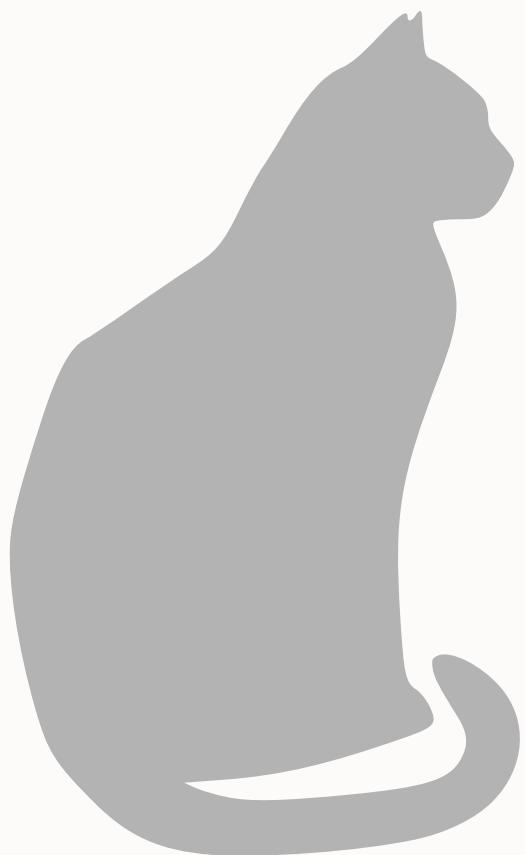


Advanced Statistics Mechanics



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CHAPTER 1 Review: Basic Concepts of Thermodynamics

1.1 Definitions

Definition 1.1.1 (Equilibrium State). 在没有外界影响的条件下，物体部分的长时间不发生变化的状态.

Definition 1.1.2 (热平衡定律). A 与 B 平衡，B 与 C 平衡，则 A 与 C 平衡.

Definition 1.1.3 (Temperature). 衡量物体间是否热平衡的物理量称为温度，一切互为热平衡的物体温度相等.

Definition 1.1.4 (温标). 确定温度具体数值的规则叫温标

Definition 1.1.5 (物态方程). 几何变量 V, A, L

力学变量 p, σ, F

电磁变量 E, p, H, M

化学变量 μ

$$T = f(p, V, \dots) \quad (1.1)$$

Definition 1.1.6 (内能). 绝热过程（没有热量/能量交换的过程）中外界对物体做功只与初态和末态有关，初态和终态的内能差 $U_2 - U_1 = W_a$ 外界对物体的绝热功

Definition 1.1.7 (热力学第一定律). 推广到非绝热过程，系统从外界吸热， $Q = U_2 - U_1 - W_0$ (能量守恒).

Definition 1.1.8 (热容).

$$C_y = \frac{dQ_y}{dT}, \quad y \text{ 是一个不变的量} \quad (1.2)$$

如果 $y = V$, 称为定容; $y = p$, 称为定压.

比热 C/V

Definition 1.1.9. 内能是态函数， $H = U + pV$, 称为焓

绝热过程中， $\Delta H = W_a$.

等压过程中， p 固定 $\Delta H = Q_p$.

Entropy: 对可逆过程，态函数

$$\Delta S = S - S_0 = \int_{\text{Initial State}}^{\text{Final State}} \frac{dQ}{T} \quad (1.3)$$

Definition 1.1.10 (热力学第二定律).

$$\Delta S \geq \int_{(i)}^{(f)} \frac{dQ}{T} \quad (1.4)$$

Definition 1.1.11 (热力学基本方程).

$$dU = T dS = \sum_i F_n dy_i p - V - T : dU = T dS - p dV \quad (1.5)$$

自由能: $F = U - TS$ $dF = dY - d(TS)$, $dF = -S dT - p dN$

Definition 1.1.12 (G.bbs 自由能: $G = F + pV$).

$$dG = -S dT + V dp \quad (1.6)$$

means 等温等压过程中, G 又不增加.

1.2 均匀系 (单相系) 的平衡

均匀系 $p - V - T$:

$$dU = T dS - p dV \quad (S, V) \quad (1.7)$$

$$df = \left(\frac{\partial f}{\partial x}\right)_y dx + \left(\frac{\partial f}{\partial y}\right)_x dy \quad (1.8)$$

$$\left(\frac{\partial T}{\partial V}\right)_S = -(PS)_V \quad (1.9)$$

同理, 对于焓

$$dH = T dS + V dP \quad (S, P) \quad (1.10)$$

$$\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P \quad (1.11)$$

$$dF = -S dT - p dV \quad (1.12)$$

$$dG = -S dT + V dP \quad (1.13)$$

Definition 1.2.1 (可测量热力学量). 1. p, V, \dots, T .

2. 响应函数: 压缩系数, 膨胀系数, ...

1.3 单元系的相变热力学

- 单相系 ∈ 单元系
- 相变：整个单详细的性质发生了变化，从一个平衡态到另一个平衡态
- 系统处于某一个相中，就是系统处于热平衡，判据 $S = S_{\max} \Leftrightarrow$ 孤立系处于平衡态. $\delta S = \delta^2 S = 0, \delta U = \delta V = \delta N = 0.$
- $\delta S = 0, \delta^2 S < 0.$
 - $\delta^3 S = 0$ 是稳定的必要条件
 - $\delta^4 S < 0 \rightarrow$ critical state
- 1. 自由能判据: T, V, N 不变, $F = F_{\min}$
- 2. Gibbs 自由能判据: T, P, N are constants, $G = G_{\min}.$
- If the number of particles is changeable, then

$$dU = T dS - p dV + (u + T_s + pV) dN \quad (1.14)$$

Here, $G/N = \mu$ is chemical potential.

- μdN

$$\mu = \left(\frac{\partial U}{\partial N} \right)_{S,V} = \left(\frac{\partial H}{\partial N} \right)_{S,P} = \left(\frac{\partial F}{\partial N} \right)_{T,V} = \left(\left(\frac{\partial G}{\partial N} \right)_{T,P} \right) \quad (1.15)$$

$$d\mu = -S dT + \sigma dP \quad (1.16)$$

- $\Psi = F - \mu N = U - T_s - \mu N = F - G$ is called the giant potential (巨势).

由平衡判据，可以得到平衡条件.

如熵极大 $T_1 = T_2$ (热平衡), $P_1 = P_2$ (力学平衡), $\mu_1 = \mu_2$ (化学平衡).

总粒子数不守恒 $\delta F = 0, P_1 = P_2, \mu_1 = \mu_2 = 0.$

由平衡判据，可以得到稳定条件

E.g.: 自由能极小

$$C_v > 0, K_T = \frac{1}{V} \left(\frac{\partial P}{\partial V} \right)_T > 0$$

- Due to equilibrium conditions, we can obtain the phase diagram.

两相平衡, $\mu^1 = \mu^2, T_1 = T_2 = T, P_1 = P_2 = P.$

$$\mu^1(T, P) = \mu^2(T, P), T, P \text{平面上}$$

Three-phase equilibrium: $\mu_1 = \mu_2 = \mu_3.$

1.4 热力学第三定律

Definition 1.4.1. 多元系的复相平衡和化学平衡 (T, P, N, \dots, N_k) $\{N_i\} \mu dN \rightarrow \sum_i \mu_i dN_i \mu_1 = \left(\frac{\partial \xi}{\partial N_i}\right)_{T, P, \{N_j \neq i\}}$

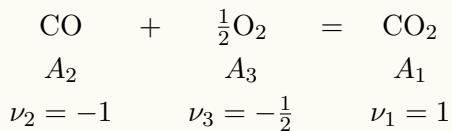
$$\int dT - V dq + \sum_i N_i d\mu_i = 0$$

$k+1$ 是独立的.

发生化学反应时,

$$\sum_{i=1}^k \nu_i A_i = 0$$

如



反应平衡条件

$$\sum_i \nu_i \mu_i = 0 \quad (1.17)$$

一些经验关系

- 等温等压条件下, 反应向放热方向进行, $\Delta H < 0$.
- 等温等压化学反应, 向着 ΔG 减小方向进行.

$$\Delta G = \Delta H - TS \Rightarrow \lim_{T \rightarrow 0} (\Delta S)_T \rightarrow 0$$

称为 Nernst Theorem.

Definition 1.4.2 (热力学第三定律). 绝对熵 $\lim_{T \rightarrow 0} S = 0$: 不可能通过有限步骤使物体冷却到绝对零度.

1.5 Linear Nonequilibrium Thermodynamics

- 能量守恒方程 -> 推广的热力学第一定律 (每一小块质心运动考虑进去) .
- 对小块, 熵的微分方程成立.
- 第二定律: $\theta = \frac{\delta S}{\delta t}$ 表示小块熵产生率.

$$\frac{dS}{dt} = -\nabla \cdot \mathbf{J}_s + \theta \cdot \mathbf{J}_s \text{ 为熵流密度}$$

$\mathbf{J}_s = \frac{\mathbf{J}_q}{T}$, \mathbf{J}_q 为热流, $\theta = \frac{K}{T^2}(\nabla T)^2 > 0$. K 为热导率.

- $\frac{\partial n}{\partial t} + \nabla \cdot \mathbf{J}_n = 0$

- 输运过程

Fourier: $\mathbf{J}_q = -K \nabla T$ Fick: $\mathbf{J}_n = -D_n \nabla n$, $\mathbf{J}_e = \sigma \mathbf{E} = -\sigma \nabla \phi$

CHAPTER 2 Concepts of Statistical Physics, Nearly Independent Particle Systems

2.1 微观状态的描写

粒子, 子系: 院子, 分子, 振子, 自旋,
 (q, p) , $q^a = 1, r, \epsilon(q, p)$

$$d\omega = d^r q d^r p$$

N : $q_1, \dots, q_s, p_1, \dots, p_s$. $s = Nr$

$$d\Omega = d^s q d^s p$$

$$\Gamma = \{(q_1, \dots, q_s; p_1, \dots, p_s)\}$$

称为相空间.

(q, p) 相空间中一个点, 叫做一个微观状态.

量子: 单粒子的量子态由一组守恒的量子数标志.

用一组可对易力学量算符的本征值描述.

例如, 自由粒子: 动量本征值

量子经典对应: 单粒子量子态 $\leftrightarrow \Delta\omega = h^r$ 的单粒子相阵积元.

全同性:

2.2 等几率原理

- 对孤立系, E, V, N 固定, 最简单朴素的假设就是等几率假设: 对于处于平衡态下的孤立系, 系统各个可能的微观状态出现的几率相等.
- 可能的微观状态是指与宏观状态 E, ν, N 相容的经典或量子态.

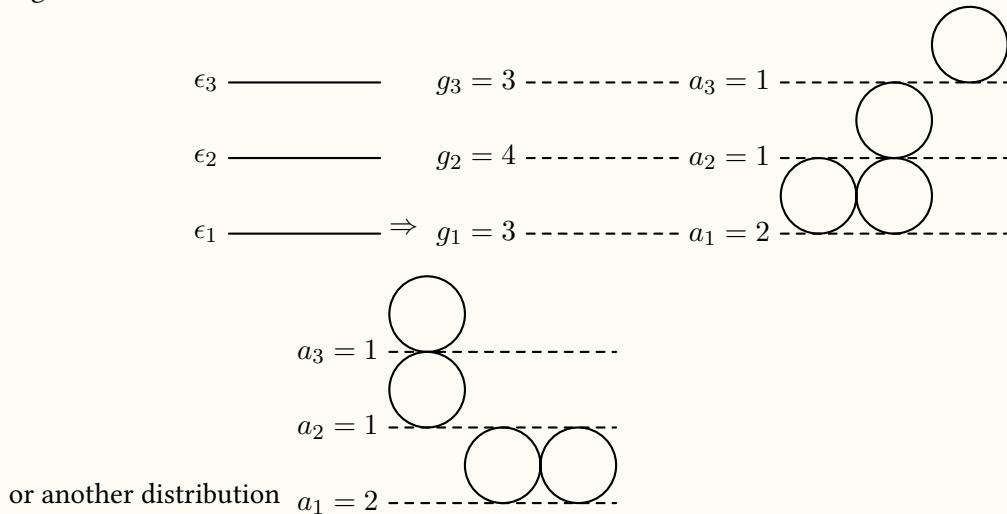
2.3 近独立粒子系统的统计物理

- 近独立是指相互作用很弱 (只对体系达到平衡起作用)

$$E = \sum_{i=1}^N \epsilon_i \tag{2.1}$$

- $\epsilon_{n,\alpha}, \alpha = 1$, 能级指标. g_α 称为简并度. a_α 指每一个能级上的占有数.

E.g.:



能级 能极简并度

- 对孤立子

$$\sum_{\alpha} a_{\alpha} = N, \sum_{\alpha} \epsilon_{\alpha} a_{\alpha} = E$$

- 对一个给定的 $\{a_{\alpha}\}$, 可以有不同的量子态. $\Rightarrow W(\{a_{\alpha}\})$ 等几率原理 $\{a_{\alpha}\}$ 出现的几率 $\propto W\{a_{\alpha}\}$.

如果可区分 $W(\{a_{\alpha}\}) = \frac{N!}{\prod_{\alpha} a_{\alpha}!} \prod_{\alpha} g_{\alpha}^{a_{\alpha}}$, Fermion $W_F(\{a_{\alpha}\}) = \prod_{\alpha} \frac{g_{\alpha}!}{a_{\alpha}!(g_{\alpha}-a_{\alpha})!}$, Boson $W_B(\{a_{\alpha}\}) = \prod_{\alpha} \frac{(g_{\alpha}+a_{\alpha}-1)!}{a_{\alpha}!(g_{\alpha}-1)!}$.

CHAPTER 3 Microregular Ensemble

平衡态统计一般理论是系综理论. 适用范围: 宏观多粒子系统.
系综: 微正则系综 (基本系综), 正则系综, 巨正则系综.

- 微正则系综: E, N, V 固定
- 正则系综: T, N, V 固定
- 巨正则系综: T, μ, V 固定

3.1 经典统计系综

经典力学的微观状态: 相空间中一个点 (q, p) 满足正则运动方程

$$\dot{q}_i = \frac{\partial H}{\partial p_i}, \dot{p}_i = -\frac{\partial H}{\partial q_i}, i = 1, \dots, s \quad (3.1)$$

$\{(q_n(t), p_n(t))\}$ 相轨道 $(\dot{q}_i(t), \dot{p}_i(t))$, 轨道上任意一点 $d\Omega = \prod_i dq_i dp_i, i = 1, \dots, s$.

设 Γ 为给定宏观物理条件下所有可能的微观状态 $\tilde{\rho} d\Omega$: $d\Omega$ 内的微观状态数, 则 $\rho d\Omega = \frac{\tilde{\rho} d\Omega}{\Gamma} = \frac{\tilde{\rho} d\Omega}{\int \tilde{\rho} d\Omega}$ 是某微观状态出现在 $d\Omega$ 内的几率, 满足归一化 $\int \rho d\Omega = 1$, ρ 为几率密度.

任何物理可观测量 O 是微观力学量 O 的统计平均.

$$\bar{O} = \int d\Omega \rho O \quad (3.2)$$

- 系统处于某一微观状态 \Leftarrow 处于该微观状态的系统
- 处于 $d\Omega$ 中的系统是 $\tilde{\rho} d\Omega$ 个 Γ 个系统的集合称为一个统计系综.
- 系综是假想的和所研究系统性质完全相同的彼此独立、各自处于某一微观状态的大量系统的集合.

3.2 系综所满足的方程: Liouville 定理

Theorem 3.2.1 (Liouville 定理). 系综的几率密度 ρ 在运动中不变,

$$\frac{d\rho}{dt} = 0, \frac{d\tilde{\rho}}{dt} = 0.$$

代表点数守恒

$$\frac{\partial \rho}{\partial t} + \nabla \cdot \mathbf{J}_\rho = 0, \mathbf{J}_\rho = \rho \mathbf{v}, \nabla = \left(\frac{\partial}{\partial q_i}, \frac{\partial}{\partial p_i} \right), \mathbf{v} = \sum_i (\dot{q}_i, \dot{p}_i) \quad (3.3)$$

$$\frac{d\tilde{\rho}}{dt} = \frac{\partial\tilde{\rho}}{\partial t} + \sum_i \mathbf{r}_i (\rho \mathbf{r}_i \mathbf{r}_i) = \frac{\partial\tilde{\rho}}{\partial t} + \sum_i \left(\left(\frac{\partial\tilde{\rho}}{\partial q} \right)_i \dot{q}_i + \left(\frac{\partial\tilde{\rho}}{\partial p} \right)_i \dot{p}_i \right) = -\tilde{\rho} \sum_i \left\{ \frac{\partial^2 H}{\partial q_i \partial p_j} - \frac{\partial^2 H}{\partial p_i \partial q_j} \right\} = 0 \quad (3.4)$$

最后得出 Liouville 方程

$$\frac{\partial\tilde{\rho}}{\partial t} + \{\tilde{\rho}, \rho\} = 0 \quad (3.5)$$

3.3 量子统计系综

- 对量子力学系统，我们用波函数 ψ_n 或态 $|n\rangle$ 来代替相空间的 (q, p)
- $A_n = \langle n | \hat{A} | n \rangle$
- 统计系综，考虑一系列的态 $|1\rangle, |2\rangle, \dots, |n\rangle$.
- 第 n 个态有 $\tilde{\rho}_n$ 个简并度，即有 $\tilde{\rho}_n$ 个系统.

总系统数 $N = \sum_n \tilde{\rho}_n$

$\rho_n = \frac{\tilde{\rho}_n}{N}$ 处于第 n 个态的几率

$$\sum_n \rho_n = 1, \bar{A} = \langle A \rangle = \sum_n \rho_n A_n$$

统计算符（密度矩阵） $\hat{\rho} = \sum_n |n\rangle \rho_n \langle n|$

$\{|i\rangle\}$ 一套正交¹完备²基.

密度矩阵

$$\rho_{ij} = \langle i | \hat{\rho} | j \rangle = \sum_n \langle i | n \rangle \rho_n \langle n | j \rangle \quad (3.6)$$

$$A_{ij} = \langle i | A | j \rangle, \bar{A} = \sum_n \rho_n \langle n | A | n \rangle = \sum_{ij} \sum_n \rho_n \langle n | j \rangle \langle j | A | i \rangle \langle i | n \rangle = \sum_{ij} \rho_{ij} A_{ji} = \text{Tr}(\hat{\rho} A)$$

$$\text{Tr} \sum_i \rho_{ii} = 1$$

$\hat{\rho}, |n\rangle$ Schrödinger eq

$$i \frac{\partial}{\partial t} |n\rangle = \hat{H} |n\rangle \quad (3.7)$$

$$i \frac{\partial}{\partial t} \hat{\rho} = \sum_n \left[\left(i \frac{\partial}{\partial t} |n\rangle \right) \rho_n \langle n| - |n\rangle \rho_n \left(-i \frac{\partial}{\partial t} \langle n| \right) \right] = \sum_n H |n\rangle \rho_n \langle n| - |n\rangle \rho_n \langle n| H = H \hat{\rho} - \hat{\rho} H = [H, \hat{\rho}]$$

Finally, we have

$$\frac{\partial}{\partial t} \hat{\rho} + i[H, \hat{\rho}] = 0 \quad (3.8)$$

即 $\hat{\rho}$ 的 Heisenberg eq. of motion.

¹即 $\delta\langle i | j \rangle = \delta_{ij}$

²即 $\sum_i |i\rangle \langle i| = \mathbb{1}$: 对于 $\{|0\rangle m|\uparrow\rangle, |\downarrow\rangle, |\uparrow\downarrow\rangle\}$, 存在 $|0\rangle \langle 0| + |\uparrow\rangle \langle \uparrow| + |\downarrow\rangle \langle \downarrow| + |\uparrow\downarrow\rangle \langle \uparrow\downarrow| = \mathbb{1}$

3.4 微正则系综

- 经典微正则系综: E, N, V 不变系综 – 孤立系.

由 Liouville 定理

$$\frac{d\rho}{dt} = 0$$

若在平衡态物理量不随时间变化, 就要求在相空间固定点, ρ 不随时间变化, 即必要条件 $\frac{\partial \rho}{\partial t} = 0$.
 \Rightarrow 在相轨道内 ρ 为常数.

但 Liouville 定理和平衡态物理量不变不能保证不同轨道的 ρ 相同.

微正则系综的基本假设

- 当 $H(q, p) = E$ 时, ρ 是常数, 即相空间中的等能面.
- 当 $H(q, p) \neq E$ 时 (存在集合 $\{p, q\}$), $\rho = 0$.

To summarize

$$\rho = \begin{cases} C & E \leq H \leq E + \Delta E, \\ 0 & otherwise \end{cases} \quad (3.9)$$

守恒条件 (Normalization of ρ)

$$\lim_{\Delta \rightarrow 0} C \int_{\Delta E} d\Omega = 1. \quad (3.10)$$

The mean value

$$\bar{O} = \lim_{\Delta E \rightarrow 0} C \int_{\Delta O d\Omega}. \quad (3.11)$$

量子微正则系综

$$H(q, p) \longrightarrow E_n \quad (3.12)$$

加入

1. 粒子的全同性

$$2. \rho_n = \begin{cases} C, & E_n = E \\ 0, & E_n \neq E \end{cases}, n \text{ 为标记量子态的量子数. } \sum_{n(E_n=E)} \rho_n = C (\sum_{n(E_n=E)} 1 = 1).$$

$$\mathcal{N}(E, V, N) = \sum_{n(E_n=E)} 1, C = \frac{1}{\mathcal{N}(E, N, V)}$$

CHAPTER 4 From Microcanonical Ensembles to Canonical Ensembles

Definition 4.0.1 (正则系综). 系统与大热源接触，达到平衡的系综， (T, V, N) 固定.

大热源的作用是提供确定的温度

- A : 就是要研究的正则系综中的系统.
- B : 大热源中的系统
- $A + B$: 孤立系.

$$E_{\text{total}} = E_A + E_B, \quad V_{\text{total}} = V_A + V_B, \quad N_{\text{total}} = N_A + N_B$$

Assume $\Omega(E_{\text{total}})$ is the number of the total state of $A + B$, then the states in A is labelled as $|n\rangle$, and A is at the $|n\rangle$ state; B has $\Omega(E_{\text{total}} - E_A)$ states. The probability that the system A at state $|n\rangle$ can be described as

$$\rho_{An} = \frac{\Omega_B(E_{\text{total}} - E_A)}{\Omega(E_{\text{total}})}. \quad (4.1)$$

and the mean value $\bar{E}_n \ll E_{\text{total}}, E_A \ll E_{\text{total}}$. It's not important that which state B is located, as well as B 's properties. Then, the freedom-particle system can be used to represent B .

Example 4.0.1 (Chapter 3, Problem 1). $\Omega_B(E_{\text{total}} - E_A) \sim (E_{\text{total}} - E_A)^M, M \sim O(N_3) \sim O(N)$. To expand it:

$$\Omega_B(E_{\text{total}} - E_A) = E_{\text{total}}^M \left(1 - \frac{E_A}{E_{\text{total}}}\right)^M = E_{\text{total}}^M \left(1 - M \frac{E_A}{E_{\text{total}}} + \dots\right)$$

we can also expand it in another way (a safer expansion)

$$\Omega_B(E_{\text{total}} - E_A) = \exp[M \ln(E_{\text{total}} - E_A)]$$

Then expand the “ln” item

$$\ln(E_{\text{total}} - E_A) = \ln E_{\text{total}} + \ln \left(1 - \frac{E_A}{E_{\text{total}}}\right) = \ln E_{\text{total}} - \frac{E_A}{E_{\text{total}}} - \frac{1}{2} \left(\frac{E_A}{E_{\text{total}}}\right)^2 + \dots$$

then we have

$$\rho_{An} = \frac{1}{\Omega(E_{\text{total}})} e^{\ln \Omega_B} = \frac{1}{\Omega(E_{\text{total}})} \exp \left[\ln \Omega_B(E_{\text{total}}) - \frac{\partial \Omega_B(E_{\text{total}})}{\partial E_{\text{total}}} E_A + \dots \right] \approx \frac{\Omega_B(E_{\text{total}})}{\Omega(E_{\text{total}})} e^{-\beta E_A} \equiv \frac{1}{Z_N} e^{-\beta E_A}$$

we define $\beta = \frac{\partial \Omega_B(E_{\text{total}})}{\partial E_{\text{total}}} \triangleq \frac{1}{k_B T}$ then remove the “ A ” index

$$\rho_{An} = \rho_n, \quad \sum_n \rho_n = 1 \Rightarrow Z_N = \sum_n e^{-\beta E_N}$$

Now, we arrive at the partition function Z_N

$$Z_N = \text{Tr } e^{-\beta H} = \sum_n \langle n | e^{-\beta H} | n \rangle = \sum_n e^{-\beta E_n} \quad (4.2)$$

Using the partition function, we have

$$\bar{A} = \sum_n A_n \rho_n = \frac{1}{Z_n} \sum_n \langle n | A | n \rangle e^{-\beta E_n} = \frac{1}{Z_n} \sum_n \langle n | A e^{-\beta H} | n \rangle = \frac{1}{Z_n} \text{Tr } A e^{-\beta H}. \quad (4.3)$$

$$\bar{E} \xrightarrow{\text{inner energy}} \sum_n E_n \rho_n = \frac{1}{Z_n} \sum_n E_n e^{-\beta E_n} = \frac{1}{Z_n} \left(-\frac{\partial}{\partial \beta} \sum_n e^{-\beta E_n} \right) = -\frac{1}{Z_n} \frac{\partial}{\partial p} Z_n = -\frac{\partial}{\partial \beta} \ln Z_n \quad (4.4)$$

$$p_n = -\frac{\partial E_n}{\partial V}, \bar{p} = \sum_n p_n \rho_n = \frac{1}{Z_n} \sum_n -\frac{\partial E_n}{\partial V} e^{-\beta E_n} = \frac{1}{\beta} \frac{\partial}{\partial V} \ln Z_N \quad (4.5)$$

$$dS = \frac{d\bar{E}}{T} + \frac{\bar{p}}{T} dN = k_B(\beta d\bar{E} + \beta \bar{p} dV) = k_B \left(-\beta \frac{\partial}{\partial \beta} d \ln Z_N + dV \frac{\partial}{\partial V} \ln Z_N \right) = d \left[k_B \left(\ln Z_N - \beta \frac{\partial}{\partial p} \ln Z_N \right) \right] \quad (4.6)$$

$$F = \bar{E} - TS = -k_B T \ln Z_N \quad (4.7)$$

4.1 能量涨落, 热力学极限, 经典极限

Definition 4.1.1 (涨落). For energy:

$$(a) \text{ 方差: } \frac{(E - \bar{E})^2}{E^2}$$

$$(b) \text{ 方均根: } \sqrt{\frac{(E - \bar{E})^2}{E^2}}$$

$$\overline{(E - \bar{E})^2} = \overline{(E^2 - 2E\bar{E} + \bar{E}^2)} = \overline{E^2} - \bar{E}^2, \overline{E^2} = \sum_n E_n^2 \rho_n = \dots = \bar{E}^2 - \frac{\partial \bar{E}}{\partial \beta} \Big|_{N,V}$$

$$\overline{(E - \bar{E})^2} = -\frac{\partial \bar{E}}{\partial \beta} \Big|_{N,V} = k_B T \left(\frac{\partial \bar{E}}{\partial T} \right)_{N,V} = k_B T^2 C_V$$

$$\frac{\sqrt{(E - \bar{E})^2}}{\bar{E}} = \frac{\sqrt{k_B + C_V}}{\bar{E}} = \frac{\sqrt{k_B c_v} + \sqrt{N}}{A + N} \propto \frac{1}{\sqrt{N}}$$

Definition 4.1.2 (热力学极限). $N, V \rightarrow \infty, n = \frac{N}{V}$ final.

Definition 4.1.3 (经典极限). 热波长 $\lambda_T = h/(2\pi m k_B T)^{1/2} \ll \delta r$ (average distance of particle).

$\Delta E = E_n - E_{n-1} \ll k_B T$ – 经典极限.

$$Z_n = \frac{1}{N! h^3} \int d\Omega e^{-\beta H(q,p)}$$

4.2 State equation of non-ideal gas

Model:

$$E = k + V = \sum_{i=1}^N \frac{\mathbf{p}_i^2}{2m} = \sum_{i < j} \phi_{ij} \quad (4.8)$$

here, $\phi_{ij} = \phi(\mathbf{r}_i - \mathbf{r}_j)$ stands for the interactions between molecule.

$$Z_N = \int (d\Omega) e^{-\beta(k+V)}, \quad (d\Omega) = \frac{1}{N! h^{3N}} \prod_i d^3 p_i d^3 r_i = \frac{1}{N! \lambda_T^{3N}} Q_N(\beta, V)$$

while $Q_N = \int d\mathbf{r}_1 \cdots d\mathbf{r}_N e^{-\beta \sum_{i < j} \phi_{ij}} = \int (d\mathbf{r}) \prod_{i < j} e^{-\beta \phi_{ij}}$.

For ideal gas, $Q_N = V^N$. The interacting force is graphed: $r^* \sim 1\text{\AA}$

$$f_{ij} = e^{-\beta p_{ij}} - 1$$

$$f(r) = \begin{cases} -1, & r \rightarrow 0, (\phi \rightarrow \infty) \\ 0, & r \rightarrow r^*(\phi \rightarrow 0) \end{cases}$$

$$Q_N = \int (d\mathbf{r}) \prod_{i < j} (1 + f_{ij}) = \int (d\mathbf{r}) \left(1 + \sum_{i < j} f_{ij} + \sum_{i < j} f_{ij} \sum_{i' < j'} f_{i'j'} + \dots \right)$$

Since $e^{-\beta \phi(r_0)} / 2 \ll 1$,

$$Q_N = \int (d\mathbf{r}) (1 + \sum_{i < j} f_{ij}) = V^N + \frac{1}{2} N(N-1) V^{N-2} \int d\mathbf{r}_1 d\mathbf{r}_2 f_{12}, \quad \mathbf{r}_1 - \mathbf{r}_2 = \mathbf{r}$$

$$\int d\mathbf{r}, d\mathbf{r}_2 f_{12} = \int d\mathbf{r}_1 \int d\mathbf{r}_2 f(|\mathbf{r}|) \approx V \int dr f(r)$$

$$Q_N \approx V^N \left(1 + f \frac{1}{2} (N^2 - N) \right) / V \int d^3 \mathbf{r} f(r) \approx V^N \left(1 + \frac{1}{2} \frac{N^2}{V} \int d\mathbf{r} f(r) \right)$$

$$\ln Q_N = N \ln V + \ln \left(1 + \frac{N^2}{2V} \int d^3 \mathbf{r} f(r) \right)$$

The pressure

$$p = \frac{1}{\beta} \frac{\partial}{\partial V} \ln N_N = \frac{1}{\beta} \frac{\partial}{\partial V} \ln Q_N = \frac{Nk_B T}{V} \left[1 - \boxed{\frac{N}{2V^2} \int d^3 \mathbf{r} f(r)} \right]$$

$$\phi(r) = \begin{cases} \infty, & r < r_0 \\ -p_0 \left(\frac{r_0}{r} \right)^b, & r \geq r_0 \end{cases}$$

$$B_2 = -\frac{N}{2} \int_0^\infty \exp \left(-\frac{-\phi(r)}{k_B T} - 1 \right) r^2 dr \approx 2\pi N \left(\frac{r_0^3}{3} - \phi_0 \frac{r_0^3}{3k_B T} \right) \equiv N_b - \frac{Na}{k_B T}$$

Substitute B_2 into p

$$p = \frac{Nk_B T}{V} \left(1 + \frac{Nb}{V} \right) - \frac{N^2 a}{V^2} \approx \frac{Nk_B T}{V(1 - Nb/V)} - \frac{N^2 a}{V^2}$$

Then we arrive at the 范德瓦耳斯 equation

$$\left(p + \frac{N^2 a}{V^2} \right) (V - Nb) = Nk_B T \quad (4.9)$$

CHAPTER 5 Grand Canonical Ensemble

(T, μ, V) 不变.

- 与正则系综类似，热库同时也是粒子源.

$$E_T = E_A + E_B, N_T = N_A + N_B \quad (5.1)$$

$$\begin{aligned} \rho_n = \rho_{AN} &= \frac{\Omega_B(N_T - N_A, E_T - E_A)}{\Omega(N_T, E_T)} = \frac{1}{\Omega(N_T, E_T)} e^{\ln \Omega_B(N_T - N_A, E_T - E_A)} \\ &= \frac{\Omega_3(N_T, E_T)}{\Omega(N_T, E_T)} \exp \left[-\frac{\partial \ln \Omega_B(N_T, E_T)}{\partial N_T} N_A - \frac{\partial \ln \Omega_B(N_T, E_T)}{\partial N_T} N_A \right] \\ &= \frac{1}{Z_G} e^{\beta \mu N_A - \beta E_A} \end{aligned}$$

即 $\rho_{N_A} = \frac{1}{Z_G} e^{-\beta(E_n - \mu_N)}$. The normalization condition

$$\sum_{N=0}^{\infty} \sum_n \rho_{Nn} = 1$$

$$Z_G = \sum_{N=0}^{\infty} e^{\beta \mu N} \sum_n e^{-\beta E_N} = \sum_{N=0}^{\infty} e^{\beta \mu N} Z_N = \text{Tr } e^{-\beta(\hat{H} - \mu N)}$$

while μ is fermion's energy.

$$\langle n | \hat{H} | n \rangle = E_n$$

$$\bar{E} = -\frac{\partial}{\partial \beta} \ln Z_G \quad (5.2)$$

$$p = \frac{1}{\beta} \frac{\partial}{\partial V} \ln Z_G \quad (5.3)$$

$$S = \alpha_B (\ln Z_G - \alpha \frac{\partial}{\partial \alpha} \ln Z_G - \beta \frac{\partial}{\partial \beta} \ln Z_G) \quad (5.4)$$

$$F = -k_B T \ln Z_G + k_B T \alpha \frac{\partial}{\partial \alpha} \ln Z_G \quad (5.5)$$

$$\psi = -k_B T \ln Z_G \quad (5.6)$$

- 经典和粒子数涨落 $\sim \frac{1}{\sqrt{N}}$.

- 经典极限 $Z_G = \sum_N e^{-\alpha N} Z_N$

Example 5.0.1 (固体表面的吸附率).

$$\theta = \frac{\bar{N}}{N_0}, N \rightarrow \bar{N}$$

(T, μ, ν) 单个分子被吸附后的能量降低 ϵ_0 .

$$E_N = -\epsilon_0 N$$

$$Z_G = \sum_{N=0}^{N_0} \sum_n e^{-\alpha N - \beta E_N} = \sum_{N=0}^{N_0} \sum_n e^{-\alpha N - \beta E_N} = \sum_{N=0}^{\infty} \sum_n e^{\beta(\beta + \epsilon_0)N}$$

其中 n 表示分子占据 N 个确定吸附中心中的 N 个时的某一特定状态

$$\sum_n = \frac{N_0!}{N!(N_0 - N)!}$$

$$Z(G) = \sum_{N=0}^{N_0} \frac{N_0!}{N!(N_0 - 1)!} e^{p(\mu + \epsilon_0)N} = (1 + x)^{N_0} = (1 + e^{\beta(\mu + \epsilon_0)})^{N_0}$$

$$\bar{N} = -\frac{\partial}{\partial x} \ln Z_G = \frac{1}{\beta} \frac{\partial}{\partial \mu} \ln Z_G|_{T_{\beta(\mu + \epsilon_0)}} = N_0 \frac{\partial}{\partial \alpha} e^{\alpha + \beta_0 \epsilon} = \frac{N_0 e^{\beta(\mu + \epsilon_0)}}{1 + e^{\beta(\mu + \epsilon_0)}}$$

这里达到平衡态 $\mu = \mu_A = \mu_B$, 这里 μ_B 可以用理想气体的化学势.

$$e^{-\beta \mu} = \frac{(2\pi m k_B T)^{3/2} k_B T}{\beta h^3}$$

$$\theta = \frac{\bar{N}}{N_0} = \frac{p h^3}{p h^3 + (2\pi m)^{3/2} - (k_B T)^{5/2} - e^{-\epsilon_0/k_B T}}$$

即 p 升高, θ 升高; T 升高; θ 下降.

CHAPTER 6 Quantum Statistics

- For dimension $d = 3$: Quantum gas could be either boson or fermion
- For dimension $d = 2$: Quantum gas could be either boson, or fermion, or anyon.
- For dimension $d = 1$: The statistic properties are related to interactions.

6.1 Bose and Fermi Statistics of free particles under GRSC

The Giant Regular System Comprehensive is

$$Z_G = \sum_{N=0}^{\infty} \sum_{\substack{s \\ N \text{ is fixed}}} e^{-\alpha N - \beta E_s} \quad (6.1)$$

Combine $E_{N_{n_1}} = E_{N_{n_2}} = \dots = E_N$ together and substitute them into Z_G

$$Z_g = \sum_{N=0}^{\infty} \sum_{E_N} \sum_{s(E_{Ns}=E_N)} e^{-\alpha N - \beta E_{Ns}}$$

For free particles

$$E_N = \sum_{\lambda} a_{\lambda} \epsilon_{\lambda}, \quad \text{and} \quad N = \sum_{\lambda} a_{\lambda}$$

ϵ_{λ} is the energy of single particle, a_{λ} is the occupation number of λ energy level, and $\{a_{\lambda}\}$ is a distribution of the number of particles after a given λ . Now, we can sum in partition

$$Z_a = \sum_{N=0}^{\infty} \sum_{E_N} \sum_{\{a_{\lambda} \mid \sum_{\lambda} a_{\lambda} \epsilon_{\lambda} = E_N\}} W(\{a_{\lambda}\}) e^{-\sum_{\lambda} (\alpha + \beta \epsilon_{\lambda}) a_{\lambda}} = \sum_{\{a_{\lambda}\}} W(\{a_{\lambda}\}) e^{-\sum_{\lambda} (\alpha + \beta \epsilon_{\lambda}) a_{\lambda}}$$

Here, $\{a_{\lambda}\}$ represent various energy level and particle numbers; W is the micro state number of distributing $\{a_{\lambda}\}$. Hence

$$Z_a = \sum_{\{a_{\lambda}\}} \prod_{\lambda} W_{\lambda} e^{-\alpha a_{\lambda} - \beta a_{\lambda} \epsilon_{\lambda}} = \prod_{\lambda} \left(\sum_{a_{\lambda}} \right) W_{\lambda} e^{-\alpha a_{\lambda} - \beta a_{\lambda} \epsilon_{\lambda}}$$

For Fermion, a state can only contain one particle

$$W_{\lambda} = \frac{g_{\lambda}!}{a_{\lambda}!(g_{\lambda} - a_{\lambda})},$$

here, g_{λ} is the degeneracy number. For Boson,

$$W_{\lambda} = \frac{(g_{\lambda} + a_{\lambda-1})!}{a_{\lambda}!(g_{\lambda} - 1)!}$$

Substitute W respectively

$$Z_{\lambda}^{(F)} = \sum_{a_{\lambda}=0}^{\infty} \frac{g_{\lambda}!}{a_{\lambda}!(g_{\lambda}-1)!} e^{-(\alpha+\beta\epsilon_{\lambda})a_{\lambda}} = (1 + e^{-\alpha-\beta\epsilon_{\lambda}})^{-g_{\lambda}} \quad (6.2)$$

$$Z_{\lambda}^{(B)} = \sum_{a_{\lambda}=0}^{\infty} \frac{(g_{\lambda}+a_{\lambda}-1)!}{a_{\lambda}!(g_{\lambda}-1)!} e^{-(\alpha+\beta\epsilon_{\lambda})a_{\lambda}} = (1 - e^{-\alpha-\beta\epsilon_{\lambda}})^{-g_{\lambda}} \quad (6.3)$$

Combine $Z_{\lambda}^{(F)}$ and $Z_{\lambda}^{(B)}$ together,

$$Z_G = \prod_{\lambda} Z_{\lambda} = \prod_{\lambda} (1 \pm e^{-\alpha-\beta\epsilon_{\lambda}})^{\pm g_{\lambda}}$$

$$\ln Z_G = \pm \sum_{\lambda} g_{\lambda} \ln(1 \pm e^{-\alpha-\beta\epsilon_{\lambda}})$$

Now, calculating the average distribution (assume that ξ is a given energy level)

$$\begin{aligned} \bar{a}_{\xi} &= \sum_N \sum_n a_{\xi} \rho_{N\xi} = \frac{1}{Z_G} \sum_{G_{\xi}} a_{\xi} W_{\xi} e^{-(\alpha+\beta\epsilon_{\xi})a_{\xi}} = \frac{1}{Z_{\xi}} \sum_{a_{\xi}} a_{\xi} W_{\xi} e^{-(\alpha+\beta\epsilon_{\xi})a_{\xi}} \\ &= -\frac{1}{Z_{\xi}} \frac{\partial}{\partial \alpha} Z_{\xi} = -\frac{\partial}{\partial \alpha} \ln Z_{\xi} = -\frac{\partial}{\partial \alpha} (\pm g_{\xi} \ln(1 \pm e^{-\alpha-\beta\epsilon_{\xi}})) = \frac{g_3}{e^{\beta(\epsilon_{\xi}-\mu)\pm 1}} \end{aligned}$$

6.2 The Symmetry of Quantum Statistic & Wave Function

For example, a wave function contains N -particle

$$\psi(\mathbf{r}_1, \dots, \mathbf{r}_N)$$

If $\mathbf{r}_i \leftrightarrow \mathbf{r}_j$, then

$$|\psi(\dots, \mathbf{r}_i, \dots, \mathbf{r}_j, \dots)|^2 = |\psi(\dots, \mathbf{r}_j, \dots, \mathbf{r}_i, \dots)|^2$$

then

$$\psi(\mathbf{r}_2, \mathbf{r}_1, \dots) = e^{i\alpha_{12}} \psi(\mathbf{r}_1, \mathbf{r}_2, \dots)$$

For Fermion, due to paul's principle, $\psi(\mathbf{r}_1, \mathbf{r}_1, \mathbf{r}_3) = 0$.

$$\lim_{\mathbf{r}_2 \rightarrow \mathbf{r}_1} \psi(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \dots) = 0$$

and $\psi(\mathbf{r}_1, \mathbf{r}_2, \dots) = -\psi(\mathbf{r}_2, \mathbf{r}_1, \dots)$. Since $e^{i\pi} = -1$, then $\alpha_{12} = \pi \pm 2n\pi$.

For Boson,

$$\lim_{\mathbf{r}_1 \rightarrow \mathbf{r}_2} \psi(\mathbf{r}_1, \mathbf{r}_2, \dots) = \lim_{\mathbf{r}_2 \rightarrow \mathbf{r}_1} \psi(\mathbf{r}_2, \mathbf{r}_1, \dots) = \psi(\mathbf{r}_1, \mathbf{r}_1, \dots) \neq 0$$

then we have $\alpha_{12} = \pm 2n\pi$.

In 3D space, rotate the particle \mathbf{r}_2 rotate around \mathbf{r}_1 has no topo barrier. $e^{i\phi} = e^{i2\pi n}$. If n is odd, then it's Fermion; or it is Boson.

In the space's dimension greater or equal than 3, only exist Bose or Fermi statistic.

6.3 Anyon (任意子), Braid Group (辫子群)

$\tau \in (0, \beta)$, then

$$\rho(x, x'; t) = \int_{(x)}^{(x')} Dx e^{-i \int_0^\infty dt \mathcal{L}}$$

where D means integral by all the paths.

In 3D space, path 1 is equivalent to path 2, since it could transform between two paths without break by the propagator; but when the paths are limited with in 2D space, it could not transform from path 1 to path 2 continuously. Now,

$$Dx \rightarrow \sum_{\alpha} \varphi_{\alpha} Dx_{\alpha}$$

where α is used to label the 有可相互连续互变的等价 in 2D space.. Since the integral is not related to the length of the path, φ_{α} is a phase factor $e^{i\theta}$, in which $|\varphi_{\alpha}| = 1$.

If there are N particles in a 2D space, that is

$$R^{2N} = \{\mathbf{r}_1, \dots, \mathbf{r}_N\} = M_N(\text{多连通})$$

and there many paths that form different 等价类 $\{\alpha\}$.

For N particles, the process of braiding form group. $B_M(\mathbb{R}^2)$: braid group, for example (2D) [!Figure]

$$(a) \quad x_i x_{i+1} = \sigma_i \quad (b) \quad \sigma_i \sigma_{i+1} \sigma_i = \sigma_{i+1} \sigma_i \sigma_{i+1}. \quad (c) \quad x_{i+1} x_i = \sigma_i^{-1}.$$

then, $\sigma_i \sigma_i^{-1} = 1$. and $\sigma_i \sigma_k = \sigma_k \sigma_i$, where $k \neq i \pm 1$. also 3D. [!Figure] (1) – (3) are the relation that a braid group needs to satisfy.

Non-abelian group.

The expression of Braid group:

$$\varphi_{\theta}(\sigma_i) = e^{-i\theta}, \quad (0 \leq \theta < 2\pi)$$

(a) $\theta = 0$, identity rep \rightarrow Boson

(b) $\theta = \pi$, Z_L rep \rightarrow Fermion

(c) $\theta = \text{rational}$ \rightarrow Fractional statistics Anyon.

Exchange: $r_i r_{i+1}$, rotate: $r_i r_{i+1} r_i$, then move $r_{i+1} r_i$. That is

$$\varphi_{\theta}(\sigma_i^{\pm 1}) = e^{\mp i\theta} = e^{-i\frac{\theta}{\pi}(\pm\pi)} = \exp\left[-i\frac{\theta}{\pi} \sum_{l < j} \Delta\phi_{lj}\right] \quad (6.4)$$

where, only $\Delta\phi_{i,i+1} = \pm\pi$, and $\Delta\phi_{lj} = 0$.

For normal α ,

$$\varphi_{\theta}(\alpha) = \exp\left(-i\frac{\theta}{\pi} \int dt \frac{d}{dt} \sum_{i < j} \phi_{ij}\right) \quad (6.5)$$

(? extra factor $\sum_\alpha \varphi_\alpha D\mathcal{L}$) For the original propagator,

$$K(r't'; rt) = \int Dr \exp \left\{ i \int_t^{t'} dt \left(\mathcal{L} - \frac{\theta}{\pi} \frac{d}{dt} \sum_{i < j} \phi_{ij} \right) \right\}$$

then

$$\psi(r't') = \int Dr K^{(0)}(r't', rt) \psi(r, t) \quad (6.6)$$

Now, define

$$\tilde{\psi}(rt) = \exp \left\{ -i \frac{\theta}{\pi} \int_r^{r^0} d\left(\sum_{i < j} \phi_{ij}\right) \right\} \psi(r, t) \quad (6.7)$$

where r^0 is some ref point. After considering braiding

$$\tilde{\psi}(r't') = \int Dr K(r't', rt) \tilde{\psi}(rt) \quad (6.8)$$

$$\tilde{\psi}(r, t) = \prod_{i < j} \frac{(z_i - z_j)^{\theta/\pi}}{|z_i - z_j|^{\theta/\pi}} \psi(r, t) = \prod_{i < j} (z_i - z_j)^{\theta/\pi} f(\theta, t) \quad (6.9)$$

where $f(\theta)$ is the exchange pair. If the two particles exchanged, then it will lead to a factor

$$(-1)^{\theta/\pi} = e^{i\frac{\theta}{\pi}\pi} = e^{i\theta}$$

that is a phase of $\exp(i\frac{\theta}{\pi} \arg(z_i - z_j))$.

6.3.1 Non-Abelian Statistics

If the wave function is s order degeneracy at a certain energy level, then for

$$\{\psi_i(\mathbf{r}_1, \dots, \mathbf{r}_N), \dots, \psi_s(\mathbf{r}_1, \dots, \mathbf{r}_N)\}$$

if we switch $\mathbf{r}_i \leftrightarrow \mathbf{r}_j$, it will lead

$$\psi_a(\mathbf{r}_1, \dots, \mathbf{r}_j, \mathbf{r}_i, \dots, \mathbf{r}_N) = \sum B_{ab} \psi_b(\mathbf{r}_1, \dots, \mathbf{r}_i, \mathbf{r}_j, \dots, \mathbf{r}_N)$$

where B_{ab} is a matrix. Write it into matrix equation form

$$\begin{pmatrix} \psi_1 \\ \vdots \\ \psi_s \end{pmatrix}_{r_j, r_i} = \begin{pmatrix} B_{11} & B_{12} & \cdots & B_{1s} \\ B_{21} & B_{22} & \cdots & B_{2s} \\ \vdots & \vdots & \ddots & \vdots \\ B_{s1} & B_{s2} & \cdots & B_{ss} \end{pmatrix} \begin{pmatrix} \psi_1 \\ \vdots \\ \psi_s \end{pmatrix}_{r_i, r_j} \quad (6.10)$$

obviously, $B_{ij}B_{jk} \neq B_{jk}B_{ij}$, which is the non-Abelian representation. of braid group. Tops Quan Computational

6.4 1D Statistics: Interaction Corresponding

For N particles with G states, how to promote Bose or Fermi Statistics.

$$W_B = \frac{[G + N - 1]!}{N!(G - 1)!}, \quad (6.11)$$

$$W_F = \frac{G!}{N!(G - 1)!}, \quad (6.12)$$

$$(6.13)$$

when $0 \leq s \leq 1$,

$$W_s = \frac{[G + (N - 1)(1 - S)]!}{N![G - SN - (1 - S)]!}$$

For a set of N : $\{N_x\}$, existing α to satisfy

$$W = \prod_{\alpha} \frac{[G_{\alpha} + N_{\alpha} - 1 - \sum_{\beta \neq \alpha} S_{\alpha\beta}(N_{\alpha} - \delta_{\alpha\beta})]!}{N_{\alpha}![G_{\alpha} - 1 - \sum_{\beta} S_{\alpha\beta}(N_{\alpha} - \delta_{\alpha})]!}, \quad (6.14)$$

let $S_{\alpha} = s\delta_{\alpha\beta}$,

i $S = 0$

$$W_B = \prod_{\alpha} \frac{(G_{\alpha} + N_{\alpha} - 1)!}{N_{\alpha}(G_{\alpha} - 1)} \quad (6.15)$$

ii $S = 1$

$$W_F = \prod_{\alpha} \frac{G_{\alpha}!}{N_{\alpha}!(G_{\alpha} - 1)!} \quad (6.16)$$

Example 6.4.1. δ -interaction Boson (Yang-Yang). For 1D, the Hamiltonian is

$$H = - \sum_{i=1}^N \frac{\partial^2}{\partial x_i^2} + 2C \sum_{i < j} \delta(x_i - x_j), \quad c \geq 0$$

Apply the Periodic Boundary Conditions, we can have the strict solution. Due to the translation conservation, apply the Fourier transformation

$$E = \sum_n K_i^2$$

while the continuous limitation

$$S_{\alpha\beta} \rightarrow S(k, k') = \delta(k - k') + \frac{1}{2\pi} \frac{d}{dk} \theta(k - k')$$

that is

$$\frac{d\theta(k - k')}{dk} = - \frac{2C}{C^2 + (k - k')^2}$$

where $\theta(k) = -2 \tan^{-1}(k/c)$.

(a) When $C \rightarrow \infty$, $\theta' = 0$, $S(k, k') = \delta(k - k')$.

(b) When $C \rightarrow 0$, then it's ideal boson.

Example 6.4.2 (Calogero-Sutherland model).

$$H = - \sum_{i=1}^N \frac{\partial}{\partial x_i} + \sum_{i < j} \lambda(\lambda - 1) \frac{\pi^2}{L^2} \sin\left(\frac{\pi}{L} \frac{x_i - x_j}{L}\right)^{-2}$$

when $L \rightarrow \infty$, the last term becomes $\lambda(\lambda - 1)/(x_i - x_j)^2$.

$$S(k, k') = \lambda\delta(k - k') = \delta(k - k') + (\lambda - 1)\delta(k - k')$$

when $\lambda = \frac{1}{2}$, it becomes a semion; when $\lambda = 2$, it becomes dual semion.

$$\epsilon(k) = \begin{cases} (k^2 - k_F^2)/\lambda, & |k| < k_F, \\ k^2 - k_F^2, & |k| > k_F \end{cases} \quad (6.17)$$

Now, the partition function becomes

$$Z_G = \prod_k \left(1 + e^{-\epsilon(k, T)/T} \right) \quad (6.18)$$

CHAPTER 7 Phase Transition, Critical Phenomenon & Renormalized Group

7.1 Categories of Phase transitions

- (a) 1 order: At the phase transition point, the chemical potential of the two phases are equal, but the partial derivation is not equal, that is

$$\mu^a - \mu^b = 0, \quad \text{and} \quad \rho_a \neq \rho_B \left(= \frac{\partial N}{\partial V}\right), S^a - S^b = -\left(\frac{\partial \mu^a}{\partial T}\right)_P + \left(\frac{\partial \mu^b}{\partial T}\right)_P \neq 0. \quad (7.1)$$

- (b) 2 order: $\Delta\mu = 0$, $\Delta S = 0$, $\Delta\rho = 0$. But the heat capacity $\frac{\partial^2 \mu}{\partial T^2}$, expansion factor $\frac{\partial^2 \mu}{\partial T \partial \beta}$, and the compression factor $\frac{\partial^2 \mu}{\partial p^2}$ are not continuous. $\Delta C_p \neq 0$, $\Delta\lambda$, $\Delta k \neq 0$

- (c) 3 order: BEC is advanced (without $K - T$ phane transition, 1 order or ∞ order)

7.2 Landau 2 order phase transition theory

描述相变：序参量，对称性破缺

序参量：用于区分两个相不同的物理量。例如：磁性物质中，有顺磁（磁化强度 $M = 0$ ），铁磁（磁化强度 $M \neq 0$ ）。

$$M = \sum (-1)^i s_i$$

[!Figure] 顺磁 [!Figure] 铁磁 \rightarrow SU(2) Conservatioin.

随 $T \downarrow$ 的相变，叫自发对称破缺。

自发破缺和序参量

- (a) 固液相变，平移不变性用 DLRO 参数表示。
- (b) 液体-液晶：转动对称性，密度的各向异性。
- (c) 超导 - Normal Metal: 基态粒子数守恒。序参量：|电子对 (Copper pair) 波函数|^2。
- (d) Boson 超流： $k = 0$ 粒子数守恒 \rightarrow ODLRO。
- (e) 二元合金固体结构相变：晶体点群 $\frac{W_1-W_2}{W_1+W_2}$

Definition 7.2.1 (序参量). 序参量概念也用到一级相变。

气 - 液相变：一级相变， $\rho_{\text{liquid}} - \rho_{\text{gas}} = 0$ 。

外磁场中的超导 - NM 相变 |超导波函数|^2

理想波色紫超流：三级相变. $k = 0$, 波色紫密度。

7.2.1 Gingbang-Landau

The Gibbs free energy of Superconductor, as a function of SC order parameter ψ .

At the critical point

$$g_s(\psi = 0) = g_n$$

and

$$g_s(\psi) = g_n + A|\psi|^2 + \frac{B}{2}|\psi|^4 + \dots$$

when $T < T_c$, $g_s < g_n$, and $A(T) < 0$ ($A(T_c) = 0$). then, around T_c

$$A(T) = (T - T_c) \left(\frac{\partial A}{\partial T} \right)_{T=T_c}$$

while $B = \text{Const}$, $B(T) = B(T_c) = B_c$.

$$\frac{dg_s(\psi)}{d\psi} = 0, \quad A + B_c|\psi|^2 = 0$$

then we have $|\psi|^2 = -A/B_c$, $g_s = g_n - A^2/2B_c$. On the other hand,

$$g_n - g_s = \mu_0 H_c^2(T)/2$$

around T_c ,

$$H_c^2(T) = \frac{A^2}{\mu_0 B_c} = \frac{(T_c - T)}{\mu_0 B_c} \left(\frac{\partial A}{\partial T} \right)_{T=T_c}, \quad H_c \propto T_c - T$$

In Landau's theory, GL: $|\psi|^2 = n_s$ should has a space distribution

$$g_s = g_n + A|\psi|^2 + \frac{B}{2}|\psi|^4 + \frac{1}{2n^*} | -i\hbar\nabla\psi |^2$$

while ψ is the pairing function. the second term becomes

$$| (i\hbar\nabla - e^* \mathbf{A})\psi |$$

where $e^* = 2e$.

$$\frac{\delta G_s}{\delta \varphi^\alpha} = 0 \Rightarrow \begin{cases} A\psi + B|\psi|^2\psi - \frac{\hbar^2}{2m^*} D^2\psi = 0 \\ \hat{n} \cdot D\psi = 0, \end{cases}$$

Consider weak field $|\mathbf{A}\psi| \gg |\Delta\psi|$. Then ignore \mathbf{A} , $\psi_0 = \sqrt{|A|/B}$. $\psi \sim \psi_0$, $f = \frac{\psi}{\psi_0}$, $f^* = f$. then we have

$$-\frac{\hbar^2}{2m_c^* A} \nabla^2 f + f - f^3 = 0.$$

To summarize

$$\begin{cases} \xi^2 \frac{d^2 f}{d\xi^2} + f - f^3 = 0 \\ f(0) = 0, \quad \frac{\partial f}{\partial z}|_{z \rightarrow 0} = 0 \\ f'(\infty) = 1, \quad \left(\frac{\partial f}{\partial z} \right)_{z \rightarrow \infty} = 1. \end{cases} \quad (7.2)$$

$$\int_{\infty}^z dx \xi^2 \left(\frac{df}{dz} \right) \frac{d}{dz} \left(\frac{df}{dz} \right) = \int_{\infty}^z dz \frac{d}{dz} \left(\frac{1}{4} f^4 - \frac{1}{2} f^2 \right)$$

Expand it

$$\frac{1}{2} \xi^2 \left(\frac{df}{dz} \right)^2 = \frac{1}{4} f^4 - \frac{1}{2} f^2 + \frac{1}{4} = \frac{1}{2} (1 - f^2)^2$$

Since $\frac{df}{dz} > 0$,

$$\frac{df}{dz} = \frac{1 - f^2}{\sqrt{2}\xi(T)}, \quad f = \operatorname{th} \frac{z}{\sqrt{2}\xi(T)}$$

where

$$\xi(T) = \frac{\hbar}{[2m^2(T_c - T) \frac{\partial A}{\partial T_c}]^{1/2}} \rightarrow \infty, \quad T \rightarrow T_c$$

The coherent long wave divergent at the critical point.

7.3 Critical Phenomenon and Critical Index

At critical point, $\xi \propto (T_c - T)^{-1/2}$.

Physics parameters behave the dependence of the power function of ΔT at the critical point, it's the so-called critical phenomenon. The power exponents are the critical exponents. $\alpha, \beta, \gamma, \delta, \nu, \eta$ stands for different physics parameters.

Since f is the function of $\epsilon = \frac{T-T_c}{T_c}$, that is

$$f(\epsilon) = \epsilon^\lambda (1 + B\epsilon^\lambda), \quad \lambda > 0$$

$\lambda = \lim_{\epsilon \rightarrow 0} \frac{\ln f(\epsilon)}{\ln \epsilon}$ is the critical exponent.

(a) β : The order parameter, which is decided with the change of temperature. $M(T) \propto (T - T_C)^\beta$

- Superconductivity: $|\psi| \propto (T - T_c)^{1/2}$
- Gas & liquid phase transition: $\Delta\rho \propto (T_c - T)^\beta$, $T \rightarrow T_c^-, p = p_c$. The order parameter $\sim |T - T_c|^\beta$.

(b) The flatness of critical isotherms δ

$$H = M^\delta \operatorname{sgn}(M) \quad (T \rightarrow T_c, H \rightarrow 0)$$

while

$$(p - p_c) \sim |\rho - \rho_c|^\delta \operatorname{sgn}(\rho - \rho_c), \quad (T = T_c, p \rightarrow p_c) \tag{7.3}$$

$$(H - H_c) \sim |\psi|^\delta \quad (T = T_c) \tag{7.4}$$

(c) χ_0, K_t, γ

$$X_0 = \left(\frac{\partial M}{\partial T} \right)_T \Big|_{H \rightarrow 0} \text{ Suspetibility, zero field magnetic ratio}$$

$$X_0 \sim (T - T_c)^{-\gamma}$$

$$K_T = -\frac{1}{V} \left(\frac{\partial V}{\partial \beta} \right)_T \text{ is isotherm compress ratio}$$

$$K_T \sim (T - T_c)^\gamma, (T \rightarrow T_c, p \rightarrow p_c)$$

$$\left. \frac{\partial \text{Order parameter}}{\partial \text{Extra field}} \right|_{\text{Extra field} \rightarrow 0} \sim (T - T_c)^{-\gamma}$$

is so-called zero-field response.

(d) Heat capacity α

- Magnetic: $C_H \sim (T - T_c)^{-\alpha}, H \rightarrow 0$
- Liquid: $C_V \sim (T - T_c)^{-\alpha}, T \rightarrow T_c, p = p_c$

(e) Correspond length ν $A(\mathbf{r}, t), B(\mathbf{r}, t)$

$$\langle (A(\mathbf{r}, t) - \langle A \rangle)(B(\mathbf{r}, t) - \langle B \rangle) \rangle$$

is called the correspond function between A and B .

$$\langle (S_i - \langle S_i \rangle)(S_j - \langle S_j \rangle) \rangle$$

$$A = B, \mathbf{r} = \mathbf{r}', t = t'$$

$$G(r, t) = \langle (A(\mathbf{r}, t) - \langle A \rangle)^2 \rangle = \langle A^2(\mathbf{r}, t) \rangle - \langle A \rangle^2$$

is called raise and fall.

MFA: $G(r) \sim \frac{1}{r} e^{-r/\xi}$, ξ is called the correspond length. At the critical point, $\xi \sim |T - T_c|^{-\nu}$.

$$f = \text{th} \frac{\delta}{\sqrt{2}\xi(T)}, f - 1 \sim e^{-\frac{\gamma}{\sqrt{2}\xi}}$$

For superconduct G-L equation, $\xi \propto |T - T_c|^{-1/2}$, $\nu = 1/2$.

But MF estimation some times has difference from the experient result.

(f) Correspond function

$$G(r) \sim r^{-d+2-\eta}, d = \text{space dimesions}$$

it should be a power law. After taking the Fourier transformation,

$$G(k) \sim k^{\eta-2}$$

- These critical exponents can be measured in experiments.
- Since the raises and falls around the critical point is large, it will take longer time to reach equilibrium (临界慢化)
- The accuracy of the measure is not good (P. 480, Lin).

These critical exponents have the relations: scaling law (标度律).

$$\alpha + 2\beta - \gamma = 2 \quad (7.5)$$

$$\gamma = \beta(\delta - 1) \quad (7.6)$$

$$\gamma = \nu(2 - \eta) \quad (7.7)$$

$$\nu d = 2 - \alpha \quad (7.8)$$

There are $6 - 4 = 2$ independent variables. 这些关系与具体的微观细节无关，具有一定的普适性（普适性假设）。

The critical behaviors of the system is determined by two variables: One is the dimension of space d , and the dimension of the order parameter n . If $d = n$, the critical phenomena are included in the same 普适类.

The order parameters of a system can be real number, complex number, or vector. If it's 实数, then $n = 1$; if it's complex number, then $n = 2$. For 3D space vector, $n = 3$.

- $n = 1$, 气液相变密度差二元合金中, 占位率差.
- $n = 2$, XY model, wave functions in superflow and superconduct.
- $n = 3$, Heisenberg model

The physics behind 普适性: The correspond length will be infinity at the critical point.

7.4 Quantum Phase Transition

Quantum Phase Transition is at the temperature of $T = 0$, the different phases of the system occur phase transition due to the change of some parameter.

For a finite system, assume $H(g)$ is Hamiltonian, g is coupling constant. Usually, $E(g)$ is the smooth function of g , means that no phase transition.

Sometimes

$$H = H_0 + gH,$$

where $[H_0, H_1] = 0$. Then, H_0, H_1 can be diagnosed at the same time, and they have the common eigenfunction

$$E_n = E_n^{(0)} + gE_n^{(1)}$$

$$E_0 = E_0^{(0)} - gE_0^{(1)}, E_1 = E_1^{(0)} - gE_1^{(1)}. \text{ At } g = g_c, E_0(g_c) = E_1(g_c), g_c = \frac{E_1^{(0)} - E_0^{(0)}}{E_0^{(1)} - E_1^{(1)}}.$$

$$E_1 = 1 + g3, E_0 = 1 + g(-2) \Rightarrow g_c = -\frac{1}{5}$$

Since $[H_0, H_1] \neq 0$. For infinite lattice system, will have the second condition,

1. Simple level crossing: 1st level phase transform
2. The opened g^a is infinite near to zero, then quantum phase transformation will take place. The correction function will have difference on 定性 before and after phase transition.

The quantum phase transition take place at the energy gap $\Delta \rightarrow 0$, or the 元激态 on the basis state.

$$\Delta \sim J|q - q_c|^{Z\nu}$$

- (a) $k_B T < \Delta$. quantum fluctuation will stronger than the heat fluctuation. Quantum critical
- (b) $k_B T > \Delta$. quantum fluctuation will weaker than the heat fluctuation.

7.5 Ising Model

Hamiltonian

$$H = -J \sum_{\langle ij \rangle} S_i^z S_j^z - B \sum_i S_i^z$$

where $S_i^z = \pm \frac{1}{2}\hbar$, $S_i^z \rightarrow \sigma_i = \pm 1$

7.5.1 Average field approximation

Hamiltonian

$$H = - \sum_i \sigma_i (B = J \sum_{\delta} S_{i+\delta})$$

Replace $\sigma_{i+\delta}$ with $\bar{\sigma} = \langle \sigma_{i+\delta} \rangle$, $\sum_{\delta} \bar{\sigma} = z\bar{\sigma}$. Now,

$$H_{MF} = - \sum_i (B + \bar{h}) \sigma_i$$

where $\bar{h} = zJ\bar{\sigma}$. Then

$$\begin{aligned} Z_{\parallel} &= \sum_{\sigma_1} \cdots \sum_{\sigma_N} \exp \left[\sum_i \beta(B + \bar{h}) \sigma_i \right] = \sum_{\sigma_1} \exp [\beta(B + \bar{h}) \sigma_1] \sum_{\sigma_2} \exp [\beta(B + \bar{h}) \sigma_2] \\ &= \prod_i \left(\sum_{\sigma_i} \exp \beta(B + \bar{h}) \sigma_i \right) = \prod_i [\exp \beta(B + \bar{h}) - \exp [-\beta(B + \bar{h})]] = \left[2 \operatorname{ch} \left(\frac{B + \bar{h}}{k_B T} \right) \right]^N \end{aligned}$$

and

$$\begin{aligned} F &= -k_B T \ln Z_N = -N k_B T \left\{ \ln z + \ln \operatorname{ch} \left[\frac{B}{k_B T} + \frac{zJ}{k_B T} \bar{\sigma} \right] \right\} \\ M &= N\bar{\sigma} = -\frac{\partial F}{\partial B} = N \operatorname{th} \left(\frac{B}{k_B T} + \frac{zJ}{k_B T} \bar{\sigma} \right) \end{aligned}$$

then we can obtain the expression of σ (it's the 自洽方程 of σ).

- If $B = 0$, then $\bar{\sigma} = \text{th}\left(\frac{ZJ}{k_B T}\bar{\sigma}\right) = \text{th}\left(\frac{T_c}{T}\bar{\sigma}\right)$, where $T_c = \frac{ZJ}{k_B}$. Denote $y = \text{th}\left(\frac{T_c}{T}\bar{\sigma}\right)$, $u' = \bar{\sigma}$. Then we can plot $y(\bar{\sigma})$: linear; Also $T > T_c$ and $T < T_c$. $\bar{\sigma} = 0$ or $\pm\sigma_0$.

In another way, $H(-\sigma_i) = H(\sigma_i)$, means Z_2 has the symmetry, leads to 自发破缺.

$$\sigma_0 = \sigma_0(T), T \sim T_C^-, \bar{\sigma}_0 \sim 0.$$

$$\text{th} \frac{T_c}{T} \bar{\sigma} \approx \frac{T_c}{T} \bar{\sigma} - \frac{1}{3} \left(\frac{T_c}{T} \bar{\sigma} \right)^3 = \bar{\sigma}$$

then we obtain $\bar{\sigma} = \sqrt{3} \left(1 - \frac{T}{T_c} \right)^{1/2}$, and $M = N\bar{\sigma} \sim (T_c - T)^{1/2}$.

$$C_B = \begin{cases} 0, & T \rightarrow T_c^+ \\ 3Nk_B T_c, & T \rightarrow T_c^- \end{cases}$$

Now $M \sim (T - T_c)^{-1}B$, $\chi = \frac{\partial M}{\partial B} \sim (T - T_c)^{-1}$, $M(T_c, B) \sim B^{1/3}$. $\beta = \frac{1}{2}$, $\alpha = 0$, $\gamma = 1$, $\delta = 3$, $T_c = \frac{zJ}{k_B}$, it's finite.

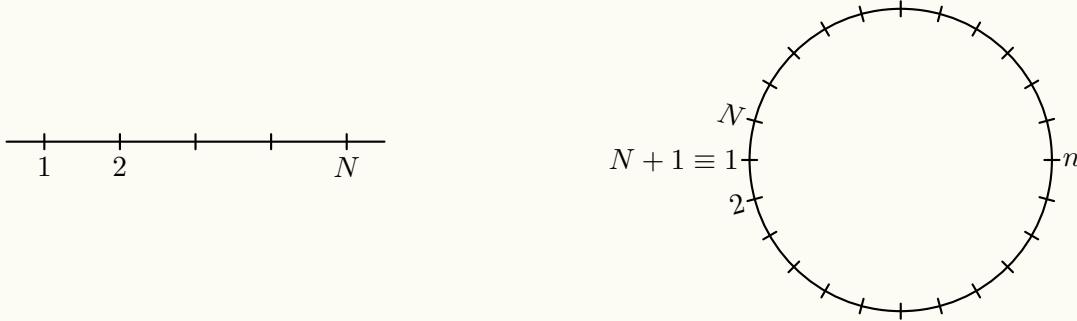
- If $B \neq 0$, then ...

7.5.2 The exact solution of 1D Ising model

The Hamiltonian

$$H = -J \sum_n \sigma_n \sigma_{n+1} - h \sum_n \sigma_n$$

with a 1D chain, or a circle (Periodic Boundary Condition $N + 1 \equiv 1$)



The partition function is

$$\begin{aligned} Z &= \sum_{\sigma_1, \dots, \sigma_N} \exp\{K \sum_n \sigma_n \sigma_{n+1}\} \exp\{B \sum_n \sigma_n\} \\ &= \sum_{\substack{\{\sigma_n\} \\ \{\sigma'_n\}}} \exp\{B\sigma_1\} \delta_{\sigma_1 \sigma'_1} \exp\{K\sigma'_1 \sigma_2\} \exp\{B\sigma_2\} \delta_{\sigma_2 \sigma'_2} \exp\{K\sigma'_2 \sigma_3\} \cdots \exp\{B\sigma_N\} \delta_{\sigma_N \sigma'_N} \exp\{K\sigma'_N \sigma_1\} \end{aligned} \quad (7.9)$$

where $K = J/kT$, and $B = h/kT$. We define $(V_1)_{\sigma_i \sigma_j} = \exp(K\sigma_i \sigma_j)$, $\sigma_i = \pm 1$, $\sigma_j = \pm 1$ stands for two directions of spins $|\uparrow\rangle$ and $|\downarrow\rangle$. Conduct a 2×2 matrix. Also for $(v_2)_{\sigma_i \sigma_j} = \exp(B\sigma_i) \delta_{\sigma_i \sigma_j}$. The matrix can be expressed as

$$V_1 = \begin{pmatrix} e^K & e^{-K} \\ e^{-K} & e^K \end{pmatrix}, \quad \text{and} \quad V_2 = \begin{pmatrix} e^B & 0 \\ 0 & e^{-B} \end{pmatrix} \quad (7.10)$$

so, we can express Z in terms of the elements of matrices

$$\begin{aligned} Z &= \sum_{\{\sigma_n\}} (V_2)_{\sigma_1 \sigma'_1} (V_1)_{\sigma'_1 \sigma_2} \cdots (V_2)_{\sigma_N \sigma'_N} (V_1)_{\sigma'_N \sigma_1} \\ &= \text{Tr}(V_2 V_1 \cdots V_2 V_1) = \text{Tr}(V_2 V_1)^N = \text{Tr}(V_2 V_1^{1/2} V_1^{1/2})^N = \text{Tr}(V_1^{1/2} V_2 V_1^{1/2})^N = \text{Tr } V^N \end{aligned} \quad (7.11)$$

where

$$V = \begin{pmatrix} e^{K+B} & e^{-K} \\ e^{-K} & e^{K-B} \end{pmatrix} = e^{K+B} I + e^{-K} \sigma_x \quad (7.12)$$

The eigenfunction

$$\det(V - \lambda) = 0, \lambda_{\pm} e^K \operatorname{ch} B \pm \sqrt{e^{2K} \operatorname{sh}^2 B + e^{-2K}} \quad (7.13)$$

Then, the trace to V^N is

$$\text{Tr}(V^N) = \text{Tr} \left[\begin{pmatrix} \lambda_+ & 0 \\ 0 & \lambda_- \end{pmatrix}^N \right] = \lambda_+^N + \lambda_-^N = \lambda_+^N [1 + (\lambda^-/\lambda_+)^N] \xrightarrow{N \rightarrow \infty} \lambda_+^N \quad (7.14)$$

From the expansion of λ_+ , we have

$$f = \frac{F}{N} = -\frac{1}{\beta^N} \ln Z = -\beta^{-1} \ln \lambda_+, \quad M \propto -\frac{\partial f}{\partial h} = \beta^{-1} \frac{\partial \ln \lambda_+}{\beta^{-1} \partial B} = \operatorname{sh} B (\operatorname{sh}^2 B + e^{-4K})^{1/2} \xrightarrow[T>0]{B \rightarrow 0} 0 \quad (7.15)$$

So, at a finite temperature, there's no phase transition, and the mean field $T_c = 2J/k_B$. In summary,

$$T = 0, \quad M = \frac{\operatorname{sh} B}{\operatorname{sh} B = 1}, \quad T_c = 0 \quad (7.16)$$

7.5.3 2D Ising Model

For 2D Ising model, $h = 0$ have exact solution. Now the matrix

$$V = \begin{pmatrix} e^K & e^{-K} \\ e^{-K} & e^K \end{pmatrix} = e^K I + e^{-K} \sigma_x = e^K (I + e^{-2K} \sigma_x) \quad (7.17)$$

we can define $\operatorname{th} a = u p e^{-2K}$. Then

$$\exp(a \sigma_x) \left(= \sum_{n=0}^{\infty} \frac{1}{n!} (a \sigma_x)^n \right) = I \operatorname{ch} a + \sigma_x \operatorname{sh} a$$

Then, we can define

$$V = A \exp(a \sigma_x) = A \operatorname{ch} a (I + \operatorname{th} a \sigma_x) = A \operatorname{ch} a (I + e^{-2k} \sigma_x)$$

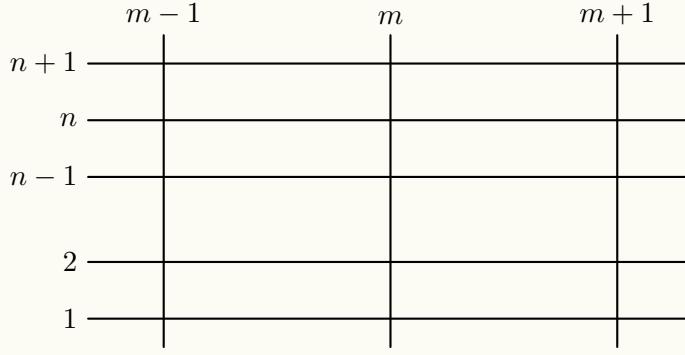
And A can be expressed as

$$A = \frac{1}{\operatorname{ch} a \sqrt{\operatorname{th} a}} = \frac{1}{\sqrt{\operatorname{ch} a \operatorname{sh} a}} = \sqrt{\frac{2}{\operatorname{sh} 2a}}$$

Since

$$\operatorname{sh} 2a \operatorname{sh} 2k = 2 \operatorname{sh} a \operatorname{ch} a \left(\frac{1}{\operatorname{th} a} - \operatorname{th} a \right) = 2(\operatorname{ch}^2 a - \operatorname{sh}^2 a) = 2, \quad \text{then} \quad A = \sqrt{\operatorname{sh} 2k}, F = \sqrt{\operatorname{sh} 2k} \exp(a \sigma_x)$$

We can draw the 2D lattice: $j = (1, 2), (2, 3), \dots, (N, 1)$.



Consider fixed the m -th column, $V \rightarrow V(m, j) = \sqrt{\sinh 2k_1} \exp(a\sigma_j^{x(m)})$; The Ising model for this column is

$$H = -J \sum_{m,n} \sigma_{mn} \sigma_{m,n+1} - J_2 \sum_{m,n} \sigma_{mn} \sigma_{m+1,n}, \quad (7.18)$$

$$Z = \sum_{\{\sigma_{m,n}\}} \exp \left(\underbrace{K_1 \sum_{mn} \sigma_{mn} \sigma_{m,n+1}}_{\prod_j V_1(j,m)} + K_2 \sum_{mn} \sigma_m \sigma_n \sigma_{m+1,n} \right) \quad (7.19)$$

and we can define $V_2(m)$

$$V_2(m) \equiv e^{K_2 \sum_j \sigma_{m,j} \sigma_{m+1,j}} V(m) = (\sinh 2k_1)^{N/2} e^{K_1 \sum_j \sigma_j^{x(m)}} \quad (7.20)$$

In terms of trace

$$Z = \text{Tr}(V_2^{1/2} V_1 V_2^{1/2})^M = \text{Tr } V^M,$$

where V_2 and V_1 are $2M \times 2M$ matrices, and

$$\{\sigma_i^a, \sigma_j^b\} = \delta^{ab}, \quad [\sigma_i^a, \sigma_j^b]_{i \neq j} = 0$$

To make it behaves as fermion, we shall

$$c_j = \exp \left(\pi i \sum_{l=1}^{j-1} \sigma_{l+} \sigma_{l-} \right) \sigma_j^- \quad (7.21)$$

$$c_j^+ = \exp \left(\pi i \sum_{l=1}^{j-1} \sigma_{l+} \sigma_{l-} \right) \sigma_j^+ \quad (7.22)$$

where $\sigma_i^\pm = \sigma_i^x \pm i\sigma_i^y$. Then we have

$$\{c_j^+, c_{j'}^-\} = \delta_{jj'}, \quad c_j^\dagger c_j = \sigma_j^+ \sigma_j^- \quad (7.23)$$

which is so-called Jordan-Wigner Transmission. To inverse, we have

$$\sigma_{j+} = \exp \left(i\pi \sum_{l=1}^{j-1} c_l^\dagger c_l \right) c_j^\dagger, \quad \sigma_j^- = \exp \left(i\pi \sum_{l=1}^{j-1} c_l^\dagger c_l \right) c_j \quad (7.24)$$

We make a transformation in V_1 , and V_2

$$(\sigma_x, \sigma_y, \sigma_z) \rightarrow (\sigma'_x, \sigma'_y, \sigma'_z) = (-\sigma_z, \sigma_y, \sigma_x) \quad (7.25)$$

i.e., $\sigma_x \sigma_y = i \sigma_z \rightarrow \sigma'_x \sigma'_y = i \sigma'_z$. Then,

$$V_1 = (\operatorname{sh} 2K_1)^{M/2} \exp \left[-2K_1 \sum_j \left(\sigma_{j+} \sigma_{j-} - \frac{1}{2} \right) \right] = (\operatorname{sh} 2k_1)^{M/2} \exp \left[-2K_1 \sum_j \left(c_j^\dagger c_j - \frac{1}{2} \right) \right] \quad (7.26)$$

In V_2 , make the transformation $\sigma_z \rightarrow \sigma_x = \sigma_+ - \sigma_-$, Then

$$V_2 = \exp \left\{ K_2 \sum_{j=1}^{M-1} (c_j^\dagger - c_j)(c_{j+1}^\dagger + c_{j+1}) - (-1)^{\hat{n}} (c_M^\dagger - c_M)(c_1^\dagger - c_1) \right\} \quad (7.27)$$

where $\hat{n} = \sum_{l=1}^M c_l^\dagger c_l$. Now,

$$\frac{F}{N} = -\beta^{-1} \left[\ln(2 \operatorname{sh} 2K_1)^{1/2} + \frac{1}{4\pi} \int_{-\pi}^{\pi} \epsilon_q dq \right] \quad (7.28)$$

where

$$\cos \epsilon_q = \operatorname{ch} 2K_2 \operatorname{ch} 2a - \operatorname{sh} 2K_2 \operatorname{sh} 2a \cos q$$

Since $\operatorname{sh} 2a = \operatorname{sh} 2K_2$ is fixed, then $J_1 = J_2$. The critical temperature now satisfies

$$\frac{k_B T_c}{J} \approx 2.7 \neq 0 \quad (7.29)$$

The heat capacity ratio

$$C \propto \ln \left| 1 - \frac{T}{T_c} \right|, \quad (7.30)$$

$$M \propto \begin{cases} (1 - T/T_c)^{1/8}, & T < T_c, \\ 0, & T > T_c, \end{cases} \quad (7.31)$$

$$g(r) \sim \begin{cases} (T - T_c)^{1/4} \frac{e^{-r/3}}{(r/3)^{1/2}}, & T > T_c, \\ (T_c - T)^{1/4} \frac{e^{-2r/3}}{(r/3)^{1/2}}, & T < T_c, \end{cases} \quad (7.32)$$

$$\chi \sim |t|^{-7/4}, \quad t = (T - T_c)/T_c \quad \xi \sim (T - T_c)^{-1}. \quad (7.33)$$

To compare with the exact solution,

Exact Solution	$\alpha = 0$ (\ln)	$\beta = 1/8$	$\gamma = 7/4$	$\nu = 1$	$\eta = 1/4$	$\delta = 15$
MF	$\alpha = 0$ (discontinuation)	$\beta = 1/2$	$\gamma = 1$	no ν	no η	$\delta = 3$

7.5.4 1D + 1D dimensional quantum Ising model

Which is so-called the Horizontal field Ising model, in a chain. The Hamiltonian is

$$H = -K \sum_n \sigma_n^z \sigma_{n+1}^z - \mathbf{h} \cdot \sum_n \boldsymbol{\sigma}_n \quad (7.34)$$

where $\mathbf{h} = (h_x, 0, 0)$, $\boldsymbol{\sigma} = (\sigma_x, \sigma_y, \sigma_z)$. Obviously, $[\sigma^z, \sigma^x] \neq 0$. We shall prove that *1D + 1D quantum Ising model is equivalent to 2D Ising model*.

Proof. Starting from the 0D + 1D single spin model is equivalent to 1D Ising model

$$Z_{1D} \longleftrightarrow \text{Tr } e^{-H_Q/kT}, \quad H_Q = -h_x \sigma_x$$

and M site lattice (K_1).

$$V = V_1 = e^{K_1} (1 + e^{-2K_1} \sigma^x) = \sqrt{\frac{M}{\beta h_x}} \left(1 + \frac{h_x \beta}{M}\right) \quad (7.35)$$

$$V^M = \left(\frac{M}{\beta h_x}\right)^{M/2} \left(1 + \frac{h_x \beta}{M} \sigma^x\right)^M = \left(\frac{M}{\beta h_x}\right)^{M/2} (1 - \Delta\tau H_Q)^{\beta/\Delta\tau} \xrightarrow{\Delta\tau \rightarrow 0} \left(\frac{M}{\beta h_x}\right)^{M/2} e^{-\beta H_Q} \quad (7.36)$$

where $\Delta\tau = \beta/M$. When $M \rightarrow \infty$,

$$Z_{1D} = \text{Tr } V^M = \text{Tr } e^{-\beta H_Q} \quad (7.37)$$

For 2D Ising model, the n -th chain

$$V_n(j) = \sqrt{\frac{M}{\beta h_x}} \left(1 + \frac{h_x \beta}{M} \sigma_n^x\right), \quad V_n^M = \left(\frac{M}{\beta h_x}\right)^{M/2} e^{-\beta h_Q(n)} \quad (7.38)$$

Concerning the couple between chains,

$$\begin{aligned} \exp\left(K_i \sum_{m,n} \sigma_{m,n}^z \sigma_{m,m-1}^z\right) &= \prod_m \exp\left(K_2 \sum_n \sigma_{m,n}^z \sigma_{m,n+1}^\delta\right) \\ &\approx \exp\left(\frac{K_2}{\Delta\tau} \beta \sum_n \sigma_n^z \sigma_{n+1}^z\right) \equiv \exp(\beta K \sum_n \sigma_n^z \sigma_{n+1}^z) \end{aligned}$$

So, we obtain the Horizontal field 2D Ising model

$$H_{2D} = \left(-K \sum_n \sigma_n^z \sigma_{n+1}^z - h_x \sum_n \sigma_n^x\right) \quad (7.39)$$

Now, back to the proof. We have $h\Delta\tau = e^{-2K_2}$, $K\Delta\tau \equiv K_\tau$. At the critical point, $\text{sh } 2K_x \text{ sh } 2K_\tau = 1$, or $\frac{2K\Delta\tau}{2h\Delta\tau} = 1$, then we have $K = h$.

$$\begin{cases} K = h, & \text{QCP} \\ K > h, & \text{FM} \\ K < h, & \text{Quantum disorder} \end{cases} \quad (7.40)$$

The Quantum 1 + 1 Ising model (such as 2D) Lagrangian is

$$\psi \bar{\psi} + \bar{\psi} \partial \bar{\psi} \quad (7.41)$$

which is very simple, where $\partial = \partial_x - i \partial_y$, $\bar{\partial} = \partial_x + i \partial_y$, and $\bar{\partial}\psi = 0$, $\partial\bar{\psi} = 0$. \square

7.6 Renormalization Group

Basic Point

- (a) 作“粗粒化”尺度变换，RG is a “half-group” (No inverse element)，找出 RG 规律.
- (b) Determine the “fixed-points”，find the fixed-points that concerning to the critial points.
- (c) Linearization the RG transformation, determine the critial index.

7.6.1 Real space RG

For the Spin model: d -space dim. Treat the integral l^d spins as a spin, i.e., for $l = 2, d = 2$,

$$\sigma : \begin{bmatrix} \uparrow & \uparrow \\ \uparrow & \uparrow \end{bmatrix} \implies \sigma' : \uparrow$$

$\sigma \rightarrow \sigma' = \pm 1$. Then the previous N sites becomes current $N = l^{-d}N$ sites.

For the spins, let $l = 2, d = 2$.

$$\left(\begin{bmatrix} \uparrow \uparrow \\ \downarrow \downarrow \\ \uparrow \downarrow \\ \downarrow \uparrow \end{bmatrix}, \begin{bmatrix} \uparrow \downarrow \\ \downarrow \uparrow \\ \uparrow \uparrow \\ \downarrow \downarrow \end{bmatrix}, \begin{bmatrix} \downarrow \downarrow \\ \uparrow \uparrow \\ \uparrow \downarrow \\ \downarrow \uparrow \end{bmatrix} \right)$$

At the beginning, $N = 24$, then $N' = 2^{-2}N = 24/4 = 6$.

$$\begin{cases} \begin{bmatrix} -1 & -1 \\ -1 & 1 \end{bmatrix} \begin{bmatrix} -1 & -1 \\ 1 & 1 \end{bmatrix} \begin{bmatrix} 1 & 1 \\ 1 & 1 \end{bmatrix} & \sigma' = 1 \\ \begin{bmatrix} -1 & 1 \\ 1 & 1 \end{bmatrix} \begin{bmatrix} 1 & -1 \\ -1 & -1 \end{bmatrix} & \sigma' = -1 \end{cases}$$

Using the decimation (消元法)

$$Z = \sum_{\{\sigma_i\}} \exp[-\beta H_N(\sigma_i)] \quad (7.42)$$

to let spins' degrees of freedom on the the $N - N'$ sites summed, then

$$Z = \sum_{\{\sigma'_i\}} \exp[-\beta H_{N'}(\sigma_i)] = Z \quad (7.43)$$

Assume H_N is a 1D Ising model. $i = 1, 2, \dots, N = 1, 3, 5, \dots, 2, 4, \dots, 6$. Then sum all the odd blocks. If the free energies at the critial point are equal in two systems,

$$N' f^{(s)}(t', h') = N f^{(s)}(t, h), \quad N' = N l^{-d}$$

where $t = (T - T_c)/T_c$, and h is the external field.

$$f^{(5)}(t, h) = l^{-d} f^{(5)}(t, h)$$

where t, t', h, h' are all small. So the linear part

$$t' = l^{y_t} t, \quad h' = l^{y_h} h$$

According to Scaling assumption, f is not sensitive to scaling. f should be a function of the following variables that have no relation l

$$\frac{h'}{|t'|^{y_h/y_t}} = \frac{h}{|t|^{y_h/y_t}} = \frac{h}{|t|^\Delta}$$

At the same time, to cancel l^{-d} , $f^{(s)}$ should have the expression

$$f^{(s)}(t', h') = |t'|^{d/y_t} \tilde{f}(h/|t|^\Delta) = l^{-d} |t'|^{d/y_t} \tilde{f}(h/|t|^\Delta) = l^{-d} |l^{y_t} t|^{d/y_t} \tilde{f}(h/|t|^\Delta) = |t|^{d/y_t} \tilde{f}(h/|t|^\Delta)$$

If these can be achieved, then

$$\begin{aligned} C_n &= \frac{\partial^2 f^{(s)}}{\partial t^2} \sim |t|^{-(2-d/y_t)} \Rightarrow \alpha = 2 - \frac{d}{y_t} \\ \frac{M}{N} &= \frac{\partial f^{(s)}}{\partial h} = |t|^{d/y_t} |t|^{-\Delta} \frac{d}{d(h/|t|^\Delta)} \tilde{f}(h/|t|^\Delta) \sim |t|^{d/y_t - \Delta} \\ \frac{\partial M}{\partial H} &= \frac{\partial^2 f^{(s)}}{\partial h^2} \sim |t|^{d/y_t - 2\Delta} \end{aligned}$$

where $\beta = \frac{(d-y_h)}{y_t} = 2 - \alpha - \Delta$, $\gamma = \frac{2y_h - d}{y_t} = -(2\alpha - 2\Delta)$, $\gamma = \beta(\delta - 1)$, $\delta = \frac{\Delta}{\beta} = y_h/(\alpha - y_h)$, $\gamma = \beta(\delta - 1)$. The correlation length $\xi' = l^{-1}\xi$. We also want

$$\xi \sim |t|^{-\nu}, \quad \xi' \sim |t'|^{-\nu}, \quad l^{-1} = (\xi'/\xi) = (t'/t)^{-\nu}, \quad \nu y_t = 1, \quad \nu = 1/y_t$$

Then, $d \cdot \nu = d/y_t = 2 - \alpha$. The Green function

$$\begin{aligned} g(r') &= \langle \sigma'(\mathbf{r}'_1) \sigma'(\mathbf{r}'_2) \rangle \sim r_{12}'^{-(d+2-\eta)}, \\ g(r) &= \langle \sigma(\mathbf{r}_1) \sigma(\mathbf{r}_2) \rangle \sim r_{12}^{-(d+2-\eta)} \end{aligned}$$

So, $\sigma'(\mathbf{r}') = l^{(d+2-\eta)/2} \sigma(\mathbf{r})$, $\gamma = (1 - \eta)\nu$, $\eta = d + 2 - 2y_h$, $\sigma'(\mathbf{r}') = l^{y_h} \sigma(\mathbf{r})$, i.e., σ and h has the same rescaling.

7.6.2 Examples: 1D Ising model

Example 7.6.1 (Exponents (Exact result in Pathria's book)).

$$Z = \sum_{\{\sigma_i\}} \exp \left[\sum_{i=1}^N \left(K_0 + K \sigma_i \sigma_{i+1} + \frac{B}{2} (\sigma_i + \sigma_{i+1}) \right) \right]$$

where $K_0 = 0$, $K = \beta J$, $B = \beta h$. Then the exponent

$$\exp[\dots] = \prod_{j=1}^{N/2} \exp[2K_0 + K(\sigma_{2j-1}\sigma_{2j} + \sigma_{2j}\sigma_{2j+1}) + \frac{1}{2}B(\sigma_{2j-1} + 2\sigma_{2j} + \sigma_{2j+1})]$$

where $\sigma_{2j} = \pm 1$. Then sum over σ_{2j}

$$\begin{aligned} &\prod_{j=1}^{N/2} \left\{ \exp \left[2K_0 + K(\sigma_{2j-1} + \sigma_{2j+1}) + \frac{1}{2}B(\sigma_{2j-1} + \sigma_{2j+1} + 2) \right] + \exp \left[2K_0 - K(\sigma_{2j} + \sigma_{2j+1}) + \frac{1}{2}B(\sigma_{2j-1} + \sigma_{2j+1}) + 3 \right] \right\} \\ &= \prod_{j=1}^{N/2} \exp \left[2K_0 + \frac{1}{2}B(\sigma_{2j-1} + \sigma_{2j+1}) \right] \cdot 2 \operatorname{ch}(K(\sigma_{2j-1} + \sigma_{2j+1}) + 3) \end{aligned}$$

Do the transformation $\sigma_{2j+1}, j = 0, 1, 2, \dots \rightarrow \sigma'_j$.

$$Z = \sum_{\{\sigma'_j\}} \prod_{j=1}^{N/2} \exp(2K_2) 2 \operatorname{ch}(K(\sigma'_j + \sigma'_{j+1}) + B) \exp\left[\frac{1}{2}B(\sigma'_j + \sigma'_{j+1})\right]$$

If we require Z is still Ising model, then

$$Z = \sum_{\{\sigma'_j\}} \exp\left\{ \sum_{j=1}^{N/2} \left[K'_0 + K' \sigma'_j \sigma'_{j+1} + \frac{1}{2} B' (\sigma'_j + \sigma'_{j+1}) \right] \right\}$$

What are K'_0 , K' , and B' ?

(a) $\sigma'_j = \sigma'_{j+1} = 1$
 $\exp(K'_0 + K' + B') = \exp(2K_0 + B) 2 \operatorname{ch}(2K + B)$

(b) $\sigma'_j = \sigma'_{j+1} = -1$
 $\exp(K'_0 + K' - B') = \exp(2K_0 - B) 2 \operatorname{ch}(-2K + B)$

(c) $\sigma'_j = \sigma'_{j+1} = \pm 1$
 $\exp(K'_0 - K') = \exp(2K_0) 2 \operatorname{ch} B$

Define $\exp(K'_0) = \alpha$, $\exp K' = y$, $\exp B' = z$. Then,

$$\begin{aligned} xyz &= 2 \exp(2K_0 + B) \operatorname{ch}(2K + B) \\ xy/2 &= 2 \exp(2K_0 - B) \operatorname{ch}(-2K + B) \\ x/2 &= 2 \exp(2K_0) \operatorname{ch} B \\ e^{K'_0} &= x = 2 e^{2K_0} [\operatorname{ch}(2K + B) \operatorname{ch}(2K - B) \operatorname{ch}^2 B]^{1/4} \\ e^{K'} &= y = [\operatorname{ch}(2K + B) \operatorname{ch}(2K - B) / \operatorname{ch}^2 B]^{1/4}, \\ e^{B'} &= z = e^B [\operatorname{ch}(2K + B) / \operatorname{ch}(2K - B)]^{1/2} \end{aligned}$$

Starting at

$$Z_N(K, B) = e^{N' K'_0} Z_{N'}(K', B')$$

where $K_0 = 0$.

$$K' = \frac{1}{4} \ln [\operatorname{ch}(2K + B) \operatorname{ch}(2K - B)] - \frac{1}{2} \ln \operatorname{ch} B \equiv R_K(K, B), \quad (7.44)$$

$$B' = B + \frac{1}{2} \ln [\operatorname{ch}(2K + B) / \operatorname{ch}(2K - B)] \equiv R_B(K, B) \quad (7.45)$$

which is so-called RG equations.

At the fixed points

$$R_K(K^*, B) = K^*, \quad R_B(K^*, B^*) = B^*$$

When $K^* = 0$, for any B , it is fixed point. The zero-interaction or $T \rightarrow \infty$. For another, $K^* \rightarrow \infty$, $B^* = 0$. Let $h = 0$, then $T \rightarrow 0$.

Around the fixed point of $T \rightarrow 0$,

$$\begin{aligned} K' &= \frac{1}{2} \ln \operatorname{ch} 2K \approx \frac{1}{2} \ln e^{2K}/2 = K - \frac{1}{2} \ln 2, \\ B' &\approx B + \frac{1}{2} \ln e^{2B} = 2B \end{aligned}$$

Define $t = \exp(-\beta K)$, for $p > 0$. Then $t^* = 0$, $t' = 2^{p/2}t$. So, $l = 2$, $y_t = p/2$, $B' = 2B$, $y_h = 1$, $\alpha = 2 - 2/p$, $\beta = 0$, $\gamma = 2/p$, $\delta = \infty$, $\eta = 1$.

For normal situation, we can expand linearly at the fixed point to get the Linearization RG. For n coupling constants, apply decimation

$$N' = l^{-d}N, \quad \xi' = l^{-1}\xi, \quad l = 1,$$

For the vector \mathbf{K}

$$\mathbf{K}' = R_l(\mathbf{K}), \quad \mathbf{k}^{(n)} = R_l(\mathbf{K}^{(n-1)}) = \dots = R_l^n(\mathbf{K}^{(0)})$$

when $n = 0$, $\mathbf{K}^{(0)} = \mathbf{K}$. Singular part of free energy per site

$$f_s^{(n)} = l^{nd} f_s^{(0)}$$

Now, the fixed point

$$R_l(\mathbf{K}^*) = \mathbf{K}^*, \quad \xi(K^*) = l^{-1}\xi(K^*)$$

then $\xi(\mathbf{K}^*) = 0$, or ∞ . $P_\xi \sim \hbar \rightarrow P_\xi \rightarrow \infty$.

- $\xi(\mathbf{K}^*) = 0$, $P - \xi \rightarrow \infty$, is so-called “UV” fixed point, high energy.
- $\xi(\mathbf{K}^*) = \infty$, $P - \xi \rightarrow 0$, is so-called “inferred” fixed point, low energy.

Around K^* ,

$$K = K^* + \delta K, \quad K' = K^* + \delta K' = R_l(K^* + \delta K), \quad \delta K' = R_l(K^* + \delta K) - K^* \quad (7.46)$$

Since δK and $\delta k'$ are small,

$$\delta K'_a = \left(\frac{dR_l}{dK'} \Big|_{K'=K^*} \right)_{ab}, \quad \delta K_b = (A_l^*)_{ab} \delta K_b$$

where A_l^* is the matrix that linearized from R_l^* . We can diagonalize A_l^* , then get the eigenvalues λ_i , and the eigenstates ϕ_i

$$\delta K = \sum_i u_i \phi_i, \quad \delta L' = \sum_i u_i A_l^* \phi_i = \sum_i u_i \lambda_i \phi_i = \sum_i u'_i \phi_i$$

In a series of transformations, we have

$$u_i^{(n)} = \lambda_i^n u_i^{(0)}$$

- (a) If $\lambda_i > 1$, then $u_i \uparrow a = n$ gets more important. We call u_i is relevant variabl. $\delta K'$ get more and more, and K' gets far away from K^* , then K^* is unstable fixed point.
- (b) If $\lambda < 1$, then u_i is irrelevant variable, K^* is stable fixed point.
- (c) If $\lambda = 1$, then marginae variable logarithmic.

7.7 Numerical Renormalized Group & DMRG

7.7.1 Momentum space renormalization

For point-particle

$$[x, p] \sim \hbar, \quad (7.47)$$

when $p \rightarrow \infty$, then $\lambda \propto \frac{1}{p}$, i.e., *UV radiation*. The divergency (Singularity) need to be excluded¹, then an offsetting term will be added for renormalization.

In momentum space, the “scaling” invariance ($\xi = 0, \xi \rightarrow \infty$). The fixed point of $\xi = 0$ ($p \rightarrow \infty$, the fixed point of UV).

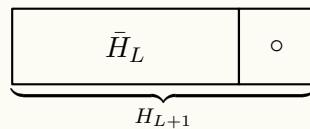
For the condensed matter, since $a = \text{finite}$, there is a “natural” cut-off, so we do not care about UV, but the infrared divergence ($p \sim \frac{1}{L}$), i.e., we consider the infrared fixed point $\xi \rightarrow \infty$.

7.7.2 Wilson’s N.R.G.

The basic concept of RG is, keep the states around the *fixed point*, i.e., integrate or sum to “cancel” the unimportant states.

In the condensed matter, the important states include 1. the basic states, 2. low-energy excited states. Wilson

1. Exactly diagonalize the L -sites subsystems (with Hamiltonian H_L) in a lattice system, with the observable variables A_L .
2. After being exact diagonalized, take n lowest energies E_i and corresponding eigenstates ψ_i , ($i = 1, 2, \dots, m$).
3. Define $O_L = (\psi_1, \psi_2, \dots, \psi_m)$, $\bar{H}_L = O_L^\dagger H_L O_L \xrightarrow{\text{diagonalization}} \begin{pmatrix} E_1 & & \\ & \ddots & \\ & & E_m \end{pmatrix}$, similarly, $\bar{A}_L = O_L^\dagger A_L O_L = (\bar{A}_{ij})_{m \times m}$.
4. Add a site, then $\bar{H}_L \rightarrow H_{L+1}$ to reconstruct the interaction between L sites and the particles on the external site.
5. Repeat the 4 steps for H_{L+1} , then $m \rightarrow Sm$.



7.7.3 Eigenstates of the $\psi_i = 1, m, L$ -site system

S. White: Enlarge the system first, and add the boundary condition to the enlarged system, which has less effect to the original system. Then, project to the original system. For non-interaction, the effect is pretty good.

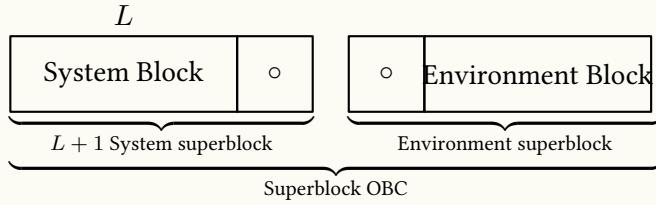
¹Normalization in QFT (actually, we consider QED).

But for the system with interaction, the result of the projection is

$$|\Psi_{Sb}\rangle \rightarrow |\Psi_L^{(1)}\rangle, \quad \text{multiple numbers}$$

$$\rightarrow |\Psi_L^{(2)}\rangle,$$

and $|\Psi_L^{(-)}\rangle$ is the most proper one. When executing the calculation,



- (a) Construct a basic state number and a superblock which needs exceed m but also small enough for exact diagonalization.
- (b) Exactly diagnose the superblock, and take the lowest eigenstate (m)
- (c) These states use system Sb basic state $|i\rangle$ and $C Sb |j\rangle$

$$|\psi\rangle = \sum_{ij} \psi_{ij} |i\rangle |j\rangle$$

then project to the reduced density matrix of the sysbm Sb

$$\rho_{ii'} = \sum_{j(\text{environment})} |\psi\rangle \langle \psi|$$

where $\text{Tr } \rho = 1$, then we can diagonalize ρ , the eigenvalues $W_\alpha \geq 0$, and $\sum_\alpha w_\alpha = 1$, and the eigenstates $|u^\alpha\rangle$.

- (d) If $\alpha = 1, \dots, s$, then
 - i. If $s \leq m$, then keep all the states;
 - ii. If $s > m$, them keep the n maximum states of w^α in the s states.

Example 7.7.1. 1D spin $1/2$ AFM Heisenberg model

$$H = \sum_i \mathbf{S}_i \mathbf{S}_{i+1}, \quad \text{let } m = S, S_{\text{tot}}^z = 0$$

the so-called antiferromagnetic model.

- (a) $L = 4$, the Superblock



contains B_L, S_L, S_R, B_R respectively in the figure, and

$$\begin{aligned} H_{B_L} &= H_{S_L} = H_{S_R} = H_{B_R} = 0 \\ S_{B_L}^z &= S_{S_L}^z = S_{S_R}^z = S_{B_L}^z = \begin{pmatrix} 1/2 & 0 \\ 0 & 1/2 \end{pmatrix} \\ S_{B_L}^+ &= S_{S_L}^+ = S_{S_R}^+ = S_{B_L}^+ = \begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix} \\ S_{B_L}^- &= \dots = \begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix} \end{aligned}$$

The 4 blocks, to keep $S_{\text{tot}}^z = 0$, there are 6 states

$$\left(\begin{array}{c} \left| \frac{1}{2}, \frac{1}{2}, -\frac{1}{2}, -\frac{1}{2} \right\rangle \\ \left| \frac{1}{2}, -\frac{1}{2}, \frac{1}{2}, -\frac{1}{2} \right\rangle \\ \left| \frac{1}{2}, -\frac{1}{2}, -\frac{1}{2}, \frac{1}{2} \right\rangle \\ \left| -\frac{1}{2}, \frac{1}{2}, \frac{1}{2}, -\frac{1}{2} \right\rangle \\ \left| -\frac{1}{2}, \frac{1}{2}, -\frac{1}{2}, \frac{1}{2} \right\rangle \\ \left| -\frac{1}{2}, -\frac{1}{2}, \frac{1}{2}, \frac{1}{2} \right\rangle \end{array} \right)$$

then, the Hamiltonian

$$\hat{H} = \mathbf{S}_{B_L} \cdot \mathbf{S}_{S_L} + \mathbf{S}_{S_L} \cdot \mathbf{S}_{S_R} + \mathbf{S}_{S_R} \cdot \mathbf{S}_{B_R} = \begin{pmatrix} \frac{1}{4} & \frac{1}{2} & 0 & 0 & 0 & 0 \\ \frac{1}{2} & -\frac{3}{4} & \frac{1}{2} & \frac{1}{2} & 0 & 0 \\ 0 & \frac{1}{2} & -\frac{1}{4} & 0 & \frac{1}{2} & 0 \\ 0 & \frac{1}{2} & 0 & -\frac{1}{4} & \frac{1}{2} & 0 \\ 0 & 0 & \frac{1}{2} & \frac{1}{2} & -\frac{1}{4} & \frac{1}{2} \\ 0 & 0 & 0 & 0 & \frac{1}{2} & \frac{1}{2} \end{pmatrix}$$

The eigenvector

$$|\psi\rangle = (0.149429, -0.557678, 0.408248, -0.557678, -0.149427)^T = \psi_{\frac{1}{2}\frac{1}{2}-\frac{1}{2}\frac{1}{2}-\frac{1}{2}-\frac{1}{2}} + \dots$$

and the density matrix element

$$\rho_{i_1, i_2, i'_1, i'_2} = \sum_{j_1 j_2} \psi_{i_1 i_2 j_1 j_2} \psi_{j_1 j_2 i'_1 i'_2}$$

from the basis

$$\{|i_1, i_2\rangle\} = \{(1/2, 1/2), (1/2, -1/2), (-1/2, 1/2), (-1/2, -1/2)\}$$

the density matrix is

$$\rho = \begin{pmatrix} -0.022329 & 0 & 0 & 0 \\ 0 & -0.477671 & 0.455342 & 0 \\ 0 & 0.455342 & -0.477671 & 0 \\ 0 & 0 & 0 & -0.022329 \end{pmatrix}.$$

Diagonalize ρ

$$W = (0.022329, 0.933013, 0.022329, 0.022329)$$

$$u^1 = (1, 0, 0, 0)^\top, u^2 = (0, \sqrt{2}/2, -\sqrt{2}/2, 0)^\top, u^3 = (0, \sqrt{2}/2, \sqrt{2}/2, 0)^\top, u^4 = (0, 0, 0, 1)^\top$$

$S = 4 \times 5$ matrix.

(b) $L = 2$.

7.8 K-T Phase Transition

The spin on a 2D plane

$$\mathbf{S} = (S_x, S_y), \quad \text{and} \quad \mathcal{H} = -J' \sum_{\langle ij \rangle} \mathbf{S}_i \cdot \mathbf{S}_j = -\underbrace{J' S^2}_{J} \sum_{\langle ij \rangle} \cos(\theta_i - \theta_j) \quad (7.48)$$

i.e., $X - Y$ model.



The partition function

$$Z = \text{Tr } e^{-\beta H} = \int_0^{2\pi} \prod_i \frac{d\theta_i}{2\pi} e^{-\beta H(\theta_i)} \xrightarrow{T \gg J/k_B} \int_0^{2\pi} \prod_i \frac{d\theta_i}{2\pi} \prod_{\langle ij \rangle} (1 + \beta J \cos(\theta_i - \theta_j) + \mathcal{O}(\beta J)^2) \quad (7.49)$$

Therefore

$$\begin{aligned} \langle \mathbf{S}_0 \cdot \mathbf{S}_1 \rangle &= S^2 \int_0^{2\pi} \prod_i \frac{d\theta}{2\pi} \prod_{\langle ij \rangle} (1 + \beta J \cos(\theta_i - \theta_j)) \cos(\theta_0 - \theta_1) \sim \left(\frac{\beta J}{2}\right)^{|\mathbf{r}|} \\ &= \exp\left(-\ln \left| \left(\frac{2}{\beta J}\right)^{|\mathbf{r}|} \right| \right) \equiv \exp\left(-\frac{|\mathbf{r}|}{\xi}\right) \end{aligned} \quad (7.50)$$

where $\xi^{-1} = \ln \frac{2}{\beta J}$. The exponential state stands for the disorder. This is so-called the *High-temperature expansion*.

For *Low-temperature expansion*, $\beta J \geq 1$. It should near a ferromagnetic state, so $\theta_i - \theta_j \ll 1$, $\cos(\theta_i - \theta_j) = 1 - \frac{1}{2}(\theta_i - \theta_j)^2$.

$$(\theta_i - \theta_{i+\delta x})^2 + (\theta_i - \theta_{i+\delta y})^2 \Rightarrow a^2(\partial_x \theta_i)^2 + a^2(\partial_y \theta_i)^2 = a^2(\nabla \theta_i)^2$$

At the continuous limit

$$\beta H = \beta E_0 - \frac{\beta J}{2} |\nabla \theta(x)|^2$$

where $\beta E_0 = 2\beta JL^2/a^2$, $\langle \cos(\theta_0 - \theta_1) \rangle \sim |\mathbf{r}/a|^{-1/(2\pi\beta J)}$. It is power law decay, we call it *Quasi-long order*, or *algebraic*, or *long range order*.

Take a peek $\frac{\delta H}{\delta \theta} = 0$, then,

$$-(\nabla \theta)^2 = \theta \nabla^2 \theta - \nabla(\theta \nabla \theta)$$

we have $\nabla^2 \theta = 0$.

- (a) $\theta = \text{Const}$
- (b) $\nabla\theta = \left(-\frac{y}{r^2}, \frac{x}{r^2}\right)$, $\theta = \arctan(\frac{y}{x})$, which satisfies $\oint \nabla\theta \cdot d\mathbf{r} = 2\pi$
- (c) Common solution: $\oint \nabla\theta \cdot d\mathbf{l} = 2\pi n$

The Hamiltonian

$$H = -\theta \nabla^2 \theta \rightarrow (\nabla\theta)^2$$

where

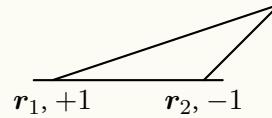
$$\nabla\theta \cdot \nabla\theta = \frac{x^2 + y^2}{r^4} = \frac{1}{r^2}$$

Then, the integral

$$\frac{J}{2} \int d^2\mathbf{r} (\nabla\theta)^2 - E_0 = \frac{J}{2} \int_a^L r dr \int_0^{2\pi} d\theta \frac{1}{r^2} = J\pi \ln \frac{L}{a}$$

This kind of solution is a high-energy excitation at $T = 0$.

Consider a pair of vertices: $\theta_1 - \theta_2 \approx 0$, $|\mathbf{r}_{12} \rightarrow \infty|$ with finite energy.



$$\begin{aligned} E_{\text{vortex-pair}} &= \int d^2\mathbf{r} [(\nabla\theta_1)^2 + (\nabla\theta_2)^2] \approx \int_{\text{core}} d^2\mathbf{r} (\nabla\theta_1)^2 \int_{\text{core}} d^2\mathbf{r} (\nabla\theta_2)^2 \\ &= \int_a^R r dr (\nabla\theta_1)^2 d\theta + \int_a^R r dr d\theta (\nabla\theta_2)^2 = 2E_{\text{core}} + 2J\pi \ln \frac{R}{a} \end{aligned}$$

The 2D Column gas

$$F = -\frac{\partial E}{\partial R} = -\frac{1}{R}$$

At a finite temperature, a vortex's square proportion to a^2 . In a square of L^2 , there can be around L^2/a^2 positions of vortices. The entropy

$$S = \ln\left(\frac{L^2}{a^2}\right)$$

then, the free energy of a vortex is

$$F = U - TS = \left(J\pi \ln \frac{L}{a} - T \ln\left(\frac{L^2}{a^2}\right)\right) = \left(J\pi - \frac{2}{\beta}\right) \ln \frac{L}{a}$$

If $J\pi - 2/\beta < 0$, then a single vortex can escape from the vortex-pair; and take a phase transition to becomes favorable. The critical temperature $T_c = J\pi/2k_B$.

CHAPTER 8 Non-equilibrium Statistic Physics

8.1 Boltzmann integral ODE

At the equilibrium state, we have a distribution function, aka a function of the energy that independent from the time

$$f_0 = f_0(\mathbf{r}) = f_0(E) \quad (8.1)$$

which only depends on r and E .

$$f_0 = \frac{1}{e^{\beta E} \pm 1} \xrightarrow{\text{Non-equilibrium}} f(\mathbf{r}, \mathbf{v}, t) \quad (8.2)$$

This is the Boltzmann equation for the classical short-term interaction thin gas.

- (a) Classical: $\lambda_T \ll |\delta r|$, $\lambda_T = \frac{h}{(2\pi m k_B T)^{1/2}}$ is the high-temperature wavelength. The gas under the standard state (0°C , 1 atm). For the Argon: $n = 2.7 \times 10^{19} \text{ cm}^{-3}$, $m \approx 6.7 \times 10^{-23} \text{ g}$. Then

$$\lambda_T = \frac{h}{\sqrt{2\pi m k_B T}} \sim 0.17 \times 10^{-8} \text{ cm}, \quad \text{and} \quad \frac{\delta r}{\lambda_T} \approx 190.$$

- (b) Thin and Short-term force $\delta r \gg d$. Most of the gas molecules are free most time. Separate the “hit” and the “motion”: There is no motion when hitting, or there will be no hitting when moving.

$$\delta r \approx 3.3 \times 10^{-7} \text{ cm}, \quad m \sim 6.7 \times 10^{-23} \text{ g}, \quad \lambda_T = \frac{h}{\sqrt{2\pi m k_B T}} \approx 0.17 \times 10^{-8} \text{ cm}$$

- (c) Three-body hitting can be omitted

Taking another simplification

- i. Omit the structure of molecules, take the rigid-sphere model to instead the Van der Waals force.
- ii. There’s no relation between the velocities of two hitting molecules.

To derive the evolution of $f(\mathbf{r}, \mathbf{v}, t)$

$$f(\mathbf{r}, \mathbf{v}, t) d^3\mathbf{r} d^3\mathbf{v}$$

is the average number of molecules around the volume unit in the phase (\mathbf{r}, \mathbf{v}) . From $t \rightarrow t + dt$

$$\frac{1}{dt} [f(\mathbf{r}, \mathbf{v}, t + dt) - f(\mathbf{r}, \mathbf{v}, t)] d^3\mathbf{r} d^3\mathbf{v} = \frac{\partial f}{\partial t} d^3\mathbf{r} d^3\mathbf{v}$$

where $\frac{\partial f}{\partial t} = \left(\frac{\partial f}{\partial t}\right)_d + \left(\frac{\partial f}{\partial t}\right)_c$: d stands for the drift, and c stands for the collision.

8.1.1 Derivation of the drift term

Since

$$df = [f(\mathbf{r} + \dot{\mathbf{r}} dt, \mathbf{v} + d\mathbf{v}, t + dt) - f(\mathbf{r}, \mathbf{v}, t)] dt = 0$$

then,

$$\frac{df}{dt} = \left(\frac{\partial f}{\partial t} \right)_d + \sum_i \left(\dot{x}_i \frac{\partial f}{\partial \dot{x}_i} + \dot{v}_i \frac{\partial f}{\partial v_i} \right) = 0$$

So, the drift term

$$\left(\frac{\partial f}{\partial t} \right)_d = -\mathbf{r} \cdot \frac{\partial f}{\partial \mathbf{r}} - \mathbf{v} \cdot \frac{\partial f}{\partial \mathbf{v}} = -\frac{\partial}{\partial \mathbf{r}} \mathbf{r} f - \frac{\partial}{\partial \mathbf{v}} \mathbf{v} f$$

8.1.2 Derivation of the collision term

To derive the collision term, consider the collision between two particles

$$\begin{aligned} m_1 \mathbf{v}_1 + m_2 \mathbf{v}_2 &= m_1 \mathbf{v}'_1 + m_2 \mathbf{v}'_2 \\ \frac{1}{2} m_1 v_1^2 + \frac{1}{2} m_2 v_2^2 &= \frac{1}{2} m_1 v'_1^2 + \frac{1}{2} m_2 v'_2^2 \end{aligned}$$

Since at the normal direction, $v'_{1\perp} = v_{1\perp}$. Then the bound condition

$$\mathbf{v}'_1 - \mathbf{v}_1 = \lambda_1 \mathbf{n}, \quad \text{and} \quad \mathbf{v}'_2 - \mathbf{v}_2 = \lambda_2 \mathbf{n}$$

For a given \mathbf{n} , we can solve

$$\begin{aligned} \mathbf{v}'_1 &= \mathbf{v}_1 + \frac{2m_2}{m_1 + m_2} [(\mathbf{v}_2 - \mathbf{v}_1) \cdot \mathbf{n}] \mathbf{n} \\ \mathbf{v}'_2 &= \mathbf{v}_2 - \frac{2m_1}{m_1 + m_2} [(\mathbf{v}_2 - \mathbf{v}_1) \cdot \mathbf{n}] \mathbf{n} \end{aligned}$$

Then, we have

$$\mathbf{v}'_2 - \mathbf{v}'_1 = \mathbf{v}_2 - \mathbf{v}_1 - 2[(\mathbf{v}_2 - \mathbf{v}_1) \cdot \mathbf{n}] \mathbf{n}, \quad (\mathbf{v}'_2 - \mathbf{v}'_1)^2 = (\mathbf{v}_2 - \mathbf{v}_1)^2, \quad v'^2_{12} = v^2_{12}.$$

To calculate $\left(\frac{\partial f}{\partial t} \right)_c$

$$f_i = f(\mathbf{r}, \mathbf{v}_i, t), \quad f'_i(\mathbf{r}, \mathbf{v}'_i, t)$$

$\Delta f_1^{(t)}$ is the collision in the $d^3 \mathbf{r}$ space during the dt time. Then,

$$\left(\frac{\partial f_1}{\partial t} \right)_c dt d^3 \mathbf{r} d^3 \mathbf{r}_1 = \Delta f_1^{(+)} - \Delta f_1^{(-)}$$

When the two molecules collide, if collide with the m_2 molecule with the centre of \mathbf{r}_2 within the volume unit of $d^3 \mathbf{r}_2$, then, the collision direction will be limited in the cubic angle $d\Omega$ with the normal vector \mathbf{n} . Then, it must be limited in a cylinder with height $v_{12} \cos \theta dt$ and with the lower square $r_{12}^2 d\Omega$. The volume of the cylinder is $r_{12}^2 d\Omega v_{12} \cos \theta dt$, where includes the number of molecules with $d^3 v_{12}$

$$(f_2 d^3 r_2) r_{12} I^2 d\Omega v_{12} \cos \theta dt$$

Multiply the number of molecules m

$$(f_1 d^3\mathbf{r} d^3\mathbf{v}_1)(f_2 d^3r_2) r_{12} d\Omega v_{12} \cos \theta dt$$

equal to the number of collisions between molecules in $d^3\mathbf{r} d^3\mathbf{v}_1$ and molecules in $d^3\mathbf{r}_2$ within the $d\Omega$ direction during time dt is equal to the number of collisions between molecules in $d^3\mathbf{r} d^3\mathbf{v}_1$ and molecules in $d^3\mathbf{r}_2$ within the domega direction.

$\delta f_1^{(-)}$ enable the decrease of molecules within $d^3\mathbf{v}_1$: $(\mathbf{v}_1, \mathbf{v}_2) \rightarrow (\mathbf{v}'_1, \mathbf{v}'_2)$

$$\delta f_1^{(+)} = [f'_1 f'_2 \lambda'_{12} d\Omega' d^3\mathbf{v}'_2] dt d^3\mathbf{r}_1 d^3\mathbf{v}'_1$$

with $(\mathbf{v}'_1, \mathbf{v}'_2, -\mathbf{n}) \rightarrow (\mathbf{v}_1, \mathbf{v}_2)$, and the transformation

$$d^3\mathbf{v}'_1 d^3\mathbf{v}'_2 = d^3v_1 d^3\mathbf{v}_2 \begin{vmatrix} \frac{\partial v_1}{\partial v'_1} & \frac{\partial v_2}{\partial v'_1} \\ \frac{\partial v_1}{\partial v'_2} & \frac{\partial v_2}{\partial v'_2} \end{vmatrix}.$$

Then,

$$\begin{aligned} \left(\frac{\partial f}{\partial t}\right)_c dt d^3\mathbf{r}_1 d^3\mathbf{v}_1 &= \Delta f_1^{(+)} - \Delta f_1^{(-)} = \int [(f'_1 f'_2 - f_1 f_2) d^3\mathbf{v}_2 \lambda_{12} d\Omega] dt d^3\mathbf{v}_1 d^3\mathbf{v}_1 \\ \frac{\partial f}{\partial t} - \left(\frac{\partial f}{\partial t}\right)_d &= \left(\frac{\partial f}{\partial t}\right)_c \\ \frac{\partial f}{\partial t} + \mathbf{v} \cdot \left(\frac{\partial f}{\partial \mathbf{r}}\right) + \mathbf{g} \cdot \frac{\partial f}{\partial \mathbf{v}} &= \int (f'_v f'_w - f_v f_w) \lambda d^3\omega d\Omega \end{aligned}$$

8.2 H-theorem, H-function and entropy

The Entropy

$$S = - \sum_i p_i \ln p_i \quad (8.3)$$

The H -function

$$H = \int f(\mathbf{r}, \mathbf{v}, t) \ln f(\mathbf{r}, \mathbf{v}, t) d^3\mathbf{v} d^3\mathbf{r} \quad (8.4)$$

The gas at the equilibrium state

$$n = N/V$$

The Maxwell distribution

$$f = n \left(\frac{m}{2\pi k_B T} \right)^{3/2} \exp \left(-\frac{mv^2}{2k_B T} \right) \quad (8.5)$$

Then, the H -function becomes

$$H = \int f \left[\ln n + \frac{3}{2} \ln \frac{m}{2\pi k_B T} - \frac{mv^2}{2k_B T} \right] d^3\mathbf{r} d^3\mathbf{v} \quad (8.6)$$

where the integral

$$\int f d^3\mathbf{r} d^3\mathbf{v} = n, \quad \frac{1}{n} \int \frac{mv^2}{2} f d^3\mathbf{v} = \frac{3}{2} k_B T$$

The entropy of single-atom ideal gas

$$S = Nk_B \left[\ln \frac{V}{N} + \frac{3}{2} \ln T + \frac{5}{2} + \frac{3}{2} \ln \left(\frac{2\pi m k_B}{h^2} \right) \right] = -k_B H + C$$

Use the Boltzmann equation to derive the H -theorem

$$\frac{dH}{dT} \leq 0 \quad (8.7)$$

The time derivative to H

$$\begin{aligned} \frac{dH}{dT} &= \int \left(\frac{\partial f}{\partial t} \ln F + f \cdot \frac{1}{f} \right) d^3r d^3v = \int (1 + \ln f) \frac{\partial f}{\partial t} d^3r d^3v \\ &= - \int (1 + \ln f) \left(\mathbf{v} \cdot \frac{\partial f}{\partial \mathbf{r}} \right) d^3r d^3v - \int (1 + \ln f) (\mathbf{q} \cdot \frac{\partial f}{\partial \mathbf{v}}) d^3r d^3v - \int (1 + \ln f) (f_1 f_2 - f'_1 f'_2) d^3v d^3v' \Lambda d\Omega \end{aligned}$$

The first term

$$\begin{aligned} \nabla \cdot (\mathbf{v} f \ln f) &= \mathbf{v} (1 + \ln f) \frac{\partial f}{\partial \mathbf{r}} \\ \int d^3r \nabla \cdot (\mathbf{v} f \ln f) &= \oint \oint \mathbf{n} \cdot (\mathbf{v} f - \ln f) d\Sigma = 0 \end{aligned}$$

The second term $\frac{\partial}{\partial \mathbf{v}} \mathbf{q} = 0$

$$\int \frac{\partial}{\partial \mathbf{v}} \mathbf{q} f \ln f d^3v = \oint \oint d\mathbf{S}_v \cdot \mathbf{q} f \ln f$$

when $v \rightarrow \infty$, $f(v)|_{v \rightarrow \infty} = 0$. The third term: $1 \leftrightarrow 2$,

$$\frac{dH}{dT} = - \int (1 + \ln f_2) (f_1 f_2 - f'_1 f'_2) d^3v_1 d^3r_2 \Lambda d\omega d^3r$$

Combine and then half

$$\frac{dH}{dt} = -\frac{1}{2} \int (2 + \ln(f_1 f_2)) (f_1 f_2 - f'_1 f'_2) d(\dots)$$

$v'_{1,2} \leftrightarrow v_{1,2}$, we have

$$\frac{dH}{dt} = -\frac{1}{2} \int (2 + \ln(f'_2 f_1)) (f'_1 f'_2 - f_1 f_2) d(\dots) = -\frac{1}{4} \underbrace{\left(\ln(f_1 f_2) - \ln(f'_1 f'_2) \right) (f_1 f_2 - f'_1 f'_2)}_{\geq 0} d(\dots)$$

Then, $\frac{dH}{dt} \leq 0$, $\frac{dS}{dt} \geq 0$. When $f_1 f_2 = f'_1 f'_2$ (Detailed equilibrium condition), they equal to zero.

8.3 Application of Boltzmann Equation

The relaxation time approximation

$$\left(\frac{\partial f}{\partial t} \right)_c = -\frac{f - f^{(0)}}{\tau} \quad (8.8)$$

where τ is the relaxation time that tends to equilibrium, independent of \mathbf{r} . Assume f is also independent of \mathbf{r} . Without the external force,

$$\frac{\partial f}{\partial t} = -\frac{f - f^{(0)}}{t}$$

Then, we have

$$\frac{d(f - f^{(0)})}{f - f^{(0)}} = -\frac{dt}{\tau},$$

$$f(\mathbf{v}) - f^{(0)}(\mathbf{v}) = [f(\mathbf{v}, 0) - f^{(0)}(\mathbf{v})] e^{-t/\tau}$$

τ is the time that required by tending to equilibrium. In the free electron gas,

$$f^{(0)}(\mathbf{p}) = \frac{1}{e^{(\epsilon(p)-\mu)/k_B T} + 1}$$

and the Fermi energy $\epsilon(p) = \frac{p^2}{2m}$.

In the unit volume, the average electron number that with in the momentum range $d^3 p$ is $2 \frac{d^3 p}{h^3} f^{(0)}$.

The Boltzmann equation

$$\frac{\partial f}{\partial t} + \frac{\mathbf{p}}{m} \cdot \frac{\partial f}{\partial \mathbf{r}} + \mathbf{F} \cdot \frac{\partial f}{\partial \mathbf{p}} = -\frac{f - f^{(0)}}{\tau}$$

where $\mathbf{F} = -e\mathbf{E}$, i.e., the ecurent is a uniform and eternal

$$\frac{\partial f}{\partial t} = 0, \quad \nabla f = 0, \quad -e\mathbf{E} \cdot \frac{\partial f}{\partial \mathbf{p}} = -\frac{f - f^{(0)}}{\tau}$$

where $f = f^{(0)} + f^{(1)} + \dots$, and we keep the first order

$$e\mathbf{E} \cdot \frac{\partial f^{(0)}}{\partial \mathbf{p}} = \frac{f^{(1)}}{\tau} \quad f^{(1)} = e\tau \mathbf{E} \cdot \mathbf{v} \frac{\partial f^{(0)}}{\partial E}$$

Hence,

$$f \approx f^{(0)} + e\tau \mathbf{E} \cdot \mathbf{v} \frac{\partial f^{(0)}}{\partial \epsilon} = f^{(0)}(\epsilon + e\tau \mathbf{E} \cdot \mathbf{v})$$

where

$$\frac{\partial f^{(0)}}{\partial \mathbf{p}} = \frac{\partial f^{(0)}}{\partial \epsilon} \frac{\partial \epsilon}{\partial \beta} = \frac{\partial f^{(0)}}{\partial \epsilon} \mathbf{v}$$

The \mathbf{E} patt through dA perpendicularly, hence

$$\int J_e dt dA = e \int v_x dt dA f \frac{2 d^3 p}{h^3}$$

where

$$J_e = nev_x = \frac{2 d^3 p}{h^3} f e v_x = 2e \int v_x (f^{(0)} + f^{(1)}) \frac{d^3 p}{h^3}$$

and we have

$$v_p = \frac{k}{m}, \quad \text{and} \quad f^{(0)}(v_x) = f^{(0)}(-v_x)$$

Now, handel $d^3 p$

$$d^3 p = p^2 dp \int d\theta \sin \theta d\varphi = 2m\epsilon d(\sqrt{2m}\sqrt{\epsilon}) \cdot 4\pi = \frac{4\pi(2m)^{3/2}}{2} \epsilon^{1/2} d\epsilon$$

Substitute it into J_e

$$J_e = 2eEt \int v_x^2 \frac{\partial f^{(0)}}{\partial \epsilon} \frac{d^3 p}{h^3} = e^2 E \tau, \quad \int v_x^2 \frac{\partial f^{(0)}}{\partial \epsilon} D(\epsilon) d\epsilon$$

where

$$D(\epsilon) = 4\pi \frac{(2m)^{3/2}}{h^3} \epsilon^{1/2}$$

Finally,

$$J_e = e^2 E \int \tau \frac{v^3}{3} \frac{\partial f^{(0)}}{\partial t} D(\epsilon) d\epsilon$$

Around $T \sim 0$, $f^{(0)} = \theta(\epsilon - \mu)$. Then,

$$J = \frac{2e^2 t}{3m} \mu D(\mu) E, \quad n = \int_0^\mu D(\epsilon) d\epsilon = \frac{2}{3} \mu D(\mu)$$

We can use it to calculate the conductivity,

$$J_e = \frac{ne^2 \tau}{m} E = \sigma E, \quad \text{where} \quad \sigma = \frac{ne\tau}{m}$$

The force

$$\mathbf{F} = -e\mathbf{E} - \frac{e}{c} \mathbf{v} \times \mathbf{B} \quad (8.9)$$

where $\mathbf{v} = (v_x, v_y)$, $v = v_x + i v_y$. The stability

$$\frac{\partial f}{\partial t} + \mathbf{v} \cdot \nabla f = 0 = -\frac{\mathbf{F}}{m} \cdot \frac{\partial f}{\partial \mathbf{v}} + \left(\frac{\partial f}{\partial t} \right)_c$$

The derivative

$$0 = \frac{d\langle v \rangle}{dt} = -\frac{eE}{m} + i\omega_c \langle v \rangle - \frac{\langle v \rangle}{\tau}, \quad \text{where} \quad \langle v \rangle = -\frac{eE/m}{1 - i\omega_c \tau}$$

Substitute $E = E_x + iE_y$, $\omega_c = \frac{eB}{mc}$, the current density

$$\mathbf{j} = \sigma \cdot \mathbf{E} = \begin{pmatrix} \sigma_{xx} & \sigma_{xy} \\ \sigma_{yx} & \sigma_{yy} \end{pmatrix} \begin{pmatrix} E_x \\ E_y \end{pmatrix} = j_x + i j_y$$

So, we have the elements of the conductivity matrix

$$\sigma_{xx} = \sigma_{yy} = \frac{\sigma_0}{1 + \omega^2 \tau^2}, \quad \sigma_{xy} = -\sigma_{yx} = -\frac{nce}{B} - \frac{\sigma_{xx}}{\omega_c \tau}$$

where $\sigma_0 = \frac{ne^2 \tau}{m}$.

8.4 Fluctuation Phenomenon: Themoral Variables

8.4.1 Regrex System

The fluctuation of energy

$$\frac{\sqrt{\langle (E - \langle E \rangle)^2 \rangle}}{\langle E \rangle} \sim \frac{1}{\sqrt{N}}, \quad \text{and} \quad n = \frac{N}{V} \quad \text{finite} \quad (8.10)$$

are all the fluctuations corresponding the microscope variable.

8.4.2 Quasi-Themoral Theory (Smoluchowski-Einstein Method)

The theromal entropy

$$\bar{S} = k_B \ln W_{\max} \quad (\text{theromal probability}) \quad (8.11)$$

where $W_{\max} = e^{\bar{S}/k_B}$.

The differ from equilibirum

$$W = e^{S/k_B} = W_{\max} e^{(S-\bar{S})/k_B} = W_{\max} e^{\Delta S/k_B}$$

(a) For dependent system, $\Delta E = 0, \Delta V = 0$.

(b) For regrex system, $\Delta E + \Delta E_e = 0, \Delta V + \Delta V_e = 0$.

$$\begin{aligned} W_T &= W_{\max} e^{(\Delta S + \Delta S_e)/k_B} = W_{\max} e^{(\Delta S + \frac{\Delta E_e + pV_e}{T})/k_B} \\ &= W_{\max} e^{(\Delta ST - \Delta E - p\Delta V)/(k_B T)} = W_{\max} e^{-(\Delta F + p\Delta V)/(k_B T)} \end{aligned}$$

The free energy

$$\Delta F = \underbrace{\left(\frac{\partial F}{\partial V}\right)_T}_{-p} \delta V + \frac{1}{2} \underbrace{\left(\frac{\partial^2 F}{\partial V^2}\right)_T}_{-\partial p/\partial V} (\Delta V)^2 + \dots \quad (8.12)$$

Then,

$$W_T \approx W_{\max} \exp \left[\frac{1}{2k_B T} \left(\frac{\partial p}{\partial V} \right)_T (\Delta V)^2 \right] \quad (8.13)$$

The probability of the quasi-themoral in regrex system

$$\langle (\Delta A)^2 \rangle = \frac{\int (\Delta A)^2 W d(\Delta A)}{\int W d(\Delta A)} \quad (8.14)$$

Example 8.4.1. Calculate $\langle (\Delta V)^2 \rangle$.

$$\begin{aligned} &\frac{\int_{-\infty}^{\infty} (\Delta V)^2 \exp \left[\frac{1}{2k_B T} \left(\frac{\partial p}{\partial V} \right)_T (\Delta V)^2 \right] d(\Delta V)}{\text{normalization factor}} \\ &= \frac{1}{\int \dots} \int_{-\infty}^{\infty} (\Delta V)^2 \frac{k_B T}{(\partial p/\partial V)_T} \frac{1}{\Delta V} d \left\{ \exp \left[\frac{1}{2k_B T} (\partial p/\partial V)_T (\Delta V)^2 \right] \right\} \\ &= \frac{1}{\int \dots} \frac{\Delta V (k_B T)}{(\partial p/\partial V)_T} \exp \left[-\frac{1}{2k_B T} \left| \left(\frac{\partial p}{\partial V} \right)_T \right| (\Delta V)^2 \right] \Big|_{-\infty}^{\infty} - k_B T \left(\frac{\partial V}{\partial p} \right)_T = -k_B T \left(\frac{\partial V}{\partial p} \right)_T \end{aligned}$$

Then, we have

$$\frac{\langle (\Delta V)^2 \rangle}{V^2} = - \frac{k_B T}{V^2} \left(\frac{\partial V}{\partial p} \right)_T$$

If the mass of the system $M = \text{Const}$, i.e., $M = pV$ is fixed. Then,

$$\Delta M = \Delta \rho V + \rho \Delta V = 0 \Rightarrow \frac{\Delta \rho}{\rho} = -\frac{\Delta V}{V}, \quad \frac{\langle (\Delta \rho)^2 \rangle}{\rho^2} = \frac{\langle (\Delta V)^2 \rangle}{V^2} = -k_B T \left(\frac{\partial V}{\partial p} \right)_T$$

$\rho = N/V$, if V is fixed, then $\Delta\rho \propto \Delta N$.

$$\begin{aligned}\left\langle \left(\frac{\Delta N}{N} \right)^2 \right\rangle &= \left\langle \left(\frac{\Delta\rho}{\rho} \right)^2 \right\rangle = -\frac{k_B T}{V^2} \left(\frac{\partial V}{\partial p} \right)_T \\ \Delta\rho &= \frac{\Delta N}{V} - \frac{N\Delta V}{V^2} \\ (\Delta\rho)^2 &= \left(\frac{\Delta N}{V} \right)^2 - \frac{2\Delta N\Delta V}{V^3} + \frac{N^2(\Delta V)^2}{V^4} \\ \langle (\Delta\rho)^2 \rangle &= \langle \left(\frac{\Delta N}{V} \right)^2 \rangle + \frac{N^2 \langle (\Delta V)^2 \rangle}{V^4} \\ \frac{\langle (\Delta\rho)^2 \rangle}{N^2} &= \frac{\langle (\Delta N)^2 \rangle}{N^2} + \frac{\langle (\Delta N)^2 \rangle}{N^2} = 2 \langle \left(\frac{\Delta N}{N} \right)^2 \rangle\end{aligned}$$

The critical point

$$\left(\frac{\partial p}{\partial V} \right)_T = \left(\frac{\partial^2 p}{\partial V^2} \right)_T = 0$$

Then,

$$\begin{aligned}\Delta F &= -p\Delta V - \frac{1}{4!} \left(\frac{\partial^3 p}{\partial V^3} \right)_T (\Delta V)^4 + \dots \\ W &= W_{\max} \exp(-\alpha x^4), \quad x = \Delta V \\ \langle (\Delta V)^2 \rangle &= \frac{\int_0^\infty x^2 e^{-\alpha x^4} dx}{\int_0^\infty e^{-\alpha x^4} dx} = \frac{\Gamma(\frac{3}{4})}{\Gamma(\frac{1}{4})} \frac{1}{\sqrt{\alpha}} = 0.338 \frac{1}{\sqrt{\alpha}}\end{aligned}$$

8.4.3 Vandé vars Gas

$$p_c = \frac{a}{27b^2}, \quad v_c = 3b, \quad T_c = \frac{8a}{27bR}$$

Substitute them into the ideal gas formula

$$\left(p + \frac{a}{v^2} \right) (v - b) = RT, \quad p = \frac{3RT}{3V - V_c} - \frac{9RT_c v_c}{8v^2}, \quad V = \frac{N}{N_a} \sigma, \quad N_a = 6.02 \times 10^{23}$$

Then,

$$p = \frac{3Nk_B T}{3V - V_c} - \frac{9Nk_B T_c V_c}{8V^2}$$

The derivatives

$$\begin{aligned}\left(\frac{\partial^3 p}{\partial V^3} \right)_T &= -\frac{486Nk_B T}{(3V - V_c)^4} + \frac{27Nk_B T_c V_c}{V^5} \\ \left(\frac{\partial^3 p}{\partial V^3} \right)_{T_c} &= -\frac{27Nk_B T_c}{8V_c^4}\end{aligned}$$

Finally, we have

$$\left(\frac{\Delta V}{V} \right)_c^2 = 0.338 \left[-\frac{V_c^4}{24kT_c} \left(\frac{\partial^3 p}{\partial V^3} \right)_c \right]^{-1/2} = 0.901/\sqrt{N}$$

Example 8.4.2 (The sky is blue (When the air is clean, not frog / haze)). The magnitude of the scatter of light

$$I \propto \frac{1}{\lambda^4} \frac{\langle (\Delta\rho)^2 \rangle}{\rho^2}$$

Example 8.4.3 (Liquid).

$$\frac{\langle I \rangle}{V} \propto \frac{1}{\lambda^4} V \left[-\frac{V^4}{24k_B T} \left(\frac{\partial^3 p}{\partial V^3} \right)_T \right]^{1/2} \propto \frac{1}{\sqrt{N}}$$

8.5 Fluctuation Phenomenon (Random External Forces, Brown Motions)

8.5.1 Langevin equation

For particles: $10^{-5} \sim 10^{-4}$ cm.

(a) For fixed external forces: Gravity, Buoyancy, Viscous Force.

(b) Random forces: 10^{-4} cm, liquid molecule density $n = 10^{22}$ cm $^{-3}$, the collisions occur 10^{22-4} /s.

For gas: $n \sim 10^{19}$, collision occurs 10^{15} s.

Fluctuation forces: the eigen time of collisions $10^{-18} \sim 10^{-15}$ s.

$$m \frac{d\mathbf{u}}{dt} = \mathbf{F}_1 + \mathbf{F}_2(t), \quad \mathbf{u} = \frac{d\mathbf{x}}{dt}, \quad \mathbf{u} = u_x$$

where F is the viscous force: $F_1 = -\alpha u$, $F_2 = x(t)$.

$$m\langle u \rangle = kT, \quad \frac{d^2\langle x^2 \rangle}{dt^2} + \frac{1}{\tau} \frac{d}{dt} \langle x^2 \rangle - \frac{2kT}{m} = 0, \quad \tau = \left(\frac{\alpha}{m} \right)^{-1}$$

Then, the solution

$$\langle x^2 \rangle = \frac{2kT\tau}{m} t + C_1 e^{-t/\tau} + C_2$$

and substitute the initial condition $t = 0$, $\langle x^2 \rangle, \frac{d}{dt}\langle x^2 \rangle = 0$. Hence,

$$\langle x^2 \rangle = \frac{2kT\tau^2}{m} \left[\frac{t}{\tau} - \left(1 - e^{-t/\tau} \right) \right] \tag{8.15}$$

i. If the observe time $t \ll \tau$,

$$\langle x^2 \rangle = \frac{2kT\tau}{m}, \quad \left(\frac{t}{\tau} - \left(1 - 1 + \frac{t}{\tau} - \frac{1}{2} \frac{t^2}{\tau^2} \right) \right) = \frac{kT}{m} t^2 = \langle u^2 \rangle t^2$$

ii. If $t \gg \tau$, then

$$\langle x^2 \rangle \approx \frac{2kT\tau}{m} t = \frac{2kT}{\alpha} t = 2Dt \propto t$$

8.5.2 The Diffusion of Brown particles

Assume $n(x, t) dx$ is in the range of $(x, x + dx)$ at time t , introduce $f(x, t) dx$ for the Brownian particle number of the unit area perpendicular to x -axis: The probability of a particle at $t = 0$ and located at $x = 0$ to time t is transformed to $(x, x + dx)$.

$$n(x, t + \tau) = \int_{-\infty}^{\infty} f(x - x', \tau) n(x', t) dx' = \int_{-\infty}^{\infty} f(\xi, \tau) n(x - \xi, t) d\xi \quad (8.16)$$

where

$$\int_{-\infty}^{\infty} dx f(x, \tau) = 1, \quad \text{and} \quad f(x, \tau) = f(-x, \tau)$$

For small τ

$$n(x, t + \tau) = n(x, t) + \tau \frac{\partial n}{\partial t} + \frac{1}{2} \tau^2 \frac{\partial^2 n}{\partial t^2} + \dots \quad (8.17)$$

For small ξ

$$n(x - \xi, t) = n(x, t) - \xi \frac{\partial n}{\partial x} + \frac{1}{2} \xi^2 \frac{\partial^2 n}{\partial t^2} + \dots \quad (8.18)$$

Assume when ξ is large, $n(x - \xi, t)$ is small. Then,

$$n(x, t + \tau) \approx n(x, t) + \tau \frac{\partial n}{\partial t} + \frac{1}{2} \tau^2 \frac{\partial^2 n}{\partial t^2} + \dots = \int_{-infy}^{\infty} d\xi f(\xi, \tau) \left(n(x, t) - \xi \frac{\partial n}{\partial x} + \frac{1}{2} \xi^2 \frac{\partial^2 n}{\partial x^2} + \xi^3 \xi^4 \right), \quad (8.19)$$

where $\frac{\partial n}{\partial t} = D \frac{\partial^2 n}{\partial x^2}$, $D = \frac{\langle \xi^2 \rangle}{2\tau}$.

$$\frac{\partial}{\partial t'} n(x, t + t') - D \frac{\partial^2}{\partial x^2} n(x, t + t') = 0 \quad (8.20)$$

$$\int_{-infy}^{\infty} \left[\frac{\partial}{\partial t'} f(x - x') - D \frac{\partial^2}{\partial x^2} f(x - x', t') \right] n(x', t) dx' = 0 \quad (8.21)$$

So, the kernel

$$\frac{\partial f(\xi, t)}{\partial t} - D \frac{\partial^2}{\partial \xi^2} f(\xi, t) = 0.$$

8.5.3 Time correlation in Brown motion

$$u(t) = g(t) e^{-t/\tau}$$

where

$$\frac{d(g e^{-t/\tau})}{dt} = -\frac{g(t) e^{-t/\tau}}{\tau} + \frac{\chi(t)}{m}$$

Then, we obtain the ODE

$$\frac{dg(t)}{dt} = e^{t/\tau} \frac{\chi(t)}{m} A(t)$$

the solution

$$[g(t) - g(0)] e^{-t/\tau} = e^{-t/\tau} \int_0^t e^{t'/\tau} A(t') dt' \quad (8.22)$$

$$u(t) = u(0) e^{-t/\tau} + e^{-t/\tau} \int_0^t e^{t'/\tau} A(t') dt' \quad (8.23)$$

$$u^2(t) = u^2(0) + 2u(0) e^{-2t/\tau} \int_0^t e^{t'/\tau} A(t') dt' + e^{2t/\tau} \int_0^t dt dt'' e^{(t'+t'')/\tau} A(t') A(t'') \quad (8.24)$$

The correlation function determines the expectation value

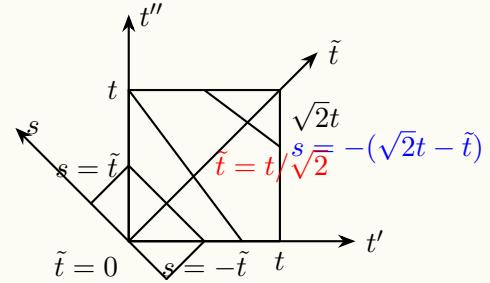
$$\langle u^2(t) \rangle = u^2(0) e^{-t/\tau} + e^{-2t/\tau} \int_0^t dt' dt'' e^{(t'+t'')/\tau} \langle A(t') A(t'') \rangle \quad (8.25)$$

Take the rotation

$$e^{(t'+t'')} \langle A(t') A(t'') \rangle \equiv e^{\sqrt{2}\tilde{t}/\tau} C(s) = \int_0^{t/\sqrt{2}} d\tilde{t} e^{\sqrt{2}\tilde{t}/\tau} \int_{-\tilde{t}}^{\tilde{t}} C(s) ds = + \int_{t/\sqrt{2}}^{\sqrt{2}t} d\tilde{t} e^{\sqrt{2}\tilde{t}/\tau} \int_{-\sqrt{2}t+\tilde{t}}^{\sqrt{2}t-\tilde{t}} C(s) ds \quad (8.26)$$

where $dt' dt'' = d\tilde{t} ds$.

$$I = \int dt' dt'' e^{\sqrt{2}\tilde{t}/\tau} C(s)$$



Brownian motion $C(s)$ Markov process

$$C(s) = C(\delta s), \quad I = \frac{Ct}{\Omega} \int_0^{\sqrt{2}t} d\tilde{t} \frac{\sqrt{2}}{2} e^{\sqrt{2}\tilde{t}/\tau} = C \frac{t}{\sqrt{2}} (e^{it/\tau} - 1)$$

Then,

$$\langle u^2(t) \rangle = u^2(0) e^{-2t/\tau} + C \frac{\tau}{\sqrt{2}} (1 - e^{-2t/\tau})$$

For $t \rightarrow \infty$, $\langle u^2(\infty) \rangle = kT/m$, $C = \frac{\sqrt{2}kT}{m\tau}$,

$$\langle u^2(t) \rangle = u^2(0) e^{-2t/\tau} + \frac{kT}{m} (1 - e^{-2t/\tau})$$

8.5.4 Fluctuation-Usage Theorem

The relation between the fluctuation of time and usage for Brownian, $\tau = (\frac{\alpha}{m})^{-1}$, so

$$\alpha = \frac{m}{\tau} = \frac{m^2}{\alpha kT} C = \frac{m^2}{\alpha kT} \int_{-\infty}^{\infty} dt \langle \delta(t) \rangle = \frac{m^2}{\alpha kT} \int_{-\infty}^{\infty} dt \langle A(0) A(t) \rangle = \frac{m^2}{\alpha kT} \int_{-\infty}^{\infty} ds \langle A(t+s) A(t) \rangle$$

We can also prove the distribution coefficient

$$D = \frac{kT}{\alpha} = \frac{1}{2} \int_{-\infty}^{\infty} du \langle u(t) u(t+s) \rangle \quad (8.27)$$

8.5.5 The themoral conductance noise and the fluctuations in voltage

In RL circuit, the KVL equation

$$L \frac{dI(t)}{dt} = -RI(t) + V(t)$$

where $V_{\text{ext}} = 0$, $\langle I(t) \rangle = 0$, $\langle V(t) \rangle = 0$. The form of Brown motation

$$I(t) \leftrightarrow u(t), \quad (8.28)$$

$$L \leftrightarrow m, \quad (8.29)$$

$$R \leftrightarrow \alpha, \quad (8.30)$$

$$V(t) \leftrightarrow \chi(t) \quad (8.31)$$

Taking the Fourier transformation

$$\tilde{V}(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} V(t) e^{-i\omega t} dt$$

and

$$\langle V(t)V(t+\delta) \rangle = C\delta(s)$$

$$\frac{1}{4\pi^2} \int d\omega d\omega' \langle \tilde{V}(\omega)\tilde{V}(\omega') \rangle e^{i\omega t+i\omega'(t+s)} = C\delta(s) = C \frac{1}{2\pi} \int d\omega' e^{i\omega's}$$

Assume

$$\begin{aligned} \langle \tilde{V}(\omega)\tilde{V}(\omega') \rangle &= \langle |\tilde{V}(\omega)|^2 \rangle \delta(\omega + \omega') = \frac{1}{4\pi^2} \int d\omega d\omega' \langle |\hat{V}(\omega)|^2 \rangle e^{i\omega t+i\omega(t+s)} \delta(\omega + \omega') \\ &= \frac{1}{4\pi^2} \int d\omega' \underset{2\pi C \rightarrow \text{Independent from } \omega}{\langle |\tilde{V}(\omega')|^2 \rangle} e^{-i\omega's} \end{aligned} \quad (8.32)$$

The fluctuation of voltage

$$\langle V^2 \rangle = \langle V^2(t) \rangle = K(0) = \int_{-\infty}^{\infty} \tilde{K}(\omega) d\omega = \int_{-\infty}^{\infty} 4\pi \tilde{K}(\nu) d\nu$$

where $\nu = 2\pi\omega$ and

- | | |
|---|---|
| (a) $S(\nu) = 4k_B T R \propto T$: Themoral noise | (c) $\langle I^2 \rangle \neq 0$ |
| (b) $S(\nu) = 4k_B T R \propto R$: Superconduct: no noise. | (d) $S(\nu)$ is independent from ν : white noise. |

8.5.6 Shot noise

- (a) The shot of electrons is random
- (b) The time between electrons released and arrive at the positive point is short, equivalent to a sudden current.

If $n(\tau)$ is the number of released electrons in unit time around time τ , then the current $j(t - \tau)$ at time τ raised from the released electrons will get weaker until 0 when $t - \tau$ is large.

$$I(t) = \int_{-\infty}^{\infty} d\tau n(\tau) i(t - \tau)$$

and the average

$$\langle I(t) \rangle = \int_{-\infty}^{\infty} d\tau \langle n \rangle i(t - \tau) = \langle n \rangle \int_{-\infty}^{\infty} i(t - \tau) d\tau = \langle n \rangle e$$

The fluctuation

$$\Delta I = I(t) - \langle I \rangle = \int_{-\infty}^{\infty} dt [n(\tau) - \langle n \rangle] i(t - \tau) dt$$

and the square

$$\langle (\Delta I)^2 \rangle = \int d\tau d\tau' \langle \Delta n(\tau) \Delta n(\tau') \rangle i(t - \tau) i(t - \tau')$$

For shot noise,

$$\begin{aligned} \langle \Delta n(\tau) \Delta n(\tau') \rangle &\propto \delta(\tau - \tau'), \\ \langle (\Delta I)^2 \rangle &= \langle n \rangle \int_{-\infty}^{\infty} |n(\tau)|^2 d\tau = \langle n \rangle 4\pi \int_0^{\infty} |S(\omega)|^2 d\omega \approx 4\pi \langle n \rangle |S(\omega)|^2 \Delta\omega \end{aligned}$$

For a scalar, $S(\omega) = \tau$ only at a given frequency.

If $\omega t \ll 1$, $e^{-i\omega t} \approx 0$.

$$S(\omega) \approx \frac{1}{2\pi} \int_{-\infty}^{\infty} i(t) dt = \frac{e}{2\pi}$$

Then, we can measure the charge e^* of a quasi-particle.

$$\langle (\Delta I)^2 \rangle = 2\langle n \rangle e^2 \Delta\nu = 2e^* \langle I \rangle \Delta\nu^*$$

In 1981: Fractional Quantum Hall Effect $\nu = \frac{1}{3}$, $e^* = \frac{e}{3}$.

8.6 Main Equation & Fock-Planck Equation

8.6.1 Master equation

Markov Process The probability at time t is only related to the former time of the nearest neighbor state.

Denote $x(t)$ a random variable $(u(t), I(t), \dots)$.

- (a) $P_1(x_1, t_1)$ denotes the probability of the value of x is x_1 at t_1 .
- (b) $P_2(x_1, t_1; x_2, t_2)$ denotes both the value of x is x_1 at t_1 and the value of x is x_2 at t_2 , is so-called the united probability.
- (c) Similarly for $P_n(x_1, t_1; \dots; x_n, t_n)$.
- (d) $P_{1/1}(x_1, t_1 | x_2, t_2)$ is for a given x , when its value is x_1 at time t_1 , the probability of the value of x is x_2 at t_2 (Conditional probability).

They satisfy the following identities

- (a) $\int P_1(x_1, t_1) dx_1 = 1.$
- (b) $\int P_n(x_1, t_1, \dots, x_n, t_n) dx_n = P_{n-1}(x_1, t_1, \dots, x_n, t_n).$
- (c) When the system is stable, $P_n(x_1, t_1; \dots, x_n, t_n) = P_n(x_1, t_1 + \tau; \dots, x_n, t_n + \tau)$ is independent from time.
- (d) $P_1(x_1, t_1)P_{1/1}(x_1, t_1 | x_2, t_2) = P_2(x_1, t_1; x_2, t_2).$
- (e) $\int P_{1/1}(x_1 t_1 | x_2 t_2) dx_2 = 1.$

In quantum mechanics,

$$P_1(x_1, t_1) = |\psi_1(x_1, t_1)|^2, \quad P_1(x_1, t_1 | x_2, t_2) = |U(x_2, t_2; x_1, t_1)|^2$$

The latter one denotes the jump probability of $|\psi_1(x_1, t_1)\rangle \rightarrow |\psi_2(x_2, t_2)\rangle$.

$$P_{n-1/1}(x_1 t_1 \dots x_{n-1} t_{n-1} | x_n, t_n) = P_{1/1}(x_{n-1} t_{n-1} | x_n, t_n)$$

Example 8.6.1.

$$\begin{aligned} P_3(x_1, t_1; x_2, t_2; x_3, t_3) &= P_2(x_1 t_1; x_2 t_2) P_{2/1}(x_1 t_1; x_2 t_2 | x_3 t_3) \\ &= P_1(x_1 t_1) P_{1/1}(x_1 t_1; x_2 t_2) P_{1/1}(x_2 t_2 | x_3 t_3) \end{aligned}$$

Integral on both sides by dx_2

$$P_2(x_1 t_1; x_3 t_2) = P_1(x_1 t_1) \int dx_2 P_{1/1}(x_1 t_1; x_2 t_2) P_{1/1}(x_2 t_2; x_3 t_3).$$

Div $P_1(x_1, t_2)$ on both sides

$$P(x_1 t_1; x_3 t_3) = \int dx_2 P(x_1 t_2; x_2 t_2) P(x_2 t_2; x_3 t_3) \tag{8.33}$$

We obtain the SCK equation. Take $t_2 = t + \tau, t_1 = t$

$$P(x_2, t + \tau) = \int P(x, t) P(xt | x_2, t + \tau) dx,$$

The derivatives

$$\frac{\partial P(x, t)}{\partial t} = \lim_{\tau \rightarrow 0} \frac{P(x, t + \tau) - P(x, t)}{\tau}, \quad \frac{\partial P(x_2, t)}{\partial t} = \lim_{\tau \rightarrow 0} \frac{1}{\tau} \int P(xt) [P(x, t | x_2, t + \tau) - P(x, t | x_2, t)]$$

If $\tau = 0$

$$P(x_2, t) = \int P(xt) P(xt | x_2 t) dx, \quad P(xt | x' t) = \delta(x - x')$$

Denote $W(x_1, x_2)$ is the jump probability density of the value of x changes from x_1 to x_2 in unit time during the time interval $t \rightarrow t + \tau$, then $\tau \int W(x_1, x) dx$ is the total probability of the value $x_1 \rightarrow x$ in time interval τ , then $[1 - \tau \int W(x_1, x) dx]$ is the probability that the jump will not occurs, if $\delta(x_1 - x_2)$ is multiplied, then it is the probability tha keep $x_1 = x_2$ and not other values of x .

$$P(x_1t|x_2t + \tau) = [1 - \tau \int W(x_1, x) dx] \delta(x_1 - x_2) + W(x_1, x_2)\tau$$

Take the time derivative

$$\frac{\partial x_0, t}{\partial t} = \frac{1}{\tau} \left[\underbrace{\int P(x_1, t) \delta(x_1 - x_2) dx_1}_{+ \tau \int P(x_1, t) W(x, x_2)} - \int P(x_1, t) \tau \int W(x_1, x) dx \delta(x_1 - x_2) dx_1 \right]$$

we obtain the Master equation

$$\frac{\partial P(x_2, t)}{\partial t} = \int [W(x_1, x_2)P(x_1, t) - P(x_2, t)W(x_2, x_1)] dx$$

Example 8.6.2. For a lonely system, its density matrix

$$\rho(t) = \sum_i w_i(t) |i\rangle \langle i|$$

and the Hamiltonian

$$H = H_0 + V, \quad H_0 |i\rangle = E_i |i\rangle.$$

$U^*(\tau)$ is time evolution operator

$$\rho(t+\tau) = \sum_i w_i(t) U(\tau) |i\rangle \langle i| U^\dagger(\tau) = \sum_{i,j,k} w_i |j\rangle \langle j| U(t) |i\rangle \langle i| U^\dagger |k\rangle \langle k| = \sum_i \sum_{j,k} w_i(t) |j\rangle \langle k| U_{ji}(\tau) U_{ki}^*(\tau)$$

Take random phase approximation (RPA)

$$\rho(t+\tau) \approx \sum_i \sum_j w_i(t) |j\rangle \langle j| U_{ji}(t) U_{ji}^*(\tau) = \sum_j w_j(t+\tau) |j\rangle \langle j|$$

That is

$$w_j(t+\tau) = \sum_i w_i(t) |U_{ji}(t)|^2, \quad w_j(t+\tau) - w_j(t) = \sum_i (w_i(t) - w_j(t)) |U_{ji}(\tau)|^2,$$

where $i = j$ canceled. $|U_{ji}|_{j \neq i}^2$.

$$|U_{ji}|^2 = \frac{1}{\hbar^2} \left(\frac{\sin(w_{ij}\tau/2)}{w_{ij}/2} \right)^2 |\langle j|V|i\rangle|^2 \approx \tau \frac{2\pi}{\hbar} \delta(E_i - E_j) |\langle j|V|i\rangle|^2$$

The derivative

$$\frac{dw_i(t)}{dt} = \frac{w_i(t+\tau) - w_i(t)}{\tau} \Big|_{\tau \rightarrow 0} = \sum_i (w_i(t) - w_j(t)) \frac{2\pi}{\hbar} \delta(E_i - E_j) |\langle j|V|i\rangle|^2$$

where $\tau = (E_i - E_j)/\hbar$, \sum_i is the sum of all the quantum states. Take $\sum_i \rightarrow \sum_{E_i, F_i}$, then

$$\sum_{E_i} \rightarrow \int dE_i n(E_i),$$

$n(E_i)$ denotes the DOE.

$$\frac{dW_{E_i F_i}(t)}{dt} = \sum_{F_i} (W_{E_j F_i} - W_{E_j F_j}) \left(\frac{2\pi}{\hbar} n(E_i) |\langle E_j F_j | V | E_j F_j \rangle|^2 P_{E_j}(E_j F_j) \right)$$

8.6.2 Forkker-Planck equation

x can be continuous, $w(x, x')$ will get weaker quickly as the increase of $|x - x'|$. We can denote $\xi = x - x'$ as a small variable, then

$$W(x', x) = W\left(\frac{x' + x}{2}, x' - x\right) \approx W(x', -\xi)$$

Take the approximation to the main equation

$$\frac{\partial P(x, t)}{\partial t} = \int [w(x', x)P(x', t) - W(x, x')P(x, t)] dx' = \int [w(x - \xi, \xi)P(x - \xi, t) - W(x, -\xi)P(x, t)] d\xi$$

Expand it

$$W(x - \xi, \xi)P(x - \xi, t) = W(x, \xi)P(x, t) - \xi \frac{\partial}{\partial x} w(x, \xi)P(x, t) + \frac{1}{2}\xi^2 \frac{\partial^2}{\partial \xi^2} [w(x, \xi)P(x, t)] + \dots$$

Substitute the expansion back

$$\frac{\partial P(x, t)}{\partial t} = \cancel{\int w(x, \xi)P(x, t) d\xi} - \int \xi \frac{\partial}{\partial x} [w(x, \xi)P(x, t)] + \frac{1}{2} \int \xi^2 \frac{\partial^2}{\partial x^2} [w(x, \xi)P(x, t)] d\xi - \cancel{\dots}$$

Rearrange

$$\frac{\partial P(x, t)}{\partial t} + \frac{\partial}{\partial x} [\alpha_1(x)P(x, t)] = \frac{1}{2} \frac{\partial^2}{\partial x^2} \alpha_2(x)P(x, t) = \int \xi^n w(x, \xi) d\xi \quad (8.34)$$

n -th matrix. Forkker-Planck equation. If $\alpha_1(x) = 0$, $\alpha_2(x) = \text{Const}$, then F-P equation is equivalent to Brownian motion equation.

Lecture #1 Homework #1 [2025-09-02]

Problem 1.1. 总结热力学的基本概念：什么叫平衡态？写出温度、温标的定义；内能的定义；热容和比热的定义；熵的定义和物理意义。

Solution.

- (a) 平衡态：在没有外界影响的条件下，物体各部分的性质长时间不发生任何变化的状态。
- (b) 温度：衡量物体间是否热平衡的物理量称为温度。
- (c) 温标：确定温度具体数值的规则叫温标。
- (d) 内能：系统所含有的能量，但不包含因外部力场而产生的系统整体之动能与势能。
- (e) 热容：在不发生相变化和化学变化的前提下，系统与环境所交换的热与由此引起的温度变化之比称为系统的热容。即 $C_\eta = \frac{dQ_\eta}{dT}$ 称为热容，其中 η 表示不变的量。
- (f) 比热：单位质量的物质在温度变化时所吸收或释放的热量与其质量之比，即 $c = C/V$ 。
- (g) 熵：一个系统内所有元素状态的总和，物理意义：用来衡量系统的无序程度。

Problem 1.2. 什么叫物态方程？写出理想气体的物态方程。写出范德瓦尔斯气体的物态方程，并解释对理想气体物态方程修正项的物理意义。

Solution.

- (a) 物态方程：物体的物理状态由几何变量 (V, A, L) ，力学变量 (p, σ, F) ，电磁变量 (E, P, H, M) 和化学变量等描述，温度与这些状态变量之间的函数关系 $T = f(p, V, \dots)$ 称为物态方程。
- (b) 理想气体状态方程： $pV = nRT = NkT$
- (c) 范德瓦尔斯气体的物态方程： $ab(p + \frac{n^2a}{V^2})(V - nb) = nRT$ 。
 - i. 体积修正 $-nb$: 分子有固有体积，活动空间减少
 - ii. 压力修正 $+an^2/V^2$: 分子间吸引力减弱对器壁的冲击

Problem 1.3. 对 $p - V - T$ 系统，依据自变量不同，写出 4 种等价的热力学微分方程，说明各自在什么条件下适用。

Solution.

- | | |
|--|------------------------------------|
| (a) $dU = T dS - p dV$ (S, V)，适用绝热过程 | (c) $dF = -S dT - p dV$ ，适用等温等容 |
| (b) $dH = T dS + V dP$ (S, P)，适用等压过程 | (d) $dG = -S dT + V dP$ ，适用等温等压、相变 |

Problem 1.4. 解释热力学第一、二、三定理的物理意义.

Solution.

- (a) 热力学第一定律: 推广到非绝热过程, 系统从外界吸热, $Q = U_2 - U_1 - W_0$, 即能量守恒
- (b) 热力学第二定律: 熵增加原理
- (c) 热力学第三定律: 不可能通过有限步骤使物体冷却到绝对零度

Problem 1.5 (林宗涵《热力学与统计物理》1.1). 设三个函数 f, g, h 都是二独立变量 x, y 的函数, 证明:

$$\begin{array}{lll} \text{(a)} \quad \left(\frac{\partial f}{\partial g}\right)_h = 1/\left(\frac{\partial g}{\partial f}\right)_h & \text{(c)} \quad \left(\frac{\partial y}{\partial x}\right)_f = -\frac{\partial f}{\partial x}/\frac{\partial f}{\partial y} & \text{(e)} \quad \left(\frac{\partial f}{\partial x}\right)_g = \frac{\partial f}{\partial x} + \frac{\partial f}{\partial y}\left(\frac{\partial y}{\partial x}\right)_g \\ \text{(b)} \quad \left(\frac{\partial f}{\partial g}\right)_x = \frac{\partial f}{\partial y}/\frac{\partial g}{\partial y} & \text{(d)} \quad \left(\frac{\partial f}{\partial g}\right)_h \left(\frac{\partial g}{\partial h}\right)_f \left(\frac{\partial h}{\partial f}\right)_g = -1 & \end{array}$$

Solution.

- (a) 对 f 取微分

$$df = \left(\frac{\partial f}{\partial g}\right)_h dg + \left(\frac{\partial f}{\partial h}\right)_g dh$$

令 $dh = 0$ 得

$$1 = \left(\frac{\partial f}{\partial g}\right)_h \left(\left(\frac{\partial g}{\partial f}\right)_h\right), \quad \left(\frac{\partial f}{\partial g}\right)_h = 1/\left(\frac{\partial g}{\partial f}\right)_h$$

- (b) $f = f(x, y(x, g))$. 由复合函数求导法则

$$\left(\frac{\partial f}{\partial g}\right)_x = \left(\frac{\partial f}{\partial y}\right)_x \left(\frac{\partial y}{\partial g}\right)_x = \left(\frac{\partial f}{\partial y}\right)_x \left(\frac{\partial g}{\partial y}\right)_x$$

这里利用了 (a) 中的结论.

- (c) $f = f(x, y)$. 令 f 的微分为 0 得

$$df = \left(\frac{\partial f}{\partial x}\right)_y dx + \left(\frac{\partial f}{\partial y}\right)_x dy = 0, \quad \left(\frac{\partial y}{\partial x}\right)_f = -\left(\frac{\partial f}{\partial x}\right)_y / \left(\frac{\partial f}{\partial y}\right)_x$$

- (d) $f = f(g, h)$. 对 (c) 中结论做变量替换

$$\left(\frac{\partial h}{\partial g}\right)_f = -\left(\frac{\partial f}{\partial g}\right)_h / \left(\frac{\partial f}{\partial h}\right)_g$$

利用 (a) 中的结论得

$$\left(\frac{\partial f}{\partial g}\right)_h \left(\frac{\partial g}{\partial h}\right)_f \left(\frac{\partial h}{\partial f}\right)_g = -1$$

- (e) $f = f(x, y(x, g))$. 由复合函数求导法则

$$\left(\frac{\partial f}{\partial x}\right)_g = \left(\frac{\partial f}{\partial x}\right)_y + \left(\frac{\partial f}{\partial y}\right)_x \left(\frac{\partial y}{\partial x}\right)_g$$

Problem 1.6 (林宗涵《热力学与统计物理》1.5). 有一铜块处于 0°C 和 1 atm 下, 经测定, 其膨胀系数和等温压缩系数分别为 $4.85 \times 10^{-5} \text{ K}^{-1}$, $\kappa_\tau = 7.8 \times 10^{-7} (\text{atm})^{-1}$, α 和 κ_τ 可以近似当成常数. 今使铜块加热至 10°C , 问

- (a) 压强要增加多少才能维持铜块体积不变? (b) 若压强增加 100 atm, 铜块的体积改变多少?

Solution.

- (a) 在温度变化 dT 和压强变化 dp 范围内, 铜块体积变化

$$dV = V(\alpha dT - \kappa dp)$$

要维持铜块体积不变, 则 $dV = 0$, 即

$$dp = \frac{\alpha}{\kappa_T} dT = 621.79 \text{ atm}$$

- (b) 对体积变化公式分离变量并积分得

$$\ln \frac{V}{V_0} = \alpha \Delta T - \kappa_T \Delta p$$

令 $V = V_0 + \Delta V$, 则

$$\ln \frac{V_0 + \Delta V}{V_0} \approx \frac{\Delta V}{V_0} = \alpha \Delta T - \kappa_T \Delta p = 4.07 \times 10^{-4}$$

即铜块体积改变 $4.07 \times 10^{-2}\%$.

Problem 1.7 (林宗涵《热力学与统计物理》1.6). 已知一理想弹性丝的物态方程为

$$\mathcal{F} = bT \left(\frac{L}{L_0} - \frac{L_0^2}{L^2} \right)$$

其中 \mathcal{F} 使张力; L 使长度, L_0 使张力为零时的 L 值, L_0 只是温度 T 的函数; b 使常数. 定义 (线) 膨胀系数为

$$\alpha \equiv \frac{1}{L} \left(\frac{\partial L}{\partial T} \right)_{\mathcal{F}}$$

等温杨氏模量为

$$Y = \frac{L}{A} \left(\frac{\partial \mathcal{F}}{\partial L} \right)_T$$

其中 A 使弹性丝的横截面积. 证明:

$$(a) Y = \frac{bT}{A} \left(\frac{L}{L_0} + \frac{2L_0^2}{L^2} \right). \quad (b) \alpha = \alpha_0 - \frac{1}{T} \frac{L^3/L_0^3 - 1}{L^3/L_0^3 + 2}, \text{ 其中 } \alpha_0 = \frac{1}{L_0} \frac{dL_0}{dT}.$$

Solution.

- (a) 将 \mathcal{F} 带入 Y 即可

$$Y = \frac{L}{A} bT \left(\frac{1}{L_0} + \frac{2L_0^2}{L^3} \right) = \frac{bT}{A} \left(\frac{L}{L_0} + \frac{2L_0^2}{L^2} \right)$$

- (b) 令 $\partial \mathcal{F} / \partial T = 0$

$$0 = b \left(\frac{L}{L_0} - \frac{L_0^2}{L^2} \right) + bT \left(\frac{1}{L_0} + \frac{2L_0^2}{L^3} \right) \left(\frac{\partial L}{\partial T} \right)_{\mathcal{F}} + bT \left(-\frac{L}{L_0^2} - \frac{2L_0}{L^2} \right) \frac{dL_0}{dT}$$

得

$$\alpha = \alpha_0 = \frac{1}{T} \frac{L^3/L_0^3 - 1}{L^3/L_0^3 + 2}$$

Problem 1.8 (林宗涵《热力学与统计物理》2.2). 证明下列关系:

- (a) $\left(\frac{\partial U}{\partial V}\right)_p = -T\left(\frac{\partial V}{\partial T}\right)_S$ (d) $\left(\frac{\partial T}{\partial p}\right)_H = T\left(\frac{\partial V}{\partial H}\right)_p - V\left(\frac{\partial T}{\partial H}\right)_p$
 (b) $\left(\frac{\partial U}{\partial V}\right)_p = -T\left(\frac{\partial p}{\partial T}\right)_S - p$ (e) $\left(\frac{\partial T}{\partial S}\right)_H = \frac{T}{C_p} - \frac{T^2}{V}\left(\frac{\partial V}{\partial H}\right)_p$
 (c) $\left(\frac{\partial T}{\partial V}\right)_U = p\left(\frac{\partial T}{\partial U}\right)_V - T\left(\frac{\partial p}{\partial U}\right)_V$.

Solution.

(a) 由热力学基本微分方程

$$dU = T dS - p dV$$

得 Maxwell 关系

$$\left(\frac{\partial V}{\partial T}\right)_S = -\left(\frac{\partial S}{\partial p}\right)_v = -\frac{\partial^2(S, V)}{\partial(p \partial V)} = -\left(\frac{\partial S}{\partial U}\right)_V \left(\frac{\partial U}{\partial p}\right)_v = -\frac{1}{T} \left(\frac{\partial U}{\partial p}\right)_V$$

即

$$\left(\frac{\partial U}{\partial p}\right)_V = -T \left(\frac{\partial V}{\partial T}\right)_S$$

(b) 将热力学基本微分方程两侧对 V 取偏微分

$$\left(\frac{\partial U}{\partial V}\right)_p = T \left(\frac{\partial S}{\partial V}\right)_p - p$$

已知

$$dH = T dS + V dp$$

得 Maxwell 关系

$$\left(\frac{\partial p}{\partial T}\right)_S = \left(\frac{\partial S}{\partial V}\right)_p$$

所以有

$$\left(\frac{\partial U}{\partial V}\right)_p = T \left(\frac{\partial p}{\partial T}\right)_S - p$$

(c) 将热力学基本微分方程写为

$$dS = \frac{1}{T} dU + \frac{p}{T} dV$$

由此得 Maxwell 关系

$$\left(\frac{\partial(1/T)}{\partial V}\right)_U = \left(\frac{\partial(p/T)}{\partial U}\right)_V$$

展开得

$$\left(\frac{\partial T}{\partial V}\right)_U = p \left(\frac{\partial T}{\partial U}\right)_V - T \left(\frac{\partial p}{\partial U}\right)_V$$

(d) 同 (iii), 使用

$$dS = \frac{1}{T} dH - \frac{V}{T} dp$$

得 Maxwell 关系

$$\left(\frac{\partial(1/T)}{\partial p}\right)_H = -\left(\frac{\partial(V/T)}{\partial H}\right)_p$$

展开得

$$\left(\frac{\partial T}{\partial p}\right)_H = T \left(\frac{\partial V}{\partial H}\right)_p - V \left(\frac{\partial T}{\partial H}\right)_p$$

(e) 由复合函数求导法则

$$\left(\frac{\partial T}{\partial S}\right)_H = \frac{\partial^2(T, H)}{\partial(S \partial p)} \cdot \frac{\partial^2(S, p)}{\partial(S \partial H)} = \frac{T}{C_p} + \left(\frac{\partial T}{\partial p}\right)_s \left(\frac{\partial p}{\partial S}\right)_H$$

令 $dH = 0$, 得

$$0 = T dS + V dp, \quad \left(\frac{\partial p}{\partial S}\right) = -\frac{T}{V}$$

使用 Maxwell 关系

$$\left(\frac{\partial T}{\partial p}\right)_s = \left(\frac{\partial V}{\partial S}\right)_p = T \left(\frac{\partial V}{\partial H}\right)_p$$

将以上两式带入求导结果

$$\left(\frac{\partial T}{\partial S}\right)_H = \frac{T}{C_p} - \frac{T^2}{V} (pdV VH)_p$$

Problem 1.9 (林宗涵《热力学与统计物理》2.3). 对 $p - V - T$ 系统, 证明

$$\frac{\kappa_T}{\kappa_S} = \frac{C_p}{C_V}$$

其中

$$\kappa_T \equiv -\frac{1}{V} \left(\frac{\partial V}{\partial p}\right)_T, \quad \kappa_S \equiv -\frac{1}{V} \left(\frac{\partial V}{\partial p}\right)_S$$

分别代表等温与绝热压缩系数.

Solution. *Proof.*

$$\frac{C_p}{C_v} = \frac{T \left(\frac{\partial S}{\partial T}\right)_p}{T \left(\frac{\partial S}{\partial T}\right)_V} = \frac{\left(\frac{\partial S}{\partial V}\right)_p \left(\frac{\partial V}{\partial T}\right)_p}{\left(\frac{\partial S}{\partial V}\right)_V \left(\frac{\partial V}{\partial T}\right)_V} = \left[-\frac{1}{V} \left(\frac{\partial V}{\partial p}\right)_T \right] / \left[-\frac{1}{V} \left(\frac{\partial V}{\partial p}\right)_S \right] = \frac{\kappa_T}{\kappa_S} \square$$

Problem 1.10 (林宗涵《热力学与统计物理》2.5).

(a) 证明

$$\left(\frac{\partial C_V}{\partial V}\right)_T = T \left(\frac{\partial^2 p}{\partial T^2}\right)_V; \quad \left(\frac{\partial C_p}{\partial p}\right)_T = -T \left(\frac{\partial^2 V}{\partial T^2}\right)_p$$

并由此导出

$$C_V = C_{V_0} + T \int_{V_0}^V \left(\frac{\partial^2 p}{\partial T^2}\right)_V dV, \quad C_p = C_{p_0} - T \int_{p_0}^p \left(\frac{\partial^2 V}{\partial T^2}\right)_p dp.$$

其中 C_{V_0} 与 C_{p_0} 分别代表体积为 V_0 时的定容热容与压强为 p_0 时的定压热容, 它们都只是温度的函数.

(b) 根据以上 C_V, C_p 两式证明, 理想气体的 C_V 与 C_p 只是温度的函数.

(c) 证明范德瓦耳斯气体的 C_V 只是温度的函数, 与体积无关.

Solution.

(a) 将 C_V 对 V 取偏导数

$$\left(\frac{\partial C_V}{\partial V}\right)_T = T \frac{\partial^2 S}{\partial T \partial V} = T \left(\frac{\partial^2 p}{\partial T^2}\right)_V$$

则 $C_V(T, V)$ 的积分分为等容过程和等压过程

$$C_V(T, V) - C_V(T_0, V_0) = \int_{T_0}^T \left(\frac{\partial C_V}{\partial T}\right)_V dT + \int_{V_0}^V \left(\frac{\partial C_V}{\partial V}\right)_T dV$$

使用 Maxwell 关系, 积分可写作

$$C_V(T, V) = C_{V_0}(T) + T \int_{V_0}^V \left(\frac{\partial^2 p}{\partial T^2}\right)_V dV.$$

同理可证

$$\left(\frac{\partial C_p}{\partial p}\right)_T = -T \left(\frac{\partial^2 V}{\partial T^2}\right)_p, \quad C_p = C_{p_0} - T \int_{p_0}^p \left(\frac{\partial^2 V}{\partial T^2}\right)_p dp.$$

(b) 由理想气体状态方程

$$pV = NRT$$

可得

$$\left(\frac{\partial^2 p}{\partial T^2}\right)_V = 0, \quad \left(\frac{\partial^2 V}{\partial T^2}\right)_p = 0.$$

带入 (a) 中结论得

$$\left(\frac{\partial C_V}{\partial V}\right)_T = 0, \quad \left(\frac{\partial C_p}{\partial p}\right)_T = 0$$

即理想气体的 C_V 与 C_p 都只是温度的函数.

(c) 由范德瓦耳斯气体的物态方程

$$\left(p + \frac{N^2 a}{V^2}\right)(V - Nb) = NRT$$

当 V 固定时, 有

$$\left(\frac{\partial^2 p}{\partial T^2}\right)_V = \left(\frac{\partial C_V}{\partial V}\right)_T = 0$$

表明范德瓦耳斯气体的 C_V 只是温度的函数, 与体积无关.

Problem 1.11 (林宗涵《热力学与统计物理》3.1). 利用无穷小的变动, 导出下列各平衡判据 (假设总粒子数不变, 且 $S > 0$)

- | | |
|-------------------------------------|-------------------------------------|
| (a) 在 U 及 V 不变的情形下, 平衡态的 S 极大 | (e) 在 S 及 p 不变的情形下, 平衡态的 H 极小 |
| (b) 在 S 及 V 不变的情形下, 平衡态的 S 极小 | (f) 在 T 及 V 不变的情形下, 平衡态的 F 极小 |
| (c) 在 S 及 U 不变的情形下, 平衡态的 V 极小 | (g) 在 F 及 T 不变的情形下, 平衡态的 V 极小 |
| (d) 在 H 及 p 不变的情形下, 平衡态的 S 极大 | (h) 在 T 及 p 不变的情形下, 平衡态的 G 极小 |

Solution.

(a) 系统孤立, 内能和体积固定. 由熵增原理, 一切自发过程朝熵增方向进行, 平衡时熵取最大值.

(b) 熵和体积固定时, 由

$$dU = T dS - p dV$$

得可逆过程 $dU = 0$. 实际不可逆过程在总熵不变时内能会减少, 平衡时内能最小.

(c) 熵与内能固定, 由

$$dU = T dS - p dV$$

得 $p dV = 0$. 考虑力学稳定性, 系统会自发收缩或抵抗膨胀, 平衡时体积最小.

(d) 焓 $H = U + pV$, 压强不变时 $dH = T dS$. 固定 H, p 则 $dS = 0$, 熵判据要求平衡时熵最大.

(e) 熵与压强固定, 由

$$dH = T dS + V dp$$

得 $dH = 0$. 系统自发趋向焓更低的状态, 平衡时焓最小.

(f) 亥姆霍兹自由能 $F = U - TS$, 固定 T, V 时

$$dF = -S dT - p dV = 0$$

自发过程 $dF < 0$, 平衡时 F 最小.

(g) 固定 F, T , 由

$$dF = -S dT - p dV$$

得 $p dV = 0$. 体积稳定性要求平衡时体积最小.

(h) 吉布斯自由能

$$G = U - TS + pV$$

固定 T, p 时 $dG = 0$ (可逆). 自发过程 $dG < 0$, 平衡时 G 最小.

Lecture #2 Homework #2 [2025-09-09]

Problem 2.1. 对独立粒子体系，用排列组合公式对可区分粒子、玻色子和费米子在给定粒子数分布 $\{a_\alpha\}$ 下的量子状态数 $W(\{a_\alpha\})$.

Solution.

(a) 可区分粒子

由于粒子可区分，能级 ε_α 有 g_α 个简并量子态. 将 N 个粒子分成若干组 $\{a_\alpha\}$ ，分配方式数为

$$\frac{N!}{\prod_\alpha a_\alpha!}$$

对能级 α ，每个粒子可占据 g_α 个态中的任意一个，因此有 $g_\alpha^{a_\alpha}$ 种占据方式. 总方式数为

$$W = \frac{N!}{\prod_\alpha a_\alpha!} \times \prod_\alpha g_\alpha^{a_\alpha} = N! \prod_\alpha \frac{g_\alpha^{a_\alpha}}{a_\alpha!}$$

(b) 玻色子

粒子全同，每个量子态占据粒子数不限. 对能级 α : 将 a_α 个全同粒子放入 g_α 个态，等价于 a_α 个粒子与 $g_\alpha - 1$ 个棒隔开不同态的排列数:

$$\frac{(a_\alpha + g_\alpha - 1)!}{a_\alpha! (g_\alpha - 1)!}$$

各能级独立，所以:

$$W = \prod_\alpha \frac{(a_\alpha + g_\alpha - 1)!}{a_\alpha! (g_\alpha - 1)!}$$

(c) 费米子

粒子全同，受泡利原理限制：每个量子态最多一个粒子，且 $a_\alpha \leq g_\alpha$. 对能级 α : 从 g_α 个态中选择 a_α 个被占据的方式数为组合数:

$$\frac{g_\alpha!}{a_\alpha! (g_\alpha - a_\alpha)!}$$

各能级独立，所以:

$$W = \prod_\alpha \frac{g_\alpha!}{a_\alpha! (g_\alpha - a_\alpha)!}$$

Problem 2.2. 用最可几分布求出上题相应的配分函数.

Solution.

(a) 可区分粒子 (MB 统计) 由 $\ln W = \ln N! + \sum_\alpha [a_\alpha \ln g_\alpha - \ln a_\alpha!]$ 及约束变分得

$$a_\alpha = g_\alpha e^{-\alpha - \beta E_\alpha}$$

代入 $\sum a_\alpha = N$ 得 $e^{-\alpha} = N/Z_1$ ，于是

$$a_\alpha = N \frac{g_\alpha e^{-\beta E_\alpha}}{Z_1}, \quad Z_N = Z_1^N$$

(或 $Z_N = Z_1^N/N!$ 以修正吉布斯佯谬)

(b) 玻色子 (BE 统计) 由 $\ln W = \sum_{\alpha} [\ln(a_{\alpha} + g_{\alpha} - 1)! - \ln a_{\alpha}! - \ln(g_{\alpha} - 1)!]$ 变分得

$$a_{\alpha} = \frac{g_{\alpha}}{e^{\alpha+\beta E_{\alpha}} - 1}$$

令 $\alpha = -\beta\mu$, 则

$$a_{\alpha} = \frac{g_{\alpha}}{e^{\beta(E_{\alpha}-\mu)} - 1}, \quad \Xi = \prod_{\alpha} \left(1 - e^{-\beta(E_{\alpha}-\mu)}\right)^{-g_{\alpha}}$$

(c) 费米子 (FD 统计) 由 $\ln W = \sum_{\alpha} [\ln g_{\alpha}! - \ln a_{\alpha}! - \ln(g_{\alpha} - a_{\alpha})!]$ 变分得

$$a_{\alpha} = \frac{g_{\alpha}}{e^{\alpha+\beta E_{\alpha}} + 1}$$

令 $\alpha = -\beta\mu$, 则

$$a_{\alpha} = \frac{g_{\alpha}}{e^{\beta(E_{\alpha}-\mu)} + 1}, \quad \Xi = \prod_{\alpha} \left(1 + e^{-\beta(E_{\alpha}-\mu)}\right)^{g_{\alpha}}$$

Problem 2.3. 一个二能级系统, $\epsilon_1 = -\epsilon$, $\epsilon_2 = \epsilon$, 且 $g_1 = g_2 = 1$. 设有 N 个独立可区分粒子处于平衡态, 求

(a) 温度 $T \rightarrow 0$ 时系统的熵.

(b) 若“粒子”是自旋 \uparrow, \downarrow 两个态, 则 $T \rightarrow 0$ 的熵值在此时的物理意义是什么?

Solution.

(a) 单粒子配分函数 $Z_1 = e^{\beta\epsilon} + e^{-\beta\epsilon} = 2 \operatorname{ch}(\beta\epsilon)$, 系统配分函数 $Z_N = Z_1^N$. 熵

$$S = Nk[\ln(2 \operatorname{ch}(\beta\epsilon)) - \beta\epsilon \operatorname{th}(\beta\epsilon)]$$

当 $T \rightarrow 0$, $\beta\epsilon \rightarrow \infty$, $\operatorname{th}(\beta\epsilon) \rightarrow 1$, $\operatorname{ch}(\beta\epsilon) \sim \frac{1}{2}e^{\beta\epsilon}$,

$$\ln(2 \operatorname{ch}(\beta\epsilon)) \rightarrow \beta\epsilon \Rightarrow S \rightarrow Nk[\beta\epsilon - \beta\epsilon] = 0$$

所以 $S(T \rightarrow 0) = 0$.

(b) 若为自旋系统, $T \rightarrow 0$ 时所有自旋处于低能态 (完全极化), 系统处于唯一基态, 微观状态数 $W = 1$, 熵为零, 符合热力学第三定律.

Problem 2.4. 论证光子气体不发生玻色 - 爱因斯坦凝聚.

Solution. 光子气体化学势 $\mu = 0$ 且 $\epsilon_{\min} = 0$, 故 μ 始终等于最低能级, 不存在随温度降低而趋近于零的过程. 同时光子数不守恒, 总粒子数由平衡条件调节, 无 BEC 所需的粒子数重新分布相变机制. 因此光子气体不发生玻色-爱因斯坦凝聚.

Problem 2.5 (林宗涵《热力学与统计物理》7.5). 计算爱因斯坦固体模型的熵.

Solution. 爱因斯坦固体模型可看作近独立子系, 每一个子系的 Maxwell-Boltzmann 分布函数为

$$Z = \sum_{n=0}^{\infty} e^{-\beta\epsilon_n} = \sum_{n=0}^{\infty} e^{-\beta(n+1/2)\hbar\omega} = \frac{e^{-\beta\hbar\omega/2}}{1 - e^{-\beta\hbar\omega}}$$

设原子总数为 N , 则总振动自由度为 $3N$. 系统的熵为

$$S = 3Nk \left(\ln Z - \beta \frac{\partial}{\partial \beta} \ln Z \right) = 3Nk \left[\frac{\hbar\omega/kT}{e^{\hbar\omega/kT} - 1} - \ln(1 - e^{\hbar\omega/kT}) \right]$$

Problem 2.6 (林宗涵《热力学与统计物理》7.7). 自旋为 $\hbar/2$ 的粒子处于磁场 \mathcal{H} 中, 粒子的磁矩为 μ , 磁矩与磁场方向平行或反平行所相应的能量分别为 $-\mu\mathcal{H}$ 与 $\mu\mathcal{H}$. 今设有 N 个这样的定域粒子处于磁场 \mathcal{H} 中, 整个系统处于温度为 T 的平衡态, 粒子之间的相互作用很弱, 可以忽略.

- (a) 求子系统的配分函数 Z .
- (b) 求系统的自由能 F , 熵 S , 内能 \bar{E} 和热容 $C_{\mathcal{H}}$.
- (c) 证明总磁矩的平均值为 $\bar{\mathcal{M}} = N\mu \operatorname{th}\left(\frac{\mu\mathcal{H}}{kT}\right)$.
- (d) 证明在高温弱场下, 亦即 $\frac{\mu\mathcal{H}}{kT} \ll 1$ 时: $\bar{\mathcal{M}} = \frac{N\mu^2}{kT}\mathcal{H}$; 磁化率 $\chi = \frac{\partial(\bar{\mathcal{M}}/V)}{\partial\mathcal{H}} = \frac{N\mu^2}{kT}$; 在低温强场下, 亦即 $\frac{\mu\mathcal{H}}{kT} \gg 1$ 时: $\bar{\mathcal{M}} = N\mu$; $\chi = 0$.

Solution.

- (a) 代入配分函数的定义得

$$Z = e^{\beta\mu\mathcal{H}} + e^{-\beta\mu\mathcal{H}} = 2 \operatorname{ch}(\beta\mu\mathcal{H})$$

- (b) i. 自由能 $F = -NkT \ln Z = -NkT \ln(2 \operatorname{ch}(\beta\mu\mathcal{H}))$.
ii. 熵 $S = Nk \left(\ln Z - \beta \frac{\partial \ln Z}{\partial \beta} \right) = Nk [\ln(2 \operatorname{ch}(\beta\mu\mathcal{H})) - \beta\mu\mathcal{H} \operatorname{th}(\beta\mu\mathcal{H})]$.
iii. 内能 $\bar{E} = -N \frac{\partial \ln Z}{\partial \beta} = -N\mu\mathcal{H} \operatorname{th}(\beta\mu\mathcal{H})$.
iv. 热容 $C_{\mathcal{H}} = \left(\frac{\partial \bar{E}}{\partial T} \right)_{\mathcal{H}} = Nk \left(\frac{\mu\mathcal{H}}{kT} \right)^2 \left\{ 1 - \operatorname{th}^2 \left(\frac{\mu\mathcal{H}}{kT} \right) \right\}$.

- (c) 设原子总数为 N . 则处于平行与反平行的概率分别为

$$P_1 = \frac{N}{Z} e^{\beta\mu\mathcal{H}}, \quad P_2 = \frac{N}{Z} e^{-\beta\mu\mathcal{H}}.$$

则磁矩的期望值为

$$\bar{\mathcal{M}} = \langle \mu \rangle = P_1\mu + P_2(-\mu) = N\mu \operatorname{th}\left(\frac{\mu\mathcal{H}}{kT}\right).$$

- (d) 由于以下极限

$$\lim_{x \rightarrow 0} \operatorname{th} x = x, \quad \lim_{x \rightarrow \infty} \operatorname{th} x = 1, \quad \lim_{x \rightarrow 0} \operatorname{ch} x = 1, \quad \lim_{x \rightarrow \infty} \operatorname{ch} x = \infty,$$

所以在高温弱场、低温强场下

$$\lim_{T \rightarrow \infty} \bar{\mathcal{M}} = \frac{N\mu^2}{kT}\mathcal{H}, \quad \text{and} \quad \lim_{T \rightarrow 0} \bar{\mathcal{M}} = N\mu,$$

磁导率的一般表达式

$$\chi = \frac{\partial(\bar{\mathcal{M}}/V)}{\partial\mathcal{H}} = \frac{N\mu^2}{kT} \frac{1}{\operatorname{ch}^2(\mu\mathcal{H}/kT)}$$

则在在高温弱场、低温强场下

$$\lim_{T \rightarrow \infty} \chi = \frac{N\mu^2}{kT}, \quad \text{and} \quad \lim_{T \rightarrow 0} \chi = 0$$

Problem 2.7 (林宗涵《热力学与统计物理》7.15). 粒子的态密度 $D(\epsilon)$ 定义为: $D(\epsilon) d\epsilon$ 代表粒子的能量处于 ϵ 与 $\epsilon + d\epsilon$ 之间的量子态数 (见原书 §7.15). 这里指考虑粒子的平动自由度所对应的态密度.

(a) 设粒子的能谱（即能量与动量的关系）是非相对论性的，试分别对下列三种空间维数，求相应的态密度 $D(\epsilon)$:

i. 粒子局限在体积为 V 的三维空间内运动

$$\epsilon = \frac{1}{2m}(p_x^2 + p_y^2 + p_z^2);$$

ii. 粒子局限在面积为 A 的二维平面内运动

$$\epsilon = \frac{1}{2m}(p_x^2 + p_y^2)$$

iii. 粒子局限在长度为 L 的一维空间内运动

$$\epsilon = \frac{p_x^2}{2m}$$

(b) 设粒子的能谱是极端相对性的，即 $\epsilon = cp, p = |\mathbf{p}|$ ，试对空间维数分别为 1. 三维 2. 二维 3. 一维三种情况，求相应的 $D(\epsilon)$.

Solution.

(a) 首先计算关系 $dp/d\epsilon$

$$\epsilon = \frac{p^2}{2m} \Rightarrow \frac{dp}{d\epsilon} = \frac{m}{p}$$

三维、二维、一维情况下的态密度分别为

$$\begin{aligned} D_{3D}(\epsilon) &= \frac{1}{d\epsilon} \int \frac{d\omega}{h^3} = \frac{1}{d\epsilon} \int \frac{dx dp_x dy dp_y dz dp_z}{h^3} = \frac{V}{h^3} 4\pi p^2 \frac{dp}{d\epsilon} = \frac{2\pi V}{h^3} (2m)^{3/2} \epsilon^{1/2} \\ D_{2D}(\epsilon) &= \frac{1}{d\epsilon} \int \frac{dx dp_x dy dp_y}{h^3} = \frac{2\pi A m}{h^2} \\ D_{1D}(\epsilon) &= \frac{L}{h} \int 2 \frac{dp}{d\epsilon} = \frac{L}{h} (2m)^{1/2} \epsilon^{-1/2} \end{aligned}$$

(b) $\epsilon = cp$ 时， $dp/d\epsilon = \frac{1}{c}$. 只需将 (a) 中的 $dp/d\epsilon$ 替换为新的 $dp/d\epsilon$ 即可. 结果分别为

$$D_{3D} = \frac{4\pi V}{(hc)^3} \epsilon^2, D_{2D} = \frac{2\pi A}{(hc)^2} \epsilon, D_{1D} = \frac{2L}{hc}.$$

Lecture #3 Homework #3 [2025-09-16]

Problem 3.1. N 个单原子分子组成的理想气体,

$$H = \sum_{i=1}^{3N} \frac{p_i^2}{2m}$$

微观状态数的定义为

$$\Omega(E) = \frac{1}{N!h^{3N}} \int_{E \leq H \leq E + \Delta E} dq_1 \cdots dq_{3N} dp_1 \cdots dp_{3N}$$

证明

$$\Omega(E) = \frac{\partial \Sigma(E)}{\partial E} \Delta E$$

其中 $\Sigma(E) = K \frac{V^N}{N!h^{3N}} (2mE)^{3N/2}$, $K = \frac{\pi^{3N/2}}{(3N/2)!}$.

Solution. *Proof.* N 个分子构成的 $3N$ 维 Euclidean 空间 (动量空间) 体积为

$$V_p^{(3N)} = \int \prod_{i=1}^{3N} dp_i = \frac{\pi^{3N/2}}{\Gamma(\frac{3}{2}N + 1)} R^{3N} = \frac{\pi^{3N/2}}{(3N/2)!} R^{3N} = KR^{3N}$$

其中 $R = \sqrt{2mE}$ 为动量空间半径. 则区间 $E \sim E + \Delta E$ 内的空间壳体积为

$$\Delta V_p^{(3N)} = \frac{\partial V_p^{(3N)}}{\partial R} \Delta R = 3NKR^{3N-1} \Delta R \xrightarrow{\Delta R = m\Delta E/R} 3mNK(2mE)^{(3N-2)/2} \Delta E$$

代入微观状态数的定义中

$$\Omega(E) = \frac{3NmKV^N}{N!h^{3N}} (2mE)^{(3N-2)/2} \Delta E$$

其中 $V^N = (\int d^3 q_i)^N$. 注意到

$$\frac{\partial \Sigma(E)}{\partial E} = \frac{3NmKV^N}{N!h^{3N}} (2mE)^{3N/2-1}$$

于是证明了 $\Omega(E) = \frac{\partial \Sigma(E)}{\partial E} \Delta E$. □

Problem 3.2. 一维谐振子

$$H = \frac{1}{2m} p^2 + \frac{k}{2} q^2$$

证明

(a) 正则方程的解是

$$q = A \cos(\omega t + \phi), \quad p = m\dot{q} = -m\omega A \sin(\omega t + \phi)$$

A 为振幅, $\omega = \sqrt{k/m}$ 是频率.

(b) 振子的能量为

$$E = \frac{1}{2} m\omega^2 A^2$$

(c) (q, p) 在相空间的轨道是

$$\frac{q^2}{\frac{2E}{m\omega^2}} + \frac{p^2}{2mE} = 1$$

(d) 求在能量区间 $E - \frac{\Delta}{2} \leq H \leq E + \frac{\Delta}{2}$, 在相空间代表点的数目

$$\int_{E-\Delta/2 \leq H \leq E+\Delta/2} dq dp$$

Solution.

(a) 由哈密顿正则方程

$$\dot{q} = \frac{p}{m}, \quad \dot{p} = -kq$$

将 \dot{q} 再次对时间求导, 得运动方程

$$\ddot{q} = \frac{\dot{p}}{m} = -\frac{k}{m}q, \quad \ddot{q} + \frac{k}{m}q = 0$$

则通解为

$$q = A \cos(\omega t + \phi), \quad p = m\dot{q} = -m\omega A \sin(\omega t + \phi)$$

其中 $\omega = \sqrt{k/m}$.

(b) 振子的能量为

$$E = K + V = \frac{p^2}{2m} + \frac{1}{2}m\omega^2q^2 = \frac{1}{2}m\dot{q}^2 + \frac{1}{2}m\omega^2q^2 = \frac{1}{2}m\omega^2A^2$$

(c) 将 p, q 表达式合并

$$\left(\frac{q}{A}\right)^2 + \left(\frac{p}{m\omega A}\right)^2 = 1$$

由 $E = \frac{1}{2}mA^2$ 得 $A^2 = 2E/m$. 代入得相空间轨道

$$\frac{q^2}{\frac{2E}{m\omega^2}} + \frac{p^2}{2mE} = 1$$

(d) (q, p) 在相空间的轨道为椭圆, 其面积为

$$A(E) = \pi ab = \pi \sqrt{\frac{2E}{m\omega^2}} \sqrt{2mE} = \frac{2\pi E}{\omega}$$

则在能量区间 $E - \frac{\Delta}{2} \leq H \leq E + \frac{\Delta}{2}$, 相空间代表点的数目即为能量区间的对应的相空间面积

$$\int_{E-\Delta/2 \leq H \leq E+\Delta/2} dq dp = A(E + \Delta/2) - A(E - \Delta/2) = \frac{2\pi\Delta}{\omega}$$

Problem 3.3. 读 Pathria 书的 §1.2, §1.3, 写一个阅读笔记.

§1.2 统计学与热力学之间的联系

(a) **系统描述与基本假设.**

- i. 两个系统 A_1 和 A_2 , 分别处于平衡态, 宏观态由 (N_1, V_1, E_1) 和 (N_2, V_2, E_2) 描述.
- ii. 系统的微观状态数分别为 $\Omega_1(N_1, V_1, E_1), \Omega_2(N_2, V_2, E_2)$.
- iii. 复合系统 $A^{(0)} = A_1 + A_2$ 的总能量守恒 $E^{(0)} = E_1 + E_2 = \text{Constant}$.

(b) **复合系统的微观状态数.** $\Omega^{(0)}(E_1, E_2) = \Omega_1(E_1) \cdot \Omega_2(E_2)$

(c) **平衡条件与最概然状态.** 平衡时, $\Omega^{(0)}$ 取最大值

$$\frac{\partial \ln \Omega_1(E_1)}{\partial E_1} = \frac{\partial \ln \Omega_2(E_2)}{\partial E_2}$$

定义 $\beta \equiv \left(\frac{\partial \ln \Omega(N, V, E)}{\partial E}\right)_{N, V}$, 则平衡条件为 $\beta_1 = \beta_2$.

(d) **熵与温度的联系.** 热力学中存在关系

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

对比统计定义 $S = k \ln \Omega$ 可得 $\beta = \frac{1}{k_B T}$, k 为玻尔兹曼常数

§1.3 统计学与热力学的进一步联系

(a) **能量与体积交换.** 若系统间可交换能量与体积, 则平衡条件为

$$\beta_1 = \beta_2 \quad \text{and} \quad \eta_1 = \eta_2$$

其中 $\eta \equiv \left(\frac{\partial \ln \Omega}{\partial V}\right)_{N, E}$.

(b) **能量、体积与粒子数交换.** 若还可交换粒子, 则平衡条件为

$$\beta_1 = \beta_2, \quad \eta_1 = \eta_2, \quad \zeta_1 = \zeta_2$$

其中 $\zeta \equiv \left(\frac{\partial \ln \Omega}{\partial N}\right)_{V, E}$.

(c) **与热力学量的对应.** 由热力学基本关系

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

可得 $\eta = \frac{P}{k_B T}, \zeta = -\frac{\mu}{k_B T}$.

(d) **统计热力学的核心公式.**

- i. 熵: $S(N, V, E) = k \ln \Omega(N, V, E)$.
- ii. 强度量: $\frac{1}{T} = \left(\frac{\partial S}{\partial E}\right)_{N, V}, \frac{P}{T} = \left(\frac{\partial S}{\partial V}\right)_{N, E}, -\frac{\mu}{T} = \left(\frac{\partial S}{\partial N}\right)_{V, E}$.

Problem 3.4. 经典单原子分子理想气体，忽略气体内自由度，用正则系综求内能，物态方程和熵。

Solution. 考虑单粒子的 Hamiltonian，对于理想气体

$$H(\mathbf{p}, \mathbf{q}) = \frac{\mathbf{p}^2}{2m}$$

无势能，与 \mathbf{q} 无关。单粒子的配分函数为

$$Z_0 = \frac{1}{h^3} \int_V d^3\mathbf{q} \int_{\mathbb{R}^3} e^{-\beta H} = \frac{V}{h^3} \left(\int_{-\infty}^{\infty} e^{-\beta p_i^2/(2m)} dp_i \right)^3$$

其中 $i = x, y, z, \beta = (k_B T)^{-1}$ 。这里利用了单粒子三个自由度之间的对称性，并引入量子相空间尺度 h^3 作无量纲化。利用 Gaussian 积分

$$\int_{-\infty}^{\infty} e^{-\beta p_i^2/(2m)} dp_i = \sqrt{\frac{2\pi m}{\beta}}$$

单粒子的配分函数可写做

$$Z_0 = \frac{V}{h^3} \left(\frac{2\pi m}{\beta} \right)^{3/2} = \frac{V}{\lambda^3}$$

其中 $\lambda \equiv \sqrt{\frac{\beta h^2}{2\pi m}}$ 为 de Broglie 波长。接下来考虑 N 个不可区分粒子的配分函数，其可近似为

$$Z_N = \frac{Z_0^N}{N!} = \frac{1}{N!} \left(\frac{V}{\lambda^3} \right)^N$$

其中因子 $N!$ 为 Gibbs 修正，为了解不可区分性。

(a) 内能

$$U = -\frac{\partial}{\partial \beta} \ln Z_N \xrightarrow[\ln Z_N = N \ln Z_0 - \ln N!]{\text{Stirling identity}} -N \frac{\partial}{\partial \beta} \ln Z_0 = \frac{3}{2} N k_B T$$

(b) 状态方程。系统的自由能

$$F = -k_B T \ln Z_N \xrightarrow[\ln Z_N = N \ln Z_0 - \ln N!]{\text{Stirling identity}} -N k_B T \left[\ln \left(\frac{V}{N \lambda^3} \right) + 1 \right]$$

由热力学关系 $p = -(\partial F / \partial V)_T$ 得

$$p = k_B T \frac{\partial}{\partial V} \ln Z_N = \frac{n k_B T}{V}$$

于是状态方程为

$$pV = N k_B T$$

(c) 熵。由 $S = -(\partial F / \partial T)_V$ 得

$$S = k_B \ln Z_N + k_B T \frac{\partial}{\partial T} \ln Z_N = N k_B \left[\ln \left(\frac{V}{N \lambda^3} + 1 \right) \right] + \frac{3}{2} k_B T = N k \left\{ \ln \left[\frac{V}{N} \left(\frac{4\pi m}{\beta h^3} \right)^{3/2} \right] + \frac{5}{2} \right\}$$

这里在 Stirling 公式的基础上做了一阶 Taylor 展开。

Problem 3.5 (林宗涵《热力学与统计物理》8.1). 设有 N 个粒子组成的系统处于平衡态, 满足经典极限条件.

- 试由正则系统的几率分布导出系统微观能量处在 E 与 $E + dE$ 之间的几率 $P(E) dE$ ($P(E)$ 为正则系综按能量的几率分布).
- 证明使 $P(E)$ 取得极大值的能量满足方程

$$\frac{\Sigma''(E)}{\Sigma(E)} = \beta$$

其中 $\Sigma(E)$ 定义为

$$\Sigma(E) = \frac{1}{N!h^s} \int_{H \leq E} d\Omega$$

$H = H(q_1, \dots, q_s; p_1, \dots, p_s)$ 为系统的 Hamiltonian.

- 将上述结果用到单原子分子理想气体, 证明

$$E = \left(\frac{3N}{2} - 1\right) \frac{1}{\beta} \approx \frac{3}{2} N k_B T.$$

这个结果说明什么?

Solution.

- 在正则系综中, 系统处于某一微观状态 i 的几率为:

$$p_i = \frac{1}{Z} e^{-\beta E_i}, \quad \text{and} \quad Z = \sum_i e^{-\beta E_i}$$

系统的微观状态数函数

$$\Sigma(E) = \frac{1}{N!h^{3N}} \int_{H \leq E} d\Omega = \frac{1}{N!h^{3N}} \int_V d^{3N}q \int_{H \leq E} d^{3N}p = \frac{V^N}{N!h^{3N}} \frac{(2\pi m E)^{3N/2}}{\Gamma(3N/2 + 1)}$$

则系统处在能量区间 $E \sim E + dE$ 之间的概率为

$$P(E) dE = p_i (\Sigma(E + dE) - \Sigma(E)) = \frac{1}{Z} e^{-\beta E_i} \Sigma'(E) dE$$

- $P(E)$ 最大时, $\frac{dP(E)}{dE} = 0$, 即

$$\frac{dP(E)}{dE} = -\frac{\beta}{Z} e^{-\beta E_i} \Sigma'(E) + \frac{1}{Z} e^{-\beta E_i} \Sigma''(E) = 0$$

由此得 $\Sigma''(E)/\Sigma'(E) = \beta$.

- 展开 (b) 中的结论

$$\frac{-\frac{3N}{2E} \Sigma(E) + \frac{3N}{2E} \frac{3N}{2E} \Sigma(E)}{\frac{3N}{2E} \Sigma(E)} = \frac{3N - 2}{2E} = \beta$$

由此得最概然能量

$$E = \frac{1}{\beta} \left(\frac{3}{2} N - 1 \right) \xrightarrow{N \gg 1} \frac{3}{2} N k_B T$$

表明使 $P(E)$ 取极大值的能量即平均能量, 体现了统计物理中的大数定律.

Problem 3.6 (林宗涵《热力学与统计物理》8.2). 有两种不同分子组成的混合理想气体, 处于平衡态. 设该气体满足经典极限条件; 且可把分子当作质点 (即忽略其内部运动自由度) . 试用正则系统求该气体的 $p, \bar{E}, S, \mu_i (i = 1, 2)$.

Solution. 设第一种与第二种分子数分别为 N_1, N_2 , 微观能量分别为 ϵ_i, ϵ_j . 则混合理想气体的微观总能量为

$$E = E_1 + E_2 = \sum_{i=1}^{N_1} \epsilon_i + \sum_{j=1}^{N_2} \epsilon_j$$

由 **Problem 3.4**: 单粒子的配分函数, 则两种分子的配分函数分别为

$$Z^{(1,2)} = \frac{Z_0^{(1,2)}}{N_{1,2}!}, \quad Z_0^{(1,2)} = \frac{V}{h^3} \left(\frac{2\pi m_{1,2}}{\beta} \right)^{3/2}$$

则系统的配分函数为

$$Z_{N_1, N_2} = Z_{N_1} Z_{N_2} = N_1 \ln Z^{(1)} - \ln N_1! + N_2 \ln Z^{(2)} - \ln N_2!$$

则气体的参数为

$$\begin{aligned} p &= \frac{1}{\beta} \frac{\partial}{\partial V} \ln Z_{N_1, N_2} = \frac{(N_1 + N_2) k_B T}{V}, \\ \bar{E} &= -\frac{\partial}{\partial \beta} \ln Z_{N_1, N_2} = (N_1 + N_2) \frac{3}{2} k_B T, \\ S &= k (\ln Z_{N_1, N_2} - \beta \frac{\partial}{\partial \beta} \ln Z_{N_1, N_2}) = \sum_{i=1,2} N_i k_B \left\{ \frac{3}{2} \ln T + \ln \frac{V}{N_i} + \left[\frac{5}{2} + \frac{3}{2} \ln \left(\frac{2\pi m_i k_B}{h^2} \right) \right] \right\}, \\ \mu_i &= \left(\frac{\partial F}{\partial N_i} \right)_{T,V} = \left(\frac{\partial \bar{E} - TS}{\partial N_i} \right)_{T,V} = -k_B T \left[\frac{3}{2} \ln T + \ln \frac{V}{N_i} + \frac{3}{2} \ln \left(\frac{2\pi m_i k_B}{h^2} \right) \right] \end{aligned}$$

Problem 3.7 (林宗涵《热力学与统计物理》8.3). 有一极端相对论性的理想气体, 粒子的能谱为 $\epsilon = cp$ ($p = |\mathbf{p}|$, c 为光速), 并满足非简并条件. 设粒子的内部运动自由度可以忽略 (即可将粒子看成质点) . 试用正则系综求该气体的 $p, \bar{E}, S, \mu, C_v, C_p$.

Solution. 此时单粒子的配分函数为

$$Z_0 = \frac{1}{h^2} \int_V d^3 q \int_{\mathbb{R}^2} d^3 q e^{-\beta \epsilon} = \frac{V}{h^3} \int_0^\infty e^{-\beta cp} 4\pi p^2 dp = \frac{8\pi V}{(hc)^3} (k_B T)^3$$

系统的配分函数仍然成立

$$Z_N = \frac{Z_0}{N!} = \frac{V^N T^{3N}}{N!} \left[\frac{8\pi k_B^3}{(hc)^3} \right]^N$$

则该系统的参数分别为

$$\begin{aligned} p &= -\left(\frac{\partial F}{\partial V} \right)_{T,N} = -\left(\frac{\partial -k_B T \ln Z_N}{\partial V} \right)_{T,N} = \frac{N k_B T}{V}, \quad \bar{E} = -T^2 \frac{\partial}{\partial T} (F/T) = 3N k_B T, \\ S &= -\left(\frac{\partial F}{\partial T} \right)_{V,N} = N k_B \left\{ 3 \ln T + \ln \frac{V}{N} + \left[4 + \ln \frac{8\pi k_B^3}{(hc)^3} \right] \right\}, \\ \mu &= -k_B T \left\{ 3 \ln T + \ln \frac{V}{N} + \ln \left[\frac{8\pi k_B^3}{(hc)^3} \right] \right\}, \quad C_v = \left(\frac{\partial \bar{E}}{\partial T} \right)_V = 3N k_B, \quad C_p = \left(\frac{\partial H}{\partial T} \right)_p = 4N k_B \end{aligned}$$

其中焓 $H \equiv \bar{E} + pV = 4N k_B T$.

Problem 3.8 (林宗涵《热力学与统计物理》8.6). 设被吸附在液体表面上的分子形成一种二维气体，分子之间相互作用为两两作用的短程力，且只与两分子的质心距离有关。试根据正则系综，证明在第二位力系数的近似下，该气体的物态方程为

$$pA = Nk_B T \left(1 + \frac{B_2}{A} \right)$$

其中 A 为液面的面积， B_2 由下式给出

$$B_2 = -\frac{N}{2} \int (e^{-\phi(r)/k_B T} - 1) 2\pi r dr$$

Solution. 气体的 Hamiltonian 为

$$H = K + \Phi = \sum_{i=1}^N \frac{\mathbf{p}_i^2}{2m} + \sum_{i < j} \phi_{ij}$$

其中 $U = \sum_{i < j} \phi(r_{ij})$ 对二维气体，配分函数为

$$Z_N = \frac{1}{N! h^{2N}} \int e^{-\beta H} d^{2N} \mathbf{q} d^{2N} \mathbf{p}$$

单个粒子的动量积分为

$$\frac{1}{h^2} \int \exp\left(-\frac{\beta p^2}{2m}\right) d^2 \mathbf{p} = \frac{2\pi m k_B T}{h^2} = \lambda_T^{-2}$$

所以气体的配分函数为

$$Z_N = \frac{1}{N! \lambda_T^{2N}} \int_{A^N} e^{-\beta \sum_{i < j} \phi_{ij}} \prod_{i=1}^N d^2 \mathbf{q}_i = \frac{1}{N! \lambda_T^{2N}} Q_N$$

其中 Q_N 为位形积分。使用 Mayer 函数 $f_{ij} = e^{-\beta \phi_{ij}} - 1$ ，位形积分在第二位力系数近似下可展开为

$$Q_N \approx \int_{A^N} \left(1 + \sum_{i < j} f_{ij} \right) \prod_{i=1}^N d^2 \mathbf{q}_i = A^N \left(1 + \frac{N^2}{2A} \int f_{12} 2\pi r dr_1 \right)$$

其中 $f_{12} = f(\mathbf{q}_1 - \mathbf{q}_2)$, $d^2 \mathbf{r}_1 = 2\pi r_1 dr_1$. 令 $B_2 = -\frac{N}{2} \int f_{12} 2\pi r dr_1$, 则位形积分的对数可写做

$$\ln Q_N = N \ln A + \ln \left(1 - \frac{N}{A} B_2 \right) \approx N \ln A - \frac{N}{A} B_2$$

对二维气体，正则系综压强为

$$p = \frac{1}{\beta} \frac{\partial}{\partial A} \ln Z_N \approx N k_B T \left(1 + \frac{B_2}{A} \right)$$

Problem 3.9 (林宗涵《热力学与统计物理》8.7). 物质磁性的起源是纯量子力学性质的，这一点可以从玻尔-范列文 (Bohr-van Leeuwen) 定理看出。该定理可以表述为：遵从经典力学和经典统计力学的系统的磁化率严格等于零。

Remark. 由公式 $\chi = \left(\frac{\partial \mathcal{M}}{\partial \mathcal{H}}\right)_{T,V}$, $\mathcal{M} = -\left(\frac{\partial F}{\partial \mathcal{H}}\right)_{T,V}$ 及 $F = -k_B T \ln Z_N$, 只需证明正则系综的配分函数 Z_N 与磁场 \mathcal{H} 无关即可. 设矢势为 \mathbf{A} (磁场由 \mathbf{A} 定出), 处于磁场中的 N 个带电粒子系统的微观总能量 (即系统的 Hamiltonian) 可以表为

$$E = \sum_{i=1}^N \frac{1}{2m} \left(\mathbf{p}_i + \frac{e_i}{c} \mathbf{A}(\mathbf{r}_i) \right)^2 + \Phi(\mathbf{r}_1, \dots, \mathbf{r}_N),$$

其中 Φ 代表粒子之间的相互作用能. 由正则系统出发, 在满足经典极限条件下, 证明 Z_N 与 \mathbf{A} 无关.

Solution. 正则系统的配分函数为

$$Z_N = \frac{1}{N! h^{3N}} \left\{ \int_{V^N} e^{-\beta \phi(\mathbf{q}_1, \dots, \mathbf{q}_N)} \prod_{i=1}^N d^3 \mathbf{q}_N \right\} \left\{ \int_{\mathbb{R}^{3N}} \exp \left[-\beta \sum_i \left(\mathbf{p}_i + \frac{e_i}{c} \mathbf{A}(\mathbf{q}_i) \right)^2 / 2m \right] \prod_{i=1}^N d^3 \mathbf{p}_i \right\}$$

做动量积分的变量变换, 令

$$\mathbf{p}'_i = \mathbf{p}_i + \frac{e_i}{c} \mathbf{A}(\mathbf{r}_i)$$

由多重积分变换

$$\prod_{i=1}^N d^3 \mathbf{p}_i = |J| \prod_{i=1}^N d^3 \mathbf{p}'_i$$

其中 Jacobian 为

$$J = \frac{\partial(p_{1_x}, p_{1_y}, p_{1_z}, \dots, p_{N_x}, p_{N_y}, p_{N_z})}{\partial(p'_{1_x}, p'_{1_y}, p'_{1_z}, \dots, p'_{N_x}, p'_{N_y}, p'_{N_z})}$$

由于 $\partial p_i / \partial \mathbf{A}(\mathbf{r}_i) = 0$, 所以 $J = 1$, Z_N 与 \mathbf{A} 无关.

Problem 3.10. 用巨正则系综计算单原子理想气体的热力学函数.

Solution. 单粒子配分函数

$$Z_1 = \frac{V}{\lambda^3}, \quad \lambda = \frac{h}{\sqrt{2\pi m k_B T}}$$

由此得巨配分函数和巨势

$$\Xi = \exp(e^{\beta\mu} Z_1) = \exp\left(e^{\beta\mu} \frac{V}{\lambda^3}\right), \quad \Omega = -k_B T \ln \Xi = -k_B T e^{\beta\mu} \frac{V}{\lambda^3}$$

粒子数

$$\langle N \rangle = -\left(\frac{\partial \Omega}{\partial \mu}\right)_{T,V} = e^{\beta\mu} \frac{V}{\lambda^3} \implies e^{\beta\mu} = \frac{\langle N \rangle \lambda^3}{V}$$

内能

$$U = \sum_{\mathbf{p}} \varepsilon_{\mathbf{p}} \langle n_{\mathbf{p}} \rangle = e^{\beta\mu} \frac{V}{h^3} \int \frac{p^2}{2m} e^{-\beta p^2/(2m)} d^3 p = \frac{3}{2\beta} e^{\beta\mu} \frac{V}{\lambda^3} = \frac{3}{2} \langle N \rangle k_B T$$

压强

$$P = -\frac{\Omega}{V} = k_B T e^{\beta\mu} \frac{1}{\lambda^3} = \frac{\langle N \rangle k_B T}{V} \implies PV = \langle N \rangle k_B T$$

由 $\Omega = U - TS - \mu \langle N \rangle$ 得熵

$$S = \frac{U - \mu \langle N \rangle - \Omega}{T} = \langle N \rangle k_B \left[\frac{5}{2} - \ln(n\lambda^3) \right], \quad n = \frac{\langle N \rangle}{V}$$

Problem 3.11 (林宗涵《热力学与统计物理》8.9). 试用巨正则系综求解题 **Problem 3.7**, 并于正则系综的结果比较.

Solution. 由 **Problem 3.7** 中单粒子的配分函数 $Z = \frac{8\pi V}{(hc)^3} \beta^{-3}$ 得巨正则系综函数

$$\Xi = \sum_{N=0}^{\infty} \frac{(e^{-\alpha} Z)^N}{N!} = \exp(e^{-\alpha} Z), \quad \ln \Xi = e^{-\alpha} Z = \frac{8\pi V}{(hc)^3} \beta^{-3}$$

利用巨正则系综求解系统的参数为

$$\begin{aligned} \bar{N} &= -\frac{\partial}{\partial \alpha} \ln \Xi = e^{-\alpha} Z, \quad \mu = -k_B T \ln \frac{Z}{\bar{N}} = -k_B T \left[3 \ln T + \ln \frac{V}{\bar{N}} + \ln \left[\frac{8\pi k^3}{(hc)^3} \right] \right], \\ \bar{E} &= -\frac{\partial}{\partial p} \ln \Xi = 3\bar{N}k_B T, \quad p = \frac{1}{\beta} \frac{\partial}{\partial V} \ln \Xi = \frac{\bar{N}k_B T}{V} = \frac{\bar{E}}{3V}, \\ S &= k_B \left(\ln \Xi - \alpha \frac{\partial}{\partial \alpha} \ln \Xi - \beta \frac{\partial}{\partial \beta} \ln \Xi \right) = \bar{N}k \left\{ 3 \ln T + \ln \frac{V}{\bar{N}} + \left[4 + \ln \left(\frac{8\pi k_B^3}{(hc)^3} \right) \right] \right\}, \\ C_V &= \left(\frac{\partial}{\partial T} \bar{E} \right)_V = 3Nk_B, \quad C_p = \left(\frac{\partial H}{\partial T} \right)_p = 4Nk_B \end{aligned}$$

结果与 **Problem 3.7** 一致.

Problem 3.12 (林宗涵《热力学与统计物理》8.10). 证明熵的下列公式.

- (a) 对正则系综, $S = -k \sum_s \rho_s \ln \rho_s$, 其中 $\rho_s = \frac{1}{Z_N} e^{-\beta E_s}$ 为正则系综的几率分布.
- (b) 对巨正则系综, $S = -k \sum_N \sum_s \rho_{Ns} \ln \rho_{Ns}$, 其中 $\rho_{Ns} = \frac{1}{\Xi} e^{-\alpha N - \beta E_s}$ 为巨正则系综的几率分布.

Solution.

(a) *Proof.* 由熵的定义出发

$$S = -\frac{\partial F}{\partial T} = -\frac{\partial -kT \ln Z}{\partial T} = k \ln Z + \frac{\langle E \rangle}{T}$$

其中 $Z = \sum_s e^{-\beta E_s}$, $\beta = (kT)^{-1}$, $\langle E \rangle = \frac{1}{Z} \sum_s E_s e^{-\beta E_s}$. 将正则系综概率分布 $\rho_s = \frac{1}{Z} e^{-\beta E_s}$ 代入题目中正则系综中 S 的右式

$$-k \sum_s \rho_s \ln \rho_s = -k \sum_s \rho_s \ln \left(\frac{1}{Z} e^{-\beta E_s} \right) = k \ln Z + k\beta \langle E \rangle$$

结果和 $S = -\partial F / \partial T$ 的表达式一致. \square

(b) *Proof.* 类似的, 从巨势 $\Omega \equiv -kT \ln \Xi$ 出发, 熵的表达式为

$$S = -\frac{\partial \Omega}{\partial T} = k \ln \Xi + \frac{\langle E \rangle - \mu \langle N \rangle}{T}$$

其中巨正则系综几率分布 $\Xi = \sum_{N,s} \exp[\beta(\mu N - E_s)]$. 从熵的定义出发可得

$$S = -k \sum_N \sum_s \rho_{Ns} \ln \rho_{Ns} = -k \sum_{N,s} \rho_{Ns} (-\ln \Xi + \beta \mu N - \beta E_s) = k \ln \Xi + k\beta \mu \langle N \rangle - k\beta \langle E \rangle$$

结果和 $S = -\partial \Omega / \partial T$ 的表达式一致. \square

Problem 3.13 (林宗涵《热力学与统计物理》8.12). 设有一 N 个相互作用可以忽略的粒子（可看成质点）组成的系统，在满足经典极限的条件下，巨正则系综的几率分布为

$$\rho_N(q_1, \dots, p_{3N}) d\Omega_N = \frac{1}{\Xi N! h^{3N}} e^{-\alpha N - \beta E_N(q_1, \dots, p_{3N})} d\Omega_N$$

(a) 试证明巨正则系综的总粒子数是 N 的几率为

$$P(N) = \frac{1}{\Xi} e^{-\alpha N} Z_N,$$

其中 Z_N 是总粒子数为 N 时的正则系综配分函数.

(b) 证明使 $P(N)$ 取极大的总粒子数满足下面的关系

$$\alpha = \frac{\partial \ln Z_N}{\partial N}.$$

(证明时，直接求 $\ln P(N)$ 的极大更方便.)

(c) 上式进一步可化为

$$N = e^{-\alpha} Z$$

其中 Z 为单粒子的配分函数，即 $Z = \frac{V}{h^3} \left(\frac{2\pi m}{\beta} \right)^{3/2}$. 上述结果说明什么？

Solution.

(a) 巨正则系综的总粒子数是 N 的几率可写做微观态的几率对相空间的积分

$$P(N) = \int \rho_N(q_1, \dots, q_{3N}; p_1, \dots, p_{3N}) d\Omega_N = \frac{1}{\Xi N! h^{3N}} \int e^{-\beta E_N} d\Omega_N$$

由于 N 个粒子的正则系综配分函数为

$$Z_N = \frac{1}{N! h^{3N}} \int e^{-\beta E_N} d\Omega_N$$

所以可得 $P(N) = \frac{1}{\Xi} e^{-\alpha N} Z_N$.

(b) 在 $P(N)$ 取极大时， $\frac{\partial P}{\partial N} = 0$. 将 (a) 中的表达式取对数并对 N 求导得

$$\frac{\partial \ln P(N)}{\partial N} = -\alpha + \frac{\partial \ln Z_N}{\partial N} = 0$$

于是得 $\alpha = \partial \ln Z_N / \partial N$.

(c) 考虑 N 个可忽略相互作用的粒子，系统的配分函数为

$$Z_N = \frac{Z_0}{N!}$$

其中 $Z_0 = \frac{V}{h^3} \left(\frac{2\pi m}{\beta} \right)^{3/2}$. 对系统的配分函数取对数并对 N 求导得

$$\frac{\partial \ln Z_N}{\partial N} = \ln Z - \ln N = \ln \frac{Z}{N} = \alpha$$

由此得 $N = e^{-\alpha} Z \bar{N}$. 即使 $P(N)$ 取极大值的 N 就是平均值 \bar{N} .

Lecture #4 Homework #4 [2025-09-23]

Problem 4.1. 理想费米气体的巨配分函数为

$$Z_G = \text{Tr} \exp \left\{ -\beta \sum_p [\epsilon(p) - \mu] \hat{n}_p \right\}$$

其中 \hat{n}_p 的本征值为 0 或 1. 证明

- (a) $Z_G = \prod_p (1 + e^{-\beta(\epsilon(p)-\mu)})$
- (b) 根据热力学关系求 $U = \sum_p \epsilon(p) \hat{n}_p$ 和 $\langle N \rangle = \sum_p \hat{n}_p$.
- (c) 若 $\epsilon(p) = \frac{p^2}{2m}$, $\sum_p \rightarrow V \int \frac{d^3 p}{(2\pi^3)}$, 求 $T = 0$ 时 $\langle N \rangle$ (设 $\mu = \epsilon_F$ 是费米能).
- (d) 证明 $T > 0$, $\beta_{\epsilon_F} \gg 1$ 时,

$$\begin{aligned} \frac{\langle N \rangle}{V} &= \frac{(2m\mu)^{1/2}}{6\pi^2} \left[1 + \frac{\pi^2}{8} (\beta\mu)^{-2} + \frac{7\pi^4}{640} (\beta\mu)^{-4} + \dots \right] \\ \frac{U}{V} &= \frac{(2m\mu)^{3/2}}{10\pi^2} \left[1 + \frac{5\pi^2}{8} (\beta\mu)^{-2} - \frac{7\pi^4}{384} (\beta\mu)^{-4} + \dots \right] \end{aligned}$$

积分公式

$$\int_0^\infty \frac{du}{e^{-\alpha+u} + 1} \left(\frac{d\varphi}{du} \right) = \varphi(u) + 2 \sum_{n=1}^{\infty} C_{2n} \left(\frac{d^{2n}\varphi}{du^{2n}} \right)_{u=\alpha}, \quad C_m = \sum_{k=1}^{\infty} \frac{(-1)^{k+1}}{k^m}, \quad C_2 = \frac{\pi^2}{12}, \quad C_4 = \frac{7\pi^2}{720}$$

Solution.

- (a) 对 $n_p = 0$ 与 $n_p = 1$ 的情况求和

$$Z_G = \prod_p \sum_{n_p=0}^1 e^{-\beta[\epsilon(p)-\mu]n_p} = \prod_p \left[1 + e^{-\beta(\epsilon(p)-\mu)} \right].$$

- (b) 巨势 $\Omega = -\frac{1}{\beta} \ln Z_G = -\frac{1}{\beta} \sum_p \ln \left[1 + e^{-\beta(\epsilon(p)-\mu)} \right]$, 由热力学关系:

$$\langle N \rangle = - \left(\frac{\partial \Omega}{\partial \mu} \right)_{T,V} = \sum_p \frac{1}{e^{\beta(\epsilon(p)-\mu)} + 1}, \quad U = \sum_p \frac{\epsilon(p)}{e^{\beta(\epsilon(p)-\mu)} + 1}.$$

- (c) $T = 0$ 时 $\mu = \epsilon_F$, $\langle n_p \rangle = \Theta(\epsilon_F - \epsilon(p))$,

$$\frac{\langle N \rangle}{V} = \frac{1}{(2\pi)^3} \int_0^{p_F} 4\pi p^2 dp = \frac{p_F^3}{6\pi^2} = \frac{(2m\epsilon_F)^{3/2}}{6\pi^2}.$$

- (d) 令 $\varphi(\epsilon) = \frac{2}{3}\epsilon^{3/2}$, 则 $\varphi'(\epsilon) = \epsilon^{1/2}$, 利用 Sommerfeld 展开:

$$\int_0^\infty \frac{\epsilon^{1/2} d\epsilon}{e^{\beta(\epsilon-\mu)} + 1} = \varphi(\mu) + 2 \sum_{n=1}^{\infty} C_{2n} \varphi^{(2n)}(\mu) \beta^{-2n},$$

其中 $C_2 = \frac{\pi^2}{12}$, $C_4 = \frac{7\pi^4}{720}$, 代入得

$$\frac{\langle N \rangle}{V} = \frac{(2m)^{3/2}}{6\pi^2} \mu^{3/2} \left[1 + \frac{\pi^2}{8} (\beta\mu)^{-2} + \frac{7\pi^4}{640} (\beta\mu)^{-4} + \dots \right].$$

对 U , 取 $\varphi(\epsilon) = \frac{2}{5}\epsilon^{5/2}$, 得:

$$\frac{U}{V} = \frac{(2m)^{3/2}}{10\pi^2} \mu^{5/2} \left[1 + \frac{5\pi^2}{8} (\beta\mu)^{-2} - \frac{7\pi^4}{384} (\beta\mu)^{-4} + \dots \right].$$

Problem 4.2. 声子的状态可用一组整数 $\{n_{k\lambda}\}$ 来表征 ($\lambda = 1, 2, 3$ 是声波的偏振方向), 能量为 $E_{\{n_{k\lambda}\}} = \sum_{k,\lambda} (n_{k\lambda} + \frac{1}{2})\omega_{0\lambda}(\mathbf{k})$. 在低能近似下, $\omega_{01,2}(\mathbf{k}) = c_T k$, $\omega_{03}(\mathbf{k}) = c_L k$.

(a) 利用 $Z = \prod_{k,\lambda} \sum_{n_{k\lambda}}^\infty e^{-\beta(n_{k\lambda} + \frac{1}{2})\omega_{0\lambda}}$, 求 Z 和 F (用 $\langle n_{k\lambda} \rangle [1 - e^{-\beta\omega_{0\lambda}}]^{-1}$ 表达).

(b) 设 ω_T 和 ω_L 是横、纵声子的频率上限, 把 ω 连续化, 写出 F .

Solution.

(a) 配分函数

$$Z = \prod_{k,\lambda} \sum_{n=0}^{\infty} e^{-\beta(n + \frac{1}{2})\omega_{0\lambda}(\mathbf{k})} = \prod_{k,\lambda} \frac{e^{-\beta\omega_{0\lambda}/2}}{1 - e^{-\beta\omega_{0\lambda}}}$$

自由能

$$F = -\frac{1}{\beta} \ln Z = \sum_{k,\lambda} \left[\frac{\omega_{0\lambda}}{2} + \frac{1}{\beta} \ln(1 - e^{-\beta\omega_{0\lambda}}) \right]$$

利用 $\langle n_{k\lambda} \rangle = (e^{\beta\omega_{0\lambda}} - 1)^{-1}$, 有

$$1 - e^{-\beta\omega_{0\lambda}} = \frac{1}{\langle n_{k\lambda} \rangle + 1}$$

因此

$$F = \sum_{k,\lambda} \left[\frac{\omega_{0\lambda}}{2} - \frac{1}{\beta} \ln(\langle n_{k\lambda} \rangle + 1) \right]$$

(b) 横模 $\omega = c_T k$ (2 支), 纵模 $\omega = c_L k$ (1 支), 频率上限分别为 ω_T , ω_L . 态密度

$$g_T(\omega) = \frac{V}{\pi^2 c_T^3} \frac{\omega^2}{c_T^3}, \quad g_L(\omega) = \frac{V}{2\pi^2 c_L^3} \frac{\omega^2}{c_L^3}$$

自由能

$$F = \frac{V}{\pi^2 c_T^3} \int_0^{\omega_T} \omega^2 \left[\frac{1}{2}\omega + \frac{1}{\beta} \ln(1 - e^{-\beta\omega}) \right] d\omega + \frac{V}{2\pi^2 c_L^3} \int_0^{\omega_L} \omega^2 \left[\frac{1}{2}\omega + \frac{1}{\beta} \ln(1 - e^{-\beta\omega}) \right] d\omega$$

Problem 4.3. 粒子数守恒的玻色子系统, 巨配分函数为 $Z_G = \prod_{N=0}^{\infty} \sum_{\{n_p\}} e^{-\beta \sum_p (\epsilon(p) - \mu)}$, 求和 $\sum_{\{n_p\}} 1 = N$.

(a) 证明 $Z_G = \prod_p [1 - e^{-\beta(\epsilon(p) - \mu)}]^{-1}$.

(b) 若 $\epsilon(p) = \frac{p^2}{2m}$, 在把求和化作积分后, 证明

$$\ln Z_G = V \left(\frac{m}{2\pi\beta} \right)^{3/2} g_{5/2}(\beta\mu), \quad g_k(\beta\mu) = \sum_{n=1}^{\infty} \frac{e^{n\beta\mu}}{n^k}$$

(c) $g_k(\nu)$ 只在 $\nu \leq 0$ 才收敛, 即对玻色子化学势最大为 0. 说明存在临界密度 $n_c = \left(\frac{m}{2\pi\beta} \right)^{3/2} g_{3/2}(0)$, 当密度 $n \leq n_c, \mu \leq 0$. 反之, 对给定 n , 有一个临界温度 $T_c^{-1} = \frac{km}{2\pi} \left(\frac{g_{3/2}(0)}{n} \right)^{2/3}$, 当 $T \geq T_c, \mu \leq 0$. 问将温度降到 $T < T_c$, 会发生什么物理现象?

(d) $\langle n \rangle = [1 - e^{-\beta(\epsilon(p)-\mu)}]^{-1}$ 在 $p = 0$ 时是无意义的, $\langle N \rangle$ 中的 $p = 0$ 部分应单独写出

$$\langle N \rangle = N_0 + \frac{(2m)^{3/2}V}{(2\pi)^2} \int_{0^+}^{\infty} d\epsilon \epsilon^{1/2} (e^{\beta\epsilon} - 1)$$

证明 $T < T_c$ 时, N_0/V 是一个宏观量

$$\frac{N_0}{V} = n \left(1 - \left(\frac{T}{T_c} \right)^{3/2} \right)$$

Solution.

(a) *Proof.* 巨正则系综对每个单粒子态独立求和 (对玻色子 $n_p = 0, 1, 2, \dots$)

$$Z_G = \prod_{\mathbf{p}} \sum_{n_p=0}^{\infty} e^{-\beta(\epsilon(\mathbf{p})-\mu)n_p}$$

于是几何级数的求和结果为

$$\sum_{n=0}^{\infty} e^{-\beta(\epsilon-\mu)n} = \frac{1}{1 - e^{-\beta(\epsilon-\mu)}}, \quad \mu < \epsilon$$

最终得到

$$Z_G = \prod_{\mathbf{p}} \left[1 - e^{-\beta(\epsilon(\mathbf{p})-\mu)} \right]^{-1} \square$$

(b) *Proof.* 已知恒等式

$$-\ln(1 - e^{-\beta(\epsilon-\mu)}) = \sum_{n=1}^{\infty} \frac{e^{n\beta\mu} e^{-n\beta\epsilon}}{n}$$

于是, 在三维连续极限下

$$\ln Z_G = - \sum_{\mathbf{p}} \ln \left[1 - e^{-\beta(\epsilon(\mathbf{p})-\mu)} \right] = \sum_{\mathbf{p}} \sum_{n=1}^{\infty} \frac{e^{n\beta\mu}}{n} e^{-n\beta p^2/(2m)}$$

对 \mathbf{p} 积分

$$\sum_{\mathbf{p}} e^{-n\beta p^2/(2m)} \rightarrow \frac{V}{(2\pi)^3} \int d^3 p e^{-n\beta p^2/(2m)} = \frac{V}{(2\pi)^3} \left(\frac{2\pi m}{n\beta} \right)^{3/2}$$

因此

$$\ln Z_G = V \left(\frac{m}{2\pi\beta} \right)^{3/2} g_{5/2}(\beta\mu), \quad g_k(z) = \sum_{n=1}^{\infty} \frac{z^n}{n^k} = \sum_{n=1}^{\infty} \frac{e^{n\beta\mu}}{n^k} \square$$

(c) 粒子数密度:

$$n = \frac{1}{V} \frac{\partial \ln Z_G}{\partial (\beta \mu)} = \frac{1}{\lambda_T^3} g_{3/2}(e^{\beta \mu}).$$

$g_{3/2}(z)$ 在 $z \leq 1$ 收敛, 故 $\mu \leq 0$ 。临界密度:

$$n_c = \frac{1}{\lambda_T^3} g_{3/2}(1) = \left(\frac{m}{2\pi\beta} \right)^{3/2} \zeta(3/2).$$

当 $n > n_c$ 或 $T < T_c$ 时发生 Bose - Einstein 凝聚, $\mu \rightarrow 0^-$, 宏观占据基态.

(d) $T < T_c$ 时 $\mu \approx 0$, 总粒子数:

$$N = N_0 + \frac{V}{\lambda_T^3} g_{3/2}(1) = N_0 + N \left(\frac{T}{T_c} \right)^{3/2},$$

所以

$$\frac{N_0}{V} = n \left[1 - \left(\frac{T}{T_c} \right)^{3/2} \right].$$

Lecture #5 Review

高等统计物理

说 明

本课程是热力学和统计物理基础上的高级课程，所以，不再系统地讲授热力学理论和近独立子系统统计物理（相当于林宗涵老师书的前七章）。对这部分内容，我会用一次课的时间回顾一下，请同学们也复习一下热统 I（重点是林老师书的第一、二、三、七章），以便更好地学新的内容。本课程内容主要包括（1）平衡态统计物理的系综理论；（2）不同空间维数的量子统计；（3）相变和临界现象：朗道理论。（4）相变和临界现象：标度理论和临界指数；（5）相变和临界现象：重整化群；（6）量子相变和 K-T 相变；（7）数值重整化群和密度矩阵重整化群简介；（8）非平衡态统计物理：Boltzmann 输运方程、H 定理和线性响应理论；（9）非平衡态统计物理：涨落现象；（10）统计物理中的数值计算方法：分子动力学简介；（11）统计物理中的中的数值计算方法：蒙特卡罗模拟；（12）量子蒙特卡罗模拟。（1）-（9）是板书，数值方法简介用 ppt. 期末考试考（1）-（9）的知识，占总成绩的 60%；（1）-（9）相关的平时习题计入平时成绩；数值计算由我在课堂主讲，作业是分组文献阅读，读一些经典的数值计算原始文章，做一些小系统的编程计算，就所得结果进行课堂交流。这部分也计入平时成绩。平时成绩占总成绩 40%。

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第一章 固体物理基础

固体和统计物理研究的是热现象。热力学是热现象的宏观唯象理论。统计物理则研究热现象的微观理论。热力学不管物体是由什么物质组成，不管微观结构，把物质看成连续介质。统计物理则一开始就考虑物质是由微观粒子组成，由微观性质出发，结合统计规律导出宏观性质。以下我们总结一下热力学和统计物理学的主要结论。

1.1 热力学的基本概念与基本规律

* 平衡态: 在没有外界影响的条件下, 物体各部分的性质长时间不发生任何变化的状态。

* 热平衡定律: A与B平衡, B与C平衡, 则A与C平衡。

* 温度: 温度物体间是否热平衡的物理量。称为温度。一切处于热平衡的物体温度相等。

* 不同温度具依赖性的规则叫温标。

* 物态方程: 物体的物理状态由几何参数 (V, A, L), 力学参数 (P, T, F), 电磁参数 (E, B, M) 和化学参数描述, 温度与这些状态变量之间的函数关系

$$T = f(P, V, \dots)$$

称为物态方程。

* 内能: 绝热(与外界没有热量交换)过程中外界对物体做功和在末态减去初态的内能。内能差 $U_2 - U_1 = W_a$ (外界对物体作功绝热)。

* 热力学第一定律: 推广到非绝热过程, 存在从外界吸热 $Q = U_2 - U_1 - W_a$, 即能守恒。

* $C_y = \frac{\partial Q_y}{\partial T}$ 表示热量, y 表示不变量, $y = V$ 容量, $y = P$ 压强, $y =$

单位质量的热量称为比热容。

* 内能是态函数, $H = U + PV$ 也是态函数。内能是绝热过程中外界没做功的情况下, $\Delta U = W_a$ 热是绝热过程中外界吸收的热量 $Q_a = W_a$

* 热：对可逆过程，志取人熵

$$\Delta S = S - S_0 = \int_{\text{初态}}^{\text{末态}(f)} \frac{dq}{T} \quad \text{与过程无关.}$$

* 直力守恒定律：

$$\Delta S \geq \int_{(i)}^{(f)} \frac{dq}{T}$$

熵增加原理.

* 直力守恒方程：第一定律 + 第二定律 单调求和

$$dU = TdS + \sum_i F_i d\gamma_i, \quad \text{但 } dU = TdS - pdV \quad \frac{pdV}{TdS}$$

例如，对 p-V-T 子集

$$dU = TdS - pdV.$$

* 自由能： $F = U - TS$.

$$dF = dU - d(TS).$$

$$\text{例如: } dF = -SdT - pdV. \quad (\text{等温准向})$$

* Gibbs 自由能：

$$G = F + PV.$$

$$\text{例如: } dG = -SdT + Vdp.$$

等温准向过程, G 不变.

~~Klern~~ 可能从单重级
基, 但不一定变为单重
基, 而产生基团能级
~~classics~~ classics
不可能把基团从低能级移到
高能级而产生基团能级

1.2 均相系(单相系)的平衡

* 均相系, 简单意义, 就是各部分性质完全一样的物体.

* 均相系的微小可逆过程由直力守恒方程描述. 依据角变量不同, 可以有 3 种表达形式,

例如对 p-V-T 子集 Maxwell 方程

$$dU = TdS - pdV \quad (S, V) \quad \left(\frac{\partial F}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V.$$

$$dH = TdS + Vdp \quad (S, p)$$

$$dF = -SdT - pdV \quad (T, V)$$

$$dG = -SdT + Vdp \quad (T, p).$$

* 可逆的直力守恒:

(1) $p, V \cdots; T$.

(2) 上物理方程程组和, 直接寻得各参数.

即各种变化量, 膨胀系数、压缩系数、
热膨胀系数, ... 可以用 (活化能, 强化能)

U, S, F, G 等不直接相关.

(3) 应用: 理想气体、麦克斯韦气体.

直幅好, 算性也好.

(复相系例水)

1.3 单之系的相变直力学 (单之系)
(复相系)

* 单相系者也是单之系(即相同的状态性质). 两相
相变, 就是整个单相系~性质发生变化, 从一个平
衡态变为另一个平衡态.

* 系统处于某一个相中, 该系统处于热力学平衡中.

热力学平衡判据: $S = S_{\max} \Leftrightarrow$ 孤立系处于平衡态.

数学表达式: $\delta S = 0, \delta^2 S < 0, \delta U = \delta V = \delta N = 0$.

δ : 热变动. 可能的变动.

* $\delta S = 0, \delta^2 S < 0$, 挑出了局域相对极大. 其它在
定是几个极大之中最大的那个. 其它相对极小.

* $\delta S = 0, \delta^2 S = 0$, 这时, $\delta^3 S = 0$ 是保证稳定性
条件. $\delta^3 S < 0$ 注定系统是否稳定. 这样的稳定性
称为临界点. 例如气-液相变的临界点.

* 热力学判据对孤立系. 从应用角度, 热力学平衡
地可用 (1) 自由能判据, (T, V, N) 不变, 自由能极小 $F = F_{\min}$.

(2) 吉布斯自由能判据, (T, P, N) 不变, $G = G_{\min}$.

(3) 内能判据: (V, S, N) 不变, $U = U_{\min}$.

④ 稳定的可变系统 ~ 热力学平衡判据

* 对单之系, 热力学可变, 则内能的基本
关系方程是: $(2T, p, V, T, \text{子集})$

$$dU = TdS - pdV + (U - Ts + Pv)dN$$

$$U - Ts + Pv = \frac{G}{N} \equiv \mu, \text{ 化学势, 1 mol m Gibbs 热能}$$

$$(U = Nu, V = Nv, S = Ns)$$

* 仅有直力学基本微分方程需加一项 μdN .

$$\mu = \left(\frac{\partial U}{\partial N}\right)_{S, V} \sim \left(\frac{\partial F}{\partial N}\right)_{S, p} = \left(\frac{\partial F}{\partial N}\right)_{T, V} = \left(\frac{\partial G}{\partial N}\right)_{T, p}.$$

$$\star \delta \mu = -SdT + Vdp.$$

* $\sigma = F - \mu N = U - TS - \mu N = F - G$ 称为
吉布斯平衡

* 仅有热力学判据都需考虑 μdN 这一项.

* 由平衡判据, 可以得出达到平衡的条件,

即状态变量之间~关系. 例如, 吉布斯判据可叙述二相之间的平衡条件是

- $T_1 = T_2, P_1 = P_2, \mu_1 = \mu_2$
 $\text{恒温} \quad \text{恒压} \quad \text{相变平衡 (不发生相变)}$
- (二组分, $S_i, U_i, V_i, N_i; i=1, 2$ 不变, 但各组分
不变, 总分子数不变, 总内能不变)
- 又例如, 若总分子数不变, 则 $\delta F = 0$ 条件
得出: $P_1 = P_2, \mu_1 = \mu_2 = 0$: 纯物质不守恒条件
简化为 0, 例如, 蒸汽、液体、固体。
- * 由平衡稳定判据, 可得稳定性条件. 稳定条件
往往有一些约束条件给出, 例如, 部分性极小,
要求密度比值 $c_1 > 0$ 和 $c_2 < 0$ 等限制于取
 $K_p = -\frac{1}{T} \left(\frac{\partial P}{\partial T} \right)_V > 0$. 举一例.
- * 根据相变平衡条件, 可以得到相同:
 例如, 二相平衡: $\mu^1 = \mu^2, T_1 = T_2, P_1 = P_2 = P$
 $\Rightarrow \mu^1(T, P) = \mu^2(T, P)$ 给出 $T-P$ 平面 $\Delta S = 0$,
 即这是二相一致平衡; 若共有三组分, $\mu^1 = \mu^2 = \mu^3$
 则完全确定了 (T, P) , 这就是三相共存. 另外,
 对于某一单质 (T, P) 在, 只有一个相是稳定的. 这样
 就是三相共存. 水的相图.

- * 在研究低温化学反应过程中, 实验发现
出规律是: 在等温等压条件下, 反应向放热
方向进行, 即 $\Delta H < 0$.
- * 热力学表明, 等温等压化学反应向着 ΔG 方向进行.
 $\Delta G = \Delta H - T \Delta S \Rightarrow \lim_{T \rightarrow 0} (\Delta S)_T \rightarrow 0$ Nernst 定理
- * 热力学第三定律:
- Nernst 定理
 - 绝对熵 $\lim_{T \rightarrow 0} S = 0$.
 - 不可逆过程有很步导致物体冷却绝热反.

1.5 非线性非平衡热力学

- * 非线性非平衡热力学: 既非即偏离平衡远
又远. 互通于宏观小、微观大区域, 可用
场论) 平衡近似.
- * 保时守恒定律 \Rightarrow 扩展的热力学第一定律 (把
小块的运动能加起来)
- * 对小块, 热力学方程仍成立.
- * 第二定律, $\Theta = \frac{\partial S}{\partial E}$ 表示小块大系统的

- * 关于相变, 我们以后将详述 (见讲义), 此处就
不继续展开.
- 1.4 相变第三定律: 多组分复相平衡和化学平衡
- * 多元系就是复相 (广义) 化学平衡的系统, 平衡
态参数是 (T, P, N_1, \dots, N_k) . $(N_1, \dots, N_k) = \sum N_i$.
- * 基本微分方程中 $dN \rightarrow \sum_i \mu_i dN_i$.
- $\mu_i = \left(\frac{\partial G}{\partial N_i} \right)_{T, P, \sum N_j \neq i}$.
- * $(T, P, \sum N_i)$ 满足 Gibbs 关系:
- $$SdT - VdP + \sum_i N_i d\mu_i = 0.$$
- 其中只有 N_i 是独立的.
- * 若不发生化学反应, 相平衡条件可类似写出.
- * 发生化学反应, $\sum_i v_i A_i = 0$, 例如
 $CO + \frac{1}{2} O_2 \rightleftharpoons CO_2, \Rightarrow v_1 = 1, v_2 = -1, v_3 = \frac{1}{2}$
 $A_1 = CO, A_2 = CO_2, A_3 = O_2$.
- 则化学平衡条件是
- $$\sum_i v_i \mu_i = 0. \quad " + " \text{ 为生成物}$$
- $$\sum_i v_i \mu_i = 0. \quad " - " \text{ 为反应物}$$

- $\mu_i \frac{\partial S}{\partial t} = - \vec{J}_s + \Theta, \quad \vec{J}_s \text{ 为大电流密度}$
- $\vec{J}_s = \frac{\vec{J}_n}{T}, \quad \vec{J}_n \text{ 为通量}, \quad \Theta = \frac{k_B}{T} (\vec{E} \cdot \vec{T}) > 0$
- * $\frac{\partial n}{\partial t} + \vec{J} \cdot \vec{J}_n = 0, \quad \text{质量守恒}$
- n 为 density. \vec{J}_n 为 particle current density.
- * 传导过程:
- 热传导 Fourier 定律: $\vec{J}_q = -k \vec{V} T$ \rightarrow 扩散
 - 扩散 Fick 定律: $\vec{J}_n = -D_n \vec{V} n$.
 - 电场定律: $\vec{J}_e = \sigma \vec{E} = -\sigma \vec{V} \phi$
- 一般 $\vec{J} = (J_1, \dots, J_n)$ 为热力学矢量, $\vec{X} = (X_1, \dots, X_n)$
 为力, 则 $J_k = \sum_i L_{ki} X_i, \quad L_{ki} - \text{动力系数}$.
- * 跳跃粘性定律: $L_{kk} = L_{kk}, \quad L \text{ 是扩散系数}$

第二章 经济物理基本概念和近独立粒子系统统计的法思想.

指的是宏观物体的现象实验基础上得出一些规律的经验总结,与物质的微观细节无关.统计物理则研究大量微观粒子,从经典、量子物理的基本原理出发,结合大量粒子呈现出的新规律:统计规律,导出宏观物作用的统计十项式.

2.1 微观状态的描述

* 经典:组成宏观物体的基本单元分子或“粒子”,可以是分子、原子,也可以是质子、中子等.我们往往称“粒子”,用广义坐标(\vec{r}, \vec{p}) ($\vec{r}^a; a=1, \dots, N$) 描述,单粒子能 $E = E(\vec{r}, \vec{p})$.一个微观大,宏观小的单粒子相空间中体积: $d\omega = d\vec{r}^a d\vec{p}^a$.

对于 N 个经典宏观粒子,广义坐标和广义动量 $(q_1, \dots, q_N; p_1, \dots, p_N)$, $S = N$ 粒子相空间体积

$$d\Omega = dq_1 \dots dq_N dp_1 \dots dp_N$$

$\{q_1, \dots, q_N; p_1, \dots, p_N\}$ = 宏观相空间,一个点就代表一个微观状态.

* 不同统计方法,造成不同的统计状态. (14)

2.2 (统计)规律

2.2 平衡态统计的等几率原理

* 宏观规则是宏观大,微观慢,宏观强,微观长,每次规则都对应于极大数目的微观状态.所以,除了微观运动规律外,统计规律不起作用.这是由宏观系统与外界的作用不可避免及随机性决定的.叫做几率决定宏观状态的宏观状态和微观状态在数量上往往由几率律相联系.

* 宏观和微观物理量的统计平均值.

* 在一定宏观状态下,微观状态出现的几率是统计物理的基本假设.

+ 对一个孤立系,即 (E, V, N) 固定一系统,最简单、朴素的假设是等几率假设,即得等几率原理:对于处于平衡态下的系统,系统有尽可能的微观状态出现的几率相等.

* 可能的微观状态是指与宏观状态 (E, V, N) 相应的微观状态数.

* 量子:单粒子状态由一组量子数标志.

即一组可对易的两个标量或矢量值描述(本征值可连结,也可互独立).例如,对自由粒子,位置和动量本征值,能本征值与经典一样,都是连续的.但在在一个盒子里,波函数 $\psi(x) \propto e^{i k x / \hbar}$, 能是离散的,能本征值为 $\hbar^2 k^2 / m$.

$$E = \frac{\hbar^2 k^2}{2m} = \frac{2\pi^2 h^2}{L^2} (n_x^2 + n_y^2 + n_z^2), \quad \vec{k} = \frac{2\pi h}{L} (n_x, n_y, n_z).$$

对于 $(3)-$ 维, 可以有不同形态, 例如 $n_x=0, n_y=1, n_z=2$, $\vec{n}=(0, \pm 1, \pm 2)$, 上它都有相同形态, 而且 $k^2 = g = 4$.

* 大量子经典对应: 单粒子状态 $\leftrightarrow \omega = \hbar^2 m$ 单粒子能.

* 量子统计的全局性: 用量子态描述宏观,无论分子、原子、电子还是质子、光子,都是全局的.

* 三维或以上空间,只有波动和量子.

+ 在 $d=2, 1$, 可以有既非波动又非量子一维, (1D 波函数)

* 全同粒子不违反 $(3)-$ 单粒子状态. (Pauli 原则)

* 如果 ψ 可以“局域化”, 则可分解. 如此, 局域在区域的区域的粒子, 不需束缚中一电子.

2.3 近独立粒子系统的统计物理

* 近独立是指相邻间作用很弱,且只对体系内起作用,但对体系外不起作用.

$$E = \sum_{i=1}^N E_i, \quad E_i \text{ 为第 } i \text{ 个粒子的能级.}$$

* 对任意的粒子, $E_i, \alpha=1, \dots, N$ 是能级指标, g_α 为能级简并度 (recall 一个 Box 中的自由粒子). 由于等价全局性, 能级不重要, 重要的是能级上占据的粒子数 a_α . 以及能级能级的组合分布

$$\begin{array}{c} \text{能级} \\ \hline \text{能级} \\ \text{能级} \\ \text{能级} \end{array} \Rightarrow \begin{array}{c} \text{能级简并度} \\ \hline \text{能级简并度} \\ \text{能级简并度} \\ \text{能级简并度} \end{array} \Rightarrow \begin{array}{c} \text{占据数} \\ \hline \text{占据数} \\ \text{占据数} \\ \text{占据数} \end{array}$$

$$g_{\alpha_1} = g_{\alpha_2} = \dots = g_{\alpha_N}$$

* 对孤立系, (E, V, N) .

$$\sum \alpha_\alpha = N, \quad \sum \epsilon_\alpha a_\alpha = E$$

* 固定一个能级占据数分布 a_α , 由于单粒子能级可能有多种不同的状态, 一个状态分布可以有不同微观状态数. 对应于 a_α 与之对应, 设 $W(a_\alpha)$ 为对应于一组微观状态数. 由等几率原理, 得出这组几率 $P(a_\alpha) \propto W(a_\alpha)$.

* 粒子态也有可区分和不可区分，对可区分的，

$$W(\{g_{\alpha}\}) = \frac{N!}{\prod g_{\alpha}!} \prod g_{\alpha}^{\alpha}$$

上式有 α 项，就是简单从 m 重取，而前一图中考虑 N 个粒子放在不同盒子中，每个盒子放 α_i 是组合数。由最概分布，可以得到配分函数，有 α_i 项，则可求出所有可能的数。这是 Boltzmann 组分法。

* 对 Fermi 子和 Bose 子，它们互不相同的性质仍是可知的，只要考虑玻尔兹曼统计中的不可分辨性即 Pauli 原理。结果是

$$(对 Fermi) W_F(\{g_{\alpha}\}) = \prod \frac{g_{\alpha}!}{\alpha_1!(g_{\alpha}-1)!}$$

$$W_B(\{g_{\alpha}\}) = \prod \frac{(g_{\alpha}+g_{\alpha}-1)!}{\alpha_1!(g_{\alpha}-1)!}$$

* 从几率分布推导出 Bose 和 Fermi 组分法

* 由独立粒子性的统计物理结果可以推广到一般情况，但最概分布的推广方式不同。这在找级主门课会讲一部分内容。

任何物理可观测量 O 是微观粒子的统计平均值

$$\bar{O} = \int d\Omega p \bar{O} \quad \int d\Omega p = 1$$

* 系统处于某一微观状态
= 这个微观状态的密度。（概率）

* 处于 $d\Omega$ 中的 $p d\Omega$ 表示该状态为一个微系综，即

系统是复数的，和研究系统性质无关。
彼此独立地处于某一微观状态的分子很多。

3.2 利维 (Liouville) 定理

利维定理：守恒的几率密度（或代表其函数）在运动中不变，即 $\frac{d\hat{p}}{dt} = 0$ 或 $\frac{dp}{dt} = 0$ 。

利维定理 ~~即~~ 代表真概率 ~~且~~ 不变

~~代表真概率~~：

$$\frac{\partial \hat{p}}{\partial t} + \nabla \cdot \vec{J}_p = 0 \quad \vec{J}_p = \vec{p} \vec{v}$$

$$\nabla = \left(\frac{\partial}{\partial p_1}, \frac{\partial}{\partial p_2} \right), \quad \vec{v} = (v_1, v_2)$$

~~用正则方程代入~~ ~~3.1 H=H(t)~~：

$$\frac{\partial \hat{p}}{\partial t} + \frac{i}{\hbar} [\hat{p}; H] = 0$$

第三章 微观力学

平衡与统计一般理论是统计理论，它适用于任何系统的宏观统计学。统计学包括微正则、麦克斯韦正则、前者是基础，但后者在实际计算中更方便。

3.1 经典统计学

经典力学的微观状态是相空间中的一点，它遵从从已知运动方程

$$\dot{q}_i = -\frac{\partial H}{\partial p_i}, \quad \dot{p}_i = -\frac{\partial H}{\partial q_i}, \quad i=1 \dots 5.$$

$(q_i^{(+)}, p_i^{(+)})$ 形成一条相轨迹，确定 (运动) 演进

$$dq = dq_1 \dots dq_5 dp = dp_1 \dots dp_5$$

是相体积。

设 Γ 为给定物理条件下所有可能的微观状态，
 $\rho d\Omega$ 为其中的微观状态密度，即

$$\rho d\Omega = \frac{\tilde{\rho} d\Omega}{\Gamma} = \frac{\tilde{\rho} d\Omega}{\int d\Omega} \text{ 是概率密度}$$

状态出现几率 \sim 常数。 $\tilde{\rho} = \frac{1}{\Gamma}$ 称为常数

因果律

~~因果律~~ $\frac{\partial \hat{p}}{\partial t} + \sum_i \vec{p}_i \cdot (\vec{v} \vec{v}_i) = 0 \quad (1)$

$$\begin{aligned} \frac{\partial \hat{p}}{\partial t} &= \frac{\partial \hat{p}}{\partial t} + \sum_i \frac{\partial \hat{p}}{\partial q_i} \dot{q}_i + \frac{\partial \hat{p}}{\partial p_i} \dot{p}_i \quad (A) \\ &= -\dot{p} \sum_i \left\{ \frac{\partial \hat{p}}{\partial q_i} + \frac{\partial \hat{p}}{\partial p_i} \right\} \quad (\text{因果律}) \end{aligned}$$

因果律

$$= -\dot{p} \sum_i \left\{ \frac{\partial H}{\partial q_i p_i} - \frac{\partial H}{\partial p_i q_i} \right\} = 0. \quad (\text{因果律})$$

另一项，~~因果律~~ $\frac{\partial \hat{p}}{\partial t} + \sum_i \vec{p}_i \cdot (\vec{v} \vec{v}_i) = 0$ 式。

$$\frac{\partial \hat{p}}{\partial t} + \sum_i \vec{p}_i \cdot (\vec{v} \vec{v}_i) = 0 \quad \text{或} \quad \frac{\partial \hat{p}}{\partial t} + \sum_i \vec{p}_i \cdot (\vec{v} \vec{v}_i) = 0.$$

* 利维定理是相空间代表类密度的运动方程。是力学定律，但之为 ~~经典~~ 量子力学提供了依据。

~~量子力学：用复数密度代替经典概率；~~
~~② Schrödinger eq. 代替波动方程；~~
~~波函数及海森堡方程：~~

$$\hat{\psi}(t) = e^{iHt/\hbar} \psi(0) e^{-iHt/\hbar}$$

$$\hat{\psi}(t) = e^{iHt/\hbar} e^{iHt/\hbar} \psi(0) e^{-iHt/\hbar} + e^{iHt/\hbar} \psi(0) e^{-iHt/\hbar}$$

$$\hat{\psi}(t) = \psi(0) [H, \psi(0)], \quad \hat{\psi}(t) \text{ 波函数}$$

$$\frac{\partial \hat{\psi}}{\partial t} + \frac{i}{\hbar} [\hat{\psi}; H] = 0 \quad \Rightarrow \text{利维方程}$$

$$\bar{\psi} = \sum_n \psi_n \langle n | \psi | m \rangle = \text{Tr } \hat{\psi} \psi$$

§3.2 量子统计力学

* 对量子力学，我们用波函数或量子态来代替经典力学的相空间的代表量。波函数波函数中认为 ψ_n 或 $|n\rangle$, 但 $|A_n\rangle = \langle n|A|n\rangle$ 是力学可观测量的平均值。

对(统计)力学，我们考虑第一子系 n 系统， $|n\rangle$, $n=1, \dots$ 其中 $N = \sum_n p_n$ 表示总概率，即有 N 系统，总概率为这样， $p_n = \frac{1}{N}$ 是一子系几率。 $\sum_n p_n = 1$.

~~①~~ ① 量子(统计)平均值为

$$\bar{A} = \langle A \rangle = \sum_n p_n A_n.$$

* 量子力学(或量子统计)

$$\hat{P} = \sum_n |n\rangle \langle n|. |n\rangle$$
 是一基波矢量。

$$\langle i|j \rangle = \delta_{ij}, \quad \hat{P} \text{ 和 } \hat{A} \text{ 是矩阵形式}$$

$$\delta P_{ij} = \langle i|\hat{P}|j \rangle = \sum_n \langle i|n \rangle \langle n|j \rangle$$

$$A_{ij} = \langle i|A|j \rangle. \quad \text{且} \quad \bar{A} = \sum_n p_n \langle n|A|n \rangle = \sum_{ij} \sum_n p_n \delta_{ij} A_{ij}$$

$$\Rightarrow \sum_{ij} p_{ij} A_{ji} = \text{Tr}(\hat{P} A), \quad \text{Tr } \hat{P} = 1.$$

§3.3 微正则力学

* 经典微正则力学，(E, N, V)不变的条件，孤立系。
时间演化 $\frac{dP}{dt} = 0$ ，若平行态物理量不随时间变，则要求 $\frac{dP}{dt} = 0$ 为必要条件。即一系相随道由， P 有本征，或是一条相随道(即一系相道)内 P 为常数。但是不能保证不同相道 P 相同。微正则力学的基本假设是，
当 $H(q, p) = E$ 时 $P = \text{Const.}$ 。当 $H \neq E$ 时 $P = 0$ 。若将 H 平移为一常数很困难，量子力学理论是

$$P = \begin{cases} C, & \text{若 } E \leq H \leq E + \Delta E \\ 0, & \text{otherwise.} \end{cases}$$

$$\lim_{\Delta E \rightarrow 0} C \int_{E-E}^E dE = 1, \quad \bar{P}(q, p) = \lim_{\Delta E \rightarrow 0} C \int_{E-E}^E 0 dE.$$

* 历史论：几率原理或微正则力学意味着只要时间足够长，(E, N, V)对宏观微观状态都可能出现。即历史论。但过去的历史是由被观察者在宏观上不能检测的另外一些相作用所决定的。而过去由 H 演变，即过去被观察者在历史论。

* \hat{P} 在力学方程

$|n\rangle$ 满足 Schrödinger eq.

$$i \frac{\partial}{\partial t} |n\rangle = \hat{H} |n\rangle$$

$$i \frac{\partial}{\partial t} \hat{P} = \sum_n \left\{ \left(i \frac{\partial}{\partial t} |n\rangle \right) \langle n| - \langle n| \left(i \frac{\partial}{\partial t} \langle n| \right) \right\}$$

$$\Leftarrow \hat{H} \hat{P} - \hat{P} \hat{H} = [H, \hat{P}]$$

$$\therefore i \frac{\partial}{\partial t} \hat{P} + i[H, \hat{P}] = 0.$$

(\hat{P} 在 Heisenberg eq.)

$$\begin{aligned} \sum_n H |n\rangle p_n \langle n| \\ - i n \rangle p_n \langle n| H \end{aligned}$$

* 量子微正则力学：① 加于该子系

$$(1) \quad P_{in} = \begin{cases} C, & E_n = E \\ 0, & E_n \neq E, \end{cases} \quad n \in \text{量子数的子集}$$

即若系统能级为 E ，则出现几率为 C ，否则为 0.

$$(2) \quad \text{由 } \sum_n P_{in} = C \left(\sum_{n \in E_n} 1 \right) = 1$$

(~~所有能级之和~~ E_n ~~之和~~ \sum_n ~~能级之和~~).

$$\begin{cases} \text{若 } E_n = E \\ \text{且 } \sum_n 1 \\ \text{本征} \end{cases} \quad N(E, V, N) = \left(\sum_{n \in E} 1 \right), \quad \text{且} \\ C = \frac{1}{N(E, V, N)}.$$

~~注：~~ 先算本征

§3.4 微正则力学中宏观统计

经典：

$$\bar{A} = \int A(q, p) P dq dp$$

$$\Rightarrow \bar{A} = \frac{1}{N!} \int_{\Omega}^{} \int_{E \leq H \leq E + \Delta E}^{} A dq dp.$$

$$\text{分子：} \quad \bar{A} = \sum_n p_n A_n$$

$$(E=E_n)$$

$$\bar{A} = \sum_n p_n A_n$$

$$(E=E_n)$$

第6章 正则系综

3.4.1 微正则系综与正则系综.

正则系综是指导体与大系统接触达到平衡的系综, (T, V, N) 固定, 大系统提供确定的温度.

① A 代表正则系综中的系统, B 代表大系统.

且 $A+B$ 是一个孤立系综 $(E_{\text{总}}, V = V_A + V_B, N = N_A + N_B)$.

若 A 和 B 互不影响, $E = E_A + E_B$. 取 $S(E)$ 为 $A+B$ 的总熵, 当 A 处于某一状态, B 处于 $S_B(E_A)$ 状态. $\therefore A$ 处于绝对热力学平衡.

$$P_A = \frac{S_B(E_A)}{S(E)}$$

条件看

E_A 对 E_A 偏离状态无影响. 由 $E_A < E_{\text{总}}$, $E_B < E_{\text{总}}$ 在推导中, B 是体积度数, 我们可用一个自由能子泛函代替规定. 由上节得式 1,

$S_B(E_A) \sim (E_A - E_A)^M$, $M \sim O(N_B) \sim O(N)$.
由于 M 很大, $E_A^M (1 - \frac{E_A}{E_{\text{总}}})^M = E_A^M (1 - \frac{E_A}{E_{\text{总}}} + \dots)$

二项式展开把二项忽略不计.

内能

$$\bar{E} = \sum_n E_n P_n = \frac{1}{Z_N} \sum_n E_n e^{-\beta E_n}$$

$$= \frac{1}{Z_N} \left(-\frac{\partial}{\partial \beta} \sum_n e^{-\beta E_n} \right) = -\frac{\partial}{\partial \beta} \ln Z_N$$

$$T \text{ 温度: } T = -\frac{\partial \bar{E}}{\partial \beta},$$

$$P = \sum_n P_n S_n = \sum_n \frac{\partial E_n}{\partial V} e^{-\beta E_n} = \frac{1}{V} \frac{\partial}{\partial V} \ln Z_N.$$

$$dS = \frac{d\bar{E}}{T} + \frac{\partial}{\partial V} dV = k_B (\beta d\bar{E} + \beta dV)$$

$$= k_B \left(-\beta \frac{\partial}{\partial \beta} \ln Z_N + dV \frac{\partial}{\partial V} \ln Z_N \right)$$

$$= k_B d \left(\ln Z_N - \beta \frac{\partial}{\partial \beta} \ln Z_N \right)$$

$$\therefore TS = k_B \left(\ln Z_N - \beta \frac{\partial}{\partial \beta} \ln Z_N \right).$$

$$F = \bar{E} - TS = -k_B T \ln Z_N.$$

3.4.3 热力学温度. 热力学极限和经典极限

(在热力学极限中, 温度用能量表示.
例如内能, 也是 E 与 \bar{E} 的方差. 或者说根. 那时
方差, $(\bar{E}-E)^2/\bar{E}^2$, 或 $\sqrt{(\bar{E}-E)^2}/\bar{E}$.

安托万方差

$$(E - \bar{E})^2 = e^{M \ln (E - \bar{E})}$$

$$\ln (E - \bar{E}) = \ln E + \ln (1 - \frac{\bar{E}}{E}) = \ln E - \frac{\bar{E}}{E} - \frac{1}{2} (\frac{\bar{E}}{E})^2 + \dots$$

这时, 可以把 $O(\frac{\bar{E}}{E})$ 忽略不计. $\therefore P_A$,
对 N_B 作同样处理. \therefore 逆温律成立.

$$P_A = \frac{1}{Z_N(E)} e^{\ln Z_N} = \frac{1}{Z_N(E)} e^{\ln Z_N(E) - \frac{\bar{E}}{E} + \dots}$$

$$\approx \frac{Z_N(E)}{Z_N(E)} e^{-\beta \bar{E}} \triangleq \frac{1}{Z_N} e^{-\beta \bar{E}}$$

其中 $\beta = \frac{\partial \ln Z_N}{\partial E}$, 由大系统决定, 从物理

角 $\beta = \frac{1}{k_B T}$. k_B 是 Boltzmann 常数, T 是温度.

$$P_A = P_n, \quad \sum_n P_n = 1, \quad \Rightarrow \sum_n e^{-\beta E_n}$$

$E_A = E_n$, \sum_n 表示正则子综的统计量.

$$\sum_n = \text{Tr} e^{-\beta H} = \sum_n \langle n | e^{-\beta H} | n \rangle = \sum_n e^{-\beta E_n}$$

3.4.2 直力子

$$\bar{A} = \frac{\text{Tr}(A e^{-\beta H})}{\sum_n} = \frac{1}{Z_N} \sum_n \frac{e^{-\beta E_n} C_n M_n}{10^{34} \text{J} \cdot \text{s} \cdot \text{C} \cdot \text{m} \cdot 10^{20} \text{kg}}$$

$$\bar{A} = \sum_n A_n P_n = \frac{1}{Z_N} \sum_n \langle n | A | n \rangle e^{-\beta E_n} \quad \begin{cases} \text{设} \\ 3 E_n = E \\ + P \end{cases}$$

$$= \frac{1}{Z_N} \sum_n \langle n | A e^{-\beta H} | n \rangle = \frac{1}{Z_N} \text{Tr}[A \hat{e}^{-\beta H}]$$

$$\overline{(E - \bar{E})^2} = \overline{(E^2 - 2\bar{E}E + \bar{E}^2)}$$

$$= \bar{E}^2 - 2\bar{E}^2 + \bar{E}^2 = \bar{E}^2 - \bar{E}^2$$

$$\bar{E}^2 = \sum_n E_n^2 P_n = \dots = \bar{E}^2 - \frac{2\bar{E}}{\partial \beta} |_{N,V}$$

$$\therefore \overline{(E - \bar{E})^2} = -\frac{\partial \bar{E}}{\partial \beta} |_{N,V} = k_B T \left(\frac{\partial \bar{E}}{\partial T} \right)_{N,V} = \frac{k_B T^2}{V} C_V$$

直力子的方程为

$$\overline{(E - \bar{E})^2} = \frac{\sqrt{k_B T^2 C_V}}{\bar{E}} \times \frac{\sqrt{N}}{N} \times \frac{1}{Z_N}$$

$$\propto T, \quad \therefore C_V, \bar{E} \text{ 为 } \propto T, \text{ 取直力子方程.}$$

$$\propto T, \quad \therefore \sqrt{k_B T N} \propto \sqrt{N} = \frac{L}{\sqrt{N}}. \quad \begin{cases} \text{单分子} \\ \text{分子} \\ \text{一般分子} \end{cases}$$

* 直力子极限值, $N, V \rightarrow \infty$, 但子数取

密度不变: $n = \frac{N}{V}$ 固定. \rightarrow 特别地它

* 我们前面都用子态表示, \therefore 热力学
极限时 $\lambda_T = h/(2\pi m k_B T)^{1/2} \ll \bar{E}$ (经典极限)

$\Delta E = E_n - E_{n+1} \ll k_B T$ 时, 可用经典力学.

$$\text{这时: } Z_N = \frac{1}{N! h^N} \int d\Omega_N e^{-\beta H(\Omega)}$$

$$A = \frac{1}{Z_N} \int d\Omega_N A e^{-\beta H}$$

多种应用：非理想气体的状态方程

$$\text{模型: } E = K + V = \sum_{i=1}^N \frac{\vec{p}_i^2}{2m} + \sum_{i,j} \phi_{ij}$$

$$\phi_{ij} = \phi(|\vec{r}_i - \vec{r}_j|) \text{ 且 } = (1 + \beta r) \sim 1/r$$

$$Z_N = \int d(\vec{p}) e^{-\beta(E+V)}$$

$$(d\vec{p}) = \frac{1}{N! V^N} \int d\vec{p}_1 \cdots d\vec{p}_N d\vec{r}_1 \cdots d\vec{r}_N$$

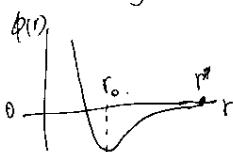
对运动积分做简单的近似积分，是积分平均法。

$$Z_N = \frac{1}{N! V^N} Q_N(\beta, V), \quad V \text{ 是恒定的。}$$

$$Q_N = \int d\vec{p}_1 \cdots d\vec{p}_N e^{-\beta \sum_{i,j} \phi_{ij}} = f(\vec{p}) \prod_{i,j} e^{-\beta \phi_{ij}}$$

是恒形函数乘积，对理想气体， $\phi_{ij} \rightarrow 0$, $Q_N \approx V^N$.

我们假设 ϕ_{ij} 是短程的，(例如， δ 势能)



r^* 表示 $\phi = \phi_0$ 时的 r 值 $\sim 10^{-8} \text{ cm} \sim 0.1 \text{ nm}$

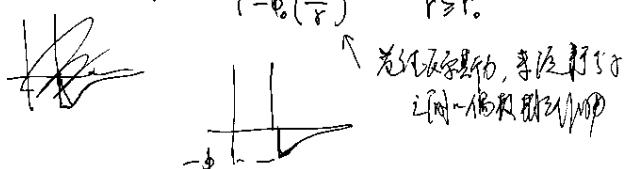
$$\left. \begin{aligned} \text{这样 } \phi_{ij} &= e^{-\beta \phi_{ij}} \\ f(r) &\Rightarrow \begin{cases} 1, & r \rightarrow 0, (\phi \rightarrow \infty) \\ 0, & r \geq r^*, (\phi \rightarrow 0) \end{cases} \end{aligned} \right\} \text{ 分开} \quad \left. \begin{aligned} r < r^*, & \text{ 分子间吸引作用} \\ r > r^*, & \text{ 分子间排斥作用} \end{aligned} \right\}$$

$$= \frac{N k_B T}{V} \left[1 - \frac{N}{2V} \int d\vec{r} f(r) \right]$$

$$B_z = -\frac{N}{2} \int d\vec{r} f(r) \quad \text{即 } f = \text{径向分布}$$

(1) 制作势能

$$\phi(r) = \begin{cases} +\infty & r < r_0 \\ -\phi_0 \left(\frac{r_0}{r}\right)^6 & r \geq r_0 \end{cases}$$



$$B_z = -\frac{N}{2} \int_0^\infty (e^{-\phi(r)/k_B T} - 1) 4\pi r^2 dr$$

$$= 2\pi N \left[\int_0^{r_0} r^2 dr - \int_{r_0}^\infty (e^{-\phi(r)/k_B T} - 1) r^2 dr \right]$$

(设 $\phi_0 \ll k_B T$)

$$\approx 2\pi N \left(\frac{r_0^3}{3} - \phi_0 \frac{r_0^3}{3k_B T} \right) = Nb - \frac{Na}{kT}$$

$$\therefore p = \frac{Nb}{V} \left(1 + \frac{Nb}{V} \right) - \frac{Na}{V^2} \approx \frac{NkT}{V(1 - \frac{Nb}{V})} - \frac{N^2 a}{V^2}$$

$$\Rightarrow \left(p + \frac{N^2 a}{V} \right) (V - Nb) = Nk_B T$$

笼子气体方程

$$Q_N = \int (d\vec{p}) \prod_{i,j} (1 + f_{ij})$$

$$= \int (d\vec{p}) \left(1 + \sum_{i,j} f_{ij} + \sum_{i,j} f_{ij} \sum_{i,j} f_{ij} + \dots \right)$$

假设 $e^{-\beta \phi(r_0)} - 1 \ll 1$. 即 $e^{-\beta \phi(r_0)/2} \ll 1$, 则在最简情况下, $f_{ij} \approx 0$ 可忽略

$$Q_N \approx \int (d\vec{p}) (1 + \sum_{i,j} f_{ij})$$

$$= V^N + \frac{1}{2} N(N-1) V^{N-2} \int d\vec{r}_1 d\vec{r}_2 f_{12}$$

体积度量变换 $\vec{r}_1 \cdot \vec{r}_2 = \vec{r}$, 空间边界效应.

$$\int d\vec{r}_1 d\vec{r}_2 f_{12} = \int d\vec{r}_1 \int d\vec{r}_2 f(r) \approx V \int d\vec{r} f(r).$$

$$\therefore Q_N \approx V^N \left(1 + \frac{1}{2} (N-1) V^0 \cdot \int d\vec{r} f(r) \right)$$

$$\approx V^N \left(1 + \frac{N^2}{2V} \int d\vec{r} f(r) \right)$$

$$\ln Q_N = N \ln V + \ln \left(1 + \frac{N^2}{2V} \int d\vec{r} f(r) \right)$$

$$\approx N \ln V + \frac{N^2}{2V} \int d\vec{r} f(r). \quad \text{化学方程: } \frac{N^2}{2V}$$

Z_E ,

$$\begin{aligned} p &= \frac{1}{\beta} \frac{\partial}{\partial V} \ln Z_N = \frac{1}{\beta} \frac{\partial}{\partial V} \ln Q_N \\ &= k_B T \left[\frac{N}{V} - \frac{N^2}{2V^2} \int d\vec{r} f(r) \right] \end{aligned}$$

第2章 固体分子

与固体分子的类似，温度同时使分子振动

$$E_T = E_A + E_B, \quad N_T = N_A + N_B.$$

$$P_n = P_{A,n} = \frac{S_B(N_A, E_A, E_B)}{S_A(N_A) S_B(E_B)}$$

$$= \frac{1}{S_A(N_A)} e^{\ln S_B(N_A, E_A, E_B)}$$

$$= \frac{S_B(N_A, E_B)}{S_A(N_A)} e^{-\frac{\partial \ln S_B(N_A, E_B)}{\partial N_A} N_A - \frac{\partial \ln S_B(N_A, E_B)}{\partial E_A} E_A}$$

$$= \frac{1}{N_A} e^{\beta E_A - \beta E_B}$$

去掉 A 的指标, $N_A \rightarrow N$, $E_A \rightarrow E_n$

$$P_{n,n} = \frac{1}{N} e^{-\beta(E_n - MN)}$$

$$\text{由 } 1/2-\text{规则}, \sum_{n=1}^N \sum_{n=1}^N P_{n,n} = 1$$

$$\Rightarrow \sum_{n=1}^N e^{\beta E_n - \beta MN} \sum_{n=1}^N e^{-\beta E_n}$$

$$= \sum_{n=1}^N e^{\beta E_n - \beta MN} Z_N = T \text{ Tr } e^{-\beta(E - MN)}$$

* 直正則系是溫度學物理中最常用。(Effective) $U = \text{Fermi energy}$.

$$\bar{N} = -\frac{\partial}{\partial \beta} \ln Z_N = -k_B T \left(\frac{\partial}{\partial \mu} \ln Z_N \right)_T$$

$$E = -\frac{\partial}{\partial \beta} \ln Z_N$$

$$P = \frac{1}{\beta} \frac{\partial}{\partial V} \ln Z_N$$

$$S = k_B \left(\ln Z_N - \alpha \frac{\partial}{\partial \mu} \ln Z_N - \beta \frac{\partial}{\partial \beta} \ln Z_N \right)$$

$$(\alpha = -\frac{\partial}{\partial \beta} P)$$

$$F = -k_B T \ln Z_N + k_B T \alpha \frac{\partial}{\partial \mu} \ln Z_N$$

$$\Phi = -k_B T \ln Z_N$$

* 能量和半導體物理 $\sim \frac{1}{N^2}$.

* 理想玻耳茲

$$Z_N = \sum_n e^{-\epsilon_n} Z_N$$

$$\sum_N = \frac{1}{N! h^3} \int d\Omega_N e^{-\beta E_N}$$

* 应用案例：固液表面吸附速率

○ 为吸附中心 (点)
○ 为吸附粒子 (点)

考慮此， $N = \frac{1}{2} N_0 \pi r^2 h^3$, 設基為理想氣體，已知 $[8.9.91]$

$$e^{-\beta \mu} = \frac{(2\pi mk_B)^{3/2} k_B T}{P h^3}$$

$$\hat{\tau}_N (\theta) = \frac{\bar{N}}{N_0} = \frac{P h^3}{P h^3 + (2\pi m)^{3/2} (k_B T)^{3/2} e^{-\epsilon_0/k_B T}}$$

$\uparrow \uparrow, \Theta \uparrow; T \uparrow, \Theta \downarrow$.

解釋：

1. 用直正則系統計計算分子理據關係~並列函數。
2. 參書 8.9, 8.10, 8.12

$$\Theta = \frac{\bar{N}}{N_0} = \frac{\text{被吸收分子數}}{\text{總分子數}}$$

(3)

總分子數部分為分子數， Θ 之部分為被吸收分子數
 $N \rightarrow \bar{N}, (T, \mu, V)$ 不變，設分子總數為 N 則有
 $-\epsilon_0$, $\text{R} \cdot E_N = -N \epsilon_0$.

$$\sum_N = \sum_{n=1}^{N_0} \sum_n e^{-\epsilon_n - \beta E_N} = \sum_{N=0}^{N_0} e^{\beta(\mu + \epsilon_0)N}$$

n 表示 N 分子出現 n 次 N_0 分子中 n 次
↑ 在 n 分子次數，這樣代表一定有

$$\frac{N_0!}{N! (N_0-N)!}$$

$$\therefore \sum_n = \frac{N_0!}{N! (N_0-N)!}$$

$$\begin{aligned} \sum_N &= \sum_{N=0}^{N_0} \frac{N_0!}{N! (N_0-N)!} e^{\beta(\mu + \epsilon_0)N} \\ &= (1 + e^{\beta(\mu + \epsilon_0)})^{N_0} \\ \bar{N} &= -\frac{\partial}{\partial \mu} \ln Z_N = \frac{1}{\beta} \frac{\partial}{\partial \mu} \ln Z_N \\ &= N_0 \frac{\partial}{\partial \mu} e^{\mu + \beta \epsilon_0} = \frac{N_0 e^{\beta(\mu + \epsilon_0)}}{1 + e^{\beta(\mu + \epsilon_0)}} \\ \therefore \Theta &= \frac{\bar{N}}{N_0} = \frac{1}{1 + e^{-\beta(\mu + \epsilon_0)}}. \end{aligned}$$

齊普塞統計 $-d=3, 2, 1$.

這章，我們討論齊普塞。若 $d=3$ ，對氣體 either bosons or fermions. 若 $d=2$ ，則 us & anyons. 若 $d=1$ ，這時狀況依賴于相對論。

3.6.1 用直正則系統計 Bose 和 Fermion (3.7P)

$$\sum_N = \sum_{N=0}^{N_0} \sum_{E_N} e^{-\epsilon_N - \beta E_N}$$

(ϵ 为能級)

若 $E_{N_01} = E_{N_02} = \dots = E_N$ 則 \sum_N 一起

$$\sum_N = \sum_{N=0}^{N_0} \sum_{E_N} \sum_{\substack{3(E_N) \\ E_{N_0}=E_N}} e^{-\epsilon_N - \beta E_N}$$

對自由能， $E_N = \sum_x a_x E_x, N = \sum_x a_x$
{ a_x, b_x 一子系統的分布}.

$$\begin{aligned} \sum_N &= \sum_{N=0}^{N_0} \sum_{E_N} \sum_{\substack{3(E_N) \\ \sum_x a_x E_x = E_N}} e^{-\epsilon_N - \beta E_N} \\ &= \sum_{\substack{3(a_x) \\ a_x \geq 0}} W(s_{\text{eff}}) e^{-\sum_x (\omega_x + \beta \epsilon_x) a_x} \end{aligned}$$

(這裡 s_{eff} 代表了所有可能分布 (各種狀態, 各種狀態).

对称粒子

$$W_\lambda = \frac{g_\lambda!}{a_\lambda!(g_\lambda-a_\lambda)!}$$

对称组合

$$W_\lambda = \frac{(g_\lambda+a_\lambda-1)!}{a_\lambda!(g_\lambda-a_\lambda)!}$$

$$\Sigma_\alpha = \sum_{\alpha > 0} \prod_\lambda [W_\lambda e^{-(\alpha+\beta_\lambda) a_\lambda}]$$

$$= \sum_{a_1} \dots \sum_{a_\lambda} \prod_\lambda [W_\lambda e^{-(\alpha+\beta_\lambda) a_\lambda}]$$

$$= \prod_\lambda \left(\sum_{a_\lambda} e^{-(\alpha+\beta_\lambda) a_\lambda} \right)$$

$$\Sigma_\alpha^{(F)} = \sum_{a_\lambda=0}^{g_\lambda} \frac{g_\lambda!}{a_\lambda!(g_\lambda-a_\lambda)!} e^{-(\alpha+\beta_\lambda) a_\lambda} = [1 + e^{-\alpha-\beta_\lambda}]^{g_\lambda}$$

($a_\lambda \leq g_\lambda$)

$$\Sigma_\alpha^{(B)} = \sum_{a_\lambda=0}^{\infty} \frac{(g_\lambda+a_\lambda-1)!}{a_\lambda!(g_\lambda-a_\lambda)!} e^{-(\alpha+\beta_\lambda) a_\lambda}$$

$$(\text{物理}) \quad (1-x)^m = \sum_{n=0}^m \frac{(m+n-1)!}{n!(m-n)!}$$

$$= (1 - e^{-\alpha-\beta_\lambda})^{g_\lambda}$$

$$\therefore \Sigma_\alpha = \prod_\lambda (1 + e^{-\alpha-\beta_\lambda})^{g_\lambda}$$

$$\therefore \psi(\vec{r}_1, \vec{r}_2, \dots) = e^{i\alpha_{12}} \psi(\vec{r}_1, \vec{r}_2, \dots)$$

对称粒子, 由 3 Pauli 波函数

$$\psi(\vec{r}_1, \vec{r}_1, \vec{r}_3, \dots) = 0.$$

$$\text{or } \lim_{\vec{r}_1 \rightarrow \vec{r}_2} \psi(\vec{r}_1, \vec{r}_2, \dots) = 0 \quad \text{反交换}$$

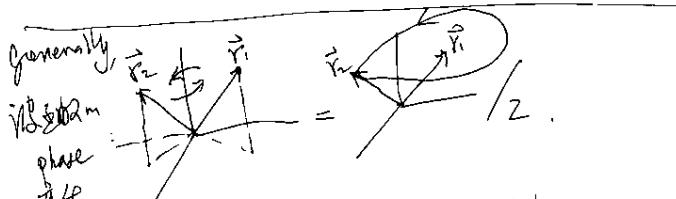
$$\text{即 } \psi(\vec{r}_1, \vec{r}_2, \dots) = -\psi(\vec{r}_2, \vec{r}_1, \dots), \text{ 即 } \alpha_{12} = \pi$$

对 Boson:

$$\lim_{\vec{r}_1 \rightarrow \vec{r}_2} \psi(\vec{r}_1, \vec{r}_2, \dots) = 0 \quad \text{不反交换}$$

$$\lim_{\vec{r}_1 \rightarrow \vec{r}_2} \psi(\vec{r}_1, \vec{r}_2, \dots) = \lim_{\vec{r}_1 \rightarrow \vec{r}_2} \psi(\vec{r}_2, \vec{r}_1, \dots) = \psi(\vec{r}_1, \vec{r}_1, \dots)$$

$$\neq 0. \quad \therefore \alpha_{12} = 0 \pm 2n\pi.$$

至二维空间, $\vec{r}_1, \vec{r}_2, \dots$ 只有一维相位障碍, 1/2 引入 α_{12} 为 0 或 π , 具有 phase

$$e^{i\alpha} = e^{i2\pi n} \Rightarrow n = \text{odd, fermion} \quad \text{或} \quad n = \text{even, boson}$$

即 $\alpha = \pi, 0$ 或 2π 只能是 boson or fermion

$$\ln Z_\alpha = \pm \sum_\lambda g_\lambda \ln (1 \pm e^{-\alpha-\beta_\lambda})$$

* 为 \bar{Z}_α (反粒子数平均值)

$$\bar{Z}_\alpha = \sum_N \sum_m g_\lambda P_{N\alpha}$$

$$= \frac{1}{Z_\alpha} \sum_\lambda g_\lambda \left(\sum_m g_\lambda W_\lambda e^{-(\alpha+\beta_\lambda) a_\lambda} \right)$$

$$\cdot \prod_{\lambda+3} \bar{Z}_\lambda$$

$$= \frac{1}{Z_\alpha} \sum_\lambda g_\lambda W_\lambda (e^{-(\alpha+\beta_\lambda) a_\lambda})$$

$$= -\frac{1}{Z_\alpha} \frac{\partial}{\partial \alpha} \bar{Z}_\lambda = -\frac{\partial}{\partial \alpha} \ln \bar{Z}_\lambda$$

$$= -\frac{\partial}{\partial \alpha} (\pm g_\lambda \ln (1 \pm e^{-\alpha-\beta_\lambda}))$$

$$= \frac{g_\lambda}{\alpha + \beta_\lambda \pm 1}$$

§ 6.2 粒子统计和波函数 (Fermion in Antiparticle)

设 $\psi(\vec{r}_1, \dots, \vec{r}_N)$ 是 N 颗粒子波函数我们取 \vec{r}_i, \vec{r}_j 为坐标, 根据假设进行 α_{ij} 计算

$$|\psi(\vec{r}_1, \dots, \vec{r}_N)|^2 = |\psi(\dots, \vec{r}_j, \dots, \vec{r}_i, \dots)|^2$$

至二维空间,

$$\circlearrowleft \neq 0. \neq \circlearrowright, \dots$$

物理上

$$\psi(\vec{r}_1, \vec{r}_2) \propto (z_1 - z_2)^2, \quad z_1 \text{ 与 } z_2 \text{ 交换}$$

$$\Rightarrow (z_1 - z_2)^2 = (-1)^2 (z_1 - z_2)^2. \quad \text{不交换}$$

phase $\propto e^{i\alpha_{12}\pi}$. 量子力学讲过讨论,

(反粒子 anyon, 顶点).

至一维空间

$\vec{r}_1, \vec{r}_2, \dots$ 在一维空间只能通过碰撞交换, \therefore 一维波函数 $\psi(\vec{r}_1, \vec{r}_2, \dots)$ 与 $\psi(\vec{r}_2, \vec{r}_1, \dots)$ 相同, \Rightarrow 我们也将其简单化一下吧.

§ 6.3 路径积分与量子力学 (3)

对已知 ψ (波函数), 算波函数
 $\langle \text{Feynman} \rangle$
 $\text{statistical mechanics}$

$$\psi = \frac{e^{-\beta H}}{\text{Tr} e^{-\beta H}}$$

$\tilde{\rho} = e^{-Ht}$ 是 t normalized 的波函数

$$-\frac{\partial \tilde{\rho}}{\partial \beta} = -\frac{\partial}{\partial \beta} (\tilde{\delta}_{ij})$$

$$= \left(-\frac{\partial}{\partial \beta} \delta_{ij} e^{-\beta E_i} \right) = (\delta_{ij} E_j e^{-\beta E_i})$$

$$= (E_i \tilde{\rho}_{ij}) = H \tilde{\rho}.$$

$$\therefore -\frac{\partial \tilde{\rho}}{\partial \beta} = H \tilde{\rho}, \quad (\tilde{\rho}(0) = 1).$$

这是守恒方程, 在任何表象都对, 在波函数表象

$$-\frac{\partial \tilde{\rho}(x, x'; \beta)}{\partial \beta} = H_x \tilde{\rho}(x, x'; \beta).$$

$$\tilde{\rho}(x, x'; 0) = \delta(x - x')$$

Formally: ~~$\tilde{\rho} = e^{-Ht/\hbar}$~~ redefine: $u = \beta \hbar t$.

~~$\tilde{\rho} = e^{-Ht/\hbar} = e^{-H\beta \hbar u / \hbar} = e^{-H\beta u}$~~

Formally: $\tilde{\rho}(u) = e^{-Hu/\hbar}$.

从 - (1) 得自由能表达式, $H = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2}$,

$$\rho(x, x'; \varepsilon) \approx \sqrt{\frac{m}{2\pi\hbar\varepsilon}} e^{-\frac{(m/\hbar\varepsilon)(x-x')^2}{2\varepsilon}}$$

$$\rho(x, x'; u) = \lim_{\varepsilon \rightarrow 0} \int \frac{dx_1}{\sqrt{2\pi\hbar/m}} \cdots \frac{dx_n}{\sqrt{2\pi\hbar/m}} e^{-\frac{m\epsilon}{2\hbar} \left[\frac{(x-x_1)^2}{\epsilon} + \cdots + \frac{(x-x_n)^2}{\epsilon} \right]}$$

$$\frac{x_n - x_{n-1}}{\epsilon} \rightarrow \frac{dx(\epsilon)}{d\epsilon} = \dot{x}(\epsilon)$$

$$\rho(x, x'; u) = \int \mathcal{D}\dot{x} e^{-S/\hbar}$$

其中 $S = \int_0^u d\epsilon L(\epsilon)$, $L(\epsilon) = \frac{m}{2} (\dot{x}(\epsilon))^2$
 自由能 L 为 ϵ 的函数。

$Z = \text{Tr } \rho$, 是 t 波函数

$$Z = \int dx \rho(x, x) = \int \mathcal{D}x(\epsilon) e^{-\int_0^u d\epsilon L}$$

这时任何相空间子空间时, 对于正则子集

$$Z_\alpha = \int \mathcal{D}x(\epsilon) e^{-S_\alpha}, \quad S_\alpha = S - \mu N.$$

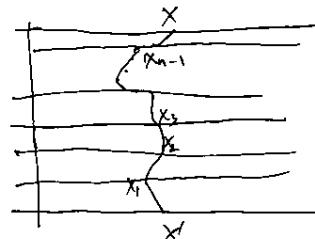
$$[t\beta] = [t], \text{ 于是 } u = \hbar \epsilon$$

$$\rho(u) = e^{-H\beta \hbar u} e^{-H\beta \hbar u} \cdots e^{-H\beta \hbar u}$$

$$= \rho_1 \cdots \rho_n.$$

坐标系表象:

$$\rho(x, x'; u) = \int \cdots \int \rho(x, x_{n-1}; \epsilon) \rho(x_{n-1}, x_{n-2}; \epsilon) \cdots \rho(x_2, x_1; \epsilon) \rho(x_1, x'; \epsilon) dx_{n-1} \cdots dx_1.$$



$$n \rightarrow \infty, \epsilon \rightarrow 0, n\epsilon = u.$$

$$\rho(x, x'; u) = \int \mathcal{D}x \Phi[x(u)]$$

$$\Phi[x(u)] = \lim_{\substack{\epsilon \rightarrow 0 \\ u = n\epsilon}} \rho(x, x_{n-1}; \epsilon) \cdots \rho(x_1, x'; \epsilon).$$

~~$\mathcal{D}x(u) \quad \mathcal{D}x(u) = \lim_{n \rightarrow \infty} dx_1 \cdots dx_{n-1}.$~~

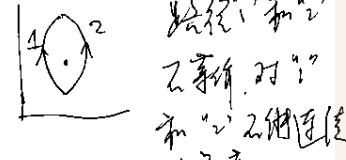
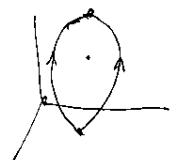
6.4 不确定度原理和 $d=2$. (2)

partition function Φ in $\epsilon \rightarrow i\hbar$, 把 ϵ 看作 \hbar 的量

中 - 于 ϵ 是 $i\hbar$ 的量。

$$\rho(x, x'; u) = \int \mathcal{D}x e^{i\int_0^u dt L}$$

$\otimes x$ 是对所有可能的路径积分。在 $i\hbar$ 的空间, 任何路径对系统状态概率都是 0 。但至 $= 0$ 的空间

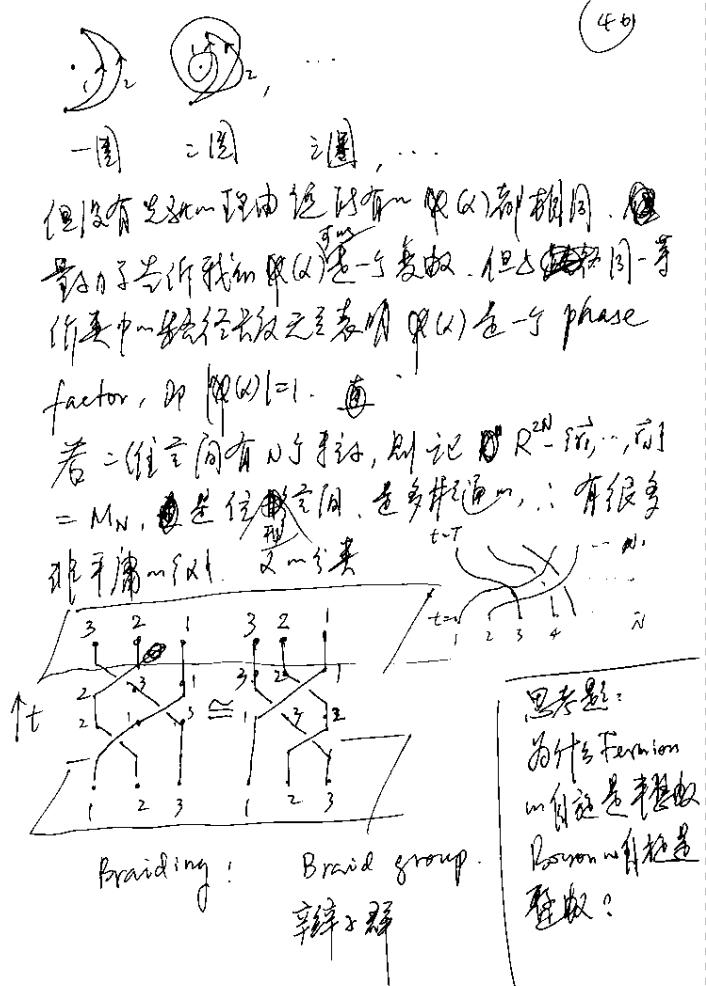


路径“1”和“2”
 和“2”2 侧边
 和底边。

$$\therefore \mathcal{D}x \rightarrow \mathcal{D}\dot{x} \Phi(\dot{x}) \mathcal{D}x$$

在于 $\mathcal{D}x$ 中 - 有路径都可以连接互通。 x 在 $i\hbar$ 的空间中只有 3 互连 - 一个物理事实。





对 N 个粒子, 在 $B_N(R^2)$. 里边,
 B_N 中一个元素叫群元 (元组, nonabelian) 都
可以用 σ_i 表示, 其中 i 是 braiding 产生的
位置, σ_i 是 x_i 及 x_{i+1} 互换时的变换, 且左乘右乘
互有逆元. 即:

$$\begin{array}{c} \sigma_i \\ x_i \quad x_{i+1} \end{array} = \sigma_i \quad \sigma_i^{-1} = \begin{array}{c} x_i \quad x_{i+1} \\ x_{i+1} \quad x_i \end{array} = I = \sigma_i \sigma_i^{-1} = \sigma_i^{-1} \sigma_i$$

从这个图看:

$\sigma_i \sigma_{i+1} \sigma_i = \sigma_{i+1} \sigma_i \sigma_{i+1}$

解:

$$\begin{array}{c} \sigma_i \\ x_i \quad x_{i+1} \end{array} \cdot \begin{array}{c} \sigma_{i+1} \\ x_{i+1} \quad x_{i+2} \end{array} = \begin{array}{c} \sigma_{i+1} \\ x_{i+1} \quad x_i \end{array} \cdot \begin{array}{c} \sigma_i \\ x_i \quad x_{i+1} \end{array}$$

群论与群论-9
Non-abelian group
但一维表示
Abelian 三值
⇒ 量子力学基础

$$\sigma_i \sigma_k = \sigma_k \sigma_i \quad (k \neq i \pm 1)$$

这就是一个群论群论的例子. 设
 $\phi_0(\sigma_i)$ 是生成元的一个表象. $\phi_0(\sigma_i) = e^{-i\theta}$
描述群论群论. ($0 \leq \theta < 2\pi$). 当 $\theta = 0$, \Rightarrow Real
情形, 当 $\theta = \pi$, \Rightarrow Fermi (三分量). $\theta = \pi/2$.
或 $\pi/4$.

(4c)

$$\begin{aligned} \vec{r}_i \vec{r}_{i+1} &\rightarrow \vec{r}_{i+1} \vec{r}_i + \vec{r}_i \vec{r}_i \\ \therefore \phi_0(\sigma_i^{\pm 1}) &= e^{\mp i\theta} = \exp \left[\mp i\frac{\theta}{\pi} \sum_j \Delta \phi_{ij} \right] \\ e^{\mp i\theta} &= \exp \left[-i\frac{\theta}{\pi} \sum_j \Delta \phi_{ij} \right] \end{aligned}$$

其中只有 $\Delta \phi_{i,i+1} = \pm \pi$, 其他 $\Delta \phi_{ij} = 0$.

推广到 n -维空间:

$$\phi_0(\omega) = \exp \left(-i \frac{\theta}{\pi} \int dt \frac{d}{dt} \sum_j \Delta \phi_{ij} \right), \quad \omega = (\vec{r}_1, \dots, \vec{r}_n).$$

\therefore 传播子 $K(r't'; rt)$

$$= \int \exp \left[i \int dt \left[L - \frac{\theta}{\pi} \frac{d}{dt} \sum_j \Delta \phi_{ij} \right] \right]$$

建立束缚状态和波函数 $\Psi(r)$ (波函数的定义)

由传播子 K 包括从 $t \rightarrow t'$ 的 braiding 项.

设 $\Psi(r, t) = \int dr K(r't; rt) \psi(r, t)$.

设 $\Psi(r, t) = \exp \left(-i \frac{\theta}{\pi} \int dt \sum_j \Delta \phi_{ij}(t) \right) \psi(r, t)$.

建立束缚状态和波函数 $\Psi(r)$ (波函数的定义)

如果 Ψ 没有 braiding 项,

$$\Psi(r') = \int dr K(r't; rt) \psi(r, t).$$

定义 $\tilde{\Psi}(r') = \exp \left\{ -i \frac{\theta}{\pi} \sum_{ij} \Delta \phi_{ij} \right\} \Psi(r')$, 因此
若无 braiding 项, 则 $\tilde{\Psi}$ 为单值, (r' 为一参数,
即 $t=0$), 否则

$$\tilde{\Psi}(r') = \int dr K(r't; rt) \tilde{\Psi}(rt)$$

K 包括从 $t \rightarrow t'$ 的 braiding 项. $\tilde{\Psi}$

若把 $\tilde{\Psi}$ 代入

$$\tilde{\Psi}(r, t) = \prod_{ij} \frac{(z_i - z_j)^{\theta/\pi}}{|z_i - z_j|^{\theta/\pi}} \tilde{\Psi}(z, t) \Psi(z, t).$$

$$= \prod_{ij} (z_i - z_j)^{\theta/\pi} f(z, t). \quad \text{其中 } f \text{ 是}$$

Ψ 的正确给出 (统计力学). 之后对称

3.6.5 一维设计：玻尔兹曼模型 (5)

在一维空间，任意两个粒子交换位置对系统相互接触，所以除自由度外，统计与相互作用相关。
 例：~~费米子~~ 基本，找的推广 Bose
 例：~~费米子~~ Fermi (3D): N particle 分布在 G 立方体上。

$W_{\text{BS}} = \frac{[G + (N-1)(1-s)]!}{N! [G - (N-1-s)!]} = W_B$

$s=0, W_0 = \frac{[G+N-1]!}{N! [G-1]!} = W_B$

$s=1, W_1 = \frac{[G+N-1]!}{N! (G-N)!} = W_F$

$0 < s < 1$, 则是玻尔兹曼 Fermi (3D) 模型。
 如图有多种分布：如果有子分布 $\{N_\alpha\}$ ，则

$N = \prod_{\alpha} N_{\alpha}! [G_{\alpha}-1 - \sum_{\beta \neq \alpha} S_{\alpha\beta} (N_{\beta} - S_{\alpha\beta})]!$

$S_{\alpha\beta} = S \delta_{\alpha\beta}, \forall s=0, s=1$

$W_0 = \prod_{\alpha} \frac{[G_{\alpha}+N_{\alpha}-1]!}{N_{\alpha}! [G_{\alpha}-1]!}, W_1 = \prod_{\alpha} \frac{G_{\alpha}}{N_{\alpha}! (G_{\alpha}-N_{\alpha})!} = W_B$

这里 $S_{\alpha\beta}$ 表示不同“坐标”指称空间的
 相互作用。
 \Rightarrow 例 1. 子相互作用波色子 ($C>0, T>0$)

$H = -\sum_{i=1}^N \frac{\partial^2}{\partial x_i^2} + 2C \sum_j \delta(x_i - x_j), C>0.$

用脚标表示 \rightarrow 量子力学的“Fourier”展开，互动空间，总能量 $E = \sum_i k_i^2$. ~~物理~~

\rightarrow 在量子论极限下， $\lambda \rightarrow k$

$\rightarrow S_{\alpha\beta} \rightarrow S(k, k') = \delta(k-k') + \frac{1}{2\pi} \theta'(k-k')$

其中 $\theta = -2\tan^{-1}(h/c)$. (Bothe Ansatz)

$\theta'(k-k') = \frac{-2c}{C + (k-k')^2}. \quad (\text{Yang-Yang})$

$\rightarrow C \rightarrow 0, \theta' \rightarrow 0, S(k, k') = \delta(k-k'). \rightarrow$ idea Fermion

$\rightarrow C \rightarrow 0, S(k, k') = -\delta(k-k'). \rightarrow$ idea Boson.

一般 C , 有 θ'/h 的修正项。

例 2: Calogero-Sutherland (Fermion) (2)

$H = -\sum_{i=1}^N \frac{\partial^2}{\partial x_i^2} + \sum_{i,j} \frac{\lambda(\lambda-1)}{x_i^2} S_{ij}^{-2} \left(\frac{\pi(x_i - x_j)}{L} \right)^2$

$\rightarrow \lambda \rightarrow 0, \theta' \rightarrow \infty \rightarrow (x_i - x_j)^2$.

$S(k, k') = \lambda \delta(k-k') = \delta(k-k') + (\lambda-1) \delta(k+k')$.

$\therefore \theta' = 2\pi(\lambda-1) \operatorname{sign}(k-k')$.

$\lambda=1 \Rightarrow \text{Fermion}, \quad \lambda=\frac{1}{2} \Rightarrow \text{semion}.$

$\lambda=2, \text{dual semion}.$

可以根据 Bothe Ansatz 写出“单粒子能级” $E(k)$ 。
 这个 $E(k)$ 一般由一个积分方程解出 (但是对 CS
 model: $E(k) = \begin{cases} (k^2 - k_F^2)/\lambda, & |k| < k_F \\ k^2 - k_F^2, & |k| > k_F \end{cases}$)

同样对于 Z_G :

$Z_G = \prod_k \left(1 + e^{-E(k)/T} \right).$

(~~物理~~)

第七章 相变、临界现象和量子群论

物理学中不同物理性质的体系都有不同的相，例如，固态、液体和气体。不同相可以相互转变，称为相变。一些特殊条件下，两种或三种可以平衡。这些参量就是相变线。于是，可以根据这些相变线，画出参量在空间的相图。根据相变量在相平行时的行为，可以判定相变。

一级相变：相变线，两相的化学势相等，但 ~~物理~~ 只有一部分做了不相等，即

$\mu^a = \mu^b = 0, \quad S^a - S^b = -\left(\frac{\partial \ln \rho}{\partial T}\right)_P + \left(\frac{\partial \ln \rho}{\partial P}\right)_T \neq 0, \dots$

二级相变： $\Delta \mu = 0, \Delta S = 0, \Delta T = 0, \dots$ 但 $\frac{\partial \ln \rho}{\partial T} = \frac{\partial \ln \rho}{\partial P}$ 不连续或发散。
 其中 $\Delta \mu, \Delta S, \Delta T$ 随时间而变化或为零。

同样可以定义二级相变。但二级相变一级只有 BEC. 三级相变 $\Delta \mu, \Delta S, \Delta T$ 都不连续或为零。
 ($T \rightarrow 0$, 有无限级相变之说)

§7.1 朗道二级相变理论简介

朗道建立描述二级相变的物理模型，引入了序参量，序参量和对称性破缺。

序参量是用于区分两个相的不同“物理量”，例如，在液体物质中，有吸引相和排斥相，在高温时，~~每个~~电子的邻居取向互无固定随机的，作为其平均值的物理量，序参量设为 $M=0$ 。随着温度降低，由于电子之间的作用，邻居的取向中的一部分能整齐划一，平均来说 $M \neq 0$ 。 $M=0$ 时 $M \neq 0$ 时是临界温度 T_c 。

$$\begin{array}{c} \nearrow \downarrow \\ \downarrow \uparrow \end{array}$$

$$\begin{array}{c} \nearrow \downarrow \\ \downarrow \uparrow \end{array}$$

对于 M 为零时液体

$$M=0$$

$$M \neq 0$$

在高温相， $M=0$ ，说明电子能取任何方向的几率都一样，~~液体~~液体

但施加转动外场时（外场的 $SU(2)$ 不变化）而在低温， $M \neq 0$ 表明电子能被强迫取向某一个方向，“转动不变性”破缺即称为“对称性破缺”。降低温度到 $M \neq 0$ 是由 A 讲的朗道理论完成的，不是

把自由能函数看成函数

朗道理论要先通过自由能函数来研究

近似序参量，通过与序参量对称的强场依赖，林纳姆图中等 $\beta = 0$ 时 $M=0$ 的例子。请看 α 的图。这里再举一个简单的例子，即所谓 GL 理论。起源于 Gibbs 自由能为序参量（对外不对称）的函数，至临界点 $g_s(\beta=0) = g_n$ 。 $g_n = f - \frac{\lambda}{2}\beta^2$ 是正源于 Gibbs free energy。展开 $g_s(\beta)$

$$g_s(\beta) = g_n + \frac{A}{2}\beta^2 + \left(\frac{B}{2}\right)\beta^4 + \dots \quad (\text{怪复数})$$

当 $T < T_c$ ， $g_s < g_n$ ， $\therefore A(T) < 0$ ，($\lambda \propto (T_c - T)$)， \therefore

$$A(T) = (T - T_c) \left(\frac{\partial A}{\partial T}\right)_{T=T_c}$$

$B(T)$ 是 β^4 的系数， $\therefore B \propto \text{const.} \cdot T^4$ 。

$$B(T) = B(T_c) = B_c.$$

在 ~~物理~~ 物理学，需求自由能极小。

$$\frac{dg_s}{d\beta} = 0, \Rightarrow A + B_c \beta^2 = 0,$$

$$\Rightarrow \beta^2 = -\frac{A}{B_c} \Rightarrow g_s = g_n - \frac{A^2}{2B_c}.$$

序参量“自发破缺”， $SU(2)$ 对称也由一个对称场引起，序参量“明显破缺”，序参量是对应的破缺的结果。这样叫“对称性”。“序参量”和“自发破缺”的例子很多：

固液相变 平移不变性 DLRO

液体-液晶 转动不变性 偏振光谱

超导-金属 磁铁磁化率恒定 [绝对温度由 χ]

玻璃-超导 $K=0$ 时服从 $\chi = \text{常数}$ ODLRO

~~液体-玻璃~~ ~~液体-玻璃~~

$$(CuZn) \quad \text{二元固溶体结构} \quad \text{滑脱孪晶时} \quad \frac{W_1 - W_2}{W_1 + W_2} \quad \frac{W_1 \Delta \varepsilon}{W_1 \Delta \mu}$$

也有一些不是二级相变，但“序参量”概念仍可用的例子：(体积突变)

气-液相变 一级相变 $P_{\text{liquid}} - P_{\text{gas}} \neq 0$

外加电场-金属相变 一级相变，(旋转电子的 $|J|$ 变化)
(电子气体模型)

理想玻色子起振 二级相变 $T=0$ 时 Ω 极化度

$$F-\text{方程}, \quad g_s - g_n = \mu_0 H_C^2(\tau)/2,$$

\therefore 在 T_c 附近

$$H_C^2(\tau) = \frac{A^2}{\mu_0 B} = \frac{(T_c - \tau)^2}{\mu_0 B_c} \left(\frac{\partial A}{\partial T}\right)_{T=T_c}^2$$

$$\Rightarrow H_C \propto T - T_c.$$

GL 理论起源于原有 Landau 里德-佩方程，假设序参量 $\psi = \psi_0$ 有空间分布，这样， g_s 也有空间分布，

$$g_s = g_n + A|\psi|^2 + \frac{B}{2}|\psi|^4 + \frac{1}{2m} \left[(-i\hbar \nabla \psi)^2 \right]$$

总自由能的自由能为

$$\left[(-i\hbar \nabla - e\vec{A})\psi \right]^2$$

$$G_s = \int d^3 r g_s(r)$$

$$\frac{\delta G_s}{\delta \psi} = 0 \Rightarrow \left\{ A\psi + B\psi^2 + \frac{1}{2m} \left[(-i\hbar \nabla - e\vec{A})\psi \right]^2 = 0 \right.$$

$$\left. \vec{n} \cdot \psi = 0 \quad (\text{单位矢}) \right.$$

GL 方程。一个简单应用 序参量相变
考虑弱场 $|\vec{A}| \ll |\vec{A}_0|$ ，则可以立 GL 方程中
忽略 A ，而 $\psi = \psi_0(\vec{r}) = \psi_0$ 很简单 定义
 $f = \frac{\psi}{\psi_0}$ ，取 $f^* = f$ ，则

$$\frac{t^2}{2m^2} \nabla^2 f + f - f^3 = 0,$$

$$\| \zeta^2(T) . \| \zeta^2 \nabla^2 f + f - f^3 = 0.$$

这是方程的解. 特殊情况:

$$f = \begin{cases} 1 & \text{Normal} \\ \zeta^2 & \end{cases}$$

$$\left\{ \begin{array}{l} \zeta^2 \frac{\partial^2 f}{\partial z^2} = -f(1-f^2) \\ f(z=0) = 0, \quad \frac{\partial f}{\partial z} \Big|_{z=0} = 0 \\ f(z=\infty) = 1 \quad \left(\frac{\partial f}{\partial z}\right)_{z=0} = 0 \end{array} \right.$$

$$\text{两边同时 } \frac{df}{dz}, \int_{-\infty}^{\infty} dz \quad \frac{d^2 f}{dz^2} = \int_{-\infty}^{\infty} dz \left(\frac{1}{4} f^4 - \frac{1}{2} f^2 \right).$$

$$\frac{1}{2} \zeta^2 \left(\frac{df}{dz} \right)^2 = \frac{1}{4} f^4 - \frac{1}{2} f^2 + \frac{1}{4} = \frac{1}{2} (1-f^2)^2.$$

$$\text{取 } \frac{df}{dz} > 0, \quad \frac{df}{dz} = \frac{1-f^2}{\sqrt{2}\zeta(T)}, \quad f = \tanh \frac{z}{\sqrt{2}\zeta(T)}.$$

至临界点附近,

$$\zeta(T) = \frac{t}{[2m^2 (T_c - T) \frac{dA}{dT_c}]^{1/2}} \rightarrow \infty, \quad T \rightarrow T_c.$$

待考由2~相变, 相变是 $\rightarrow \infty$.

(2) 临界等温线~物理量, δ . (6)

$$H = M^{\delta} \operatorname{sgn}(H), \quad (T=T_c, H \neq 0).$$

$$(p-p_c) \sim (p-p_c)^{\delta} \operatorname{sgn}(p-p_c), \quad (T \rightarrow T_c, p \neq p_c)$$

$$(H-H_c) \sim (H-H_c)^{\delta}, \quad (T=T_c). \quad \boxed{\begin{array}{c} \text{外场} \sim \text{序参量}^{\delta} \\ \downarrow \\ \text{温度} \sim T-T_c \end{array}}$$

(3) χ_0^{δ} 或 κ_T , δ .

$$\chi_0^{\delta} = \left(\frac{\partial M}{\partial H} \right)_T \Big|_{H=0}, \quad \text{susceptibility. 量级}$$

$$\left. \begin{array}{l} \xrightarrow{\text{2阶导数}} \\ \xrightarrow{\text{2阶导数}} \end{array} \right\} \chi_0^{\delta} \sim (A(T-T_c)^{-\delta}), \quad \text{无论 } (T \rightarrow T_c^+, \text{ 还是 } T \rightarrow T_c^-).$$

$$K_T = -\frac{1}{V} \left(\frac{\partial V}{\partial p} \right)_T, \quad \text{等温压缩系数}$$

$$K_T \sim (T-T_c)^{-\delta}, \quad (T \rightarrow T_c, p \neq p_c).$$

(4). 增益(耗散), α .

$$\text{增益 } C_A^{\alpha} \sim |T-T_c|^{-\alpha}, \quad \cancel{(H \neq 0)}$$

$$\text{耗散 } C_V \sim (T-T_c)^{\alpha}, \quad (T \rightarrow T_c, p=p_c).$$

(5) 关联长度 ξ

$$\text{例如对磁化率, } f \sim e^{-\xi^3}, \quad \xi \rightarrow 0.$$

§7.2 临界现象和临界指数

在上节, 我们看到在临界点, ~~物理量~~ 出现“对称性破缺”

$\zeta(T) \propto (T-T_c)^{\beta}$. 物理量在临界点出现“对称性破缺”, 依此称为临界现象, 需指出以下临界指数. 根据上节的讨论, 临界指数有 $\alpha, \beta, \gamma, \delta, \nu, \eta$.

→ 物理量从统计平均值到临界点附近按

$$\xi = \frac{T-T_c}{T_c} \text{ 展开: } f(\xi) = A \xi^{\alpha} (1+B \xi^{\beta} + \dots), \quad \xi \gg 0.$$

$$\lambda = \lim_{\xi \rightarrow 0} \frac{\ln f(\xi)}{\ln \xi} \text{ 这是临界指数.}$$

① β 等参随温度变化, 例如

$$\boxed{\begin{array}{l} \text{序参量} \sim (T-T_c)^{\beta} \\ \Delta C(M,T) \propto (T-T_c)^{\beta} \\ \Delta P^{\beta} \propto \cancel{(T-T_c)^{\beta}} \sim (T-T_c)^{\beta} \end{array}}$$

$$\text{复气液相变: } \Delta P \sim (T_c - T)^{\beta} \quad T \rightarrow T_c^-, \quad \beta = \beta_c.$$

(5) 关联长度, 临界指数 ν . (6)

对子系统~任一物理量 $A(\vec{r}, t), B(\vec{r}, t')$

统计平均值 $\langle \dots \rangle \leftrightarrow \langle \dots \rangle'$

$$\langle (A(\vec{r}, t) - \langle A \rangle)(B(\vec{r}', t') - \langle B \rangle) \rangle$$

称为 A, B 之间~关联函数, 例如对自旋系统

$$\langle (S_i - \langle S_i \rangle)(S_j - \langle S_j \rangle) \rangle \quad (\text{核壳层})$$

称为自旋-自旋关联函数.

若 $A=B$, $T=T'$,

$$G(\vec{r}) = \langle (A(\vec{r}, t) - \langle A \rangle)^2 \rangle \quad A \text{ 代表 } A(\vec{r}, t) \text{ 的关联}$$

至平均场近似下, ~~在临界点附近~~, $-A \approx 0$

$$G(\vec{r}) \sim \frac{1}{r} e^{-\xi r},$$

即 $G(\vec{r})$ 为关联函数, 到临界点附近

$$\xi \sim (T-T_c)^{-\nu}$$

$$\text{起源于 GL eq.: } \cancel{\xi \sim (T-T_c)^{-\nu}}$$

称为关联长度 $\xi \sim (T-T_c)^{-\nu}$ over estimation.

(b) 美丽指数, η (64)

② 平均场计算的美丽指数的指數
decay 率/物理量的衰减率。正确的结果是

$$\text{decay} \sim r^{-d+1} \quad \text{或} \quad G(r) \sim r^{-d+1} \quad \text{或} \quad G(k) \propto \int dr G(r) e^{ikr}$$

附近的行为

$$G(k) \sim k^{-2+\eta} \quad \text{或} \quad G(k) \propto \int dr G(r) e^{ikr}$$

这些临界指数都在实验上可测得，但由于临界附近的时间很长，往往要达到平衡所需时间很长（临界慢化），因此很困难（见书 p480）。但分析这些结果发现，不同指数之间存在一定的关系，称为标度律

$$\begin{aligned} & \alpha + 2\beta + \gamma = 2 \\ & \gamma = \beta(1-\eta) \\ & \gamma = \eta(2-\eta) \\ & \eta = 2 - \alpha \end{aligned} \quad \left| \begin{array}{l} \text{6个临界指数} \\ \text{4个约束} \\ \text{2个独立} \end{array} \right.$$

3.3 量子相变

量子相变是指 $T=0$ 时，系统不同相之间由于某一个参数的变化引起相变。对于有限系统，设 $H(g)$ 为哈密顿， g 是 coupling constant，一般来说， $E(g)$ 是光滑函数，不会发生相变。有一种情况可能： $H = H_0 + gH_1$, $[H_0, H_1] \neq 0$ 。这时， H_0 和 H_1 有共同对称角化，有 3 个特征值。
 $E_n = E_n^{(0)} + gE_n^{(1)}$.

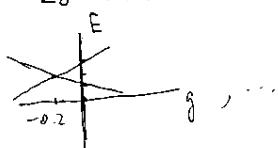
$$E_0 = E_0^{(0)} + gE_0^{(1)}, \quad E_1 = E_1^{(0)} + gE_1^{(1)} \quad \text{若} \quad g = g_c$$

$$E_0(g_c) = E_1(g_c), \quad \text{即} \quad g_c = \frac{E_1^{(0)} - E_0^{(0)}}{E_0^{(0)} - E_1^{(0)}} < 0$$

从图中：

$$E_1 = 2 + g_3$$

$$E_0 = 1 + g(-2), \quad g_c = -\frac{1}{5}$$



level crossing

一级相变

这些关系与具体系统和假设（细节无关）
有一定的普遍性。（普遍性假设）

系统临界行为分为二类决定：空间的散射和
序参量的散射。具有相似 α 和 n 的序参量 β -
一个叫普适类，具有相似 α 的临界行为。 n 不同

一个序参量可以是宏观、微观和局域。

如果在宏观， $n=1$ ，微观 $n=2$ ，局域 $n=3$ 。

$n=1$ ，气液相变中心密度差，磁铁中心磁化强度差。

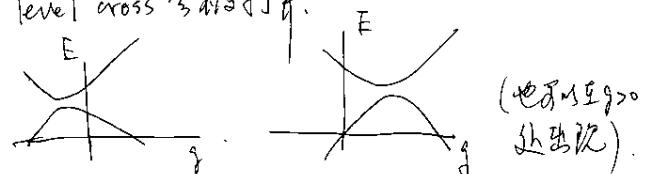
$n=2$ ，平面自旋模型（XY 模型），超流、超导中的超流速度波函数。

$n=3$ ，液体模型中的液体（液体）。

* 普遍性背后的物理原因是临界点的美丽指数
无关。这时，~~能~~ 描述子是其他特征的函数，例如，
lattice spacing, 相互作用力程及微观细节。
(晶格结构的多样性) 都不要，被普遍的参数
合作所用被摒弃。

在大多数情况下， $[H_0, H_1]$ 可以忽略，这种

level crossing 会自动打开。



在 infinite lattice 系统，有可能出现两种情况，
(i) 简单的 level crossing。这时打开 Δ 无限接近于零。
这就是量子相变。在相变前，correlation function
会有固定性。④

由此我们看到，量子相变发生无限隙 $\Delta \rightarrow 0$ 或是
在 Δ 附近发生 gapless。即

$$\Delta \sim \Gamma |g - g_c|^{\nu} \quad (\text{非线性})$$

Γ 是 non-universal，只取决于系统参数。

($g \rightarrow g_c^{\infty}$ 时不成立)

类似的，对于宏观 correlation length ζ

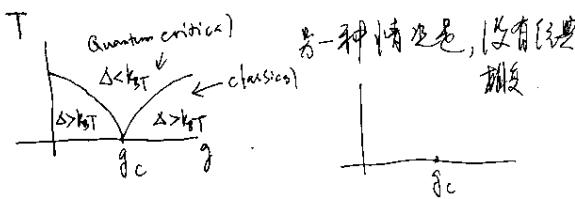
$$\zeta \sim \Gamma |g - g_c|^{\nu}$$

$$\zeta \sim \Gamma^{-2}$$

有限温度，分为两种情况，

① $k_B T > \Delta$ ，这时，量子效应要比经典效应强。
即为 Buerantum critica.

② $k_B T < \Delta$ ，这时，量子效应比经典效应弱。
即为 Dominant. 这时，会发生经典相变。



§7.4 Ising model.

为了对相变、临界现象做更直观的观察，我们讨论 Ising model.

$$H = -J \sum_{\langle i,j \rangle} S_i^z S_j^z - \frac{B}{k_B T} \sum_i S_i^z$$

$$S_i^z = \pm \frac{1}{2} (\hbar) \text{ or } S_i^z \rightarrow \sigma_i = \pm 1.$$

由题，

$$F = -k_B T \ln Z$$

$$= -N k_B T \left[\ln 2 + \ln \cosh \left(\frac{B}{k_B T} + \frac{2J}{k_B T} \bar{\sigma} \right) \right]$$

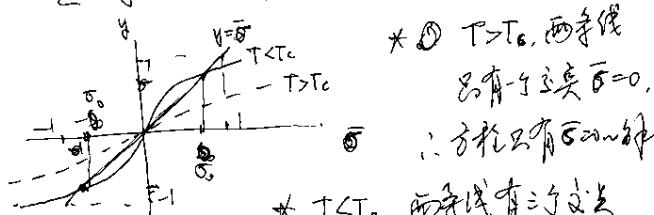
$$\therefore U = N \frac{\partial F}{\partial T} = -\frac{\partial E}{\partial T} = N \tanh \left(\frac{B}{k_B T} + \frac{2J}{k_B T} \bar{\sigma} \right)$$

$$\Rightarrow \bar{\sigma} = \tanh \left(\frac{B}{k_B T} + \frac{2J}{k_B T} \bar{\sigma} \right)$$

自然解。

$$\text{取 } B=0, \bar{\sigma} = \tanh \left(\frac{2J}{k_B T} \bar{\sigma} \right) = \tanh \left(\frac{T_c}{T} \bar{\sigma} \right).$$

$$\text{令 } y = \tanh \left(\frac{T_c}{T} \bar{\sigma} \right), y = \bar{\sigma}$$



即 $T > T_c$ 为无序相 $\bar{\sigma} = \{ \pm \} \Rightarrow \pm$
 $T < T_c$ 为有序相 $\bar{\sigma} = \pm$ \uparrow 对称性
 $\therefore \ln \cosh x \geq 0$ 且 $x=0$ 时为 0 $\therefore \bar{\sigma} = 0$ $\cancel{\text{自发磁矩}}$

§7.4.1 平均场近似。

首先让我看看平均场近似。

$$H = - \sum_i \sigma_i \left(B + J \sum_s \sigma_{is} \right)$$

$$= - \sum_i \sigma_i (B + h_i).$$

② $\langle \sigma_i \rangle$ 代入得 σ_{is} , 且因为 $\sum_s \sigma_{is} = \frac{N}{2} \bar{\sigma} = \frac{N}{2} \bar{\sigma}$.

$$(H)_M = - \sum_i (B + h_i) \sigma_i \quad h = \frac{N}{2} J \bar{\sigma}.$$

$$\text{这样, } Z_N = \sum_{\sigma_1} \cdots \sum_{\sigma_N} \exp \left[\beta \left(B + h_i \right) \sigma_i \right].$$

~~$$= \sum_{\sigma_1, \dots, \sigma_N} \prod_{i=1}^N \exp \left(B + h_i \right) \sigma_i$$~~

~~$$= \sum_{\sigma_1, \dots, \sigma_N} \prod_{i=1}^N \exp \left(B + h_i \right) \sigma_i \cdots \sum$$~~

$$= \sum_{\sigma_1} \exp \beta (B + h_1) \sigma_1 \sum_{\sigma_2} \exp \beta (B + h_2) \sigma_2 \cdots$$

$$= \prod_{i=1}^N \left(\sum_{\sigma_i} \exp \beta (B + h_i) \sigma_i \right)$$

$$= \prod_{i=1}^N \left(\exp \beta (B + h_i) + \exp -\beta (B + h_i) \right)$$

$$= \left[2 \cosh \left(B + h_i \right) / k_B T \right]^N$$

显然, $H(\sigma_i) = H(\bar{\sigma}_i)$, 有反对称性,

这说明 σ_i (含正或负) \Rightarrow 相互抵消.

~~所以 $\bar{\sigma}_i$ 是 σ_i 的平均值.~~

③ $\bar{\sigma}_i$

注意 $\bar{\sigma}_i$ 是 T 的函数, 在 $T \sim T_c$ 时, $\bar{\sigma}_i \approx 0$.

$$\therefore \tanh \frac{B}{k_B T} \approx \frac{T_c}{T} - \frac{1}{3} \left(\frac{T_c}{T} \right)^3 = \bar{\sigma}$$

$$\Rightarrow \frac{T_c}{T} - \frac{1}{3} \left(\frac{T_c}{T} \right)^3 \bar{\sigma}^2 = 1, \quad \bar{\sigma} = \sqrt{\frac{3T_c^2}{T_c^3 - T^2}} \left(\frac{T_c}{T} - 1 \right)$$

$$\bar{\sigma} = \sqrt{3} \left(\frac{T_c}{T} - 1 \right)^{\frac{1}{2}} = \sqrt{3} \left(1 - \frac{T}{T_c} \right)^{\frac{1}{2}}$$

$$\Rightarrow M \sim (T_c - T)^{\frac{1}{2}}.$$

$$\text{取 } F, \text{ 由方程组 } C_B = \begin{cases} 0, & T \rightarrow T_c \\ 3Nk_B T_c, & T \rightarrow T_c^- \end{cases}$$

$$\text{可得: } M \sim (T - T_c)^{-\frac{1}{2}} B,$$

$$X = \frac{\partial M}{\partial B} \sim (T - T_c)^{-\frac{1}{2}}, \quad \left| \begin{array}{l} \text{1st} \\ \text{d} \end{array} \right.$$

$$M(T_c, B) \sim B^{\frac{1}{2}},$$

$$\Rightarrow \text{互易场} f, \quad \beta = \frac{1}{2}, \alpha = 0, \gamma = 1, \delta = 3. \quad T_c = \frac{\sqrt{3}}{f_B} = \text{finite}.$$

§7.4.2 一维伊辛模型的精确解.

(甲) 适合吗? 用经典统计物理)

$$\textcircled{2} H = -J \sum_n \sigma_n \sigma_{n+1} - h \sum_n \sigma_n \quad (\sigma_i = \underline{\sigma_{N+i}}) \quad \text{PBC}$$

$$\Sigma = \sum_{\sigma_1, \dots, \sigma_N} \frac{\exp \left\{ K \sum_n \sigma_n \sigma_{n+1} \right\}}{Z_{kT}} \exp \left\{ B \sum_n \sigma_n \right\} \quad \text{NKT}$$

$$= \prod_{\sigma_1, \dots, \sigma_N} \exp \left\{ B \sigma_1 \sigma_2 \dots \sigma_N \right\} \exp \left\{ K \sigma_1 \sigma_2 \dots \right. \\ \left. \exp \left\{ B \sigma_2 \sigma_3 \dots \sigma_N \right\} \exp \left\{ K \sigma_2 \sigma_3 \dots \right\} \dots \right. \\ \left. \dots \exp \left\{ B \sigma_N \sigma_1 \dots \sigma_{N-1} \right\} \exp \left\{ K \sigma_N \sigma_1 \dots \right\} \right.$$

$$\text{定2 } (V_1)_{\sigma_i \sigma_j} = \exp (K \sigma_i \sigma_j) \quad (\sigma_i = \pm) \\ (V_2)_{\sigma_i \sigma_j} = \exp (B \sigma_i) \delta_{\sigma_i \sigma_j} \quad (\sigma_j = \pm) \\ \text{且 } Z = \prod_{\sigma_1, \dots, \sigma_N} (V_1)_{\sigma_1 \sigma_2} (V_1)_{\sigma_2 \sigma_3} \dots (V_1)_{\sigma_N \sigma_1} (V_2)_{\sigma_1 \sigma_2} \dots$$

$$V_1 = \begin{pmatrix} \exp k & \exp (-k) \\ \exp (k) & \exp (-k) \end{pmatrix}, V_2 = \begin{pmatrix} \exp B & 0 \\ 0 & \exp (-B) \end{pmatrix}.$$

$$\Sigma = \prod_{\sigma_1, \dots, \sigma_N} (V_2)_{\sigma_1 \sigma_2} (V_1)_{\sigma_2 \sigma_3} \dots (V_2)_{\sigma_N \sigma_1} (V_1)_{\sigma_1 \sigma_2} \\ = \text{Tr} (V_2 V_1 \dots V_2 V_1) = \text{Tr} (V_2 V_1)^N \quad \boxed{\text{PBC}} \\ = \text{Tr} (V_2^k V_1 V_1^k)^N = \text{Tr} (V^N).$$

§7.4.3 二维伊辛模型.

(10)

二维 Ising model 在 PBC, $h=0$ 时可求解.
对简单格子, 可以用经典统计物理方法求解. 办法是先解一维链, 然后再看耦合. 当 $h=0$, 一维的
经典解是

$$V = \exp(k) I + \exp(-k) \sigma_x$$

$$= \exp k (I + \exp(-2k) \sigma_x)$$

定2常数 α : $\tanh \alpha = \exp(-2k)$.

$$\text{且 } \exp(\alpha \sigma_x) = I \cosh \alpha + \sigma_x \sinh \alpha$$

现只要把 V 写成一个单 spin 形式.

$$\Delta V = A \exp(\alpha \sigma_x).$$

$$= A \cosh \alpha (I + \tanh \alpha \sigma_x)$$

$$= A \cosh \alpha (I + \exp(-2k) \sigma_x)$$

$$\Rightarrow A \cosh \alpha = e^k \quad \text{且 } = \frac{1}{\sqrt{\tanh \alpha}}$$

$$A = \frac{1}{\cosh \alpha \sqrt{\tanh \alpha}} = \frac{1}{\sqrt{\cosh \alpha \sinh \alpha}} = \sqrt{\frac{2}{2 \cosh \alpha}} \\ = \sqrt{\frac{2}{\sinh 2\alpha}}$$

$$\text{其中 } V = \begin{pmatrix} \exp(k+b) & \exp(-k) \\ \exp(-k) & \exp(k+b) \end{pmatrix}. \quad (11)$$

$$\det(V - \lambda) = 0 \Rightarrow \lambda_{\pm} = e^k \cosh B \pm \sqrt{e^{2k} \sinh^2 B + e^{2k}}$$

$$\therefore \text{Tr } V^N = \text{Tr} \left[\left(\frac{\lambda_+}{\lambda_-} \right)^N \right] = \lambda_+^N + \lambda_-^N$$

$$= \lambda_+^N (1 + \left(\frac{\lambda_-}{\lambda_+} \right)^N) \xrightarrow{N \rightarrow \infty} \lambda_+^N$$

$$\therefore f = F/N = -\frac{1}{N} \ln \Sigma = -\beta^{-1} \ln \lambda_+ \\ (\text{free energy per spin})$$

$$M \propto -\frac{\partial f}{\partial h} = \beta^{-1} \frac{\partial \ln \lambda_+}{\partial B} = \frac{\partial \ln \lambda_+}{\partial B}$$

$$= \sinh B (\sinh^2 B + e^{-2k})^{\frac{1}{2}} \\ \xrightarrow{T \rightarrow 0} 0. \quad \therefore \text{在有限温度下没有相变.}$$

$$\left(\text{而在场下, } T_c = \frac{2J}{k_B} \neq 0. \quad \therefore \text{有相变.} \right)$$

$$\text{当 } T \rightarrow 0, M \xrightarrow{\sinh B \rightarrow 0} 1. \quad \text{是有序.}$$

$\therefore T_c = 0$. 这时, 没有通常的 critical exponents
in 定2, 只 Pathria 在相变附近.

定2 § 24.2.1

$$\Sigma = \sum_{\{\sigma_{m,n}\}} e^{K_1 \sum_{m,n} \sigma_{m,n}^3 \sigma_{m+1,n}^3 + K_2 \sum_{m,n} \sigma_{m,n}^3 \sigma_{m+1,n}^3}$$

$$\text{第一部式子 } \prod_j V_1(j, m), \quad \text{第二部式子 } V_2(m)$$

$$= V(m) = (\sinh 2k_1)^{\frac{M}{2}} \exp(K_1 \sum_j \sigma_{j,x}^{(m)})$$

$$= \frac{1}{2} \sum_{j,y} \exp \left(\sum_{m,j} \sigma_{m,j}^3 \sigma_{m+1,j}^3 \right) = V_2(m) \quad \left(\frac{2M \times 2M}{2} \right)$$

$$\text{这样 } \Sigma = \text{Tr} (V_2^k V_1 V_2^k)^M = \text{Tr } V^M.$$

V_1 和 V_2 都是 $2M \times 2M$ 矩阵. ~~且 V_1 和 V_2 是对称的.~~

V 为反对称.

$$C_j = \exp \left(\pi i \sum_{l=1}^{2M} \sigma_{j+l} \sigma_{j-l} \right) \cdot \sigma_j^-$$

$$C_j^+ = \exp \left(\pi i \sum_{l=1}^{2M} \sigma_{j+l} \sigma_{j-l} \right) \cdot \sigma_j^+$$

$$\sigma_{j,\pm} = (\sigma_{j,x} + i \sigma_{j,y}) / \sqrt{2}$$

$$\{ C_j^+, C_j^-\} = \delta_{jj}, \quad \text{且 } C_j^+ C_j^- = 1.$$

$$\text{Jordan-Wigner } \frac{1}{2} \sigma_z. \quad C^+ C = \sigma_0 + \sigma_-$$

$$\text{例題: } \hat{\sigma}_{j,+} = \left[\exp\left(\beta h \sum_{k=1}^{j-1} C_k^+ C_k^- \right) \right] C_j^+ \\ \hat{\sigma}_{j,-} = \left[\quad \quad \quad \right] C_j^-.$$

~~由上式得~~ $(\sigma_x, \sigma_y, \sigma_z) \rightarrow (\bar{\sigma}_x, \bar{\sigma}_y, \bar{\sigma}_z)$
 由 Pauli matrix 与 \hat{C}_j 的关系 $\hat{C}_j = \frac{1}{2}(\sigma_x i + \sigma_y j + \sigma_z k)$
 $\therefore \bar{\sigma}_x, \bar{\sigma}_y, \bar{\sigma}_z$ 中的 $\sigma_x, \sigma_y, \sigma_z$ 为 \hat{C}_j 的线性组合。 $\bar{\sigma}_x \bar{\sigma}_y = \bar{\sigma}_z$

$$\text{这样, } V_1 = (\sinh 2k)^M \exp\left[-2k \sum_j (\bar{\sigma}_j + \bar{\sigma}_{j-\frac{1}{2}})\right] \\ = (\sinh 2k)^M \exp\left[-2k \sum_j (C_j^+ C_j^- + \frac{1}{2})\right]$$

$$\text{至 } V_2, \bar{\sigma}_j \rightarrow \sigma_x, \bar{\sigma}_j = \sigma_x \sigma_j - \sigma_j \sigma_x, \text{ 得 } \bar{\sigma}_j = \sigma_x \sigma_j. \\ V_2 = \exp\left\{ k_2 \sum_{j=1}^M (C_j^+ C_j^-) (C_{j+1}^+ + C_{j+1}^-) \right. \\ \left. - (-1)^j (C_{j+1}^+ C_j^-) (C_{j+1}^+ + C_j^-) \right\} \\ \hat{n} = \sum_{j=1}^M C_j^+ C_j^-.$$

V_1, V_2 是 $-1+1$ 体系的自由能和泛函. 两者
 一样化。

§7.4.4 $-1+1$ 体系的 Ising model. (1)

$-1+1$ 体系 (时间+空间) 为 Ising model 又称
 横场 Ising model.

$$H = -k \sum_n \sigma_n^x \sigma_{n+1}^x - h \sum_n \sigma_n^x. \\ \text{由 } [\sigma_n^x, \sigma_m^x] = 0, \therefore \text{对易, 由 } h \cdot \vec{\sigma} = h \sigma^x, \\ \text{至 } x \text{ 方向, 量子数, 2 重简并场.}$$

为证明 $-1+1$ 体系的 Ising model 与 2 重简并
 Ising model 相同, 需证明 $-1+1$ 体系的 $-1+1$ 体系
 spin 模型与 1 重简并 Ising 模型等价。

$$Z_{1D} \leftrightarrow \text{Tr } e^{-H_0/kT},$$

$$\downarrow \quad H_0 = -h_x \sigma_x, \quad \cancel{\text{由 } \sigma_x^2 = 1}$$

$$\begin{aligned} M \text{ site} & \quad h_x = e^{-2kT}, \quad (k_T \gg 1) \\ \text{lattice} & \quad \cancel{h_x^2 = 1}, \quad h_x^2/M = e^{-2kT} \end{aligned}$$

前面我们已证明了 \exists ~~两个~~ 3 重简并 $-1+1$ Ising model

$$\begin{aligned} \cancel{Z_1} &= \text{Tr } V^M \\ &= \text{Tr } \cancel{k_T} e^{k_T (H + h_x \sigma_x)} \end{aligned}$$

结果是

$$\frac{E}{N} = -\beta \left[\ln(2 \sinh 2k_T) + \frac{1}{4\pi} \int_{-T}^T E_q dq \right] \quad (16)$$

$$\cos E_q = \cosh 2k_T \cosh 2q - \sinh 2k_T \sinh 2q \cosh q.$$

$$\cancel{\cos E_q \propto T_c} \quad \sinh 2q = \sinh 2k_T \cancel{2q}$$

$$\therefore J_1 = T_c \text{ 时, } \frac{k_B T_c}{J} \approx 2.27.$$

$$\star \text{ 由 } C \propto \ln |1 - \frac{1}{T_c}|.$$

$$\star M(T) \propto \begin{cases} 0 & T < T_c \\ \infty & T > T_c. \end{cases}$$

$$\star g(r) \sim \begin{cases} (T_c - T)^{1/4} e^{-r/3} / (V_3)^{1/4} & T > T_c \\ (T_c - T)^{1/4} e^{-2r/3} / (V_3)^{1/2}, & T < T_c \end{cases}$$

$$\therefore \chi \sim |T|^{-1/4}.$$

MF

$$\begin{array}{ll} \alpha = 0 \text{ (discontinuity)} & \alpha = 0 \text{ (discontinuity)} \\ \beta = \frac{1}{8} & \beta = \frac{1}{2} \\ \gamma = \frac{7}{4} & \gamma = 1 \quad \delta = 3. \quad \text{一样.} \\ \eta = \frac{1}{4} & \eta = \frac{1}{2} \end{array}$$

$$V = V_1 = e^{kT} (1 + e^{-2kT} \delta x) \quad (1)$$

$$= \sqrt{\frac{M}{\beta h_x}} (1 + \frac{h_x \beta}{M} \delta x)$$

$$V^M = \left(\frac{M}{\beta h_x} \right)^{M/2} (1 + \frac{h_x \beta}{M} \delta x)^M$$

$$= \left(\frac{M}{\beta h_x} \right)^{M/2} (1 - \Delta \tau H_0)^{\beta/2}, \quad (\Delta \tau = \frac{\beta}{M})$$

$$= \left(\frac{M}{\beta h_x} \right)^{M/2} \left[(1 - \Delta \tau H_0)^{\frac{1}{\Delta \tau}} \right]^{\beta} = \left(\frac{M}{\beta h_x} \right)^{M/2} e^{-\beta H_0}.$$

$$\therefore M \rightarrow \infty, \quad \sum_{i=1}^M \cancel{\text{Tr } e^{-\beta H_0}}, \text{ up to a const.}$$

$$\cancel{\text{Tr } e^{-\beta H_0}} = \text{Tr } e^{-\beta H_0} \quad \cancel{\text{Tr } e^{-\beta H_0}}$$

~~这~~ $\cancel{\text{Tr } e^{-\beta H_0}}$ = 1D Ising model ~~(1)~~

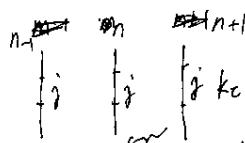
$$\cancel{\text{Tr } e^{-\beta H_0}} = \text{Tr } e^{-\beta H_0}$$

$$V = V_1 V_2 = \cancel{\text{Tr } e^{-\beta H_0}}$$

$$V = e^{kT} (1 + e^{-2kT} \delta x) \cdot e^{-kT}$$

$$= \sum_{m,n} \delta_m^{\frac{1}{2}} \delta_{m+1,n+1}^{\frac{1}{2}} \cdot \sum_{m,n} \delta_m^{\frac{1}{2}} \delta_{m+1,n+1}^{\frac{1}{2}}$$

= 1D Ising model



1D chain, ~~1D~~ - 1D Ising coupling

$$\rightarrow \text{H}(t) = \frac{M}{\beta h_x} \left(1 + \frac{h_x}{M} \sigma^x \right)$$

$$V_n(t) = \sqrt{\frac{M}{\beta h_x}} \left(1 + \frac{h_x}{M} \sigma_n^x \right)$$

$$V_n^M \sigma = \left(\frac{M}{\beta h_x} \right)^{1/2} e^{-\beta H_0(n)}, \quad H_0(n) = -h_x \sigma_n^x, \quad \frac{h_x \beta}{M} = e^{-2K}$$

链间耦合:

$$e^{K_x \sum_m \sigma_m^z \sigma_{m+1}^z} \approx e^{K_x \sum_m \sigma_m^z \sigma_{m+1}^z}$$

$$= \prod_m e^{K_x \sum_m \sigma_m^z \sigma_{m+1}^z} \approx e^{K_x \sum_n \sigma_n^z \sigma_{n+1}^z}$$

$$= e^{-K_x \sum_n \sigma_n^z \sigma_{n+1}^z}$$

$$\therefore H_{2D} = -\beta \left(-K \sum_n \sigma_n^z \sigma_{n+1}^z - h_x \sum_n \sigma_n^x \right)$$

$$Z_{2D} \Rightarrow Z = \text{Tr } e^{-\beta \left(-K \sum_n \sigma_n^z \sigma_{n+1}^z - h_x \sum_n \sigma_n^x \right)}$$

$$h_{\Delta t} = e^{-2K}, \quad K_{\Delta t} = k_x \quad (84)$$

$$\text{critical point: } \sinh 2K_x \sinh 2K_c = 1, \quad K_c \gg 1$$

$$\Rightarrow \frac{2K_x}{2h_{\Delta t}} = 1. \Rightarrow K = h. \quad \text{Quantum critical point.}$$

$K > h$, Ferromagnetic order

$K < h$, Quantum disorder.

量子态, 且 $\mu_j^z = \prod_{j \in i} \sigma_j^x$, $\mu_i^x = \sigma_i^z \sigma_{i+1}^z$,

$$\text{Tr } e^{-\beta H} = \text{Tr } e^{-\beta H'}$$

$$H' = -h \sum_i (\mu_i^z \mu_{i+1}^z - K \mu_i^x).$$

当 $h = K \alpha \beta$, self-dual. O

O I, μ^z order \Leftrightarrow μ^x disorder.

μ^x disorder \Leftrightarrow μ^z order.

\therefore critical point $\not\propto K_{ch}$.

§7.5 重叠群 RG

我们已经看到, 用平均场理论研究相变, 虽然可以得到一些直观的结果, 但在原则上往往存在各种偏差指标与实验相差甚远。精确的虽然进展有限, 但精确的物理模型很少, 且往往不能反映其实际物理学。Kadanoff首先提出了利用关联函数互相关函数发散, 子系统的物理性质已不再重合, 可以通过格致变换离散化子系统更简单, 但物理界面上不变, 从而估计临界指数。Kadanoff虽然没有建立一个完整的理论, 但用它不难改造拉格朗日方程, 使 Hamiltonian 与拉格朗日一致不容易。Wilson成功地完善了 Kadanoff 的思想, 建立重叠群理论, 该理论用 Kondo 方法, 取得非常成功(效果). 重叠群有各种不同 RG theories, 例如 JZN, 重叠群 RG, 交叉群 RG, 对称群 RG, 群论 RG, 波色 RG, DMRG, 其基本思想都是 (1) 从“粗粒化”入手变换 (2) RG 实际也是子群, 粗粒化后, 一些

(1) “平均”掉了, 不可恢复回去。∴ RG 是

1) 通过“Group”是子群), 找出 RG 变换。

(2) 通过“Group”是子群, 找出 RG 变换。

2) 通过“Group”是子群, 找出 RG 变换。

3) 通过“Group”是子群, 找出 RG 变换。

4) 通过“Group”是子群, 找出 RG 变换。

5) 通过“Group”是子群, 找出 RG 变换。

6) 通过“Group”是子群, 找出 RG 变换。

7) 通过“Group”是子群, 找出 RG 变换。

8) 通过“Group”是子群, 找出 RG 变换。

9) 通过“Group”是子群, 找出 RG 变换。

10) 通过“Group”是子群, 找出 RG 变换。

11) 通过“Group”是子群, 找出 RG 变换。

12) 通过“Group”是子群, 找出 RG 变换。

13) 通过“Group”是子群, 找出 RG 变换。

14) 通过“Group”是子群, 找出 RG 变换。

15) 通过“Group”是子群, 找出 RG 变换。

16) 通过“Group”是子群, 找出 RG 变换。

§7.5.1 Real space RG

最直观的 RG 是 RSRG. 从图中, ~~从图中~~ (Decimation)

Kadanoff block of spins. 对 1D spin model,

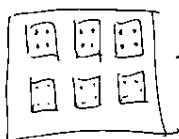
把 ℓ^d (d 是空间 dimension, ℓ 是 integer)

看成一起看作一个 spin. 例 ℓ^2 的 ~~两个~~ spin 为 1.

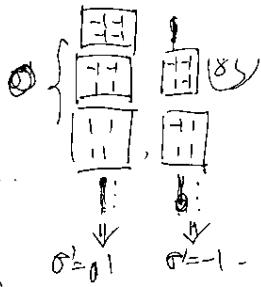
两个 spin 性质相同. 例 ℓ^2 , $\sigma \rightarrow \sigma'$ 都是 1.

原 site 的 sites, $\Rightarrow N' = \ell^{-d} N$ sites.

$$\tau' = e^{-\frac{1}{T}}$$



$$\lambda=2, d=2.$$



2D decimation (18.3.1)

$$Z = \sum_{S_i} \exp \{-\beta H_N(S_i)\}$$

求解 $N-N'$ 3 spins 艺术和掉，希望

$$Z = \sum_{S_i} \exp \{-\beta H_N(S_i)\}$$

~~例题~~ 例题，-维 Ising model. 求解并证明其解法。

如果两个子区中自由能 H / 与单格的 H 相等即

$$(S) \quad \downarrow \quad N^{\frac{1}{2}} f^{(S)}(t', h') = N \int_{t'}^{t} f^{(S)}(t, h) \quad (t = \frac{T-T_c}{T_c}),$$

~~解法~~ \Rightarrow $f^{(S)}(t', h') = t'^{-d} f^{(S)}(t, h)$.

~~解法~~ t 和 t' 都是 λ . \therefore 该方法不正确。
 $t' = \lambda^y t, h' = \lambda^y h$

y 为 y_h 的 y_t .

$$(8.4) \quad \text{解法} (8.5) \quad \text{PM 没有解} \quad (8.6)$$

$\gamma = \frac{y_h}{y_t} = y_h / (\lambda^d y_t) \quad [y = \beta(S)] \Rightarrow (9.0)$

correlation length, rescaling

$$\tilde{z}' = \lambda^{-\alpha} z.$$

而我们又希望 $\tilde{z}' \sim |t'|^{-\nu}, z' \sim |t'|^{-\nu}$.

$$t' = \left(\frac{z'}{z}\right) = \left(\frac{t}{t}\right)^{-\nu} = \lambda^{-\nu} t, \quad \nu y_t = 1, \nu = \frac{1}{y_t}.$$

$$\therefore d\nu = \frac{1}{y_t} = 2 - \alpha \quad (\bar{r} = \bar{r}_1, \bar{r}_2)$$

$$2 \quad g(r) = \langle \sigma(\vec{r}) \sigma(\vec{r}') \rangle \sim r^{-(d+2-\eta)}$$

$$g(r) = \langle \sigma(\vec{r}) \sigma(\vec{r}') \rangle \sim r^{-(d+2-\eta)}$$

$$\therefore \sigma(\vec{r}) = \lambda^{(d+2-\eta)/2} \sigma(\vec{r}')$$

\therefore scaling relation: $[Y = (2-\eta)/2]$

$$\eta = d + 2 - 2y_h.$$

$$\sigma(\vec{r}') = \lambda^{y_h} \sigma(\vec{r}')$$

即 σ' 为 h -样 rescaling.

\Leftrightarrow σ 为 h -样. ✓

根据 scaling 假设, f 为:
不成立, $\therefore f$ 为?

$$\frac{h'}{|t'|^{y_h/y_t}} = \frac{h}{|t|^{y_h/y_t}} =$$

(3) 时, 为 3 维 $\lambda^d \sim t^{-d}$, $\therefore f^{(3)}(t', h') = f(t', h')$

$$f^{(3)}(t', h') = |t'|^{y_h/y_t} f(h'/|t'|^{\alpha})$$

$$\Rightarrow (8.5) \quad f^{(3)}(t', h') = |t'|^{y_h/y_t} \tilde{f}(h'/|t'|^{\alpha}).$$

$$f^{(3)}(t, h) = \lambda^{-d} |t'|^{y_h/y_t} \tilde{f}(h/|t|^{\alpha})$$

$$= \lambda^{-d} |\lambda^y t|^{y_h/y_t} \tilde{f}(h/|t|^{\alpha})$$

$$= |t|^{y_h/y_t} \tilde{f}(h/|t|^{\alpha}).$$

如果这样都可行, 则 λ^y 为常数附近

$$C_h = \frac{\partial^2 f^{(3)}}{\partial t^2} \sim |t|^{-(2-y_h/y_t)} \Rightarrow \alpha = 2 - \frac{d}{y_t}$$

$$M = \frac{\partial f^{(3)}}{\partial h} = |t|^{y_h/y_t} |t|^{\alpha} \frac{d}{d(h/|t|^{\alpha})} \tilde{f}(h/|t|^{\alpha})$$

$$\sim |t|^{y_h/y_t - \alpha} \Rightarrow \beta = \frac{(d-y_h)}{y_t} = 2 - \alpha - \alpha$$

$$\frac{\partial M}{\partial h} = \frac{\partial^2 f^{(3)}}{\partial h^2} = |t|^{\frac{d}{y_t}} |t|^{-2\alpha} \frac{d^2}{d(h/|t|^{\alpha})^2} \tilde{f}(h/|t|^{\alpha})$$

$$\gamma = \frac{d-y_h-d}{y_t} = -2(2-2\alpha).$$

§ 2.5.2 简介: 1维 Ising model
其解法, 1维 Ising model. ✓

$$Z = \sum_{S_i} \exp \left\{ \sum_{i=1}^N \left(K_0 + K \sigma_i \sigma_{i+1} + \frac{B}{2} (\sigma_i + \sigma_{i+1}) \right) \right\},$$

($K_0 = 0, K = \beta J, B = \beta \phi h$) $\forall N = \text{even}$.

$\exp(-k)$

$$= \prod_{i=1}^{\frac{N}{2}} \exp \left[K_0 + K \sigma_i \sigma_{i+1} + \frac{1}{2} B (\sigma_i + \sigma_{i+1}) \right]$$

$$= \prod_{j=1}^{\frac{N}{2}} \exp \left\{ 2K_0 + K (\sigma_{j-1} \sigma_j + \sigma_j \sigma_{j+1}) + \frac{1}{2} B (\sigma_{j-1} + 2\sigma_j + \sigma_{j+1}) \right\}$$

$\therefore \sigma_j = \pm$ 取决

$$= \prod_{j=1}^{\frac{N}{2}} \left[\exp \left\{ 2K_0 + K_0 (\sigma_{j-1} + \sigma_{j+1}) + \frac{1}{2} B (\sigma_{j-1} + \sigma_{j+1} + 2) \right\} \right.$$

$$\left. + \exp \left\{ 2K_0 + K_0 (\sigma_{j-1} + \sigma_{j+1}) + \frac{1}{2} B (\sigma_{j-1} + \sigma_{j+1} - 2) \right\} \right]$$

$$= \prod_{j=1}^{\frac{N}{2}} \exp [2K_0 + \frac{1}{2} B (\sigma_{j-1} + \sigma_{j+1})]$$

$$2 \cosh (K_0 (\sigma_{j-1} + \sigma_{j+1}) + B).$$

$$\therefore \Sigma_N(K, B) = e^{N' K'_0} \otimes \Sigma_{N'}(K', B'). \quad \text{④}$$

Fix the form.

$$K' = \frac{1}{2} \ln [\cosh(2K+B) \cosh(2K-B)] - \frac{1}{2} \ln \tanh B.$$

$$B' = B + \frac{1}{2} \ln [\cosh(2K+B) / \cosh(2K-B)]$$

~~Fixed points~~: RG eqs.

$$\Rightarrow R(K) = K', \quad R(B) = B'.$$

Fixed points:

$$R(K^*) = K^*, \quad R(B^*) = B^*.$$

若 $K=0$, 对任何 B , fixed point 为 \exists . 但若无 fixed point, 则 trivial.

另一个 fixed point 是 $K=\infty$, $\Rightarrow B=0$.

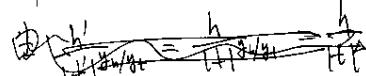
还记得说, 若 $K=0$, 那么 $T \rightarrow \infty$.

第三个 fixed point?

$$K'_0 = \frac{1}{2} \ln \cosh 2K \approx \frac{1}{2} \ln(e^{2K}/2) = K - \frac{1}{2} \ln 2.$$

$B' \approx B + \frac{1}{2} \ln e^{2B} = 2B$. (由于 $K^*=\infty$, 且 $B^*=0$)
这时, 另设 $t = \exp(-\beta K)$, ($\beta > 0$),
 $\Rightarrow t^* = 0$.

$$\text{即 } t^* = 2^{p/2}.$$



$$\therefore \lambda = 2, \quad y_t = p/2. \quad B' = 2B \Rightarrow y_h = 1.$$

$$\Rightarrow \lambda = 2 - 2/p, \quad p \approx 0, \quad \gamma = 2/p, \quad \delta = p, \quad \eta = 1.$$

So Pathria & de Gennes (§13.2)

一般 Ising model 在一个非常特别的情况下
no RG 演化可由固定点描述. (这和 RG 方程得出, 两个有 n 个 coupling constants)
于是, 作 decimation: $N' = l^{-d} N$, $\beta' = l^{-1} \beta$
重叠化解方程

$$\bar{K}' = R_e(K). \quad (K^* = \bar{K}).$$

$$K^{(n)} = R_e(\bar{K}^{(n-1)}) = \dots = R_e^n(K^*), \quad n \rightarrow \dots$$

$$\text{correlation length } \bar{\zeta}^{(n)} = l^{-n} \zeta^{(0)}$$

Singular free energy singular part of free energy / per site

$$f_s^{(0)} = \ell^{-d} f_s^{(0)}, \quad s - \text{singular}$$

$$\sigma_{2j+1, 1, 3, \dots} \rightarrow \bar{\sigma}_j: 1, 2, 3, \dots \quad \text{⑤}$$

$$\Sigma = \sum_{\sigma_j} \prod_{j=1}^N \exp(2k_0)^2 \cosh \left(K(\sigma_j + \sigma_{j+1}) + B \right) \exp \left[\frac{1}{2} B (\sigma_j + \sigma_{j+1}) \right].$$

如果要找 ~~2~~ 2D Ising model, 那

$$\Sigma = \sum_{\sigma_j} \exp \left\{ \sum_{j=1}^N \left[K_0 + K' \bar{\sigma}_j \sigma_{j+1} + \frac{1}{2} B' (\sigma_j + \sigma_{j+1}) \right] \right\}$$

还记得说: $\sigma_j = \sigma_{j+1} = 1$, $\sigma_j = \sigma_{j+1} = -1$, $\sigma_j = -\sigma_{j+1} = \pm 1$
时, ~~都~~ 都有事.

$$\exp(K_0 + K' \bar{\sigma}_j \sigma_{j+1} + \frac{1}{2} B' (\sigma_j + \sigma_{j+1})) = \exp(2K_0 + B) \cosh(2K + B).$$

$$\exp(K_0 + K' - B') = \exp(2K_0 - B) \cosh(2K - B)$$

$$\exp(K_0 - B') = \exp(2K_0) 2 \cosh B.$$

$$\text{设 } \exp(K_0) = x, \quad \exp K' = y, \quad \exp B' = z$$

$$xy = 2 \exp(2K_0 + B) \cosh(2K + B)$$

$$xz = 2 \exp(2K_0 - B) \cosh(2K - B)$$

$$xy/z = 2 \exp 2K_0 \cosh B. \quad \text{从图得}.$$

$$e^{K_0} = x = 2 e^{2K_0} [\cosh(2K + B) \cosh(2K - B) \cosh^2 B]^{1/4}$$

$$e^{K'} = y = [\cosh(2K + B) \cos(2K - B) / \cosh^2 B]^{1/4}$$

$$e^{B'} = z = [2 \cosh(2K + B) / \cosh(2K - B)]^{1/4}.$$

$$R_e(K^*) = K^* \quad \begin{cases} \text{if } K^* \neq 0 \\ \text{if } K^* = 0 \end{cases} \quad \begin{cases} \text{if } K^* \neq 0 \\ \text{if } K^* = 0 \end{cases} \quad \text{⑥}$$

fixed point. $\Rightarrow \bar{\zeta}(K^*) = l^{-1} \bar{\zeta}(K^*)$.

$\Rightarrow \bar{\zeta}(K^*) = 0$, or ∞ . 对应的 $\bar{\zeta}(K^*) = \rho$.

现在 我们看不均匀情况. 对 K^* 有

$$K = K^* + \delta K,$$

$$\Rightarrow K' = K^* + \delta K' = R_e(K^* + \delta K)$$

$$\Rightarrow K' = R_e(K^* + \delta K) - K^* = \delta K.$$

若 K 和 K' 都是 δK , R_e

$$\delta K' = \frac{dR_e}{dK'}|_{K=K^*} \delta K \equiv A_K^* \delta K.$$

A_K^* 是由 R_e 得到的 - 5 之 BPP, 设

λ_i 是极值, ϕ_i 是极值. 在一光谱, 由

$$\delta K = \sum_i u_i \phi_i$$

$$SK' = \sum_i u_i A_K^* \phi_i = \sum_i u_i \lambda_i \phi_i = \sum_i u_i' \phi_i.$$

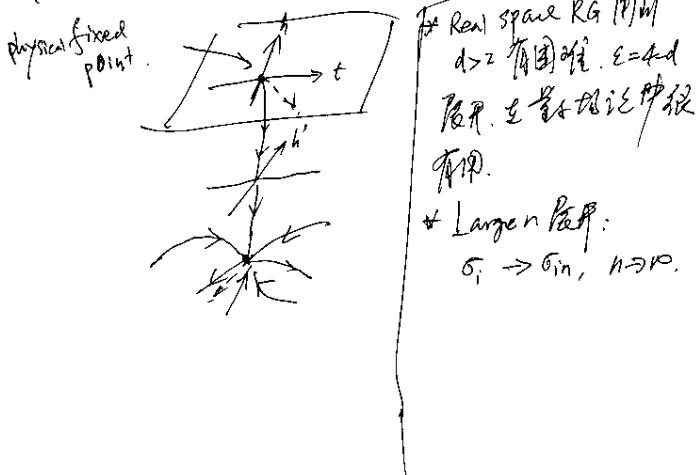
∴ 在 - 5 之 BPP 中,

$$u_i^{(n)} = \lambda_i^n u_i^{(0)},$$

(1) 若 $\lambda_i > 1$, $u_i \uparrow \text{as } n$, 越加越重要, $u_i \uparrow \dots$ (14)
 “relevant variable”. ~~相关变量~~ 带 k' 变量
 越大, 括号带离 k' . 这称为 k 为 fixed
 point.

(2). 若 $\lambda_i < 1$, u_i 是 irrelevant variable. k' 越
 小越大, 子括号带 k' , 离点不动.

(3). $\lambda_i = 1$, ~~边缘~~ marginal variable.
~~是~~ logarithmic. \Rightarrow RG 用 simple power
 law $n \rightarrow \infty$ 代替.



动量空间“Scaling”不支持. 那是错的 (14)
 长度为 $3=0$ m 不动. ($\uparrow \rightarrow \downarrow$, 等价不变)

动量空间也可以用动量空间的重正化, 但不动
 长度在“降级”, 即 \downarrow . $\uparrow \rightarrow \downarrow$, $\downarrow \rightarrow \downarrow$.
 是作做法是在 k 空间引进一个 cut off Λ , ~~把~~
~~把~~ $k > \Lambda$ 的部分去掉. 而留下 $k < \Lambda$
 部分. 这相当于在实空间中的粗粒化过程. 把 ~~粗~~
~~粗~~ 粒化程度 Λ (Λ 很大) 部分平均掉, 把其
 不同部分留下 (Λ 很小). rescaling $\Lambda \rightarrow \Lambda/b$,
 $b > 1$, ~~把~~ 在 ~~粗~~ 空间中 rescaling
 $N' = \Lambda^{-d} N$ ($\Lambda > 1$). 动量空间的重正化问题
 需要转动或连结. 把物理模型映射到 k -space
 和讨论. 用路径积分的方法来做. 通常又称为
 逆重正化群方法. ~~这是~~ 它是被广泛使用
 的. 常被用于研究强相互作用论, QFT 等.
 也是这样. 这也是数值重正化群的一种.

\Rightarrow Real space一样, 只计算 critical expts.
 也有 relevant, irr. 与 marginal.

§ 7.6 整体重整化群和 DMRG 方法 (14)

§ 7.6.1 引言

在讨论 NRG 和 DMRG 之前, 我们先 remark
 动量空间重整化群.

重整化这个概念 ~~起源于量子力学~~, ~~是~~ 由
 实际的局域场论的物理方法论 ~~在~~ 在 n 维空间
 中有“等价发散”($\uparrow \rightarrow \downarrow$). 这些发散 ~~是相~~
~~反~~ ~~对称~~ 需要重新考虑, 这就是所谓的“正规化”.
~~引入~~ 引入极限法将其去掉, 即“重整化”. 重
 整化至今在物理学中取得的非凡成功. 在此以
 后, 一般认为一个可以描述物理世界的基本
 物理都是可重整化. 具有标准模型模型
 $SU(3) \times SU(2) \times U(1)$ 的粒子论就是可重整化
 理论. 而现在四种基本相互作用中, 没有自洽
 地正规化的理论是引力理论: 量子相对论是
 不可重整化. 但即使没有作为 Λ 的选择, 通过 Λ 的
 选取可以认识清楚.

~~所有可能的理论中只有所谓重整化群~~

§ 7.6.2 Wilson's NRG. (14)

RG 的基本思想就是保留我们想研究的 fixed
 point 附近物理状态而把其它的高能态从
 物理状态“去掉”, “剥掉”. 就是说在物理而言,
 我们只关心 Λ 附近的物理性质. 把它看成 low-lying
 excitations. Wilson NRG 在此里做起来:

1. 把一个 lattice 子系统 L 有 sites 子系统拿掉,
 做精确对角化. (H_L)

2. 精确对角化 H_L 后, 取出 m 个 lowest eigenvalues
 在 eigenstates ψ_{ki} . ($i = 1, \dots, m$)

3. 做 H_L 的 transformation: $O_L^+ H_L O_L = O_L^+$

3. 定义 $O_L = (\psi_1, \dots, \psi_m)$.

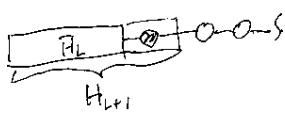
$$H_L = O_L^+ H_L O_L = \begin{pmatrix} \psi_1^+ \\ \vdots \\ \psi_m^+ \end{pmatrix} (E_1 \psi_1, \dots, E_m \psi_m) = \begin{pmatrix} E_1 & \dots & E_m \end{pmatrix}$$

$$A_L = O_L^+ A_L O_L = \begin{pmatrix} + & & \\ & \ddots & \\ & & + \end{pmatrix}$$

$$= \begin{pmatrix} \psi_1^+ A_L \psi_1 & \dots & \psi_1^+ A_L \psi_m \\ \vdots & \ddots & \vdots \\ \psi_m^+ A_L \psi_1 & \dots & \psi_m^+ A_L \psi_m \end{pmatrix} = (A_{ij})_{m \times m} \Rightarrow \bullet$$

4. 加入 g site, $\bar{H}_L \rightarrow H_{L+1}$. 这时需要
重构 L sites 与新 g site 的连接.

5. 用 H_{L+1} 代替 H_L , 重复2.



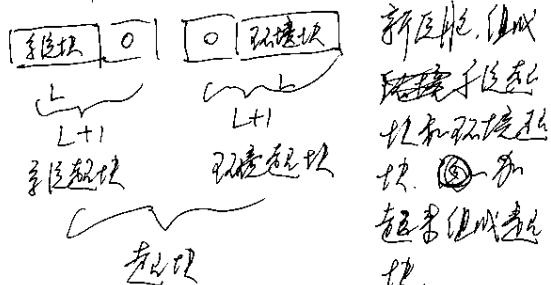
H_{L+1} 在空间上做 $L \times m \rightarrow S_m$. ~~这样~~ 由于

上一步那个 site 在空间的连接. 由 2.6.3 DMRG 算法
Wilson DMRG 中的 $\psi_i, i=1, \dots, n$ 是
 L sites 子链的基态波函数, 对于 $m-i$ sites 从
子链是断开的. 例如, 用周期边界或周期圆柱边界
计算时与之不同. ~~这样~~ 子链在空间中
边界与子链完全一样. ~~如何选择~~ 为了
与 $n-i$ sites 处理起来很方便. White 在
方法中加一些“sites”进去, 在广泛的子链中
~~这样~~ 做对角化, 再投影到没扩大的子链中.
这样, 该条件成立时~~在~~在 n -site 上, 对~~没扩大的~~
system blocks 有影响不大. ~~这样~~ 这种做法对之后之
作用子链非常有效, 及因~~该~~投影而

~~这样~~ 从 m 位移 m 位移 m - 1
m. 但对有~~相~~ 作用子链, 为 superblock
~~没~~ 投影~~①~~ 为 system blocks 位移~~位移~~:
 $|4\rangle_{Sb} \rightarrow |4\rangle^1$, 如何从中选出最合适的 $|4\rangle^1$?
这正是 DMRG 方法的核心部分.

2.6.3 DMRG 方法

我们先包简单情况. 基本的有无周期长
周期, 考虑一下子链, 为了更好的处理边界条件, 引入
上之一模一样的环境块. 对于周期和非



超周期结束可以离开边界条件.

DMRG 的计算过程如下, 首先设置一个
矩阵得由 $m \times m$. 一般为~~基态~~.

一. 首先找一个基态用起 m 个超块. 但
小于此以用精确对角化解之.

二. 精确对角化~~起始~~ 找出最低基态(一般为
基态).

三. ~~这些~~ 用 system 超块 $|i\rangle$ 和~~环境块~~ $|j\rangle$

~~基态~~ 展开是 $|4\rangle = \sum_{ij} \psi_{ij} |i\rangle |j\rangle$. 投影到
system 超块 $|i\rangle$ reduced 密级矩阵是

$$P_{ii} = \sum_j |\psi_{ij}|^2$$

$$= \sum_j \psi_{ij}^* \psi_{ij}.$$

$$\text{Tr } P = \sum_i P_{ii} = 1.$$

对角化 P , 有特征值 $\lambda_{ii} \geq 0$, $\sum \lambda_{ii} = 1$, 基态 $|4\rangle$.

四. 因第 $i=1, \dots, s$; $s < m$. 则得 s 个有
|4>. 如果 $s > m$, 则得~~该~~ $s-m$ 个.

OSG 中~~找~~ m 位移 m 位移. 用 $|4\rangle, |4\rangle^1, \dots, |4\rangle^m$ (1)

构造 $O = (O^{11}, \dots, O^{mm})$. 把 $H_{\text{sys}} \rightarrow \bar{H}_{\text{sys}} = O^T H_{\text{sys}} O$.
 $H_{\text{air}} \rightarrow \bar{H}_{\text{air}} = O^T H_{\text{air}} O$. (为了对称性的要求).

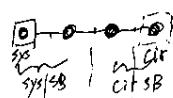
五. 用 \bar{H} 代替 H , 并~~该~~ 在 system 和 air
circumstance 之间加~~了~~ 子链. 形成~~该~~ S_m 位移 m
的环境超块. 作循环. 直到收敛~~误差~~.

例: spin 1/2 Heisenberg model

$$H = \sum_i \vec{s}_i \cdot \vec{s}_{i+1}.$$

偶数 $m=5$, ~~考虑~~ $S_{50}^z = \pm \frac{1}{2}$ 两种.

$$(1) L=4$$



$$B_L, S_L | S_R | B_R$$

且令 $\{|\frac{1}{2}\rangle, |\frac{-1}{2}\rangle\}$

$$H_{BL=1} = H_{SL=1} = H_{SR=1} = H_{BR=1} = 0$$

$$S_{B_L=1}^z = S_{S_L=1}^z = S_{SR=1}^z = S_{BR=1}^z = \left(\begin{array}{cc} \frac{1}{2} & 0 \\ 0 & -\frac{1}{2} \end{array} \right)$$

$$S_{S_L=1}^+ = S_{SR=1}^+ = S_{BR=1}^+ = \left(\begin{array}{cc} 0 & 1 \\ 0 & 0 \end{array} \right)$$

$$S_{B_L=1}^- = S_{S_L=1}^- = S_{SR=1}^- = S_{BR=1}^- = \left(\begin{array}{cc} 0 & 0 \\ 1 & 0 \end{array} \right)$$

4个格点 $S_{tot} = 0$ 的子系统 6 个基。

$$\begin{pmatrix} (\frac{1}{2}, \frac{1}{2}, -\frac{1}{2}, -\frac{1}{2}) \\ (\frac{1}{2}, -\frac{1}{2}, \frac{1}{2}, -\frac{1}{2}) \\ (\frac{1}{2}, -\frac{1}{2}, -\frac{1}{2}, \frac{1}{2}) \\ (-\frac{1}{2}, \frac{1}{2}, \frac{1}{2}, -\frac{1}{2}) \\ (-\frac{1}{2}, \frac{1}{2}, -\frac{1}{2}, \frac{1}{2}) \\ (-\frac{1}{2}, -\frac{1}{2}, \frac{1}{2}, \frac{1}{2}) \end{pmatrix}$$

$$H = \vec{S}_B \cdot \vec{S}_L + \vec{S}_L \cdot \vec{S}_R + \vec{S}_R \cdot \vec{S}_B.$$

左边的子子系统下：

$$H = \begin{pmatrix} \frac{1}{2} & \frac{1}{2} & 0 & 0 & 0 & 0 \\ \frac{1}{2} & -\frac{1}{2} & \frac{1}{2} & \frac{1}{2} & 0 & 0 \\ 0 & \frac{1}{2} & -\frac{1}{2} & -\frac{1}{2} & 0 & 0 \\ 0 & \frac{1}{2} & 0 & -\frac{1}{2} & \frac{1}{2} & 0 \\ 0 & 0 & \frac{1}{2} & \frac{1}{2} & -\frac{1}{2} & 0 \\ 0 & 0 & 0 & 0 & 0 & \frac{1}{2} \end{pmatrix}$$

~~求出~~ 求出 $\psi = (0, 149429, -0.557678, 0.408248, 0.408248, -0.557678, 0.149429)$
 $= |\psi\rangle = (|\psi_i\rangle)^+$

$$|\psi\rangle = |\psi_{\frac{1}{2}, \frac{1}{2}, -\frac{1}{2}, \frac{1}{2}, -\frac{1}{2}, -\frac{1}{2}}\rangle + \dots$$

$$= |\psi_{\frac{1}{2}, \frac{1}{2}, -\frac{1}{2}, \frac{1}{2}, -\frac{1}{2}, -\frac{1}{2}}\rangle + \dots$$

$$\Psi(i_1, i_2, i_3, i_4, i_5) = \sum_{j_1, j_2} \Psi_{i_1, i_2, j_1, j_2}^* |\psi_{j_1, j_2, i_3, i_4, i_5}\rangle$$

$$S(i_1, i_2, i_3) = \{(i_1, i_2), (i_1, -i_2), (i_2, i_3), (-i_2, -i_3)\} \text{ 为 } 4 \times 4 \text{ RDM}$$

$$\rho = \begin{pmatrix} -0.022325 & 0 & 0 & 0 \\ 0 & -0.472671 & 0.408248 & 0 \\ 0 & 0.408248 & -0.472671 & 0 \\ 0 & 0 & 0 & -0.022325 \end{pmatrix}$$

§ 7.7. K-T 相变简介 (10)

2016 年诺贝尔奖授予了三位研究拓扑相变的物理学家。

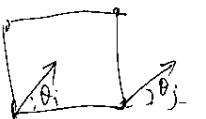
K-T 相变是通常的相变，即有序参量变化，但又不同于对称性破缺引起的相变，而是由自旋和拓扑缺陷激发引起的相变。这与我们在 ~~物理~~ 物理学中看到的相变不同，拓扑相变不是一维的，甚至拓扑相变 ~~不是~~ Thouless 在他的第一书：IQHE 中的拓扑相变 ~~不是~~ 变化。在本课程中，由于拓扑相变与统计物理的关系还不明确，我们只对 K-T 相变作一简述。

K-T 相变是从研究二维 X-Y 模型入手的。设一个 $=$ 形方格，每一边线上有一个 spin，设 x, y



$$\text{这时: } \vec{s} = (s_x, s_y).$$

$$H = -J \sum_{\langle i,j \rangle} \vec{s}_i \cdot \vec{s}_j.$$



$$= -JS^2 \sum_{\langle i,j \rangle} \cos(\theta_i - \theta_j) = -JS \sum_{\langle i,j \rangle} \cos(\theta_i - \theta_j)$$

根据 Nagaev-Mermin 定理，在低维有限尺寸

相变，但物理上这个模型的物理和低维的

对角化 P : $w = (0.022325, 0.933013, 0.022325, 0.022325)$

$$\Rightarrow u^1 = \begin{pmatrix} 1 \\ 0 \\ 0 \\ 0 \end{pmatrix}, v^2 = \begin{pmatrix} 0 \\ \frac{\sqrt{2}}{2} \\ -\frac{\sqrt{2}}{2} \\ 0 \end{pmatrix}, u^3 = \begin{pmatrix} 0 \\ \frac{\sqrt{2}}{2} \\ \frac{\sqrt{2}}{2} \\ 0 \end{pmatrix}, u^4 = \begin{pmatrix} 0 \\ 0 \\ 0 \\ 1 \end{pmatrix},$$

$S_{tot} = 0$ 全部特征。

$$O = (u^1, u^2, u^3, u^4).$$

把 ~~system~~ 转换为 ~~gauge~~ 矩阵，~~转换~~ 为 ~~向量~~ 于 ~~向量~~ 矩阵 ~~转换~~ 为 ~~向量~~ $B_L = 2$, ~~将~~ ~~从~~ system 转换 ~~到~~ ~~向量~~ 方程 $B_L = 2$: $|B_{L=2}\rangle = O(|B_{L=1}\rangle \otimes |S_L\rangle)$.

$$H_{B_{L=2}} = O(H_{B_{L=1}} + S_{B_{L=1}}^z S_{S_L}^z) O^+$$

$$S_{B_{L=2}}^z = O(I \otimes S_L^z) O^+, S_{B_{L=2}}^+ = O(I \otimes S_L^+) O^+.$$

这样得到两个全部信息: $S_L = 9$ 量子数有 8 项退级，形成 $S_{L=2}$ 和 $S_{R=2}$ ，总链长变成 36。对于 $I \otimes I + B_L = 2$ 为 $\dim = 4$, System Superblock $\dim = 4 \times 2 = 8$, 拓扑块至 $S_{tot} = 0$ 为 $\dim = 20$ 。这是 20×20 mH。

对角化，取最低能级基，输出 ψ ，输出 $O(S_{L=2}) \psi$ 为 8×8 矩阵。 $\delta > 5$. \therefore 其中最高 $m = 5$ 项 \propto $W^{1/2}$ 8 vectors. $(u^1, \dots, u^8) = O(I \otimes I \otimes I \otimes I \otimes I \otimes I \otimes I \otimes I)$ $= O(|B_{L=2} \otimes |S_L\rangle)$ 。输出 $H_{B_{L=3}}, S_{B_{L=3}}^z, S_{B_{L=3}}^+ = O(I \otimes S_L^z) O^+$

发现 $\text{Tr} e^{-\beta H} = \frac{1}{2} \pi \int_0^{2\pi} d\theta_1 d\theta_2 \dots d\theta_n$

$$Z = \text{Tr} e^{-\beta H} = \int_0^{2\pi} \dots \int_0^{2\pi} e^{-\beta H(\theta_1)}$$

$$= \int_0^{2\pi} \dots \int_0^{2\pi} \frac{d\theta_1}{2\pi} e^{-\beta H(\theta_1)}$$

$$= \int_0^{2\pi} \dots \int_0^{2\pi} \frac{d\theta_1}{2\pi} \dots \frac{d\theta_n}{2\pi} \left(1 + \beta J \cos(\theta_1 - \theta_2) + O(J^2) \right)$$

spin-spin correlation function

$$\langle \vec{s}_i \cdot \vec{s}_j \rangle = \int_0^{2\pi} \dots \int_0^{2\pi} \frac{d\theta_1}{2\pi} \dots \frac{d\theta_n}{2\pi} \left(1 + \beta J \cos(\theta_1 - \theta_2) \right) \cos(\theta_i - \theta_j)$$

$$\sim \left(\frac{J}{2}\right)^{|I|} = \exp\left[-\frac{|I|J}{2}\right],$$

$$= \exp\left(-\ln\left(\frac{2}{\beta}\right)^{|I|}\right) = \exp\left(-\frac{|I|J}{2}\right)$$

$|I|$ 是 correlation length.

另一方面，在低维极限， $(\theta_i - \theta_j)$ 是小的。 $\langle -J \vec{s}_i \cdot \vec{s}_j \rangle \sim \langle \vec{s}_i \cdot \vec{s}_j \rangle$ $\therefore \cos(\theta_i - \theta_j) = 1 - \frac{1}{2}(\theta_i - \theta_j)^2 \dots$

$$\therefore H = \frac{J}{2} \sum_{\langle i,j \rangle} (\theta_i - \theta_j)^2 \quad (1)$$

$$(\theta_i - \theta_{i+x})^2 + (\theta_i - \theta_{i+y})^2 \Rightarrow a^2 (\partial_x \theta_i)^2 + a^2 (\partial_y \theta_i)^2 = a^2 (\nabla \theta_i)^2.$$

直接求解
 $\beta H = \beta E_0 - \frac{\beta T}{2} \int d\vec{x} |\nabla \theta(\vec{x})|^2$

$$\beta E_0 = 2\beta J L^2 / a^2, \quad L \text{ is square lattice}$$

线性， a is lattice spacing

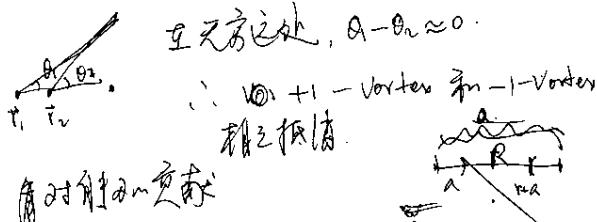
这时， $\langle \cos(\theta_i - \theta_j) \rangle = \frac{1}{2}$
 $\sim \left| \frac{\vec{r}_i - \vec{r}_j}{a} \right|$

与 exponential decay 一致，这是一次代数 decay，平方代数级数衰减。

存在一个相变点。

这个相变点对应于什么能发散到无穷大？为什么？首先，我们注意到一来，H 增起来像 θ^2 ，而 θ 不限于单值。但有 $\theta + 2\pi$ 等价， $\theta + 2\pi$ 为 θ ，是一个周期性操作。我们不能用通常的 rescale 方法去 rescale θ 。

在 zero-temperature，这种 vortex 很可能单独存在，但可能存在一对带有 charge 的 two vortices 依然有限：
~~但这个对称性， θ 变换， $\theta \rightarrow \theta + \pi$~~
 $\rightarrow \theta \rightarrow \theta + \pi$



$$\Delta U = \int_a^R r dr d\theta (\nabla \theta)^2 + \int_R^\infty r dr d\theta (\nabla \theta)^2 = 2 \ln \frac{R}{a} = 2 J \ln \frac{R}{a}.$$

R 是 vortex 位置。

是有限的。

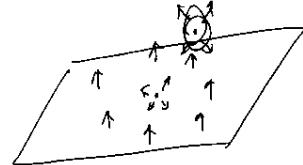
也就是说，这个相变可能进入胡乱阶段。

$$\nabla \cdot \frac{\delta H}{\delta \theta} = 0 \Rightarrow \nabla^2 \theta = 0,$$

解是：① $\theta = \text{const.}$ ② $\nabla \theta = (-\frac{1}{r}, \frac{1}{r})$.

$$\int \nabla \theta \cdot d\vec{r} = 2\pi \quad \text{一般地} \int \nabla \theta \cdot d\vec{r} = \oint d\theta = 2\pi n.$$

0 g-vortex:



$$(\nabla \theta \cdot \nabla \theta) = \left(\frac{\partial \theta}{\partial r} \right)^2 = \frac{1}{r^2}.$$

$$\therefore \text{单 g-vortex} \sim \text{常数} \quad \frac{J}{2} \int d\vec{r} (\nabla \theta)^2 = E_0$$

$$= \frac{J}{2} \int_a^L r dr d\theta \cdot \frac{1}{r^2} = J \pi \ln \left(\frac{L}{a} \right)$$

这是 log.发散。

$$E_{\text{vortex}} = \int d\vec{r} (\nabla \theta)^2 + \int d\vec{r} (\nabla \theta_r)^2 \quad (1)$$

$$\simeq \int_{\text{core}} d\vec{r} (\nabla \theta)^2 + \int_{\text{core}} d\vec{r} (\nabla \theta_r)^2 + \int_a^R r dr d\theta (\nabla \theta_r)^2 d\theta$$

$$+ \int_a^R r dr d\theta (\nabla \theta_r)^2 = 2E_{\text{core}} + 2J\pi \ln \frac{R}{a}.$$

有限级数。~~但 R 趋于无穷时 -g 会发散~~

这很容易理解，因为 XY model dual to

2 维带电度量场。charge \leftrightarrow vorticity。

K-T 相变在 critical T_c :

$$F = -\frac{\partial E}{\partial R} \approx -\frac{1}{R}$$

-g vortex 在面密度 $a^2 \theta / (2\pi)$ 。

在 L^2 面积中， $a^2 \theta / (2\pi)$ 为一个常数。

常数在 vortex 位置。

\therefore 在有限尺寸，-g vortex 在面密度 $(S = \ln(\frac{R}{a}))^2$

$$F = U - TS = (J\pi \ln \frac{L}{a} - T \ln (\frac{L}{a})^2)$$

$$= (J\pi - \frac{2}{\beta}) \ln \frac{L}{a}.$$

\therefore 当 $J\pi - \frac{2}{\beta} < 0$ 时，-g vortex 为耗散型。

发生相变。 $T_c = J\pi / 2k_B$.

~~非平衡统计物理~~

(111)

KT相变一讨论：

- ① 从低温端 \rightarrow 高温端，起流运动，即序参量有跃变。
 - ② KT相变 $F(T) = \begin{cases} \frac{1}{T} e^{-2B(T-T_K)^k}, & T \geq T_K \\ 0, & T \leq T_K \end{cases}$
- \Rightarrow 此处及台阶级函数连接。

③ \Rightarrow 宏观学相变。① \Rightarrow 一级相变。

KT相变一宏观论点：

D.J. Bishop and J.D. Reppy.

PRL 40, 1727 (1978)

起流流速 $v_s(T_K)$ - 跃变。

第八章 非平衡统计物理

§ 8.1 引言

非平衡统计物理，在我们一课程中，只讲授偏离平衡态的近平衡态。在这里耗散和涨落是一对主要矛盾。耗散包含弛豫和输运两种现象。

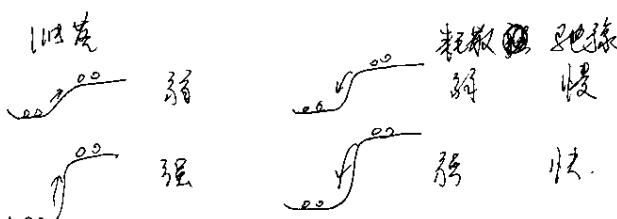
* 弛豫过程：当平衡态受到小扰动，则会偏离平衡，一旦扰动取消，系统（经过一定时间（弛豫时间）后会回到平衡。如果扰动中选取的脉冲或物场会耗散掉，则此过程叫耗散过程。

* 输运过程：适当控制外界条件，例如温差、浓度差、电位差（称为广义力或 potential），使系统维持在近平衡态，则系统内会产生持续不断，由外力或正比于“流”（热流、扩散流、电流）。这反映能流、质流和电荷的转移，称为输运过程。这类过程消耗能量或物质，所以也是耗散的过程。

* 涨落过程：涨落是系统从平衡态向非平衡态的过程，可分为二类：(i) 由物质本身（或物理状态）不连续性引起，宏观物理量围绕平衡态（或量子基态）平均值的涨落。(ii) 随机外力作用于宏观小物体导致

宏观“小物体”位置的涨落，例如布朗运动、电路中的热噪声等。

- 涨落与耗散是一对紧密联系，相辅相成的矛盾。
- (1) 二种弛豫过程：(i) 平衡态下涨落引起一个偏离会归到平衡态。(ii) 系统受外力扰动，驱动而偏离平衡态，抵抗，会回到平衡态。这两种弛豫互逆也是同样。
 - (2) 涨落越强，系统的耗散也越强。



涨落与耗散的联系由涨落-耗散定理反映。

(涨落-耗散定理表述：若有一个弛豫过程有耗散能，变化成强，则存在一个与之相关的耗散的通过程。例如：

* 弛豫耗散能 \leftrightarrow 布朗运动 (把动能转化为热能)

* 电阻和 Johnson noise (电路中的热噪声)：电阻把

电能转化成热 \leftrightarrow 电路中的热噪声转化为电能

电流。(Nyquist 定理)

* 吸吸收和辐射能：系统吸收之能 \leftrightarrow 辐射能时转化为电能吸。

非平衡统计物理的研究方法：

* 最早发展的方法是 Boltzmann 方程：单粒子分布函数的方程，即 $f(r, p, t)$ 受外力和分子之间碰撞而随时间 t 变化。用于研究耗散、弛豫和理解黑体辐射定律 (Planck)。

* 在近平衡态，Kubo 的线性响应理论成为研究输运过程提供了一个框架。Boltzmann 方程与经典力学中的守恒律相结合，线性响应理论则在经典力学中的守恒律相结合方程中体现。(用 3 维方程) 因而，后者更容易应用到量子问题。由纳维方程出发，加上因果律该定于特定的时间方向可以“证明”或“导出” Boltzmann 方程。这样可以更好的理解耗散从哪里来。纳维方程是波动部分的海森堡方程。是时间反演不变的微扰运动方程，没有耗散。耗散又来源于，对场的约束。只有纳维方程的推导是在超于平衡。

这就设定了一个固定的时间方向，破坏了时间反演不变性，造成了耗散。

* 研究非平衡统计更有效。里面的方法是用格林函数或传递矩阵，耗散的存在和相空间导致的用 Green's function 或者在时间轴下半平面叙述。

* 研究胜者问题则与系统驱动方式密切相关。从量子力学，胜者一般是一种简单的随机过程，马尔可夫过程：分布函数随时间演化成互相关分布概率分布最近邻的前一时刻的体系状态会变。分布函数随时间演化的主要方程称为主方程 (Master 方程) 中如果随机变量可以直接取值，则称为 Fokker-Planck 方程。

* 如果至胜者问题中直接研究随机运动的统计部分，则可研究全局运动的半经典方程：朗之万方程。

* 从量子观察者，Master 方程研究至 Schrödinger 理论进行，朗之万方程研究至 Heisenberg 理论进行。

* 还有平行的非平衡系理论，形为机械能非平衡统计物理研究还不够成熟，我们2.讲授。

8.2 Boltzmann 稀薄气体方程

非平衡统计需要非平衡态的分布函数。且非平衡态，分布函数 $f = f(v) = f(E)$ 与速度 v 和时间无关。例如，玻色统计 (量子统计)

$$f = \frac{1}{e^{\beta E} + 1} \quad \text{但是非平衡态, } f = f(\vec{r}, \vec{v}, t).$$

Boltzmann 方程就是研究 稀薄气体运动和碰撞的稀薄气体分布 f 。

$$(i) \text{ 经理: } \lambda_T \ll \delta r, \lambda_T = \frac{\hbar}{(2\pi mk_B)^{1/2}} - \text{一根很长}$$

即对分子可忽略。 δr 是分子平均距离。

这时在标准状况下的气体 (0°C , 1 atm) 下的气体构成。例如氢气 $n = 2.7 \times 10^{19} \text{ cm}^{-3}$,

$$\delta r \sim n^{1/3} \sim 3.3 \times 10^{-7} \text{ cm}$$

$$m \approx 6.7 \times 10^{-23} \text{ g}$$

$$\lambda_T = \frac{\hbar}{\sqrt{2\pi m k_B T}} \sim 0.17 \times 10^{-8} \text{ cm}$$

$$\therefore \frac{\delta r}{\lambda_T} \approx 0.190.$$

除了氢气外，一般的气体（密度小）都是经典。

在这一章，我们将讲解非平衡统计的全部内容。我们在这里要学习的主要内容：

- (1) Boltzmann eqs., H 定理，嫡这神义-绝对熵
- (2) 朗之万方程，胜者和扩散 DT.
- (3) 门生原理，布郎运动，Master 方程。

Langvin eq.; 布朗-耗散定理

参考书：林宗桂，苏汝铿；巨坚亮；
程稼平和吴致仁。

(ii) 稀薄和短程力: $\delta r \gg d$ (相作用)

力学)，这样，气体的大部分时间内自由运动，发生碰撞的时间短、范围小。这样，可以把“短程”和“碰撞”分开考虑。(即“运动”时无“碰撞”，“碰撞”时无“运动”。仍以氢气为例， $\delta r \sim 3.3 \times 10^{-7} \text{ cm}$ ，而相作用的半径是库仑势， $d \sim 10^{-8} \text{ cm}$ 。用这种平均自由程估计， $\lambda \sim \frac{1}{n(\delta r)} \sim 0.12 \times 10^{-3} \text{ cm}$ ， $\lambda/d \sim 10^9$ ！

(iii) 稀薄和短程地假设碰撞可以忽略。

为了写出 Boltzmann 方程，还需要进一步简化：

(i). 忽略碰撞，用刚球模型代替连续分子颗粒。

(ii). 为了减少碰撞修改，引入了碰撞速率和碰撞频率。

下面我们要导出 $f(\vec{r}, \vec{v}, t)$ 随时间变化的方程：

$f(\vec{r}, \vec{v}, t)$ 表示 t 时刻在相空间 (\vec{r}, \vec{v}) 附近体积元内的平均分子数。

$$t \rightarrow t+dt, \vec{r} + \vec{v} dt \sim \text{新位置}$$

$$[f(\vec{r}, \vec{v}, t+dt) - f(\vec{r}, \vec{v}, t)] d\vec{r} d\vec{v} = \frac{\partial f}{\partial t} d\vec{r} d\vec{v}$$

差把“运动”和“碰撞”都写了开。

$$\frac{\partial f}{\partial t} = (\frac{\partial f}{\partial t})_d + (\frac{\partial f}{\partial t})_c$$

$d = \text{drift}$, 表示作用 $2m$ 漂移。

$c = \text{collision}$.

§8.2.1 漂移项的计算

$$\cancel{\frac{\partial f}{\partial t}} = df = [f(\vec{r} + \vec{v} dt, \vec{v} + d\vec{v}, t+dt) - f(\vec{r}, \vec{v}, t)] dt = 0. \quad \begin{array}{l} \text{在“运动”中} \\ \text{分子忽略} \end{array}$$

$$\therefore \frac{\partial f}{\partial t} = (\frac{\partial f}{\partial t})_d + \sum_i \left(\vec{v}_i \cdot \frac{\partial f}{\partial \vec{v}_i} + \vec{v}_i \cdot \frac{\partial f}{\partial \vec{v}_i} \right) \Rightarrow \text{调整.}$$

$$\Rightarrow (\frac{\partial f}{\partial t})_d = - \cancel{\vec{v} \cdot \frac{\partial f}{\partial \vec{v}}} - \vec{v} \cdot \frac{\partial f}{\partial \vec{v}}$$

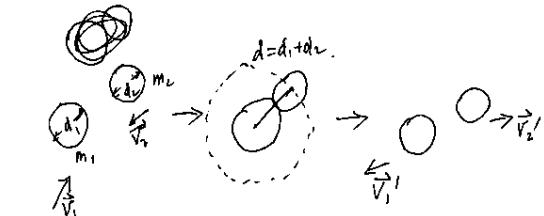
$$= \cancel{-\vec{v} \cdot \frac{\partial f}{\partial \vec{v}}} = - \frac{\partial f}{\partial \vec{v}} - \frac{\partial f}{\partial \vec{v}} (\vec{v}).$$

$\vec{v} = \vec{a} = \vec{F} / \text{单位质量的力}$

$$\therefore (\frac{\partial f}{\partial \vec{v}})_d dt d^3 \vec{r} d^3 \vec{v} = - \left(\vec{v} \cdot \frac{\partial f}{\partial \vec{v}} + \vec{F} \cdot \frac{\partial f}{\partial \vec{v}} \right) dt d^3 \vec{r} d^3 \vec{v}$$

§8.2.2 碰撞项~计算.

碰撞项~计算复杂很多。

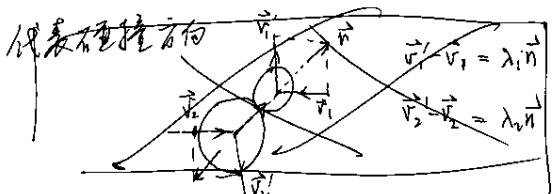


碰撞项~碰撞, 动量守恒

$$m_1 \vec{v}_1 + m_2 \vec{v}_2 = m_1 \vec{v}'_1 + m_2 \vec{v}'_2$$

$$\frac{1}{2} m_1 \vec{v}_1^2 + \frac{1}{2} m_2 \vec{v}_2^2 = \frac{1}{2} m_1 \vec{v}'_1^2 + \frac{1}{2} m_2 \vec{v}'_2^2$$

两个方程, 表示动量守恒, 另有二个任意数, 所以能

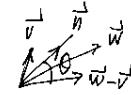
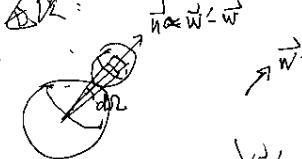


波尔兹曼方程的证明比较繁杂, 我会把证明过程讲又及应用(或见附录). (120')

现在, 我们解方程

$$(\frac{\partial f}{\partial t})_{\text{coll.}} = \int (f_v f_w' - f_v f_w) \wedge d^3 \vec{v} d^3 \vec{w}$$

泊松括号:



$$f_v = f(\vec{r}, \vec{v}, t) \quad f_w = f(\vec{r}, \vec{w}, t)$$

$$f_v' = f(\vec{r}, \vec{v}', t), \quad f_w' = \cancel{df}(\vec{r}, \vec{v}', t)$$

$$\cancel{V = V + \frac{2m_w}{m_v + m_w} [(W - V) \cdot \vec{n}] \vec{n}}$$

$$\vec{V}' = \vec{V} + \frac{2m_w}{m_v + m_w} [(\vec{W} - \vec{V}) \cdot \vec{n}] \vec{n}$$

$$\vec{W}' = \vec{W} - \frac{2m_w}{m_v + m_w} [(\vec{W} - \vec{V}) \cdot \vec{n}] \vec{n}$$

$$\vec{v}_1' - \vec{v}_1 = \lambda_1 \vec{n} \quad (121)$$

$$\vec{v}_2' - \vec{v}_2 = \lambda_2 \vec{n}$$

$\vec{n} = (0, q)$ 代表球运动方向.

(1) 在与之垂直的方向, $v_{1\perp} = v_{1\perp}'$, 表示速度不变.

(2) 没有运动.) (斜率找寻方向, 正交于运动)

上, $\vec{v}_1' - \vec{v}_1 = \vec{v}_1' \cdot \vec{n} - \vec{v}_1 \cdot \vec{n} \pm \vec{e}$ (即 m_1 与 m_2 在 n 轴的方向, 与 $m_1 \vec{v}_1' - m_1 \vec{v}_1 \propto \vec{e}$).

(3) 在 n 相反时-一个速度 $m_1 \vec{v}_1'$, 上面有的方程. (6个方程, 除速度 $= v_{1\perp}$, 有三个未知数)

(4) 与前, 动量守恒的方程合在一起, 8个方程, 有8个未知数 ($\vec{v}_1', \vec{v}_2', \lambda_1, \lambda_2$). 可解.

$$\vec{v}_1' = \vec{v}_1 + \frac{2m_w}{m_1 + m_2} [(\vec{v}_2 - \vec{v}_1) \cdot \vec{n}] \vec{n}$$

$$\vec{v}_2' = \vec{v}_2 - \frac{2m_1}{m_1 + m_2} [(\vec{v}_2 - \vec{v}_1) \cdot \vec{n}] \vec{n}$$

两式相减

$$\vec{v}_2' - \vec{v}_1' = \vec{v}_2 - \vec{v}_1 - 2 [(\vec{v}_2 - \vec{v}_1) \cdot \vec{n}] \vec{n}$$

$$\Rightarrow (\vec{v}_2' - \vec{v}_1')^2 = (\vec{v}_2 - \vec{v}_1)^2.$$

$$(\vec{v}_2'^2 = \vec{v}_2^2)$$

② 反过来, 从 $(\vec{v}_1, \vec{v}_2) \rightarrow (\vec{v}'_1, \vec{v}'_2)$ 这样
的碰撞, & $\vec{v}'_1 = \vec{v}_1 + \frac{2m_1}{m_1+m_2} [\vec{v}_1 - \vec{v}_2] \vec{n}$
 $\vec{v}'_2 = \vec{v}_2 + \frac{2m_2}{m_1+m_2} [\vec{v}_1 - \vec{v}_2] \vec{n}$

$$\vec{v}'_1 - \vec{v}_1 = \lambda_1 \vec{n} \Rightarrow \vec{v}'_1 - \vec{v}_1 = \lambda'_1 \vec{n}',$$

$$\lambda'_1 (-\vec{n}) \Rightarrow \lambda'_1 = \lambda_1 / |\vec{n}'|$$

$$\therefore \vec{v}'_1 = \vec{v}_1 + \frac{2m_1}{m_1+m_2} [(\vec{v}_2 - \vec{v}_1) \cdot (-\vec{n})] (-\vec{n})$$

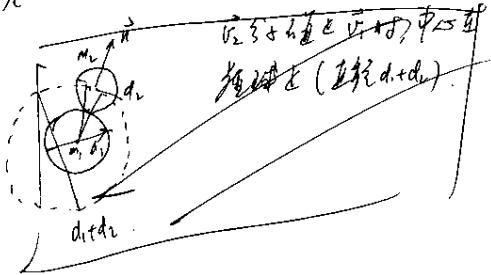
$$\vec{v}'_2 = \vec{v}_2 - \frac{2m_2}{m_1+m_2} [(\vec{v}_1 - \vec{v}_2) \cdot (-\vec{n})] (-\vec{n})$$

$$\text{由 } (\vec{v}'_2 - \vec{v}_1) \cdot \vec{n} = -(\vec{v}_2 - \vec{v}_1) \cdot \vec{n} = (\vec{v}_1 - \vec{v}_2) \cdot \vec{n}$$

与正碰撞推得.

PRF 率计算 $(\frac{\partial f}{\partial t})_c$. 记 $f_i = f(\vec{r}, \vec{v}_i, t)$,
 $f'_i(\vec{r}, \vec{v}'_i, t)$. 记 $\Delta f_i^{(+)}$ 为在 dt 时间内空间体积 d^3v_i 中
 不碰撞 (由 d^3v_i 的子集), 则撞击率为

$$(\frac{\partial f}{\partial t})_c dt d^3v_i d^3v'_i = \Delta f_i^{(+)} \Delta f_i^{(-)}$$



$\Delta f_i^{(+)}$ 为 d^3v_i 中不碰撞减少: $(\vec{v}_i, \vec{v}_i) \rightarrow (\vec{v}'_i, \vec{v}'_i)$.

对立体角积分, 即对 d^3v_i 积分, 即是碰撞 d^3v_i 中不碰撞

$$\Delta f_i^{(+)} = \left[\int f_i f'_i \Lambda_{12} d^3v_i \right] dt d^3v_i d^3v'_i.$$

同样, $(\vec{v}_1, \vec{v}_2, -\vec{n}) \rightarrow (\vec{v}'_1, \vec{v}'_2)$ 得出

$$\Delta f_i^{(+)} = \left[\int f_i f'_i \Lambda'_{12} d^3v_i d^3v'_i \right] d^3v'_i dt d^3v'_i$$

Λ'_{12} 为 Λ_{12} , d^3v_i 与 $d^3v'_i$ 一样. 只是符号要变而已.

$$d^3v'_i d^3v_i = |J| d^3v_i d^3v'_i. \quad \cancel{(J=1)}$$

$(\vec{v}_1, \vec{v}_2) \rightarrow (\vec{v}'_1, \vec{v}'_2)$ 是一个已知变换. $|J|=1$.

$$\therefore (\frac{\partial f}{\partial t})_c dt d^3v_i d^3v'_i = \Delta f_i^{(+)} - \Delta f_i^{(-)}$$

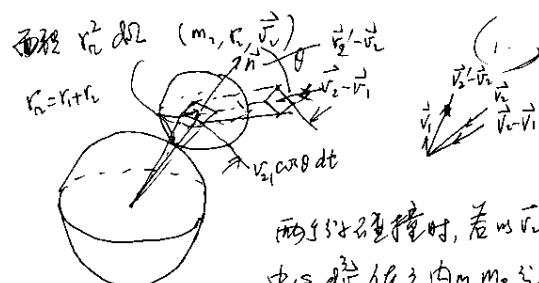
$$= \left[\int (f_i f'_i - f_i f_{i'}) \Lambda_{12} d^3v_i \right] dt d^3v_i d^3v'_i.$$

∴ Boltzmann 方程是

$$\frac{\partial f}{\partial t} - (\frac{\partial f}{\partial t})_c = (\frac{\partial f}{\partial t})_c$$

$$\frac{\partial f}{\partial t} + \vec{v} \cdot \frac{\partial f}{\partial \vec{r}} + \vec{f} \cdot \frac{\partial f}{\partial \vec{v}} = \int (f_i f'_i - f_i f_{i'}) \Lambda_{12} d^3v_i d^3v'_i.$$

$$f'_i = f_i(\vec{r}, \vec{v}'_i, t), \quad f_{i'} = f_i(\vec{r}, \vec{v}_{i'}, t).$$



而当发生碰撞时, 若 v_1 为
 中心 d^3v_i 作之由 $m_1 m_2$ 分子
 不碰撞方向看去的 \vec{n} 为该向 m_1 立体角之 $d\Omega$ 内,
 则由之碰撞 d^3v_i 为底, $d\Omega \cos \theta dt$
 为高之柱体内, 该柱体作 m_1 体积为 d^3v_i $d\Omega \cos \theta dt$
 其中包含处子 d^3v_i $d\Omega$ 中子由为

$$(f_i d^3v_i) d^3v_i d\Omega \cos \theta dt.$$

并乘以 m_1 , 以 m 为上

$$(f_i d^3v_i) (f_i d^3v_i) r_{12}^2 d\Omega \sin \theta dt$$

= dt 时内, 由 d^3v_i 由 m_1 的 $d\Omega$ 为底 d^3v_i 为高

\times 由 d^3v_i 由 m_2 的 $d\Omega$ 为底 d^3v_i 为高. ($\Delta f_i^{(+)}$)

$$\Delta f_i^{(+)} = f_i f_{i'} d^3v_i d^3v_{i'} \Lambda_{12} d\Omega dt d^3v_i$$

$$\Lambda_{12} = r_{12}^2 \sin \theta.$$

($f_i, f_{i'}$ 为相空间 m . 由 d^3v_i 为绝对值 d^3v_i)

8.3 H 定理, H 定义和熵

在很多场合, 我们用着叫熵的表达式

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

例如在信息论中叫 Shannon 熵. 其实, 这样一熵的表达式类似于 Boltzmann-H 熵:

$$H = \int f(\vec{r}, \vec{v}, t) \ln f(\vec{r}, \vec{v}, t) d^3v d^3r$$

例如, 对于平行各分子系统, $n = N/V$ 是常数,

平行各分子速度是 Maxwell 分布

$$f = n \left(\frac{m}{2\pi k_B T} \right)^{3/2} \exp \left\{ - \frac{mv^2}{2k_B T} \right\}$$

$$\Rightarrow H = \int f \left(\ln n + \frac{3}{2} \ln \frac{m}{2\pi k_B T} - \frac{mv^2}{2k_B T} \right) d^3v d^3r$$

$$\left(\int f d^3v = n, \quad \frac{1}{n} \int \frac{mv^2}{2} f d^3v = \frac{3}{2} k_B T \right)$$

$$= N \left[\ln \frac{N}{V} + \frac{3}{2} \ln \left(\frac{m}{2\pi k_B T} \right) - \frac{3}{2} \right]$$

而单粒子分子系统会大高.

$$S = N k_B \left[\ln \frac{N}{V} + \frac{3}{2} \ln T + \frac{5}{2} + \frac{3}{2} \ln \left(\frac{m}{2\pi k_B T} \right) \right]$$

$$\Rightarrow S = -k_B H + C$$

热力学的 S , $S \propto -H$, 比热容的 k_B

利用 Boltzmann 方程，可以证明

$\frac{dH}{dt} \leq 0$ ，称为 H 定理。（而且亨利王子（1923 年）通过玻耳兹曼 = 玻尔兹曼（统计物理论证明）。是 Boltzmann 方程的推论至重要。

$$\begin{aligned}\frac{dH}{dt} &= \int \left(\frac{\partial f}{\partial t} \ln f + f \frac{1}{f} \frac{\partial f}{\partial t} \right) d^3v d^3r \\ &= \int (1 + \ln f) \frac{\partial f}{\partial t} d^3v d^3r \\ \text{B. eq.} &= - \int (1 + \ln f) \left(\vec{v} \cdot \frac{\partial f}{\partial p} \right) d^3v d^3r \\ &= - \int (1 + \ln f) \left(\vec{v} \cdot \frac{\partial f}{\partial v} \right) d^3v d^3r \\ &- \int (1 + \ln f) \left(ff' - f'f' \right) d^3v d^3r / \lambda ds dr\end{aligned}$$

1. 证： $\frac{\partial}{\partial p} \cdot (\vec{v} \ln f) = \vec{v} \cdot (1 + \ln f) \frac{\partial f}{\partial p}$

而 $\int d^3r \nabla \cdot (\vec{v} \ln f) = \int \vec{v} \cdot (\vec{v} \ln f) d\Sigma = 0$

2. 证： $\frac{\partial}{\partial v} \cdot \vec{v} = 0$. ($\vec{v} = \vec{p}/m$)

$\therefore \int \frac{\partial}{\partial v} (\vec{v} \ln f) d^3v = \int \vec{v} \cdot d^3v \vec{v} \ln f$

但 $\vec{v} \rightarrow \infty$ 时 $\ln f \rightarrow \infty$, $\frac{\partial f(v)}{\partial v \rightarrow \infty} = 0$.

\Rightarrow ~~由定理~~: $n = \int f d^3v = \text{finite}$.

\therefore dynamic 量子力学 $\frac{dH}{dt} \rightarrow 0$

$\therefore \frac{dH}{dt} = - \int (1 + \ln f) (f_i f_i - f'_i f'_i) d^3v d^3r$

$\Rightarrow 1 \leftrightarrow 2$, 都是积分项. \therefore

$\frac{dH}{dt} = - \int (1 + \ln f_i) (f_i f_i - f'_i f'_i) d^3v d^3r \lambda ds dr$

$\frac{dH}{dt} = - \frac{1}{2} \int (2 + \ln(f_i f_i)) (f_i f_i - f'_i f'_i) ds \cdots$

$v'_i \leftrightarrow v_i$, $\times d(\cdots)' = d(\cdots)$

$\Rightarrow \frac{dH}{dt} = - \frac{1}{2} \int (2 + \ln(f'_i f'_i)) (f'_i f'_i - f_i f_i) ds \cdots$

$\frac{dH}{dt} =$

$\frac{dH}{dt} = - \frac{1}{4} \int [\ln(f_i f_i) - \ln(f'_i f'_i)] (f_i f_i - f'_i f'_i) ds \cdots$

≥ 0

" " 且 $f_i f_i = f'_i f'_i$ 时成立.

$\therefore \frac{dH}{dt} \leq 0 \Rightarrow \frac{ds}{dt} \geq 0$.

$f_i f_i = f'_i f'_i$ 表示平行平衡条件.

$\frac{ds}{dt} \geq 0$

* 大高流和大熵产生率 (耗散, 增生)

§ 8.4 Boltzmann 方程的应用

这里我们简单介绍 Boltzmann 方程的一些应用。

首先, Boltzmann 方程可以推广到对气体, 即

$\lambda_T \approx \bar{\lambda}_T$. 这时, $(\frac{\partial f}{\partial t})_c$ 需要修改. (参. (10.4.10))
其后, 不仅是经典和量子情形, $(\frac{\partial f}{\partial t})_c$ 是由 Boltzmann 方程中取掉 λ_T . 一般地并结合引入速度时间相关的
函数化形式

$$(1) (\frac{\partial f}{\partial t})_c \approx - \frac{f - f^{(0)}}{\tau}$$

f 为非平衡分布函数, $f^{(0)}$ 为 ~~平衡~~ (局域) 平衡分布函数, τ 为粒子平行运动的弛豫时间。

设 $\tau \propto \vec{v}^2$, 即 $f^{(0)}$ 是基态平衡函数. 记 τ 仍表示 \vec{v} 的意义. 设外力为 0, \therefore

$$\frac{\partial f}{\partial t} = - \pm \frac{f^{(0)}}{\tau} \quad \because f \propto \vec{v}^2, \therefore$$

$$\frac{df - f^{(0)}}{f^{(0)}} = - \frac{dt}{\tau}$$

$$f^{(0)(+)} - f(\vec{v}, t) - f^{(0)(-)} = [f(\vec{v}, 0) - f^{(0)(-)}] e^{-\vec{v}^2 \tau}$$

τ 是粒子平行运动时间。

在弱电场中最简单的例子是电导率

计算. 用驰豫时间方法, 可以研究金属自由电子的电导率
随电压过程. 对金属中的自由电子, $f^{(0)}$ 由 Fermi 分布

$$f^{(0)}(\vec{p}) = \frac{1}{e(E(\vec{p}) - \mu)/kT + 1}$$

$$E(\vec{p}) = \frac{p^2}{2m}, \mu \text{ 是化学势. 单位体积内粒子数}$$

即带电荷的单位体积内带电粒子数

$$2 \times \frac{N}{V} f^{(0)}, 2 \text{ 来自 spin } \uparrow, \downarrow.$$

Boltzmann eq. reads

$$\frac{\partial f}{\partial t} + \frac{\vec{p}}{m} \cdot \frac{\partial f}{\partial \vec{p}} + \vec{F} \cdot \frac{\partial f}{\partial \vec{p}} = - \frac{f - f^{(0)}}{\tau}$$

设在电场中的平衡电场中, $\vec{F} = -e\vec{E}$, \vec{E} 电场强度. 按此规律 $\frac{\partial f}{\partial \vec{p}} \rightarrow 0$, $\frac{\partial f}{\partial \vec{p}} = 0$. \therefore

$$e\vec{E} \cdot \frac{\partial f}{\partial \vec{p}} = \frac{f - f^{(0)}}{\tau}, f = f^{(0)} + f^{(1)} + \dots$$

得简化一阶:

$$e\vec{E} \cdot \frac{\partial f^{(1)}}{\partial \vec{p}} = \frac{f^{(1)}}{\tau} \Rightarrow f^{(1)} = e\vec{E} \cdot \vec{v} \frac{\partial f^{(0)}}{\partial \vec{v}}$$

$$\frac{\partial f^{(0)}}{\partial \vec{p}} = \frac{\partial f^{(0)}}{\partial \vec{E}} \frac{\partial \vec{E}}{\partial \vec{p}} = \frac{\partial f^{(0)}}{\partial \vec{E}} \vec{v}$$

$f \approx f^{(0)} + e\vec{v} \cdot \vec{E} \cdot \vec{v} \frac{\partial f^{(0)}}{\partial \vec{v}}$

若把上式看作 $f^{(0)} + e\vec{v} \cdot \vec{E} \cdot \vec{v}$, 即认为 \vec{v} 不变 shift.

现在, 取运动方向为 x 轴, 则在 dt 时间内
通过 x 方向的 dA 的电流

$$J_e dt dA = \int v_x dt dA \frac{2dp}{h^3}$$

$$(J_e = nev_x = \frac{2dp}{h^3} f^{(0)} v_x)$$

$$\text{又 } J_e = e \int v_x (f^{(0)} + f^{(1)}) \frac{2dp}{h^3},$$

$$v_x = p_x/m, f_0(-v_x) = f_0(v_x). \therefore f^{(1)}=0.$$

$$J_e = e^2 E \tau \int v_x^2 \frac{\partial f^{(0)}}{\partial E} \frac{2dp}{h^3}$$

$$\left(\int dp \frac{2dp}{h^3} = \int p^2 dp \cdot 2\pi d\theta \sin\theta d\varphi \cdot \right. \\ \left. = \int 2m E d\theta \sqrt{m/E} \cdot 4\pi \right) \\ = \frac{4\pi (2m)^{3/2}}{2} \int E^k dE \\ = e^2 E \tau \int v_x^2 \frac{\partial f^{(0)}}{\partial E} D(E) dE \\ D(E) = 4\pi \frac{(2m)^{3/2}}{h^3} E^k$$

f 在 \vec{v} 和 \vec{E} (碰撞)

$$\frac{\partial f}{\partial t} + \vec{v} \cdot \nabla f + \frac{\vec{E}}{m} \cdot \frac{\partial f}{\partial \vec{v}} = \text{coll.} \left(\frac{\partial f}{\partial t} \right)_{\text{coll.}}$$

$$\downarrow \quad \downarrow \quad \downarrow$$

$$\frac{d\langle v \rangle}{dt} = -\frac{eE}{m} + i\omega_c \langle v \rangle - \frac{\langle v \rangle}{\tau}$$

$$\langle v \rangle = -\frac{eEm}{1-i\omega_c \tau} \quad (E = E_x + iE_y) \quad \omega_c = \frac{eB}{mC}$$

$$j = -ne \langle v \rangle = \sigma_0 E / (1-i\omega_c \tau), \sigma_0 = \frac{ne^2}{m}.$$

$$\vec{j} = \vec{v} \cdot \vec{E}, \quad \vec{v} = \begin{pmatrix} \sigma_{xx} & \sigma_{xy} \\ \sigma_{yx} & \sigma_{yy} \end{pmatrix}.$$

$$\Rightarrow \sigma_{xx} = \sigma_{yy} = \frac{\sigma_0}{1+i\omega_c \tau^2},$$

$$\sigma_{xy} = -\sigma_{yx} = -\frac{nec}{B} + \frac{\sigma_0}{\omega_c \tau}.$$

* 当有温度梯度时 (碰撞), 在稳恒状态, H_0 不同
导致时间常数. 但 f 变化很慢, 用局域平衡
描述的 $f^{(0)}$ 可以导出速率. (见书)

空间坐标 x, y, z 和 $(f^{(0)})$, $v_x \rightarrow v_y \rightarrow v_z$.

$$\therefore J_e = e^2 E \tau \int T(E) \cdot \frac{4}{3} \cdot \frac{df^{(0)}}{dE} D(E) dE \\ = \frac{2e^2 E}{3m} \int T(E) E^3 \frac{2df^{(0)}}{dE} D(E) dE.$$

对 Fermi gas, $\frac{df^{(0)}}{dE}$ 只在 Fermi 面附近不为 0,
至 $T \rightarrow 0$, Fermi 面处 $\delta(E - \mu)$. \therefore

$$\frac{df^{(0)}}{dE} = \delta(E - \mu) \cdot f^{(0)} =$$

$$\therefore J_e = \frac{e^2 \tau C}{3m} M^* D(\mu) E.$$

$$\therefore n = \int_0^\mu D(E) dE \\ = \frac{2}{3} \mu D(\mu).$$

$$\therefore J_e = \frac{n e^2 F}{m} E, \quad \sigma = \frac{n e^2 F}{m}$$

正向速率 n 穿磁场的速率.

反向速率 n ,

$$\vec{F} = -e \vec{E} - \frac{e}{c} \vec{v} \times \vec{B}.$$

设 $\vec{v} = v_x \hat{x} + v_y \hat{y}$ 带入上述方程得, 且又

$$v = v_x + i v_y, \quad B \perp x-y 平面.$$

3.8.4.5 速率恒定理论: 力学扰动

Boltzmann 方程只处理稀薄、短程相互作用气体.
处理速率恒定的非平行统计理论是 Kubo 提出
的线性响应理论. 该理论不仅限于仅可以用于统计物理, 也可以用于量子力学基态. 但是, 它仅能
计算虚力子可观测值, 而可用于计算量可观测值.

线性响应理论~出发点是考虑 m+1 项级数的合成

$$H = H_0 + H_e$$

H_0 是要研究的系统~哈密顿量, $H_e(t)$ 是一个小扰动.
我们用力学方式研究问题. 于是从波函数入手

$$\text{Schrödinger eq.: } i\hbar \frac{\partial \Psi}{\partial t} = (H_0 + H_e)\Psi.$$

假设它满足

$$\Psi(t) = e^{i\frac{H_0}{\hbar}t} \Psi(0), \quad \text{Sch. eq. true}$$

$$\therefore \left(-i\frac{H_0}{\hbar}\right) e^{-i\frac{H_0}{\hbar}t} \Psi(0) + i\hbar e^{-i\frac{H_0}{\hbar}t} \dot{\Psi}$$

$$= \text{总 } H_0 e^{-i\frac{H_0}{\hbar}t} \Psi(0) + H_e e^{-i\frac{H_0}{\hbar}t} \Psi$$

$$\Rightarrow \dot{\Psi} = \frac{1}{i\hbar} \left(e^{i\frac{H_0}{\hbar}t} H_e e^{-i\frac{H_0}{\hbar}t} \right) \Psi \equiv \frac{1}{i\hbar} H_e e^{i\frac{H_0}{\hbar}t} \Psi$$

设 $t \rightarrow -\infty$ 时, $\Psi(t) = \Phi_m$, 是 Schrödinger eq.
m-宇宙态. ($t \rightarrow -\infty, H_e(t) = 0, H_0 \Phi_m = E_m \Phi$)

开始上,

$$\varphi(t) = \phi_m + \frac{1}{i\hbar} \int_0^t \tilde{H}_e(t') \varphi(t') dt'$$

是 Schrödinger eq. 的解. 量子力学中 A 在 t 时刻的值在物理上是确定的.

$$\begin{aligned} \bar{A}(t) &= \int d\vec{r} \psi^*(\vec{r}, t) A(\vec{r}) \psi(\vec{r}, t) \\ &= \int d\vec{r} \psi^*(\vec{r}, t) e^{i\frac{\tilde{H}_e}{\hbar}t} A e^{-i\frac{\tilde{H}_e}{\hbar}t} \psi(\vec{r}, t) \\ &\equiv \int d\vec{r} \psi^*(\vec{r}, t) A(t) \psi(\vec{r}, t). \end{aligned}$$

(2) 算代法

$$\varphi(t) = \phi_m + \int_{-i\hbar}^t \tilde{H}_e(t') \left(\phi_m + \int_{-i\hbar}^{t'} \tilde{H}_e(t'') \phi(t'') dt'' \right) dt'$$

仍用浅显的向量, 就是上面的 ~~算子~~ 表示.

$$\tilde{H}_e \sim \text{阶}: \varphi(t) \approx \phi_m + \int_{-i\hbar}^t \tilde{H}_e(t') \phi_m dt'.$$

$$\begin{aligned} \bar{A}_m &= \bar{A}(t) \approx \int d\vec{r} \phi_m^* A(t) \phi_m \\ &\quad + \frac{1}{i\hbar} \int_{-i\hbar}^t dt' \int d\vec{r} d\vec{r}' \phi_m^* [A(t), \tilde{H}_e(t')] \phi_m. \end{aligned}$$

$$\bar{A}(t) - \bar{A}_m < m |A| m > = \frac{1}{i\hbar} \int_{-i\hbar}^t dt' < m | [A(t), \tilde{H}_e(t')] >$$

1) Fourier 变换

$$\int \frac{d\vec{k}}{(2\pi)^3} D(\vec{k}) e^{i\vec{k} \cdot (\vec{r} - \vec{r}') - i\omega(\vec{k})t}$$

$$\delta \alpha(\vec{r}, t) = eV_0 D(\vec{k}) e^{i\vec{k} \cdot \vec{r} - i\omega(\vec{k})t}$$

对 (考虑 H_0 , $D(\vec{k})$ 可以求出, 则冲击辐射率和波函数可以求出).

例 2. 电导率. 假设我们用浅显的向量理论求电导率的一般表达式:

$$H_e = - \int d\vec{r} \vec{j} \cdot \vec{A}, \quad \vec{A} \text{ 是外电场矢量}$$

$$\vec{j} = \vec{j}_1 - \frac{e^2}{m} \hat{n}(\vec{r}) \vec{A}(\vec{r}),$$

$$\vec{j}_1 = \frac{i e}{2m} \left((\nabla - \nabla') \psi(\vec{r}) \psi^*(\vec{r}) \right)_{\vec{r}=\vec{r}'}$$

无外场时, $\langle \vec{j} \rangle = \langle \vec{j}_1 \rangle = 0$.

根据浅显的向量式:

$$\langle j_a(\vec{r}, t) \rangle = \sum_{b=1}^3 \int d\vec{r} dt' K_{ab}(\vec{r}, t; \vec{r}', t') A_b(\vec{r}', t')$$

如果 $\nu \sim k_F$, $\langle j_a j_b \rangle \neq 0$, 很多结果将更复杂.

对统计学

$$\langle \bar{A} \rangle_T = \sum_m \frac{1}{Z_A} e^{-(E_m - \mu)/k_B T} \bar{A}_m$$

$$(Z_A \text{ 是 } \bar{A} \text{ 的配分函数}, \frac{1}{Z_A} e^{-(E_m - \mu)/k_B T} = p_m)$$

$$= \sum_m p_m \bar{A}_m = \text{Tr } P \bar{A}$$

Kubo 的线性响应理论也可 ~~推~~ ^{LC} 得到相同的结果. 由出发 ~~得出~~ (见苏进书), 和那书.)

下面举二例.

例 1. 对电子气加冲击型脉冲扰动.

$$V(\vec{r}, t) = V_0 e^{i\vec{Q} \cdot \vec{r}} \delta(t)$$

$$H_e = -eV_0 \int d\vec{r} \hat{n} e^{i\vec{Q} \cdot \vec{r}} \delta(t).$$

\hat{n} 是粒子密度算符. 接前面讨论

$$\delta \bar{A}(\vec{r}, t) = ie \nabla V_0 \int d\vec{r}' \langle [\hat{n}(\vec{r}, t), \hat{n}(\vec{r}', 0)] \rangle_{t \rightarrow 0} e^{i\vec{Q} \cdot \vec{r}'}$$

$$i \langle [\hat{n}(\vec{r}, t), \hat{n}(\vec{r}', 0)] \rangle_{t \rightarrow 0}$$

是惟一的非零结果. 如果考虑长期, 它是 $\vec{r} - \vec{r}'$, $t \rightarrow m$ 项.

$$K_{ab} = -\frac{e^2 n}{m} \delta(\vec{r} - \vec{r}') \delta(t - t') \delta_{ab}$$

$$+ i \langle [j_a(\vec{r}, t), j_b(\vec{r}', t')] \rangle \delta(t - t')$$

2) Fourier 变换

$$\langle j_a(\vec{r}, t) \rangle = \int \frac{d\vec{k} dv}{(2\pi)^3} j_a(\vec{k}, v) e^{i\vec{k} \cdot \vec{r} - ivt}$$

$$\xrightarrow{\text{傅立叶变换}} K_{ab}(\vec{r} - \vec{r}', t - t') = \int \frac{d\vec{k} dv}{(2\pi)^3} K_{ab}(\vec{k}, v) e^{i\vec{k} \cdot (\vec{r} - \vec{r}') - iv(t - t')}$$

$$A_b(\vec{r}, t) = \int \frac{d\vec{k} dv}{(2\pi)^3} A_b(\vec{k}, v) e^{i\vec{k} \cdot \vec{r} - ivt}$$

$$\therefore j_a(v) = \sum_{b=1}^3 K_{ab}(\vec{v}, v) A_b(\vec{v}, v)$$

看电场是否周期性

$$A_b(\vec{v}, v) = \frac{1}{\sqrt{V}} E_b(v) \delta(\vec{v})$$

$$j_a(v) = \sum_{b=1}^3 K_{ab}(0, v) E_b(v) / \sqrt{V}$$

$$\sigma_{ab}(v) = \frac{1}{\sqrt{V}} K_{ab}(0, v) \text{ 是电导率张量.}$$

$$\text{进一步得: } \sigma_e = \frac{e^2}{3V} \int_0^\infty dt \int_0^B d\vec{x} \text{Tr } \vec{J} \cdot \vec{J} e^{-iLt} \rho_0.$$

3.8. 6 线性响应原理数：量子扰动

前面讲的是传播算符扰动后线性响应，这里由于引入梯度，波函数表示扰动不能用一个由微扰的密度表示，这时，传播算符直接与局域平行。我们称传播算符为扰动（见前讲义，即之后书）。传播 Hamiltonian 是

$$\begin{aligned} \langle \vec{q} = m\vec{v} \rangle & H = \int H(\vec{r}) d\vec{r} \\ \text{或 } \hat{\vec{p}} &= -i\hbar\nabla \\ (\text{从 } \hat{H} = \frac{1}{2m} \nabla^2 + \mu(\vec{r}), \text{ 得 } H(\vec{r}) = \sum_{i=1}^N E_i \delta(\vec{r} - \vec{r}_i)) \\ E_i &= \frac{p_i^2}{2m} + \frac{1}{2} \sum_{j \neq i} U(\vec{r}_i - \vec{r}_j) \end{aligned}$$

是传播算符

$$N = \int d\vec{r} N(\vec{r}).$$

\vec{r} 是一个微扰量，应该与传播算符 N 在同一内，传播算符平行态。对每一个 i 对于 local，局域平行态与线性响应算符

$$\hat{S}_i(t) \sim e^{-iE_i t / \hbar}$$

$$P(\vec{r}) \sim e^{-\beta(\vec{r}) H_0(\vec{r})}$$

$$H_0(\vec{r}) = H(\vec{r}) - \mu(\vec{r}) N(\vec{r}).$$

(19)

$$\delta P = -\frac{i}{\hbar} \int_{-\infty}^t dt' (L P_L + L \delta P(t'))$$

用替代法

$$\begin{aligned} \delta P &= -\frac{i}{\hbar} \int_{-\infty}^t dt' L P_L + -\frac{i}{\hbar} \int_{-\infty}^t dt' \left(\frac{-i}{\hbar} \int_{-\infty}^{t'} dt'' (L P_L + L \delta P(t'')) \right) \\ &= -\frac{i}{\hbar} \int_{-\infty}^t dt' L P_L + \left(\frac{-i}{\hbar} \right)^2 \int_{-\infty}^t dt' L \left(\frac{-i}{\hbar} \int_{-\infty}^{t'} dt'' L P_L \right. \\ &\quad \left. + \left(\frac{-i}{\hbar} \right)^3 \int_{-\infty}^{t'} dt'' L \int_{-\infty}^{t''} dt''' L \int_{-\infty}^{t'''} dt'''' L P_L \right) + \dots \\ &\equiv -\frac{i}{\hbar} \int_{-\infty}^t dt' e^{-\frac{i}{\hbar} L(t-t')} L P_L = -\frac{i}{\hbar} \int_0^P e^{-\frac{i}{\hbar} L(t-t')} L P_L dt' \end{aligned}$$

$$\cancel{\frac{i}{\hbar} L P} \quad \dot{S}_q = -\frac{i}{\hbar} L S_q$$

$$= -\frac{i}{\hbar} \left[H, \int \beta(\vec{r}) (H(\vec{r}) - \mu(\vec{r}) N(\vec{r})) d\vec{r} \right]$$

$$\begin{aligned} &= -\frac{i}{\hbar} [H, \bar{\beta} S_q] + -\frac{i}{\hbar} \left[H, \int \frac{\partial \beta(\vec{r})}{\partial \vec{r}} \cdot \nabla (H - \mu N) d\vec{r} \right] \\ &= \cancel{\frac{i}{\hbar} \beta} = -\frac{i}{\hbar} L \int \frac{\partial \beta}{\partial \vec{r}} \cdot \nabla (H - \mu N) d\vec{r}. \end{aligned}$$

P, 正比于 $\bar{\beta}$ 或 βM 的梯度。

系统处于局域平衡态的密度矩阵 (14)

$$\rho_L = N_L^{-1} e^{-\beta S_q}$$

$$S_q = \int \beta(\vec{r}) [H(\vec{r}) - \mu(\vec{r}) N(\vec{r})] d\vec{r}.$$

N_L 是归一化因子， $\beta(\vec{r}) = 1/k_B T(\vec{r})$ ， $M(\vec{r})$ 是 local 电子数。 $T(\vec{r})$ ， $\mu(\vec{r})$ 在空间上均是连续的，但局域平行态 ρ_L 不能直接求出它的实值， ρ_L 是密度矩阵的全部，还需要加修正项：

$$\rho = \rho_L + \delta \rho,$$

P 满足时间方程。

$$i \hbar \frac{\partial \rho}{\partial t} = \cancel{H}, [\rho, \rho] = L \rho$$

||

$$i \hbar \frac{\partial \delta \rho}{\partial t} = L \rho_L + L \delta \rho$$

$$\therefore \delta \rho(t) = \frac{i}{\hbar} \int_0^t dt' e^{-iL(t-t')/\hbar} \cancel{L(t-t')/\hbar} \delta \rho(0) \quad (\text{因 } \hbar = 1).$$

$$[H, \rho_L] = [H, \frac{1}{N_L} e^{-S_q}]$$

$$= \frac{1}{N_L} [H, -S_q] + \frac{1}{N_L} [H, (S_q)_{h.c.}] + \dots$$

$$= -\frac{1}{\hbar} L S_q + \frac{1}{N_L} \cancel{L(S_q) \delta S_q} + \dots$$

$$= -L S_q \left(\frac{1}{N_L} (1 - S_q + \dots) \right) = -L S_q \rho_L.$$

$$\left(\text{由 } L S_q \text{ 为 } \frac{\partial \beta}{\partial \vec{r}}, \text{ 是小量, } \therefore \cancel{P_L} \approx P_0. \right)$$

$$\approx -L S_q P_0$$

$$= - \int d\vec{r} \left[\beta(\vec{r}) [H(\vec{r}) - \mu(\vec{r}) N(\vec{r})] \right] P_0.$$

$$P_0 = e^{-\bar{\beta}(H - \bar{\mu}N)} / \text{Tr} e^{-\bar{\beta}(H - \bar{\mu}N)}$$

$\bar{\beta}$ 和 $\bar{\mu}$ 是 $\beta(\vec{r})$ 和 $\mu(\vec{r})$ 在空间平均值。

由能守恒律： $\frac{\partial H(\vec{r})}{\partial t} + \vec{J} \cdot \vec{B}(\vec{r}) = 0$

守恒律： $\frac{\partial N}{\partial t} + \vec{J} \cdot \vec{J}(\vec{r}) = 0$.

$$\Rightarrow -\frac{i}{\hbar} L H(\vec{r}) = -\vec{J} \cdot \vec{B}(\vec{r}), -\frac{i}{\hbar} L N(\vec{r}) = -\vec{J} \cdot \vec{J}(\vec{r})$$

$\vec{B}(\vec{r})$ 和 $\vec{J}(\vec{r})$ 是随壳层转动的。

$$\therefore L_{\text{ext}} = \int d\vec{r} \hat{F}$$

$$\begin{aligned} L_{\text{ext}} &= -i \int d\vec{r} [\beta(\vec{r}) \nabla \cdot \vec{Q}(\vec{r}) - \beta^* \nabla \cdot \vec{J}(\vec{r})] \rho_0 \\ &= -i \int d\vec{r} [\vec{Q} \cdot \nabla \beta(\vec{r}) - \vec{J} \cdot \nabla (\beta^*)] \rho_0 \\ &= i \int d\vec{r} [\vec{J}_e \cdot \nabla \beta - \beta \nabla \cdot \vec{J}_e] \rho_0 \\ &\quad \vec{J}_e = \vec{Q}(\vec{r}) - h \vec{T}(\vec{r}), h = \mu - T \left(\frac{\partial \beta}{\partial T} \right)_h. \end{aligned}$$

$h(\vec{r})$ 是 loca 约数, n 是子波函数.

对一个物理量 $\vec{B}(\vec{r})$, 例如 \vec{B} , \vec{Q} 或 \vec{J} , 在区域 Ω , 且平均得 $\langle \vec{B} \rangle = \text{Tr } \vec{B}(\vec{r}) \rho_0 = 0$. \therefore

$$\begin{aligned} \langle \vec{B}(\vec{r}) \rangle &= \text{Tr} (\vec{B}(\vec{r}) \rho_0) \\ &= -i \int_0^\infty dt' \text{Tr} \vec{B}(\vec{r}) e^{-iLt'} L_{\text{ext}} \\ &= \int_0^\infty dt' d\vec{r}' \text{Tr} \vec{B}(\vec{r}') e^{-iLt'} [\vec{J}_e(\vec{r}') \cdot \nabla \beta \\ &\quad - \beta \left(\frac{\partial n}{\partial T} \right) \vec{T}(\vec{r}') \cdot \nabla \vec{n}] \rho_0 \end{aligned}$$

若 $T(\vec{r})$ 是空间常数, $\frac{\partial n}{\partial T} \neq 0$, 则 \vec{J}_e 为:

$$\langle \vec{J}_e \rangle = -D \nabla n, D$$
 为扩散系数

$$\begin{aligned} D &= \beta \left(\frac{\partial n}{\partial T} \right)_T \frac{1}{3V} \int_0^\infty dt \text{Tr} \vec{J} \cdot \vec{J} e^{-iLt} \rho_0 \\ &= \frac{1}{e^2} \left(\frac{\partial n}{\partial T} \right)_T e^2 \beta \sigma_e \\ \sigma_e &= \frac{e^2 \beta}{30V} \int_0^\infty dt \text{Tr} \vec{J} \cdot \vec{J} e^{-iLt} \rho_0. \quad (S.2.10) \end{aligned}$$

是电导率. ($\propto \sigma_{ab}(v) = \frac{1}{iV} K_{ab}(0, v)$ 为 v)

$$\boxed{\text{由 } \frac{d\vec{J}}{dt} = -\nabla \vec{V} \rightarrow \vec{J} = -\vec{V} \rightarrow \vec{V} = \frac{1}{\rho} = \vec{T}.}$$

粒子运动造成的 \vec{J} 与 \vec{V} 有直接关系与耗散系数 (例如热导率、扩散系数) 的关系 $\vec{J} = \frac{e}{m} \vec{V}$ 有时称为 (一) 耗散-速度关联律. (\because 从 \vec{J} 与 \vec{V} 及 \vec{J} 与 \vec{V} 的相关性推导出 \vec{J} 与 \vec{V}). 布朗运动 (即 \vec{J} 与 \vec{V} 的相关系数 $\propto \vec{J} \cdot \vec{V}$ 为零) 存在耗散系数 η 与 $\vec{J} = \frac{e}{m} \vec{V}$ 的关系. 通过 $\vec{J} = \frac{e}{m} \vec{V}$ 可以推导出 \vec{J} 与 \vec{V} 的相关性. 这时 \vec{V} 为随机的 \vec{J} 为确定的.

若 \vec{J} 为零, \vec{V} 是空间常数. (1.1)

$$\langle \vec{B} \rangle = \frac{1}{V} \int_0^\infty dt \text{Tr} \vec{B} e^{-iLt} [\vec{J}_e \cdot \nabla \beta - \beta \left(\frac{\partial n}{\partial T} \right) \vec{T} \cdot \nabla \vec{n}] \rho_0.$$

$$\vec{B} = \int d\vec{r} \vec{B}(\vec{r}), \vec{J}_e = \int d\vec{r} \vec{J}_e(\vec{r}),$$

若只有 \vec{J}_e 为常数, 但 $\vec{J}_e \neq 0$, 则 $\vec{J}_e = \vec{Q}$, $\vec{J} = \vec{Q}$, 则 $\langle \vec{B} \rangle = \frac{1}{V} \int_0^\infty dt \text{Tr} (\vec{Q} \cdot \nabla \beta) \vec{Q} e^{-iLt} \rho_0.$

$$\langle \vec{Q} \rangle = \cancel{K \nabla T} + \cancel{K \nabla \beta} + \cancel{K \nabla \vec{J}} + \cancel{K \nabla \vec{B}}$$

$$\langle \vec{Q} \rangle = -K \nabla T = -K \nabla \frac{1}{\beta} = +K T^2 \nabla \beta \quad (k_B = 1)$$

$$\begin{aligned} \text{另一方面}, (\nabla \beta \cdot \vec{Q}) \vec{Q} &= \vec{Q} (\vec{A} \cdot \vec{Q}) \vec{Q} = (A_x Q_x \& A_y Q_y \& A_z Q_z) \vec{Q} \\ \text{因 } \vec{Q} \text{ 为常数} \& \vec{Q} \cdot \vec{Q} = A_x Q_x \& A_y Q_y \& A_z Q_z \end{aligned}$$

$$\therefore \langle \vec{Q} \rangle = \underbrace{\left(\frac{1}{3k_B T^2 V} \int_0^\infty \text{Tr} \vec{Q} \cdot \vec{Q} e^{-iLt} \rho_0 dt \right)^2}_{K} \nabla \beta$$

括号

§ 8.4 液体性质: ~~液体~~ 153 (153) (153)

液体是一般近代物理学中都单独立一章. 液体和气体属于经典统计力学. 而液体和固体偏重于平行和距离有固定联系. 同时, 我们把液体和固体归于一类. 因为液体和固体都是无序的. 由物质状态的不连续性引起. (由 ~~单相~~ 引起). 另一类是随外力引起. (这一类是确定的). 在讨论分子运动时, 我们说正则系综和大通量接触, 通过能会用到平衡状态的性质:

$$\sqrt{E-E_0}/E \sim \frac{1}{\sqrt{N}}$$

至多子极限 ($n = \frac{N}{V}$ fixed when N and $V \rightarrow \infty$). 这种广泛的 $E-E_0/E$ 的变化. 至多子极限, 可以同时有耗散系数 η 和扩散系数 σ_e , 都 $\sim \frac{1}{\sqrt{N}}$. 这些系数用分子有规则运动 \vec{J} 广泛地表示时, 这些计算很直接, 但一些没有物理意义, 例如熵和张量 \vec{J} / \vec{V} , 不适用. 在这里我们只讨论 \vec{J} 与 \vec{V} 的相关系数, 及讨论它们的物理意义.

3.8.1. 热力学子系统

(Smoluchowski-Einstein 方程)

对于处于平衡态的子系统，玻尔兹曼分布平衡态
概率是 $S = k_B \ln W_{\max}$, 且 $W_{\max} = e^{\frac{S}{k_B}}$

$$\text{偏离平衡: } W = e^{S/k_B}$$

$$\therefore W = W_{\max} e^{(\bar{S}-S)/k_B} = W_{\max} e^{-\Delta S/k_B}$$

系统分子的能量差 $\Delta E = 0$, $\Delta V = 0$.

对已知子系，条件是 $\Delta E + \Delta E_e = 0$, $\Delta V + \Delta V_e = 0$.

$e^{\frac{E}{k_B T}}$ 表示外部力矩 F . ($F = V + V_e$ 和 $E = E_e + E$)

$$\therefore W_T = W_{\max, T, \max} = e^{(\Delta S + \Delta F) / k_B T}$$

$$= W_{\max} e^{(\Delta S + \frac{\Delta E + p\Delta V}{T}) / k_B T}$$

$$= W_{\max} e^{(\Delta S - \Delta E - p\Delta V) / k_B T}$$

$$= W_{\max} e^{-(\Delta F + p\Delta V) / k_B T}$$

$$\Delta F = \left(\frac{\partial F}{\partial V} \right)_{\text{ext}} \Delta V + \frac{1}{2} \left(\frac{\partial^2 F}{\partial V^2} \right)_{\text{ext}} (\Delta V)^2 + \dots$$

$$-pV - \frac{\partial p}{\partial V}$$

由单分子 N 和 $M = \text{const}$, $N/V = P$ 且 $P = \rho V$.

$$\Rightarrow \Delta M = \Delta P V + P \Delta V \Rightarrow \frac{\Delta P}{P} = -\frac{\Delta V}{V}$$

$$\therefore \frac{(\Delta P)^2}{P^2} = \frac{(\Delta V)^2}{V^2} = -k_B T \left(\frac{\partial V}{\partial P} \right)_T$$

$$P = \frac{N}{V}, \text{且 } V \text{ 固定, } \text{且 } \Delta P \propto \Delta N.$$

$$\therefore \frac{(\Delta N)^2}{N^2} = \frac{(\Delta P)^2}{P^2} = -\frac{k_B T}{V^2} \left(\frac{\partial V}{\partial P} \right)_T$$

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$$\Delta P = \frac{\Delta N}{V} - \frac{N \Delta V}{V^2}$$

$$(\Delta P)^2 = \left(\frac{\Delta N}{V} \right)^2 - 2 \frac{\Delta N}{V} \frac{N \Delta V}{V^2} + \frac{N^2 (\Delta V)^2}{V^4}$$

$$\frac{(\Delta P)^2}{P^2} = \frac{(\Delta N)^2}{N^2} + \frac{(\Delta N)^2}{N^2} = 2 \left(\frac{\Delta N}{N} \right)^2.$$

对理想气体, $\left(\frac{\partial V}{\partial P} \right)_T = -\frac{1}{P} = -\frac{V^2}{N k_B T}$

$$\Rightarrow \frac{(\Delta P)^2}{P^2} - \frac{k_B T}{V^2} \left(-\frac{V^2}{N k_B T} \right) \propto \frac{1}{N}.$$

与理想气体结果一致.

$$W_T \approx W_{\max, T} \exp \left(\frac{1}{2k_B T} \left(\frac{\partial P}{\partial V} \right)_T (\Delta V)^2 \right)$$

这就是玻尔兹曼分布概率. 但 ΔV 取分子偏移可以忽略不计.

$$\langle \Delta A \rangle^2 = \int (\Delta A)^2 W d(AA) / \int W d(AA) \text{ d}AA.$$

$$\langle \Delta V \rangle^2 = \frac{\int_{-\infty}^{+\infty} (\Delta V)^2 \exp \left[-\frac{1}{2k_B T} \left(\frac{\partial P}{\partial V} \right)_T (\Delta V)^2 \right] d(\Delta V)}{\int_{-\infty}^{+\infty} \exp \left[-\frac{1}{2k_B T} \left(\frac{\partial P}{\partial V} \right)_T (\Delta V)^2 \right] d(\Delta V)}$$

$$= \frac{\int_{-\infty}^{+\infty} (\Delta V)^2 \frac{k_B T}{(\frac{\partial P}{\partial V})_T} \frac{1}{2V} d(\exp \left(-\frac{1}{2k_B T} \left(\frac{\partial P}{\partial V} \right)_T (\Delta V)^2 \right))}{\int_{-\infty}^{+\infty} \exp \left(-\frac{1}{2k_B T} \left(\frac{\partial P}{\partial V} \right)_T (\Delta V)^2 \right) d(\Delta V)}$$

$$= \Rightarrow \frac{\Delta V (k_B T)}{(\frac{\partial P}{\partial V})_T} \exp \left(-\frac{1}{2k_B T} \left(\frac{\partial P}{\partial V} \right)_T (\Delta V)^2 \right) \Big|_{-\infty}^{+\infty}$$

$$- k_B T \left(\frac{\partial V}{\partial P} \right)_T = - k_B T \left(\frac{\partial V}{\partial P} \right)_T.$$

$$\therefore \frac{(\Delta V)^2}{V^2} = - \frac{k_B T}{V^2} \left(\frac{\partial V}{\partial P} \right)_T.$$

以上计算得到的结果是正确的. 因为 $(\frac{\partial P}{\partial V})_T = (\frac{\partial^2 F}{\partial V^2})_T = 0$, 所以 $\Delta F \propto M(\Delta V)^2$.

$$\Delta F = -p\Delta V - \frac{1}{2} \left(\frac{\partial^2 P}{\partial V^2} \right)_T (\Delta V)^2 + \dots$$

$$\therefore W = W_{\max} \exp [-\alpha X^2],$$

$$\alpha = \frac{1}{2k_B T} \left| \left(\frac{\partial^2 P}{\partial V^2} \right)_T \right|, X = \Delta V.$$

$$\langle \Delta V \rangle^2 = \frac{\int_0^\infty X^2 e^{-\alpha X^2} dX}{\int_0^\infty e^{-\alpha X^2} dX} = \frac{\Gamma(\frac{3}{2})}{\Gamma(\frac{1}{2})} \frac{1}{\alpha^{\frac{1}{2}}} = 0.338 \left[\frac{1}{2k_B T} \left(\frac{\partial^2 P}{\partial V^2} \right)_T \right]^{\frac{1}{2}}$$

对实际分子热气.

$$P_C = \frac{a}{27b^2}, V_C = 3b, T_C = \frac{8a}{27bR}.$$

$$\text{理想气体方程: } (P + \frac{a}{V})(V - b) = RT$$

$$\Rightarrow P = \frac{3RT}{3V - V_C} - \frac{9RT_C V_C}{8V^2}$$

$$\therefore V = \frac{N}{N_A} V_C, \left(V_C = \frac{N}{N_A} V_C \right), N_A = 6.02 \times 10^{23}$$

$$P = \frac{3NkT}{3V - V_C} - \frac{9NkT_C V_C}{8V^2}$$

$$\left(\frac{\partial P}{\partial V^3} \right)_T = -\frac{48NkT}{(3V - V_C)^2} + \frac{27NkT_C V_C}{V^3}, \left(\frac{\partial P}{\partial V^3} \right)_{T_C} = -\frac{27NkT_C}{8V_C^4}$$

$$\left(\frac{V}{V_0}\right)_c = 0.338 \left[-\frac{V^4}{24kT_c} \left(\frac{\partial^3}{\partial V^3} \right)_{T_c} \right]^{-k}$$

$$= 0.901 / \text{km}$$

一般情况 $\frac{V}{V_0} \propto$ 光的吸收，而吸收量大得多。当光束穿过多层大气时，吸收量比单层大气要大许多倍。

~~吸收系数~~ \propto ~~吸收量~~ \propto ~~光的吸收量~~ \propto ~~光的吸收量~~

两点应用：

① 测定空气中杂质时，可以解释为什么天是蓝色的。我们考虑空气是干净的情况，这时，漫射光强度不随引出距离而变，吸收的强度

$\propto \frac{1}{x} \frac{\Delta P^2}{P^2}$ (且假设，绝对吸收不随引出距离而变)

② 没有杂质的话，则没有吸收光的强度会越强，散射越强。蓝色波长短，所以看到的强度相对是蓝色的 \Rightarrow 蓝天。③ 太阳，无论何时哪里看到时，杂质散射占比大，所以看到的是蓝天。

$x=0$ 时 S 取极大值，

(16)

$$\therefore \frac{\partial S}{\partial x} \Big|_{x=0} = 0, \quad \frac{\partial^2 S}{\partial x^2} \Big|_{x=0} < 0.$$

$$\therefore W(x) dx \approx A e^{-\frac{3x^2}{2k_B T}} dx, \quad 3 = -\frac{\partial S}{\partial x} \Big|_{x=0} > 0.$$

$$\int_{-\infty}^{+\infty} W(x) dx = 1, \quad \Rightarrow A = \sqrt{\frac{3}{2\pi k}}$$

$$W(x) dx = \sqrt{\frac{3}{2\pi k}} e^{-\frac{3x^2}{2k_B T}} dx$$

即在 x 出现偏移的高斯分布，Gauss 分布。

$$\text{且} \quad \bar{x} = \sqrt{\frac{3}{2\pi k}} \int_{-\infty}^{+\infty} x^2 e^{-\frac{3x^2}{2k_B T}} dx = \frac{k}{3}.$$

$$\therefore 3^2 = k/\bar{x}, \quad \therefore$$

$$W(x) dx = \frac{1}{\sqrt{2\pi k^2}} e^{-\frac{x^2}{2\bar{x}^2}} dx.$$

* 高斯分布可以推广到多维空间。

* 高斯分布对于小体积中 $n \gg n - \bar{n}$ 。

- 一般情况下，用泊松分布。

④ ④ 8天，但至清晨和傍晚，太阳光穿过多层大气才能发生散射，但蓝光早被大气吸收，只有漫射光能经穿透过来， \therefore 太阳 \Rightarrow 白光。

⑤ 对液体，至临界处

$$\langle I \rangle \propto \frac{1}{x} \sqrt{-\frac{V^4}{24kT} \left(\frac{\partial^3}{\partial V^3} \right)_T}^{-k}$$

与吸收系数比正常情况下大 k 倍。

液体透明的液体由于光吸收变成乳白色。

3.8.3.2 高斯分布

对任意粒子 $\alpha, X, \alpha x = X - \bar{X}$ ，高斯是独立变量 X 的 S ： $S = S(X)$ 。

$$\Delta S = S - \bar{S} = S(X) - S(\bar{X}) = \Delta S(X).$$

类似于体积情况 X 出现偏移的分布

$$W(x) dx \approx e^{\frac{\Delta S(x)}{k_B T}} dx.$$

且 \bar{x} 是常数。

$$\Delta S = \Delta S(0) + \frac{\partial S}{\partial x} \Big|_{x=0} x + \frac{1}{2} \frac{\partial^2 S}{\partial x^2} \Big|_{x=0} x^2 + \dots$$

3.8.3.3 附录：空间关联

在临界点，粒子和空间位置的浓度变化很强烈，意义上，由空间点，关联长度很长，不同空间的粒子之间的影响可以导致更强的关联。我的连续介质理论中已经指出 $\langle n(r) n(r') \rangle$ 与空间点的引入 $\langle n(r) n(r') \rangle$ 与 $\langle n(r) \rangle$ 和 $\langle n(r') \rangle$ 的关系。但线性响应理论没有指出 $\langle n(r) n(r') \rangle$ 与 $\langle n(r) \rangle$ 和 $\langle n(r') \rangle$ 的关系。在线的用连续介质理论方法到研究实际分子的密度关联函数。

且 $\langle n(r) n(r') \rangle = \langle n(r) \rangle \langle n(r') \rangle + \langle \Delta n(r) \Delta n(r') \rangle$

$$\begin{aligned} C(r, r') &= \langle (n(r) - \langle n(r) \rangle)(n(r') - \langle n(r') \rangle) \rangle \\ &= \langle \Delta n(r) \Delta n(r') \rangle. \end{aligned}$$

$$\langle \Delta n(r) \rangle = 0.$$

\therefore 只要 $\Delta n(r) \propto \Delta n(r')$ 是独立的，即 $C(r, r')$

$$= \langle \Delta n(r) \rangle \langle \Delta n(r') \rangle = 0 \Rightarrow$$
 无关。

$C(r, r') \neq 0$ ，则空间的浓度有关联。

考虑大的液体， $\langle \Delta n(r) \rangle = \bar{n}$ ，太无关。由物理意义， $C(r, r') = C(r-r')$ ，若垂直向同轴。

$$C(r-r') = C(|r-r'|) \text{，且两个无关。}$$

$\therefore \nabla^2 \vec{r} = 0$,

$$C(\vec{r}) = \langle \Delta n(\vec{r}) \Delta n(0) \rangle$$

$$\text{设 } \Delta n(\vec{r}) = \frac{1}{V} \sum_i \tilde{n}_i e^{i\vec{q} \cdot \vec{r}}$$

$$\Delta n^*(\vec{r}) = \Delta n(\vec{r}) \Rightarrow \tilde{n}_i^* = \tilde{n}_i$$

$$|\tilde{n}_i|^2 = \int d\vec{p} d\vec{P}' \langle \Delta n(\vec{r}) \Delta n(\vec{r}') \rangle e^{-i\vec{q} \cdot (\vec{r}-\vec{r}')}}$$

$$\begin{aligned} \langle |\tilde{n}_i|^2 \rangle &= \int d\vec{r} d\vec{P}' \langle \Delta n(\vec{r}) \Delta n(\vec{r}') \rangle e^{-i\vec{q} \cdot (\vec{r}-\vec{r}')} \\ &= V \int d\vec{R} \langle \Delta n(\vec{R}) \Delta n(0) \rangle e^{-i\vec{q} \cdot \vec{R}} = V C(\vec{q}). \end{aligned}$$

$$\therefore C(\vec{r}) = \frac{1}{V} \sum_i \langle |\tilde{n}_i|^2 \rangle e^{i\vec{q} \cdot \vec{r}}$$

$$\begin{aligned} \text{由 } \cancel{\text{只对 } T=0}, \quad &- (\Delta F + p\Delta V)/kT \\ \text{由 } W = W_{\max} e^{- (\Delta F + p\Delta V)/kT} &\stackrel{V \neq 0}{=} W_{\max} e^{- \Delta F/kT}. \\ \Delta F = \int (f - \bar{f}) d\vec{r}. & \end{aligned}$$

$f(\vec{r})$ 是单位体积 local Free energy. 若 $T \neq 0$, Δf 可得 Δn 为:

$$\Delta f = \frac{a}{2} (\Delta n)^2 - \frac{b}{2} (\Delta n). \quad \left(\int_{n=0}^{\infty} (n-\bar{n})^2 e^{-\frac{n}{kT}} \right)$$

($\cancel{\text{只对 } T=0}$), 由内能展开最低阶是 Δn .

Δf 对 n 有 Δf 在空间依赖. Δn 等于 0.

这是 Landau-Ginzburg 理论.

$$\langle |\tilde{n}_i|^2 \rangle = \int_{\vec{q}} \frac{d\vec{q}}{(2\pi)^3} |\tilde{n}_i|^2 W / \int_{\vec{q}} \frac{d\vec{q}}{(2\pi)^3} W. \quad (16)$$

$$\stackrel{\text{由}}{=} \int_{-\infty}^{+\infty} dq_1 |\tilde{n}_i|^2 W / \int_{-\infty}^{+\infty} dq_1 W \quad (\text{Gauss 分布})$$

$$= \frac{\sqrt{kT}}{a+bq^2}.$$

$$\begin{aligned} \therefore C(\vec{r}) &= \frac{kT}{V} \sum_i \frac{1}{a+bq^2} e^{i\vec{q} \cdot \vec{r}} \\ &= \Rightarrow kT \frac{1}{(2\pi)^3} \int d\vec{q} \frac{1}{a+bq^2} e^{i\vec{q} \cdot \vec{r}} \\ &= \frac{kT}{(2\pi)^3} \int d\vec{q} \frac{1}{a+bq^2} \int_0^{2\pi} d\theta e^{iqr \cos \theta} \\ &= \frac{kT}{4\pi b} \frac{1}{r} e^{-r/\lambda}, \quad \lambda = \sqrt{\frac{b}{a}}. \sim (T-T_c)^{1/2}. \end{aligned}$$

这 mean field 也是对. 具体表达式.

至 $\cancel{\text{只对 } T=0}$ 时, 我们讲了冲量型标积
标积, $D(\vec{q})$ 在对 \vec{q} 的平均值, 至 $\cancel{\text{只对 } T=0}$
至 $\cancel{\text{只对 } T=0}$, 这可以由 $\langle |\tilde{n}_i|^2 \rangle$ 推导.

由热力学, $a = \frac{1}{n} \left(\frac{\partial P}{\partial n} \right)_T$ (见书 570)

而到能级之 $\left(\frac{\partial P}{\partial n} \right)_T = 0 \therefore a = a_0(T-T_c)$.

$$\nabla n(\vec{r}) = \nabla \Delta n(\vec{r}) = \cancel{\frac{1}{V} \sum_i \tilde{n}_i^* e^{i\vec{q} \cdot \vec{r}}} = \frac{1}{V} \sum_i \tilde{n}_i^* e^{i\vec{q} \cdot \vec{r}}$$

$$= \frac{1}{V} \sum_i \tilde{n}_i^* i\vec{q} e^{i\vec{q} \cdot \vec{r}} = \frac{1}{V} \sum_i \tilde{n}_i^* (i\vec{q}) e^{-i\vec{q} \cdot \vec{r}}$$

$$(\nabla n(\vec{r}))^2 = \frac{1}{V} \sum_i \tilde{n}_i^* \tilde{n}_i^* i\vec{q} \cdot i\vec{q} e^{-i\vec{q} \cdot \vec{r}}.$$

$$\therefore \Delta f = \frac{1}{V} \sum_i \tilde{n}_i^* \tilde{n}_i^* \left(\frac{a}{2} + \frac{b}{2} \vec{q} \cdot \vec{q} \right) e^{-i\vec{q} \cdot \vec{r}}.$$

$$\begin{aligned} \Delta F &= \int d\vec{q} d\vec{P} \Delta f = \frac{1}{2V} \sum_{\vec{q}, \vec{P}} \tilde{n}_i^* \tilde{n}_i^* \left(\frac{a}{2} + \frac{b}{2} \vec{q} \cdot \vec{q} \right) \delta_{\vec{q}, \vec{P}} \\ &= \frac{1}{2V} \sum_{\vec{q}} (a + b\vec{q} \cdot \vec{q}) |\tilde{n}_i|^2. \end{aligned}$$

$$\therefore W = W_{\max} \exp \left(- \frac{1}{2kT} \sum_{\vec{q}} (a + b\vec{q} \cdot \vec{q}) |\tilde{n}_i|^2 \right)$$

$$= W_{\max} \prod_{\vec{q}} \exp \left(- \frac{a + b\vec{q} \cdot \vec{q}}{2kT} |\tilde{n}_i|^2 \right).$$

这式子表明, 宏观性质在空间是 local 的. 不同
方向 \vec{q} 之间是独立的. 是 Gauss 分布. (小许修改).

3.8.1. 随机运动: 随机坐标和布朗运动

关于布朗运动, 我们已经了解到不少故事. 说的是在
荷兰植物学家, 微观生物学家随机运动. 最早由
斯托克斯通过年正确地解释了布朗运动. 对分子
相互性, 或说颗粒与分子间的作用力作用. 现在,
“布朗运动”代表广义的“微粒”在广泛的随机
“场”作用下随机运动. 是一类重要的物理现象.

3.8.1. 随机方程

用随机方程可以对布朗运动作一些预言和
预测. ~~随机方程~~ 布朗运动 $\sim 10^{-5} \text{--} 10^{-4} \text{ cm}$
~~随机方程~~ 大小. 受 ~~随机方程~~ 两种力作用

① 确定性驱动力, 如电, 磁力, 引力, 流体-粘滞力,
等.

② 随机引起碰撞、相互作用, 例如 $10^{-4} \text{ cm}^2/\text{sec}$,
液体与速率 10^{-2} cm/sec , 对碰撞次数为 $10^{22-4}/\text{秒}$
气体与速率 10^{-3} cm/sec , “ ” “ ” “ ” “ ” “ ”
∴ $\sim 10^{-18} \text{ Sec}$ 为直接打靶时间. 可以这种
方式随机引起 10^{-5} 起.

3. 布朗运动满足牛顿第二定律

$$m \frac{d\vec{u}}{dt} = \vec{F}_0 + \vec{F}_1(t) + \vec{F}_2(t). \quad (\text{考虑重力})$$

例如，考虑在水平方向(x)上的投影，运动方程简化，
中只有粘滞力 $-\alpha u_x \equiv -\alpha u$, $F_1(t) = X(t)$.

$$m \frac{du}{dt} = -\alpha u + X(t)$$

这是微分方程.

$$m \frac{dx}{dt} = -\alpha x \frac{dx}{dt} + X(t),$$

$$\frac{m}{2} \frac{d^2x^2}{dt^2} - m \left(\frac{dx}{dt} \right)^2 = -\frac{\alpha}{2} \frac{d^2x^2}{dt^2} + X(t)$$

对大数布朗运动求解平均

$$\frac{m}{2} \frac{d^2}{dt^2} \langle x^2 \rangle - m \langle \ddot{x} \rangle = -\frac{\alpha}{2} \frac{d^2 \langle x^2 \rangle}{dt^2} + \langle X(t) \rangle = 0.$$

由能的泛化, $m \bar{v}^2 = kT$.

$$\frac{d^2}{dt^2} \langle x^2 \rangle + \frac{1}{\tau} \frac{d}{dt} \langle x \rangle - \frac{2kT}{m} = 0, \quad \tau = \left(\frac{\alpha}{m} \right)^{-1}$$

$$\Rightarrow \langle x^2 \rangle = \frac{2kT}{m} t + C_1 e^{-t/\tau} + C_2.$$

若且 $t=0$, 则 $\langle x \rangle$ 和 $\frac{d}{dt} \langle x \rangle = 0$. 则

$$\langle x^2 \rangle = \frac{2kT}{m} \left(\frac{t}{\tau} - (1 - e^{-t/\tau}) \right)$$

$$\begin{aligned} \therefore n(x, t+\tau) &= \int_{-\infty}^{+\infty} f(x-x', \tau) n(x', t) dx' \\ &= \int_{-\infty}^{+\infty} f(\tilde{x}, \tau) n(x-\tilde{x}, t) d\tilde{x} \\ x, \tilde{x}, x' \quad \text{满足:} \quad &\int_{-\infty}^{+\infty} \tilde{x} f(\tilde{x}, \tau) d\tilde{x} = 1 \\ \tilde{x} = x-x' &f(x, \tau) = f(-x, \tau). \end{aligned}$$

又很慢, 则

$$n(x, t+\tau) = n(x, t) + \tau \frac{\partial n}{\partial t} + \frac{1}{2} \tau^2 \frac{\partial^2 n}{\partial x^2} + \dots$$

$$n(x-3\tau, t) = n(x, t) - 3 \frac{\partial n}{\partial x} + \frac{1}{2} 3^2 \frac{\partial^2 n}{\partial x^2} + \dots$$

设 \oplus $n(x-3\tau, t)$ 在 τ 大时很快, 则

$$n(x, t+\tau) \approx n(x, t) + \tau \frac{\partial n}{\partial t} + \frac{1}{2} \tau^2 \frac{\partial^2 n}{\partial x^2} + \dots$$

$$\int_{-\infty}^{+\infty} f(\tilde{x}, \tau) \left(n(x, t) - \frac{3}{2} \frac{\partial n}{\partial x} + \frac{1}{2} 3^2 \frac{\partial^2 n}{\partial x^2} \right) d\tilde{x}$$

$$= n(x, t) + \frac{1}{2} \langle \tilde{x}^2 \rangle \frac{\partial n}{\partial x^2}$$

$$\frac{\partial n}{\partial t} = D \frac{\partial^2 n}{\partial x^2}, \quad D = \frac{\langle \tilde{x}^2 \rangle}{20} \quad \text{扩散系数.}$$

∴ 布朗运动是扩散过程.

$$\text{若 } t \ll \tau, \text{ 则 } \langle x \rangle = \int \frac{2kT\tilde{x}}{m} \quad (\text{)}$$

$$\left(\frac{2kT}{m} - (X - X_0 + \frac{1}{2} \frac{dX}{dt} \tau) \right) = \frac{kT}{m} \tau^2 = \langle x \rangle \tau^2$$

这就是说, 当观察时间 $t \ll \tau$ 时, 布朗运动服从

运动. 而 $t \gg \tau$,

$$\langle x^2 \rangle \approx 2 \frac{kT}{m} \tau = \frac{2kT}{\alpha} t \equiv 2Dt.$$

爱因斯坦通过计算 $\langle x^2 \rangle \propto t$ 为分子扩散
附录. (因为计算时水中大分子 $\sim 10^{-5} \text{ cm m}^{-2}$,
 $\tau \sim 10^{-7} \text{ s}$, 这些速率比记录一个粒子位置
在给定时间要小得多)

3.8.2 布朗运动扩散

布朗运动用微粒扩散解释地可以更好地
地说明其他类似的过程, 而且可以推广到各种
过程.

设 $n(x, t) dx$ 是在时刻 t 在 x 与 $x+dx$ 之间
且 x 和 $x+dx$ 内 Brownian 粒子数
 $n(x, t)$ 是随时间变化的, $\int f(x, t) dx$ 是在时刻
 t 由于 $x \rightarrow x+dx$ 时被转移进 $(x, x+dx)$ 内
几率. 称为转移率.

上面方程地写成

$$\frac{\partial}{\partial t} n(x, t+\tau) = -D \frac{\partial^2}{\partial x^2} (x, t+\tau) = 0$$

$$\int_{-\infty}^{+\infty} \left[\frac{\partial}{\partial t} f(x-x', t') - D \frac{\partial^2}{\partial x^2} f(x-x', t') \right] n(x', t) dx' = 0$$

$$\therefore \frac{\partial}{\partial t} f(x-x', t) - D \frac{\partial^2}{\partial x^2} f(x-x', t) = 0$$

$$\frac{\partial}{\partial t} f(x, t) - D \frac{\partial^2}{\partial x^2} f(x, t) = 0.$$

设 $f(x, 0) = 0$ 且 $\lim_{x \rightarrow \pm\infty} f(x, 0) = 0$

由 $\int_{-\infty}^{+\infty} f(x, 0) dx = 1$ 和 $f(x, 0) = 0$, if $x \neq 0$,

$$\therefore f(x, 0) = \delta(x).$$

$$\therefore f(x, t) = \frac{1}{2\pi Dt} e^{-x^2/4Dt}.$$

$\Rightarrow \langle x^2 \rangle = 2Dt$. 这是爱因斯坦
的结果.

以后将证明, 这方程是随机过程
Master 方程 对 Brown 运动的解
例.

讲义方程 \Leftrightarrow Master 方程, 因为分子数, 一旦受到碰撞或散失,
将随机地受到新的运动方程. 由于是 Schrödinger 方程, 对于没有碰撞或散失
碰撞-运动方程. 后者更易于推广出扩散方程.

§8.8.3 布朗运动中时间函数

在讲惯性论时，我们看到是能函数可以
空间和时间一起极。在 Brownian 运动中，随和 $\vec{F}(t)$
被设成 $\vec{F}(t)$ 是时间无关的。但布朗运动 $\vec{F}(t)$ 是 $m \vec{v}(t)$
是取什么样子呢？为此，我们考虑 $\langle u(t) \rangle$ 。

$$\text{胡方程中取 } u(t) = g(t) e^{-tk}$$

$$\frac{dg(t)}{dt} e^{-tk} = -\frac{g(t)}{\tau} + \frac{x(t)}{m}$$

$$\Rightarrow \frac{dg(t)}{dt} = e^{tk} (x(t)/m) = A(t)$$

$$\begin{aligned} \langle g(t) \rangle e^{-tk} &= e^{-tk} \int_0^t e^{t''k} A(t'') dt' \\ u(t) &= e^{-tk} \int_0^t dt' \int_{t'}^t dt'' e^{(t-t'')k} A(t') A(t'') \end{aligned}$$

$$u(t) = u(0) e^{-tk} + e^{-tk} \int_0^t e^{t''k} A(t'') dt'$$

$$\begin{aligned} \tilde{u}(t) &= u(0) e^{-2tk} + 2u(0) e^{-tk} \int_0^t e^{t''k} A(t'') dt' \\ &\quad + e^{-tk} \int_0^t dt' dt'' e^{(t-t'')k} A(t') A(t'') \end{aligned}$$

$$\langle u^2(t) \rangle = u(0)^2 e^{-2tk} + e^{\frac{\tau}{m}} (1 - e^{-2tk})$$

$$t \rightarrow \infty, \langle u^2(\infty) \rangle = kT/m,$$

$$\Rightarrow C = \frac{\sqrt{kT}}{mc}$$

$$\langle u^2(t) \rangle = u(0)^2 e^{-2tk} + \frac{kT}{m} (1 - e^{-2tk})$$

§8.8.4 电场-耗散论

我们在前面已经对耗散力的强度与耗散系数
进行了讨论。耗散力强度是空间的。因此，我们
可以用时间平均耗散系数来表示。对 Brownian
运动， $\tau = (\frac{d}{m})^2 \Rightarrow d = \frac{m}{\tau} = \frac{m^2}{2kT} C$ 。

$$= \frac{m^2}{2kT} \int_{-\infty}^{+\infty} dt C \delta(t)$$

$$= \frac{m^2}{2kT} \int_{-\infty}^{+\infty} dt \langle A(0) A(t) \rangle$$

$$= \frac{m^2}{2kT} \int_{-\infty}^{+\infty} ds \langle A(t) A(s) \rangle$$

即随和 $\vec{A}(t)$ 与随和 $\vec{A}(s)$ 的相关
为零 - 耗散论。

$$\langle u^2(t) \rangle = u(0)^2 e^{-2tk}$$

$$+ e^{-2tk} \int_0^t dt' dt'' e^{(t-t'')k} \langle A(t') A(t'') \rangle$$

$\therefore \tilde{t} = t + t_0, s = \frac{t-t_0}{\sqrt{2}}$, 以 t_0 为常数

$$e^{(t-t')k} \langle A(t) A(t') \rangle = e^{t k} C(s)$$

$$dt' dt'' = dt ds$$

: 因为

$$\begin{aligned} I &= \int dt' dt'' \dots \\ &= \int_0^{t_0} dt' \int_{-t'}^{t-t'} ds C(s) ds \\ &\quad + \int_{t_0}^{t-t'} dt' \int_{-t+t'}^{t-t'} ds C(s) ds \end{aligned}$$

对 Brownian 运动， $C(s) = C \delta(s)$ 。
同时，(Markov 过程)， $C(s) = C \delta(s)$ 。

$$\therefore I = \int_0^{t_0} dt' e^{\sqrt{2} t' k} = C \frac{t_0}{\sqrt{2}} (e^{2t_0 k} - 1)$$

运动论的扩散系数 (耗散)

$$D = kT/\tau = \frac{1}{2} \int_{-\infty}^{+\infty} du \langle u(t) u(t+s) \rangle$$

在耗散论中 D 由层-层扩散
决定的该量，此时这里 $u(t)$ 是时间函数。

在 Kubo 线性论中，扩散系数可以
是时间和空间的函数。

§8.8.5 Markov 过程

§8.8.5 布朗运动的物理过程：

电路中的电荷和电压的性质。



$$L \frac{dI(t)}{dt} = -RI(t) + V(t)$$

\therefore 若外电压为 0，即电池失电，

在一直流下，仍存在电压 $V(t)$ 和电流
 $I(t)$ ， $\langle I(t) \rangle = \langle V(t) \rangle = 0$ 。

这时电流声不仅随电压方程且
有布朗运动形式

$$I(t) \leftrightarrow u(t)$$

$$L \leftrightarrow h$$

$$R \leftrightarrow \alpha$$

$$V(t) \leftrightarrow X(t).$$

作练习, 请参考教材书 - (11.6.6)-(11.6.7).

在电路中, 请 请 (即时间 \sim Fourier 变换) 等
式改写为 Brownian motion 形式. 令 $V(t)$
in Fourier 变换.

$$\tilde{V}(w) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} V(t) e^{-iwt} dt$$

(电场噪声等效变换)
 $\langle V(t) V(t+s) \rangle = \frac{1}{4\pi} \int dw \tilde{V}(w) e^{iwt+iws}$

$$\Leftrightarrow \langle V(t) V(t+s) \rangle = C S(s)$$

$$\frac{1}{4\pi} \int dw dw' \langle \tilde{V}(w) \tilde{V}(w') \rangle e^{iwt+iw'(t+s)} = C S(s)$$

$$= C \int dw e^{iws}$$

(1) 随温度 T , $=$ 电噪声

(2) $\propto R$, 噪声无电噪声. (3) $\langle \bar{V}^2 \rangle \neq 0$, 即
 $\langle \bar{V} \rangle \neq 0$, (4) $S(v)$ 为常数, 为 white noise . (类似白光, 各种频率成分
随机分布).

这种噪声又称为 Johnson noise, $S(v) = 4kTR$
称为 Nyquist 定理

§8.8.7 shot noise (颗粒噪声)

另一种电噪声称为 shot noise. 由灯丝发射电子
到达阳极而引起一大噪声. (见图)

* 电子发射是随机的.

* 电子从发射到阳极的时间极短, 相当于瞬时电流.

$n(t)$ 为单位时间内的发射的电子数. 此时

无附近发射粒子引起的电流为

$i(t-t')$. $i(t-t')$ 在 $t-t'$ 大时很快衰减到 0. 重积分

没有 $\overline{i^2}$, 电子发射引起电流是

$$I(t) = \int_{-\infty}^{+\infty} dt n(t) G(t-t').$$

$$\begin{aligned} \text{④ } \langle \tilde{V}(w) \tilde{V}(w') \rangle &= \langle |\tilde{V}(w)|^2 \delta(w+w') \rangle \quad (\because) \\ &= \frac{1}{4\pi} \int dw dw' \langle |\tilde{V}(w)|^2 \rangle \delta(w+w') e^{iws} \\ &= \frac{1}{4\pi} \int dw \langle |\tilde{V}(w)|^2 \rangle e^{iws} \end{aligned}$$

$$\Leftrightarrow \langle |\tilde{V}(w)|^2 \rangle = C. \propto w^2.$$

$$\text{即 } K(s) = \langle V(t) V(t+s) \rangle$$

$$= \int_{-\infty}^{+\infty} dw \tilde{K}(w) e^{iws}$$

$$\Rightarrow \tilde{K}(w) = \frac{C}{2\pi} = \frac{2kTR}{2\pi} = \frac{kTR}{\pi}$$

$$\therefore \bar{V}^2 = \overline{V^2} = K(0) = \int_{-\infty}^{+\infty} \tilde{K}(w) dw$$

$$= 2 \int_0^\infty \tilde{K}(0) dw = \int_0^\infty 4\pi \tilde{K}(0) dw$$

$$(w=2\pi v) \Rightarrow \int_0^\infty dv S(v)$$

$$\therefore S(v) = 4kTR \text{ 是电噪声的 } \frac{1}{v^2} \text{ 分布}$$

(1) $\langle n \rangle$ 为平均值, 则

$$\langle I(t) \rangle = \int_{-\infty}^{+\infty} \langle n \rangle i(t-t') dt$$

$$= \bar{n} \int_{-\infty}^{+\infty} i(t-t') dt = \bar{n} \cdot e$$

($i(t-t') = \frac{dG(t-t')}{dt}$) 由于积分, 因此 $i(t-t') \approx$
集中至 $t=0$ 附近. \therefore 能源为一个电子-电荷

$$\Delta I = I(t) - \langle I \rangle = \int_{-\infty}^{+\infty} [n(t) - \bar{n}] i(t-t') dt$$

$$\langle \Delta I^2 \rangle = \int dt dt' \langle (\Delta n(t)) (\Delta n(t')) \rangle$$

$$i(t-t') i(t-t')$$

由于 $\Delta n(t)$ 为 Shot noise, 且 $\Delta n(t)$ 随机

$$\therefore \langle \Delta n(t) \Delta n(t') \rangle \propto \delta(t-t')$$

(平稳地, $\langle \Delta n(t) \Delta n(t') \rangle = \langle n \rangle \delta(t-t')$, $\langle n \rangle$

物理意义为从 t 到 t' 的平均电子数

$$n \propto t, \therefore \langle n^2 \rangle = \bar{n}^2$$

$$\langle \Delta I^2 \rangle = \bar{n} \int_{-\infty}^{+\infty} |G(t-t')|^2 dt = \bar{n} \int_{-\infty}^{+\infty} |G(t)|^2 dt$$

Campbell 定律

请教：

$$G(t) = \int S(\omega) e^{i\omega t} d\omega$$

$$\int_{-\infty}^{+\infty} |A(t)|^2 dt = 4\pi \int_{-\infty}^{+\infty} |S(\omega)|^2 d\omega$$

$$\therefore \langle |I|^2 \rangle = 4\pi \bar{n} \int_0^{+\infty} |S(\omega)|^2 d\omega.$$

对 \$I\$ 的方程仪，假设放大器，\$S(\omega)\$ 是在频率 \$\omega\$ 处的功率，\$\therefore\$

$$\langle |I|^2 \rangle = 4\pi \bar{n} |S(\omega)|^2 d\omega.$$

另一方面，\$S(\omega) = \frac{1}{2\pi} \sum_{t=0}^{+\infty} G(t) e^{i\omega t} dt

若 \$\omega t \ll 1\$，\$e^{-i\omega t} \approx 1\$。

$$S(\omega) \approx \frac{1}{2\pi} \int_0^{+\infty} G(t) dt = \frac{\bar{G}}{2\pi}.$$

$$\therefore \langle |I|^2 \rangle = \bar{n} \bar{G}^2 \Delta \omega \quad (\Delta \omega = 2\pi \Delta \omega).$$

$$= 2\bar{G}\bar{I}\Delta \omega \quad (\bar{I} = \bar{n}\bar{G}).$$

由 \$\langle I \rangle\$, \$\langle |I|^2 \rangle\$ 和 \$\Delta \omega\$ 在系统中是确定的，可以用来测 \$\bar{G}\$。在射频和微波中，shot noise 中发射带电粒子是 quasi-particle，\$n\$ 及 \$e\$ 都应由 \$\bar{n}\$ 及 \$\bar{G}\$ 代替。

可测得的有。

(iii) 作子推定时，\$P_n(x_i; t_i; t_b)\$ 时¹⁸

$$\text{无}, \quad P_n(x_i; t_i; t_b) = P_n(x_i; t_i; t_b).$$

$$(iv) \quad P_1(x_i; t_i) P_{11}(x_i; t_i; x_i; t_i) = P_2(x_i; t_i; x_i; t_i).$$

$$(v) \quad \int P_{11}(x_i; t_i; x_i; t_i) dx_i = 1.$$

16: $\int P_2(x_i; t_i; x_i; t_i)$

$$\begin{aligned} & \int \int P_1(x_i; t_i) P_{11}(x_i; t_i; x_i; t_i) dx_i dx_i \\ &= \int \int P_2(x_i; t_i; x_i; t_i) dx_i = \int P_2(x_i; t_i) dx_i = 1 \end{aligned}$$

$$\int P_1(x_i; t_i) \left[\int dx_i P_{11}(x_i; t_i; x_i; t_i) \right] dx_i$$

由图及推论，得

$$\begin{aligned} & P_3(x_i; t_i; x_i; t_i; x_i; t_i) \\ &= P_2(x_i; t_i; x_i; t_i) P_{21}(x_i; t_i; x_i; t_i; x_i; t_i) \\ &= P_1(x_i; t_i) P_{11}(x_i; t_i; x_i; t_i) P_{11}(x_i; t_i; x_i; t_i) \end{aligned}$$

3.8.4 定方程和福克-普朗克方程

3.8.4.1 Master eq. and Fokker-Planck eq.

定方程是分布函数 (也是) 一般性方程。Generally, 这是一个很复杂的方程。这里我们只研究 Markov 过程中的方程。Markov 过程是指分子在 t 时刻的位置只与 t 时刻最近的前一时刻的物理状态有关，而更早的物理状态都没有影响。例如，在布朗运动中的速度 \$u(t)\$, Johnson noise 中的电流 \$I(t)\$。设 \$x(t)\$ 为随机变量 \$(u(t), I(t), \dots)\$, \$P_i(x_i, t_i)\$ 表示在 \$t_i\$ 时刻取 \$x_i\$ 时的几率，\$P_{ij}(x_i, t_i; x_j, t_j)\$ 表示在 \$t_i\$ 时刻取值 \$x_i\$，至 \$t_j\$ 取 \$x_j\$ 的联合几率，\$\dots, P_n(x_1, t_1, \dots, x_n, t_n)\$。条件几率 \$P_{ij}(x_i, t_i; x_j, t_j)\$ 为给定 \$x_i\$ 时 \$x_j\$ 在 \$t_j\$ 时的条件下，至 \$t_j\$ 时刻取值为 \$x_j\$ 的几率。\$P_{ijk}(x_i, t_i; x_j, t_j; x_k, t_k)\$ 表示在 \$x_i\$ 及 \$x_j\$ (\$1 \leq i \leq k\$) 时取 \$x_k\$ 在 \$t_k\$ 时的条件下，在 \$t_{k+1}\$ (\$1 \leq j \leq k\$) 时刻取值 \$x_{k+1}\$ 的几率。

$$(i) \quad \int P_i(x_i, t_i) = 1.$$

$$(ii) \quad \int \underbrace{P_n(x_1, t_1; \dots; x_n, t_n)}_{\propto} dx_n = P_{n-1}(x_1, t_1; \dots; x_{n-1}, t_{n-1})$$

我们用对称于语言来理解 -1:

$$P_i(x_i, t_i) = |\psi_i(x_i, t_i)|^2 \quad (\text{见前面})$$

$$P_2(x_i, t_i; x_i, t_i) = |\psi_2(x_i, t_i; x_i, t_i)|^2 \dots$$

条件几率：\$P_{ij}(x_i; x_j, t_i)\$ 为理解为 \$|\psi_i(x_i, t_i)|^2 \times |\psi_j(x_i, t_i)|^2\$

$$\rightarrow = |\psi_i(x_i)|^2 \times |\psi_j(x_i)|^2 = |\psi_i(x_i, t_i)|^2$$

初态 \$x_i + x_j \rightarrow\$ 等于末态

$$P_{ij}(x_i, t_i; x_j, t_j) = \left| \psi(x_i, t_i) \psi(x_j, t_j) \right|^2$$

\$\psi(x_i, t_i)\$ 是 \$\psi_i(x_i, t_i)\$

\$\psi(x_j, t_j)\$ 是 \$\psi_j(x_j, t_j)\$

这样，我们把很容易理解推论 (i) - (v)。

~~由图及推论，得~~

$$P_3(x_i, t_i; x_i, t_i; x_i, t_i)$$

$$= P_2(x_i, t_i; x_i, t_i) P_{21}(x_i, t_i; x_i, t_i; x_i, t_i)$$

$$= P_1(x_i, t_i) P_{11}(x_i, t_i; x_i, t_i) P_{11}(x_i, t_i; x_i, t_i)$$

~~且 \$t_i < t_2 < t_3\$，所以~~

$$P_2(x_i, t_i; x_i, t_i) = \int dx_i P_{11}(x_i, t_i; x_i, t_i) P_{11}(x_i, t_i; x_i, t_i)$$

以 $P_{k|x}(x_1, \dots, x_{n+k} | x_{n+k+1}, \dots)$ 表之
 t_{k+1}, \dots, t_{n+k} 时刻 $\geq t_1, \dots, t_k$ 时刻 \rightarrow 无关.

四 马尔可夫过程:

$$P_{n-y_1}(x_1, \dots, x_{n+m} | x_{n+m}) \\ = P_{y_1}(x_{n+m} | x_n), \text{ 即 } t_n \text{ 时刻} \geq t \\ t_{n-1} \text{ 时刻有关. 即 } P_{y_1}(x_{n+m} | x_n) \text{ 有 } P_1(x_1, t) \\ \text{ 和 } P_2 P_3(x_1, x_2, t) \text{ 无关. 由}$$

$$P_3(x_1, t_1; x_2, t_2; x_3, t_3) \\ = P_2(x_1, t_1; x_2, t_2) P_{y_1}(x_1, t_1; x_2, t_2 | x_3, t_3) \\ = P_1(x_1) P_{y_1}(x_1, t_1) P_{y_1}(x_2, t_2 | x_3, t_3). \quad \therefore \text{即马尔可夫} \\ \text{过程中, } x_3 \text{ 无关}$$

$$P_2(x_1, t_1; x_3, t_3) = \frac{P_1(x_1)}{P_1(x_1)} \int dx_2 P_{y_1}(x_1, t_1; x_2, t_2) P_{y_1}(x_2, t_2) \\ P_2(x_1, t_1; x_3, t_3) = \int dx_2 P_{y_1}(x_1, t_1; x_2, t_2) P_{y_1}(x_2, t_2; x_3, t_3)$$

Markov 过程 m. Smoluchowski-Chapman
 - Kolmogorov 方程.

$x_1 \rightarrow$ 离散取值 m 概率. $[1 - \int W(x_1, x) dx]$ 是
 不发生跃迁概率. $\cancel{\text{是}}$
 $\therefore [1 - \int W(x_1, x) dx] \delta(x_1 - x_2)$ 是不发生从 x_1 到
 跃迁. 离子从 x_1 m 概率是 $\tau W(x_1, x_2)$.
 $[1 - \int W(x_1, x) dx] \delta(x_1 - x_2)$ 是不发生从 x_1 到
 保持至 $x_2 = x_1$ m 概率, $\delta \tau W(x_1, x_2)$ 称为, $\tau x_1 = x_2$
 和 $x_1 \neq x_2$ m 概率之和.

$$P(x_1, t | x_n, t+\tau) = [1 - \int W(x_1, x) dx] \delta(x_1 - x_2) + W(x_1, x_2) \tau \\ = \delta(x_1 - x_2) - \tau \int W(x_1, x) dx \cdot \delta(x_1 - x_2) + W(x_1, x_2) \tau. \\ \text{代入 } \frac{\partial P(x_1, t)}{\partial t} = \frac{1}{\tau} \left[\int P(x_1, t) \delta(x_1 - x_2) \delta(x_1) \right. \\ \left. - \int P(x_1, t) \delta(x_1 - x_2) dx_1 \right] \\ = \int P(x_1, t) W(x_1, x_2) - \int P(x_1, t) W(x_2, x_1) dx_1 \\ = \int [W(x_1, x_2) P(x_1, t) - P(x_2, t) W(x_2, x_1)] dx_1. \\ \text{Master eq.}$$

定理 23 Markov chain, 找到 $P_j(x_i, t_i)$ $P(x_i, t_i)$

$$\frac{\partial P(x_i, t_i)}{\partial t} = \lim_{\tau \rightarrow 0} \frac{P(x_i, t_i + \tau) - P(x_i, t_i)}{\tau} \\ \frac{\partial P(x_i, t_i)}{\partial t} = \lim_{\tau \rightarrow 0} \frac{1}{\tau} \left\{ \int P(x_i, t_i) \right. \\ \left. P(x_i + \tau, t_i + \tau) - P(x_i, t_i) \right\}$$

由 $P(x_i, t_i + \tau) = P(x_i, t_i)$, $t_i = t$, 由图 (iv),

$$P(x_i, t + \tau) = \int P(x_i, t) P(x_i + \tau | x_i, t + \tau) dx$$

$$\frac{\partial P(x_i, t)}{\partial t} = \int P(x_i, t) \frac{\partial P(x_i + \tau | x_i, t + \tau)}{\partial t} dx$$

$$\frac{\partial P(x_i, t)}{\partial t} = \lim_{\tau \rightarrow 0} \frac{P(x_i, t + \tau) - P(x_i, t)}{\tau}$$

$$\frac{\partial P(x_i, t)}{\partial t} = \lim_{\tau \rightarrow 0} \frac{1}{\tau} \int P(x_i, t) [P(x_i + \tau | x_i, t + \tau) - P(x_i, t + \tau | x_i, t)] dx$$

$$\text{R } \tau = 0, P(x_i, t) = \int P(x_i, t) P(x_i + \tau | x_i, t) dx$$

$$\Rightarrow P(x_i + \tau | x_i, t) = \delta(x - x')$$

即 $W(x_i, x_i) \approx \tau + \tau + \text{time interval}$, x 取值 x_i
 在 x_i m 经过中单位时间 m 跳迁概率.

$\therefore \tau W(x_i, x_i) \int W(x_i, x) dx$ 是 τ 的跳迁概率

主方程 m 一阶表示从其他态跃迁到
 x_m m 概率密度; 第二阶表示从 x_m 跳迁到其他态
 m 概率密度. 在链子中, 既有因 m 跳迁 m 动
 学机制, 也有涉及子链子 m 跳迁. 是普遍的.

下面举一个例子: 对于分子系统. (F. Schwab)
 密度矩阵: $P(t) = \sum_i W_i(t) |i\rangle \langle i|$.

$H = H_0 + V, \quad H_0 |i\rangle = E_i |i\rangle, \quad F_i |i\rangle$

$F_i |i\rangle = F_i |i\rangle$ 是守恒量. V 是微扰哈密顿.

$U(t)$ 是时间 m 波函数

$$P(t+\tau) = \sum_i W_i(t) U(t) |i\rangle \langle i| U^\dagger(t) \quad (\sum_j |j\rangle \times j |i\rangle = 1) \\ = \sum_i \sum_j W_i(t) |j\rangle \langle j| U(t) |i\rangle \langle i| U^\dagger(t) \cancel{|k\rangle \langle k| U^\dagger(t) |k\rangle} \\ = \sum_i \sum_j W_i(t) |j\rangle \langle j| U(t) |i\rangle \langle i| U^\dagger(t)$$

$$\therefore U_j(t) = \langle j | U(t) | i \rangle$$

取随机相近 m, 即忽略非对角项贡献,

$$P(t+\tau) \approx \sum_i \sum_j W_i(t) |j\rangle \langle j| U_{ij}(t) U_{ji}^\dagger(t).$$

$$\equiv \sum_j W_j(t+\tau) |U_{j,i}(t)|^2$$

$$\text{即 } W_j(t+\tau) = \sum_i W_i(t) |U_{j,i}(t)|^2$$

$$\therefore W_j(t+\tau) - W_j(t) = \sum_i (W_i(t) - W_j(t)) |U_{j,i}(t)|^2$$

(∵ $\sum_i |U_{j,i}(t)|^2 = 1$) ($i=j$, $|U_{j,j}(t)|^2$ 不为 0)
出现重叠)

由 $|U_{j,i}|^2$, 用微扰论, (Fermi Golden rule)

$$|U_{j,i}|^2 = \frac{1}{\hbar} \left(\frac{\sin \omega_{j,i} \tau}{\omega_{j,i}} \right)^2 |\langle j | V | i \rangle|^2$$

$$\approx \tau \frac{2\pi}{\hbar} \delta(E_i - E_j) |\langle j | V | i \rangle|^2$$

$$W_{ij} = E_i - E_j / \hbar. \quad (\cancel{E_i - E_j / \hbar} \rightarrow \frac{1}{\hbar})$$

$$(\approx (E_i - E_j) \tau \ll 1, \tau \gg 1/\Delta E \quad \Delta E \text{ 很大})$$

$$\text{由 } \frac{W_j(t+\tau) - W_j(t)}{\tau} \Big|_{\tau \gg 0} = \frac{d W_j(t)}{d t}$$

$$\sum_i (W_i(t) - W_j(t)) \frac{2\pi}{\hbar} \delta(E_i - E_j) |\langle j | V | i \rangle|^2.$$

得:

$$\frac{\partial P(x,t)}{\partial t} = \int_{-\infty}^{+\infty} W(x, z) P(x, t) dz$$

$$- \int z \frac{\partial}{\partial x} [W(x, z) P(x, t)] dz + \frac{1}{2} \int z^2 \frac{\partial^2}{\partial x^2} [W(x, z) P(x, t)] dz$$

$$- \int_{-\infty}^{+\infty} W(x, -z) P(x, t) dz$$

$$- \int_{+\infty}^{-\infty} W(x, z') P(x, t) dz' \quad ||$$

$$\therefore \frac{\partial P(x,t)}{\partial t} + \frac{\partial}{\partial x} [\alpha_1(x) P(x,t)] = \frac{1}{2} \frac{\partial^2}{\partial x^2} [\alpha_2(x) P(x,t)]$$

$$(\alpha_1(x) = \int z^n W(x, z) dz, n \text{ 很大})$$

Fokker-Planck eq.

$\lim_{n \rightarrow \infty} \alpha_1(x) = 0, \alpha_2(x) = \text{const.}$ 由 F-P 方程

相当于 ~~Brownian motion~~ Brownian motion in f' 空间。

这里 \sum_i 表示对 E_i 和 f_i 求和。

$$\sum_{E_i} \rightarrow \int dE_i \delta n(E_i), \quad n(E_i) = D \delta E$$

$$\text{由 } \frac{dW_{E_i, F_i}(t)}{dt} = \sum_{E_j} (W_{F_j, F_i} - W_{E_j, F_j})$$

$$\left(\frac{2\pi}{\hbar} n(E_i) |\langle F_j | V | E_j \rangle|^2 \right)$$

$$P_{E_j, F_j, F_i} = P_{E_j}(F_j, F_i).$$

§ 8.1.2 Fokker-Planck eq.

分子的 x 可以选择取值, $W(x', x)$ 是随 $|x' - x|$ 很快衰减的函数。设 $z = x - x'$ 是小量, $W(x', x) = W(x-z, x)$

$$= W(\frac{x+z}{2}, x-z) \approx W(x, -z).$$

$$\text{于是 } \frac{\partial P(x,t)}{\partial t} = \int [W(x-z, z) P(x-z, t) - W(x, z) P(x, t)] dz$$

$$= \int [W(x-z, z) P(x-z, t) - W(x, -z) P(x, t)] dz$$

$$\text{展开 } W(x-z, z) P(x-z, t) = W(x, z) P(x, t) - z \frac{\partial}{\partial x} [W(x, z) P(x, t)] + \frac{1}{2} z^2 \frac{\partial^2}{\partial x^2} [W(x, z) P(x, t)] + \dots$$

第九章 统计物理中计算方法简介

- Numerical Simulation in Statistical Physics, Pascal Viot
<http://www.lptmc.jussieu.fr/user/viot/COURS/simulation.pdf>
- 分子模拟 陈正隆
- 统计物理中的蒙特卡罗模拟方法, Binder等
- 以密度泛函为代表的第一性原理计算是计算物理课的主要内容, 这里不讲
- AI正在深刻地影响计算物理, 但由于我学识的原因, 本课程不讲
- 量子计算; 经典-量子计算混合算法, 我们不讲

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引言

- 计算机技术的进步各位可能比我了解更多。这使得计算物理已经成为连接理论物理和实验物理的**桥梁或独立检验的第三方**
- 计算物理方法可以作为一个**独立研究工具**。例如, 很多重要的物理模型是没有解析严格解或可控近似解的。数值模拟可以提供对模型物理性质定量或定性的了解, 例如, **密度矩阵重整化群**计算可以非常精确地计算一些凝聚态一维强关联电子系统的基态; **精确对角化**计算可以得到较小的有限体系精确性质; **变分Monte Carlo**方法可以在系统中各种可能的基态变分波函数形式已知的情况下比解析方法更好地确定相图。**Quantum Monte Carlo**可以用于玻色多体系统和无符号问题的费米多体系统的无偏向性的定量计算。

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引言

- 在量子化学、材料物理和凝聚态物理中, 我们要了解组成物质的**大量原子、分子及其电子的性质**。
- 在**凝聚态材料设计和固态量子化学**中, 基于量子力学的从头计算(**ab initio**)和第一性原理计算, 包括能带论中以Hartree-Fock自洽场计算为基础的**ab initio**从头计算, 和密度泛函理论(**DFT**)计算可以计算**电子性质**。已经有很多商用软件, 例如VASP(Vienna Ab-initio Simulation Package)。考虑弱的关联效应, 发展了一些改进的平均场方法: **DMF+U**, 动力学平均场(**DMFT**), 等
- 在凝聚态物理中, 计算物理方法已经成为预言新**电子态**的重要手段, 例如, **量子自旋霍尔效应**, **三维拓扑绝缘体**, **量子反常霍尔效应**, **Weyl半金属**, **三分量费米子**等都是**第一性原理**计算先预言精准或相关的材料, 再由实验证实的
- AI**加持的计算方法正在改变整个计算物理

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引言

- 原则上, 以上提到的计算模拟方法都涉及大量粒子体系, 属于统计物理相关领域。
- ✓ 在讲重整化群时, 已经提了**DMRG**计算的基本原理, 但实际操作、编程技术难度较高。
- ✓ 第一性原理计算是计算凝聚态物理课的内容
- ✓ 现行**狭义的统计物理计算方法**主要包括**分子动力学方法**和**蒙特卡罗方法**。前者用于分子体系, 后者则可以广泛地应用于各种物理体系, 特别是凝聚态相互作用多电子系统。我们下面将对它们做简介。

- 本章引言
- 分子动力学简介
- 经典Monte Carlo 方法
- 量子 Monte Carlo方法

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引言

- 一些直观物理认为不可能的物理现象经常是通过数值模拟首先实现, 然后在理论上或实验上验证的。一个著名例子是仅有强的短程排斥作用而无任何吸引的球状粒子是否可以形成晶体? 最早计算模拟得到Yes被普遍怀疑, 现在已经是一个常识。
- 在高能物理中, 计算物理从方法发展成一个独立的物理研究领域。**格点规范理论**是了解非微扰强相互作用物理的唯一理论方法。主要模拟手段是**量子Monte Carlo**方法。由于4维空间的计算量非常大, 需要超级计算机和为格点规范计算特别设计的计算机。

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引言

- 由于**符号问题**, 一些重要的二维强关联**电子**模型, 如Hubbard模型, 和有阻错的自旋模型是不能用**Quantum Monte Carlo**去计算的。**DMRG**对二维体系不适用。人们正在发展**DMRG**方法的推广: **张量网络算法**。
- 分子动力学方法**是用计算模拟的方法解相互作用牛顿粒子(经典力学)的运动方程, 确定**原子**或**分子**的轨迹。用于计算**化学物理**、**材料科学**和**模拟生物分子**, 特别是气体和非晶固体(生物分子、聚合物、金属和非金属。对晶体, 晶格动力学方法和声子可以较好描述之)
- 与分子动力学模拟类似地一种方法是**布朗动力学模拟**, 适用于大分子溶液体系
- 用经典力学Hamilton描述代替牛顿方程, 用保辛结构的**辛算法**研究分子动力学最近得到了极大的发展。辛算法在整体性、结构性、精确性和长期跟踪稳定性方面都超过了传统的方法。(冯康)

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分子动力学简介

- 历史上把**Monte Carlo(MC)**模拟用到统计物理问题要早于分子动力学(**MD**)方法。采用先讲**MD**完全是因为我个人的原因: **MD**我以前几乎没有接触过, 而**MC**方面多少接触。所以, **MD**放在前面讲, 只作一些简介, **MC**则讲得稍微多点。
- **MD的基本假设:** 原子的Schrodinger equation

$$H\psi(R, r) = E\psi(R, r)$$

分子动力学简介

- Born-Oppenheimer近似，即绝热近似：电子运动如此之快，以致它们感受不到原子核在动。它们只感受到原子核的势场，电子的 Schrodinger方程是

$$(H_e + V_{NN})\psi_e(R, r) = E_e \psi_e(R, r) \quad (1)$$
- V_{NN} 是effective potential。把R看作慢变参数，把 V_{NN} 看作外力场，作经验拟合，这构成量子化学中分子力学的基础。固体物理中电子结构也是由此方程出发做计算的（多体，周期势，相互作用，等等）

分子动力学简介

- MD计算，典型地，有 10^4 个粒子。这样，在一条线上平均有 $10000^{1/3} = 21 \sim 22$ 。
- 这意味着若要得到热力学性质，应该取周期边条件。（边界效应）。
- 远离临界点的气体的关联长度远小于21个粒子的间距。但在相变区域，关联长度会很长。MD不太适合于研究相变

分子动力学简介

- 对分子气体 $\tau \sim 10^{-14}$ sec, 例如，氩气
 $\sigma = 3 \text{ \AA}$, $m = 6.63 \cdot 10^{-23} \text{ kg}$ and $\epsilon = 1.64 \cdot 10^{-20} \text{ J}$,
 $\tau = 2.8 \cdot 10^{-14} \text{ s}$
- 解牛顿运动方程，对微分方程的积分step应比 τ 小得多，如 $\Delta t = 10^{-15} \text{ sec}$.
- 在一次simulation run中，总的时间steps为 $10^4 \sim 10^7$. 所以，对一个原子，duration是 10^{-8} .
- 多数原子系统的弛豫时间要远小于 10^{-8} . 所以，MD是对于研究其动力学和热力学性质是很好的工具。
- 但对某些glass体系的glass transition，弛豫时间 10^{-3} sec . 这时，就要coarse-grain一些微观自由度

分子动力学简介

- Equations of motion

$$\frac{d^2 \mathbf{r}_i}{dt^2} = - \sum_{j \neq i} \nabla_{\mathbf{r}_i} u(\mathbf{r}_{ij}).$$
- Periodic boundary condition in order to simulate an infinite system
- 对一个给定的粒子，用truncated potential with in distance r_c

$$u^{trunc}(r) = \begin{cases} u(r) - u(r_c) & r < r_c \\ 0 & r \geq r_c. \end{cases}$$

分子动力学简介

- 原子核的Schrodinger方程是

$$(T_\alpha + E_e)\psi_N(R) = E_N \psi_N(R) \quad (2)$$
- 用经典的牛顿方程代替(2)，势能 E_e 用力场拟合，就构成了分子力学的基础。
- 历史上最早用计算机解多体问题是“曼哈顿计划”的需要。Monte Carlo方法首先被使用（下面会讲）。但Monte Carlo方法只能计算统计平均值，无法得到体系的动力学性质。

分子动力学简介

- 我们设质量为m的分子间的van der Waals力由Lennard-Jones potential给出

$$u(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right]$$

- σ 是分子直径， ϵ 是微观能量scale，则系统的特征时间为

$$\tau = \sigma \sqrt{\frac{m}{\epsilon}}$$

分子动力学简介

- 分子间的作用力或分子的总势能包括
 $\text{范德瓦尔斯非键结合能} + \text{键伸缩势能} + \text{键角弯曲势能} + \text{双面角扭曲势能} + \text{离平面振动势能} + \text{库伦静电能}$
- MD的一个重要步骤是根据分子结构决定有效力场。Typical Example: 除van der Waals力(Lennard-Jones potential)外，其他的力都很小。
- 确定一个正确的计算方法。

分子动力学简介

- 选择Verlet algorithm: 数值解，第一步是连续变量的离散化。一个crucial的要求是，对一个孤立系统，在simulation中，总能量要保持守恒。（这是一个微正则系综）The Verlet's algorithm one of first methods and remains one most used nowadays. 但在能量守恒上有点问题。

分子动力学简介

- 考虑N个全同粒子， $\mathbf{r}=(\mathbf{r}_1, \dots, \mathbf{r}_N)$ 是 $3N$ vector, \mathbf{r}_i 是第*i*个粒子位置。
- Formally, 系统演化方程是

$$m \frac{d^2 \mathbf{r}}{dt^2} = \mathbf{f}(\mathbf{r}(t)).$$

精确到 $O(\Delta t^4)$,

$$\mathbf{r}(t + \Delta t) = \mathbf{r}(t) + \mathbf{v}(t)\Delta t + \frac{\mathbf{f}(\mathbf{r}(t))}{2m}(\Delta t)^2 + \frac{d^3 \mathbf{r}}{dt^3}(\Delta t)^3 + O((\Delta t)^4)$$

$$\mathbf{r}(t + \Delta t) + \mathbf{r}(t - \Delta t) = 2\mathbf{r}(t) + \frac{\mathbf{f}(\mathbf{r}(t))}{m}(\Delta t)^2 + O((\Delta t)^4).$$

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分子动力学简介

- Verlet algorithm是时间反演不变的。这是微观理论的要求，但round-off errors也会积累。
- 对一个Hamilton系统，相空间的体积是不变的。Numerical simulation也必须如此，否则能量就不守恒。Verlet algorithm满足能量守恒吗？

分子动力学简介

- 离散化后，速度定义是

$$\mathbf{v}(t) = \frac{\mathbf{r}(t + \Delta t) - \mathbf{r}(t - \Delta t)}{2\Delta t} + O((\Delta t)^2)$$

- Verlet algorithm的计算精度是

$$\Delta t^4 N_t$$

N_t 是总的积分steps. 总的simulation时间为 $\Delta t N_t$ 。

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分子动力学简介

- 要计算能量，我们首先来看速度，根据速度定义，我们有

$$\mathbf{v}(t + \Delta t/2) = \frac{\mathbf{r}(t + \Delta t) - \mathbf{r}(t)}{\Delta t},$$

$$\mathbf{v}(t - \Delta t/2) = \frac{\mathbf{r}(t) - \mathbf{r}(t - \Delta t)}{\Delta t},$$

- 为什么是 $\Delta t/2$?

$$\mathbf{r}(t + \Delta t) = \mathbf{r}(t) + \mathbf{v}(t + \Delta t/2)\Delta t$$

$$\mathbf{r}(t - \Delta t) = \mathbf{r}(t) - \mathbf{v}(t - \Delta t/2)\Delta t.$$

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分子动力学简介

- 用 $\mathbf{r}(t + \Delta t) + \mathbf{r}(t - \Delta t)$ 有

$$\mathbf{v}(t + \Delta t/2) = \mathbf{v}(t - \Delta t/2) + \frac{\mathbf{f}(t)}{m}\Delta t + O((\Delta t)^3).$$

- 所以，velocities are calculated on half-integer time intervals, and positions are obtained on integer time intervals

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分子动力学简介

- 但这会造成问题：在计算热力学量时，平均势能是按 Δt 整数计算的，而动能是按 Δt 半整数计算的。这造成能量不守恒。
- 需要更严格的算法
- 辛算法：可以保相空间体积，从而总能量守恒。（数学理论上，冯康的贡献）

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分子动力学简介

- 辛算法的出发点是刘维定理（§ 3.2）
- 设 $f^{(N)}(\mathbf{r}^N, \mathbf{p}^N, t)$ 是N粒子几率分布函数，刘维定理

$$\frac{\partial f^{(N)}(\mathbf{r}^N, \mathbf{p}^N, t)}{\partial t} = -i\mathcal{L}f^{(N)}$$

$$\mathcal{L} = i\{H_N, \} = \sum_{i=1}^N \left(\left(\frac{\partial \mathcal{H}_N}{\partial \mathbf{r}_i} \right) \frac{\partial}{\partial \mathbf{p}_i} - \left(\frac{\partial \mathcal{H}_N}{\partial \mathbf{p}_i} \right) \frac{\partial}{\partial \mathbf{r}_i} \right)$$

- 形式解

$$f^{(N)}(\mathbf{r}^N, \mathbf{p}^N, t) = \exp(-i\mathcal{L}t)f^{(N)}(\mathbf{r}^N, \mathbf{p}^N, 0).$$

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分子动力学简介

- 任何 $A = A(\mathbf{r}^N, \mathbf{p}^N)$,

$$A(\mathbf{r}^N(t), \mathbf{p}^N(t)) = \exp(i\mathcal{L}t)A(\mathbf{r}^N(0), \mathbf{p}^N(0)).$$

- 只是一个形式解，explicit 解一般是写不出来的
- 定义 $\mathcal{L} = \mathcal{L}_r + \mathcal{L}_p$

$$i\mathcal{L}_r = \sum_i \frac{d\mathbf{r}_i}{dt} \frac{\partial}{\partial \mathbf{r}_i} \quad i\mathcal{L}_p = \sum_i \frac{d\mathbf{p}_i}{dt} \frac{\partial}{\partial \mathbf{p}_i}$$

分子动力学简介

- 设 $i\mathcal{L}_p = \sum_i \frac{d\mathbf{p}_i}{dt} \frac{\partial}{\partial \mathbf{p}_i} = 0$

- A的时间演化为

$$A(\mathbf{r}(t), \mathbf{p}(t)) = \exp(i\mathcal{L}_r^0 t) A(\mathbf{r}(0), \mathbf{p}(0))$$

$$i\mathcal{L}_r^0 = \sum_i \frac{d\mathbf{r}_i}{dt}(0) \frac{\partial}{\partial \mathbf{r}_i}$$

- 作指数展开

$$A(\mathbf{r}^N(t), \mathbf{p}^N(t)) = A(\mathbf{r}^N(0), \mathbf{p}^N(0)) + i\mathcal{L}_r^0 A(\mathbf{r}^N(0), \mathbf{p}^N(0)) + \frac{(i\mathcal{L}_r^0)^2}{2!} A(\mathbf{r}^N(0), \mathbf{p}^N(0)) + \dots$$

$$= \sum_{n=0}^{\infty} \sum_i \frac{\left(\frac{d\mathbf{r}_i}{dt}(0)t\right)^n}{n!} \left(\frac{\partial^n}{\partial \mathbf{r}_i^n}\right) A(\mathbf{r}(0), \mathbf{p}(0))$$

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分子动力学简介

- 为了做数值模拟，我们也要离散化刘维方程

- Trotter identity ($\exp(\mathcal{L}t) \neq \exp(\mathcal{L}_r t) \exp(\mathcal{L}_p t)$)

$$\exp(B+C) = \lim_{P \rightarrow \infty} \left(\exp\left(\frac{B}{2P}\right) \exp\left(\frac{C}{P}\right) \exp\left(\frac{B}{2P}\right) \right)^P.$$

- For a finite P

$$\exp(B+C) = \left(\exp\left(\frac{B}{2P}\right) \exp\left(\frac{C}{P}\right) \exp\left(\frac{B}{2P}\right) \right)^P \exp\left(\mathcal{O}\left(\frac{1}{P^2}\right)\right)$$

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分子动力学简介

- By definition, 指数算子的作用

$$e^{i\mathcal{L}_p \Delta t / 2} A(\mathbf{r}^N(0), \mathbf{p}^N(0)) =$$

$$A\left(\mathbf{r}^N(0), \left(\mathbf{p}(0) + \frac{\Delta t}{2} \frac{d\mathbf{p}(0)}{dt}\right)^N\right)$$

$$e^{i\mathcal{L}_r \Delta t} A\left(\mathbf{r}^N(0), \left(\mathbf{p}(0) + \frac{\Delta t}{2} \frac{d\mathbf{p}(0)}{dt}\right)^N\right) =$$

$$A\left(\left(\mathbf{r}(0) + \Delta t \frac{d\mathbf{r}(\frac{\Delta t}{2})}{dt}\right)^N, \left(\mathbf{p}(0) + \frac{\Delta t}{2} \frac{d\mathbf{p}(0)}{dt}\right)^N\right)$$

分子动力学简介

- 但刘维定理得到的结果是通过幺正变换得到的，所以，变换的Jacobi行列式为1。这样，这些变换是保相空间体积的，所以，能量是守恒的。这个算法称为symplectic algorithm。
- Symplectic form: $\omega = \sum_i d\mathbf{p}_i \wedge d\mathbf{q}_i$ 在幺正变换下不变。

分子动力学简介

- 这相当于空间平移

$$A(\mathbf{r}^N(t), \mathbf{p}^N(t)) = A\left(\left(\mathbf{r}_i + \frac{d\mathbf{r}_i}{dt}(0)t\right)^N, \mathbf{p}^N(0)\right)$$

- 这正是无相互的自由粒子

- 如果 $\mathcal{L}_r^0 = 0$ 则得到动量空间的“平移”

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分子动力学简介

- 取

$$\Delta t = t/P, \quad \frac{B}{P} = \frac{i\mathcal{L}_p t}{P}, \quad \frac{C}{P} = \frac{i\mathcal{L}_r t}{P}$$

- 用于刘维方程的解，对每一步

$$e^{i\mathcal{L}_p \Delta t / 2} e^{i\mathcal{L}_r \Delta t} e^{i\mathcal{L}_p \Delta t / 2}$$

- Again，我们看到坐标是1步，动量是半步

- 由于 \mathcal{L}_r 和 \mathcal{L}_p 是厄米的，相应的指数算子是么正的。由此可以得到保相空间体积的算法，即辛算法

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分子动力学简介

- $e^{i\mathcal{L}_p \Delta t / 2} e^{i\mathcal{L}_r \Delta t} e^{i\mathcal{L}_p \Delta t / 2}$. 作用后 $A(\mathbf{r}^N(0), \mathbf{p}^N(0))$ 变为

$$A\left(\left(\mathbf{r}(0) + \Delta t \frac{d\mathbf{r}(\frac{\Delta t}{2})}{dt}\right)^N, \left(\mathbf{p}(0) + \frac{\Delta t}{2} \frac{d\mathbf{p}(0)}{dt} + \frac{\Delta t}{2} \frac{d\mathbf{p}(\Delta t)}{dt}\right)^N\right)$$

- Summary:

这recovered

Verlet算法
的结果

$$\mathbf{p}(\Delta t) = \mathbf{p}(0) + \frac{\Delta t}{2} (\mathbf{f}(\mathbf{r}(0)) + \mathbf{f}(\mathbf{r}(\Delta t)))$$

$$\mathbf{r}(\Delta t) = \mathbf{r}(0) + \Delta t \frac{d\mathbf{r}(\Delta t/2)}{dt}$$

分子动力学简介

- 其他算法: Andersen algorithm; Nose-Hoover algorithm

- 布朗力学: 对两种分子的混合体，如果分子体积相差很大，大分子的运动可以看作是布朗运动。例如，生物分子的水溶液；稀释纳米颗粒（铁电液体等）

- 离散化朗之万方程。

- 用解随机微分方程的Euler algorithm

蒙特卡罗方法：概说

- 计算配分函数是统计物理的出发点

$$Z = \sum_i \exp(-\beta U(i))$$

- 求和指数i run all over all configurations. 对一个线度为10, a lattice gas with two degrees of freedom per site has the configuration number $2^{100} \sim 10^{30}$. 对一个连续模型, 离散化后, 选10点for每一个坐标点in 3-D, 对100个particles, 这样一共有 10^{300} 个点数。
- 做精确计算是不可能的。用Monte Carlo方法可以 evaluates这个“高维积分”。

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蒙特卡罗方法：概说

- Monte Carlo方法就是随机地从configuration space取出有限的点，在给定的精度内，估算要做的积分。
- 取样的方法会很大程度上决定计算的有效性和精度。

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蒙特卡罗方法：Uniform and weighted sampling

- 一维积分

$$I = \int_a^b dx f(x).$$

- 重写

$$I = (b - a) \langle f(x) \rangle$$

- 随机地，均匀地在[a,b]中取N_r个点，积分可以用以下公式估计

$$I_{N_r} = \frac{(b - a)}{N_r} \sum_{i=1}^{N_r} f(x_i).$$

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蒙特卡罗方法：均匀或权重取样

- 设w(x)>0, defining du=w(x)dx with u(a)=a, u(b)=b, 则

$$I = \int_a^b du \frac{f(x(u))}{w(x(u))},$$

- Randomly

$$I \simeq \frac{(b - a)}{N_r} \sum_{i=1}^{N_r} \frac{f(x(u_i))}{w(x(u_i))}$$

- 方差是

$$\sigma^2 = \frac{1}{N_r} \left(\left\langle \left(\frac{f(x(u))}{w(x(u))} \right)^2 \right\rangle - \left\langle \frac{f(x(u))}{w(x(u))} \right\rangle^2 \right)$$

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蒙特卡罗方法：均匀或权重取样

- 这个方法的收敛性可以通过方差估算

$$\sigma^2 = \frac{1}{N_r} \langle f(x)^2 \rangle - \langle f(x) \rangle^2.$$

- 收敛度 $1/N_r$ 是很慢的，但对uniform取样，似乎没有好的改进办法。

- 重写积分

$$I = \int_a^b dx \frac{f(x)}{w(x)} w(x).$$

w(x)dx意味着取样有权重

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蒙特卡罗方法：对平衡体系的马尔可夫链取样

- 统计物理中，我们要计算

$$\langle A \rangle = \frac{\sum_i A_i \exp(-\beta U_i)}{Z} = \sum_i A_i p_i$$

$$p_i = \frac{\exp(-\beta U_i)}{Z} \quad p_i \text{ is strictly positive and } \sum_i p_i = 1$$

- 如果由p_i这个权重产生N_r个configurations,

$$\langle A \rangle \simeq \frac{1}{N_r} \sum_i^{N_r} A_i$$

- 这样，热平均变成了算术平均。

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蒙特卡罗方法：对平衡体系的马尔可夫链取样

- Metropolis等发展了所谓的重要性取样。他们引入一个 stochastic Markovian process between相继的configurations, 可以收敛到平衡的distribution p_{eq}.

- 记p(i,t)是t时刻有i configuration的几率。正如我们上一章讲的，p(i,t)满足 Master eq.

$$p(i, t + dt) = p(i, t) + \sum_j (W(j \rightarrow i) P(j, t) - W(i \rightarrow j) p(i, t)) dt$$

W(i→j)dt是条件几率或转移几率。

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- At time t = 0, the system is in an initial configuration i₀: The initial probability distribution is p(i) = δ_{i0,i}, which means that we are far from the equilibrium distribution.

- 在平衡态，p(i,t)与时间无关，Master eq变成

$$\sum_j W(j \rightarrow i) p_{eq}(j) = p_{eq}(i) \sum_j W(i \rightarrow j)$$

- 一个简单的解是（细致平衡条件）

$$W(j \rightarrow i) p_{eq}(j) = W(i \rightarrow j) p_{eq}(i)$$

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蒙特卡罗方法：对平衡体系的马尔可夫链取样

- 等价地

$$\frac{W(i \rightarrow j)}{W(j \rightarrow i)} = \frac{p_{eq}(j)}{p_{eq}(i)} = \exp(-\beta(U(j) - U(i))).$$

$W(i \rightarrow j)$ 与 partition function 无关，而只与 Boltzmann 因子有关。

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蒙特卡罗方法：Metropolis algorithm

- 要求满足 detailed balance 的转移矩阵，注意到 Monte Carlo 的动力学是两步的序列：
 - 从一个 configuration i 出发，根据某一个事先给定的几率 $\alpha(i \rightarrow j)$ 随机地得到一个新的 configuration j 。
 - This new configuration is accepted with a probability $\Pi(i \rightarrow j)$.

- Thus

$$W(i \rightarrow j) = \alpha(i \rightarrow j)\Pi(i \rightarrow j).$$

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蒙特卡罗方法：Metropolis algorithm

- Originally, Metropolis et al 等选择

$$\alpha(i \rightarrow j) = \alpha(j \rightarrow i)$$

- Then $\frac{\Pi(i \rightarrow j)}{\Pi(j \rightarrow i)} = \exp(-\beta(U(j) - U(i)))$

- 一个特解是

$$\Pi(i \rightarrow j) = \begin{cases} \exp(-\beta(U(j) - U(i))) & \text{if } U(j) > U(i) \\ 1 & \text{if } U(j) \leq U(i) \end{cases}$$

- 重要性抽样：从 i 构型到 j 构型发生的概率由上式给出。第二行表示绝对变，而第一行由能量差给出一个构型的几率（实际执行中，变与不变由这个几率与一个随机数比较确定）。

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蒙特卡罗方法：Metropolis algorithm

- 初始构型总是远离平衡的，所以，MC 总是分两步，(1) 预热，让初始构型弛豫到平衡，也就是说，预热阶段得到构型不记录。(2) 到平衡附近，再记录每一个构型，用于计算热力学量。

$$\langle A \rangle \simeq \frac{1}{N_r} \sum_i A_i$$

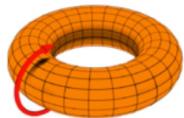
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蒙特卡罗方法：Ising model

- Two-dimensional Ising model with $S_i = \pm 1$

$$\mathcal{H} = -J \sum_{\langle i,j \rangle} S_i S_j - H \sum_{i=1}^N S_i$$

- Periodic boundary condition: two-dimensional lattice torus



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蒙特卡罗方法：Ising model

- Metropolis algorithm: 更新构型。如果构型与前一个差别太大，很有可能由于几率太小“跑不出去”。所以，通常是随机地选一个格点，翻转其 spin。
- 计算新构型的能量
- 若 $U_{new} < U_{old}$, 接受这个新构型
- 若 $U_{new} > U_{old}$, 产生一个随机数 r (在 0 和 1 之间), 若 $r < \exp[-\beta(U_{new} - U_{old})]$, 接受新构型, 反之, 拒绝接受, 留在旧构型。
- 继续, 迭代。
- 在足够多个平衡态构型 (除去“预热”构型) 后, 用这些构型计算热力学量
- 通常, Metropolis algorithm MC 在远离相变点是有效的。

$$\langle A \rangle \simeq \frac{1}{N_r} \sum_i A_i$$

蒙特卡罗方法：Ising model

- Metropolis algorithm: initial 构型 (1) the ground state。(2) 有限温度, 对每个 site, 赋予一个随机数 $r(i)$. $0 < r(i) < 0.5$, spin = +1, $0.5 < r(i) < 1$, spin = -1

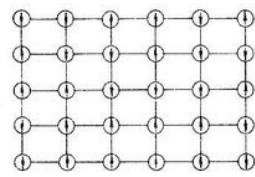
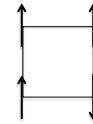


图 1 二维伊辛模型



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蒙特卡罗方法：Ising model

- 我这里非常粗糙地讲了 Metropolis algorithm for Ising model. 实际计算中为了提高效率、缩短时间、减小误差、提高精度, 由很多技术。我不去细讲。大家可以参考有关参考文献。

相变和蒙特卡罗模拟

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- Monte Carlo 模拟在临界点附近可以计算各种临界指数
- Review:** For 2-D Ising model, near the critical point $t = (T - T_c)/T_c$, 磁化强度

$$m(t, h) = \frac{1}{N} \sum_{i=1}^N \langle S_i \rangle$$

$$m(t, h=0) = \begin{cases} 0 & t > 0 \\ A|t|^\beta & t < 0 \end{cases}$$

$$m(t=0, h) = \begin{cases} -B|h|^{1/\delta} & h < 0 \\ B|h|^{1/\delta} & h > 0 \end{cases}$$

相变和蒙特卡罗模拟

- 比热

$$c_v(t, h=0) = \begin{cases} C|t|^{-\alpha} & t < 0 \\ C'|t|^{-\alpha'} & t > 0 \end{cases}$$

- 磁化率

$$\chi_T(h=0) \sim |t|^{-\gamma},$$

- 关联函数

关联长度

$$g(r) \sim \frac{\exp(-r/\xi)}{r^{d-2+\eta}},$$

$$\xi \sim |t|^{-\nu},$$

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相变和蒙特卡罗模拟

- 四个约束: 6个临界指数只有2个独立

$$\alpha + 2\beta + \gamma = 2.$$

$$\beta\delta = \beta + \gamma.$$

$$2 - \alpha = d\nu,$$

$$\gamma = (2 - \eta)\nu.$$

相变和蒙特卡罗模拟

- 有限尺寸标度理论: 重整化群理论表明, 在临界点附近, 有限线度 L 系统的热力学量与 t 和 h 的关系是与线度 L/ℓ 的系统的热力学量 for $t \ell^{\gamma_t}$ 和 $h \ell^{\gamma_h}$ 的关系一样的。
- 在相变点附近

$$f_s(t, h, \dots L^{-1}) = l^{-d} f_s(t l^{\gamma_t}, h l^{\gamma_h}, \dots, (l/L)^{-1})$$

- 对零场($h=0$)比热

$$c_v(t, L^{-1}) = |t|^{-\alpha} F_c^\pm(|t|^{-\nu}/L)$$

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相变和蒙特卡罗模拟

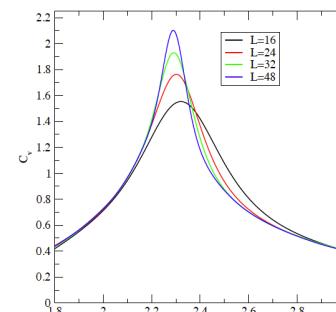
- 由于是 finite size, t 趋于 0 时, 无发散, 要求 $F_c^\pm(|t|^{-\nu}/L)) = (|t|^{-\nu}/L)^{-\kappa} D^\pm(L t^\nu)$ with $D^\pm(0)$ finite $\kappa = \alpha/\nu$
- 所以

$$c_v(t, L^{-1}) = L^{\alpha/\nu} D(L|t|^\nu).$$

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相变和蒙特卡罗模拟

- Monte Carlo simulation for finite systems



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相变和蒙特卡罗模拟

- 在 $T_c(L)$,

$$T_c(L) - T_c \sim L^{-1/\nu}$$

- 此时比热最大

$$C_v(T_c(L), L^{-1}) \sim L^{\alpha/\nu}$$

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相变和蒙特卡罗模拟

- The absolute value of magnetization, the isothermal susceptibility, the second susceptibility, Binder's parameter are defined by

$$\langle |m| \rangle = \frac{1}{N} \langle \left| \sum_{i=1}^N S_i \right| \rangle$$

$$k_B T \chi = N(\langle m^2 \rangle - \langle m \rangle^2).$$

$$k_B T \chi' = N(\langle m^2 \rangle - \langle |m| \rangle^2)$$

$$U = 1 - \frac{\langle m^4 \rangle}{3 \langle m^2 \rangle^2}$$

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相变和蒙特卡罗模拟

- The scaling laws are

$$\begin{aligned}\langle |m(t, 0, L^{-1})| \rangle &= L^{-\beta/\nu} F_m^\pm(tL^{1/\nu}) \\ k_B T \chi(t, 0, L^{-1}) &= L^{\gamma/\nu} F_\chi^\pm(tL^{1/\nu}) \\ k_B T \chi'(t, 0, L^{-1}) &= L^{\gamma/\nu} F_{\chi'}^\pm(tL^{1/\nu}) \\ U(t, 0, L^{-1}) &= F_U^\pm(tL^{1/\nu})\end{aligned}$$

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相变和蒙特卡罗模拟

- 在临界点附近，很大标度的涨落存在，弛豫时间 τ 变长。由于关联长度是唯一的scale，有一个新的临界指数出现

$$\tau \sim (\xi(t))^z$$

- z 称为动力学临界指数，typically, $z=2\sim 5$ 。

$$\xi \sim |t|^{-\nu} \sim |t|^{-\nu z}$$

- For finite system, $\tau \sim L^z$; 随 L 变大，算法失效。这称为临界慢化

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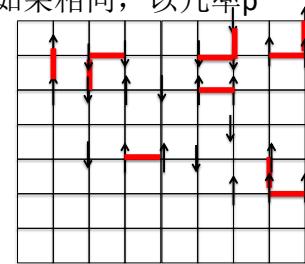
相变和蒙特卡罗模拟

- 这样，我们可以确定critical temperature和所有critical exponents.
- MC模拟与有效尺寸效应不但可以计算普适量，例如，临界指数，还能计算非universal量，例如，临界温度
- 临界慢化：上面我们假设MC在临界点可用。但Metropolis algorithm在临界点还是一个好的算法吗？

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相变和蒙特卡罗模拟

- 改进办法：Cluster algorithm(Wang-Landau algorithm)把spins bond起来：如果最邻近自旋相反，不bond。如果相同，以几率 p bond,几率 $(1-p)$ 不bond. (对反铁磁，相反)。



相变和蒙特卡罗模拟

- 变化构型时随机地翻转一个 bonded cluster. Swendsen and Wang发现可以克服临界慢化。
- 可以进一步改进，例如，小的cluster没贡献，用Wolff算法。
- Monte Carlo method with multiple Markov chains

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变分蒙特卡罗

参考书：Morten Hjorth-Jensen, Computational Physics

<http://vdisk.weibo.com/s/DdqkzLldy1Rb>

变分蒙特卡罗

- 量子力学问题。猜一个带参数的波函数，(如 α)，能量期待值：

$$\langle \hat{H} \rangle = \frac{\int d\mathbf{R} \Psi^*(\mathbf{R}) H(\mathbf{R}) \Psi(\mathbf{R})}{\int d\mathbf{R} \Psi^*(\mathbf{R}) \Psi(\mathbf{R})} = \int P(\mathbf{R}; \alpha) \hat{E}_L(\mathbf{R}; \alpha) d\mathbf{R}.$$

$$P(\mathbf{R}; \alpha) = \frac{|\psi_T(\mathbf{R}; \alpha)|^2}{\int |\psi_T(\mathbf{R}; \alpha)|^2 d\mathbf{R}}.$$

$$\hat{E}_L(\mathbf{R}; \alpha) = \frac{1}{\psi_T(\mathbf{R}; \alpha)} \hat{H} \psi_T(\mathbf{R}; \alpha)$$

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变分蒙特卡罗

- 我们用MC来计算积分：用 $P(\mathbf{R}, \alpha)$ 作为抽样的几率，得到configurations

$$\langle \hat{E}_L \rangle = \int P(\mathbf{R}) \hat{E}_L(\mathbf{R}) d\mathbf{R} \approx \frac{1}{N} \sum_{i=1}^N E_L(x_i),$$

$$\langle \hat{E}_L^2 \rangle = \int P(\mathbf{R}) \hat{E}_L^2(\mathbf{R}) d\mathbf{R} \approx \frac{1}{N} \sum_{i=1}^N E_L^2(x_i).$$

- 对不同的 α ，计算积分，找能量的minimum，就是变分过程。

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变分蒙特卡罗

- 一维谐振子（自然单位）精确基态

$$H = -\frac{d^2}{dx^2} + x^2, \quad \Psi_0(x) = \frac{1}{\pi^{1/4}} e^{-x^2/2} \quad E_0 = 1$$

- 猜变分波函数是

$$\Psi_T(x) = \frac{\sqrt{\alpha}}{\pi^{1/4}} e^{-x^2\alpha^2/2}.$$

$$E_L(x) = \alpha^2 + x^2(1 - \alpha^4).$$

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变分蒙特卡罗

- 变分能量

$$\langle E_L \rangle = \frac{\int_{-\infty}^{\infty} dx e^{-x^2\alpha^2} \alpha^2 + x^2(1 - \alpha^4)}{\int_{-\infty}^{\infty} dx e^{-x^2\alpha^2}}.$$

- 因为积分可以解析算出

$$\int_{-\infty}^{\infty} dx e^{-x^2\alpha^2} = \sqrt{\frac{\pi}{\alpha^2}}, \quad \langle E_L \rangle = \frac{\alpha^2}{2} + \frac{1}{2\alpha^2}, \quad \sigma^2 = \frac{(\alpha^4 - 1)^2}{2\alpha^4}.$$

- Exactly, $\alpha=1$ 是minimal, 与精确解一致。

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变分蒙特卡罗

- 我们也可用MC来计算积分：用 $P(\mathbf{R}, \alpha)$ 作为抽样的几率，得到configurations

$$\langle \hat{\mathbf{E}}_L \rangle = \int P(\mathbf{R}) \hat{\mathbf{E}}_L(\mathbf{R}) d\mathbf{R} \approx \frac{1}{N} \sum_{i=1}^N E_L(x_i),$$

$$\langle \hat{\mathbf{E}}_L^2 \rangle = \int P(\mathbf{R}) \hat{\mathbf{E}}_L^2(\mathbf{R}) d\mathbf{R} \approx \frac{1}{N} \sum_{i=1}^N E_L^2(x_i).$$

- 对不同的 α , 计算积分，找能量的minimum, 就是变分过程。

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变分蒙特卡罗

- 氢原子一电子和质子，2粒子系统。六维。在质心坐标系，三维：

$$H = -\frac{\hbar^2}{2m} \nabla^2 - \frac{e^2}{r}$$

$$\mathbf{r} = \mathbf{r}_e - \mathbf{r}_p$$

$$m = m_e m_p / (m_e - m_p)$$

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变分蒙特卡罗

- 想求基态：角动量守恒和基态波函数球对称，在球坐标

$$H = -\frac{\hbar^2}{2m} \left[\frac{d^2}{dr^2} + \frac{2}{r} \frac{d}{dr} \right] - \frac{e^2}{r}$$

- 问题是精确可解的：

$$E_0 = -\frac{e^2}{2a_0}, \quad \psi_0(r) \sim e^{-r/a_0} \quad a_0 = \frac{\hbar^2}{me^2}$$

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变分蒙特卡罗

- 变分计算： trial ground state wave function

$$\psi_{T,\alpha}(r) = e^{-\alpha r}$$

- Local energy: (自然单位)

$$E_L(r) = \frac{1}{\psi_{T,\alpha}} H \psi_{T,\alpha}(r) = -\frac{1}{2} \left[\alpha^2 - \frac{2\alpha}{r} \right] - \frac{1}{r}$$

- 与谐振子一样，可以用MC计算 E_L 的期待值，得到 $\alpha=1$ 的极小值。解析地作积分，求极值，也可得同样的结果。

- 也可以根据角动量守恒用VMC求激发态。

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变分蒙特卡罗

- 氦原子， M_N 是 m_e 的7300多倍，所以，可以认为是不动的，电子的哈密顿是（自然单位）

$$H = -\frac{1}{2} \nabla_1^2 - \frac{1}{2} \nabla_2^2 - \frac{2}{r_1} - \frac{2}{r_2} + \frac{1}{r_{12}},$$

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变分蒙特卡罗

- 若电子间无相互作用，则就是两个简单的类氢原子问题

$$E_0 = -\frac{Z^2}{2}, \quad \psi_0 \sim e^{-Zr}$$

$$\psi(\mathbf{r}_1, \mathbf{r}_2) \sim e^{-2r_1} e^{-2r_2}$$

- 取变分波函数为

$$\Psi_{T,\alpha} = e^{-\alpha r_1} e^{-\alpha r_2}$$

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变分蒙特卡罗

- 由此可得

$$\left\langle -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - \frac{2}{r_1} - \frac{2}{r_2} \right\rangle = 2 \times \frac{\alpha^2}{2} - 2 \times \alpha,$$

- 直接解, minimum at $\alpha=1, E_0=-1$. 实验测量是 $E_0=-2.904$. 这个近似不好。

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变分蒙特卡罗

- 把电子电子相互作用加上

$$\left\langle -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - \frac{2}{r_1} - \frac{2}{r_2} + \frac{1}{r_{12}} \right\rangle = \alpha^2 - \frac{27}{8}\alpha$$

- 直接解, minimum at $\alpha=27/16, E_0=-2.8477$. Much better! 电子间的排斥相互作用 lowers ground state energy.

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变分蒙特卡罗

- 更好的变分波函数: Pade-Jastrow wave function (加一个Jastrow factor)

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = e^{-2r_1} e^{-2r_2} e^{\frac{r_{12}}{2(1+\alpha r_{12})}}$$

$$E_L(\mathbf{r}_1, \mathbf{r}_2) = -4 + \frac{\alpha}{(1+\alpha r_{12})} + \frac{\alpha}{(1+\alpha r_{12})^2} + \frac{\alpha}{(1+\alpha r_{12})^3}$$

$$- \frac{1}{4(1+\alpha r_{12})^4} + \frac{\hat{\mathbf{r}}_{12} \cdot (\hat{\mathbf{r}}_1 - \hat{\mathbf{r}}_2)}{(1+\alpha r_{12})^2}.$$

- 这时, 解析求积分就难点了, 但用MC做变分, 难度并不增加。

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变分蒙特卡罗

- The expectation value of O is

$$\langle O \rangle = \frac{\langle \psi | O | \psi \rangle}{\langle \psi | \psi \rangle} = \sum_{\alpha, \beta} \langle \alpha | O | \beta \rangle \frac{\langle \psi | \alpha \rangle \langle \beta | \psi \rangle}{\langle \psi | \psi \rangle}$$

where α and β are 具有确定电子自旋构型。例如, 两个sets

$$\{R_1, \dots, R_{N_e/2}\} \text{ and } \{R'_1, \dots, R'_{N_e/2}\}$$

这两个sets的交就是double occupied sites

$$\{R_1, \dots, R_{N_e/2}\} \cap \{R'_1, \dots, R'_{N_e/2}\} = \{R_1^d, \dots, R_D^d\}$$

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变分蒙特卡罗

- 蒙特卡罗方法也可处理量子多体系统。如果可以猜到量子多体系统的基态变分波函数的形式, 通过MC方法最优化变分参数, 可以得到变分基态波函数。用这种办法, 可以决定量子相图。
- 考虑相互作用 N_e 电子体系, 一个量子态 $|\psi\rangle$ 和可观察量 O
- 参考文献: arXiv 0707.1020

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变分蒙特卡罗

- The state $|\alpha\rangle$ is given by

$$|\alpha\rangle = c_{R_1, \uparrow}^\dagger \cdots c_{R_{N_e/2}, \uparrow}^\dagger c_{R'_1, \downarrow}^\dagger \cdots c_{R'_{N_e/2}, \downarrow}^\dagger |0\rangle$$

- 重写 $\langle O \rangle$

$$\sum_{\alpha} \left(\sum_{\beta} \frac{\langle \alpha | O | \beta \rangle \langle \beta | \psi \rangle}{\langle \alpha | \psi \rangle} \right) \frac{|\langle \psi | \alpha \rangle|^2}{\langle \psi | \psi \rangle} = \sum_{\alpha} f(\alpha) \rho(\alpha)$$

$$f(\alpha) = \sum_{\beta} \frac{\langle \alpha | O | \beta \rangle \langle \beta | \psi \rangle}{\langle \alpha | \psi \rangle}, \quad \rho(\alpha) = \frac{|\langle \psi | \alpha \rangle|^2}{\langle \psi | \psi \rangle}$$

$$\rho(\alpha) \geq 0, \quad \sum_{\alpha} \rho(\alpha) = 1.$$

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变分蒙特卡罗

- 对这样一个系统, 在电子构型空间sample $|\alpha\rangle$ 态, 做 Metropolis algorithm, 就可以算出 $\langle O \rangle$.
- The error bars are given by

$$\sqrt{\frac{1}{N_r - 1} \sum_{l=1}^{N_r} (\langle O \rangle_l - \overline{\langle O \rangle})^2}$$

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变分蒙特卡罗

- There is a given expression of $|\psi\rangle$ with several free parameters. For example, $|\psi\rangle$ is a d-wave pairing state with gap parameters Δ_d . It can also be a generalized pairing wave function with Δ_d 和 antiferromagnetic order parameter Δ_{ad} . (用于 Hubbard model 或 t-J model, 见参考文献 arXiv 0707.1020).
- 变化 Δ_d 和 Δ_{ad} , 用 MC, 可以画出 $E(\Delta_d, \Delta_{ad})$ 。这样, 就可以确定 supercond-AF 相图。

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扩散蒙特卡罗

- Diffusion Monte Carlo: 把Schrodinger equation写成虚时，这时，与粒子的扩散方程比较，波函数就象扩散粒子的密度。用MC解这个扩散方程，所以叫DMC。这实际上是粒子的随机行走问题，所以，又叫随机行走MC。

$$\frac{\partial \psi}{\partial \tau} = -\hat{H}\psi,$$

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扩散蒙特卡罗

- 用一组本征态展开
$$\psi = \sum_i^{\infty} c_i \phi_i, \quad \hat{H}\phi_i = \epsilon_i \phi_i,$$
- 形式解 $\psi(\tau_1 + \delta\tau) = e^{-\hat{H}\delta\tau}\psi(\tau_1)$

$$\psi(\delta\tau) = \sum_i^{\infty} c_i e^{-\epsilon_i \delta\tau} \phi_i.$$
- 长时间演化后
$$\lim_{\tau \rightarrow \infty} \psi(\delta\tau) = c_0 e^{-\epsilon_0 \tau} \phi_0.$$

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扩散蒙特卡罗

- 把空间坐标明显写出来($\mathbf{R} = (\mathbf{r}_1, \dots, \mathbf{r}_n)$)

$$\lim_{\tau \rightarrow \infty} \psi(\mathbf{R}, \delta\tau) = c_0 e^{-\epsilon_0 \tau} \phi_0(\mathbf{R}).$$

- 设哈密顿量是动能加势能，得到“扩散方程”

$$-\frac{\partial \psi(\mathbf{R}, \tau)}{\partial \tau} = \left[\sum_i^N -\frac{1}{2} \nabla_i^2 \psi(\mathbf{R}, \tau) \right] + (V(\mathbf{R}) - E_T) \psi(\mathbf{R}, \tau).$$

$$E_0 - E_T \approx 0$$

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扩散蒙特卡罗

- 引进了一个试探波函数（可以用VMC或其他办法得到） $\psi_G(\mathbf{R})$ 定义分布

$$f(\mathbf{R}, t) = \psi_G(\mathbf{R}) \psi(\mathbf{R}, t)$$

$$-\frac{\partial f(\mathbf{R}, t)}{\partial t} = -\frac{1}{2} \nabla^2 f(\mathbf{R}, t) + \nabla \cdot [\mathbf{V}(\mathbf{R}) f(\mathbf{R}, t)] - S(\mathbf{R}) f(\mathbf{R}, t)$$

$$\mathbf{V}(\mathbf{R}) = \frac{\nabla \psi_G(\mathbf{R})}{\psi_G(\mathbf{R})} \quad S(\mathbf{R}) = E_T - E_L(\mathbf{R})$$

$$E_L(\mathbf{R}) = -\frac{\nabla^2 \psi_G(\mathbf{R})}{2\psi_G(\mathbf{R})} + \mathcal{V}(\mathbf{R})$$

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扩散蒙特卡罗

- 分布的扩散方程的形式解

$$f(\mathbf{R}', t + \tau) = e^{\tau E_T(t + \tau)} \int d\mathbf{R} \tilde{G}(\mathbf{R}', \mathbf{R}, \tau) f(\mathbf{R}, t)$$

- \tilde{G} 是 $E_T=0$ 时的 Green's function

$$\begin{aligned} \tilde{G}(\mathbf{R}', \mathbf{R}, \tau) &= \frac{1}{(2\pi\tau)^{3n/2}} \int d\mathbf{R}'' e^{-[(\mathbf{R}' - \mathbf{R}'')^2/2\tau]} \\ &\times \delta(\mathbf{R}'' - \mathbf{R} - \mathbf{V}(\mathbf{R})\tau) \\ &\times e^{-(1/2)[E_L(\mathbf{R}') + E_L(\mathbf{R})]\tau} + \mathcal{O}(\tau^2). \end{aligned}$$

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扩散蒙特卡罗

- 用一个n-粒子随机行走来迭代解上面的方程，即由一个 $f(\mathbf{R})$ 出发，diffuse 到 $f(\mathbf{R}')$ ，随机行走是否 do，即是否接受 \mathbf{R}' 由重要性抽样决定。经过这样的MC，最后可以得到 ground state 的分布。
- 扩散MC，又称Green函数MC的short time近似。
J. Chem. Phys. 77, 349 (1982). J. Chem. Phys. 77, 5593 (1982).
- 与VMC比较，DMC可以修正f的形式，求基态比VMC好，但无法求激发态。

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扩散蒙特卡罗

- 基态波函数 $H\Psi_0(x) = E_0 \Psi_0(x)$,
- Green函数 $HG(x, y) = \delta(x - y)$,
- $G(x, y) = G(y, x)$,
- 用MC方法求解以下方程称为Green函数MC
$$\Psi_0(y) = E_0 \int \Psi_0(x) G(x, y) dx.$$
- 扩散MC是一个例子，其他的，如贝塞尔函数MC，库仑格林函数MC，等等，主要是用的Green函数不同

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量子蒙特卡罗

- QMC方法是 simulating 强相互作用玻色和费米多体问题的强有力工具。
- 变分蒙特卡罗是 QMC 的一种，但只考虑了某些特定的量子构型，是有明显偏向的。DMC 是求基态用加强版的 VMC。
- 无偏向的 QMC 是要在整个量子态空间做抽样。但 MC 的权重是经典的，这会在处理量子问题时遇到很多麻烦。
- 对相互作用玻色体系，主要问题是抽样的效率问题。对相互作用费米子体系，几乎对实际物理上重要的系统，都会有所谓的经典权重的负符号问题，甚至是 phase 问题，即对某些构型，经典权重是负的或者是复的，这使 MC 算法失效。

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量子蒙特卡罗

- Sign problems: QMC有两类sign problems
- 一类是相互作用费米子体系，由费米子的反对易关系引起（见以后讨论）
- 另一类是spin或玻色子系统中lattice几何引起的。反铁磁耦合会导致负的MC几率。对双子格lattice, 总可使spin flip为偶数，所以，没有符号问题，但对有阻错的格子，例如，三角、Kagome等会有奇数spin flip的update从而出现负几率存在，求和会出现零配分函数。

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量子蒙特卡罗：相互作用玻色子， SSE算法

- 重写H $H = -J \sum_{b=1}^M [H_{1,b} - H_{2,b}]$

$$H_{1,b} = C - \Delta S_{i(b)}^z S_{j(b)}^z + \frac{h}{2J} (S_{i(b)}^z + S_{j(b)}^z),$$

$$H_{2,b} = \frac{1}{2} (S_{i(b)}^+ S_{j(b)}^- + S_{i(b)}^- S_{j(b)}^+).$$
- 在一个无阻错的lattice (如2D square lattice)，任何常数C都是允许的。取C>0.

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量子蒙特卡罗：相互作用玻色子， SSE算法

- 重新arrange求和

$$Z = \sum_{\alpha} \sum_{S_L} \frac{\beta^n (L-n)!}{L!} \left\langle \alpha \left| \prod_{i=1}^L H_{a_i, b_i} \right| \alpha \right\rangle (-1)^{n_2}.$$

$$H_{0,0} = 1 \quad S_L = [a_1, b_1]_1, [a_2, b_2]_2, \dots, [a_L, b_L]_L$$

with $a_i \in \{1,2\}$ and $b_i \in \{1, \dots, M\}$, or $[a_i, b_i] = [0, 0]$
 n denotes the number of non-[0,0] elements in S_L
 n_2 is the total number of [2,b] elements in S_L

对无阻错lattice, $n_2=\text{even}$. 取做够大的C, 没有符号问题 93

量子蒙特卡罗：相互作用玻色子， SSE算法

- A. Sandvik, PRB 59, R14157 (1999), Stochastic series expansion method with operator-loop update
- 这个算法解决了很多玻色子和自旋模型的计算问题. 但对有阻错的格子，仍会有负符号问题。
- 有些有阻错的格子，例如三角格子，也会有无负符号问题的模型

$$H = \sum_{(i,j)} \{ J_z S_i^z S_j^z - \frac{J_{\pm}}{2} (S_i^+ S_j^- + h.c.) - \frac{J_{\pm\pm}}{2} (S_i^+ S_j^+ + h.c.) \} + J_h \sum_i S_i^z$$

量子蒙特卡罗：相互作用玻色子， SSE算法

- 我们首先介绍对玻色子随机扩展数序列(SSE)展开的原理。要计算 $\langle \hat{A} \rangle = \frac{1}{Z} \text{Tr}\{\hat{A} e^{-\beta \hat{H}}\}$
- 为简单，我们考虑一个XXZ model $H = J \sum_{(i,j)} \left[\Delta S_i^z S_j^z + \frac{1}{2} (S_i^+ S_j^- + S_i^- S_j^+) \right] - h \sum_i S_i^z$
- 记*i,j>=b*为一个bond, 对2维方格子, bond数M=2N.

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量子蒙特卡罗：相互作用玻色子， SSE算法

- 展开配分函数 $Z = \sum_{\alpha} \sum_{n=0}^{\infty} \frac{(-\beta)^n}{n!} \langle \alpha | H^n | \alpha \rangle, \quad \{|\alpha\rangle\} = \{|S_1^z, S_2^z, \dots, S_N^z\rangle\}$
- 由于 $(-\beta)^n$, 一般情况下，即使玻色（或自旋）系统也存在符号问题。Sandvik发现，对无组错系统，这个符号问题不存在。

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量子蒙特卡罗：相互作用玻色子， SSE算法

- 于是，量子问题转化为一个经典问题

$$\langle \hat{A} \rangle = \frac{\sum_{\alpha} \sum_{n=0}^{\infty} \sum_{S_L} A(\alpha, S_L), W(\alpha, S_L)}{\sum_{\alpha} \sum_{n=0}^{\infty} \sum_{S_L} W(\alpha, S_L)}$$

$$W(\alpha, S_L) = \frac{\beta^n (L-n)!}{L!} \left\langle \alpha \left| \prod_{i=1}^L H_{a_i, b_i} \right| \alpha \right\rangle$$

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量子蒙特卡罗：相互作用费米子

- 对费米子，也可做类似的展开，但可以发现，一般情况下存在负符号问题。如果负符号“几率”与正符号几率出现的次数几乎相等，配分函数就会非常小，造成MC概率发散，从而引起极大的误差。

$$\langle A \rangle = \frac{\sum_i A_i W_i}{\sum_i W_i} = \sum_i A_i \rho_i$$

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量子蒙特卡罗：相互作用费米子

- 举二个例子，Determinantal QMC and continuous time MC .
- Determinant MC: 以量子杂质模型为例，

$$H = \sum_s \epsilon_0 c_{0\sigma}^\dagger c_{0\sigma} + Un_{0\uparrow}n_{0\downarrow} + \sum_{p>0\sigma} [V_{0p}c_{0\sigma}^\dagger c_{p\sigma} + V_{0p}^*c_{p\sigma}^\dagger c_{0\sigma}] + \sum_{p>0,\sigma} \epsilon_p c_{p\sigma}^\dagger c_{p\sigma}$$

- 除了第二项，杂质on-site 库伦相互作用，其他都是二次型，可精确解。U=0，杂质的

Green's function是 $G^0 = (\omega - \epsilon_0 - \sum_{p>0} \frac{V_{0p}^* V_{p0}}{\omega - \epsilon_p})^{-1}$

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量子蒙特卡罗：相互作用费米子

- (3) 把费米子自由度求和掉，只留下 $s=\pm 1$ 的自由度，Ising自由度，full Green's function

$$G = \frac{\sum_{\{s\}} \text{Det}[g^{-1}]g}{\sum_{\{s\}} \text{Det}[g^{-1}]} \cdot g^{-1} = \begin{pmatrix} 1 & 0 & \dots & 0 & B_{L-1} \\ -B_0 & 1 & \dots & \dots & 0 \\ 0 & -B_1 & 1 & \dots & \dots \\ \dots & \dots & \dots & \dots & \dots \\ \dots & \dots & \dots & 1 & 0 \\ \dots & \dots & \dots & -B_{L-2} & 1 \end{pmatrix}$$

$$B_l = e^{-\Delta\tau h^0} e^{\lambda s_l \sigma \delta_{i=j=0}}$$

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量子蒙特卡罗：相互作用费米子

- 把 H 分为两项 $H = H^0 + H^i$
- 三个重要步骤：
- (1) 把 β 分为很多小间隔 $\Delta\tau L = \beta$

$$Z \approx \text{Tr} \left[\prod_{l=0}^{L-1} e^{-\Delta\tau H^0} e^{-\Delta\tau H^i} \right] + O(\Delta\tau^2 U)$$

- (2) Discrete Hubbard-Stratonovich 变换

$$e^{-\Delta\tau U[n_{0\uparrow}n_{0\downarrow} - \frac{1}{2}(n_{0\uparrow} + n_{0\downarrow})]} = \frac{1}{2} \sum_{s=\pm 1} e^{\lambda s(n_{0\uparrow} - n_{0\downarrow})}$$

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量子蒙特卡罗：相互作用费米子

量子蒙特卡罗：相互作用费米子

- DQMC, $\det g^{-1}$ 不能保证是非负的，sign problem!!

- 对给定的电子自旋 σ ,

$$G_\sigma = \frac{\sum_{\{s\}} \rho g_\sigma}{\sum_{\{s\}} \rho}$$

$$\rho = \text{Det}[g_\uparrow^{-1}] \text{Det}[g_\downarrow^{-1}]$$

- 已严格证明对单杂质问题，两个行列式的积 ρ 总是正的。No sign problem

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量子蒙特卡罗：相互作用费米子

- 对 Hubbard model, DQMC 也可用，

$$H = -t \sum_{\langle i,j \rangle, \sigma} (c_{i\sigma}^\dagger c_{j\sigma} + c_{j\sigma}^\dagger c_{i\sigma}) + U \sum_i (n_{i+} - \frac{1}{2})(n_{i-} - \frac{1}{2}) - \mu \sum_i (n_{i+} + n_{i-})$$

- 当 $U < 0$ 时，无 sign problem

- 当 $U > 0$, 只有 $\mu = 0$, 即 Hubbard band 半满时才没有 sign problem

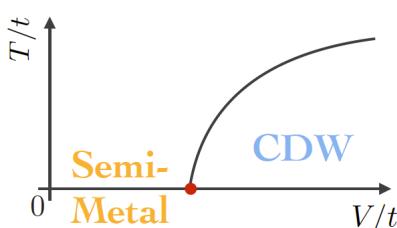
- 很遗憾，物理上最感兴趣的 $U > 0$, finite μ , 存在 sign problem, 且 U 越大越严重。

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量子蒙特卡罗：相互作用费米子

- Phase diagram



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量子蒙特卡罗：相互作用费米子

- CT-QMC, Z_0 is non-interacting partition function

$$Z = Z_0 \sum_{k=0}^{\infty} \frac{(-V)^k}{k!} \int_0^\beta d\tau_1 \int_0^\beta d\tau_2 \dots \int_0^\beta d\tau_{2k} \delta(\tau_1 - \tau_2) \dots \delta(\tau_{2k-1} - \tau_{2k}) \times$$

$$\left\langle \left(\hat{n}_{i_1}(\tau_1) - \frac{1}{2} \right) \left(\hat{n}_{i_2}(\tau_2) - \frac{1}{2} \right) \dots \left(\hat{n}_{i_{2k-1}}(\tau_{2k-1}) - \frac{1}{2} \right) \left(\hat{n}_{i_{2k}}(\tau_{2k}) - \frac{1}{2} \right) \right\rangle_0$$

$$= Z_0 \sum_{k=0}^{\infty} \frac{(-V)^k}{k!} \int_0^\beta d\tau_2 \int_0^\beta d\tau_4 \dots \int_0^\beta d\tau_{2k} \det(G^k),$$

$$\langle \dots \rangle_0 = \mathcal{T} \text{Tr}(e^{-\beta \hat{H}_0} \dots) / Z_0$$

$$G_{pq}^k = \mathcal{G}_{i_p i_q}^0(\tau_p - \tau_q) - \delta_{pq}/2, \quad \mathcal{G}_{ij}^0(\tau) = \langle \hat{c}_i(\tau) \hat{c}_j^\dagger \rangle_0$$

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量子蒙特卡罗：相互作用费米子

- G 是 $2k \times 2k$ matrix.
- 由于 $(-V)^k$, 在 k 为 odd, $V > 0$, 一般情况下, 有 sign problem.
- 对六角格子, 可以证明, 对 $V > 0$

$$w(\mathcal{C}) = \frac{(-V)^k}{k!} \int_0^\beta d\tau_2 \int_0^\beta d\tau_4 \dots \int_0^\beta d\tau_{2k} \det(G^k) > 0$$

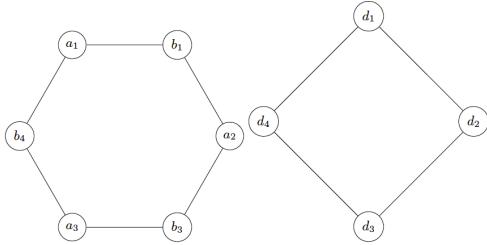
$$\mathcal{C} = \{i_1, i_2; \tau_2\}, \{i_3, i_4; \tau_4\} \dots \{i_{2k-1}, i_{2k}; \tau_{2k}\}$$

$$Z = Z_0 \sum_{\mathcal{C}} w(\mathcal{C})$$

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量子蒙特卡罗：相互作用费米子

- Mapping



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路径积分蒙特卡罗

- 作为路径积分MC中的一个重要例子, 简介一下格点规范理论。粒子物理中的强相互作用理论SU(3)QCD, 在高能端相互作用耦合常数趋于零, 即所谓的渐近自由, 可以用微扰论处理, 即微扰QCD。
- 色自由度在强如LHC这样的加速器(相比渐近自由能标, 仍是低能)中也没有显现出来, 表明在低能下色是禁闭的, 即所谓的夸克禁闭。所以, 低能是强相互作用区。

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路径积分蒙特卡罗

$$S = \beta \sum_{\text{plaquette}} \left[1 - \frac{1}{2N} \text{Tr}(\Omega_p + \Omega_p^*) \right]$$

- 这个作用量在 $a \rightarrow 0$ (连续极限), 回到通常我们熟悉的SU(3)Yang-Mill作用量

$$\beta = \frac{2N}{g^2}$$

$$\Omega_p = U_{n,\mu} U_{n+\mu,\nu} U_{n+\nu,\mu}^{-1} U_{n,\nu}^{-1}$$

$$U_{n,\mu} = e^{i a g A_{\mu}^{\alpha} \tau_{\alpha}}$$

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量子蒙特卡罗：相互作用费米子

- 无自旋费米子 no sign problem 似乎很奇怪。因为DQMC中的经验是两个自旋相反的费米子 determinants 互为复共轭才导致无 sign problem. 而且是 negative U.
- 事实上, 这是与 negative U Hubbard model 相关的: 把六角格子 spinless fermion model with positive V 可以映射到一个四方格子上 负自旋1/2费米子模型 with Hubbard U=-V.

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路径积分蒙特卡罗

- 路径积分蒙特卡罗 (顾昌鑫—计算物理学)
 - 把泛函积分在欧氏空间写出
- $$Z_{fi} = \int e^{-S[x]/\hbar} [dx], \quad S = \int_0^T \left[\frac{m}{2} \left(\frac{dx}{dt} \right)^2 + V(x) \right] dt$$
- 离散化 $Z_{fi} = \sum_{\text{paths}} e^{-S[x]/\hbar}$,
 - 与求配分函数类似, 在一下边界条件下用 MC 求泛函积分

$$x(0) = x_i, x(T) = x_f$$

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路径积分蒙特卡罗

- 强相互作用只能用非微扰方法处理, 格点规范是唯一行之有效的方法: 把4维时空离散化, 通常先研究虚时问题, 即在4维离散欧氏空间, 或四维格子中研究SU(3)规范理论。
- 最早是 Wilson 提出了 LGT 的规范不变的 Wilson 做用量

$$S = \beta \sum_{\text{plaquette}} \left[1 - \frac{1}{2N} \text{Tr}(\Omega_p + \Omega_p^*) \right]$$

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路径积分蒙特卡罗

- 路径积分量子化

$$Z = \int D A_\mu e^{-S(U_\mu)}$$

- 离散化

$$Z = \sum_{\{U_\mu\}} e^{-S(U_\mu)}$$

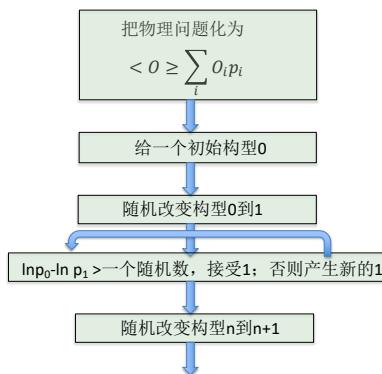
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路径积分蒙特卡罗

- 有多种LGT作用量的选择，都可以回到连续极限
- 4维lattice, Hilbert空间的维数是 4^N ，还不包括内部自由度。计算量超大。
- 放夸克，有符号问题。
- 要重整合到红外临界点，要求LGT有正确的scaling行为。计算上要克服临界慢化。

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蒙特卡罗模拟框图



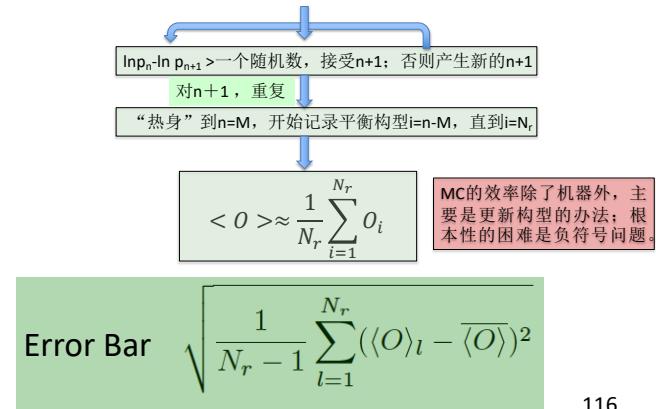
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路径积分蒙特卡罗

- Wilson证明在 $\beta \rightarrow 0, (g \rightarrow \infty)$, 即强耦合极限，任何规范理论都是禁闭的。
- 所以，要证明，U(1)LGT理论用confinement-deconfinement相变，电荷不禁闭。
- SU(3) 色规范理论是禁闭的，没有相变。

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蒙特卡罗模拟框图



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谢谢！

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