NATIONAL UNIVERSITY OF SINGAPORE

PC5202 ADVANCED STATISTICAL MECHANICS

(Semester II: AY 2010-11)

Time Allowed: 2 Hours

INSTRUCTIONS TO CANDIDATES

1. This examination paper contains 5 questions and comprises 3 printed pages.
2. Answer all the questions.
3. Answers to the questions are to be written in the answer books.
4. This is an OPEN BOOK examination.
5. Each question carries 20 marks.

1. Answer concisely the following questions:
   a. Define the Kelvin scale.
   b. Is the Helmholtz free energy F as a function of temperature T convex or concave?
   c. Give the argument leading to the Maxwell construction (of the van der Waals equation for gas).
   d. Explain the concept of "universality" in critical phenomena.

   a. *The temperature absolute 0 is fixed by nature (entropy is then 0); the triple point of water is defined to be 273.16 K. The rest of the temperature can be uniquely determined by the 2nd law of thermodynamics (with Carnot cycle).*
   b. *F is concave in T, because S=- $\partial F/\partial T$, $\partial S/\partial T$ = - $\partial^2 F/\partial T^2$ > 0 (entropy is an increasing function of T).*
   c. *The equal area law of Maxwell is obtained by the requirement that chemical potentials μ of the gas phase and liquid phase are equal, assuming that the van der Waals equation is also valid in the unstable region. We need the Gibbs-Guhem equation to show this.*
   d. *The critical exponents, α, β, γ, etc., do not depend on the details of the systems but only depend on the space dimensionality d, dimensionality of the order parameter n, and the range of interactions. This fact can be explained by the renormalization group theory of the second order phase transitions.*

2. Consider a collection of N (one-dimensional) harmonic oscillators all with the same intrinsic frequency ω_0 treated with classical "microcanonical" ensemble. The Hamiltonian is

$$H = \sum_{j=1}^{N} \frac{1}{2}\left(p_j^2 + \omega_0^2 q_j^2\right).$$

   a. Using the Boltzmann's principle, determine the entropy $S(U,N)$.
   b. Calculate the heat capacity based on S.
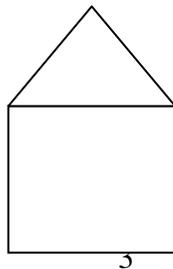
a. Entropy $S = k_B \ln \Omega$ (by Boltzmann's principle)

$$\Omega = \frac{1}{h^N} \int\limits_{H<U} dp_1 dp_2 \cdots dp_N dq_1 dq_2 \cdots dq_N$$

$$= \frac{1}{(h\omega_0)^N} \int\limits_{\sum_{j=1}^{N}(p_j^2+x_j^2)<2U} dp_1 dp_2 \cdots dp_N dx_1 dx_2 \cdots dx_N$$

$$= \left(\frac{2\pi U}{h\omega_0}\right)^N \frac{1}{N!}$$

We have introduced new variable $x_j = \omega_0\, q_j$, and used the formula for the hyper-volume of 2N-dimensional sphere of radius $\sqrt{2U}$.

b. $T=\partial U/\partial S = U/(k_B N)$, or $U = N\,k_B\,T$. Heat capacity is $C = \partial U/\partial T = k_B N$ (same as that given by equal partition theorem).

3. Consider the ferromagnetic Ising model with coupling constant J and nearest neighbor interaction (without magnetic field) defined on a finite network of five sites as shown below.
   a. Determine the high-temperature expansion of the partition function Z in variable $x = \tanh(K)$, $K = \beta J = J/(k_B T)$.
   b. Draw a dual lattice to the five-site system, and give the Hamiltonian associated with the dual lattice so that duality relation holds.
   c. Give the low-temperature expansion of the partition function Z on the dual lattice.

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a. $Z = 2^5 cosh^6(K)(1 + x^3 + x^4 + x^5)$.

b. Dual lattice has 3 sites, call it A for the center of square, B for the center triangle and C for a site outside, then $H^* = - J^*(\sigma_A\sigma_B + 2\,\sigma_B\sigma_C + 3\sigma_A\sigma_C)$.

c. $Z^* = 2\,e^{6K^*}(1 + e^{-6K^*} + e^{-8K^*} + e^{-10K^*})$.

4. Consider a system where the velocity $v(t)$ is governed by some stochastic dynamics similar to the Langevin equation (actual form is not given). We assume that $v(t)$ is a smooth, bounded function of time t, and the velocity correlation $\langle v(t)v(t')\rangle$ can be calculated. The position displacement variable will be called $x(t)$ at time t, and assuming $x(0) = 0$.

   a. Determine the approximate time dependence of $\langle x(t)^2\rangle$ when time t is small.

   b. Work out the expression of $\langle x(t)^2\rangle$ in terms of velocity correlation when t is large, assuming the velocity correlation is time translationally invariant.

   a. *Since $v(t)$ is a smooth function, and $x(t) = \int_0^t v(s)ds$, we can make a Taylor expansion of $x(t)$ in time t, $x(t) = x(0) + v(0)t + O(t^2)$. $x(0) = 0$. We obtain $<x(t)^2> \approx <v(0)^2>t^2$.*

   b. *$<x(t)^2> = <\int_0^t v(t')dt' \int_0^t v(t'')dt''>$. Using translational invariance, $<v(t)v(t'')> = <v(0)v(t'-t'')>$. Changing the integration variables from t', t'', to t' and s=t''-t', and considering carefully the new limits, we obtain*
   $<x(t)^2> =2 \int_0^t (t-s) < v(0)v(s) > ds$. *In the large time limit, it is*
   $<x(t)^2> =2t \int_0^\infty < v(0)v(s) > ds$.

5. Consider the Boltzmann's *H*-theorem. The time-dependent "Boltzmann entropy" is defined by the equation

$$S_B(t) = -k_B \int f \ln f\, d^3\mathbf{r}\,d^3\mathbf{p}\ ,$$

where $f = f(\mathbf{r},\mathbf{p},t)$ is the distribution function of molecules having position $\mathbf{r}$ and momentum $\mathbf{p}$ at time t. The function f satisfies the Boltzmann equation:

$$\frac{\partial f}{\partial t} + \frac{\mathbf{p}}{m}\cdot\nabla_{\mathbf{r}}f + \mathbf{F}\cdot\nabla_{\mathbf{p}}f = \left(\frac{\partial f}{\partial t}\right)_{coll}.$$

a. Show that if the molecules do not collide, i.e., if $\left(\dfrac{\partial f}{\partial t}\right)_{coll} = 0$, then the entropy S_B does not change with time.

b. Explain qualitatively (i.e., no equations) why entropy S_B always increases if there are molecular collisions.

a. *Exchange the order of differentiation of time with the phase space integration, and using the Boltzmann equation when the collision term is zero, we have ($d\mathbf{r} = dxdydz$, $d\mathbf{p} = dp_x\,dp_y\,dp_z$)*

$$\frac{dS_B}{dt} = -k_B \int \frac{\partial}{\partial t}\left(f \ln f\right) d\mathbf{r}d\mathbf{p}$$

$$= -k_B \int \left(1 + \ln f\right)\frac{\partial f}{\partial t} d\mathbf{r}d\mathbf{p}$$

$$= -k_B \int \left[-\frac{\mathbf{p}}{m}\cdot\nabla_{\mathbf{r}} f - \mathbf{F}\cdot\nabla_{\mathbf{p}} f\right]\left(1 + \ln f\right) d\mathbf{r}d\mathbf{p}$$

Note that because $\mathbf{p}$ and $\mathbf{r}$ are independent variables, we can rewrite the expression as an integral of a divergence. Using Gaussian theorem, divergence of a volume integral can be written as integral over the surface. For example, focus on the partial x term, we have

$$\int \frac{\partial}{\partial x}\left(\frac{p_x f}{m}\right)\left(1 + \ln f\right) d\mathbf{r}d\mathbf{p}$$

$$= \int \frac{\partial}{\partial x}\left(\frac{p_x}{m} f \ln f\right) d\mathbf{r}d\mathbf{p}$$

$$= \int \frac{p_x}{m} f \ln f \Big|_{-\infty}^{+\infty} dydzd\mathbf{p} = 0$$

Similarly for y and z components, and p_x, p_y, p_z. We have assumed that outside the box, or when momentum is very large, $f = 0$, and F is a function of $\mathbf{r}$ only.

b. *First, the Boltzmann equation is not time-reversible symmetric due to the assumption of molecular chaos of the collision term. Second, collision causes a redistribution in the space of $\mathbf{r}$ and $\mathbf{p}$. So the distribution is more and more uniform in space (thus larger entropy) and more close to Maxwell distribution for the velocity. Third, the function f is a reduced description of the system, not a full description – information is "lost" as time goes on. Thus, under collision, S_b increases as shown quantitatively by the Boltzmann H-theorem.*

-- End of Paper --   [WJS]