

# 第一章 Homework

## 1.1 Homework 2

### 1. Show that the volume element

$$d\omega = \prod_{i=1}^{3N} (dq_i dp_i)$$

of the phase space remains invariant under a canonical transformation of the (generalized) coordinates  $(q, p)$  to any other set of (generalized) coordinates  $(Q, P)$ .

[Hint: Before considering the most general transformation of this kind, which is referred to as a contact transformation, it may be helpful to consider a point transformation - one in which the new coordinates  $Q_i$  and the old coordinates  $q_i$  transform only among themselves.]

$$(Q, P) = (Q(q, p), P(q, p))$$

So the volume element is

$$d\omega' = \prod_{i=1}^{3N} dQ_i dP_i = \left| \frac{\partial(Q, P)}{\partial(q, p)} \right| \prod_{i=1}^{3N} dq_i dp_i$$
$$J = \frac{\partial(Q, P)}{\partial(q, p)} = \begin{bmatrix} \frac{\partial Q}{\partial q} & \frac{\partial Q}{\partial p} \\ \frac{\partial P}{\partial q} & \frac{\partial P}{\partial p} \end{bmatrix}$$

Since canonical transformations preserve the Poisson brackets

$$\{Q_i, Q_j\} = 0, \quad \{P_i, P_j\} = 0, \quad \{Q_i, P_j\} = \delta_{ij},$$

which gives the Jacobian matrix  $J$

$$J^T \Omega J = \Omega, \quad \Omega = \begin{bmatrix} 0 & I \\ -I & 0 \end{bmatrix}$$

So  $\det \Omega = 1$ , which means  $\det J = 1$ .

Therefore we have  $d\omega' = d\omega$ , or

$$\prod_{i=1}^{3N} dQ_i dP_i = \prod_{i=1}^{3N} dq_i dp_i$$

Comments:

这道题目展示了相空间体积守恒, 或者说 "刘维尔定理". 它揭示了在哈密顿力学中, 若对系统作正则变换, 则像空间的体积元素依然保持不变. 这表明哈密顿力学将是一个可逆演化的系统, 即统计力学中的微观可逆性基础. 在量子力学中, 它还可对应于量子力学中的么正演化.

2. The generalized coordinates of a simple pendulum are the angular displacement  $\theta$  and the angular momentum  $ml^2\dot{\theta}$ . Study, both mathematically and graphically, the nature of the corresponding trajectories in the phase space of the system, and show that the area  $A$  enclosed by a trajectory is equal to the product of the total energy  $E$  and the time period  $\tau$  of the pendulum. With  $\theta$  and  $L = m\dot{\theta}l^2$ , the Hamiltonian of the simple pendulum is

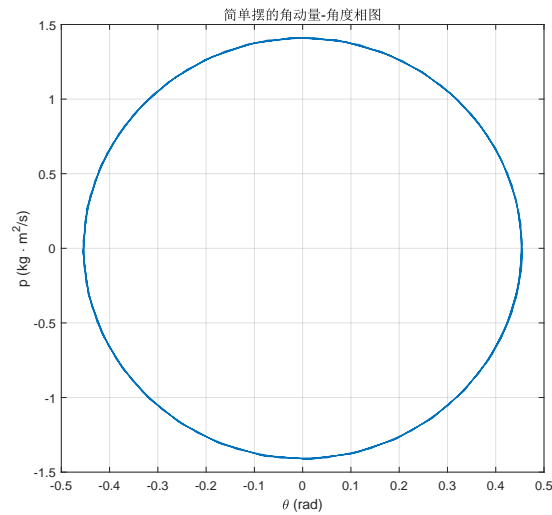
$$H = \frac{L^2}{2ml^2} + mgl(1 - \cos \theta)$$

So the area  $A$  enclosed by a trajectory is computed using the integral of  $Ld\theta$ :

$$A = \oint Ld\theta.$$

Derivative of  $A$  with respect to  $E$  gives the time period  $\tau$ :

$$\begin{aligned} \frac{dA}{dE} &= \frac{d}{dE} \oint Ld\theta = \oint \frac{\partial L}{\partial E} d\theta \\ \frac{\partial H}{\partial L} &= \frac{L}{ml^2} = \dot{\theta} \\ \Rightarrow \frac{dA}{dE} &= \oint \frac{1}{\dot{\theta}} d\theta = \tau \\ \Rightarrow A &= E\tau. \square \end{aligned}$$



Comments:

相空间中轨迹所围面积其实正是动作变量. 这也是对刘维尔定理的直观体现. 另外这也表明了, 能量-时间, 角动量-角度, 和坐标-动量之间存在着奇异的对偶联系, 我们从不确定性原理/诺特定理中也可以瞥见这种特别的联系, 暗示着更加深刻的物理规律.

## 1.2 Homework 3

### 1.2.1 1-D Harmonic Oscillators

Derive

1. **an asymptotic expression for the number of ways in which a given energy  $E$  can be distributed among a set of  $N$  one-dimensional harmonic oscillators, the energy eigenvalues of the oscillators being  $\left(n + \frac{1}{2}\right) \hbar\omega; n = 0, 1, 2, \dots$ ;**

The ground state energy for  $N$  oscillators is

$$E_{\text{ground}} = N \cdot \frac{1}{2} \hbar\omega = \frac{N}{2} \hbar\omega.$$

So the excitation energy above the ground state is

$$E^* = E - E_{\text{ground}} = E - \frac{N}{2} \hbar\omega.$$

So we need to distribute  $E^*$  among  $N$  oscillators, or

$$\sum_{i=1}^N = M, \quad \text{where } M = \frac{E^*}{\hbar\omega} = \frac{E}{\hbar\omega} - \frac{N}{2}.$$

So the number of ways, or the microstates, is given by the combinatorics

$$\Omega = \binom{M + N - 1}{N - 1}$$

With the Stirling approximation, we have

$$\begin{aligned} \ln \Omega &\approx (M + N) \ln (M + N) - M \ln M - N \ln N - \frac{1}{2} \ln (2\pi MN) \\ \Omega &\approx \frac{(M + N)^{M+N}}{M^M N^N} \sqrt{\frac{M + N}{2\pi MN}} \end{aligned}$$

Apply  $M = \frac{E}{\hbar\omega} - \frac{N}{2}$  to the above equation, we have

$$\Omega \approx \frac{\left(\frac{E}{\hbar\omega} + \frac{N}{2}\right)^{\frac{E}{\hbar\omega} + \frac{N}{2}}}{\left(\frac{E}{\hbar\omega} - \frac{N}{2}\right)^{\frac{E}{\hbar\omega} - \frac{N}{2}} N^N} \sqrt{\frac{\frac{E}{\hbar\omega} + \frac{N}{2}}{2\pi\left(\frac{E}{\hbar\omega} - \frac{N}{2}\right)N}}$$

If  $\frac{E}{\hbar\omega} \gg N$ , the number of states can be approximated as

$$\Omega \approx \frac{1}{N!} \left(\frac{E}{\hbar\omega}\right)^N.$$

2. **and the corresponding expression for the "volume" of the relevant region of the phase space of this system. Establish the correspondence between the two results, showing that the conversion factor  $\omega_0$  is precisely  $h^N$ .**

For a one-dimensional harmonic oscillator with energy  $E_i$ , its Hamiltonian is a elliptic curve:

$$H_i = \frac{p_i^2}{2m} + \frac{1}{2} m \omega^2 x_i^2 = E_i$$

So the phase space volume is given by the integral of the Hamiltonian over the energy surface:

$$\Gamma_i = \iint H_i dp_i dx_i = \pi \cdot \sqrt{\frac{2E_i}{m}} \cdot m \cdot \frac{1}{\omega} \sqrt{\frac{2E_i}{m}} = \frac{2\pi E_i}{\omega}$$

So the total phase space volume is given by

$$\Gamma = \int_{\sum E_i \leq E} \prod_{i=1}^N \frac{2\pi E_i}{\omega} dE_1 \cdots dE_N = \frac{(2\pi/\omega)^N E^N}{N!} = \frac{1}{N!} \left( \frac{2\pi E}{\omega} \right)^N$$

The classical microstate is

$$\Omega = \frac{1}{N!} \left( \frac{E}{\hbar\omega} \right)^N = \frac{1}{N!} \left( \frac{2\pi E}{h\omega} \right)^N = \frac{1}{h^N} \Gamma$$

So we get

$$\boxed{\omega_0 = h^N}$$

### 3. On the basis of Problem 1, derive the entropy and temperature. Comment on the result.

Since the number of microstates  $\Omega$  is given by

$$\Omega \approx \frac{\left(\frac{E}{\hbar\omega} + \frac{N}{2}\right)^{\frac{E}{\hbar\omega} + \frac{N}{2}}}{\left(\frac{E}{\hbar\omega} - \frac{N}{2}\right)^{\frac{E}{\hbar\omega} - \frac{N}{2}} N^N} \sqrt{\frac{\frac{E}{\hbar\omega} + \frac{N}{2}}{2\pi\left(\frac{E}{\hbar\omega} - \frac{N}{2}\right)N}},$$

we can calculate the entropy  $S$  using the Boltzmann entropy formula with Stirling approximation:

$$\boxed{S = k_B \left[ \left( \frac{E}{\hbar\omega} + \frac{N}{2} \right) \ln \left( \frac{E}{\hbar\omega} + \frac{N}{2} \right) - \left( \frac{E}{\hbar\omega} - \frac{N}{2} \right) \ln \left( \frac{E}{\hbar\omega} - \frac{N}{2} \right) - N \ln N \right]}$$

With the thermodynamic connection  $\frac{1}{T} = \frac{\partial S}{\partial E}$ , we have

$$\begin{aligned} \frac{1}{T} &= \frac{k_B}{\hbar\omega} \ln \left( \frac{\frac{E}{\hbar\omega} + \frac{N}{2}}{\frac{E}{\hbar\omega} - \frac{N}{2}} \right) \\ \Rightarrow T &= \frac{\hbar\omega}{k_B} \left[ \ln \left( \frac{E + \frac{N}{2}\hbar\omega}{E - \frac{N}{2}\hbar\omega} \right) \right]^{-1} \end{aligned}$$

Comments:

- **Role of Zero-Point Energy:** The derived expressions explicitly include the zero-point energy  $\frac{1}{2}\hbar\omega$  per oscillator, a quantum mechanical feature absent in classical treatments. This ensures that the total energy  $E$  cannot drop below  $\frac{N\hbar\omega}{2}$ , even at absolute zero, preserving the quantum ground state. The entropy and temperature formulas inherently account for this residual energy, distinguishing them from classical results.
- **High-Temperature Classical Limit:** At high energies  $E \gg \frac{N\hbar\omega}{2}$ , the zero-point energy becomes negligible. The entropy and temperature expressions reduce to classical results, aligning with the correspondence principle. For instance, the logarithmic terms simplify, leading to a linear relationship between  $E$  and  $T$ , consistent with the classical equipartition theorem.
- **Phase Space Quantization:** The phase space volume  $\Gamma \propto \left(\frac{E}{\omega}\right)^N$  and its conversion to quantum states via  $h^N$  underscores Planck's constant  $h$  as the fundamental unit of phase space volume. This bridges classical and quantum descriptions, emphasizing  $h^N$  as the natural measure for counting microstates in quantum systems.
- **Validity of Approximations:** The use of Stirling's approximation assumes  $N \gg 1$ , which is valid for macroscopic systems. The derived entropy  $S$  exhibits logarithmic scaling with energy, characteristic of systems with extensive degrees of freedom. This ensures consistency with thermodynamic expectations for large  $N$ .
- **Temperature-Energy Relationship:** The inverse logarithmic dependence of  $T$  on  $E$  reflects how energy distribution among oscillators governs thermal behavior. At low energies, quantum effects dominate, while high energies recover classical proportionality between  $E$  and  $T$ .

## 1.2.2 Helmholtz Free Energy

Making use of the fact that the Helmholtz free energy  $A(N, V, T)$  of a thermodynamic system is an extensive property of the system, show that

$$N \left( \frac{\partial A}{\partial N} \right)_{V,T} + V \left( \frac{\partial A}{\partial V} \right)_{N,T} = A$$

[Note that this result implies the well-known relationship:  $N\mu = A + PV (\equiv G)$ .]

Since the Helmholtz free energy  $A(N, V, T)$  satisfies the scaling relation

$$A(\lambda N, \lambda V, T) = \lambda A(N, V, T) \quad \text{for any } \lambda > 0,$$

so  $A(N, V, T)$  is homogeneous of degree 1 in  $N$  and  $V$ . So apply the Euler theorem for homogeneous functions to show that

$$N \left( \frac{\partial A}{\partial N} \right)_{V,T} + V \left( \frac{\partial A}{\partial V} \right)_{N,T} = A(N, V, T).$$

Since the chemical potential  $\mu$  is defined as  $\mu = \left( \frac{\partial A}{\partial N} \right)_{V,T}$ , and the pressure  $P$  is defined as  $P = - \left( \frac{\partial A}{\partial V} \right)_{N,T}$ , so we have the relation between the Helmholtz free energy and the chemical potential and pressure:

$$N\mu + V(-P) = A \Rightarrow N\mu = A + PV \equiv G.$$

## 1.2.3 Dilute Hard Sphere Gas

Assume there's a dilute hard sphere system, where exists  $N$  hard spheres with radius  $a$ , or volume  $\omega_e = \frac{4}{3}\pi(2a)^3$ . The system is at thermal equilibrium at temperature  $T$ . The total energy is  $E$ , and the system is in a container with volume  $V$ . Derive

1. entropy  $S(E, V)$ . [Hint: For an  $n$ -dimensional sphere with radius  $R$ , its  $(n - 1)$ -dimensional sphere area  $S^{(n-1)}$  is

$$\text{Area} = \frac{2\pi^{n/2}}{\Gamma(n/2)} R^{n-1}$$

The number of microstates is given by

$$\Omega(E, V, N) = \frac{1}{N!h^{3N}} \int_{\mathcal{D}} d^{3N}q d^{3N}p \delta \left( E - \sum_{i=1}^N \frac{p_i^2}{2m} \right), \quad \text{where } \mathcal{D} : |\vec{q}_i - \vec{q}_j| \geq 2a, \quad \forall i < j.$$

At dilute gas limit, the free volume can be considered as the rest volume:

$$V_{\text{free}} \approx V - \frac{N\omega_e}{2}.$$

So for the real space integral part, we have

$$\int_{\mathcal{D}} d^{3N}q \approx \left( V - \frac{N\omega_e}{2} \right)^N.$$

Since the energy consists of the kinetic energy only, as

$$E = \sum_{i=1}^N \frac{p_i^2}{2m},$$

the momentum integral part can be calculated:

$$\int d^{3N}p \delta \left( E - \sum_{i=1}^N \frac{p_i^2}{2m} \right) = \int d\Omega_{3N} \int_0^\infty dp p^{3N-1} \delta \left( E - \frac{p^2}{2m} \right), \quad p = \sqrt{\sum_{i=1}^{3N} p_i^2}$$

where  $d\Omega_{3N}$  is the angle integral part of the  $3N$ -dimensional sphere. As the hint gives, we have

$$S_{3N-1}(R) = \frac{2\pi^{3N/2}}{\Gamma(3N/2)} R^{3N-1}$$

Let  $R = \sqrt{2mE}$ , and remember that  $\delta(E - \frac{p^2}{2m}) = \frac{m}{p} \delta(p - \sqrt{2mE})$ , we have

$$\int d^{3N}p \delta\left(E - \sum_{i=1}^N \frac{p_i^2}{2m}\right) \propto (2mE)^{3N/2-1}$$

So the number of microstates is given by

$$\Omega(E, V, N) \approx \frac{1}{N! h^{3N}} \left(V - \frac{N\omega_e}{2}\right)^N \frac{(2\pi m)^{3N/2}}{\Gamma(3N/2)} E^{3N/2-1}$$

So the Boltzmann entropy is given by

$$S(E, V, N) = k_B \left\{ -\ln N! - 3N \ln h + N \ln \left(V - \frac{N\omega_e}{2}\right) + \left(\frac{3N}{2} - 1\right) \ln E + \frac{3N}{2} \ln(2\pi m) - \ln \Gamma\left(\frac{3N}{2}\right) \right\}$$

With thermodynamic limit  $N \rightarrow \infty$  and Stirling approximation  $\ln N! \approx N \ln N - N$ , we have

$$S(E, V, N) \sim N k_B \ln \left(V - \frac{N\omega_e}{2}\right) + \frac{3N}{2} k_B \ln E + \dots$$

## 2. guess the equation of state.

Since only the volume changed from  $V$  to  $V - \frac{N\omega_e}{2}$ , the state equation can be compared with the ideal gas one:

$$P \left(V - \frac{N\omega_e}{2}\right) = N k_B T.$$

## 3. calculate the equation of state.

With the thermodynamic relation  $\frac{1}{T} = \left(\frac{\partial S}{\partial E}\right)_{V,N}$  and  $\frac{P}{T} = \left(\frac{\partial S}{\partial V}\right)_{E,N}$ , we have

$$S(E, V, N) \sim N k_B \ln \left(V - \frac{N\omega_e}{2}\right) + \dots$$

$$\frac{P}{T} = \left(\frac{\partial S}{\partial V}\right)_{E,N} \sim \frac{N k_B}{V - \frac{N\omega_e}{2}} \dots$$

So we have the equation of state for the dilute hard sphere system:

$$\boxed{P \left(V - \frac{N\omega_e}{2}\right) = N k_B T}$$

# 1.3 Homework 4

## 1.3.1 Van der Waals equation

1. Derive for the dimensionless van der Waals equation of state from the original vdW equation  $P = \frac{RT}{v-b} - \frac{a}{v^2}$ .

The conditions for the critical point are

$$\left(\frac{\partial P}{\partial v}\right)_T = 0, \quad \left(\frac{\partial^2 P}{\partial v^2}\right)_T = 0.$$

So compute the derivatives of the pressure  $P$ :

$$\begin{cases} \frac{\partial P}{\partial v} &= -\frac{RT}{(v-b)^2} + \frac{2a}{v^3}, \\ \frac{\partial^2 P}{\partial v^2} &= \frac{2RT}{(v-b)^3} - \frac{6a}{v^4}. \end{cases}$$

At the critical point, let  $v = v_c$ ,  $P = P_c$ ,  $T = T_c$ , and we have the following equations:

$$\begin{cases} \frac{RT_c}{(v_c-b)^2} - \frac{2a}{v_c^3} = 0, \\ \frac{2RT_c}{(v_c-b)^3} - \frac{6a}{v_c^4} = 0. \end{cases} \Rightarrow \begin{cases} RT_c = \frac{2a(v_c-b)^2}{v_c^3}, \\ RT_c = \frac{3a(v_c-b)^3}{v_c^4}. \end{cases} \Rightarrow v_c = 3b$$

Since  $v_c$  has been determined, we can substitute it into the first equation to get:

$$RT_c = \frac{2a(3b-b)^2}{(3b)^3} = \frac{8a}{27b} \Rightarrow T_c = \frac{8a}{27Rb}$$

$$P_c = \frac{RT_c}{v_c-b} - \frac{a}{v_c^2} = \frac{a}{27b^2}.$$

Rescale the variables with the critical conditions:

$$P_r = \frac{P}{P_c}, \quad v_r = \frac{v}{v_c}, \quad T_r = \frac{T}{T_c}.$$

$$\Leftrightarrow P = P_r P_c = P_r \cdot \frac{a}{27b^2}, \quad v = v_r v_c = v_r \cdot 3b, \quad T = T_r T_c = T_r \cdot \frac{8a}{27Rb}.$$

So the van der Waals equation of state come to be

$$P_r \cdot \frac{a}{27b^2} = \frac{RT_r \cdot \frac{8a}{27Rb}}{v_r \cdot 3b - b} - \frac{a}{(v_r \cdot 3b)^2}$$

$$\Rightarrow P_r = \frac{8T_r}{3v_r - 1} - \frac{3}{v_r^2}.$$

2. **Plot typical curves  $P(v)$  at high and low temperature. In the derivation, one should identify the critical point. Show all your work.**

*% Define the reduced volume range*

`v_r = linspace(0.5, 10, 1000);`

*% High temperature ( $T_r > 1$ , e.g.,  $T_r = 1.5$ )*

`T_r_high = 1.5;`

`P_r_high = 8 * T_r_high ./ (3 * v_r - 1) - 3 ./ (v_r.^2);`

*% Low temperature ( $T_r < 1$ , e.g.,  $T_r = 0.8$ )*

`T_r_low = 0.8;`

`P_r_low = 8 * T_r_low ./ (3 * v_r - 1) - 3 ./ (v_r.^2);`

*% Critical isotherm ( $T_r = 1$ )*

`T_r_critical = 1;`

`P_r_critical = 8 * T_r_critical ./ (3 * v_r - 1) - 3 ./ (v_r.^2);`

*% Plotting*

**figure;**

**hold on;**

**plot(v\_r, P\_r\_high, 'b', 'LineWidth', 2, 'DisplayName', 'High\_T\_r(1.5)');**

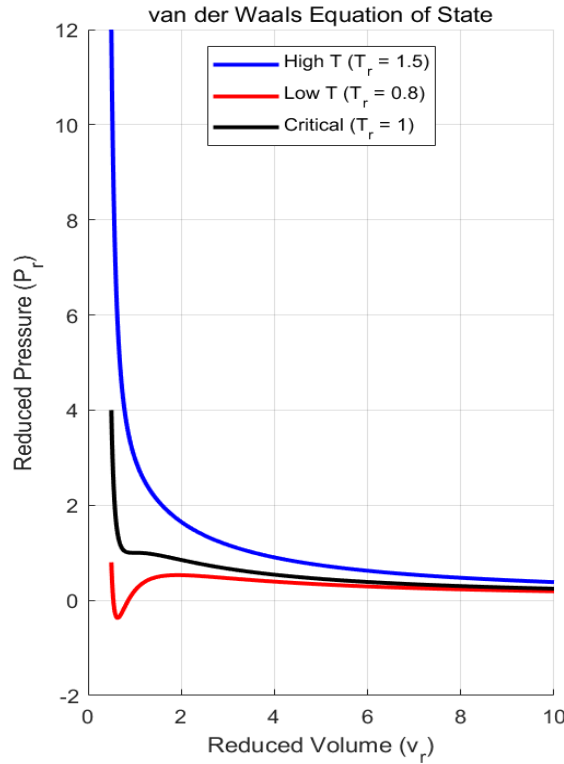
**plot(v\_r, P\_r\_low, 'r', 'LineWidth', 2, 'DisplayName', 'Low\_T\_r(0.8)');**

```

plot(v_r, P_r_critical, 'k', 'LineWidth', 2, 'DisplayName', 'Critical (T_r=1)');
xlabel('Reduced Volume (v_r)');
ylabel('Reduced Pressure (P_r)');
title('van der Waals Equation of State');
legend('Location', 'best');
grid on;
hold off;

```

The figure is shown below:



### 1.3.2 Maxwell Equal Area Construction

**Derive for the Maxwell equal area construction.**

The van der Waals equation of state for a non-ideal gas is given by

$$P = \frac{RT}{v - b} - \frac{a}{v^2}$$

The Maxwell construction replaces an unphysical "loop" with a horizontal line (Constant  $P$ ), representing liquid-vapor coexistence. Conditions for phase equilibrium are:

$$P(T, V_g) = P(T, V_l) = P_{\text{sat}}, \quad V_{g/l}: \text{ the molar volume of gas/liquid phases.}$$

$$\mu_g(T, P) = \mu_l(T, P)$$

Since  $G = \mu N$  and  $dG = -SdT + VdP$ , we have:

$$\mu_g - \mu_l = \int_{V_l}^{V_g} \left( \frac{\partial \mu}{\partial V} \right)_T dV = \int_{V_l}^{V_g} v dP = 0$$

Since  $P$  is constant ( $P_{\text{sat}}$ ) along the coexistence line, we can write:

$$\int_{V_l}^{V_g} v dP = P_{\text{sat}}(V_g - V_l) - \int_{P_l}^{P_g} P dV = 0$$



And we know that  $P_l = P_g = P_{\text{sat}}$ , so this reduces to

$$\int_{V_l}^{V_g} P dV = P_{\text{sat}}(V_g - V_l),$$

which is the conclusion to be derived.

### 1.3.3 Virial Expansion

Assume that in the virial expansion

$$\frac{Pv}{kT} = 1 - \sum_{j=1}^{\infty} \frac{j}{j+1} \beta_j \left( \frac{\lambda^3}{v} \right)^j,$$

where  $\beta_j$  are the irreducible cluster integrals of the system, only terms with  $j = 1$  and  $j = 2$  are appreciable in the critical region.

#### 1. Determine the relationship between $\beta_1$ and $\beta_2$ at the critical point, and

Since only the first two terms are appreciable, we can write the virial expansion as:

$$\frac{Pv}{kT} \simeq 1 - \left( \frac{1}{2} \beta_1 \frac{\lambda^3}{v} + \frac{2}{3} \beta_2 \frac{\lambda^6}{v^2} \right) = 1 - \frac{\beta_1 \lambda^3}{2v} - \frac{2\beta_2 \lambda^6}{3v^2}.$$

Or we can write it as a pressure function  $P$  of variable  $v$ :

$$P = kT \left( v^{-1} - \frac{\beta_1 \lambda^3}{2} v^{-2} - \frac{2\beta_2 \lambda^6}{3} v^{-3} \right)$$

So list the derivatives of  $P$  with respect to  $v$ :

$$\begin{aligned} \frac{\partial P}{\partial v} &= kT(-v^{-2} + \beta_1 \lambda^3 v^{-3} + 2\beta_2 \lambda^6 v^{-4}) (= 0), \\ \frac{\partial^2 P}{\partial v^2} &= kT(2v^{-3} - 3\beta_1 \lambda^3 v^{-4} - 8\beta_2 \lambda^6 v^{-5}) (= 0), \end{aligned}$$

which brings the critical point conditions:

$$\begin{aligned} -v_c^{-2} + \beta_1 \lambda^3 v_c^{-3} + 2\beta_2 \lambda^6 v_c^{-4} &= 0, \\ 2v_c^{-3} - 3\beta_1 \lambda^3 v_c^{-4} - 8\beta_2 \lambda^6 v_c^{-5} &= 0. \end{aligned}$$

We can rewrite the equations as

$$-v_c^2 + \beta_1 \lambda^3 v_c + 2\beta_2 \lambda^6 = 0, \tag{1.1}$$

$$2v_c^2 - 3\beta_1 \lambda^3 v_c - 8\beta_2 \lambda^6 = 0. \tag{1.2}$$

So the target is to eliminate terms like  $v_c$ . (1.3)  $\times 2 + (1.5)$  gives

$$\begin{aligned} (2v_c^2 - 2v_c^2) &= (3\beta_1 \lambda^3 v_c - 2\beta_1 \lambda^3 v_c) + (8\beta_2 \lambda^6 - 4\beta_2 \lambda^6) \\ \Rightarrow 0 &= \beta_1 \lambda^3 v_c + 4\beta_2 \lambda^6 \Rightarrow \boxed{\beta_1 = -\frac{4\beta_2 \lambda^3}{v_c}}. \end{aligned}$$

Substitute this into (1.3) gives:

$$\begin{aligned} v_c^2 &= \left( -4\beta_2 \frac{\lambda^3}{v_c} \right) \lambda^3 v_c + 2\beta_2 \lambda^6 \\ \Rightarrow v_c^2 &= -2\beta_2 \lambda^6 \Rightarrow \boxed{v_c = \sqrt{-2\beta_2 \lambda^3}} \end{aligned}$$

This connects  $\beta_1$  and  $\beta_2$ :

$$\beta_1 = -\frac{4\beta_2 \lambda^3}{\sqrt{-2\beta_2 \lambda^3}} = 2\sqrt{-2\beta_2}.$$

So we have  $\boxed{\beta_1 = 2\sqrt{-2\beta_2}}$ .

2. **show that**  $\frac{kT_c}{P_c v_c} = 3$ .

From the previous problem, we have  $\beta_1 = \frac{2v_c}{\lambda^3}$  and  $\beta_2 = -\frac{v_c^2}{2\lambda^6}$ . Substituting these into the virial expansion gives:

$$\begin{aligned}\frac{P_c v_c}{kT_c} &\simeq 1 - \frac{2v_c}{\lambda^3} \cdot \frac{\lambda^3}{2v_c} - \left(-\frac{v_c^2}{2\lambda^6}\right) \frac{2\lambda^6}{3v_c^2} \\ &= 1 - 1 + \frac{1}{3} = \frac{1}{3}\end{aligned}$$

So we have  $\boxed{\frac{kT_c}{P_c v_c} = 3}$

## 1.4 Homework 5

### 1.4.1 Partition Function

**Show that the partition function of an Ising lattice can be written as**

$$Q_N(B, T) = \sum_{N_+, N_{+-}} g_N(N_+, N_{+-}) \exp\{-\beta H_N(N_+, N_{+-})\},$$

**where**

$$H_N(N_+, N_{+-}) = -J \left( \frac{1}{2} qN - 2N_{+-} \right) - \mu B(2N_+ - N), \quad (1.3)$$

**while other symbols have their usual meanings; compare these results to equations**

$$H_N(N_+, N_{++}) = -J(N_{++} + N_{--} - N_{+-}) - \mu B(N_+ - N_-) \quad (1.4)$$

$$= -J \left( \frac{1}{2} qN - 2qN_+ + 4N_{++} \right) - \mu B(2N_+ - N) \quad (1.5)$$

**and**

$$Q_N(B, T) = \sum_{N_+, N_{++}} g_N(N_+, N_{++}) \exp\{-\beta H_N(N_+, N_{++})\}.$$

The Hamiltonian of the Ising model is given by

$$H = -J \sum_{\langle i, j \rangle} \sigma_i \sigma_j - \mu B \sum_i \sigma_i, \quad \sigma_i = \pm 1 \quad \forall i.$$

The total number of neighbor pairs is

$$N_{++} + N_{--} + N_{+-} = \frac{1}{2} qN$$

So the interaction energy component of the Hamiltonian becomes

$$-J \sum_{\langle i, j \rangle} \sigma_i \sigma_j = -J(N_{++} + N_{--} - N_{+-}),$$

where  $\sigma_i \sigma_j = +1$  for  $N_{++}$  and  $N_{--}$ , and  $\sigma_i \sigma_j = -1$  for  $N_{+-}$ .

The magnetic energy component is

$$-\mu B \sum_i \sigma_i = -\mu B(N_+ - N_-) = -\mu B(2N_+ - N), \quad N_- = N - N_+.$$

Combining these two components gives the total Hamiltonian

$$H_N = -J(N_{++} + N_{--} - N_{+-}) - \mu B(2N_+ - N)$$

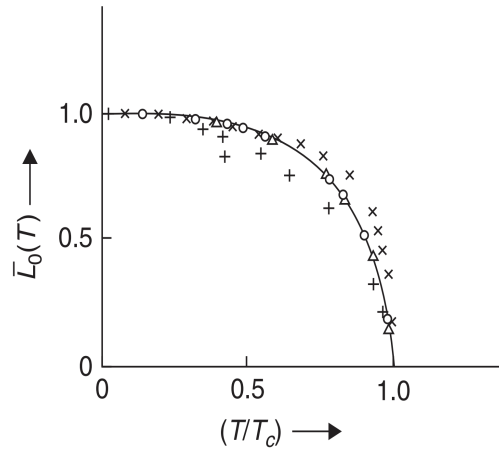


Figure 1.1: The spontaneous magnetization of a Weiss ferromagnet as a function of temperature. The experimental points (after Becker) are for iron (x), nickel (o), cobalt ( $\Delta$ ), and magnetite (+).

Using the relation  $N_{++} + N_{--} = \frac{1}{2}qN - N_{+-}$ , we can rewrite the Hamiltonian as

$$H_N = -J \left( \frac{1}{2}qN - 2N_{+-} \right) - \mu B(2N_+ - N),$$

So the partition function can be expressed as

$$\begin{aligned} Q_N(B, T) &= \sum_{N_+, N_{+-}} g_N(N_+, N_{+-}) \exp\{-\beta H_N(N_+, N_{+-})\} \\ &= \sum_{N_+, N_{+-}} g_N(N_+, N_{+-}) \exp\left\{-\beta \left[ -J \left( \frac{1}{2}qN - 2N_{+-} \right) - \mu B(2N_+ - N) \right]\right\} \end{aligned}$$

which matches the provided expression.

To prove that (1.3) and (1.5) are equivalent, we can use the relation between  $N_{+-}$  and  $N_{++}$ :

$$qN_+ = 2N_{++} + N_{+-} \Rightarrow N_{+-} = qN_+ - 2N_{++}$$

Substituting this into (1.3) gives:

$$\begin{aligned} H_N(N_+, N_{+-}) &= -J \left[ \frac{1}{2}qN - 2(qN_+ - 2N_{++}) \right] - \mu B(2N_+ - N) \\ &= -J \left( \frac{1}{2}qN - 2qN_+ + 4N_{++} \right) - \mu B(2N_+ - N) \end{aligned}$$

### 1.4.2 Equation of State

Show that the curve in 1.1 hits the horizontal and vertical axes at right angle according to the equation of state

$$\bar{L}_0 = \tanh\left(\frac{qJ\bar{L}_0}{kT}\right).$$

To show that the curve given by the equation of state  $\bar{L}_0 = \tanh\left(\frac{qJ\bar{L}_0}{kT}\right)$  hits the horizontal and vertical axes at right angles, we need to analyze the slope of the curve at the boundaries ( $T = 0$  and  $T = T_c = \frac{qJ}{k}$ ).

Differentiate both sides of the equation with respect to  $T$ , with chain rule:

$$\begin{aligned}\frac{d\bar{L}_0}{dT} &= \text{sech}^2\left(\frac{qJ\bar{L}_0}{kT}\right) \left(\frac{qJ}{kT} \frac{d\bar{L}_0}{dT} - \frac{qJ\bar{L}_0}{kT^2}\right) \\ \left[1 - \text{sech}^2\left(\frac{qJ\bar{L}_0}{kT}\right) \frac{qJ}{kT}\right] \frac{d\bar{L}_0}{dT} &= -\text{sech}^2\left(\frac{qJ\bar{L}_0}{kT}\right) \frac{qJ\bar{L}_0}{kT^2} \\ \frac{d\bar{L}_0}{dT} &= \frac{\text{sech}^2\left(\frac{qJ\bar{L}_0}{kT}\right) \frac{qJ\bar{L}_0}{kT^2}}{\text{sech}^2\left(\frac{qJ\bar{L}_0}{kT}\right) \frac{qJ}{kT} - 1}\end{aligned}$$

1. At  $T = 0$ . Define  $x = \frac{qJ\bar{L}_0}{kT}$ , we have:

$$\begin{aligned}\lim_{T \rightarrow 0} \tanh\left(\frac{qJ\bar{L}_0}{kT}\right) &= \lim_{x \rightarrow \infty} \tanh x = 1, \quad \forall \bar{L}_0 \neq 0 \\ &\Rightarrow \lim_{T \rightarrow 0} \bar{L}_0 = 1 \\ \lim_{T \rightarrow 0} \text{sech}^2\left(\frac{qJ\bar{L}_0}{kT}\right) &= \lim_{x \rightarrow \infty} \text{sech}^2 x = 0, \quad \forall \bar{L}_0 \neq 0 \\ &\Rightarrow \lim_{T \rightarrow 0} \frac{d\bar{L}_0}{dT} = \boxed{0}\end{aligned}$$

Thus the curve hits the horizontal axis horizontally at  $T = 0$ .

2. At  $T = T_c$ . We have  $\bar{L}_0 = 0$ , and  $\lim_{x \rightarrow 0} \tanh x = x - \frac{x^3}{3} + o(x^3)$ .

$$\begin{aligned}\lim_{\bar{L}_0 \rightarrow 0} \tanh\left(\frac{qJ\bar{L}_0}{kT}\right) &= \frac{qJ\bar{L}_0}{kT} - \frac{1}{3} \left(\frac{qJ\bar{L}_0}{kT}\right)^3 \\ &\Rightarrow \bar{L}_0 \left(1 - \frac{qJ}{kT}\right) = -\frac{1}{3} \left(\frac{qJ}{kT}\right)^3 \bar{L}_0^3\end{aligned}$$

Define  $T_c = \frac{qJ}{k}$ , so that  $t = \frac{T}{T_c} = \frac{kT}{qJ}$  to substitute into the equation:

$$\bar{L}_0 \left(1 - \frac{1}{t}\right) = -\frac{\bar{L}_0^3}{3t^3}$$

Let  $t = 1 + \epsilon$  while  $\epsilon \rightarrow 0$ , we have  $1 - \frac{1}{t} \approx \epsilon$ . Then rewrite the equation as:

$$\begin{aligned}\bar{L}_0 \epsilon &= -\frac{1}{3} \bar{L}_0^3 \Rightarrow \bar{L}_0 \approx \sqrt{3} \sqrt{1 - \frac{T}{T_c}} \\ &\Rightarrow \lim_{T \rightarrow T_c^-} \frac{d\bar{L}_0}{dT} \approx -\frac{\sqrt{3}}{2} \frac{1}{\sqrt{1 - \frac{T}{T_c}}} \frac{1}{T_c} = \boxed{\infty}\end{aligned}$$

Therefore the curve hits the vertical axis vertically at  $T = T_c$ .

## 1.5 Homework 6

### 1.5.1 Landau's Theory

Derive the critical exponents based on Landau's theory for second-order phase transition.

$$\psi_0(t, m_0) = q(t) + r(t)m_0^2 + s(t)m_0^4 + \dots \quad \left(t = \frac{T - T_c}{T_c}, |t| \ll 1\right);$$

Assuming that

- Symmetry: The free energy is even in  $m_0$ ;
- Analyticity:  $\psi_0$  is analytic in  $m_0$  and  $t$ , which allows a Taylor expansion;
- Critical behavior: Near  $T_c$ , the coefficients behave as  $r(t) \approx r_0 t$ ,  $s(t) \approx s_0 > 0$ .

The exponents are given by:

$$m_0 \sim (-t)^\beta, \quad \chi \sim |-t|^{-1}, \quad m_0 \sim h^{1/\delta}, \quad \xi \sim |t|^{-\nu}$$

The equilibrium order parameter  $m_0$  minimizes the free energy:

$$\begin{aligned} \frac{\partial \psi_0}{\partial m_0} = 0 &\Rightarrow 2r(t)m_0 + 4s(t)m_0^3 = 0 \\ &\Rightarrow m_0[r(t) + 2s(t)m_0^2] = 0 \end{aligned}$$

So

- Disordered phase ( $T > T_c$ ):  $m_0 = 0$ , since  $r(t) > 0$ ;
- Ordered phase ( $T < T_c$ ):  $m_0^2 = -\frac{r(t)}{2s(t)} \approx -\frac{r_0 t}{2s_0}$ , since  $r(t) \approx r_0 t$  and  $s(t) \approx s_0$ .

$$1. \text{ For } T < T_c, t < 0, m_0 \sim \sqrt{-t} \Rightarrow m_0 \sim (-t)^{1/2} \Rightarrow \boxed{\beta = \frac{1}{2}}$$

$$2. \text{ Susceptibility } \chi, \text{ which is defined as } \chi^{-1} = \left. \frac{\partial^2 \psi_0}{\partial m_0^2} \right|_{m_0=m_{eq}}.$$

- For  $T > T_c$ ,  $m_0 = 0$ .  $\chi^{-1} = 2r(t) \approx 2r_0 t \Rightarrow \chi \sim t^{-1}$
- For  $T < T_c$ ,  $m_0^2 = -\frac{r(t)}{2s(t)}$ :

$$\begin{aligned} \frac{\partial^2 \psi_0}{\partial m_0^2} &= 2r(t) + 12s(t)m_0^2 = 2r(t) + 12s(t) \left[ -\frac{r(t)}{2s(t)} \right] = -4r(t) \\ \chi^{-1} &= -4r(t) \approx -4r_0 t \Rightarrow \chi \sim (-t)^{-1} \Rightarrow \boxed{\gamma = 1} \end{aligned}$$

3. Specific heat.

- For  $T > T_c$ ,  $\psi_0 = q(t)$ ;
- For  $T < T_c$ ,  $\psi_0 = q(t) + r(t)m_0^2 + s(t)m_0^4 = q(t) - \frac{r(t)^2}{4s(t)}$ . And the specific heat is defined as  $C = -T \frac{\partial^2 \psi_0}{\partial T^2}$ . Since  $r(t) \sim t$ , the singular part is  $C$ , which jumps at  $t = 0$ . So  $\boxed{\alpha = 0}$ .

4. Critical isotherm. At  $T = T_c$ , the free energy is  $\psi_0 = q(0) + s(0)m_0^4 + \dots$ . Applying an external field  $h$ , the equilibrium condition is

$$h = \frac{\partial \psi_0}{\partial m_0} = 4s(0)m_0^3 \Rightarrow m_0 \sim h^{1/3} \Rightarrow \boxed{\delta = 3}.$$

$$5. \text{ Correlation length, which is defined as } \xi \sim \sqrt{\frac{c}{r(t)}} \sim t^{-1/2} \Rightarrow \boxed{\nu = \frac{1}{2}}$$

## 1.6 Homework 7

### 1.6.1 Stretched String

A string of length  $l$  is stretched, under a constant tension  $F$ , between two fixed points  $A$  and  $B$ . Show that the mean square (fluctuational) displacement  $y(x)$  at point  $P$ , distant  $x$  from  $A$ , is given by

$$\overline{\{y(x)\}^2} = \frac{kT}{Fl} x(l-x)$$

Further show that, for  $x_2 \geq x_1$ ,

$$\overline{y(x_1)y(x_2)} = \frac{kT}{Fl} x_1(l-x_2).$$

[Hint : Calculate the energy,  $\Phi$ , associated with the fluctuation in question; the desired probability distribution is then given by  $p \propto \exp(-\Phi/kT)$ , from which the required averages can be readily evaluated.]

Boundary conditions:  $y(0) = y(l) = 0$ . Energy of the fluctuation:  $\Phi[y(x)] = \frac{F}{2} \int_0^l \left( \frac{dy}{dx} \right)^2 dx$ .

Therefore  $P[y(x)] \propto \exp \left( -\frac{\Phi[y(x)]}{kT} \right) = \exp \left[ -\frac{F}{2kT} \int_0^l \left( \frac{dy}{dx} \right)^2 dx \right]$ .

Expand  $y(x)$  in eigenmodes which satisfies the boundary conditions:  $y(x) = \sum_{n=1}^{\infty} a_n \sin \left( \frac{n\pi x}{l} \right)$ , so the derivative becomes  $\frac{dy}{dx} = \sum_{n=1}^{\infty} a_n \frac{n\pi}{l} \cos \left( \frac{n\pi x}{l} \right)$ .

Substitute into the energy:  $\Phi = \frac{F}{2} \int_0^l \left( \frac{dy}{dx} \right)^2 dx = \frac{F}{2} \sum_{n=1}^{\infty} a_n^2 \left( \frac{n\pi}{l} \right)^2 \frac{l}{2} = \sum_{n=1}^{\infty} \frac{F\pi^2 n^2}{4l} a_n^2$ .

The probability distribution is  $p(\{a_n\}) \propto \exp \left[ -\sum_{n=1}^{\infty} \frac{F\pi^2 n^2}{4l} a_n^2 \right]$ , which is a product of independent Gaussian distribution for each

$a_n$ . And the variance of each  $a_n$  can be extracted from the exponent term:  $\overline{a_n^2} = \frac{2kT}{Fl} \left( \frac{l}{n\pi} \right)^2 = \frac{2kTl}{F\pi^2 n^2}$ .

Fourier expand  $\overline{y(x)^2} = \sum_{n=1}^{\infty} \sum_{m=1}^{\infty} \overline{a_n a_m} \sin \left( \frac{n\pi x}{l} \right) \sin \left( \frac{m\pi x}{l} \right)$ . Since  $\overline{a_n a_m} = \overline{a_n^2} \delta_{nm}$ ,  $\overline{y(x)^2} = \frac{2kTl}{F\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \sin^2 \left( \frac{n\pi x}{l} \right)$ .

Use the identity  $\sum_{n=1}^{\infty} \frac{\cos 2n\theta}{n^2} = \frac{\pi^2}{6} - \frac{\pi\theta}{2} + \frac{\theta^2}{2}$  and  $\sin^2 \theta = \frac{1 - \cos(2\theta)}{2}$ , the summation term:

$$\sum_{n=1}^{\infty} \frac{1}{n^2} \sin^2 \left( \frac{n\pi x}{l} \right) = \frac{1}{2} \sum_{n=1}^{\infty} \frac{1}{n^2} - \frac{1}{2} \sum_{n=1}^{\infty} \frac{1}{n^2} \cos \left( \frac{2n\pi x}{l} \right) = \frac{\pi^2}{12} - \frac{1}{2} \left( \frac{\pi^2}{6} - \frac{\pi^2 x}{2l} + \frac{\pi^2 x^2}{2l^2} \right) = \frac{\pi^2 x}{2l} - \frac{\pi^2 x^2}{2l^2} = \frac{\pi^2}{2l^2} x(l-x)$$

Substitute it back into the expansion to get  $\overline{y(x)^2} = \frac{2kTl}{F\pi^2} \times \frac{\pi^2}{2l^2} x(l-x) = \boxed{\frac{kT}{Fl} x(l-x)}$

Similarly,  $\overline{y(x_1)y(x_2)} = \sum_{n=1}^{\infty} \overline{a_n^2} \sin \left( \frac{n\pi x_1}{l} \right) \sin \left( \frac{n\pi x_2}{l} \right) = \frac{2kTl}{F\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \sin \left( \frac{n\pi x_1}{l} \right) \sin \left( \frac{n\pi x_2}{l} \right)$ .

Use the identity  $\sum_{n=1}^{\infty} \frac{\cos(n\theta)}{n^2} = \frac{\pi^2}{6} - \frac{\pi\theta}{2} + \frac{\theta^2}{4}$  and  $\sin A \sin B = \frac{\cos(A-B) - \cos(A+B)}{2}$ , the summation term:

$$\sum_{n=1}^{\infty} \frac{1}{n^2} \sin \left( \frac{n\pi x_1}{l} \right) \sin \left( \frac{n\pi x_2}{l} \right) = \frac{1}{2} \sum_{n=1}^{\infty} \frac{1}{n^2} \cos \left[ \frac{n\pi(x_1 - x_2)}{l} \right] - \frac{1}{2} \sum_{n=1}^{\infty} \frac{1}{n^2} \cos \left[ \frac{n\pi(x_1 + x_2)}{l} \right]$$

So define  $\theta_1 = \frac{\pi(x_1 - x_2)}{l}$ ,  $\theta_2 = \frac{\pi(x_1 + x_2)}{l}$ , the summation term becomes

$$\begin{aligned} \sum_{n=1}^{\infty} \frac{\cos(n\theta_1)}{n^2} &= \frac{\pi^2}{6} - \frac{\pi|\theta_1|}{2} + \frac{\theta_1^2}{4}, \quad \sum_{n=1}^{\infty} \frac{\cos(n\theta_2)}{n^2} = \frac{\pi^2}{6} - \frac{\pi\theta_2}{2} + \frac{\theta_2^2}{4}. \text{ Therefore} \\ \sum_{n=1}^{\infty} \frac{1}{n^2} \sin \left( \frac{n\pi x_1}{l} \right) \sin \left( \frac{n\pi x_2}{l} \right) &= \frac{1}{2} \left[ \frac{\pi^2}{6} - \frac{\pi^2|x_1 - x_2|}{2l} + \frac{\pi^2(x_1 - x_2)^2}{4l^2} \right] - \frac{1}{2} \left[ \frac{\pi^2}{6} - \frac{\pi^2(x_1 + x_2)}{2l} + \frac{\pi^2(x_1 + x_2)^2}{4l^2} \right] \\ &= \frac{\pi^2(x_1 + x_2 - |x_1 - x_2|)}{4l} + \frac{\pi^2[(x_1 - x_2)^2 - (x_1 + x_2)^2]}{8l^2} \quad x_2 \geq x_1 \quad \frac{\pi^2(2x_1)}{4l} + \frac{\pi^2(-4x_1x_2)}{8l^2} \end{aligned}$$

Substitute it back into the expansion to get  $\overline{y(x_1)y(x_2)} = \frac{2kTl}{F\pi^2} \times \left( \frac{\pi^2 x_1}{2l} - \frac{\pi^2 x_1 x_2}{2l^2} \right) = \boxed{\frac{kT}{Fl} x_1(l-x_2)}$

## 1.6.2 Derive the Onsager's Reciprocal Relations

**Derive for the Onsager's reciprocity relation. [Refer to Section 15.7 @ Pathria & Beale]**

Forces  $X_i$  and the current  $\dot{x}_i$ :  $\dot{x}_i = \gamma_{ij} X_j$ .

$$S(x_i) = S(\tilde{x}_i) + \left( \frac{\partial S}{\partial x_i} \right)_{x_i=\tilde{x}_i} (x_i - \tilde{x}_i) + \frac{1}{2} \left( \frac{\partial^2 S}{\partial x_i \partial x_j} \right)_{x_i,j=\tilde{x}_i,j} (x_i - \tilde{x}_i) (x_j - \tilde{x}_j), \quad \left( \frac{\partial S}{\partial x_i} \right)_{x_i=\tilde{x}_i} = 0$$

$$\Delta S \equiv S(x_i) - S(\tilde{x}_i) = -\frac{1}{2} \beta_{ij} (x_i - \tilde{x}_i) (x_j - \tilde{x}_j), \quad \beta_{ij} = - \left( \frac{\partial^2 S}{\partial x_i \partial x_j} \right)_{x_i,j=\tilde{x}_i,j} = \beta_{ji}$$

The driving forces  $X_i$  can be defined as the second law of thermodynamics:  $X_i = \left( \frac{\partial S}{\partial x_i} \right) = -\beta_{ij} (x_j - \tilde{x}_j)$

$$\langle x_i X_j \rangle = \frac{\int_{-\infty}^{+\infty} (x_i X_j) \exp \left\{ -\frac{1}{2k} \beta_{ij} (x_i - \tilde{x}_i) (x_j - \tilde{x}_j) \right\} \prod_i dx_i}{\int_{-\infty}^{+\infty} \exp \left\{ -\frac{1}{2k} \beta_{ij} (x_i - \tilde{x}_i) (x_j - \tilde{x}_j) \right\} \prod_i dx_i}, \text{ where}$$

$$\langle x_i \rangle = \frac{\int_{-\infty}^{+\infty} x_i \exp \left\{ -\frac{1}{2k} \beta_{ij} (x_i - \tilde{x}_i) (x_j - \tilde{x}_j) \right\} \prod_i dx_i}{\int_{-\infty}^{+\infty} \exp \left\{ -\frac{1}{2k} \beta_{ij} (x_i - \tilde{x}_i) (x_j - \tilde{x}_j) \right\} \prod_i dx_i} = \tilde{x}_i, \quad \frac{\partial \langle x_i \rangle}{\partial x_j} = 0 \Rightarrow \langle x_i X_j \rangle = -k \delta_{ij}.$$

According to time reversal symmetry (in microscopic process),

$$\langle x_i(0) x_j(s) \rangle = \langle x_i(0) x_j(-s) \rangle, \quad \langle x_i(0) x_j(-s) \rangle = \langle x_i(s) x_j(0) \rangle \Rightarrow \langle x_i(0) x_j(s) \rangle = \langle x_i(s) x_j(0) \rangle. \text{ Let } s \rightarrow 0 \text{ to get: } \langle x_i(0) \dot{x}_j(0) \rangle =$$

Substitute the force-current relation, and get  $\langle x_i(0) \gamma_{jl} X_l(0) \rangle = -k \gamma_{jl} \delta_{il} = -k \gamma_{ji}$   
 $\langle \gamma_{il} X_l(0) x_j(0) \rangle = -k \gamma_{il} \delta_{jl} = -k \gamma_{ij} \Rightarrow \boxed{\gamma_{ij} = \gamma_{ji}}.$