

NATIONAL UNIVERSITY OF SINGAPORE

PC5202 ADVANCED STATISTICAL MECHANICS

(Semester II: AY 2011-12)

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 a CLOSED BOOK examination.
5. Each question carries 20 marks.

1. Explain briefly the following concepts or terms:

- a. Heat, according to thermodynamics
 - b. Ergodic hypothesis
 - c. Boltzmann's principle
 - d. Rushbrook's scaling law
 - e. White noise
- a. *The heat Q is defined by the first law of thermodynamics – heat absorbed $Q = \Delta U - W$, where ΔU is the increase in internal energy and W is the work done to the system. It is the energy transferred by non-mechanical means. Alternatively, it can be related to entropy by $\delta Q = TdS$ in a reversible process.*
 - b. *Ergodic hypothesis assumes time average equals ensemble average, i.e.*

$$\lim_{T \rightarrow \infty} \frac{1}{T} \int_0^T A(t) dt = \int \rho(\Gamma) A(\Gamma) d\Gamma .$$
 - c. *Boltzmann's principle is $S = k_B \ln \Omega$ where Ω is the number of microscopic states consistent with given macroscopic (external) constraints.*
 - d. *Rushbrook's scaling law is $\alpha + 2\beta + \gamma = 2$ (heat capacity, order parameter, and susceptibility exponents, for α, β, γ , respectively).*
 - e. *White noise is a stochastic (random) variable with $\langle R(t) \rangle = 0$ and $\langle R(t) R(t') \rangle = C \delta(t-t')$.*

2. Consider small vibrations of a one-dimensional chain of N atoms with the following Hamiltonian:

$$H = \sum_{j=1}^N \frac{1}{2m} p_j^2 + \sum_{j=0}^N \frac{1}{2} k (x_j - x_{j+1})^2, \quad x_0 = x_{N+1} = 0,$$

where, x_j is the displacement away from equilibrium and p_j is associated conjugate momentum for site j , m is mass, and k is force constant. Note that site 0 and $N+1$ are fixed, and the dynamic equations apply only for the sites from 1 to N .

- a. Compute the heat capacity of the classical system based on the equipartition theorem (in a canonical ensemble).
- b. Assuming a solution of the form $x_j = A \sin(jq) \cos(\omega_q t)$, determine the possible vibrational angular frequencies ω_q .
- c. Repeat the heat capacity calculation but for the corresponding quantum system.

- a. Since the system is quadratic, we can always diagonalize the system using normal mode coordinates. Each quadratic form gives $(1/2) k_B T$ for energy, the total energy is $U=2N(1/2)kT = Nk_B T$, the heat capacity is thus $C=dU/dT = Nk_B$.
- b. Because $x_{N+1}=0$, we must have $\sin(q(N+1)) = 0$, or $(N+1)q=k\pi$, or

$$q = \frac{k\pi}{N+1}, \quad k = 1, 2, \dots, N.$$

The value k specifies the N linearly independent solutions of normal mode vibrations. Substituting the solution $x_j=A \sin(qj) \cos(\omega_q t)$ into the equation of motion

$$m\ddot{x}_j = k(x_{j-1} - 2x_j + x_{j+1}),$$

$$\begin{aligned} m\ddot{x}_j &= -m\omega_q^2 x_j = kA\{\sin(q(j+1)) + \sin(q(j-1)) - 2\sin(qj)\} \cos(\omega_q t) \\ &= k \operatorname{Im} \left[e^{iq(j+1)} + e^{iq(j-1)} - 2e^{iqj} \right] A \cos(\omega_q t) \\ &= k \operatorname{Im} \left[(e^{iq} + e^{-iq} - 2)e^{iqj} \right] A \cos(\omega_q t) \\ &= 2k(\cos(q) - 1) \operatorname{Im} \left[e^{iqj} \right] A \cos(\omega_q t) = 2k(\cos(q) - 1) A \sin(qj) \cos(\omega_q t) \\ &= 2k(\cos(q) - 1)x_j \end{aligned}$$

we find

$$\omega_q^2 = \frac{2k}{m}(1 - \cos(q)).$$

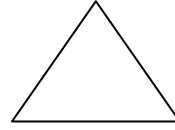
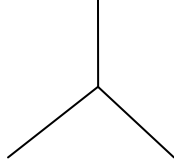
- c. The energy of a set of quantum harmonic oscillators is

$$U = \sum_q \left(f_q + \frac{1}{2} \right) \hbar \omega_q, \quad f_q = \frac{1}{e^{\beta \hbar \omega_q} - 1}. \quad \text{The heat capacity is obtained by taking}$$

derivative with respect to temperature T ,

$$C = \frac{dU}{dT} = \sum_q \hbar \omega_q \frac{df_q}{dT} = k_B \sum_q \frac{(\beta \hbar \omega_q)^2 e^{\beta \hbar \omega_q}}{(e^{\beta \hbar \omega_q} - 1)^2}, \text{ where } q \text{ takes the value } k\pi/(N+1) \text{ for } k = 1, 2, \dots, N.$$

3. Consider the ferromagnetic Ising model with 4 sites (left) and 3 sites (right) as shown below, with coupling constants J and J' for the nearest neighbor interactions (without magnetic field) defined on a finite network of sites indicated by the lines.
- Determine the high-temperature expansion of the partition function Z and Z' in variable $x = \tanh(K)$, $K = \beta J = J/(k_B T)$, for the 4-site model, and similarly for the 3 sites with primed variable $x' = \tanh(K')$.
 - If the center site in the 4-site model is first summed, then it becomes a model identical to the 3-sited model with a different coupling. Determine the relation between K and K' such that the two models can be mapped into each other.



a. The partition function for the 4 sites can be expanded as

$$Z = \cosh^3(K) \sum_{\sigma_0 \sigma_1 \sigma_2 \sigma_3} (1 + \sigma_0 \sigma_1 x)(1 + \sigma_0 \sigma_2 x)(1 + \sigma_0 \sigma_3 x) = 2^4 \cosh^3(K).$$

Similarly for the 3 sites,

$$\begin{aligned} Z' &= \cosh^3(K') \sum_{\sigma_1 \sigma_2 \sigma_3} (1 + \sigma_1 \sigma_2 x')(1 + \sigma_2 \sigma_3 x')(1 + \sigma_3 \sigma_1 x') \\ &= \cosh^3(K') \sum_{\sigma_1 \sigma_2 \sigma_3} [1 + x'^3 + (x' + x'^2)(\sigma_1 \sigma_2 + \sigma_2 \sigma_3 + \sigma_3 \sigma_1)] \\ &= \cosh^3(K') 2^3 (1 + x'^3) \end{aligned}$$

b. Sum over $\sigma_0 = +1$ or -1 in Z , we get

$$\begin{aligned} Z &= \cosh^3(K) \sum_{\sigma_1 \sigma_2 \sigma_3} [(1 + \sigma_1 x)(1 + \sigma_2 x)(1 + \sigma_3 x) + (1 - \sigma_1 x)(1 - \sigma_2 x)(1 - \sigma_3 x)] \\ &= \cosh^3(K) \sum_{\sigma_1 \sigma_2 \sigma_3} [2 + 2x^2(\sigma_1 \sigma_2 + \sigma_2 \sigma_3 + \sigma_3 \sigma_1)] \end{aligned}$$

Compare with the second line of Z' in part a, we find

$$1 + x'^3 = 2A$$

$$x' + x'^2 = 2x^2 A$$

Eliminating A , we can simplify the transformation x' to x as $\exp(4K') = 2 \cosh(2K) - 1$.

4. Consider the standard one-dimensional Langevin equation

$$\frac{dv(t)}{dt} = -\gamma v(t) + \frac{R(t)}{m},$$

where $v(t)$ is velocity, γ is the damping constant, m is mass, and $R(t)$ is the random force with the usual white noise correlation.

a. Find the solution $v(t)$ of the stochastic differential equation in terms of the random force $R(t)$.

b. Compute the velocity random-force correlation, i.e., compute $\langle v(t)R(t') \rangle$ in the long-time limit. Pay attention to the case $t < t'$ and $t > t'$.

a. If $R = 0$, the solution is $v = v_0 \exp(-\gamma t)$. Let $v(t) = A(t) \exp(-\gamma t)$, substituting into the equation we can solve for A . Given solution, in the long time limit

$$v(t) = \int_{-\infty}^t \frac{R(\tau)}{m} e^{\gamma(\tau-t)} d\tau .$$

b. The velocity-random force correlation is

$$\begin{aligned} \langle v(t)R(t') \rangle &= \left\langle \int_{-\infty}^t \frac{R(\tau)}{m} e^{\gamma(\tau-t)} R(t') d\tau \right\rangle \\ &= \frac{C}{m} \int_{-\infty}^t \delta(\tau-t') e^{\gamma(\tau-t)} d\tau = \begin{cases} 0 & \text{if } t < t', \\ \frac{C}{m} e^{-\gamma(t-t')} & \text{if } t > t'. \end{cases} \end{aligned}$$

5. The time-dependent Boltzmann entropy for a gas 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 , while the Gibbs entropy is defined by a similar formula with the full phase space variables $\Gamma = (\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N, \mathbf{p}_1, \mathbf{p}_2, \dots, \mathbf{p}_N)$ and the phase space probability distribution $\rho(\Gamma, t)$,

$$S_G = -k_B \int \rho \ln \rho d\Gamma .$$

- Write down the relation between f and ρ .
- Based on the fact that ρ satisfies the Liouville equation, show that S_G is a constant that does not change with time.
- Explain qualitatively, why S_B increases with time as given by the Boltzmann's H -theorem, while S_G does not.

a. f and ρ are related by integrating all variables except one particle, i.e.,

$$f(\mathbf{r}, \mathbf{p}, t) = N \int \rho(\mathbf{r}, \mathbf{r}_2, \mathbf{r}_3, \dots, \mathbf{r}_N, \mathbf{p}, \mathbf{p}_2, \mathbf{p}_3, \dots, \mathbf{p}_N) d\mathbf{r}_2 d\mathbf{r}_3 \dots d\mathbf{p}_N .$$

b. Using Liouville's theorem,

$$\frac{D\rho}{Dt} = \frac{\partial\rho}{\partial t} + \sum_j \left(\dot{q}_j \frac{\partial\rho}{\partial q_j} + \dot{p}_j \frac{\partial\rho}{\partial p_j} \right) = 0,$$

we have

$$\begin{aligned} \frac{dS_G}{dt} &= -k_B \int \frac{\partial(\rho \ln \rho)}{\partial t} d\Gamma = -k_B \int (1 + \ln \rho) \frac{\partial\rho}{\partial t} d\Gamma \\ &= k_B \int \left[\sum_j \dot{q}_j \frac{\partial\rho}{\partial q_j} (1 + \ln \rho) + \sum_j \dot{p}_j \frac{\partial\rho}{\partial p_j} (1 + \ln \rho) \right] d\Gamma \\ &= k_B \int \left[\sum_j \frac{\partial(\dot{q}_j \rho \ln \rho)}{\partial q_j} + \sum_j \frac{\partial(\dot{p}_j \rho \ln \rho)}{\partial p_j} \right] d\Gamma = 0 \end{aligned}$$

In the last step, we assumed that dq/dt is a function p only and dp/dt is a function of q only. Now the integrand is a divergence which can be converted into a surface integral using Gaussian theorem. We assume ρ is zero at far away surface, which give us 0 for dS_G/dt .

- c. The equation for f is not time-reversal symmetric, while the Liouville's equation for ρ is time-reversal symmetric. f is a coarse grained description of the system, while ρ contains the full information of the system. Using f , information is lost, which can be interpreted as producing entropy.

-- End of Paper --

[WJS]