two bodies are brought into thermal contact, and then equilibrate, the temperatures of the two bodies must be the same.
    c. Continue on the above, show that the Clausius statement that 'heat flows from hot body to cold body', is implied by the Callen postulates.

    The answers are in Callen, "Thermodynamics and an introduction to …", 2nd ed, Chap.1.10, page 27-28; Chap.2-4 & 2-5, 43-46.

2. Consider two classical non-interacting Hamiltonian systems with a total Hamiltonian $H = H_1 + H_2$. We define the phase space volume less than a given energy of each system by $\Gamma_j(E_j) = \int_{H_j<E_j} dp_j dq_j$ where $j = 1,2$, and $dp_j dq_j$ represents all the momenta and coordinates of the system j.
    a. Give an expression for the phase space volume Γ of the combined system associated with H less than a given energy E in terms of $\Gamma_1(E_1)$ and $\Gamma_2(E_2)$.
    b. Work in canonical ensemble with the partition functions Z_j, show that entropy is additive, i.e., $S = S_1 + S_2$.
    c. Comment on a similar statement of part b in micro-canonical ensemble starting from the result of part a (i.e., is entropy additive in micro-canonical ensemble?)

    a. *This problem was first discussed in A. I. Khinchin's book "Mathematical Foundations of Statistical Mechanics," (Dover 1949), Sec.7-8, the result is on page 41. Let's assume that energy is bounded below by 0, i.e., 0 < H_1 or H_2, then*

    $$\begin{aligned}\Gamma(E) &= \int_{H_1+H_2<E} dq_1 dp_1 dq_2 dp_2 \\ &= \int dq_1 dp_1 \int_{H_2<E-H_1(q_1,p_1)} dq_2 dp_2 \\ &= \int dq_1 dp_1 \Gamma_1(E-H_1) = \int dE_1 \Gamma_1'(E_1)\Gamma_2(E-E_1) \\ &= \int_{0<E_1+E_2<E} dE_1 dE_2 \Gamma_1'(E_1)\Gamma_2'(E_2)\end{aligned}$$

    The prime means derivative with respect to the argument.

    b. *For partition function it is easy to show $Z = Z_1Z_2$, if Hamiltonian is $H=H_1+H_2$ so this implies additivity to entropy, since $S = -\frac{\partial F}{\partial T}$, $F = -k_B T \ln Z$.*

    c. *No, unless thermodynamic limit is taken.*

3. To a first order approximation, a piece of solid can be thought of as a collection of N independent harmonic oscillators, with a classical Hamiltonian $H = \frac{1}{2}\sum_{j=1}^{N}\left(P_j^2 + \Omega_j^2 Q_j^2\right)$, where P_j, Q_j are the conjugate pairs of dynamic variables, and Ω_j is the angular frequency. Treated as a classical system, compute a) partition function Z, b) entropy S, c) internal energy U, and finally d) heat capacity C (which should recover the Dulong-Petit law).

   The answers are in my notes, http://staff.science.nus.edu.sg/~phywjs/PC5202/stat-mech-1.pdf page 69-71.

4. One way to derive the mean-field theory more rigorously is to use Jensen's inequality, $\overline{\varphi(x)} \ge \varphi(\bar{x})$.
   a. State the condition need for the validity of the Jensen's inequality.
   b. Based on the Jensen inequality or quantum version of the Feynman-Jensen (or Bogoliubov) inequality: $F \le F_0 + \langle (H - H_0)\rangle_0$, derive the mean-field estimation of the free energy (the right-hand side) for a simplified Heisenberg model $H = -J\sum_{\langle i,j\rangle} S_i^z S_j^z - h\sum_{i=1}^{N} S_i^z$, here $S_i^z = -S, -S+1, \cdots, S-1, S$, where S is either an integer or half integer. i or j denotes lattice site on hyper-cubic lattice in D dimensions and the first sum is over the nearest neighbors only.

   a. *Need a continuous convex function, so that the straight line is always above the function for x inside the interval.*
   b. *We need first to define H*$_0$. *Let* $H_0 = -\tilde{h}\sum_{i=1}^{N} S_i^z$, $S_i^z = -S, -S+1, \ldots, S-1, S$. *The partition function associated with H*$_0$ *is* $Z_0 = z^N$,

$$z = \sum_{S^z} e^{\beta\tilde{h}S^z} = e^{-\beta\tilde{h}S} + e^{-\beta\tilde{h}S+\beta\tilde{h}} + e^{-\beta\tilde{h}S+2\beta\tilde{h}} + \cdots e^{\beta\tilde{h}(S-1)} + e^{\beta\tilde{h}S}$$

$$= \frac{e^{-\beta\tilde{h}S}\left(1-e^{\beta\tilde{h}(2S+1)}\right)}{1-e^{\beta\tilde{h}}} = \frac{\sinh\left(\beta\tilde{h}(S+1/2)\right)}{\sinh(\beta\tilde{h}/2)} .$$

$F_0 = -k_B T N \ln z$, $\langle (H-H_0)\rangle_0 = -JND\langle S^z\rangle_0^2 - (h-\tilde{h})N\langle S^z\rangle_0$. *Define* $\Phi = F_0 + \langle (H - H_0) \rangle_0$, *we need to minimize* Φ *with respect to* $\tilde{h}$ *and* $\langle S^z\rangle$, *which gives us mean field equations:*

$$\frac{\partial\Phi}{\partial\langle S^z\rangle} = 0 \quad \Rightarrow \quad \tilde{h} = h + 2JD\langle S^z\rangle,$$

$$\frac{\partial\Phi}{\partial\tilde{h}} = 0 \quad \Rightarrow \quad \langle S^z\rangle = \frac{1}{z}\frac{\partial z}{\partial(\beta\tilde{h})} = \frac{S+1/2}{\tanh\left(\beta\tilde{h}(S+1/2)\right)} - \frac{1}{2\tanh(\beta\tilde{h}/2)}$$

PC5202 Advanced Statistical Mechanics

Midterm test, closed book, 5 March 2014

1.
   a. Explain the meaning of "Schrödinger picture" and "Heisenberg picture" in the contexts of time-dependent classical statistical-mechanical averages.
   b. State the von Neumann equation for the quantum-mechanical density matrix ρ.
   c. State the Maxwell construction used in the van der Waals equation describing gas-liquid phase transition; then sketch the reasoning/proof of the Maxwell construction.

2. Consider a general quantum system of identical particles with the Hamiltonian of the form $H = \sum_{i=1}^{N} \frac{\mathbf{p}_i^2}{2m} + V = K + V$, where m is the mass, $\mathbf{p}_\mathrm{i}$ is momentum, and V is potential energy operator that only depends on coordinates. Let the grand partition function be $\Omega = \mathrm{Tr}\exp\left[-\beta(H-\mu N)\right]$. Show that the average total kinetic energy K of the system can be expressed as $\langle K \rangle = mk_BT\frac{\partial \ln \Omega}{\partial m}$.

3. Beside the micro-canonical, canonical, and grand-canonical ensembles, other ensembles can be defined. Corresponding to the Legendre transform of the thermal dynamic potentials from the Helmholtz free energy to Gibbs free energy, $G = F + p\,V$, one can construct an isobaric-isothermal ensemble with fixed temperature T, pressure p, and number of particles N.
   a. Show that $\Xi(T,p,N) = \int_0^\infty dV\,\mathrm{Tr}\exp\left[-\beta\left(\hat{H}+pV\right)\right]$ is consistent with the above mentioned Legendre transform with $G = -k_\mathrm{B}T\ln\Xi$.
   b. Compute Ξ for a classical ideal gas.
   c. Determine the equation of state by $\partial G/\partial p = V$, and show that it is the same as the ideal gas law.

4.
   a. State the Jensen inequality and condition of its validity.
   b. State the Feynman-Jensen (also known as Bogoliubov) inequality.
   c. Using the above, determine the best mean-field estimate of the free energy F for the N spin Ising model with q number of nearest neighbors with the standard Hamiltonian $H = -J\sum_{<ij>}\sigma_i\sigma_j - h\sum_{i=1}^{N}\sigma_i$ and $H_0 = -h_{eff}\sum_{i=1}^{N}\sigma_i$.

5. Bonus question: state the names of authors of textbooks on statistical mechanics, for which you have read at least one chapter from.

PC5202, Advanced Statistical Mechanics

Midterm Test, 9 March 2013

1. Consider thermodynamic problems.
   a. Derive the Gibbs-Duhem relation for fluid system.
   b. Use the result above to prove the Clapeyron equation, $\mathrm{d}P/\mathrm{d}T = \ell/(T\,\Delta v)$, for the slope of the phase-coexistence curve in a P-T diagram, where P is pressure, and T is absolute temperature. Interpret the meanings of ℓ and Δv.

a. Using the extensivity property, $U(\lambda S,\lambda V,\lambda N)=\lambda U(S,V,N)$, by making derivative with respect to λ and setting $\lambda=1$, we get the Euler equation $U=TS-pV+\mu N$. Differentiate this (i.e. $dU = \ldots$) and together with the fundamental thermodynamic equation $dU=TdS-pdV+\mu dN$, we find the Gibbs-Duhem relation $SdT - Vdp + Nd\mu=0$.

b. We have two Gibbs-Duhem equations, one for the gas phase and one for liquid phase. Subtracting the two after dividing by N, and noting that in phase equilibrium on the phase coexistence line, temperature T, pressure p, and chemical potential μ must be the same. We get the Clapeyron equation, where ℓ is the latent heat needed to vaporize liquid per mole, and $\Delta v=v_g-v_l$ is the volume change per mole. All are positive quantities.

For more details, see page 59-62, and 228-231 of the textbook of Callen, "thermodynamics and an intro to thermostatistics", 2nd ed.

2. With respect to Liouville's theorem:
   a. Explain in words that the microcanonical ensemble is consistent with the theorem.
   b. Let $D(t)$ be the Jacobian determinant defined by the transform $\gamma_0 = (p,q)$ to $\Gamma(t) = (p(t), q(t))$ where $\Gamma(t)$ is the solution of the Hamilton equations of motion with initial condition γ_0. Using the integral form of Liouville's theorem, show that $D(t) = 1$.
   c. Show that $\mathrm{d}D(t)/\mathrm{d}t|_{t=0} = 0$ as a consequence of the Hamilton equations of motion.

a. If the phase space distribution function ρ is a function of the Hamiltonian H only, then ρ satisfies the Liouville's equation $\partial\rho/\partial t=(H,\rho) = 0$. The microcanonical distribution, ρ=const if $E < H < E + \Delta E$ and 0 otherwise is a function of H only, so it is consistent with Liouville's equation. But so does the canonical distribution. Liouville says the phase space volume is invariant under the Hamiltonian dynamics. This implies that if the density was initially uniform (constant in a region), it will stay so, so microcanonical ensemble is stationary and consistent with Liouville theorem.

b. Let Ω_0 be a set of phase space points at initial time t=0. This region moves to Ω_t by time t. There is a one-to-one map from points Ω_0 to Ω_t. The Liouville theorem says (see, e.g., V.I. Arnold, "mathematical methods of classical Mechanics," 2nd ed, page 69):

$$\int_{\Omega_0} d\gamma_0 = \int_{\Omega_t} d\Gamma_t$$

However, according to the usual rule of change of integration variables, we need

$$\int_{\Omega_t} d\Gamma_t = \int_{\Omega_0} \det\left(\frac{\partial\Gamma_t}{\partial\gamma_0}\right) d\gamma_0 = \int_{\Omega_0} D(t)\, d\gamma_0$$

Compare the two, we conclude that the Jacobian determinant D(t) must be 1 for all t.

c. D(t) is the determinant of matrix elements $\frac{\partial\Gamma_i}{\partial\gamma_j}$ *(where Γ is at time t and γ at time 0).*

Expand Γ for small time t using the Hamilton's equation, and taking the time derivative of the determinant and set time to 0, we obtain.

$$\left.\frac{dD(t)}{dt}\right|_{t=0} = \sum_{i=1}^{2N} \left.\frac{d}{dt}\left(\frac{\partial\Gamma_i}{\partial\gamma_i}\right)\right|_{t=0}$$

Using the solution of Hamilton's equation near t=0, e.g., $P_i = p^0_i - t\, \partial H/\partial q^0_i + O(t^2)$, we can show the sum above is zero due to the fact that the second order mixed derivative to H are equal, where $\Gamma = \begin{pmatrix} \Gamma_1 \\ \Gamma_2 \\ \cdots \\ \Gamma_{2N} \end{pmatrix} = \begin{pmatrix} P_1 \\ P_2 \\ \cdots \\ P_N \\ Q_1 \\ Q_2 \\ \cdots \\ Q_N \end{pmatrix}$ *and similarly for the small γ version.*

3. Consider a non-interacting gas of N monatomic molecules in a cylinder with horizontal cross-section area of A and vertical height L in a uniform gravitational field. The total volume is $V=AL$. In addition to the usual kinetic energy term $p^2/(2m)$, there is also a

potential energy of mgz, $0<z<L$, for each molecule of mass m. Where g is the gravitational acceleration constant.

a. Give the expression for the Boltzmann entropy S in microcanonical ensemble in terms of some integral with proper integral limit or constraint (You need not perform the integral analytically).
b. Determine the partition function Z of the canonical ensemble.
c. What is the pressure P at bottom (z=0) and top (z=L) of the cylinder?

a. Boltzmann entropy is $S=k_B \ln W$, *where*

$$W=\frac{A^N}{N!h^{3N}}\int_{U<\sum_{i=1}^{N}\left(\frac{\mathbf{p}_i^2}{2m}+mgz_i\right)<U+\Delta} dz_1dz_2\ldots dz_N d^3\mathbf{p}_1 d^3\mathbf{p}_2\cdots d^3\mathbf{p}_N$$

where $0<z_i<L$.

b. $Z=z^N/N!$,

$$\begin{aligned} z&=\frac{1}{h^3}\iint_A dxdy\int_{z_0}^{z_1}dz\int_{-\infty}^{+\infty}dp_x\int_{-\infty}^{+\infty}dp_y\int_{-\infty}^{+\infty}dp_z e^{-\beta\left(\frac{p_x^2+p_y^2+p_z^2}{2m}+mgz\right)} \\ &=\frac{A}{h^3}\left(\frac{2\pi m}{\beta}\right)^{3/2}\frac{e^{-\beta mgz_0}-e^{-\beta mgz_1}}{\beta mg} \end{aligned}$$

where z_0 *is close to 0 and* z_1 *close to L. The reason that we don't set exactly to 0 and L is because we like to see how the free energy varies with the locations of the top and bottom of the cylinder so that pressure there can be calculated.*

c. The pressure is the force per unit area, f/A. The work done to the system is force times the displacement. So we have $dF = f_0\, dz_0 - f_1\, dz_1 - SdT$, $F = -k_BT \ln Z$. *Differentiate with respect to* z_0 *or* z_1, *we get the pressure at the bottom and top as*

$$P(z=0)=\frac{Nmg}{(1-e^{-\beta mgL})A},$$

$$P(z=L)=\frac{Nmg}{(e^{\beta mgL}-1)A}.$$

4. Consider an idealized boson gas (free particle) such that each quantum particle can take only two non-degenerate quantum state, either the ground state with energy $\varepsilon_0 = 0$, or excited state with energy ε_1, at a chemical potential μ.
   a. Determine the grand partition function Ξ.
   b. Determine if such a simple system shows Bose-Einstein condensation phase transition. If it does, determine the transition temperature T_c. If not, discuss why

it does not have a phase transition as comparing to the usual problem of non-interacting Bose particles in a box.

a. The grand partition function is

$$\begin{aligned}\Xi &= \sum_{\text{All Fock states}} e^{-\beta(H_N-\mu N)} \\ &= \sum_{n_0=0,1,2,\cdots,n_1=0,1,2,\cdots} e^{-\beta(\varepsilon_0 n_0+\varepsilon_1 n_1-\mu n_0-\mu n_1)} \\ &= \frac{1}{1-e^{\beta\mu}}\cdot\frac{1}{1-e^{\beta(\mu-\varepsilon_1)}}\end{aligned}$$

b. The occupation number of the two levels are $<n_0>=1/(\exp(-\beta\mu)-1)$, $<n_1>=1/(\exp(\beta(\varepsilon_1-\mu))-1)$*. Thus the total* $N = <n_0>+<n_1>$*. This equation can be used to determine the chemical potential* μ *as a function of T, which is a smooth function of T. Alternatively, one can calculate heat capacity C, which is a smooth function of T again. The reason that the usual particle-in-a-box boson particles have phase transition is that there are infinite numbers of excited states. So the total number of particle is determined by a separate term for the ground state, plus an integral for all the excited states. The chemical potential is not a smooth function of T due to this.*

PC5202 Advanced Statistical Mechanics

Midterm Test (closed book), Saturday, 3 March 2012

1. Thermodynamics
    a. State the Postulate II of Callen on thermodynamics, and use it to show that heat flows from a hot body to a cold body.
    b. State the Gibbs phase rule. At the triple point of pure water, the temperature T and pressure P have unique values, explain from the fundamental thermodynamic point of view why this is so.

2. Foundations of statistical mechanics.
    a. State the Liouville equation for classical dynamics. Explain the meaning of symbols used.
    b. Show that the Jacobian of the transform, Γ_0 to Γ_t for fixed time t, is 1, where $\Gamma=(q_1, q_2, \ldots q_N, p_1, p_2, \ldots p_N)$ is a phase space point and the time dependence follows the Hamiltonian dynamics.

3. Consider a two-dimensional oscillator with the classical Hamiltonian

$$H = \frac{1}{2}\left(p_x^2 + p_y^2 + x^2 + y^2\right).$$

    a. Compute the entropy $S(U)$ of the system as a function of the total energy U using the classical microcanonical ensemble. [You may use the fact that the volume of a four-dimensional hyper-sphere of a unit radius is $\pi^2/2$.]
    b. Using the result in a, determine the heat capacity C of the system.
    c. Is the result consistent with the equipartition theorem?

4. Assuming that the Helmhotz free energy of a fluid (the van der Waals fluid) is given by the equation

$$F = -a\frac{N^2}{V} - Nk_B T\ln(V - Nb) + Nk_B T\left[\ln\left(\lambda^3 N\right) - 1\right],$$

$$\lambda = \frac{h}{\sqrt{2\pi m k_B T}},$$

where a, b, are constants, N is the number of particles, T is temperature, k_B is the Boltzmann constant, and λ is the thermal wavelength, m is the mass, and h is the Planck constant.

   a. Compute the internal energy U.
   b. Compute the heat capacity at constant volume, C_v, at the critical volume V_c.
   c. Compute approximately (asymptotically close to T_c) the heat capacity at constant pressure, C_p, at the critical pressure P_c.

PC5202 Advanced Statistical Mechanics

midterm test, closed book, 5 March 2011

1. Thermodynamics:
    a. Give at least two equivalent definitions of the chemical potential μ.
    b. Using Callen's maximum entropy postulates I, II, and III, show or argue that when two phases are in coexistence, e.g., ice in coexistence with liquid water, the chemical potentials of the two phases must be equal.
    c. State the Gibbs phase rule.

Ans:

a) $\mu = \left(\frac{\partial U}{\partial N}\right)_{S,V} = \left(\frac{\partial F}{\partial N}\right)_{T,V} = -T\left(\frac{\partial S}{\partial N}\right)_{U,V} = \frac{G}{N}$

b) Let the two subsystems called 1 and 2, then we have

$$dS_1 = \frac{dU_1}{T_1} + \frac{P_1}{T_1} dV_1 - \frac{\mu_1}{T_1} dN_1,$$

$$dS_2 = \frac{dU_2}{T_2} + \frac{P_2}{T_2} dV_2 - \frac{\mu_2}{T_2} dN_2$$

Since the system as a whole are closed, we have $d(U_1+U_2) = 0$, $d(V_1+V_2)=0$, $d(N_1+N_2)=0$, but total entropy S_1+S_2 must be a maximum with respect to the change of U_1, V_1 or N_1, i.e.,

$$d(S_1+S_2) = \left(\frac{1}{T_1} - \frac{1}{T_2}\right) dU_1 + \left(\frac{P_1}{T_1} - \frac{P_2}{T_2}\right) dV_1 - \left(\frac{\mu_1}{T_1} - \frac{\mu_2}{T_2}\right) dN_1 = 0,$$

we find $T_1=T_2$, $P_1=P_2$, and $\mu_1=\mu_2$.

c) $f = r - M + 2$ where f is the number of degrees of freedom of intensive variables (varying of which do not lead to change of phases), r is the number of chemical components, and M is the number of coexisting phases. (see Callen's book, page 245-248).

2. The quantum-mechanical mixed state (density operator) is of the form

$$\rho = \sum_i w_i |\Psi_i\rangle\langle\Psi_i| .$$

    a. What condition do we must impose for ρ to be a valid density matrix?
    b. Give the equation that ρ satisfies.
    c. What is ρ in a grand canonical ensemble?

Ans:

a) For the formula to represent a valid density matrix (read Chap 8 of K. Huang), one must have w_i a real number and $w_i \geq 0, \quad \sum_i w_i = 1.$

b) The von Neumann equation, $\frac{d\rho}{dt} = (\hat{H}, \rho) = \frac{1}{i\hbar}[\hat{H}, \rho]$

c) $\rho = \frac{e^{-\beta(\hat{H}-\mu\hat{N})}}{\Xi}$. The grand partition function Ξ is fixed by Tr[ρ]=1. The trace is over the Fock space.

3. Consider a collection of bosonic particles moving in a 1D parabolic trap such that the energy levels of a single particle are given by $E_n = (n+1/2)\hbar\omega$, n=0, 1, 2, …
    a. Compute the grand partition function Ξ as a function of temperature T and chemical potential μ.
    b. What is a typical fluctuation in the number of particles if the trap contains one particle on average; what if there are 10^6 particles. Answer quantitatively based on result in part (a).

Ans:

a)

$$\begin{aligned}
\Xi &= \mathrm{Tr}[e^{-\beta(H_N-\mu N)}] \\
&= \sum_{\{n_0,n_1,n_2,\cdots\}} e^{-\beta\sum\limits_{i=0,1,2,\cdots}(\varepsilon_i-\mu)n_i} \\
&= \prod_{i=0}^{\infty}\sum_{n_i=0,1,2,\cdots} e^{-\beta(\varepsilon_i-\mu)n_i} \\
&= \prod_{i=0}^{\infty}\frac{1}{1-e^{-\beta(\varepsilon_i-\mu)}}, \qquad\qquad \varepsilon_i = (i+\frac{1}{2})\hbar\omega
\end{aligned}$$

b)

$$\langle N\rangle = \frac{\partial \ln\Xi}{\partial(\beta\mu)} = \sum_{i=0}^{\infty}\frac{1}{e^{\beta(\varepsilon_i-\mu)}-1},$$

$$\langle N^2\rangle - \langle N\rangle^2 = \frac{\partial^2 \ln\Xi}{\partial(\beta\mu)^2} = \sum_{i=0}^{\infty}\frac{e^{\beta(\varepsilon_i-\mu)}}{(e^{\beta(\varepsilon_i-\mu)}-1)^2} = \langle N\rangle + \sum_{i=0}^{\infty}\frac{1}{(e^{\beta(\varepsilon_i-\mu)}-1)^2}$$

If the occupation number per state is low (high T), the second term can be ignored. We have that

$\langle N^2\rangle - \langle N\rangle^2 \approx \langle N\rangle$. If we have 1 particle on average, the standard deviation (square root of the variance) in the particle number is of order 1 (percentage deviation is 100%). If we have 10^6 particles, the standard deviation (fluctuation) in the particle numbers is of order $\sqrt{N} \approx 10^3$ (0.1 percents).

4. Consider the problem of a mean-field theory of an infinite long one-dimensional Ising model, with the classical Hamiltonian (energy) given by $H = -J\sum_i \sigma_i\sigma_{i+1} - h\sum_i \sigma_i$, $\sigma=\pm1$. Let us have the spins of site 1 and 2 treated explicitly and exactly and the rest of the spins of site …, -2, -1, 0, and 3, 4, 5, …, replaced by average, $m=\langle\sigma_i\rangle$.
   a. Derive the mean-field equations for the average of two spins $\langle\sigma_1\rangle$ and $\langle\sigma_2\rangle$.
   b. If $\langle\sigma_1\rangle = \langle\sigma_2\rangle = m$, discuss if there is a phase transition at $h=0$, in the sense that $m>0$ for $T < T_c$ and $m=0$ for $T > T_c$ with $T_c > 0$.

a) The effective Hamiltonian is obtained by replacing all other spins by the average m: $H_{\text{eff}} = -J\sigma_1\sigma_2 - Jm\sigma_1 - Jm\sigma_2 - h\sigma_1 - h\sigma_2 + \text{const}$. The partition function (drop the constant term) is

$$Z = \sum_{\sigma_1,\sigma_2} e^{-\beta H_{eff}} = e^{\beta[2(Jm+h)+J]} + e^{\beta[-2(Jm+h)+J]} + 2e^{-\beta J}$$

$$m = \langle\sigma_1\rangle = \langle\sigma_2\rangle = \frac{1}{Z}\sum_{\sigma_1,\sigma_2}\sigma_1 e^{-\beta H_{eff}} = \frac{1}{Z}\left(e^{\beta[2(Jm+h)+J]} - e^{\beta[-2(Jm+h)+J]}\right)$$

$$= \frac{\sinh[2\beta(mJ+h)]}{\cosh[2\beta(mJ+h)] + e^{-2\beta J}}$$

b) Yes, there is a phase transition at nonzero T_c. Because if $\beta=1/(k_B T)$ is large (low temperature T), the equation becomes approximately the same as the standard one discussed in class. One can draw two curves of the right and left side to see if there is an intersection point for m or not.

- The end -

PC5202 Advanced Statistical Mechanics, Midterm Test, 6 March 2010

(closed book, 90 min)

1. Consider two bodies initially isolated and in respective equilibrium at temperatures T_1 and T_2 (with $T_1 \approx T_2$). A thermal contact allows the exchange of energy through a diathermal wall. Using Callen's postulates about the entropy, show that heat flows from hot body to cold body.

2. Consider a general Hamiltonian $H = \sum_j \frac{p_j^2}{2m_j} + V$ with s-degrees of freedom. Show that in the canonical ensemble, equipartition theorem is valid for a classical system, i.e., $<(1/2)\, m_j v_j^2> = 1/2\, k_B T$. v is j-th component of the velocity.

3. Consider a particle in a one-dimensional box confined in an infinite potential well, $V(x) = 0$ if $0 < x < L$, and $V(x) = +\infty$ otherwise, such that the quantum-mechanical wavefunction is give by $\psi = A \sin(n \pi x/L)$, $0 < x < L$, $n = 1, 2, 3, ..$
    a. give the eigenenergy of the particle of mass m.
    b. Consider a collection of boson particles in such a potential well. Calculate the grand partition function of the system (expressed as a sum over n).
    c. Derive a system of equations which give the force of the particle acting on the wall as function of temperature and fixed total particle number N.

4. The Helmhotz free energy of the van der Waals theory for fluid is

$$F = -a\frac{N^2}{V} - Nk_B T \ln(V - bN) + \frac{3}{2} Nk_B T \ln(T/c) + \text{const} \ .$$

The constants a, b, c, const are independent of both volume V and temperature T. Calculate the heat capacity at constant pressure, C_p. Give the asymptotic value near critical point at a fixed pressure P_c.

PC5202 Advanced Statistical Mechanics

Midterm Test, Saturday, 7 March 2009

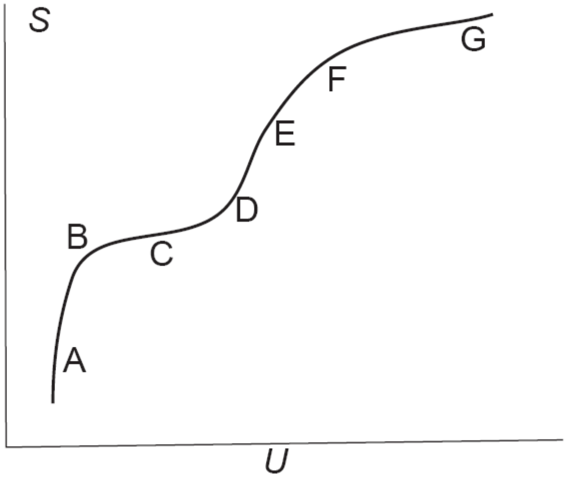
1. Answer briefly with one sentence or one formula
   a. Give one definition of the (electro-) chemical potential μ.
   b. Give the Gibbs-Duhem relation (without derivation).
   c. Which one is NOT correct: the ensemble average at time t for a (implicitly) time-dependent quantity A can be calculated from (i) $\int d\Gamma A(\Gamma,t)\rho(\Gamma)$, (ii) $\int d\Gamma A(\Gamma,t)\rho(\Gamma,t)$, (iii) $\int d\Gamma A(\Gamma)\rho(\Gamma,t)$.
   d. What is Boltzmann's principle?
   e. Give the equation for the ergodic hypothesis.
   f. Consider the microcanonical distribution in the limit when the shell thickness Δ goes to 0. What is the probability of finding the system in a small area of $d\sigma$ on the energy hypersurface (of $2N-1$ dimensions)?
   g. What is the heat capacity of a heat bath?
   h. Give the formula for the thermal wavelength.

a. $\mu = \left(\frac{\partial U}{\partial N}\right)_{S,V} = \left(\frac{\partial F}{\partial N}\right)_{T,V} = \frac{G}{N}$ *b.* $SdT - Vdp + Nd\mu = 0$ *c. (ii) is not correct d.* $S = k_B \ln \Omega$

e. time average equals ensemble average, $\langle A\rangle = \frac{1}{t}\int_0^t A(t')dt' = \int A(\Gamma)\rho(\Gamma)d\Gamma$ *f. the probability in an area of* $d\sigma$ *is proportional to* $d\sigma/|\nabla H|$ *g. The heat capacity of a heat-bath is infinite,* *h.* $\lambda = \frac{h}{\sqrt{2\pi m k_B T}}$.

2. (a) Derive the equation $\frac{\partial^2 S}{\partial U^2} = -\frac{1}{CT^2}$, where S is entropy, T is temperature, and C is heat capacity; the number of particle N and volume V are fixed.

(b) The figure shown below for entropy versus internal energy U is not correct, where at point C and E we have $\frac{\partial^2 S}{\partial U^2} = 0$, $\frac{\partial^2 S}{\partial U^2} > 0$ between C and E, and at point B and F, the slopes are equal. (i) Modify the curve (in the spirit similar to Maxwell's construction) so that the figure becomes physical acceptable. (ii) What happens when system move from point A to point G?



a. Since $\partial S/\partial U = 1/T$, take one more derivative with respect to U and use the definition for heat capacity, C = dU/dT, we obtain the result. b. (i) connect with a straight line from B to F. See Callen, page 205. (ii) There is a (first-order) phase transition from B to F. (draw a curve U vs T will show clearly). On the straight line BF, there is a two-phase coexistence, A to B, or F to G is a single phase.

3. Consider N independent, distinguishable one-dimensional harmonic oscillators with the classical Hamiltonian $H = \sum_{i=1}^{N}\left(\frac{p_i^2}{2m} + \frac{1}{2}k x_i^2\right)$, where m is the mass and k is the spring constant. Note that the volume of a unit hypersphere of n dimensions is $\frac{\pi^{n/2}}{(n/2)!}$.

   a. Compute the entropy in microcanonical ensemble in the thermodynamic limit.
   b. Is the result above the same as that calculated in canonical ensemble (answer yes or no, no actual calculation is required)?

$S = k_B \ln \Gamma$, where

$$
\begin{aligned}
\Gamma &= \frac{1}{h^N}\int_{H<U} dp_1 dp_2 \cdots dp_N dx_1 dx_2 \cdots dx_N \\
&= \frac{1}{h^N}\left(\frac{m}{k}\right)^{N/2} \int_{y_1^2+y_2^2+\cdots y_{2N}^2<2U} dy_1 dy_2 \cdots dy_{2N} \\
&= \left(\frac{2\pi U}{h}\sqrt{\frac{m}{k}}\right)^N \frac{1}{N!}
\end{aligned}
$$

we have used transformations, $p_1 = \sqrt{m}y_1,\ p_2 = \sqrt{m}y_2, \cdots, p_N = \sqrt{m}y_N,$ *and*

$x_1 = \frac{1}{\sqrt{k}}y_{N+1},\ x_2 = \frac{1}{\sqrt{k}}y_{N+2}, \cdots, x_N = \frac{1}{\sqrt{k}}y_{2N}$. *Using the Sterling formula, ln N! = N ln N – N, taking the large limit, we obtain* $S = Nk_B \ln\left(\frac{Ue}{\hbar\omega N}\right), \hbar = h/(2\pi), \omega = \sqrt{\frac{k}{m}}$.

b. yes. (the result was derived in class).

-- The End --

PC5202 midterm test, 8 March 2008

(25 marks for each question)

1. Answer briefly:

- (a) What is the precise definition of Kelvin scale for temperature?
- (b) Consequence of the Euler equation for internal energy U (derivation not needed);
- (c) Explain the meaning of equation of motion, $\dot{A} = (A, H)$, in classical and quantum terms;
- (d) What is ergodic hypothesis?
- (e) What is a Maxwell construction.

2. (a) Fixing the number of particles N and volume V as constants, show that

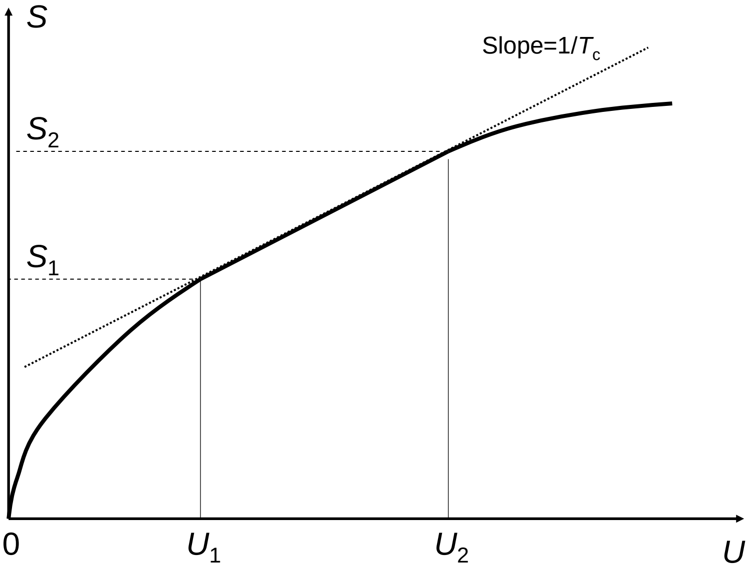
$$\frac{\partial^2 S}{\partial U^2} = -\frac{1}{CT^2},$$

where T is temperature and C is heat capacity.

(b) For a thermodynamic system with the fundamental relation shown schematically in the figure, draw a figure of internal energy U on the vertical axis and temperature T on the horizontal axis. In the figure below, the energy U and entropy S start from 0 and the entropy increases with an infinite slope and smoothly goes to the point (U_1,S_1), it is then connected by a straight line segment to the point (U_2,S_2), followed by another smooth curve with decreasing slope.

(c) What is the significance of T_c , U_1 and U_2? what is the heat capacity at T_c?

(d) What is the heat Q absorbed by the system if the temperature is increased from slightly below T_c to slightly above T_c?



3. The vibration of certain type of molecules is described by a Hamiltonian of coupled harmonic oscillators:

$$H = \frac{1}{2}\left(p_x^2 + p_y^2\right) + \frac{1}{2}\left(x^2 + y^2 + xy\right),$$

Compute (a) the canonical partition function Z, (b) the Helmholtz free energy F. The following Gaussian integral may be helpful:

$$\int_{-\infty}^{+\infty} e^{-\frac{x^2}{2}} dx = \sqrt{2\pi}\ .$$

4. Consider a system of N monomers in one dimension. The monomers are strongly attractive, and when they meet and become nearest neighbor, an energy of $(-\varepsilon)$ is gained. Neglecting kinetic energy, the N monomers form a polymer chain with energy $-(N-1)\varepsilon$. We also assume that each monomer has a chemical potential μ, and the polymer chain stays only in its ground state. The monomers are not conserved and are supplied from the gas phase. (a) Compute the grand partition function Ω of the system, (b) give the grand potential Ψ, (c) compute the average number of monomers of a chain $\langle N \rangle$.

--- the End ---

PC5202 Advanced Statistical Mechanics

Midterm test (close book), 3 March 2007

1. (a) In Callen's Postulate I of thermodynamics, an equilibrium state for a simple homogeneous and anisotropic system is uniquely determined by three macroscopic parameters. Name the three parameters.
   (b) State the Postulate II.

   (c) A set of four properties (monotonicity, extensivity, concavity, and third law of thermodynamics) exists for entropy which can be written as mathematical expressions or conditions. Give these four equations.

2. The entropy S of a hypothetical system as a function of internal energy U has the following form:

$$S = \begin{cases} a\sqrt{UN}, & U < U_1 \\ bU + c, & U_1 \le U \le U_2 \\ a'\sqrt{UN} + dU, & U_2 < U \end{cases}$$

   where N is the number of particles; a, a', b, c, and d are some positive constants. It turns out that these constants can not be chosen arbitrarily but is uniquely determined by a', U_1 and U_2.

   (a) Draw a qualitatively correct plot of S as a function of U.
   (b) Compute temperature T as a function of U. Draw a qualitatively correct plot of U as a function of temperature T.
   (c) Write down a set of four equations determining the parameters a, b, c, and d. Solution is not required.
   (d) The straight line segment in S vs. U represents a first-order phase transition. Determine the latent heat of the phase transition.
   (e) The straight line segment also represents a coexistence of two phases. Explain briefly why?

3. Consider a one-dimensional classical harmonic oscillator with the Hamiltonian

$$H = \frac{p^2}{2m} + \frac{1}{2} m\omega^2 q^2 .$$

   (a) Compute the partition function Z of canonical ensemble, the Helmholtz free energy F, the entropy S, and the internal energy U as functions of temperature T.

   (b) Compute in micro-canonical ensemble the number of microstates using two different definitions for the number of microstates and entropy:

$$\Gamma(U) = \int_{H<U} dpdq, \qquad S = k_B \ln \Gamma(U)$$

$$\Omega(U) = \int_{U<H<U+\Delta} dpdq, \qquad S' = k_B \ln \Omega(U)$$

   Again give results for F, S, and U.

   (c) Explain why the two definitions give different results?

   (d) Apparently, the ensemble equivalence is violated here. Are you able to resolve the contradictions in (a) and (b) where the different ensembles and different definitions of entropy give different results [Hint: consider a set of N independent oscillators].

4. (a) State the three conditions that a liquid phase and its gaseous phase can be in coexistence.

   (b) Using the maximum entropy principle, derive the conditions stated in (a) for equilibrium between the two phases.

   (c) Using one of the conditions stated in (a), give a brief derivation (justification) of the Maxwell construction of the isotherms of the van der Waals equation (i.e., cut the P-V curve in such a way so that the areas above and below a line are equal).