NATIONAL UNIVERSITY OF SINGAPORE

PC5202 ADVANCED STATISTICAL MECHANICS

(Semester II: AY 2015-16)

Time Allowed: 2 Hours

INSTRUCTIONS TO STUDENTS

1. Please write your student number only. Do not write your name.

2. This assessment paper contains 4 questions and comprises 2 printed pages.

3. Students are required to answer ALL the questions.

4. Students should write the answers for each question on a new page.

5. This is a CLOSED BOOK examination.

6. Each question carries 25 marks.

1. (a) Consider the triple point of water where three phases coexist – liquid water, water vapor, and ice. Give the Gibbs-Duhem relation and use it to argue that at the triple point, it has unique values of temperature T and pressure p.
(b) State the concavity condition for entropy S as a function of energy E (ignore possible dependence of the entropy on other variables). Use the concavity condition to show that heat capacity at constant volume, C_v, must be non-negative.
(c) Continue from (b), draw a schematic plot of S vs E to show a first order phase transition situation when temperature changes.

(a) *The Gibbs-Duhem relation can be derived from the Euler equation and the fundamental thermodynamic equation. The derivations are not necessary; the required equation is S dT − V dP + N dμ = 0. This equation applies to the homogeneous phases of liquid, gas, and solid, respectively. At the triple point, since the three phases coexist, in order to be thermodynamically stable, the three phases must have the same T, P, and μ. Since we have three equations, one for each phase, and S, V, N are different in each phase, the only solutions to these equations are dT = dP = dμ = 0, i.e., the temperature and pressure are fixed. Alternatively, one can argue with the Gibbs phase rule.*

(b) *Concavity: $\lambda S(E_1) + (1 - \lambda)S(E_2) \le S(\lambda E_1 + (1 - \lambda)E_2)$, where $0 < \lambda < 1$. If S is smooth, this is equivalent to $\frac{\partial^2 S}{\partial E^2} < 0$. C=δQ/δT = T dS/dT = dE/dT (fixing volume). So $\frac{\partial^2 S}{\partial E^2} = \frac{\partial}{\partial E}\frac{1}{T} = -\frac{1}{T^2 C} < 0$. This implies C > 0. Note that only in constant volume, C = dE/dT. We need to relate C to the second derivative of S.*

(c) *S vs E need to be concave. A straight line segment in an otherwise parabolic-like curve indicate a first order phase transition. At the transition, temperature stays constant with a jump in energy.*

2. Consider the benzene molecule simplified as 6 point masses, each with mass m located on a circle of radius R, with a potential energy between two neighboring pair of points i and $i+1$ as $\left(\frac{k}{2}\right)(\theta_i - \theta_{i+1})^2$, where θ_i is a small deviation from equilibrium of equally spaced angles of $\frac{\pi}{3}$, and k is coupling constant.
(a) Give the Lagrangian L and Hamiltonian H of the system.
(b) Compute the eigenmodes of the system, thus determine the normal mode coordinates.
(c) Compute the (classical) partition function Z of the system in the canonical ensemble.

(a) *Lagrangian $L = \frac{1}{2}mR^2 \sum_{i=1}^{6} \dot{\theta}_i^2 - \frac{k}{2}\sum_{i=1}^{6}(\theta_i - \theta_{i+1})^2 = K - V$, Hamiltonian $H = \frac{1}{2mR^2}\sum_{i=1}^{6} p_{\theta_i}^2 + \frac{k}{2}\sum_{i=1}^{6}(\theta_i - \theta_{i+1})^2 = K + V$, where $\theta_7 = \theta_1$. $p_{\theta_i} = mR^2 \dot{\theta}_i$.*

(b) *The equation of motion can be written as $\ddot{\theta}_i + \frac{k}{mR^2}(2\theta_i - \theta_{i-1} - \theta_{i+1}) = 0$. To solve this equation, we try wave-like solution: $\theta_j = A\lambda^j e^{-i\omega t}$. Putting into the equation, we find the dispersion relation, $\omega^2 = \frac{k}{mR^2}(2 - \lambda - 1/\lambda)$. We can fix λ by periodic boundary condition, i.e., $\theta_7 = \theta_1$, or $\lambda^6 = 1$, this implies that $\lambda = e^{\frac{i2\pi k}{6}}$, for k = 0, 1, 2, ... 5, given the 6 normal*

   (c) *We compute the contribution of each mode separately, then $Z = \prod_{k=0}^{5} Z_k$. However, there are two problems here. First, the mode with k=0 has 0 as the frequency; this corresponds to pure translation (in fact rotation), not vibration. This term has to be treated separately. Second the angle θ is in a compact domain of $[0,2\pi]$. If we integrate from $-\infty$ to $+\infty$ it is not quite correct. But I have no better solution to offer, as the expression in the bounded domain does not have closed form. Within small oscillation approximation, we do the usual Gaussian integrals, and results are standard, i.e., $Z_k = \frac{k_B T}{\hbar \omega_k}$.*

3. Consider a magnetic system near critical point. The equation of state has the following form $H \approx a\, M(t + bM^2)^\theta$, where H is magnetic field, M is magnetization, $t = (T - T_c)/T_c$, $1 < \theta < 2$, and $a, b > 0$.
   (a) Find the critical exponents β, γ, and δ, where β is the order parameter (magnetization) exponent, and γ is associated with the magnetic susceptibility, and δ determines the isothermal curve near the critical point.
   (b) Show that the exponents satisfy $\gamma = \beta(\delta - 1)$.

We need the basic definitions of critical exponents, $M \sim (-t)^\beta$, $\chi \sim t^{-\gamma}$, $H \sim M^\delta$. To get β, we set H=0, and solve for M in terms of t, we find $M=(-t/b)^{1/2}$, so $\beta = 1/2$. Take derivative with respect to H for fixed t on both sides of the equation of states, consider the high temperature side so M=0, we found $1 = a\chi t^\theta$, so $\gamma = \theta$. Lastly, to find δ, we set t=0 in the equation of states, we identify $\delta = 1 + 2\theta$. Part (b) is easily verified.

Note that this problem has nothing to do with Landau theory or mean-field free energy. The important point is that β and γ are defined at H=0, and δ is defined at t=0.

4. Consider a diatomic molecule moving in a one-dimensional space immersed in an environment modelled as white noises. The equations of motion of the diatomic molecule are given as
   $m\frac{d^2 x_1}{dt^2} = -k(x_1 - x_2) - \gamma \frac{dx_1}{dt} - R_1(t)$, $m\frac{d^2 x_2}{dt^2} = +k(x_1 - x_2) - \gamma \frac{dx_2}{dt} - R_2(t)$, where $R_1(t)$ and $R_2(t)$ are independent noises, $\langle R_i(t) R_j(t') \rangle = C\delta_{ij}\delta(t - t')$.
   (a) Determine the rate of change of the total energy of the molecule, $E(t) = \frac{m}{2}\left(\left(\frac{dx_1}{dt}\right)^2 + \left(\frac{dx_2}{dt}\right)^2\right) + \frac{k}{2}(x_1 - x_2)^2$, with time. Compute the long-time average of $\frac{dE(t)}{dt}$.
   (b) Consider the overly-damped case, i.e., γ is much larger than the mass m so that we can set $m = 0$ in the equations of motion. Solve formally $x_1(t)$ and $x_2(t)$, in terms of random noises $R_1(t)$ and $R_2(t)$.
   (c) For the overly-damped case in part (b), determine the associated Fokker-Planck equation for the probability distribution of the positions $\langle P(x_1, x_2) \rangle$.

(a) We take the derivation and use the equations of motion, find: $\frac{dE}{dt} = -\gamma \dot{x}_1^2 - \gamma \dot{x}_2^2 - \dot{x}_1 R_1 -$ $\dot{x}_2 R_2$. The average is $\langle \frac{dE}{dt} \rangle = 0$. This is because the energy is bounded. Or the dissipation energy proportional to the velocity squared gets cancelled by the work done by the random force. Since we have thermal noise, the energy of the particles does not go to zero, but stay at a constant. The rate of change is 0. In particular, $\langle \dot{x}_1 R_1 \rangle$ is not 0, as x_1 is not independent of R_1 and average cannot be factored.

(b) The equations because particularly simple if we take the sum $X = x_1 + x_2$, and difference $x = x_1$-x_2. They are $\gamma \dot{X} = R_1 + R_2$, and $\gamma \dot{x} = -2kx + R_1 - R_2$. Although X and x are decoupled and look independent, but they are not, as they depend on the same random noises. The solutions are $X(t) = X(0) + \frac{1}{\gamma} \int_0^t (R_1(s) + R_2(s)) ds$, and $x(t) = x(0) e^{-2(\frac{k}{\gamma})t} +$ $\frac{1}{\gamma} \int_0^t (R_1(s) - R_2(s)) e^{-2(\frac{k}{\gamma})(t-s)} ds$. We can rewrite back in $x_1 = (X+x)/2$, and $x_2 = (X-x)/2$.

(c) Since equation is simpler in X and x, we can work in P(X,x). Skip the detail derivation, the final equation is $\frac{\partial P}{\partial t} = \frac{\partial}{\partial x} \left(\frac{2kx}{\gamma} P \right) + \frac{C}{\gamma^2} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial X^2} \right) P$.

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