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.

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

- 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.

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

1.1.1.1.2 Maximum Work

- isothermal process, $A \to B$:

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

- $A \to B, U_A = U_B$: $\Delta W_{\text{max}} = T(S_B - S_A)$. 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) $\leftrightarrow$ $J=1$:

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

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

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

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

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

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

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

1.1.2 Some Key Concepts in Thermodynamics

1.1.2.1 Temperature

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

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

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

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

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

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

*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 $\frac{1}{2}k_B T$ 的能量.

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

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

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

1.1.2.2 Entropy

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

[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

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

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

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

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.

$$
\begin{aligned}
&U = cL_0T, \quad U\sim T\\
&\tau = bT\frac{L-L_0}{L_1-L_0}, \quad \text{self-consistent condition: } \frac{\partial^2 S}{\partial U\partial V} = \frac{\partial^2 S}{\partial V\partial U}\\
\Rightarrow\ &\mathrm{d}S = \frac{1}{T}\mathrm{d}U - \frac{\tau}{T}\mathrm{d}L = cL_0\frac{\mathrm{d}U}{U} - b\frac{L-L_0}{L_1-L_0}\mathrm{d}L \overset{\int}{\Longrightarrow} S = S_0 + cL_0\ln\frac{U}{U_0} - b\frac{(L-L_0)^2}{2(L_1-L_0)}, \quad \text{entropy elasticity}
\end{aligned}
$$

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.

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

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

随着时间推移, $H = \displaystyle\int f\ln f$ 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 $\displaystyle\prod_{\alpha=1}^{n_k}\Delta\vec{q}_\alpha\Delta\vec{p}_\alpha = \prod_{\alpha=1}^{n_k}\omega_k = \omega_k^{n_k}$. 因此所有粒子所占据的空间为 $\displaystyle\prod_k \omega_k^{n_k}$

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: $W' = \dfrac{N!}{\prod_k n_k!}\displaystyle\prod_k\omega_k^{n_k}$. 该体积和状态数成正比, 那么寻找在 $\displaystyle\sum_k n_k = N, \quad \sum_k \varepsilon_k n_k = E$ 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: $V\left(B_R^n\right) = C_n R^n, \quad C_n = \dfrac{\pi^{\frac{n}{2}}}{\Gamma\left(\frac{n}{2}+1\right)}, \quad \Gamma(z+1) \equiv \int_0^{\infty} t^{-z} e^{-t} \mathrm{d}t \overset{z\in\mathbb{Z}}{=} z! \approx \sqrt{2\pi z}\left(\dfrac{z}{e}\right)^z$

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

设两共心球半径分别为 $R, R(1+\varepsilon)$. 求夹层(Shell)体积为 $V_{\text{shell}} = V(R)[(1+\varepsilon)^n - 1^n]$. 即使 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 $\int_{-R}^{R} \rho(x)\mathrm{d}x = \int_{-R}^{R} V\left(B_{R'}^{n-1}\right)\mathrm{d}x = V\left(B_R^n\right)$, 求 $\rho(x)$ 表达式.

$\dfrac{V\left(B_{R'}^{n-1}\right)}{V\left(B_R^{n-1}\right)} = \left(\dfrac{R'}{R}\right)^{n-1} = \left(1-\dfrac{x^2}{R^2}\right)^{\frac{n-1}{2}} \simeq e^{-(n-1)x^2/2R^2}$; 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: $\text{Area} = \lim_{\epsilon\to 0} \dfrac{V(C+\epsilon B) - V(C)}{\epsilon}$. 不等式: $V(C+\epsilon B)^{1/n} \geq V(C)^{1/n} + V(\epsilon B)^{1/n} = V(B)^{1/n} + (\epsilon^n V(B))^{1/n} \Rightarrow \text{Area} \geq \lim_{\epsilon\to 0} \dfrac{[(1+\epsilon)^n - 1]}{\epsilon} V(B) \approx n\cdot V(B)$, 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 interpretted 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: $C_N^{NM_N} = C_N^k$.

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

$S = k_B \ln C_N^k$

[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: $f_i=f_\alpha,\quad\forall i\in\alpha$.

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

Formal presentation: in equilibrium,

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

不同情况下的 microstate: 1. In Γ-space($6N$-dim), (q,p); 2. $|n\rangle$; 3. $\sigma=\pm1$; 4. $\sigma=\{0,1\}$...

Representative point $\leftrightarrow$ one gas. Density function(continuum description) $\sum\limits_i\delta(x-x_i)\to\rho(x)$.

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

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 $\displaystyle\int_\omega\rho(q,p,t)\mathrm{d}\omega$ 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

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

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: $\displaystyle\frac{\mathrm{D}\rho(q,p,t)}{\mathrm{D}t}=\frac{\partial\rho}{\partial t}+\vec{v}\cdot\nabla\rho=\frac{\partial\rho}{\partial t}+\sum_i\left(\dot{q}_i\frac{\partial\rho}{\partial\rho_i}+\dot{p}_i\frac{\partial\rho}{\partial p_i}\right)$

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

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

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

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

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

若ρ为H函数$\rho(H)$, 则$\{\rho,H\}=0\Rightarrow\dfrac{\partial\rho}{\partial t}=0$, 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:

$\overset{\text{1st particle}}{\underline{p_{1x}^2+p_{1y}^2+p_{1z}^2}}+p_{2x}^2+\cdots+p_{Nz}^2\overset{\text{ideal gas}}{=}2mE,\quad P_z=\displaystyle\sum_{i=1}^{N}p_{1z}\to0$, due to high dimension.

[Example] 2-state system. $|1\rangle:N_1,|2\rangle:N_2.\quad P_1=\dfrac{N_1}{N_1+N_2},P_2=\dfrac{N_2}{N_1+N_2}\Rightarrow\langle f\rangle=f_1P_1+f_2P_2.$

Equilibrium density function? $\rho(q,p)=\begin{cases}\text{const.}\quad H(q,p)\in\lim\limits_{\Delta\to0}\left[E-\dfrac{\Delta}{2},E+\dfrac{\Delta}{2}\right]\\0,\quad\text{others}\end{cases}$

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

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

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

$\Rightarrow$ 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: $\displaystyle\sum_{i=1}^{N}|\vec{p}_i|^2=2mE$. 等能面为 $(3N-1)$ 维球面, 且球面半径约为 $\sqrt{E}$. 那么相空间体积/微观态数 $\Omega\sim(\sqrt{E})^{3N-1}\sim E^{3N/2}$. 克劳修斯熵 $S=k_B\ln\Omega=\dfrac{3}{2}k_BN\ln E+\text{const.}$; 1st law: $\dfrac{1}{T}=\left(\dfrac{\partial S}{\partial E}\right)_V\Rightarrow E=\dfrac{3}{2}Nk_BT$.

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 $\Omega\sim\dfrac{(\sqrt{E})^{3N-1}}{(\delta p)^{3N}}\overset{V\sim L^3}{\longrightarrow}\left(E^{3/2}V\right)^N$,

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

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

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

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

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

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 $\frac{U}{\hbar\omega_0}$ 个竖隔板插入由 $3N$ 个球间隔出的 $(3N-1)$ 的缝隙中.

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

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

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

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

1.2.4 Canonical Ensemble

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

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

$\sum_i\left(\dot{q}_i\frac{\partial\rho}{\partial q_i} + \dot{p}_i\frac{\partial\rho}{\partial q_i}\right) = 0 \Rightarrow \sum_i\left(\frac{\partial H}{\partial p_i}\frac{\partial\rho}{\partial q_i} - \frac{\partial H}{\partial q_i}\frac{\partial\rho}{\partial q_i}\right) = 0$. 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 $E_r + E_{r'} = E^{(0)} = \text{const.}$; 设 Ω' 为环境微观态数, 则体系处于态 $|r\rangle$ 的概率 $P_r \propto \Omega'(E_{r'}) = \Omega'(E^{(0)} - E_r)$. 假定体系所占能量足够小, 即 $E_r \ll E^{(0)}$, 则可 Taylor 展开: $\ln\Omega'(E^{(0)}-E_r) = \ln\Omega'(E^{(0)}) + \left.\frac{\partial\ln\Omega'}{\partial E'}\right|_{E'=E^{(0)}}\overbrace{(E_{r'}-E^{(0)})}^{-E_r} + \cdots = \text{const.} - \beta E_r$

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 $\sum_r n_r = N, \quad \sum_r n_r E_r = NU = N\langle E_r\rangle$. 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. $\exists\{n_r\}, \quad \text{s.t. } W = \dfrac{N!}{\prod_\alpha n_\alpha!}$

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

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

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

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

[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: $U = -\frac{\partial}{\partial\beta}\left(\ln\sum_r e^{-\beta E_r}\right)$. 若再对 U 求一次 β 偏导, 则有

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

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

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

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

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

[Example] Reletive fluctuation of speed in Maxwell distribution. $f(v) = A\exp\left\{-\frac{mv^2}{2k_BT}\right\}v^2\mathrm{d}v$, 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. $H = \sum_{i=1}^N \frac{\vec{p}_i^2}{2m}$.

1. **使用正则系综方法**. 配分函数为

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

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

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

记 $n = \frac{N}{V}$, 则 $\frac{F}{V} = nk_BT\left[\ln\left(\frac{n}{f}\right)-1\right] \Rightarrow P = \left(\frac{\partial F}{\partial V}\right)_{N,T} = \frac{Nk_BT}{V}$, 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.

$S = -\left(\frac{\partial F}{\partial T}\right)_{N,V} = k_B V \left[-n \ln\left(\frac{n}{f}\right) + \frac{5}{2}n\right]$, 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 $\rightarrow$ analyze a single particle. 底数 3: 3 种颜色/状态. 2. $S_{\text{tot}} = S_{\{q,p\}} + S_{\text{color}}$. 新的自由度独立于 (q,p), 则熵直接相加.

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

$\widetilde{S}_{\text{mix}} = -k_B \sum_{r=1}^{2} P_r \ln P_r == -k_B[r \ln r + (1-r)\ln(1-r)]$. 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.

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

$Q(Z,V,T) = \sum_{N_r=0}^{\infty} Z^{N_r} Q_{N_r}(V,T), \quad Z \equiv e^{-\alpha}$, 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 $P = \frac{k_B T}{V}q = Zk_B Tf(T)$; 粒子数 $N = -\frac{\partial q}{\partial \alpha} = ZVf(T)$; 内能 $U = -\frac{\partial q}{\partial \beta} = ZVk_B T^2 f'(T)$; 状态方程 $PV = Nk_B T$.

[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 $P_n = \dfrac{\sum_s e^{-\alpha n - \beta E_n^{(s)}}}{Q}$. 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: $P_1 = \dfrac{v}{V}, \quad P_0 = 1 - \dfrac{v}{V}$. 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

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

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

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

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

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

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

1.3.1.1.1 Simpler Argument

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

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

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

1.3.2 Phase Diagram

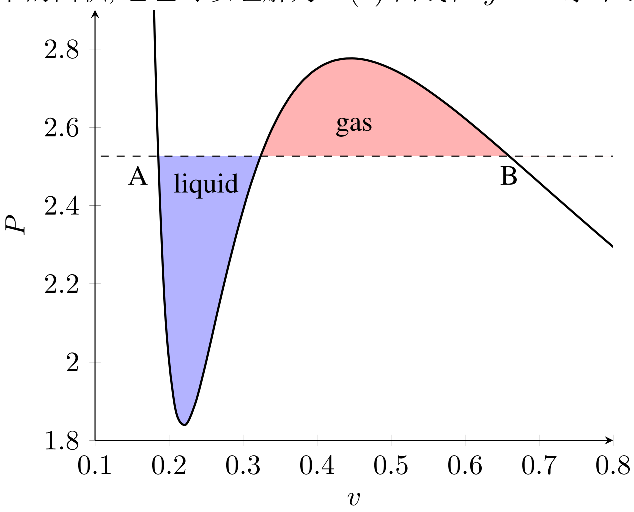
Van der Waals equation: real gas.

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

$P = \frac{RT}{v-b} - \frac{a}{v^2}$ 数学上是一个 v 的三次方程. 存在三个解代表的是 gas-liquid coexistence. $v_1 = v_l, v_3 = v_g$. 特殊情况: $v_1, v_2, v_3 \to v_c$, 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 $\Delta G = \int_A^B V\mathrm{d}P = \int_A^B [\mathrm{d}(PV) - P\mathrm{d}V] = P(V_B - V_A) - \int_{V_A}^{V_B} P\mathrm{d}V = 0$, 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: $v_0 = xv_l + (1-x)v_g \Rightarrow x = \frac{v_g - v_0}{v_g - v_l}$, 即 lever rule. $\frac{\partial P}{\partial v} > 0$ 是热力学不稳定的.

1.3.2.2 Critical Behavior

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

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

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

1.3.2.2.1 Along the isothermal curve at $t = 0 (T = T_c)$

$\pi = -\frac{3}{2}\Psi^3$, 3: critical exponent.

1.3.2.2.2 Ψ_l 和 Ψ_g 对 critical point 的逼近行为

$\pi = 4t - 6t\Psi + \frac{3}{2}\Psi^3 \Rightarrow \begin{cases} \pi = 4t - 6t\Psi_l + \frac{3}{2}\Psi_l^3 \\ \pi = 4t - 6t\Psi_g + \frac{3}{2}\Psi_g^3 \end{cases}$. 原始的 v_l 和 v_g 是通过 Maxwell construction $\int \mathrm{d}G = 0 \Rightarrow P(V_B - V_A) - \int_{V_A}^{V_B} P\mathrm{d}V = 0$ 得到的. 使用 (π, Ψ, t) 重构:

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

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

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

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

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

[Discussion] $Q(Z,V,T)=\sum_{N=0}^{N_{\max}}Z^NQ_N(V,T)$, $\quad P=\frac{k_BT}{V}\ln Q$. 级数各项表达式均为解析的. 若要产生奇点(singularity), 应要求 Thermodynamic limit(热力学极限), 即 $\lim_{N_{\max},V\to\infty}$ 的同时 $\frac{N}{V}=$ finite const..

1.3.3 Ising Model: From Thermodynamic Approach to Statistical Approach

$H(\{\sigma_i\})=-J\sum_{\langle i,j\rangle}\sigma_i\sigma_j-\mu B\sum_i\sigma_i,\quad \sigma_i=\pm1$(binary variable)

1.3.3.1 Preliminary Analysis

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

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

设 q 是各自旋的配位数(对于 Ising Model 即 2), 存在约束关系 $N=N_++N_-$, $qN_+=2N_{++}+N_{+-}$, $qN_-=2N_{--}+N_{+-}$. 因此只有两个独立变量.

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

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

1.3.3.2 Mean-Field Approximation

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

[Discussion] 为了照顾到 $L=0$ 中"前半全 $\uparrow$, 后半全 $\downarrow$"的特殊情况, 可以进一步定义新的序参量 $S=\frac{N_{++}+N_{--}-N_{+-}}{\frac{1}{2}qN}$. 即相邻自旋方向相同为有序, 反之为无序. 因此序参量依赖于对 "序" 的定义.

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

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

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

等式两边同 ln, 且引入 $\operatorname{arctanh}x=\frac{1}{2}\ln\left(\frac{1+x}{1-x}\right)$, 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 $\rho(\vec r)=\sum_s e_sn_{s_0}e^{-\frac{e_s\phi(\vec r)}{k_BT}}$, $\nabla^2\phi(\vec r)=-4\pi\rho(\vec r)$.
2. 在 $\overline{L}\to0$ 时, 即有 $\overline{L}\sim M\propto B$, 即 paramagnetism(顺磁). 非线性项 $\to$ ferromagnetism(铁磁).

1.3.3.2.1 $B=0$ 下的 $\overline{L}$

令 $L_0=\overline{L}(B=0)$, 得到无外场条件下的状态方程 $\overline{L}_0=\tanh\left(\beta Jq\overline{L}_0\right)$. $\overline{L}_0\to0$ 代表可相变.

使用极限 $\lim_{x\to0}\tanh(x)\simeq x-\frac{x^3}{3}+O(x^5)$, 展开状态方程: $(\beta qJ-1)\overline{L}_0=\frac{1}{3}\left(\beta qJ\overline{L}_0\right)^3$. 若 $\beta qJ-1>0\Leftrightarrow T<\frac{qJ}{k_B}=T_c$,

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 $y=\tanh(\beta Jqx)$ 的交点. 在高温时只有 1 个交点, 而低温时则能产生 3 个交点.

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

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 $\lim\limits_{T\to T_c^-}\overline{L}_0=\overline{L}_0\frac{T_c}{T}-\frac{1}{3}\overline{L}_0^3\left(\frac{T_c}{T}\right)^3\Rightarrow\overline{L}_0\simeq3^{\frac{1}{2}}\left(1-\frac{T}{T_c}\right)^{\frac{1}{2}}.$

2. 在 $T\to0$ 时, 有近似 $\lim\limits_{T\to0}\overline{L}_0\simeq1-2\exp\left(-\frac{2T_c}{T}\right)$, 斜率 $\frac{\mathrm{d}\overline{L}_0}{\mathrm{d}T}\to0$.

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

热容为内能偏导 $c_0=\frac{\partial U_0}{\partial T}=-qJN\overline{L}_0\frac{\mathrm{d}\overline{L}_0}{\mathrm{d}T}$. 可见其依赖于 $\frac{\mathrm{d}\overline{L}_0}{\mathrm{d}T}$; 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 $\frac{\partial}{\partial T}$, 得到 $c_0=k_BN\frac{T_c}{T}\overline{L}_0^2\frac{1-\overline{L}_0^2}{\frac{T}{T_c}-\left(1-\overline{L}_0^2\right)}\simeq\frac{3}{2}Nk_B$

研究在 $B=0$ 时的熵 S_0. 1. Statistical method. 熵 $S_0(T\geq T_c)=k_B\ln\left(2^N\right)=Nk_B\ln2$.

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

$=Nk_B\int_0^1\operatorname{arctanh}\left(\overline{L}_0\right)\mathrm{d}\overline{L}_0=Nk_B\ln2$

研究 $B=0$ 时的磁化率 χ_0.

$\chi_0=\left(\frac{\partial M}{\partial B}\right)_T\Rightarrow\lim\limits_{T\to T_c^+}\chi_0\simeq\frac{NM^2}{k_B}\frac{1}{T-T_c},\quad\lim\limits_{T\to T_c^-}\chi_0\simeq\frac{NM^2}{2k_B}\frac{1}{T_c-T},\quad\lim\limits_{T\to0}\chi_0\simeq\frac{4NM^2}{k_BT}\exp\left\{-\frac{2T_c}{T}\right\}.$

1.3.3.2.2 Weak External Field $B\to0$

在 $T\geq T_c$ 时, 有 $\overline{L}\simeq\frac{\mu\beta}{1-\beta qJ}B=\frac{\mu}{k_B(T-T_c)}B\Rightarrow\overline{L}\propto B$, 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 $P_{++}=\frac{N_{++}}{\frac{1}{2}qN}$ 是否等价于单自旋↑概率乘积 $\frac{N_+}{N}\times\frac{N_+}{N}=P_+\times P_+$? 通过 MFT 给出的 $U_0=-\frac{1}{2}qJN\overline{L}_0^2, N_+=\frac{1}{2}N(1+\overline{L}_0), H_N(N_+,N_{++})$ 进行验证($\surd$).

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

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

1.3.3.3.2 涨落检验

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

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

在处理时运用了 $\delta\sigma_i\delta\sigma_j\to0$ 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]:

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

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

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

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

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

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

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

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

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. $H_{q+1}=-\mu B\sigma_0-\mu\left(B+B'\right)\sum_{j=1}^{q}\sigma_j-J\sum_{j=1}^{q}\sigma_0\sigma_j$. Requirement: $\overline{\sigma}_0=\overline{\sigma}_j,\quad\forall j$.

$Z=\sum_{\sigma_0=\pm1}\sum_{\sigma_j=\pm1}e^{-\beta H_{q+1}}\overset{\sigma_0=+1}{=}Z_+ + \overset{\sigma_0=-1}{Z_-},\quad Z_\pm=e^{\pm\alpha}\left[2\cosh\left(\alpha+\alpha'\pm\gamma\right)\right]^q,\quad \alpha=\frac{\mu B}{k_BT},\quad \alpha'=\frac{\mu B'}{k_BT},\quad \gamma=\frac{J}{k_BT}$.

$\overline{\sigma}_0=(+1)\frac{Z_+}{Z}+(-1)\frac{Z_-}{Z},\quad \overline{\sigma}_j=\langle\frac{1}{q}\sum_j\sigma_j\rangle=\frac{1}{q}\frac{1}{Z}\frac{\partial Z}{\partial\alpha'}$ (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 $\overline{\sigma}_0=\overline{\sigma}_j\Rightarrow e^{2\alpha'}=\left[\frac{\cosh\left(\alpha+\alpha'+\gamma\right)}{\cosh\left(\alpha+\alpha'-\gamma\right)}\right]^{q-1}$. $\alpha'=\alpha'(\alpha,\gamma)$.

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, $q=2\Rightarrow T_c=0$.

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

若 $\alpha=0$, 则 $\lim_{\alpha'\to0}\overline{\sigma}_0=\frac{2\alpha'}{1+e^{-2\gamma_c}}=\left[\frac{q^2}{q-1}\frac{J}{k_BT_c}3\left(1-\frac{T}{T_c}\right)\right]^{\frac{1}{2}}$. 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 $Z=\sum_{\sigma_0=\pm1}\sum_{\sigma_1\pm1}\left(\sum_{\sigma_2,\sigma_3,\cdots,\sigma_q=\pm1}\right)=Z_{++}+Z_{+-}+Z_{--}$. 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 $\dfrac{N_{++}N_{--}}{N_{+-}^2} = \dfrac{1}{4} \overset{\text{correlation}}{e^{4\gamma}}$, $\gamma = \dfrac{J}{k_B T}$

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

1. **矩阵法推导**: $Q_N = \sum\limits_{\{\sigma_i\}} \exp\left\{\beta \sum\limits_i \left[J\sigma_i\sigma_{i+1} + \dfrac{1}{2}\mu B(\sigma_i + \sigma_{i+1})\right]\right\} = \sum\limits_{\{\sigma_i\}} \prod\limits_i \exp\left\{\beta \left[J\sigma_i\sigma_{i+1} + \dfrac{1}{2}\mu B(\sigma_i + \sigma_j)\right]\right\}$,

观察到可将其写作矩阵元形式: $Q_N = \sum\limits_{\{\sigma_i\}} \prod\limits_i \langle \sigma_i | P | \sigma_{i+1} \rangle = \sum\limits_{\{\sigma_i\}} \langle \sigma_1 | P \underbrace{|\sigma_2\rangle\langle\sigma_2|}_{\mathbb{I}} P | \sigma_3 \rangle \cdots \langle \sigma_{N-1} | P \underbrace{|\sigma_N\rangle\langle\sigma_N|}_{\mathbb{I}} P | \sigma_{N+1} \rangle$

$= \sum\limits_{\sigma_1 = \pm 1} \langle \sigma_1 | P^N | \sigma_1 \rangle = \operatorname{Tr} P^N = \lambda_+^N + \lambda_-^N \overset{\lambda_+ \gg \lambda_-}{\approx} \lambda_+^N$. 其中 $\lambda_\pm$ 是矩阵 P 的特征值.

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

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

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

$F(B,T) = -Nk_BT\ln Q_N = -NJ - Nk_BT\ln\left\{\cosh(\beta\mu B) + \left[e^{-4\beta J} + \sinh^2(\beta\mu B)\right]^{\frac{1}{2}}\right\}$, $M = \left(\dfrac{\partial F}{\partial B}\right)$, $\lim\limits_{B\to 0} M = 0$

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

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

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

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

$$\langle \sigma_k \sigma_{k+r} \rangle \overset{\sigma_i^2 = 1}{=} \langle \sigma_k\sigma_{k+1} \cdot \sigma_{k+1}\sigma_{k+2} \cdots \sigma_{k+r-1}\sigma_{k+r} \rangle = \frac{1}{Q_N} \frac{\partial}{\beta\partial J_k} \frac{\partial}{\beta\partial J_{k+1}} \cdots \frac{\partial}{\beta\partial J_{k+r-1}} Q_N = \prod_{i=k}^{k+r-1} \tanh(\beta J_i) = \tanh^r(\beta J)$$
$$= e^{-r/\xi}, \quad \text{correlation length: } \xi = \frac{1}{\ln[\coth(\beta)]} \Rightarrow \text{随距离增大而迅速衰减.} \quad \lim_{T\to 0} \xi = \infty, \quad \lim_{T\to\infty} \xi = 0 .$$

1.3.3.7 Phase Transition & Space Dimension

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

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

1.3.3.8 Development of Ising Model

1.3.3.8.1 Spin Glass

$H = -\sum\limits_{\langle i,j \rangle} J_{ij}\sigma_i\sigma_j - h\sum\limits_i \sigma_i$, 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).

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

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

[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, $\mathrm{d}F = -S\mathrm{d}T - M\mathrm{d}H, \quad M = -\left(\dfrac{\partial F}{\partial H}\right)_T \Rightarrow F(T,H,M)$, let $\dfrac{\partial F(T,H,M)}{\partial M}\Big|_{\text{equilibrium}} = 0$. M acts as a constraint.

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

Free energy (analytic function of m_0): $\lim\limits_{t, m_0 \to 0} \psi_0(t, m_0) = q(t) + r(t) m_0^2 + s(t) m_0^4 + \cdots, t = \dfrac{T - T_c}{T_c}$,

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 $\dfrac{\partial \psi_0}{\partial m_0}\Big|_{m_0 = 0} \neq 0$.

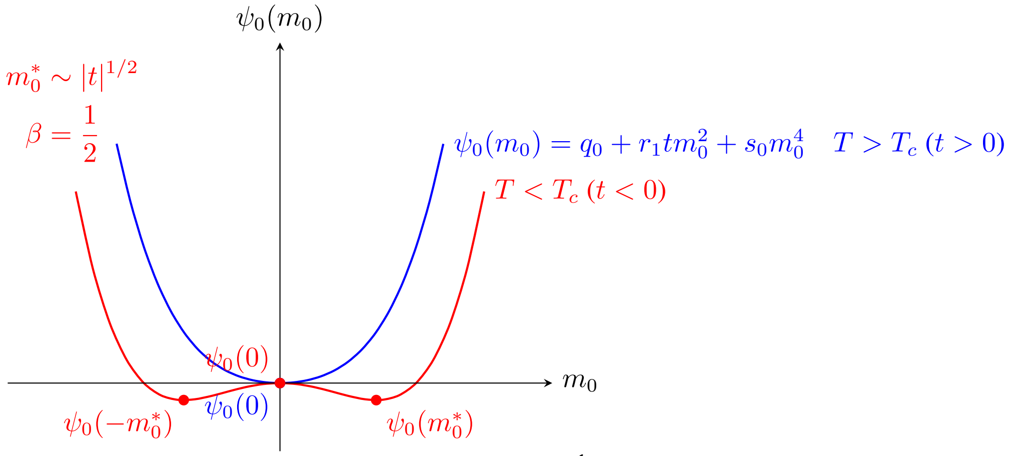
化学势 μ 全微分: $\mathrm{d}\mu(T,p,h) = -S\mathrm{d}T + v\mathrm{d}p - m\mathrm{d}h$. 加入外场 h 得到约化的化学势: $\widetilde{\mu} = \mu + mh$,

其全微分为 $\mathrm{d}\widetilde{\mu} = -S\mathrm{d}T + v\mathrm{d}p - h\mathrm{d}m$. 那么 $\mu = \widetilde{\mu} - mh = \underbrace{\widetilde{\mu}_0(T,p) + \alpha(T,p)m^2 + \beta(T,p)m^4}^{\text{Gibbs Free Energy}} - mh$.

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).



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

[Discussion] Wriss model @ 1907

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

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

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

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

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

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

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

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

[Discussion] Fluctuation & Response Theorem.

1. 热容 $C_v = \left.\dfrac{\partial \langle E \rangle}{\partial T}\right|_V = \dfrac{\langle (\Delta E)^2 \rangle}{k_B T^2}$;
2. 等温压缩率 $\kappa_T = -\dfrac{1}{\langle V \rangle}\left.\dfrac{\partial \langle V \rangle}{\partial P}\right|_T = \dfrac{\langle (\Delta V)^2 \rangle}{k_B T \langle V \rangle}$.

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

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

[Discussion] **Linear Response**. $H=H_0[m(x)]-\int \mathrm{d}x m(x)h(x)$, 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 $\lim\limits_{h\to0,t\to0^+}\xi\sim t^{-\nu},\quad C(r)\Big|_{t=0}\sim r^{-(d-2+\eta)}$.

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

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 $\lim\limits_{d<4,t\to0}C_f=\infty$, 和 1. 中表述一致.

1.3.5 Scale Transformation

对 2D spin lattice 进行标度变换: $\begin{bmatrix}x&o&x\\o&o&x\\x&x&x\end{bmatrix}\xrightarrow{N_x>N_o}X$. 观察发现, 对于 Critical state($\xi\to\infty$), 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), Single 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 $\psi^{(s)}(t,h) = l^{-d}\psi^{(s)}\left(l^{y_t}t, l^{y_h}h\right)$ 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 $\dfrac{h}{|t|^\alpha} = \dfrac{h'}{|t'|^\alpha}$, $\quad |t|^\beta = l^{-d}\,|t'|^\beta$. 因此指数间存在关系 $\alpha = \dfrac{y_h}{y_t}$, $\quad \beta = \dfrac{d}{y_t}$.

1.3.5.2 Scale Transformation in 1D & 2D Ising Models

1.3.5.2.1 1D Ising Model 研究 $J \to J'$, $\quad B \to B'$ 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: $\sigma_{2j} = \sigma_{2j+1} = \pm 1 \Rightarrow \sigma_j' = \pm 1$; $\quad \sigma_{2j} = -\sigma_{2j+1} \Rightarrow \sigma_j' = 0$, 作为约束方程.
解得 $\vec{K} \to \vec{K}'$ 的具体表达式:
$e^{K_0'} = 2e^{2K_0}\left[\cosh\left(2K_1 + K_2\right)\cosh\left(2K_1 - K_2\right)\cosh^2 K_2\right]^{\frac{1}{4}} = \sharp_0(K_0, K_1, K_2)$, $\quad e^{K_1'} = \sharp_1(K_1, K_2)$, $\quad e^{K_2'} = \sharp_2(K_1, K_2)$
[Discussion] 研究无外场条件($K_2 = 0$)下各量. 配分函数变换为 $Q_N(K_1, K_2) = e^{N'K_0'}Q_{N'}(K_1', K_2)'$,
因此自由能变换为 $F_N(K_1, K_2) = -N'K_0' + F_{N'}(K_1', K_2')$.
设单自旋自由能为 $f(K_1, K_2)$ 形式: $f(K_1; K_2 = 0) = -\dfrac{1}{2}\ln\left[2\cosh^{\frac{1}{2}}(2K_1)\right] + \dfrac{1}{2}f\left(K_1' = \ln\left[\cosh^{\frac{1}{2}}(2K_1)\right]; K_2' = 0\right)$
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 $f(x) = -\ln\left[2y(x)\right]$, 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 $\boxed{f(K_1; K_2 = 0) = -\ln\left(2\cosh K_1\right)}$.

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 $\xi\left[K^{(n)}\right]$, 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 $\xi\left[K^{(n)}\right]$ 递减, 其仍发散说明初项 $\xi\left[K^{(0)}\right] = \infty$.
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: $\vec{K}' = \vec{K}^* + \vec{k}' = R_l\left(\vec{K}^* + \vec{k}\right) = R_l\left(\vec{K}^*\right) + \left.\dfrac{\partial R_l(\vec{q})}{\partial \vec{q}}\right|_{\vec{q}=\vec{K}^*} \vec{k} + \cdots$,

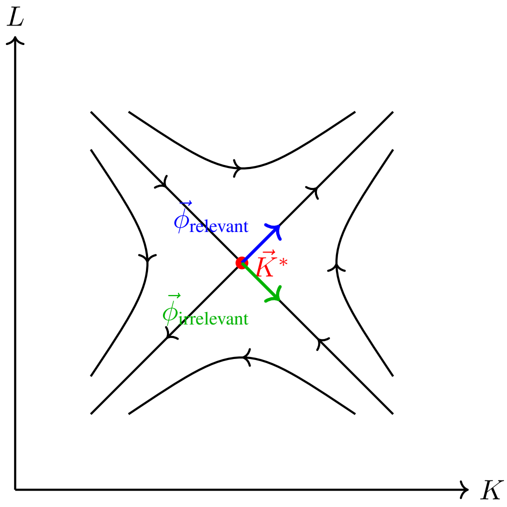
其中 $\vec{k}' = A_l\vec{k}$, $\quad A_l = \left.\dfrac{\partial R_l(\vec{q})}{\partial \vec{q}}\right|_{\vec{q}=\vec{K}^*}$. 将 $\vec{k}$ 以基矢展开 $\vec{k} = \sum\limits_i u_i\hat{\phi}_i$, 则变换式 $\vec{k}' = A_l\vec{k}$ 即可写作 $\sum\limits_i u_i'\hat{\phi}_i = A_l\sum\limits_i u_i\hat{\phi}_i$.

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 $\dfrac{\mathrm{d}u}{\mathrm{d}t} = -2u\left(u^2 - 1\right)$ 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-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

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

于是迁移概率为 $P_1\propto\exp\left(-\dfrac{\Delta E-T\Delta S+p\Delta V}{k_BT}\right)$. 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:

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

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 $P\propto\exp\left(-\dfrac{\Delta T\Delta S-\Delta P\Delta V}{2k_BT}\right)$, 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. $\Delta P=\left(\dfrac{\partial P}{\partial T}\right)_V\Delta T+\left(\dfrac{\partial P}{\partial V}\right)_T\Delta V=\left(\dfrac{\partial P}{\partial T}\right)_V\Delta T-\dfrac{1}{\kappa_TV}\Delta V$, 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 $P\propto\exp\left[-\dfrac{C_v}{2k_BT^2}(\Delta T)^2-\dfrac{1}{2k_Bk_TTV}(\Delta V)^2\right]$.

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

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:

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

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

$k_BT\kappa_TV\left(\frac{\partial E}{\partial V}\right)^2_{TN}=k_BT\kappa_TNv\left(\frac{\partial\widetilde{\varepsilon}}{\partial v}\right)^2_T=k_BT\kappa_TNn^3\left(\frac{\partial\widetilde{\varepsilon}}{\partial n}\right)^2_T$, 其中粒子数密度 $n=\frac{N}{V}=\frac{1}{v}$.

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

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

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

1.4.1.2 Time Analysis of Fluctuations

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

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** $g_{ij}\xrightarrow{\text{in equilibrium}}$ Response χ;
2. **时间关联函数** $\phi(t)\xrightarrow{\text{out of equilibrium}}$ conductivity, viscosity(粘度).

[Example] 测量 k_B. 分光出点光源, 凸透镜聚焦后散射至垂吊镜面, 相机收集其反射光. 镜子受空气撞击即布朗运动(视为热浴). 热平衡下 $\frac{1}{2}L\langle\theta^2\rangle=\frac{1}{2}k_BT\Rightarrow\langle\theta^2\rangle=\frac{k_BT}{L}$. (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 $\phi\left(t'-t\right)=\left\langle x\left(t'\right)x(t)\right\rangle=\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty}\left\langle\widetilde{x}(\omega)\widetilde{x}\left(\omega'\right)\right\rangle e^{-i\left(\omega t+\omega't'\right)}\mathrm{d}\omega\mathrm{d}\omega'$,

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

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

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

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

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

1.4.2 Relaxation of Weakly Non-equilibrium State

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

$\langle x_i(t)\rangle\Rightarrow\frac{\mathrm{d}x_i(t)}{\mathrm{d}t}=-\sum_k\lambda_{ik}x_k(t)$. 延拓 $\phi_{ik}\left(t'-t\right)=\left\langle x_i\left(t'\right)x_k(t)\right\rangle=\left\langle x_k(t)x_i\left(t'\right)\right\rangle=\phi_{ki}\left(t-t'\right)\Rightarrow\boxed{\phi_{ik}(t)=\phi_{ki}(-t)}$.

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

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

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

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

1.4.2.2 Onsager's Reciprocal Relation

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

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

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 $H = -\dfrac{1}{2} J \sum\limits_{\langle i,j \rangle}\left\langle \vec{S}_i \cdot \vec{S}_j \right\rangle$, 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

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

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

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

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 $\sqrt{\langle\vec{R}^2\rangle} \sim L^{\frac{1}{2}+\delta}$, 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 $\left(10^{-6}, 10^{-5}\right)$ m^2/s, 在液体中约 $\left(10^{-10}, 10^{-9}\right)$ 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 $t \sim \frac{\langle(\Delta x)^2\rangle}{D} \sim 10^6\ \text{s} \approx 11$ 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 $\langle S_n \rangle = \sum_{i=1}^{n} \langle X_i \rangle = nl(2p-1)$.

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

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 $\left\langle r^2 \right\rangle = \sum_{\alpha=1}^{d} \left\langle x_\alpha^2 \right\rangle$, 各轴 $\left\langle x_\alpha^2 \right\rangle = a^2 \sum_{i=1}^{} \langle \cos\theta_i \rangle + \cancel{a^2 \sum_{i\neq j}^{\langle \cos\theta_i \rangle = 0} \langle \cos\theta_i \cos\theta_j \rangle} = Na^2 \left\langle \cos^2\theta \right\rangle$.

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

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 $\left\langle r^2 \right\rangle$ 与维数无关.

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

1.4.3.2 Stochastic process

Static continuous random variable $X_i: \quad \overset{t_0}{\{x_0\}} \to \overset{t_1}{[x_1, x_1 + \mathrm{d}x]} \to \overset{t_2}{[x_2, x_2 + \mathrm{d}x]} \to \cdots$

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

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

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

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 $\text{Prob}\left(x_0 \overset{n\text{ steps}}{\longrightarrow} x\right) = P_n(x_0|x)$, 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

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

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

$$\begin{aligned}P(n,s)&=\sum_{m,m_1,m_2,\cdots,m_{s-1}}P(\overset{m\to m_1\to m_2\to\cdots\to m_{s-1}}{m,0)P(m,0|m_1,1)P(m_1,1|m_2,2)\cdots P(m_{s-1},s-1|n,s})\\&=\sum_{m,m_1,m_2,\cdots,m_{s-1}}P(m,0)Q_{mm_1}(1)Q_{m_1m_2}(2)\cdots Q_{m_{s-1}n}(s-1)=\sum_m P(m,0)\left(Q^S\right)_{mn},P(m,s_0|n,s)=(Q^{s-s_0})_{mn}\end{aligned}$$

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

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

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

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

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

1.4.3.5 Langevin's Theory

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

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

随机力满足 $\langle F(t)\rangle=0,\quad\left\langle\vec{F}(t)\vec{F}\left(t'\right)\right\rangle=C_1\delta\left(t-t'\right)$.
[Discussion] 回忆 Ideal gas: $\langle\delta n(x)\delta n\left(x'\right)\rangle=c\delta\left(x-x'\right)$, 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 $\dfrac{\mathrm{d}}{\mathrm{d}t}\left(\overset{K(t)}{\dfrac{1}{2}M\left\langle v(t)^2\right\rangle}\right)+M\tau^{-1}\left\langle v(t)^2\right\rangle=\langle v(t)F(t)\rangle$, 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: $\dfrac{\mathrm{d}K(t)}{\mathrm{d}t}=0\Rightarrow\langle v(t)F(t)\rangle=\dfrac{2}{\tau}K_0=\dfrac{2}{\tau}\cdot\dfrac{d}{2}k_BT$, 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 $\boxed{v(t)=\dfrac{1}{M}\displaystyle\int_0^t\mathrm{d}t'e^{-(t-t')/\tau}F\left(t'\right)}$.

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

平衡态: $\dfrac{C_1}{2M}=\dfrac{2}{\tau}\cdot\dfrac{1}{2}k_BT\Rightarrow\boxed{C_1=\dfrac{2k_BT}{B}}$, **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

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

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

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

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

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

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

Requires $\dfrac{1}{2}M\langle v^2(t)\rangle = \dfrac{3}{2}k_BT \Rightarrow C = \dfrac{6k_BT}{B}$.. 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 $\rho(x) = q\delta(x-x_0)$, $\displaystyle\int \rho(x)\mathrm{d}x = q$. 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: $\dfrac{1}{\delta t}\left[\sum\limits_i n_i(t+\delta t) - \sum\limits_i n_i\right] = \sum\limits_i\left(\sum\limits_{i\neq j} n_jP_{j\to i} - \sum\limits_{i\neq j} n_iP_{i\to j}\right) = 0.$

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

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

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**: $\displaystyle\int_{-\infty}^{+\infty} f(x,t)\mathrm{d}x = 1$;

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

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

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

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

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

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

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

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

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 $\langle x^2(t)\rangle=\left\langle\left(\displaystyle\int_0^t\mathrm{d}u_1v(u_1)\right)\left(\int_0^t\mathrm{d}u_1v(u_1)\right)\right\rangle=\int_0^t\mathrm{d}u_1\int_0^t\mathrm{d}u_2\,\langle v(u_1)v(u_2)\rangle$. 利用微积分性质 $\dfrac{\mathrm{d}}{\mathrm{d}t}\displaystyle\int_0^t f(u)\mathrm{d}u=f$

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

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

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

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 $\langle v(t)v(0)\rangle=\displaystyle\int_{-\infty}^{+\infty}S(\omega)e^{-i\omega t}\frac{\mathrm{d}\omega}{2\pi}$.

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

第二章　Homework

2.1　Homework 2

1. **Show that the volume element**

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

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

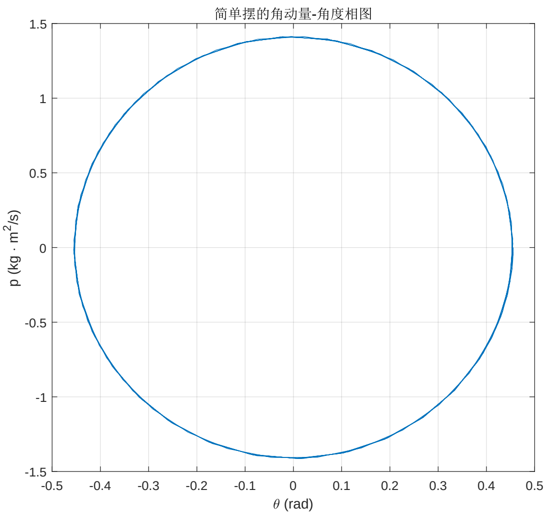
$$H = \frac{L^2}{2ml^2} + mgl(1 - \cos\theta)$$

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:

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



2.2 Homework 3

2.2.1 1-D Harmonic Oscillators

Derive

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

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

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

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

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

2. **and the corresponding expression for the "volume" of the relevant region of the phase space of this system. Establish the correspondence between the two results, showing that the conversion factor 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

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

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

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

   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 $\dfrac{1}{T}=\dfrac{\partial S}{\partial E}$, 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 $\mu=\left(\dfrac{\partial A}{\partial N}\right)_{V,T}$, and the pressure P is defined as $P=-\left(\dfrac{\partial A}{\partial V}\right)_{N,T}$, 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 $=\dfrac{2\pi^{n/2}}{\Gamma(n/2)}R^{n-1}s$]**

   The number of microstates is given by

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

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

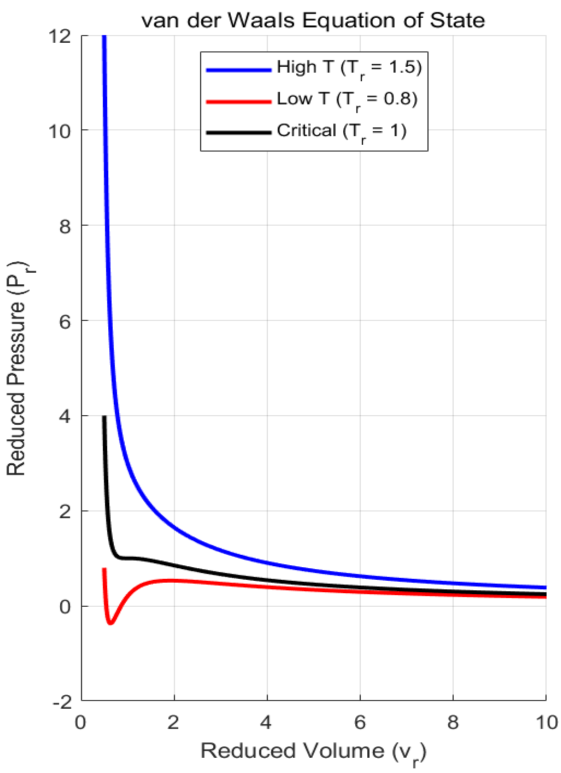
$$P_r \cdot \frac{a}{27b^2} = \frac{RT_r \cdot \frac{8a}{27Rb}}{v_r \cdot 3b - b} - \frac{a}{(v_r \cdot 3b)^2}$$
$$\Rightarrow P_r = \frac{8T_r}{3v_r - 1} - \frac{3}{v_r^2}.$$

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 coexistence. Conditions for phase equilibrium are:

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

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:

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

   which brings the critical point conditions:

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

   We can rewrite the equations as

   $$-v_c^2+\beta_1\lambda^3v_c+2\beta_2\lambda^6=0, \tag{2.1}$$
   $$2v_c^2-3\beta_1\lambda^3v_c-8\beta_2\lambda^6=0. \tag{2.2}$$

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:

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

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

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

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

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

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

2.4 Homework 5

2.4.1 Partition Function

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

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

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

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

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

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

which matches the provided expression.

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

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

Substituting this into (2.3) gives:

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

2.4.2 Equation of State

Show that the curve in 2.1 hits the horizontal and vertical axes at right angle according to the equation of state

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

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

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

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

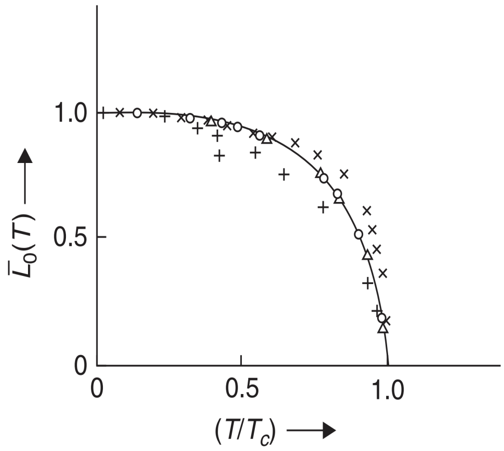


Figure 2.1: The spontaneous magnetization of a Weiss ferromagnet as a function of temperature. The experimental points (after Becker) are for iron (x), nickel (o), cobalt (Δ), and magnetite (+).

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

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

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

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

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

   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:

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

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

2.5 Homework 6

2.5.1 Landau's Theory

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

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

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:

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

So

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

1. For $T < T_c, t < 0$, $m_0 \sim \sqrt{-t} \Rightarrow m_0 \sim (-t)^{1/2} \Rightarrow \boxed{\beta = \frac{1}{2}}$
2. Susceptibility χ, which is defined as $\chi^{-1} = \left.\frac{\partial^2 \psi_0}{\partial m_0^2}\right|_{m_0 = m_{eq}}$.
   - For $T > T_c$, $m_0 = 0$. $\chi^{-1} = 2r(t) \approx 2r_0 t \Rightarrow \chi \sim t^{-1}$
   - For $T < T_c$, $m_0^2 = -\frac{r(t)}{2s(t)}$:

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

3. Specific heat.
   - For $T > T_c$, $\psi_0 = q(t)$;
   - For $T < T_c$, $\psi_0 = q(t) + r(t)m_0^2 + s(t)m_0^4 = q(t) - \frac{r(t)^2}{4s(t)}$. And the specific heat is defined as $C = -T\frac{\partial^2 \psi_0}{\partial T^2}$. Since $r(t) \sim t$, the singular part is C, which jumps at $t = 0$. So $\boxed{\alpha = 0}$.
4. Critical isotherm. At $T = T_c$, the free energy is $\psi_0 = q(0) + s(0)m_0^4 + \cdots$. 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 $\xi \sim \sqrt{\frac{c}{r(t)}} \sim t^{-1/2} \Rightarrow \boxed{\nu = \frac{1}{2}}$

2.6 Homework 7

2.6.1 Stretched String

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

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

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

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

[Hint : Calculate the energy, 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: $\Phi[y(x)] = \dfrac{F}{2}\displaystyle\int_0^l \left(\frac{\mathrm{d}y}{\mathrm{d}x}\right)^2 \mathrm{d}x$.

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

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

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

The probability distribution is $p(\{\}) \propto \exp\left[-\displaystyle\sum_{n=1}^{\infty} \frac{F\pi^2 n^2}{4l} a_n^2\right]$, which is a product of independent Gaussian distribution for each a_n. And the variance of each a_n can be extracted from the exponent term: $\overline{a_n^2} = \dfrac{2kT}{Fl}\left(\dfrac{l}{n\pi}\right)^2 = \dfrac{2kTl}{F\pi^2 n^2}$.

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

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

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

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

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

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

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

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

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

$$\begin{aligned}\sum_{n=1}^{\infty}\frac{1}{n^2}\sin\left(\frac{n\pi x_1}{l}\right)\sin\left(\frac{n\pi x_2}{l}\right) &= \frac{1}{2}\left[\frac{\pi^2}{6} - \frac{\pi^2|x_1-x_2|}{2l} + \frac{\pi^2(x_1-x_2)^2}{4l^2}\right] - \frac{1}{2}\left[\frac{\pi^2}{6} - \frac{\pi^2(x_1+x_2)}{2l} + \frac{\pi^2(x_1+x_2)^2}{4l^2}\right] \\ &= \frac{\pi^2(x_1+x_2-|x_1-x_2|)}{4l} + \frac{\pi^2[(x_1-x_2)^2-(x_1+x_2)^2]}{8l^2} \overset{x_2\geq x_1}{=} \frac{\pi^2(2x_1)}{4l} + \frac{\pi^2(-4x_1x_2)}{8l^2}\end{aligned}$$

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

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

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

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

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

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

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

According to time reversal symmetry(in microscopic process),

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

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 $\begin{matrix} \langle x_i(0)\gamma_{jl}X_l(0)\rangle = -k\gamma_{jl}\delta_{il} = -k\gamma_{ji} \\ \langle \gamma_{il}X_l(0)x_j(0)\rangle = -k\gamma_{il}\delta_{jl} = -k\gamma_{ij} \end{matrix} \Rightarrow \boxed{\gamma_{ij} = \gamma_{ji}}$.

Theoretical Statistical Physics (MKTP1)
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1 Introduction to probability theory

Bayes' theorem

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

Expactation and covariance

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

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

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

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

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

Poisson distribution

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

Information entropy

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

2 The microcanonical ensemble

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

The fundamental postulate

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

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

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

n_0 different particles

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

Equilibrium conditions

Entropy S must be maximal

Thermal contact

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

Contact with volume excahnge

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

Contact with exchange of particle number

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

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

Ideal Gas

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

microcanonical partition sum for an ideal gas

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

$$S = k_BN\left\{\ln\left[\left(\frac{V}{N}\right)\left(\frac{4\pi mE}{3h^2N}\right)^{3/2}\right] + \frac{5}{2}\right\}$$

Equations of state fo ideal gas

$$\frac{1}{T} = \left(\frac{\partial S}{\partial E}\right)_{N,V} = \frac{3}{2}\frac{Nk_B}{E} \to U = \frac{3}{2}Nk_BT$$

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

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

$$\lambda = \frac{h}{\sqrt{2\pi mk_BT}} \quad \text{Thermal de Broglie}$$

Einstein model for specific heat of a solid

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

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

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

Entropic elasticity of polymers

$N_+ - N_- = \frac{L}{a} = m \to N_+ = \frac{1}{2}(N+m)$

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

if both directions are possible $x2$

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

Statistical deviation from average

Two ideal gases in thermal conact $T_1 = T_2$

$$S_i = \frac{3}{2}k_BN_i\ln(E_i) + \text{independent of} E_i$$
$$S = S_1 + S_2$$
$$dS = 0 \to \frac{\partial S_1}{\partial E_1} = \frac{\partial S_2}{\partial E_2}$$
$$\to \overline{E}_1 = \frac{N_1}{N}E$$

consider small deviation:

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

$$S(\overline{E}_1 + \Delta E) \approx \frac{3}{2}k_B\left[N_1\ln\overline{E}_1 + N_2\ln\overline{E}_2 - \frac{N_1}{2}\left(\frac{\Delta E}{\overline{E}_1}\right)^2 - \frac{N_2}{2}\left(\frac{\Delta E}{\overline{E}_2}\right)^2\right]$$

$$\to \Omega = \overline{\Omega}e^{\left[-\frac{3}{4}\left(\frac{\Delta E}{E}\right)^2N^2\left(\frac{1}{N_1}+\frac{1}{N_2}\right)\right]}$$

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:

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

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

For common Hamiltonian:

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

Free energy

$$F(T,V,N) = -k_BT\ln Z_N(T,V)$$

$$\langle E\rangle = U = -\partial_\beta\ln Z_N$$

total differential:

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

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 j^{th} state of the i^{th} element

$$Z = \sum_{j1}\sum_{j2}\ldots\sum_{jN} e^{-\beta\sum_{i=1}^{N}\epsilon_{ij_i}}$$
$$= \left(\sum_{j1} e^{-\beta\epsilon_{1j_1}}\right)\ldots\left(\sum_{jN} e^{-\beta\epsilon_{Nj_1N}}\right)$$
$$= z_1\cdot\ldots\cdot z_N = \prod_{i=1}^{N} z_i$$
$$\to F = -k_BT\sum_{i=1}^{N}\ln(z_i) = -k_BT\ln(Z)$$

$$Z = z^N, \qquad F = -k_BTNln(z)$$

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 $f_{dof} = 2$

$$\mathcal{H} = Aq^2 + Bp^2$$
$$z \propto \int dqdpe^{-\beta\mathcal{H}}$$
$$= \left(\frac{\pi}{A\beta}\right)^{\frac{1}{2}}\cdot\left(\frac{\pi}{B\beta}\right)^{\frac{1}{2}} \propto \left(T^{\frac{1}{2}}\right)^{f_{dof}}$$

For sufficiently high temperture (classical limit), each quadratic term in the Hamiltonian contributes a factor $T^{\frac{1}{2}}$ to the partition sum ('equipartition theorem')

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

Molecular gases

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

Vibrational modes

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

An exact solution of the Schrödinger equation gives:
$E_n = \hbar\omega_0\left(n+\frac{1}{2}\right) - \frac{\hbar^2\omega_0^2}{eE_0}\left(n+\frac{1}{2}\right)^2$
$\omega_0 = \frac{\alpha}{2\pi}\sqrt{\frac{2E_0}{\mu}}, \quad \mu = \frac{m}{2}$

For $\hbar\omega_0 \ll E_0$ we can use the harmonic approximation:
$z_{vib} = \frac{e^{-\beta\hbar\omega/2}}{1-e^{-\beta\hbar\omega_0}}$
$T_{vib} \approx \frac{\hbar\omega_0}{k_B} \approx 6.140K$ for H_2

Rotational modes

standart approximation is the one of a rigid rotator. The moment of inertia is given as:
$I = \mu r_0^2 \quad T_{rot} = \frac{\hbar^2}{Ik_B} \quad \omega_n = (2J+1)$
$\to E_l = \frac{\hbar^2}{2I}l(l+1)$

Nuclear contributions: ortho- and parahydrogen

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

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Specific heat of a solid

Debye model

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

Debye frequency:

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

density of states in ω-space:

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

count modes in frequency-space:

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

partition sum:

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

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

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

4 The grandcanonical ensemble

$T, \mu = const.$

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

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

Mean phase space observable

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

mean particle number:

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

pressure:

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

energy U**:**

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

Grandcanonical potential

grandcanonical potential:

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

p is maximal, if Ψ is minimal.
Total differential:

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

Equations of state:

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

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

$$Z_N(T,V) = \frac{1}{N!}\left(\frac{V}{\lambda^3}\right)^N, \ \lambda = \frac{h}{(2\pi mk_B T)^{\frac{1}{2}}}$$
$$\Xi = \sum_{N=0}^\infty Z_N(T,V)z^N$$
$$= \sum_{N=0}^\infty \frac{1}{N!}\left(e^{\beta\mu}\frac{V}{\lambda^3}\right)^N$$
$$= e^{z\frac{V}{\lambda^3}} \quad \text{fugacity: } z := e^{\beta\mu}$$
$$\langle N\rangle = \frac{1}{\beta}\partial_\mu\ln(Z_G) = \frac{V}{\lambda^3}d^{\beta\mu}$$
$$\mu = k_B T\ln\left(\frac{N\lambda^3}{V}\right)$$

Molecular adsorption onto a surface

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

5 Quantum fluids

Fermion vs. bosons

1. Fermions: Pauli-principle + not distinguishable
2. Bosons: symetric wave function + not distinguishable
3. Boltzmann: particles are distinguishable

Canonical ensemble

$\omega_n \rightarrow$ degeneracy of state n

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

Grand canonical ensemble

only two states $0, \epsilon$

Fermions:

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

average occupation number n_F:

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

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

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

Bosons:

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

average occupation number n_B:

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

- Fermions tend to fill up energy states one after the other
- Bosons tend to condense all into the same low energy state

The ideal Fermi fluid

density of states:

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

Fermi energy

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

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

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

specific heat

$$\mu = \epsilon_F\left[1 - \frac{\pi^2}{12}\left(\frac{k_B T}{\epsilon_F}\right)^2\right] \text{ for } T \ll \frac{\epsilon_F}{k_B}$$
$$c_V = \frac{\partial E}{\partial T}\bigg|_V = N\frac{\pi^2}{3}k_B^2 D(\epsilon_F)T$$
$$c_V = N\frac{\pi^2}{2}\frac{k_B T}{\epsilon_F}k_B$$

Fermi pressure

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

The ideal Bose fluid

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

$$N = \frac{N}{\lambda^3}g_{\frac{3}{2}}(z)$$
$$z = e^{\beta\mu}, \ \lambda = \frac{h}{(2\pi mk_B T)^{\frac{1}{2}}}$$
$$T_c = \frac{2\pi}{\left(\zeta\left(\frac{3}{2}\right)\right)^{\frac{3}{2}}}\frac{\hbar^2\rho^{\frac{2}{3}}}{k_B m}$$
$$E = \frac{3}{2}k_B T\frac{V}{\lambda^3}g_{\frac{5}{2}}(z) = \frac{3}{2}k_B TN_e\frac{g_{\frac{5}{2}}(z)}{g_{\frac{3}{2}}(z)}$$
$$c_V = \frac{15}{4}k_B N\left(\frac{T}{T_c}\right)^{\frac{3}{2}}\frac{\zeta\left(\frac{5}{2}\right)}{\zeta\left(\frac{3}{2}\right)} \ (\text{ for } T \le T_c)$$
$$c_V = \frac{15}{4}k_B N\frac{g_{\frac{5}{2}}(z)}{g_{\frac{3}{2}}(z)} - \frac{9}{4}k_B N\frac{g_{\frac{3}{2}}(z)}{g_{\frac{1}{2}}(z)} \ (T > T_c)$$

Classical limit

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

$$n_{F/B} = \frac{1}{e^{\beta(\epsilon-\mu)}\pm 1} \rightarrow e^{\beta\mu}e^{-\beta\epsilon}$$
$$N = g\frac{V}{\lambda^3}e^{\beta\mu}$$
$$E = \frac{3}{2}k_B TN$$

6 Phase transitions

Ising model

Hamiltonian

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

special cases:

Ferromagnetic systems:
$\mathcal{H} = -J\sum_{\langle i,j\rangle}\vec{J}_i\vec{J}_j - \mu\vec{B}\sum_i\vec{J}_i$
lattice gases:
$\mathcal{H} = -\sum_{\langle i,j\rangle}J_{ij}S_iS_j$

1. Dimensional

Only Next Neighbor and $B_0 = 0$
$J_{i,i+1} \rightarrow J_i, \quad \mathcal{H} = -\sum_{i=1}^{N-1}J_iS_iS_{i+1}, \quad j_i = \beta J_i$

$$Z_N = \sum_{S_1}\dots\sum_{S_N}\exp\left(\sum_{i=1}^{N-1}j_iS_iS_{i+1}\right)$$
$$= 2^N\prod_{i=1}^{N-1}\cosh(\beta J_i)$$

Spin correlation function:

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

spontanious magnetisation:

$$M_S(T) = \mu\langle S\rangle$$
$$M_S^2(T) = \mu^2\lim_{j\rightarrow\infty}\langle S_iS_{i+1}\rangle$$

No phase transition for $T > 0$. But for $T = 0$
$M_S(T=0) = \mu$

Transfer matrix

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

$$T_{i,i+1} = e^{jS_iS_{i+1}+\frac{1}{2}b(S_i+S_{i+1})}$$
$$\rightarrow e^{-\beta\mathcal{H}} = T_{1,2}\cdot T_{2,3}\dots T_{N,1}$$
$$T = \begin{pmatrix} T(+1,+1) & T(+1,-1) \\ T(-1,+1) & T(-1,-1)\end{pmatrix}$$
$$Z_N = \lambda_1^N + \lambda_2^N = E_+^N + E_-^N$$

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

Renormalization of the Ising chain

$$K' = \frac{1}{2}\ln(\cosh(2K))$$

Renormalization of the 2d Ising model

$$\overline{K}' = K' + K_1 = \frac{3}{8}\ln(\cosh(4K))$$

The 2d Ising model

$$\beta\mathcal{H} = -K\sum_{r,c} S_{r,c}S_{r+1,c} - K\sum_{r,c} S_{r.c}S_{r,c+1}$$

$$1 = \sinh(2K_c)$$

$$K_c = \frac{1}{2}\ln\left(1+\sqrt{2}\right) \approx 0.4407$$

$$T_c = 2J/\ln\left(1+\sqrt{2}\right) \approx 2.269J/k_B$$

Perturbation theory

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

Mean field theory for the Ising model

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

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

$$\begin{aligned}
F_0 &= -Nk_BT\ln\left(e^{\beta B} + e^{-\beta B}\right)\\
&= -Nk_BT\ln(2\cosh(\beta B))\\
F &\leq F_0 + \langle\mathcal{H} - \mathcal{H}_0\rangle_0\\
&= -Nk_BT\ln(2\cosh(\beta B)) - N\frac{z}{2}\langle S\rangle_0^2\\
&+ N\langle S\rangle_0 = F_u\\
&\rightarrow z = 2\cdot\text{dimension}\\
B &= Jz\langle S\rangle_0 = Jz\tanh(\beta B)
\end{aligned}$$

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

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7 Classical fluids

Virial expansion

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

$$p = \rho k_BT\left[1 + B_2\rho\right]$$

Second virial coefficient

$$B_2(T) = -2\pi\int r^2 dr\left(e^{-\beta U(r)} - 1\right)$$

8 Others

Stirling's formula

$$\ln(n!) = n\ln(n) - n + \frac{1}{2}\ln(2\pi n)$$

de Broglie relation

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

Energies

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

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