

# **ADVANCED STATISTICAL MECHANICS**

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# 第一章 课堂讲义

## 1.1 Introduction

### 1.1.1 Review of Thermodynamics

#### 1.1.1.1 Central Theme of Thermodynamics: Work & Heat

**1.1.1.1.1 The Four Laws** 0th: If two systems are in thermal equilibrium with a third system, they are in thermal equilibrium with each other.

1st: The change in internal energy of a closed system is equal to the heat added to the system minus the work done by the system.

2nd: The total entropy of an isolated system can never decrease over time. In any reversible process, the total entropy of the system and its surroundings remains constant.

3rd: As the temperature approaches absolute zero, the entropy of a perfect crystal approaches a constant minimum.

$$\begin{array}{ccccc} \text{increase of internal energy} & & \text{input heat} & & \text{output work} \\ dU & = & \delta Q & - & \delta W \end{array}$$

- reversible process:  $dU = TdS - PdV$
- mechanical system:  $\delta W = f dx = -dV(x)$ ;
- *adiabatic process*(绝热过程):  $\delta W = PdV = -dU$ .  $U$ : thermodynamic/adiabatic potential.
- *isothermal process*(等温过程).  $F$ : isothermal potential.

$$F \equiv U - TS, \quad dF = -SdT - PdV, \quad \left. \delta W \right|_T = PdV = -dF$$

#### 1.1.1.1.2 Maximum Work

- isothermal process,  $A \rightarrow B$ :

$$\text{1st law: } \Delta W = -\Delta U + \Delta Q$$

$$\text{2nd law: } \Delta Q \leq T(S_B - S_A)$$

$$\Delta W \leq U_A - U_B + T(S_B - S_A) = -\Delta F, \quad \Delta F = F_B - F_A$$

- $A \rightarrow B, U_A = U_B$ :  $\Delta W_{\max} = T(S_B - S_A)$ . Example: Rubber band(橡皮筋), shrinking:  $S \uparrow$ .

**1.1.1.1.3 Extensivity(广延)** 形如  $E = E_1 + E_2$  的广延性在传统热力学中要求短程相互作用. Assume extensive quantity  $X$ ,

$$U(\lambda S, \lambda X) = \lambda U(S, X) \xrightarrow{\partial_\lambda} \frac{\partial U(\lambda S, \lambda X)}{\partial(\lambda S)} \dot{S} + \frac{\partial U(\lambda S, \lambda X)}{\partial(\lambda X)} \dot{X} = U(S, X)$$

$$\text{let } \lambda = 1, \quad \frac{\partial U}{\partial S} \dot{S} + \frac{\partial U}{\partial X} \dot{X} = U \Rightarrow U = TS + QX, \quad Q = \frac{\partial U}{\partial X}$$

Introduce physics:  $U = TS - PV + \mu N \Rightarrow dU = TdS + SdT - PdV - VdP + \mu dN + Nd\mu$

$$\text{Since } dU = TdS - PdV + \mu dN$$

$$\text{So new physics: } d\mu = -sdT + vdP, \quad s = \frac{S}{N}, \quad v = \frac{V}{N}, \quad s = \left( \frac{\partial \mu}{\partial T} \right)_P, \quad v = \left( \frac{\partial \mu}{\partial P} \right)_T$$

一/二级相变分类依据: 化学势  $\mu$  的导数连续性

一级相变.  $s$  突变: 潜热;  $v$  突变: 水结冰; 二级相变.  $\frac{\partial s}{\partial T}$  突变: 热容  $\left(T \frac{\partial S}{\partial T}\right)$  变化;  $\frac{\partial v}{\partial P}$  压缩率  $\left(\frac{1}{v} \frac{\partial v}{\partial P}\right)$  变化

### 1.1.1.2 Jacobian & Thermodynamics Relations

**1.1.1.2.1 Definition of Jacobian**  $(x, y)$  plane, functions:  $\xi(x, y), \eta(x, y)$ . relative functions:  $x(\xi, \eta), y(\xi, \eta)$ .

$$\begin{aligned} dx &= \frac{\partial x}{\partial \xi} d\xi + \frac{\partial x}{\partial \eta} d\eta, \quad dy = \frac{\partial y}{\partial \xi} d\xi + \frac{\partial y}{\partial \eta} d\eta \\ dx \wedge dy &= \frac{\partial(x, y)}{\partial(\xi, \eta)} d\xi \wedge d\eta, \quad \text{Jacobian matrix: } \frac{\partial(x, y)}{\partial(\xi, \eta)} = \begin{vmatrix} \frac{\partial x}{\partial \xi} & \frac{\partial x}{\partial \eta} \\ \frac{\partial y}{\partial \xi} & \frac{\partial y}{\partial \eta} \end{vmatrix} = \begin{vmatrix} J_{11} & J_{12} \\ J_{21} & J_{22} \end{vmatrix} \end{aligned}$$

正则变换:  $J = 1$ , 相空间体积不变. State function  $\leftrightarrow$  total differential(全微分)  $\leftrightarrow J = 1$ :

$$\begin{aligned} dU &= TdS - PdV = \frac{\partial U}{\partial x} dx + \frac{\partial U}{\partial y} dy \Rightarrow T = \left(\frac{\partial U}{\partial S}\right)_V, -P = \left(\frac{\partial U}{\partial V}\right)_S \\ \frac{\partial^2 U}{\partial V \partial S} &= \frac{\partial^2 U}{\partial S \partial V}, \quad \text{derivative exchange symmetry} \\ \left(\frac{\partial T}{\partial V}\right)_S &= -\left(\frac{\partial P}{\partial S}\right)_V \Rightarrow \frac{\partial(T, S)}{\partial(P, V)} = 1, \quad \text{Maxwell's relation(s)} \\ dT \wedge dS &= \frac{\partial(T, S)}{\partial(P, V)} dP \wedge dV, \quad J = 1 \text{ 和温标选取对应} \end{aligned}$$

### 1.1.1.2.2 Property of Jacobian Matrix

1.  $\frac{\partial(T, S)}{\partial(P, V)} = \frac{\partial(T, S)}{\partial(\mu, \nu)} \frac{\partial(\mu, \nu)}{\partial(P, V)} = 1$ , to produce numerous Maxwell's relations;

[Example] let  $(\mu, \nu) = (V, S)$ ,  $\frac{\partial(T, S)}{\partial(V, S)} \frac{\partial(V, S)}{\partial(P, V)} = 1 \Rightarrow \left(\frac{\partial T}{\partial V}\right)_S \cdot \left(-\frac{\partial S}{\partial P}\right)_V = 1 \Rightarrow \left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V$

As  $\left(\frac{\partial \gamma}{\partial \mu}\right)_\nu$ , variables  $\gamma, \mu, \nu$  as  $P, V, T, S$ .  $\frac{1}{2}A_4^3 = 12$ . Write down these elements as a big matrix:

$$\begin{bmatrix} \left(\frac{\partial V}{\partial P}\right)_T & \left(\frac{\partial P}{\partial T}\right)_V & \left(\frac{\partial V}{\partial P}\right)_T \\ \vdots & \vdots & \vdots \end{bmatrix}_{4 \times 3}, \quad \text{Only 3 elements are independent.}$$

$$2. \frac{\partial(x, y)}{\partial(\xi, y)} = \left(\frac{\partial x}{\partial \xi}\right)_y; 3. \frac{\partial(y, x)}{\partial(\xi, \eta)} = -\frac{\partial(x, y)}{\partial(\xi, \eta)}$$

### 1.1.1.3 Exterior derivative(外微分)

$p$ -form  $\xrightarrow{d} p + 1$ -form. 0-form:  $f(x) \rightarrow df(x) = \frac{df(x)}{dx} dx$ ;

1-form:  $g(x, y)dx \rightarrow d[g(x, y)dx] = \left(\frac{\partial g}{\partial x} dx + \frac{\partial g}{\partial y} dy\right) \wedge dx = \frac{\partial g}{\partial y} dy \wedge dx, \quad dx \wedge dy = -dy \wedge dx \Rightarrow d^2 = 0$ ;

2-form:  $f(x, y)dx \wedge dy$

$$dU = TdS - PdV \Rightarrow d(dU) = d(TdS) - d(PdV) \Rightarrow 0 = dT \wedge dS - dP \wedge dV \Rightarrow dT \wedge dS = dP \wedge dV$$

$$d^2 = 0 \Rightarrow dT \wedge \left[ \left(\frac{\partial S}{\partial V}\right)_T dV + \left(\frac{\partial S}{\partial T}\right)_V dT \right] = \left[ \left(\frac{\partial P}{\partial V}\right)_T dV + \left(\frac{\partial P}{\partial T}\right)_V dT \right] \wedge dV \Rightarrow \left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$$

## 1.1.2 Some Key Concepts in Thermodynamics

### 1.1.2.1 Temperature

**1.1.2.1.1 Thermodynamic Perspective**  $dU = TdS - PdV, T \equiv \left( \frac{\partial U}{\partial S} \right)_V$ , thermodynamic definition of temperature.

1st law:  $E = E_1 + E_2 = \text{const.}$

$$\frac{dS}{dE_1} = 0, \quad \text{condition of thermal equilibrium}$$

$$\frac{dS_1}{dE_1} + \frac{dS_2}{dE_1} = \frac{dS_1}{dE_1} + \frac{dS_2}{dE_2} \frac{dE_2}{dE_1} = \frac{dS_1}{dE_1} - \frac{dS_2}{dE_2} = 0 \Rightarrow \frac{dS_1}{dE_1} = \frac{dS_2}{dE_2} \leftrightarrow \frac{1}{T_1} = \frac{1}{T_2}$$

$$\text{2nd law: } \frac{dS}{dt} \geq 0 \Rightarrow \frac{dS}{dE_1} \frac{dE_1}{dt} \geq 0 \Rightarrow \left( \frac{dS_1}{dE_1} - \frac{dS_2}{dE_2} \right) \frac{dE_1}{dt} \geq 0 \Rightarrow \left( \frac{1}{T_1} - \frac{1}{T_2} \right) \frac{dE_1}{dt} \geq 0$$

$$\text{if } T_2 > T_1, \quad \frac{1}{T_1} - \frac{1}{T_2} > 0 \Rightarrow \frac{dE_1}{dt} \geq 0$$

\*Gibbs' geometric viewpoint of thermodynamics  $U(S, V)$ .

**1.1.2.1.2 Kinetic Viewpoint** Microscopic structure of the system needed. Ideal gas, Maxwell distribution(3D):

$$P(\vec{v})d^3\vec{v} = A \exp \left[ -\frac{mv^2/2}{k_B T} \right] d^3\vec{v}$$

$$\frac{1}{2}m\langle v^2 \rangle = \frac{1}{2}m(\langle v_x^2 \rangle + \langle v_y^2 \rangle + \langle v_z^2 \rangle) = \frac{3}{2}k_B T, \quad \langle v_x^2 \rangle = \int v_x^2 P(\vec{v})d^3\vec{v}$$

[Example] Rod particles in thermal equilibrium. 若棒的长轴为  $z$  轴, 则角动量  $\vec{J}$  倾向于 平行/ 垂直 于  $z$  轴. 每个自由度都是分得  $\frac{1}{2}k_B T$  的能量.

$$\frac{1}{2}I_z \overline{\omega_z^2} = \frac{1}{2}k_B T, \quad \frac{1}{2}I_x \overline{\omega_x^2} = \frac{1}{2}k_B T$$

$$I_z \ll I_x = I_y \Rightarrow \overline{\omega_z^2} \gg \overline{\omega_x^2} = \overline{\omega_y^2}$$

$$\frac{J_z}{J_x} = \frac{I_z \omega_z}{I_x \omega_x} \approx \frac{\omega_z}{\omega_x} \ll 1 \Rightarrow J_z \ll J_x \Rightarrow \vec{J} \text{ 主要在 } x-y \text{ 平面}$$

### 1.1.2.2 Entropy

**1.1.2.2.1 Thermodynamic Perspective** For a reversible cyclic process,  $\oint \frac{\delta Q}{T} = 0$ .  $\delta Q$ : heat absorbed by the system.

$$\forall \text{ reversible process, } \int_{\Gamma_{A \rightarrow B}} \frac{\delta Q}{T} + \int_{\Gamma_{B \rightarrow A}} \frac{\delta Q}{T} = 0 \Rightarrow \int_{\Gamma_{A \rightarrow B}} \frac{\delta Q}{T} \text{ is independent of the path.}$$

State variable  $dS \equiv \frac{\delta Q}{T}$  reflects intrinsic property of the system. 熔化热(相变潜热), 吸热而  $T$  不变(change of state).

$$\text{2nd law: } \oint \frac{\delta Q}{T} \leq 0, \quad \forall \text{ process}$$

$$\int_{\gamma_{A \rightarrow B}^{(I)}} \frac{\delta Q}{T} + \int_{\gamma_{B \rightarrow A}^{(R)}} \frac{\delta Q}{T} \leq 0, \quad \text{(I) for Irreversible, (R) for reversible}$$

$$\Rightarrow S(B) - S(A) \geq \int_{\Gamma_{A \rightarrow B}^{(I)}} \frac{\delta Q}{T} \Rightarrow \text{isolated system: } S(B) - S(A) \geq 0$$

**1.1.2.2.2 Boltzmann's Entropy** Statistical interpretation of thermodynamics.  $S = k \ln W$ ,

1. closed/isolated system.  $W$ : number of microstates. states:  $(q, p); (0, 1); |n\rangle$ , distinguishable(等价, 不可区分).

2. 两系统微观态数  $W_1, W_2$ . 熵广延性  $S = S_1 + S_2 = k \ln W_1 + k \ln W_2 = k \ln (W_1 W_2)$ .  $\ln$ : 化 $\times$ 为 $+$ .

3.  $W = e^{S/k} \sim e^{O(N)}$ ,  $W$ : thermodynamic probability.

[Example] Closed system consisted of  $N$  non-interacting oscillators. 各振子  $k$  处于  $|k\rangle$  状态. 总能量为  $E$ . distribution of energy?  $n_k$  为处于  $|k\rangle$  状态的振子数目且充分大.



$$\sum_k \varepsilon_k n_k = E = \text{const.}, \quad \sum_k n_k = N$$

$$\exists \{n_k\} \text{ s.t. } W = \frac{N!}{\prod_k n_k!} \text{ reaches max } \xrightarrow{\ln M! = M \ln M - M} \ln W = - \sum_k n_k \ln \frac{n_k}{N}, \quad (\# \ln \#)$$

拉格朗日乘子法:  $I = \ln W - \alpha \sum_k n_k - \beta \sum_k n_k \varepsilon_k$ ,  $\delta n_k \rightarrow \delta I = 0 \Rightarrow n_k^* = \frac{e^{-\beta \varepsilon_k}}{\sum_k e^{-\beta \varepsilon_k}}$ , Boltzmann factor

Stirling's formula:  $\ln N! = N \ln N - N$

$$N! = \Gamma(N+1) = \int_0^\infty e^{-x} x^N dx = \int_0^\infty e^{-S(x)} dx$$

$$S(x) \approx S(x_0) + \frac{1}{2} \frac{\partial^2 S(x)}{\partial x^2} \Big|_{x_0} (x - x_0)^2 + \dots, \quad \frac{\partial S_x}{\partial x} \Big|_{x_0} = 0$$

$$\Rightarrow N! \simeq N^N e^{-N} (2\pi N)^{\frac{1}{2}}$$

**1.1.2.2.3 Gibbs' Entropy** Open system:  $S = -k_B \sum_i P_i \ln P_i$ . 微观态处于  $|i\rangle$  的概率为  $P_i$ .

1. 使得  $S$  最大的  $\{P_i\}$  为等概率分布. [Example] 两状态系统.

2.  $P_i = \frac{e^{-\beta E_i}}{\sum_i e^{-\beta E_i}} = \frac{e^{-\beta E_i}}{Z}$ ,  $S = \frac{\langle E \rangle}{T} + k_B \ln Z$ ,  $-k_B T \ln Z = \langle E \rangle - TS$ .

## 1.1.3 Learn Thermodynamics by Examples/Applications

### 1.1.3.1 Ideal Gas

#### 1.1.3.1.1 Entropy

$$dU = TdS - PdV \Leftrightarrow TdS = dU + PdV$$

If  $V = \text{const.}$ :  $dU = TdS \Rightarrow \frac{\partial S(U, V)}{\partial U} \Big|_V = T(U, V)$

$$S(U, V) - S(U_0, V) = \int_{U_0}^U \frac{1}{T(U, V)} dU, \quad \text{ideal gas: } U = \frac{3}{2} k_B T N$$

$$\Rightarrow S(U, V) - S(U_0, V) = \frac{3}{2} N k_B \ln \left( \frac{U}{U_0} \right);$$

$$\text{similarly, } S(T, V) - S(T_0, V) = \frac{3}{2} N k_B \ln \left( \frac{T}{T_0} \right)$$

[Discussion] 1. Extensivity:  $S \propto N$ ; Dimension(量纲); 2. Physics: log-dependence on  $U$  and  $T$  @ high  $T$  (low response)

#### 1.1.3.2 Electromagnetic Radiation @ Thermodynamic Viewpoint

$$\text{Stafan-Boltzmann Law: } U = bVT^4, \quad b = 7.65 \times 10^{-16} \text{ J/m}^3 \text{K}^4$$

$$dU = TdS - PdV \xrightarrow{\frac{dV}{dV}} \frac{\partial U(T, V)}{\partial V} = T \frac{\partial S(T, V)}{\partial V} - P \quad \frac{\partial S(T, V)}{\partial V} = \frac{\partial P(T, V)}{\partial T} \quad bT^4 = T \frac{\partial P(T, V)}{\partial T} - P \Rightarrow P = \frac{b}{3} T^4$$

$$U = TS - PV \quad (\text{for extensive system}) \Rightarrow P = \frac{1}{3} \frac{U}{V}, \quad S = \frac{4}{3} b^{\frac{1}{4}} U^{\frac{3}{4}} V^{\frac{1}{4}} \sim T^3$$

对光子而言, "化学势" 为 0. 所以很容易因为升温激发出光子.

[Example] 更多高响应体系的例子: 1. Bending rigidity:  $B \sim h^3$ ; 2. Power in fusion:  $\sim B^4$ ;

### 1.1.3.3 Rubber Band

前置: 1. thermodynamic laws(general); 2. equation of state, molecular/microscopic model

**1.1.3.3.1 定性分析** 假定为快速拉伸, 即设  $\Delta Q = 0$ . 拉长后构型减少, 即其构型熵  $S_{\text{conf}}$  减少,  $T\Delta S_{\text{conf}} \downarrow$ ; 长链分子本身也在振动, 振动熵  $S_{\text{vib}}$  上升使得总热量为 0. 因此温度  $T \uparrow$ . 相应地, 一个绷直的橡皮筋快速收缩会  $T \downarrow$ .

假定橡皮筋垂吊一重物  $G$ . 可将其视为一(低效)热机. 收缩之后, 其构型熵增加. 所以若要使得其收缩/做功, 令其吸热即可.

**1.1.3.3.2 定量分析**  $L$ : 长度;  $\tau$ : tension(张力);  $T$ : 温度,  $U$ : 内能.

$L_0 < L < L_1$ ,  $U$  对  $L$  无关;  $\tau$  随着  $T$  升高而增大.

$$U = cL_0T, \quad U \sim T$$

$$\tau = bT \frac{L - L_0}{L_1 - L_0}, \quad \text{self-consistent condition: } \frac{\partial^2 S}{\partial U \partial V} = \frac{\partial^2 S}{\partial V \partial U}$$

$$\Rightarrow dS = \frac{1}{T}dU - \frac{\tau}{T}dL = cL_0 \frac{dU}{U} - b \frac{L - L_0}{L_1 - L_0} dL \xrightarrow{f} S = S_0 + cL_0 \ln \frac{U}{U_0} - b \frac{(L - L_0)^2}{2(L_1 - L_0)}, \quad \text{entropy elasticity}$$

## 1.2 Ensemble Theory

### 1.2.1 Space

描述 gas model 的方法: 列出所有气体粒子的  $(q, p)$ .

#### 1.2.1.1 $\mu$ -space by Ehrenfest

$(x, y, z, v_x, v_y, v_z)$  6-dim space. 其中的一个点描述的是一个粒子的状态. 共需  $N \sim N_A$  个点进行描述.

$$\sum_i \delta(x - x_i) \delta(y - y_i) \delta(z - z_i) \delta(v_x - v_{xi}) \delta(v_y - v_{yi}) \delta(v_z - v_{zi})$$

$$\text{Distribution function: } f(\vec{x}, \vec{v}, t) d^3\vec{x} d^3\vec{v}$$

随着时间推移,  $H = \int f \ln f$  总是趋向于减小. 在达成最小/细致平衡时:  $\vec{x}$ : 均匀;  $\vec{v}$ : Maxwell 分布.

[Discussion] 质疑: 令某一时刻  $t$  下  $\vec{v} \rightarrow -\vec{v}$ , 难道不会使  $H$  回升吗?

#### 1.2.1.2 $\Gamma$ -space

$\{q_1, q_2, q_3, p_1, p_2, p_3, q_4, q_5, q_6, p_4, p_5, p_6, \dots\}$ ,  $6N$ -dim. 空间中的一个点描述的是整团气体某时刻下的状态. 系统的演化即点的运动.

在  $\mu$ -空间中的通过 course-graining 分割的一个  $|k\rangle$  状态格子中, 有着  $n_k$  个粒子. 该格子的体积为 6-dim phase volume  $\omega_k = \Delta \vec{q}_k \Delta \vec{p}_k$ . 相应地, 在  $\Gamma$  空间中由这  $n_k$  个粒子所占据的空间体积为  $\prod_{\alpha=1}^{n_k} \Delta \vec{q}_\alpha \Delta \vec{p}_\alpha = \prod_{\alpha=1}^{n_k} \omega_k = \omega_k^{n_k}$ . 因此所有粒子所占据的空间为  $\prod_k \omega_k^{n_k}$

在给定的  $\{n_k\}$  中, 同状态  $|k\rangle$  的粒子间交换不会产生新的状态数, 因此修正:  $W' = \frac{N!}{\prod_k n_k!} \prod_k \omega_k^{n_k}$ . 该体积和状态数成正比, 那么寻找在  $\sum_k n_k = N$ ,  $\sum_k \varepsilon_k n_k = E$  约束下使得空间体积/状态数极大的  $n_k^* = A \omega_k e^{-\beta \varepsilon_k}$ .

### 1.2.1.3 Geomtry of High-Dimensional Space

#### 1.2.1.3.1 An Illustrative Example: Sphere in $n$ -dim Space

3-dim space:  $S^2, B^3$ ;  $n$ -dim space:  $S^{n-1}, B^n$ .

在  $n$ -dim 欧式空间中的一个点  $x = (x_1, x_2, \dots, x_n)$ .  $\vec{x}$  的长度为  $|x| = \sqrt{\sum_{i=1}^n x_i^2}$ .

体积:  $V(B_R^n) = C_n R^n$ ,  $C_n = \frac{\pi^{\frac{n}{2}}}{\Gamma(\frac{n}{2} + 1)}$ ,  $\Gamma(z+1) \equiv \int_0^\infty t^{-z} e^{-t} dt \stackrel{z \in \mathbb{Z}}{=} z! \approx \sqrt{2\pi z} \left(\frac{z}{e}\right)^z$

$$C_n \stackrel{n \text{ even}}{=} \frac{\pi^{n/2}}{\left(\frac{n}{2}\right)!} \Rightarrow V(B_R^n) \simeq \frac{1}{\sqrt{n\pi}} \left(\sqrt{\frac{2\pi e}{n}}\right)^n R^n, \quad \text{unit sphere: } V(B_R^n) = 1 \Leftrightarrow R = \sqrt{\frac{n}{2\pi e}}$$

设两共心球半径分别为  $R, R(1+\varepsilon)$ . 求夹层(Shell)体积为  $V_{\text{shell}} = V(R)[(1+\varepsilon)^n - 1^n]$ . 即使  $\varepsilon$  很小, 也会随着  $n \uparrow$  使得  $V[R(1+\varepsilon)]$  急剧上升. 即高维空间中体积集中在"边缘".

[Example] 高维酒杯. 要求填满圆锥形酒杯的一半, 随着维度升高, 酒面高度也会升高, 趋近于酒杯边缘.

[Example] 密度均匀,  $n$ -dim, 半径为  $R$  的高维球  $B_R^n$ . 只取单个轴  $x$ , 另一个轴作为垂直  $x$  分量的  $B_R^n$  球切片  $B_{R'}^{n-1}$ , 其中  $R' = R\sqrt{1 - \frac{x^2}{R^2}}$ . 存在  $\int_{-R}^R \rho(x) dx = \int_{-R}^R V(B_{R'}^{n-1}) dx = V(B_R^n)$ , 求  $\rho(x)$  表达式.

$$\frac{V(B_{R'}^{n-1})}{V(B_R^{n-1})} = \left(\frac{R'}{R}\right)^{n-1} = \left(1 - \frac{x^2}{R^2}\right)^{\frac{n-1}{2}} \simeq e^{-(n-1)x^2/2R^2}; \text{ For a unit ball, } R = \sqrt{\frac{n}{e}} \Rightarrow \rho(x) \simeq e^{-ex^2/2} V(B_1^{n-1})$$

#### 1.2.1.3.2 The Geometric Deviation Principle

Minkowski 求和. 点集  $A+B$  对应于  $\vec{a} + \vec{b}$ .  $A, B$  本身具有一定的形状.

Brunn-Minkowski inequality:  $[V(A+B)]^{1/n} \geq [V(A)]^{1/n} + [V(B)]^{1/n}$ .  $A$  和  $B$  为齐形凸体, 即  $A = \alpha B + x$  时取等.

Isoperimetric principle: 等面积, 求周长最小; 等体积, 求表面积最小.

设  $n$ -dim 无定形点集  $C$  和  $n$ -dim 球点集  $B$ , 两者体积相同  $V(C) = V(B) = V(B_R^n)$ . 设  $\epsilon \rightarrow 0$ ,  $C + \epsilon B$  使得在  $C$  表面增加薄壳. 那么  $C$  的  $(n-1)$ -dim 表面积(Area)可借该薄壳体积除以厚度  $\epsilon$  得到:  $\text{Area} = \lim_{\epsilon \rightarrow 0} \frac{V(C + \epsilon B) - V(C)}{\epsilon}$ . 不等式:  $V(C + \epsilon B)^{1/n} \geq V(C)^{1/n} + V(\epsilon B)^{1/n} = V(C)^{1/n} + (\epsilon^n V(B))^{1/n} \Rightarrow \text{Area} \geq \lim_{\epsilon \rightarrow 0} \frac{[(1+\epsilon)^n - 1]}{\epsilon} V(B) \approx n \cdot V(B)$ ,  $C$  为球时取等. 于是"等体积, 表面积最小时为球"得证.

[Example] 取两铁环沾肥皂水, 铁环间由肥皂水薄膜相连. 几何: curvature; 物理: surface tension. Laplace preessure:  $p \propto \sigma \bar{H}$ .

[Example] 悬链线(Catenary Curve).

类比不等式  $\frac{x+y}{2} \geq \sqrt{xy}$ , 那么  $\sqrt{[V(C)V(D)]} \leq V\left[\frac{C+D}{2}\right] \leq \left(1 - \frac{\epsilon^2}{8}\right)^n V(B)$ .  $\epsilon$  为不对齐程度.

设单位体积球点集  $B$ , 而  $C$  占据  $B$  体积的  $\frac{1}{2}$ , 剩下的  $\frac{1}{2}$  体积为  $D$ . 即有  $V(C) = \frac{1}{2}V(B)$ . 那么  $M = \frac{C+D}{2}$  所能占据的体积是有限的. 代入  $V(B) = 1$  得  $V(D) \leq 2(1 - \frac{1}{8}\epsilon^2)^{2n} \times V(B) = 2e^{-n\epsilon^2/4}V(B)$ .

[Example] 考虑  $n$ -dim 球的球面  $S^{n-1}$ , 在球面上有一分布函数  $f$  且随球面坐标缓慢变化. 找到  $f$  的中位数  $M$ , 分界为  $S_1(f < M)$  和  $S_2(f > M)$ . 令  $S_1$  向  $S_2$  方向膨胀微薄一层, 得到  $f = M + \epsilon$  界线; 同样地,  $S_2$  向  $S_1$  方向膨胀后, 得到  $f = M - \epsilon$  界线. 因为  $V(S_1) \ll V(S^{n-1})$  且  $V(S_2) \ll V(S^{n-1})$ , 说明球面上大部分数值都集中在中值  $M$  附近.

#### 1.2.1.3.3 Probability Perspective @ Levy, 1980

Uniform distribution of dots  $\rightarrow$  volume interpreted as the probability.

[Example] Probability theory of large deviation. Toss coin(抛掷硬币):  $X_i = 0, 1$ ; 均值  $M_N = \frac{1}{N} \sum_{i=1}^N X_i$ . 令  $x \in \left(\frac{1}{2}, 1\right)$ ,

$P(M_N > x) < e^{-NI(x)}$ , 其中  $I(x) = x \ln x + (1-x) \ln(1-x) + \ln 2$ . 令  $x = \frac{1}{2} + \epsilon$ , 则  $P(M_N > \frac{1}{2} + \epsilon) < e^{-2N\epsilon^2}$ .

$M_N$ , "macrostate". microstates:  $C_N^{NM_N} = C_N^k$ .

$$C_N^k = \frac{N!}{k!(N-k)!} \Rightarrow \ln C_k = \ln \left[ \frac{N!}{k!(N-k)!} \right] \simeq -N \ln x \ln x - N(1-x) \ln(1-x) = -N[I(x) - \ln 2]$$

$$S = k_B \ln C_N^k$$

[Example]  $[-1, 1] \otimes [-1, 1]$  空间内随机撒点. 设  $x + y = 0$  分割线, 该线上的点有  $\lim_{n \rightarrow \infty} \sum_i^n x_i = 0$ ; 相应地, 若  $\lim_{n \rightarrow \infty} x + y = \epsilon$  描述了偏离中心线的程度.

## 1.2.2 From Dynamics to Probability Description

Measurement: time-average. Phase space with macroscopic constraint: ensemble-average. Poincare recurrence theorem(庞加莱回归定理)

$$\text{时间平均: } \langle f \rangle_t = \frac{\sum_i f_i \tau_i}{\sum_i \tau_i}$$

Course-grained description of phase space:  $f_i = f_\alpha, \quad \forall i \in \alpha.$

$$\begin{aligned} \langle f \rangle_t &= \frac{1}{T} \sum_\alpha f_\alpha t_\alpha, \quad t_\alpha = \sum_{i \in \alpha} \tau_i \\ &= \sum_\alpha f_\alpha \times \left( \frac{t_\alpha}{T} \right) = \sum_\alpha f_\alpha p_\alpha, \quad \text{prob description: } p_\alpha = \frac{t_\alpha}{T} \end{aligned}$$

Formal presentation: in equilibrium,

$$\begin{aligned} \text{ensemble average} \\ \langle f \rangle_e &= \langle \langle f \rangle_e \rangle_t = \langle \langle f \rangle_t \rangle_e \\ \left\langle \lim_{T \rightarrow \infty} \langle f \rangle_t \right\rangle_e &= \lim_{T \rightarrow \infty} \langle f \rangle_t : \quad \text{ergodic(各态历经), 初态无关} \\ \langle f \rangle_e &= \lim_{T \rightarrow \infty} \langle f \rangle_t \end{aligned}$$

不同情况下的 microstate: 1. In  $\Gamma$ -space( $6N$ -dim),  $(q, p)$ ; 2.  $|n\rangle$ ; 3.  $\sigma = \pm 1$ ; 4.  $\sigma = \{0, 1\}$ ...

Representative point  $\leftrightarrow$  one gas. Density function(continuum description)  $\sum_i \delta(x - x_i) \rightarrow \rho(x).$

$$\langle f \rangle = \frac{\sum_\alpha f_\alpha p_{\alpha,t}}{\sum_\alpha p_{\alpha,t}} \Rightarrow \frac{\int f(q, p) \rho(q, p, t) d^{3N} q d^{3N} p}{\int \rho(q, p, t) d^{3N} q d^{3N} p}$$

equilibrium condition:  $\langle f \rangle$  time-invariant  $\rightarrow \frac{\partial \rho}{\partial t} = 0$

[Discussion] 若  $\rho(q, p, t) = g(q, p) f(t)$ ,  $\langle f \rangle$  在数学上也是平衡的. 这种情况下需要考虑到

$$\int g(q, p) f(t) d^{3N} q d^{3N} p = N \Rightarrow f(t) = \text{const.} \Rightarrow \frac{\partial \rho}{\partial t} = 0.$$

### 1.2.2.1 Dynamics

#### 1.2.2.1.1 A Single Representative Point in $\Gamma$ -Space

Hamiltonian 力学:  $\dot{q}_i = \frac{\partial H}{\partial p_i}, \quad \dot{p}_i = -\frac{\partial H}{\partial q_i}$ . 特征: 1. 轨迹不可能自相交; 2. 回归定理.

1.2.2.1.2 Multiple Representative Points 在  $\Gamma$ -空间中选取一个体积  $\omega$ , 将会有  $\int_\omega \rho(q, p, t) d\omega$  个代表点. 其表面为  $\partial\omega$ . 代表点在  $\Gamma$ -空间中的运动速度为  $\vec{v}_i = \{\dot{q}_i, \dot{p}_i\}$ . 那么存在关系

$$\begin{aligned} \frac{\partial}{\partial t} \int_\omega \rho(q, p, t) d\omega &= - \int_{\partial\omega} \rho \vec{v} \cdot \hat{n} d\sigma = - \int_\omega \nabla \cdot (\rho \vec{v}) d\omega, \quad \nabla = \left( \frac{\partial}{\partial \mathbf{q}}, \frac{\partial}{\partial \mathbf{p}} \right) \\ \Rightarrow \frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \vec{v}) &= 0, \quad \text{Continuity Equation} \end{aligned}$$

Material derivative. 设  $g(\vec{x}, t)$ , flow field:  $\vec{v}(\vec{x}, t)$ .

$$g(\vec{x} + \delta\vec{x}, t + \delta t) - g(\vec{x}, t) = g(\vec{x}, t) + \delta\vec{x} \frac{\partial g}{\partial \vec{x}} + \delta t \frac{\partial g}{\partial t} - g(\vec{x}, t) = \delta\vec{x} \frac{\partial g}{\partial \vec{x}} + \delta t \frac{\partial g}{\partial t} = \delta t \left( \vec{v} \cdot \frac{\partial g}{\partial \vec{x}} + \frac{\partial g}{\partial t} \right)$$

$$\frac{Dg}{Dt} \equiv \frac{g(\vec{x} + \delta\vec{x}, t + \delta t) - g(\vec{x}, t)}{\delta t} = \vec{v} \cdot \frac{\partial g}{\partial \vec{x}} + \frac{\partial g}{\partial t}$$

Liouville's theorem:  $\frac{D\rho(q, p, t)}{Dt} = \frac{\partial \rho}{\partial t} + \vec{v} \cdot \nabla \rho = \frac{\partial \rho}{\partial t} + \sum_i \left( \dot{q}_i \frac{\partial \rho}{\partial p_i} + \dot{p}_i \frac{\partial \rho}{\partial q_i} \right)$

$$= \frac{\partial \rho}{\partial t} + \sum_i \left( \frac{\partial H}{\partial p_i} \frac{\partial \rho}{\partial p_i} - \frac{\partial H}{\partial q_i} \frac{\partial \rho}{\partial q_i} \right) = \boxed{\frac{\partial \rho}{\partial t} + \{\rho, H\} = 0}$$

[Discussion] How to understand  $\frac{D\rho}{Dt} = 0$ ? 1. canonical transform; 2. incompressibility ( $\nabla \cdot \vec{v} = 0$ )

$$\frac{\partial \rho}{\partial t} + \nabla(\rho \vec{v}) = 0 \Rightarrow \frac{\partial \rho}{\partial t} + \vec{v} \cdot \nabla \rho + \rho \nabla \cdot \vec{v} = 0 \Rightarrow \nabla \cdot \vec{v} = 0$$

check:  $\nabla \cdot \vec{v} = \sum_i \left( \frac{\partial}{\partial q_i} \dot{q}_i + \frac{\partial}{\partial p_i} \dot{p}_i \right) = \sum_i \left( \frac{\partial}{\partial q_i} \frac{\partial H}{\partial p_i} - \frac{\partial}{\partial p_i} \frac{\partial H}{\partial q_i} \right) = 0$

$H$ -dynamics  $\Leftrightarrow$  incompressibility of representative points.

若  $\rho$  为  $H$  函数  $\rho(H)$ , 则  $\{\rho, H\} = 0 \Rightarrow \frac{\partial \rho}{\partial t} = 0$ , 即达成 equilibrium; 两种可能: 1.  $\rho = \text{const.}$ ; 2. @Gibbs: canonical  $\Rightarrow \ln \rho \propto H$

### 1.2.3 Microcanonical Ensemble

气体模型 macrostate:  $(E, N, V)$ , to construct an ensemble of microstates. surface of  $(6N - 1)$ -dim.

[Discussion] 可能总动量  $\vec{P} \neq \vec{0}$ , 总角动量  $\vec{L} \neq \vec{0}$ . 以动量为例子:

$$\underbrace{p_{1x}^2 + p_{1y}^2 + p_{1z}^2}_{\text{1st particle}} + p_{2x}^2 + \cdots + p_{Nz}^2 \stackrel{\text{ideal gas}}{=} 2mE, \quad P_z = \sum_{i=1}^N p_{iz} \rightarrow 0, \text{ due to high dimension.}$$

[Example] 2-state system.  $|1\rangle : N_1, |2\rangle : N_2. \quad P_1 = \frac{N_1}{N_1 + N_2}, P_2 = \frac{N_2}{N_1 + N_2} \Rightarrow \langle f \rangle = f_1 P_1 + f_2 P_2.$

Equilibrium density function?  $\rho(q, p) = \begin{cases} \text{const.} & H(q, p) \in \lim_{\Delta \rightarrow 0} \left[ E - \frac{\Delta}{2}, E + \frac{\Delta}{2} \right] \\ 0, & \text{others} \end{cases}$

Foudation of equilibrium: 等概率假设, 且为 ergodicity(各态历经).

Closed system:  $S = k_B \ln \Omega, \quad \Omega = \frac{\omega}{\omega_0}, \quad \omega$ : allowed region of motion,  $\omega_0$ : some constant

$$\delta q \delta p \sim h \Rightarrow (\delta \mathbf{q} \delta \mathbf{p}) \sim h^{3N} \Rightarrow \omega_0 = h^{3N}$$

$$\Omega = \frac{1}{N! h^{3N}} \int_{\omega} d^3 \vec{q}_1 d^3 \vec{q}_2 \cdots d^3 \vec{q}_N d^3 \vec{p}_1 d^3 \vec{p}_2 \cdots d^3 \vec{p}_N, \quad \text{N! to make } S \text{ is extensive}$$

$\Rightarrow$  indistinguishability of microscopic particles

#### 1.2.3.1 Equation of State for Ideal Gas

Derive the equation of state by microcanonical ensemble method.

理想气体的内能表达式:  $\sum_{i=1}^N |\vec{p}_i|^2 = 2mE$ . 等能面为  $(3N - 1)$  维球面, 且球面半径约为  $\sqrt{E}$ . 那么相空间体积/微观态数

$$\Omega \sim (\sqrt{E})^{3N-1} \sim E^{3N/2}. \text{ 克劳修斯熵 } S = k_B \ln \Omega = \frac{3}{2} k_B N \ln E + \text{const.}; \text{ 1st law: } \frac{1}{T} = \left( \frac{\partial S}{\partial E} \right)_V \Rightarrow E = \frac{3}{2} N k_B T.$$

在 1D 下存在关系  $p \cdot L \sim \pi \Rightarrow p \sim \frac{1}{L} \Rightarrow \delta p \sim \frac{1}{L}$ , 则更良的微观态数表达式为  $\Omega \sim \frac{(\sqrt{E})^{3N-1}}{(\delta p)^{3N}} \xrightarrow{V \sim L^3} (E^{3/2} V)^N$ ,

$$S = k_B \ln \Omega = N k_B \left( \frac{3}{2} \ln E + \ln V + \text{const.} \right) \Rightarrow \left( \frac{\partial S}{\partial V} \right)_E = \frac{N k_B}{V} \Rightarrow dS = \frac{3}{2} N k_B \frac{dE}{E} + N k_B \frac{dV}{V} = \frac{dE}{T} + \frac{PdV}{T},$$

观察比较得到  $N k_B \frac{dV}{V} = \frac{PdV}{T} \Rightarrow P = \frac{N}{V} k_B T.$

### 1.2.3.2 Dilute Hard Sphere System

各小球可占体积为因各自体积而相互减少. 设小球半径为  $a$ , 体积为  $\omega_e = \frac{4}{3}\pi(2a)^3$ . 接触距离至少为球心间距所以是  $2a$ .

微观态数为  $\Omega = \frac{1}{N!h^N} \int d^3\vec{q}_1 d^3\vec{q}_2 \cdots d^3\vec{q}_N d^3\vec{p}_1 d^3\vec{p}_2 \cdots d^3\vec{p}_N$ , 其中

$$\int d^3\vec{q}_1 \cdots d^3\vec{q}_N = V(V - \omega_e)(V - 2\omega_e) \cdots [V - (N-1)\omega_e] = \prod_{i=0}^{N-1} (V - i\omega_e) \stackrel{\ln}{\Rightarrow} \ln \prod_{i=0}^{N-1} (V - i\omega_e) = \sum_{i=0}^{N-1} \ln(V - i\omega_e).$$

使用极限  $\ln(x + \delta x) \Leftrightarrow \ln x + \frac{1}{x}\delta x$ , 则  $\sum_{i=0}^{N-1} \ln(V - i\omega_e) = \sum_{i=0}^{N-1} \left( \ln V - \frac{i\omega_e}{V} \right) = N \ln V - \frac{\omega_e}{V} \frac{(N-1)N}{2}$

$$\simeq N \left( \ln V - \frac{\omega_e N}{2V} \right) \simeq N \ln \left( V - \frac{\omega_e N}{2} \right) \Rightarrow \int d^{3N}q = \left( V - \frac{\omega_e N}{2} \right)^N$$

[Exercise] 设有  $N$  个硬球, 半径  $a$ , 约定  $\omega_e = \frac{4}{3}\pi(2a)^3$ , 体系能量为  $E$ , 总体积为  $V$ , 温度为  $T$ . 尝试计算  $S(E, V)$ , 状态方程.

$$[\text{Hint: Area}(S^{n-1}) = \frac{2\pi^{\frac{n}{2}}}{\Gamma(\frac{n}{2})} R^{n-1}]$$

### 1.2.3.3 Einstein's Model for Heat Capacity of Solid(1907)

Excitations  $\rightarrow$  Solid property? Quantum?

$N$  atoms, 等效于  $3N$  independent oscillators. Total energy:  $U$ , distributed to  $3N$  oscillators. 等效为将  $\frac{U}{\hbar\omega_0}$  个竖隔板插入由  $3N$  个球间隔出的  $(3N-1)$  的缝隙中.

$$\text{微观态数 } W = \frac{\left[ (3N-1) + \left( \frac{U}{\hbar\omega_0} \right) \right]!}{(3N-1)! \left( \frac{U}{\hbar\omega_0} \right)!}, \text{ 则每 1 mol 原子的熵为 } s(u) = k_B \ln W \simeq 3R \left[ \ln \left( 1 + \frac{u}{u_0} \right) + \frac{u}{u_0} \ln \left( 1 + \frac{u_0}{u} \right) \right],$$

其中  $s = \frac{S}{N/N_A}$ ,  $u = \frac{U}{N/N_A}$ ,  $u_0 = 3N_A \hbar\omega_0$ . 压强是某量对体积的偏导数  $P = \frac{\partial \sharp}{\partial V}$ ,  $\sharp: U, S \cdots$ , 热容则是  $c = T \frac{\partial S}{\partial T}$ .

温度  $\frac{1}{T} = \left[ \frac{\partial S(U)}{\partial U} \right] = \frac{k_B}{\hbar\omega_0} \ln \left( 1 + \frac{3}{u} \hbar\omega_0 \right)$ , 代入即有  $\frac{1}{3N_A} u(T) = \frac{\hbar\omega_0}{e^{\hbar\omega_0/k_B T} - 1}$ , 正是 Boson 行为.

$$\text{热容为 } c = \frac{\partial u}{\partial T} = 3N_A k_B \left( \frac{\hbar\omega_0}{k_B T} \right)^2 e^{-\frac{\hbar\omega_0}{k_B T}}.$$

## 1.2.4 Canonical Ensemble

Macrostate:  $(N, V, T)$ . 能量允许涨落. 又名: Entropy representation.

Equilibrium density function? @Gibbs:  $\frac{\partial \rho}{\partial t} = -\vec{v} \cdot \nabla \rho$ . If equilibrium  $\frac{\partial \rho}{\partial t} = 0$ , then  $\vec{v} \cdot \nabla \rho = 0$ .

$$\sum_i \left( \dot{q}_i \frac{\partial \rho}{\partial q_i} + \dot{p}_i \frac{\partial \rho}{\partial p_i} \right) = 0 \Rightarrow \sum_i \left( \frac{\partial H}{\partial p_i} \frac{\partial \rho}{\partial q_i} - \frac{\partial H}{\partial q_i} \frac{\partial \rho}{\partial p_i} \right) = 0. \text{ 若 } \rho \text{ 为 } H \text{ 函数 } \rho(H), \text{ 则方程自动满足.}$$

$$\rho_{1+2} = \rho_1 \times \rho_2, \quad H_{1+2} = H_1 + H_2 \Rightarrow \ln \rho \propto \alpha H \Rightarrow \rho \propto e^{\alpha H}$$

### 1.2.4.1 Connection to Microcanonical Ensemble

**1.2.4.1.1 Environment & System Perspective** 设环境为  $A'$ , 处于态  $|r'\rangle$ ; 体系为  $A$ , 处于态  $|r\rangle$ ,  $A + A'$  整体是孤立系统. 那么有  $E_r + E_{r'} = E^{(0)} = \text{const.}$ ; 设  $\Omega'$  为环境微观态数, 则体系处于态  $|r\rangle$  的概率  $P_r \propto \Omega'(E_{r'}) = \Omega'(E^{(0)} - E_r)$ . 假定体系所占能量足够小, 即  $E_r \ll E^{(0)}$ , 则可 Taylor 展开:  $\ln \Omega'(E^{(0)} - E_r) = \ln \Omega'(E^{(0)}) + \frac{\partial \ln \Omega'}{\partial E'} \bigg|_{E'=E^{(0)}} (-E_r) + \cdots = \text{const.} - \beta E_r$

$$\text{于是得到 Boltzmann factor/Canonical distribution } P_r = \frac{e^{-\beta E_r}}{\sum_r e^{-\beta E_r}}.$$

[Discussion] Taylor 展开时, 为何不需要保留更高次?  $\Rightarrow$  为了保持  $S$  的广延性.

**1.2.4.1.2 Multiple Systems Perspective** 制备  $N$  个正则系综, 整体组成一个微正则系综. 设  $n_r$  个系统处于状态  $|r\rangle$ , 能量为  $E_r$ . 则存在约束条件  $\sum_r n_r = N$ ,  $\sum_r n_r E_r = NU = N\langle E_r \rangle$ . 微观态数为  $W = \frac{N!}{\prod_r n_r!}$ , 寻找  $\{n_r\}$  使得  $W$  最大化.

$$\Rightarrow \frac{n_r^*}{N} = \frac{e^{-\beta E_r}}{\sum_r e^{-\beta E_r}}.$$

[Discussion] Why is  $\ln \rho \propto \alpha E \Rightarrow \rho \propto e^{\alpha E}$  simple: 1. No dynamics information; 2. Time-reversal symmetry. Detailed-balance(细致平衡); 3. 具有可加性. 引申为  $\ln \rho = \alpha + \beta E$ ; 4. 设  $f(\epsilon)$  为体系处于能量  $\epsilon$  的概率, 则有  $\frac{f(\epsilon_1)}{f(\epsilon_2)} = \frac{f(\epsilon_1 + \epsilon)}{f(\epsilon_2 + \epsilon)}$ . 定义

$$f(\epsilon) = g(\epsilon - \epsilon_2) \Rightarrow g(\epsilon)g(\epsilon_1 - \epsilon_2) = g(0)g(\epsilon_1 - \epsilon_2 - \epsilon) \Rightarrow g(\epsilon) = g(0)e^{-\beta\epsilon} \Rightarrow \frac{f(\epsilon_1)}{f(\epsilon_2)} = e^{-\beta(\epsilon_1 - \epsilon_2)}$$

## 1.2.4.2 Revisit Maxwell Distribution

### 1.2.4.2.1 Galton's Statistical Model

**1.2.4.2.2 Based on Symmetry** 各向同性:  $f(\vec{v}) = f(v) = f_0(v_x)f_0(v_y)f_0(v_z)$

**1.2.4.2.3 Boltzmann** 能量离散化.  $\exists \{n_r\}$ , s.t.  $W = \frac{N!}{\prod_\alpha n_\alpha!}$

**1.2.4.2.4 Based on Ensemble Theory** 能量中动量和位置分离:  $E(q, p) = K(p) + U(q)$

因此统计独立:  $\rho(q, p) \propto e^{-\beta E(q, p)} \Rightarrow \rho(q, p) = A e^{-\beta[K(p) + U(q)]} = A e^{-\beta K(p)} \cdot e^{-\beta U(q)}$ .

其中动能部分:  $e^{-\beta K(p)} = \exp \left[ -\beta \left( \frac{p_1^2}{2m} + \frac{p_1^2}{2m} + \dots + \frac{p_N^2}{2m} \right) \right] = e^{-\beta \frac{p_{1x}^2}{2m}} e^{-\beta \frac{p_{1y}^2}{2m}} e^{-\beta \frac{p_{1z}^2}{2m}} \dots e^{-\beta \frac{p_{Nz}^2}{2m}}.$

New perspective on gas model: 将各粒子单独视为一个系统, 只有  $E$  交换而没有  $N$  交换:  $\rho_1 = A e^{-\beta \frac{p_1^2}{2m}}$

**1.2.4.2.5 Geometric Viewpoint** 在  $(p_{1x}, p_{1y}, p_{1z}, p_{2x}, p_{2y}, \dots)$   $3N$ -dim 空间中, 挑任意一轴(以  $p_{1x}$  为例), 系统处于该轴上的概率分布为?  $\Rightarrow \rho(p_{1x}) \sim e^{-\beta p_{1x}^2}$  (Energy partition theorem).

[Example] 受热浴谐振子:  $H = \alpha p^2 + \beta q^2$ ;  $\langle \alpha p^2 \rangle = \int \alpha p^2 A^{-\beta H} dq dp = \frac{1}{2} k_B T$ .

[Example] 推广:  $H = \sum_i \alpha p_i^n$ ,  $E_i = \alpha p_i^n$ ,  $\langle E_i \rangle = \int E_i e^{-\beta E_i} dE_i / \int e^{-\beta E_i} dE_i = -\frac{\partial}{\partial \beta} \ln \left( \int e^{-\beta E_i} dp_i \right)$ .

Let  $y = \beta^{\frac{1}{n}} p_i \Rightarrow \int e^{-\beta E_i} dp_i = \beta^{-\frac{1}{n}} \int e^{-\alpha y^n} dy \Rightarrow \langle E_i \rangle = \frac{1}{n} k_B T$ .

## 1.2.4.3 Thermodynamics

[Discussion] 已知 1st law:  $dU = TdS - pdV$ , 如何将  $U(V, S)$  转变为  $V$  和  $T$  的未知函数  $U(V, T)$ .

定义  $F \equiv U - TS$ , 全微分  $dF = -pdV - SdT \Rightarrow F(V, T)$ . 因此正则系综  $(N, V, T)$  也被称作  $F$ -representation.

类似地, 定义  $G \equiv F + PV$  从而得到  $P$  和  $T$  的函数  $G(P, T)$ .  $G = \mu N$ .

$$\text{平均能量 } \langle E_r \rangle = \frac{\sum_r E_r e^{-\beta E_r}}{\sum_r e^{-\beta E_r}} = -\frac{\partial}{\partial \beta} \ln \left( \sum_r e^{-\beta E_r} \right)$$

$$\text{内能 } U = F + TS = F - T \left( \frac{\partial F}{\partial T} \right)_{N, V} = \frac{\partial}{\partial (1/T)} \left( \frac{F}{T} \right)_{N, V}$$

记  $\beta = \frac{1}{k_B T}$ , 则自由能  $F = -k_B T \ln Q_N(V, T)$ , 其中正则配分函数对状态  $|r\rangle$  求和形式为  $Q_N = \sum_r e^{-\beta E_r}$ .

求  $\langle \ln P_r \rangle = \left\langle \ln \left( \frac{e^{-\beta E_r}}{Q_N} \right) \right\rangle = -\ln Q_N - \beta \langle E_r \rangle = \beta(F - U) = -\frac{S}{k_B} \Rightarrow S = -k_B \sum_r P_r \ln P_r$ , 正是 Gibbs entropy 形式.

对能量  $i$  求和形式:  $Q_N = \sum_i g_i e^{-\beta E_i} = \int g(E) e^{-\beta E} dE$ , 其中  $g_i$  为 degeneracy of energy level  $E_i$  (能级的简并度).

微观态数/Γ-相空间体积的形式:  $Q_N = \frac{1}{N! h^{3N}} \int e^{-\beta H(q,p)} d^{3N} q d^{3N} p$

[Discussion]  $Q_N = \sum_r e^{-\beta E_r}$ , 根据  $e^{-\beta E_r}$  能定论  $E_r = 0$  是概率最高的能量吗?  $(E_r)_{\text{most prob}} = U$ . 因为还存在着  $g(E)$  调控了概率, 使得  $U$  才是真正概率最高的能量.  $e^{-\beta U} e^{S/k_B}$ .

#### 1.2.4.4 Fluctuations

已知内能  $U$  可通过对正则配分函数求  $\beta$  偏导得到:  $U = -\frac{\partial}{\partial \beta} \left( \ln \sum_r e^{-\beta E_r} \right)$ . 若再对  $U$  求一次  $\beta$  偏导, 则有

$$\frac{\partial U}{\partial \beta} = -\frac{\sum_r E_r^2 e^{-\beta E_r}}{\sum_r e^{-\beta E_r}} + \left( \frac{\sum_r E_r e^{-\beta E_r}}{\sum_r e^{-\beta E_r}} \right)^2 = -\langle E^2 \rangle + \langle E \rangle^2 \equiv \langle (\Delta E)^2 \rangle = k_B T^2 C_v$$

定义相对变化量/涨落为  $\frac{\sqrt{\langle (\Delta E)^2 \rangle}}{\langle E \rangle} = \frac{\sqrt{k_B T^2 C_v}}{U} \sim N^{-\frac{1}{2}}$

[Example] Classical harmonic oscillator ( $\varepsilon_n = n h \nu$ ). Single oscillator:

$$\langle E_1 \rangle = \frac{\sum_n \varepsilon_n e^{-\beta \varepsilon_n}}{\sum_n e^{-\beta \varepsilon_n}} = \frac{h \nu}{e^{\beta h \nu} - 1}. \quad \langle E_1^2 \rangle = (h \nu)^2 \frac{1 + e^{\beta h \nu}}{(e^{\beta h \nu} - 1)^2}, \quad \langle (\Delta E_1)^2 \rangle = (h \nu)^2 \frac{e^{\beta h \nu}}{(e^{\beta h \nu} - 1)^2}, \quad \frac{\sqrt{\langle (\Delta E_1)^2 \rangle}}{\langle E_1 \rangle} = e^{\frac{1}{2} \beta h \nu}. \quad T \rightarrow 0,$$

涨落趋于发散.

$$N \text{ oscillators: } \langle (\Delta E)^2 \rangle = N \langle (\Delta E_1)^2 \rangle, \quad \frac{\sqrt{\langle (\Delta E)^2 \rangle}}{\langle E \rangle} = N^{-\frac{1}{2}} \frac{\sqrt{\langle (\Delta E_1)^2 \rangle}}{\langle E_1 \rangle}.$$

[Example] Relative fluctuation of speed in Maxwell distribution.  $f(v) = A \exp \left\{ -\frac{m v^2}{2 k_B T} \right\} v^2 dv$ , where  $v^2$  for 3D gas.

$$\langle g(v) \rangle = \frac{\int g(v) f(v) dv}{\int f(v) dv}, \quad \frac{\sqrt{\langle v^2 \rangle}}{\langle v \rangle} = \sqrt{\frac{3\pi}{8} - 1}$$

[Example] Ideal gas.  $H = \sum_{i=1}^N \frac{\vec{p}_i^2}{2m}$ .

1. 使用正则系综方法. 配分函数为

$$Q_N(V, T) = \sum_r e^{-\beta E_r} = \frac{1}{N! h^{3N}} \int e^{-\beta \sum_{i=1}^N \frac{\vec{p}_i^2}{2m}} d^{3N} q d^{3N} p = \frac{1}{N!} \left( \frac{1}{h^3} \int_{-\infty}^{+\infty} e^{-\beta \frac{p_1^2}{2m}} 4\pi p_1^2 dp_1 \underbrace{\int_V d^3 \vec{q}_1}_V \right)^N = \frac{Q_1(T, V)^N}{N!},$$

即各粒子统计独立. 单粒子配分函数  $Q_1 = \frac{V}{h^3} (2\pi m k_B T)^{\frac{3}{2}} = \frac{V}{\lambda_T^3}$ , 其中  $\lambda_T = \frac{h}{\sqrt{2\pi m k_B T}}$  为热波长. 粒子间平均间距可估算为  $a \sim \left( \frac{V}{N} \right)^{\frac{1}{3}}$ . 若  $\lambda_T \ll a$ , 即可认为  $h \rightarrow 0$ , 无量子效应. 更一般性地, 若 Hamiltonian 仅为动量  $p$  的函数  $H = H(p)$ , 则单粒子配分函数形为  $Q_1 = V f(T)$ . 当  $H = \sum_i \frac{p_i^2}{2m}$  特殊情形时, 有  $f(T) = \lambda_T^{-3}$ . 继续一般性的讨论:

$$\ln Q_N = \ln \left[ \frac{(V f(T))^N}{N!} \right] = N \ln f(T) + \ln \frac{V^N}{N!} = N \ln f(T) + \ln \left( \frac{e^N}{N^N} V^N \right) = N \ln f(T) + N \ln \left( \frac{eV}{N} \right)$$

记  $n = \frac{N}{V}$ , 则  $\frac{F}{V} = n k_B T \left[ \ln \left( \frac{n}{f} \right) - 1 \right] \Rightarrow P = \left( \frac{\partial F}{\partial V} \right)_{N, T} = \frac{N k_B T}{V}$ , 和理想气体相同. 这说明满足该形式的状态方程,



真正重要的是各粒子统计独立.

$$S = - \left( \frac{\partial F}{\partial T} \right)_{N,V} = k_B V \left[ -n \ln \left( \frac{n}{f} \right) + \frac{5}{2} n \right], \text{ extensive by adding } N!$$

2. 通过态密度分析配分函数.  $Q_N = \int g(E) e^{-\beta E} dE$ ,  $g(E) \sim E^{\frac{3N}{2}-1}$ . 那么概率则是  $P(E) dE = g(E) e^{-\beta E} dE$

概率  $P(E)$  对能量  $E$  导数为 0 以寻找极值点  $E_0$ :

$$\begin{aligned} \frac{\partial}{\partial E} [g(E) e^{-\beta E}] &= g'(E) e^{-\beta E} + g(E) (-\beta) e^{-\beta E} = \left( \frac{3N}{2} - 1 \right) E^{\frac{3N}{2}-2} e^{-\beta E} + E^{\frac{3N}{2}-1} (-\beta) e^{-\beta E} \\ &= \left[ \left( \frac{3N}{2} - 1 \right) E^{-1} - \beta \right] \times \# = 0 \Rightarrow E_0 = \left( \frac{3N}{2} - 1 \right) \frac{1}{\beta} \Rightarrow \lim_{N \rightarrow \infty} E_0 = \frac{3N}{2} k_B T \end{aligned}$$

[Example] Colored Ideal Gas.  $N$  red atoms,  $N$  blue atoms,  $N$  green atoms. Statistically independent. microstate:  $(q, p, \text{color})$

1. 存在三种颜色时的熵  $S_{3c}$ : 单种颜色的配分函数  $Q_N(T, V) = \frac{1}{N!} \left( \frac{V}{\lambda_T} \right)^N$ , 则三种颜色总共的配分函数为  $Q = Q_N^3$ . 那

么自由能为  $F = -k_B T \ln Q = -3k_B T \ln \left( \frac{V}{N \lambda_T} \right)$ . 熵为  $S_{3c} = - \left( \frac{\partial F}{\partial T} \right)_{N,V} = 3N k_B \ln \left( \frac{eV}{N} \right) - 3N f'(T)$

2. 只存在一种颜色时的熵  $S_{1c}$ :  $S_{1c} = 3N k_B \ln \left( \frac{eV}{3N} \right) - 3N f'$

比较以上两个结果, 就会发现由于多出颜色自由度产生的混合熵  $\Delta S = S_{3c} - S_{1c} = k_B \ln 3^{3N}$ .

[Discussion] 1. How to understand  $\ln 3^{3N}$ ? statistically independent  $\rightarrow$  analyze a single particle. 底数 3: 3 种颜色/状态. 2.

$S_{\text{tot}} = S_{\{q,p\}} + S_{\text{color}}$ . 新的自由度独立于  $(q, p)$ , 则熵直接相加.

[Example] 2-state.  $|1\rangle : P_1 = r; |2\rangle : P_2 = 1 - r$ . For a single particle,

$$\tilde{S}_{\text{mix}} = -k_B \sum_{r=1}^2 P_r \ln P_r = -k_B [r \ln r + (1-r) \ln (1-r)]. \text{ 取极值: } r = \frac{1}{2} \Rightarrow \tilde{S}_{\text{mix}} = k_B \ln 2$$

## 1.2.5 Grand Canonical Ensemble

exchange energy, matter.  $(T, V, \mu)$ .  $|rs\rangle$ : 粒子数为  $N_r$ , 能量为  $E_r$ . 令该系统  $A$  与环境  $A'$  整体组成一个孤立系统.

$$P_{rs} = \frac{e^{-\alpha N_r - \beta E_s}}{\sum_{r,s} e^{-\alpha N_r - \beta E_s}}$$

系综中能量的延拓:  $U(S, V, N) \xrightarrow{F=U-TS} F(T, V, N) \xrightarrow{\Phi=F-\mu N} \Phi(T, V, \mu)$ , 即 Grand potential.

$$\langle N \rangle = \sum_{r,s} N P_{rs} = \frac{\sum_{r,s} N_r e^{-\alpha N_r - \beta E_s}}{\sum_{r,s} e^{-\alpha N_r - \beta E_s}} = - \frac{\partial q}{\partial \alpha}, q = \ln \left( \sum_{r,s} e^{-\alpha N_r - \beta E_s} \right). \text{ 可类比于 } \langle E \rangle = - \frac{\partial q}{\partial \beta} \Rightarrow \text{q-potential}$$

$$Q(Z, V, T) = \sum_{N_r=0}^{\infty} Z^{N_r} Q_{N_r}(V, T), \quad Z \equiv e^{-\alpha}, \text{ fugacity(逸度)}$$

导出 Gibbs entropy(for open system):  $\langle \ln P_{rs} \rangle = \sum_{r,s} P_{rs} (\ln P_{rs}) \Rightarrow S = -k_B \sum_{r,s} P_{rs} \ln P_{rs}$ .

$$\text{粒子数涨落: } \langle (\Delta N)^2 \rangle = \frac{\langle N \rangle^2 k_B T \kappa_T}{V} \Rightarrow \frac{\langle (\Delta n)^2 \rangle}{\langle n^2 \rangle} = \frac{k_B T}{V} \kappa_T, \quad \kappa_T = - \frac{1}{V} \left( \frac{\partial V}{\partial T} \right).$$

[Example] **Ideal gas**.  $Q_N(V, T) = \frac{Q_1^N}{N!}$ ,  $Q_1(V, T) = \frac{1}{h^3} \int e^{-\beta \frac{p^2}{2m}} d^3 \vec{q} d^3 \vec{p} = \frac{V}{\lambda_T^3}$ . 若  $H = H(p)$ , 则形式为  $Q_1(V, T) = V f(T)$ .

从巨正则系综角度出发, 配分函数为  $Q(Z, V, T) = \sum_{N_r=0}^{\infty} Z^{N_r} \frac{[V f(T)]^{N_r}}{N_r!} = e^{Z V f(T)}$ , 其中  $Z = e^{-\alpha}$ .

那么 q-potential 为  $q(Z, V, T) = \ln Q = Z V f(T)$ . 各热力学量根据与  $q$  的关系分别导出: 压强  $\langle P \rangle = \frac{k_B T}{V} q = Z k_B T f(T)$ ;

粒子数  $\langle N \rangle = - \frac{\partial q}{\partial \alpha} = Z V f(T)$ ; 内能  $\langle U \rangle = - \frac{\partial q}{\partial \beta} = Z V k_B T^2 f'(T)$ ; 状态方程  $\langle P \rangle V = \langle N \rangle k_B T$ .

[Example] Fluctuation of number of particles. 考虑体系  $(V, N)$  中的小区域  $\Omega$ , 体积为  $v$ , 粒子数为  $n$ . 则  $\Omega$  中有  $n$  个粒子的概率  $P_n = \frac{\sum_s e^{-\alpha n - \beta E_n^{(s)}}}{Q}$ . 猜测平均粒子数为  $\langle n \rangle = \frac{N}{V}v$ . 独立同分布. 单个粒子在/不在  $\Omega$  中的概率:  $P_1 = \frac{v}{V}$ ,  $P_0 = 1 - \frac{v}{V}$ . 则  $\Omega$  中有  $n$  个粒子的概率为  $P(n) = \frac{N!}{(N-n)!n!} P_1^n P_0^{N-n}$ ,  $\lim_{N \rightarrow \infty} P(n)$  将化为 Poisson 分布:  $P(n) = \frac{\langle n \rangle^n}{n!} e^{-\langle n \rangle}$ , 其中  $\langle n \rangle = \frac{N}{V}v$ .

## 1.3 Phase Transition

A system containing many degrees of freedom  $\rightarrow$  exhibits collective behavior.

[Example] 1. condensation of water vapor; 2. critical behavior; 3. magnetic system. ferromagnetism(自发磁化). 加热后化为 paramagnetism  $M \propto H$ . 这些相变存在着共性. 4. fluid-superfluid phase transition(He-3 fermion,  $T_c = 2.491$  mK; He-4 boson,  $T_c = 2172$  K) fermion pair 才可以产生凝聚, 而产生 fermion pair 需要极低温; 5. social/crowd behavior, market price...

$d\mu = v dP - s dT$ , 化学势的一阶导数突变为一级相变(水结冰), 二阶导数突变为二级相变.

### 1.3.1 Van der Waals Theory

motivation: to find the universal law for gas-liquid phase transition.

分子间相互作用势: 近程排斥, 远程吸引. 临界点  $r_0$ . 修正 ideal gas:  $P = \frac{RT}{v-b} - \frac{a}{v^2}$ .  $b$ : hard-core repulsion(硬球排斥);  $a$ : attraction,  $\frac{a}{v^2} \sim n^2 = \left(\frac{N}{V}\right)^2$ . 1.  $T \gg |\varepsilon_0|$ , 可忽略相互作用; 2.  $T \downarrow$ , interaction  $\uparrow$ , condensed state(liquid state); 3.  $T \rightarrow 0$ , crystal state/amorphous state (mechanical in equilibrium).

#### 1.3.1.1 Derivation of Van der Waals Equation

$$Q_N(T, V) = \frac{1}{N! h^{3N}} \int \prod_{i=1}^N d^3 \vec{q}_i d^3 \vec{p}_i \exp \left\{ -\beta \sum_i \frac{p_i^2}{2m} - \beta \sum_{i < j} V(\vec{q}_i - \vec{q}_j) \right\} = \frac{1}{N!} \underbrace{\lambda_T^{3N}}_{\int d^3 \vec{p}} \underbrace{\left( V - \frac{N\omega}{2} \right)^N}_{\text{hard-core repulsion}} e^{-\beta \bar{U}}$$

$$\bar{U} = \frac{1}{2} \sum_{i,j} V_{\text{attract}}(\vec{q}_i - \vec{q}_j) = \frac{1}{2} \int d^3 \vec{r}_1 d^3 \vec{r}_2 n(\vec{r}_1) n(\vec{r}_2) V_{\text{attract}}(\vec{r}_1 - \vec{r}_2) = \frac{1}{2} n^2 V \underbrace{\int V_{\text{attract}}(\vec{r}) d^3 \vec{r}}_u = \frac{1}{2} \frac{N^2}{V} u$$

$$F = -k_B T \ln Q_N(V, T) = -N k_B T \ln \left( V - \frac{N\omega}{2} \right) + N k_B T \ln \left( \frac{N}{e} \right) + 3N k_B T \ln \lambda_T - u \frac{N^2}{2V}$$

$$\Rightarrow P = - \left( \frac{\partial F}{\partial V} \right)_{T, N} = \frac{N k_B T}{V - \frac{N\omega}{2}} - \underbrace{\frac{u}{2}}_a \frac{N^2}{V^2}$$

使用 cluster expansion 对  $V(\vec{q}_i - \vec{q}_j)$  进行处理.

[Example]  $U(r) = \begin{cases} \infty, & r \leq r_0 \\ -U_0 \left( \frac{r_0}{r} \right)^6, & r > r_0 \end{cases}$ .  $B(T) = -2\pi \int_0^\infty [e^{-U(r)/k_B T} - 1] r^2 dr = \frac{2\pi r_0^2}{3} \left( 1 - \frac{U_0}{k_B T} \right)$ ,

$$a = \frac{2\pi r_0^3 U_0}{3}, \quad b = \frac{2\pi r_0^3}{3}$$

**1.3.1.1.1 Simpler Argument** Statistical independence of particles  $\rightarrow$  consider a single particle. Accessible volume(repulsion):  $V - V_0$ ,  $V_0 \propto N \Rightarrow V_0 = bN$ ; potential energy(attraction):  $u \propto \frac{N}{V} = n \Rightarrow u = -a \frac{N}{V}$ .

$$Q_1(V, T) = f(T) \int_{V-V_0} e^{aN/V^T} d^3 \vec{r} = f(T) (V - bN) e^{aN/V^T},$$

$$P = - \left( \frac{\partial F}{\partial V} \right)_{T, N} = k_B T \frac{\partial \ln Q_N}{\partial V} \Big|_{T, N} = k_B T \frac{\partial}{\partial V} \left( \ln \frac{Q_1^N}{N!} \right)_{T, N} \stackrel{\frac{\partial N}{\partial V} = 0}{=} k_B T N \frac{\partial \ln Q_1}{\partial V}$$

### 1.3.2 Phase Diagram

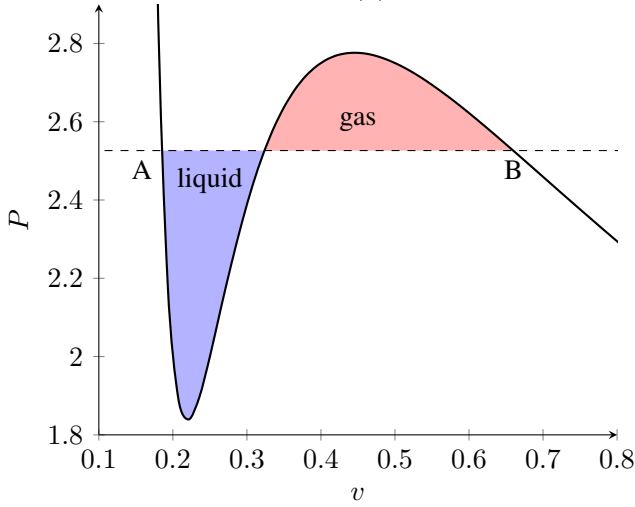
Van der Waals equation: real gas.

Other ways to describe:  $PV = RT \left( 1 + \frac{A_2}{V} + \frac{A_3}{V^2} + \dots \right)$ , or  $\frac{Pv}{k_B T} = 1 + \frac{B(T)}{v} + \frac{C(T)}{v^2} + \dots$

$P = \frac{RT}{v-b} - \frac{a}{v^2}$  数学上是一个  $v$  的三次方程. 存在三个解代表的是 gas-liquid coexistence.  $v_1 = v_l, v_3 = v_g$ . 特殊情况:  $v_1, v_2, v_3 \rightarrow v_c$ , 即 critical point.

#### 1.3.2.1 Maxwell Construction

$G = \mu N$ . 在等温曲线上,  $dG = -SdT + VdP$ . 设  $y = P$  水平线与  $P(v)$  交点左右分别为  $A, B$ . 那么从  $A$  到  $B$  的自由能变化量为  $\Delta G = \int_A^B VdP = \int_A^B [d(PV) - PdV] = P(V_B - V_A) - \int_{V_A}^{V_B} PdV = 0$ , 前后分别是  $y = P$  直线下矩形面积和  $P(v)$  曲线下的面积, 它也可以理解为  $P(v)$  曲线在  $y = P$  水平线上下两面积相等. 也就是说, 在这条水平线上 liquid-gas coexistence.



计算气液两相所占体积:  $v_0 = xv_l + (1-x)v_g \Rightarrow x = \frac{v_g - v_0}{v_g - v_l}$ , 即 lever rule.  $\frac{\partial P}{\partial v} > 0$  是热力学不稳定的.

#### 1.3.2.2 Critical Behavior

Critical point:  $\left. \frac{\partial P}{\partial v} \right|_c = 0$ ,  $\left. \frac{\partial^2 P}{\partial v^2} \right|_c = 0 \Rightarrow P_c = \frac{a}{27b^2}$ ,  $T_c = \frac{8a}{27bR}$ ,  $v_c = 3b$ , material dependent;  $\frac{RT_c}{P_c v_c} = \frac{8}{3}$ , material independent.

$P_r = \frac{P}{P_c}$ ,  $v_r = \frac{v}{v_c}$ ,  $T_r = \frac{T}{T_c} \Rightarrow \left( P_r + \frac{3}{v_r^2} \right) (3v_r - 1) = 8T_r$ . 所以即使是不同类的 Van der Waals gas, 也可以通过判断  $(P_r, v_r)$  相等而判断其处于 corresponding state.

进一步使用小量:  $P_r = 1 + \pi$ ,  $v_r = 1 + \Psi$ ,  $T_r = 1 + t$ , 从而使用  $(\pi, \Psi, t)$  描述临界点附近状态.

**1.3.2.2.1 Along the isothermal curve at  $t = 0 (T = T_c)$**   $\pi = -\frac{3}{2}\Psi^3$ , 3: critical exponent.

**1.3.2.2.2  $\Psi_l$  和  $\Psi_g$  对 critical point 的逼近行为**  $\pi = 4t - 6t\Psi + \frac{3}{2}\Psi^3 \Rightarrow \begin{cases} \pi = 4t - 6t\Psi_l + \frac{3}{2}\Psi_l^3 \\ \pi = 4t - 6t\Psi_g + \frac{3}{2}\Psi_g^3 \end{cases}$ . 原始的  $v_l$  和  $v_g$  是通过

Maxwell construction  $\int dG = 0 \Rightarrow P(V_B - V_A) - \int_{V_A}^{V_B} PdV = 0$  得到的. 使用  $(\pi, \Psi, t)$  重构:

$$\int_{\Psi_l}^{\Psi_g} \pi(\Psi; t) d\Psi = \pi(\Psi_g - \Psi_l) \Rightarrow 4t - 3t(\Psi_g + \Psi_l) - \frac{3}{8}(\Psi_g + \Psi_l)(\Psi_g^2 + \Psi_l^2) = \pi.$$

联立方程组得到  $2\pi = 8t - 6t(\Psi_l + \Psi_g) - \frac{3}{2}(\Psi_l^2 + \Psi_g^2) \Rightarrow (\Psi_g + \Psi_l)(\Psi_g - \Psi_l) = 0 \Rightarrow \Psi_g = -\Psi_l$ .

因此在临界点附近,  $\Psi_l$  和  $\Psi_g$  对称地分布在临界点两侧.

**1.3.2.2.3 Isothermal Compressibility Near the Critical State**  $-\left(\frac{\partial \Psi}{\partial \pi}\right)_t = \begin{cases} \frac{1}{6}t^{-1}, & t > 0 \\ \frac{1}{12}|t|^{-1}, & t < 0 \end{cases}$ ,  $-1$ : critical exponent.

[Example] First observation of critical phenomenon. Water:  $T_c = 373.946^\circ\text{C}$ ,  $P_c = 217.7$  atm.

[Discussion]  $Q(Z, V, T) = \sum_{N=0}^{N_{\max}} Z^N Q_N(V, T)$ ,  $P = \frac{k_B T}{V} \ln Q$ . 级数各项表达式均为解析的. 若要产生奇点(singularity), 应

要求 Thermodynamic limit(热力学极限), 即  $\lim_{N_{\max}, V \rightarrow \infty}$  的同时  $\frac{N}{V} = \text{finite const.}$ .

### 1.3.3 Ising Model: From Thermodynamic Approach to Statistical Approach

$$H(\{\sigma_i\}) = -J \sum_{\langle i, j \rangle} \sigma_i \sigma_j - \mu B \sum_i \sigma_i, \quad \sigma_i = \pm 1 (\text{binary variable})$$

#### 1.3.3.1 Preliminary Analysis

设  $N_+$  个自旋  $\uparrow$ ,  $N_-$  个自旋  $\downarrow$ ; 又令  $N_{++}$  为相邻  $\uparrow\uparrow$  的数,  $N_{--}$  为相邻  $\downarrow\downarrow$  的数,  $N_{+-}$  为相邻  $\uparrow\downarrow$  与  $\downarrow\uparrow$  的数.

通过这些参数重构哈密顿量:  $H_N = -J(N_{++} + N_{--} - N_{+-}) - \mu B(N_+ - N_-)$ .

设  $q$  是各自旋的配位数(对于 Ising Model 即 2), 存在约束关系  $N = N_+ + N_-$ ,  $qN_+ = 2N_{++} + N_{+-}$ ,  $qN_- = 2N_{--} + N_{+-}$ .

因此只有两个独立变量.

$(N_+, N_{++})$  不是单个微观态, 存在着简并. 因此  $H_N(N_+, N_{++}) = -J \left( \frac{1}{2}qN - 2qN_+ + 4N_{++} \right) - \mu B(N_+ - N)$ ,

$$Q_N = \sum_{(N_+, N_{++})} e^{-\beta H_N(N_+, N_{++})} g_N(N_+, N_{++})$$

#### 1.3.3.2 Mean-Field Approximation

Order parameter(序参量):  $L = \frac{1}{N} \sum_i \sigma_i = \frac{N_+ - N_-}{N} \in [-1, +1]$ . 而  $M = \mu(N_+ - N_-) = \mu N L$ .

[Discussion] 为了照顾到  $L = 0$  中“前半全  $\uparrow$ , 后半全  $\downarrow$ ”的特殊情况, 可以进一步定义新的序参量  $S = \frac{N_{++} + N_{--} - N_{+-}}{\frac{1}{2}qN}$ .

即相邻自旋方向相同为有序, 反之为无序. 因此序参量依赖于对“序”的定义.

$$\begin{aligned} H(\{\sigma_i\}) &= -J \sum_{\langle i, j \rangle} \sigma_i \sigma_j - \mu B \sum_i \sigma_i = -\frac{J}{2} \sum_i \left( \sum_{\langle j \rangle} \sigma_j \right) \sigma_i - \mu B \sum_i \sigma_i \\ &= -\frac{J}{2} \sum_i (q\bar{\sigma}) \sigma_i - \mu B \sum_i \sigma_i = -\mu \left( B + \frac{1}{2}B' \right) \sum_i \sigma_i, \quad B' = \frac{qJ}{\mu} \bar{\sigma}, \quad \text{Effective field} \end{aligned}$$

spin flip( $\uparrow \leftrightarrow \downarrow$ ) 引起能量变化  $\delta \varepsilon = \varepsilon_- - \varepsilon_+ = \left( -J \sum_{\langle j \rangle} \sigma_i - \mu B \sigma_i \right)_{\sigma_i=-1} - \left( -J \sum_{\langle j \rangle} \sigma_i - \mu B \sigma_i \right)_{\sigma_i=+1} = 2\mu(B + B')$ .

记  $\bar{N}_{\pm} = N \frac{e^{-\beta \varepsilon_{\pm}}}{\sum_{+, -} e^{-\beta \varepsilon_i}}$ , 则有 **self-consistency function**(自洽方程):  $\frac{\bar{N}_-}{\bar{N}_+} = \frac{1 - \bar{L}}{1 + \bar{L}} = e^{-2\beta(\mu B + qJ\bar{L})}$ ,  $\bar{L} = \bar{\sigma} = \frac{1}{N} \sum_i \sigma_i$ .

等式两边同  $\ln$ , 且引入  $\text{arctanh } x = \frac{1}{2} \ln \left( \frac{1+x}{1-x} \right)$ , 得到  $\beta(qJ\bar{L} + \mu B) = \text{arctanh}(\bar{L})$ , 即  $\bar{L}$  形式的 **Equation of State**.

[Example] 其它使用 Mean-Field approximation 的例子

1. 溶液中 electric potential  $\phi(\vec{r})$ , 粒子分布  $\rho(\vec{r}) = \sum_s e_s n_{s0} e^{-\frac{e_s \phi(\vec{r})}{k_B T}}$ ,  $\nabla^2 \phi(\vec{r}) = -4\pi \rho(\vec{r})$ .

2. 在  $\bar{L} \rightarrow 0$  时, 即有  $\bar{L} \sim M \propto B$ , 即 paramagnetism(顺磁). 非线性项  $\rightarrow$  ferromagnetism(铁磁).

**1.3.3.2.1**  $B = 0$  下的  $\bar{L}$  令  $L_0 = \bar{L}(B = 0)$ , 得到无外场条件下的状态方程  $\bar{L}_0 = \tanh(\beta J q \bar{L}_0)$ .  $\bar{L}_0 \rightarrow 0$  代表可相变.

使用极限  $\lim_{x \rightarrow 0} \tanh(x) \simeq x - \frac{x^3}{3} + O(x^5)$ , 展开状态方程:  $(\beta q J - 1)\bar{L}_0 = \frac{1}{3}(\beta q J \bar{L}_0)^3$ . 若  $\beta q J - 1 > 0 \Leftrightarrow T < \frac{qJ}{k_B} = T_c$ ,

则存在顺磁解  $\bar{L}_0 = 0$ ; 同时还存在着 2 个非零解, 代表系统可自发磁化.

[Discussion] 几何观点:  $y = x$  和  $y = \tanh(\beta J q x)$  的交点. 在高温时只有 1 个交点, 而低温时则能产生 3 个交点.

根据中值定理, 为产生交点, 应存在  $\left. \frac{d \tanh(\beta J \bar{L}_0)}{d \bar{L}_0} \right|_{\bar{L}_0 > 0} = 1 \Rightarrow \frac{qJ}{k_B T_c} = 1$ .

对于  $L_0$ - $T$  相图. 这是一种 continuous phase transition, 属于二阶相变. symmetry abrupt change(对称性突变).

1. 在  $T_c$  左邻域, 有近似  $\lim_{T \rightarrow T_c^-} \bar{L}_0 = \bar{L}_0 \frac{T_c}{T} - \frac{1}{3} \bar{L}_0^3 \left( \frac{T_c}{T} \right)^3 \Rightarrow \bar{L}_0 \simeq 3^{\frac{1}{2}} \left( 1 - \frac{T}{T_c} \right)^{\frac{1}{2}}$ .

2. 在  $T \rightarrow 0$  时, 有近似  $\lim_{T \rightarrow 0} \bar{L}_0 \simeq 1 - 2 \exp \left( -\frac{2T_c}{T} \right)$ , 斜率  $\frac{d \bar{L}_0}{dT} \rightarrow 0$ .

研究在  $B = 0$  时的 Specific Heat(热容). 无外场时系统内能为  $H(\{\sigma_i\}) = -\frac{J}{2} \sum_i (q \bar{\sigma}) \sigma_i = -\frac{1}{2} q J N \bar{L}_0^2$ ;

热容为内能偏导  $c_0 = \frac{\partial U_0}{\partial T} = -q J N \bar{L}_0 \frac{d \bar{L}_0}{dT}$ . 可见其依赖于  $\frac{d \bar{L}_0}{dT}$ ; 因此 1.  $T > T_c$  时,  $c_0 = 0$ ;

2.  $\lim_{T \rightarrow T_c^-}$  时, 对物态方程两边都  $\frac{\partial}{\partial T}$ , 得到  $c_0 = k_B N \frac{T_c}{T} \bar{L}_0^2 \frac{1 - \bar{L}_0^2}{\frac{T_c}{T} - (1 - \bar{L}_0^2)} \simeq \frac{3}{2} N k_B$

研究在  $B = 0$  时的熵  $S_0$ . 1. Statistical method. 熵  $S_0(T \geq T_c) = k_B \ln(2^N) = N k_B \ln 2$ .

2. Thermodynamic method.  $S_0(T \geq T_c) = \int_0^T \frac{c_0(T) dT}{T} = \int_0^{T_c} \frac{c_0(T) dT}{T} + \int_{T_c}^T \frac{c_0(T) dT}{T} = -q J N \int_1^0 \frac{\bar{L}_0}{T} d \bar{L}_0$   
 $= N k_B \int_0^1 \operatorname{arctanh}(\bar{L}_0) d \bar{L}_0 = N k_B \ln 2$

研究  $B = 0$  时的磁化率  $\chi_0$ .

$\chi_0 = \left( \frac{\partial M}{\partial B} \right)_T \Rightarrow \lim_{T \rightarrow T_c^+} \chi_0 \simeq \frac{N M^2}{k_B} \frac{1}{T - T_c}$ ,  $\lim_{T \rightarrow T_c^-} \chi_0 \simeq \frac{N M^2}{2 k_B} \frac{1}{T_c - T}$ ,  $\lim_{T \rightarrow 0} \chi_0 \simeq \frac{4 N M^2}{k_B T} \exp \left\{ -\frac{2 T_c}{T} \right\}$ .

**1.3.3.2.2 Weak External Field**  $B \rightarrow 0$  在  $T \geq T_c$  时, 有  $\bar{L} \simeq \frac{\mu \beta}{1 - \beta q J} B = \frac{\mu}{k_B (T - T_c)} B \Rightarrow \bar{L} \propto B$ , 即 Curie's law.

### 1.3.3.3 Lost Correlation under Mean-Field Approximation

**1.3.3.3.1 概率检验** 取任意两相邻格点  $\langle i, j \rangle$ , 其自旋均为  $\uparrow$  的概率  $P_{++} = \frac{N_{++}}{2^q N}$  是否等价于单自旋  $\uparrow$  概率乘积

$\frac{N_+}{N} \times \frac{N_+}{N} = P_+ \times P_+$ ? 通过 MFT 给出的  $U_0 = -\frac{1}{2} q J N \bar{L}_0^2$ ,  $N_+ = \frac{1}{2} N (1 + \bar{L}_0)$ ,  $H_N(N_+, N_{++})$  进行验证( $\checkmark$ ).

同理  $P_{--} = P_-^2$ ,  $P_{+-} = 2 P_+ P_-$ . 如果 Random mixing(完全随机):  $\frac{N_{++} N_{--}}{N_{+-}^2} = \frac{P_{++} P_{--}}{(P_{+-} + P_{-+})^2} = \frac{P_+^2 P_-^2}{4 P_+^2 P_-^2} = \frac{1}{4}$ .

因此若该值偏离  $\frac{1}{4}$ , 则存在着某种自旋间的 correlation.

**1.3.3.3.2 涨落检验** 将  $\sigma_i$  视为 continuous variable  $\sigma = \langle \sigma_i \rangle + \delta \sigma_i = m + \delta \sigma_i$ , 则

$H = -J \sum_{\langle i, j \rangle} \sigma_i \sigma_j = -J \sum_{\langle i, j \rangle} (m + \delta \sigma_i)(m + \delta \sigma_j) = -J m q \sum_i \delta \sigma_i = -J m q \sum_i (\sigma_i - m) = -J m q \sum_i \sigma_i + \text{const.}$

在处理时运用了  $\delta \sigma_i \delta \sigma_j \rightarrow 0$  的技巧, 这也意味着 lost of correlation of fluctuation.

### 1.3.3.4 Derivation of Equation of State in Terms of Order Parameter $L$

Also as an [Exercise]:

$$\begin{aligned}
 \frac{N_+}{N} &= \frac{1}{2}(1+L), \quad \frac{N_-}{N} = \frac{1}{2}(1-L), \quad L = \frac{N_+ - N_-}{N} \\
 \frac{N_{++}}{\frac{1}{2}qN} &= \left(\frac{N_+}{N}\right)^2 \rightarrow \frac{N_{++}}{N} = \frac{q}{8}(1+L)^2, \quad \text{similarly } \frac{N_{--}}{N} = \frac{q}{8}(1-L)^2, \quad \frac{N_{+-}}{N} = \frac{q}{4}(1-L^2) \\
 U(L) &= -\frac{1}{2}qJNL^2 - \mu BNL \\
 S &= k_B \ln \left( \frac{N!}{N_+!N_-!} \right) \stackrel{N \rightarrow \infty}{\approx} -k_B N \left[ \frac{1+L}{2} \ln \left( \frac{1+L}{2} \right) + \frac{1-L}{2} \ln \left( \frac{1-L}{2} \right) \right] \\
 F(L) &= U - TS = -\frac{1}{2}qJNL^2 - \mu BNL + k_B TN \left[ \frac{1+L}{2} \ln \left( \frac{1+L}{2} \right) + \frac{1-L}{2} \ln \left( \frac{1-L}{2} \right) \right] \\
 \frac{\partial F}{\partial L} &= 0 \Rightarrow -qJNL - \mu BN + \frac{1}{2}k_B TN \left[ \ln \left( \frac{1+L}{2} \right) + 1 - \ln \left( \frac{1-L}{2} \right) - 1 \right] = 0 \\
 &\Rightarrow -qJNL - \mu BN + \frac{1}{2}k_B TN \ln \left( \frac{1+L}{1-L} \right) = 0 \Rightarrow \frac{1}{2} \ln \left( \frac{1+L}{1-L} \right) = \frac{qJL + \mu B}{k_B T} \\
 &\Rightarrow \operatorname{arctanh} L = \beta(qJL + \mu B), \quad \beta = \frac{1}{k_B T}
 \end{aligned}$$

### 1.3.3.5 1st-Order Approximation-Bethe's Method @ 1935

$(q+1)$  system.  $\sigma_0$  感受到  $q$  个  $\sigma_i$  的作用.  $H_{q+1} = -\mu B\sigma_0 - \mu(B+B') \sum_{j=1}^q \sigma_j - J \sum_{j=1}^q \sigma_0 \sigma_j$ . Requirement:  $\bar{\sigma}_0 = \bar{\sigma}_j, \quad \forall j$ .

$$Z = \sum_{\sigma_0=\pm 1} \sum_{\sigma_j=\pm 1} e^{-\beta H_{q+1}} = \bar{Z}_+^{\sigma_0=+1} + \bar{Z}_-^{\sigma_0=-1}, \quad Z_{\pm} = e^{\pm \alpha} [2 \cosh(\alpha + \alpha' \pm \gamma)]^q, \quad \alpha = \frac{\mu B}{k_B T}, \quad \alpha' = \frac{\mu B'}{k_B T}, \quad \gamma = \frac{J}{k_B T}.$$

$$\bar{\sigma}_0 = (+1) \frac{\bar{Z}_+}{Z} + (-1) \frac{\bar{Z}_-}{Z}, \quad \bar{\sigma}_j = \left\langle \frac{1}{q} \sum_j \sigma_j \right\rangle = \frac{1}{q} \frac{1}{Z} \frac{\partial Z}{\partial \alpha'} \quad (\text{类比巨正则系综 } Z = \sum_{r,s} e^{-\alpha N_r - \beta E_s}, \quad \langle N \rangle = -\frac{\partial \ln Z}{\partial \alpha}).$$

$$\text{要求 } \bar{\sigma}_0 = \bar{\sigma}_j \Rightarrow e^{2\alpha'} = \left[ \frac{\cosh(\alpha + \alpha' + \gamma)}{\cosh(\alpha + \alpha' - \gamma)} \right]^{q-1}. \quad \alpha' = \alpha'(\alpha, \gamma).$$

若  $\alpha = 0$  (no external field), 此时  $\alpha' = 0$  解存在(顺磁). 非零解:  $\alpha' = (q-1) \tanh \gamma \left( \alpha' - \operatorname{sech}^2 \gamma \frac{\alpha'^2}{3} \right)$ . 根据中值定理,

$$\text{有解即要求斜率 } \left( \frac{\partial}{\partial \alpha'} \right) \text{ 满足 } (q-1) \tanh \gamma > 1. \text{ 解得 } \gamma_c = \frac{1}{2} \ln \left( \frac{q}{q-2} \right), \quad T_c = \frac{2J}{k_B} \frac{1}{\ln \left( \frac{q}{q-2} \right)}.$$

$$\left[ \text{回忆之前通过 MFT 得到的 } T_c = \frac{qJ}{k_B} \right] \lim_{q \rightarrow \infty} T_c = \lim_{q \rightarrow \infty} \frac{2J}{k_B} \frac{1}{\ln \left( \frac{1}{1-2/q} \right)} \simeq \frac{qJ}{k_B}, \text{ 即 MFT.}$$

检验发现对于 1-dim Ising Model,  $q = 2 \Rightarrow T_c = 0$ .

$$\alpha'(T \leq T_c) = \left[ 3(q-1) \frac{J}{k_B T_c} \left( 1 - \frac{T}{T_c} \right) \right]^{\frac{1}{2}}, \quad \bar{\sigma}_0 = \frac{(+1) \cdot \bar{Z}_+ + (-1) \cdot \bar{Z}_-}{\bar{Z}_+ + \bar{Z}_-} = \frac{\frac{\bar{Z}_+}{\bar{Z}_-} - 1}{\frac{\bar{Z}_+}{\bar{Z}_-} + 1} = \frac{\sinh(2\alpha + 2\alpha')}{\cosh(2\alpha + 2\alpha') + e^{-2\gamma}}.$$

若  $\alpha = 0$ , 则  $\lim_{\alpha' \rightarrow 0} \bar{\sigma}_0 = \frac{2\alpha'}{1 + e^{-2\gamma_c}} = \left[ \frac{q^2}{q-1} \frac{J}{k_B T_c} 3 \left( 1 - \frac{T}{T_c} \right) \right]^{\frac{1}{2}}$ . 无论是否存在关联  $q$ , 都存在于  $T = T_c$  附近的发散斜率.

#### 1.3.3.5.1 Correlation of Spin 对于 no correlation 体系, $\frac{N_{++}N_{--}}{N_{+-}^2} = \frac{1}{4}$ .

$$\text{将求和形式写作 } Z = \sum_{\sigma_0=\pm 1} \sum_{\sigma_1=\pm 1} \left( \sum_{\sigma_2, \sigma_3, \dots, \sigma_q=\pm 1} \right) = Z_{++} + Z_{+-} + Z_{--}. \text{ 存在键数约束 } N_{++} + N_{--} + N_{+-} = \frac{1}{2}qN.$$

$$\text{可解得 } (N_{++}, N_{--}, N_{+-}) = \frac{qN}{4[e^\gamma \cosh(2\alpha + 2\alpha') + e^{-\gamma}]} \left( e^{2\alpha+2\alpha'+\gamma}, e^{-2\alpha-2\alpha'+\gamma}, 2e^{-\gamma} \right).$$

代入检验自旋关联  $\frac{N_{++}N_{--}}{N_{+-}^2} = \frac{1}{4} e^{4\gamma}$ ,  $\gamma = \frac{J}{k_B T}$

**1.3.3.5.2 Specific Heat** 无外场内能为  $U_0 = -\frac{1}{2}qJN \frac{\cosh(2\alpha') - e^{-2\gamma}}{\cosh(2\alpha') + e^{-2\gamma}}$ . 在  $T > T_c$  时, 等效平均场为  $\alpha' = 0$ . 此时热容为  $\frac{c_0}{Nk_B} = \frac{1}{2}q\gamma^2 \text{sech}^2 \gamma > 0$  [回忆 MFT 给出的  $c_0 \propto \bar{L}_0 \frac{d\bar{L}_0}{dT} = 0$  和此处结果相悖, 显然是忽略了涨落关联造成的]

### 1.3.3.6 Exact Solution of 1-D Ising Model

考虑周期性条件 ( $\sigma_{N+1} = \sigma_1$ ), 哈密顿量  $H_N(\{\sigma_i\}) = -J \sum_{\langle i,j \rangle} \sigma_i \sigma_j - \mu B \sum_{i=1}^N \sigma_i = -J \sum_{i=1}^N \sigma_i \sigma_{i+1} - \frac{1}{2} \mu B \sum_{i=1}^N (\sigma_i + \sigma_{i+1})$

1. 矩阵法推导:  $Q_N = \sum_{\{\sigma_i\}} \exp \left\{ \beta \sum_i \left[ J \sigma_i \sigma_{i+1} + \frac{1}{2} \mu B (\sigma_i + \sigma_{i+1}) \right] \right\} = \sum_{\{\sigma_i\}} \prod_i \exp \left\{ \beta \left[ J \sigma_i \sigma_{i+1} + \frac{1}{2} \mu B (\sigma_i + \sigma_{i+1}) \right] \right\},$

观察到可将其写作矩阵元形式:  $Q_N = \sum_{\{\sigma_i\}} \prod_i \langle \sigma_i | P | \sigma_{i+1} \rangle = \sum_{\{\sigma_i\}} \langle \sigma_1 | P | \sigma_2 \rangle \langle \sigma_2 | P | \sigma_3 \rangle \cdots \langle \sigma_{N-1} | P | \sigma_N \rangle \langle \sigma_N | P | \sigma_{N+1} \rangle$

$= \sum_{\sigma_1=\pm 1} \langle \sigma_1 | P^N | \sigma_1 \rangle = \text{Tr } P^N = \lambda_+^N + \lambda_-^N \stackrel{\lambda_+ \gg \lambda_-}{\approx} \lambda_+^N$ . 其中  $\lambda_{\pm}$  是矩阵  $P$  的特征值.

定义基矢  $|\sigma = +1\rangle = \begin{bmatrix} 1 \\ 0 \end{bmatrix}$ ,  $|\sigma = -1\rangle = \begin{bmatrix} 0 \\ 1 \end{bmatrix} \Rightarrow P = \begin{bmatrix} P_{++} & P_{+-} \\ P_{-+} & P_{--} \end{bmatrix} = \begin{bmatrix} e^{\beta(J+\mu B)} & e^{-\beta J} \\ e^{-\beta J} & e^{\beta(J-\mu B)} \end{bmatrix}$ .

$P$  有两个特征值  $\lambda_{\pm} = e^{\beta J} \cosh(\beta \mu B) \pm [e^{-2\beta J} + e^{2\beta J} \sinh^2(\beta \mu B)]^{\frac{1}{2}} = e^{\beta J} \left[ \cosh(\beta \mu B) \pm \sqrt{e^{-4\beta J} + \sinh^2(\beta \mu B)} \right]$ .

$\ln Q_N \approx N \ln \lambda_+ = N \beta J + N \ln \left\{ \cosh(\beta \mu B) + [e^{-4\beta J} + \sinh^2(\beta \mu B)]^{\frac{1}{2}} \right\}$

$F(B, T) = -k_B T \ln Q_N = -N J - N k_B T \ln \left\{ \cosh(\beta \mu B) + [e^{-4\beta J} + \sinh^2(\beta \mu B)]^{\frac{1}{2}} \right\}$ ,  $M = \left( \frac{\partial F}{\partial B} \right)$ ,  $\lim_{B \rightarrow 0} M = 0$

2. 递推法导出配分函数. 将  $J$  写作形式  $J_i$ , 在无外场 ( $B = 0$ ) 下:  $Q_N = \sum_{\{\sigma_i\}} \prod_i e^{\beta J_i \sigma_i \sigma_{i+1}}$ . 分离出最后一项

$\sum_{\sigma_N=\pm 1} e^{\beta J_{N-1} \sigma_{N-1} \sigma_N} = e^{\beta J_{N-1} \sigma_{N-1}} + e^{-\beta J_{N-1} \sigma_{N-1}} = 2 \cosh(\beta J_{N-1} \sigma_{N-1}) \stackrel{\text{even function}}{=} 2 \cosh(\beta J_{N-1})$

于是有递推关系:  $Q_N = 2 \cosh(\beta J_{N-1}) Q_{N-1}$ ,  $Q_1 = \sum_{\sigma_1=\pm 1} (1) = 2 \Rightarrow Q_N = Q_1 \prod_{i=1}^{N-1} 2 \cosh(\beta J_i)$

类比  $\langle E \rangle = -\frac{\partial \ln Q}{\partial \beta}$ , 通过求偏导得到空间关联  $\langle \sigma_k \sigma_{k+1} \rangle = -\frac{1}{\beta} \frac{\partial \ln Q_N}{\partial J_k} = \tanh(\beta J_k)$ ,

$\langle \sigma_k \sigma_{k+r} \rangle \stackrel{\sigma_i^2=1}{=} \langle \sigma_k \sigma_{k+1} \cdot \sigma_{k+1} \sigma_{k+2} \cdots \sigma_{k+r-1} \sigma_{k+r} \rangle = \frac{1}{Q_N} \frac{\partial}{\partial J_k} \frac{\partial}{\partial J_{k+1}} \cdots \frac{\partial}{\partial J_{k+r-1}} Q_N = \prod_{i=k}^{k+r-1} \tanh(\beta J_i) = \tanh^r(\beta J)$

$= e^{-r/\xi}$ , correlation length:  $\xi = \frac{1}{\ln[\coth(\beta)]} \Rightarrow$  随距离增大而迅速衰减.  $\lim_{T \rightarrow 0} \xi = \infty$ ,  $\lim_{T \rightarrow \infty} \xi = 0$

### 1.3.3.7 Phase Transition & Space Dimension

spin flip: energetically unfavored, entropically favored.  $F = 2J - k_B T \ln N < 0 \Rightarrow T > \frac{2J}{k_B \ln N}$ .

1D: (+, +, -, +, +) 染色元素翻转  $+\rightarrow -$ , 不会消耗能量; 2D:  $\begin{pmatrix} - & - & - & - & - \\ - & - & - & - & - \\ - & + & + & + & - \\ - & - & - & - & - \end{pmatrix}$  染色元素翻转, 需要消耗能量.

### 1.3.3.8 Development of Ising Model

**1.3.3.8.1 Spin Glass**  $H = - \sum_{\langle i,j \rangle} J_{ij} \sigma_i \sigma_j - h \sum_i \sigma_i$ , metastable state.

**1.3.3.8.2 Hopfield Network** Learning & Computation.  $V_i \rightarrow \begin{cases} 1, & \text{if } \sum_j \omega_{ij} V_j > U \\ 0, & \text{if } \sum_j \omega_{ij} V_j < U \end{cases}$

**1.3.3.8.3 Boltzmann Machine**  $V_i = 0 \rightarrow 1, \quad \frac{P_{V_i=0}}{P_{V_i=1}} = e^{-\Delta E_i / k_B T}.$

### 1.3.4 Landau's Theory (of 2nd Order Phase Transition)

Critical exponents:  $\alpha, \beta, \gamma, \delta$ . External field  $h$ ; Order parameter:  $m_0 = m(h=0)$ ;

Response functions:  $C_0$  (热容),  $\chi_0 \sim \frac{\partial m}{\partial h}$  (磁化率).

$$\lim_{h \rightarrow 0, T \rightarrow T_c^-} m_0 \sim (T_c - T)^\beta, \quad \lim_{h \rightarrow 0} \chi_0 \sim \begin{cases} (T - T_c)^{-\gamma}, & T \rightarrow T_c^+ \\ (T_c - T)^{-\gamma'}, & T \rightarrow T_c^- \end{cases},$$

$$\lim_{h \rightarrow 0} m \Big|_{T=T_c} \sim h^{1/\delta}, \quad \lim_{h \rightarrow 0} C_0 \sim \begin{cases} (T - T_c)^{-\alpha}, & T \rightarrow T_c^+ \\ (T_c - T)^{-\alpha'}, & T \rightarrow T_c^- \end{cases}$$

[Example] 1. superfluid He:  $\alpha \approx -0.01294$ ; 2. 0th approximation of Ising Model & Van der Waals theory of gas-liquid phase transition:  $\alpha = \alpha' = 0, \quad \beta = \frac{1}{2}, \gamma = \gamma' = 1, \delta = 3$ ; 3. CO2:  $\beta = 0.34, \quad \delta = 0.42, \quad \gamma = 1.32$ . N2:  $\beta = 0.33, \quad \delta = 0.42, \quad \gamma = 1.35$

[Discussion] Critical exponents. 考虑稳定性条件, 导出其关系  $\alpha' + 2\beta + \gamma' \geq 2$  (Rushbrooke's inequality).

#### 1.3.4.1 Constrained Free Energy

平衡态下,  $dF = -SdT - MdH, \quad M = -\left(\frac{\partial F}{\partial H}\right)_T \Rightarrow F(T, H, M)$ , let  $\frac{\partial F(T, H, M)}{\partial M} \Big|_{\text{equilibrium}} = 0$ .  $M$  acts as a constraint.

Continuous variable  $m_0$ :  $m_0 = 0 \xrightarrow{\text{phase transition}} m_0 \neq 0$ .

Free energy (analytic function of  $m_0$ ):  $\lim_{t, m_0 \rightarrow 0} \psi_0(t, m_0) = q(t) + r(t)m_0^2 + s(t)m_0^4 + \dots, t = \frac{T - T_c}{T_c}$ ,

其中  $q(t), r(t), s(t)$  是 phenomenological parameters (唯象参数).

一级相变:  $m_0$ - $T$  相图中,  $m_0$  出现骤降. 在 gas-liquid PT 中,  $m_0 = \rho_l - \rho_g$ .

[Discussion]  $\psi_0$  是对  $m_0$  的偶函数, 因为要求系统具有:

1. symmetry: 能量不应依赖于磁化的方向, 即  $\psi_0(m_0) = \psi_0(-m_0)$ ;

2. 稳定性: 自由能需要在  $m_0 = 0$  (高温相) 取得极小值, 若有奇次项则使得  $\frac{\partial \psi_0}{\partial m_0} \Big|_{m_0=0} \neq 0$ .

化学势  $\mu$  全微分:  $d\mu(T, p, h) = -SdT + vdp - mdh$ . 加入外场  $h$  得到约化的化学势:  $\tilde{\mu} = \mu + mh$ ,

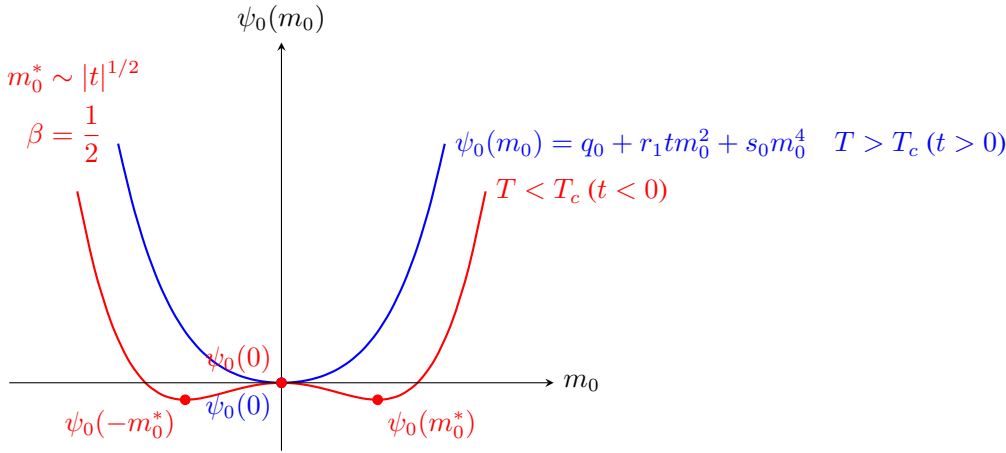
其全微分为  $d\tilde{\mu} = -SdT + vdp - hdm$ . 那么  $\mu = \tilde{\mu} - mh = \overbrace{\tilde{\mu}_0(T, p)}^{\text{Gibbs Free Energy}} + \alpha(T, p)m^2 + \beta(T, p)m^4 - mh$ .

平衡态:  $\frac{\partial \psi_0}{\partial m_0} = r(t)m_0 + 2s(t)m_0^3 = 0 \Rightarrow m_0 = 0, \pm \sqrt{\frac{-r(t)}{s(t)}}$ . 将  $r(t), s(t)$  以  $t$  阶数展开:

$r(t) = r_0 + \boxed{r_1 t} + r_2 t^2 + \dots, \quad s(t) = \boxed{s_0} + s_1 t + s_2 t^2 + \dots$ . 仅取框选项, 即

$\psi_0 = q_0 + r_1 t m_0^2 + s_0 m_0^4, \quad r_1 > 0, \quad s_0 > 0$ . 存在关系  $\sqrt{\frac{-r(t)}{2s(t)}} \simeq \sqrt{\frac{r_1 |t|}{2s_0}} \Rightarrow \beta = \frac{1}{2}, \quad m_0 \sim t^\beta$  ( $\beta$  的定义).





$$\text{热容 } c_0 \sim \frac{\partial \text{Entropy}}{\partial t}, \quad \text{Entropy} = \frac{\partial \psi_0}{\partial t} \simeq r_1 m_0^2 \begin{cases} 0, & t > 0 \\ m_0 \sim |t|^{\frac{1}{2}}, & t < 0 \end{cases}$$

[Discussion] The concept of "Universality Class(普适类)". 以 critical exponents 对相变进行分类. 比如 Ising Model 和 Van der Waals gas 属于同类( $\alpha = \alpha' = 0, \beta = \frac{1}{2}, \gamma = \gamma' = 1, \delta = 3$ ).  $q(t), r(t), s(t)$  不影响 critical exponents, 而是描述具体实验.

[Discussion] Weiss model @ 1907

$$F = U - TS, \quad dU = - \int H dM, \quad H = H_{\text{ext}} + b, \quad b \propto M : \text{mean field} \Rightarrow U = -H_{\text{ext}}M + \alpha M^2$$

$$S = S(m), \quad m = \frac{N_+ - N_-}{N}, \quad S(m) = -Nk_B \sum_j P_j \ln P_j, \quad P_{\pm}(m) = \frac{1 \pm m}{2}$$

$$F = -hm + \alpha m^2 - Nk_B T[(1+m) \ln(1+m) + (1-m) \ln(1-m)]$$

$$\text{Landau Free Energy 物态方程: } \left. \frac{\partial F}{\partial m} \right|_{m_0} = 0 \Rightarrow h = 2r_1 m + 4s_0 m^3 \Rightarrow |m_0| = \sqrt{\frac{r_1 |t|}{2s_0}}, \quad t \rightarrow 0^-.$$

$$2^{\frac{1}{2}} \left[ 2 \operatorname{sgn}(t) \left( \frac{m}{r_1^{\frac{1}{2}} |t|^{\frac{1}{2}} / s_0^{\frac{1}{2}}} \right) + 4 \left( \frac{m}{r_1^{\frac{1}{2}} |t|^{\frac{1}{2}} / s_0^{\frac{1}{2}}} \right)^3 \right] = \frac{h}{r_1^{\frac{3}{2}} |t|^{\frac{3}{2}} s_0^{\frac{1}{2}}} \Leftrightarrow 2^{\frac{1}{2}} [2 \operatorname{sgn}(t) \tilde{m} + \tilde{m}^3] = \tilde{h}, \quad \tilde{\psi} = -\tilde{h} \tilde{m} + \operatorname{sgn}(t) \tilde{m}^2 + \tilde{m}^4$$

$$\text{约化自由能: } \tilde{\psi} = \frac{\psi}{r_1^2 |t|^2 / s_0} \sim \tilde{h}, \text{ 或 } \frac{\psi}{|t|^2} \sim \frac{h}{|t|^{\frac{3}{2}}}. \text{ 于是有 } \boxed{\psi = C_2 |t|^2 f\left(\frac{C_1 h}{|t|^{\frac{3}{2}}}\right)}.$$

$$\text{Beyond MFT: 将指数延拓为 } \psi = C_2 |t|^{2-\alpha} f\left(\frac{C_1 h}{|t|^{\Delta}}\right), m_0 \sim \lim_{h \rightarrow 0} \left( \frac{\partial \psi}{\partial h} \right) \sim \lim_{h \rightarrow 0} |t|^{2-\alpha-\Delta} f'\left(\frac{C_1 h}{|t|^{\Delta}}\right) \Rightarrow \beta = 2 - \alpha - \Delta$$

$$\gamma = \gamma' = \alpha + 2\Delta - 2, \quad \delta = \frac{\Delta}{\beta}. \text{ 不需要知道具体的 Hamiltonian.}$$

### 1.3.4.2 Fluctuations & Correlation Functions

无关联体系:  $\langle \sigma_i \sigma_j \rangle = \langle \sigma_i \rangle \langle \sigma_j \rangle$ . 定义关联函数  $g_{ij} = \langle \sigma_i \sigma_j \rangle - \langle \sigma_i \rangle \langle \sigma_j \rangle = \langle \delta \sigma_i \delta \sigma_j \rangle$ , 其中  $\delta \sigma = \sigma - \langle \sigma \rangle$ .

配分函数为  $Q_N(H, T) = \sum_{\{\sigma_i\}} \exp \left( \beta J \sum_{\langle i, j \rangle} \sigma_i \sigma_j + \beta \mu H \sum_i \sigma_i \right)$ , 通过对  $\ln Q_N$  求偏导以得到期望值:

$$\frac{\partial \ln Q_N}{\partial H} = \beta \mu \left\langle \sum_i \sigma_i \right\rangle = \beta \langle M \rangle, \quad \frac{\partial^2 \ln Q_N}{\partial H^2} = \beta^2 (\langle M^2 \rangle - \langle M \rangle^2);$$

$$\chi = \frac{\partial \bar{M}}{\partial H} = \frac{\partial}{\partial H} \left( \frac{1}{\beta} \frac{\partial \ln Q_N}{\partial H} \right) = \beta (\langle M^2 \rangle - \langle M \rangle^2) = \beta \mu^2 \sum_{ij} g_{ij},$$

[Discussion] Fluctuation & Response Theorem.

$$1. \text{ 热容 } C_v = \left. \frac{\partial \langle E \rangle}{\partial T} \right|_V = \frac{\langle (\Delta E)^2 \rangle}{k_B T^2};$$

$$2. \text{ 等温压缩率 } \kappa_T = -\frac{1}{\langle V \rangle} \left. \frac{\partial \langle V \rangle}{\partial P} \right|_T = \frac{\langle (\Delta V)^2 \rangle}{k_B T \langle V \rangle}.$$

For homogeneous system,  $g_j = g(\vec{r})$ ,  $\chi = \beta \mu^2 N \sum_{\vec{r}} g(\vec{r}) = N \beta \mu^2 \frac{1}{a^d} \int d^d \vec{r} g(\vec{r})$ ,  $a$ : lattice constant. 也可理解为再乘上

$e^{i\vec{k}\cdot\vec{r}}$  进行傅里叶变换得到  $\tilde{g}(\vec{k})$ , 但仅取  $\vec{k} = 0$  的分量, 即  $\tilde{g}(\vec{k} = 0) \rightarrow \chi$ .

[Discussion] **Linear Response.**  $H = H_0[m(x)] - \int dx m(x)h(x)$ , 其中  $m(x)$  和  $h(x)$  是 linear coupling 的. 那么

$$F = -k_B T \ln Q, \quad \chi(x, x') = \frac{\partial m(x')}{\partial h(x)} = -\frac{\partial^2 F}{\partial h(x) \partial h(x')} = \beta (\langle m(x)m(x') \rangle - \langle m(x) \rangle \langle m(x') \rangle)$$

### 1.3.4.2.1 Generalized Landau Free Energy Correlation Function 一般性地, 自由能 $F = \int d^d \vec{x} \{ a m(\vec{x})^2 + b [\nabla m(\vec{x})]^2 \}$ ,

$m(\vec{x})$  为 order parameter, 其中  $a = kt$ , 于是存在关联长度  $\xi = \sqrt{\frac{b}{kt}}$ . 尝试求解序参量  $m(\vec{x})$  的关联函数  $\langle m(\vec{x}) m(\vec{x}') \rangle$ .

可使用 Fourier 变换  $m(\vec{x}) = \frac{1}{(2\pi)^d} \int d^d \vec{q} e^{i\vec{q}\cdot\vec{x}} \tilde{m}(\vec{q})$ ,  $\tilde{m}(\vec{q}) = \int d^d \vec{x} e^{-i\vec{q}\cdot\vec{x}} m(\vec{x})$  将其在  $\vec{q}$  空间中处理.

规定  $\int e^{i(\vec{q}-\vec{q}')\cdot\vec{x}} d^d \vec{x} = (2\pi)^d \delta(\vec{q}-\vec{q}')$ . 变换后自由能为  $F[\tilde{m}(\vec{q})] = \int \frac{d^d \vec{q}}{(2\pi)^d} (kt + bq^2) \tilde{m}(\vec{q}) \tilde{m}(-\vec{q})$ .

记关联函数  $C(\vec{x}) \equiv \langle m(\vec{x}) m(0) \rangle = \frac{1}{(2\pi)^d} \int d^d \vec{q} e^{i\vec{q}\cdot\vec{x}} \langle |\tilde{m}(\vec{q})|^2 \rangle$ , 其 Fourier 变换后形式为:

$$\tilde{C}(\vec{q}) = \frac{\int |\tilde{m}(\vec{q})|^2 \exp\{-\beta F[\tilde{m}(\vec{q})]\} d^d \vec{q}}{\int \exp\{-\beta F[\tilde{m}(\vec{q})]\} d^d \vec{q}} = \frac{(2\pi)^d}{2} \frac{T}{kt + bq^2} = \frac{(2\pi)^d}{2} \frac{T}{kt(1 + \xi^2 q^2)}$$

重新变换回  $\vec{x}$  空间, 得到  $C(\vec{x}) = \frac{T}{2} \int d^d \vec{q} e^{i\vec{q}\cdot\vec{x}} \frac{1}{kt + bq^2}$ .

1.  $d = 1$ : Residue theorem.  $\lim_{r \gg \xi} C(r) \propto r^{-(d-1)/2} e^{-r/\xi}$ ;

2.  $d = 3$ :  $C(r) \sim \frac{1}{r} e^{-r/\xi}$ .

[Discussion] New critical exponents. 对于关联现象存在  $\lim_{h \rightarrow 0, t \rightarrow 0^+} \xi \sim t^{-\nu}$ ,  $C(r) \Big|_{t=0} \sim r^{-(d-2+\eta)}$ .

### 1.3.4.2.2 Validity of Mean-Field Approximation 平均场理论的生效范围

1. 涨落 v.s. 效应. 选任意一点  $\sigma_0$ , 设范围尺度(半径)为  $\xi$ , 圈出范围  $\Omega$ . 范围内其余自旋为  $\sigma_r$ .

If  $\int_{\Omega} \langle \delta \sigma_r \delta \sigma_0 \rangle d^d \vec{r} \ll \int_{\Omega} \langle \sigma_r \rangle \langle \sigma_0 \rangle d^d \vec{r} \Leftrightarrow T\chi \ll m^2 \xi^d \Leftrightarrow T(T_c - T)^{-\gamma} \ll (T_c - T)^{2\beta} (T_c - T)^{-\nu d} \Rightarrow \gamma < \nu d - 2\beta$ ,

即涨落相对效应很小, 则 MFT( $\gamma = 1, \beta = \nu = \frac{1}{2}$ ) 较好  $\Rightarrow \boxed{d > 4}$ .

2. 涨落/关联贡献. 对相变/关联有贡献的内能:  $U_f = -J \sum_{i,j} (\langle \sigma_i \sigma_j \rangle - \langle \sigma_i \rangle \langle \sigma_j \rangle) = -J \sum_{i,j} g(r_{ij})$ ,

其中  $g(r) \sim \int d^d(\vec{q}a) \frac{e^{-i\vec{q}\cdot\vec{r}}}{t(1 + \xi^2 q^2)}$  为关联函数. 关联/涨落部分的热容与  $C_f = -\frac{\partial g(r)}{\partial t} = \int q^{d-1} \frac{e^{-i\vec{q}\cdot\vec{r}}}{t^2(1 + \xi^2 q^2)} dq$  有关.

考虑 Long wavelength limit (small  $q \sim \frac{1}{\xi}$ ):  $\Rightarrow C_f \sim \int dq \frac{q^{d-1}}{t^2(1 + \xi^2 q^2)} \sim \xi^{-d} t^{-2} \sim \left(t^{-\frac{1}{2}}\right)^{-d} t^{-2} \sim t^{-(d-4)/2}$ ,

发现  $\lim_{d < 4, t \rightarrow 0} C_f = \infty$ , 和 1. 中表述一致.

## 1.3.5 Scale Transformation

对 2D spin lattice 进行标度变换:  $\begin{bmatrix} x & o & x \\ o & o & x \\ x & x & x \end{bmatrix} \xrightarrow{N_x > N_o} X$ . 观察发现, 对于 Critical state( $\xi \rightarrow \infty$ ), 会保持 Scale invariance.

[Discussion] Symmetry consideration (**Noether's theorem**).

$L = (\dot{x}^2 + \dot{y}^2) + V(x - y)$ , 对  $(x, y) \rightarrow (x + \delta, y + \delta)$  表现出平移不变性;  $L = \dot{x}^2 + \dot{y}^2 + x^2 + y^2$ , 表现出旋转不变性.

### 1.3.5.1 Implement Scale Transformation

存在两种尺度变换思路:

1. Block-spin transformation:  $\begin{bmatrix} o & o & o & o \\ o & o & o & o \\ o & o & o & o \\ o & o & o & o \end{bmatrix} \xrightarrow{l=2} \begin{bmatrix} \bullet & \bullet \\ \bullet & \bullet \end{bmatrix}$ , 晶格常数  $a \rightarrow a' = la (l=2)$ ; 自旋个数  $N \rightarrow N' = l^{-d}N (d=2)$ ;

尺度  $r \rightarrow r' = l^{-1}r$ . Number density invariant:  $\frac{N}{a^d} = \frac{N'}{(a')^d}$ .  $\sigma = \pm 1 \rightarrow \sigma' = \pm 1$ .

2.  $\begin{bmatrix} \phi & o & \phi & o & \phi & o \\ o & \phi & o & \phi & o & \phi \\ \phi & o & \phi & o & \phi & o \\ o & \phi & o & \phi & o & \phi \\ \phi & o & \phi & o & \phi & o \\ o & \phi & o & \phi & o & \phi \end{bmatrix}$ ,  $Q_N = \sum_{\sigma_i} \exp[-\beta H_N(\{\sigma_i\}, J)] = \sum_{\sigma'_j} \exp[-\beta H_{N'}(\{\sigma'_j\}, J')]$ ,  $N' = \frac{N}{2}$ ,  $a' = \sqrt{2}a$ ,  $l = \frac{a'}{a} = \sqrt{2}$ .

考察对相变有贡献的自由能(Landau 自由能是 Helmholtz 自由能), **Single point**:  $N'\psi^{(s)}(t', h') = N\psi^{(s)}(t, h)$ ,

类比  $N \rightarrow N' = l^{-d}N$ , 线性假设  $t \rightarrow t' = l^{y_t}t$ ,  $h \rightarrow h' = l^{y_h}h$ . 于是将  $\psi^{(s)}$  变换写作  $\psi^{(s)}(t, h) = l^{-d}\psi^{(s)}(l^{y_t}t, l^{y_h}h)$  形式.

已知自由能  $\psi^{(s)}(t, h) = |t|^\beta \tilde{\psi}\left(\frac{h}{|t|^\alpha}\right)$ , 变换前后分别代入得  $|t|^\beta \tilde{\psi}\left(\frac{h}{|t|^\alpha}\right) = l^{-d} |t'|^\beta \tilde{\psi}\left(\frac{h'}{|t'|^\alpha}\right)$ ,

比较可得  $\frac{h}{|t|^\alpha} = \frac{h'}{|t'|^\alpha}$ ,  $|t|^\beta = l^{-d} |t'|^\beta$ . 因此指数间存在关系  $\alpha = \frac{y_h}{y_t}$ ,  $\beta = \frac{d}{y_t}$ .

### 1.3.5.2 Scale Transformation in 1D & 2D Ising Models

**1.3.5.2.1 1D Ising Model** 研究  $J \rightarrow J'$ ,  $B \rightarrow B'$  变换的具体形式. 将配分函数写作形式:

$$Q_N = \sum_{\sigma} \exp \left\{ \beta \sum_i \left[ J \sigma_i \sigma_{i+1} + \frac{1}{2} \mu B (\sigma_i + \sigma_{i+1}) \right] \right\} = \sum_{\sigma} \exp \left\{ \sum_i \left[ K_0 + K_1 \sigma_i \sigma_{i+1} + \frac{1}{2} K_2 (\sigma_i + \sigma_{i+1}) \right] \right\}$$

将系数写作矢量形式  $\vec{K} = (K_0, K_1, K_2) = (0, \beta J, \beta \mu B)$ . 可知变换时有  $\vec{K} \rightarrow \vec{K}'$ , 其蕴含具体变换的信息.

不妨假定总自旋数  $N$  为偶数, 则取自旋链环中所有偶数位置, 则自旋数变换:  $N \rightarrow N' = \frac{N}{2}$ . 变换前后的配分函数相等:

$$Q_N = \sum_{\sigma'_j} \prod_{j=1}^{\frac{N}{2}} e^{2K_0} e^{\frac{1}{2} K_2 (\sigma'_j + \sigma'_{j+1})} 2 \cosh [K_1 (\sigma'_j + \sigma'_{j+1}) + K_2] = \sum_{\sigma'_j} \prod_{j=1}^{\frac{N}{2}} e^{K'_0 + K'_1 \sigma'_j \sigma'_{j+1} + \frac{1}{2} K'_2 (\sigma'_j + \sigma'_{j+1})}$$

$\sigma \rightarrow \sigma'$  的变换即相邻自旋求和, 涉及 3 类情况:  $\sigma_{2j} = \sigma_{2j+1} = \pm 1 \Rightarrow \sigma'_j = \pm 1$ ;  $\sigma_{2j} = -\sigma_{2j+1} \Rightarrow \sigma'_j = 0$ , 作为约束方程.

解得  $\vec{K} \rightarrow \vec{K}'$  的具体表达式:

$$e^{K'_0} = 2e^{2K_0} [\cosh(2K_1 + K_2) \cosh(2K_1 - K_2) \cosh^2 K_2]^{\frac{1}{4}} = \sharp_0(K_0, K_1, K_2), \quad e^{K'_1} = \sharp_1(K_1, K_2), \quad e^{K'_2} = \sharp_2(K_1, K_2)$$

[Discussion] 研究无外场条件( $K_2 = 0$ )下各量. 配分函数变换为  $Q_N(K_1, K_2) = e^{N'K'_0} Q_{N'}(K'_1, K'_2)'$ ,

因此自由能变换为  $F_N(K_1, K_2) = -N'K'_0 + F_{N'}(K'_1, K'_2)$ .

设单自旋自由能为  $f(K_1, K_2)$  形式:  $f(K_1; K_2 = 0) = -\frac{1}{2} \ln [2 \cosh^{\frac{1}{2}}(2K_1)] + \frac{1}{2} f(K'_1 = \ln [\cosh^{\frac{1}{2}}(2K_1)]; K'_2 = 0)$

令  $x = K_1$ , 即有  $f(x) = -\frac{1}{2} \ln [2 \cosh^{\frac{1}{2}}(2x)] + \frac{1}{2} f(\ln [\cosh^{\frac{1}{2}}(2x)])$ , 代入  $x = 0$  发现  $f(0) = -\ln 2$ .

猜测  $f(x) = -\ln [2y(x)]$ , 代入单自旋自由能变换式:  $\frac{y^2(x)}{y \left\{ \ln [\cosh^{\frac{1}{2}}(2x)] \right\}} = \cosh^{\frac{1}{2}}(2x)$ , 解得  $y(x) = \cosh(x)$ .

因此  $\boxed{f(K_1; K_2 = 0) = -\ln(2 \cosh K_1)}$ .

**1.3.5.2.2 2D Ising Model**  $Q_N = e^{NK_0} \sum_{\sigma_i} \exp \left\{ K \sum_{\langle i, j \rangle} \sigma_i \sigma_j + L \sum \sigma_i \sigma_j + M \sum \sigma_j \sigma_r \sigma_l \sigma_m \right\}$

**1.3.5.2.3 Origin of Fixed Point** 变换  $K' = R_l(K)$  可以视为点在  $\vec{K}$  空间中的 flow(轨迹).

那么可能存在点  $K^*$ , 使得  $R_l(K^*) = K^*$ . 这类点即 **Fixed Point**.

[Example]  $X_{i+1} = \lambda X_i (1 - X_i)$ , 存在两个不动点  $X^* = 0, 1$ .

变换对应于矩阵, 即可用特征值来进行描述. 令变换无穷小, 则  $R_{l_2}[R_{l_1}(K)] = R_{l_1 * l_2}(K) \rightarrow \lambda_{l_1} \lambda_{l_2} = \lambda_{l_1 * l_2}$ .

这说明特征值可能为  $\lambda(l) \sim l^\alpha$  形式, 从而满足  $l_1^\alpha l_2^\alpha = (l_1 \cdot l_2)^\alpha$ .

研究  $\vec{K}$  的连续变换. 记  $R_l^n(K^*) = K^{(n)}$  为对  $\vec{K}$  进行了  $n$  次  $R_l$  变换的结果. 那么关联长度将会满足变换式  $\xi^{(n)} = l^{-n}\xi^{(0)}$ . 对于不动点  $K^*$  而言, 将会有  $\xi(K^*) = l^{-1}\xi(K^*)$ . 该方程具有两个解  $\{0^{\text{trivial}}, \infty^{\text{critical}}\}$ .

[Discussion] 若经过  $n$  次变换后的关联长度  $\xi[K^{(n)}]$ , 能推导出初始点  $K^{(0)} = R_l^0(K)$  的关联长度  $\xi(K^{(0)}) = \infty$  吗? 由于  $l > 1$ , 则关联长度有  $\xi(K') = l^{-1}\xi(K) < \xi(K)$ . 可见  $\xi[K^{(n)}]$  递减, 其仍发散说明初项  $\xi[K^{(0)}] = \infty$ . 可见  $\xi = \infty$  不仅会在不动点/Critical point 出现, 也会在  $\vec{K}$  空间中连续出现而形成 **Critical Curve**.

#### 1.3.5.2.4 RG Flow Near the Critical/Fixed Point in $\vec{K}$ Space

研究不动点附近的  $\vec{K} = \vec{K}^* + \vec{k}$ , 其中  $\vec{k} \rightarrow \vec{0}$ .

那么可将  $K \rightarrow K'$  变换写作 Taylor 展开:  $\vec{K}' = \vec{K}^* + \vec{k}' = R_l(\vec{K}^* + \vec{k}) = R_l(\vec{K}^*) + \left. \frac{\partial R_l(\vec{q})}{\partial \vec{q}} \right|_{\vec{q}=\vec{K}^*} \vec{k} + \dots$ ,

其中  $\vec{k}' = A_l \vec{k}$ ,  $A_l = \left. \frac{\partial R_l(\vec{q})}{\partial \vec{q}} \right|_{\vec{q}=\vec{K}^*}$ . 将  $\vec{k}$  以基矢展开  $\vec{k} = \sum_i u_i \hat{\phi}_i$ , 则变换式  $\vec{k}' = A_l \vec{k}$  即可写作  $\sum_i u'_i \hat{\phi}_i = A_l \sum_i u_i \hat{\phi}_i$ .

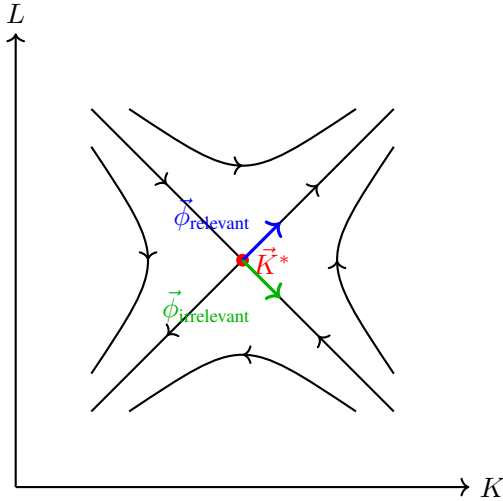
特征方程  $A_l \hat{\phi}_i = \lambda_i \hat{\phi}_i$ , 代入为  $\sum_i u'_i \hat{\phi}_i = \sum_i u_i \lambda_i \hat{\phi}_i$ , 即得分量变换式  $u_i \rightarrow u'_i = \lambda_i u_i = l^{y_i} u_i$ .

$n$  次变换后, 分量  $u_i^{(n)} = l^{ny_i} u_i^{(0)} = \lambda_i^n u_i^{(0)}$ ; 可见:

1.  $\lambda_i > 1$ , 则分量发散, 此时  $u_i$  为 **Relevant Variable**(有相变贡献);
2.  $\lambda_i < 1$ , 则分量收敛于 0, 此时  $u_i$  为 **Irrelevant Variable**(无相变贡献).

[Discussion] Scale transformation 是一个信息丢失的过程, 所以重整化群严格来说不能被称为群结构.

现在研究 2D Ising Model 中的 RG flow. 取公式中的  $K$  和  $L$  作为坐标轴, 得到大致的 RG flow 示意图:



在不动点附近存在  $\vec{\phi}_{\text{relevant}}$  和  $\vec{\phi}_{\text{irrelevant}}$ , 两本征矢所指的方向. 亦即, 若要流沿着指向  $K^*$  的曲线移动, 要求分量  $u_{\text{relevant}} \rightarrow 0$ .

[Discussion] Emergence of Non-analyticity/singularity

1. 回忆: 在研究配分函数时, 每一项都是解析的, 若要产生 singularity(奇点), 则要求和项数无穷大, 而某些物理量保持有极限(e.g.  $\lim_{N, V \rightarrow \infty} n = \frac{N}{V} = n_0$ );
2. 不动点也是通过无穷连续变换产生的;
3. 微分方程  $\frac{du}{dt} = -2u(u^2 - 1)$  的精确解为  $u(t) = \frac{u_0}{\sqrt{u_0^2 - (u_0^2 - 1)e^{-4t}}}$ , 其中  $u_0 = u|_{t=0}$ . 存在不动点  $u^* = \pm 1$ , 通过  $\lim_{t \rightarrow \infty} u(t) = \text{sgn}(u_0)$  逼近.

[Example] RG Equ. of 2D Ising Model:  $\begin{cases} K' = 2K^2 + L \\ L' = K^2 \end{cases}$ , 通过  $\begin{cases} K' = K \\ L' = L \end{cases}$  解得  $\begin{cases} K^* = \frac{1}{3} \\ L^* = \frac{1}{9} \end{cases}$ . 取不动点附近  $\begin{cases} K = K^* + k_1 \\ L = L^* + k_2 \end{cases}$ ,

小量变换满足  $\begin{cases} k'_1 = \frac{4}{3}k_1 + k_2 \\ k'_2 = \frac{2}{3}k_1 \end{cases}$ . 将其写作矩阵形式:  $\vec{k}' = A_l \vec{k} \Rightarrow A_l = \begin{bmatrix} 4/3 & 1 \\ 2/3 & 0 \end{bmatrix}$ . 该矩阵的特征值为  $\lambda_{1,2} = \frac{2 \pm \sqrt{14}}{3}$ .

( $\lambda_1 > 1$ , 则  $u_1$  是 **Relevant Variable**, 表现为  $u_1 \neq 0$  时, RG flow 趋于发散.)

特征矢量  $\vec{\phi}_{1,2} = \begin{bmatrix} 2 \pm \sqrt{10} \\ 2 \end{bmatrix}$ ; 将其作为基矢, 则小量  $\vec{k} = \begin{bmatrix} k_1 \\ k_2 \end{bmatrix} = u_1 \vec{\phi}_1 + u_2 \vec{\phi}_2$ . 反解得到  $u_1 = 2k_1 + (\sqrt{10} - 2)k_2$ .

令  $u_1 = 0$ , 则  $\lambda_1 > 1$  不影响流的轨迹经过不动点  $(K^*, L^*)$ . 此时得到  $K$ - $L$  空间中的一条斜线  $2k_1 + (\sqrt{10} - 2)k_2 = 0$ , 该斜线将与  $K$  轴相交于  $K_c \simeq 0.3979$ .

[Discussion] Complexity? Universal behavior?

形如  $x_{j+1} = f(x_i, \lambda)$  的迭代方程. 如  $x_{i+1} = \lambda x_i(1 - x_i)$ , 随着  $\lambda$  值变化出现不动点  $x^*$  的分形.

定义  $\delta_n = \frac{x_{n+1} - x_n}{x_n - x_{n-1}}$ , 发现其存在规律  $\lim_{n \rightarrow \infty} \delta_n = 4.6692 \dots$ .

## 1.4 Non-equilibrium Statistical Physics

Fluctuations. 1. Equilibrium state: thermodynamic level/quantities  $(N, T, P)$ , 随机变量存在概率分布  $\rightarrow$  涨落  $N = N_0 + \delta N$ ;

2. Non-equilibrium state, thermodynamic level: 时空不均匀,  $T(x, t), n(x, t)$ . 通过局域平衡假设分析.  $\frac{\partial n}{\partial x} \rightarrow$  flux. Relaxation(弛豫); Transportation(输运). force-flux 关系.

### 1.4.1 Analyze Fluctuations

[Example] Classical nucleation theory: 若  $\mu_{\text{vapor}} > \mu_{\text{liquid}}$ , 则凝结发生. Local fluctuation of density  $\rho$ : grow/decay.

$G = -\alpha \uparrow |\Delta\mu| R^3 + \beta \sigma \downarrow R^2$ . 需要足够大的凝结核.

#### 1.4.1.1 Static Thermodynamic Analysis

研究发生  $f_0^{\text{equilibrium}} \rightarrow f_0 + \delta f^{\text{fluctuated}}$  的概率.

令系统 1 和系统 2 状态分别为  $(E_1, V_1), (E_2, V_2)$ , 且满足  $E_1 \ll E_2, V_1 \ll V_2$ ;  $\begin{cases} E_1 + E_2 = E \\ V_1 + V_2 = V \end{cases}$ .

设平衡态熵为  $S_0$ , 涨落态熵为  $S_f$ . 熵变  $\Delta S = S_f - S_0$ . 处于涨落态的概率  $P \propto e^{\Delta S/k_B}$ , 可近似  $P_2 \simeq P_0, T_2 \simeq T_0$ , 得

$$\Delta S = \Delta S_1 + \Delta S_2 = \Delta S_1 + \int_0^f \frac{dE_2 + P_2 dV_2}{T_2} \simeq \Delta S_1 - \frac{\Delta E_1 + P_0 \Delta V_1}{T_0}$$

于是迁移概率为  $P_1 \propto \exp\left(-\frac{\Delta E - T \Delta S + p \Delta V}{k_B T}\right)$ . 因此涨落态可用  $(\Delta E, \Delta S, \Delta V)$  描述. 将  $\Delta E$  在平衡态附近展开:

$$\Delta E(S, V) = \left(\frac{\partial E}{\partial S}\right)_0 \Delta S + \left(\frac{\partial E}{\partial V}\right)_0 \Delta V + \frac{1}{2} \left[ \left(\frac{\partial^2 E}{\partial S^2}\right)_0 (\Delta S)^2 + 2 \left(\frac{\partial^2 E}{\partial S \partial V}\right)_0 \Delta S \Delta V + \left(\frac{\partial^2 E}{\partial V^2}\right)_0 (\Delta V)^2 \right] + \dots$$

将展开式代入分子:  $\Delta E - T \Delta S + p \Delta V = \frac{1}{2} \left[ \Delta \left(\frac{\partial E}{\partial S}\right)_0 \Delta S + \Delta \left(\frac{\partial E}{\partial V}\right)_0 \Delta V \right] = \frac{1}{2} [\Delta T \Delta S - \Delta p \Delta V]$ ,

于是得到  $P \propto \exp\left(-\frac{\Delta T \Delta S - \Delta p \Delta V}{2k_B T}\right)$ , 即三个  $\Delta$  中只有两个独立. 类似的关系还有:

$$1. \Delta S = \left(\frac{\partial S}{\partial T}\right)_V \Delta T + \left(\frac{\partial S}{\partial V}\right)_T \Delta V = \frac{C_v}{T} \Delta T + \left(\frac{\partial S}{\partial V}\right)_T \Delta V;$$

$$2. \Delta P = \left(\frac{\partial P}{\partial T}\right)_V \Delta T + \left(\frac{\partial P}{\partial V}\right)_T \Delta V = \left(\frac{\partial P}{\partial T}\right)_V \Delta T - \frac{1}{\kappa_T V} \Delta V, \text{ 其中等温压缩率 } \kappa_T = -\frac{1}{V} \left(\frac{\partial V}{\partial P}\right)_T.$$

使用 Maxwell Relation  $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$ , 迁移概率化为  $P \propto \exp\left[-\frac{C_v}{2k_B T^2} (\Delta T)^2 - \frac{1}{2k_B \kappa_T T V} (\Delta V)^2\right]$ .

$$\text{计算涨落: } \langle (\Delta T)^2 \rangle = \frac{\int (\Delta T)^2 P(\Delta T, \Delta V) d(\Delta T)}{\int P(\Delta T, \Delta V) d(\Delta T)} = \frac{k_B T^2}{C_v} \propto \frac{1}{V}, \quad \langle (\Delta V)^2 \rangle = k_B T \kappa_T V \propto V$$

定义相对涨落为  $\frac{\sqrt{\langle (\Delta A)^2 \rangle}}{\langle A \rangle}$ .  $(\Delta E)^2 = \left[ \left(\frac{\partial E}{\partial T}\right)_{VN} \Delta T + \left(\frac{\partial E}{\partial V}\right)_{TN} \Delta V \right]^2$ , 等式两边同取期望值  $\langle \cdot \rangle$ , 忽略交叉项:

$$\langle(\Delta E)^2\rangle = \langle(C_v\Delta T)^2\rangle + \left\langle\left[\left(\frac{\partial E}{\partial V}\right)_{TN}\Delta V\right]^2\right\rangle + \overset{\text{fluctuation of particle numbers}}{\text{cross terms}\rightarrow 0} = C_v k_B T^2 + k_B T \kappa_T V \left(\frac{\partial E}{\partial V}\right)_{TN}^2.$$

[Discussion] 令 internal energy per particle  $\tilde{\varepsilon}$  与 volume per particle  $v$ .

$$k_B T \kappa_T V \left(\frac{\partial E}{\partial V}\right)_{TN}^2 = k_B T \kappa_T N v \left(\frac{\partial \tilde{\varepsilon}}{\partial v}\right)_T^2 = k_B T \kappa_T N n^3 \left(\frac{\partial \tilde{\varepsilon}}{\partial n}\right)_T^2, \text{ 其中粒子数密度 } n = \frac{N}{V} = \frac{1}{v}.$$

回忆巨正则系综:  $\langle(\Delta E)^2\rangle = k_B T^2 C_v$ , 即 canonical 项. 将其和粒子数涨落项  $\langle(\Delta N)^2\rangle$  分离, 从而写作

$$\langle(\Delta E)^2\rangle = \langle(\Delta E)^2\rangle_{\text{canonical}} + \left(\frac{\partial \langle E \rangle}{\partial N}\right)_{TV}^2 \langle(\Delta N)^2\rangle, \text{ 其中 } \langle(\Delta N)^2\rangle = \frac{\langle N \rangle^2 k_B T \kappa_T}{V}$$

观察相对涨落与体积  $V$  关系为  $\frac{\sqrt{\langle(\Delta T)^2\rangle}}{\langle T \rangle} \sim \frac{1}{\sqrt{V}}, \quad \frac{\sqrt{\langle(\Delta V)^2\rangle}}{\langle V \rangle} \propto \frac{1}{\sqrt{V}}$ . 因此 MFT 难以用于小尺度系统.

#### 1.4.1.2 Time Analysis of Fluctuations

$x_0 \rightarrow x_f(t)$ . 视涨落为含时信号  $A(t)$ . 时间平均  $\langle A \rangle = \frac{1}{T} \int_0^T A(t) dt$ ; 定义时间关联函数  $\phi(t) = \frac{1}{T} \int_0^T \delta A(u) \delta A(u+t) du$ .

假定 ergodic (各态历经), 时间平均化为系综平均:  $\phi(t_1, t_2) = \langle \delta A(t_1) \delta A(t_2) \rangle^{\text{ensemble}}$ . 时间平移不变性:  $\phi(t_1, t_2) \rightarrow \phi(t_2 - t_1)$ .

时间平移不变性 in Joint probability  $P_n(x_1, t_1; x_2, t_2; \dots; x_n, t_n) = P_n(x_1, t_1 + \Delta t; x_2, t_2 + \Delta t; \dots; x_n, t_n + \Delta t)$

[Discussion] Correlation & Macroscopic properties.

1. 空间关联函数  $g_{ij} \xrightarrow{\text{in equilibrium}}$  Response  $\chi$ ;

2. 时间关联函数  $\phi(t) \xrightarrow{\text{out of equilibrium}}$  conductivity, viscosity (粘度).

[Example] 测量  $k_B$ . 分光出点光源, 凸透镜聚焦后散射至垂吊镜面, 相机收集其反射光. 镜子受空气撞击即布朗运动 (视为热浴). 热平衡下  $\frac{1}{2} L \langle \theta^2 \rangle = \frac{1}{2} k_B T \Rightarrow \langle \theta^2 \rangle = \frac{k_B T}{L}$ . (能均分定理: Hamiltonian  $\propto$  自由度平方) 分别在 1 atom 和  $10^{-4}$  mmHg 进行实验. 前者相比后者的偏转产生频率高得多. 但只要温度一样, 仅凭  $\langle \theta^2 \rangle$  无法区分. 类比于价格/股票的含时变化.

##### 1.4.1.2.1 Spectral Analysis [Discussion] 使用三棱镜分光, 实际上就是一种频谱分析.

$$\tilde{x}(\omega) = \int_{-\infty}^{+\infty} x(t) e^{i\omega t} dt, \quad x(t) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} \tilde{x}(\omega) e^{-i\omega t} d\omega$$

对 statistically stationary signal (稳态信号), 关联函数  $\phi(t' - t) = \langle x(t') x(t) \rangle = \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \langle \tilde{x}(\omega) \tilde{x}(\omega') \rangle e^{-i(\omega t + \omega' t')} d\omega d\omega'$ ,

可推断频域内关联函数为  $\langle \tilde{x}(\omega) \tilde{x}(\omega') \rangle = 2\pi [\tilde{x}^2(\omega)] \delta(\omega - \omega')$ , 那么变换回时域形式:  $\phi(t) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} \tilde{x}^2(\omega) e^{-i\omega t} d\omega$ ,

其中  $\tilde{x}^2(\omega)$  是  $x^2(t)$  的傅里叶变换. 令  $\tilde{x}^2(\omega)$  对频域积分并归一化, 得到

$\phi(0) = \langle x^2(t) \rangle = \int_{-\infty}^{+\infty} \tilde{x}^2(\omega) \frac{d\omega}{2\pi} = 2 \int_0^{+\infty} \tilde{x}^2(\omega) \frac{d\omega}{2\pi}$ , 即得出 **Wiener-Khinchin theorem** (for random process & statistically stationary signal).

[Example]  $\phi(t) = \langle x(0)x(t) \rangle = \langle x(0)^2 \rangle e^{-\lambda|t|}$ .  $\tilde{x}^2(\omega) = \langle x(0)^2 \rangle \frac{2\lambda}{\omega^2 + \lambda^2}$ ,  $\langle x^2(t) \rangle = \left\langle 2 \int_0^{+\infty} \tilde{x}^2(\omega) \frac{d\omega}{2\pi} \right\rangle$ ,

$$\int_0^{+\infty} \frac{\lambda}{\omega^2 + \lambda^2} d\omega = \int_0^{+\infty} \frac{1}{\omega'^2 + 1} d\omega' = \frac{\pi}{2} \Rightarrow \langle x^2(t) \rangle = \langle x^2(0) \rangle.$$

#### 1.4.2 Relaxation of Weakly Non-equilibrium State

形如  $\frac{dx(t)}{dt} = -\lambda x(t) \Rightarrow x(t) = x(0)e^{-\lambda t}$  的 (描述性) Relaxation equation. 物质输运和热量输运是耦合的, 则

$$\langle x_i(t) \rangle \Rightarrow \frac{dx_i(t)}{dt} = - \sum_k \lambda_{ik} x_k(t). \text{ 延拓 } \phi_{ik}(t' - t) = \langle x_i(t') x_k(t) \rangle = \langle x_k(t) x_i(t') \rangle = \phi_{ki}(t - t') \Rightarrow \boxed{\phi_{ik}(t) = \phi_{ki}(-t)}.$$

若  $x_i(-t) = x_i(t)$ ,  $\phi_{ik}(t' - t) = \langle x_i(t') x_k(t) \rangle = \langle x_i(-t') x_k(-t) \rangle = \phi_{ik}[-t' - (-t)] = \phi_{ik}(t - t') \Rightarrow \phi_{ik}(t) = \phi_{ik}(-t)$

因此时间反演对称下, 有  $\boxed{\phi_{ik}(t) = \phi_{ki}(t)}$

### 1.4.2.1 Flux & Force

求和约定:  $\dot{x}_i(t) = -\lambda_{ik}x_k(t)$ , 定义共轭量  $X_i = \frac{\partial S}{\partial x_i}$  以引入熵  $S(x_1, x_2, \dots, x_n)$ .  $\dot{x}_i(t), X_i(t)$  分别为 flux 和 force.

Taylor 展开:  $S(x_i) = S(0) + \left( \frac{\partial S}{\partial x_i} \right)_{x_i=0} x_i + \frac{1}{2} \left( \frac{\partial^2 S}{\partial x_i \partial x_j} \right)_{x_i=x_j=0} x_i x_j + \dots = S(0) - \frac{1}{2} \beta_{ij} x_i x_j$ , 其中  $\beta_{ij} = \beta_{ji}$ .

代入展开式:  $X_i = \frac{\partial S}{\partial x_i} = \frac{\partial}{\partial x_i} \left[ S(0) - \frac{1}{2} \beta_{jk} x_j x_k \right] = -\frac{\beta_{jk}}{2} \frac{\partial}{\partial x_i} (x_j x_k) = -\frac{\beta_{jk}}{2} (\delta_{ij} x_k + x_j \delta_{ik}) = -\beta_{ik} x_k$ .

于是 Force  $X_i = -\beta_{ik} x_k$ , 从而得到 **Force-Flux** 关系  $\dot{x}_i = \gamma_{ik} X_k$ , 其中  $\gamma_{ik} = \lambda_{il} (\beta^{-1})_{lk}$  是 **Kinetic Coefficient**.

比如写作二阶形式的  $\begin{bmatrix} \dot{x}_1 \\ \dot{x}_2 \end{bmatrix} = \begin{bmatrix} \gamma_{11} & \gamma_{12} \\ \gamma_{21} & \gamma_{22} \end{bmatrix} \begin{bmatrix} X_1 \\ X_2 \end{bmatrix}$ . 若常数项  $S(0) = 0$ , 则熵可写作共轭量乘积:  $S = \frac{1}{2} X_i x_i$ ,

变化率为  $\frac{dS}{dt} = \frac{1}{2} (\dot{X}_i x_i + X_i \dot{x}_i)$ . 利用 force-flux 关系处理  $x_i \dot{X}_i = x_i (-\beta_{ik} \dot{x}_k) = x_i (-\beta_{ki} \dot{x}_k) = X_k \dot{x}_k$ ,

因此  $\dot{S} = X_i \dot{x}_i = \frac{\partial S}{\partial x_i} \dot{x}_i$ , 显然就是链式求导规则.

[Example] 考虑铜棒, 忽略体积变化 ( $dV = 0$ ). 存在热流  $\vec{J}_h$ . Internal energy per volume:  $u(x, y, z, t)$ . 则有

$$\frac{\partial u}{\partial t} + \nabla \cdot \vec{J}_h = 0 \xrightarrow{du=TdS} \frac{\partial S}{\partial t} = -\frac{1}{T} \nabla \cdot \vec{J}_h \Rightarrow \frac{\partial S}{\partial t} + \nabla \cdot \left( \frac{\vec{J}_h}{T} \right) = -\frac{1}{T^2} \vec{J}_h \cdot \nabla T.$$

等式右边为 rate of entropy production ( $\neq 0$  时为非平衡过程), 即为 0 时形成对  $S$  的连续性方程.

### 1.4.2.2 Onsager's Reciprocal Relation

平衡态时,  $\langle \dot{x}_i \rangle = 0, \langle x_i \rangle = \tilde{x}_i$ .  $\langle x_i X_j \rangle = \text{Tr} [x_i X_j A e^{\Delta S(x_1, x_2, \dots, x_n)/k_B}] = \text{Tr} [x_i X_j A e^{\frac{1}{2k_B} \beta_{ij} (x_i - \tilde{x}_i)(x_j - \tilde{x}_j)}]$

$$\frac{\partial \langle x_i \rangle}{\partial \tilde{x}_j} = \delta_{ij} = \frac{\partial}{\partial \tilde{x}_j} \text{Tr} [x_i A e^{-\frac{1}{2k_B} \beta_{ij} (x_i - \tilde{x}_i)(x_j - \tilde{x}_j)}] = \text{Tr} \left[ x_i \frac{-X_j}{k_B} A e^{-\frac{1}{2k_B} \beta_{ij} (x_i - \tilde{x}_i)(x_j - \tilde{x}_j)} \right] = -\frac{1}{k_B} \langle x_i X_j \rangle.$$

于是得到关系  $\langle x_i X_j \rangle = -k_B \delta_{ij}$ .

Time reversal symmetry of  $x_i$ :  $\langle x_i(0) x_j(t) \rangle = \langle x_i(t) x_j(0) \rangle \xrightarrow{t=0} \langle x_i(0) \dot{x}_j(0) \rangle = \langle \dot{x}_i(0) x_j(0) \rangle$ .

等式两边分别代入 force-flux 关系:  $\begin{cases} \langle x_i(0) \gamma_{jl} X_l(0) \rangle = -k_B \gamma_{jl} \delta_{il} = -k_B \gamma_{ji} \\ \langle \gamma_{il} X_l(0) x_j(0) \rangle = -k_B \gamma_{il} \delta_{jl} = -k_B \gamma_{ij} \end{cases}$ , 联立即得  $\gamma_{ij} = \gamma_{ji}$ .

若将  $\dot{x}_i = \gamma_{ij} X_j$  定义为  $\frac{\partial f}{\partial X_i}$ , 则有  $f = \frac{1}{2} \gamma_{ij} X_i X_j$ . 熵变化率可表述为  $\frac{dS}{dt} = X_i \dot{x}_i = X_i \frac{\partial f}{\partial X_i} = 2f$

[Discussion] Dynamics of fluctuation  $x_i = 0 \rightarrow x_i \neq 0$ . 若过程可表述为  $\dot{x}_i = -\Gamma_{ik} x_k$ ;

1. 且  $\Gamma_{ik}$  可对角化, 则可进一步写作 decay  $\dot{x}'_i = -\lambda_i x'_i$ ;
2. 且  $\Gamma_{ik}$  antisymmetric (特征值纯虚数), 即  $\dot{x}_i = -\lambda_{ik}^A x_k$ , 则动力学为 oscillatory (振荡).

### 1.4.2.3 Fluctuation Phenomena

1.4.2.3.1 XY Model Hamiltonian  $H = -\frac{1}{2} J \sum_{\langle i, j \rangle} \langle \vec{S}_i \cdot \vec{S}_j \rangle$ , 其中自旋形式为  $\vec{S}_i = (\cos \theta_i, \sin \theta_i)$ .

相比一般的 Ising model 多了  $\theta$  进行控制. 选定  $\vec{R}$  处一格点, 设  $\theta$  足够小. 则 Hamiltonian 为

$$\lim_{\theta \rightarrow 0} H = \frac{J}{4} \sum_{\vec{R}} \sum_{\vec{a}} \left[ \theta(\vec{R}) - \theta(\vec{R} + \vec{a}) \right]^2; \text{使用 Fourier 变换 } \theta_{\vec{k}} = \frac{1}{\sqrt{N}} \sum_{\vec{R}} \theta(\vec{R}) e^{-i\vec{k} \cdot \vec{R}},$$

将 Hamiltonian 写作动量  $\vec{k}$  形式  $H = \frac{1}{2} \sum_{\vec{k}} J_{\vec{k}} |\theta_{\vec{k}}|^2$ , 其中  $J_{\vec{k}} = 2J \sum_{\vec{a}} \left[ 1 - \cos(\vec{k} \cdot \vec{a}) \right]$ .

$$\langle \vec{S}(\vec{R}) \cdot \vec{S}(\vec{0}) \rangle = \begin{cases} \exp\left(-\frac{T}{a} \frac{R}{a}\right), & d=1, \text{ short range order} \\ (R/a)^{-\frac{\alpha}{T/2\pi\alpha}}, & d=2, \text{ quasi-long-range order} \\ \exp\left[-\frac{T k_D a}{\pi^2 \alpha}\right] \left(1 + \frac{\pi}{4k_D R}\right), & d=3, \text{ long range order} \end{cases}$$



### 1.4.2.3.2 Topological Defects 拓扑缺陷: vortex. 通过矢量场分析(汇源, winding number).

[Example] 二维点电荷电场, 点电荷所在位置即 defect core. 沿着圆周电场矢量方向旋转 360 度(规定旋转方向和圆周旋转方向相同为+, 反之为-). 则 winding number 为 +1. 匀强电场则为 0. 即  $\oint d\theta = 2\pi k, k \in \mathbb{Z}$ .

根据  $H \sim \int (\nabla\theta)^2$  可知, 拓扑缺陷的激发需要能量, 并且和角度梯度有关. 设  $\frac{\partial\theta}{\partial r} = 0 \Rightarrow \nabla\theta = \frac{1}{r} \frac{\partial\theta}{\partial\phi} \hat{e}_\phi + \frac{\partial\theta}{\partial r} \hat{e}_r$ ,

$$\oint d\theta = \oint \nabla\theta \cdot d\vec{l} = \frac{1}{r} \frac{\partial\theta}{\partial\phi} 2\pi r = 2\pi k \Rightarrow \frac{\partial\theta}{\partial\phi} = k \Rightarrow \theta = k\phi + c_0, c_0 \text{ 使得全局相位偏移.}$$

对  $H \sim \int (\nabla\theta)^2$  使用变分法, 即  $\delta H = 0 \Rightarrow \nabla^2\theta = 0$

$$1. \text{ One defect: } E = \varepsilon_0(a) + \frac{K}{2} \int (\nabla\theta)^2 d^2\vec{x} \stackrel{\theta=k\phi}{=} \varepsilon_0(a) + \pi K k^2 \ln\left(\frac{R}{a}\right)$$

2. Two defects.  $r$  为两缺陷间距,  $E_{\text{int}} = 2\pi k_1 k_2 K \ln\left(\frac{R}{r}\right)$ , 可类比二维形式的 Coulomb 势能(但不完全等效),  $k_1, k_2$  acts as charge. 温度从 0K 升高, 涨落变强, 激发出结构.

[Discussion] KPZ 方程(fluctuation/growth of interfaces).  $h(\vec{x}, t)$  为界面厚度.

$$\frac{\partial h(\vec{x}, t)}{\partial t} = \nu \nabla^2 h + \lambda (\nabla h)^2 + \eta(\vec{x}, t), \quad \eta = \text{white noise} \quad \langle \eta(\vec{x}, t) \rangle = 0$$

## 1.4.3 Brownian Motion

[Discussion] 墨滴在水中的扩散并不完全是布朗运动, 较大的影响因素是 flux. Brownian motion 本质是可以写出 Hamiltonian 的, 应当是一个完全确定系统. 随机性的来源: 观察的时间间隔  $\Delta t$ . 散点连线后是完全无规律的. 长链分子(Polymer) 的空间结构也可类比于布朗运动, 但不完全相同(需要考虑之前分子所占体积, 亦即 Self Avoidance); 特征是  $\sqrt{\langle \vec{R}^2 \rangle} \sim L^{\frac{1}{2}+\delta}$ , 其中  $\delta$  为分子自身体积产生的.

### 1.4.3.1 Random walk model

$$\langle r^2 \rangle \propto t.$$

#### 1.4.3.1.1 $n$ steps on 1D lattice $n$ 步后处于第 $m$ 格的概率为

$$P_n(m) = C_n^{\frac{n+m}{2}} \left(\frac{1}{2}\right)^{\frac{n+m}{2}} \left(\frac{1}{2}\right)^{\frac{n-m}{2}}, \text{ 设 } k = \frac{n+m}{2} \text{ 检验归一化: } \sum_{m=-n}^n P_n(m) = \sum_{k=0}^n C_n^k P_L^k P_R^{n-k} = 1.$$

$$\langle m \rangle = \sum_{m=-n}^n m P_n(m) = 0, \quad \langle m^2 \rangle = \sum_{m=-n}^n m^2 P_n(m) = n \rightarrow \langle x^2 \rangle \propto t.$$

极限下取高斯分布  $\lim_{n \rightarrow \infty} P_n(m) = \frac{1}{\sqrt{2\pi n}} \exp\left(-\frac{m^2}{2n}\right)$ . 使用  $\begin{cases} x = ml \\ t = n\tau \end{cases}$  连续化为  $P(x, t)dx = \frac{dx}{\sqrt{4\pi Dt}} \exp\left(-\frac{x^2}{4Dt}\right)$ , 其中扩散系数  $D = \frac{l^2}{2t}$ , 在气体中约  $(10^{-6}, 10^{-5}) \text{ m}^2/\text{s}$ , 在液体中约  $(10^{-10}, 10^{-9}) \text{ m}^2/\text{s}$ .

[Discussion] 从单粒子到粒子群. 设  $N$  particles, 且均为  $\delta(x, 0)$  分布. 经过时段  $t_1$  后, 则有分布函数  $P(x, t_1)dx \rightarrow n(\vec{x}, t)dx$ . 这就是扩散现象.

$$\text{连续性方程 } \frac{\partial n(\vec{x}, t)}{\partial t} = -\nabla \cdot \vec{j}(\vec{x}, t), \text{ Fick's law } \vec{j}(\vec{x}, t) = -D\nabla n(\vec{x}, t), \text{ 从而导出扩散方程 } \frac{\partial n(\vec{x}, t)}{\partial t} = D\nabla^2 n(\vec{x}, t).$$

$$\text{一维扩散方程解为 } n(\vec{x}, t) = \frac{N}{(4\pi Dt)^{d/2}} \exp\left(-\frac{|\vec{x}|^2}{4Dt}\right).$$

$$\langle x \rangle = 0, \langle x^2 \rangle = \frac{1}{N} \int_{-\infty}^{+\infty} x^2 n(\vec{x}, t) d^d\vec{x} = \boxed{2dDt}, \text{ 可见各轴分量独立.}$$

$$\langle (\Delta x)^2 \rangle \sim Dt, \text{ 纯粹依靠扩散作用在空气中传播 } 1\text{m} \text{ 需耗时 } t \sim \frac{\langle (\Delta x)^2 \rangle}{D} \sim 10^6 \text{ s} \approx 11 \text{ days.}$$

[Discussion]  $\sqrt{\langle (\Delta x)^2 \rangle} \sim t^\gamma$ .  $\gamma > \frac{1}{2}$ : super diffusion;  $\gamma < \frac{1}{2}$ : sub diffusion. e.g. cloud size:  $\gamma \approx \frac{3}{2}$ .

一种解释  $\gamma \neq \frac{1}{2}$  非 normal diffusion 的思路: Levy flight(令步长为概率分布).



**Galton Board.** 每层都是  $X_i = \pm 1$  的离散随机变量. 最后位置  $S_n = \sum_{i=1}^n X_i$ , 处于  $k$  的概率  $P(S = k) = C_n^k p^k (1-p)^{n-k}$ .

一般性地, 步长期望  $\langle X_i \rangle = (+1) \times p + (-1) \times (1-p) = l(2p-1)$ , 最后位置期望为  $\langle S_n \rangle = \sum_{i=1}^n \langle X_i \rangle = nl(2p-1)$ .

$$\langle S_n^2 \rangle = \langle \sum_{ij} X_i X_j \rangle = \sum_i \langle X_i^2 \rangle + \sum_{i \neq j} \langle X_i X_j \rangle = [l^2 p + l^2 (1-p)] n + \sum_{i \neq j} \langle X_i \rangle \langle X_j \rangle = nl^2 + n(n-1)(2p-1)^2 l^2$$

**1.4.3.1.2 d-Dim Off-Lattice Random Walk** 将位矢  $\vec{r}$  展开为基矢形式  $\vec{r} = \sum_{\alpha=1}^d x_{\alpha} \hat{e}_{\alpha}$ , 其中  $x_{\alpha} = \sum_{i=1}^N \vec{a}_i \cdot \vec{e}_{\alpha} = a_i \sum_{i=1}^N \cos \theta_i$ .

根据独立性有  $\langle r^2 \rangle = \sum_{\alpha=1}^d \langle x_{\alpha}^2 \rangle$ , 各轴  $\langle x_{\alpha}^2 \rangle = a^2 \sum_{i=1}^N \langle \cos^2 \theta_i \rangle + a^2 \sum_{i \neq j} \langle \cos \theta_i \cos \theta_j \rangle = Na^2 \langle \cos^2 \theta \rangle$ .

对2维球面  $d\Omega = \sin \theta d\theta d\phi$ , 推广至  $(d-1)$  维球面:  $d\Omega = \sin^{d-2} \theta_1 \sin^{d-3} \theta_2 \cdots \sin^1 \theta_{d-2} d\theta_1 d\theta_2 \cdots d\theta_{d-1} d\phi$ .

于是归一化条件  $\int P(\{\theta\}) d\Omega = 1$  应写为

$$\int P_0(\sin \theta_1)^{d-2} (\sin \theta_2)^{d-3} \cdots (\sin \theta_{d-2})^1 d\theta_1 d\theta_2 \cdots d\theta_{d-1} = \left[ \int P_0(\sin \theta_1)^{d-1} d\theta_1 \right] \times \Omega'(\theta_2, \theta_3, \cdots, \theta_{d-1}) = 1.$$

$$\text{计算 } \langle \cos^2 \theta_1 \rangle = \int \cos^2 \theta_1 P_0 d\Omega = \Omega' \int_0^{\pi} P_0 \cos^2 \theta_1 \sin^{d-2} \theta_1 d\theta_1 = \frac{1}{d}, \text{ 于是 } \langle r^2 \rangle = \sum_{\alpha=1}^d Na^2 \langle \cos^2 \theta \rangle = Na^2 \sum_{\alpha=1}^d \frac{1}{d} = Na^2.$$

即极高  $d$  维下, 矢量集中在球面的"赤道"上, 这是因为高维下赤道附近的"面积"更集中. 最后所得  $\langle r^2 \rangle$  与维数无关.

$$[\text{Discussion}] \text{ Random unit vector } \vec{n} \text{ in } n\text{-dim space. } \vec{n} = \sum_{\alpha=1}^d n_{\alpha} \hat{e}_{\alpha}, \langle n_{\alpha}^2 \rangle = \sum_{\alpha=1}^d \langle n_{\alpha}^2 \rangle = d \langle n_1^2 \rangle = d \langle \cos^2 \theta \rangle = 1 \Rightarrow \langle n_1^2 \rangle = \frac{1}{d}$$

### 1.4.3.2 Stochastic process

Static continuous random variable  $X_i: \{x_0\} \xrightarrow{t_0} [x_1, x_1 + dx] \xrightarrow{t_1} [x_2, x_2 + dx] \rightarrow \cdots$

令  $P_1(x, t) = \text{Prob}[x < x(t) < x + dx]$  为  $t$  时刻  $x \in (x, x + dx)$  的概率,

$$P_n(x_0, t_0; x_1, t_1; \cdots; x_{n-1}, t_{n-1}) dx_0 \cdots dx_{n-1} = \text{Prob}[x_0 < x(t_0) < x_0 + dx_0, \cdots, x_{n-1} < x(t_{n-1}) < x_{n-1} + dx_{n-1}]$$

$$\text{定义 Transition Probability: } \text{Prob}[(x_0, t_0) \rightarrow (x_1, t_1)] dx_1 = \frac{P_2(x_0, t_0; x_1, t_1) dx_1}{P_1(x_0, t_0)}.$$

$$\text{该语言下的关联函数为 } \langle x_0(t_0) x_1(t_1) \rangle = \int x_0(t_0) x_1(t_1) P_n(x_0, t_0; x_1, t_1, \cdots) \prod_{k=0}^{n-1} dx_k.$$

### 1.4.3.3 Smoluchowski's Approach

从  $x_0$  出发, 经过  $n$  步后到达  $x$  的概率为  $\text{Prob}(x_0 \xrightarrow{n \text{ steps}} x) = P_n(x_0|x)$ , 可写作递推形式( $n \geq 1$ )  $\sum_{z=-\infty}^{+\infty} P_{n-1}(x_0|z) P_1(z|x)$ ,

即从  $x_0$  出发, 经过  $n-1$  步到达任意位置  $z$ , 再经过 1 步到达  $x$ . 对于位置  $z$ , 要求

$$P_1(z|x) = \frac{1}{2} (\delta_{z, x+1} + \delta_{z, x-1}), P_0(z|x) = \delta_{z, x}, \text{ 代入递推得 } P_n(x_0|x) = \frac{1}{2} P_{n-1}(x_0|x-1) + \frac{1}{2} P_{n-1}(x_0|x+1).$$

构造辅助函数  $Q_n(\xi) \equiv \sum_{x=-\infty}^{+\infty} P_n(x_0|x) \xi^{x-x_0}$ , 将其递推化:

$$Q_n(\xi) = \sum_{x=-\infty}^{+\infty} \left[ \frac{1}{2} P_n(x_0|x-1) \xi^{x-x_0} + \frac{1}{2} P_{n-1}(x_0|x+1) \xi^{x-x_0} \right] = \frac{1}{2} \xi Q_{n-1}(\xi) + \frac{1}{2} \xi^{-1} Q_{n-1}(\xi) = \frac{1}{2} (\xi + \xi^{-1}) Q_{n-1}(\xi)$$

$$\text{代入初始条件 } Q_0(\xi) = 1 \text{ 解得 } Q_n(\xi) = \left( \frac{1}{2} \right)^n \sum_{|x-x_0| \leq n} C_n^{[n+(x-x_0)]/2} \xi^{x-x_0}.$$

$$\text{通过同构可知 } P_n(x_0|x) = \left( \frac{1}{2} \right)^n C_n^{[n+(x-x_0)]/2}, \text{ 其中 } |x-x_0| \leq n.$$

#### 1.4.3.4 State of System(Markov Procss, History-Independent)

态:  $n = 1, 2, 3, \dots, M$ ; 态为  $n$  的概率:  $y(n)$ ; 时间:  $t = s\tau, s = 0, 1, 2, \dots$  系统在  $t = s\tau$  时刻处于状态  $n$  的概率:  $P(n, s)$ .

**Markov Chain:**  $P(n, s) \rightarrow P(n, s+1) \rightarrow P(n, s+2) \rightarrow \dots$ , 即依赖于前一时刻的状态, 和历史无关.

前文所谈则是 history-dependent  $P(n, s) = f[P(n, s-1), P(n, s-2), \dots, P(n, 0)]$ .

定义 Conditional Prob:  $P(n_1, s_1 | n_2, s_2)$ . 则从  $s_0$  时刻的状态  $n_0$  迁移至  $(s_0 + 1)$  时刻的状态  $n$  的概率为

$$P(n_0, s_0 | n, s+1) = \sum_{m=1}^M P(n_0, s_0 | m, s) P(m, s | n, s+1) = \sum_{m=1}^M P(n_0, s_0 | m, s) Q_{mn}(s).$$

那么系统在  $s$  时刻处于状态  $n$  的概率为  $P(n, s) = \sum_{m=1}^M P(m, s-1) P(m, s-1 | n, s)$ , 重复该递推直至化为形式:

$$\begin{aligned} P(n, s) &= \sum_{m, m_1, m_2, \dots, m_{s-1}} P(m, 0) P(m, 0 | m_1, 1) P(m_1, 1 | m_2, 2) \cdots P(m_{s-1}, s-1 | n, s) \\ &= \sum_{m, m_1, m_2, \dots, m_{s-1}} P(m, 0) Q_{mm_1}(1) Q_{m_1 m_2}(2) \cdots Q_{m_{s-1} n}(s-1) = \sum_m P(m, 0) (Q^S)_{mn}, \\ P(m, s_0 | n, s) &= (Q^{s-s_0})_{mn} \end{aligned}$$

其中运用了类似于矩阵乘法  $\sum_j A_{ij} B_{jk} = (AB)_{ik}$ .

[Example]  $N$ -ring [ $P(N+1) \equiv P(1)$ ]. 将 Random Walk 近似为 Markov Process.  $Q_{n,n+1} = Q_{n+1,n} = \frac{1}{2}, n \in \mathbb{N}$ .

$$P(n, s) = P(n-1, s-1) Q_{n-1,n} + P(n+1, s-1) Q_{n+1,n} = \frac{1}{2} [P(n-1, s-1) + P(n+1, s-1)]$$

$$\begin{aligned} \text{Define } \delta P(n, s) &\equiv P(n, s) - P(n, s-1) = P(n-1, s-1) Q_{n-1,n} + P(n+1, s-1) Q_{n+1,n} - P(n, s-1) \\ &= \frac{1}{2} [P(n-1, s-1) + P(n+1, s-1) - 2P(n, s-1)] \end{aligned}$$

Let  $t$  be continuous:  $\tau \frac{dP_n(t)}{dt} = \frac{1}{2} [P_{n-1}(t) + P_{n+1}(t) - 2P_n(t)]$ ; Then let  $n$  be continuous:

$$\tau \frac{dP_n(t)}{dt} = \frac{a^2 P_{n-1}(t) + P_{n+1}(t) - 2P_n(t)}{a^2} \Rightarrow \frac{\partial P(x, t)}{\partial t} = D \frac{\partial^2 P(x, t)}{\partial x^2}, \quad D \sim \frac{a^2}{2\tau}. \text{ 正是 Feynmann Kac formula.}$$

#### 1.4.3.5 Langevin's Theory

忽略粒子间关联(flux). Based on force & dynamics, equation of motion.  $x(t + \delta t) - x(t) = f(t)\delta t \Rightarrow \dot{x}(t) = f$ , random force.

$$\text{介观(mesosopic) level: } M \frac{d\vec{v}}{dt} = -\frac{\vec{v}}{B} + \vec{F}(t). \quad f_{\text{stokes}} = f\left(\frac{\text{半径}}{a}, \frac{\text{粘度}}{\eta}, \frac{\text{速度}}{v}, \frac{\text{质量}}{m}\right) = 6\pi\eta a v \Rightarrow B = \frac{1}{6\pi\eta a}$$

$$\text{随机力满足 } \langle F(t) \rangle = 0, \quad \langle \vec{F}(t) \vec{F}(t') \rangle = C_1 \delta(t - t').$$

[Discussion] 回忆 Ideal gas:  $\langle \delta n(x) \delta n(x') \rangle = c \delta(x - x')$ , 形式与随机力的二阶矩相似.

只有一阶矩和二阶矩非零, 则可使用 Gaussian distribution 描述.

$$\text{[Example] Irregular part(noise) of collective electron motion in circuit. } L \frac{dI}{dt} = -RI + V(t)$$

两边同乘  $\vec{v}$  且求期望  $\langle \cdot \rangle$ , 有  $\frac{d}{dt} \left( \frac{1}{2} M \langle v(t)^2 \rangle \right) + M\tau^{-1} \langle v(t)^2 \rangle = \langle v(t) F(t) \rangle$ , 即得到动能形式的 Langevin 方程.

$$\frac{dK(t)}{dt} = \langle v(t) F(t) \rangle - \frac{2}{\tau} K(t). \text{ 其中 } \tau = MB. \text{ 平衡态: } \frac{dK(t)}{dt} = 0 \Rightarrow \langle v(t) F(t) \rangle = \frac{2}{\tau} K_0 = \frac{2}{\tau} \cdot \frac{d}{2} k_B T, d \text{ 为维数.}$$

$$\text{在 } d=1 \text{ 情况下, 定义 } v(t) = e^{-t/\tau} u(t), \text{ 其中 } \tau = MB. \text{ 将其代入方程后解得 } v(t) = \frac{1}{M} \int_0^t dt' e^{-(t-t')/\tau} F(t').$$

$$\text{那么 } \langle v(t) F(t) \rangle = \frac{C_1}{2M}, \text{ 其中 } C_1 \text{ 来自于 } \langle \vec{F}(t) \vec{F}(t') \rangle = C_1 \delta(t - t').$$

$$\text{平衡态: } \frac{C_1}{2M} = \frac{2}{\tau} \cdot \frac{1}{2} k_B T \Rightarrow \boxed{C_1 = \frac{2k_B T}{B}}, \text{ Fluctuation-Dissipation Theorem(涨落耗散定理).}$$

#### 1.4.3.5.1 Analysis of Particle Position 检查 Langevin 语言下的 $\langle r^2(t) \rangle = 2dDt$ 是否仍然满足.

方程写作  $\frac{d\vec{v}}{dt} = -\frac{\vec{v}}{\tau} + \vec{A}(t)$ , 其中  $\vec{A}(t) = \frac{\vec{F}}{M}$ . 因为  $\frac{d^2 r^2}{dt^2} = 2v^2 + 2\vec{r} \cdot \frac{d\vec{r}}{dt}$ , 等号两边同乘  $\vec{r}$  后求系综平均  $\langle \cdot \rangle$ , 有

$$\frac{d^2}{dt^2} r^2 + \frac{1}{\tau} \frac{d}{dt} r^2 = 2v^2 + \vec{r} \cdot \vec{A} \Rightarrow \frac{d^2}{dt^2} \langle r^2 \rangle + \frac{1}{\tau} \frac{d}{dt} \langle r^2 \rangle + 2 \langle v^2 \rangle + \langle \vec{r} \cdot \vec{A} \rangle = 0$$

因为  $\vec{A}$  和  $\vec{r}$  无关, 所以该期望项为 0.

三维动能均值为  $\frac{1}{2} M \langle v^2 \rangle = \frac{1}{2} k_B T \times 3$ , 解得位移方均  $\langle r^2(t) \rangle = \frac{6k_B T \tau^2}{M} \left[ \frac{t}{\tau} - (1 - e^{-t/\tau}) \right]$

1.  $t \ll \tau$ ,  $\langle r^2(t) \rangle = \frac{3k_B T}{M} t^2 = \langle v^2 \rangle t^2$ , 即 Ballistic motion(弹道运动). 然而 Langevin 方程在  $t \rightarrow 0$  时有效性存疑.

2.  $t \gg \tau$ ,  $\langle r^2(t) \rangle = \frac{6k_B T \tau}{M} t = 6Bk_B T t \stackrel{d=3}{=} 6Dt \Rightarrow \boxed{D = Bk_B T}$ ,  $\forall d$ , another form of **Fluctuation-Dissipation Theorem**, or **Einstein's Relation**.

#### 1.4.3.5.2 Analysis of Particle Velocity $\vec{v}(t)$

$\langle v^2(t) \rangle = \left\langle \left[ v(0) + \frac{1}{M} \int_0^t dt' e^{-(t-t')/\tau} F(t') \right]^2 \right\rangle = v^2(0) e^{-2t/\tau} + \frac{C}{M^2} \frac{\tau}{2} (1 - e^{-2t/\tau})$ , 其中带入了  $v(t)$  表达式.

Requires  $\frac{1}{2} M \langle v^2(t) \rangle = \frac{3}{2} k_B T \Rightarrow C = \frac{6k_B T}{B}$ . Let  $x \equiv \langle v^2(t) \rangle - \langle v^2(\infty) \rangle$ , 则  $\frac{dx}{dt} = -\frac{2}{\tau} x$

[Discussion] 速度发散  $\lim_{\delta t \rightarrow 0} \frac{\langle |x(t+\delta t) - x(t)| \rangle}{\delta t} \sim \lim_{\delta t \rightarrow 0} \frac{(\delta t)^{\frac{1}{2}}}{\delta t} \rightarrow \infty$ . Solution:

1. Stochastic Differential Equation 严格化;

2. 从场的观点出发. 将随机性转移至概率分布函数(particle-based approach  $\rightarrow$  field-based approach). 场  $f(x, t)$ , 则位置为

$\rho(x) = q\delta(x - x_0)$ ,  $\int \rho(x) dx = q$ . 如果是匀速直线运动, 则  $f(x, t) = \delta(x - vt)$ . 若粒子  $x \rightarrow x + \delta x$ , 则  $f(x, t) = \langle \delta[x - x(t)] \rangle$ , 即场与粒子观点的转换.

约束  $\sum_i n_i = N$ . 态迁移率(transition rate) 为  $\frac{n_i(t+\delta t) - n_i(t)}{\delta t} = -\sum_{j \neq i} n_i(t) P_{i \rightarrow j} + \sum_{j \neq i} n_j(t) P_{j \rightarrow i}$ , 这类方程被称为

**Master equation**.

1. 假定为 Markov Process;

2. 粒子数守恒:  $\frac{1}{\delta t} \left[ \sum_i n_i(t+\delta t) - \sum_i n_i \right] = \sum_i \left( \sum_{j \neq i} n_j P_{j \rightarrow i} - \sum_{i \neq j} n_i P_{i \rightarrow j} \right) = 0$ .

[Application] 2-state system.  $n_+ : |+\rangle$ ,  $n_- : |-\rangle$ . 迁移速率  $\omega_{\pm}$ . 平衡态:  $\frac{n_+^0}{n_-^0} = \frac{\omega_+}{\omega_-}$

$\frac{dn_+}{dt} = -n_+ \omega_- + n_- \omega_+$ ,  $\frac{dn_-}{dt} = -n_- \omega_+ + n_+ \omega_-$

Relaxation dynamics: 设  $n(t) = n_- - n_+$ . 则微分方程化为  $\frac{dn(t)}{dt} = \frac{1}{\tau} [n(t) - n^0]$ , 其中  $\tau = \frac{1}{\omega_+ + \omega_-}$ ,  $n^0 = n_-^0 - n_+^0$ .

[Discussion] 连续变量 Master Equation. 前提: 1. 归一化条件:  $\int_{-\infty}^{+\infty} f(x, t) dx = 1$ ;

2. 概率函数定义:  $f(x, t) dx$  是粒子在  $t$  时刻处于  $[x, x + dx]$  的概率.

3. 动力学:  $\frac{\partial f(x, t)}{\partial t} = \int_{-\infty}^{+\infty} [-f(x, t) W(x, x') + f(x', t) W(x', x)] dx'$ ,  $W(x, x') dx'$  是  $x \rightarrow x'$  的迁移概率.

以上动力学方程可改写为  $\frac{\partial}{\partial t} f(x, t) = -\frac{\partial}{\partial x} (\mu_1(x) f(x, t)) + \frac{1}{2} \frac{\partial^2}{\partial x^2} [\mu_2(x) f(x, t)]$ , 即 **Fokker-Planck** 方程.

其中矩系数  $\mu_1(x) = \int_{-\infty}^{+\infty} d\xi \xi W(x, \xi) = \frac{\langle \delta x \rangle_{\delta t}}{\delta t} = \langle v_x \rangle$ ,  $\mu_2(x) = \int_{-\infty}^{+\infty} d\xi \xi^2 W(x, \xi) = \frac{\langle (\delta x)^2 \rangle_{\delta t}}{\delta t}$ .

写作概率流形式:  $\frac{\partial}{\partial t} f(x, t) = -\frac{\partial}{\partial x} j(x, t)$ ,  $j(x, t) = \mu_1(x) f(x, t) - \frac{1}{2} \frac{\partial}{\partial x} [\mu_2(x) f(x, t)]$ .

[Example] 粘液中振子. 矩系数信息为  $\mu_1(x) = -\lambda B x$ ,  $\mu_2(x) = \frac{\langle \delta x^2 \rangle}{\delta t} = 2Bk_B T$

Fokker-Planck 方程为  $\frac{\partial f(x, t)}{\partial t} = \lambda B \frac{\partial}{\partial x} (x f(x, t)) + Bk_B T \frac{\partial^2 f(x, t)}{\partial x^2}$

平衡态解:  $\lambda B \frac{\partial}{\partial x} (x f(x, \infty)) + B k_B T \frac{\partial^2}{\partial x^2} f(x, \infty) = 0 \Rightarrow f(x, \infty) = \left( \frac{\lambda}{2\pi k_B T} \right)^{\frac{1}{2}} e^{-\frac{\lambda x^2}{2k_B T}}.$

$$\langle x \rangle = 0, \quad \langle x^2 \rangle = \int_{-\infty}^{+\infty} x^2 f(x, \infty) dx = \frac{k_B T}{\lambda}$$

设初始为  $\delta x$  分布, 则一般含时解为  $f(x, t) = \left[ \frac{\lambda}{2\pi k_B T (1 - e^{-2\lambda B t})} \right]^{\frac{1}{2}} \exp \left[ -\frac{\lambda x^2}{2k_B T (1 - e^{-2\lambda B t})} \right].$

该模型对应的 Langevin 方程为  $\eta \frac{dx}{dt} = -U'(x) + F(t)$ , 其中  $U(x) = \frac{1}{2} \lambda x^2$ ,  $U'(x) = \lambda x$  为势能的导数.

#### 1.4.3.5.3 Time Correlation of Velocity $v(t)$ . 令时间变量 $u_1, u_2$ .

则位移方均  $\langle x^2(t) \rangle = \left\langle \left( \int_0^t du_1 v(u_1) \right) \left( \int_0^t du_2 v(u_2) \right) \right\rangle = \int_0^t du_1 \int_0^t du_2 \langle v(u_1) v(u_2) \rangle$ . 利用微积分性质  $\frac{d}{dt} \int_0^t f(u) du = f(t)$

$$\text{得到 } \frac{d \langle x^2(t) \rangle}{dt} = 2 \int_0^t du \langle v(u) v(t) \rangle \stackrel{\text{time reversal symmetry}}{=} 2 \int_{-t}^0 du \langle v(u) v(0) \rangle = 2 \int_0^t du \langle v(u) v(0) \rangle = 2D$$

观察对比得到  $\int_0^t \langle v(u) v(0) \rangle du = D t.$

$$\frac{\partial f(x, t)}{\partial t} = \frac{1}{\eta} \frac{\partial}{\partial x} (U'(x) f(x, t)) + \frac{k_B T}{\eta} \frac{\partial^2}{\partial x^2} f(x, t)$$

#### 1.4.3.5.4 Fourier Transformation of Langevin Equation .

约化 Langevin 方程形为  $\frac{dv(t)}{dt} = -\frac{v(t)}{\tau} + A(t)$ , 其中  $\langle A(t) A(t') \rangle = C_1' \delta(t - t')$ .

速度变换为  $\tilde{v}(\omega) = \frac{\tilde{A}(\omega)}{-i\omega + \tau^{-1}}$ , 约化随机力变换后满足  $\langle \tilde{A}(\omega) \tilde{A}(\omega') \rangle = 2\pi C_1' \delta(\omega + \omega')$

频域内速度关联为  $\langle \tilde{v}^*(\omega) \tilde{v}(\omega') \rangle = S(\omega) \delta(\omega + \omega')$ , 其中  $S(\omega) = \frac{2\pi C_1}{\tau^{-2} + \omega^2}$ . 令速度关联在  $\omega'$  域积分,

得到  $\langle \tilde{v}^*(\omega) \tilde{v}(t=0) \rangle = S(\omega)$ ; 再令其在  $\omega$  域积分, 得到  $\langle v(t) v(0) \rangle = \int_{-\infty}^{+\infty} S(\omega) e^{-i\omega t} \frac{d\omega}{2\pi}.$

令自由参数  $t = 0$ , 则  $\langle v(0)^2 \rangle = \int_{-\infty}^{+\infty} \frac{d\omega}{2\pi} S(\omega)$ ; 根据对称性,  $S(0) = 2 \int_0^{+\infty} d\omega \langle v(t) v(0) \rangle = \frac{2\pi C_1}{\tau^{-2}} = 2D.$

## 第二章 Homework

### 2.1 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

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

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

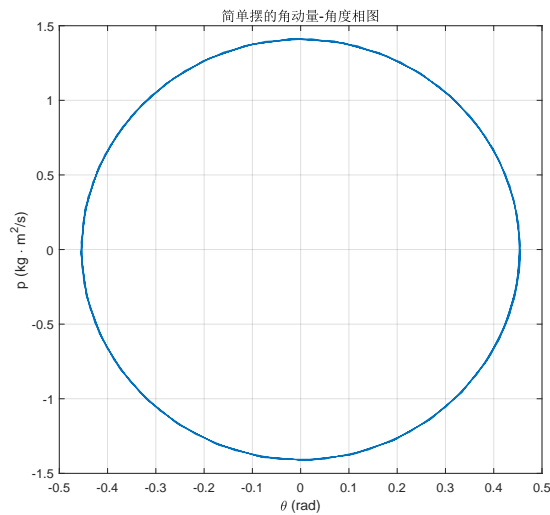
$$H = \frac{L^2}{2ml^2} + mgl(1 - \cos \theta)$$

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

$$A = \oint L d\theta.$$

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

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



## 2.2 Homework 3

### 2.2.1 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

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

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

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

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:

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

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

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

### 2.2.2 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:

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

### 2.2.3 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:

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

## 2.3 Homework 4

### 2.3.1 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 ( $T_r = 1$ )*

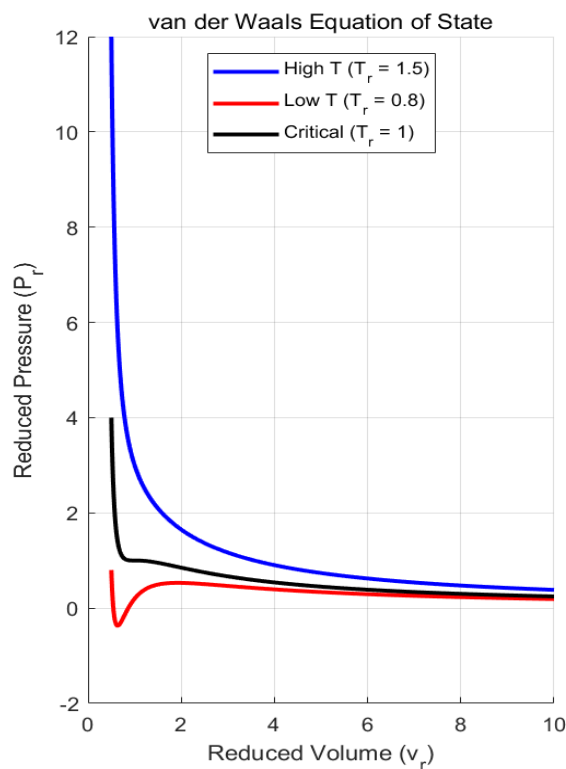
```

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 (T_r = 1.5)');
plot(v_r, P_r_low, 'r', 'LineWidth', 2, 'DisplayName', 'Low T (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:



### 2.3.2 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 coexis-

tence. 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

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

which is the conclusion to be derived.

### 2.3.3 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  $v$ :

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

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

which brings the critical point conditions:

$$-v_c^{-2} + \beta_1 \lambda^3 v_c^{-3} + 2\beta_2 \lambda^6 v_c^{-4} = 0,$$

$$2v_c^{-3} - 3\beta_1 \lambda^3 v_c^{-4} - 8\beta_2 \lambda^6 v_c^{-5} = 0.$$

We can rewrite the equations as

$$-v_c^2 + \beta_1 \lambda^3 v_c + 2\beta_2 \lambda^6 = 0, \tag{2.1}$$

$$2v_c^2 - 3\beta_1 \lambda^3 v_c - 8\beta_2 \lambda^6 = 0. \tag{2.2}$$

So the target is to eliminate terms like  $v_c$ . (2.3)  $\times$  2 + (2.5) gives

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

Substitute this into (2.3) gives:

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

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:

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

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

## 2.4 Homework 5

### 2.4.1 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

$$H_N(N_+, N_{+-}) = -J \left( \frac{1}{2} qN - 2N_{+-} \right) - \mu B (2N_+ - N), \quad (2.3)$$

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

$$H_N(N_+, N_{++}) = -J(N_{++} + N_{--} - N_{+-}) - \mu B (N_+ - N_-) \quad (2.4)$$

$$= -J \left( \frac{1}{2} qN - 2qN_+ + 4N_{++} \right) - \mu B (2N_+ - N) \quad (2.5)$$

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

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

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 (2.3) and (2.5) are equivalent, we can use the relation between  $N_{+-}$  and  $N_{++}$ :

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

Substituting this into (2.3) gives:

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

## 2.4.2 Equation of State

Show that the curve in 2.1 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:

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

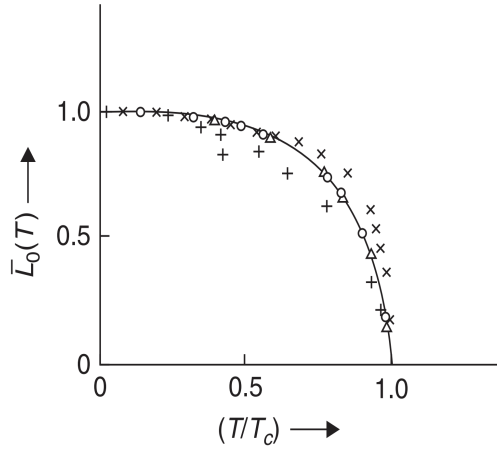


Figure 2.1: The spontaneous magnetization of a Weiss ferromagnet as a function of temperature. The experimental points (after Becker) are for iron (x), nickel (o), cobalt ( $\Delta$ ), and magnetite (+).

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

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

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

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  $T = T_c$ .

## 2.5 Homework 6

### 2.5.1 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

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

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



## 2.6 Homework 7

### 2.6.1 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

$$\sum_{n=1}^{\infty} \frac{\cos(n\theta_1)}{n^2} = \frac{\pi^2}{6} - \frac{\pi|\theta_1|}{2} + \frac{\theta_1^2}{4}, \quad \sum_{n=1}^{\infty} \frac{\cos(n\theta_2)}{n^2} = \frac{\pi^2}{6} - \frac{\pi\theta_2}{2} + \frac{\theta_2^2}{4}. \text{ Therefore}$$

$$\begin{aligned} \sum_{n=1}^{\infty} \frac{1}{n^2} \sin \left( \frac{n\pi x_1}{l} \right) \sin \left( \frac{n\pi x_2}{l} \right) &= \frac{1}{2} \left[ \frac{\pi^2}{6} - \frac{\pi^2 |x_1 - x_2|}{2l} + \frac{\pi^2 (x_1 - x_2)^2}{4l^2} \right] - \frac{1}{2} \left[ \frac{\pi^2}{6} - \frac{\pi^2 (x_1 + x_2)}{2l} + \frac{\pi^2 (x_1 + x_2)^2}{4l^2} \right] \\ &= \frac{\pi^2 (x_1 + x_2 - |x_1 - x_2|)}{4l} + \frac{\pi^2 [(x_1 - x_2)^2 - (x_1 + x_2)^2]}{8l^2} \stackrel{x_2 \geq x_1}{=} \frac{\pi^2 (2x_1)}{4l} + \frac{\pi^2 (-4x_1 x_2)}{8l^2} \end{aligned}$$

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

## 2.6.2 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:  $X_i = \left( \frac{\partial S}{\partial x_i} \right) = -\beta_{ij} (x_j - \tilde{x}_j)$

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

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

According to time reversal symmetry (in microscopic process),

$$\langle x_i(0) x_j(s) \rangle = \langle x_i(0) x_j(-s) \rangle, \quad \langle x_i(0) x_j(-s) \rangle = \langle x_i(s) x_j(0) \rangle \Rightarrow \langle x_i(0) x_j(s) \rangle = \langle x_i(s) x_j(0) \rangle.$$

Let  $s \rightarrow 0$  to get:  $\langle x_i(0) \dot{x}_j(0) \rangle = \langle \dot{x}_i(0) x_j(0) \rangle$ .

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

## 第三章 往年试卷

### 3.1 2025 Spring

#### 3.1.1 概念解释

1. University class.
2. Fluctuation-dissipation theorem.
3. Thermodynamic limit.
4. 等概率原理?

#### 3.1.2 相空间

刘维尔定理在非平衡条件下是否仍然成立, 分析具体原因.

#### 3.1.3 Virial Expansion

修正后的状态方程为  $P = \frac{NkT}{V} \left[ 1 + \frac{N}{V} B_2(T) \right]$ , 该修正下的热容为  $C_V = \frac{3}{2}Nk - \frac{N^2k}{V} f(T)$ . 用  $B_2(T)$  表示  $f(T)$ .

#### 3.1.4 二能级系统

$$N(E_0 = 0) = n_0, N(E_1) = n_1, n_1 + n_2 = N.$$

1. 求  $S(U)$ ,  $U$  为内能.
2. 求粒子数  $N$  时的热容  $C_V$ .

#### 3.1.5 Ising Model

3-spin 环.

1. 配分函数.
2. 磁化率.

#### 3.1.6 Langevin Dynamics

证明  $\langle (\Delta x)^2 \rangle = \frac{Tt}{\lambda}$ , 其中  $\lambda$  为阻力系数,  $T$  为温度,  $t$  为时间.

1 Introduction to probability theory

Bayes' theorem

$$p(B|A) = \frac{p(A|B) \cdot p(B)}{p(A)} = \frac{p(A|B) \cdot p(B)}{\sum_B p(A|B) \cdot p(B')}$$

Expectation and covariance

$$\langle f \rangle = \sum_i f(i) p_i \text{ or } \langle f \rangle = \int f(x) p(x) dx$$
$$\mu = \langle x \rangle = \sum_i i p_i \text{ or } \mu = \langle x \rangle = \int x p(x) dx$$

$$\sigma^2 = \langle i^2 \rangle - \langle i \rangle^2$$
$$\sigma_{ij}^2 = \langle ij \rangle - \langle i \rangle \langle j \rangle$$

Binomial distribution

$$\frac{N!}{(N-i)!i!} = \binom{N}{i} \text{ binomial coefficient}$$
$$p_i = \binom{N}{i} \cdot p^i q^{N-i} \text{ distribution}$$
$$\mu = \langle i \rangle = N \cdot p$$
$$\langle i^2 \rangle = p \cdot N + p^2 \cdot N \cdot (N-1)$$
$$\sigma^2 = N \cdot p \cdot q$$
$$\sum_{i=0}^N p_i = \sum_{i=0}^N \binom{N}{i} \cdot p^i q^{N-i} = (p+q)^N = 1$$

Gauss distribution

$$p(x) = \frac{1}{\left(2\pi\sigma^2\right)^{\frac{1}{2}}} \cdot e^{-\frac{x-\mu}{2\sigma^2}}, \quad \langle x^2 \rangle = \sigma^2$$

Poisson distribution

$$p(k; \mu) = \frac{\mu^k}{k!} e^{-\mu}, \quad E[k] = \mu, \quad V[k] = \mu$$

Information entropy

$$S = - \sum_i p_i \ln(p_i)$$

2 The microcanonical ensemble

$E \approx \text{const}, V = \text{const}, N = \text{const}.$

The fundamental postulate

$$\Omega(E) = \sum_{n: E \leq E_n \leq E} 1$$
$$\Omega(E; \delta E) = \frac{1}{h^3 N!} \iint_{E-\delta E \leq \mathcal{H}(\vec{q}, \vec{p}) \leq E} d\vec{q} d\vec{p}$$
$$S = -k_B \sum_{i=1}^{\Omega} p_i \ln(p_i) = k_B \ln(\Omega)$$

$n_0$  different particles

$$\Omega = \frac{1}{h^{3N} \prod_{j=0}^{n_0} N_j!} \iint_{E-\delta E \leq \mathcal{H}(\vec{q}, \vec{p}) \leq E} d\vec{q} d\vec{p}$$

Equilibrium conditions

Entropy  $S$  must be maximal

Thermal contact

$$\frac{\partial S(E, V, N)}{\partial E} \Big|_{V, N} = \frac{1}{T(E, V, N)}$$

Contact with volume exachnge

$$\frac{\partial S(E, V, N)}{\partial V} \Big|_{E, N} = \frac{p(E, V, N)}{T(E, V, N)}$$

Contact with exchange of particle number

$$\frac{\partial S(E, V, N)}{\partial N} \Big|_{E, V} = - \frac{\mu(E, V, N)}{T(E, V, N)}$$

Equations of state

$$dE = T dS - p dV + \mu dN$$

Specific heat

$$c_v = \frac{dE}{dT}$$

solution concept

- Set up Hamiltonian
  - Calculate phasevolume  $\Omega$
  - Calculate entropy  $S$
  - determine  $T, p, \mu$
  - Calculate  $U = \langle E \rangle$
  - thermodynamic potentials:

$$F(T, V, N) = U - TS$$
$$\hat{H}(S, p, N) = U + pV$$
$$G(T, p, N) = U + pV - TS$$

Ideal Gas

$$\mathcal{H} = \sum_{i=1}^{3N} \frac{p_i^2}{2m} + V(q_1, \dots, q_{3N})$$

microcanonical partition sum for an ideal gas

$$\Omega(E) = \frac{V^N \pi^{3N/2} (2mE)^{3N/2}}{h^{3N} N! \left(\frac{3N}{2}\right)!}$$

$$S = k_B N \left\{ \ln \left[ \left( \frac{V}{N} \right) \left( \frac{4\pi m E}{3 l^2 N} \right)^{3/2} \right] + \frac{5}{2} \right\}$$

Equations of state fo ideal gas

$$\frac{1}{T} = \left( \frac{\partial S}{\partial E} \right)_{N, V} = \frac{3}{2} \frac{N k_B}{E} \rightarrow U = \frac{3}{2} N k_B T$$
$$p = T \left( \frac{\partial S}{\partial V} \right)_{E, N} = T N k_B \frac{1}{V} \rightarrow p V = N k_B T$$
$$\mu = k_B T \ln \left( \frac{N \lambda^3}{V} \right) \text{ chemical potential}$$
$$\lambda = \frac{h}{\sqrt{2\pi m k_B T}} \quad \text{Thermal de Broglie}$$

Einstein model for specific heat of a solid

$$E = \hbar \omega \left( \frac{N}{2} + Q \right) \rightarrow Q = \left( \frac{E}{\hbar \omega} - \frac{N}{2} \right)$$
$$\Omega(E, N) = \frac{(Q+N)!}{Q! N!}$$

$$S = k_B \left[ Q \ln \left( \frac{Q+N}{Q} \right) + N \ln \left( \frac{Q+N}{N} \right) \right]$$
$$= k_B N \left[ \left( e + \frac{1}{2} \right) \ln \left( e + \frac{1}{2} \right) - \left( e - \frac{1}{2} \right) \ln \left( e - \frac{1}{2} \right) \right]$$
$$e = E/E_0; E_0 = N \hbar \omega; \beta = \hbar \omega/k_B T$$

$$\frac{1}{T} = \frac{\partial S}{\partial E} \Rightarrow E = N \hbar \omega \left( \frac{1}{2} + \frac{1}{e^{\beta} - 1} \right)$$

Entropic elasticity of polymers

$$N_+ - N_- = \frac{L}{a} = m \rightarrow N_+ = \frac{1}{2} (N + m)$$
$$\Omega = \frac{N!}{N_+! N_-!} = \frac{N!}{\left(\frac{1}{2}(N+m)\right)! \left(\frac{1}{2}(N-m)\right)!}$$

if both directions are possible x2

$$S = -k_B \left( N_+ \ln \left( \frac{N_+}{N} \right) + N_- \ln \left( \frac{N_-}{N} \right) \right)$$

Statistical deviation from average

Two ideal gases in thermal conact  $T_1 = T_2$

$$S_i = \frac{3}{2} k_B N_i \ln(E_i) + \text{independent of } E_i$$
$$S = S_1 + S_2$$

$$dS = 0 \rightarrow \frac{\partial S_1}{\partial E_1} = \frac{\partial S_2}{\partial E_2}$$
$$\rightarrow \bar{E}_1 = \frac{N_1}{N} E$$

consider small deviation:

$$E_1 = \bar{E}_1 + \Delta E, \quad E_2 = \bar{E}_2 - \Delta E$$
$$S(\bar{E}_1 + \Delta E) \approx \frac{3}{2} k_B \left[ N_1 \ln \bar{E}_1 + N_2 \ln \bar{E}_2 - \frac{N_1}{2} \left( \frac{\Delta E}{\bar{E}_1} \right)^2 - \frac{N_2}{2} \left( \frac{\Delta E}{\bar{E}_2} \right)^2 \right]$$
$$\rightarrow \Omega = \bar{\Omega} e^{\left[ -\frac{3}{4} \left( \frac{\Delta E}{\bar{E}} \right)^2 N^2 \left( \frac{1}{N_1} + \frac{1}{N_2} \right) \right]}$$

3 The canonical ensemble

$T = \text{const}, V = \text{const}, N = \text{const}.$

Boltzmann distribution

$$p_i = \frac{1}{Z} e^{-\beta E_i} \quad \text{Boltzmann distribution}$$
$$Z = \sum_i e^{-\beta E_i} \quad \text{partition sum}$$

For classical Hamiltonian systems:

$$p(\vec{q}, \vec{p}) = \frac{1}{Z N! h^{3N}} e^{-\beta \mathcal{H}(\vec{q}, \vec{p})}$$
$$Z_N(T, V) = \frac{1}{N! h^{3N}} \iint d\vec{q} d\vec{p} e^{-\beta \mathcal{H}(\vec{q}, \vec{p})}$$

For common Hamiltonian:

$$Z_N(T, V) = \frac{1}{\lambda^{3N} N!} \int d\vec{q} e^{-\beta \hat{V}(\vec{q})}$$

Free energy

$$F(T, V, N) = -k_B T \ln Z_N(T, V)$$
$$\langle E \rangle = U = -\partial_{\beta} \ln Z_N$$

total differential:

$$dF = dE + d(TS) = -SdT - pdV + \mu dN$$

equations of state

$$S = -\frac{\partial F}{\partial T}, \quad p = -\frac{\partial F}{\partial V}, \quad \mu = \frac{\partial F}{\partial N}$$

Non-interacting systems

$\epsilon_{ij}$  is the  $j^{th}$  state of the  $i^{th}$  element

$$Z = \sum_i \sum_j \dots \sum_{j^N} e^{-\beta \sum_{i=1}^N \epsilon_{ij}}$$
$$= \left( \sum_{j_1} e^{-\beta \epsilon_{1j_1}} \right) \dots \left( \sum_{j_N} e^{-\beta \epsilon_{Nj_N}} \right)$$
$$= z_1 \cdot \dots \cdot z_N = \prod_{i=1}^N z_i$$

$$\rightarrow F = -k_B T \sum_{i=1}^N \ln(z_i) = -k_B T \ln(Z)$$

$$Z = z^N, \quad F = -k_B T N \ln(z)$$

Ideal Gas

$$\mathcal{H} = \sum_{i=1}^N \frac{\vec{p}_i^2}{2m}$$
$$Z_N(T, V) = \frac{V^N}{N!} \left( \int_{-\infty}^{+\infty} \frac{dp}{h} e^{-\beta \frac{p^2}{2m}} \right)^{3N}$$
$$= \frac{1}{N!} \left( \frac{V}{\lambda^3} \right)^{3N}$$

Equipartition theorem

$f_{dof}$  are the degrees of freedom.

harmonic Hamiltonian with  $f_{dof} = 2$

$$\mathcal{H} = A q^2 + B p^2$$
$$z \propto \int dq dp e^{-\beta \mathcal{H}}$$
$$= \left( \frac{\pi}{A \beta} \right)^{\frac{1}{2}} \cdot \left( \frac{\pi}{B \beta} \right)^{\frac{1}{2}} \propto \left( T^{\frac{1}{2}} \right)^{f_{dof}}$$

For sufficiently high temperature (classical limit), each quadratic term in the Hamiltonian contributes a factor  $T^{\frac{1}{2}}$  to the partition

sum ('equipartition theorem')

$$F = -k_B T \ln(z) = -\frac{f_{dof}}{2} k_B T \ln(T)$$
$$S = -\frac{\partial F}{\partial T} = \frac{f_{dof}}{2} k_B (\ln(T) + 1)$$
$$U = -\partial_{\beta} \ln(z) = \frac{f_{dof}}{2} k_B T$$
$$c_v = \frac{dU}{dT} = \frac{f_{dof}}{2} k_B$$
$$c_p = \frac{f_{dof} + 2}{2} k_B$$

Molecular gases

$N$  molecules;  $x$  different mode types:  
 $Z = Z_{trans} \cdot Z_{vib} \cdot Z_{rot} \cdot Z_{elec} \cdot Z_{nuc}$   
 $Z_x = z_x^N$

Vibrational modes

often described by the Morse potential:  
 $V(r) = E_0 \left( 1 - e^{-\alpha(r-r_0)} \right)^2$

An exact solution of the Schrödinger equation gives:

$$E_n = \hbar \omega_0 \left( n + \frac{1}{2} \right) - \frac{\hbar^2 \omega_0^2}{e E_0} \left( n + \frac{1}{2} \right)^2$$
$$\omega_0 = \frac{\alpha}{2\pi} \sqrt{\frac{2E_0}{\mu}}, \quad \mu = \frac{m}{2}$$

For  $\hbar \omega_0 \ll E_0$  we can use the harmonic approximation:  
 $z_{vib} = \frac{1 - e^{-\beta \hbar \omega_0}}{e^{-\beta \hbar \omega_0/2}}$

$$T_{vib} \approx \frac{\hbar \omega_0}{k_B} \approx 6.140 \text{ K for } H_2$$

Rotational modes

standard approximation is the one of a rigid rotator. The moment of inertia is given as:

$$I = \mu r_0^2 \quad T_{rot} = \frac{\hbar^2}{I k_B} \quad \omega_n = (2J+1)$$
$$\rightarrow E_l = \frac{\hbar^2}{2I} l(l+1)$$

Nuclear contributions: ortho- and parahydrogen

$$S = 1, z_{ortho} = \sum_{l=1,3,5,\dots} (2l+1) e^{-\frac{l(l+1)T_{rot}}{T}}$$
$$S = 0, z_{para} = \sum_{l=0,2,4,\dots} (2l+1) e^{-\frac{l(l+1)T_{rot}}{T}}$$

Specific heat of a solid  
Debye model

$$\rightarrow \omega(k) = \left(\frac{4\kappa}{m}\right)^{\frac{1}{2}} \left|\sin\left(\frac{ka}{2}\right)\right|$$
$$\omega = \frac{2\pi}{T}, \quad k = \frac{2\pi}{\lambda}$$

Debye frequency:

$$\omega_D = c_s \left(\frac{6\pi^2 N}{V}\right)^{\frac{1}{3}}$$
$$c_s = \frac{d\omega}{dk}\Big|_{k=0} = \sqrt{\frac{\kappa}{m}} a$$

density of states in  $\omega$ -space:

$$D(\omega) = 3 \frac{\omega^2}{\omega_D^3} \quad \text{for } \omega \leq \omega_D$$

count modes in frequency-space:

$$\sum_{modes} (...) = 3 \sum_k (...) = 3N \int_0^{\omega_D} d\omega D(\omega) (...)$$

partition sum:

$$z(\omega) = \frac{e^{-\beta\hbar\omega/2}}{1 - e^{-\beta\hbar\omega}}$$
$$\rightarrow Z = \prod_{modes} z(\omega)$$
$$\rightarrow E = -\partial_\beta \ln(Z) = \sum_{modes} \hbar\omega \left(\frac{1}{e^{\beta\hbar\omega} - 1} + \frac{1}{2}\right)$$
$$= E_0 + 3N \int_0^{\omega_D} d\omega \frac{\hbar\omega}{e^{\beta\hbar\omega} - 1} \frac{3\omega^2}{\omega_D^3}$$
$$c_v(T) = \frac{\partial E}{\partial T}$$
$$= \frac{3\hbar^2 N}{k_B T^2} \int_0^{\omega_D} d\omega \frac{3\omega^2}{\omega_D^3} \frac{e^{\beta\hbar\omega} \omega^2}{\left(e^{\beta\hbar\omega} - 1\right)^2}$$
$$u = \beta \hbar \omega$$
$$c_v(T) = \frac{9 N k_B}{u_m^3} \int_0^{u_m} \frac{e^u u^4}{(e^u - 1)^2} du$$

the limit for  $\hbar\omega_D \ll k_B T$ :

$$c_v(T) = 3Nk_B$$

the limit for  $k_B T \ll \hbar\omega_D$ : ( $T_D = \frac{\hbar\omega_D}{k_B}$ )

$$c_v(T) = \frac{12\pi^4}{5} Nk_B \left(\frac{T}{T_D}\right)^3$$

Black body radiation

$$E = \frac{4\sigma}{c} VT^4, \quad \sigma = \frac{\pi^2 k_B^4}{60\hbar^3 c^2}$$
$$c_v = \frac{16\sigma}{c} VT^3$$

$$J = \frac{P}{A} = \sigma T^4 \quad \text{Stefan- Boltzmann law}$$

Planck's law for black body radiation

$$u(\omega) := \frac{\hbar}{\pi^2 c^3} \frac{\omega^3}{e^{\hbar\omega/(k_B T)} - 1}$$

The Plank distribution has a maximum at:

$$\hbar\omega_{max} = 2.82k_B T \quad \text{Wien's displacement law}$$

4 The grandcanonical ensemble  
 $T, \mu = const.$

$$p_N(q, p) = \frac{1}{\Xi_\mu(T, V)} e^{-\beta(H_N(q, p) - \mu N)}$$
$$\Xi_\mu(T, V) = \sum_{N=0}^\infty \frac{1}{h^{3N} N!} \iint d^{3N} q d^{3N} p e^{-\beta(H_N - \mu N)}$$
$$\rightarrow \Xi_z = \sum_{N=0}^\infty z^N Z_N(T, V)$$
$$z = e^{\beta\mu} \rightarrow \text{Fugacity}$$
$$\text{Mean phase space observable}$$
$$\langle F \rangle = \frac{1}{\Xi_\mu(T, V)} \sum_{N=0}^\infty \frac{1}{h^{3N} N!} \iint d^{3N} q d^{3N} p \dots$$
$$\dots e^{-\beta(H_N - \mu N)} F_N(q, p)$$
$$\text{mean particle number:}$$
$$\langle N \rangle = \frac{1}{\beta} \left( \frac{\partial}{\partial \mu} \ln \left( \Xi_\mu(T, V) \right) \right)_{T, V}$$
$$= z \left( \frac{\partial}{\partial z} \ln \left( \Xi_z(T, V) \right) \right)_{T, V}$$
$$\text{pressure:}$$
$$p = - \left( \frac{\partial H}{\partial V} \right) = - \left( \frac{\partial}{\partial \beta} \ln \left( \Xi_\mu(T, V) \right) \right)_{\mu, V}$$
$$\text{energy } U:$$
$$U = \langle H \rangle = - \left( \frac{\partial}{\partial \beta} \ln \left( \Xi_\mu(T, V) \right) \right)_{\mu, V} + \mu \langle N \rangle$$
$$= - \left( \frac{\partial}{\partial \beta} \ln \left( \Xi_z(T, V) \right) \right)_{z, V}$$

Grandcanonical potential  
grandcanonical potential:

$$\Psi(T, V, \mu) = -k_B T \ln \left( \Xi_\mu(T, V) \right)$$

p is maximal, if  $\Psi$  is minimal.

Total differential:

$$d\Psi = -SdT - pdV - \langle N \rangle d\mu$$

Equations of state:

$$S = -\frac{\partial \Psi}{\partial T}, p = -\frac{\partial \Psi}{\partial V}, N = -\frac{\partial \Psi}{\partial \mu}$$

Fluctuations

$$\sigma_N^2 = \langle N^2 \rangle - \langle N \rangle^2 = \frac{1}{\beta^2} \left( \partial_\mu^2 \ln(\Xi_\mu) \right)$$
$$\frac{\sigma_N}{\langle N \rangle} \propto \frac{1}{\sqrt{N}}$$

Ideal gas

$$Z_N(T, V) = \frac{1}{N!} \left( \frac{V}{\lambda^3} \right)^N, \quad \lambda = \frac{h}{(2\pi mk_B T)^{\frac{1}{2}}}$$

$$\Xi = \sum_{N=0}^\infty Z_N(T, V) z^N$$

$$= \sum_{N=0}^\infty \frac{1}{N!} \left( e^{\beta\mu} \frac{V}{\lambda^3} \right)^N$$

$$= z \frac{V}{\lambda^3} \quad \text{fugacity: } z := e^{\beta\mu}$$

$$\langle N \rangle = \frac{1}{\beta} \partial_\mu \ln(Z_G) = \frac{V}{\lambda^3} d^{\beta\mu}$$

$$\mu = k_B T \ln \left( \frac{N \lambda^3}{V} \right)$$

Molecular adsorption onto a surface

$$Z_G = z_G^N; z_G = 1 + e^{-\beta(\epsilon - \mu)}$$

$$\langle n \rangle = \frac{1}{e^{-\beta(\mu - \epsilon)} + 1} \quad \text{per site}$$
$$\langle \epsilon \rangle = \epsilon \langle n \rangle$$

5 Quantum fluids

- Fermion vs. bosons**
1. Fermions: Pauli-principle + not distinguishable

2. Bosons: symmetric wave function + not distinguishable

3. Boltzmann: particles are distinguishable

Canonical ensemble

$\omega_n \rightarrow$  degeneracy of state  $n$

$$z = \sum_n \omega_n \exp(-\beta E_n)$$

Grand canonical ensemble

only two states 0,  $\epsilon$

Fermions:

$$z_F = 1 + e^{-\beta(\epsilon - \mu)}$$

average occupation number  $n_F$ :

$$n_F = \frac{1}{e^{\beta(\epsilon - \mu)} + 1} \quad \text{Fermi function}$$

For  $T \rightarrow 0$ , the fermi function approaches a step function:

$$n_F = \Theta(\mu - \epsilon)$$

Bosons:

$$z_B = \frac{1}{e^{-\beta(\epsilon - \mu)}} = e^{\beta(\epsilon - \mu)}$$

average occupation number  $n_B$ :

$$n_B = \frac{1}{e^{\beta(\epsilon - \mu)} - 1}$$

- Fermions tend to fill up energy states one after the other

Bosons tend to condense all into the same low energy state

The ideal Fermi fluid  
density of states:

$$D(\epsilon) = \frac{V}{2\pi N} \left( \frac{2m}{\hbar^2} \right)^{\frac{3}{2}} \sqrt{\epsilon}$$

Fermi energy

$$N = \sum_{\vec{k}, m_s} n_{\vec{k}, m_s} = N \int_0^\infty d\epsilon D(\epsilon) n_F(\epsilon)$$

Limit  $T \rightarrow 0$ .  $\mu(T = 0)$  is called Fermi energy:

$$\epsilon_F = (3\pi^2)^{\frac{2}{3}} \frac{\hbar^2 \rho^{\frac{2}{3}}}{2m}$$

specific heat

$$\mu = \epsilon_F \left[ 1 - \frac{\pi^2}{12} \left( \frac{k_B T}{\epsilon_F} \right)^2 \right] \quad \text{for } T \ll \frac{\epsilon_F}{k_B}$$

$$c_V = \frac{\partial E}{\partial T} \Big|_V = N \frac{\pi^2}{3} k_B^2 D(\epsilon_F) T$$

$$c_V = N \frac{\pi^2}{2} \frac{k_B T}{\epsilon_F}$$

Fermi pressure

$$p \xrightarrow{T \rightarrow 0} \frac{2}{5} \frac{N}{V} \epsilon_F = \frac{(2\pi^2)^{\frac{2}{3}}}{5} \frac{\hbar^2}{m v^{\frac{5}{3}}}$$

The ideal Bose fluid

$\epsilon = \frac{\hbar^2 k^2}{2m}$  and conserved particle number  $N$ .

$$N = \frac{N}{\lambda^3} g_{\frac{3}{2}}(z)$$

$$z = e^{\beta\mu}, \quad \lambda = \frac{h}{(2\pi mk_B T)^{\frac{1}{2}}}$$

$$T_c = \frac{2\pi}{\left( \zeta\left(\frac{3}{2}\right) \right)^2} \frac{\hbar^2 \rho^{\frac{2}{3}}}{k_B m}$$

$$E = \frac{3}{2} k_B T \frac{V}{\lambda^3} g_{\frac{5}{2}}(z) = \frac{3}{2} k_B T N_c \frac{g_{\frac{5}{2}}(z)}{g_{\frac{3}{2}}(z)}$$

$$c_V = \frac{15}{4} k_B N \left( \frac{T}{T_c} \right)^{\frac{3}{2}} \frac{\zeta\left(\frac{5}{2}\right)}{\zeta\left(\frac{3}{2}\right)} \quad (\text{for } T \leq T_c)$$

$$c_V = \frac{15}{4} k_B N \frac{g_{\frac{5}{2}}(z)}{g_{\frac{3}{2}}(z)} - \frac{9}{4} k_B N \frac{g_{\frac{3}{2}}(z)}{g_{\frac{1}{2}}(z)} \quad (T > T_c)$$

Classical limit

$\mu \rightarrow -\infty$  the two grandcanonical distr. become the Maxwell-Boltzmann distr.

$$n_{F/B} = \frac{1}{e^{\beta(\epsilon - \mu)} \pm 1} \rightarrow e^{\beta\mu} e^{-\beta\epsilon}$$

$$N = g \frac{V}{\lambda^3} e^{\beta\mu}$$

$$E = \frac{3}{2} k_B T N$$

6 Phase transitions  
Ising model  
Hamiltonian

$$\mathcal{H} = - \sum_{i,j} J_{ij} S_i S_j - \mu B_0 \sum_i S_i$$

special cases:

Ferromagnetic systems:

$$\mathcal{H} = -J \sum_{\langle i,j \rangle} \vec{J}_{ij} \vec{J} - \mu \vec{B} \sum_i \vec{J}_i$$

lattice gases:

$$\mathcal{H} = - \sum_{\langle i,j \rangle} J_{ij} S_i S_j$$

1. Dimensional

Only Next Neighbor and  $B_0 = 0$

$$J_{i,i+1} \rightarrow J_{ij}, \quad \mathcal{H} = - \sum_{i=1}^{N-1} J_{ij} S_i S_{i+1}, \quad j_i = \beta J_i$$

$$Z_N = \sum_{S_1} \dots \sum_{S_N} \exp \left( \sum_{i=1}^{N-1} J_i S_i S_{i+1} \right)$$

$$= 2^N \prod_{i=1}^{N-1} \cosh(\beta J_i)$$

Spin correlation function:

$$\langle S_i S_{i+1} \rangle = \tanh(\beta J)$$

spontaneous magnetisation:

$$M_S(T) = \mu \langle S \rangle$$

$$M_S^2(T) = \mu^2 \lim_{j \rightarrow \infty} \langle S_i S_{i+1} \rangle$$

No phase transition for  $T > 0$ . But for  $T = 0$

$$M_S(T = 0) = \mu$$

Transfer matrix

$$j = \beta J, \quad b = \beta \mu B_0, \quad S_i = \pm 1$$

$$T_{i,i+1} = e^{j S_i S_{i+1} + \frac{1}{2} b (S_i + S_{i+1})}$$

$$\rightarrow e^{-\beta \mathcal{H}} = T_{1,2} \cdot T_{2,3} \dots T_{N,1}$$

$$T = \begin{pmatrix} T(+1,+1) & T(+1,-1) \\ T(-1,+1) & T(-1,-1) \end{pmatrix}$$

$$Z_N = \lambda_1^N + \lambda_2^N = E_+^N + E_-^N$$

for  $N \gg 1 \rightarrow E_+ \gg E_-$

Renormalization of the Ising chain

$$K' = \frac{1}{2} \ln(\cosh(2K))$$

Renormalization of the 2d Ising model

$$\overline{K}' = K' + K_1 = \frac{3}{8} \ln(\cosh(4K))$$

The 2d Ising model

$$\beta \mathcal{H} = -K \sum_{r,c} S_{r,c} S_{r+1,c} - K \sum_{r,c} S_{r,c} S_{r,c+1}$$

$$1 = \sinh(2K_c)$$

$$K_c = \frac{1}{2} \ln \left( 1 + \sqrt{2} \right) \approx 0.4407$$

$$T_c = 2J / \ln \left( 1 + \sqrt{2} \right) \approx 2.269 J / k_B$$

Perturbation theory

$$F \leq F_H = F_0 + \langle \mathcal{H}_1 \rangle_0 \text{ Bogoliubov inequality}$$

Mean field theory for the Ising model

$$\mathcal{H} = -J \sum_{\langle i,j \rangle} S_i S_j$$

$$\mathcal{H}_0 = -B \sum_i S_i$$

$$F_0 = -N k_B T \ln \left( e^{\beta B} + e^{-\beta B} \right)$$

$$= -N k_B T \ln (2 \cosh(\beta B))$$

$$F \leq F_0 + \langle \mathcal{H} - \mathcal{H}_0 \rangle_0$$

$$= -N k_B T \ln (2 \cosh(\beta B)) - N \frac{z}{2} \langle S \rangle_0^2$$

$$+ N \langle S \rangle_0 = F_u$$

$$\rightarrow z = 2 \cdot \text{dimension}$$

$$B = J z \langle S \rangle_0 = J z \tanh(\beta B)$$

$$K_c = \frac{1}{z} \rightarrow T_c = \frac{zJ}{k_B}$$

7 Classical fluids

Virial expansion

$$F = N k_B T \left[ \ln(\rho \lambda^3) - 1 + B_2 \rho \right]$$

$$p = \rho k_B T \left[ 1 + B_2 \rho \right]$$

Second virial coefficient

$$B_2(T) = -2\pi \int r^2 dr \left( e^{-\beta U(r)} - 1 \right)$$

8 Others

Stirling's formula

$$\ln(n!) = n \ln(n) - n + \frac{1}{2} \ln(2\pi n)$$

de Broglie relation

$$\epsilon = \frac{p^2}{2m} = \frac{\hbar^2 k^2}{2m}$$

Energies

$$E_{kin} = \frac{1}{2} M \overline{v^2}$$

$$E_{rot} = \frac{1}{2} I \omega^2$$