NATIONAL UNIVERSITY OF SINGAPORE

PC5202 ADVANCED STATISTICAL MECHANICS

(Semester II: AY 2017-18)

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 3 printed pages.
3. Students are required to answer ALL the questions.
4. Each question carries 25 marks.
5. Students should write the answers for each question on a new page.
6. This is a CLOSED BOOK examination.

1. Consider the TPN (isothermal-isobaric) ensemble, where the temperature T, pressure p, and number of particles N are fixed fundamental thermodynamic variables. We define the partition function in the TPN ensemble as $Z_G(T,p,N) = \int_0^\infty \beta p dV \int \frac{d\Gamma}{N!\, h^{3N}} e^{-\beta(H+pV)}$, here the volume V is an integration variable, $\beta = 1/(k_B T)$, $d\Gamma = dq_1 dq_2 \cdots dq_{3N} dp_1 \cdots dp_{3N}$, H is the Hamiltonian, and h is the Planck constant.
   a. Show that the Gibbs free energy is given by $G = -\frac{1}{\beta}\ln Z_G$.
   b. Considering the ideal gas with $= \sum_{j=1}^{3N} \frac{p_j^2}{2m}$, compute Z_G. You may need the definition of the Gamma function $\Gamma(x+1) \equiv x! = \int_0^\infty t^x e^{-t} dt$.
   c. Using the thermodynamic relation, determine the chemical potential μ; and show that the ideal gas law, $pV = Nk_BT$, is valid.
   d. Show that the entropy S obtained from G agrees with the usual Sackur-Tetrode formula.

a) The integration over the phase space Γ can be changed as integration over energy with the density of states N(E) of the energy. By Boltzmann principle, we can write exp(S(E)/k) = N(E). Then the values of two dimensional integrals over the volume V and E is dominated by the maxima (multiplied by a gaussian), so $-\frac{1}{\beta}\ln Z_G \approx -\frac{1}{\beta}\ln e^{\frac{S}{k}-\beta(E+pV)} = -TS + E + pV = G.$

b) The $d\Gamma$ *integral gives* $\int d\Gamma e^{-\beta H} = V^N \left(\frac{2\pi m}{\beta}\right)^{3N/2}$. *Using the given formula for x! we cancel the N! in the denominator. Find* $Z_G = \left(\frac{2\pi m}{\beta h^2}\right)^{3N/2}\left(\frac{1}{\beta P}\right)^N$.

c) Since $G(T,p,N) = -kT\ln Z_G$, *and take derivative with respect to N we get* $\mu = \frac{\partial G}{\partial N} = -\frac{1}{\beta}\ln\left[\left(\frac{2\pi m}{\beta h^2}\right)^{\frac{3}{2}}\frac{1}{\beta P}\right]$. *Take derivative with respect to p, we get V =* $\frac{\partial G}{\partial p} = N/(\beta p)$. *Or the ideal gas law* $pV = NkT$.

d) Entropy is obtained by taking partial derivative with respect to temperature T. We got two terms which can be simplified to the standard Sackur-Tetrode form: $S = Nk\ln\frac{V}{N\lambda^3} + \frac{5}{2}Nk$, *where* $\lambda = \frac{h}{\sqrt{2\pi m\, kT}}$ *is the thermal wavelength.*

2. We consider the application of the mean-field theory in the framework of the Feynman-Jensen-Bogoliubov (FJB) formulation to the spin S Heisenberg model. The Heisenberg model on a cubic lattice is $\hat{H} = -J\sum_{<ij>}\left(S_i^x S_j^x + S_i^y S_j^y + S_i^z S_j^z\right) - g\mu_B B\sum_i S_i^z$. Here the first term sums over the nearest neighbor pairs only, g is the Landé factor, μ_B is the Bohr magneton, B is applied external magnetic field in z direction, and the spin operators satisfy the usual commutation relations, with the eigenvalues of S^z taking $-S, -S+1, \cdots, S-1, S$. Let's choose the non-interacting Hamiltonian to be $\hat{H}_0 = -h\sum_i S_i^z$. Here h is the mean field to be determined.

a. Write down the quantum version of the FJB inequality for the Helmholtz free energy F, no need to give a proof.
b. Show that in the canonical ensemble defined by $\widehat{H}_0$, the average values of x and y components of the spins are 0, i.e., $\langle S_i^x \rangle_0 = \langle S_i^y \rangle_0 = 0$.
c. Prove that $\langle S_i^z \rangle_0 = SB_S(\eta)$, here $\eta = S\beta g\mu_B B$, and the Brillouin function is $B_S(\eta) = \frac{2S+1}{2S}\coth\left(\frac{2S+1}{2S}\eta\right) - \frac{1}{2S}\coth\left(\frac{1}{2S}\eta\right)$.
d. Compute the right-hand side of the Feynman-Jensen-Bogoliubov inequality, i.e., the estimate of the free energy of the original interacting system.

a) The Feynman-Jensen-Bogoliubov inequality is $F \leq F_0 + \langle H - H_0 \rangle_0$. *Here subscript 0 for the brackets means we average over the ensemble governed by* H_0.

b) Using S^+ *and* S^-, $S^\pm = S^x \pm iS^y$, *and* $\langle m|S^\pm|m\rangle = 0$, *we get,* $\langle S_i^x \rangle_0 = \langle S_i^y \rangle_0 = 0$, this is purely due to quantum mechanics.

c) Define the partition function as $Z = \sum_j e^{\beta h S_j}$, *sum over the all possible values of S from –S, -S+1, …, S-1, S, we get,* $Z = \frac{e^{-\beta h S} - e^{\beta h(S+1)}}{1-e^{\beta h}} = \frac{\sinh\left(S+\frac{1}{2}\right)x}{\sinh\frac{x}{2}}$, *here* $x = \beta h$. *Then if we take log derivative of Z with respect to x, we get the average value of z component of the spin, which in turn derive the Brillouin function.*

d) Since x and y average is 0, and spins are uncorrelated in the mean field approximation, we find, $F_0 = -NkT\ln Z$, *and* $\langle H - H_0 \rangle_0 = -JM^2Nd - g\,\mu_B BNM + hNM$. *Here we define* $M = \langle S_i^z \rangle_0$.

3. Consider the standard Langevin equation for the velocity, $\frac{dv}{dt} = -\gamma v + \frac{R(t)}{m}$, with $\langle R(t) \rangle = 0$, and $\langle R(t)R(t') \rangle = 2\gamma m k_B T \delta(t-t')$. Here m is particle mass, γ is the damping parameter.
a. Solve the equation formally, assuming steady state is reached, and thus ignoring the transient term to obtain an expression of the velocity $v(t)$ as an integral involving the random noise R. Obtain the position $x(t)$ formally, by integrating the velocity.
b. Determine the correlation function between the noise and the position, i.e., compute $\langle R(t)x(t') \rangle$, assuming steady state so the result should be a function of the time difference, $t - t'$, only. From this result, show explicitly that equal-time correlation $\langle R(t)x(t) \rangle = 0$, justifying Langevin's assumption.
c. Define a new variable $z = \frac{d\langle x^2 \rangle}{dt}$, here the average is over the random noise R. Show that z satisfies the equation $\frac{dz}{dt} + \gamma z = \frac{2k_B T}{m}$. Here equipartition theorem is assumed, $m\langle \dot{x}^2 \rangle = k_B T$, for all time t, as well as the conclusion obtained in (b).

a) Ignore the transient term, the noise part of the solution is $v(t) = \int_{-\infty}^{t} \frac{e^{-\gamma(t-t')}R(t')}{m} dt'$. *We can verify this is indeed the solution by substituting back to the equation. Position x(t) is obtained by double integral over time.*

b) Using the property of R correlation, we can do the integral with delta function, the result is $\langle R(t)x(t') \rangle = 2kT\left(1 - e^{-\gamma(t'-t)}\right)\theta(t'-t)$. *When* $t' \leq t$, *we get 0.*

c) *Take the derivative of z, we get* $\frac{dz}{dt} = \frac{d}{dt}\langle 2x\dot{x}\rangle = 2\langle \dot{x}^2\rangle + 2\langle x\ddot{x}\rangle$. *Using equipartition theorem for the first term since it is velocity square average and replace the second derivative by the equation of motion, and using the result in b) we get the required equation for z. Clearly,* $\frac{dx^2}{dt} = 2x\frac{dx}{dt}$. *And taking average and take time derivative commute.*

4. Linear response theory is a very general theory to describe transport or changes of a system under small perturbation. Let's consider an unperturbed, time-independent Hamiltonian to be $\widehat{H}_0$ and the small perturbation is $\widehat{H}' = -a(t)\,\hat{A}$, here $a(t)$ is a time-dependent c-number and $\hat{A}$ is a time-independent operator.
   a. Starting at thermal equilibrium at $t = -\infty$ with canonical distribution proportional to $\exp(-\beta\widehat{H}_0)$, show that an observable $\widehat{B}$ at time t is given by $\langle\widehat{B}(t)\rangle = -\int_{-\infty}^{t} G(t-t')a(t')dt'$. Give the precise definition of the Green's function G.
   b. Work out an explicit linear response formula for a simple quantum harmonic oscillator with $\widehat{H}_0 = \frac{\hat{p}^2}{2m} + \frac{1}{2}m\Omega^2\hat{x}^2$ under the drive of an external force, such that $\widehat{H}' = -f(t)\hat{x}$, and the observable $\widehat{B} = \hat{x}$, i.e., the position of the harmonic oscillator responding to the external force $f(t)$.

a) *We solve the equation for the density matrix ρ in interaction picture and compute the average. Detail, see Pottier's textbook.*

b) *For the harmonic oscillator, the required Green's function is* $G(t,t') = -\frac{i}{\hbar}\theta(t-t')\langle[x(t),x(t')]\rangle$. *The position is related to the ladder operator by* $x = \sqrt{\frac{\hbar}{2m\Omega}}(a+a^{+})$. *The time variation for a is,* $a(t) = ae^{-i\Omega t}$. *Putting this result in, we obtain,* $G(t,t') = -\frac{\theta(t-t')\sin\Omega(t-t')}{m\Omega}$.

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