NATIONAL UNIVERSITY OF SINGAPORE

PC5202 Advanced Statistical Mechanics

(Semester II: AY 2006-07, 23 April 07)

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 TRUE or FALSE for the following statements:

(a) Classical mechanics when combined with statistical-mechanical principles is consistent with first, second, and third laws of thermodynamics.
(b) Mean-field critical exponents are correct when spatial dimensions $d \geq 4$.
(c) Thermodynamic limit means that temperature T approaches 0.
(d) Different ensembles are not equivalent at the point of phase transitions.
(e) The Fermi-Dirac distribution function, $\{\exp[\beta(\varepsilon-\mu)]+1\}^{-1}$, is valid even if the fermions have interactions.
(f) The triple point of water has a unique temperature T and pressure P.
(g) The Maxwell construction is not needed if the P-V curve is calculated exactly (for a macroscopically large system).
(h) In Langevin equation, the frictional force and random force must be related.
(i) Boltzmann equation is time-reversal symmetric.
(j) Duality can be used to determine the critical temperature T_c of a triangular lattice Ising model.

(a) false (e.g., entropy goes to negative infinity, inconsistent with 3rd law), (b) true, (c) false (system size approaches infinity), (d) true, (e) false, (f) true, (g) true (van der Waals loop is an artifact of approximation), (h) true (related by fluctuation-dissipation theorem), (i) false (molecular chaos approximation breaks the symmetry), (j) false (triangular lattice is not self-dual).

2. Consider the adsorption of atoms on a crystal surface in a column-like fashion such that if the site i adsorbed n_i atoms the energy associated with the configuration is εn_i, $n_i = 0, 1, 2, 3, \ldots$, independent of the number of atoms adsorbed on other sites. There are all together N such adsorbing sites. Using grand-canonical ensemble, compute

(a) The grand-canonical partition function Ξ;
(b) The entropy S;
(c) The average number of atoms adsorbed,

as functions of temperature T and chemical potential μ.

(a) Let $\beta = 1/(k_B T)$, the grand partition function is (discrete energy levels)

$$\Xi = \sum_{n_1, n_2, \cdots, n_N} e^{-\beta\left(\sum_{i=1}^{N}(\varepsilon n_i - \mu n_i)\right)} = \sum_{n_1} e^{-\beta(\varepsilon-\mu)n_1)} \sum_{n_2} e^{-\beta(\varepsilon-\mu)n_2)} \cdots$$

$$= \left[\sum_{n=0}^{\infty} e^{-\beta(\varepsilon-\mu)n)}\right]^N = \left[\frac{1}{1-e^{-\beta(\varepsilon-\mu)}}\right]^N$$

(b) Use the relation $\Psi = -k_B T \ln \Xi$ and $d\Psi = -SdT - pdV - \langle N \rangle d\mu$, we get entropy

$$S = \frac{\partial}{\partial T}\left(k_B T \ln \Xi\right) = -Nk_B \ln(1-e^{-\beta(\varepsilon-\mu)}) - N\frac{\varepsilon-\mu}{T}\frac{1}{e^{\beta(\varepsilon-\mu)}-1}.$$

(c) similarly, the average numbers of particles adsorbed is

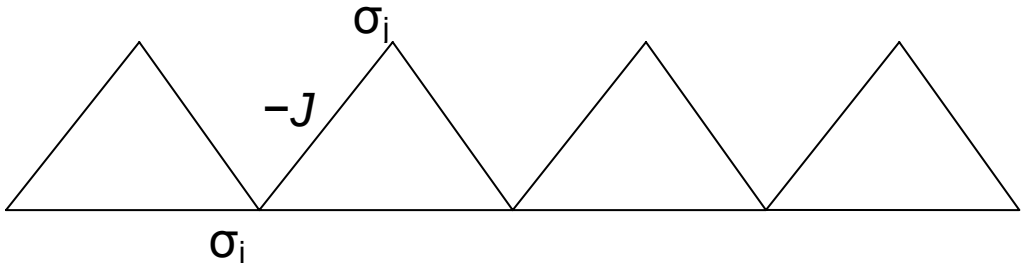
$$\langle N\rangle = \frac{\partial k_B T \ln \Xi}{\partial \mu} = \frac{\partial}{\partial \mu}\left[-Nk_B T \ln\left(1-e^{-\beta(\varepsilon-\mu)}\right)\right]$$

$$= N\frac{1}{e^{\beta(\varepsilon-\mu)}-1}.$$

3. Consider a quasi-one-dimensional chain of the Ising model shown below. The Ising spins $\sigma_i=\pm 1$ are defined on the vertices of the triangles. Each line signifies a term of the form $-J\sigma_i\sigma_j$.

(a) Express the canonical partition function *Z* in terms of a transfer matrix *P*, give the matrix elements.

(b) Compute the eigenvalues λ of the transfer matrix, and give the free energy *F* in the thermodynamic limit.



(a) Consider one triangle, label the bottom two spins as 1 and 2, the top one as 3, then exponential factor is $e^{K(\sigma_1\sigma_2+\sigma_1\sigma_3+\sigma_2\sigma_3)}$*, where K =J/(k_BT). The spin 3 appears only in this factor which can be summed over, getting* $P(\sigma_1;\sigma_2) = e^{K\sigma_1\sigma_2}\,2\cosh[K(\sigma_1+\sigma_2)]$. *Thus the transfer matrix is*

$$P = \begin{bmatrix} e^{3K}+e^{-K} & 2e^{-K} \\ 2e^{-K} & e^{3K}+e^{-K} \end{bmatrix}.$$

Partition function $Z = Tr(P^N)$.

(b) The eigenvalues satisfy $|P-\lambda I|=0$, *which gives* $\lambda_1 = e^{3K}+3e^{-K}$, $\lambda_2 = e^{3K}-e^{-K}$. *The free energy is* $F = -NkT\ln\lambda_1$.

Alternatively, one can also use two spins as matrix indices. The bottom two spins are called 1, and 2, the top two with a prime. We get

$$P(\sigma_1\sigma_1';\sigma_2\sigma_2') = e^{K(\frac{1}{2}\sigma_1\sigma_1'+\frac{1}{2}\sigma_2\sigma_2'+\sigma_1\sigma_2+\sigma_1'\sigma_2)}$$
$$= \begin{bmatrix} e^{3K} & e^{2K} & e^{-2K} & e^{-K} \\ 1 & e^{-K} & e^{-K} & 1 \\ 1 & e^{-K} & e^{-K} & 1 \\ e^{-K} & e^{-2K} & e^{2K} & e^{3K} \end{bmatrix} .$$

Two of the eigenvalues are zero, the rest is identical as in (b) above. A third possibility is to include the complete triangle as a repeating unit and not sharing the sides:

$$P(\sigma_1\sigma_1';\sigma_2\sigma_2') = e^{K(\sigma_1\sigma_1'+\sigma_1\sigma_2+\sigma_1'\sigma_2)}$$
$$= \begin{bmatrix} e^{3K} & e^{3K} & e^{-K} & e^{-K} \\ e^{-K} & e^{-K} & e^{-K} & e^{-K} \\ e^{-K} & e^{-K} & e^{-K} & e^{-K} \\ e^{-K} & e^{-K} & e^{3K} & e^{3K} \end{bmatrix}.$$

4. Consider the Landau theory for ferromagnetic phase transitions. The Gibbs free energy as a function of temperature T and total magnetization M is assumed to be

$$G = (T - T_c)aM^2 + bM^4,$$

where a, b, and T_c are some positive constants.

(a) Give the corresponding expression for the Helmholtz free energy F as a function of temperature T and magnetic field h.

(b) Let $T = T_c$, show that $F(T_c, h) \propto h^{4/3}$.

(c) At $h = 0$, $T < T_c$, show that $F(T, 0) \propto (T - T_c)^2$.

(d) Assuming a scaling form for the Helmholtz free energy

$$F(t,h) = b^{-4}F(b^Y t, b^X h), \quad t = T - T_c,$$

and using the information obtained in (b) and (c), determine the scaling exponents X and Y.

(a) F(T,h) = G − hM where $h = \partial G / \partial M = (T - T_c)2aM + 4bM^3$. *Formally, F will be a function of T and h only, if we solve the above equation for M in terms of h.*

(b) at $T = T_c$, $h = 4bM^3$, *so* $F = bM^4 - hM \propto h^{4/3}$.

(c) at h = 0, we have $(T - T_c)a + 2bM^2 = 0$, *so* $M \propto (T - T_c)^{1/2}$.

$F = G = (T - T_c)aM^2 + bM^4 \propto (T - T_c)^2$.

(d) set t = 0, $b^X h = 1$, *we have* $F(0,h) = h^{4/X}F(0,1)$, *compare with (b) 4/3 = 4/X, so X = 3. Similarly,* $F(t,0) = t^{4/Y}F(1,0)$, *compare with (c) 4/Y = 2, so Y = 2.*

5. Consider the standard Langevin equation in one dimension

$$m\frac{dv}{dt} = -m\gamma v + R(t),$$
$$\langle R(t)\rangle = 0,$$
$$\langle R(t)R(t')\rangle = C\delta(t'-t).$$

Energy dissipated or work done in unit time is force times velocity.

(a) Applying the equipartition theorem, express the average power dissipation P due to the frictional force in terms of the temperature T.

(b) Show that the average energy input per unit time due to random noise is $I = C/(2m)$.

(c) As a consequence of the Langevin equation, show that $P = I$.

(a) $P = \langle m\gamma v \cdot v\rangle = \gamma\langle mv^2\rangle = \gamma k_B T$.

(b) Using the solution for Langevin equation $v(t) = v(0)e^{-\gamma t} + \int_0^t \frac{R(\tau)}{m} e^{-\gamma(t-\tau)} d\tau$,

we get $I = \langle R(t)v(t)\rangle = \int_0^t \langle R(t)R(\tau)\rangle \frac{1}{m} e^{-\gamma(t-\tau)} d\tau = \frac{C}{m}\int_0^t \delta(\tau - t)d\tau = \frac{C}{2m}$. *The* $\langle R(t)v(0)\rangle$ *term is zero assuming the random noise and initial condition are uncorrelated. The delta function is an idealization, integration exactly to the middle of a delta-function is ill-defined, but we imagine that it is a broad peak.*

(c) Fluctuation-dissipation theorem gives $C = 2m\gamma k_B T$, *thus* $P = I$. *Alternatively, multiplying v to both side of the Langevin equation, and integrate (average) over time, we get*

$$vm\frac{dv}{dt} = -m\gamma v^2 + R(t)v,$$
$$\frac{1}{T}\int_0^T \frac{d}{dt}\left(\frac{1}{2}mv^2\right)dt = \frac{E(t)-E(0)}{T} = \frac{1}{T}\int_0^T (-m\gamma v^2)dt + \frac{1}{T}\int_0^T R(t)v dt = -P + I$$

Taking the limit $T \to \infty$, *assuming that the energy E(t) of the system is bounded, we get P=I. We have assumed ergodicity, so that time average is equal to the ensemble average* $\langle \ldots \rangle$.

-- the end --

[WJS]