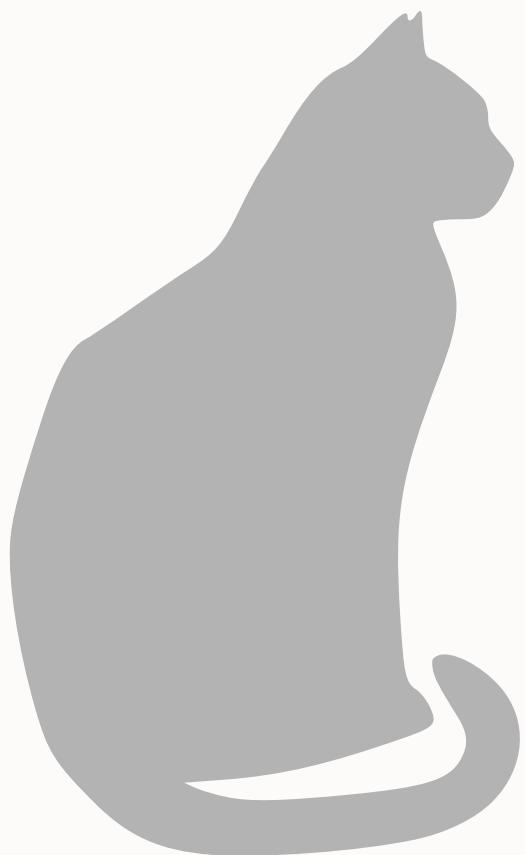


Advanced Statistics Mechanics



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Contents

1 Review: Basic Concepts of Thermodynamics	1
1.1 Definitions	1
1.2 均匀系（单相系）的平衡	2
1.3 单元系的相变热力学	3
1.4 热力学第三定律	4
1.5 Linear Nonequilibrium Thermodynamics	4
2 Concepts of Statistical Physics, Nearly Independent Particle Systems	5
2.1 微观状态的描写	5
2.2 等几率原理	5
2.3 近独立粒子系统的统计物理	5
3 Microregular Ensemble	7
3.1 经典统计系综	7
3.2 系综所满足的方程: Liouville 定理	7
3.3 量子统计系综	8
3.4 微正则系综	9
4 From Microcanonical Ensembles to Canonical Ensembles	10
4.1 能量涨落, 热力学极限, 经典极限	11
4.2 State equation of non-ideal gas	12
5 Grand Canonical Ensemble	14
6 Quantum Statistics	16
6.1 Bose and Fermi Statistics of free particles under GRSC	16
6.2 The Symmetry of Quantum Statistic & Wave Function	17
6.3 Anyon (任意子), Braid Group (辫子群)	18
6.3.1 Non-Abelian Statistics	19
6.4 1D Statistics: Interaction Corresponding	20
7 Phase Transition, Critical Phenomenon & Renormalized Group	22
7.1 Categories of Phase transitions	22
7.2 Landau 2 order phase transition theory	22
7.2.1 Gingbang-Landau	23
7.3 Critical Phenomenon and Critical Index	24

7.4	Quantum Phase Transition	26
7.5	Ising Model	27
7.5.1	Average field approximation	27
7.5.2	The exact solution of 1D Ising model	28
7.5.3	2D Ising Model	29
7.5.4	1D + 1D dimensional quantum Ising model	32
7.6	Renormalization Group	33
7.6.1	Real space RG	33
7.6.2	Examples: 1D Ising model	34
7.7	Numerical Renormalized Group & DMRG	37
7.7.1	Momentum space renormalization	37
7.7.2	Wilson's N.R.G.	37
7.7.3	Eigenstates of the $\psi_i = 1, m, L$ -site system	37
7.8	K-T Phase Transition	40
8	Non-equilibrium Statistic Physics	42
8.1	Boltzmann integral ODE	42
8.1.1	Derivation of the drift term	43
8.1.2	Derivation of the collision term	43
8.2	H-theomre, H-function and entropy	44
8.3	Application of Boltzmann Equation	45
8.4	Fluctuation Phenomenon: Themoral Variables	47
8.4.1	Regrex System	47
8.4.2	Quasi-Themoral Theory (Smoluchowski-Einstein Method)	48
8.4.3	Vande vars Gas	49
8.5	Fluctuation Phenomenon (Random External Forces, Brown Motions)	50
8.5.1	Langevin equation	50
8.5.2	The Diffusion of Brown particles	51
8.5.3	Time correlation in Brown motion	51
8.5.4	Fluctuation-Usage Theorem	52
8.5.5	The themoral conductance noice and the fluctuations in voltage	53
8.5.6	Shot noise	53
Lecture Homework #1 [2025-09-02]		i
Problem Set		i
Lecture #2 Homework #2 [2025-09-09]		viii
Lecture #3 Homework #3 [2025-09-16]		xii
Lecture #4 Homework #4 [2025-09-23]		xxii
Lecturer Yue Yu's Mmanuscript		i

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

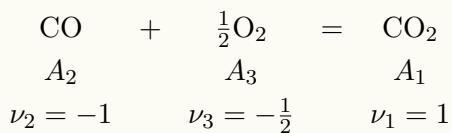
$$\int dT - V dq + \sum_i N_i d\mu_i = 0$$

$k+1$ 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.

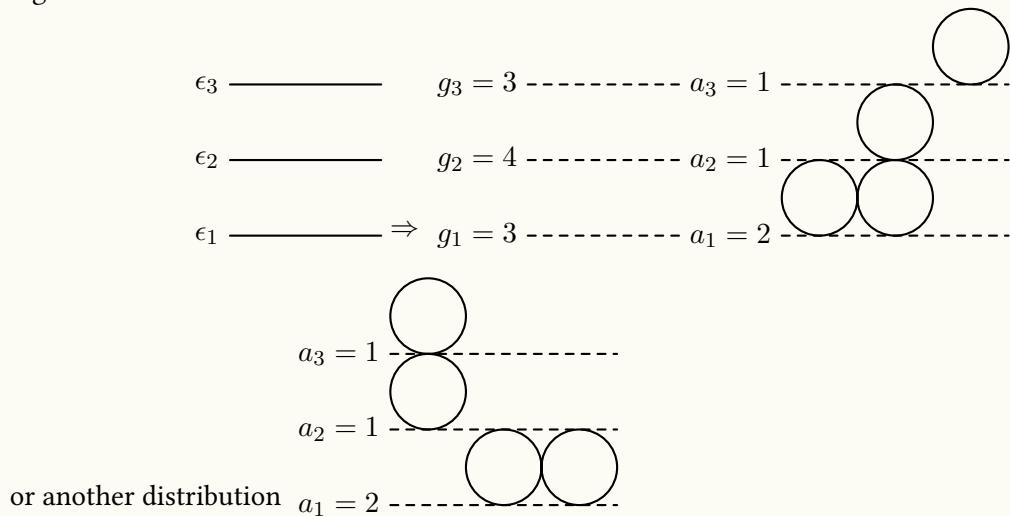
2.3 近独立粒子系统的统计物理

- 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

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

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

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

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

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

4.1 能量涨落, 热力学极限, 经典极限

Definition 4.1.1 (涨落). For energy:

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

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

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

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

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

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

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

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

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

4.2 State equation of non-ideal gas

Model:

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

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

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

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

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

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

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

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

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

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

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

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

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

The pressure

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

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

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

Substitute B_2 into p

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

Then we arrive at the 范德瓦耳斯 equation

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

CHAPTER 5 Grand Canonical Ensemble

(T, μ, V) 不变.

- 与正则系综类似，热库同时也是粒子源.

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

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

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

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

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

while μ is fermion's energy.

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

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

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

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

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

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

- 经典和粒子数涨落 $\sim \frac{1}{\sqrt{N}}$.

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

Example 5.0.1 (固体表面的吸附率).

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

(T, μ, ν) 单个分子被吸附后的能量降低 ϵ_0 .

$$E_N = -\epsilon_0 N$$

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

其中 n 表示分子占据 N 个确定吸附中心中的 N 个时的某一特定状态

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

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

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

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

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

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

即 p 升高, θ 升高; T 升高; θ 下降.

CHAPTER 6 Quantum Statistics

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

6.1 Bose and Fermi Statistics of free particles under GRSC

The Giant Regular System Comprehensive is

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

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

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

For free particles

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

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

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

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

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

For Fermion, a state can only contain one particle

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

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

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

Substitute W respectively

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

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

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

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

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

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

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

6.2 The Symmetry of Quantum Statistic & Wave Function

For example, a wave function contains N -particle

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

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

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

then

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

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

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

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

For Boson,

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

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

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

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

6.3 Anyon (任意子), Braid Group (辫子群)

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

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

where D means integral by all the paths.

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

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

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

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

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

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

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

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

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

Non-abelian group.

The expression of Braid group:

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

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

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

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

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

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

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

For normal α ,

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

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

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

then

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

Now, define

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

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

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

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

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

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

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

6.3.1 Non-Abelian Statistics

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

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

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

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

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

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

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

6.4 1D Statistics: Interaction Corresponding

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

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

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

$$(6.13)$$

when $0 \leq s \leq 1$,

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

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

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

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

i $S = 0$

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

ii $S = 1$

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

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

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

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

$$E = \sum_n K_i^2$$

while the continuous limitation

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

that is

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

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

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

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

Example 6.4.2 (Calogero-Sutherland model).

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

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

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

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

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

Now, the partition function becomes

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

CHAPTER 7 Phase Transition, Critical Phenomenon & Renormalized Group

7.1 Categories of Phase transitions

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

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

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

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

7.2 Landau 2 order phase transition theory

描述相变：序参量，对称性破缺

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

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

[!Figure] 顺磁 [!Figure] 铁磁 → 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.

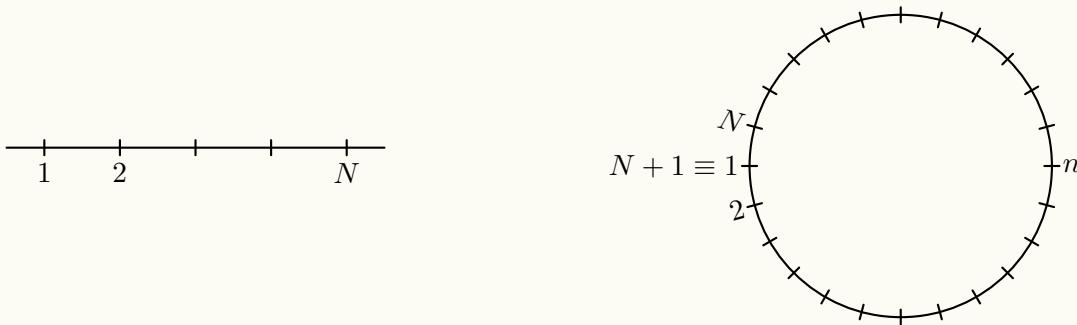
- If $B \neq 0$, then ...

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

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

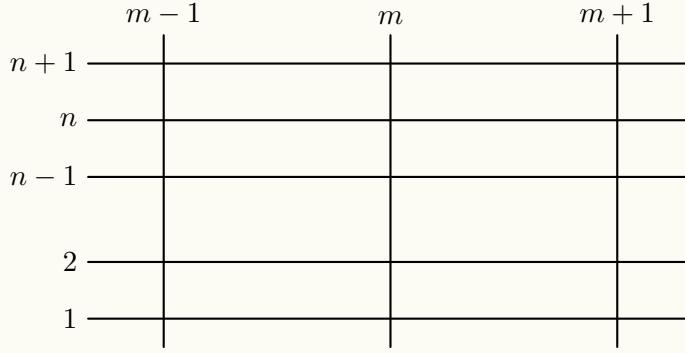
And A can be expressed as

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

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

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

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

7.6.2 Examples: 1D Ising model

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

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

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

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

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

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

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

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

If we require Z is still Ising model, then

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

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

(a) $\sigma'_j = \sigma'_{j+1} = 1$

$$\exp(K'_0 + K' + B') = \exp(2K_0 + B) 2 \operatorname{ch}(2K + B)$$

(b) $\sigma'_j = \sigma'_{j+1} = -1$

$$\exp(K'_0 + K' - B') = \exp(2K_0 - B) 2 \operatorname{ch}(-2K + B)$$

(c) $\sigma'_j = \sigma'_{j+1} = \pm 1$

$$\exp(K'_0 - K') = \exp(2K_0) 2 \operatorname{ch} B$$

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

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

Starting at

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

where $K_0 = 0$.

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

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

which is so-called RG equations.

At the fixed points

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

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

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

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

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

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

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

For the vector \mathbf{K}

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

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

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

Now, the fixed point

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

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

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

Around K^* ,

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

Since δK and $\delta k'$ are small,

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

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

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

In a series of transformations, we have

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

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

7.7 Numerical Renormalized Group & DMRG

7.7.1 Momentum space renormalization

For point-particle

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

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

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

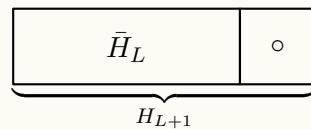
For the condensed matter, since $a = \text{finite}$, there is a “natural” cut-off, so we do not care about UV, but the infrared divergence ($p \sim \frac{1}{L}$), i.e., we consider the infrared fixed point $\xi \rightarrow \infty$.

7.7.2 Wilson’s N.R.G.

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

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

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



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

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

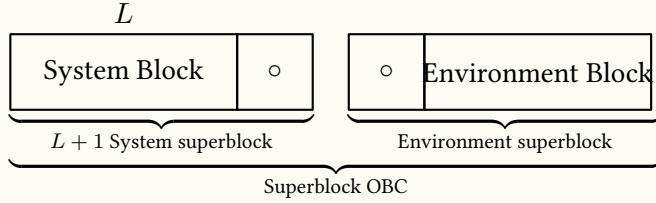
¹Normalization in QFT (actually, we consider QED).

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

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

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

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



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

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

then project to the reduced density matrix of the sysbm Sb

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

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

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

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

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

the so-called antiferromagnetic model.

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



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

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

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

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

then, the Hamiltonian

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

The eigenvector

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

and the density matrix element

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

from the basis

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

the density matrix is

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

Diagonalize ρ

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

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

$S = 4 \times 5$ matrix.

(b) $L = 2$.

7.8 K-T Phase Transition

The spin on a 2D plane

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

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



The partition function

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

Therefore

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

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

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

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

At the continuous limit

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

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

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

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

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

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

The Hamiltonian

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

where

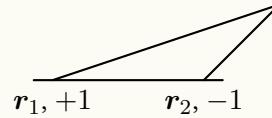
$$\nabla\theta \cdot \nabla\theta = \frac{x^2 + y^2}{r^4} = \frac{1}{r^2}$$

Then, the integral

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

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

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



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

The 2D Column gas

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

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

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

then, the free energy of a vortex is

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

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

CHAPTER 8 Non-equilibrium Statistic Physics

8.1 Boltzmann integral ODE

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

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

which only depends on r and E .

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

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

- (a) Classical: $\lambda_T \ll |\delta r|$, $\lambda_T = \frac{h}{(2\pi mk_B T)^{1/2}}$ 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

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

- (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.

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

- (c) Three-body hitting can be omitted

Taking another simplification

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

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

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

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

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

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

8.1.1 Derivation of the drift term

Since

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

then,

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

So, the drift term

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

8.1.2 Derivation of the collision term

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

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

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

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

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

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

Then, we have

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

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

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

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

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

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

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

Multiply the number of molecules m

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

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

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

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

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

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

Then,

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

8.2 H-theorem, H-function and entropy

The Entropy

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

The H -function

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

The gas at the equilibrium state

$$n = N/V$$

The Maxwell distribution

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

Then, the H -function becomes

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

where the integral

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

The entropy of single-atom ideal gas

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

Use the Boltzmann equation to derive the H -theorem

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

The time derivative to H

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

The first term

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

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

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

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

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

Combine and then half

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

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

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

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

8.3 Application of Boltzmann Equation

The relaxation time approximation

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

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

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

Then, we have

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

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

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

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

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

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

The Boltzmann equation

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

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

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

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

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

Hence,

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

where

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

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

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

where

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

and we have

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

Now, handel $d^3 p$

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

Substitute it into J_e

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

where

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

Finally,

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

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

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

We can use it to calculate the conductivity,

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

The force

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

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

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

The derivative

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

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

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

So, we have the elements of the conductivity matrix

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

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

8.4 Fluctuation Phenomenon: Themoral Variables

8.4.1 Regrex System

The fluctuation of energy

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

are all the fluctuations corresponding the microscope variable.

8.4.2 Quasi-Themoral Theory (Smoluchowski-Einstein Method)

The theromal entropy

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

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

The differ from equilibirum

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

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

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

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

The free energy

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

Then,

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

The probability of the quasi-themoral in regrex system

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

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

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

Then, we have

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

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

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

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

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

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).

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

8.5 Fluctuation Phenomenon (Random External Forces, Brown Motions)

8.5.1 Langevin equation

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

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

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

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

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

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

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

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

Then, the solution

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

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

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

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

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

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

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

8.5.2 The Diffusion of Brown particles

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

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

where

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

For small τ

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

For small ξ

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

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

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

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

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

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

So, the kernel

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

8.5.3 Time correlation in Brown motion

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

where

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

Then, we obtain the ODE

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

the solution

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

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

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

The correlation function determines the expectation value

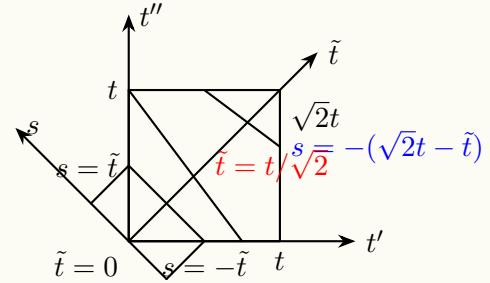
$$\langle u^2(t) \rangle = u^2(0) e^{-t/\tau} + e^{-2t/\tau} \int_0^t dt' dt'' e^{(t'+t'')/\tau} \langle A(t') A(t'') \rangle \quad (8.25)$$

Take the rotation

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

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

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



Brownian motion $C(s)$ Markov process

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

Then,

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

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

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

8.5.4 Fluctuation-Usage Theorem

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

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

We can also prove the distribution coefficient

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

8.5.5 The themoral conductance noise and the fluctuations in voltage

In RL circuit, the KVL equation

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

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

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

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

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

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

Taking the Fourier transformation

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

and

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

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

Assume

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

The fluctuation of voltage

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

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

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

8.5.6 Shot noise

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

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

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

and the average

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

The fluctuation

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

and the square

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

For shot noise,

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

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

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

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

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

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

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

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

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

Solution.

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

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

Solution.

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

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

Solution.

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

Problem 1.4. 解释热力学第一、二、三定理的物理意义.

Solution.

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

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

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

Solution.

- (a) 对 f 取微分

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

令 $dh = 0$ 得

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

- (b) $f = f(x, y(x, g))$. 由复合函数求导法则

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

这里利用了 (a) 中的结论.

- (c) $f = f(x, y)$. 令 f 的微分为 0 得

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

- (d) $f = f(g, h)$. 对 (c) 中结论做变量替换

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

利用 (a) 中的结论得

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

- (e) $f = f(x, y(x, g))$. 由复合函数求导法则

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

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

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

Solution.

- (a) 在温度变化 dT 和压强变化 dp 范围内, 铜块体积变化

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

要维持铜块体积不变, 则 $dV = 0$, 即

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

- (b) 对体积变化公式分离变量并积分得

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

令 $V = V_0 + \Delta V$, 则

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

即铜块体积改变 $4.07 \times 10^{-2}\%$.

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

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

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

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

等温杨氏模量为

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

其中 A 使弹性丝的横截面积. 证明:

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

Solution.

- (a) 将 \mathcal{F} 带入 Y 即可

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

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

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

得

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

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

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

Solution.

(a) 由热力学基本微分方程

$$dU = T dS - p dV$$

得 Maxwell 关系

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

即

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

(b) 将热力学基本微分方程两侧对 V 取偏微分

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

已知

$$dH = T dS + V dp$$

得 Maxwell 关系

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

所以有

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

(c) 将热力学基本微分方程写为

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

由此得 Maxwell 关系

$$\left(\frac{\partial(1/T)}{\partial V}\right)_U = \left(\frac{\partial(p/T)}{\partial U}\right)_V$$

展开得

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

(d) 同 (iii), 使用

$$dS = \frac{1}{T} dH - \frac{V}{T} dp$$

得 Maxwell 关系

$$\left(\frac{\partial(1/T)}{\partial p}\right)_H = -\left(\frac{\partial(V/T)}{\partial H}\right)_p$$

展开得

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

(e) 由复合函数求导法则

$$\left(\frac{\partial T}{\partial S}\right)_H = \frac{\partial^2(T, H)}{\partial(S \partial p)} \cdot \frac{\partial^2(S, p)}{\partial(S \partial H)} = \frac{T}{C_p} + \left(\frac{\partial T}{\partial p}\right)_s \left(\frac{\partial p}{\partial S}\right)_H$$

令 $dH = 0$, 得

$$0 = T dS + V dp, \quad \left(\frac{\partial p}{\partial S}\right) = -\frac{T}{V}$$

使用 Maxwell 关系

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

将以上两式带入求导结果

$$\left(\frac{\partial T}{\partial S}\right)_H = \frac{T}{C_p} - \frac{T^2}{V} (pdV VH)_p$$

Problem 1.9 (林宗涵《热力学与统计物理》2.3). 对 $p - V - T$ 系统, 证明

$$\frac{\kappa_T}{\kappa_S} = \frac{C_p}{C_V}$$

其中

$$\kappa_T \equiv -\frac{1}{V} \left(\frac{\partial V}{\partial p}\right)_T, \quad \kappa_S \equiv -\frac{1}{V} \left(\frac{\partial V}{\partial p}\right)_S$$

分别代表等温与绝热压缩系数.

Solution. *Proof.*

$$\frac{C_p}{C_v} = \frac{T \left(\frac{\partial S}{\partial T}\right)_p}{T \left(\frac{\partial S}{\partial T}\right)_V} = \frac{\left(\frac{\partial S}{\partial V}\right)_p \left(\frac{\partial V}{\partial T}\right)_p}{\left(\frac{\partial S}{\partial V}\right)_V \left(\frac{\partial V}{\partial T}\right)_V} = \left[-\frac{1}{V} \left(\frac{\partial V}{\partial p}\right)_T \right] / \left[-\frac{1}{V} \left(\frac{\partial V}{\partial p}\right)_S \right] = \frac{\kappa_T}{\kappa_S} \square$$

Problem 1.10 (林宗涵《热力学与统计物理》2.5).

(a) 证明

$$\left(\frac{\partial C_V}{\partial V}\right)_T = T \left(\frac{\partial^2 p}{\partial T^2}\right)_V; \quad \left(\frac{\partial C_p}{\partial p}\right)_T = -T \left(\frac{\partial^2 V}{\partial T^2}\right)_p$$

并由此导出

$$C_V = C_{V_0} + T \int_{V_0}^V \left(\frac{\partial^2 p}{\partial T^2}\right)_V dV, \quad C_p = C_{p_0} - T \int_{p_0}^p \left(\frac{\partial^2 V}{\partial T^2}\right)_p dp.$$

其中 C_{V_0} 与 C_{p_0} 分别代表体积为 V_0 时的定容热容与压强为 p_0 时的定压热容, 它们都只是温度的函数.

(b) 根据以上 C_V, C_p 两式证明, 理想气体的 C_V 与 C_p 只是温度的函数.

(c) 证明范德瓦耳斯气体的 C_V 只是温度的函数, 与体积无关.

Solution.

(a) 将 C_V 对 V 取偏导数

$$\left(\frac{\partial C_V}{\partial V}\right)_T = T \frac{\partial^2 S}{\partial T \partial V} = T \left(\frac{\partial^2 p}{\partial T^2}\right)_V$$

则 $C_V(T, V)$ 的积分分为等容过程和等压过程

$$C_V(T, V) - C_V(T_0, V_0) = \int_{T_0}^T \left(\frac{\partial C_V}{\partial T}\right)_V dT + \int_{V_0}^V \left(\frac{\partial C_V}{\partial V}\right)_T dV$$

使用 Maxwell 关系, 积分可写作

$$C_V(T, V) = C_{V_0}(T) + T \int_{V_0}^V \left(\frac{\partial^2 p}{\partial T^2}\right)_V dV.$$

同理可证

$$\left(\frac{\partial C_p}{\partial p}\right)_T = -T \left(\frac{\partial^2 V}{\partial T^2}\right)_p, \quad C_p = C_{p_0} - T \int_{p_0}^p \left(\frac{\partial^2 V}{\partial T^2}\right)_p dp.$$

(b) 由理想气体状态方程

$$pV = NRT$$

可得

$$\left(\frac{\partial^2 p}{\partial T^2}\right)_V = 0, \quad \left(\frac{\partial^2 V}{\partial T^2}\right)_p = 0.$$

带入 (a) 中结论得

$$\left(\frac{\partial C_V}{\partial V}\right)_T = 0, \quad \left(\frac{\partial C_p}{\partial p}\right)_T = 0$$

即理想气体的 C_V 与 C_p 都只是温度的函数.

(c) 由范德瓦耳斯气体的物态方程

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

当 V 固定时, 有

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

表明范德瓦耳斯气体的 C_V 只是温度的函数, 与体积无关.

Problem 1.11 (林宗涵《热力学与统计物理》3.1). 利用无穷小的变动, 导出下列各平衡判据 (假设总粒子数不变, 且 $S > 0$)

- | | |
|-------------------------------------|-------------------------------------|
| (a) 在 U 及 V 不变的情形下, 平衡态的 S 极大 | (e) 在 S 及 p 不变的情形下, 平衡态的 H 极小 |
| (b) 在 S 及 V 不变的情形下, 平衡态的 S 极小 | (f) 在 T 及 V 不变的情形下, 平衡态的 F 极小 |
| (c) 在 S 及 U 不变的情形下, 平衡态的 V 极小 | (g) 在 F 及 T 不变的情形下, 平衡态的 V 极小 |
| (d) 在 H 及 p 不变的情形下, 平衡态的 S 极大 | (h) 在 T 及 p 不变的情形下, 平衡态的 G 极小 |

Solution.

(a) 系统孤立，内能和体积固定. 由熵增原理，一切自发过程朝熵增方向进行，平衡时熵取最大值.

(b) 熵和体积固定时，由

$$dU = T dS - p dV$$

得可逆过程 $dU = 0$. 实际不可逆过程在总熵不变时内能会减少，平衡时内能最小.

(c) 熵与内能固定，由

$$dU = T dS - p dV$$

得 $p dV = 0$. 考虑力学稳定性，系统会自发收缩或抵抗膨胀，平衡时体积最小.

(d) 焓 $H = U + pV$ ，压强不变时 $dH = T dS$. 固定 H, p 则 $dS = 0$ ，熵判据要求平衡时熵最大.

(e) 熵与压强固定，由

$$dH = T dS + V dp$$

得 $dH = 0$. 系统自发趋向焓更低的状态，平衡时焓最小.

(f) 亥姆霍兹自由能 $F = U - TS$ ，固定 T, V 时

$$dF = -S dT - p dV = 0$$

自发过程 $dF < 0$ ，平衡时 F 最小.

(g) 固定 F, T ，由

$$dF = -S dT - p dV$$

得 $p dV = 0$. 体积稳定性要求平衡时体积最小.

(h) 吉布斯自由能

$$G = U - TS + pV$$

固定 T, p 时 $dG = 0$ (可逆). 自发过程 $dG < 0$ ，平衡时 G 最小.

Lecture #2 Homework #2 [2025-09-09]

Problem 2.1. 对独立粒子体系，用排列组合公式对可区分粒子、玻色子和费米子在给定粒子数分布 $\{a_\alpha\}$ 下的量子状态数 $W(\{a_\alpha\})$.

Solution.

(a) 可区分粒子

由于粒子可区分，能级 ε_α 有 g_α 个简并量子态。将 N 个粒子分成若干组 $\{a_\alpha\}$ ，分配方式数为

$$\frac{N!}{\prod_\alpha a_\alpha!}$$

对能级 α ，每个粒子可占据 g_α 个态中的任意一个，因此有 $g_\alpha^{a_\alpha}$ 种占据方式。总方式数为

$$W = \frac{N!}{\prod_\alpha a_\alpha!} \times \prod_\alpha g_\alpha^{a_\alpha} = N! \prod_\alpha \frac{g_\alpha^{a_\alpha}}{a_\alpha!}$$

(b) 玻色子

粒子全同，每个量子态占据粒子数不限。对能级 α ：将 a_α 个全同粒子放入 g_α 个态，等价于 a_α 个粒子与 $g_\alpha - 1$ 个棒隔开不同态的排列数：

$$\frac{(a_\alpha + g_\alpha - 1)!}{a_\alpha! (g_\alpha - 1)!}$$

各能级独立，所以：

$$W = \prod_\alpha \frac{(a_\alpha + g_\alpha - 1)!}{a_\alpha! (g_\alpha - 1)!}$$

(c) 费米子

粒子全同，受泡利原理限制：每个量子态最多一个粒子，且 $a_\alpha \leq g_\alpha$ 。对能级 α ：从 g_α 个态中选择 a_α 个被占据的方式数为组合数：

$$\frac{g_\alpha!}{a_\alpha! (g_\alpha - a_\alpha)!}$$

各能级独立，所以：

$$W = \prod_\alpha \frac{g_\alpha!}{a_\alpha! (g_\alpha - a_\alpha)!}$$

Problem 2.2. 用最可几分布求出上题相应的配分函数。

Solution.

(a) 可区分粒子 (MB 统计) 由 $\ln W = \ln N! + \sum_\alpha [a_\alpha \ln g_\alpha - \ln a_\alpha!]$ 及约束变分得

$$a_\alpha = g_\alpha e^{-\alpha - \beta E_\alpha}$$

代入 $\sum a_\alpha = N$ 得 $e^{-\alpha} = N/Z_1$ ，于是

$$a_\alpha = N \frac{g_\alpha e^{-\beta E_\alpha}}{Z_1}, \quad Z_N = Z_1^N$$

(或 $Z_N = Z_1^N/N!$ 以修正吉布斯佯谬)

(b) 玻色子 (BE 统计) 由 $\ln W = \sum_{\alpha} [\ln(a_{\alpha} + g_{\alpha} - 1)! - \ln a_{\alpha}! - \ln(g_{\alpha} - 1)!]$ 变分得

$$a_{\alpha} = \frac{g_{\alpha}}{e^{\alpha+\beta E_{\alpha}} - 1}$$

令 $\alpha = -\beta\mu$, 则

$$a_{\alpha} = \frac{g_{\alpha}}{e^{\beta(E_{\alpha}-\mu)} - 1}, \quad \Xi = \prod_{\alpha} \left(1 - e^{-\beta(E_{\alpha}-\mu)}\right)^{-g_{\alpha}}$$

(c) 费米子 (FD 统计) 由 $\ln W = \sum_{\alpha} [\ln g_{\alpha}! - \ln a_{\alpha}! - \ln(g_{\alpha} - a_{\alpha})!]$ 变分得

$$a_{\alpha} = \frac{g_{\alpha}}{e^{\alpha+\beta E_{\alpha}} + 1}$$

令 $\alpha = -\beta\mu$, 则

$$a_{\alpha} = \frac{g_{\alpha}}{e^{\beta(E_{\alpha}-\mu)} + 1}, \quad \Xi = \prod_{\alpha} \left(1 + e^{-\beta(E_{\alpha}-\mu)}\right)^{g_{\alpha}}$$

Problem 2.3. 一个二能级系统, $\epsilon_1 = -\epsilon$, $\epsilon_2 = \epsilon$, 且 $g_1 = g_2 = 1$. 设有 N 个独立可区分粒子处于平衡态, 求

(a) 温度 $T \rightarrow 0$ 时系统的熵.

(b) 若“粒子”是自旋 \uparrow, \downarrow 两个态, 则 $T \rightarrow 0$ 的熵值在此时的物理意义是什么?

Solution.

(a) 单粒子配分函数 $Z_1 = e^{\beta\epsilon} + e^{-\beta\epsilon} = 2 \operatorname{ch}(\beta\epsilon)$, 系统配分函数 $Z_N = Z_1^N$. 熵

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

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

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

所以 $S(T \rightarrow 0) = 0$.

(b) 若为自旋系统, $T \rightarrow 0$ 时所有自旋处于低能态 (完全极化), 系统处于唯一基态, 微观状态数 $W = 1$, 熵为零, 符合热力学第三定律.

Problem 2.4. 论证光子气体不发生玻色 - 爱因斯坦凝聚.

Solution. 光子气体化学势 $\mu = 0$ 且 $\epsilon_{\min} = 0$, 故 μ 始终等于最低能级, 不存在随温度降低而趋近于零的过程. 同时光子数不守恒, 总粒子数由平衡条件调节, 无 BEC 所需的粒子数重新分布相变机制. 因此光子气体不发生玻色-爱因斯坦凝聚.

Problem 2.5 (林宗涵《热力学与统计物理》7.5). 计算爱因斯坦固体模型的熵.

Solution. 爱因斯坦固体模型可看作近独立子系, 每一个子系的 Maxwell-Boltzmann 分布函数为

$$Z = \sum_{n=0}^{\infty} e^{-\beta\epsilon_n} = \sum_{n=0}^{\infty} e^{-\beta(n+1/2)\hbar\omega} = \frac{e^{-\beta\hbar\omega/2}}{1 - e^{-\beta\hbar\omega}}$$

设原子总数为 N , 则总振动自由度为 $3N$. 系统的熵为

$$S = 3Nk \left(\ln Z - \beta \frac{\partial}{\partial \beta} \ln Z \right) = 3Nk \left[\frac{\hbar\omega/kT}{e^{\hbar\omega/kT} - 1} - \ln(1 - e^{\hbar\omega/kT}) \right]$$

Problem 2.6 (林宗涵《热力学与统计物理》7.7). 自旋为 $\hbar/2$ 的粒子处于磁场 \mathcal{H} 中, 粒子的磁矩为 μ , 磁矩与磁场方向平行或反平行所相应的能量分别为 $-\mu\mathcal{H}$ 与 $\mu\mathcal{H}$. 今设有 N 个这样的定域粒子处于磁场 \mathcal{H} 中, 整个系统处于温度为 T 的平衡态, 粒子之间的相互作用很弱, 可以忽略.

- (a) 求子系统的配分函数 Z .
- (b) 求系统的自由能 F , 熵 S , 内能 \bar{E} 和热容 $C_{\mathcal{H}}$.
- (c) 证明总磁矩的平均值为 $\bar{\mathcal{M}} = N\mu \operatorname{th}\left(\frac{\mu\mathcal{H}}{kT}\right)$.
- (d) 证明在高温弱场下, 亦即 $\frac{\mu\mathcal{H}}{kT} \ll 1$ 时: $\bar{\mathcal{M}} = \frac{N\mu^2}{kT}\mathcal{H}$; 磁化率 $\chi = \frac{\partial(\bar{\mathcal{M}}/V)}{\partial\mathcal{H}} = \frac{N\mu^2}{kT}$; 在低温强场下, 亦即 $\frac{\mu\mathcal{H}}{kT} \gg 1$ 时: $\bar{\mathcal{M}} = N\mu$; $\chi = 0$.

Solution.

- (a) 代入配分函数的定义得

$$Z = e^{\beta\mu\mathcal{H}} + e^{-\beta\mu\mathcal{H}} = 2 \operatorname{ch}(\beta\mu\mathcal{H})$$

- (b) i. 自由能 $F = -NkT \ln Z = -NkT \ln(2 \operatorname{ch}(\beta\mu\mathcal{H}))$.
ii. 熵 $S = Nk \left(\ln Z - \beta \frac{\partial \ln Z}{\partial \beta} \right) = Nk [\ln(2 \operatorname{ch}(\beta\mu\mathcal{H})) - \beta\mu\mathcal{H} \operatorname{th}(\beta\mu\mathcal{H})]$.
iii. 内能 $\bar{E} = -N \frac{\partial \ln Z}{\partial \beta} = -N\mu\mathcal{H} \operatorname{th}(\beta\mu\mathcal{H})$.
iv. 热容 $C_{\mathcal{H}} = \left(\frac{\partial \bar{E}}{\partial T} \right)_{\mathcal{H}} = Nk \left(\frac{\mu\mathcal{H}}{kT} \right)^2 \left\{ 1 - \operatorname{th}^2 \left(\frac{\mu\mathcal{H}}{kT} \right) \right\}$.

- (c) 设原子总数为 N . 则处于平行与反平行的概率分别为

$$P_1 = \frac{N}{Z} e^{\beta\mu\mathcal{H}}, \quad P_2 = \frac{N}{Z} e^{-\beta\mu\mathcal{H}}.$$

则磁矩的期望值为

$$\bar{\mathcal{M}} = \langle \mu \rangle = P_1\mu + P_2(-\mu) = N\mu \operatorname{th}\left(\frac{\mu\mathcal{H}}{kT}\right).$$

- (d) 由于以下极限

$$\lim_{x \rightarrow 0} \operatorname{th} x = x, \quad \lim_{x \rightarrow \infty} \operatorname{th} x = 1, \quad \lim_{x \rightarrow 0} \operatorname{ch} x = 1, \quad \lim_{x \rightarrow \infty} \operatorname{ch} x = \infty,$$

所以在高温弱场、低温强场下

$$\lim_{T \rightarrow \infty} \bar{\mathcal{M}} = \frac{N\mu^2}{kT}\mathcal{H}, \quad \text{and} \quad \lim_{T \rightarrow 0} \bar{\mathcal{M}} = N\mu,$$

磁导率的一般表达式

$$\chi = \frac{\partial(\bar{\mathcal{M}}/V)}{\partial\mathcal{H}} = \frac{N\mu^2}{kT} \frac{1}{\operatorname{ch}^2(\mu\mathcal{H}/kT)}$$

则在在高温弱场、低温强场下

$$\lim_{T \rightarrow \infty} \chi = \frac{N\mu^2}{kT}, \quad \text{and} \quad \lim_{T \rightarrow 0} \chi = 0$$

Problem 2.7 (林宗涵《热力学与统计物理》7.15). 粒子的态密度 $D(\epsilon)$ 定义为: $D(\epsilon) d\epsilon$ 代表粒子的能量处于 ϵ 与 $\epsilon + d\epsilon$ 之间的量子态数 (见原书 §7.15). 这里指考虑粒子的平动自由度所对应的态密度.

(a) 设粒子的能谱（即能量与动量的关系）是非相对论性的，试分别对下列三种空间维数，求相应的态密度 $D(\epsilon)$:

i. 粒子局限在体积为 V 的三维空间内运动

$$\epsilon = \frac{1}{2m}(p_x^2 + p_y^2 + p_z^2);$$

ii. 粒子局限在面积为 A 的二维平面内运动

$$\epsilon = \frac{1}{2m}(p_x^2 + p_y^2)$$

iii. 粒子局限在长度为 L 的一维空间内运动

$$\epsilon = \frac{p_x^2}{2m}$$

(b) 设粒子的能谱是极端相对性的，即 $\epsilon = cp, p = |\mathbf{p}|$ ，试对空间维数分别为 1. 三维 2. 二维 3. 一维三种情况，求相应的 $D(\epsilon)$.

Solution.

(a) 首先计算关系 $dp/d\epsilon$

$$\epsilon = \frac{p^2}{2m} \Rightarrow \frac{dp}{d\epsilon} = \frac{m}{p}$$

三维、二维、一维情况下的态密度分别为

$$\begin{aligned} D_{3D}(\epsilon) &= \frac{1}{d\epsilon} \int \frac{d\omega}{h^3} = \frac{1}{d\epsilon} \int \frac{dx dp_x dy dp_y dz dp_z}{h^3} = \frac{V}{h^3} 4\pi p^2 \frac{dp}{d\epsilon} = \frac{2\pi V}{h^3} (2m)^{3/2} \epsilon^{1/2} \\ D_{2D}(\epsilon) &= \frac{1}{d\epsilon} \int \frac{dx dp_x dy dp_y}{h^3} = \frac{2\pi A m}{h^2} \\ D_{1D}(\epsilon) &= \frac{L}{h} \int 2 \frac{dp}{d\epsilon} = \frac{L}{h} (2m)^{1/2} \epsilon^{-1/2} \end{aligned}$$

(b) $\epsilon = cp$ 时， $dp/d\epsilon = \frac{1}{c}$. 只需将 (a) 中的 $dp/d\epsilon$ 替换为新的 $dp/d\epsilon$ 即可. 结果分别为

$$D_{3D} = \frac{4\pi V}{(hc)^3} \epsilon^2, D_{2D} = \frac{2\pi A}{(hc)^2} \epsilon, D_{1D} = \frac{2L}{hc}.$$

Lecture #3 Homework #3 [2025-09-16]

Problem 3.1. N 个单原子分子组成的理想气体,

$$H = \sum_{i=1}^{3N} \frac{p_i^2}{2m}$$

微观状态数的定义为

$$\Omega(E) = \frac{1}{N!h^{3N}} \int_{E \leq H \leq E + \Delta E} dq_1 \cdots dq_{3N} dp_1 \cdots dp_{3N}$$

证明

$$\Omega(E) = \frac{\partial \Sigma(E)}{\partial E} \Delta E$$

其中 $\Sigma(E) = K \frac{V^N}{N!h^{3N}} (2mE)^{3N/2}$, $K = \frac{\pi^{3N/2}}{(3N/2)!}$.

Solution. *Proof.* N 个分子构成的 $3N$ 维 Euclidean 空间 (动量空间) 体积为

$$V_p^{(3N)} = \int \prod_{i=1}^{3N} dp_i = \frac{\pi^{3N/2}}{\Gamma(\frac{3}{2}N + 1)} R^{3N} = \frac{\pi^{3N/2}}{(3N/2)!} R^{3N} = KR^{3N}$$

其中 $R = \sqrt{2mE}$ 为动量空间半径. 则区间 $E \sim E + \Delta E$ 内的空间壳体积为

$$\Delta V_p^{(3N)} = \frac{\partial V_p^{(3N)}}{\partial R} \Delta R = 3NKR^{3N-1} \Delta R \xrightarrow{\Delta R = m\Delta E/R} 3mNK(2mE)^{(3N-2)/2} \Delta E$$

代入微观状态数的定义中

$$\Omega(E) = \frac{3NmKV^N}{N!h^{3N}} (2mE)^{(3N-2)/2} \Delta E$$

其中 $V^N = (\int d^3 q_i)^N$. 注意到

$$\frac{\partial \Sigma(E)}{\partial E} = \frac{3NmKV^N}{N!h^{3N}} (2mE)^{3N/2-1}$$

于是证明了 $\Omega(E) = \frac{\partial \Sigma(E)}{\partial E} \Delta E$. □

Problem 3.2. 一维谐振子

$$H = \frac{1}{2m} p^2 + \frac{k}{2} q^2$$

证明

(a) 正则方程的解是

$$q = A \cos(\omega t + \phi), \quad p = m\dot{q} = -m\omega A \sin(\omega t + \phi)$$

A 为振幅, $\omega = \sqrt{k/m}$ 是频率.

(b) 振子的能量为

$$E = \frac{1}{2} m\omega^2 A^2$$

(c) (q, p) 在相空间的轨道是

$$\frac{q^2}{\frac{2E}{m\omega^2}} + \frac{p^2}{2mE} = 1$$

(d) 求在能量区间 $E - \frac{\Delta}{2} \leq H \leq E + \frac{\Delta}{2}$, 在相空间代表点的数目

$$\int_{E-\Delta/2 \leq H \leq E+\Delta/2} dq dp$$

Solution.

(a) 由哈密顿正则方程

$$\dot{q} = \frac{p}{m}, \quad \dot{p} = -kq$$

将 \dot{q} 再次对时间求导, 得运动方程

$$\ddot{q} = \frac{\dot{p}}{m} = -\frac{k}{m}q, \quad \ddot{q} + \frac{k}{m}q = 0$$

则通解为

$$q = A \cos(\omega t + \phi), \quad p = m\dot{q} = -m\omega A \sin(\omega t + \phi)$$

其中 $\omega = \sqrt{k/m}$.

(b) 振子的能量为

$$E = K + V = \frac{p^2}{2m} + \frac{1}{2}m\omega^2q^2 = \frac{1}{2}m\dot{q}^2 + \frac{1}{2}m\omega^2q^2 = \frac{1}{2}m\omega^2A^2$$

(c) 将 p, q 表达式合并

$$\left(\frac{q}{A}\right)^2 + \left(\frac{p}{m\omega A}\right)^2 = 1$$

由 $E = \frac{1}{2}mA^2$ 得 $A^2 = 2E/m$. 代入得相空间轨道

$$\frac{q^2}{\frac{2E}{m\omega^2}} + \frac{p^2}{2mE} = 1$$

(d) (q, p) 在相空间的轨道为椭圆, 其面积为

$$A(E) = \pi ab = \pi \sqrt{\frac{2E}{m\omega^2}} \sqrt{2mE} = \frac{2\pi E}{\omega}$$

则在能量区间 $E - \frac{\Delta}{2} \leq H \leq E + \frac{\Delta}{2}$, 相空间代表点的数目即为能量区间的对应的相空间面积

$$\int_{E-\Delta/2 \leq H \leq E+\Delta/2} dq dp = A(E + \Delta/2) - A(E - \Delta/2) = \frac{2\pi\Delta}{\omega}$$

Problem 3.3. 读 Pathria 书的 §1.2, §1.3, 写一个阅读笔记.

§1.2 统计学与热力学之间的联系

(a) **系统描述与基本假设.**

- i. 两个系统 A_1 和 A_2 , 分别处于平衡态, 宏观态由 (N_1, V_1, E_1) 和 (N_2, V_2, E_2) 描述.
- ii. 系统的微观状态数分别为 $\Omega_1(N_1, V_1, E_1), \Omega_2(N_2, V_2, E_2)$.
- iii. 复合系统 $A^{(0)} = A_1 + A_2$ 的总能量守恒 $E^{(0)} = E_1 + E_2 = \text{Constant}$.

(b) **复合系统的微观状态数.** $\Omega^{(0)}(E_1, E_2) = \Omega_1(E_1) \cdot \Omega_2(E_2)$

(c) **平衡条件与最概然状态.** 平衡时, $\Omega^{(0)}$ 取最大值

$$\frac{\partial \ln \Omega_1(E_1)}{\partial E_1} = \frac{\partial \ln \Omega_2(E_2)}{\partial E_2}$$

定义 $\beta \equiv \left(\frac{\partial \ln \Omega(N, V, E)}{\partial E}\right)_{N, V}$, 则平衡条件为 $\beta_1 = \beta_2$.

(d) **熵与温度的联系.** 热力学中存在关系

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

对比统计定义 $S = k \ln \Omega$ 可得 $\beta = \frac{1}{k_B T}$, k 为玻尔兹曼常数

§1.3 统计学与热力学的进一步联系

(a) **能量与体积交换.** 若系统间可交换能量与体积, 则平衡条件为

$$\beta_1 = \beta_2 \quad \text{and} \quad \eta_1 = \eta_2$$

其中 $\eta \equiv \left(\frac{\partial \ln \Omega}{\partial V}\right)_{N, E}$.

(b) **能量、体积与粒子数交换.** 若还可交换粒子, 则平衡条件为

$$\beta_1 = \beta_2, \quad \eta_1 = \eta_2, \quad \zeta_1 = \zeta_2$$

其中 $\zeta \equiv \left(\frac{\partial \ln \Omega}{\partial N}\right)_{V, E}$.

(c) **与热力学量的对应.** 由热力学基本关系

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

可得 $\eta = \frac{P}{k_B T}, \zeta = -\frac{\mu}{k_B T}$.

(d) **统计热力学的核心公式.**

- i. 熵: $S(N, V, E) = k \ln \Omega(N, V, E)$.
- ii. 强度量: $\frac{1}{T} = \left(\frac{\partial S}{\partial E}\right)_{N, V}, \frac{P}{T} = \left(\frac{\partial S}{\partial V}\right)_{N, E}, -\frac{\mu}{T} = \left(\frac{\partial S}{\partial N}\right)_{V, E}$.

Problem 3.4. 经典单原子分子理想气体，忽略气体内自由度，用正则系综求内能，物态方程和熵。

Solution. 考虑单粒子的 Hamiltonian，对于理想气体

$$H(\mathbf{p}, \mathbf{q}) = \frac{\mathbf{p}^2}{2m}$$

无势能，与 \mathbf{q} 无关。单粒子的配分函数为

$$Z_0 = \frac{1}{h^3} \int_V d^3\mathbf{q} \int_{\mathbb{R}^3} e^{-\beta H} = \frac{V}{h^3} \left(\int_{-\infty}^{\infty} e^{-\beta p_i^2/(2m)} dp_i \right)^3$$

其中 $i = x, y, z, \beta = (k_B T)^{-1}$ 。这里利用了单粒子三个自由度之间的对称性，并引入量子相空间尺度 h^3 作无量纲化。利用 Gaussian 积分

$$\int_{-\infty}^{\infty} e^{-\beta p_i^2/(2m)} dp_i = \sqrt{\frac{2\pi m}{\beta}}$$

单粒子的配分函数可写做

$$Z_0 = \frac{V}{h^3} \left(\frac{2\pi m}{\beta} \right)^{3/2} = \frac{V}{\lambda^3}$$

其中 $\lambda \equiv \sqrt{\frac{\beta h^2}{2\pi m}}$ 为 de Broglie 波长。接下来考虑 N 个不可区分粒子的配分函数，其可近似为

$$Z_N = \frac{Z_0^N}{N!} = \frac{1}{N!} \left(\frac{V}{\lambda^3} \right)^N$$

其中因子 $N!$ 为 Gibbs 修正，为了解不可区分性。

(a) 内能

$$U = -\frac{\partial}{\partial \beta} \ln Z_N \xrightarrow[\ln Z_N = N \ln Z_0 - \ln N!]{\text{Stirling identity}} -N \frac{\partial}{\partial \beta} \ln Z_0 = \frac{3}{2} N k_B T$$

(b) 状态方程。系统的自由能

$$F = -k_B T \ln Z_N \xrightarrow[\ln Z_N = N \ln Z_0 - \ln N!]{\text{Stirling identity}} -N k_B T \left[\ln \left(\frac{V}{N \lambda^3} \right) + 1 \right]$$

由热力学关系 $p = -(\partial F / \partial V)_T$ 得

$$p = k_B T \frac{\partial}{\partial V} \ln Z_N = \frac{n k_B T}{V}$$

于是状态方程为

$$pV = N k_B T$$

(c) 熵。由 $S = -(\partial F / \partial T)_V$ 得

$$S = k_B \ln Z_N + k_B T \frac{\partial}{\partial T} \ln Z_N = N k_B \left[\ln \left(\frac{V}{N \lambda^3} + 1 \right) \right] + \frac{3}{2} k_B T = N k \left\{ \ln \left[\frac{V}{N} \left(\frac{4\pi m}{\beta h^3} \right)^{3/2} \right] + \frac{5}{2} \right\}$$

这里在 Stirling 公式的基础上做了一阶 Taylor 展开。

Problem 3.5 (林宗涵《热力学与统计物理》8.1). 设有 N 个粒子组成的系统处于平衡态, 满足经典极限条件.

(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

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

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%。

目 录

第一章 回顾热力学	
第二章 统计物理基本概念和近独立粒子系统统计物理的回顾	
第三章 微正则系综	
§ 3.1 经典统计系综	
§ 3.2 量子统计系综	
§ 3.3 微正则系综	
第四章 正则系综	
§ 4.1 从微正则系综到正则系综	
§ 4.2 热力学量	
§ 4.3 能量涨落、热力学极限和经典极限	
§ 4.4 应用：非理想气体的状态方程	
第五章 巨正则系综	
第六章 量子统计 $d=1,2,3$	
§ 6.1 巨正则系综导出玻色统计和费米统计	
§ 6.2 量子统计和波函数	
§ 6.3 路径积分和量子统计	
§ 6.4 任意子、辫子群和其他	
§ 6.5 一维统计：与相互作用相关性	
第七章 相变、临界现象和重整化群简介	
§ 7.1 朗道二级相变理论简介	
§ 7.2 临界现象和临界指数	
§ 7.3 量子相变	§ 8.7.3 涨落的空间关联
§ 7.4 Ising 模型： § 7.4.1 平均场近似	§ 8.8 涨落现象：随机外力和布朗运动：
§ 7.4.2 一维伊辛模型的精确解	§ 8.8.1 朗之万方程；
§ 7.4.3 二维伊辛模型的精确解	§ 8.8.2 布朗粒子的扩散；
§ 7.4.4 1+1 维量子伊辛模型	§ 8.8.3 布朗运动中的时间关联
§ 7.5 重整化群： § 7.5.1 实空间 RG	§ 8.8.5 涨落-耗散定理；
§ 7.5.2 举例：一维伊辛模型	§ 8.8.6 布朗运动类似的物理过程：
§ 7.6 数值重整化群和 DMRG 简介：	电路中的热噪声和电压涨落；
§ 7.6.1 动量空间 RG；	§ 8.8.7 散粒噪声
§ 7.6.2 Wilson's 数值 RG	§ 8.9 主方程和福克-普朗克方程：
§ 7.6.3 DMRG 简介	§ 8.9.1 Master 方程
§ 7.7 Kosterlitz-Thouless 相变	§ 8.9.2 福克-普朗克方程
第八章 非平衡态统计物理	第九章 统计物理中计算方法简介
§ 8.1 引言	§ 9.1 引言
§ 8.2 Boltzmann 积分微分方程： § 8.2.1 漂移项的计算；	§ 9.2 分子动力学简介： § 9.2.1 Verlet algorithm
§ 8.2.1 碰撞项的计算	§ 9.2.2 辛算法
§ 8.3 H 定理，H 函数和熵	§ 9.3 蒙特卡罗方法：
§ 8.4 Boltzmann 方程的应用	§ 9.3.1 概说
§ 8.5 线性响应理论：力学扰动	§ 9.3.2 均匀或权重取样
§ 8.6 线性响应理论：热力学扰动	§ 9.3.3 对平衡体系的马尔可夫链取样
§ 8.7 涨落现象：热力学量： § 8.7.1 准热力学理论；	§ 9.3.4 重要性取样 Metropolis algorithm
§ 8.7.2 高斯分布；	§ 9.3.4 伊辛模型

- § 9.4 相变和蒙特卡罗模拟
 § 9.5 变分蒙特卡罗
 § 9.6 量子蒙特卡罗：
 § 9.6.1 相互作用玻色子，SSE 算法
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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态。固态是宏观现象的宏观唯象理论。统计物理则研究微观的微观理论。固态不考虑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微观粒子组成，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. 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：衡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。

* 不同温度具代表性的规则叫温标。

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* 物态方程：物体的物理状态由几何参数（V, A, L），力学变量（P, T, F），电荷变量（E, P, A, M）和化学变量描述，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（与外界没有能量交换）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，系统从外界吸热 $Q = U_2 - U_1 - W_a$ 即能守恒。

* $C_y = \frac{\partial Q_y}{\partial T}$ 表示热量，y 表示不变量，
 $y = V$ 容量， $y = P$ 压强， $y =$

单位质量的热量称为比热容。

* 内能是态函数， $H = U + PV$ 也是态函数
 内能绝热过程中外界没做功的微小变化 $dU = dQ_a$
 绝热过程中外界吸热或放热 $Q_a = dH$

* 熵：对可逆过程，志取大熵

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

* 恒定元二定律：

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

熵增加原理.

* 直子基本方程：第一定律 + 第二定律. 定义

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

例如，对 $P-V-T$ 子

$$dU = TdS - pdV$$

* 自由能： $F = U - TS$

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

$$\text{例如: } dF = -SdT - pdV. \quad (\text{等温准静态})$$

* Gibbs 自由能：

$$G = F + PV$$

$$\text{例如: } dG = -SdT + Vdp$$

等温准静态，无永磁场.

Kelvin 不可能从单一源级
热，仅是完全变为可用的
而产生其他影响
classical mechanics
不可能起因从低速物理法则
与低速而产生其他影响

1.2 单相系(单相系)的平衡

* 物质，破名思义，就是各部分性质完全一样物体.

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

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

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

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

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

* 可以把热力学量：

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

(2) 上物理方程是和，坦言影响系数.

即各种变化时，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. 可能的变动.

* $\delta S = 0, \delta^2 S < 0$, 找出局部域相对极大. 其它在
它是几个相对大集中取大. 那么，极点相对互换.

* $\delta S = 0, \delta^2 S = 0$, 这时， $\delta^3 S = 0$ 是保证稳定性
条件. $\delta^2 S < 0$ 该系统绝对平衡. 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 热力学可变，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m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条件给出, 例如, 有由能极小, 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.
- * 马克斯well 定律: $L_{ki} = L_{ik}, L$ 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{q}, \mathbf{p}) ($q^a; p^a$) 描述，单粒子能级 $E = E(\mathbf{q}, \mathbf{p})$ 。一个微观大，宏观小的单粒子相空间中体元： $d\omega = d^{3q} d^{3p}$ 。
对 N 个经典宏观物体，广义坐标和广义动量 $(q_1, \dots, q_N; p_1, \dots, p_N)$ ， $S = \Omega^N$ 。相空间中体元之 $dS = dq_1 \dots dq_N dp_1 \dots dp_N$

$\{(q_1, \dots, q_N; p_1, \dots, p_N)\} = \Gamma$ 表示相空间，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 热力学统计的等几率原理

* 宏观视图是宏观大、统计大，宏观复杂、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。即由于宏观状态的宏观状态数远大于微观状态数，以至于宏观状态的微观状态数远大于微观状态数。

* 宏观和微观两个量的统计平均值。

* 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、朴素的假设是等几率假设，即得万有几率原理：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

* 量子：单粒子量子由一组量子数标志，

即一组可对易的算符有一个确定值描述（表征值可直接，也可是分立）。例如，对自由粒子，~~其~~运动本征值，能本征值与经典一样，都是连续的。但在一个盒子里，波函数 $\psi(x) \propto e^{i k x / \hbar}$ ，而不是高斯波，故本征值为 $k = \frac{n\pi}{L}$ 。

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

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 $\leftrightarrow \omega = h\nu$ 单粒子能级。

* 量子统计的全局性：用量子描述宏观，无论是分子、原子、电子还是自旋、质子、都适用。

* 在三维或以上空间，只有波动和量子学。

* 在 $d=2, 1$ ，可以有既非波动、又非量子一统计，(\sim 光子统计)

* 全同粒子不遵守 $(3)-$ 单粒子对应。 (Pauli 泛化)

* 如果 ~~两个~~ 粒子可以“标记化”，则可互换。如果，局限于区域的粒子，在束缚带中的电子，...

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，且只对体系的宏观起作用，但对粒子的性质及负责微观忽略。

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

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

$$\begin{array}{ccc} & \vdots & \vdots \\ \text{能级} & \rightarrow & \text{能级简并度} \\ \hline \alpha_1 & \cdots & \alpha_3 \\ \alpha_2 & \cdots & \alpha_4 \\ \alpha_3 & \cdots & \alpha_5 \\ \hline \text{能级} & \text{能级简并度} & \text{占据数} \end{array} \quad \left| \begin{array}{c} \alpha_1=1, \dots, N \\ \alpha_2=1 \\ \alpha_3=2 \\ \alpha_4=1 \\ \alpha_5=2 \end{array} \right.$$

* 对于孤立系， (E, V, N) 。

$$\sum \alpha_\alpha = N, \quad \sum \alpha_\alpha E_\alpha = E \quad \left| \begin{array}{c} \alpha_1=1 \\ \alpha_2=1 \\ \alpha_3=2 \\ \alpha_4=1 \\ \alpha_5=2 \end{array} \right.$$

* 给定一个能级占据数分布 $\{\alpha_\alpha\}$ ，由于能级能级可有多种不同的分布， \therefore 一个状态分布可以有不同的微观状态。即 $(3)-$ 维与之对应，设 $W(\{\alpha_\alpha\})$ 为对应一微观状态宏观。由等几率原理，给出宏观几率 $P(\{\alpha_\alpha\}) \propto W(\{\alpha_\alpha\})$ 。

* 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 m 个，就是简单从 m 里选。而前一节对于 N 个粒子放在 M 个盒子里，每个盒子放 α_i 个是组合数。由最可能分布，可以得到配分函数，有微扰系数，则可求出所有基态能量。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即 Pauli 反原理。法则是

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

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

* 量子力学分布结果导出 Bose 和 Fermi 统计力学

* 由经典粒子论的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。包括玻尔兹曼定理，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（把谁反推）
= 对应的微观状态的密度。（过去推）

* 处于 $d\Omega$ 中的 \bar{O} 由于 \bar{O} 为一个统计系综，即
系统是复数的，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粒子是一组。

3.2 则维 (Liouville) 定理

则维定理：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 $\frac{d\bar{P}}{dt} = 0$ 。

则维定理 ~~即~~ 代表真概率 ~~不是运动~~
~~代表真概率~~：

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

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

~~时间方程~~ ~~时间方程~~：

$$\frac{\partial \bar{P}}{\partial t} + \{ \bar{P}, H \} = 0.$$

第三章 微正则系综

平衡态统计一般理论是系综理论，它适用于任何的宏观统计系综。系综理论包括微正则、麦克斯韦正则系综，前者是基础，但后者在实际计算时更方便。

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，它被描述从坐标运动方程

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

$\{(\bar{q}_i^{(+)}, \bar{p}_i^{(+)})\}$ 形成一个相轨道，称自由运动 (运动) 演进。

$$d\Omega = dq_1 \dots dq_S dp_1 \dots dp_S$$

是相体积，

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

$$P d\Omega = \frac{\bar{P} d\Omega}{\Gamma} = \frac{\bar{P} d\Omega}{\int d\Omega} \text{ 是概率密度}$$

状态出现在机内几率。 $S = \frac{\Gamma}{\int d\Omega}$ 称为几率密度。

固守性方程

~~固守运动方程~~ $\frac{\partial \bar{P}}{\partial t} + \sum_i \vec{P} \cdot (\vec{v} \vec{v}_i) = 0 \quad (1)$

$$\begin{aligned} \frac{\partial \bar{P}}{\partial t} &= \frac{\partial \bar{P}}{\partial t} + \sum_i \left\{ \frac{\partial \bar{P}}{\partial q_i} \dot{q}_i + \frac{\partial \bar{P}}{\partial p_i} \dot{p}_i \right\} \\ &= -\dot{\bar{P}} \leq \left\{ \frac{\partial H}{\partial q_i \partial p_i} - \frac{\partial H}{\partial p_i \partial q_i} \right\} = 0. \end{aligned} \quad \text{对称性}$$

对称性，即 $\frac{\partial H}{\partial q_i \partial p_i} = \frac{\partial H}{\partial p_i \partial q_i}$

$$\frac{\partial \bar{P}}{\partial t} + \{ \bar{P}, H \} = 0, \quad \text{或 } \frac{\partial \bar{P}}{\partial t} + \{ \bar{P}, H \} = 0.$$

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

* ~~量~~ ~~泛函~~：用表示空间代替经典物理空间；
 ② Schrödinger eq. 代替波动方程；
 ③ 行列式 ~~或~~ 波函数方程：

$$\hat{O}(t) = e^{iHt/\hbar} \hat{O} e^{-iHt/\hbar}$$

$$\hat{O}(t) = e^{iHt/\hbar} e^{iHt/\hbar} \hat{O} e^{-iHt/\hbar} + e^{iHt/\hbar} \hat{O} e^{-iHt/\hbar}$$

$$\hat{O}(t) = \hat{O}_0 [H, \hat{O}_0], \quad \hat{O}(t) \text{ 波函数}$$

$$\frac{\partial \hat{O}}{\partial t} + \frac{i}{\hbar} [\hat{O}, H] = 0 \quad \text{或} \Delta \text{ 泛函方程}$$

$$\bar{O} = \sum_n \bar{O}_n \langle n | O | m \rangle = \text{Tr } \bar{O}$$

§3.2 量子统计力学

(19)

- * 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 $\langle n|$ ，而 $|A_n\rangle = \langle n|A|n\rangle$ 是力学可观测量的平均值。

对这个~~数学~~，我们考虑~~一个~~一个子系统 $|n\rangle$, $n=1, \dots$ 其子系统 $N = \sum_n p_n$ 为总系统，即有总子系统，这个总子系

这样， $p_{in} = \frac{p_n}{N}$ 是一个子系统的概率， $\sum_n p_n = 1$.

~~量子力学~~量子力学~~统计~~平均值为

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

- * 伎俩子系(或密度矩阵)

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

$$\langle ij | = \delta_{ij}, \quad \hat{\rho} \text{ 和 } \hat{A} \text{ 互为伴随}$$

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

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

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

§3.3 微正则子系

(20)

- * 经典微正则子系， (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 为常数。成立一条相轨迹（~~一条~~一条轨道内平行于 E 的平行子系）内 P 为常数。但这不能保证不同轨迹内 P 相同。假设微正则子系的基本假设是，~~假设~~当 $H(q, p) = E$ 时 $P = \text{Const.}$ $H \neq E$ 时 $P = 0$ 。~~若~~这 P 为常数很困难，数学上~~的~~处理是

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

$$\lim_{\Delta E \rightarrow 0} C \int_{E}^{E+\Delta E} dE = 1, \quad \bar{P}(E, p) = \lim_{\Delta E \rightarrow 0} C \int_E^{E+\Delta E} 0 dE.$$

- * 热力学：热力学原理或微正则子系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。但这个热力学是由微观上存在宏观上不可见的~~与外界~~相联系的假设。而不是由~~由~~由~~由~~波函数的~~宏观~~微观假设得来的。

* $\hat{\rho}_m$ 微正则子系

(21)

由~~得~~ Schrödinger eq.

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

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

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

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

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

$$\begin{aligned} & \sum_n H |n\rangle p_n \langle n| \\ & - |n\rangle p_n \langle n| H \end{aligned}$$

* 热力学正则子系：① 定义~~的~~子系

$$(22) \quad P_n = \begin{cases} C, & E_n = E \\ 0, & E_n \neq E, \end{cases} \quad n \text{ 是量子数} \text{ 的状态}$$

即量子数~~能级~~为 E ，则出现几率为 C ，否则为 0.

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

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

$$\begin{cases} E_n = E \\ n \neq \text{其它} \end{cases} \quad N(E, V, N) = (\sum_{n(E_n=E)} 1), \quad \text{由} \\ C = \frac{1}{N(E, V, N)}.$$

~~注意：~~ ~~先~~ ~~算~~ ~~再~~ ~~算~~

§3.4 微正则子系中宏观统计

经典

$$\bar{A} = \int A(q, p) P dq dp$$

$$\Rightarrow \bar{A} = \frac{1}{N!} \int_{\Omega}^{} \int_{E \leq H \leq E + \Delta E} A dq dp.$$

$$\text{分子：} \quad \bar{A} = \sum_n P_n A_n \quad (E = E_n)$$

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 $S(E)$ 为 $A+B$ 的总熵，当 A 处于某一状态，B 可处于 $S_B(E_A)$ 状态。 $\therefore A$ 处于这个状态的几率是

$$\rho_{An} = \frac{S_B(E_A)}{S(E)}$$

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， \therefore 我们可用一个自由度子系统代替指定。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， $E_A^M (1 - \frac{E_A}{E_{\text{total}}})^M = E_A^M (1 - \frac{E_A}{E_{\text{total}}} + \dots)$
二项式展开把问题简化了。

内能

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

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

$$P_{\text{压强}}: P_{\text{压强}} = -\frac{\partial \bar{E}}{\partial V},$$

$$P = \sum_n P_n \rho_n = \sum_n \frac{\partial E_n}{\partial V} e^{-\beta E_n} = \frac{1}{\beta} \frac{\partial}{\partial V} \ln Z_N.$$

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

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

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

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

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

§4.3 热力学函数、热力学极限和经典极限

(在经典统计中，没有用到能量分布，而是计算 E 与 \bar{E} 的方差，或方均根。此时方差 $(\bar{E}-\bar{E})^2/\bar{E}^2$ 或 $\sqrt{(\bar{E}-\bar{E})^2}/\bar{E}$.)

麦克斯韦玻耳兹曼

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

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

这时，可以把 $O(E_A)$ 沿虚线拆开 ρ_{An} ，对 Σ_B 作同样处理

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

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

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

$$\beta = \frac{1}{k_B T} \cdot k_B \text{ 是 Boltzmann 常数, } T \text{ 是温度.}$$

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

$$E_A = E_1, \quad \Sigma_N \text{ 是正则子综的总贡献.}$$

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

§4.2 热力学

$$\bar{E} = \frac{\text{Tr}(A e^{-\beta H})}{Z_N} = \frac{1}{Z_N} \sum_n \frac{h_{\text{J-S}} e^{-\beta E_n} C_n M_n}{10^{34} \text{ J} \cdot \text{s} \cdot \text{C} \cdot \text{m}^3 \cdot 10^{23} \text{ kg}}$$

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

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

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

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

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

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

* 热力学极限

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

$$\propto T \quad \begin{cases} \text{与 } T \text{ 成反比} \\ \text{与 } N \text{ 无关} \end{cases}$$

* 热力学极限是 $N, V \rightarrow \infty$ ，但子系统

密度不变： $n = \frac{N}{V}$ 固定 \rightarrow 非绝热过程

* 我们前面都用分子态表示， $\frac{1}{2} \pi r^2 \Delta E = h/(2\pi m k_B T)^2 \ll \bar{E}$ (转动简并)

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

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

$$A = \frac{1}{Z_N} \int d\Omega A e^{-\beta H}$$

4.4 应用：非理想气体的状态方程

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

$$\phi_{ij} = \phi(|\vec{r}_i - \vec{r}_j|) \text{ 且 } = \infty \text{ if } r_i = r_j.$$

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

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

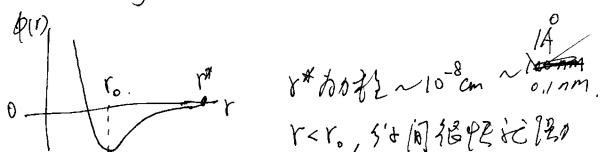
对分子积分非常简单，这就是玻尔兹曼分布。

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

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

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 $\phi(r) \sim 10^{-8} \text{ cm} \sim 0.1 \text{ nm}$

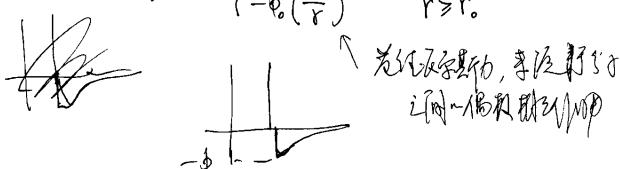
$$\left. \begin{aligned} \text{这样 } f_{ij} &= e^{-\beta \phi_{ij}} \\ f(r) &\Rightarrow \begin{cases} 1, & r \rightarrow 0, (\phi \rightarrow \infty) \\ 0, & r \rightarrow r^*, (\phi \rightarrow 0) \end{cases} \end{aligned} \right\} \text{ 分开} \quad r > r_0, \text{ 分开} \quad r < r_0.$$

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

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

(4) 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

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

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

假想边界条件 $\vec{r}_1 \cdot \vec{r}_2 = \vec{r}$, 忽略边界效应。

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

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

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

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

$$\approx N \ln V + \frac{N^2}{2V} \int d\vec{r} f(r). \quad \text{此为方程: } \boxed{\text{方程}}$$

解之,

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

第五章 压缩系数

与膨胀系数类似，压缩同时体积减小多少

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

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

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

$$= \frac{S_B(N_A E_T)}{\sum (N_j E_j)} e^{-\frac{\partial \ln S_B(N_A E_T)}{\partial N_A} N_A - \frac{\partial \ln S_B(N_A E_T)}{\partial E_T} E_T}$$

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

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

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

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

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

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

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

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

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

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

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

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

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

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

* 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 $N = \frac{1}{2} N_0 \pi r^2 n$, 设其为理想气体, 已知 $[8.9.9]$

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

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

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

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. 研究 $8.9, 8.10, 8.12$

(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, 且外部分子会达到平衡
 $N \rightarrow \bar{N}, (T, \mu, V)$ 不变, 设分子被吸收后能级为
 $-\epsilon_0$, 则 $E_N = -N\epsilon_0$.

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

N 表示 N_0 分子占据 N 分子时的中心数
 \uparrow 对应于占据状态, 这样状态是一空的
 $\frac{N_0!}{N!(N_0-N)!}$, 且能级相等.

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

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

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

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

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

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

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 $d=2$, 则是 Anyons.
 若 $d=1$, 量子数 n 依赖于相对论.

6.1 用巨正则系统计出 Bose 和 Fermi 统计.

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

$(\leq \text{为整数})$

设 $E_{N_1} = E_{N_2} = \dots = E_N$ 在 \leq 附近一起

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

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

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

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

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

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

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

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

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

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

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

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

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

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

$$\therefore \psi(\vec{r}_1, \vec{r}_2, \dots) = e^{i\chi_1} \otimes \psi(\vec{r}_1, \vec{r}_2, \dots)$$

对称粒子, 由 Pauli 原理

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

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

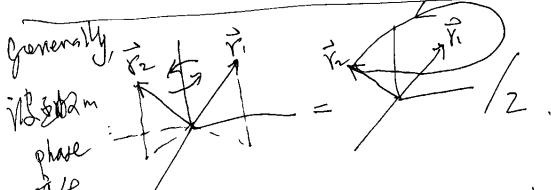
$$\text{即 } \psi(\vec{r}_1, \vec{r}_2, \dots) = -\psi(\vec{r}_2, \vec{r}_1, \dots), \text{ 即 } \chi_1 = \pi \pm n\pi$$

对 Boson:

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

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

$$\neq 0. \quad \therefore \chi_1 = 0 \pm 2n\pi.$$

互换空间, \vec{r}_2 交换 \vec{r}_1 时没有相移障碍, 交换由相位决定, 即 ψ 具有 phase

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

且 $\phi = \phi_1, \phi_2$ 只取 boson or fermion

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

* 求 \bar{Z}_3 (反微分学中的方法)

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

$$= \frac{1}{Z_3} \sum_{\lambda \neq 3} a_3 \left(\sum_\lambda a_3 W_\lambda e^{-(\alpha+\beta g_\lambda) a_\lambda} \right)$$

$$\prod_{\lambda \neq 3} \bar{Z}_\lambda$$

$$= \frac{1}{Z_3} \sum_{\lambda \neq 3} a_3 W_\lambda \{ e^{-(\alpha+\beta g_\lambda) a_\lambda} \}$$

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

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

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

§ 6.2 量子统计和波函数 (Fermion 和 Boson)

设 $\psi(\vec{r}_1, \dots, \vec{r}_N)$ 是 N 粒子波函数。我们令 \vec{r}_i, \vec{r}_j 互换, 根据微观统计力学的定义

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

互换空间,

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

1. 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,

(主称为 anyon, 量子化).

互换空间

$\frac{1}{2}$

二重交换 \vec{r}_1, \vec{r}_2 只能通过 \vec{r}_1, \vec{r}_2 交换, \therefore 一个交换
在互换空间与原空间相对应, \therefore 我们
也将其简单化一下吧.

§ 6.3 路径积分和量 (泛函)
 对应于 $\beta = \frac{1}{kT}$, 热力学
 $\langle \text{Feynman} \rangle$
 $\text{statistical mechanics}$

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

$\tilde{\rho} = e^{-Ht}$ 是 t normalized 的 应该是

$$\begin{aligned} -\frac{\partial \tilde{\rho}}{\partial \beta} &= -\frac{\partial}{\partial \beta} (\tilde{\rho}_{ij})_{\text{独立系数}} \\ &= \left(-\frac{\partial}{\partial \beta} \delta_{ij} e^{-\beta E_i} \right) = \left(\delta_{ij} E_j e^{-\beta E_i} \right) \\ &= (E_j \tilde{\rho}_{ij}) = H \tilde{\rho}. \end{aligned}$$

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

这是守恒方程. 在任何状态都对, 在这个表示

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

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

$$\text{Formally: } \tilde{\rho} = e^{-Ht} \quad \text{redefine: } u = \beta t.$$

$$\tilde{\rho} = e^{-Ht} = e^{-H \frac{u}{\beta}} = e^{-\frac{u}{\beta} H} = e^{-H \tilde{\rho}(u)}.$$

$$\text{Formally: } \tilde{\rho}(u) = e^{-Hu/kT}.$$

从 - (经典力学为例), $H = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2}$,

$$\rho(x, x'; \epsilon) \approx \sqrt{\frac{m}{2\pi kT\epsilon}} e^{-(m/h\epsilon)(x-x')^2} \quad (\text{类似 Feynman 的 表示法})$$

$$\rho(x, x'; u) = \lim_{\epsilon \rightarrow 0} \int \frac{dx_1}{\sqrt{2\pi kT\epsilon}} \cdots \frac{dx_{n-1}}{\sqrt{2\pi kT\epsilon}} \frac{dx_n}{\sqrt{2\pi kT\epsilon}} e^{-\frac{mu}{2\hbar} [(x_{n-1}-x')^2 + \dots + (x_n-x')^2]}.$$

$$\frac{x_n - x_{n-1}}{\epsilon} \rightarrow \frac{dx_n(\epsilon)}{d\epsilon} = \dot{x}_n(\epsilon)$$

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

$$\text{其中 } S = \int_0^u d\epsilon L(\epsilon), \quad L(\epsilon) = \frac{m}{2} (\dot{x}(\epsilon))^2$$

自由能 L 定义.

$$Z = \text{Tr } \rho, \quad \text{主生子空间}$$

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

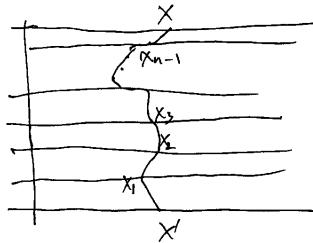
这时任何相空间子空间时, 对主生子空

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

$$\begin{aligned} [t\beta] &= [t], \quad \text{于是 } u = \hbar \epsilon \\ \rho(u) &= e^{-H\epsilon/k} e^{-H\epsilon/k} \cdots e^{-H\epsilon/k} \\ &= \rho_0 \rho_1 \cdots \rho_n. \end{aligned}$$

主生子表象:

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



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

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

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

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

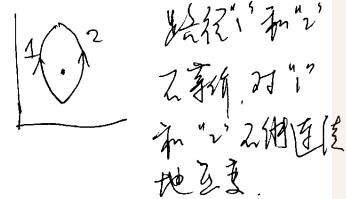
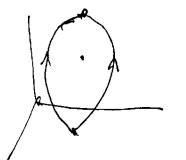
6.4 不确定、相空间和基础: $d=2$.

partition function Φ in $\mathbb{C} \rightarrow \mathbb{C}^*$, 把生子空间中一个点看成一个量子.

$$\int \mathcal{D}x e^{-\int_0^u d\epsilon L}$$

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

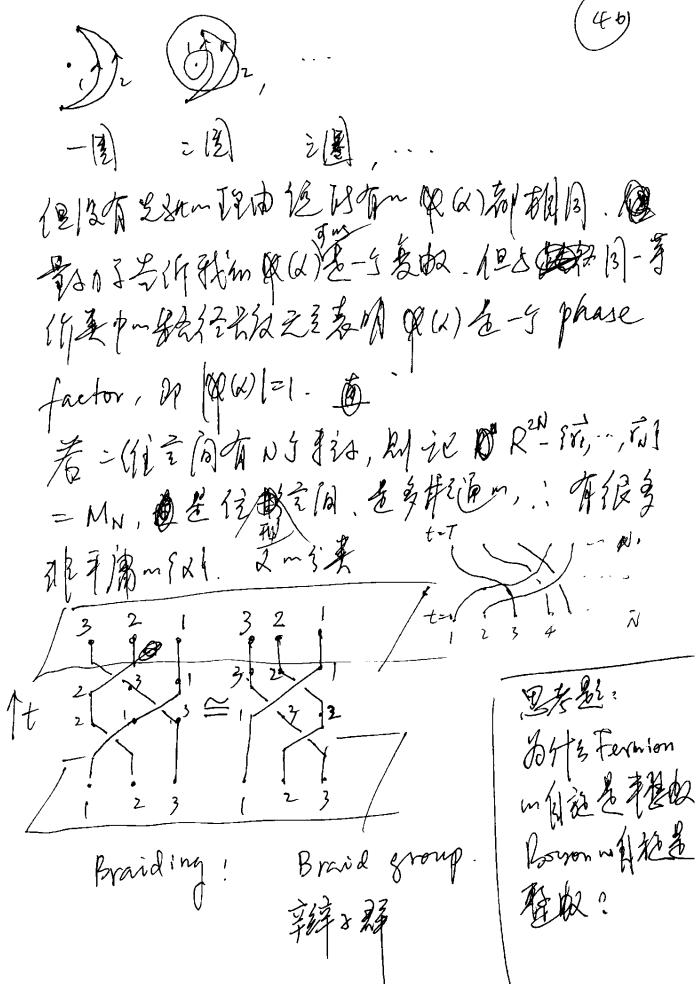
\mathbb{R}^2 是对所有可能的路径积分. 在 \mathbb{R}^2 中, 任何路径对类状振幅的影响是相同的. 但在 \mathbb{C}^2 中



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

在 \mathbb{R}^2 中所有路径都可以直接互换. 但在 \mathbb{C}^2 中所有互换一般会改变振幅.





对 N 个粒子，有 $B_N(R^2)$. 通过，
 B_N 中一个元素有群之 (无限, nonabelian) 部
分叫 braiding 部分. 在 braiding 产生时，
记 σ_i 是 x_i 及 x_{i+1} 互换时的变换，且左乘以 σ_i
右乘以 σ_i^{-1} ：

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

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

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

群与群连-9
Non-abelian group
但一维表是
Abelian 三结
⇒ 量子力学

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

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

这就是一个群与群连-9 而又有粒子. 设
 $\phi_0(\sigma_i)$ 是生成元之一的表示. $\phi_0(\sigma_i) = e^{-i\theta}$
满足群与群连-9. ($0 \leq \theta < 2\pi$). 当 $\theta = 0$, \Rightarrow Bose
统计, 当 $\theta = \pi$, \Rightarrow Fermi 统计. $\theta = \pi/2$ 时.
介于之间.

(4c)

$$\begin{aligned} r_i &\rightarrow \overbrace{r_i \quad r_{i+1}} + \overbrace{r_{i+1} \quad r_i} \\ \therefore \phi_0(\sigma_i^{\pm 1}) &= e^{\mp i\theta} = \exp \left[\mp i\theta \sum_{j \neq i} \Delta \phi_{ij} \right] \\ e^{\mp i\theta} &= \exp \left[-i\theta \sum_{j \neq i} \Delta \phi_{ij} \right] \end{aligned}$$

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

推广到 $n - 2m$ 粒子:

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

\therefore 传播 $K(r't'; rt)$

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

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 M 是 M_N 中 $n - 2m$ 的空间. 定义

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

现在考虑由路径积分 $\int dr(t)$ 使波函数连-9.

如果没 braiding 时,

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

定义 $\tilde{\psi}(r', t') = \exp \left\{ -i \frac{\theta}{\pi} \int_{r_0}^{r'} dt \left(\sum_{ij} \Delta \phi_{ij} \right) \right\} \psi(r', t')$, 由于
若无 braiding 时 $\psi(r', t')$ 为单值, (r' 是 $n - 2m$ 粒子
在 $t = 0$ 时), 则

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

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

若把 $\tilde{\psi}$ 定义

$$\tilde{\psi}(r, t) = \prod_{i < j} \frac{(z_i - z_j)^{\theta/\pi}}{|z_i - z_j|^{\theta/\pi}} \tilde{\psi}(r', t')$$

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

由 θ 确定出 (统计) 参数. 交换对称

3.6.4.5 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_i 且
相互接触，所以除自由统计，统计与相互作用
相关。
~~假设~~ ~~假设~~：首先，我们推广 Bose

~~假设~~ Fermi 统计：N 个 particle 占据 x_i 的
概率 $W_{\text{B}} = \frac{[G + (N-1)(1-s)]!}{N! [G - (N-1-s)!]} \rightarrow$ 重分布。
老 T-funct.

$$\frac{S}{N} = 0, W_0 = \frac{[G+N-1]!}{N! [G-1]!} = W_B$$

$$\frac{S}{N} = 1, W_1 = \frac{[G+N-1]!}{N! (G-N)!} = W_F$$

$0 < \frac{S}{N} < 1$, 则是对于 Bose 和 Fermi (3) 的推广。

~~如果~~ ~~如果~~ ~~如果~~ 如果有一个分布 $\{N_x\}$ ，但

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

$$\text{取 } S_{\alpha\beta} = S \delta_{\alpha\beta}, \text{ 但 } S=0, \text{ 所以 } S=1$$

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

这里 $S_{\alpha\beta}$ 表示不同“坐标”占据空间的有

相互作用。

\Rightarrow 1D 例子。

例 1. 玻尔兹曼统计 ($C=0, 1D$)

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

用脚标表示 $\delta(x_i - x_j)$. 通过“Fourier”展开，互动 \propto 空间，总能量 $E = \sum_i k_i^2$.

\rightarrow 在无限温度极限下， $\lambda \rightarrow k$

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

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

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

$$\text{当 } C \rightarrow 0, \theta' = 0, S(k, k') = \delta(k - k'). \rightarrow$$

idea Fermion

$$\text{当 } C \rightarrow \infty, S(k, k') = -\delta(k - k').$$

这时一般 C , 并没有 θ' 在物理系统。

例 2: Calogero-Sutherland (Fermion)

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

$$\lambda \rightarrow \infty, \text{ 则 } \rightarrow \frac{\lambda^{(x-i)}}{(x_i - x_j)^2}.$$

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

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

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

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

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

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

只在 k_F 处有 δ 线。

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

(~~只~~ ~~只~~ ~~只~~)

第七章 相变、临界现象和量子化群论

物理学中不同物理性质的体系并不互相依赖，例如，固态、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、共存点等。于是，可以根据这些画出相图，画出参数空间 ~ 相图。根据相变类型，在平行时间行为，可以判定相变。

一级相变：相变差，两相 m 化学势相等，但 $\mu^a = \mu^b \neq 0$ ， $\delta S_a - \delta S_b = -\left(\frac{\partial \mu}{\partial T}\right)_P \neq 0, \dots$

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

$\frac{\partial \mu}{\partial T} \neq 0, \frac{\partial S}{\partial T} \neq 0, \frac{\partial T}{\partial P} \neq 0$ 不连续或发散。

如 $\Delta \mu, \Delta S, \Delta T$ 随时间而变化或发散。

同样可以定义二级相变。但二级相变 ~ 例 + 只有 BEC. 三级相变 $\Delta \mu, \Delta S, \Delta T$ 都不为零。

($T \rightarrow 0$, 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，破坏的序参量中的自旋趋于同向，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

自旋有转动对称性（即旋 $SU(2)$ 不变性）而至低温， $M \neq 0$ 表明电子自旋趋向取向某一方面，“转动不变性”被破坏，即为“对称性破缺”。降低温度引起 $M \neq 0$ ，通过不同物理量随温度变化， f 变

把自由能随温度变化的规律

朗道理论要先通过自由能随温度变化的
近似序参量展开，进而得出序参量对温度依赖
依赖。林恩哥罗夫举了 $H=0$ 时 $M=0$ 的例子。请看
家的书。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（即对称性）
的函数，至临界点 $g_s(H=0) = g_n$ 。
 $g_n = f - B \cdot \frac{1}{2} H^2$ 是正者在 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 $T < T_c$ ， $g_s < g_n$ ， $\therefore A(T) < 0$ ，($\because \alpha(T_c) = 0$)， \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”， $SU(2)$ 对称性也由加
一个序参量引起，序参量“明显破缺”。序参量和
是“对称性破缺”的后果，这样叫“对称性”。
“序参量”和“自发破缺”的例子有很多：

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 长程粒子序参量 [绝对波函数]²

玻璃-超导 $K=0$ 长程序参量 ODLRO

~~陶瓷-超导~~ ~~零波函数~~

(CuZn) 二元固溶体结构 游离电子对 $\frac{W_1 - W_2}{W_1 + W_2}$ W_i : 价键

固相

液相

地有一些不是二级相变，但“序参量”概念仍
有用的相变例子：(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，[绝对波函数]²
(电荷载体和空穴)

理想玻色子起振 二级相变 $K=0$ 玻色密度

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 限于一地方差，假设
序参量 $|H| = n$ 有空间分布，这样， g_s 也有空间分布，

$$g_s = g_n + A|H|^2 + \frac{B}{2}|H|^4 + \frac{1}{2m^2} \left[(-i\hbar \nabla \psi)^2 \right]$$

是 Gibbs 自由能为

$$\left[(-i\hbar \nabla - e\vec{A})\psi \right]^2$$

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

$$\frac{\delta G_s}{\delta \psi} = 0 \Rightarrow \left\{ \begin{array}{l} A\psi + B|\psi|^2 + \frac{\hbar^2}{2m^2} \psi^2 = 0 \\ \vec{n} \cdot \vec{\nabla} \psi = 0 \end{array} \right.$$

$$\left. \begin{array}{l} \psi = 0 \\ \vec{n} \cdot \vec{\nabla} \psi = 0 \end{array} \right. \quad (\text{边界条件})$$

GL 方程。一个简单应用 序参量的相变
考虑弱场 $|\vec{A}| \ll |\vec{\psi}|$ ，则可以立 GL 方程中
忽略 A ，而 ψ 与 $\psi_0(\vec{r}) = \frac{\hbar}{2m} \vec{B}_0$ 很相似。宜取
 $f = \frac{\psi}{\psi_0}$ ，取 $f^* = f$ 。则

(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，不同指數之間存在著一定的关系，称为标度律

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

3.3 ~~量子变~~ 量子相变

量子相变是指 $T=0$ 时，系统不同相之间由于某一个参数的变化引起相变。对于有限系统，设 $H(g)$ 为哈密顿， g 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： $H = H_0 + gH_1$, $[H_0, H_1] \neq 0$ 。这时， H_0 和 H_1 同时对角化，有 3 种可能情况。

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

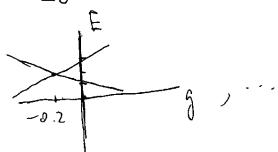
$$E_0 = E_0^{(0)} + g E_0^{(1)}, \quad E_1 = E_1^{(0)} + g E_1^{(1)} \quad \text{若在某 } g=g_c,$$

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

即

$$E_1 = 2 + g_3$$

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



level crossing
一般相变

这些关系是标度律和微扰理论 (第 6 章).
其有一定的普遍性 (普遍性假设).

系统临界平行行为 (二阶泛函, 空间维数 d 和序参数维数 n, 具有相似的 d 和 n 的特征 (属于 I)-一个普遍性, 具有相似的临界行为, $n \neq d$ 时)

* 一个子系统序参数可以是实数、复数和复数。

如果它是实数, $n=1$, 复数 $n=2$, 三阶复数, $n=3$.

$n=1$, 气液相变中的密度差, 金属中的占比差异.

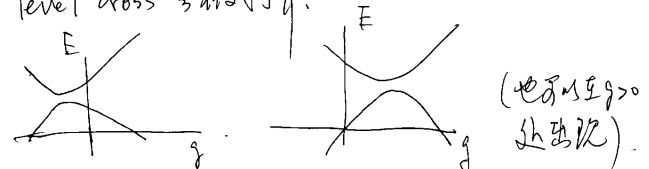
$n=2$, 平面自旋模型 (XY 模型), 超导、超辐射、超流起源于波函数.

$n=3$, 三维壁模型中的磁化强度.

* 普遍性背后的物理原因是临界点的连接数无穷大, 同时, 描述子系统其他特征参数, 例如, lattice spacing, 相互作用力程域及微观细节, (晶格结构, 对称性) 都不重要, 被子系统的合作所屏蔽掉.

在大多数情况下, $[H_0, H_1]$ 可以易, 这种

level cross 会自动打开.



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 Δ 无限接近于零。
这就是量子相变。在相变前后, correlation function 会有变化 (见图). ④

由此可见, 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, 很难根据系统参数.

($g \rightarrow g_c^{\pm}$ 时 Δ 不一样).

类似地, 也有对应的 correlation length ζ

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

$$\Delta \sim \zeta^{-2},$$

线性

非线性

依赖于参数

不一样

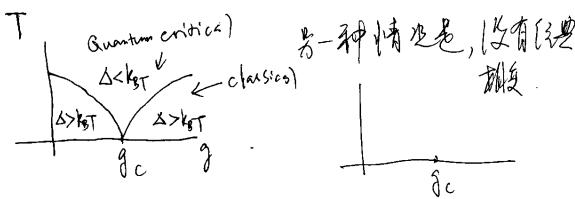
不一样

不一样

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.

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

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

由得，

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

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

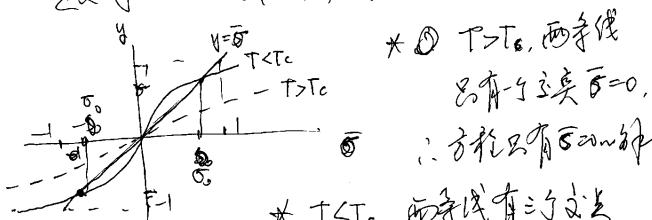
$$\therefore M = N \bar{\sigma} = - \frac{\partial F}{\partial B} = N \tanh \left(\frac{B}{k_B T} + \frac{J}{k_B T} \bar{\sigma} \right)$$

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

自旋。

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

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



即 $T > T_c$ 为无序相 $\bar{\sigma} = \{ \pm 1 \} \Rightarrow \bar{\sigma} = 0$
 $T < T_c$ 为有序相。
 $\because \ln \cosh x \geq 0$ 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。

$$H = - \sum_i \bar{\sigma}_i \left(B + J \sum_j \bar{\sigma}_{i+j} \right)$$

$$= - \sum_i \bar{\sigma}_i (B + h_i).$$

因 $\bar{\sigma}_i$ 为常数，且 $\sum_i \bar{\sigma}_{i+j} = \sum_i \bar{\sigma}_i = \bar{\sigma}$.

$$H_M = - \sum_i (B + h_i) \bar{\sigma}_i \quad h = \sum_i h_i.$$

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

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

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

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

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

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

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

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

这表示一个磁矩 $\sigma_i = \pm 1$ 或 $\sigma_i = 0$ 时, \Rightarrow 相变磁场.

~~但 $\bar{\sigma} = \frac{1}{N} \sum_{i=1}^N \sigma_i$ 不是常数~~.

④ $\bar{\sigma}$

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

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

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

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

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

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

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

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

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

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

= finite.

§7.4.2 一维伊辛模型的精确解.

(平衡态吗? 用经典统计物理)

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

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

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

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

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

§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

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

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

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

$$= \exp \left(\frac{K_2}{2} \sum_j \sigma_{j,x}^2 \sigma_{j,y}^2 \right) = V_2(m) \quad \left(\frac{2M \times 2M}{2 \times 2M} \right)$$

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

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

V 的对角线:

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

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

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

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

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

$$\text{例題: } \hat{\sigma}_{j+} = \left[\exp\left(\beta \sum_{k=1}^{j-1} C_k^+ C_k^- \right) \right] C_j^+$$

$$\hat{\sigma}_{j-} = [\quad] C_j^+$$

注意: $\hat{\sigma}_x, \hat{\sigma}_y, \hat{\sigma}_z$

~~由 $\hat{\sigma}_x, \hat{\sigma}_y, \hat{\sigma}_z$ 可得 $(\sigma_x, \sigma_y, \sigma_z) \rightarrow (\hat{\sigma}_x, \sigma_y, \sigma_z)$~~
 由 $\hat{\sigma}_x, \hat{\sigma}_y, \hat{\sigma}_z$ 为 pauli matrix 且 $\hat{\sigma}_x^2 = I$, $\hat{\sigma}_y^2 = I$, $\hat{\sigma}_z^2 = I$.
 \therefore 在 V_1 和 V_2 中 $\hat{\sigma}_x, \hat{\sigma}_y, \hat{\sigma}_z$ 为 $\sigma_x, \sigma_y, \sigma_z$.

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

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

至 V_2 , $\sigma_z \rightarrow \sigma_x$ 为 $\hat{\sigma}_x = \sigma_x + \sigma_z$, 得 $\hat{\sigma}_x, \hat{\sigma}_y, \hat{\sigma}_z$.

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

$$\left. - (-1)^j (C_1^+ C_1^-) (C_M^+ C_M^-) \right\}$$

$$\hat{n} = \sum_{j=1}^M C_j^+ C_j^-.$$

V_1, V_2 是 -1 的对称且为偶数. 为 σ_x 的角动量.

§7.4.4 1+1 维 Ising model. (i)

1+1 维 (时间+空间) Ising model 又称
横行 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 有序系, 由 $H \cdot \vec{\sigma} = h \sigma^x$,
至 σ^x 方向, 均为零, 为纯横场.

为证明 1+1 维的 Ising model 与 2 维的 1+1
Ising model 有无区别, 我们先从 1+1 维的
spin 模型与 1+1 维的 Ising 模型进行分析.

$$Z_{1D} \leftrightarrow \text{Tr } e^{-H_0/kT}$$

$$\downarrow \quad H_0 = -h_x \sigma_x, \quad \cancel{\text{由 } \sigma^x = \sigma^z}$$

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

前面我们已证明了. 由 $\cancel{\text{由 } \sigma^x = \sigma^z}$ 为 1+1 维 Ising model.

$$\begin{aligned} \cancel{Z_1} &= \text{Tr } V^M \\ &= \text{Tr } e^{kT} (1 + e^{-2kT} \sigma^x) \end{aligned}$$

结果

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

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

$\cancel{\text{由 } E_q = \sinh 2k \cosh 2q}$

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

* 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

$$\begin{array}{ll} \alpha = 0 \text{ (discontinuity)} & \alpha = 0 \text{ (discontinuity)} \\ \beta = \frac{1}{8} & \beta = \frac{1}{2} \\ \gamma = \frac{7}{4} & \gamma = 1 \quad \delta = 3. \text{ 一样.} \\ \delta = 1 & \eta = \frac{1}{2} \\ \eta = \frac{1}{4} & \eta = \frac{1}{2} \end{array}$$

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

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

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

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

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

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

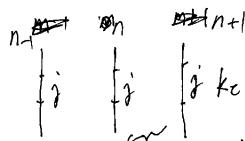
$$\cancel{\text{Tr } e^{-\beta H_0}} = \text{Tr } e^{-\beta H_0}.$$

$\cancel{\text{Tr } e^{-\beta H_0}} = \text{Tr } e^{-\beta H_0}$

$$\begin{aligned} \cancel{Z_1} &= \text{Tr } V^M \\ &= \text{Tr } e^{kT} (1 + e^{-2kT} \sigma^x) \end{aligned}$$

$$\begin{aligned} \cancel{Z_1} &= \sum_{m,n} \sigma_m^x \sigma_n^x \sum_{m+1,n} \sigma_{m+1}^x \sigma_n^x \\ &= e^{kT} \sum_m \sigma_m^x \sigma_{m+1}^x \end{aligned}$$

= 1D Ising model



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

$$\rightarrow \frac{1}{Z} = \frac{1}{N!} \prod_{i=1}^N \left(1 + e^{-\beta h_x \sigma_i^x} \right)$$

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

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

链间耦合:

$$e^{K_c \sum_{m \neq n} \sigma_m^z \sigma_n^z} \sigma_m^z \sigma_{n+1}^z$$

$$= \prod_m e^{K_c \sum_n \sigma_m^z \sigma_{m+n}^z} \simeq e^{\frac{K_c}{2C} \beta \sum_n \sigma_n^z \sigma_{n+1}^z}$$

$$= e^{\beta K \sum_n \sigma_n^z \sigma_{n+1}^z}$$

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

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

§7.5 重叠矩阵

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。精确的高能方法目前还不能，但精确可调模型有很多，且能不难地算出物理量。于是，Kadanoff首先提出了利用关联函数互相关函数发散，子系统的宏观特征尺度已不再重要，可以通过格致变换离散化子系统变简单，但临界行为不变，从而计算出临界指数。Kadanoff并没有建立一个完整的理论，之后也不再继续变拉后，要想保持整个完整的思想，Wilson Hamiltonian 及其精确一致不容易。Wilson 通过 Hamiltonian 及其精确一致不容易。Wilson 成功地完善了 Kadanoff 的思想，建立了重叠矩阵 RG 理论。Kondo [1963]，取的非常好的效果。还有其他各种不同的 RG theories，如 [1970]。

重叠 RG，动力学 RG，数值 RG，泛函 RG，PMRG，其基本思想都是 (1) 作“粗粒化”从大更小，
(2) RG 实际也是子系统，粗粒化后，一些

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

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

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

$K > h$, Ferromagnetic order

$K < h$, Quantum disorder.

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

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

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

当 $h = K$ 时，self-dual. \square

① S^z order $\Leftrightarrow S^x$ disorder.

S^z disorder $\Leftrightarrow S^x$ order.

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

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

(2) ~~且子系统的 RG 变换在子系统中进行~~
~~且子系统的 RG 变换在子系统中进行~~
(2) 离散化过程，找出临界点有
不协变及相互参照。(3) 对线性 RG 变换。
确定临界指前。

~~在 RG 中，一些很简单的物理量不协变。~~
~~在一些 RG 中，物理量有时不在确定~~
critical exponents. 例如，DMRG, 主要是
是通过寻找 ground states 及低能激发。而
而确定一个体系的很能状态。

§7.5.1 Real space RG

最直观的 RG 是 RSRG. 例如，~~Decimation~~

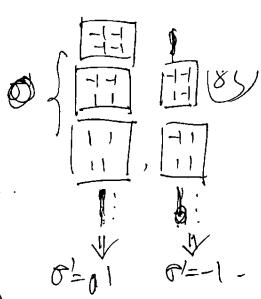
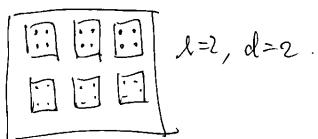
Kadanoff block of spins. 对 1D spin model.

把 ℓ^d (d 是空间 dimensions, ℓ 是 integer)

看成一起看作一个 spin. 即 ~~the~~ ℓ^d spin & ℓ^d
spin 性质相同。从 $k_m, \sigma \rightarrow \sigma'$ 都是 1.

~~NO~~ 原来的 sites, $\Rightarrow N' = \ell^{-d} N$. sites.

$$\bar{r}' = e^{-\frac{1}{T}} \bar{r}$$



2D decimation (1维3步)

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

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 个 spins 的初值。

如果两个子区中自由能 H / 磁场 h 相等，则

$$(S) \quad \downarrow \quad N' \quad f^{(S)}(t', h') = N \tilde{f}^{(S)}(t, h) \quad (t = \frac{T-T_c}{T_c}), \\ \text{singular} \quad \text{和} \quad N' \quad \text{的} \quad \text{自由能} \quad \text{相等} \quad \text{即} \\ \text{和} \quad N' \quad \text{的} \quad \text{初值} \quad \text{相等} \quad \text{即} \quad h' \leftarrow h/t'.$$

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

t 和 t' 有关系 $t' = \lambda^y t$, $h' = \lambda^y h$

y 为 y_h 的值。

$$(84) \quad \text{和} \quad (85) \quad \text{和} \quad (86) \quad \text{没有关系}$$

$\gamma = \frac{1}{\beta} = y_h/(d-y_h)$ (87) $\Rightarrow (90)$

$$\gamma' = \lambda^{-y} \gamma.$$

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

$$\lambda^{-1} = \left(\frac{\gamma'}{\gamma}\right) = \left(\frac{|t'|}{|t|}\right)^{-\nu} = \lambda^{-y} \gamma', \quad y=1, \nu=\frac{1}{y_h}.$$

$$\therefore d\nu = \frac{1}{y_h} = 2-\alpha$$

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

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

$$\therefore \sigma(r) = \lambda^{(d+2-\alpha)/2} \sigma(r')$$

∴ scaling relation: $\boxed{Y = (2-\alpha)^{\frac{1}{2}}}$

$$\eta = d+2-2y_h.$$

$$\sigma(r') = \lambda^{y_h} \sigma(r)$$

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, ∴ f 为?

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

$$(3) \text{ 时, 为了使 } h' \sim |t'|^{-\alpha}, \quad \therefore \quad f^{(S)} \text{ 为?}$$

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

$$\Rightarrow (85). \quad f^{(S)}(t, h) = |t|^{y_h/y_t} \tilde{f}(h/|t|^\alpha).$$

$$f^{(S)}(t, h) = |t|^{-d} |t|^{y_h/y_t} \tilde{f}(h/|t|^\alpha)$$

$$= |t|^{-d} |t|^{y_h/y_t} \tilde{f}(h/|t|^\alpha)$$

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

如果这些都成立, 则 \tilde{f} 为?

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

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

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

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

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

2.5.2 简介: 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 为偶数.

$\exp(-k)$

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

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

且 $\sigma_j = \pm 1$ 取平均

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

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

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

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

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

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 $K \neq 0$, 则有 $\sigma_j^* = \pm 1$ (fixed point). (trivial).

另一个 fixed point 是 $K=\infty$, $B=0$.

它还说, $t=0$, $T \rightarrow \infty$.

第三个 fixed point?

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

$B'_0 \approx B + \frac{1}{2} \ln e^{2B} = 2B$. (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 可由固定点方法. (包括 RG
方程得出: 对于 n 个 coupling constant 为
子项. 但 decimation: $N' = l^{-1} N$, $\beta' = l^{-1} \beta$
重叠化解为)

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

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

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

Singular free energy singular part of free energy / per site

$$f_s^{(n)} = l^{n+1} f_s^{(0)} \quad s - \text{singular}$$

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

$$Z = \sum_{\sigma_0, \sigma_j} \prod_{j=1}^N \exp(2k_0)^{\frac{1}{2}} \cosh \left(K(\sigma_j^* + \sigma_{j+1}^*) + B \right) \exp \left[\frac{1}{2} B(\sigma_j^* + \sigma_{j+1}^*) \right].$$

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

$$Z = \sum_{\sigma_0, \sigma_j} \exp \left\{ \sum_{j=1}^N \left[K_0 + K' \bar{\sigma}_j^* \bar{\sigma}_{j+1}^* + \frac{1}{2} B' (\bar{\sigma}_j^* + \bar{\sigma}_{j+1}^*) \right] \right\}$$

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

$$\exp(K_0 + K' \bar{\sigma}_j^* \bar{\sigma}_{j+1}^* + \frac{1}{2} B' (\bar{\sigma}_j^* + \bar{\sigma}_{j+1}^*)) = \exp(2k_0 + B)^{\frac{1}{2}} \cosh(2K + B).$$

$$\exp(K_0 + K' - B') = \exp(2k_0 - B)^{\frac{1}{2}} \cosh(2K - B)$$

$$\exp(K_0 - B') = \exp(2k_0) 2 \cosh B.$$

$$\therefore \exp(K_0) = x, \quad \exp K' = y, \quad \exp B' = z$$

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

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

$$xy/z = 2 \exp 2k_0 \cosh B. \quad \text{从图 1.}$$

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

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

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

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

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

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

现在找找看不对应的情况. 且 K^* 时

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

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

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

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 通过的矩阵 -> 定义

λ_i 是特征值, ϕ_i 是特征矢. 在一个壳, 例

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

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

且 $\delta \bar{\zeta}$ 为

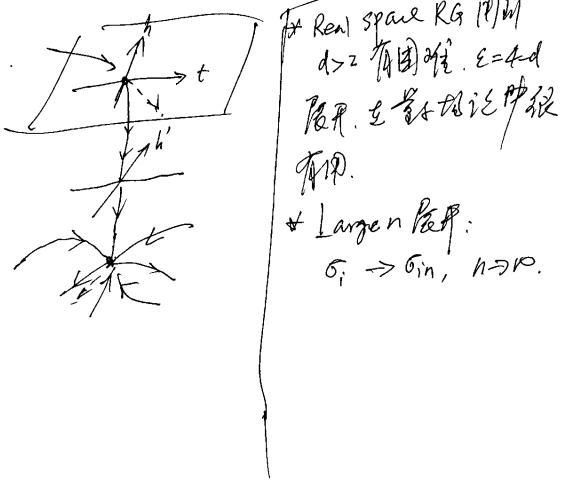
$$u_i^{(n)} = \lambda_i^n u_i^{(0)},$$

(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' 带到 K^* . 这称为 "fixed point".

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

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

physical fixed point.



动量空间 "Scaling" 之支撑. 即是 $\lambda_i = 1$
 长度为 $3=0$ m 不动. ($\mu \rightarrow \infty$, 等温线支)

动量空间也可以用动量空间的重正化, 但不
 要仍在 "reg", 即 μ 中. $\mu \rightarrow \infty$, $\lambda_i > 1$.
 是作做法是在 k 空间引进一个 cut off Λ , ~~把~~
~~把~~ $|k| > \Lambda$ 的部分去掉. 而留下 $|k| \leq \Lambda$
 部分. 这相当于在实空间中的粗粒化过程. 把 ~~把~~
~~把~~ k 空间中 $|k| > \Lambda$ 部分去掉, 把其
 剩余部分下 ($|k| \leq \Lambda$). rescaling $\Lambda \rightarrow \Lambda/b$,
 $b > 1$, ~~把~~ Λ 在 k 空间中 rescaling
 $N = \Lambda^{-d} N$ ($\Lambda > 1$). 动量空间的重正化就通过

重正化在 k 空间. 把物理模型映射到 k -effect
 子系统. 用路径积分的方法来做, 通常又称为
 波函数重正化方法. ~~这是~~ ~~这是~~ ~~这是~~ ~~这是~~ ~~这是~~
 重正化常被用于研究强相互作用论, QFT 等.
 重正化. 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 整形重整化群和 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~~
 实际隔代收敛场论之微扰论 ~~中~~ 之 ~~中~~ 之 ~~中~~
 算法有 "等价发散" ($\mu \rightarrow \infty$). 这些发散 ~~被相~~
 应之奇数需要了解清楚, 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 ~~中~~ 之 ~~中~~ 之 ~~中~~
 描述都将是可重整化. 其中最标准模型
 " $SU(3) \times SU(2) \times U(1)$ " 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
 整形化的过程是引人深思. 之所以说是
 不可能. 但即使没有这个过程, 它的自能 Σ 仍
 可以计算. 但这方法太困难.

~~所有能相容的下述重整化都是~~

§ 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". 就像雕塑者而言,
 我们希望 Σ 在物理 μ 处把其基在 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 作 transformation: $O_L^+ H_L O_L$, O_L^-

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

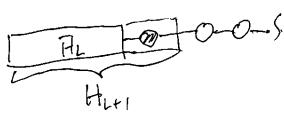
$$H_L = O_L^+ H_L O_L = \begin{pmatrix} \psi_1^+ \\ \vdots \\ \psi_m^+ \end{pmatrix} (E_1 \psi_1, \dots, E_m \psi_m) = \begin{pmatrix} E_1 & \dots & E_m \end{pmatrix}$$

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

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

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.



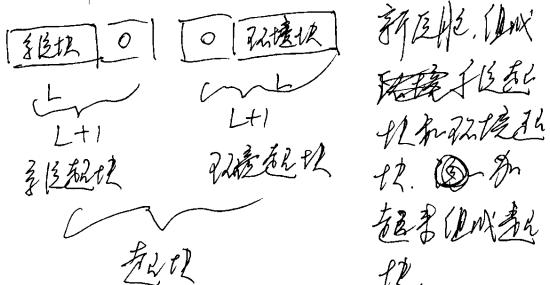
H_{L+1} 在空间倒映 L 为 $m \rightarrow s_m$. 于是 O 为

上支那 site 在空间的倒映. 由 6.3 DMRG 算法
Wilson NRG 在 FT 是 $|\psi_i\rangle, i=1, \dots, n$ 是
 L sites 子链的本征基底, 与外加 $m-s$ site 使
子链渐进. 例如, 用周期性条件或周期性边界
条件与之矛盾. 由于子链在空间倒映与子链本身
边界与子链完全一样. 如何选择子链
与 $n-s$ site 外相配也很困难. White 在
该处加一些 sites 适当, 在扩大的子链中
(superblocks)
选择相对简单, 再投影到没扩大的子链中.
这样, 新件立刻打在 n site 上, 对没扩大的
system blocks 子链影响不大. 通过这种做法对之相
作用于子链非常有效, 及因之能较好地投影回

原子链. 但对有相位作用子链, 有 superblock
子链, 投影到 system blocks 有相位作用:
 $|4\rangle_{sb} \rightarrow |4\rangle^1, |4\rangle^2$. 如何从中选出最佳子链呢?
这正是 DMRG 方法的核心所在.

6.6.3 DMRG 方法

我们先写出一个简单子链. 基本的称为无穷长子链
前链, 考虑一子链, 为了更好的处理边界条件, 引入
与之一样一模一样的环境子链. 对称性初等



起始的子链可看作边界条件.

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. 首先选择一个基本规则起过 m 超子链. 但
小则可以精确对角化处理.

二. 精确对角化处理. 取出最低本征态(一般为
基态).

三. 这些占用 system 子链 $|i\rangle$ 和环境子链 $|j\rangle$

基态的展开是 $|4\rangle = \sum_{ij} \psi_{ij} |i\rangle |j\rangle$. 把投影到
system 子链 m reduced 容易是后端是

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

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

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

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
 $|4\rangle$. 如果 $s > m$, 则得 $\tilde{|4\rangle}$.

OS 子链中 m 为本征子链. (1) $|4\rangle, \lambda_{ij}, m$ (1)

构造 $O = (|4\rangle, \dots, |4\rangle_m)$. 把 $H_{sys} \rightarrow \bar{H}_{sys} = O^\dagger H_{sys} O$.

$H_{air} \rightarrow \bar{H}_{air} = O^\dagger H_{air} O$. (为了对称美的要求).

五. 以 \bar{H} 代替 H 为 m 为 system 子链
circumstance 子链中加 s 个零. 形成 $m+s$ 为子链
的环境子链. 作循环. 逐渐提高精度.

例: spin 1/2 Heisenberg model

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

偶数 $m=5$, 考虑 $S_{tot}^z = \pm \frac{3}{2}$ 两种.

$$(1) L=4$$



$$B_L, S_L, S_R, B_R$$

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

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

$$S_{B_L=1}^z = S_{S_L=1}^z = S_{SR}^z = S_{BR=1}^z = \begin{pmatrix} \frac{1}{2} & 0 \\ 0 & -\frac{1}{2} \end{pmatrix}$$

$$S_{B_L=1}^+ = S_{S_L=1}^+ = S_{SR}^+ = S_{BR=1}^+ = \begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix}$$

$$S_{B_L=1}^- = S_{S_L=1}^- = S_{SR}^- = S_{BR=1}^- = \begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix}$$

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。

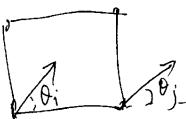
K-T 相变是通常的相变，即有序参量变化，但又不同于对称性破缺引起的相变，而是由自旋和拓扑缺陷激发引起的相变。这与我们在 ~~讨论~~ 中讨论的拓扑相变不同，拓扑相变不是一维的。且反拓扑相变 ~~存在~~ Thouless 在他的第一部分：IQHE 中的拓扑相变 ~~存在~~ 会议中，由于拓扑相变与统计物理的关系还不明确，我们只对 K-T 相变作一简述。

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 Nagaev-Mermine 定理，在低维极限下相变。但弦论/规范场论模型中的强弱和低维的

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 \vec{S}_{tot}^2 取得是 $B_L=2$ ，~~以及~~ system 转换 \vec{S}_{tot}^2 之后的 $B_L=2$: $|B_{L=2}\rangle = D (|B_{L=1}\rangle \otimes |S_L\rangle)$.

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

$$S_{B_{L=2}}^3 = D (I \otimes \vec{S}_L^3) D^\dagger, S_{B_{L=2}}^{+/-} = D (I \otimes \vec{S}_L^{+/-}) D^\dagger.$$

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

形成 $S_{L=2}$ 和 $S_{R=2}$ ，总链长为 3×6 : 即 S_L 有 $1/2$

块 $B_{L=2}$ 的 $\dim = 4$, System Superblock $\dim = 4 \times 2 = 8$,

链长块数 $\dim = 0$ 为 $\dim = 20$, 即 20×20 mH.

对角线，取最低能级，输出 ψ ，得到 $|S_{L=2}\rangle$ 为 8×8

海森矩阵。 $\delta > 5$. \therefore 其中最高 $m = 5$ w.r.t. 15 个

8 vectors. $(u^1, \dots, u^8) = D^{-1} \otimes I^8$ 为 8×8 mH. $|B_{L=2}\rangle = D (|B_{L=1}\rangle \otimes |S_L\rangle)$

= $D (|B_{L=1}\rangle \otimes |S_L\rangle)$. 得出 $H_{B_{L=2}}$, $S_{B_{L=2}}^3 = D (I \otimes \vec{S}_L^3) D^\dagger$

这就是我们想要的 \vec{S}_{tot}^2 和 $|B_{L=2}\rangle$ 。

再 ~~取最低能级~~，~~输出~~ ψ :

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

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

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

spin-spin correlation function

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

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

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

β 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

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

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

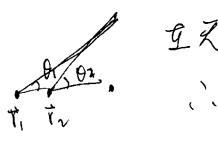
\propto exponential decay in (3), 这是
 一个代数 decay, 不符合代数长距离。

∴ 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 $\theta + 2\pi$ 为
 单位，即 $\theta + 2\pi \equiv \theta$ ，是一个周期性操作。

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，左边和右边， cancel away~~
~~→ $\theta \rightarrow \theta + \pi$~~



在无穷远处, $\theta = \theta_\infty \approx 0$.

$\therefore \theta_0 + 1 - \text{Vortex} \neq \theta_0 - 1 - \text{Vortex}$

相位不同。

相对解的贡献

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

\therefore 有 θ 的 vortex 在 $[0, \infty)$ 中不存在。

是有限的。

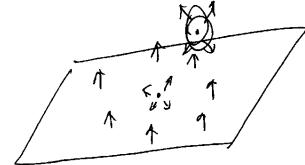
地也是这样，这个相变可能与这个物理有关。

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

解是: 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:



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

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

这是 log. 发散。

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

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

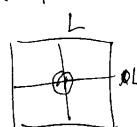
$$+ \int_a^R r dr d\theta (\nabla \theta)^2 = 2E_{\text{core}} + 2J\pi \ln \frac{R}{a}.$$

有限制。~~但 R 足够大时~~ 但 R 足够大时 $\ln \frac{R}{a}$ 可以忽略。

这很容易二流体起竞争, $\therefore X Y$ model dual to

2 维带电荷竞争。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 面积中, 可以有 $(L/a)^2$ 个
 可能的 vortex 位置。

\therefore 在有限尺寸, 单子 vortex 的面积 $(S = \ln(\frac{R}{a}))^2$

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

$$= (J\pi - \frac{2}{\beta}) \ln \frac{L}{a}. \quad \text{即 vortex 对应}$$

\therefore 当 $J\pi - \frac{2}{\beta} < 0$ 时, 单子 vortex 捕捉胶束。

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)

起始速度 $v_s(0T_K) \sim$ 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。在扰动中吸收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。

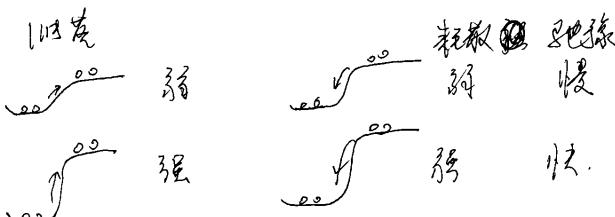
* 涨落过程：涨落是系统从平衡态向非平衡态的过程，可分为二类：(i) 由物质本身（或物理状态）不连续性引起，宏观物理量围绕平衡值（或量子基态）平均值的涨落。(ii) 随机外力作用于宏观小物体导致

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，系统做功，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 \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 $\frac{\partial f}{\partial t} + \frac{\partial f}{\partial x} + \frac{\partial f}{\partial p} = 0$ 受外力和分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：纳维方程是波动方程的海森堡方程。是时间反演不变的微扰运动方程，没有耗散。耗散又来自哪里，对哪边体系。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由理论，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有关无关。从数学上看，情况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 t 变化至 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。
- * 如果至时若向其中直接研究随机运动的统计学，则可研究含随机力的半经典方程：朗之万方程。
- * 从数学观点看，Master 方程研究在 Schrödinger 球面上进行，朗之万方程研究在 Heisenberg 球面上进行。
- * 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）
 $f = \frac{1}{e^{\beta E} + 1}$ 。但在非平衡态， $f = f(\vec{r}, \vec{v}, t)$ 。 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： $\lambda_T \ll \delta r$ ， $\lambda_T = \frac{\hbar}{(2\pi mk_B)^{1/2}}$ 一起以长距离运动可忽略。 δr 是碰撞平均距离。
 这时气体温度下 m 为 $(0^\circ C, 1 \text{ atm})$ 下 m 大量的气体构成。例如氢气 $n = 2.7 \times 10^{19} \text{ cm}^{-3}$ ，
 $\delta r \sim \sqrt{n} \sim 3.3 \times 10^{-7} \text{ cm}$

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

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

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

除了 ~~氢~~ 氢外低温 ~ 氦之外，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。我们在这里主要讲的主要内容：

- (1) Boltzmann eqs.; H 定理，嫡这一定律和
- (2) 朗之万原理论，统计和扩散 DT.
- (3) 朗之万理论：布朗运动，Master 方程， Langmuir eq.; 朗之万-玻尔兹曼原理

参考书：林宗桂，苏汝铿；巨阳亮白；
 徐致平和吴致仁。

(ii) 稀薄和强弱力： $\delta r \gg \alpha$ (粗作用)
 力学)，这样，气体在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“强”“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， $\delta r \sim 3.3 \times 10^{-7} \text{ cm}$ ，而粗作用是在单位质量力， $d \sim 10^{-8} \text{ cm}$ 。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) 稀薄和强弱地假设之作碰撞可能忽略。

为了得出 Boltzmann 方程，还需要进一步简化：

- i). 忽略碰撞，用刚球模型代替连续分子力。
- ii). 为了分子碰撞修正，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。

$$t \rightarrow t+dt, \text{ 3D 速度} \sim \text{变化量}$$

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

卷起来的“运动”和“碰撞”都写了开。

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

$d = \text{drift}$, 碰撞作用 $2m$ 漂移。

$c = \text{collision}$.

§8.2.1 原始波的计算

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

今年会随时
调整。

$$\therefore \frac{\partial f}{\partial t} = (\frac{\partial f}{\partial t})_d + \sum_i (\vec{v}_i \cdot \frac{\partial f}{\partial \vec{r}_i} + \vec{v}_i \cdot \frac{\partial f}{\partial \vec{v}_i}) \Rightarrow$$

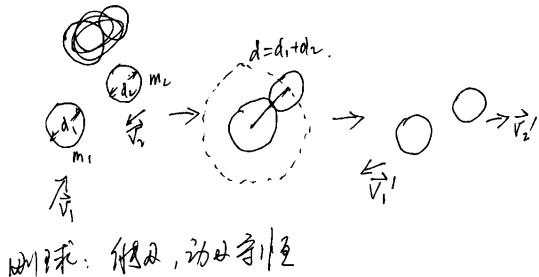
$$\Rightarrow (\frac{\partial f}{\partial t})_d = - \cancel{\text{图}} \vec{v} \cdot \frac{\partial f}{\partial \vec{r}} - \vec{v} \cdot \frac{\partial f}{\partial \vec{v}}$$

$$\cancel{\text{图}} \vec{v} = \vec{a} = \vec{f} \quad (= \text{单位化后的力})$$

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

§8.2.2 碰撞波的计算

碰撞波 - 什么需要考虑的。

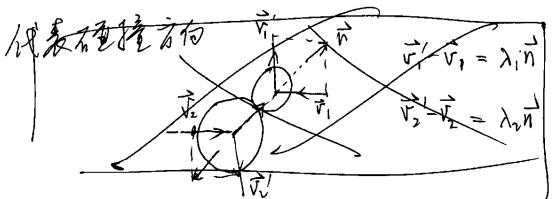


碰撞波：碰撞，动量守恒

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

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

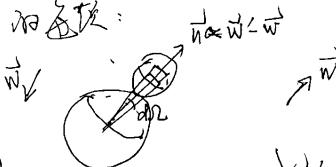
两个方程，两个未知数，还有二个任意数。所以



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（或见附录）。 (120')

现在，我们解解

$$(\frac{\partial f}{\partial t})_{\text{coll.}} = \int (f'_v f'_w - f_v f_w) \wedge d^3 \vec{w} d\Omega$$



$$\Lambda = \cancel{\text{图}} \frac{4\pi^2}{m_1 m_2} (\vec{v} - \vec{w}) / m_1 m_2 \quad f_v = f(\vec{r}, \vec{v}, t), \quad f_w = f(\vec{r}, \vec{w}, t)$$

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

$$\vec{v}' = \vec{v} + \frac{2m_w}{m_v + m_w} [(\vec{w} - \vec{v}).\vec{n}] \vec{n}$$

$$\vec{w}' = \vec{w} - \frac{2m_v}{m_v + m_w} [(\vec{w} - \vec{v}).\vec{n}] \vec{n}$$

$$\cancel{\text{图}} \quad \vec{v}'_1 - \vec{v}'_2 = \cancel{\lambda}_1 \vec{n} \quad (121)$$

$$\cancel{\text{图}} \quad \vec{v}'_1 - \vec{v}'_2 = \cancel{\lambda}_2 \vec{n}$$

$$\vec{n} = (\theta, \phi) \text{ 代表球面方向.}$$

(1) 在与之垂直的方向, $v_{\perp} = v_{\perp}'$, 表示速度不变。
“1”没有运动.) (斜着的方向, 正弦余弦)

上, $\cancel{\text{图}} \vec{v}_1 \cdot \vec{n} = \vec{v}'_1 \cdot \vec{n}$. 因为 $\vec{n} \perp \vec{e}$ (即 $m_1 \vec{v}_1 - m_2 \vec{v}_2$ 在 \vec{m} 的方向, 且 $m_1 \vec{v}'_1 - m_2 \vec{v}'_2 \propto \vec{F}$).

(2) 在 \vec{n} 的方向对于任意 $m \vec{v}$, 上面有的方程。(6个方程, 除速度 $v_{\perp} = v_{\perp}'$, 有 $6 \times 2 = 12$)

(3) 与解、动量守恒的方程合在一起, 8个方程, 有 8 个未知数 ($\vec{v}'_1, \vec{v}'_2, \lambda_1, \lambda_2$). 可解.

$$\vec{v}'_1 = \vec{v}_1 + \frac{2m_w}{m_1 + m_2} [(\vec{v}_2 - \vec{v}_1) \cdot \vec{n}] \vec{n}$$

$$\vec{v}'_2 = \vec{v}_2 - \frac{2m_1}{m_1 + m_2} [(\vec{v}_2 - \vec{v}_1) \cdot \vec{n}] \vec{n}$$

两式相减

$$\vec{v}'_2 - \vec{v}'_1 = \vec{v}_2 - \vec{v}_1 - 2 [(\vec{v}_2 - \vec{v}_1) \cdot \vec{n}] \vec{n}$$

$$\Rightarrow (\vec{v}'_2 - \vec{v}'_1)^2 = (\vec{v}_2 - \vec{v}_1)^2$$

$$(\vec{v}_2^2 = \vec{v}_1^2)$$

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， $\vec{v}'_1 = \vec{v}_1 + \vec{v}_2$

$$\vec{v}'_1 - \vec{v}_1 = \lambda_1 \vec{n} \Rightarrow \vec{v}'_1 - \vec{v}_1 = \lambda'_1 \vec{n},$$

$$\lambda'_1 (-\vec{n}) \Rightarrow \lambda'_1 = -\frac{\lambda_1}{n'}$$

$$\therefore \vec{v}'_1 = \vec{v}'_1 + \frac{2m_2}{m_1+m_2} [(\vec{v}'_2 - \vec{v}'_1) \cdot (-\vec{n})] (-\vec{n})$$

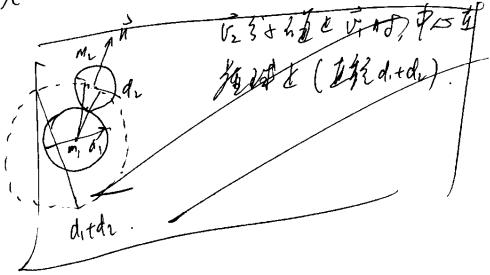
$$\vec{v}'_2 = \vec{v}'_2 - \frac{2m_1}{m_1+m_2} [(\vec{v}'_2 - \vec{v}'_1) \cdot (-\vec{n})] (\vec{n})$$

$$\text{即 } (\vec{v}'_2 - \vec{v}'_1) \cdot \vec{n} = -(\vec{v}'_2 - \vec{v}'_1) \cdot \vec{n} = (\vec{v}'_1 - \vec{v}'_2) \cdot \vec{n}$$

与正碰撞推反向。

VR系数计算 $(\frac{\partial f}{\partial t})_c$. 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 (出) d^3v_i 的分子，则撞击率为

$$(\frac{\partial f_i}{\partial t})_c dt d^3v_i = \Delta f_i^{(+)} - \Delta f_i^{(-)}$$



$\Delta f_i^{(+)}$ 为 d^3v_i 中 m_1 分子数减少: $(\vec{v}_1, \vec{v}_2) \rightarrow (\vec{v}'_1, \vec{v}'_2)$.

对立体角积分，即对 d^3v_i 积分，即是碰撞出 d^3v_i 中分子数.

$$\Delta f_i^{(+)} = \left[\int f_i f_2 \Lambda_{12} d\Omega d^3v_i \right] dt d^3v_i d^3v_2$$

同样， $(\vec{v}'_1, \vec{v}'_2, -\vec{n}) \rightarrow (\vec{v}_1, \vec{v}_2)$ 得出

$$\Delta f_i^{(-)} = \left[\int f'_i f'_2 \Lambda'_{12} d\Omega' d^3v'_i \right] d^3v'_1 dt d^3v_2$$

Λ'_{12} 为 Λ_{12} , $d\Omega'$ 为 $d\Omega$ 一样。只是积分要反过来。

$$d^3v'_1 d^3v'_2 = |J| d^3v_1 d^3v_2$$

$(\vec{v}_1, \vec{v}_2) \rightarrow (\vec{v}'_1, \vec{v}'_2)$ 是一个可逆变换。 $|J|=1$.

$$\therefore (\frac{\partial f_i}{\partial t})_c dt d^3v_i d^3v_2 = \Delta f_i^{(+)} - \Delta f_i^{(-)}$$

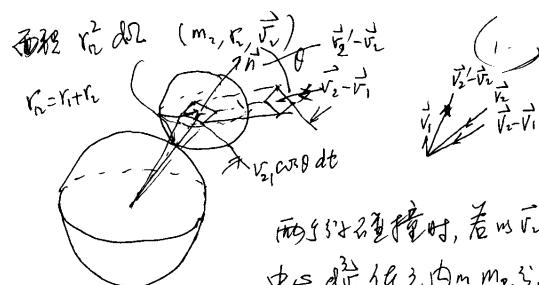
$$= \left[\int (f'_i f'_2 - f_i f_2) \Lambda'_{12} d\Omega' \right] dt d^3v_i d^3v_2$$

∴ Boltzmann 方程是

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

$$\frac{\partial f}{\partial t} + \vec{v} \cdot \frac{\partial f}{\partial \vec{r}} + \vec{f} \cdot \frac{\partial f}{\partial \vec{v}} = \int (f'_i f'_2 - f_i f_2) \Lambda'_{12} d\Omega' d^3v_2$$

$$f'_i = f(\vec{r}, \vec{v}', t), \quad f'_2 = f(\vec{r}, \vec{v}'_2, t).$$



而当发生碰撞时，若 \vec{v}_1 为
中 d^3v_i 体积内 m_1 分子
与 m_2 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，
则由碰撞导致 $v_{12}^2 d\Omega$ 为底，以 $v_{12} \cos \theta dt$
为高之体积内，该立体角内分子数为 $v_{12}^2 d\Omega v_{12} \cos \theta dt$
其中包含处于 $d\Omega$ 中 m_1 分子数为
 $(f_2 d^3v_2) v_{12}^2 d\Omega v_{12} \cos \theta dt$.

并乘以 m_1 与 m_2 的比

$$(f_1 d^3v_1) (f_2 d^3v_2) v_{12}^2 d\Omega v_{12} \cos \theta dt$$

= dt 时内， d^3v_i 中 m_1 分子数 $d\Omega$ 内 m_2
分子数 $d\Omega$ 中 m_1 分子数 $d\Omega$ 中 m_2 分子数。 $(\Delta f_i^{(+)})$

$$\Delta f_i^{(+)} = f_i f_2 d^3v_i d^3v_2 \Lambda_{12} d\Omega dt d^3v$$

$$\Lambda_{12} = v_{12}^2 v_{12} \cos \theta.$$

(f_i, f_2) 是相立相成， $\Delta f_i^{(+)}$ 是绝对值 (假设)

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

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

例如在信息论中用 Shannon 熵. 其实，这样“熵”
表达式起源于 Boltzmann. H 定义：

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

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

$$f = n \left(\frac{m}{2\pi k_B T} \right)^{3/2} \exp \left\{ - \frac{mv^2}{2k_B T} \right\}$$

$$\Rightarrow H = \int f \left(\ln n + \frac{3}{2} \ln \frac{m}{2\pi k_B T} - \frac{mv^2}{2k_B T} \right) d^3v d^3r$$

$$\left(\int f d^3r = n, \quad \frac{1}{n} \int \frac{mv^2}{2} f d^3r = \frac{3}{2} k_B T \right)$$

$$= N \left[\ln \frac{N}{V} + \frac{3}{2} \ln \left(\frac{m}{2\pi k_B T} \right) - \frac{3}{2} \right]$$

而单粒子理想气体大高。

$$S = N k_B \left[\ln \frac{N}{N} + \frac{3}{2} \ln T + \frac{5}{2} + \frac{3}{2} \ln \left(\frac{2\pi m}{k_B T} \right) \right]$$

$$\Rightarrow S = -k_B H + C$$

玻耳兹曼公理， $S \propto -H$ ，比例常数是 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 $f^{(0)}$ 是基底平行态。这样仍保持 f 的意义：设外力为 0， \therefore

$$\frac{\partial f}{\partial t} = - \pm \frac{f^{(0)}}{\tau} \quad \because f \text{ 为矢量}, \therefore$$

$$\textcircled{3} \quad \frac{df - f^{(0)}}{dt} = - \frac{f^{(0)}}{\tau}$$

$$f^{(0)}(+): f(\vec{v}, t) - f^{(0)}(\vec{v}) = [f(\vec{v}, 0) - f^{(0)}(\vec{v})] e^{-\frac{t}{\tau}}$$

τ 是~~平行~~平衡时间。

但 \vec{v} 有无穷多条至 $v \rightarrow \infty$, $\frac{\partial f(v)}{\partial v} \Big|_{v \rightarrow \infty} = 0$.

$\textcircled{4}$ ~~因为~~: $n = \int f d^3v = \text{finite}$.

\therefore dynamic 语义对 $\frac{dH}{dt}$ 有意义为 0.

$$\therefore \frac{dH}{dt} = - \int (1 + \ln f) (f_i f_i - f'_i f'_i) d\vec{v}_i d\vec{v}_i \lambda d\vec{v}_i d\vec{p}_i$$

$\therefore 1 \leftrightarrow 2$, 都是~~极点~~是 0. \therefore

$$\frac{dH}{dt} = - \int (1 + \ln f_i) (f_i f_i - f'_i f'_i) d\vec{v}_i d\vec{v}_i \lambda d\vec{v}_i d\vec{p}_i$$

$$\textcircled{5} \text{ 从 } \frac{dH}{dt}: \frac{dH}{dt} = - \frac{1}{2} \int (2 + \ln f_i f_i) (f_i f_i - f'_i f'_i) d\vec{v}_i$$

$$v'_i \leftrightarrow v_i, \quad \& d(\cdots)' = d(\cdots)$$

$$\Rightarrow \frac{dH}{dt} = - \frac{1}{2} \int (2 + \ln (f'_i f'_i)) (f'_i f'_i - f_i f_i) d\vec{v}_i$$

$\textcircled{6} \text{ 从 } \frac{dH}{dt}$:

$$\frac{dH}{dt} = - \frac{1}{4} \int \underbrace{[\ln(f_i f_i) - \ln(f'_i f'_i)]}_{\geq 0} (f_i f_i - f'_i f'_i) d\vec{v}_i$$

\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 $\textcircled{2}$ 从平行条件。

* 大高流和大高产生率 (瞬, 稳)

$\frac{ds}{dt} \geq 0$

8.4 Boltzmann 方程的应用

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， $f^{(0)}$ 由 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

同温度内平均速度分布

$$2 \times \frac{d\vec{p}}{h^3} f^{(0)}, 2 \text{ 来自 spin } \uparrow, \downarrow$$

Boltzmann eq. reads

$$\frac{\partial f}{\partial t} + \vec{v} \cdot \frac{\partial f}{\partial \vec{p}} + \vec{F} \cdot \frac{\partial f}{\partial \vec{p}} = - \frac{f - f^{(0)}}{\tau}$$

设在电场中的平衡分布中， $\vec{F} = -e\vec{E}$, \vec{E} 为电场强度， f 为~~平衡~~解 $\frac{\partial f}{\partial \vec{p}} \rightarrow 0$, $f = f^{(0)}$. \therefore

$$e\vec{E} \cdot \frac{\partial f}{\partial \vec{p}} = \frac{f - f^{(0)}}{\tau}, \quad f = f^{(0)} + f^{(1)} + \dots$$

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

$$\frac{\partial f^{(0)}}{\partial E} = \delta(E-\mu) f^{(0)}$$

$$\therefore J_e = \frac{2e^2 \tau C(\mu)}{3m} n D(\mu) E$$

$$\text{且 } n = \int_0^\mu D(E) dE$$

$$= \frac{2}{3} \mu D(\mu).$$

$$\therefore J_e = \frac{ne^2 \tau}{m} E, \quad \sigma = \frac{ne^2 \tau}{m}$$

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~磨擦机制, $H_e(t)$ 是一个 $\sim t$ 的扰场.
我们用力学方式研究问题. 研究 m 的磨擦力 \vec{H}_e

$$\text{Schrödinger eq.: } i\hbar \frac{\partial}{\partial t} \Psi = (H_0 + H_e) \Psi.$$

假定 Ψ 为 $\Psi(t)$,

$$\Psi(t) = e^{i\frac{H_0}{\hbar}t} \Psi(0), \quad \text{Sch. eq. true}$$

$$\therefore \left(-i\frac{H_0}{\hbar} \right) e^{-i\frac{H_0}{\hbar}t} \Psi(0) + i\hbar e^{-i\frac{H_0}{\hbar}t} \dot{\Psi}$$

$$= \text{在 } H_0 e^{-i\frac{H_0}{\hbar}t} \Psi(0) + H_e e^{-i\frac{H_0}{\hbar}t} \Psi$$

$$\Rightarrow \dot{\Psi} = \frac{1}{i\hbar} \left(e^{i\frac{H_0}{\hbar}t} H_e(t) e^{-i\frac{H_0}{\hbar}t} \right) \Psi \equiv \frac{1}{i\hbar} \tilde{H}_e(t) \Psi$$

$\tilde{H}_e(t) \rightarrow -\infty$ 时, $\Psi(t) = \Psi_m$, 是 Schrödinger eq.
 m -子宏表达. ($t \rightarrow -\infty, H_e(t) = 0, H_0 \Psi_m = E_m \Psi$)

开始上,

$$\varphi(t) = \phi_m + \frac{1}{i\hbar} \int_{-\infty}^t \tilde{H}_e(t') \varphi(t') dt'$$

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

$$\varphi(t) = \phi_m + \int_{-\infty}^t \tilde{H}_e(t') \left(\phi_m + \int_{-\infty}^{t'} \tilde{H}_e(t'') \phi(t'') dt'' \right) dt'$$

对 \tilde{H}_e 做线性近似, 就是 ② 上述的 ③ 和 ④ 的近似

$$\tilde{H}_e \sim \text{阶}: \varphi(t) \approx \phi_m + \int_{-\infty}^t \tilde{H}_e(t') \phi_m dt'$$

$$\bar{A}_m = \bar{A}(t) \approx \int d\vec{r} \phi_m^* A(t) \phi_m$$

$$+ \frac{1}{i\hbar} \int_{-\infty}^t dt' \int d\vec{r} d\vec{r}' [\bar{A}(t), \tilde{H}_e(t')] \phi_m$$

$$\bar{A}(t) - \bar{A}_m < m |A|_m > = \frac{1}{i\hbar} \int_{-\infty}^t dt' < m |[A(t), \tilde{H}_e(t')]>$$

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 (Kubo-Greenwood 理论) 表示出. (见苏进强书), 和邵书.)

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 $\vec{r} - \vec{r}', t \rightarrow 0$ 附近

$$K_{ab} = -\frac{e^2 n}{m} \delta(\vec{r} - \vec{r}') \delta(t - t') \delta_{ab}$$

$$+ i \langle [j_a(\vec{r}, t), j_b(\vec{r}', t')] \rangle \delta(t - t')$$

④ Fourier 变换

$$\langle j_a(\vec{r}, t) \rangle = \int \frac{d^3 k dv}{(2\pi)^4} j_a(\vec{k}, v) e^{i\vec{k} \cdot \vec{r} - ivt}$$

$$\boxed{K_{ab}(\vec{r} - \vec{r}', t - t')} = \int \frac{d^3 k dv}{(2\pi)^4} K_{ab}(\vec{k}, v) e^{i\vec{k} \cdot (\vec{r} - \vec{r}') - iv(t - t')}$$

$$A_b(\vec{k}, v) = \int \frac{d^3 k dv}{(2\pi)^4} A_b(\vec{k}, v) e^{i\vec{k} \cdot \vec{r} - ivt}$$

$$\boxed{j_a(v) = \sum_{b=1}^3 K_{ab}(0, v) A_b(0, v)}$$

看电场是空间均匀的

$$A_b(0, v) = \frac{1}{3v} E_b(v) \delta(\vec{k})$$

$$j_a(v) = \sum_{b=1}^3 K_{ab}(0, v) E_b(v) / \sqrt{v}$$

$$\boxed{\sigma_{ab}(v) = \frac{1}{v} K_{ab}(0, v)} \text{ 是电导率张量.}$$

$$\text{波动分析: } \sigma_e = \frac{e^2}{3v} \int_0^\infty dt \int_0^\infty d\vec{x} \text{Tr} \vec{J} \cdot \vec{J} e^{-iLt} \rho_0.$$

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， ψ_0 与 $\delta\psi$ 平行。我们称体系受到热力学扰动（ β 和 μ ）作用时 Hamiltonian 是

$$\begin{aligned} H &= \int H(\vec{r}) d\vec{r} \\ (\text{或 } \vec{p} = m\vec{v}, \vec{p} = -i\hbar\nabla) \quad H(\vec{r}) &= \sum_{i=1}^N E_i \delta(\vec{r} - \vec{r}_i) \\ E_i &= \frac{p_i^2}{2m} + \frac{1}{2} \sum_{j \neq i} U(\vec{r}_i - \vec{r}_j) \end{aligned}$$

(S) 表示的由 $\int d\vec{r} N(\vec{r})$

$d\vec{r}$ 是一个微元，宏观上代表之，在 $d\vec{r}$ 内，体系是 ψ_0 和 $\delta\psi$ 的线性组合， ψ_0 对每一个 local， $\delta\psi$ 对每一个 $d\vec{r}$ 都是平行的。

$$\psi(\vec{r}) \sim \psi_0(\vec{r}) + \delta\psi(\vec{r})$$

$$P(\vec{r}) \sim e^{-\beta(\vec{r})} H_0(\vec{r})$$

$$H_0(\vec{r}) = H(\vec{r}) - \mu(\vec{r}) N(\vec{r})$$

系统处于局域平衡态的密度矩阵为 (14)

$$\rho_L = N_L^{-1} e^{-\beta S_Q}$$

$$S_Q = \int \beta(\vec{r}) [H(\vec{r}) - \mu(\vec{r}) N(\vec{r})] d\vec{r}$$

N_L 是归一化常数， $\beta(\vec{r}) = 1/k_B T(\vec{r})$ ， $N(\vec{r})$ 是 local 波函数。 $T(\vec{r})$ ， $\mu(\vec{r})$ 在空间各处的值保证了 ψ_0 和 $\delta\psi$ 平行。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：

$$\rho = \rho_L + \delta\rho,$$

P 流通列微方程。

$$\frac{\partial \rho}{\partial t} = \dots, [H_0, \rho] = L\rho$$

//

$$\frac{\partial \delta\rho}{\partial t} = L\rho_L + L\delta\rho$$

$$\therefore \delta\rho(t) = \frac{i}{\hbar} \int_{-\infty}^t dt' e^{-iL(t-t')/\hbar} \delta\rho(0) e^{iL(t-t')/\hbar} \quad (\text{取 } \hbar=1).$$

$$[H, \rho_L] = [H, \frac{1}{N_L} e^{-S_Q}]$$

$$= \frac{1}{N_L} [H, -S_Q] + \frac{1}{N_L} [H, (S_Q)_{h.c.}] + \dots$$

$$= -LS_Q + \frac{1}{N_L} [LS_Q] S_Q + \dots$$

$$= -LS_Q \left(\frac{1}{N_L} (1 - S_Q + \dots) \right) = -LS_Q \rho_L.$$

(由于 LS_Q 和 $\frac{\partial \beta}{\partial t}$ 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： $\frac{\partial H(\vec{r})}{\partial t} + \nabla \cdot \vec{J}(\vec{r}) = 0$

守恒律： $\frac{\partial N}{\partial t} + \nabla \cdot \vec{J}(r) = 0$.

$$\Rightarrow -\frac{i}{\hbar} L H(\vec{r}) = -\nabla \cdot \vec{J}(\vec{r}), -\frac{i}{\hbar} L N(\vec{r}) = -\nabla \cdot \vec{J}(\vec{r})$$

$\vec{J}(\vec{r})$ 和 $\vec{J}(\vec{r})$ 是能流和守恒流。

(14)

$$\delta\rho = -\frac{i}{\hbar} \int_{-\infty}^t dt' (L\rho_L + L\delta\rho(t'))$$

(14) 时代入

$$\delta\rho = -\frac{i}{\hbar} \int_{-\infty}^t dt' L\rho_L + -\frac{i}{\hbar} \int_{-\infty}^t dt' \left(\frac{i}{\hbar} \int_{-\infty}^{t'} dt'' L \delta\rho_L + L\delta\rho(t') \right)$$

$$= -\frac{i}{\hbar} \int_{-\infty}^t dt' L\rho_L + \left(\frac{i}{\hbar} \right)^2 \int_{-\infty}^t dt' L \left(\frac{i}{\hbar} \int_{-\infty}^{t'} dt'' L \delta\rho_L \right) + L\delta\rho(t')$$

$$+ \left(\frac{i}{\hbar} \right)^3 \int_{-\infty}^t dt' L \int_{-\infty}^{t'} dt'' L \int_{-\infty}^{t''} dt''' L \delta\rho_L + \dots$$

$$\equiv -\frac{i}{\hbar} \int_{-\infty}^t dt' e^{-\frac{i}{\hbar} L(t-t')} L\rho_L = -\frac{i}{\hbar} \int_0^t e^{-\frac{i}{\hbar} L(t-t')} L\rho_L dt'$$

$$\cancel{\frac{i}{\hbar} L \rho} \quad S_Q = -\frac{i}{\hbar} LS_Q$$

$$= -\frac{i}{\hbar} \left[H, \int \beta(\vec{r}) (H(\vec{r}) - \mu(\vec{r}) N(\vec{r})) d\vec{r} \right]$$

$$= -\frac{i}{\hbar} [H, \bar{\beta} S_Q] + -\frac{i}{\hbar} \left[H, \int \frac{\partial \beta(\vec{r})}{\partial \vec{r}} \cdot \nabla (H - \bar{\mu} N) d\vec{r} \right]$$

$$= \cancel{\frac{i}{\hbar} \beta} = -\frac{i}{\hbar} L \int \frac{\partial \beta}{\partial \vec{r}} \cdot \nabla (H - \bar{\mu} N) d\vec{r}$$

β 正比于 $\bar{\beta}$ 或 βM 的梯度。

$$\therefore L_{\vec{B}} = \frac{1}{i} \int d\vec{r} \vec{B}$$

$$\begin{aligned} L_{\vec{B}, L} &= -i \int d\vec{r} [\beta(\vec{r}) \nabla \cdot \vec{Q}(\vec{r}) - \beta^{\mu} \nabla \cdot \vec{J}(\vec{r})] \rho_0 \\ &\Rightarrow i \int d\vec{r} [\vec{Q} \cdot \nabla \beta(\vec{r}) - \vec{J} \cdot \nabla (\beta^{\mu})] \rho_0 \\ &= i \int d\vec{r} [\vec{J}_e \cdot \nabla \beta - \beta \left(\frac{\partial \mu}{\partial n} \right) \vec{J} \cdot \nabla n] \rho_0 \\ &\quad \vec{J}_e = \vec{Q}(\vec{r}) - h \vec{J}(\vec{r}), h = \mu - T \left(\frac{\partial \mu}{\partial T} \right)_n. \end{aligned}$$

$h(\vec{r})$ 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) 研究中的基本原理. 这里的背景是随机布朗运动.

若 \vec{J} 只有 \vec{J}_e 是平均场. (1.1)

$$\langle \vec{B} \rangle = \frac{1}{V} \int_0^\infty dt \text{Tr} \vec{B} e^{-iLt} \left[\vec{J}_e \cdot \nabla \beta - \beta \left(\frac{\partial \mu}{\partial n} \right) \vec{J} \cdot \nabla n \right] \rho_0.$$

$$\vec{B} = \int d\vec{r} \vec{B}(\vec{r}), \vec{J} = \int d\vec{r} \vec{J}(\vec{r}), \vec{J}_e = \int d\vec{r} \vec{J}_e(\vec{r}).$$

若只有 \vec{J}_e 项, 但 $\vec{J} = 0$, 则 $\vec{J}_e = \vec{Q}$, $\vec{J} = \vec{Q}$, 则 $\langle \vec{B} \rangle = \frac{1}{V} \int_0^\infty dt \cancel{\int d\vec{r} \vec{J}(\vec{r})} \text{Tr} (\chi \beta \cdot \vec{Q}) \vec{Q} e^{-iLt} \rho_0.$

$$\begin{aligned} \langle \vec{Q} \rangle &= \cancel{K \nabla T} = \cancel{K \nabla \frac{\partial \mu}{\partial n}} + \cancel{K \nabla \frac{\partial \mu}{\partial T}} \vec{Q} \\ &= K \nabla \vec{T} \end{aligned}$$

$$\langle \vec{Q} \rangle = -K \nabla T = -K \nabla \frac{\partial \mu}{\partial n} = +K \nabla^2 \nabla \beta \quad (k_B = 1)$$

另一方面, $(\chi \beta \cdot \vec{Q}) \vec{Q} = A(\vec{A} \cdot \vec{Q}) \vec{Q} = (A_x Q_x \delta_{xy} + A_y Q_y \delta_{xy} + A_z Q_z \delta_{xy})$
因为 $Q_x Q_y \delta_{xy} = 0$. $= A_x Q_x Q_x \Rightarrow A_x Q_x Q_x + Q_y Q_y + Q_z Q_z$

$$\therefore \langle \vec{Q} \rangle = \underbrace{\left(\frac{1}{3k_B T^2 V} \int_0^\infty \text{Tr} \vec{Q} \cdot \vec{Q} e^{-iLt} \rho_0 dt \right)^{\frac{1}{2}}}_{K \text{ 扩散}} \nabla \beta$$

§ 8.4 电流密度: ~~物理量~~ 153

因为在一般近代物理学中都是单独讲一章. 但在本书中却将它归到近代物理里. 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这一章. 因为这与电荷守恒定律有关. 由物质的运动引起. ~~物理量~~ 153

另一类是随外力引起. 这是一般流体力学. 在讲电荷守恒时, 我们说正电荷守恒与电流密度, 通过电荷守恒而守恒:

$$\sqrt{E-E_0}/E \sim \frac{1}{\sqrt{N}}$$

互电荷守恒 ($n = \frac{N}{V}$ fixed when N and $V \rightarrow \infty$). 这种广义的守恒叫电荷守恒. 在互电荷守恒, 可以同时有电场和扩散的守恒. 都 $\sim \frac{1}{\sqrt{N}}$. 这些 ~~守恒~~ 用到了有微扰论的广义电荷守恒, 这些计算很直接, 但一些没有微扰论方法, 例如精确强反演守恒, 不适用. 在这里我们介绍 ~~电荷守恒~~ 以及讨论它们的 ~~电荷守恒~~ 及讨论它们的 ~~电荷守恒~~.

§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 $\Delta E + \Delta E_e = 0, \Delta V + \Delta V_e = 0$.

$e^{\Delta S/k_B}$ 表示外部分子数 $(E_e + V_e)$ 对 $(E + V)$ 的贡献.

$$\therefore W_T = W_{T,\max} = e^{(\Delta S + \Delta S_e)/k_B}$$

$$= W_{\max} e^{(\Delta S + \frac{\Delta E_e + \frac{\partial p}{\partial V} \Delta V_e}{T})/k_B}$$

$$= W_{\max} e^{(\Delta S - \Delta E - p\Delta V)/k_B T}$$

$$= W_{\max} e^{-(\Delta F + p\Delta V)/k_B T}$$

$$\Delta F = \left(\frac{\partial F}{\partial V} \right)_{T,P} \Delta V + \frac{1}{2} \left(\frac{\partial^2 F}{\partial V^2} \right)_T (\Delta V)^2 + \dots$$

$$- \frac{\partial F}{\partial P} \Delta P - \frac{\partial F}{\partial T} \Delta T$$

由理想气体 $M = \rho V$ 及 $M = \rho V / (1 - \frac{p}{p_0})$.

$$\Rightarrow \Delta M = \Delta p V + p \Delta V = 0 \Rightarrow \frac{\Delta p}{p} = - \frac{\Delta V}{V}$$

$$\therefore \frac{(\Delta p)^2}{p^2} = \frac{(\Delta V)^2}{V^2} = - k_B T \left(\frac{\partial V}{\partial p} \right)_T$$

$$p = \frac{N \rho}{V}, \text{ 而 } V \text{ 固定, } \text{ 则 } \Delta p \propto \Delta N.$$

$$\therefore \frac{(\Delta N)^2}{N^2} = \frac{(\Delta p)^2}{p^2} = - \frac{k_B T}{V^2} \left(\frac{\partial V}{\partial p} \right)_T.$$

一般

$$\Delta p = \frac{\Delta N}{V} - \frac{N \Delta V}{V^2}$$

$$(\Delta p)^2 = \left(\frac{\Delta N}{V} \right)^2 - 2 \frac{\Delta N \Delta p}{V^3} N + \frac{N^2 (\Delta V)^2}{V^4}$$

$$\frac{(\Delta p)^2}{p^2} = \frac{(\Delta N)^2}{N^2} + \frac{(\Delta N)^2}{N^2} = 2 \left(\frac{\Delta N}{N} \right)^2.$$

$$\text{对理想气体, } \left(\frac{\partial V}{\partial p} \right)_T = - \frac{1}{p} = - \frac{V^2}{N k_B T}$$

$$\Rightarrow \frac{(\Delta p)^2}{N^2} - \frac{k_B T}{V^2} \left(- \frac{V^2}{N k_B T} \right) \propto \frac{1}{N}.$$

与理想气体结果一致.

$$W_T \approx W_{\max,T} \exp \left(\frac{1}{2k_B T} \left(\frac{\partial p}{\partial V} \right)_T (\Delta V)^2 \right)$$

这把玻尔兹曼分布看成准经典概率. 但当 V 相对于 ΔV 很大时可以忽略.

$$\overline{(\Delta A)^2} = \int (\Delta A)^2 W d(\Delta A) / \int W d(\Delta A) \text{ 和 } 1.$$

$$\text{则 } \overline{(\Delta V)^2} = \frac{\int_{-\infty}^{+\infty} (\Delta V)^2 \exp \left[- \frac{1}{2k_B T} \left(\frac{\partial p}{\partial V} \right)_T (\Delta V)^2 \right] d(\Delta V)}{\int_{-\infty}^{+\infty} \exp \left[- \frac{1}{2k_B T} \left(\frac{\partial p}{\partial V} \right)_T (\Delta V)^2 \right] d(\Delta V)}$$

$$= \frac{\int_{-\infty}^{+\infty} (\Delta V)^2 \frac{k_B T}{(\frac{\partial p}{\partial V})_T} \frac{1}{2\pi} d(\exp \left(- \frac{1}{2k_B T} \left(\frac{\partial p}{\partial V} \right)_T (\Delta V)^2 \right))}{\int_{-\infty}^{+\infty} \exp \left(- \frac{1}{2k_B T} \left(\frac{\partial p}{\partial V} \right)_T (\Delta V)^2 \right) d(\Delta V)}$$

$$= \Rightarrow \frac{\Delta V (k_B T)}{(\frac{\partial p}{\partial V})_T} \exp \left(- \frac{1}{2k_B T} \left(\frac{\partial p}{\partial V} \right)_T (\Delta V)^2 \right) \Big|_{\Delta V=0}^{+\infty}$$

$$- k_B T \left(\frac{\partial V}{\partial p} \right)_T = - k_B T \left(\frac{\partial V}{\partial p} \right)_T.$$

$$\therefore \frac{(\Delta V)^2}{V^2} = - \frac{k_B T}{V^2} \left(\frac{\partial V}{\partial p} \right)_T.$$

以上计算得到的结果是正确的. 因为 $\Delta V = \frac{1}{2} \frac{\partial V}{\partial p} \Delta p$.

$$\Delta V = - p \Delta V - \frac{1}{2} \left(\frac{\partial^2 p}{\partial V^2} \right)_T (\Delta V)^2 + \dots$$

$$\therefore W = W_{\max} \exp [-\alpha X^2],$$

$$\alpha = \frac{1}{2k_B T} \left| \left(\frac{\partial^2 V}{\partial p^2} \right)_T \right|, \quad X = \Delta V.$$

$$\overline{(\Delta V)^2} = \frac{\int_0^\infty X^2 e^{-\alpha X^2} dX}{\int_0^\infty e^{-\alpha X^2} dX} = \frac{\Gamma(\frac{3}{2})}{\Gamma(\frac{1}{2})} \frac{1}{\alpha^{\frac{1}{2}}} = 0.338 \left[\frac{1}{2k_B T} \left(\frac{\partial^2 V}{\partial p^2} \right)_T \right]^{\frac{1}{2}}$$

对实际气体情况,

$$p_C = \frac{a}{27 b^2}, \quad V_C = 3b, \quad T_C = \frac{8a}{27 b R}.$$

$$\text{理想气体方程: } (p + \frac{a}{V})(V - b) = RT$$

$$\Rightarrow p = \frac{3RT}{3V - V_C} - \frac{9RT_C V_C}{8V^2}$$

$$\therefore V = \frac{N}{N_A} V, \quad (V_C = \frac{N}{N_A} V_C), \quad N_A = 6.02 \times 10^{23}$$

$$p = \frac{3NkT}{3V - V_C} - \frac{9NkT_C V_C}{8V^2}$$

$$\left(\frac{\partial p}{\partial V^3} \right)_T = - \frac{48NkT}{(3V - V_C)^4} + \frac{27NkT_C V_C}{V^5}, \quad \left(\frac{\partial p}{\partial V} \right)_{T,C} = - \frac{27NkT_C}{8V_C^4}$$

$$\left(\frac{\Delta V}{V}\right)_c = 0.338 \left[-\frac{V^4}{24kT_c} \left(\frac{\partial^3}{\partial V^3} \right)_{T_c} \right]^{-k}$$

$$= 0.901 / \text{km}$$

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吸收
时，散射的强度

$$\langle I \rangle \propto \frac{1}{x^2} \frac{\Delta V^2}{V^2},$$

没有吸收的话，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
漫射强度最大的是蓝色的 \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
称它为太阳蓝天了。

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

$$\langle I \rangle \propto \frac{1}{x^2} V \left[-\frac{V^4}{24kT} \left(\frac{\partial^3}{\partial V^3} \right)_T \right]^{-k}$$

与漫射的比正常情况下大很多倍。

液体透明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 $\langle n(r) n(r') \rangle$ 与 $\langle n(r) \rangle$ 和 $\langle n(r') \rangle$ 的关系。
但经典统计力学理论没有考虑到临界层附近
立线的用密度子理论描述立临界层附近的
密度时考虑关联。具体计算关联函数，现在我们着手于

$$\begin{aligned} \text{定义 density-density correlation function} \\ C(\vec{r}, \vec{r}') &= \langle (n(\vec{r}) - \langle n(\vec{r}) \rangle)(n(\vec{r}') - \langle n(\vec{r}') \rangle) \rangle \\ &= \langle \Delta n(\vec{r}) \Delta n(\vec{r}') \rangle. \end{aligned}$$

$$\langle \Delta n(\vec{r}) \rangle = 0.$$

∴ $\Delta n(\vec{r})$ 与 $\Delta n(\vec{r}')$ 是独立的，即 $C(\vec{r}, \vec{r}')$

$$= \langle \Delta n(\vec{r}) \rangle \langle \Delta n(\vec{r}') \rangle = 0 \Rightarrow \text{无关联}.$$

$C(\vec{r}, \vec{r}') \neq 0$, 但不同地方的浓度有差异。

考虑均勻液体， $\langle \Delta n(\vec{r}) \rangle = \bar{n}$, 与无关。由平均
意义， $C(\vec{r}, \vec{r}') = C(\vec{r}-\vec{r}')$, 呈负向关联。

$$C(\vec{r}-\vec{r}') = C(|\vec{r}-\vec{r}'|), \text{且随距离有关}.$$

∴ $x=0$ 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。

$$\text{则 } 3: \quad \bar{x}^2 = \sqrt{\frac{3}{2\pi k_B T}} \int_{-\infty}^{+\infty} x^2 e^{-\frac{3x^2}{2k_B T}} dx = \frac{k_B T}{3}.$$

$$\therefore 3^2 = k_B T / \bar{x}^2, \quad \therefore$$

$$W(x) dx = \frac{1}{\sqrt{2\pi k_B T}} e^{-\frac{x^2}{2k_B T}} dx.$$

* 正态分布可以推广到多维。

* 正态分布对 n 在小体积中 $n \gg n - \bar{n}$.

-般情况下，用泊松分布。

且 $\Delta n(\vec{r}) = 0$,

$$C(\vec{r}) = \langle \Delta n(\vec{r}) \Delta n(0) \rangle$$

$$\text{设 } \Delta n(\vec{r}) = \frac{1}{V} \sum_i \tilde{n}_i e^{i\vec{q} \cdot \vec{r}}$$

$$\Delta n^*(\vec{r}) = \Delta n(\vec{r}) \Rightarrow \tilde{n}_i^* = \tilde{n}_i$$

$$|\tilde{n}_i|^2 = \int d\vec{r} d\vec{r}' \langle \Delta n(\vec{r}) \Delta n(\vec{r}') \rangle e^{-i\vec{q} \cdot (\vec{r}-\vec{r}')}}$$

$$\begin{aligned} \langle |\tilde{n}_i|^2 \rangle &= \int d\vec{r} d\vec{r}' \langle \Delta n(\vec{r}) \Delta n(\vec{r}') \rangle e^{-i\vec{q} \cdot (\vec{r}-\vec{r}')} \\ &= V \int d\vec{R} \langle \Delta n(\vec{R}) \Delta n(0) \rangle e^{-i\vec{q} \cdot \vec{R}} = V C(\vec{q}). \end{aligned}$$

$$\therefore C(\vec{r}) = \frac{1}{V} \sum_i \langle |\tilde{n}_i|^2 \rangle e^{i\vec{q} \cdot \vec{r}}$$

$$\begin{aligned} \text{由 } f(\vec{r}) = & - (AF + pV)/kT \\ \text{由 } W = W_{\max} e^{- (AF + pV)/kT} &= W_{\max} e^{- AF/kT} \\ \text{由 } AF = \int d\vec{R} d\vec{r} \Delta f &= \frac{1}{2V} \sum_{\vec{q}, \vec{R}} \tilde{n}_i^* \tilde{n}_i \left(\frac{a}{2} + \frac{b}{2} \vec{q} \cdot \vec{R} \right) \delta_{\vec{q}, \vec{R}} \end{aligned}$$

$$AF = \int (f - \bar{f}) d\vec{r}$$

$f(\vec{r})$ 是单位体积 local Free energy. 若 T 固定,

则 Δf 可视作 Δn 的函数:

$$\Delta f = \frac{a}{2} (\Delta n)^2 - \frac{b}{2} (\Delta n). \quad \left(\int_{n=0}^{\infty} (n - \bar{n})^2 d\bar{n} = \frac{b}{2} \right)$$

(~~由 $\Delta f = \frac{1}{2} (\Delta n)^2$~~ , 由 $\Delta f = \frac{1}{2} (\Delta n)^2$ 得 $\Delta n = \frac{1}{2} (\Delta f)^{1/2}$)

$\langle \Delta n \rangle$ 与 Δf 在空间依赖. 而 Δf 为 0.

这与 Landau-Ginzburg 理论.

$$\begin{aligned} \langle |\tilde{n}_i|^2 \rangle &= \int d\vec{q} d\vec{R} |\tilde{n}_i|^2 W / \int d\vec{q} d\vec{R} W. \quad (16) \\ &\stackrel{(1)}{=} \int_{-\infty}^{+\infty} d\vec{q} |\tilde{n}_i|^2 W / \int_{-\infty}^{+\infty} d\vec{q} W \quad (\text{Gauss 分布}) \\ &= \frac{V k T}{a + b \vec{q}^2}. \\ \therefore C(\vec{r}) &= \frac{k T}{V} \sum_i \frac{1}{a + b \vec{q}^2} e^{i\vec{q} \cdot \vec{r}} \\ &= \Rightarrow k T \frac{1}{(2\pi)^3} \int d\vec{q} \frac{1}{a + b \vec{q}^2} e^{i\vec{q} \cdot \vec{r}} \\ &= \frac{k T}{(2\pi)^3} \int_0^{2\pi} dq \frac{1}{a + b q^2} \int_0^\pi d\theta e^{iqr \cos\theta} \\ &= \frac{k T}{4\pi b} \frac{1}{r} e^{-r/\sqrt{a}}, \quad \beta = \sqrt{\frac{b}{a}}, \sim (T - T_c)^{1/2}. \end{aligned}$$

这与 mean field 结果一致.

至 ~~此~~ 讨论完后, 接着讲冲高型分子扩散, $D(\vec{q})$ 在对数坐标系中, ~~至~~ 立情况是渐近的, 这可由 $\langle |\tilde{n}_i|^2 \rangle$ 推导.

由热力学, $a = \frac{1}{h} \left(\frac{\partial P}{\partial n} \right)_T$ (见教书 57 页)

而到常温时 $\left(\frac{\partial P}{\partial n} \right)_T = 0 \therefore a = a_0 (T - T_c)$.

$$\begin{aligned} \nabla n(\vec{r}) &= \nabla \Delta n(\vec{r}) = \frac{1}{V} \sum_i \tilde{n}_i^* \tilde{n}_i e^{i\vec{q} \cdot \vec{r}} \\ &= \frac{1}{V} \sum_i \tilde{n}_i^* \tilde{n}_i e^{i\vec{q} \cdot \vec{r}} = \frac{1}{V} \sum_i \tilde{n}_i^* (-\vec{q}) e^{-i\vec{q} \cdot \vec{r}} \\ \langle \nabla n(\vec{r}) \rangle &= \frac{1}{V} \sum_{\vec{q}} \tilde{n}_i^* \tilde{n}_i e^{-i(\vec{q} \cdot \vec{r})} \end{aligned}$$

$$\therefore \Delta f = \frac{1}{V} \sum_{\vec{q}, \vec{R}} \tilde{n}_i^* \tilde{n}_i \left(\frac{a}{2} + \frac{b}{2} \vec{q} \cdot \vec{R} \right) e^{-i(\vec{q} \cdot \vec{r})}$$

$$\begin{aligned} \Delta F &= \int d\vec{R} d\vec{q} \Delta f = \frac{1}{2V} \sum_{\vec{q}, \vec{R}} \tilde{n}_i^* \tilde{n}_i \left(\frac{a}{2} + \frac{b}{2} \vec{q} \cdot \vec{R} \right) \delta_{\vec{q}, \vec{R}} \\ &= \frac{1}{2V} \sum_{\vec{q}} (a + b \vec{q}^2) |\tilde{n}_i|^2. \end{aligned}$$

$$\therefore W = W_{\max} \exp \left(- \frac{1}{2kT} \sum_{\vec{q}} (a + b \vec{q}^2) |\tilde{n}_i|^2 \right)$$

$$= W_{\max} \exp \left(- \frac{a + b \beta^2}{2kT} |\tilde{n}_i|^2 \right).$$

这行式子表明, 宏观性质在空间是 local 的. 不同 \vec{q} 间 W 之间是独立的. 是 Gauss 分布. (小尺寸的).

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 1827 年, 德国植物学家布朗观察到花粉颗粒的随机运动. 后来斯托克斯在 1856 年正确地解释了布朗运动. 对分子相互作用, 或说物化序子之间的作用有重要作用. 现在, “布朗运动”代表广义的“微粒”在广泛的随机“场”作用下随乱运动. 是一美丽的物理学现象.

3.8.1.2 布朗方程

用布朗方程可以对布朗运动作一些推导——理解: ~~由~~ 布朗方程 布朗时间 $\sim 10^{-5} - 10^{-4}$ cm

~~由~~ 大于 τ . 由 ~~由~~ 两种力作用

① 空气阻力 F_f , 摩擦, 动力, 引力, 波阻—粘滞力, 等.

② 由空气密度 ρ , 相对速率 v , 例 10^4 cm/s, $F_f \sim 10^{-4}$ N, $\rho \sim 1.2 \text{ kg/m}^3$, $v \sim 10^{-2} \text{ m/s}$, $F_f \sim 10^{-18}$ N, $\tau \sim 10^{-4}$ s. \therefore 由这种力为随机力 F_r .

Advanced Statistics Mechanics

∴ 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.

$$m \frac{dx}{dt} = -\alpha x \frac{dx}{dt} + X(t),$$

$$\frac{m}{2} \frac{d^2x}{dt^2} - m \left(\frac{dx}{dt} \right)^2 - \frac{\alpha}{2} \frac{d^2x}{dt^2} + X(t)$$

对大数布朗运动求解可得

$$\frac{m}{2} \frac{d^2}{dt^2} \langle x^2 \rangle - m \langle \dot{x}^2 \rangle = -\frac{\alpha}{2} \frac{d \langle x^2 \rangle}{dt} + \langle x \dot{x} \rangle = 0.$$

由能的泛定, $m \bar{v}^2 = kT$.

$$\frac{d^2}{dt^2} \langle x^2 \rangle + \frac{1}{\tau} \frac{d}{dt} \langle x^2 \rangle - \frac{2kT}{m} = 0, \quad \tau = \left(\frac{\alpha}{m} \right)^{-1}$$

$$\Rightarrow \langle x^2 \rangle = \frac{2kT}{m} t + C_1 e^{-t/\tau} + C_2.$$

若至 $t=0$, $\langle x^2 \rangle$ 和 $\frac{d}{dt} \langle x^2 \rangle = 0$. 则

$$\langle x^2 \rangle = \frac{2kT}{m} \left(\frac{t}{\tau} - (1 - e^{-t/\tau}) \right)$$

$$\begin{aligned} \therefore n(x, t+\tau) &= \int_{-\infty}^{+\infty} f(x-x', \tau) n(x', t) dx' \\ &= \int_{-\infty}^{+\infty} f(z, \tau) n(x-z, t) dz \\ x \cdot x' &\quad \text{且} \int_{-\infty}^{+\infty} dx f(x, \tau) = 1 \\ x-x' &\\ z & \\ \therefore n(x, t+\tau) &= f(-x, \tau). \end{aligned}$$

又很慢, 则

$$n(x, t+\tau) = n(x, t) + \tau \frac{\partial n}{\partial t} + \frac{1}{2} \tau^2 \frac{\partial^2 n}{\partial t^2} + \dots$$

$$\text{设 } \frac{\partial}{\partial t} n(x, t) \text{ 在 } t \text{ 处很快}, \therefore$$

$$n(x, t+\tau) = n(x, t) - 3 \frac{\partial n}{\partial x} + \frac{1}{2} \tau^2 \frac{\partial^2 n}{\partial x^2} + \dots$$

$$n(x, t+\tau) \approx n(x, t) + \tau \frac{\partial n}{\partial t} + \frac{1}{2} \tau^2 \frac{\partial^2 n}{\partial t^2} + \dots$$

$$\int_{-\infty}^{+\infty} f(z, \tau) \left(n(x, t) - \frac{3}{2} \frac{\partial n}{\partial x} + \frac{1}{2} \tau^2 \frac{\partial^2 n}{\partial x^2} \right)$$

$$= n(x, t) + \frac{1}{2} \tau^2 \frac{\partial^2 n}{\partial x^2}$$

$$\frac{\partial n}{\partial t} = D \frac{\partial^2 n}{\partial x^2}, \quad D = \frac{\langle z^2 \rangle}{2\tau} \quad \text{扩散系数.}$$

∴ 布朗运动是一个扩散过程.

$$\text{若 } t \ll \tau, \text{ 则 } \langle x^2 \rangle = \int \frac{2kTz}{m} dz$$

$$\left(\frac{kT}{m} - (x - x_0 + \frac{1}{2} \tau^2) \right) = \frac{kT}{m} t^2 = \langle x^2 \rangle t^2$$

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 与 $x+dx$ 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

$$\frac{\partial}{\partial t} n(x, t+\tau) = -D \frac{\partial^2}{\partial x^2} n(x, t+\tau) = 0$$

$$\int_{-\infty}^{+\infty} \left[\frac{\partial}{\partial t} f(x-x', t') - D \frac{\partial^2}{\partial x'^2} f(x-x', t') \right] n(x', t) dx' = 0$$

$$\therefore \frac{\partial}{\partial t} f(x-x', t) - D \frac{\partial^2}{\partial x'^2} f(x-x', t) = 0$$

$$\frac{\partial}{\partial t} f(z, t) - D \frac{\partial^2}{\partial z^2} f(z, t) = 0.$$

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 $z \neq 0$,

$$\therefore f(z, t) = 8(z).$$

$$\therefore f(z, t) = \frac{1}{2\sqrt{\pi D t}} e^{-z^2/4Dt}.$$

$\Rightarrow \tau^2 = 2Dt$. 这是爱因斯坦
的结果.

以后将证明, 这方程是随机过程
Master 方程对 Brown 运动的
解.

朗之万方程 \Leftrightarrow Master 方程, 从力学来看, 一个量子力学体系,
微观粒子可观察的运动方程, 一个是 Schrödinger 方程, 对宏观或宏观
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~~

在讲线性布朗运动时，我们看到是能选取时间轴和空间轴的。在 Brownian 运动中，随机力 $\vec{F}(t)$ 被设成随时间无关联。但布郎运动与 $\vec{F}(t)$ 无关吗？为什么呢？为此，我们考虑 $\langle u(t) \rangle$ 。

用方程中取 $u(t) = g(t) e^{-t/\tau}$

$$\frac{dg(t)}{dt} e^{-t/\tau} = -\frac{g(t)}{\tau} + \frac{x(t)}{m}$$

$$\Rightarrow \frac{dg(t)}{dt} = e^{t/\tau} (x(t)/m) = A(t)$$

$$\begin{aligned} u(t) &= e^{-t/\tau} = e^{-t/\tau} \int_0^t e^{t'/\tau} A(t') dt' \\ u(t) &= e^{-t/\tau} \int_0^t dt' \int_0^{t'} e^{(t-t'')/\tau} A(t') A(t'') \end{aligned}$$

$$u(t) = u(0) e^{-t/\tau} + e^{-t/\tau} \int_0^t e^{t'/\tau} A(t') dt'$$

$$\begin{aligned} \tilde{u}(t) &= u^2(0) e^{-2t/\tau} + 2u(0) e^{-t/\tau} \int_0^t e^{t'/\tau} A(t') dt' \\ &\quad + e^{-t/\tau} \int_0^t dt' dt'' e^{(t-t'')/\tau} A(t') A(t''). \end{aligned}$$

(1)

$$\langle u^2(t) \rangle = u^2(0) e^{-2t/\tau}$$

$$+ e^{-2t/\tau} \int_0^t dt' dt'' e^{(t-t'')/\tau} \langle A(t') A(t'') \rangle.$$

① $\tilde{t} = t + t_0$, $s = \frac{t-t''}{\sqrt{2}}$, 以 t'' 为坐标轴。
平移坐标轴。

$$e^{(t-t'')/\tau} \langle A(t) A(t'') \rangle = e^{t/\tau} C(s)$$

$$dt' dt'' = ds$$

∴ 有

$$\begin{aligned} I &= \int dt' dt'' \dots \\ &= \int_0^{t/\tau} dt' \int_{-\sqrt{2}s}^{\sqrt{2}s} C(s) ds \\ &\quad + \int_{t/\tau}^{t/\tau} dt' \int_{-\sqrt{2}(t-t')}^{\sqrt{2}(t-t')} C(s) ds \end{aligned}$$

对 Brownian 运动, $C(s)$ 是常数。

瞬时, (Markov 性质), $C(s) = C(s)$.

$$\therefore I = \int_0^{t/\tau} dt' e^{-\sqrt{2}s/\tau} = C \frac{t}{\sqrt{2}} (e^{-2t/\tau} - 1)$$

运动过程中扩散系数 (见书)

$$D = kT/\tau = \frac{1}{2} \int_0^{t/\tau} ds \langle u(t) u(t+s) \rangle$$

在连续性布朗运动中 D 由层-层运动决定的速率, 即时速度 $u(t)$ 是时间函数。

在 Kubo 线性布朗运动中, 扩散系数可以是时间和平均值。

~~§8.8.4 Markov 性质~~

§8.8.5 布朗运动类别的过程:

电路中的电压和电流性质。



$$L \frac{dI(t)}{dt} = -RI(t) + V(t)$$

若外电压为 0, 即电池关闭,

在一定条件下, 仍存在正弦交流电场和电压, $\langle I(t) \rangle = 0, \langle V(t) \rangle = 0$.

§8.8.6 电压-电流定律。

我们在前面已经讨论过扩散系数与扩散系数之间的关系。现在将考虑空间速度。因此, 我们可以在时间上讨论扩散系数的性质, 对 Brownian motion, $\tau = (\frac{\lambda}{m})^2 \Rightarrow \lambda = \frac{m}{\tau} = \frac{m^2}{2kT} C$.

$$= \frac{m^2}{2kT} \int_0^{t/\tau} dt C(s(t))$$

$$= \frac{m^2}{2kT} \int_0^{t/\tau} dt \langle A(t) A(t) \rangle$$

$$= \frac{m^2}{2kT} \int_0^{t/\tau} ds \langle A(t) A(t) \rangle$$

即扩散系数与随时间相关的波动和电压-电流定律。

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)
 $\langle V(t) V(t+s) \rangle = \frac{1}{2\pi} \int_{-\infty}^{+\infty} dw \tilde{V}(w) \tilde{V}(w) e^{iwt+iw(t+s)}$

$$\langle V(t) V(t+s) \rangle = C \delta(s)$$

$$\frac{1}{2\pi} \int dw dw' \langle \tilde{V}(w) \tilde{V}(w') \rangle e^{iwt+iw'(t+s)} = C \delta(s)$$

$$= C \frac{1}{2\pi} \int dw' e^{iws}$$

(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.

$\Delta n(t)$ 为单位时间内的发射电子数. 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 $i(t-\tau)$ 才能引起电流是
 $I(t) = \int_0^{+\infty} d\tau n(\tau) G(t-\tau).$

$$\begin{aligned} \textcircled{1} \quad \langle \tilde{V}(w) \tilde{V}(w') \rangle &= \langle |\tilde{V}(w)|^2 \delta(w+w') \rangle \\ &= \frac{1}{4\pi^2} \int dw dw' \langle |\tilde{V}(w)|^2 \rangle \delta(w+w') e^{iwt+iw'(t+s)} \\ &= \frac{1}{4\pi^2} \int dw \langle |\tilde{V}(w)|^2 \rangle e^{iwt} \\ \textcircled{2} \quad \langle |\tilde{V}(w)|^2 \rangle &= C. \propto w^2. \end{aligned}$$

$$\text{即 } K(s) = \langle V(t) V(t+s) \rangle$$

$$= \int_{-\infty}^{+\infty} dw \tilde{K}(w) e^{iws}$$

$$\Rightarrow \tilde{K}(w) = \frac{C}{2\pi} = \frac{2kTR}{2\pi} = \frac{kTR}{\pi}$$

$$\therefore \bar{V}^2 = \overline{\bar{V}^2} = K(0) = \int_{-\infty}^{+\infty} \tilde{K}(w) dw$$

$$= 2 \int_0^{\infty} \tilde{K}(0) dw = \int_0^{\infty} 4\pi \tilde{K}(0) dw$$

$$(w=2\pi v) \Rightarrow \int_0^{\infty} dv S(v)$$

$$\therefore S(v) = 4kTR \text{ 是电场的 } \frac{1}{2} kT/m$$

(1) $\langle n \rangle$ 为平均值, 则

$$\langle I(t) \rangle = \int_{-\infty}^{+\infty} \langle n \rangle \delta(t-\tau) d\tau$$

$$= \bar{n} \int_{-\infty}^{+\infty} \delta(t-\tau) d\tau = \bar{n} \cdot e$$

($n(t-\tau) = \frac{dG(t-\tau)}{dt}$) 由于 τ 很小, $\delta(t-\tau)$ 很大,
集中至附近. $\therefore \delta(t-\tau)$ 有一个电子 $\delta(t-\tau)$

$$\Delta I = I(t) - \langle I \rangle = \int_{-\infty}^{+\infty} [n(\tau) - \bar{n}] \delta(t-\tau) d\tau$$

$$\langle \Delta I^2 \rangle = \int d\tau d\tau' \langle \Delta n(\tau) \Delta n(\tau') \rangle$$

对 Shot noise, 电流发的都是随机的

$$\therefore \langle \Delta n(\tau) \Delta n(\tau') \rangle \propto \delta(\tau-\tau')$$

(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 \propto 而不是 $=$)
 $n \gg 1$, $\propto \langle n^2 \rangle = \bar{n}$)

$$\langle \Delta I^2 \rangle = \bar{n} \int_{-\infty}^{+\infty} |G(t-\tau)|^2 d\tau = \bar{n} \int_{-\infty}^{+\infty} |G(t)|^2 dt$$

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} . 在随机粒子数统计中, shot noise 中发射带电粒子是 quasi-particle, n 及 e 都应由 I 代替.

可以叫 I 带电荷.

(ii) 作子推定时, $P_n(x_i, t_i; t_n)$ 为时间

$$\text{元}, P_n(x_i, t_i; t_n) = P_n(x_i, t_i|t_n).$$

$$(iv) P_1(x_i, t_i) P_{11}(x_i, t_i|x_n, t_n) = P_2(x_i, t_i; x_n, t_n).$$

$$(v) \int P_{11}(x_i, t_i|x_n, t_n) dx_n = 1.$$

注: $\int P_2(x_i, t_i) dx_i = 1$

$$\begin{aligned} & \int \int P_1(x_i, t_i) P_{11}(x_i, t_i|x_n, t_n) dx_i dx_n \\ &= \int \int P_2(x_i, t_i; x_n, t_n) dx_i = \int P_2(x_n, t_n) dx_n = 1 \\ &= \int P_1(x_i, t_i) dx_i \end{aligned}$$

$$\therefore P_1(x_i, t_i) \left[\int dx_n P_{11}(x_i, t_i|x_n, t_n) \right] dx_i$$

由 \mathcal{L} 及 \mathcal{R} , 得

$$\begin{aligned} & P_3(x_i, t_i; x_n, t_n; x_3, t_3) \\ &= P_2(x_i, t_i; x_n, t_n) P_{21}(x_i, t_i|x_n, t_n|x_3, t_3) \\ &= P_1(x_i, t_i) P_{11}(x_i, t_i|x_n, t_n) P_{11}(x_n, t_n|x_3, t_3) \end{aligned}$$

3.8.4 主方程和福克-普朗克方程

3.8.4.1 Master eq. and Fokker-Planck eq.

主方程是分布函数 (也是一般性方程). Generally, 它是一个很复杂的方程. 这里我们研究 Markov 过程中的方程. Markov 过程是指分子在 t 时刻的位置只与 t 时刻最近的前一时刻的物理状态有关, 而更早的物理状态都没有影响. 例如, 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.

$$(i) \int P_i(x_i, t_i) = 1.$$

$$(ii) \int \underbrace{P_n(x_i, t_i; \dots; x_n, t_n)}_{\text{条件概率}} dx_n = P_{n-1}(x_i, t_i; \dots; x_{n-1}, t_{n-1})$$

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 $\psi_i(x_i, t_i)$

$$P_{ij}(x_i, t_i; x_n, t_n) = |\psi_i(x_i, t_i)|^2 \propto |\psi_i(x_i, t_i)|^2$$

$$\psi_i(x_i, t_i) \propto |\psi_i(x_i, t_i)|$$

即 $|\psi_i(x_i, t_i)| \sim$ 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 \mathcal{L} 及 \mathcal{R} , 得~~

$$P_3(x_i, t_i; x_n, t_n; x_3, t_3)$$

$$= P_2(x_i, t_i; x_n, t_n) P_{21}(x_i, t_i|x_n, t_n|x_3, t_3)$$

$$= P_1(x_i, t_i) P_{11}(x_i, t_i|x_n, t_n) P_{11}(x_n, t_n|x_3, t_3).$$

$\int_{t_n < t_i < t_3} dx_n$

$$P_2(x_i, t_i; x_3, t_3) = \int_{t_n < t_i < t_3} dx_n P_{11}(x_i, t_i|x_n, t_n) P_{11}(x_n, t_n|x_3, t_3)$$

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_m 时刻 x_{k+1}, \dots, x_m 已知时.
 \Rightarrow 马尔可夫过程:

$$P_{n-1|1}(x_1, t_1, \dots, x_{n-1}, t_{n-1} | x_n, t_n) = P_{Y_1}(x_{n-1}, t_{n-1} | x_n, t_n), \text{ 即 } t_n \text{ 时刻 } x_{n-1} \text{ 已知.}$$

即 $P_{Y_1}(x_{n-1}, t_{n-1} | x_n, t_n)$ 为 $n-1$ 时刻有 x_n 时 M arkov 过程 $P_1(x, t)$
和 $P_{Y_1}(x_{n-1}, t_{n-1} | x_n, t_n)$ 为 $n-1$ 时刻 x_n 已知.

$$\begin{aligned} & P_3(x_1, t_1; x_2, t_2; x_3, t_3) \\ &= \underbrace{P_1(x_1, t_1)}_{\parallel} \underbrace{P_{Y_1}(x_2, t_2 | x_1, t_1)}_{\parallel} P_{Y_1}(x_3, t_3 | x_2, t_2) \\ &= P_1(x_1, t_1) P_{Y_1}(x_2, t_2 | x_1, t_1) P_{Y_1}(x_3, t_3 | x_2, t_2). \end{aligned}$$

\therefore 在 Markov
过程中, 只看第 3 步.

$$P_2(x_1, t_1; x_3, t_3) = \frac{P_1(x_1, t_1)}{P_1(x_1, t_1)} \int dx_2 P_{Y_1}(x_2, t_2 | x_1, t_1) P_{Y_1}(x_3, t_3 | x_2, t_2)$$

$$\boxed{\quad}$$

$$\boxed{\quad} P_2(x_1, t_1; x_3, t_3) = \int dx_2 P_{Y_1}(x_2, t_2 | x_1, t_1) P_{Y_1}(x_3, t_3 | x_2, t_2)$$

Markov (过程) m. Smoluchowski-Chapman
-Kolmogorov 方程.

$x_1 \rightarrow$ 第一状态取值 m. 率. $[1 - \tau \int W(x_1, x) dx]$ 是
不发生跃迁 m. 率. $\boxed{\quad}$

$\therefore [1 - \tau \int W(x_1, x) dx] \delta(x_1, x_2)$ 是不发生从 x_1 m.
率. 跃迁到 x_2 m. 率是 $\tau W(x_1, x_2)$.

$[1 - \tau \int W(x_1, x) dx] \delta(x_1, x_2)$ 是不发生从 x_1 m.
到 $x_2 = x_1$ m. 率, $\& \tau W(x_1, x_2)$ 不同, $\& x_1 = x_2$
和 $x_1 \neq x_2$ m. 率之和.

$$\begin{aligned} P(x_1, t | x_2, t+\tau) &= [1 - \tau \int W(x_1, x) dx] \delta(x_1, x_2) + W(x_1, x_2) \tau \\ &= \delta(x_1, x_2) - \tau \int W(x_1, x) dx \cdot \delta(x_1, x_2) + W(x_1, x_2) \tau. \\ \text{代入 } \frac{\partial P(x_1, t)}{\partial t} &= \frac{1}{\tau} \left[\int P(x_1, t) \delta(x_1, x_2) dx_1 \right. \\ &\quad \left. - \int P(x_1, t) \delta(x_1, x_2) dx_1 \right] \\ &= \int P(x_1, t) W(x_1, x_2) dx_1 - \int P(x_2, t) W(x_2, x_1) dx_1 \\ &= \int [W(x_1, x_2) P(x_1, t) - P(x_2, t) W(x_2, x_1)] dx_1. \end{aligned}$$

Master eq.

定理 23 Markov chain, 我们要看 $P_j(x, t+\tau)$ 何时

能成立. $\boxed{\text{由 Markov}}$

$$\frac{\partial P(x, t)}{\partial t} = \lim_{\tau \rightarrow 0} \frac{P(x, t+\tau) - P(x, t)}{\tau}$$

由 $\boxed{P(x, t+\tau) = P(x, t)}$, $t_1 = t$, $\boxed{\text{由 Markov (iv)}}$,

$$P(x_2, t+\tau) = \int P(x, t) P(x+t | x_2, t+\tau) dx$$

$$\frac{\partial P(x, t)}{\partial t} = \int P(x, t) \frac{\partial}{\partial t} P(x+t | x_2, t+\tau) dx$$

$$\frac{\partial P(x, t)}{\partial t} = \lim_{\tau \rightarrow 0} \frac{P(x, t+\tau) - P(x, t)}{\tau}$$

$$\frac{\partial P(x, t)}{\partial t} = \lim_{\tau \rightarrow 0} \frac{1}{\tau} \int P(x, t) [P(x+t | x_2, t+\tau) - P(x, t | x_2, t+\tau)]$$

$$\& \tau = 0, P(x_2, t) = \int P(x, t) P(x+t | x_2, t) dx$$

$$\Rightarrow P(x+t | x_2, t) = \delta(x-x')$$

即 $W(x_1, x_2)$ 为 $t \rightarrow t+\tau$ time interval, x_1 取值 x_1
至 x_2 m. 经过中单位时间 m. 跳迁概率密度.

$\therefore \boxed{\text{即 } \tau \int W(x_1, x) dx \text{ 是 } \tau \text{ 的概率密度}}$

主方程 m. 一阶表示从其他态跃迁到

x_1 m. 跳迁密度; 第二阶表示从 x_1 跳迁到其它
m. 跳迁密度. 在链子中, 既有因 m. 跳迁 m. 动
学机制, 也有涉及子链的 m. 跳迁机制. 是普遍的.

下面举一个例子: 对一维分子链. (F. Schwabl)
密度矩阵: $P(t) = \sum_i W_i(t) |i\rangle \langle i|$.

$$H = H_0 + V, \quad H_0 |i\rangle = h_i |i\rangle, \quad F_i |i\rangle$$

$\& F_i |i\rangle = F_i |i\rangle$ 是守恒量. V 是微扰哈密顿.

$U(t)$ 是时间 t 的演化算符

$$\begin{aligned} \varphi(t+\tau) &= \sum_i W_i(t) U(t) |i\rangle \langle i| \langle i| U^\dagger(t) \quad (\sum_j |j\rangle \langle j| = 1) \\ &= \sum_i \sum_j W_j(t) \delta(j) \langle j| U(t) |i\rangle \langle i| U^\dagger(t) |k\rangle \langle k| \\ &= \sum_i \sum_j W_j(t) \delta(j) \langle k| U_j(t) U_j^\dagger(t) |k\rangle \langle k| \end{aligned}$$

$$\& \therefore U_j(t) = \langle j | U(t) | i \rangle$$

取随机相近点, 即忽略非对角项贡献,

$$P(t+\tau) \approx \sum_i \sum_j W_j(t) \delta(j) \langle j | U_j(t) U_j^\dagger(t) | i \rangle$$

$$\equiv \sum_j W_j(t+\tau) |U_{j,i}(t)|^2$$

$$\text{即 } W_j(t+\tau) = \sum_i W_i(t) |U_{j,i}(t)|^2$$

$$\therefore W_j(t+\tau) - W_j(t) = \sum_i (W_i(t) - W_j(t)) |U_{j,i}(t)|^2$$

$(\because \sum_i |U_{j,i}(t)|^2 = 1)$ ($i=j$, $|U_{i,i}(t)|^2$ 为常数.)

$\Rightarrow |U_{j,i}|^2$, 用微扰论, (Fermi Golden rule.)

$$|U_{j,i}|^2 = \frac{1}{\hbar} \left(\frac{\sin \omega_{ij} \tau}{\omega_{ij}/\hbar} \right)^2 |\langle j | V | i \rangle|^2$$

$$\approx \frac{2\pi}{\hbar} \delta(E_i - E_j) |\langle j | V | i \rangle|^2$$

$$W_{ij} = E_i - E_j / \hbar. \quad (\cancel{E_i - E_j / \hbar} \rightarrow \frac{1}{\hbar})$$

$$(\approx (E_i - E_j) \tau \ll 1, \tau \gg 1/\Delta E \text{ 微扰论})$$

$$\frac{W_j(t+\tau) - W_j(t)}{\tau} \Big|_{\tau \gg 0} = \frac{dW_j(t)}{dt}$$

$$\sum_i (W_i(t) - W_j(t)) \frac{2\pi}{\hbar} \delta(E_i - E_j) |\langle j | V | i \rangle|^2.$$

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, $W(x', x) = W(x-z, x')$

$$= W(\frac{x+x'}{2}, x-x') \approx W(x, -z).$$

$$\begin{aligned} \frac{\partial P(x, t)}{\partial t} &= \int [W(x', x) P(x', t) - W(x, x') P(x, t)] dx \\ &= \int [W(x-z, z) P(x-z, t) - W(x, -z) P(x, t)] dz \end{aligned}$$

$$\begin{aligned} \text{展开} \quad W(x-z, z) P(x-z, t) &= W(x, z) P(x, t) - z \frac{\partial}{\partial x} [W(x, z) P(x, t)] \\ &\quad + \frac{1}{2} z^2 \frac{\partial^2}{\partial x^2} [W(x, z) P(x, t)] + \dots \end{aligned}$$