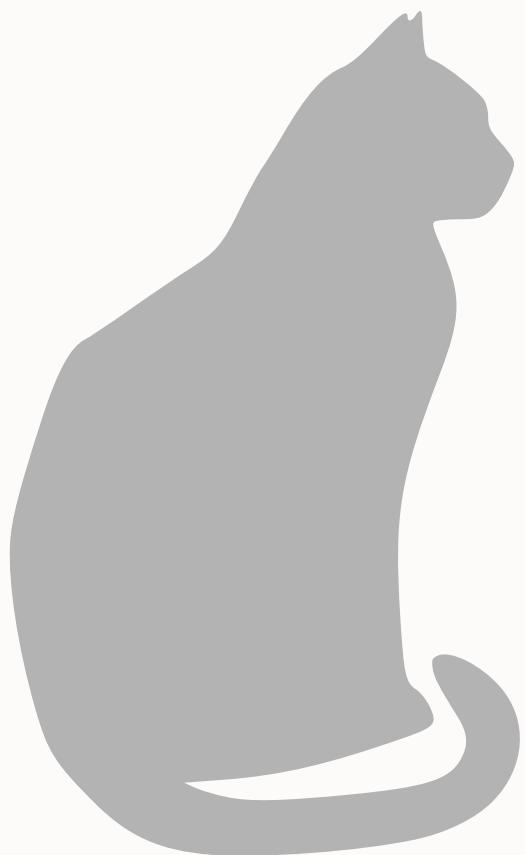


Advanced Statistics Mechanics



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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) $\{N_i\} \mu dN \rightarrow \sum_i \mu_i dN_i \mu_1 = \left(\frac{\partial \xi}{\partial N_i}\right)_{T, P, \{N_j \neq i\}}$

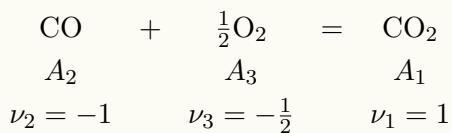
$$\int dT - V dq + \sum_i N_i d\mu_i = 0$$

$k+1$ 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.

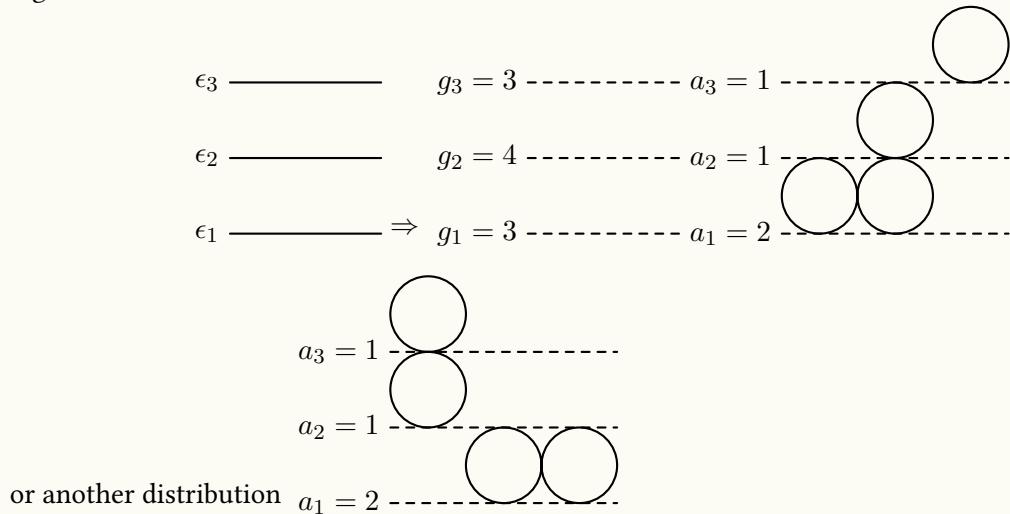
2.3 近独立粒子系统的统计物理

- 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

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

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

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

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

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

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

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

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

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

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

4.1 能量涨落, 热力学极限, 经典极限

Definition 4.1.1 (涨落). For energy:

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

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

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

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

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

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

$$\{\psi_1(\mathbf{r}_1, \dots, \mathbf{r}_N), \dots, \psi_s(\mathbf{r}_1, \dots, \mathbf{r}_N)\}$$

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 → 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 → 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} , $\psi_0 = \sqrt{|A|/B}$. $\psi \sim \psi_0$, $f = \frac{\psi}{\hbar}\psi$, $f^* = f$. 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.

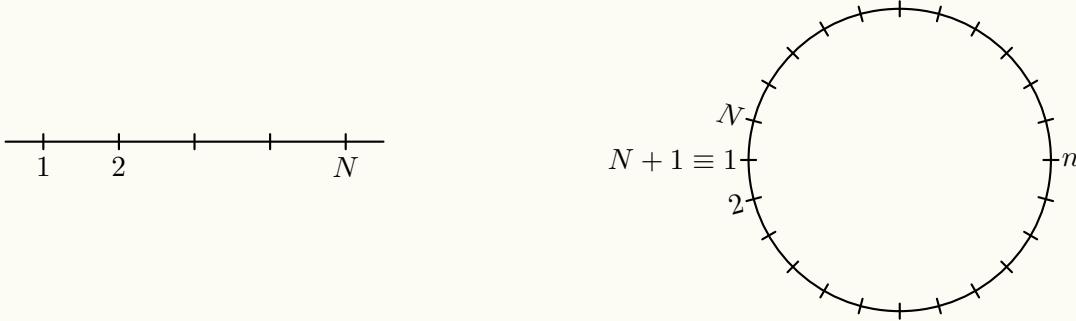
- If $B \neq 0$, then ...

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

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

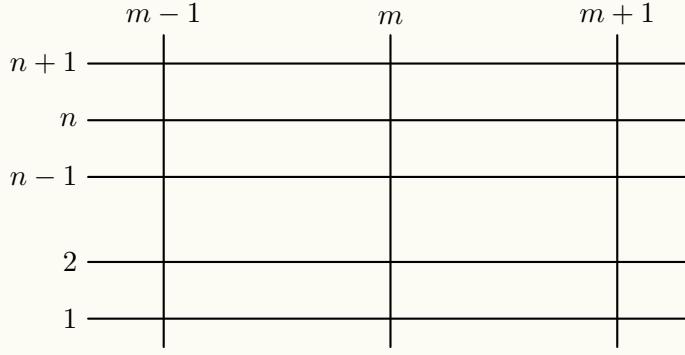
And A can be expressed as

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

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 $l = 2, d = 2$.

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

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

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

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' ?

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

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

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

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).

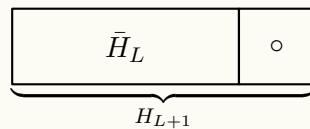
For the condensed matter, since $a = \text{finite}$, there is a “natural” cut-off, so we do not care about UV, but the infrared divergence ($p \sim \frac{1}{L}$), i.e., we consider the infrared fixed point $\xi \rightarrow \infty$.

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.

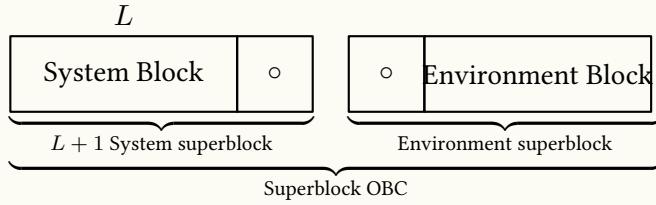
¹Normalization in QFT (actually, we consider QED).

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

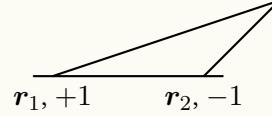
$$\nabla\theta \cdot \nabla\theta = \frac{x^2 + y^2}{r^4} = \frac{1}{r^2}$$

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 -theomre, 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 equilirum 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 $\Delta\rho \propto \Delta N$.

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

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).

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

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

$$S = Nk[\ln(2 \operatorname{ch}(\beta\epsilon)) - \beta\epsilon \operatorname{th}(\beta\epsilon)]$$

$$\text{当 } T \rightarrow 0, \beta\epsilon \rightarrow \infty, \operatorname{th}(\beta\epsilon) \rightarrow 1, \operatorname{ch}(\beta\epsilon) \sim \frac{1}{2}e^{\beta\epsilon},$$

$$\ln(2 \operatorname{ch}(\beta\epsilon)) \rightarrow \beta\epsilon \Rightarrow S \rightarrow Nk[\beta\epsilon - \beta\epsilon] = 0$$

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.

(a) 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).

(b) 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.

(c) 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.

(a) 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

$$P(E) dE = p_i (\Sigma(E + dE) - \Sigma(E)) = \frac{1}{Z} e^{-\beta E_i} \Sigma'(E) dE$$

(b) $P(E)$ 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 $\Sigma''(E)/\Sigma'(E) = \beta$.

(c) 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

$$\begin{aligned} \bar{N} &= -\frac{\partial}{\partial \alpha} \ln \Xi = e^{-\alpha} Z, \quad \mu = -k_B T \ln \frac{Z}{\bar{N}} = -k_B T \left[3 \ln T + \ln \frac{V}{\bar{N}} + \ln \left[\frac{8\pi k_B^3}{(hc)^3} \right] \right], \\ \bar{E} &= -\frac{\partial}{\partial p} \ln \Xi = 3\bar{N}k_B T, \quad p = \frac{1}{\beta} \frac{\partial}{\partial V} \ln \Xi = \frac{\bar{N}k_B T}{V} = \frac{\bar{E}}{3V}, \\ S &= k_B \left(\ln \Xi - \alpha \frac{\partial}{\partial \alpha} \ln \Xi - \beta \frac{\partial}{\partial \beta} \ln \Xi \right) = \bar{N}k \left\{ 3 \ln T + \ln \frac{V}{\bar{N}} + \left[4 + \ln \left(\frac{8\pi k_B^3}{(hc)^3} \right) \right] \right\}, \\ C_V &= \left(\frac{\partial}{\partial T} \bar{E} \right)_V = 3Nk_B, \quad C_p = \left(\frac{\partial H}{\partial T} \right)_p = 4Nk_B \end{aligned}$$

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

$$\frac{N_0}{V} = n \left[1 - \left(\frac{T}{T_c} \right)^{3/2} \right].$$

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固体。固体是宏观现象的宏观唯象理论。统计物理则研究更微观的微观理论。固体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。统计物理一开始就在考虑物质是由大颗粒组成，由微观性质出发，然后统计推导出宏观性质。以下我们总结一下固体和统计物理学的主要结论。

1.1 固体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。

* 平衡定律: A与B平衡, B与C平衡, 则A与C平衡。

* 温度: 测量物体间是否平衡的物理量称为温度。一切处于平衡状态的物体温度相等。

* 温度温标是数值化的规则叫温标。

* 物态方程: 物体的物理状态由几何参数(体积、面积、形状), 力学变量(位置、速度、加速度)和化学变量(质量、浓度)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时初态和末态的内能差 $U_2 - U_1 = W_a$ (外界对物体作功绝热)。

* 固体第一定律: 推广的非绝热过程, 存在从外界吸热 $Q = U_2 - U_1 - W_a$, 即能守恒。

* $C_y = \frac{\partial Q_y}{\partial T}$ 称为比容, y 表示不变量, $y = V$ 容积, $y = p$ 压强, $y =$ 质量。

单位质量的比容称为比热容。

* 内能是标量, $H = U + pV$ 也是标量。内能是绝热过程中外界没做功的情况下, $\Delta U = W_a$ 。内能是在过程中外界吸热或放热 $Q_p = \Delta H$ 。

* 熵：对可逆过程，志取大熵

$$\Delta S = S - S_0 = \int_{\text{初态}}^{\text{末态}} \frac{dq}{T} \quad \text{与过程无关.}$$

* 恒定子二定律：

$$\Delta S \geq \int_{(i)}^{(f)} \frac{dq}{T}$$

熵增加原理.

* 直子基本方程：第一定律 + 第二定律. 定调子

$$dU = TdS + \sum_i F_i dg_i, \quad \text{例: } dU = TdS - pdV$$

例如，对 $P-V-T$ 子

$$dU = TdS - pdV$$

* 自由能： $F = U - TS$

$$dF = dU - d(TS)$$

$$\text{例: } dF = -SdT - pdV \quad (\text{等温准向})$$

* Gibbs 自由能：

$$G = F + PV$$

$$\text{例: } dG = -SdT + Vdp$$

等温准向过程， $\delta G = 0$.

Kelvin 不可能从单一同级
退，但必定变为不可逆的
而产生其他影响
classical classical
不可能起因从低级到高级
与低级而产生其他影响

1.2 单相系(单相系)的平衡

* 单相系，顾名思义，就是各部分性质完全一样的物体。

* 单相系的微小可逆过程由热力学基本微分方程
描述。根据前面对应不同，可以有3种表达描述，
例如对 $P-V-T$ 子

$$dU = TdS - pdV \quad (S, V) \quad \left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V$$

$$dH = TdS + Vdp \quad (S, p)$$

$$dF = -SdT - pdV \quad (T, V)$$

$$dG = -SdT + Vdp \quad (T, p)$$

* 可逆的热力学量：

(1) $P, V, \dots; T$.

(2) 上物理方程是和，坦言影响系数。

即各种变化如，膨胀系数、压缩系数、
压缩系数，… 可见。 (强度强，很弱)

U, S, F, G 等不直接相关。

(3) 应用：理想气体、麦克斯韦气体。

互易性、称性很好。

(复相)，例如水

1.3 单之系的相变热力学 (单之系)-“res”
(复相)

* 单相系者也是单之系(即相同的状态性质). 例如
相变，就是整个单相系的性质发生变化，从一个平
衡态变为另一个平衡态。

* 系统处于某一相中，该系统处于热力学平衡中。

热力学平衡的判据： $S = S_{\max} \Leftrightarrow$ 孤立系处于平衡态。

数学表达为： $\delta S = 0, \delta^2 S < 0, \delta U = \delta V = \delta N = 0$.

S : 热变功. 可能的变功。

* $\delta S = 0, \delta^2 S < 0$, 找出局部域相对极大. 其它在
它是几个相对大集中最大的那个. 基本上称为互换。

* $\delta S = 0, \delta^2 S = 0$, 这时, $\delta^3 S = 0$ 是保证稳定性
条件. $\delta^2 S < 0$ 保证系统是互换. 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， $U = U_{\min}$.

热力学可变系的热力学判据

* 对单之系， λ 可变，则内能的基东
数方程是：(对 $P-V-T$ 子)

$$dU = TdS - pdV + (U - Ts + Pv)dN$$

$$U - Ts + Pv = \frac{G}{N} \equiv \mu, \text{ 化学势, 1 mol m Gibbs函数}$$

$$(U = Nu, V = Nv, S = Ns)$$

* 仅有热力学平衡的方程高一阶 μdN .

$$\mu = \left(\frac{\partial U}{\partial N}\right)_{S,V} = \left(-\frac{\partial F}{\partial N}\right)_{S,p} = \left(\frac{\partial F}{\partial N}\right)_{T,V} = \left(\frac{\partial G}{\partial N}\right)_{T,p}$$

$$\delta \mu = -SdT + Vdp.$$

$$\pi = F - \mu N = U - TS - \mu N = F - G \text{ 称为}$$

巨势 平衡

* 仅有热力学判据都需考虑 μdN 这一项。

* 由平衡判据，可以得到达到平衡的条件。

即状态变量之间的关系，例如，升高热力学
判据可得 $\frac{\partial \mu}{\partial T} = \frac{\partial G}{\partial T}$ 二相之间的平衡条件是

- $T_1 = T_2, P_1 = P_2, \mu_1 = \mu_2$
 $\text{恒压平行} \quad \text{相变平行 (不发生相变)}$
- (二元相, $S_i, U_i, V_i, N_i : i=1, 2$ 都可变, 但各体积不变, 总体积不变, 总内能不变)
 又例如, 若总内能不变, 则 $\delta F = 0$ 条件
 得出: $P_1 = P_2, \mu_1 = \mu_2 = 0$: 相变不守恒条件
 m化系数为0, 例如, 蒸汽, 液体.
- * 由平衡了稳定性判据, 可得稳定性条件. 稳定条件往往由一些响应系数给出, 例如, 弹性模极小, 稳定度高比例 $C_0 > 0$ 和等温压缩系数的 $K_T = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T > 0$. 等.
- * 根据相变平行条件, 可以得到相同:
 例如, 二相平衡: $\mu^1 = \mu^2, T_1 = T_2, P_1 = P_2 = P$.
 则 $\mu^1(T, P) = \mu^2(T, P)$ 给出 $T-P$ 平面两条曲线, 这就是二相~3界线; 若共有三元相, $\mu^1 = \mu^2 = \mu^3$ 则完全确定了 (T, P) , 这就是三相共存. 另外, 对于某一单 (T, P) 点, 只有一个相是稳定的. 这样一来是以前错误. 水 m相固.

- * 在研究低温化学反应过程中, 実验显示
 出现规律是: 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

- * 热力学三定律:
- Nernst 定理
 - 绝对熵 $\lim_{T \rightarrow 0} S = 0$.
 - 不可逆通过有限步导致物体冷却绝对零度.

1.5 线性非平衡热力学

- * 线性非平衡热力学: 仅限于偏离平衡远. 在一个宏观小、微观大的区域, 可用局域平衡近似.
- * 保时守恒定律 \Rightarrow 推广的热力学第一定律 (把小块的质点加起来)
- * 对小块, 热力学方程仍成立.
- * 不守律, $\Theta = \frac{\partial S}{\partial E}$ 表示小块的熵产率

- * 关于相变, 我们以后将译成国际, 所以就不继续展开.
- 1.4 热力学第三定律: 多元的复相平衡和化学平衡
- * 多元系就是不同化学 (广泛) 组分的系统, 平衡态又可以是 (T, P, N_1, \dots, N_k) . $(N_1, \dots, N_k) = \{N\}$.
- * 基本微分方程中 $dN \rightarrow \sum_i \mu_i dN_i$.
- $\mu_i = \left(\frac{\partial G}{\partial N_i} \right)_{T, P, \{N_j\}}$.
- * $(T, P, \{N\})$ 满足 Gibbs 关系:
- $$SdT - VdP + \sum_i N_i d\mu_i = 0.$$
- 其中只有 $k+1$ 个是独立的.
- * 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
 $CO + \frac{1}{2} O_2 \rightleftharpoons CO_2, \Rightarrow v_1 = 1, v_2 = -1, v_3 = \frac{1}{2}$
 $A_1 = CO_2, A_2 = CO, A_3 = O_2$.
- m化平衡条件是
 $\sum_i v_i \mu_i = 0$. “+”为生成物
“-”为反应物

- $\rho_n \frac{\partial \vec{J}_s}{\partial t} = - \nabla \cdot \vec{J}_s + \Theta, \vec{J}_s$ 为大电流密度
- $\vec{J}_s = \frac{\vec{J}_n}{T}, \vec{J}_n$ 为速度, $\Theta = \frac{k}{T} \left(\frac{\partial T}{\partial t} \right) > 0$
- * $\frac{\partial n}{\partial t} + \nabla \cdot \vec{J}_n = 0$, 电子守恒.
- n 为 density. \vec{J}_n 为 particle current density.
- * 电荷守恒:
- 热传导 Fourier 定律: $\vec{J}_q = -k \nabla T$.
 - 扩散 Fick 定律: $\vec{J}_n = -D_n \nabla n$.
 - 电场定律: $\vec{J}_e = \sigma \vec{E} = -\sigma \nabla \phi$
- 一般 $\vec{J} = (J_1, \dots, J_n)$ 为热力学量, $\vec{X} = (X_1, \dots, X_n)$ 为力, 则 $J_k = \sum_i L_{ki} X_i, L_{ki}$ 为动力学量.
- * 马赫拉得关系: $L_{kj} = L_{ik}, L$ 是对称矩阵

第3章 统计物理基本概念和近独立粒子系统统计的因果回溯

指对于宏观物体的现象实验基础上得出一些规律的经验定律，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，结合大量实验提出的统计律：统计规律，导出宏观物性的理论十全十美。

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、自旋等。我们往往称“粒子”，用广义坐标 (\mathbf{r}, \mathbf{p}) ($\mathbf{r}^a; a=1, \dots, r$) 描述，单粒子能级 $E = E(\mathbf{r}, \mathbf{p})$ 。一个微观大，宏观小的单粒子相空间中体积： $d\omega = d^{3r} \mathbf{d}^3 p$ 。对 N 个经典宏观物体，广义坐标和广义动量 $(q_1, \dots, q_s; p_1, \dots, p_s)$, $S = \Omega^N$ 。~~在~~ 空间相体积之积 $dS = dq_1 \dots dq_s dp_1 \dots dp_s$

$\{(q_1, \dots, q_s; p_1, \dots, p_s)\}$ = 相空间，一个点就代表着一个微观状态。

* 不同统计的条件，造成不同的统计量。 (14)

2.2 ~~统计规律~~

2.2 平衡态统计的几率率原理

* 宏观视图是宏观大、统计大，宏观稳定、微观长，每次观测都对应于极大数目的微观状态。所以，除了微观运动规律外，统计规律也起作用。这是由宏观系统与外界的作用不可避免及随机性决定的。叫做几率分布宏观状态的宏观状态和微观状态的联系由几率率相联。

* 宏观和微观可观测量的统计平均值。

* 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给出的。

* 对一个孤立系，即 (E, V, N) 固定系统 最简单、朴素的假设是几率率假设，即得几率率原理：对于处于平衡态下的孤立系，系统有尽可能的微观状态在出现的几率相等。

* 可能的微观状态是指占有宏观状态 (E, V, N) 的宏观微观状态数

* 原子：单粒子量由一组量子数标志，

即一组可对易力学算符的一组本征值描述 (本征值可连结，也可互独立)。例如，对自由粒子，~~所有~~ 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 $\psi(x) \propto e^{i k x / \hbar}$ ，而不是高斯波，波数也是离散的。

$$E = \frac{\hbar^2}{2m} = \frac{2\pi^2 h^2}{L^2} (n_x^2 + n_y^2 + n_z^2), \quad \Psi = \frac{2\pi h}{L} (n_x, n_y, n_z).$$

对于 $(3)-$ 维，可以有不同的量子态，例如 $n_x=0, n_y=1, n_z=2, \vec{n}=(0, \pm 1, \pm 2)$ ，上它都有相同的能级，简并度 $g=4$ 。

* 能量经典对应：单粒子状态 $\leftrightarrow \omega = h^2 m$ 单粒子能级。

* 能量量子化的全局性：用量子描述能级，无论是分子、原子、电子还是自旋、质子、都是一样的。

* 在三维或以上空间，只有波动和量子力学。

* 在 $d=2, 1$ ，可以有既非波动、又非量子力学，(ω 为常数)

* 全同粒子不违反 $(3)-$ 单粒子对应。 (Pauli 泛化)

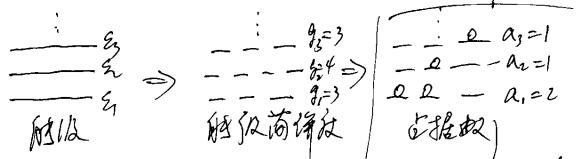
* 如果 ~~两个~~ 粒子可以“简并化”，则可互交换。如果，局域在不同区域的粒子，不能在带中运动，...

2.3 近独立粒子系统的统计物理

* 近独立是相邻的相邻很弱，且只对体系的宏观性质起作用，但对粒子的运动及微观的运动。

$$E = \sum_{i=1}^N E_i, \quad E_i \text{ 为第 } i \text{ 个粒子的能级。}$$

* 对于能级的粒子， $E_\alpha, \alpha=1, \dots, r$ 是能级指标， α 为能级的简并度 (recall 量子 Box 中的自由粒子)。由于能级的全局性，指标不重要，重要的是能级上占据的粒子数。以及粒子的占据数的统计分布



* 对于孤立系， (E, V, N) 。

$$\sum_{\alpha} \alpha_{\alpha} = N, \quad \sum_{\alpha} E_{\alpha} \alpha_{\alpha} = E$$

* 给定一个能级占据数分布 $\{\alpha_{\alpha}\}$ ，由于能级能级可能有多个不同的量子态，一个能级分布可以有不同微观看状态 $\{\alpha_{\alpha}\}$ 与之对应，设 $W(\{\alpha_{\alpha}\})$ 为对应一能级观看状态数。由几率率原理，给出其几率 $P(\{\alpha_{\alpha}\}) \propto W(\{\alpha_{\alpha}\})$ 。

* 粒子态也有可区分和不可区分，对可区分的，

$$W(\{\alpha_{\alpha}\}) = \frac{N!}{\prod \alpha_i!} \prod g_{\alpha_i}^{\alpha_i}$$

上 g_{α_i} 有差 m 级，就是简单从 m 级抽。而前一节对于 N 个粒子放在 M 盒子中，每个盒子放 α_i 是 m 级抽。由最可能分布，可以得到配分函数，有微扰系数，则可求出附加热力学量。这是 Boltzmann 统计力学

* 对 Fermi 子和 Bose 子，它们在不同阶段仍是不可分辨的，只考虑泡利不相容原理中的不可分辨性称 Pauli 反馈。法则是

$$(2) \text{Fermion: } W_F(\{\alpha_{\alpha}\}) = \prod \frac{g_{\alpha_i}!}{\alpha_i!(g_{\alpha_i}-\alpha_i)!}$$

$$W_B(\{\alpha_{\alpha}\}) = \prod \frac{(g_{\alpha_i}+\alpha_i-1)!}{\alpha_i!(g_{\alpha_i}-1)!}$$

* 假设几率分布得出 Bose 和 Fermi 统计力学

* 由玻尔兹曼统计物理结果可以推广到一般情况，但最可能分布的推导方式不同。包括玻耳兹曼定理，要讲一部分内容。

任何物理可观测项 \bar{O} 是微观粒子数的统计平均值

$$\bar{O} = \int d\Omega \bar{O} \quad \int d\Omega = 1$$

* 系统处于某一微观状态（把宏观理解为处于该微观状态的几率）

* 处于 $d\Omega$ 中的 \bar{O} 由于系统会存在一个统计系综，即

系统是随机的，和研究系统性质完全相同。

彼此独立地处于某一微观状态的概率是一样的。

3.3.2 列维 (Liouville) 定理

列维定理：系综的几率密度（或代表其密度）在运动中不变，即 $\frac{d\bar{O}}{dt} = 0$ 或 $\frac{d\bar{P}}{dt} = 0$ 。

列维定理 ~~假设~~ 代表真概率 ~~不是运动~~

~~代表真概率~~：

$$\frac{\partial \bar{P}}{\partial t} + \nabla \cdot \vec{J}_{\bar{P}} = 0, \quad \vec{J}_{\bar{P}} = \bar{P} \vec{v}$$

$$\vec{v} = \left(\frac{\partial \bar{P}}{\partial p_i}, \frac{\partial \bar{P}}{\partial q_i} \right), \quad \vec{v} = (\dot{q}_i, \dot{p}_i).$$

~~列维方程~~ ~~3.3.2~~：

$$\frac{\partial \bar{P}}{\partial t} + \frac{i}{\hbar} [\bar{P}; H] = 0$$

第三章 微观统计学

平衡态统计一般理论是麦克斯韦理论，它适用于任何的微观粒子系统。统计系综包括玻耳兹曼统计、亚统计和正则统计系综，前者是基础，但后者在实际计算中更方便。

3.3.1 经典统计系综

经典力学的微观状态是坐标空间中一个点，它变化遵从牛顿运动方程

$$\dot{q}_i = -\frac{\partial H}{\partial p_i}, \quad \dot{p}_i = -\frac{\partial H}{\partial q_i}, \quad i=1, \dots, S.$$

$\{q_i^{(+)}, p_i^{(+)}\}$ 形成一个相轨道，称为 (主) 演进

$$ds = dq_1 \dots dq_S dp_1 \dots dp_S$$

是相体积元，

设 Γ 为给定物理条件下所有可能的微观状态， $\tilde{\rho} d\Omega$ 为其中的微观状态数，即

$$\tilde{\rho} d\Omega = \frac{\tilde{\rho} d\Omega}{\Gamma} = \frac{\tilde{\rho} d\Omega}{\int d\Omega} \text{ 是概率密度}$$

状态出现在机内几率。 $\tilde{\rho} = \frac{1}{\Gamma}$ 称几率密度。

固有性质

~~因为运动方程~~ $\frac{\partial \tilde{\rho}}{\partial t} + \sum_i \tilde{\rho} \frac{\partial}{\partial q_i} \cdot (\vec{v} \vec{v}_i) = 0 \quad (1)$

$$\begin{aligned} \frac{\partial \tilde{\rho}}{\partial t} &= \frac{\partial \tilde{\rho}}{\partial t} + \sum_i \tilde{\rho} \frac{\partial}{\partial q_i} \cdot \vec{v}_i + \frac{\partial \tilde{\rho}}{\partial p_i} \cdot \vec{p}_i \stackrel{!}{=} 0 \\ &= -\tilde{\rho} \sum_i \left\{ \frac{\partial \vec{v}_i}{\partial q_i} + \frac{\partial \vec{p}_i}{\partial p_i} \right\} \end{aligned}$$

(忽略高阶项)

$$\begin{aligned} &\text{忽略高阶项} \\ &= -\tilde{\rho} \sum_i \left\{ \frac{\partial H}{\partial q_i p_i} - \frac{\partial H}{\partial p_i q_i} \right\} = 0. \quad \text{忽略高阶项} \\ &\text{另一方面, } \frac{\partial \tilde{\rho}}{\partial t} + \sum_i \tilde{\rho} \frac{\partial}{\partial q_i} \cdot \vec{v}_i = 0. \quad \text{忽略高阶项} \end{aligned}$$

$$\frac{\partial \tilde{\rho}}{\partial t} + \sum_i \tilde{\rho} \frac{\partial}{\partial q_i} \cdot \vec{v}_i = 0, \quad \text{或 } \frac{\partial \tilde{\rho}}{\partial t} + \sum_i \tilde{\rho} \frac{\partial}{\partial p_i} \cdot \vec{p}_i = 0.$$

* 列维定理是相空间代表类密度的运动方程是力学定律，但它的假定假设提供了依据。

* ~~量子力学~~：用相空间代替经典相空间；
~~② Schrödinger eq. 代替波动方程；~~
~~波函数是几率密度：~~
 ~~$\psi(t) = e^{iHt/\hbar} \psi_0 e^{-iHt/\hbar}$~~
 ~~$\tilde{\rho}(t) = \psi(t) \tilde{\rho}_0 \psi^*(t)$~~
 ~~$\frac{\partial \tilde{\rho}}{\partial t} + \frac{i}{\hbar} [\tilde{\rho}; H] = 0$~~
~~或~~
 ~~$\bar{O} = \sum_n \tilde{\rho}_n \langle n | O | n \rangle = \text{Tr } \tilde{\rho} O$~~

§3.2 量子统计力学

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- * 对量子力学，我们用波函数或态矢量来代替经典力学的相空间的代数量。波函数波函数中人有 $|n\rangle$ 或 $\langle n|$, 但 $|A_n = \langle n|A|n\rangle$ 是力学量的可观测量的平均值。

对这个~~力学量~~，我们寄希望于一个~~力学量~~， $|n\rangle$, $n=1, \dots$ 其中 n 有 p_n 与之~~有关~~，即有~~力学量~~，这个~~力学量~~为

$$\text{这样}, p_n = \sum_n p_n \quad \text{是一系列几率} \quad \sum_n p_n = 1.$$

~~分子~~ $\bar{A} = \langle A \rangle = \sum_n p_n A_n$.

- * 伎俩存在(或密度矩阵)

$$\hat{\rho} = \sum_n |n\rangle \langle n|. \quad |n\rangle \text{ 是一基波矢量}.$$

$$\langle i|j \rangle = \delta_{ij}, \quad \hat{\rho} \text{ 和 } \hat{A} \text{ 互换阵是}$$

$$\hat{\rho}_{ij} = \langle i|\hat{\rho}|j \rangle = \sum_n \langle i|n \rangle \langle n|j \rangle$$

$$A_{ij} = \langle i|A|j \rangle. \quad \text{由 } \bar{A} = \sum_n p_n \langle n|A|n \rangle = \sum_{ij} \sum_n p_n \langle i|j \rangle A_{ij}$$

$$\Rightarrow \hat{\rho}_{ij} A_{ji} = \text{Tr}(\hat{\rho} A), \quad \text{Tr } \hat{\rho} = 1.$$

§3.3 微正则力学

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- * 经典微正则力学, (E, N, V) 不变的条件, 孤立系。
刘维定理 $\frac{dP}{dt} = 0$, 若平行态物理量不随时间变, 则要求 $\frac{dP}{dt} = 0$ 为必要条件。即在一条相轨迹内, P 有常数, 成立一条相轨迹(~~且~~一条轨道)内 P 为常数, 但这不能保证不同轨迹~~且~~相交。微正则力学的基本假设是, ~~且~~当 $H(q, p) = E$ 时 $P = \text{Const}$. $H \neq E$ 时, $P = 0$.
而 E 平衡为一常数很困难, 数学上~~且~~处理是

$$P = \begin{cases} C, & \text{当 } E \leq H < E + \Delta E \\ 0, & \text{otherwise.} \end{cases}$$

$$\lim_{\Delta E \rightarrow 0} C \int_{AE} d\omega = 1, \quad D(E, P) = \lim_{\Delta E \rightarrow 0} \int_{AE} 0 d\omega.$$

- * 热力学：等几率原理或微正则力学意味着只要时间足够长, (E, N, V) 对应的微观状态都可能出现。即热力学。但这与热力学是由微观上存在宏观上不可逆的~~且~~外界~~且~~相联系的假设。而不是由~~且~~演化。即不是玻尔兹曼的~~且~~微观假设。

* $\hat{\rho}_m$ 的微方程由 $\hat{\rho}$ 满足 Schrödinger eq.

$$i \frac{\partial}{\partial t} |\psi\rangle = \hat{H} |\psi\rangle$$

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

$$\Leftarrow \hat{H} \hat{\rho} - \hat{\rho} \hat{H} = [H, \hat{\rho}]$$

$$\therefore \frac{\partial}{\partial t} \hat{\rho} + i[H, \hat{\rho}] = 0.$$

($\hat{\rho}_m$ Heisenberg eq.)

$$\sum_n H |n\rangle p_n \langle n| - \langle n| p_n \langle n| H$$

* 等几率统计力学: ① 加平均值~~且~~和

$$(2) \quad p_n = \begin{cases} C, & E_n = E \\ 0, & E_n \neq E, \end{cases} \quad N \text{ 是等效的粒子数}$$

即等效~~且~~粒子数为 E , 则发生几率为 C , 必然为 0.

$$(C \text{ 由 } \sum_n p_n = C \quad (\sum_{n(E_n=E)} 1) = 1)$$

$$(\text{由 } \sum_n p_n = 1 \quad (\sum_{n(E_n=E)} 1) = 1). \quad \text{令}$$

$$\begin{cases} E_n = E \\ n \neq \text{总 } n \end{cases} \quad N(E, V, N) = \left(\sum_n 1 \right), \quad N(E = E) \\ C = \frac{1}{N(E, V, N)}. \end{math>$$

~~注意: 等几率~~§3.4 微正则力学中宏观~~且~~统计经典~~且~~:

$$\bar{A} = \int A(q, p) P d\omega$$

$$\Rightarrow \bar{A} = \frac{1}{N!} \int_{\Omega}^S A d\omega$$

$$\text{分子: } \bar{A} = \sum_n p_n A_n$$

 $(E = E_n)$

$$\bar{A} = \sum_n p_n A_n$$

 $(E = E_n)$

第6章 正则系综

§4.1 从微正则系综到正则系综

正则系综是指导系统与大面积接触达到平衡的系综， (T, V, N) 固定，大面积提供确定的温度。

① A 代表正则系综中的系统，B 代表大面积。

且 $A+B$ 是一个孤立系综 $(E_{\text{total}}, V_{\text{total}} = V_A + V_B, N_{\text{total}} = N_A + N_B)$ 。

若 A 和 B 互不影响，则 $E_{\text{total}} = E_A + E_B$ 。设 $S(E_{\text{total}})$ 为 $A+B$ 的总熵，若 A 处于某一状态， B 可处于 $S_B(E_A)$ 状态。 $\therefore A$ 以及处于这个状态的几率

$$\rho_{An} = \frac{S_B(E_A)}{S(E_{\text{total}})}$$

E_A 对 E_A 偏离状态的贡献率。由 $E_A < E_{\text{total}}$ ， $E_A < E_B$ ， E_A 贡献率高。B 有多种状态，我们取其中一个自由能子级来代替指定。由上部的推导，

$S_B(E_A) \sim (E_A - E_A)^M$, $M \sim O(N_B) \sim O(N)$ 。
由于 M 很大，“ $E_A^M (1 - \frac{E_A}{E_{\text{total}}})^M = E_A^M (1 - \frac{E_A}{E_{\text{total}}} + \dots)$ ”二项式展开把 E_A 视为常数。

内能

$$\bar{E} = \sum_n E_n \rho_n = \frac{1}{Z_N} \sum_n E_n e^{-\beta E_n}$$

$$= \frac{1}{Z_N} \left(-\frac{\partial}{\partial \beta} \sum_n e^{-\beta E_n} \right) = -\frac{\partial}{\partial \beta} \ln Z_N$$

$$\text{热强度: } P_{vn} = -\frac{\partial \bar{E}_n}{\partial V},$$

$$P = \sum_n P_{vn} \rho_n = \sum_n \frac{\partial \bar{E}_n}{\partial V} e^{-\beta E_n} = \frac{1}{\beta} \frac{\partial}{\partial V} \ln Z_N.$$

$$dS = \frac{d\bar{E}}{T} + \frac{P}{T} dV = k_B (\beta d\bar{E} + \beta P dV)$$

$$= k_B \left(-\beta \frac{\partial}{\partial \beta} \ln Z_N + \frac{\partial}{\partial V} \frac{\partial}{\partial V} \ln Z_N \right)$$

$$= k_B \left(\ln \frac{1}{Z_N} - \beta \frac{\partial}{\partial \beta} \ln Z_N \right)$$

$$\therefore S = k_B \left(\ln \frac{1}{Z_N} - \beta \frac{\partial}{\partial \beta} \ln \frac{1}{Z_N} \right)$$

$$F = \bar{E} - TS = -k_B T \ln Z_N.$$

§4.3 热力学函数、热力学极限和经典极限

在经典统计中，温度用能量表示。例如 E ，或是 E 与 \bar{E} 的方差。或方均根。此时方差， $(\bar{E}-\bar{E})^2/\bar{E}^2$ ，或 $\sqrt{(\bar{E}-\bar{E})^2}/\bar{E}$ 。

安乐定系综

$$(E_A - E_A)^M = e^{M \ln (E_A - E_A)}$$

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

这时，可以把 $O(E_A^M)$ 视为常数 ρ_{An} ，对 Σ_B 作同样处理

$$\rho_{An} = \frac{1}{\Sigma_B(E_A)} e^{\ln \Sigma_B} = \frac{1}{\Sigma_B(E_A)} e^{\ln \Sigma_B(E_A) - \frac{\partial \Sigma_B}{\partial E_A} E_A + \dots}$$

$$\approx \frac{\Sigma_B(E_A)}{\Sigma_B(E)} e^{-\beta E_A} \triangleq \frac{1}{Z_N} e^{-\beta E_A}$$

其中 $\beta = \frac{\partial \Sigma_B}{\partial E_A}$ ， β 大概没变，从而得

而 $\beta = \frac{1}{k_B T}$ 。 k_B 是 Boltzmann 常数， T 是温度。

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

$E_A = E_n$ ， \sum_n 表示正则子综的总贡献。

$$\sum_n = \text{Tr} e^{-\beta H} = \sum_n \langle n | e^{-\beta H} | n \rangle = \sum_n e^{-\beta E_n}$$

§4.2 热力学

$$\bar{E} = \frac{\text{Tr}(A e^{-\beta H})}{\sum_n} = \frac{\sum_n}{n} \frac{e^{-\beta E_1} C_1 + e^{-\beta E_2} C_2 + \dots + e^{-\beta E_N} C_N}{10^{34} \text{J} \cdot \text{s} \cdot \text{C} \cdot \text{m}^2 \cdot \text{K}^2}$$

$$\bar{A} = \sum_n A_n \rho_n = \frac{1}{Z_N} \sum_n \langle n | A | n \rangle e^{-\beta E_n} \quad \begin{cases} \text{没有} \\ \text{3} F_n = E_n \\ \text{+ P&H} \end{cases}$$

$$= \frac{1}{Z_N} \sum_n \langle n | A e^{-\beta H} | n \rangle = \text{Tr}[A \hat{\rho}]$$

$$\overline{(E - \bar{E})^2} = \overline{(E^2 - 2\bar{E}E + \bar{E}^2)}$$

$$= \bar{E}^2 - 2\bar{E}^2 + \bar{E}^2 = \bar{E}^2 - \bar{E}^2$$

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

$$\therefore \overline{(E - \bar{E})^2} = -\frac{\partial \bar{E}}{\partial \beta} |_{N, V} = k_B T \left(\frac{\partial \bar{E}}{\partial T} \right)_{N, V} = \frac{1}{\beta} T^2 C_V$$

热力学极限

$$\overline{(E - \bar{E})^2} = \frac{\sqrt{k_B T^2 C_V}}{\bar{E}} \times \frac{1}{N} \frac{1}{C_V}$$

$$\therefore \frac{\partial \bar{E}}{\partial T} = \frac{\sqrt{k_B T N}}{AT} \propto \frac{\sqrt{N}}{N} = \frac{1}{\sqrt{N}} \quad \begin{cases} \text{实际} \\ \text{只对} \\ \text{一般情况适用} \end{cases}$$

* 热力学极限是假， $N, V \rightarrow \infty$ ，但子级数

密度不变： $n = \frac{N}{V}$ 固定 \rightarrow 非理想气体

* 我们前面都用分子态表示， $\frac{h}{2\pi m k_B T} \ll \sqrt{r}$ (分子间距离)

$\Delta E = E_n - E_{n-1} \ll k_B T$ 时，可用经典力学。

$$\text{这时: } Z_N = \frac{1}{N! h^3} \int d\Omega e^{-\beta H(\Omega)}$$

$$A = \frac{1}{N! h^3} \int d\Omega A e^{-\beta H}$$

3.4.4 应用：非理想气体的状志方程

$$\text{模型: } E = k + V = \sum_{i=1}^N \frac{\vec{p}_i^2}{2m} + \sum_{i,j} \phi_{ij}$$

$$\phi_{ij} = \phi(|\vec{r}_i - \vec{r}_j|) \text{ 且 } = \epsilon + (n/a) \sim 1/r^3$$

$$Z_N = \int d\vec{p}_1 \dots e^{-\beta(E+k+V)}$$

$$(d\Omega) = \frac{1}{N! V^N} \int d\vec{p}_1 \dots d\vec{p}_N d\vec{r}_1 \dots d\vec{r}_N$$

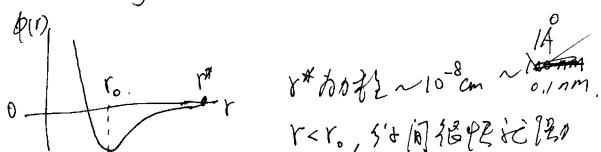
对分子积分非常简单，这就是玻尔兹曼分布。

$$Z_N = \frac{1}{N! V^N} Q_N(\beta, V), \quad V \text{ 是体积。}$$

$$Q_N = \int d\vec{p}_1 \dots d\vec{p}_N e^{-\beta \sum_{i,j} \phi_{ij}} = \int (d\vec{r}) \prod_{i,j} e^{-\beta \phi_{ij}}$$

是径向函数乘积。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 $\phi(r) \sim 10^{-8} \text{ cm} \sim 0.1 \text{ nm}$

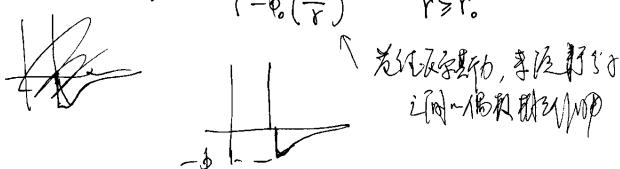
$$\left. \begin{aligned} \text{这样 } f_{ij} &= e^{-\beta \phi_{ij}} \\ f(r) &\Rightarrow \begin{cases} 1, & r \rightarrow 0, (\phi \rightarrow \infty) \\ 0, & r \rightarrow r^*, (\phi \rightarrow 0) \end{cases} \end{aligned} \right\} \text{ 分开} \quad r > r_0, \text{ 分开} \quad r < r_0.$$

$$= \frac{Nk_B T}{V} \left[1 - \frac{N}{2V} \left(\int d\vec{r} f(r) \right) \right]$$

$$B_z = -\frac{N}{2} \int d\vec{r} f(r) \quad \text{即 } f = \text{径向分布}$$

(3) 径向分布

$$\phi(r) = \begin{cases} +\infty & r < r_0 \\ -b_0 \left(\frac{r_0}{r}\right)^6 & r \geq r_0 \end{cases}$$



$$B_z = -\frac{N}{2} \int_0^\infty (e^{-\phi(r)/k_B T} - 1) 4\pi r^2 dr$$

$$= 2\pi N \left[\int_0^{r_0} r^2 dr - \int_{r_0}^\infty (e^{-\phi(r)/k_B T} - 1) r^2 dr \right]$$

(设 $\phi_0 \ll k_B T$)

$$\approx 2\pi N \left(\frac{r_0^3}{3} - b_0 \frac{r_0^3}{3k_B T} \right) = Nb - \frac{Na}{k_B T}$$

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

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

范德瓦尔斯方程

$$Q_N = \int (d\vec{r}) \prod_{i,j} (1 + f_{ij})$$

$$= \int (d\vec{r}) \left(1 + \sum_{i,j} f_{ij} + \sum_{i,j} f_{ij} \sum_{i,j} f_{ij} + \dots \right)$$

假设 $e^{-\beta \phi(r_0)} - 1 \ll 1$. 即 $e^{\beta \phi(r_0)/2} \ll 1$, 则在极限情况下， $f_{ij} \rightarrow 0$ 时可忽略

$$Q_N \approx \int (d\vec{r}) (1 + \sum_{i,j} f_{ij})$$

$$= V^N + \frac{1}{2} N(N-1) V^{N-2} \int d\vec{r}_1 d\vec{r}_2 f_{12}$$

假想一个球对称 $\vec{r}_1 \cdot \vec{r}_2 = \vec{r}$, 球的边界半径 R .

$$\int d\vec{r}_1 d\vec{r}_2 f_{12} = \int d\vec{r}_1 \int d\vec{r}_2 f(r) d\Omega \approx V \int d\vec{r} f(r)$$

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

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

$$\approx N \ln V + \frac{N^2}{2V} \int d\vec{r} f(r). \quad \text{将之整理: } \boxed{\text{分子}}$$

化简,

$$\rho = \frac{1}{\beta} \frac{\partial}{\partial V} \ln Z_N = \frac{1}{\beta} \frac{\partial}{\partial V} \ln Q_N = k_B T \left[\frac{N}{V} - \frac{N^2}{2V^2} \int d\vec{r} f(r) \right]$$

第5章 压缩系数

与膨胀系数类似，压缩同时气体分子间相互作用

$$E_T = E_A + E_B, \quad N_T = N_A + N_B.$$

$$\rho_n = \rho_{A,n} = \frac{S_B(N_A, E_T, E_B)}{\sum (N_j E_j)}$$

$$= \frac{1}{\sum (N_j E_j)} e^{\ln S_B(N_A, E_T, E_B)}$$

$$= \frac{S_B(N_A E_T)}{S_B(N_A E_T) + S_B(N_B E_B)} e^{-\frac{\partial \ln S_B(N_A E_T)}{\partial N_A} N_A - \frac{\partial \ln S_B(N_A E_T)}{\partial E_T} E_T}$$

$$= \frac{1}{N_A} e^{+\mu N_A - \beta E_A}$$

去掉 A 的指标， $N_A \rightarrow N$, $E_A \rightarrow E_n$

$$\rho_{n,n} = \frac{1}{N} \frac{\partial}{\partial N} e^{-\beta(E_n - \mu N)}$$

$$\text{由 1/2-规则, } \sum_{n=0}^N \sum_{n=0}^N \rho_{n,n} = 1$$

$$\Rightarrow \sum_{n=0}^N e^{\beta E_n} \sum_{n=0}^N e^{-\beta E_n}$$

$$= \sum_{n=0}^N e^{\beta E_n} Z_N = T \text{Tr } e^{-\beta(\hat{A} - \mu \hat{N})}$$

* 直到目前为止在统计物理中最常用。
 $(\text{effective}) \mu = \text{Fermi energy}$.

$$\bar{N} = -\frac{\partial}{\partial \beta} \ln Z_N = -k_B T \left(\frac{\partial}{\partial \mu} \ln Z_N \right)_T$$

$$\bar{E} = -\frac{\partial}{\partial \beta} \ln Z_N$$

$$\beta = \frac{1}{k_B} \frac{\partial}{\partial V} \ln Z_N$$

$$S = k_B \left(\ln Z_N - \alpha \frac{\partial}{\partial \mu} \ln Z_N - \beta \frac{\partial}{\partial \beta} \ln Z_N \right)$$

$$(\alpha = -\frac{\partial \mu}{\partial \beta})$$

$$F = -k_B T \ln Z_N + k_B T \alpha \frac{\partial}{\partial \mu} \ln Z_N$$

$$U = -k_B T \ln Z_N$$

* 能级和半能级数随 $\sim \frac{1}{\sqrt{N}}$.

* 经典极限下

$$Z_N = \sum_n e^{-\beta E_n} Z_n$$

$$Z_N = \frac{1}{N! h^3} \int d\Omega_N e^{-\beta E_N}$$

* 应用举例：固体表面的吸附率

考虑 N , $N = \text{分子数}$, 设其为理想气体, 已知 [8.9.9]

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

$$\text{于是 } \Theta = \frac{\bar{N}}{N_0} = \frac{1}{N_0} \frac{1}{h^3} \frac{1}{(2\pi m)^{3/2} (k_B T)^{3/2}} e^{-\epsilon_0/k_B T}$$

$\uparrow \uparrow, \Theta \uparrow; T \uparrow, \Theta \downarrow$.

简并度

1. 用巨正则系统计算单分子理想气体的绝对温度.

2. 看书 8.9, 8.10, 8.12

(3)

$$\Theta = \frac{\bar{N}}{N_0} = \frac{\text{被吸收分子平均数}}{\text{总分子数}}$$

根据部分子数大于总数, 与外部分子达到平衡
 $N \rightarrow \bar{N}$. (T, μ, V) 不变, 设分子服从玻尔兹曼分布
 $-E_0$, 则 $E_N = -N\epsilon_0$.

$$\sum_{E_N} = \sum_{n=1}^{N_0} \sum_n e^{-\alpha N - \beta E_N} = \sum_{N=0}^{N_0} e^{\beta(\mu + \epsilon_0)N}$$

n 表示 N 分子占据 N_0 分子中的 n 个
 \uparrow 对应于量子状态, 这样状态一定有 $\frac{N_0!}{N!(N_0-N)!}$, 且能分排开.

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

$$\sum_{E_N} = \sum_{N=0}^{N_0} \frac{N_0!}{N!(N_0-N)!} e^{\beta(\mu + \epsilon_0)N}$$

$$= (1 + e^{\beta(\mu + \epsilon_0)})^{N_0}$$

$$\bar{N} = -\frac{\partial}{\partial \mu} \ln Z_N = \frac{1}{\beta} \frac{\partial}{\partial \mu} \ln Z_N$$

$$= N_0 \frac{\partial}{\partial \mu} e^{\mu + \beta \epsilon_0} = \frac{N_0 e^{\beta(\mu + \epsilon_0)}}{1 + e^{\beta(\mu + \epsilon_0)}}$$

$$\therefore \Theta = \frac{\bar{N}}{N_0} = \frac{1}{1 + e^{-\beta(\mu + \epsilon_0)}}$$

考虑量子统计 $-d=3, 2, 1$.

这里, 我们讨论量子统计. 若 $d=3$, 量子数 n either bosons or fermions. 若 $d=2$, 电子 & anyons.
 若 $d=1$, 电子数依赖于相空间.

§ 6.1 用巨正则系统计出 Bose 和 Fermi 统计

$$Z_N = \sum_{N=0}^{N_0} \sum_{E_N \text{ (fixed)}} e^{-\alpha N - \beta E_N}$$

(\leq 为整数)

设 $E_{N_1} = E_{N_2} = \dots = E_N$ 在 \sum_{E_N} 中一起

$$\sum_{E_N} = \sum_{N=0}^{N_0} \sum_{E_N} \sum_{\substack{3(E_N) \\ E_{N_1}=E_N}} e^{-\alpha N - \beta E_N}$$

对自由粒子, $E_N = \sum_x a_x E_x$, $N = \sum_x a_x$
 $\{a_x\}$ 是一个量子数分布.

$$\begin{aligned} \sum_{E_N} &= \sum_{N=0}^{N_0} \sum_{E_N} \sum_{\substack{3(E_N) \\ \sum_x a_x E_x = E_N}} W(s, g, f) e^{-\sum_x a_x \epsilon_x - \beta \sum_x a_x E_x} \\ &= \sum_{\{a_x\}} W(s, g, f) e^{-\sum_x (\omega_x + \beta \epsilon_x) a_x} \end{aligned}$$

这里 $\{a_x\}$ 代表了所有可能分布 (各种可能, 各种状态).

对称粒子

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

对称波函数

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

$$\Sigma_\alpha = \sum_{\{\alpha\}} \prod_\lambda [W_\lambda e^{-(\alpha+\beta g_\lambda) a_\lambda}]$$

$$= \sum_{a_1} \dots \sum_{a_\lambda} \prod_\lambda [W_\lambda e^{-(\alpha+\beta g_\lambda) a_\lambda}]$$

$$= \prod_\lambda \left(\sum_{a_\lambda} e^{-(\alpha+\beta g_\lambda) a_\lambda} \right)$$

$$\Sigma_\lambda^{(F)} = \sum_{a_\lambda=0}^{g_\lambda} \frac{g_\lambda!}{a_\lambda!(g_\lambda-a_\lambda)!} e^{-(\alpha+\beta g_\lambda) a_\lambda} = [1 + e^{-\alpha-\beta g_\lambda}]^{g_\lambda}$$

($a_\lambda \leq g_\lambda$)

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

$$(利用) (1-x)^m = \sum_{n=0}^m \frac{(m+n-1)!}{n!(m-n)!}$$

$$= (1 - e^{-\alpha-\beta g_\lambda})^{g_\lambda}$$

$$\therefore \Sigma_\alpha = \prod_\lambda (\pm e^{-\alpha-\beta g_\lambda})^{g_\lambda}$$

$$\therefore \psi(\vec{r}_1, \vec{r}_2, \dots) = e^{i\chi_{12}} \otimes \psi(\vec{r}_1, \vec{r}_2, \dots)$$

对称粒子, 由 Pauli 原理

$$\psi(\vec{r}_1, \vec{r}_1, \vec{r}_3, \dots) = 0.$$

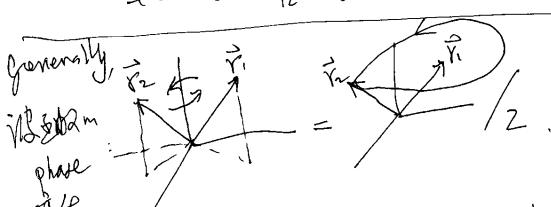
$$\text{or } \lim_{\vec{r}_1 \rightarrow \vec{r}_2} \psi(\vec{r}_1, \vec{r}_2, \dots) = 0 \quad \text{反交换}$$

$$\text{即 } \psi(\vec{r}_1, \vec{r}_2, \dots) = -\psi(\vec{r}_2, \vec{r}_1, \dots), \text{ 即 } \chi_{12} = \pi \quad \Rightarrow \psi(\vec{r}_1, \vec{r}_2, \dots) = \pi \# \psi(\vec{r}_2, \vec{r}_1, \dots)$$

对 Boson:

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

$$\therefore 0. \quad \because \chi_{12} = 0 \pm 2n\pi.$$

互换空间, \vec{r}_2 交换 \vec{r}_1 时没有相移

障碍, 15 年由 Wigner 提出 phase

$$e^{i\phi} = e^{i2\pi n} \Rightarrow n = \text{odd, fermion} \quad \text{或} \quad n = \text{even, boson}$$

且只有 boson or fermion

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

* 求 \bar{Z}_3 (简单推导)

$$\bar{Z}_3 = \sum_n \sum_m a_3 q_m$$

$$= \frac{1}{Z_3} \sum_{\lambda \neq \lambda'} a_3 \left(\sum_\lambda a_\lambda W_\lambda e^{-(\alpha+\beta g_\lambda) a_\lambda} \right)$$

$$\prod_{\lambda \neq \lambda'} \bar{Z}_3$$

$$= \frac{1}{Z_3} \sum_{\lambda} a_\lambda W_\lambda \{ e^{-(\alpha+\beta g_\lambda) a_\lambda} \}$$

$$= -\frac{1}{Z_3} \frac{\partial}{\partial \alpha} \bar{Z}_3 = -\frac{\partial}{\partial \alpha} \ln \bar{Z}_3.$$

$$= -\frac{\partial}{\partial \alpha} (\pm g_\lambda \ln (\pm e^{-\alpha-\beta g_\lambda}))$$

$$= \frac{g_\lambda}{\alpha + \beta g_\lambda \pm 1}$$

§ 6.2 量子统计和波函数 (Fermion 和 Boson)

设 $\psi(\vec{r}_1, \dots, \vec{r}_N)$ 是 N 电子波函数。我们令 \vec{r}_i, \vec{r}_j 互换, 根据假设进行计算

$$|\psi(\vec{r}_1, \dots, \vec{r}_N)|^2 = |\psi(\dots, \vec{r}_j, \dots, \vec{r}_{i-1}, \dots)|^2.$$

互换空间,

$$\circlearrowleft \neq Q \cdot \neq \circlearrowright, \dots$$

161 例

$$\psi(\vec{r}_1, \vec{r}_2) \propto (z_1 - z_2)^\alpha, \quad z_1 \text{ 与 } z_2 \text{ 交换}$$

$$\Rightarrow (z_2 - z_1)^\alpha = (-1)^\alpha (z_1 - z_2)^\alpha. \quad \text{有一个任意数}$$

phase $\propto e^{i\alpha\pi}$. 下面将详细讨论之。
(互换为 anyon, 顶点子).

互换空间

$\frac{1}{2}$

二重交换的交错只能通过相位来实现, 因此如果在空间中交换了两个点, 我们必须简单地乘以一个介词。

§ 6.3 路径积分和量 (泛函)

(Feynman
statistical mechanics)

对正则力学，路径积分

$$\varphi = \frac{e^{-PH}}{\text{Tr} e^{PH}} \quad \varphi(\beta) \text{ 是温度的函数.}$$

$\tilde{\varphi} = e^{-Ht}$ 是 正常化 在 度量矩阵

$$-\frac{\partial \tilde{\varphi}}{\partial \beta} = -\frac{\partial}{\partial \beta} (\tilde{\delta}_{ij})$$

$$= \left(-\frac{\partial}{\partial \beta} \delta_{ij} e^{-\beta E_i}\right) = \left(\delta_{ij} E_j e^{-\beta E_i}\right)$$

$$= (E_i \tilde{\delta}_{ij}) = H \tilde{\varphi}.$$

$$\therefore -\frac{\partial \tilde{\varphi}}{\partial \beta} = H \tilde{\varphi}, \quad (\tilde{\varphi}(0) = 1).$$

这是守恒方程，在任何表象都对，在这行表示

$$-\frac{\partial \tilde{\varphi}(x, x'; \beta)}{\partial \beta} = H x \tilde{\varphi}(x, x'; \beta).$$

$$\tilde{\varphi}(x, x'; 0) = \delta(x - x').$$

Formally: ~~$\tilde{\varphi} = e^{-Ht}$~~ $\tilde{\varphi} = e^{-Ht/\hbar}$, redefine: $u = \beta t$.

~~$\tilde{\varphi} = e^{-Ht/\hbar} = e^{-H\beta u/\hbar} = e^{-H\tilde{\varphi}(u)}$~~

Formally: $\tilde{\varphi}(u) = e^{-Hu/\hbar}$.

us - (假想由路径为例), $H = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2}$,

$$\varphi(x, x'; \varepsilon) \approx \sqrt{\frac{m}{2\pi\hbar\varepsilon}} e^{-(m/\hbar\varepsilon)(x-x')^2}$$

$$\varphi(x, x'; u) = \lim_{\varepsilon \rightarrow 0} \int \frac{dx_1}{\sqrt{2\pi\hbar\varepsilon}} \cdots \frac{dx_{n-1}}{\sqrt{2\pi\hbar\varepsilon}} e^{-\frac{m\varepsilon}{2\hbar} [(x-x_1)^2 + \cdots + (x_{n-1}-x_n)^2]}$$

$$\frac{x_n - x_{n-1}}{\varepsilon} \rightarrow \frac{dx(\varepsilon)}{d\varepsilon} = \dot{x}(\varepsilon)$$

$$\varphi(x, x'; u) = \int \mathcal{D}x e^{-S/\hbar}$$

其中 $S = \int_0^u d\varepsilon L(\varepsilon)$, $L(\varepsilon) = \frac{m}{2} (\dot{x}(\varepsilon))^2$
自由能 L 找到.

$$Z = \text{Tr } \varphi, \text{ 正生子方向}$$

$$Z = \int dx \varphi(x, x) = \int \mathcal{D}x e^{-\int_0^u d\varepsilon L}$$

这时任何相空间子空间时，对正则子得

$$Z_G = \int \mathcal{D}x(u) e^{-S_G}, \quad S_G = S - \mu N.$$

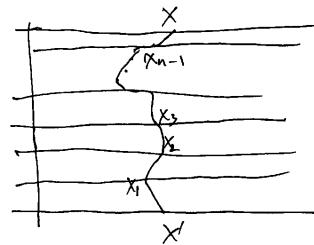
$$[t\beta] = [t], \text{ 于是 } u = \hbar\varepsilon$$

$$\varphi(u) = e^{-He/\hbar} e^{-He/\hbar} \cdots e^{-He/\hbar}$$

$$= \varphi_0 \varphi_1 \cdots \varphi_n.$$

正生子表象:

$$\varphi(x, x'; u) = \int \cdots \int \varphi(x, x_{n-1}; \varepsilon) \varphi(x_{n-1}, x_{n-2}; \varepsilon) \cdots \varphi(x_2, x_1; \varepsilon) \varphi(x_1, x'; \varepsilon) dx_{n-1} \cdots dx_1.$$



$$n \rightarrow \infty, \varepsilon \rightarrow 0, \quad n\varepsilon = u.$$

$$\varphi(x, x'; u) = \int \mathcal{D}x \Phi[x(u)]$$

$$\Phi[x(u)] = \lim_{\substack{\varepsilon \rightarrow 0 \\ u = n\varepsilon}} \varphi(x, x_{n-1}; \varepsilon) \cdots \varphi(x_1, x'; \varepsilon).$$

~~$\Phi[x(u)] \quad \mathcal{D}x(u) = \lim_{n \rightarrow \infty} dx_1 \cdots dx_{n-1}$~~

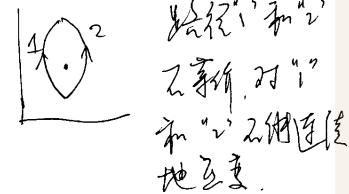
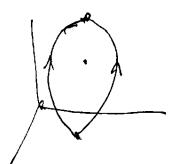
6.4 不确定、相空间和基础: $d=2$. (2)

partition function Φ in $\mathbb{C} \rightarrow i\mathbb{R}$, 把 x 看成复数

中一个点 x 的位置.

$$\varphi(x, x'; u) = \int \mathcal{D}x e^{i \int_0^u dt L}$$

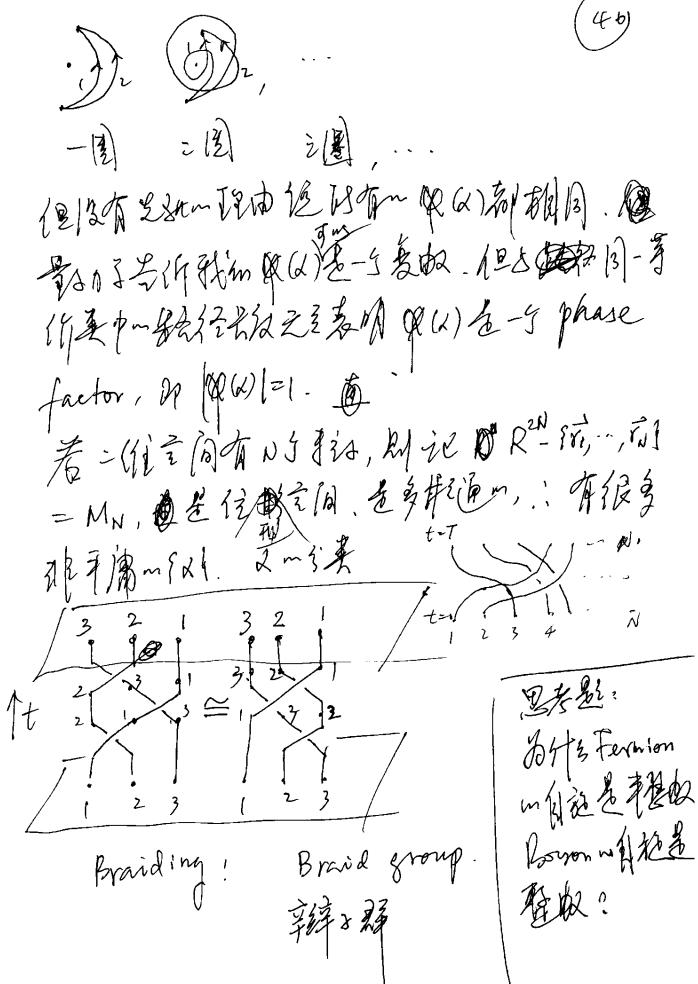
$\mathbb{R}x$ 是对所有可能的路径积分. 在之 (偏空间),
任何路径对类状振幅的影响是之. 但至 = (偏空间)



$$\therefore \mathcal{D}x \rightarrow \mathcal{D}x \Phi(x) \mathcal{D}x$$

在 $\mathcal{D}x$ 中只有路径都可时连接互通. x 在
二偏空间中有且只有一条路径可得.





对 N 个粒子，有 $B_N(R^2)$. 但是，
 B_N 中一般没有群之 (无限, nonabelian) 部
分，同时被邻近于 π 线的 braiding 所生成，
记 σ_i 是 x_i 及 x_{i+1} 间的对换，且左乘以 σ_i
右乘以 σ_i^{-1} ：

$$\begin{array}{c} \sigma_i \\ x_i \end{array} = \sigma_i, \quad \begin{array}{c} \sigma_i^{-1} \\ x_i x_{i+1} \end{array} = I_i = \sigma_i \sigma_i^{-1} = \sigma_i^2.$$

从而有 $\sigma_i \sigma_j = \sigma_j \sigma_i$

$$\sigma_i \sigma_{i+1} \sigma_i = \sigma_{i+1} \sigma_i \sigma_{i+1}$$

特别：

$$\begin{array}{c} \sigma_i \\ x_i \end{array} = \begin{array}{c} \sigma_i \\ x_i x_{i+1} \end{array}$$

群与群连-9
Non-abelian group
但一维表
Abelian 三结
⇒ 带电荷的弦

$$\sigma_i \sigma_k = \sigma_k \sigma_i \quad (k \neq i \pm 1)$$

这就是一个群与群连-9 例子。设

$\phi_0(\sigma_i)$ 是生成元之一的表象。 $\phi_0(\sigma_i) = e^{-i\theta}$
满足群与群连-9. ($0 \leq \theta < 2\pi$). 当 $\theta=0$, \Rightarrow Bose
统计, 当 $\theta=\pi$, \Rightarrow Fermi (反). $\theta=2\pi$ 为
自由 (统计).

(4c)

$$\begin{aligned} r_i &\rightarrow \begin{cases} r_i & \text{if } i \neq i+1 \\ r_{i+1} & \text{if } i = i+1 \end{cases} + \dots \end{aligned}$$

$$\therefore \phi_0(\sigma_i^{\pm 1}) = e^{\mp i\theta} = \exp\left[\mp i\theta \sum_{j \neq i} \Delta\phi_{ij}\right]$$

$$e^{\mp i\theta (\pm \pi)} = \exp\left[-i\theta \sum_{j \neq i} \Delta\phi_{ij}\right]$$

其中只有 $\Delta\phi_{ii+1} = \pm \pi$, 其他 $\Delta\phi_{ij} = 0$.

推广到 $n-2m$ 维:

$$\phi_0(\omega) = \exp\left(-i\frac{\theta}{\pi} \int dt \frac{d}{dt} \sum_{ij} \Delta\phi_{ij}\right), \quad r = (r_1, \dots, r_n).$$

\therefore 传播 $K(r't'; rt)$

$$K(r't'; rt) = \int \exp\left[i \int_r^{r'} dt \left[L - \frac{\theta}{\pi} \frac{d}{dt} \sum_{ij} \Delta\phi_{ij}\right]\right] d^N r$$

现在来考虑路径积分 $\int dr(t)$ 使波函数连-9.

由传播子 K 及 $\phi_0(\omega)$ 定义 $\psi(r, t)$ 是单值的 (single-valued).

$$\psi(r, t) = \int_M dr K(r't'; rt) \psi(r, t).$$

这在 M_N 中是一个闭合类. 定义

$$\tilde{\psi}(r, t) = \exp\left(-i\frac{\theta}{\pi}\right) \int_{r_0}^{r_0} dt \left(\sum_{ij} \Delta\phi_{ij}(t)\right) \psi(r, t).$$

现在考虑由路径积分的波函数的表象.

如果没 braiding 时,

$$\psi(r') = \int dr K^{(0)}(r't'; rt) \psi(r, t).$$

定义 $\tilde{\psi}(r') = \exp\left\{-i\frac{\theta}{\pi} \int_{r_0}^{r'} dt \left(\sum_{ij} \Delta\phi_{ij}\right)\right\} \psi(r', t)$, 因此
若无 braiding 时 ψ 为波函数, (r' 是一个参数,
从 $t=0$ 到 $t=t'$), 则

$$\tilde{\psi}(r') = \int dr \tilde{K}(r't'; rt) \tilde{\psi}(rt)$$

K 包括从 $t \rightarrow t'$ 的 braiding 时. \tilde{K}

若把 ψ 为

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

$$= \prod_{i < j} (z_i - z_j)^{\theta/\pi} f(z, t). \quad \text{其中 } f$$

由 θ 的正确给出 (统计) 波函数. 之后对称

3.6.5 一级统计：玻尔兹曼统计 (5)

在一维空间，任意的粒子需占据位置 x_1, x_2, \dots, x_N
相互接触，所以除自由统计，统计与相互作用
相关。
 假设 N 个 Fermi (费米) 粒子， N 个 particle 与自由度。
 $W_{\text{tot}} = \frac{[G + (N-1)(1-s)]!}{N! [G - (N-1-s)!]} = W_B$

$$\text{若 } s=0, W_0 = \frac{[G+N-1]!}{N! [G-1]!} = W_F$$

$s < 1$ ，则是对 Bose 和 Fermi (玻色和费米)。
如果 $s=1$ 如果有二分布 $\{N_x\}$ ，即

$$N = \prod_{\alpha} N_{\alpha}! [G_{\alpha}-1 - \sum_{\beta \neq \alpha} S_{\alpha\beta} (N_{\beta} - S_{\alpha\beta})]$$

$$\text{取 } S_{\alpha\beta} = S \delta_{\alpha\beta}, \text{ 且 } s=0, S=1$$

$$W_0 = \prod_{\alpha} \frac{(G_{\alpha}+N_{\alpha}-1)!}{N_{\alpha}! [G_{\alpha}-1]!}, W_1 = \prod_{\alpha} \frac{G_{\alpha}}{N_{\alpha}! (G_{\alpha}-N_{\alpha})!} = W_B$$

这里 $S_{\alpha\beta}$ 表示不同“坐标”指称空间的
相互作用。

等于 1 时。

例 1. 子相互作用波色子 ($C=0, \text{玻色}$)

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

用脚标表示。进行“Fourier”展开，互动
空间，总能量 $E = \sum_i k_i^2$ 。
~~但~~

\rightarrow 在限制极限下， $\lambda \rightarrow k$

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

$$\text{其中 } \theta = -2 \tan^{-1}(h/c). \quad (\text{Bothe Ansatz})$$

$$\theta'(k-k') = \frac{-2c}{c^2 + (k-k')^2}. \quad (\text{Yang-Yang})$$

$$\text{若 } c \rightarrow \infty, \theta' \rightarrow 0, S(k, k') = \delta(k-k').$$

idea Fermion

$$\text{若 } c \rightarrow 0, S(k, k') = -\delta(k-k').$$

这时一般 C ，称为 Bose 在理想系统。

3.6.6 Calogero-Sutherland (Fermion) (2)

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

$$\rightarrow \infty, \text{ 相互作用} \rightarrow \propto (x_i - x_j)^2.$$

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

$$\therefore \theta = 2\pi(\lambda-1) \operatorname{sign}(k-k')$$

$$\lambda=1 \Rightarrow \text{Fermion}, \quad \lambda=\frac{1}{2} \Rightarrow \text{semion}.$$

$$\lambda=2, \text{ dual semion.}$$

可以根据 Bethe Ansatz 写出“单粒子能级” $E(k)$ 。
这个 $E(k)$ 一般由一阶方程得出 (但是 CS
模型)。

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

只对 k_F 而言。

$$Z_G = \prod_k \left(1 + e^{-E(k)/T} \right).$$

(~~只对~~)

第七章 相变、临界现象和量子化群商

物理学中不同物理性质的体系并不互相依赖，例如，
固体、液体和气体。不同相可以相互转换，称为相变。
在一些特殊条件下，两相或三相可以平衡。这些
条件就是相变线。于是，可以根据这些相
变线，画出参数空间——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：相变差，两相变化导致相变，但 ~~没有~~
~~两个~~ 有一阶相变不相容，即

$$\mu^a - \mu^b = 0, \quad S^a - S^b = -\left(\frac{\partial \mu^a}{\partial T}\right)_P + \left(\frac{\partial \mu^b}{\partial T}\right)_P \neq 0, \dots$$

二级相变： $\Delta \mu = 0, \Delta S = 0, \Delta T = 0, \dots$ 但

$$\frac{\partial \mu}{\partial T} \frac{\partial \mu}{\partial \mu}, \frac{\partial \mu}{\partial \mu} \text{ 不连续或发散}.$$

即 $\Delta \mu, \Delta S, \Delta T$ 随温度而变化。

同样可以定义二级相变。但二级相变 \rightarrow 只有
BEC。三级相变 \rightarrow 相变在量子层面上发生。

($T \rightarrow 0$, 有无限级相变之说)

§7.1 朗道=假想度理论简介

朗道建立描述二级相变的假想理论，引入了
一个新概念：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-固体中，有序破坏和铁磁性，至高温时，~~每个~~每个电子的自旋取向在空间是随机的，作为其平均值的物理量，序参量强度 $M = 0$ 。随着温度降低，由于电子之间的作用，铁磁性在其中开始趋于同向，平均来说 $M \neq 0$ 。 $M = 0$ 时 $M \neq 0$ 时这就是临界温度 T_c 。

$$\begin{array}{c} \nearrow \downarrow \\ \downarrow \uparrow \\ \vdots \end{array}$$

$$\begin{array}{c} \nearrow \downarrow \\ \downarrow \uparrow \\ \vdots \end{array}$$

对于 M 为铁磁体序参量

$$M = 0$$

$$M \neq 0$$

至高温相， $M = 0$ ，说明
电子自旋取向任一方向的几率都一样，~~这样~~这样

倒施有转动对称性（倒施的 $SU(2)$ 不对称）而至低温， $M \neq 0$ 表明电子自旋趋向于某一方，“转动不变性”破缺意味着“对称性破缺”。降低温度引起 $M \neq 0$ ，且随温度降低而增加， $M \neq 0$

把自由能简化为序参量

朗道理论要先通过自由能至相变点

近似序参量展开，进而得出序参量对温度依赖性。林恩哥书中举了 $H=0$ 时 M 的例子。请看。这里再举一个简单的例子，即所谓 GL 理论。超导体 Gibbs 自由能为序参量（绝对零度时）的函数，至临界点 $g_s(H=0) = g_n$ 。 $g_n = f - B$ 是正考夫 Gibbs free energy。展开 $g_s(H)$

$$g_s(H) = g_n + A|H|^2 + \frac{B}{2}|H|^4 + \dots \quad (\text{4级多项})$$

当 $T < T_c$ ， $g_s < g_n$ ， $\therefore A(T) < 0$ ，($\because \lambda(T_c) = 0$)， \therefore

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

$B(T)$ 是 $|H|$ 的系数， \therefore 取 const. 即可。

$$B(T) = B(T_c) = B_c.$$

在物理上，需求自由能极小。

$$\frac{dg_s}{dH} = 0, \Rightarrow A + B_c|H|^2 = 0,$$

$$\Rightarrow |H|^2 = -\frac{A}{B_c}. \Rightarrow g_s = g_n - \frac{A^2}{2B_c}.$$

序参量“自发破缺”， $SU(2)$ 对称也由加一个磁场引起，序参量“明显破缺”。序参量是“对称性破缺”的后果，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 液晶的各向异性

超导-金属 马约拉纳对称性 [绝对温度时]
玻璃-超导 $K=0$ 时对称性 ODLRO

~~陶瓷-金属~~ ~~陶瓷-超导~~

$$\text{二次固相结构} \quad \text{滑脱层时} \quad \frac{W_1 - W_2}{W_1 + W_2}, \quad \begin{matrix} W_1: \text{柱径} \\ W_2: \text{壁厚} \end{matrix}$$

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， $P_{\text{liquid}} - P_{\text{gas}} \neq 0$.

补偿超导-金属相变 一级相变，[绝对温度时] $|f|$
(电子气体和空穴)

理想玻色子起振 二级相变 $K=0$ 时波长突变。

$$\text{另一方面, } g_n - g_s = \mu_0 H_C^2(\tau)/2,$$

\therefore 在 T_c 附近

$$H_C^2(\tau) = \frac{A^2}{\mu_0 B_c} = \frac{(T_c - \tau)^2}{\mu_0 B_c} \left(\frac{\partial A}{\partial T}\right)_{T=T_c}^2.$$

$$\Rightarrow H_C \propto T - T_c.$$

GL 理论起源于原有 Landau 限低一地方差，假设序参量 $|4| = n$ 有空间分布，这样， g_s 也有空间分布，

$$g_s = g_n + A|4|^2 + \frac{B}{2}|4|^4 + \frac{1}{2m^2} |(-i\hbar \nabla 4)|^2$$

是 Gibbs 自由能为

$$|(-i\hbar \nabla - e\vec{A})4|^2$$

$$G_s = \int d\vec{r} g_s(\vec{r})$$

$$\frac{\delta G_s}{\delta 4} = 0 \Rightarrow \left\{ \begin{array}{l} A4 + B|4|^2 + \frac{1}{2m^2} \vec{D}4 = 0 \\ \vec{D}4 = 0 \end{array} \right.$$

$$\vec{D}4 = 0 \quad (\text{直接解})$$

GL 方程。一个简单应用 序参量的相变

考虑弱场 $|\vec{A}| \ll |4|$, 则可以立 GL 方程中忽略 A , 而 $4 = 4_0(r) = \frac{f}{r}$ 很简单。又

$$f = \frac{4_0}{r}, \text{ 取 } f^* = f. \text{ 则}$$

$$\frac{\hbar^2}{2m^2} \nabla^2 f + f - f^3 = 0,$$

$$\zeta^2(T) \cdot \zeta^2(T) \nabla^2 f + f - f^3 = 0.$$

这是方程的解. 半无限长轴.

$$\begin{aligned} & \text{Normal} \quad \left\{ \begin{array}{l} \zeta^2 \frac{\partial^2 f}{\partial z^2} = -f(1-f^2), \\ f(z=0)=0, \quad \frac{\partial f}{\partial z} \Big|_{z=0} = 0 \\ f(z=\infty)=1 \quad \left(\frac{\partial f}{\partial z}\right)_{z=\infty}=0 \end{array} \right. \\ & \text{而对 } \frac{df}{dz}, \int_{-\infty}^{\infty} dz \end{aligned}$$

$$\int_{-\infty}^{\infty} \zeta^2 \frac{1}{2} \frac{d}{dz} \left(\frac{\partial f}{\partial z} \right) = \int_{-\infty}^{\infty} dz \left(\frac{1}{4} f^4 - \frac{1}{2} f^2 \right).$$

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

$$\text{取 } \frac{df}{dz} > 0, \quad \frac{df}{dz} = \frac{1-f^2}{\sqrt{2}\zeta(T)}, \quad f = \tanh \frac{z}{\sqrt{2}\zeta(T)}.$$

至临界点附近,

$$\zeta(T) = \frac{\hbar}{[2m^2 (T_c - T) \frac{dA}{dT}]^{1/2}} \rightarrow \infty, \quad T \rightarrow T_c.$$

许多物理量的收敛速度是 $\rightarrow \infty$.

(2) 临界等温线的物理量, δ .

60

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

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

$$(H-H_c) \sim (H-H_c)^\delta, \quad (T=T_c). \quad \left\{ \begin{array}{l} \text{外场} \sim \text{序参量}^\delta \\ \downarrow \\ T=T_c \end{array} \right.$$

(3) χ_0^δ 或 κ_T ; δ .

$$\chi_0^\delta = \left(\frac{\partial M}{\partial H} \right)_T \Big|_{H \rightarrow 0}, \quad \text{susceptibility. 磁化率.}$$

$$\left. \begin{array}{l} \text{等温线} \\ \text{等温线附近} \\ \sim |T-T_c|^{-\delta} \end{array} \right\} \chi_0^\delta \sim (\alpha (T-T_c))^{-\delta}, \quad \text{无论 } (T \rightarrow T_c^+) \text{ 还是 } (T \rightarrow T_c^-).$$

$$K_T = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T, \quad \text{等温压缩系数.}$$

$$K_T \sim (T-T_c)^{-\delta}, \quad (T \rightarrow T_c, p \rightarrow p_c).$$

(4). 抵抗 (比热), λ .

$$\text{抵抗 } C_A^\delta \sim |T-T_c|^{-\delta}, \quad (H \rightarrow 0)$$

$$\text{比热 } C_V \sim (T-T_c)^\delta, \quad (T \rightarrow T_c, p=p_c).$$

(5) 关联长度 ξ

$$\text{关联长度: } f \sim e^{-\xi} \quad \delta \rightarrow 0$$

§7.2 临界现象和临界指数

(一)

在上节, 我们看到在临界点, ~~物理量在临界点出现时~~ ^(二级相变) ~~物理量在临界点附近~~ ^(一级相变) 在 T_c 附近, 物理量在临界点附近时 f 的 $\frac{df}{dz}$ 为零, 但 f 不为零, 有临界现象, 需指出 f 为临界指数. 根据 $\frac{df}{dz} \neq 0$, 由物理量, 临界指数为 $\alpha, \beta, \gamma, \delta, \nu, \eta$.

\rightarrow 物理量从 ∞ 收敛到临界点附近

$$\varepsilon = \frac{T-T_c}{T_c} \text{ 放大: } f(\varepsilon) = A \varepsilon^\alpha (1+B\varepsilon^\beta + \dots), \quad \varepsilon \gg 0.$$

$$\lambda = \lim_{\varepsilon \rightarrow 0} \frac{\ln f(\varepsilon)}{\ln \varepsilon} \text{ 这是临界指数.}$$

(1) β 序参量随温度变化, 例如

$$\begin{aligned} \text{液体} & \quad \Delta C(M(T)) \propto (T-T_c)^\beta. \\ \sim |T-T_c|^\beta & \quad 1/T^\beta \propto \cancel{(T-T_c)^\beta}. \end{aligned}$$

$$\text{气液相变: } \Delta p \sim (T_c-T)^\beta$$

$$T \rightarrow T_c^-, \quad \beta = \beta_c.$$

(5) 关联长度, 临界指数 ν .

(二)

~~对于~~ 对于系统中任一物理量 $A(\vec{r}, t), B(\vec{r}, t')$

其物理值 $\left\langle \frac{A(\vec{r}, t)}{B(\vec{r}, t')} \right\rangle$

$$\left\langle (A(\vec{r}, t) - \langle A \rangle)(B(\vec{r}, t') - \langle B \rangle) \right\rangle$$

称为 A, B 之间的关联函数, 例如对自旋系统

$$\left\langle (S_i - \langle S_i \rangle)(S_j - \langle S_j \rangle) \right\rangle \quad (\text{核磁共振})$$

称为自旋-自旋关联函数.

若 $A=B$, $\vec{r}=\vec{r}'$,

$$G(\vec{r}) = \left\langle (A(\vec{r}, t) - \langle A \rangle)^2 \right\rangle \text{ 则代表 } A(\vec{r}, t) \text{ 的方差.}$$

在平均场论下, ~~在~~ $\sim |T-T_c|^{-\delta}$, 一般地

$$G(\vec{r}) \sim \frac{1}{r} e^{-r/\xi},$$

$$\text{则 } \xi \text{ 为关联长度. 到处 } f-1 \sim e^{-r/\xi}$$

$$\xi \sim |T-T_c|^{-\nu},$$

起源于 GL eq.: ~~起源于~~ $\xi \sim |T-T_c|^{-\nu}$ over estimation.

与实验结果有明显偏差. 平均场论 \rightarrow estimation.

(b) 美丽指数, η (64)

平均场计算的美丽指数的指數

decay 立方根是正确的, 正确的结果是

$$\text{decay} \sim r^{-d+2-\eta} \quad \eta \text{ 是美丽指数}$$

則動量空間

$$G(k) \sim k^{-2+\eta} \quad G(k) \propto \int dr \delta(r)e^{ikr}$$

這些临界指數都未实现到固體，但由於临界附近的时间很长，所以从达到平衡所需时间很长（临界慢化），例如铁磁石（见书 p480）。但分析这些结果发现，不同指數之間存在一些关系，称为标度律

$$\begin{aligned} & 2 + 2\beta + \gamma = 2 \\ & \gamma = \beta(\beta-1) \\ & \gamma = \nu(2-\eta) \\ & \nu d = 2 - \eta \end{aligned} \quad \left\{ \begin{array}{l} \text{6个临界指數,} \\ \text{4个约束,} \\ \text{2个独立.} \end{array} \right.$$

3.3 量子相变和隙

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 为 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： $H = H_0 + gH_1$, $[H_0, H_1] = 0$ 。这时， H_0 和 H_1 同时对角化，有 3 种可能情况。

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

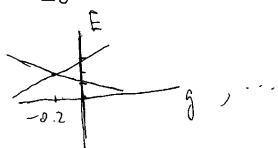
$$E_0 = E_0^{(0)} + g E_0^{(1)}, \quad E_1 = E_1^{(0)} + g E_1^{(1)} \quad \text{若在 } g=g_c,$$

$$E_0(g_c) = E_1(g_c), \quad \text{但 } E_0^{(1)} \neq E_1^{(1)} \quad (\neq 0) \quad \text{即}$$

从图

$$E_1 = 2 + g_3$$

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



level crossing
—般相变

这些关系是标度律和隙 (gap)。 (65)
其有一定的普遍性：(普遍性假设)。

系统临界平行行为二分法决定：空间维数 d 和序參數的維數 n 。具有相似 d 和 n 的序參數 η 有一个普遍性。具有相似 d 的临界行为。 $n=1$ (液体)

* 一个序參數可以是实数、复数和复数。

如果它是实数, $n=1$, 复数 $n=2$, 三維 $n=3$ 。

$n=1$, 气液相变中的密度差, 金属中的占比率。

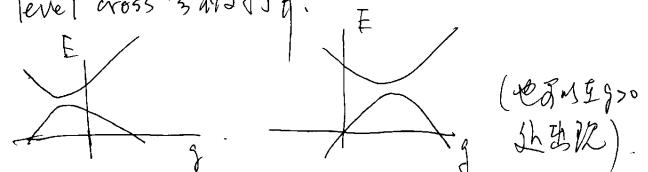
$n=2$, 平面自旋模型 (XY 模型), 超导、超辐射、超流起源于波函数。

$n=3$, 三维自旋模型中的磁化强度。

* 普遍性背后的物理原因是临界点的连接线无奇点，能描述子系统其他特征参数，例如，lattice spacing, 相互作用力程及微观细节。(晶格结构, 对称性) 都不要被子系统参数合作而崩溃掉。

在大多数情况下， $[H_0, H_1]$ 不对易，这种

level crossing 会自动打开。



（也可至 $g > 0$ ）

（这里说 $g < 0$ ）

在 infinite L 的情况下，有可能出现两种情况，(i) 简单的 level cross, (ii) 打开 gap 无限接近于零。这就是量子相变。在相变前，correlation function 会有定性变化。

由此我们看到，量子相变发生在间隙 $\Delta \rightarrow 0$ 或是 $\Delta \rightarrow \infty$ 时发生 gapless。即

$$\Delta \sim \Gamma (g - g_c)^{\frac{1}{2}} \quad (\text{非线性})$$

Δ 是 non-universal，依赖于具体的系统。

($g \rightarrow g_c^{\pm 0}$ 时不同)

类似地， ζ 与 Δ 有 correlation length ζ

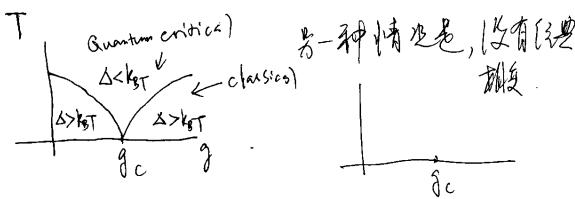
$$\zeta \sim \Gamma^{-1} (g - g_c)^{-\nu}$$

$$\text{则 } \Delta \sim \zeta^{-2}$$

有限温度，分为两种情况，

① $k_B T > \Delta$ ，这时，量子效应比经典效应强。
称为 Buetant critics.

② $k_B T < \Delta$ ，这时，量子效应比经典效应弱，
称为 Dominant。这时，会发现经典相变。



§7.4 Ising model.

为了对相变、临界指前，量相变有一个更直观的感受，我们讨论 Ising model.

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

$$S_i^z = \pm \frac{1}{2} (h) \text{ or } S_i^z \rightarrow \sigma_i = \pm 1.$$

由上，

$$F = -k_B T \ln Z$$

$$= -N k_B T \left[\ln 2 + \ln \cosh \left(\frac{B}{k_B T} + \frac{J}{k_B T} \bar{\sigma} \right) \right]$$

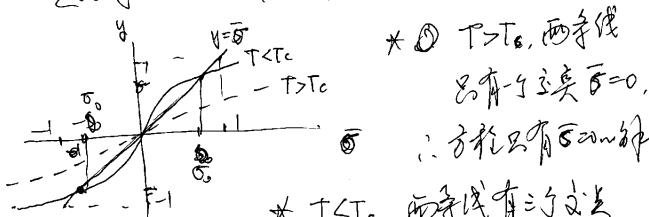
$$\therefore M = N \frac{\partial F}{\partial B} = -\frac{\partial F}{\partial B} = N \tanh \left(\frac{B}{k_B T} + \frac{J}{k_B T} \bar{\sigma} \right)$$

$$\Rightarrow \bar{\sigma} = \tanh \left(\frac{B}{k_B T} + \frac{J}{k_B T} \bar{\sigma} \right)$$

自然能。

$$\text{取 } B=0, \bar{\sigma} = \tanh \left(\frac{J}{k_B T} \bar{\sigma} \right) = \tanh \left(\frac{J}{T} \bar{\sigma} \right).$$

$$\text{令 } y = \tanh \left(\frac{J}{T} \bar{\sigma} \right), y = \bar{\sigma}$$



即 $T > T_c$ 为无序相 $\bar{\sigma} = \{ \pm \} \Rightarrow \bar{\sigma} = 0$
 $T < T_c$ 为有序相 $\bar{\sigma} = \pm$

$\because \ln \cosh x \geq 0$ 且 $x=0$ 时 $\ln \cosh x = 0$ 故 $\bar{\sigma} = 0$

§7.4.1 平均场近似。

首先让我介绍平均场近似。

$$H = - \sum_i \sigma_i \left(B + J \sum_j \sigma_{j+\delta} \right)$$

$$= - \sum_i \sigma_i (B + h_i).$$

因 $\sum_i \sigma_{i+\delta}$ 代替 $\sum_j \sigma_{j+\delta}$, 且因 $\sum_i \sigma_{i+\delta} = \sum_i \bar{\sigma} = \frac{1}{2} N$.

$$(H)_M = - \sum_i (B + h_i) \sigma_i \quad h = \frac{1}{2} J \bar{\sigma}$$

$$\text{这样, } Z_N = \sum_{\sigma_1} \cdots \sum_{\sigma_N} \exp \left[\beta \left(B + h_i \right) \sigma_i \right]$$

~~$$= \sum_{\sigma_1, \dots, \sigma_N} \prod_{i=1}^N \exp \left(B + h_i \right) \sigma_i$$~~

~~$$= \sum_{\sigma_1, \dots, \sigma_N} \prod_{i=1}^N \exp \left(B + h_i \right) \sigma_i \cdots \sum$$~~

$$= \sum_{\sigma_1} \exp \beta (B + h) \sigma_1 \sum_{\sigma_2} \exp \beta (B + h) \sigma_2 \cdots$$

$$= \prod_{i=1}^N \left(\sum_{\sigma_i} \exp \beta (B + h) \sigma_i \right)$$

$$= \prod_{i=1}^N \left(\exp \beta (B + h) + \exp -\beta (B + h) \right)$$

$$= \left[2 \cosh \left(B + h \right) / k_B T \right]^N$$

显然, $H(\sigma_i) = h(\sigma_i)$, 有无序性,

这表示一个状态 $\sigma_i = \pm$ 或 $\sigma_i = 0$, \Rightarrow 相变破坏。

~~相变 = 有序 + 无序 = 有序 + 无序~~。

② 有序

注意 $\bar{\sigma}$ 是 T 的函数, 于 $T \sim T_c$ 时, $\bar{\sigma} \sim 0$.

$$\therefore \tanh \frac{J}{T} \bar{\sigma} \approx \frac{T_c}{T} \bar{\sigma} - \frac{1}{3} \left(\frac{T_c}{T} \bar{\sigma} \right)^3 = \bar{\sigma}$$

$$\Rightarrow \frac{T_c}{T} - \frac{1}{3} \left(\frac{T_c}{T} \bar{\sigma} \right)^2 = 1, \quad \bar{\sigma} = \frac{3}{T_c} \left(\frac{T_c}{T} - 1 \right)$$

$$\bar{\sigma} = \sqrt{3} \left(1 - \frac{T}{T_c} \right)^{\frac{1}{2}}$$

$$\Rightarrow M \sim (T_c - T)^{\frac{1}{2}}$$

$$\text{取 } F, \text{ 由上计算 } C_B = \begin{cases} 0, & T \rightarrow T_c^+ \\ 3Nk_B T_c, & T \rightarrow T_c^- \end{cases}$$

$$\text{不可证明: } M \sim (T - T_c)^{-1} B,$$

$$X = \frac{\partial M}{\partial B} \sim (T - T_c)^{-1}, \quad \boxed{1^{\text{节}}}$$

$$M(T_c, B) \sim B^{\frac{1}{2}},$$

$$\Rightarrow \text{互易场 } f, \quad \beta = \frac{1}{2}, \alpha = 0, \gamma = 1, \delta = 3. \quad T_c = \frac{\sqrt{3}}{k_B}$$

§7.4.2 一维伊辛模型的精确解.

(平衡态吗? 用经典统计物理)

$$\textcircled{2} \quad H = -J \sum_n \sigma_n \sigma_{n+1} - h \sum_n \sigma_n \quad (\underbrace{\sigma_i = \sigma_{N+i}}_{\text{PBC}})$$

$$\Sigma = \sum_{\sigma_1, \dots, \sigma_N} \frac{\exp \left\{ K \sum_n \sigma_n \sigma_{n+1} \right\}}{Z_{kT}} \exp \left\{ B \sum_n \sigma_n \right\}$$

$$= \sum_{\sigma_1, \dots, \sigma_N} \exp \left\{ B \sigma_1 \delta_{\sigma_0, 1} \exp \left\{ K \sigma'_1 \sigma'_2 \right\} \right. \\ \left. \exp \left\{ B \sigma_2 \delta_{\sigma_1, 2} \exp \left\{ K \sigma'_2 \sigma'_3 \right\} \dots \right. \right. \\ \left. \left. \dots \exp \left\{ B \sigma_N \delta_{\sigma_{N-1}, N} \exp \left\{ K \sigma'_N \sigma'_1 \right\} \right. \right. \right.$$

$$\text{定义 } (V_1)_{\sigma_i \sigma_j} = \exp \left(K \sigma_i \sigma_j \right) \quad (\sigma_i = \pm 1) \\ (V_2)_{\sigma_i \sigma_j} = \exp \left(B \sigma_i \right) \delta_{\sigma_i, \sigma_j} \quad (\sigma_j = \pm 1) \\ \text{且 } V_1 = \begin{pmatrix} \exp k & \exp(-k) \\ \exp(k) & \exp(k) \end{pmatrix}, V_2 = \begin{pmatrix} \exp B & 0 \\ 0 & \exp(-B) \end{pmatrix}.$$

$$\Sigma = \prod_{\sigma_1, \dots, \sigma_N} (V_1)_{\sigma_1 \sigma'_1} (V_1)_{\sigma'_1 \sigma_2} \dots (V_1)_{\sigma_N \sigma'_N} (V_1)_{\sigma'_N \sigma'_1} \\ = \text{Tr} (V_2 V_1 \dots V_2 V_1) = \text{Tr} (V_2 V_1)^N \quad \boxed{\text{PBC}} \\ = \text{Tr} (V_2^N V_1^N)^M = \text{Tr} (V^N).$$

§7.4.3 二维伊辛模型.

(10)

二维 Ising model 在 PBC, $h=0$ 时有精确解.
对四方格子, 可以用转移矩阵法求精确解. 办法是先解一维链, 然后再看耦合. 当 $h=0$, 一维的转移矩阵

$$V = \exp(K) I + \exp(-K) \sigma_x \\ = \exp K (I + \exp(-2k) \sigma_x)$$

定义常数 α : $\tanh \alpha = \exp(-2k)$.

$$\Rightarrow \exp(\alpha \sigma_x) = I \cosh \alpha + \sigma_x \sinh \alpha$$

现在要把 V 写成一个单 spin 形式.

$$\Delta V = A \exp(\alpha \sigma_x).$$

$$= A \cosh \alpha (I + \tanh \alpha \sigma_x)$$

$$= A \cosh \alpha (I + \exp(-2k) \sigma_x)$$

$$\Rightarrow A \cosh \alpha = e^K \quad \text{或} \quad = \frac{1}{\sqrt{\tanh \alpha}}$$

$$A = \frac{1}{\cosh \alpha \sqrt{\tanh \alpha}} = \frac{1}{\sqrt{\cosh \alpha \sinh \alpha}} = \sqrt{\frac{2}{3 \cosh \alpha}} \\ = \sqrt{\frac{2}{\sinh 2\alpha}}$$

其中 $V = \begin{pmatrix} \exp(K+B) & \exp(-K) \\ \exp(-K) & \exp(K+B) \end{pmatrix}$ (11)

$$\det(V - \lambda) = 0 \Rightarrow \lambda_{\pm} = e^K \cosh B \pm \sqrt{e^{2K} \sinh^2 B + e^{2K}}$$

$$\therefore \text{Tr } V^N = \text{Tr} \left[\left(\frac{\lambda_+}{\lambda_-} \right)^N \right] = \lambda_+^N + \lambda_-^N$$

$$= \lambda_+^N (1 + \left(\frac{\lambda_-}{\lambda_+} \right)^N) \xrightarrow{N \rightarrow \infty} \lambda_+^N$$

$$\therefore f = F/N = -\frac{1}{N} \ln \Sigma = -\beta^{-1} \ln \lambda_+ \\ (\text{free energy per spin})$$

$$M \propto -\frac{\partial f}{\partial h} = \beta^{-1} \frac{\partial \ln \lambda_+}{\partial B} = \frac{\partial \ln \lambda_+}{\partial B}$$

$$= \sinh B (\sinh^2 B + e^{-2K})^{-\frac{1}{2}} \\ \xrightarrow[B \rightarrow 0]{T \rightarrow 0} 0. \quad \therefore \text{在有限温度下有相变.}$$

$$\left(\text{而在场下, } T_c = \frac{2J}{k_B} \neq 0. \quad \therefore \text{有相变.} \right)$$

$$\text{当 } T \rightarrow 0, \quad M \xrightarrow{\sinh B \rightarrow 0} 1. \quad \text{是有序.}$$

$\therefore T_c = 0$. 这时, 没有通常的 critical exponents
in 二维, 但 Pathria 在相变附近.

这样子写

$$\Sigma = \sum_{\{\sigma_{m,n}\}} e^{K_1 \sum_{m,n} \sigma_{m,n}^3 \sigma_{m+1,n}^3 + K_2 \sum_{m,n} \sigma_{m,n}^2 \sigma_{m+1,n}^2}$$

$$\text{第一部式子 } \prod_j V_1(j, m), \quad \text{第二部式子 } \prod_j V_2(j, m)$$

$$= V(m) = (\sinh 2K_1)^{\frac{M}{2}} \exp(K_1 \sum_j \sigma_{j,x}^{(m)})$$

$$= e^{\frac{M}{2} \sum_j \sigma_{j,x}^2} \sum_j \sigma_{j,x}^3 = V_2(m) \quad \left(\frac{2M \times 2M}{2M \times 2M} \right).$$

$$\text{这样 } \Sigma = \text{Tr} (V_2^M V_1 V_2^M)^M = \text{Tr } V^M.$$

V_1 和 V_2 都是 $2M \times 2M$ 矩阵. Σ 是 $2M \times 2M$.

V 的对角线:

$$C_j = \exp \left(\pi i \sum_{l=1}^{2M} \sigma_{j+l} \sigma_{j-l} \right) \cdot O_j^-$$

$$C_j^+ = \exp \left(\pi i \sum_{l=1}^{2M} \sigma_{j+l} \sigma_{j-l} \right) \cdot O_j^+$$

$$O_{j\pm} = (\sigma_{j,x} + i \sigma_{j,y}) / \sqrt{2}$$

$$\{ C_j^+, C_j^-\} = \delta_{jj}, \quad \text{且 } C_j^+ C_j^- = 1.$$

$$\text{Jordan-Wigner 变换. } C^+ C = O^+ O^-$$

$$\text{例題: } C_{j,+} = \left[\exp\left(\beta \sum_{k=1}^{M-1} C_k^+ C_k^- \right) \right] C_j^+ \\ C_{j,-} = [\quad] C_j^+$$

注意

~~$\sigma_x, \sigma_y, \sigma_z$~~ , $(\sigma_x, \sigma_y, \sigma_z) \rightarrow (\sigma_x, \sigma_y, \sigma_x)$

不是 pauli matrix 但符合 $\sigma_x^2 + \sigma_y^2 + \sigma_z^2 = 1$. \therefore 在 V_1 和 V_2 中有相同的規律. $\sigma_x \sigma_y = i \sigma_z$.

這樣, $V_1 = (\sinh 2k)^{\frac{M}{2}} \exp\left[-2k \sum_j (\sigma_j^+ \sigma_j^- - \frac{1}{2})\right]$
 $= (\sinh 2k)^{\frac{M}{2}} \exp\left[-2k \sum_j (C_j^+ C_j^- - \frac{1}{2})\right]$

至 V_2 , $\sigma_z \rightarrow \sigma_x$ ~~且~~ $= \sigma_+ - \sigma_-$, 從而沒有規律.

$$V_2 = \exp \left\{ k \sum_{j=1}^M (C_j^+ C_j^-) (C_{j+1}^+ C_{j+1}^-) \right. \\ \left. - (-1)^j (C_1^+ C_1^-) (C_M^+ C_M^-) \right\}$$
 $\hat{n} = \sum_{j=1}^M C_j^+ C_j^-.$

 V_1, V_2 是 ~~一樣~~ 不同的由來和不同. 只是
規律.

§7.4.4 1+1 维 Ising model. (i)

1+1 维 (时间+空间) ~~且~~ Ising model 又称
横轴 Ising model.

$$H = -k \sum_n \sigma_n^x \sigma_{n+1}^x - h \sum_n \sigma_n^x.$$

由 $[\sigma_n^x, \sigma_m^x] = 0$, \therefore 有序, 由于 $H \cdot \vec{\sigma} = h \sigma^x$,
在 x 方向, 均匀垂直, 为纯横场.为证明 1+1 维且 Ising model 与 2 维 Ising
Ising model 一样, 需要从 ~~且~~ 2 维的 0+1 维
spin 模型与 1 维的 Ising 模型等价.

$$Z_1 \leftrightarrow \text{Tr } e^{-H_0/kT}$$

$$\downarrow \quad H_0 = -h_x \sigma_x, \quad \cancel{\text{且}} \quad \cancel{\sigma_x}$$

$$\begin{aligned} M &\text{ site} & h_x &= \cancel{e^{-2kT}}, \quad (k \gg 1) \\ \text{lattice} & & \cancel{h_x} &= M, \quad h_x \beta/M = e^{-2kT} \end{aligned}$$

前面我们已证明了. \therefore 从 3D 的 0+1 维 Ising model

$$\cancel{\bullet} \quad Z_1 = \text{Tr } V^M \\ = \text{Tr } \cancel{k} e^{kT} (1 + e^{-2kT} \sigma^x)$$

結果

$$\frac{E}{N} = -\beta \left[\ln(2 \sinh 2k) + \frac{1}{4\pi} \int_{-\pi}^{\pi} E_q dq \right] \quad (16)$$

$$\cos E_q = \cosh 2k \cosh 2q - \sinh 2k \sinh 2q.$$

~~\therefore 且~~ $E_q = \sinh 2k \cosh 2q$

$$\therefore J_1 = J_2 \text{ 时}, \quad \frac{k_B T_c}{J} \approx 2.27.$$

* 特性 $c \propto \ln |1 - \frac{E}{T_c}|$.

$$* M(T) \propto \begin{cases} (1 - \frac{T}{T_c})^{\frac{1}{2}} & T < T_c \\ 0 & T > T_c. \end{cases}$$

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

$$\lambda \sim (T_c - T)^{\frac{1}{4}}$$

$$\chi \sim |T|^{-\frac{1}{4}}.$$

MF

$$\begin{array}{ll} \alpha = 0 \quad (\text{discontinuation}) & \alpha = 0 \\ \beta = \frac{1}{8} & \beta = \frac{1}{2} \\ \gamma = \frac{1}{4} & \gamma = 1 \quad \delta = 3. \quad \text{完全一样.} \\ \eta = \frac{1}{4} & \eta = \frac{1}{2} \end{array}$$

$$V = V_1 = e^{kT} (1 + e^{-2kT} \sigma^x) \quad (i)$$

$$= \sqrt{\frac{M}{\beta h_x}} (1 + \frac{h_x \beta}{M} \sigma^x)$$

$$V^M = \left(\frac{M}{\beta h_x} \right)^{\frac{M}{2}} (1 + \frac{h_x \beta}{M} \sigma^x)^M$$

$$= \left(\frac{M}{\beta h_x} \right)^{\frac{M}{2}} (1 - \Delta \tau H_0)^{\frac{M}{2}}, \quad (\Delta \tau = \frac{\beta}{M})$$

$$= \left(\frac{M}{\beta h_x} \right)^{\frac{M}{2}} \left[(1 - \Delta \tau H_0)^{\frac{1}{\Delta \tau}} \right]^{\frac{M}{\Delta \tau}} = \left(\frac{M}{\beta h_x} \right)^{\frac{M}{2}} e^{-\beta H_0}.$$

 $\therefore M \rightarrow \infty, \quad \sum_{i=1}^M \cancel{\text{Tr } V^M} \sim \text{Tr } e^{-\beta H_0}, \text{ up to a const.}$

~~∴ $Z_1 = \text{Tr } e^{-\beta H_0}$~~

$$= \text{Tr } e^{-\beta \cancel{V}}$$

 ~~\therefore 且~~ $Z_1 = \text{Tr } e^{-\beta \cancel{V}}$

$$\cancel{\bullet} \quad \text{Tr } e^{-\beta \cancel{V}} = \text{Tr } e^{-\beta N}$$

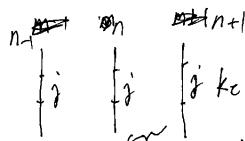
$$V = V_1 V_2 = \cancel{\text{Tr } e^{-\beta \cancel{V}}}$$

$$V = e^{kT} (1 + e^{-2kT} \sigma^x) \cdot e^k$$

$$\cancel{\bullet} \quad \sum_{m,n} \sigma_m^x \sigma_n^x = \cancel{\text{Tr } e^{-\beta \cancel{V}}}$$

$$\sum_{m,n} \sigma_m^x \sigma_{m+1,n}^x = e^{\sum_m \sigma_m^x \sigma_{m+1}^x}$$

= 1D Ising model



1D Ising chain, ~~with~~ - 1D Ising coupling

$$\rightarrow \text{H}(i) = \frac{M}{\beta h_x} \left(1 + \frac{h_x}{M} \sigma_i^x \right)$$

$$V_n(i) = \sqrt{\frac{M}{\beta h_x}} \left(1 + \frac{h_x}{M} \sigma_i^x \right)$$

$$V_n^M \sigma = \left(\frac{M}{\beta h_x} \right)^{1/2} e^{-\beta H_Q(n)}, \quad H_Q(n) = -h_x \sigma_i^x, \quad \frac{h_x \beta}{M} = e^{-2K}$$

链间耦合:

$$e^{K \sum_{m \neq n} \sigma_m^z \sigma_{m+1}^z} e^{K \sum_n \sigma_m^z \sigma_{m+1}^z} \approx e^{\frac{K}{2} \beta \sum_n \sigma_n^z \sigma_{n+1}^z}$$

$$= \prod_m e^{K \sum_n \sigma_m^z \sigma_{m+1}^z}$$

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

$$Z_{2D} \Rightarrow \Sigma = \text{Tr } e^{-\beta \left(-K \sum_n \sigma_n^z \sigma_{n+1}^z - h_x \sum_n \sigma_n^x \right)}$$

§7.5 重叠算符

我们已经看到，用平均场理论研究相变，虽然可以得到一些定性的结果，但定量上计算的各种临界指数与实验相差甚远。精确的高能重整化群，但精确可调模型很少，且往往不能反映其实际物理子性。Kadanoff首先提出了利用关联函数互相关函数发散，子系统的物理特征尺度已不再重合，可以通过格致变换离散化子系统变简单，但临界行为不变，从而估计临界指数。Kadanoff并没有建立一个完整的理论，之后也不再继续变拉后，要想保持整个重整化理论，之间也不再接续变拉后，要想保持整个重整化理论，之间也不再接续。

Wilson 通过 Hamiltonian 变换前一致不容易。Wilson 成功地完善了 Kadanoff 的思想，建立了重整化群理论，这是应用 Kondo 模型，取的非常好的效果。但是，也有各种不同的 RG theories，到底哪个好。

空间 RG，动量空间 RG，密度 RG，泛函 RG，PMRG，其基本思想都是 (1) 作“粗粒化”从大更拉，
(2) RG 实际也是子系统，粗粒化后，一些

$$h_{\Delta x} = e^{-2K}, \quad K_{\Delta x} = k_x \quad (84)$$

$$\sinh 2K_x \sinh 2K_x = 1, \quad K_x \gg 1$$

$$\Rightarrow \frac{2K_{\Delta x}}{2h_{\Delta x}} = 1. \Rightarrow K = h. \quad \text{Quantum critical point.}$$

$K > h$, Ferromagnetic order

$K < h$, Quantum disorder.

$$\text{量子态, 有 } M_j^S = \prod_{j \in i} \sigma_j^x, \quad M_i^X = \sigma_i^x \sigma_{i+1}^x,$$

$$\text{则 } \text{Tr } e^{-\beta H} = \text{Tr } e^{-\beta H}$$

$$H = -h \sum_i (M_i^S M_{i+1}^S - K M_i^X).$$

当 $h = K$ 时，self-dual. \square

① M^S order $\Leftrightarrow \sigma^S$ disorder.

M^S disorder $\Leftrightarrow \sigma^S$ order.

\therefore critical point \nexists . $K = h$.

(1) “平均”掉了，不可微开圆弧。 \therefore RG 是 \square
(2) 通过“Group”是子系统，找出 RG 变换。

(3) 通过 RG 变换，找出临界点和
临界指数及相互参数。(3) 通过 RG 变换。
确定临界指数。

在 RG 中，一些物理量有时不在确定
critical exponents. 例如，DMRG，主要用
是确定系统 Groundstates 及低能激发。而
而确定一个体系的很能特征。

§7.5.1 Real space RG

最直观的 RG 是 RSRG. 例如，~~Decimation~~

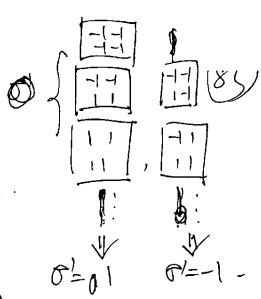
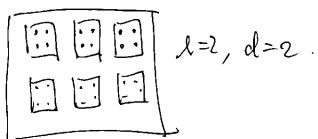
Kadanoff block of spins. 对 1D spin model.

把 ℓ^d (d 是空间 dimensions, ℓ 是 integer)

看成一起看作一个 spin. 即 $\text{the sum of } \ell^d$ spin & 2
个 spin 性质相同。从 $k_m, \sigma \rightarrow \sigma'$ 都是 1.

∇ 原来的 sites, $\Rightarrow N' = \ell^{-d} N$. sites.

$$\tau' = \ell^{-1} \tau$$



2D decimation (1834)

$$Z = \sum_{\{\sigma_i\}} \exp \{-\beta H_N \{\sigma_i\}\}$$

求解其中 $N-N'$ 个 spins 的初值，希望

$$Z = \sum_{\{\sigma_i\}} \exp \{-\beta H_N \{\sigma_i\}\}$$

~~像~~ 例 Ising model ，求解 $N-N'$ 个 spins 的初值，希望

如果两个子区中自由能 H / 磁场 h 相等，即

$$(S) \quad \downarrow \quad N' f^{(S)}(t', h') = N f^{(S)}(t, h) \quad (t = \frac{T-T_c}{T_c}), \\ \text{singular} \quad \text{if } t' \ll t, \quad \text{if } t' \gg t.$$

$$\Rightarrow f^{(S)}(t, h) = \ell^{-d} f^{(S)}(t', h').$$

~~因为~~ t 和 t' 都是 ℓ 的倍数， \therefore 该结论成立。

y_t 和 $y_{t'}$ 一样。

$$(84) \quad \text{求解 } (87) \quad \text{PM 没有考虑 } \quad (85)$$

$\gamma = \frac{1}{\beta} = y_t / (d-y_t)$. $\boxed{\gamma = \beta(S+1)}$ $\Rightarrow (90)$

$$\text{correlation length, rescaling} \quad \bar{z}' = \ell^{-\gamma} z.$$

而我们又希望 $\bar{z}' \sim |t|^{-\nu}$, $\bar{z}' \sim |t'|^{-\nu}$.

$$\ell' = \left(\frac{\bar{z}'}{\bar{z}}\right) = \left(\frac{|t'|}{|t|}\right)^{-\nu} = \ell^{-\nu} y_t, \quad \forall y_t = 1, \nu = \frac{1}{y_t}.$$

$$\therefore \boxed{\nu = 1/y_t = 2 - \alpha} \quad (\bar{z} = \bar{z}_1 \bar{z}_2)$$

$$\text{且 } g(r) = \langle \sigma(r) \sigma(r') \rangle \sim r^{-(d+2-\nu)}.$$

$$g(r) = \langle \sigma(r) \sigma(r') \rangle \sim r^{-(d+2-\nu)}.$$

$$\therefore \sigma(r) = \ell^{(d+2-\nu)/2} \sigma(\bar{r})$$

\therefore scaling relation: $\boxed{Y = (2-\nu)^{\eta}}$

$$\eta = d + 2 - 2/y_t.$$

$$\sigma(r) = \ell^{y_t} \sigma(\bar{r})$$

即 σ 和 h 不一样 rescaling.

$\langle \sigma \rangle$ 和 h 一样. ✓

根据 scaling 假设, f 为:
不成立, $\therefore f$ 为?

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

$$(3) \text{ 时, 为了使 } h \propto |t|^{-\alpha}, \therefore \boxed{f} \text{ 为 } f^{(S)} \text{ 为常数}$$

$$f^{(S)}(t', h') = |t'|^{y_t/y_t} f(h'/|t'|^{\alpha})$$

$$\Rightarrow \boxed{(S)} \quad f^{(S)}(t, h) = |t|^{\frac{1}{y_t/y_t}} f(h/|t|^{\alpha}).$$

$$f^{(S)}(t, h) = \ell^{-\alpha} |t|^{\frac{1}{y_t/y_t}} f(h/|t|^{\alpha})$$

$$= \ell^{-\alpha} |\ell^{\frac{1}{y_t/y_t}} t|^{\frac{1}{y_t/y_t}} f(h/|t|^{\alpha})$$

$$= |t|^{\frac{1}{y_t/y_t}} f(h/|t|^{\alpha}).$$

如果这些都成立，则 f 为常数附近

$$C_h = \frac{\partial^2 f^{(S)}}{\partial t^2} \sim |t|^{-(2-\frac{1}{y_t/y_t})} \Rightarrow \alpha = 2 - \frac{d}{y_t}$$

$$M = \frac{\partial f^{(S)}}{\partial h} = |t|^{\frac{1}{y_t/y_t}} |t|^{\alpha} \frac{d}{d(h/|t|^{\alpha})} f(h/|t|^{\alpha})$$

$$\sim |t|^{\frac{d}{y_t/y_t}-\alpha} \Rightarrow \beta = \frac{(d-y_t)}{y_t} = 2-\alpha-\alpha$$

$$\frac{\partial M}{\partial h} = \frac{\partial^2 f^{(S)}}{\partial h^2} = |t|^{\frac{1}{y_t}} |t|^{-2\alpha} \frac{d^2}{d(h/|t|^{\alpha})^2} f(h/|t|^{\alpha})$$

$$\gamma = \boxed{\frac{d-y_t}{y_t} = -\frac{2\alpha}{d-2\alpha}}.$$

3.2.5.2 简介: 1维 Ising model
其解法, 1维 Ising model. ✓

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

($K_0=0$, $K=\beta J$, $B=\beta \phi h$) 且 $N=\text{even}$.

$\exp(-k)$

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

$$= \prod_{j=1}^{\frac{N}{2}} \exp \left\{ 2K_0 + K \left(\sigma_{j-1} \sigma_j + \sigma_j \sigma_{j+1} \right) + \frac{1}{2} B \left(\sigma_{j-1} + 2\sigma_j + \sigma_{j+1} \right) \right\}$$

$\therefore \sigma_j = \pm 1$ 取决

$$= \prod_{j=1}^{\frac{N}{2}} \left[\exp \left\{ 2K_0 + K_0 (\sigma_{j-1} + \sigma_{j+1}) + \frac{1}{2} B (\sigma_{j-1} + \sigma_{j+1} + 2) \right\} \right.$$

$$\left. + \frac{1}{2} B (\sigma_{j-1} + \sigma_{j+1} - 2) \right\}$$

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

$$2 \cosh \left(K_0 (\sigma_{j-1} + \sigma_{j+1}) + B \right).$$

hyper scaling relation!!!!

✓

$$\sigma(r) = \ell^{y_t} \sigma(\bar{r})$$

即 σ 和 h 不一样 rescaling.

$\langle \sigma \rangle$ 和 h 一样. ✓

$$\therefore Z_N(K, B) = e^{N' K'_0} \otimes Z_{N'}(K', B'). \quad (1)$$

Fix the form.

$$K' = \frac{1}{2} \ln [\cosh(2K+B) \cosh(2K-B)] - \frac{1}{2} \ln \cosh B.$$

$$B' = B + \frac{1}{2} \ln [\cosh(2K+B) / \cosh(2K-B)]$$

Fixed points: RG eqs.

$$\Rightarrow R(K) = K', \quad R(B) = B'.$$

Fixed points:

$$R(K^*) = K^*, \quad R(B^*) = B^*.$$

若 $K=0$, 对称 B , fixed point 为 $\sigma_j^* = \pm 1$.
若 $K \neq 0$, 固定点 $\sigma_j^* = \pm 1$ (trivial).

另一个 fixed point 是 $K=\infty$, $B=0$.

它还说, $h=0$, $T \rightarrow \infty$.

另一个 fixed point 为

$$K'_0 = \frac{1}{2} \ln \cosh 2K \approx \frac{1}{2} \ln (e^{2K}/2) = K - \frac{1}{2} \ln 2.$$

$B'_0 \approx B + \frac{1}{2} \ln e^{2B} = 2B$. (由 $K^* = 0$, 且 $B^* = 0$)
这时, 反 $t = \exp(-\beta K)$, ($\beta > 0$),
 $\Rightarrow t^* = 0$.

即 $t^* = 2^{1/2} t$.



$$\therefore \lambda = 2, \quad \gamma_t = \pi/2. \quad B'_0 = 2B \Rightarrow y_h = 1.$$

$$\Rightarrow \lambda = 2 - 2/p, \quad \beta = 0, \quad \gamma = 2/p, \quad \delta = p, \quad \eta = 1.$$

5 Pathria 书上 exact 结果 -> (§13.2)

-维 Ising model 在一个非常特别的情况下 -般
no RG 可以由固定点方法. (包括 RG
方程得出: 对于 n 有 coupling constant 为
子级. 例如 decimation: $N' = l^{-1} N$, $\beta' = l^{-1} \beta$
重叠化解方法)

$$\bar{K}' = R_\ell(\bar{K}). \quad (\bar{K}' = \bar{K}).$$

$$\bar{K}^{(n)} = R_\ell(\bar{K}^{(n-1)}) = \dots = R_\ell^n(\bar{K}^{(0)}), \quad n \geq 0, \dots$$

$$\text{correlation length } \bar{\zeta}^{(n)} = l^{-n} \bar{\zeta}^{(0)}$$

Singular free energy singular part of free energy / per site

$$f_s^{(n)} = l^{n\alpha} f_s^{(0)} \quad s - \text{singular}$$

$$\sigma_{j+1, 1, 3, \dots} \rightarrow \bar{\sigma}_j^*: 1, 2, 3, \dots \quad (1)$$

$$Z = \sum_{\sigma_j^*} \prod_{j=1}^N \exp(2k_0)^{\frac{1}{2}} \cosh \left(K(\sigma_j^* + \sigma_{j+1}^*) + B \right) \exp \left[\frac{1}{2} B(\sigma_j^* + \sigma_{j+1}^*) \right].$$

如果要找 $\bar{\sigma}_j^*$ 为描述 Ising model, 那

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

结论是: $\sigma_j^* = \bar{\sigma}_{j+1}^* = 1$, $\sigma_j^* = \bar{\sigma}_{j+1}^* = -1$, $\sigma_j^* = -\bar{\sigma}_{j+1}^* = \pm 1$
时, Z 为常数.

$$\exp(K'_0 + K' + B') = \exp(2k_0 + B)^{\frac{1}{2}} \cosh(2K + B).$$

$$\exp(K'_0 + K' - B') = \exp(2k_0 - B)^{\frac{1}{2}} \cosh(2K - B)$$

$$\exp(2k_0 - B') = \exp(2k_0) 2 \cosh B.$$

$$\text{设 } \exp(K'_0) = x, \quad \exp K' = y, \quad \exp B' = z$$

$$xy/z = 2 \exp(2k_0 + B) \cosh(2K + B)$$

$$xy/z = 2 \exp(2k_0 - B) \cosh(2K - B)$$

$$x/z = 2 \exp 2k_0 \cosh B. \quad \text{从图 18.}$$

$$e^{K'_0} = x = 2 e^{2k_0} [\cosh(2K + B) \cosh(2K - B) \cosh^2 B]^{\frac{1}{4}}$$

$$e^{K'} = y = [\cosh(2K + B) \cos(2K - B) / \cosh^2 B]^{\frac{1}{4}}$$

$$e^B = z = [\cosh(2K + B) / \cosh(2K - B)]^{\frac{1}{2}}$$

$$R_\ell(K^*) = K^* \quad \begin{cases} \text{若 } K^* \neq 0 \\ \text{若 } K^* = 0 \end{cases} \quad \begin{cases} \text{若 } K^* \neq 0 \\ \text{若 } K^* = 0 \end{cases} \quad (1)$$

$$\text{fixed point.} \Rightarrow \bar{\zeta}(K^*) = l^{-1} \bar{\zeta}(K^*).$$

$$\Rightarrow \bar{\zeta}(K^*) = 0, \text{ or } \infty. \quad \text{对称 } \bar{\zeta}, \bar{\zeta}(K^*) = 0.$$

现在我们看不对应情况. 对 K^* 有

$$K = K^* + \delta K,$$

$$\Rightarrow K' = K^* + \delta K' = R_\ell(K^* + \delta K)$$

$$\Rightarrow K' = R_\ell(K^* + \delta K) - K^* = \delta K.$$

若 K 和 K' 都是 δK , 则

$$\delta K' = \frac{dR_\ell}{dK'}|_{K=K^*} \delta K \equiv A_\ell^* \delta K.$$

A_ℓ^* 是由 R_ℓ 通过微分 -5 得到的, 即

λ_i 是极值, ϕ_i 是极值. 在一个壳中

$$\delta K = \sum_i u_i \phi_i.$$

$$\delta K' = \sum_i u_i A_\ell^* \phi_i = \sum_i u_i \lambda_i \phi_i = \sum_i u_i' \phi_i.$$

即 δK 在 $\delta K'$ 中是线性的,

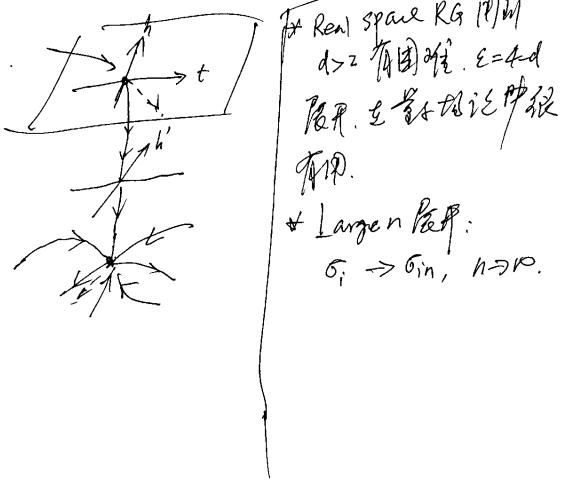
$$u_i^{(n)} = \lambda_i^n u_i^{(0)},$$

(1) 若 $\lambda_i > 1$, $u_i \uparrow \propto n$, 越做越重要, $u_i \uparrow \propto n^{(1)}$
 "relevant variable". ~~如带 K' 变量~~
 越大, 把 K' 变量看成 fixed point.

(2). 若 $\lambda_i < 1$, u_i 是 irrelevant variable. K' 越
 小则 u_i 越固定在 K' , 稳定不动.

(3). $\lambda_i = 1$, ~~是 marginal variable~~.
 是 logarithmic. \Rightarrow RG 用 simple power
 law $n \rightarrow \infty$ 优去.

physical fixed point.



动量空间 "Scaling" 之支柱. 即是 λ 为 1
 长度为 $3=0$ m 不动. ($\mu \rightarrow 0$, 等价不变)

动量空间也可以用动量空间的重正化, 但不
 要仍在 "fixed", 而是 μ . $\mu \rightarrow 0$, $\lambda > 1$.
 是作做法是在 k 空间引进一个 cut off Λ ,
~~并把~~ 把 $|k| > \Lambda$ 的部分去掉. 而留下 $|k| \leq \Lambda$ 部分. 这相当于在实空间中进行粗粒化过程. 把 ~~粗~~
~~大~~ 空间中 $(|k| > \Lambda)$ 部分平均掉, 把其
~~粗~~ 部分留下 ($|k| \leq \Lambda$). rescaling $\Lambda \rightarrow \Lambda/b$,
 $b > 1$, ~~把~~ 在 k 空间中 rescaling
 $N = \Lambda^{-d} N$ ($\Lambda > 1$). 动量空间的重正化就通过

重正化而简化. 把物理模型映射到 Λ -effect
 子系统. 用路径积分的方法来做, 通常又称为
 适应性重整化方法. ~~这是~~ 这是种对称性
 重整化被用于研究强电弱电统一论, QCD 等.
 它很复杂. 这也是数值重整化群的一种.

\Rightarrow Real space 一样, 只计算 critical expts.
 也有 relevant, irr. 与 marginal.

§ 7.6 整数重整化群和 DMRG 方法 (1)

§ 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.

重整化这概念起源于量子力学, ~~是~~
 真的隔代遗传学之微扰论 ~~是~~ 之间
 有 "等级发散" ($\mu \rightarrow 0$). 这些发散 ~~是~~ 相
 应于需要重新定义, 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
 整化至今已成功地取到了非凡成就. 在此以
 后, 一般认为一个物理描述将从此世界 ~~是~~ 为
 所谓新世界所取代. 其中最著名的模型
 "SL(3) \times SU(2) \times U(1)" 被发现它是一个可重整
 模型. 而且这四种基本相互作用中, 没有自能
 重整化是引人深思. 之所以说是
 不可能. 但即使没有自能重整化, 通过 RG
 依然可以认识清楚.

所有的能相空间下所谓重整化是 ~~是~~

§ 7.6.2 Wilson's NRG. (1)

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他的变成不太
 物理状态 "丢掉", "砍掉". 就像整数空间而言,
 我们关心 low-lying 特征值在 low-lying
 excitations. Wilson NRG 在此思想上发展:

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 , 取出 m 个 lowest eigenvalues
 在 eigenstates ψ_i , ($i = 1, \dots, m$) .

3. 把 H_L 的 transformation: $O_L^+ H_L O_L$, O_L^-

3. 定义 $O_L = (\psi_1, \dots, \psi_m)$, ~~是~~

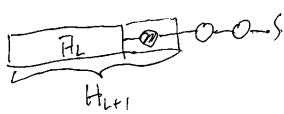
$$H_L = O_L^+ H_L O_L = \begin{pmatrix} \psi_1^+ \\ \vdots \\ \psi_m^+ \end{pmatrix} (E_1 \psi_1, \dots, E_m \psi_m) = \begin{pmatrix} E_1 & \dots & E_m \end{pmatrix}$$

$$A_L = O_L^+ A_L O_L = \begin{pmatrix} \psi_1^+ \\ \vdots \\ \psi_m^+ \end{pmatrix} \begin{pmatrix} A_{11} & \dots & A_{1m} \\ \vdots & \ddots & \vdots \\ A_{m1} & \dots & A_{mm} \end{pmatrix} \begin{pmatrix} \psi_1 \\ \vdots \\ \psi_m \end{pmatrix}$$

$$= \begin{pmatrix} \psi_1^+ A_{11} \psi_1 & \dots & \psi_1^+ A_{1m} \psi_m \\ \vdots & \ddots & \vdots \\ \psi_m^+ A_{m1} \psi_1 & \dots & \psi_m^+ A_{mm} \psi_m \end{pmatrix} = (A_{ij})_{m \times m} \Rightarrow \text{mxm matrix}$$

4. 加 n -site, $\bar{H}_L \rightarrow H_{L+1}$. 这时需要
重构 L sites 与新 site 的相位图.

5. 用 H_{L+1} 代替 H_L , 重复 2.



H_{L+1} 在空间倒映 L 为 $m \rightarrow s_m$. ~~这样~~

上步那个 site 在空间倒映. 由 6.3 DMRG 算
Wilson NRG 在 FT 是 $|\psi_i\rangle, i=1, \dots, n$ 是
 L sites 子链的本征基底, 与外部 $m-1$ sites 有
子链渐近. 例如, 用周期性条件或周期性边界
条件与之相连. ~~这样~~ 子链在空间倒映与
边界及子链完全一样. 如何选择子链
与 $n-1$ sites 复相配也很关键. White 在
这里加一些 sites 适当, 在扩大的子链中
(superblocks) 使对角化, 再投影到没扩大的子链中.
这样, 新件立刻打在 n site 上, 对 n 个 site
block 在空间影响不大. ~~这样~~ 这种做法有时又称为
作用于链非常有效, 及因 ~~其~~ 投影而

DMRG 的计算过程如下, 首先设置一个
矩阵得由 m 由 m . 一般为 m .

一. 首先在子基底用起过 m 越快. 但
小则必须用精确对角化方法.

二. 精确对角化起过. 取出最低本征 (一般为
基底).

三. 这些起用 system 起过 $|i\rangle$ 和 $|j\rangle$ 从

~~基底~~ 展开是 $|i\rangle = \sum_j \psi_{ij} |j\rangle$. 把投影
system 起过 m reduced ~~密~~ 得后得是

$$P_{ij} = \sum_{\text{基底}} |\psi_{ij}\rangle \langle \psi_{ij}|$$

$$= \sum_j \psi_{ij}^* \psi_{ij}.$$

$$\text{Tr } P = \sum_i P_{ii} = 1.$$

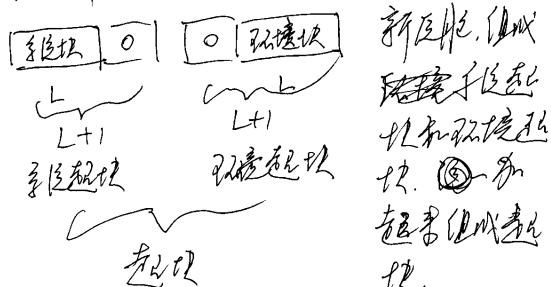
对角化 P , 有本征值 $\lambda_{ij} \geq 0$, $\sum_i \lambda_{ij} = 1$, 本征向量.

四. 因第 $i=1, \dots, s$; $s < m$. 则得留有
 $|i\rangle$. 如果 $s > m$, 则得 ~~无~~ ~~无~~ ~~无~~ ~~无~~.

~~这样~~ 没法在 m 空间找 $|i\rangle$
m. 但对有相位作用子链, i 是 superblock
的本征, 投影到 system blocks 有 $|i\rangle$:
 $|i\rangle_{\text{sb}} \rightarrow |i\rangle^1, |i\rangle^2, \dots$ 如何从中选出最高 $|i\rangle$?
这涉及 DMRG 方法的技巧.

6.6.3 DMRG 方

我们先写出一个简单子链. 基底的行数无穷大
前, 考虑子链后, 为了更好的处理边界条件, 引入
与之相匹配的环境子链. 对称性初等



起始的子链可看作边界条件.

OS 中 m 为本征子链. (1) $|1\rangle, |2\rangle, \dots, |m\rangle$

构造 $O = (|1\rangle, \dots, |m\rangle)$. 把 $H_{\text{sys}} \rightarrow \bar{H}_{\text{sys}} = O^\dagger H_{\text{sys}} O$.

$H_{\text{air}} \rightarrow \bar{H}_{\text{air}} = O^\dagger H_{\text{air}} O$. (力学对称性的要求).

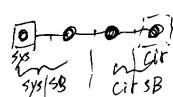
五. 以 H 代替 H_{air} , 在 m 为 system 子链
circumstance 下中取 $n-1$ 个基底. 形成 m 为子链下
的环境子链. 作循环. 直到精度满足.

例: spin 1/2 Heisenberg model

$$H = \sum_i \vec{S}_i \cdot \vec{S}_{i+1}.$$

偶数 $m=5$, ~~考虑~~ $S_{\text{tot}}^z = \pm \frac{3}{2}$ 间.

$$(1) L=4$$



$$B_L, S_L, S_R, B_R$$

且令 $\{|\frac{1}{2}\rangle, |\frac{1}{2}\rangle\}$

$$H_{BL=1} = H_{SL=1} = H_{SR} = H_{BR=1} = 0$$

$$S_{B_L=1}^z = S_{S_L=1}^z = S_{SR}^z = S_{BR=1}^z = \left(\begin{array}{cc} \frac{1}{2} & 0 \\ 0 & -\frac{1}{2} \end{array} \right)$$

$$S_{B_L=1}^+ = S_{S_L=1}^+ = S_{SR}^+ = S_{BR=1}^+ = \left(\begin{array}{cc} 0 & 1 \\ 0 & 0 \end{array} \right)$$

$$S_{B_L=1}^- = S_{S_L=1}^- = S_{SR}^- = S_{BR=1}^- = \left(\begin{array}{cc} 0 & 0 \\ 1 & 0 \end{array} \right)$$

4个格点 $S_{tot} = 0$ 的子系统.

$$\begin{pmatrix} (\frac{1}{2}, \frac{1}{2}, -\frac{1}{2}, -\frac{1}{2}) \\ (\frac{1}{2}, -\frac{1}{2}, \frac{1}{2}, -\frac{1}{2}) \\ (\frac{1}{2}, -\frac{1}{2}, -\frac{1}{2}, \frac{1}{2}) \\ (-\frac{1}{2}, \frac{1}{2}, \frac{1}{2}, -\frac{1}{2}) \\ (-\frac{1}{2}, \frac{1}{2}, -\frac{1}{2}, \frac{1}{2}) \\ (-\frac{1}{2}, -\frac{1}{2}, \frac{1}{2}, \frac{1}{2}) \end{pmatrix}$$

$$H = \vec{S}_{B_1} \cdot \vec{S}_{B_2} + \vec{S}_{B_2} \cdot \vec{S}_{B_3} + \vec{S}_{B_3} \cdot \vec{S}_{B_4}.$$

左边的子子系统下:

$$H = \begin{pmatrix} \frac{1}{2} & \frac{1}{2} & 0 & 0 & 0 & 0 \\ t & -\frac{3}{2} & \frac{1}{2} & 0 & 0 & 0 \\ 0 & \frac{1}{2} & -\frac{1}{2} & 0 & \frac{1}{2} & 0 \\ 0 & \frac{1}{2} & 0 & -\frac{1}{2} & \frac{1}{2} & 0 \\ 0 & 0 & \frac{1}{2} & \frac{1}{2} & -\frac{3}{2} & t \\ 0 & 0 & 0 & 0 & \frac{1}{2} & \frac{1}{2} \end{pmatrix}$$

~~解~~ 求出 $\psi = (0, 149429, -0.557678, 0.408248, 0.408248, -0.557678, 0.149429)$

$$= |\psi\rangle = (|\psi_i\rangle)^+$$

$$|\psi\rangle = \cancel{(|\frac{1}{2}, \frac{1}{2}, -\frac{1}{2}, -\frac{1}{2}\rangle + \dots)} + 0.149429$$

$$= \psi_{\frac{1}{2}, \frac{1}{2}, -\frac{1}{2}, -\frac{1}{2}} + \dots$$

$$\Psi(i_1, i_2, i_3, i_4) = \sum_{j_1 j_2} \psi_{i_1 i_2 j_1 j_2}^* \psi_{i_3 i_4 j_1 j_2}$$

$$\{i_1, i_2, i_3, i_4\} = \{(\frac{1}{2}, \frac{1}{2}), (\frac{1}{2}, -\frac{1}{2}), (-\frac{1}{2}, \frac{1}{2}), (-\frac{1}{2}, -\frac{1}{2})\}. \text{ 简化 } 4 \times 4 \text{ RDM}$$

$$P = \begin{pmatrix} -0.022325 & 0 & 0 & 0 \\ 0 & -0.472671 & 0.455342 & 0 \\ 0 & 0.455342 & -0.472671 & 0 \\ 0 & 0 & 0 & -0.022325 \end{pmatrix}$$

§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。

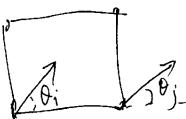
K-T 相变是通常的相变，即有序参量变化，但又不同于对称性破缺引起的相变，而是由自旋和拓扑缺陷激发引起的相变。这与我们在 ~~讨论~~ 中讨论的拓扑相变不同，拓扑相变不是一维的，且反拓扑相变 ~~存在~~ Thouless 在他的第一部分：IQHE 中的拓扑相变 ~~存在~~ 会议中，由于拓扑相变与统计物理的关系还不明确，我们只对 K-T 相变作一简述。

K-T 相变是从研究二维 X-Y 模型入手的。设一个 = 行方格，每一条边上有一个 spin。设只有 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 Nagaoka-Mermin 定理，在低维极限下相变，但弦论/色散模型的低维和低维的

对角线 P : $w = (0.022325, 0.933013, 0.022325, 0.022325)$

$$\Rightarrow u^1 = \begin{pmatrix} 1 \\ 0 \\ 0 \\ 0 \end{pmatrix}, u^2 = \begin{pmatrix} 0 \\ \frac{\sqrt{2}}{2} \\ -\frac{\sqrt{2}}{2} \\ 0 \end{pmatrix}, u^3 = \begin{pmatrix} 0 \\ \frac{\sqrt{2}}{2} \\ \frac{\sqrt{2}}{2} \\ 0 \end{pmatrix}, u^4 = \begin{pmatrix} 0 \\ 0 \\ 0 \\ 1 \end{pmatrix}.$$

~~所以~~ 全部得道。

$$D = (u^1, u^2, u^3, u^4).$$

把 system 转换为 \vec{S}_{tot}^2 之后，~~这个~~ 问题就变成了 $B_L=2$ ，~~这个~~ 是 system 转换 \vec{S}_{tot}^2 之后的一个步骤: $|B_L=2\rangle = D (|B_L=1\rangle \otimes |S_2\rangle)$.

$$H_{B_L=2} = D (H_{B_L=1} + \vec{S}_{B_L=1} \cdot \vec{S}_{S_L}) D^\dagger$$

$$S_{B_L=2}^3 = D (I \otimes S_2^3) D^\dagger, S_{B_L=2}^+ = D (I \otimes S_2^+) D^\dagger.$$

这样我们有了全部信息: $D = \vec{S}_{tot}^2$ 和 $H_{B_L=1}$ 。

形成 $S_{L=2}$ 和 $S_{R=2}$ ，总链长为 36。即有了 \vec{S}_{tot}^2 和 $B_L=2$ 的 dim=4, System Superblock dim=4x2=8,

链长链块至 $S_{tot}^2 = 0$ 为 dim=20, 即为 20×20 mH.

对角线，取最低能级，输出 ψ ，得到 $S_{L=2}$ 的 8x8

海森矩阵。 $\delta > 5$. \therefore 其中最高 m5 项为 W5 8 vectors. $(u^1, \dots, u^8) = D^{-1} S_{L=2}^2 D$.

$|B_L=2\rangle = D (|B_L=1\rangle \otimes |S_2\rangle)$ 。输出 $H_{B_L=3}$, $S_{B_L=3}^3 = D (I \otimes S_2^3) D^\dagger$

这就是我们所说的 K-T 相变， χ^2 为 $\chi^2 = 1/3$ 。

相。相 ~~相~~ 相变 ~~相~~ 相变。

$$Z = \text{Tr} e^{-\beta H} = \int_0^{2\pi} \frac{d\theta_1}{2\pi} \int_0^{2\pi} \frac{d\theta_2}{2\pi} \dots \int_0^{2\pi} \frac{d\theta_n}{2\pi} e^{-\beta H(\theta_1)}$$

$$Z = \text{Tr} e^{-\beta H} = \int_0^{2\pi} \frac{d\theta_1}{2\pi} \int_0^{2\pi} \frac{d\theta_2}{2\pi} \dots \int_0^{2\pi} \frac{d\theta_n}{2\pi} e^{-\beta H(\theta_1)}$$

$$= \int_0^{2\pi} \frac{d\theta_1}{2\pi} \int_0^{2\pi} \frac{d\theta_2}{2\pi} \dots \int_0^{2\pi} \frac{d\theta_n}{2\pi} \left(1 + \beta J \cos(\theta_1 - \theta_2) + O(J^2) \right)$$

spin-spin correlation function

$$\langle \vec{s}_i \cdot \vec{s}_j \rangle = \int_0^{2\pi} \frac{d\theta_1}{2\pi} \int_0^{2\pi} \frac{d\theta_2}{2\pi} \dots \int_0^{2\pi} \frac{d\theta_n}{2\pi} \left(1 + \beta J \cos(\theta_1 - \theta_2) \right) \cos(\theta_1 - \theta_2)$$

$$\sim \left(\frac{J}{2}\right)^{|I|} = \sim \exp\left[-\frac{|I|}{3}\right],$$

$$= \exp\left(-\ln\left(\frac{2}{\beta J}\right)^{|I|}\right) = \exp\left(-\frac{|I|}{3}\right)$$

$|I|$ 是 correlation length.

另一方面，在低维极限， $(\theta_i - \theta_j)$ 是小的。 $\langle -J \vec{s}_i \cdot \vec{s}_j \rangle$, $\vec{s}_i \cdot \vec{s}_j \rangle$: $\cos(\theta_i - \theta_j) = 1 - \frac{1}{2} (\theta_i - \theta_j)^2 \dots$

$$\therefore H = \frac{J}{2} \sum_i (\theta_i - \theta_{i+1})^2 \quad (1)$$

$$(\theta_i - \theta_{i+1})^2 + (\theta_i - \theta_{i+2})^2 \Rightarrow a^2 (\partial_x \theta_i)^2 + a^2 (\partial_y \theta_i)^2 = a^2 (\nabla \theta_i)^2.$$

左边是物理
 $\beta H = \beta E_0 - \frac{J}{2} \int d\vec{x} |\nabla \theta(\vec{x})|^2$

$$\beta E_0 = 2\beta J L^2 / a^2, \quad L \text{ is square lattice}$$

线性， a is lattice spacing

$$\text{这时, } \langle \cos(\theta_i - \theta_j) \rangle = \frac{1}{2\pi J}$$

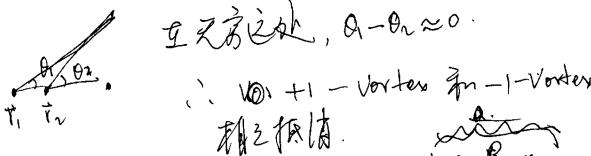
$$\sim \left| \frac{\vec{r}_i - \vec{r}_j}{a} \right|$$

\propto exponential decay in (3), 这是
 一个代数 decay, 不符合代数长距离。

∴ 存在一个相变点。

这相变点对称性自发破缺的物理过程。怎样
 来实现呢？首先，我们注意到一来， H 看起来
 像一个梯度场，但带有额外的角速度。但有 $\theta + 2\pi$ 的周期性，即 $\theta + 2\pi \equiv \theta$ 。还有一个周期性项。
 我们不能用通常的 $\theta \rightarrow \theta + 2\pi$ 方式去 rescale θ 。

∴ 在 zero-temperature, 这种 vortex 很可能
 单独存在。但可以有一个对称性破缺 charge
 和 two vortices 体能有限：
~~两个方向，左边一个，右边一个~~, ~~constant~~ ~~over~~



$$\Delta U = \int_a^R r dr d\theta (\nabla \theta)^2 + \int_a^{R+a} r dr d\theta (\nabla \theta)^2 = 2 \ln \frac{R}{a} + 2 J \ln \frac{R}{a}.$$

\therefore 有 $\theta_1 + \theta_2 \approx 0$ 时，
 两个 vortices 之间没有能量。

是有限的。

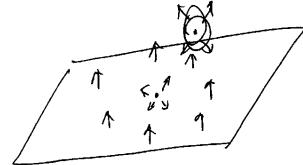
地在左边, 这样相变可能由这个原因引起。

$$\nabla \cdot \frac{\nabla H}{8\theta} = 0 \Rightarrow \nabla^2 \theta = 0,$$

解得: ① $\theta = \text{const.}$ ② $\nabla \theta = (-\frac{y}{r}, \frac{x}{r})$.

$$\int \nabla \theta \cdot d\vec{r} = 2\pi \quad \text{一般地} \int \nabla \theta \cdot d\vec{r} = \int d\theta = 2\pi n.$$

∴ 是 $-g$ vortex:



$$(\nabla \theta \cdot \nabla \theta) = \left(\frac{x^2 n^2}{r^2} \right) = \frac{1}{r^2}.$$

$$\begin{aligned} \therefore \text{单子 vortex } &\sim \frac{J}{2} \int d\vec{r} (\nabla \theta)^2 - E_0 \\ &= \frac{J}{2} \int_a^L r dr \int_0^{2\pi} d\theta \cdot \frac{1}{r^2} = J\pi \ln \left(\frac{L}{a} \right) \end{aligned}$$

这是 log. 发散。

$$E_{\text{vortex}} = \int d\vec{r} (\nabla \theta)^2 + \int d\vec{r} (\nabla \theta)^2 \quad (1)$$

$$\simeq \int_{\text{core}} d\vec{r} (\nabla \theta)^2 + \int_{\text{core}} d\vec{r} (\nabla \theta)^2 + \int_a^R r dr d\theta (\nabla \theta)^2 d\theta$$

$$+ \int_a^R r dr d\theta (\nabla \theta)^2 = 2E_{\text{core}} + 2J\pi \ln \frac{R}{a}.$$

有限制。
 ∵ 有 $\theta_1 + \theta_2 \approx 0$ 时，
 θ_1 很大 = 强束缚态， θ_2 很小 = 弱束缚态

∴ 很容易二能级分支条件, $\therefore X Y$ model dual to

2 个带电荷条件, charge \leftrightarrow vorticity.

K-T 相变 in critical T_c : $F = -\frac{\partial E}{\partial R} \approx -\frac{1}{R}$

\therefore vortex 在面积是 a^2 的 L^2 中，
 在 L^2 中面积中，只有 $(L/a)^2$ 面积
 可能有 vortex 在 L^2 中。

∴ 在有限尺寸， $-g$ vortex 在面积是 $(S = \ln(\frac{L}{a}))^2$

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

$$= (J\pi - \frac{2}{\beta}) \ln \frac{L}{a}.$$

\therefore 当 $J\pi - \frac{2}{\beta} < 0$ 时， $-g$ vortex 在 L^2 中消失。

发生相变。 $T_c = J\pi / 2k_B$.

~~非平衡统计物理~~

(111)

KT相变~ 手写:

① 从低温端 \rightarrow 高温端，起始速率，即序号有跃变。

$$\text{② } KT \text{附近 } F(T) = \begin{cases} \frac{1}{T} e^{-2B(T-T_K)^2}, & T \geq T_K \\ 0, & T \leq T_K \end{cases}$$

 \Rightarrow 此处及台阶级函数连续。③ \Rightarrow 宏观许相变。① \Rightarrow 一级相变。

KT相变~ 宏观论点:

D. J. Bishop and J. D. Reppy.

PRL 40, 1727 (1978)

起始速率 $P_s(0T_K) \sim$ 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“课件”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）后会回归平衡。从扰动中获取的能量或物质会被耗散掉。

* 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，则系统内会产生扩散运动，外部力或正比于“层”（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。

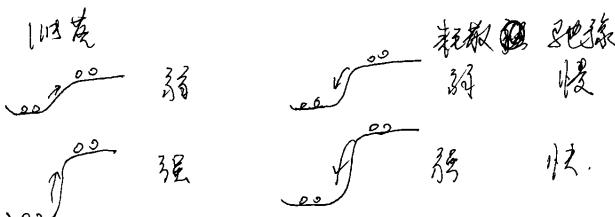
* 涨落过程：涨落是系统从平衡态向非平衡态的过程，可分为二类：(i) 由物质本身（或物理状态）不连续性引起，宏观物理量围绕平衡值（或量子基态）平均值的涨落。(ii) 随机外力作用于宏观小物体导致

导致“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，相辅相成的矛盾对立面。

(一) 三种弛豫过程：(1) 平衡至下限态引起一个瞬时过程；归结到平衡态。(2) 系统受外力扰动，导致非平衡态，撤掉外力，会回到平衡态。这两种弛豫过程本质上是一样的。

(3) 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：若有一个弛豫过程消耗能量，转化为热能，则存在一个与该过程有关的弛豫过程。例如

* 阻尼耗散运动能 \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

电能转化为热能 \leftrightarrow 电路中的热噪声转化为电能

电流。(Nyquist 定理)

* 吸收和辐射：系统吸收之能变热 \leftrightarrow 辐射时转化为电能吸。

非平衡统计物理的研究方法：

* 最早发展的方法是 Boltzmann 方程：单粒子分布函数的微分方程，即 $\frac{\partial f}{\partial t} + \frac{\partial f}{\partial p_i} \cdot \nabla_{p_i}$ 受外力和粒子之间碰撞而随时间 t 变化。用了研究耗散、弛豫和理解黑体辐射定律 (Planck 定律)。

* 在近平衡态，Kubo 的线性响应理论成为研究输运过程描述性更好的框架。Boltzmann 方程与经典力学中的牛顿第二定律相似，线性响应理论则与经典力学中的牛顿第二定律相似。(用 3D 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。这样可以更好的地理解耗散从哪里来：纳维方程是密度矩阵的海森堡方程。是时间反演不变的微分运动方程，没有耗散。耗散又来自哪里，对哪没体系。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波函数，耗散的存储与相空间坐标用 Green's function 在某点至 \vec{r} 的平面下半平面泛函。

- * 研究胜者问题则与系统驱动方式密切相关。从量子力学，似乎是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到 t 时刻的分布概率只与最近邻的前一时刻的体系状态有关。分布函数随时间演化的主要方程（Master 方程）中如果随机变量可以直接取值，则称为 Fokker-Planck 方程。
- * 如果在时间范围内直接研究随机运动的统计学，则可研究含随机力的牛顿方程：朗之万方程。
- * 从量子论来看，Master 方程研究在 Schrödinger 球壳上进行，朗之万方程研究在 Heisenberg 球壳上进行。
- * 还有平行的非平衡系理论，称为非线性非平衡统计物理。研究还不够成熟，我们不讲授。

3.8.2 Boltzmann 粒子统计方程

非平衡统计要确定非平衡态的分布函数。非平衡态，分布函数 $f = f(v) = f_0(E)$ 与能量和时间无关。例如，玻色统计（量子统计）

$$f_0 = \frac{1}{e^{\beta E} + 1} \quad \text{但是非平衡态, } f = f(\vec{r}, \vec{v}, t).$$

Boltzmann 方程就是研究 ~~经典~~ 经典统计和 ~~非平衡~~ 稀薄气体的 f 。

(i) 气体： $\lambda_T \ll \delta r$, $\lambda_T = \frac{\hbar}{(2\pi mk_B)^{1/2}}$ 一起增长，则对分子可忽略。 δr 是分子平均距离。

这时气体温度下 m 为 $(0^\circ\text{C}, 1 \text{ atm})$ 下 m 大约 n 为 $2.7 \times 10^{19} \text{ cm}^{-3}$,

$$\delta r \sim \sqrt{n} \sim 3.3 \times 10^{-7} \text{ cm}$$

$$m \approx 6.7 \times 10^{-23} \text{ g}$$

$$\lambda_T = \frac{\hbar}{\sqrt{2\pi mk_B}} \sim 0.17 \times 10^{-8} \text{ cm}$$

$$\therefore \frac{\delta r}{\lambda_T} \approx 0.190.$$

除了 ~~氢~~ 氢和水以外，一般的气体（密致气体）都是经典。

在这一章，我们将讲解非平衡统计的全部内容。我们在这里主要讲主要内容：

- (1) Boltzmann eqs.; H 定理，嫡这神义和绝对熵
- (2) 朗之万原理，嫡这和扩散 DT.
- (3) 朗之万理论，布朗运动，Master 方程，Langvin eq.; 嫉这—扩散原理

参考书：林宗桂，苏汝霖；巨阳亮；
程稼平和吴致仁。

(ii) 稀薄和强弱力： $\delta r \gg \alpha$ (相作用力)

力学)，这样，气体会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“运动”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， $\delta r \sim 3.3 \times 10^{-7} \text{ cm}$ ，而相作用力是范德瓦尔斯力， $d \sim 10^{-8} \text{ cm}$ 。用这种平均自由程估计， $\lambda \sim \frac{1}{n(\delta r)} \sim 0.12 \times 10^{-3} \text{ cm}$ ， $\lambda/d \sim 10^4$ 。

(iii) 稀薄和强弱地彼此之间碰撞可能忽略。

为了得出 Boltzmann 方程，还需要进一步简化：

- i). 忽略分子结构，用刚球模型代替连续分子模型。
- ii). 为了分子间碰撞修改，引入碰撞速率和速度分布函数。

下面我们将导出 $f(\vec{r}, \vec{v}, t)$ 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。

$$t \rightarrow t+dt, \text{ 速度 } \vec{v} \text{ 和 } \vec{r} \text{ 都会变化}$$

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

考虑“运动”和“碰撞”都写了

$$\frac{\partial f}{\partial t} = (\frac{\partial f}{\partial t})_d + (\frac{\partial f}{\partial t})_c$$

$d = \text{drift}$, 即力作用下 m 漂移.

$c = \text{collision}$.

§8.2.1 原始波的计算

~~$$\frac{\partial f}{\partial t} = [f(\vec{r} + \vec{v} dt, \vec{v} + d\vec{v}, t+dt) - f(\vec{r}, \vec{v}, t)] dt = 0. \quad \text{在“运动”中}$$~~

$$\therefore \frac{\partial f}{\partial t} = (\frac{\partial f}{\partial t})_d + \sum_i (\vec{v}_i \frac{\partial f}{\partial \vec{v}_i} + \vec{v}_i \frac{\partial f}{\partial \vec{v}_i}) \Rightarrow \text{碰撞时}$$

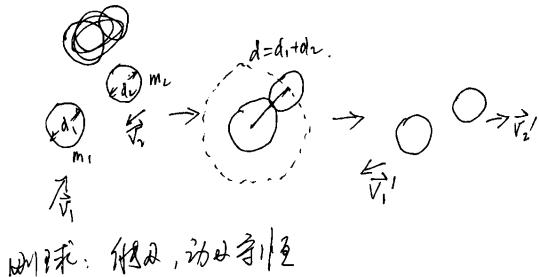
$$\Rightarrow (\frac{\partial f}{\partial t})_d = - \vec{v} \cdot \frac{\partial f}{\partial \vec{v}} - \vec{v} \cdot \frac{\partial f}{\partial \vec{v}}$$
~~$$= - \cancel{\vec{v} \cdot \frac{\partial f}{\partial \vec{v}}} = - \frac{\partial f}{\partial \vec{v}} - \frac{\partial f}{\partial \vec{v}}$$~~

$\vec{v} = \vec{a} = \vec{0}$ (单位向量)

$$\therefore (\frac{\partial f}{\partial \vec{v}})_d dt d^3 \vec{r} d^3 \vec{v} = - \left(\vec{v} \cdot \frac{\partial f}{\partial \vec{v}} + \vec{v} \cdot \frac{\partial f}{\partial \vec{v}} \right) dt d^3 \vec{r} d^3 \vec{v}$$

§8.2.2 碰撞波的计算

碰撞波 - 什么需要考虑.

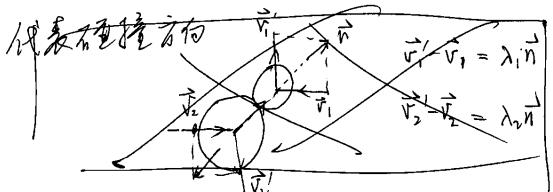


碰撞波: 什么, 动量守恒?

$$m_1 \vec{v}_1 + m_2 \vec{v}_2 = m_1 \vec{v}'_1 + m_2 \vec{v}'_2$$

$$\frac{1}{2} m_1 \vec{v}_1^2 + \frac{1}{2} m_2 \vec{v}_2^2 = \frac{1}{2} m_1 \vec{v}'_1^2 + \frac{1}{2} m_2 \vec{v}'_2^2$$

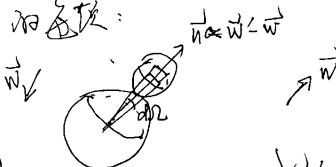
两个方程, 两个未知数. 还有二个任意数. 所以



波尔兹曼方程的证明比较繁杂, 我会把证明过程讲又发给大家(或见书本). (120')

现在, 我们解解

$$(\frac{\partial f}{\partial t})_{\text{coll.}} = \int (f'_v f'_w - f_v f_w) \Lambda d\vec{w} d\vec{v}$$



$$\Lambda = \int (\vec{v} - \vec{w}) / (m_v + m_w) d\vec{v} d\vec{w}$$

$$f_v = f(\vec{r}, \vec{v}, t), \quad f_w = f(\vec{r}, \vec{w}, t)$$

$$f'_v = f(\vec{r}, \vec{v}', t), \quad f'_w = f(\vec{r}, \vec{w}', t)$$

$$\vec{v}' = \vec{v} + \frac{2m_w}{m_v + m_w} [(\vec{w} - \vec{v}).\vec{n}] \vec{n}$$

$$\vec{w}' = \vec{w} - \frac{2m_w}{m_v + m_w} [(\vec{w} - \vec{v}).\vec{n}] \vec{n}$$

$$\vec{v}' = \vec{v} + \frac{2m_w}{m_v + m_w} [(\vec{w} - \vec{v}).\vec{n}] \vec{n}$$

$$\vec{w}' = \vec{w} - \frac{2m_w}{m_v + m_w} [(\vec{w} - \vec{v}).\vec{n}] \vec{n}$$

$$\vec{v}' - \vec{v}_1 = \lambda_1 \vec{n}$$

$$\vec{v}' - \vec{v}_2 = \lambda_2 \vec{n}$$

$$\vec{n} = (0, \varphi) \text{ 代表球运动方向.}$$

(1) 在与之垂直的方向, $v_{1\perp} = v_{1\perp}'$, 表示速度不变.
“1”没有运动.) (斜率 - 方向, 正弦余弦)

上, $\vec{v}_1 \cdot \vec{n} = \vec{v}'_1 \cdot \vec{n}$. 因为 $\vec{n} \perp \vec{e}$ (即 $m_1 \vec{v}_1$ 在 m_1 伸缩方向, & $m_1 \vec{v}'_1 - m_1 \vec{v}_1 \propto \vec{F}$).

(2) 在与之平行的方向 - 于伸缩 $m_1 \vec{v}_1$, 上面有的方程. (6个方程, 除速度 $v_{1\perp} = v_{1\perp}'$, 有6个未知数 m_1)

① & ② 与动、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.

$$\vec{v}'_1 = \vec{v}_1 + \frac{2m_w}{m_1 + m_2} [(\vec{v}_2 - \vec{v}_1) \cdot \vec{n}] \vec{n}$$

$$\vec{v}'_2 = \vec{v}_2 - \frac{2m_1}{m_1 + m_2} [(\vec{v}_2 - \vec{v}_1) \cdot \vec{n}] \vec{n}$$

两边都减

$$\vec{v}'_2 - \vec{v}'_1 = \vec{v}_2 - \vec{v}_1 - 2 [(\vec{v}_2 - \vec{v}_1) \cdot \vec{n}] \vec{n}$$

$$\Rightarrow (\vec{v}'_2 - \vec{v}'_1)^2 = (\vec{v}_2 - \vec{v}_1)^2$$

$$(\vec{v}_2^2 - \vec{v}_1^2)$$

② 反过来说，如果 $(\vec{v}_1, \vec{v}_2) \rightarrow (\vec{v}'_1, \vec{v}'_2)$ 逆行
而碰撞后， $\vec{v}'_1 = \vec{v}_1 + \vec{v}_2$

$$\vec{v}'_1 - \vec{v}_1 = \lambda_1 \vec{n} \Rightarrow \vec{v}'_1 - \vec{v}_1 = \lambda'_1 \vec{n},$$

$$\lambda'_1 (-\vec{n}) \Rightarrow \lambda'_1 = -\frac{\lambda_1}{n'}$$

$$\therefore \vec{v}'_1 = \vec{v}'_1 + \frac{2m_2}{m_1+m_2} [(\vec{v}'_2 - \vec{v}'_1) \cdot (-\vec{n})] (-\vec{n})$$

$$\vec{v}'_2 = \vec{v}'_2 - \frac{2m_1}{m_1+m_2} [(\vec{v}'_2 - \vec{v}'_1) \cdot (-\vec{n})] (\vec{n})$$

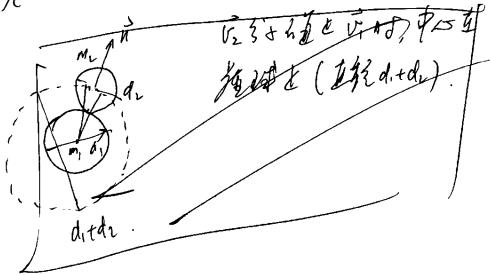
$$\text{即 } (\vec{v}'_2 - \vec{v}'_1) \cdot \vec{n} = -(\vec{v}'_2 - \vec{v}'_1) \cdot \vec{n} = (\vec{v}'_1 - \vec{v}'_2) \cdot \vec{n}$$

与正碰撞推反合。

VR速率计算 $(\frac{\partial f}{\partial t})_c$. 记 $f_i = f(\vec{r}, \vec{v}_i, t)$,
 $f'_i(\vec{r}, \vec{v}'_i, t)$. 记 $\Delta f_i^{(+)}$ 为至 dt 时间内立空间体积 d^3v_i 中

不通过 (\vec{v}_i, \vec{v}'_i) 的分子，则速变化为

$$(\frac{\partial f_i}{\partial t})_c dt d^3v_i = \Delta f_i^{(+)} - \Delta f_i^{(-)}$$



$\Delta f_i^{(+)}$ 为 $d\vec{v}_i$ 中 m_1 分子数减少: $(\vec{v}_i, \vec{v}_i) \rightarrow (\vec{v}'_i, \vec{v}'_i)$.

对立体角积分，即对 d^3v_i 积分，即是碰撞出 $d\vec{v}_i$ 中分子数.

$$\Delta f_i^{(+)} = \left[\int f_i f_2 \Lambda_{12} d\Omega d\vec{v}_i \right] dt d^3v_i d\vec{v}_i$$

同样， $(\vec{v}'_i, \vec{v}'_i, -\vec{n}) \rightarrow (\vec{v}_i, \vec{v}_i)$ 得出

$$\Delta f_i^{(-)} = \left[\int f_i f'_2 \Lambda_{12} d\Omega d\vec{v}_i \right] d\vec{v}'_i dt d^3v_i$$

Λ_{12} 为 Λ_n , $d\Omega$ 为 $d\Omega$ 是一样的。只是积分要反过来。

$$d\vec{v}'_i dt d^3v_i = |J| d\vec{v}_i d\vec{v}_i$$

$(\vec{v}_i, \vec{v}_i) \rightarrow (\vec{v}'_i, \vec{v}'_i)$ 是一个逆过程。 $|J|=1$.

$$\therefore (\frac{\partial f_i}{\partial t})_c dt d^3v_i d\vec{v}_i = \Delta f_i^{(+)} - \Delta f_i^{(-)}$$

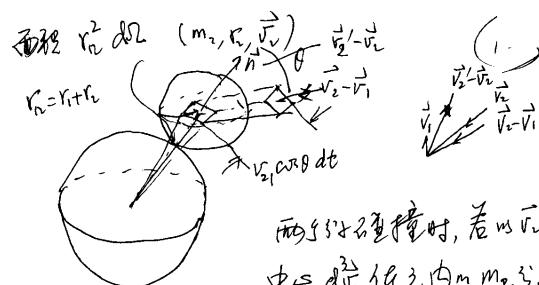
$$= \left[\int (f_i f'_2 - f_i f_2) \Lambda_{12} d\Omega \right] dt d^3v_i d\vec{v}_i$$

∴ Boltzmann 方程是

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

$$\frac{\partial f}{\partial t} + \vec{v} \cdot \frac{\partial f}{\partial \vec{r}} + \vec{f} \cdot \frac{\partial f}{\partial \vec{v}} = \int (f'_v f'_w - f_v f_w) \Lambda d^3v d\Omega.$$

$$f'_v = f(\vec{r}, \vec{v}, t), \quad f'_w = f(\vec{r}, \vec{v}', t).$$



而当发生碰撞时，若 m_1 为
中性 d^3v_i 中之 m_2 分子
与 m_1 分子碰撞后，
碰撞方向垂直于 \vec{n} 为碰撞 m_1 立体角之 $d\Omega$ 内，则由碰撞可得 $r_{12}^2 d\Omega$ 为底，以 $v_{12} \cos \theta dt$ 为高，在 $d\Omega$ 立体角内，该立体角作平行移转 $r_{12}^2 d\Omega v_{12} \cos \theta dt$ 是中包含处于 $d\vec{v}_i$ 中 m_1 分子数为

$$(f_1 d^3v_i) r_{12}^2 d\Omega v_{12} \cos \theta dt.$$

并乘以 m_1 与 m_2 的比

$$(f_1 d^3v_i) (f_2 d^3v_i) r_{12}^2 d\Omega v_{12} \cos \theta dt$$

= dt 时内， d^3v_i 中 m_1 分子数 $d\vec{v}_i$ 内 m_2 分子数 $d\vec{v}_i$ 中 m_1 分子数的 $d\vec{v}_i$ 中 m_2 分子数。 $(\Delta f_1^{(+)})$

$$\Delta f_1^{(+)} = f_1 f_2 d\vec{v}_i d\vec{v}_i \Lambda_{12} d\Omega dt d^3v_i$$

$$\Lambda_{12} = r_{12}^2 v_{12} \cos \theta.$$

$(f_1 \Delta f_1^{(+)})$ 是相立相成， $(f_2 \Delta f_2^{(+)})$ 是相立相成

8.3 H 定理, H 定义和熵

在很多场合，我们用香农熵的表达式

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

例如在信息论中 Shannon 熵. 其实，这样“熵”一词正式起源于 Boltzmann. H 不对：

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

例如，对于平行态分子系统， $n = \frac{N}{V}$ 是常数，平行态分布是 Maxwell 分布

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

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

$$\left(\int f d^3r = n, \quad \frac{1}{n} \int \frac{mv^2}{2} f d^3r = \frac{3}{2} k_B T \right)$$

$$= N \left[\ln \frac{N}{V} + \frac{3}{2} \ln \left(\frac{m}{2\pi k_B T} \right) - \frac{3}{2} \right]$$

而单分子理想热气的熵大。

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

$$\Rightarrow S = -k_B H + C$$

玻耳兹曼公理， $S \propto -H$ ，比例系数是 k_B

利用 Boltzmann 方程，可以证明

$\frac{dH}{dt} \leq 0$ ，称为 H 定理。（而且本节主要讨论的）这代表任何子系统都是“~~平衡~~”（统计物理里证明）。是 Boltzmann 方程物理意义的直接推论。

$$\frac{dH}{dt} = \int \left(\frac{\partial f}{\partial t} \ln f + f \frac{1}{f} \frac{\partial f}{\partial t} \right) d\vec{r} d\vec{p}$$

$$= \int (1 + \ln f) \frac{\partial f}{\partial t} d\vec{r} d\vec{p}$$

$$\text{B. eq. } = - \int (1 + \ln f) \left(\vec{v} \cdot \frac{\partial f}{\partial \vec{p}} \right) d\vec{r} d\vec{p}$$

$$= - \int (1 + \ln f) \left(\vec{v} \cdot \frac{\partial f}{\partial \vec{v}} \right) d\vec{v} d\vec{r}$$

$$= - \int (1 + \ln f) (ff' - f'f') d\vec{v} d\vec{v} d\vec{r} d\vec{p}$$

~~1. 证~~
~~方法：~~ $\frac{\partial}{\partial \vec{p}} \cdot (\vec{v} \ln f) = \vec{v} \cdot (1 + \ln f) \frac{\partial f}{\partial \vec{p}}$

而 $\int d\vec{r} \nabla \cdot (\vec{v} f \ln f) = \oint \vec{n} \cdot (\vec{v} f \ln f) d\Sigma = 0$

方法： $\vec{n} \cdot \vec{p} = 0$. (~~且~~ $\vec{v} = \vec{p}/m$)

$$\therefore \int \frac{\partial}{\partial \vec{v}} (f f \ln f) d\vec{v} = \oint d\Sigma \vec{v} \cdot f f \ln f$$

§ 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 方程可以推广到非气体，即 $\lambda_T \approx \bar{\lambda}_T$. 这时， $(\frac{\partial f}{\partial t})_c$ 需要修改。（参见 10.4.10）其次，不仅考虑经典和量子情形， $(\frac{\partial f}{\partial t})_c$ 是由 Boltzmann 方程导出的，一般来讲还要引入驰豫时间的近似。那就叫做耗散性。

$$\textcircled{2} \quad (\frac{\partial f}{\partial t})_c \approx - \frac{f - f^{(0)}}{\tau}$$

f 为非平衡分布函数， $f^{(0)}$ 为~~平衡~~（局域）平衡分布函数， τ 表示了平行的弛豫时间。

设 f 为矢量，即 $f^{(0)}$ 是基底平行函数。这样仍保持 \vec{v} 的意义：设外力为 0， \therefore

$$\frac{\partial f}{\partial t} = - \frac{f - f^{(0)}}{\tau} \quad \because f \text{ 为矢量}, \therefore$$

$$\textcircled{3} \quad \frac{df - f^{(0)}}{dt} = - \frac{f - f^{(0)}}{\tau}$$

$$f^{(0)(+)} \quad f(\vec{v}, t) - f^{(0)}(\vec{v}) = [f(\vec{v}, 0) - f^{(0)}(\vec{v})] e^{-\frac{t}{\tau}}$$

τ 是~~平行~~需要的时间。

但 \vec{v} 为~~平行~~且 $v \rightarrow \infty$, $\frac{\partial f(v)}{v \rightarrow \infty} = 0$.

\Rightarrow ~~因为~~: $n = \int f d^3 v = \text{finite}$.

\therefore dynamic 语义对 $\frac{dH}{dt}$ 有意义。

$$\therefore \frac{dH}{dt} = - \int (1 + \ln f) (f_i f_i - f'_i f'_i) d\vec{v}_i d\vec{v}_i d\vec{p}_i$$

$\Rightarrow 1 \leftrightarrow 2$, 都是~~平行~~意义。 \therefore

$$\frac{dH}{dt} = - \int (1 + \ln f_i) (f_i f_i - f'_i f'_i) d\vec{v}_i d\vec{v}_i d\vec{p}_i$$

$$\text{耗散/1: } \frac{dH}{dt} = - \frac{1}{2} \int (2 + \ln f_i f_i) (f_i f_i - f'_i f'_i) d\vec{v}_i$$

$$v'_i \leftrightarrow v_i, \quad \& d(\cdots)' = d(\cdots)$$

$$\Rightarrow \frac{dH}{dt} = - \frac{1}{2} \int (2 + \ln (f'_i f'_i)) (f'_i f'_i - f_i f_i) d\vec{v}_i$$

耗散/2:

$$\frac{dH}{dt} = - \frac{1}{4} \int \underbrace{[\ln(f_i f_i) - \ln(f'_i f'_i)]}_{\geq 0} (f_i f_i - f'_i f'_i) d\vec{v}_i$$

\therefore ~~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~~1~~两个平行条件。

* 大高流和大高产生率~~率~~（耗散，~~且~~）

8.4 Boltzmann 方程中的电荷平衡

计算。用驰豫时间 τ_{fr} ，可以研究金属自由电子的~~平衡~~过程。对金属中的自由电子， $f^{(0)}$ 为~~平衡~~ Fermi 分布

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

$E(\vec{p}) = \frac{p^2}{2m}$, μ 是化学势。单位体积内~~粒子数~~子数

[同温度下] 内~~单位体积内~~ 等于

$$2 \times \frac{p^2}{h^3} f^{(0)}, \quad 2 \text{ 来自 spin } \uparrow, \downarrow.$$

Boltzmann eq. reads

$$\frac{\partial f}{\partial t} + \vec{v} \cdot \frac{\partial f}{\partial \vec{p}} + \vec{F} \cdot \frac{\partial f}{\partial \vec{p}} = - \frac{f - f^{(0)}}{\tau}$$

设~~在~~电子在外部电场中， $\vec{F} = -e\vec{E}$, \vec{E} 为电场强度。~~且~~ $\frac{\partial f}{\partial \vec{p}} \gg \frac{\partial f}{\partial t}$, $\frac{\partial f}{\partial \vec{p}} \gg \frac{\partial f}{\partial \vec{v}}$, $\therefore f \approx f^{(0)}$.

$$e\vec{E} \cdot \frac{\partial f}{\partial \vec{p}} = \frac{f - f^{(0)}}{\tau}, \quad f = f^{(0)} + f^{(1)} + \dots;$$

代入~~一~~式：

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

$$\frac{\partial f^{(0)}}{\partial \vec{p}} = \frac{\partial f^{(0)}}{\partial \vec{E}} \frac{\partial \vec{E}}{\partial \vec{p}} = \frac{\partial f^{(0)}}{\partial \vec{E}} \vec{v}$$

$f \approx f^{(0)} + e\vec{v} \cdot \vec{E} \cdot \vec{v} \frac{\partial f^{(0)}}{\partial \vec{v}}$

若把上式积分 $\int (f^{(0)} + e\vec{v} \cdot \vec{E} \cdot \vec{v}) dt$, 即能得到 $\rightarrow \text{J. m shift.}$

现在, 取运动方向为 x 轴, 则在 dt 时间内

速度沿 x 方向的 dA 在 E 层流

$$J_e dt dA = \int v_x dt dA + \frac{2dp}{h^3}$$

$$(J_e = nev_x = \frac{2dp}{h^3} f e^{v_x})$$

$$\text{即 } J_e = e \int v_x (f^{(0)} + f^{(1)}) \frac{2dp}{h^3},$$

$$v_x = p_x/m, f_0(-v_x) = f_0(v_x). \therefore f^{(1)}=0.$$

$$J_e = e^2 E \tau \int v_x^2 \frac{\partial f^{(0)}}{\partial E} \frac{2dp}{h^3}$$

$$\left(\begin{aligned} \int dp = & \int p d\phi \cdot d\theta \sin\theta d\psi \\ = & 2\pi E d\phi \sqrt{m/E} \cdot 4\pi \\ = & 4\pi \frac{(2m)^{3/2}}{2} \int E^k dE \\ = & e^2 E \tau \int v_x^2 \frac{\partial f^{(0)}}{\partial E} D(E) dE \\ D(E) = & 4\pi \frac{(2m)^{3/2}}{h^3} E^k \end{aligned} \right)$$

f 为 \vec{r} 和 t (振动)

$$\frac{\partial f}{\partial t} + \vec{v} \cdot \nabla f + \frac{\vec{E}}{m} \cdot \frac{\partial f}{\partial \vec{v}} = \frac{\partial f}{\partial t} \text{coll.}$$

$$\downarrow \quad \downarrow \quad \downarrow$$

$$\frac{d\langle v \rangle}{dt} = -\frac{eE}{m} + i\omega_c \langle v \rangle - \frac{\langle v \rangle}{\tau}$$

$$\langle v \rangle = -\frac{eE/m}{1-i\omega_c \tau} \quad (E = E_x + iE_y)$$

$$j = -ne\langle v \rangle = \sigma_0 E / (1-i\omega_c \tau), \sigma_0 = \frac{ne^2}{m}.$$

$$\vec{j} = \vec{v} \cdot \vec{E}, \quad \vec{v} = \begin{pmatrix} \sigma_{xx} & \sigma_{xy} \\ \sigma_{yx} & \sigma_{yy} \end{pmatrix}.$$

$$\Rightarrow \sigma_{xx} = \sigma_{yy} = \frac{\sigma_0}{1+i\omega_c \tau^2},$$

$$\sigma_{xy} = -\sigma_{yx} = -\frac{nec}{B} + \frac{\sigma_0}{\omega_c \tau}.$$

* 当有吸收辐射时 (辐射), 在稳恒状态, H_0 可用
弛豫时间近似. 但 f 不依赖于 t , 用局域平均
值近似 $f^{(0)}$. 可得出速率. (见书)

选择 x, y, z 轴, (f 不变), $v_x \rightarrow v_f \rightarrow v_g$.

$$\therefore J_e = e^2 E \tau \int C(E) \frac{2p^2}{3} \frac{\partial f^{(0)}}{\partial E} D(E) dE$$

$$= \frac{2e^2 E}{3m} \int C(E) E^3 \frac{\partial f^{(0)}}{\partial E} D(E) dE$$

对 Fermi gas, $\frac{\partial f^{(0)}}{\partial E}$ 只在 Fermi 面附近不为 0,
且 $T \rightarrow 0$, Fermi 面处 $\delta(E-\mu)$. \therefore

$$\frac{\partial f^{(0)}}{\partial E} = \delta(E-\mu) f^{(0)}$$

$$\therefore J_e = \frac{2e^2 \tau C(\mu)}{3m} n D(\mu) E$$

$$\text{对 } n = \int_0^\mu D(E) dE$$

$$= \frac{2}{3} \mu D(\mu).$$

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

正向速率 n 纯粹由速率决定.

反向速率也时,

$$\vec{F} = -e \vec{E} - \frac{e}{c} \vec{v} \times \vec{B}.$$

设 $\vec{v} = v_x + i v_y$ 考虑一维空间情况, 且

$$v = v_x + i v_y, \quad B \perp x-y \text{ 平面.}$$

3.8.4.5 速率响应理论: 力学扰动

Boltzmann 方程只处理稀薄、短程相互作用气体.
这里还用到非平衡统计理论是 Kubo 提出的
线性响应理论. 该理论不仅可以用分子
动力学方法, 也可以用量子力学基态. 但是, 它仅限
于纯热力学可观察量, 也可用于计算量子力学可观察量.

线性响应理论~出发点是考虑 m 的磨擦力可以写成

$$H = H_0 + h(t)$$

H_0 是要研究的系统~磨擦力, $H_0(t)$ 是一个 $\sim t$ 的扰动.
我们用力学方式研究问题. 研究 m 的磨擦力 H

$$\text{Schrödinger eq.: } i\hbar \frac{\partial}{\partial t} \Psi = (H_0 + H_e) \Psi.$$

假定 Ψ 为 $\Psi(t)$,

$$\Psi(t) = e^{i\frac{H_0}{\hbar}t} \Psi(0), \quad \text{Sch. eq. true}$$

$$\therefore \left(-i\frac{H_0}{\hbar} \right) e^{-i\frac{H_0}{\hbar}t} \Psi(0) + i\hbar e^{-i\frac{H_0}{\hbar}t} \dot{\Psi}$$

$$= \text{在 } H_0 e^{-i\frac{H_0}{\hbar}t} \Psi(0) + H_e e^{-i\frac{H_0}{\hbar}t} \Psi$$

$$\Rightarrow \dot{\Psi} = \frac{1}{i\hbar} \left(e^{i\frac{H_0}{\hbar}t} H_e \Psi + e^{-i\frac{H_0}{\hbar}t} \right) \Psi = \frac{1}{i\hbar} \tilde{H}_e e^{i\frac{H_0}{\hbar}t} \Psi$$

$\therefore t \rightarrow -\infty$ 时, $\Psi(t) = \Psi_m$, 是 Schrödinger eq.
 m -子宏态. ($t \rightarrow -\infty, H_e(t) = 0, H_0 \Psi_m = E_m \Psi$)

开始上,

$$\phi(t) = \phi_m + \frac{1}{i\hbar} \int_{-\infty}^t \tilde{H}_e(t') \phi(t') dt'$$

是 Schrödinger eq. 的解. 量力学守恒 A ①
在 t 时刻 n 能级值在物理上是确定的.

$$\bar{A}(t) = \int d\vec{r} \psi^*(\vec{r}, t) A(\vec{r}, t) \psi(\vec{r}, t)$$

$$= \int d\vec{r} \psi^*(\vec{r}, t) e^{i\frac{\tilde{H}_e}{\hbar}t} A e^{-i\frac{\tilde{H}_e}{\hbar}t} \psi(\vec{r}, t)$$

$$= \int d\vec{r} \psi^*(\vec{r}, t) A(t) \psi(\vec{r}, t)$$

② 代入

$$\phi(t) = \phi_m + \int_{-\infty}^t \tilde{H}_e(t') \left(\phi_m + \int_{-\infty}^{t'} \tilde{H}_e(t'') \phi(t'') dt'' \right) dt'$$

对 \tilde{H}_e 做线性近似, 就是 ② 上述的 ③ 和 ④ 的近似

$$\tilde{H}_e \sim \text{阶}: \phi(t) \approx \phi_m + \int_{-\infty}^t \tilde{H}_e(t') \phi_m dt'$$

$$\bar{A}_m = \bar{A}(t) \approx \int d\vec{r} \phi_m^* A(t) \phi_m$$

$$+ \frac{1}{i\hbar} \int_{-\infty}^t dt' \int d\vec{r} d\vec{r}' [\bar{A}(t), \tilde{H}_e(t')] \phi_m$$

$$\bar{A}(t) - \bar{A}_m < m |A|_m > = \frac{1}{i\hbar} \int_{-\infty}^t dt' < m |[A(t), \tilde{H}_e(t')]>$$

③ Fourier 变换

$$\int \frac{d^3 k}{(2\pi)^3} D(\vec{k}) e^{i\vec{k} \cdot (\vec{r} - \vec{r}')} - i\omega(\vec{k}) t$$

$$\delta \alpha(\vec{r}, t) = eV_0 D(\vec{k}) e^{i\vec{k} \cdot \vec{r} - i\omega(\vec{k}) t}$$

对 \tilde{H}_e 中 H_0 , $D(\vec{k})$ 可以求出, 则冲击辐射率
密度函数可以求出.

例 2. 电导率. 假设我们用线性响应
理论求电导率的一般表达式:

$$H_e = - \int d\vec{r} \vec{j} \cdot \vec{A}, \quad \vec{A} \text{ 是外电场矢量}$$

$$\vec{j} = \vec{j}_1 - \frac{e^2}{m} \hat{n}(\vec{r}) \bar{A}(\vec{r}),$$

$$\vec{j}_1 = \frac{i e}{2m} \left((\nabla - \nabla') \Psi(\vec{r}) \Psi(\vec{r}') \right)_{\vec{r}=\vec{r}'}$$

在外场时, $\langle \vec{j} \rangle = \langle \vec{j}_1 \rangle = 0$.

根据经典物理学公式:

$$\langle j_a(\vec{r}, t) \rangle = \sum_{b=1}^3 \int d\vec{r} dt' K_{ab}(\vec{r}, t; \vec{r}', t') A_b(\vec{r}', t')$$

如果 $v \sim k_F$, $\langle j \rangle \downarrow 0$, 微观粒子向反向
运动.

对统计系统

$$\langle \bar{A} \rangle_T = \sum_m \frac{1}{Z_G} e^{-(E_m - \mu)/k_B T} \bar{A}_m$$

$$(Z_G \text{ 是 } E \text{ 配分函数}, \frac{1}{Z_G} e^{-(E_m - \mu)/k_B T} = p_m)$$

$$= \sum_m p_m \bar{A}_m = \text{Tr} P \bar{A}$$

Kubo 在线性响应理论中推导出 (见书上推导)
程出发得出. (见苏进强书), 和那书上)

下面举二例.

例 1. 对电子气做冲击型脉冲扰动.

$$V(\vec{r}, t) = V_0 e^{i\vec{Q} \cdot \vec{r}} \delta(t)$$

$$H_e = -eV_0 \int d\vec{r} \hat{n} e^{i\vec{Q} \cdot \vec{r}} \delta(t).$$

\hat{n} 是粒子数密度算符. 接前面讨论

$$\delta \hat{n}(\vec{r}, t) = i e V_0 \int d\vec{r}' \langle [\hat{n}(\vec{r}, t), \hat{n}(\vec{r}', 0)] \rangle_{t \rightarrow 0} e^{i\vec{Q} \cdot \vec{r}'}$$

$$i \langle [\hat{n}(\vec{r}, t), \hat{n}(\vec{r}', 0)] \rangle_{t \rightarrow 0}$$

是描述跃迁概率矩阵, 如果考虑平均场,
它在 $\vec{r} - \vec{r}'$, $t \rightarrow 0$ 时为

$$K_{ab} = -\frac{e^2 n}{m} \delta(\vec{r} - \vec{r}') \delta(t - t') \delta_{ab}$$

$$+ i \langle [j_a(\vec{r}, t), j_b(\vec{r}', t')] \rangle \delta(t - t')$$

④ Fourier 变换

$$\langle j_a(\vec{r}, t) \rangle = \int \frac{d^3 k dv}{(2\pi)^4} j_a(\vec{k}, v) e^{i\vec{k} \cdot \vec{r} - ivt}$$

$$\boxed{K_{ab}(\vec{r} - \vec{r}', t - t')} = \int \frac{d^3 k dv}{(2\pi)^4} K_{ab}(\vec{k}, v) e^{i\vec{k} \cdot (\vec{r} - \vec{r}') - iv(t - t')}$$

$$A_b(\vec{r}, t) = \int \frac{d^3 k dv}{(2\pi)^4} A_b(\vec{k}, v) e^{i\vec{k} \cdot \vec{r} - ivt}$$

$$\boxed{j_a(v) = \sum_{b=1}^3 K_{ab}(\vec{v}, v) A_b(\vec{v}, v)}$$

看电场是空间均匀的

$$A_b(\vec{v}, v) = \frac{1}{3V} E_b(v) \delta(\vec{v})$$

$$\boxed{j_a(v) = \sum_{b=1}^3 K_{ab}(0, v) E_b(v) / \hbar v}$$

$$\boxed{\sigma_{ab}(v) = \frac{1}{\hbar v} K_{ab}(0, v)} \text{ 是电导率张量.}$$

$$\text{动力学平均: } \sigma_e = \frac{e^2}{3V} \int_0^\infty dt \int_0^B d\vec{x} \text{Tr} \vec{J} \cdot \vec{J} e^{-iLt} \rho_0.$$

3.8.6 线性响应理论：热力学扰动

前面讲的是直接外加扰动后线性响应，这里由于是微扰，波函数和扰动不能用一个 ψ 表示，由 $\psi = \psi_0 + \delta\psi$ 表示，这时，体系状态是 ψ_0 和 $\delta\psi$ 的线性组合，而 ψ_0 与 $\delta\psi$ 垂直，所以 ψ_0 与 $\delta\psi$ 平行。我们称 ψ_0 为真热力学扰动（ ψ_0 和 H 平行， ψ_0 和 N 垂直）。 ψ_0 的 Hamiltonian 是

$$\begin{aligned} H &= \int H(\vec{r}) d\vec{r} \\ (\text{或 } \vec{p} = m\vec{v}, \vec{r} = \vec{r} + \vec{p}\tau) \quad H(\vec{r}) &= \sum_{i=1}^N E_i \delta(\vec{r} - \vec{r}_i) \\ E_i &= \frac{p_i^2}{2m} + \frac{1}{2} \sum_{j \neq i} U(\vec{r}_i - \vec{r}_j) \end{aligned}$$

(14)

ψ_0 的形式

$$N = \int d\vec{r} N(\vec{r}).$$

$d\vec{r}$ 是一个微元，假设中只考虑在 $d\vec{r}$ 内，体系是 ψ_0 平行态。对每一个 $d\vec{r}$ ， ψ_0 对每一个 local， ψ_0 局域平衡态。局域平衡态下 ψ_0 有

$$\psi_0(\vec{r}) \sim e^{-\beta(\vec{r}) H_0(\vec{r})}$$

$$H_0(\vec{r}) = H(\vec{r}) - \mu(\vec{r}) N(\vec{r}).$$

系统处于局域平衡态的密度矩阵为 (14)

$$\rho_L = N_L^{-1} e^{-\beta(\vec{r}) S_Q}$$

$$S_Q = \int \beta(\vec{r}) [H(\vec{r}) - \mu(\vec{r}) N(\vec{r})] d\vec{r}.$$

N_L 是归一化常数， $\beta(\vec{r}) = 1/k_B T(\vec{r})$ ， $N(\vec{r})$ 是 local 波函数。 $T(\vec{r})$ ， $\mu(\vec{r})$ 在空间上均是连续的，但局域平衡态 ρ_L 不能直接求出它的密度矩阵， ρ_L 不是密级矩阵的元素，还需要加修正项：

$$\rho = \rho_L + \delta\rho,$$

ρ 满足演化方程。

$$i\hbar \frac{\partial \rho}{\partial t} = \dots, [H_0, \rho] = L\rho$$

//

$$i\hbar \frac{\partial \delta\rho}{\partial t} = L\rho_L + L\delta\rho$$

$$\therefore \delta\rho(t) = \frac{i}{\hbar} \int_{-\infty}^t dt' e^{-iL(t-t')/\hbar} L\rho_L e^{iL(t-t')/\hbar} \quad (\text{取 } \hbar=1).$$

$$[H, \rho_L] = [H, \frac{1}{N_L} e^{-S_Q}]$$

$$= \frac{1}{N_L} [H, -S_Q] + \frac{1}{N_L} [H, (S_Q)_{h.c.}] + \dots$$

$$= -LS_Q + \frac{1}{N_L} [LS_Q] S_Q + \dots$$

$$= -LS_Q \left(\frac{1}{N_L} (1 - S_Q + \dots) \right) = -LS_Q \rho_L.$$

(由于 LS_Q 和 $\frac{\partial \beta}{\partial p}$ 是小量， $\therefore \rho_L \approx \rho_0$)

$$\simeq -LS_Q \rho_0$$

$$= - \int d\vec{r} \left[[H(\vec{r}) - \beta(\vec{r}) \mu(\vec{r})] N(\vec{r}) \right] \rho_0.$$

$$\rho_0 = e^{-\beta(H - \bar{\mu}N)} / \text{Tr} e^{-\beta(H - \bar{\mu}N)}$$

$\bar{\mu}$ 和 $\bar{\mu}$ 是 $\beta(\vec{r})$ 和 $\mu(\vec{r})$ 在空间平均值。

由能守恒： $\frac{\partial H(\vec{r})}{\partial t} + \vec{J} \cdot \vec{B}(\vec{r}) \Rightarrow$

守恒律： $\frac{\partial N}{\partial t} + \nabla \cdot \vec{J}(\vec{r}) = 0$.

$$\Rightarrow -\frac{i}{\hbar} L H(\vec{r}) = -\nabla \cdot \vec{B}(\vec{r}), -\frac{i}{\hbar} L N(\vec{r}) = -\nabla \cdot \vec{J}(\vec{r})$$

$\vec{B}(\vec{r})$ 和 $\vec{J}(\vec{r})$ 是能流和守恒流。

$$\delta\rho = -\frac{i}{\hbar} \int_{-\infty}^t dt' L[\rho_L + \delta\rho(t')]$$

(14)

$$\begin{aligned} \delta\rho &= -\frac{i}{\hbar} \int_{-\infty}^t dt' L\rho_L + -\frac{i}{\hbar} \int_{-\infty}^t dt' \left(\frac{i}{\hbar} \int_{-\infty}^{t'} dt'' L[\rho_L + \delta\rho(t'')] \right) \\ &= -\frac{i}{\hbar} \int_{-\infty}^t dt' L\rho_L + \left(\frac{i}{\hbar} \right)^2 \int_{-\infty}^t dt' L \left(\frac{i}{\hbar} \int_{-\infty}^{t'} dt'' L[\rho_L + \delta\rho(t'')] \right) \\ &\quad + \left(\frac{i}{\hbar} \right)^3 \int_{-\infty}^t dt' L \int_{-\infty}^{t'} dt'' L \int_{-\infty}^{t''} dt''' L[\rho_L + \dots] \\ &\equiv -\frac{i}{\hbar} \int_{-\infty}^t dt' e^{-iL(t-t')} L\rho_L = -\frac{i}{\hbar} \int_0^\infty e^{-iLt'} L\rho_L dt' \end{aligned}$$

$$\cancel{\frac{i}{\hbar} L Q} \quad S_Q = -\frac{i}{\hbar} LS_Q$$

$$= -\frac{i}{\hbar} \left[H, \int \beta(\vec{r}) (H(\vec{r}) - \mu(\vec{r}) N(\vec{r})) d\vec{r} \right]$$

$$= -\frac{i}{\hbar} [H, \bar{\mu} S_Q] + -\frac{i}{\hbar} \left[H, \int \frac{\partial \beta(\vec{r})}{\partial \vec{r}} \cdot \nabla (H - \bar{\mu} N) d\vec{r} \right]$$

$$= \cancel{\frac{i}{\hbar} L Q} = -\frac{i}{\hbar} L \int \frac{\partial \beta}{\partial \vec{r}} \cdot \nabla (H - \bar{\mu} N) d\vec{r}.$$

β 正比于 $\bar{\mu}$ 或 $\beta \propto \bar{\mu}$ 在样证。

$$\therefore L_{\vec{B}} = \frac{1}{i} \int d\vec{r} \vec{B}$$

$$\begin{aligned} L_{\vec{B}, L} &= -i \int d\vec{r} [\beta(\vec{r}) \nabla \cdot \vec{Q}(\vec{r}) - \beta^{\mu} \nabla \cdot \vec{J}(\vec{r})] \rho_0 \\ &\Rightarrow i \int d\vec{r} [\vec{Q} \cdot \nabla \beta(\vec{r}) - \vec{J} \cdot \nabla (\beta^{\mu})] \rho_0 \\ &= i \int d\vec{r} [\vec{J}_e \cdot \nabla \beta - \beta \left(\frac{\partial \mu}{\partial n} \right) \vec{J} \cdot \nabla n] \rho_0 \\ &\quad \vec{J}_e = \vec{Q}(\vec{r}) - h \vec{J}(\vec{r}), h = \mu - T \left(\frac{\partial \mu}{\partial T} \right)_n. \end{aligned}$$

$h(\vec{r})$ 是 local 项, n 是平均密度.

对 \vec{J} 的积分 $\vec{B}(\vec{r})$, 例如在 \vec{J} 层的区域层, 在平均场时 $\text{Tr } \vec{B}(\vec{r}) \rho_0 = 0 \dots$

$$\begin{aligned} \langle \vec{B}(\vec{r}) \rangle &= \text{Tr} (\vec{B}(\vec{r}) \rho_0) \\ &= -i \int_0^\infty dt' \text{Tr} \vec{B}(\vec{r}) e^{-iLt'} L_{\vec{B}} \rho_0 \\ &= \int_0^\infty dt' \int d\vec{r}' \text{Tr} \vec{B}(\vec{r}') e^{-iLt'} \left[\vec{J}_e(\vec{r}') \cdot \nabla \beta \right. \\ &\quad \left. - \beta \left(\frac{\partial \mu}{\partial n} \right) \vec{J}(\vec{r}'). \nabla n \right] \rho_0 \end{aligned}$$

若 $T(\vec{r})$ 是平均场, $\frac{\partial n}{\partial r} \neq 0$, 则 $\vec{J} \neq 0$.

$$\langle \vec{J} \rangle = -D \nabla n, \text{ 扩散系数}$$

$$\begin{aligned} D &= \beta \left(\frac{\partial \mu}{\partial n} \right)_T \frac{1}{3V} \int_0^\infty dt \text{Tr} \vec{J} \cdot \vec{J} e^{-iLt} \rho_0 \\ &= \frac{1}{e^2} \left(\frac{\partial n}{\partial r} \right) \cancel{\int d\vec{r} e^2 \beta \sigma_e} \\ \sigma_e &= \frac{e^2 \beta}{30V} \int_0^\infty dt \text{Tr} \vec{J} \cdot \vec{J} e^{-iLt} \rho_0. \quad (S.2.10) \end{aligned}$$

是电导率. ($\propto \sigma_{ab}(v) = \frac{1}{iV} K_{ab}(0, v)$ 为 v^2)

$$\cancel{\int d\vec{r} \vec{J} \cdot \vec{J}} = \vec{J} \cdot \vec{J}. \quad ; \vec{V} \rightarrow \frac{1}{i} \beta = T.$$

扩散运动造成的 \vec{J} 与 \vec{Q} 及 \vec{J} 的关系是扩散系数 (例如扩散率、扩散系数) 的主要部分. 有时称为第一系数-扩散定律. (\because 第二系数-扩散系数等于零). 布朗运动 (扩散运动) 和力 \vec{F} (速度与 \vec{Q} 存在强联系) 是力学 (力学) 研究的主要问题. 这里的背景是随机振动 \vec{J} 的方程.

若 \vec{J} 只有 \vec{J}_e 是平均场. (154)

$$\langle \vec{B} \rangle = \frac{1}{V} \int_0^\infty dt \text{Tr} \vec{B} e^{-iLt} \left[\vec{J}_e \cdot \nabla \beta - \beta \left(\frac{\partial \mu}{\partial n} \right) \vec{J} \cdot \nabla n \right] \rho_0.$$

$$\vec{B} = \int d\vec{r} \vec{B}(\vec{r}), \vec{J} = \int d\vec{r} \vec{J}(\vec{r}), \vec{J}_e = \int d\vec{r} \vec{J}_e(\vec{r}).$$

若只有 \vec{J}_e 有移位, 但 $\vec{J} = 0$, 则 $\vec{J}_e = \vec{Q}$, $\vec{J} = \vec{Q}$, 则 $\vec{B} = \vec{Q}$. 但 $\vec{J}_e = \vec{Q}$, $\vec{J} = \vec{Q}$, 则 $\langle \vec{B} \rangle = \frac{1}{V} \int_0^\infty dt \cancel{\int d\vec{r} \vec{J}(\vec{r})} \text{Tr} (\vec{X} \beta \cdot \vec{Q}) \vec{Q} e^{-iLt} \rho_0.$

$$\begin{aligned} \langle \vec{Q} \rangle &= \cancel{K \nabla T} = \cancel{K \nabla \frac{1}{\beta}} = \cancel{K \frac{1}{\beta} \nabla T} + \cancel{K \frac{1}{\beta} \nabla \vec{B}} \\ &= K \frac{1}{\beta} \nabla T \end{aligned}$$

$$\langle \vec{Q} \rangle = -K \nabla T = -K \nabla \frac{1}{\beta} = +K \frac{1}{\beta^2} \nabla \beta \quad (k_B = 1)$$

另一方面, $(\nabla \cdot \vec{Q}) \vec{Q} = \vec{Q} \cdot (\vec{A} \cdot \vec{Q}) \vec{Q} = (A_x Q_x \partial_x + A_y Q_y \partial_y + A_z Q_z \partial_z) \vec{Q} = A_x Q_x \partial_x \vec{Q} + A_y Q_y \partial_y \vec{Q} + A_z Q_z \partial_z \vec{Q}$

而 \vec{Q} 为单位矢量. $= A_x Q_x \partial_x \vec{Q} + A_y Q_y \partial_y \vec{Q} + A_z Q_z \partial_z \vec{Q} = \frac{1}{3} \vec{Q} \cdot \vec{Q} = \frac{1}{3}$

$$\therefore \langle \vec{Q} \rangle = \underbrace{\left(\frac{1}{3} \frac{1}{k_B T^2 V} \int_0^\infty \text{Tr} \vec{Q} \cdot \vec{Q} e^{-iLt} \rho_0 dt \right)^{\frac{1}{2}}}_{K \text{ 扩散}} \beta \rho_0$$

§ 8.4 电流密度: ~~物理量~~ ~~物理量~~ (153)

因为在一般近代物理书中都是单独讲一章. 但在普通电学和力学中讲得很少. 而且讲的时候偏重于平行和垂直有相互联系. 所以, 我们把电流密度讲在一起. 因为这与电荷守恒律有关. 由物质的运动引起. ~~物理量~~ ~~物理量~~ 另一类是随机运动引起的. 这是一类很复杂的. 在讲电荷守恒时, 我们说正电荷守恒与负电荷守恒, 通过电荷守恒来讲电荷守恒. 通过电荷守恒来讲电荷守恒:

$$\sqrt{E-E_0}/E \sim \frac{1}{\sqrt{N}}$$

互电荷守恒 ($n = \frac{N}{V}$ fixed when N and $V \rightarrow \infty$). 这种广义的电荷守恒叫电荷守恒. 在互电荷守恒, 可以同时有电荷守恒. 互电荷守恒. $\sim \frac{1}{\sqrt{N}}$. 这些叫电荷守恒. 用以有微扰时广义电荷守恒时, 这些计算很直接, 但一些没有微扰时不能用, 例如嫡和强反向电荷守恒, 不适用. 在这里我们讲电荷守恒及电荷守恒, 及讨论化归电荷守恒的偏微分方程.

§8.4.1 活塞热力学

(Smoluchowski-Einstein 方程)

对于处于平衡态的分子系，玻尔兹曼分布平衡态
概率是 $S = k_B \ln W_{\max}$, 且 $W_{\max} = e^{S/k_B}$

$$\text{偏离平衡: } W = e^{S/k_B}$$

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

满足 $\frac{\partial}{\partial E} \ln W = 0$ 的条件 $\Delta E = 0, \Delta V = 0$.

对已知系统，条件变为 $\Delta E + \Delta E_e = 0, \Delta V + \Delta V_e = 0$.

$e^{\Delta F}$ 表示外部功 ΔF . ($E = V + V_e$ 和 $E = E_e + E_e$ 为 ΔF)

$$\therefore W_T = W_{T,\max} = e^{(\Delta S + \Delta F) / k_B T}$$

$$= W_{\max} e^{(\Delta S + \frac{\Delta E_e + \frac{\partial}{\partial V} \Delta V_e}{T}) / k_B T}$$

$$= W_{\max} e^{(\Delta S - \Delta E - \frac{\partial}{\partial V} \Delta V) / k_B T}$$

$$= W_{\max} e^{-(\Delta F + \frac{\partial}{\partial V} \Delta V) / k_B T}$$

$$\Delta F = \left(\frac{\partial F}{\partial V} \right)_T \Delta V + \frac{1}{2} \left(\frac{\partial^2 F}{\partial V^2} \right)_T (\Delta V)^2 + \dots$$

$$- \frac{\partial}{\partial V}$$

$$- \frac{\partial^2 F}{\partial V^2}$$

由 $N \neq \infty$ 且 $M = \text{const}$, 则 $M = \rho V$ 且 $\Delta M = \Delta \rho V + \rho \Delta V = 0$.

$$\Rightarrow \Delta M = \Delta \rho V + \rho \Delta V = 0 \Rightarrow \frac{\Delta \rho}{\rho} = -\frac{\Delta V}{V}$$

$$\therefore \overline{(\Delta \rho)^2} = \overline{\left(\frac{\Delta V}{V}\right)^2} = -k_B T \left(\frac{\partial V}{\partial P} \right)_T$$

$$\rho = \frac{N \cdot \rho_0}{V}, \text{且 } \rho \propto V, \text{且 } \Delta \rho \propto \Delta N.$$

$$\therefore \overline{(\Delta N)^2} = \overline{(\Delta \rho)^2} = -\frac{k_B T}{V^2} \left(\frac{\partial V}{\partial P} \right)_T$$

一般

$$\Delta \rho = \frac{\Delta N}{V} - \frac{N \Delta V}{V^2}$$

$$(\Delta \rho)^2 = \left(\frac{\Delta N}{V} \right)^2 - 2 \frac{\Delta N \Delta P}{V^3} N + \frac{N^2 (\Delta V)^2}{V^4}$$

$$\overline{(\Delta \rho)^2} = \frac{(\Delta N)^2}{V^2} + \frac{N^2 (\Delta V)^2}{V^4}$$

$$\overline{\left(\frac{\Delta \rho}{\rho} \right)^2} = \frac{(\Delta N)^2}{N^2} + \frac{(\Delta N)^2}{N^2} = 2 \left(\frac{\Delta N}{N} \right)^2$$

对理想气体, $\left(\frac{\partial V}{\partial P} \right)_T = -\frac{1}{P} = -\frac{V^2}{N k_B T}$

$$\Rightarrow \overline{\left(\frac{\Delta \rho}{\rho} \right)^2} = -\frac{k_B T}{V^2} \left(-\frac{V^2}{N k_B T} \right) \propto \frac{1}{N}. \quad \checkmark$$

对理想气体 - 2.

$$W_T \approx W_{\max,T} \exp \left(\frac{1}{2k_B T} \left(\frac{\partial P}{\partial V} \right)_T (\Delta V)^2 \right)$$

这把玻耳兹曼分布看成准静态过程. ① $\frac{\partial}{\partial V}$ 做功和偏移可以忽略

$$\overline{(\Delta A)^2} = \int (\Delta A)^2 W d(\Delta A) / \int W d(\Delta A) \text{ 和 } 1.$$

$$\text{则 } \overline{(\Delta V)^2} = \frac{\int_{-\infty}^{+\infty} (\Delta V)^2 \exp \left[\frac{1}{2k_B T} \left(\frac{\partial P}{\partial V} \right)_T (\Delta V)^2 \right] d(\Delta V)}{\int_{-\infty}^{+\infty} \exp \left[\frac{1}{2k_B T} \left(\frac{\partial P}{\partial V} \right)_T (\Delta V)^2 \right] d(\Delta V)}$$

$$= \frac{\int_{-\infty}^{+\infty} (\Delta V)^2 \frac{k_B T}{(\frac{\partial P}{\partial V})_T} \frac{1}{2V} d \left(\exp \left(\frac{1}{2k_B T} \left(\frac{\partial P}{\partial V} \right)_T (\Delta V)^2 \right) \right)}{\int_{-\infty}^{+\infty} \exp \left(\frac{1}{2k_B T} \left(\frac{\partial P}{\partial V} \right)_T (\Delta V)^2 \right) d(\Delta V)}$$

$$= \Rightarrow \frac{\Delta V (k_B T)}{(\frac{\partial P}{\partial V})_T} \exp \left(\frac{-1}{2k_B T} \left(\frac{\partial P}{\partial V} \right)_T (\Delta V)^2 \right) \Big|_{-\infty}^{+\infty}$$

$$- k_B T \left(\frac{\partial V}{\partial P} \right)_T = - k_B T \left(\frac{\partial V}{\partial P} \right)_T$$

$$\therefore \overline{(\Delta V)^2} = - \frac{k_B T}{V^2} \left(\frac{\partial V}{\partial P} \right)_T$$

以上计算得到的结果是正确的. 因为 $\frac{\partial}{\partial V} \left(\frac{\partial P}{\partial V} \right)_T = \left(\frac{\partial^2 P}{\partial V^2} \right)_T = 0$, 所以 $\Delta F \propto M (\Delta V)^2$.

$$\Delta F = -p \Delta V - \frac{1}{2} \left(\frac{\partial^2 P}{\partial V^2} \right)_T (\Delta V)^2 + \dots$$

$$\therefore W = W_{\max} \exp [-\alpha X^2],$$

$$\alpha = \frac{1}{24k_B T} \left| \left(\frac{\partial^3 P}{\partial V^3} \right)_T \right|, \quad X = \Delta V.$$

$$\overline{(\Delta V)^2} = \frac{\int_0^\infty X^2 e^{-\alpha X^2} dX}{\int_0^\infty e^{-\alpha X^2} dX} = \frac{\Gamma(\frac{3}{2})}{\Gamma(\frac{1}{2})} \frac{1}{\alpha^{\frac{1}{2}}} = 0.338 \left[\frac{1}{24k_B T} \left(\frac{\partial^3 P}{\partial V^3} \right)_T \right]^{-\frac{1}{2}}$$

对实际气体

$$P_C = \frac{a}{27b^2}, \quad V_C = 3b, \quad T_C = \frac{8a}{27bR}.$$

$$\text{理想气体方程: } (P + \frac{a}{V})(V - b) = RT$$

$$\Rightarrow P = \frac{3RT}{3V - V_C} - \frac{9RT_C V_C}{8V^2}$$

$$\therefore V = \frac{N}{N_A} V, \quad (V_C = \frac{N}{N_A} V_C), \quad N_A = 6.02 \times 10^{23}$$

$$P = \frac{3NkT}{3V - V_C} - \frac{9NkT_C V_C}{8V^2}$$

$$\left(\frac{\partial P}{\partial V^3} \right)_T = -\frac{48NkT}{(3V - V_C)^4} + \frac{27NkT_C V_C}{V^5}, \quad \left(\frac{\partial P}{\partial V^2} \right)_{TC} = -\frac{27NkT_C}{8V_C^4}$$

$$\left(\frac{\Delta V}{V}\right)_c = 0.338 \left[-\frac{V^4}{24kT_c} \left(\frac{\partial^3}{\partial V^3} \right)_{T_c} \right]^{-k}$$

$$= 0.901 / \text{km}$$

一般情况 $\frac{\Delta V}{V} \propto$ 高度，然而随高度
变大很多。∴临界层厚度要到至深入分子 phase
的内部才足够。

8.4.1. 色散和吸收
两点应用：

① 由于空气中存在分子振动能级，可以解释为什么
云天是蓝色的。我们考虑空气是干净的
情况，这时，漫射光强度不会引起散射
时，散射的强度

$$\langle I \rangle \propto \frac{1}{x^4} \frac{\Delta V^2}{V^2},$$

没有散射的话，则没有散射光。光的强度
会越强，散射越强。蓝色波长短，∴我们看到
漫射强度散射是蓝色的 \Rightarrow 蓝天。② 来自，互作用
太阳光中 中子辐射时，杂质散射占优，所以
称它为太阳蓝天。

天空颜色是由穿过大气层
的光散射决定的。

(在太空中是黑色的)

④ ④ 天空，但在清晨和傍晚，太阳
光穿过滤较厚的大气层才能发生散射，
但蓝光早被大气吸收，只有很长的
红色穿透过来，∴太阳 \Rightarrow 红色。

⑤ 对液体，立临界层处

$$\langle I \rangle \propto \frac{1}{x^4} V \left[-\frac{V^4}{24kT} \left(\frac{\partial^3}{\partial V^3} \right)_T \right]^{-k}$$

与漫射的比正常情况下大很多倍。

漫射的液体由于光散射变成乳白色。

8.4.2 高斯分布

对任意粒子 x , X , $\Delta x = X - \bar{x}$; 高斯是
单独立子 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 出现偏差的几率

$$W(x) dx \approx e^{\frac{\Delta S(x)}{k_B T}} dx.$$

∴ x 是子场。

$$\Delta S = \Delta S(0) + \frac{\partial S}{\partial x} \Big|_{x=0} x + \frac{1}{2} \frac{\partial^2 S}{\partial x^2} \Big|_{x=0} x^2 + \dots$$

8.4.3 液体空间关联

立临界层，我们看到，粒子和立临界层的浓度差
以很慢的速度，事实上，由于立临界层，关联长度很长，不
同空间的粒子数之间的关联可叫做远场的关联。
我们在经典统计力学中已经看到立临界层
的物理引起 $\langle n(\vec{r}) n(\vec{r}') \rangle$ 与密度平均值的关系。
但经典统计力学理论没有考虑到临界层附近
立线的用经典统计力学理论描述立临界层附近
的关联。具体计算关联函数，现在我们着手于

密度关联函数

$$C(\vec{r}, \vec{r}') = \langle (n(\vec{r}) - \langle n(\vec{r}) \rangle)(n(\vec{r}') - \langle n(\vec{r}') \rangle) \rangle$$

$$= \langle \Delta n(\vec{r}) \Delta n(\vec{r}') \rangle.$$

$$\langle \Delta n(\vec{r}) \rangle = 0.$$

\therefore 只有 $\Delta n(\vec{r})$ 和 $\Delta n(\vec{r}')$ 是独立的，即 $C(\vec{r}, \vec{r}')$

$$= \langle \Delta n(\vec{r}) \rangle \langle \Delta n(\vec{r}') \rangle = 0 \Rightarrow$$
 无关。

$C(\vec{r}, \vec{r}') \neq 0$, 说明它们的密度在立临界层附近有关系。

考虑均勻液体， $\langle \Delta n(\vec{r}) \rangle = \bar{n}$, 与无关。由统计
方法， $C(\vec{r}, \vec{r}') = C(\vec{r}-\vec{r}')$, 呈呈向关联。

$$C(\vec{r}-\vec{r}') = C(|\vec{r}-\vec{r}'|),$$
 且随距离有关。

$\because x > 0$ 时 S 取极大值,

(b)

$$\therefore \frac{\partial S}{\partial x} \Big|_{x=0} = 0, \quad \frac{\partial^2 S}{\partial x^2} \Big|_{x=0} < 0.$$

$$\therefore W(x) dx \approx A e^{-\frac{3x^2}{2k_B T}}, \quad 3 = -\frac{\partial^2 S}{\partial x^2} \Big|_{x=0} > 0.$$

$$\int_{-\infty}^{+\infty} W(x) dx = 1, \Rightarrow A = \sqrt{\frac{3}{2\pi k_B T}}.$$

$$W(x) dx = \sqrt{\frac{3}{2\pi k_B T}} e^{-\frac{3x^2}{2k_B T}} dx$$

即在 x 出现偏差的密度分布，Gauss 分布。

$$\therefore 3 = \sqrt{\frac{3}{2\pi k_B T}} \int_0^{+\infty} x^2 e^{-\frac{3x^2}{2k_B T}} dx = \frac{k_B T}{3}.$$

$$\therefore 3^2 = k_B T / \bar{n}, \quad \therefore$$

$$W(x) dx = \frac{1}{\sqrt{2\pi k_B T}} e^{-\frac{x^2}{2k_B T}} dx.$$

* 正态分布可以推广到多维。

* 正态分布对于小体积中 $n \gg \bar{n}$.

-般情况下，用泊松分布。

且 $\Delta n(\vec{r}) = 0$,

$$\begin{aligned} C(\vec{r}) &= \langle \Delta n(\vec{r}) \Delta n(0) \rangle \\ \text{设 } \Delta n(\vec{r}) &= \frac{1}{V} \sum_i \tilde{n}_i e^{i\vec{q} \cdot \vec{r}} \\ \Delta n^*(\vec{r}) &= \Delta n(\vec{r}) \Rightarrow \tilde{n}_i^* = \tilde{n}_{-i} e^{-i\vec{q} \cdot (\vec{r}-\vec{r}')} \\ |\tilde{n}_i|^2 &= \int d\vec{r} d\vec{r}' \langle \Delta n(\vec{r}) \Delta n(\vec{r}') \rangle e^{-i\vec{q} \cdot (\vec{r}-\vec{r}')} \\ \langle |\tilde{n}_i|^2 \rangle &= \int d\vec{r} d\vec{r}' \langle \Delta n(\vec{r}) \Delta n(\vec{r}') \rangle e^{-i\vec{q} \cdot (\vec{r}-\vec{r}')} \\ &= V \int d\vec{R} \langle \Delta n(\vec{R}) \Delta n(0) \rangle e^{-i\vec{q} \cdot \vec{R}} = V C(\vec{q}) \\ \therefore C(\vec{r}) &= \frac{1}{V} \sum_i \langle |\tilde{n}_i|^2 \rangle e^{i\vec{q} \cdot \vec{r}} \end{aligned}$$

$$\begin{aligned} \text{由 } \frac{\partial f}{\partial T} = -\frac{\partial F}{\partial T}, \quad F = -kT \ln Z & \Rightarrow F = -kT \ln \left(\sum_i e^{-\beta E_i} \right) \\ \text{由 } W = W_{\max} e^{-\frac{(F + \mu N)}{kT}} & \stackrel{V \rightarrow \infty}{=} W_{\max} e^{-\frac{\Delta F}{kT}} \\ \Delta F &= \int (f - \bar{f}) d\vec{r} \end{aligned}$$

$f(\vec{r})$ 是单位体积 local Free energy. 若 $T \rightarrow \infty$, Δf 可得 Δn 为 δ 函数:

$$\Delta f = \frac{a}{2} (\Delta n)^2 - \frac{b}{2} (\nabla n)^2. \quad \left(\int_{n=0}^{\infty} (n - \bar{n})^2 e^{-\frac{n-\bar{n}}{kT}} \right)$$

(~~由 Δf 表明~~, 分子密度分布函数是 Δn .)

Δn 与 Δf 在空间依赖. 而 ∇f 为 0.

这叫 Landau-Ginzburg 理论.

$$\begin{aligned} \langle |\tilde{n}_i|^2 \rangle &= \int \frac{d\vec{q}}{V} |\tilde{n}_i|^2 W / \int \frac{d\vec{q}}{V} W. \quad (16) \\ &\stackrel{\text{Gauss}}{=} \int_{-\infty}^{+\infty} d\tilde{n}_i |\tilde{n}_i|^2 W / \int_{-\infty}^{+\infty} d\tilde{n}_i W \quad (\text{Gauss}) \\ &= \frac{\sqrt{kT}}{a+b\tilde{q}^2}. \\ \therefore C(\vec{r}) &= \frac{kT}{V} \sum_i \frac{1}{a+b\tilde{q}^2} e^{i\vec{q} \cdot \vec{r}} \\ &= \Rightarrow kT \frac{1}{(2\pi)^3} \int d\vec{q} \frac{1}{a+b\tilde{q}^2} e^{i\vec{q} \cdot \vec{r}} \\ &= \frac{kT}{(2\pi)^3} \int_0^{2\pi} dq \frac{1}{a+b\tilde{q}^2} \int_0^\pi d\theta e^{iqr \cos\theta} \\ &= \frac{kT}{4\pi b} \frac{1}{r} e^{-r/\zeta}, \quad \zeta = \sqrt{\frac{a}{b}}. \sim (T-T_c)^{1/2}. \end{aligned}$$

这叫 mean field 说法. 其他方法.

至 ~~此~~ 计算结果与前讲的冲高型模型
相符合, $D(\vec{q})$ 在对数中是常数, Δn
在 ~~此~~ 是常数, 这叫 $\langle |\tilde{n}_i|^2 \rangle$ 模型.

由热力学, $a = \frac{1}{h} \left(\frac{\partial F}{\partial n} \right)_T$ (见书 57 页)

而到 n 有 $\frac{\partial n}{\partial q} = 0 \Rightarrow a = a_0(T-T_c)$.

$$\begin{aligned} \nabla n(\vec{r}) &= \nabla \Delta n(\vec{r}) = \sum_i \tilde{n}_i^* e^{i\vec{q} \cdot \vec{r}} \\ &= \frac{1}{V} \sum_i \tilde{n}_i^* \tilde{n}_i e^{i\vec{q} \cdot \vec{r}} = \frac{1}{V} \sum_i \tilde{n}_i^* (-\vec{q}) e^{-i\vec{q} \cdot \vec{r}} \\ \langle \nabla n(\vec{r}) \rangle &= \frac{1}{V} \sum_i \tilde{n}_i^* \tilde{n}_i \vec{q} e^{-i\vec{q} \cdot \vec{r}} \end{aligned}$$

$$\therefore \Delta f = \frac{1}{V} \sum_i \tilde{n}_i^* \tilde{n}_i \left(\frac{a}{2} + \frac{b}{2} \vec{q} \cdot \vec{q} \right) e^{-i\vec{q} \cdot \vec{r}}$$

$$\begin{aligned} \Delta F &= \int d\vec{q} \Delta f = \frac{1}{2V} \left| \sum_i \tilde{n}_i^* \tilde{n}_i \left(\frac{a}{2} + \frac{b}{2} \vec{q} \cdot \vec{q} \right) \delta_{\vec{q}\vec{q}} \right|^2 \\ &= \frac{1}{2V} \sum_i (a+b\tilde{q}^2) |\tilde{n}_i|^2. \end{aligned}$$

$$\begin{aligned} \therefore W &= W_{\max} \exp \left(-\frac{1}{2kT} \sum_i (a+b\tilde{q}^2) |\tilde{n}_i|^2 \right) \\ &= W_{\max} \exp \left(-\frac{a+b\tilde{q}^2}{2kT} |\tilde{n}_i|^2 \right). \end{aligned}$$

(~~由~~ 式 ~~表~~ 明, 宏观性质是 ~~由~~ Δn 决定的. 不同
温度 ~~在~~ \tilde{q} 之间是独立. 是 Gauss 分布. (小 ~~于~~ \tilde{q})).

3.8.1.1 布朗运动: 随机运动和布朗运动

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, 微观大师做随机的布朗运动. 爱因
斯坦在他的青年正确地解释了布朗运动. 对分子
相互性, 或说分子间作用力有重要作用. 现在,
“布朗运动”代表 ~~广义~~ “微粒”在广义的随机
“场”~~下~~ 下随布朗运动. 是一美丽的物理学史.

3.8.1.2 布朗方程

用布朗方程可以对布朗运动 τ 作非常直接的
理解: ~~由~~ 布朗方程 布朗时间 $\sim 10^{-5} - 10^{-4}$ cm
~~由~~ 大于 ~~由~~ 两种力作用

① 线性阻力 $\propto v$, 刹车, 阻力, 摩擦, 流体-粘滞力,
等.

② 用用 $\propto v^2$ 碰撞、耗散系数, 例如 10^{-4} cm/m²s,
液体 \propto 密度 $\propto 10^{-2}$ cm⁻³, 固体碰撞次数 $\propto 10^{22-4}$ /cm²
气体 \propto 密度 $\propto 10^{15}$ cm⁻³, “ ” “ ” “ ” “ ” “ ”
∴ 布朗 $\sim 10^{-18}$ sec 为碰撞打靶时间. 可以这种
力为随机 $\propto 10^{-18}$ 力.

∴ 布朗运动满足牛顿第二定律

$$m \frac{d\vec{u}}{dt} = \vec{F}_1 + \vec{F}_2(t). \quad (\text{由牛顿第二定律})$$

例如，考虑在水平方向 (x) 上投影，运动和速度只有粘滞力 $-\alpha u_x = -\alpha u$, $F_2(t) = X(t)$.

$$m \frac{du}{dt} = -\alpha u + X(t)$$

这是二阶方程.

$$m \frac{dx}{dt} = -\alpha x + X(t),$$

$$\frac{d^2x}{dt^2} - m \left(\frac{dX}{dt} \right) = -\frac{\alpha}{2} \frac{dX^2}{dt^2} + X \ddot{X}$$

对大数布朗运动求解可得

$$\frac{m}{2} \frac{d^2}{dt^2} \langle x^2 \rangle - m \langle \ddot{x} \rangle = -\frac{\alpha}{2} \frac{d \langle X^2 \rangle}{dt^2} + \langle X \ddot{X} \rangle = 0.$$

由能的泛定, $m \bar{v}^2 = kT$.

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

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

若至 $t=0$, $\langle x \rangle = 0$ 且 $\frac{d}{dt} \langle x \rangle = 0$. 则

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

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

$$\begin{aligned} x & \cdot x' \\ x-x' & \end{aligned} \quad \text{且} \quad \int_{-\infty}^{+\infty} dx f(x, \tau) = 1$$

$$f(x, \tau) = f(-x, \tau).$$

又很慢, 则

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

$$\text{若} \quad \int_{-\infty}^{+\infty} f(z, \tau) dz = 1, \quad n(x, t+\tau) = n(x, t) - 3 \frac{\partial n}{\partial x} + \frac{1}{2} \frac{\partial^2 n}{\partial x^2} + \dots$$

设 $\frac{\partial}{\partial t} n(x, t)$ 在 t 处很快, 则

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

$$\int_{-\infty}^{+\infty} f(z, \tau) \left(n(x, t) - \frac{3}{2} \frac{\partial n}{\partial x} + \frac{1}{2} \frac{\partial^2 n}{\partial x^2} \right) dz$$

$$= n(x, t) + \frac{1}{2} \langle z^2 \rangle \frac{\partial n}{\partial x}$$

$$\frac{\partial n}{\partial t} = D \frac{\partial^2 n}{\partial x^2}, \quad D = \frac{\langle z^2 \rangle}{2\tau} \quad \text{扩散系数.}$$

∴ 布朗运动是一个扩散过程.

$$\text{若 } t \ll \tau, \text{ 则 } \langle x \rangle = \int \frac{2kTz}{m} dz$$

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

这就是说, 在观察时间 $t \ll \tau$ 时, 布朗运动满足牛顿第二定律.

而 $t \gg \tau$,

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

爱因斯坦通过计算 $\langle x^2 \rangle \propto t$ 为分子扩散附着. (可以估算, 对水中大分子 $\sim 10^{-5} \text{ cm m}^{-2}$, $\tau \sim 10^{-7} \text{ s}$, 这些速率比记录一个粒子位置所需要的时间要小得多.)

8.8.2 布朗运动的扩散

布朗运动用微粒扩散解释地讲可以更好地推广到其他类似的过程, 而且可以推广到扩散过程.

设 $n(x, t) dx$ 是在时刻 t 在 x 和 $x+dx$ 之间单位垂直面上的 Brownian 粒子数, 则 $n(x, t)$ 是随时间变化的, 从 t 时刻到 $t+\tau$ 时刻被移进 $(x, x+dx)$ 内的几率. 称为扩散率.

上面方程也可写成

$$\frac{\partial}{\partial t} n(x, t+\tau) = -D \frac{\partial^2}{\partial x^2} (x, t+\tau) = 0$$

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

$$\therefore \frac{\partial}{\partial t} f(x-x', t) - D \frac{\partial^2}{\partial x'^2} f(x-x', t) = 0$$

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

设 $f(z, 0) = 0$, 则 $\lim_{z \rightarrow \infty} f(z, t) = 0$

由 $\int_{-\infty}^{+\infty} f(z, t) dz = 1$, 则 $f(z, 0) = 0$, if $z \neq 0$,

$$\therefore f(z, t) = g(z, t).$$

$$\therefore f(z, t) = \frac{1}{2\sqrt{\pi Dt}} e^{-z^2/4Dt}.$$

$\Rightarrow \langle z^2 \rangle = 2Dt$. 这是爱因斯坦在结果.

以后将证明, 这方程是随机过程 Master 方程对 Brown 运动的解.

朗之万方程 \Leftrightarrow Master 方程, 从力学来看, 一个量子力学系统, 一次可观测的运动过程, 一个是 Schrödinger 方程, 对于经典或宏观系统~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~~

(1)

§8.8.3 布朗运动中时间函数.

在讲线性布朗运动时，我们看到是能函数可以
空间和时间一起做。在 Brownian 运动中，随和 $\bar{F}(t)$
被设成 ~~时间无关~~。但布郎运动 $\bar{F}(t)$ 和 $\bar{f}(t)$ 是什么
关系有什么关系呢？为此，我们考虑 $\langle U(t) \rangle$ 。

用方程中取 $U(t) = f(t) e^{-\tau t}$

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

$$\Rightarrow \frac{d g(t)}{dt} = e^{\tau t} (X(t)/m) = A(t)$$

$$\begin{aligned} \cancel{U(t)} &= \cancel{g(t)} e^{-\tau t} = e^{-\tau t} \int_0^t e^{\tau t'} A(t') dt' \\ \cancel{U(t)} &= e^{-\tau t} \int_0^t dt' \int_0^{t'} e^{\tau t''} A(t') A(t'') \end{aligned}$$

$$U(t) = U(0) e^{-\tau t} + e^{-\tau t} \int_0^t e^{\tau t'} A(t') dt'$$

$$\begin{aligned} \tilde{U}(t) &= U(0) e^{-2\tau t} + 2U(0) e^{-\tau t} \int_0^t e^{\tau t'} A(t') dt' \\ &\quad + e^{-\tau t} \int_0^t dt' dt'' e^{(\tau t'+\tau t'')} A(t') A(t''). \end{aligned}$$

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

$$t \rightarrow \infty, \langle U^2(\infty) \rangle = kT/m,$$

$$\Rightarrow C = \frac{\sqrt{kT}}{mc}$$

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

§8.8.4 电流-电压定理.

我们前面已经做过对电场力 F 与电势 V 的讨论。电场力随位置是空间函数。因此，我们可以有时间依赖与电势 V 的关系，对 Brownian motion, $F = (\frac{d}{dt})V \Rightarrow F = \frac{m}{\tau} V = \frac{m^2}{2kT} C$.

$$= \frac{m^2}{2kT} \int_{-\infty}^{+\infty} dt C \delta(t)$$

$$= \frac{m^2}{2kT} \int_{-\infty}^{+\infty} dt \langle A(t) A(t) \rangle$$

$$= \frac{m^2}{2kT} \int_{-\infty}^{+\infty} ds \langle A(s) A(s) \rangle$$

即随位置 s 与随和 $\bar{F}(t)$ 随着 t 的变化
而随位置 s 与随和 $\bar{F}(t)$ 随着 t 的变化

$$\langle U^2(t) \rangle = U(0)^2 e^{-2\tau t}$$

$$+ e^{-2\tau t} \int_0^t dt' dt'' e^{(\tau t'+\tau t'')} \langle A(t') A(t'') \rangle$$

① $\cancel{t} = t_1 + t_2, s = \frac{t_1 - t_2}{\pi^2}$, 以 t 为轴 t_1, t_2
~~平行~~ 平移 t 轴。

$$e^{(\tau t'+\tau t'')} \langle A(t') A(t'') \rangle = e^{\tau t''} C(s)$$

$$dt' dt'' = ds$$

∴ 为 S

$$\begin{aligned} I &= \int dt' dt'' \dots \\ &= \int_0^{\pi^2} dt' \int_{-\pi^2}^{\pi^2} C(s) ds \\ &\quad + \int_{\pi^2}^{\pi^2} dt' \int_{-\pi^2}^{\pi^2} C(s) ds \end{aligned}$$

对 Brownian 运动, $C(s)$ 不是常数

瞬时, (Markov 性质), $C(s) = C \delta(s)$.

$$\therefore I = \int_0^{\pi^2} dt' e^{\tau t'} = C \frac{\pi^2}{2} (e^{2\tau t} - 1)$$

运动运动的扩散系数 (见书)

$$D = kT/\tau = \frac{1}{2} \int_{-\infty}^{+\infty} du \langle U(t) U(t+s) \rangle$$

运动线性布朗运动中 D 由层-层运动
决定的速率, 同时这里 $U(t)$ 是时间函数。

在 Kubo 线性布朗运动中, 扩散系数可以
是时间和空间的函数。

~~§8.8.5 Markov 性质~~

§8.8.5 布朗运动遵循的过程:

电路中的电压和电流的关系。



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

若外电压为 0, 即电池关闭,

在一定条件下, 仍存在正弦交流电源和电压
电流, $\langle I(t) \rangle = \langle V(t) \rangle = 0$.

这时电流声可以用波动方程表示
有布朗运动形式

$$I(t) \leftrightarrow U(t)$$

$$L \leftrightarrow m$$

$$R \leftrightarrow \omega$$

$$V(t) \leftrightarrow X(t).$$

作练习, 请参考复教材 (11.6.6)-(11.6.17).

在电路中, 请将即时间 Fourier 变换需要
此过程是 Brownian 运动中方便很多. 由 $V(t)$
in Fourier 变换.

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

(电场强度的频谱)
 $\langle V(t) V(t+s) \rangle = \frac{1}{4\pi^2} \int dw dw' \langle \tilde{V}(w) \tilde{V}(w') \rangle e^{iwt+iw'(t+s)}$

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

$$\frac{1}{4\pi^2} \int dw dw' \langle \tilde{V}(w) \tilde{V}(w') \rangle e^{iwt+iw'(t+s)} = C \delta(s)$$

$$= C \frac{1}{2\pi} \int dw' e^{iws}$$

(1) $\propto T$, = 逆噪声

(2) $\propto R$, 噪声与无逆噪声. (3) $\langle \bar{V}^2 \rangle \neq 0$, 即
 $\langle \bar{V} \rangle \neq 0$, (4) $S(v) \propto v$ 无关, 即 $S(v)$ 为常数
white noise. (类似于白光, 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 定律

§8.8. shot noise (散粒噪声)

另一种逆噪声称为 shot noise. 由灯丝发射电子
到达阳极而引起噪声. (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.

$\Delta n(t)$ 为单位时间内发射的电子数. 此时
刻发射一个电子引起电流为
 $i(t-\tau)$. $i(t-\tau)$ 在 $t-\tau$ 大时很快衰减到 0. 且积分

只有 $i(t-\tau)$ 才能引起电流. 电子发射引起电流是

$$I(t) = \int_0^{+\infty} d\tau n(\tau) i(t-\tau).$$

$$\begin{aligned} \text{④ } \langle \tilde{V}(w) \tilde{V}(w') \rangle &= \langle |\tilde{V}(w)|^2 \delta(w+w') \rangle \\ &= \frac{1}{4\pi^2} \int dw dw' \langle |\tilde{V}(w)|^2 \rangle \delta(w+w') e^{iws} \\ &= \frac{1}{4\pi^2} \int dw \langle |\tilde{V}(w)|^2 \rangle e^{iws} \\ \Rightarrow \langle |\tilde{V}(w)|^2 \rangle &= C. \quad \delta w \approx 0. \end{aligned}$$

$$\text{即 } K(s) = \langle V(t) V(t+s) \rangle$$

$$= \int_{-\infty}^{+\infty} dw \tilde{K}(w) e^{iws}$$

$$\Rightarrow \tilde{K}(w) = \frac{C}{2\pi} = \frac{2kTR}{2\pi} = \frac{kTR}{\pi}.$$

$$\therefore \bar{V}^2 = \overline{V^2} = K(0) = \int_{-\infty}^{+\infty} \tilde{K}(w) dw$$

$$= 2 \int_0^{\infty} \tilde{K}(0) dw = \int_0^{\infty} 4\pi \tilde{K}(0) dw$$

$$(w=2\pi v) \Rightarrow \int_0^{\infty} dv S(v)$$

$$\therefore S(v) = 4kTR \quad \text{是电场强度的方差}$$

(1) $\langle n \rangle$ 为平均值, 则

$$\begin{aligned} \langle I(t) \rangle &= \int_0^{+\infty} \langle n \rangle i(t-\tau) d\tau \\ &= \bar{n} \int_0^{+\infty} i(t-\tau) d\tau = \bar{n} \cdot e \end{aligned}$$

($i(t-\tau) = \frac{dG(t-\tau)}{dt}$ 为 $t-\tau$ 时的瞬时电流, $\therefore i(t-\tau) \propto t$,
其中至 $t-\tau$ 附近, \therefore 离子流由一个电子组成)

$$\Delta I = I(t) - \langle I \rangle = \int_0^{+\infty} [n(\tau) - \bar{n}] i(t-\tau) d\tau$$

$$\langle (\Delta I)^2 \rangle = \int d\tau d\tau' \langle \Delta n(\tau) \Delta n(\tau') \rangle$$

对 ΔI 对 $\Delta n(\tau)$ 和 $\Delta n(\tau')$ 都是随机的

$$\therefore \langle \Delta n(\tau) \Delta n(\tau') \rangle \propto \delta(\tau-\tau')$$

(严格地, $\langle \Delta n(\tau) \Delta n(\tau') \rangle = \langle n \rangle \delta(\tau-\tau')$, $\langle n \rangle$
物理意义从 n 为大数时近似为常数
 $n \gg 1$, $\therefore \langle n^2 \rangle = \bar{n}$)

$$\langle (\Delta I)^2 \rangle = \bar{n} \int_0^{+\infty} |G(t-\tau)|^2 d\tau = \bar{n} \int_0^{+\infty} |G(t)|^2 dt$$

Campbell 定律

请教导:

$$G(t) = \int S(\omega) e^{i\omega t} d\omega$$

$$\int_{-\infty}^{+\infty} |G(t)|^2 dt = 4\pi \int_{-\infty}^{+\infty} |S(\omega)|^2 d\omega$$

$$\therefore \langle \langle I \rangle \rangle = 4\pi \bar{n} \int_0^{+\infty} |S(\omega)|^2 d\omega.$$

2. 2-3 (注意 m 仪因, 例因放大器, $S(\omega)$ 只在 (注意 m 放大器为 0), \therefore

$$\langle \langle I \rangle \rangle = 4\pi \bar{n} |S(\omega)|^2 d\omega.$$

另一方面, $S(\omega) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} G(t) e^{-i\omega t} dt$

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

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

$$\therefore \langle \langle I \rangle \rangle = 4\pi \bar{n} e^2 \Delta \nu \quad (\Delta \nu = 2\pi \Delta \omega). \\ = 2eI \Delta \nu \quad \langle \bar{I} \rangle = \bar{n} e.$$

由 $\langle I \rangle$, $\langle \langle I \rangle \rangle$ 和 $\Delta \nu$ 在实验中是确定的, 所以用 I 表示 \bar{n} . 在随机粒子数 n 中, shot noise 中发射带电粒子是 quasi-particle, n 及 e 都应由 n 及 e 代替.

可以叫 n 带电荷.

(ii) 作子推定时, $P_n(x_i, t_i; t_n)$ 与时间无关

$$\text{无理}, P_n(x_i, t_i; t_n) = P_n(x_i, t_i).$$

$$(iv) P_1(x_i, t_i) P_{11}(x_i, t_i | x_n, t_n) = P_2(x_i, t_i; x_n, t_n).$$

$$(v) \int P_{11}(x_i, t_i | x_n, t_n) dx_n = 1.$$

注: $\int P_2(x_i, t_i)$

$$\begin{aligned} & \int \int P_1(x_i, t_i) P_{11}(x_i, t_i | x_n, t_n) dx_n dx_i \\ &= \int \int P_2(x_i, t_i; x_n, t_n) dx_i = \int P_2(x_n, t_n) dx_n = 1 \\ &= \int P_1(x_i, t_i) dx_i \end{aligned}$$

$$\therefore \int P_1(x_i, t_i) \left[\int dx_n P_{11}(x_i, t_i | x_n, t_n) \right] dx_i$$

由 $\int P_1(x_i, t_i)$

$$\begin{aligned} & P_3(x_i, t_i; x_n, t_n; x_3, t_3) \\ &= P_2(x_i, t_i; x_n, t_n) P_{21}(x_i, t_i | x_n, t_n | x_3, t_3) \\ &= P_1(x_i, t_i) P_{11}(x_i, t_i | x_n, t_n) P_{11}(x_n, t_n | x_3, t_3) \end{aligned}$$

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, 它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位置有关, 而更早的过去位置都沒有影响. 例如, 电子运动中的速度 $u(t)$, 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 的概率. $P_{ij}(x_i, t_i; x_j, t_j)$ 表示在 t_i 时刻取值 x_i , 在 t_j 取 x_j 的概率. $\dots, P_n(x_i, t_i, \dots, x_n, t_n)$. 条件概率 $P_{ij}(x_i, t_i | x_n, t_n)$ 表示在 t_i 时刻取值为 x_i 的条件下, 在 t_j 时刻取值为 x_j 的概率. $P_{ijk}(x_i, t_i; x_j, t_j; x_k, t_k)$ 表示在 t_i, t_j, t_k 时刻取值 x_i, x_j, x_k 的概率. 在 t_{k+1} ($1 \leq k \leq l$) 时刻取值 x_{k+1} 的概率.

$$(i) \int P_i(x_i, t_i) = 1.$$

$$(ii) \int \underbrace{P_n(x_1, t_1; \dots; x_n, t_n)}_{\propto} dx_n = P_{n-1}(x_1, t_1; \dots; x_{n-1}, t_{n-1})$$

找话用对分子语言来理解 - 1:

$$P_i(x_i, t_i) = |\psi_i(x_i, t_i)|^2$$

(见前面
m 161(2))

$$P_2(x_i, t_i; x_n, t_n) = |\psi_2(x_i, t_i; x_n, t_n)|^2 \dots$$

条件概率: $P_{ij}(x_i, t_i | x_n, t_n)$ 可以理解为 $\psi_i(x_i, t_i)$ 与 $\psi_j(x_n, t_n)$ 的乘积

$$\rightarrow = |\psi_i(x_i, t_i)| \cdot |\psi_j(x_n, t_n)| = |\psi_i(x_i, t_i)|$$

初态 $\psi_i(x_i, t_i)$ 是 $\psi_i(x_i, t_i)$

$$P_{ij}(x_i, t_i; x_n, t_n) = |\psi_i(x_i, t_i) \psi_j(x_n, t_n)|^2 \propto |\psi_i(x_i, t_i)|^2$$

$$\int (x_i, t_i; x_n, t_n) \propto |\psi_i(x_i, t_i)|^2$$

即 $|\psi_i(x_i, t_i)|^2 \sim$ 恒定 $\psi_i(x_i, t_i)$ 线性.

这样, 我们把很容易理解的推论 (i) - (v).

~~由 $\int P_1(x_i, t_i)$~~

$$P_3(x_i, t_i; x_n, t_n; x_3, t_3)$$

$$= P_2(x_i, t_i; x_n, t_n) P_{21}(x_i, t_i | x_n, t_n | x_3, t_3)$$

$$= P_1(x_i, t_i) P_{11}(x_i, t_i | x_n, t_n) P_{11}(x_n, t_n | x_3, t_3).$$

$$\int_{t_n < t_3} dx_n P_{11}(x_i, t_i | x_n, t_n) P_{11}(x_n, t_n | x_3, t_3)$$

$$P_2(x_i, t_i; x_3, t_3) = \int dx_n P_{11}(x_i, t_i | x_n, t_n) P_{11}(x_n, t_n | x_3, t_3)$$

以 $P_{k|x}(x_1, t_1, \dots, x_k | t_k | x_{k+1}, \dots)$ 表明
在 t_{k+1}, \dots, t_n 时刻 x_{k+1}, \dots, x_n 已知时， x_1, \dots, t_k 时刻 x_1, \dots, t_k 的条件概率。

② 马尔可夫过程：

$$P_{n-1|1}(x_1, t_1, \dots, x_{n-1} | t_{n-1} / x_n | t_n) \\ = P_{Y_1}(x_{n-1} | t_{n-1} / x_n | t_n), \text{ 若 } t_n \text{ 时刻 } x_n \text{ 已知} \\ t_{n-1} \text{ 时刻 } x_{n-1}. \text{ 即 } -\text{Markov 过程} \Leftrightarrow P_i(x_i, t)$$

$$P_3(x_1, t_1; x_2, t_2; x_3, t_3) \\ = P_2(x_1, t_1; x_2, t_2) P_{Y_1}(x_3, t_3 | x_2, t_2) \\ = P_1(x_1, t_1) P_{Y_1}(x_2, t_2) P_{Y_1}(x_3, t_3). \quad (\because \text{在 Markov} \\ \text{过程中, 只看第 3 步})$$

$$P_2(x_1, t_1; x_3, t_3) = \frac{P_1(x_1, t_1)}{P_1(x_1, t_1)} \int dx_2 P_{Y_1}(x_1, t_1; x_2, t_2) P_{Y_1}(x_2, t_2; x_3, t_3)$$

$$\int P_2(x_1, t_1; x_3, t_3) = \int dx_2 P_{Y_1}(x_1, t_1; x_2, t_2) P_{Y_1}(x_2, t_2; x_3, t_3)$$

Markov (Markovian Smoluchowski-Chapman-Kolmogorov 方程).

$x_1 \rightarrow$ 第一状态取值 δ 概率。 $[1 - \tau \int W(x_1, x) dx]$ 表示
不发生跳跃的概率。
 $\therefore [1 - \tau \int W(x_1, x) dx] \delta(x_1, x_2)$ 表示从 x_1 到 x_2
概率。该概率 $\delta(x_1, x_2)$ 在 τ 时间内
 $[1 - \tau \int W(x_1, x) dx] \delta(x_1, x_2)$ 表示不发生从 x_1 到
 x_2 的概率， $\delta \tau W(x_1, x_2)$ 表示，若 $x_1 = x_2$
和 $x_1 \neq x_2$ 的概率之和。

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

$$\text{代入 } \frac{\partial P(x_1, t)}{\partial t} = \frac{1}{\tau} \left[\int P(x_1, t) \delta(x_1, x_2) dx_2 \right. \\ \left. - \int P(x_1, t) \delta(x_1, x_2) dx_1 \right]$$

$$= \int P(x_1, t) W(x_1, x_2) dx_2 - \int P(x_2, t) W(x_2, x_1) dx_1 \\ = \int [W(x_1, x_2) P(x_1, t) - P(x_2, t) W(x_2, x_1)] dx.$$

Master eq.

定理 23 Markov chain, 我们有 $P_j(x_i, t_i) P(x_i, t_i)$

(iii) m 步。即, Markov

$$\frac{\partial P(x, t)}{\partial t} = \lim_{\tau \rightarrow 0} \frac{P(x, t+\tau) - P(x, t)}{\tau}$$

由 $P(x, t) \Delta t = t+\tau, t_i=t$, 由得 (iv),

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

~~$$\frac{\partial P(x, t)}{\partial t} = \int P(x, t) \frac{\partial}{\partial t} P(x | t) dx$$~~

$$\frac{\partial P(x, t)}{\partial t} = \lim_{\tau \rightarrow 0} \frac{P(x, t+\tau) - P(x, t)}{\tau}$$

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

$$\text{若 } \tau=0, P(x_2, t) = \int P(x, t) P(x | x_2, t) dx$$

$$\Rightarrow P(x | x_2, t) = \delta(x - x_2).$$

即 $W(x_1, x_2)$ 为 $t \rightarrow t+\tau$ time interval, x_1 取值 x_1
至 x_2 在 τ 时间中单位时间 m 跳跃概率。

$\therefore \lim_{\tau \rightarrow 0} \int W(x_1, x) dx$ 是 τ 的 τ 间隔由 τ

主方程的一般表示从其他法推导

x_1 在概率密度； x_2 在概率密度从 x_1 跳跃到 x_2 在
 m 是概率密度。在概率中，被用到的跳跃运动
学机制，涉及到分子的运动速度是普遍的。

下面举一个例子：对 $-$ 式子 F (F. Schwab).
stat. Mech.

$$\text{密度矩阵: } P(t) = \sum_i W_i(t) |i\rangle \langle i|.$$

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

$F |i\rangle = F_i |i\rangle$ 是守恒的。V 是微扰哈密顿。

$U(t)$ 是时间的演化算符

$$P(t+\tau) = \sum_i W_i(t) U(t) |i\rangle \langle i| U^\dagger(t) \quad (\sum_j |j\rangle \langle j| = 1) \\ = \sum_i \sum_j W_j(t) \delta(j) \langle j | U(t) |i\rangle \times \delta(i | U^\dagger(t) | k) \\ = \sum_i \sum_k W_k(t) |j\rangle \langle k| U_j(t) U_k^\dagger(t)$$

$$\therefore U_j(t) = \langle j | U(t) | i \rangle$$

取随机相近点，即忽略非对角项贡献，

$$P(t+\tau) \approx \sum_i \sum_j W_j(t) \delta(j) \langle j | U_j(t) U_j^\dagger(t)$$

$$\equiv \sum_j W_j(t+\tau) |U_{j,i}(t)|^2$$

$$\text{即 } W_j(t+\tau) = \sum_i W_i(t) |U_{j,i}(t)|^2$$

$$\therefore W_j(t+\tau) - W_j(t) = \sum_i (W_i(t) - W_j(t)) |U_{j,i}(t)|^2$$

$(\because \sum_i |U_{j,i}(t)|^2 = 1)$ ($i=j$, $|U_{i,i}(t)|^2$ 为常数.)

$|U_{j,i}|^2$, 用微扰论, (Fermi Golden rule.)

$$|U_{j,i}|^2 = \frac{1}{\hbar} \left(\frac{\sin \omega_{ij} \tau}{\omega_{ij}/\hbar} \right)^2 |\langle j | V | i \rangle|^2$$

$$\approx \frac{2\pi}{\hbar} \delta(E_i - E_j) |\langle j | V | i \rangle|^2$$

$$W_{ij} = E_i - E_j / \hbar. \quad (\cancel{E_i - E_j / \hbar} \rightarrow \frac{1}{\hbar})$$

$$(\simeq (E_i - E_j) \tau \ll 1, \tau \gg 1/\Delta E \text{ 微扰论})$$

$$\frac{W_j(t+\tau) - W_j(t)}{\tau} \Big|_{\tau \gg 0} = \frac{dW_j(t)}{dt}$$

$$\sum_i (W_i(t) - W_j(t)) \frac{2\pi}{\hbar} \delta(E_i - E_j) |\langle j | V | i \rangle|^2.$$

得:

$$\frac{\partial P(x,t)}{\partial t} = \int_{-\infty}^{+\infty} W(x, z) P(x, t) dz$$

$$- \int z \frac{\partial}{\partial x} [W(x, z) P(x, t)] dz + \frac{1}{2} \int z^2 \frac{\partial^2}{\partial x^2} [W(x, z) P(x, t)] dz$$

$$- \int_{-\infty}^{+\infty} W(x, -z) P(x, t) dz$$

$$- \int_{+\infty}^{-\infty} W(x, z') P(x, t) dz' = \int_{-\infty}^{+\infty} W(x, z') P(x, t) dz'$$

$$\therefore \frac{\partial P(x,t)}{\partial t} + \frac{\partial}{\partial x} [\alpha_1(x) P(x,t)] = \frac{1}{2} \frac{\partial^2}{\partial x^2} (\alpha_2(x) P(x,t))$$

$$(\alpha_n(x) = \int z^n W(x, z) dz. — n \text{ 阶矩.})$$

Fokker-Planck eq.

即 $\alpha_1(x) = 0, \alpha_2(x) = \text{const.}$ 的 F-P 方程

相等 ~~于~~ Brownian motion in \mathbb{R}^n 的方程.

这里 \sum_i 表示对 E_i 和 f_i 求和.

$$\sum_{E_i} \rightarrow \int dE_i \otimes n(E_i). \quad n(E_i) = D(E)$$

$$\text{由 } \frac{dW_{E_i, F_i}(t)}{dt} = \sum_{F_i} (W_{F_j, F_i} - W_{E_j, F_i})$$

$$\left(\frac{2\pi}{\hbar} n(E_i) |\langle E_j, F_i | V | E_j, F_i \rangle|^2 \right)$$

$$P_{E_j, F_i, F_j} = P_{E_j}(F_j, F_i).$$

§8.1.2 Fokker-Planck eq.

易于看出 x 可以选择取值, $W(x', x)$ 是随 $|x' - x|$ 增加而减小的函数. 取 $z = x - x'$ 是小量, $W(x', x) = W(x-z, x')$

$$= W(\frac{x+x'}{2}, x-x') \approx W(x, -z).$$

$$\text{于是 } \frac{\partial P(x,t)}{\partial t} = \int [W(x', x) P(x', t) - W(x, x') P(x, t)] dz$$

$$= \int [W(x-z, z) P(x-z, t) - W(x, -z) P(x, t)] dz$$

$$\begin{aligned} \text{展开 } W(x-z, z) P(x-z, t) &= W(x, z) P(x, t) - z \frac{\partial}{\partial x} [W(x, z) P(x, t)] \\ &+ \frac{1}{2} z^2 \frac{\partial^2}{\partial x^2} [W(x, z) P(x, t)] + \dots \end{aligned}$$