ADVANCED STATISTICAL MECHANICS

https://github.com/Muatyz/review-sheet

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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.

$$\underset{\text{increase of internal energy}}{\mathrm{d}U} = \underset{\text{input heat}}{\delta Q} - \underset{\text{output work}}{\delta W}$$

- reversible process: $\mathrm{d}U = T\mathrm{d}S - P\mathrm{d}V$

- mechanical system: $\delta W = f\mathrm{d}x = -\mathrm{d}V(x)$;

- *adiabatic process*(绝热过程): $\delta W = P\mathrm{d}V = -\mathrm{d}U$. U: thermodynamic/adiabatic potential.

- *isothemal process*(等温过程). F: isothermal potential.

$$F \equiv U - TS, \quad \mathrm{d}F = -S\mathrm{d}T - P\mathrm{d}V, \quad \left.\delta W\right|_T = P\mathrm{d}V = -\mathrm{d}F$$

1.1.1.1.2　Maximum Work

- isothermal process, $A \to B$:

$$\text{1st law: } \Delta W = -\Delta U + \Delta Q$$
$$\text{2nd law: } \Delta Q \leq T(S_B - S_A)$$
$$\Delta W \leq U_A - U_B + T(S_B - S_A) = -\Delta F, \quad \Delta F = F_B - F_A$$

- $A \to B, U_A = U_B$: $\Delta W_{\max} = T(S_B - S_A)$. 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,

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

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

Introduce physics: $U = TS - PV + \mu N \Rightarrow \mathrm{d}U = T\mathrm{d}S + S\mathrm{d}T - P\mathrm{d}V - V\mathrm{d}P + \mu\mathrm{d}N + N\mathrm{d}\mu$

Since $\mathrm{d}U = T\mathrm{d}S - P\mathrm{d}V + \mu\mathrm{d}N$

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

一/二级相变分类依据: 化学势 μ 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. $\dfrac{\partial s}{\partial T}$ 突变: 热容 $\left(T\dfrac{\partial S}{\partial T}\right)$ 变化; $\dfrac{\partial v}{\partial P}$ 压缩率 $\left(\dfrac{1}{v}\dfrac{\partial v}{\partial P}\right)$ 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: $x(\xi, \eta)$, $y(\xi, \eta)$.

$$\mathrm{d}x = \frac{\partial x}{\partial \xi}\mathrm{d}\xi + \frac{\partial x}{\partial \eta}\mathrm{d}\eta, \quad \mathrm{d}y = \frac{\partial y}{\partial \xi}\mathrm{d}\xi + \frac{\partial y}{\partial \eta}\mathrm{d}\eta$$

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

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

$$\mathrm{d}U = T\mathrm{d}S - P\mathrm{d}V = \frac{\partial U}{\partial x}\mathrm{d}x + \frac{\partial U}{\partial y}\mathrm{d}y \Rightarrow T = \left(\frac{\partial U}{\partial S}\right)_V, \quad -P = \left(\frac{\partial U}{\partial V}\right)_S$$

$$\frac{\partial^2 U}{\partial V \partial S} = \frac{\partial^2 U}{\partial S \partial V}, \quad \text{derivative exchange symmetry}$$

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V \Rightarrow \frac{\partial(T, S)}{\partial(P, V)} = 1, \quad \text{Maxwell's relation(s)}$$

$$\mathrm{d}T \wedge \mathrm{d}S = \frac{\partial(T, S)}{\partial(P, V)}\mathrm{d}P \wedge \mathrm{d}V, \quad J = 1\text{和温标选取对应}$$

1.1.1.2.2 Property of Jacobian Matrix .

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

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

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

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

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

1.1.1.3 Exterior derivative(外微分)

p-form $\xrightarrow{\mathrm{d}}$ $p + 1$-form. 0-form: $f(x) \to \mathrm{d}f(x) = \dfrac{\mathrm{d}f(x)}{\mathrm{d}x}\mathrm{d}x$;

1-form: $g(x, y)\mathrm{d}x \to \mathrm{d}[g(x, y)\mathrm{d}x] = \left(\dfrac{\partial g}{\partial x}\mathrm{d}x + \dfrac{\partial f}{\partial y}\mathrm{d}y\right) \wedge \mathrm{d}x = \dfrac{\partial f}{\partial y}\mathrm{d}y \wedge \mathrm{d}x, \quad \mathrm{d}x \wedge \mathrm{d}y = -\mathrm{d}y \wedge \mathrm{d}x \Rightarrow \mathrm{d}^2 = 0$;

2-form: $f(x, y)\mathrm{d}x \wedge \mathrm{d}y$

$\mathrm{d}U = T\mathrm{d}S - P\mathrm{d}V \Rightarrow \mathrm{d}(\mathrm{d}U) = \mathrm{d}(T\mathrm{d}S) - \mathrm{d}(P\mathrm{d}V) \Rightarrow 0 = \mathrm{d}T \wedge \mathrm{d}S - \mathrm{d}P \wedge \mathrm{d}V \Rightarrow \mathrm{d}T \wedge \mathrm{d}S = \mathrm{d}P \wedge \mathrm{d}V$

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

1.1.2 Some Key Concepts in Thermodynamics

1.1.2.1 Temperature

1.1.2.1.1 Thermodynamic Perspective $\mathrm{d}U = T\mathrm{d}S - P\mathrm{d}V, T \equiv \left(\dfrac{\partial U}{\partial S}\right)_V$, thermodynamic definition of temperature.

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

$$\frac{\mathrm{d}S}{\mathrm{d}E_1} = 0, \quad \text{condition of thermal equilibrium}$$

$$\frac{\mathrm{d}S_1}{\mathrm{d}E_1} + \frac{\mathrm{d}S_2}{\mathrm{d}E_1} = \frac{\mathrm{d}S_1}{\mathrm{d}E_1} + \frac{\mathrm{d}S_2}{\mathrm{d}E_2}\frac{\mathrm{d}E_2}{\mathrm{d}E_1} = \frac{\mathrm{d}S_1}{\mathrm{d}E_1} - \frac{\mathrm{d}S_2}{\mathrm{d}E_2} = 0 \Rightarrow \frac{\mathrm{d}S_1}{\mathrm{d}E_1} = \frac{\mathrm{d}S_2}{\mathrm{d}E_2} \leftrightarrow \frac{1}{T_1} = \frac{1}{T_2}$$

2nd law: $\dfrac{\mathrm{d}S}{\mathrm{d}t} \geq 0 \Rightarrow \dfrac{\mathrm{d}S}{\mathrm{d}E_1}\dfrac{\mathrm{d}E_1}{\mathrm{d}t} \geq 0 \Rightarrow \left(\dfrac{\mathrm{d}S_1}{\mathrm{d}E_1} - \dfrac{\mathrm{d}S_2}{\mathrm{d}E_2}\right)\dfrac{\mathrm{d}E_1}{\mathrm{d}t} \geq 0 \Rightarrow \left(\dfrac{1}{T_1} - \dfrac{1}{T_2}\right)\dfrac{\mathrm{d}E_1}{\mathrm{d}t} \geq 0$

$$\text{if } T_2 > T_1, \quad \frac{1}{T_1} - \frac{1}{T_2} > 0 \Rightarrow \frac{\mathrm{d}E_1}{\mathrm{d}t} \geq 0$$

*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):

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

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

[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/ $\boxed{\text{垂直}}$ 于 z 轴. 每个自由度都是分得 $\dfrac{1}{2}k_B T$ 的能量.

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

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

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

1.1.2.2 Entropy

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

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

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

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

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

$\Rightarrow \color{red}{S(B) - S(A)} \geq \displaystyle\int_{\Gamma_{A\to B}^{(I)}} \frac{\delta Q}{T} \Rightarrow$ 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); $(0, 1)$; $|n\rangle$, disdinguishable(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×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.

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

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

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

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

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

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

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

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

1.1.3 Learn Thermodynamics by Examples/Applications

1.1.3.1 Ideal Gas

1.1.3.1.1 Entropy

$$\mathrm{d}U = T\mathrm{d}S - P\mathrm{d}V \Leftrightarrow T\mathrm{d}S = \mathrm{d}U + P\mathrm{d}V$$

$$\text{If } V = \text{const.}: \quad \mathrm{d}U = T\mathrm{d}S \Rightarrow \frac{\partial S(U,V)}{\partial U}\bigg|_V = T(U,V)$$

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

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

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

[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

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

$$\mathrm{d}U = T\mathrm{d}S - P\mathrm{d}V \overset{\frac{1}{\mathrm{d}V}}{\Longrightarrow} \frac{\partial U(T,V)}{\partial V} = T \frac{\partial S(T,V)}{\partial V} - P \overset{\frac{\partial S(T,V)}{\partial V} = \frac{\partial P(T,V)}{\partial T}}{\Longrightarrow} bT^4 = T \frac{\partial P(T,V)}{\partial T} - P \Longrightarrow P = \frac{b}{3} T^4$$

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

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_{conf} 减少, $T\Delta S_{\text{conf}} \downarrow$; 长链分子本身也在振动, 振动熵 S_{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; τ: tension(张力); T: 温度, U: 内能.

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

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

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

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

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 μ-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.

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

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

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 $\vec{v} \to -\vec{v}$, 难道不会使 H 回升吗?

1.2.1.2 Γ-space

$\{q_1, q_2, q_3, p_1, p_2, p_3, q_4, q_5, q_6, p_4, p_5, p_6, \cdots\}$, $6N$-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 μ-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 Γ 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: $W' = \dfrac{N!}{\prod_k n_k!}\prod_k \omega_k^{n_k}$. 该体积和状态数成正比, 那么寻找在 $\sum_k n_k = N, \quad \sum_k \varepsilon_k n_k = E$ 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 Geomatry 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 $x = (x_1, x_2, \cdots, x_n)$. $\vec{x}$ 的长度为 $|x| = \sqrt{\sum_{i=1}^{n} x_i^2}$.

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

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

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 ε 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 $R' = R\sqrt{1 - \dfrac{x^2}{R^2}}$. 存在 $\int_{-R}^{R} \rho(x)\mathrm{d}x = \int_{-R}^{R} V(B_{R'}^{n-1})\,\mathrm{d}x = V(B_R^n)$, 求 $\rho(x)$ 表达式.

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

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 $\epsilon \to 0$, $C + \epsilon B$ 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 ϵ 得到: $\text{Area} = \lim\limits_{\epsilon \to 0} \dfrac{V(C + \epsilon B) - V(C)}{\epsilon}$. 不等式: $V(C + \epsilon B)^{1/n} \geq V(C)^{1/n} + V(\epsilon B)^{1/n} = V(B)^{1/n} + (\epsilon^n V(B))^{1/n} \Rightarrow \text{Area} \geq \lim\limits_{\epsilon \to 0} \dfrac{[(1+\epsilon)^n - 1]}{\epsilon} V(B) \approx n \cdot V(B)$, 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: $p \propto \sigma \overline{H}$.
[Example] 悬链线(Catenary Curve).

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

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

[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 $\to$ volume interpreted as the probability.

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

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

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

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

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

[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 $\lim\limits_{n\to\infty} \sum\limits_{i}^{n} x_i = 0$; 相应地, 若 $\lim\limits_{n\to\infty} x+y = \epsilon$ 描述了偏离中心线的程度.

1.2.2 From Dynamics to Probability Description

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

时间平均: $\langle f \rangle_t = \dfrac{\sum\limits_{i} f_i \tau_i}{\sum\limits_{i} \tau_i}$

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

$$\langle f \rangle_t = \frac{1}{T} \sum_\alpha f_\alpha t_\alpha, \quad t_\alpha = \sum_{i \in \alpha} \tau_\alpha$$

$$= \sum_\alpha f_\alpha \times \left(\frac{t_\alpha}{T} \right) = \sum_\alpha f_\alpha p_\alpha, \quad \text{prob description: } p_\alpha = \frac{t_\alpha}{T}$$

Formal presentation: in equilibrium,

$$\overset{\text{ensemble avarage}}{\langle f \rangle_e} = \langle \langle f \rangle_e \rangle_t = \langle \langle f \rangle_t \rangle_e$$

$$\left\langle \lim_{T\to\infty} \langle f \rangle_t \right\rangle_e = \lim_{T\to\infty} \langle f \rangle_t : \quad \text{ergodic(各态历经), 初态无关}$$

$$\langle f \rangle_e = \lim_{T\to\infty} \langle f \rangle_t$$

不同情况下的 microstate: 1. In Γ-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) $\sum\limits_{i} \delta(x - x_i) \to \rho(x)$.

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

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

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

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

1.2.2.1 Dynamics

1.2.2.1.1 A Single Representative Point in Γ-Space .

Hamiltonian 力学: $\dot{q}_i = \dfrac{\partial H}{\partial p_i}, \quad \dot{p}_i = -\dfrac{\partial H}{\partial q_i}$. 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 Γ-空间中选取一个体积 ω, 将会有 $\int_\omega \rho(q,p,t)\mathrm{d}\omega$ 个代表点. 其表面为 $\partial\omega$. 代表点在 Γ-空间中的运动速度为 $\vec{v}_i = \{\dot{q}_i, \dot{p}_i\}$. 那么存在关系

$$\frac{\partial}{\partial t} \int_\omega \rho(q,p,t)\mathrm{d}\omega = -\int_{\partial\omega} \rho\vec{v} \cdot \hat{n}\mathrm{d}\sigma = -\int_\omega \nabla \cdot (\rho\vec{v})\mathrm{d}\omega, \quad \nabla = \left(\frac{\partial}{\partial \mathbf{q}}, \frac{\partial}{\partial \mathbf{p}} \right)$$

$$\Rightarrow \frac{\partial \rho}{\partial t} + \nabla \cdot (\rho\vec{v}) = 0, \quad \text{Continuity Equation}$$

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

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

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

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

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

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

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

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

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

若ρ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 = $ 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:

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

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

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

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

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

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

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

$$\Rightarrow \text{indisdinguishability of microscopic particles}$$

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: $\sum\limits_{i=1}^N |\vec{p}_i|^2 = 2mE$. 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

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

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

$S = k_B\ln\Omega = Nk_B\left(\dfrac{3}{2}\ln E + \ln V + \text{const.}\right) \Rightarrow \left(\dfrac{\partial S}{\partial V}\right)_E = \dfrac{Nk_B}{V} \Rightarrow \mathrm{d}S = \dfrac{3}{2}Nk_B\dfrac{\mathrm{d}E}{E} + {\color{red}Nk_B\dfrac{\mathrm{d}V}{V}} = \dfrac{\mathrm{d}E}{T} + {\color{red}\dfrac{P\mathrm{d}V}{T}}$,

观察比较得到 $Nk_B\dfrac{\mathrm{d}V}{V} = \dfrac{P\mathrm{d}V}{T} \Rightarrow P = \dfrac{N}{V}k_B T$.

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

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

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

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

[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.

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

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

Excitations $\to$ Solid property? Quantum?

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

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

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

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

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

1.2.4 Canonical Ensemble

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

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

$$\sum_i\left(\dot{q}_i\frac{\partial\rho}{\partial q_i} + \dot{p}_i\frac{\partial\rho}{\partial q_i}\right) = 0 \Rightarrow \sum_i\left(\frac{\partial H}{\partial p_i}\frac{\partial\rho}{\partial q_i} - \frac{\partial H}{\partial q_i}\frac{\partial\rho}{\partial q_i}\right) = 0.$$ 若 ρ 为 H 函数 $\rho(H)$, 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)} = $ const.; 设 Ω' 为环境微观数, 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)}) + \dfrac{\partial\ln\Omega'}{\partial E'}\bigg|_{E'=E^{(0)}} \overset{-E_r}{(E_{r'} - E^{(0)})} + \cdots = $ const. $- \beta E_r$

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

[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 $W = \dfrac{N!}{\prod_r n_r!}$, 寻找 $\{n_r\}$ 使得 W 最大化.

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

[Dsicussion] 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 ϵ 的概率, 则有 $\dfrac{f(\epsilon_1)}{f(\epsilon_2)} = \dfrac{f(\epsilon_1 + \epsilon)}{f(\epsilon_2 + \epsilon)}$. 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. $W = \dfrac{N!}{\prod_\alpha n_\alpha!}$

1.2.4.2.4 Based on Ensemble Theory   能量中动量和位置分离: $E(q,p) = \overset{\text{kinetic}}{K(p)} + \overset{\text{potential}}{U(q)}$

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

其中动能部分: $e^{-\beta K(p)} = \exp\left[-\beta\left(\dfrac{p_1^2}{2m} + \dfrac{p_1^2}{2m} + \cdots + \dfrac{p_N^2}{2m}\right)\right] = \overset{e^{-\beta \frac{p_{1x}^2}{2m}} e^{-\beta \frac{p_{1y}^2}{2m}} e^{-\beta \frac{p_{1z}^2}{2m}}}{e^{-\beta \frac{p_1^2}{2m}}} \cdot e^{-\beta \frac{p_2^2}{2m}} \cdot e^{-\beta \frac{p_3^2}{2m}} \cdots e^{-\beta \frac{p_N^2}{2m}}$.

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: $\rho_1 = Ae^{-\beta \frac{p_1^2}{2m}}$

1.2.4.2.5 Geometric Viewpoint   在 $(p_{1x}, p_{1y}, p_{1z}, p_{2x}, p_{2y}, \cdots)$ $3N$-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: $H = \alpha p^2 + \beta q^2$; $\langle \alpha p^2 \rangle = \int \alpha p^2 A^{-\beta H} \mathrm{d}q \mathrm{d}p = \dfrac{1}{2}k_B T$.

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

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

1.2.4.3 Thermodynamics

[Discussion] 已知 1st law: $\mathrm{d}U = T\mathrm{d}S - p\mathrm{d}V$, 如何将 $U(V,S)$ 转变为 V 和 T 的未知函数 ?(V,T).

定义 $F \equiv U - TS$, 全微分 $\mathrm{d}F = -p\mathrm{d}V - S\mathrm{d}T \Rightarrow F(V,T)$. 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 $G(P,T)$. $G = \mu N$.

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

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

记 $\beta = \dfrac{1}{k_B T}$, 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 $\langle \ln P_r \rangle = \left\langle \ln \left(\dfrac{e^{-\beta E_r}}{Q_N} \right) \right\rangle = -\ln Q_N - \beta \langle E_r \rangle = \beta(F - U) = -\dfrac{S}{k_B} \Rightarrow S = -k_B \sum_r P_r \ln P_r$, 正是 Gibbs entropy 形式.

对能量 i 求和形式: $Q_N = \sum_i g_i e^{-\beta E_i} = \int g(E) e^{-\beta E} \mathrm{d}E$, 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: $Q_N = \dfrac{1}{N! h^{3N}} \int e^{-\beta H(q,p)} \mathrm{d}^{3N} q \mathrm{d}^{3N} p$

[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 β 偏导得到: $U = -\dfrac{\partial}{\partial \beta} \left(\ln \sum_r e^{-\beta E_r} \right)$. 若再对 U 求一次 β 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 $\dfrac{\sqrt{\langle (\Delta E)^2 \rangle}}{\langle E \rangle} = \dfrac{\sqrt{k_B T^2 C_v}}{U} \sim N^{-\frac{1}{2}}$

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

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

涨落趋于发散.

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

[Example] Reletive fluctuation of speed in Maxwell distribution. $f(v) = A \exp \left\{ -\dfrac{mv^2}{2 k_B T} \right\} v^2 \mathrm{d}v$, where v^2 for 3D gas.

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

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

1. 使用正则系综方法. 配分函数为

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

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

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

记 $n = \dfrac{N}{V}$, 则 $\dfrac{F}{V} = n k_B T \left[\ln \left(\dfrac{n}{f} \right) - 1 \right] \Rightarrow P = \left(\dfrac{\partial F}{\partial V} \right)_{N,T} = \dfrac{N k_B T}{V}$, 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.** $Q_N = \int g(E)e^{-\beta E}\mathrm{d}E, \quad g(E) \sim E^{\frac{3N}{2}-1}$. 那么概率则是 $P(E)\mathrm{d}E = g(E)e^{-\beta E}\mathrm{d}E$

概率 $P(E)$ 对能量 E 导数为 0 以寻找极值点 E_0:
$$\frac{\partial}{\partial E}\left[g(E)e^{-\beta E}\right] = g'(E)e^{-\beta E} + g(E)(-\beta)e^{-\beta E} = \left(\frac{3N}{2}-1\right)E^{\frac{3N}{2}-2}e^{-\beta E} + E^{\frac{3N}{2}-1}(-\beta)e^{-\beta E}$$
$$= \left[\left(\frac{3N}{2}-1\right)E^{-1} - \beta\right] \times \sharp = 0 \Rightarrow E_0 = \left(\frac{3N}{2}-1\right)\frac{1}{\beta} \Rightarrow \lim_{N\to\infty}E_0 = \frac{3N}{2}k_B T$$

[Example] Colored Ideal Gas. N red atoms, N blue atoms, N green atoms. Statistically independent. microstate: (q, p, 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 $S_{3c} = -\left(\frac{\partial F}{\partial T}\right)_{N,V} = 3Nk_B\ln\left(\frac{eV}{N}\right) - 3Nf'(T)$

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

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

1.2.5 Grand Canonical Ensemble

exchange energy, matter. (T, V, μ). $|rs\rangle$: 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.

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

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

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

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

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

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

粒子数 $\langle N\rangle = -\frac{\partial q}{\partial\alpha} = ZVf(T)$; 内能 $\langle U\rangle = -\frac{\partial q}{\partial\beta} = ZVk_B T^2 f'(T)$; 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 Ω, 体积为 v, 粒子数为 n. 则 Ω 中有 n 个粒子的概率 $P_n = \dfrac{\sum\limits_s e^{-\alpha n - \beta E_n^{(s)}}}{Q}$. 猜测平均粒子数为 $\langle n \rangle = \dfrac{N}{V} v$. 独立同分布. 单个粒子在/不在 Ω 中的概率: $P_1 = \dfrac{v}{V}$, $P_0 = 1 - \dfrac{v}{V}$. 则 Ω 中有 n 个粒子的概率为 $P(n) = \dfrac{N!}{(N-n)!n!} P_1^n P_0^{N-n}$, $\lim\limits_{N \to \infty} P(n)$ 将化为 Poisson 分布: $P(n) = \dfrac{\langle n \rangle^n}{n!} e^{-\langle n \rangle}$, 其中 $\langle n \rangle = \dfrac{N}{V} v$.

1.3   Phase Transition

A system containing many degrees of freedom $\to$ 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-superfulid 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...

$\mathrm{d}\mu = v\mathrm{d}P - s\mathrm{d}T$, 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: $P = \dfrac{RT}{v-b} - \dfrac{a}{v^2}$. b: hard-core repulsion(硬球排斥); a: attraction, $\dfrac{a}{v^2} \sim n^2 = \left(\dfrac{N}{V}\right)^2$. 1. $T \gg |\varepsilon_0|$, 可忽略相互作用; 2. $T \downarrow$, interaction $\uparrow$, condensed state(liquid state); 3. $T \to 0$, crystal state/amorphous state (mechanical in equilibrium).

1.3.1.1   Derivation of Van der Waals Equation

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

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

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

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

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

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

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

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

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

1.3.2 Phase Diagram

Van der Waals equation: real gas.

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

$P = \dfrac{RT}{v-b} - \dfrac{a}{v^2}$ 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: $v_1, v_2, v_3 \to v_c$, 即 critical point.

1.3.2.1 Maxwell Construction

$G = \mu N$. 在等温曲线上, $\mathrm{d}G = \cancel{-S\mathrm{d}T} + V\mathrm{d}P$. 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 $\Delta G = \displaystyle\int_A^B V\mathrm{d}P = \int_A^B [\mathrm{d}(PV) - P\mathrm{d}V] = P(V_B - V_A) - \int_{V_A}^{V_B} P\mathrm{d}V = 0$, 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.
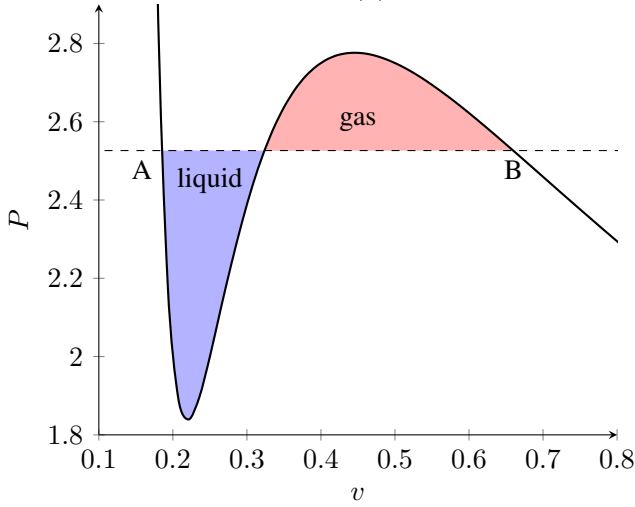
计算气液两相所占体积: $v_0 = xv_l + (1-x)v_g \Rightarrow x = \dfrac{v_g - v_0}{v_g - v_l}$, 即 lever rule. $\dfrac{\partial P}{\partial v} > 0$ 是热力学不稳定的.

1.3.2.2 Critical Behavior

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

$P_r = \dfrac{P}{P_c}$, $v_r = \dfrac{v}{v_c}$, $T_r = \dfrac{T}{T_c} \Rightarrow \left(P_r + \dfrac{3}{v_r^2} \right) (3v_r - 1) = 8T_r$. 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 (π, Ψ, t) 描述临界点附近状态.

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

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

Maxwell construction $\displaystyle\int \mathrm{d}G = 0 \Rightarrow P(V_B - V_A) - \int_{V_A}^{V_B} P\mathrm{d}V = 0$ 得到的. 使用 (π, Ψ, t) 重构:

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

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

因此在临界点附近, Ψ_l 和 Ψ_g 对称地分布在临界点两侧.

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

[Example] First observation of critical phenomenon. Water: $T_c = 373.946°C$, $P_c = 217.7$ atom.

[Discussion] $Q(Z,V,T) = \displaystyle\sum_{N=0}^{N_{\max}} Z^N Q_N(V,T), \quad P = \dfrac{k_B T}{V}\ln Q$. 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 $\displaystyle\lim_{N_{\max}, V \to \infty}$ 的同时 $\dfrac{N}{V} = $ 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↑, N_- 个自旋↓; 又令 N_{++} 为相邻 ↑↑ 的数, N_{--} 为相邻 ↓↓ 的数, N_{+-} 为相邻 ↓↑ 与 ↑↓ 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 $H_N(N_+, N_{++}) = -J\left(\dfrac{1}{2}qN - 2qN_+ + 4N_{++}\right) - \mu B(N_+ - N)$,

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

1.3.3.2 Mean-Field Approximation

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

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

$$H(\{\sigma_i\}) = -J\sum_{\langle i,j\rangle}\sigma_i\sigma_j - \mu B\sum_i \sigma_i = -\frac{J}{2}\sum_i\left(\sum_{\langle j\rangle}\sigma_j\right)\sigma_i - \mu B\sum_i \sigma_i$$

$$= -\frac{J}{2}\sum_i(q\overline{\sigma})\sigma_i - \mu B\sum_i \sigma_i = -\mu\left(B + \frac{1}{2}B'\right)\sum_i \sigma_i, \quad B' = \frac{qJ}{\mu}\overline{\sigma}, \quad \text{Effective field}$$

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

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

等式两边同 ln, 且引入 $\operatorname{arctanh} x = \dfrac{1}{2}\ln\left(\dfrac{1+x}{1-x}\right)$, 得到 $\beta\left(qJ\overline{L} + \mu B\right) = \operatorname{arctanh}\left(\overline{L}\right)$, 即 $\overline{L}$ 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 $\rho(\vec{r}) = \displaystyle\sum_s e_s n_{s_0}e^{-\frac{e_s\phi(\vec{r})}{k_B T}}$, $\nabla^2\phi(\vec{r}) = -4\pi\rho(\vec{r})$.

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

1.3.3.2.1 $B = 0$ 下的 $\overline{L}$ $\quad$ 令 $L_0 = \overline{L}(B = 0)$, 得到无外场条件下的状态方程 $\overline{L}_0 = \tanh\left(\beta Jq\overline{L}_0\right)$. $\overline{L}_0 \to 0$ 代表可相变.

使用极限 $\displaystyle\lim_{x\to 0}\tanh(x) \simeq x - \dfrac{x^3}{3} + O(x^5)$, 展开状态方程: $(\beta qJ - 1)\overline{L}_0 = \dfrac{1}{3}\left(\beta qJ\overline{L}_0\right)^3$. 若 $\beta qJ - 1 > 0 \Leftrightarrow T < \dfrac{qJ}{k_B} = T_c$,

则存在顺磁解 $\overline{L}_0 = 0$; 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 $\dfrac{\mathrm{d}\tanh\left(\beta J \overline{L}_0\right)}{\mathrm{d}\overline{L}_0}\bigg|_{\overline{L}_0 > 0} = 1 \Rightarrow \dfrac{qJ}{k_B T_c} = 1$.

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 $\lim\limits_{T \to T_c^-} \overline{L}_0 = \overline{L}_0 \dfrac{T_c}{T} - \dfrac{1}{3}\overline{L}_0^3 \left(\dfrac{T_c}{T}\right)^3 \Rightarrow \overline{L}_0 \simeq 3^{\frac{1}{2}} \left(1 - \dfrac{T}{T_c}\right)^{\frac{1}{2}}$.

2. 在 $T \to 0$ 时, 有近似 $\lim\limits_{T \to 0} \overline{L}_0 \simeq 1 - 2\exp\left(-\dfrac{2T_c}{T}\right)$, 斜率 $\dfrac{\mathrm{d}\overline{L}_0}{\mathrm{d}T} \to 0$.

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

热容为内能偏导 $c_0 = \dfrac{\partial U_0}{\partial T} = -qJN\overline{L}_0 \dfrac{\mathrm{d}\overline{L}_0}{\mathrm{d}T}$. 可见其依赖于 $\dfrac{\mathrm{d}\overline{L}_0}{\mathrm{d}T}$; 因此 1. $T > T_c$ 时, $c_0 = 0$;

2. $\lim\limits_{T \to T_c^-}$ 时, 对物态方程两边都 $\dfrac{\partial}{\partial T}$, 得到 $c_0 = k_B N \dfrac{T_c}{T}\overline{L}_0^2 \dfrac{1 - \overline{L}_0^2}{\dfrac{T}{T_c} - \left(1 - \overline{L}_0^2\right)} \simeq \dfrac{3}{2}Nk_B$

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

2. Thermodynamic method. $S_0(T \geq T_c) = \displaystyle\int_0^T \dfrac{c_0(T)\mathrm{d}T}{T} = \int_0^{T_c} \dfrac{c_0(T)\mathrm{d}T}{T} + \cancel{\int_{T_c}^T \dfrac{c_0(T)\mathrm{d}T}{T}} = -qJN\int_1^0 \dfrac{\overline{L}_0}{T}\mathrm{d}\overline{L}_0$

$= Nk_B \displaystyle\int_0^1 \operatorname{arctanh}\left(\overline{L}_0\right)\mathrm{d}\overline{L}_0 = Nk_B \ln 2$

研究 $B = 0$ 时的磁化率 χ_0.

$\chi_0 = \left(\dfrac{\partial M}{\partial B}\right)_T \Rightarrow \lim\limits_{T \to T_c^+} \chi_0 \simeq \dfrac{NM^2}{k_B} \dfrac{1}{T - T_c}, \quad \lim\limits_{T \to T_c^-} \chi_0 \simeq \dfrac{NM^2}{2k_B} \dfrac{1}{T_c - T}, \quad \lim\limits_{T \to 0} \chi_0 \simeq \dfrac{4NM^2}{k_B T} \exp\left\{-\dfrac{2T_c}{T}\right\}$.

1.3.3.2.2 Weak External Field $B \to 0$ 在 $T \geq T_c$ 时, 有 $\overline{L} \simeq \dfrac{\mu\beta}{1 - \beta qJ}B = \dfrac{\mu}{k_B(T - T_c)}B \Rightarrow \overline{L} \propto B$, 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 ↑ 的概率 $P_{++} = \dfrac{N_{++}}{\dfrac{1}{2}qN}$ 是否等价于单自旋 ↑ 概率乘积

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

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

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

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

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

在处理时运用了 $\delta\sigma_i\delta\sigma_j \to 0$ 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]:

$$\frac{N_+}{N} = \frac{1}{2}(1+L), \quad \frac{N_-}{N} = \frac{1}{2}(1-L), \quad L = \frac{N_+ - N_-}{N}$$

$$\frac{N_{++}}{\frac{1}{2}qN} = \left(\frac{N_+}{N}\right)^2 \to \frac{N_{++}}{N} = \frac{q}{8}(1+L)^2, \quad \text{similarly } \frac{N_{--}}{N} = \frac{q}{8}(1-L)^2, \quad \frac{N_{+-}}{N} = \frac{q}{4}(1-L^2)$$

$$U(L) = -\frac{1}{2}qJNL^2 - \mu BNL$$

$$S = k_B \ln\left(\frac{N!}{N_+!N_-!}\right) \overset{N\to\infty}{=} -k_B N \left[\frac{1+L}{2}\ln\left(\frac{1+L}{2}\right) + \frac{1-L}{2}\ln\left(\frac{1-L}{2}\right)\right]$$

$$F(L) = U - TS = -\frac{1}{2}qJNL^2 - \mu BNL + k_B TN\left[\frac{1+L}{2}\ln\left(\frac{1+L}{2}\right) + \frac{1-L}{2}\ln\left(\frac{1-L}{2}\right)\right]$$

$$\frac{\partial F}{\partial L} = 0 \Rightarrow -qJNL - \mu BN + \frac{1}{2}k_B TN\left[\ln\left(\frac{1+L}{2}\right) + 1 - \ln\left(\frac{1-L}{2}\right) - 1\right] = 0$$

$$\Rightarrow -qJNL - \mu BN + \frac{1}{2}k_B TN\ln\left(\frac{1+L}{1-L}\right) = 0 \Rightarrow \frac{1}{2}\ln\left(\frac{1+L}{1-L}\right) = \frac{qJL + \mu B}{k_B T}$$

$$\Rightarrow \operatorname{arctanh} L = \beta(qJL + \mu B), \quad \beta = \frac{1}{k_B T}$$

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

$(q+1)$ system. σ_0 感受到 q 个 σ_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: $\overline{\sigma}_0 = \overline{\sigma}_j, \quad \forall j$.

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

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

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

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,

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

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

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

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

若 $\alpha = 0$, 则 $\lim_{\alpha'\to 0}\overline{\sigma}_0 = \frac{2\alpha'}{1+e^{-2\gamma_c}} = \left[\frac{q^2}{q-1}\frac{J}{k_B T_c}3\left(1-\frac{T}{T_c}\right)\right]^{\frac{1}{2}}$. 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, $\frac{N_{++}N_{--}}{N_{+-}^2} = \frac{1}{4}$.

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

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

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

1.3.3.5.2 Specific Heat 无外场内能为 $U_0 = -\dfrac{1}{2}qJN\dfrac{\cosh(2\alpha') - e^{-2\gamma}}{\cosh(2\alpha') + e^{-2\gamma}}$. 在 $T > T_c$ 时, 等效平均场为 $\alpha' = 0$. 此时热容为

$\dfrac{c_0}{Nk_B} = \dfrac{1}{2}q\gamma^2 \operatorname{sech}^2 \gamma > 0$ $\left[\text{回忆 MFT 给出的 } c_0 \propto \overline{L}_0 \dfrac{\mathrm{d}\overline{L}_0}{\mathrm{d}T} = 0 \text{ 和此处结果相悖, 显然是忽略了涨落关联造成的}\right]$

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 $H_N(\{\sigma_i\}) = -J\sum_{\langle i,j\rangle}\sigma_i\sigma_j - \mu B\sum_{i=1}^{N}\sigma_i = -J\sum_{i=1}^{N}\sigma_i\sigma_{i+1} - \dfrac{1}{2}\mu B\sum_{i=1}^{N}(\sigma_i + \sigma_{i+1})$

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

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

$= \sum_{\sigma_1=\pm1}\langle\sigma_1|P^N|\sigma_1\rangle = \operatorname{Tr}P^N = \lambda_+^N + \lambda_-^N \overset{\lambda_+\gg\lambda_-}{\approx}\lambda_+^N$. 其中 $\lambda_\pm$ 是矩阵 P 的特征值.

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

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

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

$F(B,T) = -k_B T\ln Q_N = -NJ - Nk_B T\ln\left\{\cosh(\beta\mu B) + [e^{-4\beta J} + \sinh^2(\beta\mu B)]^{\frac{1}{2}}\right\}, \quad M = \left(\dfrac{\partial F}{\partial B}\right), \quad \lim_{B\to0}M = 0$

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

$\sum_{\sigma_N=\pm1}e^{\beta J_{N-1}\sigma_{N-1}\sigma_N} = e^{\beta J_{N-1}\sigma_{N-1}} + e^{-\beta J_{N-1}\sigma_{N-1}} = 2\cosh(\beta J_{N-1}\sigma_{N-1}) \overset{\text{even function}}{=} 2\cosh(\beta J_{N-1})$

于是有递推关系: $Q_N = 2\cosh(\beta J_{N-1})Q_{N-1}, \quad Q_1 = \sum_{\sigma_1=\pm1}(1) = 2 \Rightarrow Q_N = Q_1\prod_{i=1}^{N-1}2\cosh(\beta J_i)$

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

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

$= e^{-r/\xi}, \quad$ correlation length: $\xi = \dfrac{1}{\ln[\coth(\beta)]} \Rightarrow$ 随距离增大而迅速衰减. $\quad\lim_{T\to0}\xi = \infty, \quad \lim_{T\to\infty}\xi = 0$

1.3.3.7 Phase Transition & Space Dimension

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

1D: $(+,+,-,\textcolor{red}{+},+)$ 染色 元素翻转 $+\to-$, 不会消耗能量; 2D: $\begin{pmatrix}- & - & - & - & -\\- & - & - & - & -\\- & + & + & \textcolor{red}{+} & -\\- & - & - & - & -\end{pmatrix}$ 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. $V_i \to \begin{cases} 1, & \text{if } \sum_j \omega_{ij} V_j > U \\ 0, & \text{if } \sum_j \omega_{ij} V_j < U \end{cases}$.

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

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), $\chi_0 \sim \dfrac{\partial m}{\partial h}$ (磁化率).

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

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

[Example] 1. superfluid He: $\alpha \approx -0.01294$; 2. 0th approximation of Ising Model & Van der Waals theory of gas-liquid phase transition: $\alpha = \alpha' = 0, \quad \beta = \dfrac{1}{2}, \gamma = \gamma' = 1, \delta = 3$; 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, $dF = -SdT - MdH, \quad M = -\left(\dfrac{\partial F}{\partial H}\right)_T \Rightarrow F(T, H, M)$, let $\dfrac{\partial F(T, H, M)}{\partial M}\bigg|_{\text{equilibrium}} = 0$. 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): $\lim_{t, m_0 \to 0} \psi_0(t, m_0) = q(t) + r(t) m_0^2 + s(t) m_0^4 + \cdots, t = \dfrac{T - T_c}{T_c}$,

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] ψ_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 $\dfrac{\partial \psi_0}{\partial m_0}\bigg|_{m_0=0} \neq 0$.

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

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

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

$r(t) = r_0 + \boxed{r_1 t} + r_2 t^2 + \cdots, \quad s(t) = \boxed{s_0} + s_1 t + s_2 t^2 + \cdots$. 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 $\sqrt{\dfrac{-r(t)}{2s(t)}} \simeq \sqrt{\dfrac{r_1 |t|}{2s_0}} \Rightarrow \beta = \dfrac{1}{2}, \quad m_0 \sim t^\beta (\beta$ 的定义).

图中标注：

$\psi_0(m_0)$ (纵轴)

$m_0^* \sim |t|^{1/2}$

$\beta = \dfrac{1}{2}$

$\psi_0(m_0) = q_0 + r_1 t m_0^2 + s_0 m_0^4 \quad T > T_c \ (t > 0)$

$T < T_c \ (t < 0)$

$\psi_0(0)$

$\psi_0(0)$

$\psi_0(-m_0^*)$

$\psi_0(m_0^*)$

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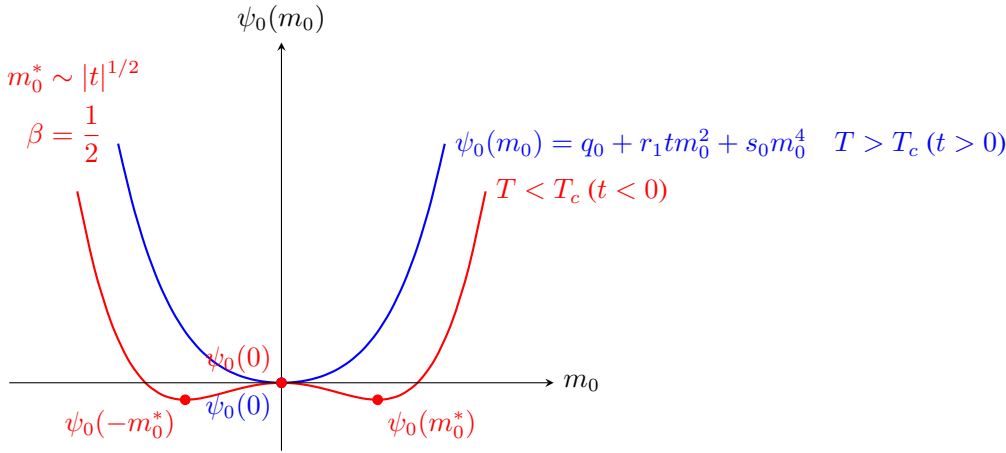
热容 $c_0 \sim \dfrac{\partial \, \text{Entropy}}{\partial t}$, $\quad$ Entropy $= \dfrac{\partial \psi_0}{\partial t} \simeq r_1 m_0^2 \begin{cases} 0, & t > 0 \\ m_0 \sim |t|^{\frac{1}{2}}, & t < 0 \end{cases}$

[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($\alpha = \alpha' = 0, \beta = \dfrac{1}{2}, \gamma = \gamma' = 1, \delta = 3$). $q(t), r(t), s(t)$ 不影响 critical exponents, 而是描述具体实验.

[Discussion] Wriss model @ 1907

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

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

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

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

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

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

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

$\gamma = \gamma' = \alpha + 2\Delta - 2, \quad \delta = \dfrac{\Delta}{\beta}$. 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 $Q_N(H, T) = \displaystyle\sum_{\{\sigma_i\}} \exp\left(\beta J \sum_{\langle i,j \rangle} \sigma_i \sigma_j + \beta\mu H \sum_i \sigma_i \right)$, 通过对 $\ln Q_N$ 求偏导以得到期望值:

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

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

[Discussion] Fluctuation & Response Theorem.

1. 热容 $C_v = \dfrac{\partial \langle E \rangle}{\partial T}\bigg|_V = \dfrac{\langle (\Delta E)^2 \rangle}{k_B T^2}$;

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

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

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

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

$$F=-k_BT\ln Q,\quad \chi(x,x')=\frac{\partial m(x')}{\delta h(x)}=-\frac{\partial^2 F}{\partial h(x)\partial h(x')}=\beta\left(\langle m(x)m(x')\rangle-\langle m(x)\rangle\langle m(x')\rangle\right)$$

1.3.4.2.1 Generalized Landau Free Energy Correlation Function

一般性地, 自由能 $F=\int\mathrm{d}^d\vec{x}\left\{am\left(\vec{x}\right)^2+b\left[\nabla m\left(\vec{x}\right)\right]^2\right\}$,

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

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

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

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

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

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

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

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

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

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 σ_0, 设范围尺度(半径)为 ξ, 圈出范围 Ω. 范围内其余自旋为 σ_r.

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

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

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

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

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

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

1.3.5 Scale Transformation

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

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

$L=\left(\dot{x}^2+\dot{y}^2\right)+V(x-y)$, 对 $(x,y)\to(x+\delta,y+\delta)$ 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 $a \to a' = la(l=2)$; 自旋个数 $N \to N' = l^{-d}N(d=2)$;

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

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

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

类比 $N \to N' = l^{-d}N$, 线性假设 $t \to t' = l^{y_t}t, h \to h' = l^{y_h}h$. 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 $\psi^{(s)}(t, h) = |t|^\beta \widetilde{\psi}\left(\dfrac{h}{|t|^\alpha}\right)$, 变换前后分别代入得 $|t|^\beta \widetilde{\psi}\left(\dfrac{h}{|t|^\alpha}\right) = l^{-d}|t'|^\beta \widetilde{\psi}\left(\dfrac{h'}{|t'|^\alpha}\right)$,

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

1.3.5.2 Scale Transformation in 1D & 2D Ising Models

1.3.5.2.1 1D Ising Model

研究 $J \to J'$, $B \to B'$ 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 $\vec{K} \to \vec{K}'$, 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: $N \to N' = \dfrac{N}{2}$. 变换前后的配分函数相等:

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

$\sigma \to \sigma'$ 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 $\vec{K} \to \vec{K}'$ 的具体表达式:

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

[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: $f(K_1; K_2 = 0) = -\dfrac{1}{2}\ln\left[2\cosh^{\frac{1}{2}}(2K_1)\right] + \dfrac{1}{2}f\left(K'_1 = \ln\left[\cosh^{\frac{1}{2}}(2K_1)\right]; K'_2 = 0\right)$

令 $x = K_1$, 即有 $f(x) = -\dfrac{1}{2}\ln\left[2\cosh^{\frac{1}{2}}(2x)\right] + \dfrac{1}{2}f\left(\ln\left[\cosh^{\frac{1}{2}}(2x)\right]\right)$, 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: $\dfrac{y^2(x)}{y\left\{\ln\left[\cosh^{\frac{1}{2}}(2x)\right]\right\}} = \cosh^{\frac{1}{2}}(2x)$, 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 $R_{l_2}[R_{l_1}(K)] = R_{l_1 * l_2}(K) \longrightarrow \lambda_{l_1}\lambda_{l_2} = \lambda_{l_1 * l_2}$.

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 $\{\overset{\text{trivial}}{0}, \overset{\text{critical}}{\infty}\}$.

[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 $\vec{k} \to \vec{0}$.

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

其中 $\vec{k}' = A_l\vec{k}$, $\quad A_l = \left.\dfrac{\partial R_l(\vec{q})}{\partial \vec{q}}\right|_{\vec{q}=\vec{K}^*}$. 将 $\vec{k}$ 以基矢展开 $\vec{k} = \sum\limits_i u_i\hat{\phi}_i$, 则变换式 $\vec{k}' = A_l\vec{k}$ 即可写作 $\sum\limits_i u_i'\hat{\phi}_i = A_l\sum\limits_i u_i\hat{\phi}_i$.
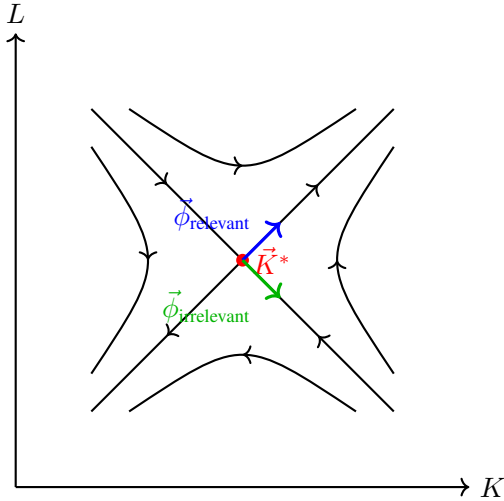
特征方程 $A_l\hat{\phi}_i = \lambda_i\hat{\phi}_i$, 代入为 $\sum\limits_i u_i'\hat{\phi}_i = \sum\limits_i u_i\lambda_i\hat{\phi}_i$, 即得分量变换式 $u_i \to u_i' = \lambda_i u_i = l^{y_i}u_i$.

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 $u_{\text{relevant}} \to 0$.

[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), 则需要求和项数无穷大, 而某些物理量保持有限值(e.g. $\lim\limits_{N,V\to\infty} n = \dfrac{N}{V} = n_0$);

2. 不动点也是通过无穷连续变换产生的;

3. 微分方程 $\dfrac{\mathrm{d}u}{\mathrm{d}t} = -2u(u^2 - 1)$ 的精确解为 $u(t) = \dfrac{u_0}{\sqrt{u_0^2 - (u_0^2 - 1)e^{-4t}}}$, 其中 $u_0 = u\Big|_{t=0}$. 存在不动点 $u^* = \pm 1$, 通过 $\lim\limits_{t\to\infty} u(t) = \mathrm{sgn}(u_0)$ 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 $\begin{cases} K^* = \dfrac{1}{3} \\ L^* = \dfrac{1}{9} \end{cases}$. 取不动点附近 $\begin{cases} K = K^* + k_1 \\ L = L^* + k_2 \end{cases}$,

小量变换满足 $\begin{cases} k_1' = \dfrac{4}{3}k_1 + k_2 \\ k_2' = \dfrac{2}{3}k_1 \end{cases}$. 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 $\lambda_{1,2} = \dfrac{2 \pm \sqrt{14}}{3}$.

($\lambda_1 > 1$, 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 $K\text{-}L$ 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 λ 值变化出现不动点 x^* 的分形.

定义 $\delta_n = \dfrac{x_{n+1} - x_n}{x_n - x_{n-1}}$, 发现其存在规律 $\lim\limits_{n \to \infty} \delta_n = 4.6692 \cdots$.

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 $\to$ 涨落 $N = N_0 + \delta N$; 2. Non-equilibrium state, thermodynamic level: 时空间不均匀, $T(x, t), n(x, t)$. 通过局域平衡假设分析. $\dfrac{\partial n}{\partial x} \to$ 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 fluactuation of density ρ: grow/decay.

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

1.4.1.1　Static Thermodynamic Analysis

研究发生 $\overset{\text{equilibrium}}{f_0} \to \overset{\text{fluactuated}}{f_0 + \delta f}$ 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

$$\Delta S = \Delta S_1 + \Delta S_2 = \Delta S_1 + \int_0^f \frac{\mathrm{d}E_2 + P_2\mathrm{d}V_2}{T_2} \quad \begin{cases} \Delta E_2 = -\Delta E_1 \\ \Delta V_2 = -\Delta V_1 \end{cases} \simeq \quad \Delta S_1 - \frac{\Delta E_1 + P_0\Delta V_1}{T_0}$$

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

$$\Delta E(S, V) = \left(\overset{T}{\frac{\partial E}{\partial S}}\right)_0 \Delta S + \left(\overset{-p}{\frac{\partial E}{\partial V}}\right)_0 \Delta V + \frac{1}{2}\left[\left(\frac{\partial^2 E}{\partial S^2}\right)_0 (\Delta S)^2 + 2\left(\frac{\partial^2 E}{\partial S \partial V}\right)_0 \Delta S \Delta V + \left(\frac{\partial^2 E}{\partial V^2}\right)_0 (\Delta V)^2\right] + \cdots$$

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

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

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

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

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

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

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

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

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

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

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

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

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

1.4.1.2 Time Analysis of Fluctuations

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

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

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

[Discussion] Correlation & Macroscopic properties.

1. 空间关联函数 g_{ij} $\overset{\text{in equilibrium}}{\longrightarrow}$ Response χ;

2. 时间关联函数 $\phi(t)$ $\overset{\text{out of equilibrium}}{\longrightarrow}$ 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 $\dfrac{1}{2}L\langle\theta^2\rangle = \dfrac{1}{2}k_B T \Rightarrow \langle\theta^2\rangle = \dfrac{k_B T}{L}$. (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.

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

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

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

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

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

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

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

1.4.2 Relaxation of Weakly Non-equilibrium State

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

$\langle x_i(t)\rangle \Rightarrow \dfrac{\mathrm{d}x_i(t)}{\mathrm{d}t} = -\displaystyle\sum_k \lambda_{ik}x_k(t)$. 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 $X_i = \dfrac{\partial S}{\partial x_i}$ 以引入熵 $S(x_1, x_2, \cdots, x_n)$. $\dot{x}_i(t), X_i(t)$ 分别为 flux 和 force.

Taylor 展开: $S(x_i) = \overset{\text{equilibrium}}{S(0)} + \cancel{\left(\dfrac{\partial S}{\partial x_i}\right)_{x_i=0} x_i} + \dfrac{1}{2}\left(\dfrac{\partial^2 S}{\partial x_i \partial x_j}\right)_{x_i = x_j = 0} x_i x_j + \cdots = S(0) - \dfrac{1}{2}\beta_{ij}x_i x_j$, 其中 $\beta_{ij} = \beta_{ji}$.

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

于是 Force $X_i = -\beta_{ik}x_k$, 从而得到 **Force-Flux 关系** $\boxed{\dot{x}_i = \gamma_{ik}X_k}$, 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: $S = \dfrac{1}{2}X_i x_i$,

变化率为 $\dfrac{\mathrm{d}S}{\mathrm{d}t} = \dfrac{1}{2}\left(\dot{X}_i x_i + X_i \dot{x}_i\right)$. 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 $\dot{S} = X_i \dot{x}_i = \dfrac{\partial S}{\partial x_i}\dot{x}_i$, 显然就是链式求导规则.

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

$$\dfrac{\partial u}{\partial t} + \nabla \cdot \vec{J}_h = 0 \overset{\mathrm{d}u = T\mathrm{d}S}{\Longrightarrow} \dfrac{\partial S}{\partial t} = -\dfrac{1}{T}\nabla \cdot \vec{J}_h \Rightarrow \dfrac{\partial S}{\partial t} + \nabla \cdot \left(\dfrac{\vec{J}_h}{T}\right) = -\dfrac{1}{T^2}\vec{J}_h \cdot \nabla T.$$

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, $\langle \dot{x}_i \rangle = 0, \langle x_i \rangle = \widetilde{x}_i$. $\langle x_i X_j \rangle = \underset{x_i}{\mathrm{Tr}}\left[x_i X_j A e^{\Delta S(x_1, x_2, \cdots, x_n)/k_B}\right] = \underset{x_i}{\mathrm{Tr}}\left[x_i X_j A e^{\frac{1}{2k_B}\beta_{ij}(x_i - \widetilde{x}_i)(x_j - \widetilde{x}_j)}\right]$

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

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

Time reversal symmetry of x_i: $\overset{\phi_{ij}(-t)}{\langle x_i(0)x_j(t)\rangle} = \overset{\phi_{ij}(t)}{\langle x_i(t)x_j(0)\rangle} \overset{t=0}{\Longrightarrow} \langle x_i(0)\dot{x}_j(0)\rangle = \langle \dot{x}_i(0)x_j(0)\rangle.$

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 $\boxed{\gamma_{ij} = \gamma_{ji}}$.

若将 $\dot{x}_i = \gamma_{ij}X_j$ 定义为 $\dfrac{\partial f}{\partial X_i}$, 则有 $f = \dfrac{1}{2}\gamma_{ij}X_i X_j$. 熵变化率可表述为 $\dfrac{\mathrm{d}S}{\mathrm{d}t} = X_i \dot{x}_i = X_i \dfrac{\partial f}{\partial X_i} = 2f$

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

1. 且 Γ_{ik} 可对角化, 则可进一步写作 decay $\dot{x}'_i = -\lambda_i x'_i$;

2. 且 Γ_{ik} antisymmetric(特征值纯虚数), 即 $\dot{x}_i = -\lambda^A_{ik}x_k$, 则动力学为 oscillatory(振荡).

1.4.2.3 Fluactuation Phenomena

1.4.2.3.1 XY Model

Hamiltonian $H = -\dfrac{1}{2}J\sum_{\langle i,j \rangle}\left\langle \vec{S}_i \cdot \vec{S}_j \right\rangle$, 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 θ 进行控制. 选定 $\vec{R}$ 处一格点, 设 θ 足够小. 则 Hamiltonian 为

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

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

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

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 $\oint \mathrm{d}\theta = 2\pi k, k \in \mathbb{Z}$.

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 $\frac{\partial\theta}{\partial r} = 0 \Rightarrow \nabla\theta = \frac{1}{r}\frac{\partial\theta}{\partial\phi}\hat{e}_\phi + \cancel{\frac{\partial\theta}{\partial r}\hat{e}_r}$,

$\oint \mathrm{d}\theta = \oint \nabla\theta \cdot \mathrm{d}\vec{l} = \frac{1}{r}\frac{\partial\theta}{\partial\phi}2\pi r = 2\pi k \Rightarrow \frac{\partial\theta}{\partial\phi} = k \Rightarrow \theta = k\phi + c_0, c_0$ 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. One defect: $E = \overset{\text{core energy}}{\varepsilon_0(a)} + \frac{K}{2}\int (\nabla\theta)^2 \mathrm{d}^2\vec{x} \overset{\theta=k\phi}{=} \varepsilon_0(a) + \pi K k^2 \ln\left(\frac{R}{a}\right)$

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(fluactuation/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 Δt. 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 $\sqrt{\left\langle\vec{R^2}\right\rangle} \sim L^{\frac{1}{2}+\delta}$, 其中 δ 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

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

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

极限下取高斯分布 $\lim_{n\to\infty} P_n(m) = \frac{1}{\sqrt{2\pi n}}\exp\left(-\frac{m^2}{2n}\right)$. 使用 $\begin{cases} x = ml \\ t = n\tau \end{cases}$ 连续化为 $P(x,t)\mathrm{d}x = \frac{\mathrm{d}x}{\sqrt{4\pi Dt}}\exp\left(-\frac{x^2}{4Dt}\right)$, 其中扩散系数 $D = \frac{l^2}{2t}$, 在气体中约 $(10^{-6}, 10^{-5})$ m^2/s, 在液体中约 $(10^{-10}, 10^{-9})$ m^2/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 $P(x,t_1)\mathrm{d}x \to n(\vec{x},t)\mathrm{d}x$. 这就是扩散现象.

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

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

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

$\langle(\Delta x)^2\rangle \sim Dt$, 纯粹依靠扩散作用在空气中传播 1m 需耗时 $t \sim \frac{\langle(\Delta x)^2\rangle}{D} \sim 10^6$ s ≈ 11 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 $P(S = k) = C_n^k p^k (1-p)^k$.

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

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

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 $\langle x_\alpha^2 \rangle = a^2 \sum_{i=1}^{\langle \cos \theta_i \rangle = 0} \langle \cos \theta_i \rangle + a^2 \sum_{i \neq j} \langle \cos \theta_i \cos \theta_j \rangle = Na^2 \langle \cos^2 \theta \rangle$.

对2维球面 $\mathrm{d}\Omega = \sin \theta \overset{[0,\pi]}{\mathrm{d}\theta} \overset{[0,2\pi]}{\mathrm{d}\phi}$, 推广至 $(d-1)$ 维球面: $\mathrm{d}\Omega = \sin^{d-2} \theta_1 \sin^{d-3} \theta_2 \cdots \sin^1 \theta_{d-2} \mathrm{d}\theta_1 \mathrm{d}\theta_2 \cdots \mathrm{d}\theta_{d-1} \mathrm{d}\phi$.

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

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

计算 $\langle \cos^2 \theta_1 \rangle = \int \cos^2 \theta_1 P_0 \mathrm{d}\Omega = \Omega' \int_0^\pi P_0 \cos^2 \theta_1 \sin^{d-2} \theta_1 \mathrm{d}\theta_1 = \frac{1}{d}$, 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.

[Discussion] Random unit vector $\vec{n}$ in $n-$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: $\{\overset{t_0}{x_0}\} \to [x_1, \overset{t_1}{x_1} + \mathrm{d}x] \to [x_2, \overset{t_2}{x_2} + \mathrm{d}x] \to \cdots$

令 $P_1(x, t) = \mathrm{Prob}\left[x < x(t) < x + \mathrm{d}x \right]$ 为 t 时刻 $x \in (x, x + \mathrm{d}x)$ 的概率,

$P_n(x_0, t_0; x_1, t_1; \cdots; x_{n-1}, t_{n-1}) \mathrm{d}x_0 \cdots \mathrm{d}x_{n-1} = \mathrm{Prob}\left[x_0 < x(t_0) < x_0 + \mathrm{d}x_0, \cdots, x_{n-1} < x(t_{n-1}) < x_{n-1} + \mathrm{d}x_{n-1} \right]$

定义 **Transition Probability**: $\mathrm{Prob}\left[(x_0, t_0) \to (x_1, t_1) \right] \mathrm{d}x_1 = \dfrac{P_2(x_0, t_0; x_1, t_1) \mathrm{d}x_1}{P_1(x_0, t_0)}$.

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

1.4.3.3   Smoluchowski's Approach

从 x_0 出发, 经过 n 步后到达 x 的概率为 $\mathrm{Prob}\left(x_0 \overset{n \text{ steps}}{\longrightarrow} x \right) = P_n(x_0 | x)$, 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

$P_1(z | x) = \frac{1}{2} \left(\delta_{z, x+1} + \delta_{z, x-1} \right)$, $P_0(z | x) = \delta_{z, x}$, 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:

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

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

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

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

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

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

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

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

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

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

$$P(n, s) = \sum_{m, m_1, m_2, \cdots, m_{s-1}} \overset{m \to m_1 \to m_2 \to \cdots \to m_{s-1}}{P(m, 0) P(m, 0 | m_1, 1) P(m_1, 1 | m_2, 2) \cdots P(m_{s-1}, s-1 | n, s)}$$

$$= \sum_{m, m_1, m_2, \cdots, m_{s-1}} P(m, 0) Q_{mm_1}(1) Q_{m_1 m_2}(2) \cdots Q_{m_{s-1} n}(s-1) = \sum_{m} P(m, 0) \left(Q^S\right)_{mn}, P(m, s_0 | n, s) = (Q^{s-s_0})_{mn}$$

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. $Q_{n,n+1} = Q_{n+1,n} = \dfrac{1}{2}, n \in \mathbb{N}$.

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

Define $\delta P(n, s) \equiv P(n, s) - P(n, s-1) = P(n-1, s-1) Q_{n-1,n} + P(n+1, s-1) Q_{n+1,n} - P(n, s-1)$

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

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

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

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.

介观(mesoscopic) level: $M \dfrac{\mathrm{d}\vec{v}}{\mathrm{d}t} = -\overset{\text{viscosity}}{\dfrac{\vec{v}}{B}} + \overset{\text{random}}{\vec{F}(t)} \cdot f_{\text{stokes}} = f(\overset{\text{半径}}{a}, \overset{\text{粘度}}{\eta}, \overset{\text{速度}}{v}, \overset{\text{质量}}{m}) = 6\pi\eta a v \Rightarrow B = \dfrac{1}{6\pi\eta a}$

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

[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.

[Example] Irregular part(noise) of collective electron motion in circuit. $L \dfrac{\mathrm{d}I}{\mathrm{d}t} = \overset{\text{dissipation}}{-RI} + \overset{\text{fluactuation}}{V(t)}$

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

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

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

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

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

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

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

$$\dfrac{\mathrm{d}^2}{\mathrm{d}t^2}r^2 + \dfrac{1}{\tau}\dfrac{\mathrm{d}}{\mathrm{d}t}r^2 = 2v^2 + \vec{r}\cdot\vec{A} \Rightarrow \dfrac{\mathrm{d}^2}{\mathrm{d}t^2}\langle r^2\rangle + \dfrac{1}{\tau}\dfrac{\mathrm{d}}{\mathrm{d}t}\langle r^2\rangle + 2\langle v^2\rangle + \langle\cancel{\vec{r}\cdot\vec{A}}\rangle,$$ 因为 $\vec{A}$ 和 $\vec{r}$ 无关, 所以该期望项为 0.

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

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

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

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

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

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

[Discussion] 速度发散 $\lim\limits_{\delta t\to 0}\dfrac{\langle|x(t+\delta t) - x(t)|\rangle}{\delta t} \sim \lim\limits_{\delta t\to 0}\dfrac{(\delta t)^{\frac{1}{2}}}{\delta t} \to \infty$. 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 → field-based approach). 场 $f(x,t)$, 则位置为 $\rho(x) = q\delta(x - x_0)$, $\int \rho(x)\mathrm{d}x = q$. 如果是匀速直线运动, 则 $f(x,t) = \delta(x - vt)$. 若粒子 $x \to x + \delta x$, 则 $f(x,t) = \langle\delta[x - x(t)]\rangle$, 即场与粒子观点的转换.

约束 $\sum\limits_i n_i = N$. **态迁移率(transition rate)** 为 $\dfrac{n_i(t+\delta t) - n_i(t)}{\delta t} = -\sum\limits_{j\neq i}n_i(t)P_{i\to j} + \sum\limits_{j\neq i}n_j(t)P_{j\to i}$, 这类方程被称为 **Master equation**.

1. 假定为 Markov Process;

2. 粒子数守恒: $\dfrac{1}{\delta t}\left[\sum\limits_i n_i(t+\delta t) - \sum\limits_i n_i\right] = \sum\limits_i\left(\sum\limits_{i\neq j}n_j P_{j\to i} - \sum\limits_{i\neq j}n_i P_{i\to j}\right) = 0$.

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

$$\dfrac{\mathrm{d}n_+}{\mathrm{d}t} = -n_+\omega_- + n_-\omega_+, \qquad \dfrac{\mathrm{d}n_-}{\mathrm{d}t} = -n_-\omega_+ + n_+\omega_-$$

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

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

2. **概率函数定义**: $f(x,t)\mathrm{d}x$ 是粒子在 t 时刻处于 $[x, x+\mathrm{d}x]$ 的概率.

3. **动力学**: $\dfrac{\partial f(x,t)}{\partial t} = \int_{-\infty}^{+\infty}\left[-f(x,t)W(x,x') + f(x',t)W(x',x)\right]\mathrm{d}x'$, $W(x,x')\mathrm{d}x'$ 是 $x \to x'$ 的迁移概率.

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

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

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

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

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

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

$$\langle x\rangle = 0, \quad \langle x^2\rangle = \int_{-\infty}^{+\infty}x^2 f(x,\infty)\mathrm{d}x = \dfrac{k_BT}{\lambda}$$

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

该模型对应的 Langevin 方程为 $\eta\dfrac{\mathrm{d}x}{\mathrm{d}t} = \overset{\text{potential}}{-U'(x)} + \overset{\text{random}}{F(t)}$, 其中 $U(x) = \dfrac{1}{2}\lambda x^2, U'(x) = \lambda x$ 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 $\langle x^2(t)\rangle = \left\langle\left(\int_0^t \mathrm{d}u_1 v(u_1)\right)\left(\int_0^t \mathrm{d}u_1 v(u_1)\right)\right\rangle = \int_0^t \mathrm{d}u_1 \int_0^t \mathrm{d}u_2\,\langle v(u_1)v(u_2)\rangle$. 利用微积分性质 $\dfrac{\mathrm{d}}{\mathrm{d}t}\int_0^t f(u)\mathrm{d}u = f$

得到 $\dfrac{\mathrm{d}\langle x^2(t)\rangle}{\mathrm{d}t} = 2\int_0^t \mathrm{d}u\langle v(u)v(t)\rangle \overset{\text{time reversal symmetry}}{=} 2\int_{-t}^0 \mathrm{d}u\,\langle v(u)v(0)\rangle = 2\int_0^t \mathrm{d}u\,\langle v(u)v(0)\rangle = 2Dd$

观察对比得到 $\int_0^t \langle v(u)v(0)\rangle\mathrm{d}u = Dd$.

$$\dfrac{\partial f(x,t)}{\partial t} = \dfrac{1}{\eta}\dfrac{\partial}{\partial x}(U'(x)f(x,t)) + \dfrac{k_BT}{\eta}\dfrac{\partial^2}{\partial x^2}f(x,t)$$

1.4.3.5.4 Fourier Transformation of Langevin Equation .

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

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

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

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

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

第二章 Homework

2.1 Homework 2

1. **Show that the volume element**

$$\mathrm{d}\omega = \prod_{i=1}^{3N}(\mathrm{d}q_i\mathrm{d}p_i)$$

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 ti 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

$$\mathrm{d}\omega' = \prod_{i=1}^{3N}\mathrm{d}Q_i\mathrm{d}P_i = \left|\frac{\partial(Q,P)}{\partial(q,p)}\right|\prod_{i=1}^{3N}\mathrm{d}q_i\mathrm{d}p_i$$

$$J = \frac{\partial(Q,P)}{\partial(q,p)} = \begin{bmatrix} \dfrac{\partial Q}{\partial q} & \dfrac{\partial Q}{\partial p} \\ \dfrac{\partial P}{\partial q} & \dfrac{\partial P}{\partial p} \end{bmatrix}$$

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 $\mathrm{d}\omega' = \mathrm{d}\omega$, or

$$\prod_{i=1}^{3N}\mathrm{d}Q_i\mathrm{d}P_i = \prod_{i=1}^{3N}\mathrm{d}q_i\mathrm{d}p_i$$

2. **The generalized coordinates of a simple pendulum are the angular displacement θ 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 τ of the pendulum.** With θ and $L = m\dot{\theta}l^2$, the Hamiltonian of the simple pendulum is
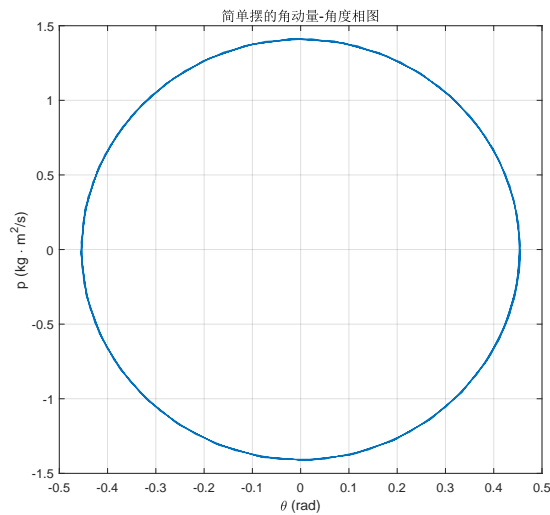
$$H = \frac{L^2}{2ml^2} + mgl(1 - \cos\theta)$$

So the area A enclosed by a trajectory is computed using the integral of $L\mathrm{d}\theta$:

$$A = \oint L\mathrm{d}\theta.$$

Deriative of A with respect to E gives the time period τ:

$$\frac{\mathrm{d}A}{\mathrm{d}E} = \frac{\mathrm{d}}{\mathrm{d}E} \oint L\mathrm{d}\theta = \oint \frac{\partial L}{\partial E}\mathrm{d}\theta$$

$$\frac{\partial H}{\partial L} = \frac{L}{ml^2} = \dot{\theta}$$

$$\Rightarrow \frac{\mathrm{d}A}{\mathrm{d}E} = \oint \frac{1}{\dot{\theta}}\mathrm{d}\theta = \tau$$

$$\Rightarrow A = E\tau.\square$$

简单摆的角动量-角度相图

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 $\left(n + \dfrac{1}{2}\right)\hbar\omega; n = 0, 1, 2, \cdots$;**

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

$$\ln\Omega \approx (M+N)\ln(M+N) - M\ln M - N\ln N - \frac{1}{2}\ln(2\pi MN)$$

$$\Omega \approx \frac{(M+N)^{M+N}}{M^M N^N}\sqrt{\frac{M+N}{2\pi MN}}$$

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

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

If $\dfrac{E}{\hbar\omega} \gg N$, 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 ω_0 is precisely h^N.**

For a one-dimensinal 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:

$$\Gamma_i = \iint H_i \mathrm{d}p_i \mathrm{d}x_i = \pi \cdot \sqrt{\frac{2E_i}{m}} \cdot m \cdot \frac{1}{\omega}\sqrt{\frac{2E_i}{m}} = \frac{2\pi E_i}{\omega}$$

So the total phase space volume is given by

$$\Gamma = \int_{\sum E_i \leq E} \prod_{i=1}^{N} \frac{2\pi E_i}{\omega}\mathrm{d}E_1\cdots\mathrm{d}E_N = \frac{(2\pi/\omega)^N E^N}{N!} = \frac{1}{N!}\left(\frac{2\pi E}{\omega}\right)^N$$

The classical microstate is

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

So we get

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

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

Since the number of microstates Ω is given by

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

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

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

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

$$\frac{1}{T} = \frac{k_B}{\hbar\omega} \ln\left(\frac{\frac{E}{\hbar\omega} + \frac{N}{2}}{\frac{E}{\hbar\omega} - \frac{N}{2}}\right)$$

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

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 μ 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 Area $= \frac{2\pi^{n/2}}{\Gamma(n/2)} R^{n-1}$s]**

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 consideres as the rest volume:

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

So for the real space integral part, we have

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

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:

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

where $\mathrm{d}\Omega_{3N}$ is the angle interal 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

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

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 $N \to \infty$ and Stirling approximation $\ln N! \approx N \ln N - N$, we have

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

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

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

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

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** $P = \dfrac{RT}{v-b} - \dfrac{a}{v^2}$.

   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:
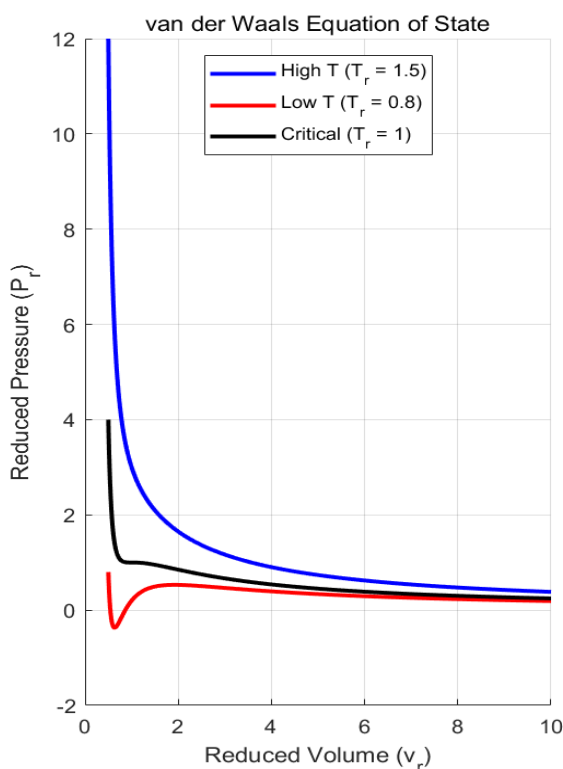
2.3.2   Maxwell Equal Area Construction

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), reprensenting 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 $\mathrm{d}G = -S\mathrm{d}T + V\mathrm{d}P$, we have:

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

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

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

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

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

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 β_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 β_1 and β_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)×2+(2.5) gives

$$(2v_c^2 - 2v_c^2) = (3\beta_1\lambda^3 v_c - 2\beta_1\lambda^3 v_c) + (8\beta_2\lambda^6 - 4\beta_2\lambda^6)$$

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

Substitute this into (2.3) gives:

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

$$\Rightarrow v_c^2 = -2\beta_2\lambda^6 \Rightarrow \boxed{v_c = \sqrt{-2\beta_2}\lambda^3}$$

This connects β_1 and β_2:

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

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

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

From the previous problem, we have $\beta_1 = \dfrac{2v_c}{\lambda^3}$ and $\beta_2 = -\dfrac{v_c^2}{2\lambda^6}$. 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 $\boxed{\dfrac{kT_c}{P_c v_c} = 3}$

2.4 Homework 5

2.4.1 Partition Function

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

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

where

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

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

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

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

and

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

The Hamiltonian of the Ising model is given by

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

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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

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

So the partition function can be expressed as

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

$$= \sum_{N_+,N_{+-}} g_N(N_+, N_{+-})\exp\left\{-\beta\left[-J\left(\frac{1}{2}qN - 2N_{+-}\right) - \mu B(2N_+ - N)\right]\right\}$$

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:

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

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

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:

$$\frac{d\bar{L}_0}{dT} = \operatorname{sech}^2\left(\frac{qJ\bar{L}_0}{kT}\right)\left(\frac{qJ}{kT}\frac{d\bar{L}_0}{dT} - \frac{qJ\bar{L}_0}{kT^2}\right)$$

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

$$\frac{d\bar{L}_0}{dT} = \frac{\operatorname{sech}^2\left(\frac{qJ\bar{L}_0}{kT}\right)\frac{qJ\bar{L}_0}{kT^2}}{\operatorname{sech}^2\left(\frac{qJ\bar{L}_0}{kT}\right)\frac{qJ}{kT} - 1}$$
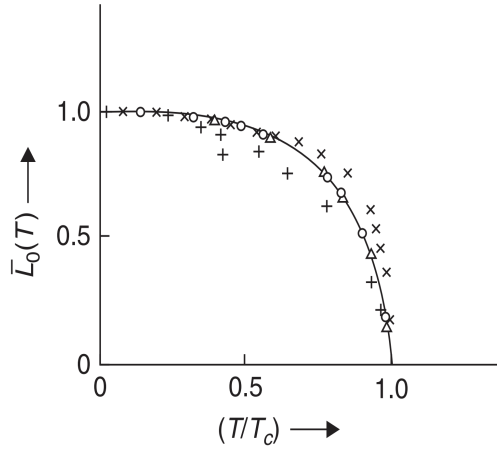
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Figure 2.1: The spontaneous magnetization of a Weiss ferromagnet as a function of temperature. The experimental points (after Becker) are for iron (x), nickel (o), cobalt (Δ), and magnetite (+).

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

$$\lim_{T \to 0} \tanh\left(\frac{qJ\bar{L}_0}{kT}\right) = \lim_{x \to \infty} \tanh x = 1, \quad \forall \bar{L}_0 \neq 0$$

$$\Rightarrow \lim_{T \to 0} \bar{L}_0 = 1$$

$$\lim_{T \to 0} \operatorname{sech}^2\left(\frac{qJ\bar{L}_0}{kT}\right) = \lim_{x \to \infty} \operatorname{sech}^2 x = 0, \quad \forall \bar{L}_0 \neq 0$$

$$\Rightarrow \lim_{T \to 0} \frac{\mathrm{d}\bar{L}_0}{\mathrm{d}T} = \boxed{0}$$

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

2. At $T = T_c$. We have $\bar{L}_0 = 0$, and $\lim\limits_{x \to 0} \tanh x = x - \dfrac{x^3}{3} + o(x^3)$.

$$\lim_{\bar{L}_0 \to 0} \tanh\left(\frac{qJ\bar{L}_0}{kT}\right) = \frac{qJ\bar{L}_0}{kT} - \frac{1}{3}\left(\frac{qJ\bar{L}_0}{kT}\right)^3$$

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

Define $T_c = \dfrac{qJ}{k}$, so that $t = \dfrac{T}{T_c} = \dfrac{kT}{qJ}$ 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 $\epsilon \to 0$, we have $1 - \dfrac{1}{t} \approx \epsilon$. Then rewrite the equation as:

$$\bar{L}_0 \epsilon = -\frac{1}{3}\bar{L}_0^3 \Rightarrow \bar{L}_0 \approx \sqrt{3}\sqrt{1 - \frac{T}{T_c}}$$

$$\Rightarrow \lim_{T \to T_c^-} \frac{\mathrm{d}\bar{L}_0}{\mathrm{d}T} \approx -\frac{\sqrt{3}}{2}\frac{1}{\sqrt{1 - \frac{T}{T_c}}}\frac{1}{T_c} = \boxed{\infty}$$

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.

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

Assuming that

- Symmetry: The free energy is even in m_0;

- Analticity: ψ_0 is analytic in m_0 and t, which allows a Taylor expansion;

- Critical behavior: Near T_c, the coefficients behave as $r(r) \approx r_0 t$, $\quad s(t) \approx s_0 > 0$.

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:

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

So

- Disordered phase($T > T_c$): $m_0 = 0$, since $r(t) > 0$;

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

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

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

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

    - For $T < T_c$, $m_0^2 = -\dfrac{r(t)}{2s(t)}$:

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

3. Specific heat.

    - For $T > T_c$, $\psi_0 = q(t)$;

    - For $T < T_c$, $\psi_0 = q(t) + r(t)m_0^2 + s(t)m_0^4 = q(t) - \dfrac{r(t)^2}{4s(t)}$. And the specific heat is defined as $C = -T\dfrac{\partial^2 \psi_0}{\partial T^2}$. 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 $\psi_0 = q(0) + s(0)m_0^4 + \cdots$. 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. Correlation length, which is defined as $\xi \sim \sqrt{\dfrac{c}{r(t)}} \sim t^{-1/2} \Rightarrow \boxed{\nu = \dfrac{1}{2}}$

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, Φ, 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 fluactuation: $\Phi[y(x)] = \dfrac{F}{2}\displaystyle\int_0^l \left(\dfrac{\mathrm{d}y}{\mathrm{d}x}\right)^2 \mathrm{d}x$.

Therefore $P[y(x)] \propto \exp\left(-\dfrac{\Phi[y(x)]}{kT}\right) = \exp\left[-\dfrac{F}{2kT}\displaystyle\int_0^l \left(\dfrac{\mathrm{d}y}{\mathrm{d}x}\right)^2 \mathrm{d}x\right]$.

Expand $y(x)$ in eigenmodes which satisfies the boundary conditions: $y(x) = \displaystyle\sum_{n=1}^\infty a_n \sin\left(\dfrac{n\pi x}{l}\right)$,

so the derivative becomes $\dfrac{\mathrm{d}y}{\mathrm{d}x} = \displaystyle\sum_{n=1}^\infty a_n \dfrac{n\pi}{l}\cos\left(\dfrac{n\pi x}{l}\right)$.

Substitute into the energy: $\Phi = \dfrac{F}{2}\displaystyle\int_0^l \left(\dfrac{\mathrm{d}y}{\mathrm{d}x}\right)^2 \mathrm{d}x = \dfrac{F}{2}\displaystyle\sum_{n=1}^\infty a_n^2 \left(\dfrac{n\pi}{l}\right)^2 \dfrac{l}{2} = \displaystyle\sum_{n=1}^\infty \dfrac{F\pi^2 n^2}{4l}a_n^2$.

The probability distribution is $p(\{\}) \propto \exp\left[-\displaystyle\sum_{n=1}^\infty \dfrac{F\pi^2 n^2}{4l}a_n^2\right]$, 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: $\overline{a_n^2} = \dfrac{2kT}{Fl}\left(\dfrac{l}{n\pi}\right)^2 = \dfrac{2kTl}{F\pi^2 n^2}$.

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

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

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

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

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

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

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

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

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

$$\sum_{n=1}^\infty \dfrac{1}{n^2}\sin\left(\dfrac{n\pi x_1}{l}\right)\sin\left(\dfrac{n\pi x_2}{l}\right) = \dfrac{1}{2}\left[\dfrac{\pi^2}{6} - \dfrac{\pi^2|x_1-x_2|}{2l} + \dfrac{\pi^2(x_1-x_2)^2}{4l^2}\right] - \dfrac{1}{2}\left[\dfrac{\pi^2}{6} - \dfrac{\pi^2(x_1+x_2)}{2l} + \dfrac{\pi^2(x_1+x_2)^2}{4l^2}\right]$$

$$= \dfrac{\pi^2(x_1+x_2 - |x_1-x_2|)}{4l} + \dfrac{\pi^2[(x_1-x_2)^2 - (x_1+x_2)^2]}{8l^2} \overset{x_2\geqq x_1}{=} \dfrac{\pi^2(2x_1)}{4l} + \dfrac{\pi^2(-4x_1 x_2)}{8l^2}$$

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

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 $\dot{x}_i$: $\dot{x}_i = \gamma_{ij} X_j$.

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

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

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

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

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

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

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

1 Introduction to probability theory

Bayes' theorem

$$p(B|A) = \frac{p(A|B)\cdot p(B)}{p(A)}, \quad \frac{p(A|B)\cdot p(B)}{\sum_{B'} p(A|B')\cdot p(B')}$$

Expactation and covariance

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

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

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

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

$$p(x) = \frac{1}{(2\pi\sigma^2)^{\frac12}}\cdot e^{-\frac{x-\mu}{2\sigma^2}}, \quad \langle x^2 \rangle = \sigma^2$$

Poisson distribution

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

Information entropy

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

2 The microcanonical ensemble

$E \approx const$, $V = const$, $N = const.$

The fundamental postulate

$$\Omega(E) = \sum_{n:E-\delta E\leq E_n\leq E} 1$$

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

$$S = -k_B\sum_{i=1}^{\Omega} p_i\ln(p_i) = k_B\ln(\Omega)$$

---

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 exchange

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

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

$$dE = TdS - pdV + \mu dN$$

Specific heat

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

solution concept

- Set up Hamiltonian
- Calculate phasevolume Ω
- Calculate entropy S
- determine T, p, μ
- Calculate $U = \langle E\rangle$
- thermodynamic potentials:
- $F(T,V,N) = U - TS$
- $H(S,p,N) = U + pV$
- $G(T,p,N) = U + pV - TS$

Ideal Gas

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

microcanonical partition sum for an ideal gas

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

$$S = k_B N\left\{\ln\left[\left(\frac{V}{N}\right)\left(\frac{4\pi mE}{3h^2 N}\right)^{3/2}\right] + \frac52\right\}$$

Equations of state fo ideal gas

$$\frac{1}{T} = \left(\frac{\partial S}{\partial E}\right)_{N,V} = \frac32\frac{Nk_B}{E} \to U = \frac32 Nk_B T$$

$$p = T\left(\frac{\partial S}{\partial V}\right)_{E,N} = TNk_B\frac{1}{V} \to pV = Nk_B T$$

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

$$\lambda = \frac{h}{\sqrt{2\pi mk_B T}} \ \text{Thermal de Broglie}$$

Einstein model for specific heat of a solid

$$E = \hbar\omega\left(\frac{N}{2}+Q\right) \to Q = \left(\frac{E}{\hbar\omega}-\frac{N}{2}\right)$$

$$\Omega(E,N) = \frac{(Q+N)!}{Q!N!}$$

$$S = k_B\left[Q\ln\left(\frac{Q+N}{Q}\right) + N\ln\left(\frac{Q+N}{N}\right)\right]$$

$$= k_B N\left[\left(e+\tfrac12\right)\ln\left(e+\tfrac12\right) - \left(e-\tfrac12\right)\ln\left(e-\tfrac12\right)\right]$$

$$e = E/E_0;\ E_0 = N\hbar\omega;\ \beta = \hbar\omega/k_B T$$

$$\frac{1}{T} = \frac{\partial S}{\partial E} \to E = N\hbar\omega\left(\frac12 + \frac{1}{e^\beta - 1}\right)$$

Entropic elasticity of polymers

$$N_+ - N_- = \frac{L}{a} = m \to N_+ = \frac12(N+m)$$

$$\Omega = \frac{N!}{N_+!N_-!} = \frac{N!}{\left(\frac12(N+m)\right)!\left(\frac12(N-m)\right)!}$$

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 $T_1 = T_2$

$$S_i = \frac32 k_B N_i\ln(E_i) + \text{independent of } E_i$$

$$S = S_1 + S_2$$

$$dS = 0 \to \frac{\partial S_1}{\partial E_1} = \frac{\partial S_2}{\partial E_2}$$

$$\to \overline{E}_1 = \frac{N_1}{N}E$$

consider small deviation:

$$E_1 = \overline{E}_1 + \Delta E, \quad E_2 = \overline{E}_2 - \Delta E$$

$$S(\overline{E}_1 + \Delta E) \approx \frac32 k_B\left[N_1\ln\overline{E}_1 + N_2\ln\overline{E}_2\right]$$

$$-\frac{N_1}{2}\left(\frac{\Delta E}{\overline{E}_1}\right)^2 - \frac{N_2}{2}\left(\frac{\Delta E}{\overline{E}_2}\right)^2$$

$$\to \Omega = \overline{\Omega}e^{\left[-\frac34\left(\frac{\Delta E}{E}\right)^2 N^2\left(\frac{1}{N_1}+\frac{1}{N_2}\right)\right]}$$

---

3 The canonical ensemble

$T = const$, $V = const$, $N = const.$

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:

$$p(\vec{q},\vec{p}) = \frac{1}{ZN!h^{3N}}e^{-\beta\mathcal{H}(\vec{q},\vec{p})}$$

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

For common Hamiltonian:

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

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

ϵ_{ij} is the jth state of the ith element

$$Z = \sum_{j_1}\sum_{j_2}\ldots\sum_{jN}e^{-\beta\sum_{i=1}^N\epsilon_{ij_i}}$$

$$= \left(\sum_{j_1}e^{-\beta\epsilon_{1j_1}}\right)\cdots\left(\sum_{jN}e^{-\beta\epsilon_{Nj_N}}\right)$$

$$= z_1\cdots z_N = \prod_{i=1}^N z_i$$

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

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

Ideal Gas

$$\mathcal{H} = \sum_{i=1}^N\frac{\vec{p_i}^2}{2m}$$

$$Z_N(T,V) = \frac{V^N}{N!}\left(\int_{-\infty}^{+\infty}\frac{dp}{h}e^{-\beta\frac{p^2}{2m}}\right)^{3N}$$

$$= \frac{1}{N!}\left(\frac{V}{\lambda^3}\right)^N$$

Equipartition theorem

f_{dof} are the degrees of freedom.
harmonic Hamiltonian with $f_{dof} = 2$

$$\mathcal{H} = Aq^2 + Bp^2$$

$$z \propto \int dq\,dp\,e^{-\beta\mathcal{H}}$$

$$= \left(\frac{\pi}{A\beta}\right)^{\frac12}\cdot\left(\frac{\pi}{B\beta}\right)^{\frac12} \propto \left(T^{\frac12}\right)^{f_{dof}}$$

---

sum ('equipartition theorem')

$$F = -k_B T\ln(z) = -\frac{f_{dof}}{2}k_B T\ln(T)$$

$$\frac{\partial F}{\partial T} = \frac{f_{dof}}{2}k_B(\ln(T)+1)$$

$$S = -\frac{\partial F}{\partial T} = \frac{f_{dof}}{2}k_B(\ln(T)+1)$$

$$U = -\partial_\beta\ln(z) = \frac{f_{dof}}{2}k_B T$$

$$\frac{dU}{dT} = \frac{f_{dof}}{2}k_B$$

$$c_v = \frac{f_{dof}}{2}k_B$$

$$c_p = \frac{f_{dof}+2}{2}k_B$$

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:

$$V(r) = E_0\left(1 - e^{-a(r-r_0)}\right)^2$$

An exact solution of the Schrödinger equation gives:

$$E_n = \hbar\omega_0\left(n+\frac12\right) - \frac{\hbar^2\omega_0^2}{eE_0}\left(n+\frac12\right)^2$$

$$\omega_0 = \frac{\alpha}{2\pi}\sqrt{\frac{2E_0}{\mu}}, \quad \mu = \frac{m}{2}$$

For $\hbar\omega_0 \ll E_0$ we can use the harmonic approximation:

$$z_{vib} = \frac{e^{-\beta\hbar\omega/2}}{1-e^{-\beta\hbar\omega_0}}$$

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

Rotational modes

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

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

$$\to E_l = \frac{\hbar^2}{2I}l(l+1)$$

Nuclear contributions: ortho- and parahydrogen

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

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

For sufficiently high temperature (classical limit), each quadratic term in the Hamiltonian contributes a factor $T^{\frac12}$ to the partition

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Specific heat of a solid
Debye model

$$\to \omega(k) = \left(\frac{4\kappa}{m}\right)^{\frac{1}{2}}\left|\sin\left(\frac{ka}{2}\right)\right|$$

$$\omega = \frac{2\pi}{T},\quad k = \frac{2\pi}{\lambda}$$

Debye frequency:

$$\omega_D = c_s\left(\frac{6\pi^2 N}{V}\right)^{\frac{1}{3}}$$

$$c_s = \frac{d\omega}{dk}\Big|_{k=0} = \sqrt{\frac{\kappa}{m}}a = \sqrt{\frac{\kappa}{m}}$$

density of states in ω-space:

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

count modes in frequency-space:

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

partition sum:

$$z(\omega) = \frac{e^{-\beta\hbar\omega/2}}{1 - e^{-\beta\hbar\omega}}$$

$$\to Z = \prod_{modes} z(\omega)$$

$$\to E = -\partial_\beta\ln(Z) = \sum_{modes}\hbar\omega\left(\frac{1}{e^{\beta\hbar\omega}-1}+\frac{1}{2}\right)$$

$$= E_0 + 3N\int_0^{\omega_D}d\omega\frac{\hbar\omega}{e^{\beta\hbar\omega}-1}\frac{3\omega^2}{\omega_D^3}$$

$$c_V(T) = \frac{\partial E}{\partial T}$$

$$= \frac{3\hbar^2 N}{k_B T^2}\int_0^{\omega_D}d\omega\frac{3\omega^2}{\omega_D^3}\frac{e^{\beta\hbar\omega}\omega^2}{(e^{\beta\hbar\omega}-1)^2}$$

$$u = \beta\hbar\omega$$

$$c_V(T) = \frac{9Nk_B}{u_m^3}\int_0^{u_m}\frac{e^u u^4}{(e^u-1)^2}du$$

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

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

$$c_v = \frac{16\sigma}{c}VT^3$$

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

Plank'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:

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

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

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

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

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

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

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

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

4 The grandcanonical ensemble

$T,\mu = const.$

$$P_N(q,p) = \frac{1}{\Xi_\mu(T,V)}e^{-\beta(H_N(q,p)-\mu N)}$$

$$\Xi_\mu(T,V) = \sum_{N=0}^\infty\frac{1}{h^{3N}N!}\iint d^{3N}q\, d^{3N}p\, e^{-\beta(H_N-\mu N)}$$

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

$z = e^{\beta\mu} \to$ Fugacity

Mean phase space observable

$$\langle F\rangle = \frac{1}{\Xi_\mu(T,V)}\sum_{N=0}^\infty\frac{1}{h^{3N}N!}\iint d^{3N}q\, d^{3N}p\ldots$$

$$\ldots e^{-\beta(H_N-\mu N)}F_N(q,p)$$

mean particle number:

$$\langle N\rangle = \frac{1}{\beta}\left(\frac{\partial}{\partial\mu}\ln(\Xi_\mu(T,V))\right)_{T,V}$$

$$= z\left(\frac{\partial}{\partial z}\ln(\Xi_z(T,V))\right)_{T,V}$$

pressure:

$$p = -\left\langle\frac{\partial H}{\partial V}\right\rangle = \frac{1}{\beta}\left(\frac{\partial}{\partial V}\ln(\Xi_\mu(T,V))\right)$$

energy U:

$$U = \langle H\rangle = -\left(\frac{\partial}{\partial\beta}\ln(\Xi_\mu(T,V))\right)_{\mu,V} + \mu\langle N\rangle$$

$$= -\left(\frac{\partial}{\partial\beta}\ln(\Xi_z(T,V))\right)_{z,V}$$

Grandcanonical potential

grandcanonical potential:

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

p is maximal, if Ψ is minimal.

Total differential:

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

Equations of state:

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

Molecular adsorption onto a surface

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

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

$$\langle\epsilon\rangle = \epsilon\langle n\rangle$$

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

$\omega_n \to$ 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 $T \to 0$, the fermi function approaches a step function:

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

Bosons:

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

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

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

specific heat

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

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

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

Fermi pressure

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

The ideal Bose fluid

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

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

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

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

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

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

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

Classical limit

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

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

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

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

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:

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

lattice gases:

$$\mathcal{H} = -\sum_{\langle i,j\rangle} J_{ij} S_i S_j$$

1. Dimensional

Only Next Neighbor and $B_0 = 0$

$$I_{i,i+1} \to I_i,\quad \mathcal{H} = -\sum_{i=1}^{N-1} J_i S_i S_{i+1},\quad j_i = \beta J_i$$

$$Z_N = \sum_{S_1}\cdots\sum_{S_N} \exp\left(\sum_{i=1}^{N-1} j_i S_i S_{i+1}\right)$$

$$= 2^N \prod_{i=1}^{N-1}\cosh(\beta J_i)$$

Spin correlation function:

$$\langle S_i S_{i+1}\rangle = \tanh(\beta J)$$

spontaneous magnetisation:

$$M_S(T) = \mu\langle S\rangle$$

$$M_S^2(T) = \mu^2 \lim_{j\to\infty}\langle S_i S_{i+1}\rangle$$

No phase transition for $T > 0$. But for $T = 0$

$$M_S(T=0) = \mu$$

Transfer matrix

$$j = \beta J,\quad b = \beta\mu B_0,\quad S_i = \pm 1$$

$$T_{i,i+1} = e^{jS_iS_{i+1}+\frac{1}{2}b(S_i+S_{i+1})}$$

$$\to e^{-\beta\mathcal{H}} = T_{1,2}\cdot T_{2,3}\ldots T_{N,1}$$

$$T = \begin{pmatrix} T(+1,+1) & T(+1,-1) \\ T(-1,+1) & T(-1,-1) \end{pmatrix}$$

$$Z_N = \lambda_1^N + \lambda_2^N = E_+^N + E_-^N$$

for $N \gg 1 \to E_+ \gg E_-$

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

$$F \leq F_u = F_0 + \langle \mathcal{H}_1 \rangle_0 \text{ Bogoliubov inequality}$$

Mean field theory for the Ising model

$$\mathcal{H} = -J \sum_{\langle i,j \rangle} S_i S_j$$

$$\mathcal{H}_0 = -B \sum_i S_i$$

$$F_0 = -N k_B T \ln\left(e^{\beta B} + e^{-\beta B}\right)$$

$$= -N k_B T \ln(2\cosh(\beta B))$$

$$F \leq F_0 + \langle \mathcal{H} - \mathcal{H}_0 \rangle_0$$

$$= -N k_B T \ln(2\cosh(\beta B)) - N \frac{z}{2} \langle S \rangle_0^2$$

$$+ N \langle S \rangle_0 = F_u$$

$$\rightarrow z = 2 \cdot \text{dimension}$$

$$B = Jz \langle S \rangle_0 = Jz \tanh(\beta B)$$

$$K_c = \frac{1}{z} \longrightarrow T_c = \frac{zJ}{k_B}$$

7 Classical fluids
Virial expansion

$$F = N k_B T \left[\ln(\rho \lambda^3) - 1 + B_2 \rho\right]$$

$$p = \rho k_B T [1 + B_2 \rho]$$

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

$$\epsilon = \frac{p^2}{2m} \qquad \frac{\hbar^2 k^2}{2m}$$

Energies

$$E_{kin} = \frac{1}{2} M \overline{v^2}$$

$$E_{rot} = \frac{1}{2} I \overline{\omega^2}$$