

量统近独立子系. F.D/B.E.

理想玻色气体 (非相对论性)

1. 自由而非相对论性玻色气体.

$$\epsilon = \frac{p^2}{2m} \sim \frac{\hbar^2}{2m} \left(\frac{2\pi}{L}\right)^2 n^2. \quad (\vec{p} = \hbar \vec{k}, \quad \vec{k} = \left(\frac{2\pi}{L}\right) \vec{n})$$

$$\Delta \epsilon \sim \frac{\hbar^2}{mL}, \quad \Delta \epsilon \ll k_B T \rightarrow \text{准连续能谱.}$$

我们知道, 对于 Boson,  $\ln Z = -\sum_s \ln(1 - e^{-\alpha - \beta \epsilon_s})$

考虑  $V = L^3$  中,  $d^3\vec{p}$  中的量子态个数. 为

$$\text{态密度 } g(\epsilon) d\epsilon = \frac{V d^3\vec{p}}{\hbar^3} = \frac{4\pi V p^2 dp}{\hbar^3} = 2\pi \frac{V}{\hbar^3} (2m)^{\frac{3}{2}} \epsilon^{\frac{1}{2}} d\epsilon.$$

$$g(\epsilon) = \frac{2\pi V}{\hbar^3} (2m)^{\frac{3}{2}} \epsilon^{\frac{1}{2}}, \quad \text{这里忽略了自旋,}$$

$$\Rightarrow \ln Z = \frac{2\pi V}{\hbar^3} (2m)^{\frac{3}{2}} \int_0^{+\infty} \ln(1 - e^{-\alpha - \beta \epsilon}) \epsilon^{\frac{1}{2}} d\epsilon.$$

$$\stackrel{x = \beta \epsilon}{=} \frac{2\pi V}{\hbar^3} (2m k_B T)^{\frac{3}{2}} \int_0^{+\infty} \ln(1 - e^{-\alpha - x}) x^{\frac{1}{2}} dx$$

$$\alpha = -\frac{\mu}{k_B T} \Rightarrow e^{-\alpha} = e^{\frac{\mu}{k_B T}} \equiv z, \quad \text{逸度 (fugacity).}$$

$$\text{我们知道, } \ln(1+x) = \sum_{n=1}^{\infty} \frac{x^n}{n} \Rightarrow \ln(1 - e^{-\alpha - x}) x^{\frac{1}{2}} = \sum_{n=1}^{\infty} -\frac{z^{-n} x^{\frac{1}{2}}}{n} x^{\frac{1}{2}}$$

积分得

$$\ln \Xi = \frac{V}{h^3} (2\pi m k_B T)^{3/2} \sum_{j=1}^{\infty} \frac{z^j}{j^{5/2}}$$

定义  $g_5(z) = \sum_{j=1}^{\infty} \frac{z^j}{j^5}$ , 实际上,  $g_5(1) = \underbrace{\zeta(5)}_{\text{Riemann Zeta function.}}$

定义:  $\lambda_T = \frac{h}{(2\pi m k_B T)^{1/2}}$

则  $\ln \Xi = \frac{V}{\lambda_T^3} g_5(z)$

随后由热力学函数与巨正则系综配分函数的关系

$$\bar{N} = - \frac{\partial \ln \Xi}{\partial \alpha} = \frac{V}{\lambda_T^3} g_{5/2}(z)$$

$$U = - \frac{\partial \ln \Xi}{\partial \beta} = \frac{3}{2} k_B T \left( \frac{V}{\lambda_T^3} \right) g_{5/2}(z)$$

$$S = k_B \left( \frac{5}{2} \ln \Xi + \bar{N} \alpha \right)$$

$$E_{热} = k_B T \ln \Xi = PV = k_B T \left( \frac{V}{\lambda_T^3} \right) g_{5/2}(z)$$

我们引入无量纲常数  $y = \frac{\bar{N}}{V} \lambda_T^3 = n \lambda_T^3$

则  $\bar{N} \Rightarrow y = g_{5/2}(z) = z + \frac{z^2}{2^{5/2}} + \frac{z^3}{3^{5/2}} + \dots \xRightarrow{\text{反解}} z = y - \frac{y^2}{2^{5/2}} + \left( \frac{1}{4} - \frac{1}{3^{5/2}} \right) y^3$

$y \ll 1$  时, 称为弱简并气体 (粒子间距离较大)

弱简并气体的物态方程.

$$\frac{PV}{N k_B T} = 1 - \frac{y}{2^{5/2}} - \left( \frac{2}{3^{5/2}} - \frac{1}{8} \right) y^2 - \dots$$

强简并气体的 B-E 凝聚.

$$y_{\max} \text{ 发生在 } z=1, y_{\max} = C_e(3/2) \approx 2.612 \quad (\mu \geq 0)$$

(why?)

$$\text{由 B-E 分布, } \bar{\alpha}_s = \frac{1}{e^{\frac{e_s - \mu}{k_B T}} - 1}$$

若  $\mu > 0$ , 总能找到  $e_s = \mu$ ,  $\bar{\alpha}_s \rightarrow \infty$ .

故  $\mu \leq 0$ ,  $\mu_{\max} = 0$ .

$$\text{但, 由 } y = \frac{\bar{N} h^3}{V} (2\pi m k_B T)^{-3/2}, \quad T \rightarrow 0 \text{ 时, } y \text{ 可以 } \rightarrow +\infty$$

矛盾!

(基态.)  
问题:  $T \rightarrow 0$  时, 对于低能态的处理不严谨.

我们之前的求和, 都基于基态上粒子数远小于激发态. 粒子数之和

但  $T \rightarrow 0$  时, 基态上占据了可与  $\bar{N}$  比拟的粒子, 之前的求和不能直接近似!

改进: 将基态与激发态粒子分开处理.

$$\bar{N} = \bar{N}_{e=0} + \bar{N}_{e>0}$$

$$(\ln \bar{N})_{e>0} = - \frac{2\pi V}{h^3} (2\pi m k_B T)^{3/2} \int_0^{+\infty} \ln(1 - e^{-\alpha x}) x^{1/2} dx.$$

$$(\ln \bar{N})_{e=0} = - \ln(1 - e^{-\alpha}). \quad \ln \bar{N} = - \frac{V}{\lambda_T^3} \int_0^{+\infty} \ln(1 - e^{-\alpha x}) x^{1/2} dx - \ln(1 - e^{-\alpha})$$

B-E 凝聚时,

$$\bar{N}_{e>0} = \frac{V}{\lambda_T^3} g_{3/2}(z=1)$$

$$\bar{N}_{e=0} = \bar{N} - \bar{N}_{e>0} = n \left(1 - \left(\frac{T}{T_c}\right)^{3/2}\right)$$

$$\text{其中, } T_c \text{ 的定义由 } n \lambda_{T_c}^3 = C_e(3/2) \text{ 得出, } T_c = \frac{2\pi}{C_e(3/2)^{2/3}} \frac{h^2}{m k_B} n^{2/3}.$$

其他物理量也可类似讨论.

例如: 对于压强与内能,  $U_{e=0}$  和  $P_{e=0} = 0$

$$P = \frac{2}{3} \frac{U}{V} = \begin{cases} \frac{k_B T}{\lambda_T^3} g_{5/2}(z) = n k_B T \frac{g_{5/2}(z)}{g_{3/2}(z)} & (T > T_c) \\ \frac{k_B T}{\lambda_T^3} \zeta(\frac{5}{2}), = n k_B T \frac{\zeta(\frac{5}{2})}{\zeta(\frac{3}{2})} \left(\frac{T}{T_c}\right)^{3/2} & (T < T_c) \end{cases}$$

$$C_V = \left( \frac{\partial U}{\partial T} \right)_V = \begin{cases} \frac{15}{4} \frac{g_{5/2}(z)}{g_{3/2}(z)} - \frac{9}{4} \frac{g_{3/2}(z)}{g_{3/2}(z)} & , T > T_c \\ \frac{15}{4} \frac{\zeta(5/2)}{\zeta(3/2)} \left(\frac{T}{T_c}\right)^{3/2} & T < T_c \end{cases}$$

$C_V$  连续,  $\frac{dC_V}{dT}$  不连续.



# 黑体辐射的统计理论.

两种图像: 光子气体 ② 电磁场简正模式.

先从简正模式出发:

$$\vec{B}, \vec{E} \sim e^{i\vec{k} \cdot \vec{r} - i\omega t}.$$

$$\omega_k = ck, \quad \vec{k} = \left(\frac{2\pi}{L}\right) \vec{n}.$$

对于各模式求和有  $E = \sum_{\vec{k}, s} (n_{\vec{k}, s} + \frac{1}{2}) \hbar \omega_{\vec{k}, s}$ . (谐振子).

$$Z = \sum_{\{n_{\vec{k}, s}\}} e^{-\beta E} = \prod_{\vec{k}, s} Z_{\vec{k}, s}$$

$$\text{where } Z_{\vec{k}, s} = \sum_{n_s=0}^{\infty} e^{-\beta (n_s + \frac{1}{2}) \hbar \omega_{\vec{k}}} = \frac{e^{-\beta \hbar \omega_{\vec{k}}/2}}{1 - e^{-\beta \hbar \omega_{\vec{k}}}}$$

$$\text{则 } U = -\frac{\partial \ln Z}{\partial \beta} = \sum_{\vec{k}, s} \left( -\frac{\partial \ln Z}{\partial \beta} \right) = U_0 + 2 \sum_{\vec{k}} \frac{\partial}{\partial \beta} \ln(1 - e^{-\beta \hbar \omega_{\vec{k}}})$$

$$\sum_{\vec{k}} \xrightarrow{\text{宏观近似}} \int d^3 \vec{k}$$

对于  $(\vec{k}, \vec{k} + d\vec{k})$  内的电磁模式数有

$$\frac{8\pi V k^2 dk}{(2\pi)^3} \uparrow.$$

$$\Rightarrow \frac{U(\omega, T) d\omega}{V} = \frac{1}{\pi^2 c^3} \frac{\hbar \omega^3}{e^{\frac{\hbar \omega}{k_B T}} - 1} \quad \text{Planck 能量密度.}$$

② 视作光子气体.

$$p = \frac{1}{3} \epsilon, \quad \epsilon = \hbar \omega, \quad \text{Boson.}$$

我们知道对于 Boson,  $\bar{a}_i = \frac{\overline{\epsilon_i}}{e^{\beta \hbar \omega} - 1}$  振动模式数.

$$U(\omega, T) = \bar{a}_i d\omega = \frac{\epsilon_i}{e^{\beta \hbar \omega} - 1} d\omega = \frac{1}{\pi^2 c^3} \frac{V \hbar \omega \cdot \omega^2 d\omega}{e^{\beta \hbar \omega} - 1} \quad (\epsilon_i = \frac{8\pi \hbar^3 \omega^3}{(2\pi)^3})$$

高频 ( $\hbar \omega \gg k_B T$ ):

$$U(\omega, T) d\omega = \frac{V}{\pi^2 c^3} \hbar \omega^3 e^{-\frac{\hbar \omega}{k_B T}} d\omega \quad \text{Wien law} \quad \text{指数衰减.}$$

低频 ( $\hbar \omega \ll k_B T$ ):

$$U(\omega, T) d\omega = \frac{V}{\pi^2 c^3} \omega^2 k_B T d\omega \quad (\text{能均分定理}).$$

Rayleigh - Jeans 公式.

Planck 提出 PRR 的过程

Rayleigh - Jeans 与 Wien:  $\omega \rightarrow 0, \omega \rightarrow \infty$  分别不能解释

① 内插, 得到一个纯数学上的结论 —— 发现与实验非常符合.

② 假设能量不连续,  $\epsilon = \hbar \omega$ , 由此可以从热力学公式推出谱.

普朗克 - 公式的变革.

$\frac{1}{10}$  子 振动.

Einstein 模型

$$\epsilon_n = (n + \frac{1}{2}) \hbar \omega.$$

$3N$  个 振子,  $U = -3N \frac{\partial \ln Z}{\partial \beta}$  where  $Z = \sum_n e^{-\beta(n + \frac{1}{2}) \hbar \omega}.$

$$U = \frac{3N}{2} \hbar \omega + \frac{3N \hbar \omega}{e^{\beta \hbar \omega} - 1}$$

$$C_V = \left( \frac{\partial U}{\partial T} \right)_V = 3N k_B \left( \frac{\hbar \omega}{k_B T} \right)^2 \frac{e^{\beta \hbar \omega}}{(e^{\beta \hbar \omega} - 1)^2} \sim 3N k_B \left( \frac{\hbar \omega}{k_B T} \right)^2 e^{-\frac{\hbar \omega}{k_B T}}$$

高温下,  $C_V = 3N k_B$ . Dulong - Petit 定律.

低温下,  $\rightarrow 0$ , 但衰减速度太快.

1912 - Debye 模型

① 声波 分为纵波与横波两种.

$$\omega = c_L k \quad \omega = c_T k$$

$$\Rightarrow g(\omega) d\omega = \frac{V}{2\pi^2} \left( \underbrace{\frac{1}{c_L^3}}_{\sim \frac{1}{\omega^3}} + \underbrace{\frac{2}{c_T^3}}_{\sim \frac{1}{\omega^3}} \right) \omega^2 d\omega.$$

② 截止频率,  $\omega_D$ .

满足  $\int_0^{\omega_D} g(\omega) d\omega = 3N$

$$U = U_0 + \int_0^{\omega_D} g(\omega) \frac{\hbar \omega}{e^{\beta \hbar \omega} - 1} d\omega.$$

$$\beta(\lambda) y = \frac{\hbar \omega}{k_B T}, \quad x = \frac{\hbar \omega_D}{k_B T}, \quad \text{记}$$

$$U = U_0 + 3Nk_B T D(x)$$

$$\text{Debye function, } D(x) = \frac{1}{x^3} \int_0^x \frac{y^3 dy}{e^y - 1}$$

$$\text{再令 } u = \frac{1}{x}, \text{ 则}$$

$$f_0(u) = 3u^2 \int_0^u \frac{y^4 e^y dy}{(e^y - 1)^2}$$

$$C_V = 3Nk_B f_0\left(\frac{T}{\Theta_D}\right), \quad \Theta_D \text{ 为德拜温度 } \Theta_D = \frac{\hbar \omega_D}{k_B}$$

$$\text{低温下, } D(x) \sim \frac{\pi^4}{15 x^3}$$

$$\begin{cases} U = U_0 + 3Nk_B \left(\frac{\pi^4}{15}\right) \frac{T^4}{\Theta_D^4} \end{cases}$$

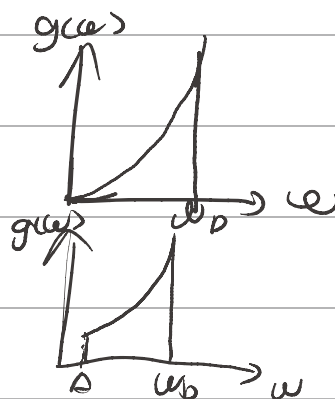
$$\begin{cases} C_V = 3Nk_B \frac{4\pi^5}{15} \left(\frac{T}{\Theta_D}\right)^3 \propto T^3 \text{ Debye } T^3 \text{ law.} \end{cases}$$

phonon

gapless:  $\omega = ck, k \rightarrow 0, \omega \rightarrow 0$

gap:  $\omega = A + ck^\alpha, k \rightarrow 0, \omega \rightarrow 0$

有能隙  $\rightarrow \omega_{\min} = \Delta$ , Einstein



对于晶体没有问题

若有自由电子:  $C_V \sim aT + bT^3$   
低温占主导

若为绝缘体:  $C_V \sim T^3$

实际声子谱: 非常复杂, 可以用中子衍射来表征

## 理想费米气体

弱简并费米气体: (自旋  $s$ ,  $e = \frac{p^2}{2m}$ )

$$\ln \Xi = \frac{2\pi^{3/2} V}{h^3} (2mk_B T)^{3/2} \int_0^\infty \ln(H e^{-\alpha-x}) dx.$$

简并度

由 Pauli 不相容原理, 不会出现如 Bose 样的凝聚现象.

展开系数, 写作  $\ln \Xi = \frac{(2s+1)V}{h^3} (2\pi mk_B T)^{3/2} \sum_{j=1}^{\infty} (-1)^{j-1} \frac{e^{-j\alpha}}{j^{5/2}}$

$$N = - \frac{\partial \ln \Xi}{\partial \alpha} = \frac{(2s+1)V}{h^3} (2\pi mk_B T)^{3/2} \sum_{j=1}^{\infty} (-1)^{j-1} \frac{e^{-j\alpha}}{j^{3/2}}$$

$$U = - \frac{\partial \ln \Xi}{\partial \beta} = \frac{3}{2} k_B T \ln \Xi.$$

$$p = \frac{1}{\beta} \frac{\partial \ln \Xi}{\partial V} = \frac{2}{3} \frac{U}{V}$$

$$S = k_B \left( \frac{5}{2} \ln \Xi + N \alpha \right)$$

$$\frac{1}{2} z = e^{-\alpha}, \text{ 定义: } f_s(z) = \sum_{k=1}^{\infty} (-1)^{k-1} \frac{z^k}{k^s}$$

$$\text{令 } y = \frac{N h^3}{(2s+1)(2\pi m k_B T)^{3/2}} \quad \text{则有 } f_s(z) = y \overset{\text{解}}{\Rightarrow} z = y + \frac{1}{2^{s/2}} y^2 + \dots$$

$(y < 1)$





# 北京大学

于是有状态方程

$$\frac{PV}{Nk_B T} = \frac{2U}{3Nk_B T} = \frac{\ln Z}{N} = \ln \frac{1}{2^{5/2}} y - \left( \frac{2}{5^{5/2}} - \frac{1}{8} \right) y^2 + \dots$$

Boson:  $1 - \frac{1}{2^{5/2}} y + \dots$  只差符号

与理想经典气体相比, 有一个增大, 似乎有一种排斥作用

这是由泡利不相容原理造成的.

Fermi/Dirac 分布是在1926年发表的

实际上, 最简并 Fermi 气体不常见, 更有实际意义的是简并 Fermi 气



# 北京大学

强简并 Fermi 理想气体.

金属中电子气 (自由/巡游/ Bloch 电子)

电子气的数密度  $\bar{N}$  相当大  $\rightarrow y \ll 1$  不成立.

实际上, 金属中的 Coulomb 势能相当大, 应当对电子气产生显著影响

~~Drude~~ 自由电子气模型能够预测金属热容? ~~与实验不符~~  
经典理想



Sommerfeld Fermi 气体模型.



Fermion - Pauli 不相容

$\rightarrow$  Fermi 面.

只有在低温下, 只有 Fermi 面附近的电子能够发生跃迁, 贡献  $C_v$ .

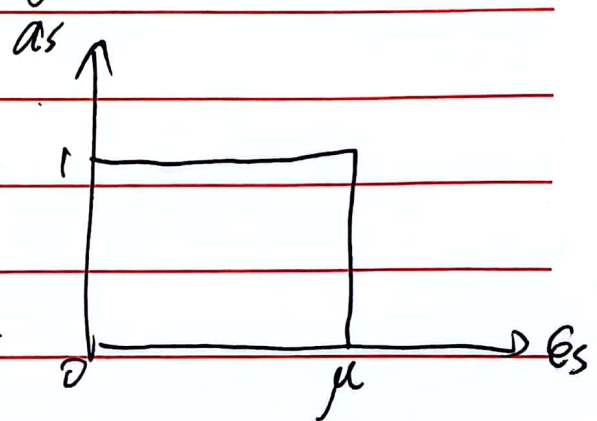
定量计算:

① 室温对典型金属,  $y \sim \frac{10^7}{T^{3/2}}$   
 $T=0$ .

$y \sim 3400 \gg 1$ ! 强简并.

Fermi 分布  $\bar{a}_s = \frac{1}{e^{\frac{E_s - \mu}{k_B T}} + 1}$

$T=0$  导致  $\bar{a}_s$  在  $E_s = \mu$  处发生阶跃.



我们知道  $\bar{N} = \int_0^{\mu} \frac{4\pi V}{h^3} (2m)^{3/2} e^{\frac{1}{2}} dE$ , 这里已经考虑简并:  $2s+1=2$

积分得  $\mu_0 = E_F = \frac{\hbar^2}{2m} (3\pi^2 \bar{N})^{2/3} = \frac{\hbar^2 k_F^2}{2m}$   
Fermi 能级 where  $k_F = \sqrt{3\pi^2 \bar{N}}$

( $s = \frac{1}{2}$ , 电子自旋)





# 北京大学

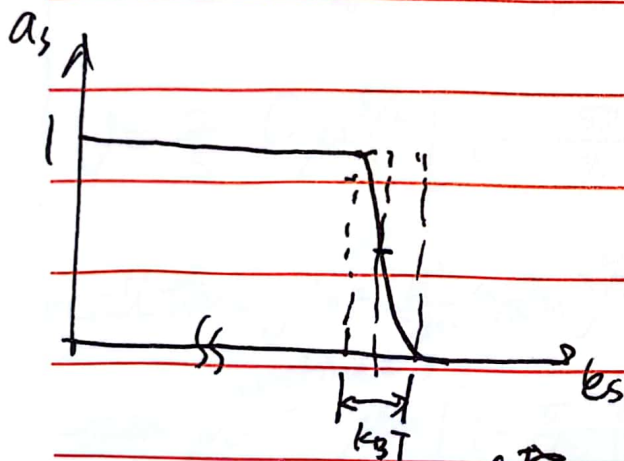
Fermi 能量  $\mu = E_F$

还可以计算其他物理量

$$U = \int_0^{\mu_0} \frac{4\pi V}{h^3} (2m)^{3/2} e^{3/2} de = \frac{3}{5} \bar{N} E_F$$

$$p = \frac{2}{3} \frac{U}{V} = \frac{2}{5} n E_F, \text{ 费米压.}$$

②  $T \neq 0$  且  $k_B T \ll E_F = \mu_0$



$$\bar{N} = \frac{4\pi V}{h^3} (2m)^{3/2} \int_0^{\infty} \frac{e^{\frac{\epsilon}{2}}}{e^{\frac{\epsilon - \mu}{k_B T}} + 1} d\epsilon$$

$$U = \frac{4\pi V}{h^3} (2m)^{3/2} \int_0^{\infty} \frac{e^{\frac{3}{2}\epsilon}}{e^{\frac{\epsilon - \mu}{k_B T}} + 1} d\epsilon$$





ideal contribution of Sommerfeld:

$$I = \int_0^\infty \frac{\eta(x) dx}{e^{\frac{x-\mu}{k_B T}} + 1} \quad \text{的展开式} - \text{Sommerfeld 展开.}$$

$$I = \int_0^\mu \eta(x) dx + \frac{\pi^2}{6} (k_B T)^2 \eta'(\mu) \left( + \frac{7\pi^4}{720} (k_B T)^4 \eta'''(\mu) + \dots \right)$$

由此可以计算得

$$\begin{cases} N = \frac{2}{3} \cdot \frac{4\pi V}{h^3} (2m)^{3/2} \cdot \mu^{3/2} \left[ 1 + \frac{\pi^2}{8} \left( \frac{k_B T}{\mu} \right)^2 \right] \\ U = \frac{2}{5} C \mu^{5/2} \left[ 1 + \frac{5\pi^2}{8} \left( \frac{k_B T}{\mu} \right)^2 \right] \end{cases}$$

recall that  $\mu_0 = \frac{\hbar^2}{2m} (3\pi^2 n)^{2/3}$

then  $\mu^{(\text{refined})} = \mu_0 \left[ 1 - \frac{\pi^2}{12} \left( \frac{k_B T}{\mu_0} \right)^2 \right]$

$$\Rightarrow U = \frac{2}{5} N \mu_0 \left[ 1 + \frac{5\pi^2}{12} \left( \frac{k_B T}{\mu_0} \right)^2 \right]$$

$$\Rightarrow C_V = \left( \frac{\partial U}{\partial T} \right)_V = \cancel{N k_B} N k_B \frac{\pi^2}{2} \left( \frac{k_B T}{\mu_0} \right)$$

与晶格引起的  $C_V$  对比: 低温下  $\rightarrow 0$ , 常温下  $\propto T$ .  
Constant



# 北京大学

磁场中的强简并理想气体.  
(较弱)

电子磁矩 Bohr 磁子  $\mu_B$ . 引入能量  $\mu_B B$ .

讨论 ①  $\mu_B \ll k_B T \ll \epsilon_F$ . 极弱磁场

②  $\mu_B \sim k_B T \ll \epsilon_F$  中强磁场.

③ 自旋效应.

Bohr 磁子,  $\mu_B = \frac{e\hbar}{2mc}$

$$\vec{\mu} = g \mu_B \vec{S} \quad (\text{电子: } g = -2)$$

$$E = \frac{p^2}{2m} \pm \mu_B B.$$

$\uparrow \rightarrow +$  :  $\uparrow \downarrow$  - :  $\uparrow \uparrow$

$$g_+(E) = g_-(E) = g_0(E) = \frac{2\pi V}{h^3} (2m)^{3/2} E^{1/2}$$

$$N_{\pm} = \int_{\pm \mu_B B}^{\mu_0} g_{\pm}(E \mp \mu_B B_0) dE = \int_0^{\mu_0 \mp \mu_B B_0} g_{\pm}(E) dE.$$

( $\mu_0 = 0$  at  $\pm \mu_B B_0$ )

$$N = N_+ + N_- = \frac{4\pi V}{3h^3} (2m)^{3/2} [(\mu + \mu_B B)^{3/2} + (\mu - \mu_B B)^{3/2}]$$

$$M = \frac{\mu_B}{V} (N_- - N_+) = \frac{4\pi}{3h^3} (2m)^{3/2} \mu^{3/2} \cdot 2 \cdot \frac{3}{2} \mu_B \left( \frac{\mu_B B}{\mu} \right) = \left( \frac{3n\mu_B^2}{2\epsilon_F} \right) B_0$$

顺磁磁化率

- Pauli 顺磁化率  $\chi = \frac{3n\mu_B^2}{2\epsilon_F}$





# 北京大学

CH7 经典流体.

(不包含/包含相互作用).

经典理想气体. (双原子分子的热容量)

不考虑相互作用. (近独立子系)

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

$$Z = \sum_S e^{-\beta E_S} = Z^N \Rightarrow Z = \frac{1}{N! h^{3N}} \int \prod_{i=1}^N (d^3 r_i d^3 p_i) e^{-\sum_{i=1}^N \frac{p_i^2}{2m}}$$

$$= \frac{1}{N!} \cdot \left( \frac{1}{h^3} \int d^3 r d^3 p e^{-\frac{p^2}{2m}} \right)^N$$
$$= \frac{1}{N!} \cdot \left[ V \left( \frac{2\pi m}{\beta h^2} \right)^{\frac{3}{2}} \right]^N$$

$$\Rightarrow P = \frac{1}{\beta} \frac{\partial}{\partial V} \ln Z = \frac{N k_B T}{V}$$

$$U = - \frac{\partial}{\partial \beta} \ln Z = \frac{3}{2} N k_B T$$

$$S = k_B \left( \ln Z - \alpha \beta \frac{\partial}{\partial \beta} \ln Z \right) = \frac{3}{2} N k_B \ln T + N k_B \ln \frac{V}{N} + \frac{3}{2} N k_B \left[ \frac{5}{2} + \ln \left( \frac{2\pi m k_B}{h^2} \right) \right]$$



# 北京大学

轨道运动引起的磁矩.

Hamiltonian  $H = \frac{1}{2m} (\vec{p} - e\vec{A})^2$

$\vec{p} = \vec{p} - \frac{e}{c}\vec{A}$      $\vec{p}^2 = p_{\parallel}^2 + p_{\perp}^2$      $p_{\parallel} \sim \left(\frac{p_{\perp}}{L}\right) r_{\parallel}$

$\Rightarrow E = \frac{p_{\perp}^2}{2m} + (n + \frac{1}{2})\hbar\omega_B = \frac{p_{\perp}^2}{2m} + (n + \frac{1}{2})\mu_B B_0$

利用配分函数  $J = -k_B T \ln Z$  (自由能  $F = -k_B T \ln Z$ ) 计算得

$\chi = \frac{1}{V} \frac{\partial}{\partial B_0} (k_B T \ln Z)$

可以算得  $k_B T \ln Z \approx \frac{2}{5} N \mu_B^2 \left[ 1 - \frac{5}{32} \left( \frac{\mu_B B_0}{E_F} \right)^2 \right]$

则  $\chi_{dia} = -n \frac{\mu_B^2}{2E_F} = -\frac{1}{3} \chi_{para}$

Landau 抗磁磁化率

↓ 真实情况

$\chi = \chi_{para} + \chi_{dia} = \frac{n \mu_B^2}{E_F}$

$\chi_{dia} = -\frac{1}{3} \left( \frac{m_e}{m_{eff}} \right)^2 \chi_{para}$

$m_{eff}$ : 在能带理论中引入的等效电子质量



# 北京大学

双原子分子

$$E = \sum_{i=1}^N (e_i^{(t)} + e_i^{(r)} + e_i^{(v)})$$

where  $e_i^{(t)} = \frac{p_i^2}{2m}$

$$e_i^{(r)} = \frac{j_i^2}{2m}$$

$$e_i^{(v)} = \frac{p_i^2}{2\mu} + \frac{1}{2}\mu\omega^2 x^2$$

$$Z = \frac{1}{N!} Z^N \quad \text{where } Z = Z^{(t)} + Z^{(r)} + Z^{(v)}$$

$$\Rightarrow U = U^{(t)} + U^{(r)} + U^{(v)}$$

$$\Rightarrow C_V = C_V^{(t)} + C_V^{(r)} + C_V^{(v)}$$

且  $C_V^{(t)} = \frac{3}{2} N k_B$  ✓

$$U^{(v)} = \frac{N\hbar\omega}{2} + \frac{N\hbar\omega}{e^{\beta\hbar\omega} - 1}$$

(Einstein 振子)

$$\Rightarrow C_V^{(v)} = N k_B \left( \frac{\theta_v}{T} \right)^2 e^{-\frac{\theta_v}{T}} \quad \text{where } \theta_v = \frac{\hbar\omega}{k_B}$$

低温下,  $C_V^{(v)} \rightarrow 0$ .

简并度  $\omega_j = 2j+1$ .

$$e_j^{(r)} = \frac{j(j+1)\hbar^2}{2I}$$

~~$\Rightarrow Z^{(r)} = \sum_{j=0}^{\infty} (2j+1) e^{-\frac{j(j+1)\hbar^2}{2Ik_B T}}$~~

$$Z^{(r)} = \sum_{j=0}^{\infty} (2j+1) e^{-\frac{j(j+1)\hbar^2}{2Ik_B T}}$$





# 北京大学

转动特征温度  $\theta_r = \frac{h^2}{2Ik_B}$

$$\Rightarrow Z^{(r)} = \sum_{j=0}^{\infty} (2j+1) e^{-\frac{j(j+1)\theta_r}{T}}$$

考虑高温、低温近似.

高温下, 可用积分替代 ( $x = j(j+1)\frac{\theta_r}{T}$ ,  $(\frac{\theta_r}{T}) \ll 1$ )

$$Z^{(r)} = \int_0^{\infty} dx e^{-x} = \frac{2I}{\beta h^2} = \frac{2Ik_B T}{h^2} = \frac{T}{\theta_r}$$

$$\Rightarrow \overline{U} = N \frac{\partial \ln Z}{\partial \beta} = N k_B T \Rightarrow C_V = N k_B$$

低温下, 数值计算.

$\frac{\theta_r}{T} \approx 1$  时数值计算给出的结果与实验相符 ( $H_2$  便是如此).



# 北京大学

同核双原子分子:  $H_2, O_2, N_2$ .

异核双原子分子:  $HCl$  ...

高温下, 无差别

低温下, 同核双原子分子, 以  $H_2$  为例.

$H$  原子核为费米子. 两质子的交换, 波函数反对称.

$$\Psi_{\text{总}} = \Psi_{\text{轨道}} \times \Psi_{\text{自旋}} \quad (\text{轨道分离})$$

两个  $p$  的自旋共 4 种状态.

S 3 个三重态 ( $p+p=1$ )  $\Rightarrow |\uparrow\uparrow\rangle, |\downarrow\downarrow\rangle, \frac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle)$  交换对称

A 1 个单态 ( $p+p=0$ )  $\downarrow$   $S_z=1$   $S_z=-1$   $S_z=0$ .

$\frac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle)$  交换反对称.  
 $S_z=0$ .

当 spin 对称, orbit 需反对称.

当 spin 反对称, orbit 需对称.

由于氢分子的开成只依赖于经电核相互作用, 可认为纯随机

$$\Rightarrow P(\Psi_{\text{orbit}}^A) \approx P(\Psi_{\text{spin}}^A) = \frac{1}{4} \quad P(\Psi_{\text{orbit}}^A) \approx P(\Psi_{\text{spin}}^S) = \frac{3}{4}$$



# 北京大学

$j$  为偶数: 偶宇称  
↓  
对称

$j$  为奇数: 奇宇称  
↓  
反对称

故: 同核双原子

$$Z_{\text{rot}}^{(H)} = \frac{1}{4} \sum_{j=1,3,\dots}^{\infty} (2j+1) e^{-\frac{j(j+1)\theta_r}{T}} + \frac{1}{4} \sum_{j=2,4,\dots}^{\infty} (2j+1) e^{-\frac{j(j+1)\theta_r}{T}}$$

$$C_v^{(r)} = \frac{3}{4} C_{v0}^{(r)} + \frac{1}{4} C_{vp}^{(r)}$$

$^2H$  原子核为 Boson.

对于任意自旋  $S$ .

有  $\frac{S+1}{2S+1}$  的对称, 与  $\frac{S}{2S+1}$  的反对称.

对于氦气, 有  $\frac{2}{3}$  的对称态和  $\frac{1}{3}$  的反对称态:

$$Z^{(H)} = \frac{2}{3} \sum_{j=2,4,\dots}^{\infty} (2j+1) e^{-\frac{j(j+1)\theta_r}{T}} + \frac{1}{3} \sum_{j=1,3,\dots}^{\infty} (2j+1) e^{-\frac{j(j+1)\theta_r}{T}}$$





# 北京大学

实际上, 分子的电子能级也是存在的但其特征温度  $\theta_e \sim 10^4 K$ , 又难以被激发故认为系统存在基态

Born-Oppenheimer 近似.

$$\Delta E^{(e)} \sim 1 \sim 10 eV$$

快自由度 - 电子

$$\Delta E^{(v)} \sim 10^{-1} eV$$

缓慢自由度 - 核.

$$\Delta E^{(r)} \sim 10^{-4} \sim 10^{-3} eV$$

混合理想气体. 化学反应.

考虑  $k$  个组元的理想气体.  $N = \sum_{i=1}^k N_i$

$$E = \sum_{i=1}^k \sum_{j=1}^{N_i} (e_{ij}^{(e)} + e_{ij}^{(v)} + e_{ij}^{(r)} + \dots) = \sum_{i=1}^k \sum_{j=1}^{N_i} (e_{ij}^{(e)} + e_{ij}^{(v)})$$

$$\Xi = \sum_{\{N_i\}} \sum_S e^{-\alpha_1 N_1 - \alpha_2 N_2 - \dots - \alpha_k N_k} \cdot e^{-\beta E_S}$$

如果只考虑平动,

$$\Xi = \sum_{\{N_i\}} e^{-\alpha_1 N_1 - \alpha_2 N_2 - \dots - \alpha_k N_k} \cdot \frac{1}{N_1! N_2! \dots N_k!} \prod_{ij} \left( \int \frac{d^3 \vec{p}_{ij}}{h^3} \frac{d^3 \vec{r}_{ij}}{V} e^{-\beta \frac{\vec{p}_{ij}^2}{2m_i}} \right) \sum_{e_{ij}} e^{-\beta e_{ij}}$$

$$\Rightarrow Z_i = Z_i^{(e)} \cdot Z_i^{(v)}$$

$$\text{where } Z_i^{(v)} = V \left( \frac{2\pi m_i}{\beta h^2} \right)^{3/2}$$

$$\Xi = \sum_{\{N_i\}} e^{-\alpha_1 N_1 - \alpha_2 N_2 - \dots - \alpha_k N_k} \frac{Z_1^{N_1} \dots Z_k^{N_k}}{N_1! N_2! \dots N_k!} \Rightarrow \ln \Xi = \sum_{i=1}^k e^{-\alpha_i} Z_i$$



# 北京大学

$$\bar{N}_i = e^{-\alpha_i} z_i$$

$$P = \frac{1}{\beta} \frac{\partial \ln Z}{\partial V} = \sum_{i=1}^k p_i \quad \text{where} \quad p_i = \frac{\bar{N}_i k_B T}{V}$$

$$U = - \frac{\partial \ln Z}{\partial \beta} = \sum_{i=1}^k \bar{N}_i \left( \frac{3}{2} k_B T - \frac{d \ln z_i}{d \beta} \right)$$

$$S = k_B \sum_{i=1}^k \bar{N}_i \left( \frac{5}{2} + \alpha_i - \beta \frac{d \ln z_i}{d \beta} \right)$$

$$= k_B \sum_{i=1}^k \bar{N}_i \left( \underbrace{(1 + \beta \bar{e}_i - \phi_i(T) - \ln p)}_{RT \lambda \alpha_i = -\frac{\mu_i}{k_B T}} \right) - k_B \sum_{i=1}^k \bar{N}_i \ln x_i \quad \text{where} \quad x_i = \frac{\bar{N}_i}{N}$$

$$\mu_i = k_B T \ln \left[ \frac{p_i}{k_B T z_i} \left( \frac{h^2}{2\pi m_i k_B T} \right)^{3/2} \right]$$

$$\Downarrow$$

$$\mu_i = RT [\phi_i(T) + \ln p_i] \Rightarrow \phi_i(T) = \ln \left[ \left( \frac{h^2}{2\pi m_i k_B T} \right)^{3/2} \frac{1}{k_B T z_i} \right]$$

在热力学中已讨论, 化学平衡条件  $\sum \nu_i \mu_i = 0$ .





# 北京大学

非理想气体/流体 - 存在相互作用

迈耶 - 集团展开理论

单原子单元系

$$H = \sum_{i=1}^N \frac{\vec{p}_i^2}{2m} + \sum_{i < j} \phi(r_{ij}) \quad \text{where } r_{ij} = |\vec{r}_i - \vec{r}_j|$$

↓ 对相互作用

$$\sum_{i < j} \phi(r_{ij})$$

假设  $\phi(r)$  在  $r \rightarrow 0$  时较快趋于 0.

$$E = \sum_{N=0}^{\infty} \left( \frac{z}{\Omega_1^3} \right)^N Q_N(T, V) \quad \text{where } z = e^{-\alpha}, \text{ 逸度.}$$

$\lambda_T^3$  来自动量空间积分.

$$Q_N = \frac{1}{N!} \int \cdots \int e^{-\beta \sum_{i < j} \phi(r_{ij})} d^3\vec{r}_1 \cdots d^3\vec{r}_N \quad \text{位型积分}$$

$$\text{令 } f_{ij} = e^{-\beta \phi(r_{ij})} - 1$$

$$\text{则 } Q_N = \frac{1}{N!} \int \cdots \int \prod_{i < j} (1 + f_{ij}) d^3\vec{r}_1 \cdots d^3\vec{r}_N$$

$\phi(r_{ij})$  衰减极快  $\rightarrow$  短程.

将  $f_{ij}$  看作小量. 领头项:  $Q_N = \frac{1}{N!} \int \cdots \int d^3\vec{r}_1 \cdots d^3\vec{r}_N = V^N$

$(i, j)$  共  $\frac{N(N-1)}{2}$  对, 其中可任选几项保留其余取作 1.



# 北京大学

Mayer 集团展开.

$$Z = \sum_{N=0}^{\infty} \left( \frac{z}{\lambda_T} \right)^N Q_N(T, V)$$

where  $Q_N = \frac{1}{N!} \int \dots \int d^3r_1 \dots d^3r_N \exp(-\beta \sum_{i < j} \phi(r_{ij}))$

def  $f_{ij} = e^{-\beta \phi(r_{ij})} - 1 \Rightarrow e^{-\beta \phi(r_{ij})} = f_{ij} + 1$

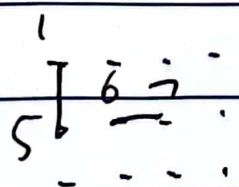
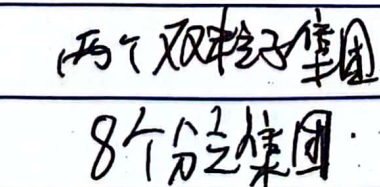
$$\Rightarrow Q_N = \frac{1}{N!} \int \dots \int d^3r_1 \dots d^3r_N \prod_{i < j} (1 + f_{ij})$$

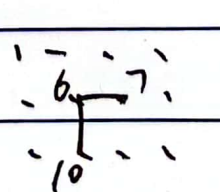
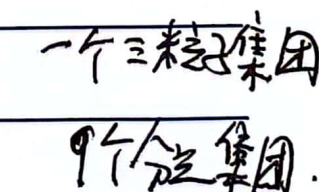
$$= \frac{1}{N!} \int \dots \int d^3r_1 \dots d^3r_N \left( 1 + \sum_{i < j} f_{ij} + \sum_{\substack{i < j \\ k < l \\ (i,j) \neq (k,l)}} f_{ij} f_{kl} + \dots \right)$$

利用图像表示展开过程.

$$\begin{matrix} 1 & 2 & \dots & N \\ \vdots & \vdots & & \vdots \\ 1 & 2 & \dots & N \end{matrix} \int \dots \int d^3r_1 \dots d^3r_N f_{12} = V^{N-2} \iint d^3r_1 d^3r_2 f_{12} = V^{N-1} \int d^3r f_{12}(\vec{r})$$

$f_{12}$

 两个双粒子集团  
 8个分子集团

 一个三粒子集团  
 9个分子集团.

$$\int \dots \int$$



# 北京大学

集团积分.

$$b(\tau) = \frac{1}{n_c! V} \sum_p \int d\vec{r}_1 \cdots d\vec{r}_{n_c} \prod_{l \in L} f_l$$

$c$ : 集团

$n_c$ : 集团  $c$  中点的数目.

$L$ : 链集

$l$ : 一个链节

$\sum_p$ : 粒子作轮换.

例.

$c = \text{"."}$

$$b_c(\tau) = \frac{1}{V} \sum_p \int d\vec{r}_i = 1$$

$c = \text{"--"}$

$$b_c(\tau) = \frac{1}{2V} \int d\vec{r}_1 d\vec{r}_2 f_{12}$$

$c = \text{"^"}$

$$b_c(\tau) = \frac{1}{3!V} \int d\vec{r}_1 d\vec{r}_2 d\vec{r}_3 (f_{12}f_{23} + f_{13}f_{23} + f_{12}f_{13})$$

对于  $N$  粒子系统,  $N = \sum_c m_c n_c$ ,  $m_c$  为 " $c$ " 出现的次数.

于是可将  $b_N$  按集团展开:





# 北京大学

restraint  $N = \sum_c m_c n_c$ .

$$Q_N = \sum_{\{m_c\}} \frac{1}{N!} \left( \frac{N!}{\prod_c m_c! (n_c!)^{m_c}} \right) \left( \prod_c [V n_c! b_c(\tau)]^{m_c} \right)$$

全同性      组合数      每个  $c$  的贡献

$$E = \sum_{m=0}^{\infty} \left( \frac{z}{\lambda T^3} \right)^{\sum_c m_c n_c} \sum_{\{m_c\}} \prod_c \frac{[V b_c(\tau)]^{m_c}}{m_c!}$$

$$= \sum_{\{m_c\}} \left( \frac{z}{\lambda T^3} \right)^{\sum_c m_c n_c} \prod_c \frac{[V b_c(\tau)]^{m_c}}{m_c!} = \sum_{\{m_c\}} \prod_c \frac{\left[ \left( \frac{z}{\lambda T^3} \right)^{n_c} V b_c(\tau) \right]^{m_c}}{m_c!}$$

无限限制  
无约束

~~$$= \prod_c \sum_{m_c} \left( \frac{z}{\lambda T^3} \right)^{\sum_c m_c n_c} \frac{[V b_c(\tau)]^{m_c}}{m_c!}$$~~

$$= \prod_c \sum_{m_c} \frac{\left[ \left( \frac{z}{\lambda T^3} \right)^{n_c} V b_c(\tau) \right]^{m_c}}{m_c!}$$

$$= \prod_c \exp \left[ \left( \frac{z}{\lambda T^3} \right)^{n_c} V b_c(\tau) \right] !!! \quad NB.$$

$$\ln Z = \sum_c \left( \frac{z}{\lambda T^3} \right)^{n_c} V b_c(\tau)$$



# 北京大学

$$Q_N = \sum_{\{m_c\}} \underbrace{\frac{1}{N!}}_{\text{全同性}} \underbrace{\left( \frac{N!}{\prod_c m_c! (n_c!)^{m_c}} \right)}_{\text{组合数}} \underbrace{\left( \prod_c [V n_c! b_c(\tau)]^{m_c} \right)}_{\text{每个 } c \text{ 的贡献}}$$

restraint  $N = \sum_c m_c n_c$ .

$$Z = \sum_{N=0}^{\infty} \left( \frac{z}{\lambda_T^3} \right)^N \sum_{\{m_c\}} \prod_c \frac{[V b_c(\tau)]^{m_c}}{m_c!}$$

$$= \sum_{\{m_c\}} \left( \frac{z}{\lambda_T^3} \right)^{\sum_c m_c n_c} \prod_c \frac{[V b_c(\tau)]^{m_c}}{m_c!} = \sum_{\{m_c\}} \prod_c \frac{\left[ \left( \frac{z}{\lambda_T^3} \right)^{n_c} V b_c(\tau) \right]^{m_c}}{m_c!}$$

无限限制  
无约束

~~$$= \prod_c \sum_{m_c} \left( \frac{z}{\lambda_T^3} \right)^{\sum_c m_c n_c} \frac{[V b_c(\tau)]^{m_c}}{m_c!}$$~~

$$= \prod_c \sum_{m_c} \frac{\left[ \left( \frac{z}{\lambda_T^3} \right)^{n_c} V b_c(\tau) \right]^{m_c}}{m_c!}$$

$$= \prod_c \exp \left[ \left( \frac{z}{\lambda_T^3} \right)^{n_c} V b_c(\tau) \right] \quad !!! \quad NB.$$

$$\ln Z = \sum_c \left( \frac{z}{\lambda_T^3} \right)^{n_c} V b_c(\tau)$$



# 北京大学

$$\Rightarrow \frac{P}{k_B T} = \frac{1}{V} \ln Z = \frac{1}{V} \ln \left[ \sum_c \left( \frac{2}{\pi T^3} \right)^{n_c} b_c(T) \right]$$

$$n = \frac{\bar{N}}{V} = - \frac{1}{V} \frac{\partial}{\partial \alpha} \ln Z = \sum_c n_c \left( \frac{2}{\pi T^3} \right)^{n_c} b_c(T).$$

最低阶:  $b_c(T) \equiv$

$$b_0(T) = \frac{1}{2V} \int d^3 \vec{r}_1 d^3 \vec{r}_2 f_{12}$$

$$= \frac{1}{2} \int d^3 \vec{r} f_{12}(r)$$

$$= \frac{1}{2} \int d^3 r [e^{-\beta \phi(r)} - 1]$$

位力展开:

$$\frac{P}{k_B T} = n + B_2(T)n^2 + B_3(T)n^3 + \dots$$

$$B_1 = 1$$

$$B_2(T) = - \frac{1}{2} \int d^3 r f(r)$$

$$B_3(T) = - \frac{1}{3V} \int d^3 \vec{r}_1 d^3 \vec{r}_2 d^3 \vec{r}_3 f_{123} \quad \triangle$$

...

可以证明, 有无穷小的扰动结构是单粒子不可约的。  
对位力系数





# 北京大学

problem: 在相变过程中 (临界点), ~~系统~~ 集团展开发散.

根据  $n = \sum_c n_c b_c(\tau) \left(\frac{z}{\lambda_T^3}\right)^{n_c}$  反解  $z(n)$ :

$$\frac{1}{\lambda_T^3} x = \frac{z}{\lambda_T^3}$$

$$n = n_1 b_1(\tau) x^{n_1} + n_2 b_2(\tau) x^{n_2} + 3 b_3(\tau) x^3 + \dots$$

$$n = x + 2b_2(\tau)x^2 + 3b_3(\tau)x^3$$

↓ 反解.

假设  $x = n + a_2 n^2 + a_3 n^3 + \dots$

代入  $n(x)$ , 对比系数即可得展开系数  $k_i$ .

$$n = (n + a_2 n^2 + a_3 n^3) + 2b_2(n + a_2 n^2 + a_3 n^3)^2 + \dots$$

$$\Rightarrow \begin{cases} a_2 + 2b_2 = 0 \\ a_3 + 4b_2 a_2 + 3b_3 = 0 \\ \dots \end{cases} \Rightarrow \begin{cases} a_2 = -2b_2 \\ a_3 = 8b_2^2 - 3b_3 \\ \dots \end{cases}$$

代回  $\frac{p}{k_B T} = \sum_c \left(\frac{z}{\lambda_T^3}\right)^{n_c} b_c(\tau)$ , 发现

$b_3$  的情形被消去

只留下  $\triangle$  的贡献



# 北京大学

$$\frac{p}{k_B T} = n + B_2 n^2 + B_3 n^3$$

- Onnes equation

计算  $B_2, B_3 \dots$

需要知道  $\phi(r)$  的表达式

采用  $\phi(r) = \phi_0 \left[ \left( \frac{r_0}{r} \right)^{12} - 2 \left( \frac{r_0}{r} \right)^6 \right]$  "12-6" 式

简化为  $\phi(r) = \begin{cases} \infty, & r < r_0 \\ -\phi_0 \left( \frac{r_0}{r} \right)^6, & r > r_0 \end{cases}$

$$B_2(T) = -\frac{1}{2} \int d^3r \phi(r)$$

$$= -\frac{1}{2} \int d^3r \left[ e^{-\beta \phi(r)} - 1 \right]$$

$$= -2\pi \int_{r_0}^{\infty} r^2 dr \left[ e^{-\beta \phi_0 \left( \frac{r_0}{r} \right)^6} - 1 \right] + \frac{1}{2} \int_0^{r_0} 4\pi r^2 dr$$

$$= -2\pi \int_{r_0}^{\infty} r^2 dr \left[ e^{-\beta \phi_0 \left( \frac{r_0}{r} \right)^6} - 1 \right] + \frac{2}{3} \pi r_0^3$$

假设  $\phi_0$  很小, 将  $e^{-\beta \phi_0 \left( \frac{r_0}{r} \right)^6}$  展开, 得

$$B_2(T) = -2\pi \int_{r_0}^{\infty} r^2 dr \cdot \beta \phi_0 \left( \frac{r_0}{r} \right)^6 + \frac{2}{3} \pi r_0^3$$

$$= b - \frac{a}{N k_B T} \quad \text{where } b = \frac{2}{3} \pi N r_0^3$$

$$a = \frac{2}{3} \pi N^2 \phi_0 r_0^3$$





# 北京大学

液体热力学性质.

★ 集团展开对于  $N$  很大的情形不适用.

设经典相互作用  $U(\vec{r}_i - \vec{r}_j)$

$N$  粒子共分布 ~~概率~~ 常数密度函数

$$P(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N) = \frac{1}{N! Q_N(T, V)} \exp\left[-\beta \sum_{i < j} U(\vec{r}_i - \vec{r}_j)\right]$$

单粒子分布函数

$$n_1(\vec{x}) = \sum_{i=1}^N \langle \delta(\vec{x} - \vec{r}_i) \rangle$$

两体  $n_2(\vec{x}_1, \vec{x}_2) = \sum_{i < j} \langle \delta(\vec{x}_1 - \vec{r}_i) \delta(\vec{x}_2 - \vec{r}_j) \rangle$

若系统是各向同性的:

$$n_2(\vec{x}_1, \vec{x}_2) = n_2(|\vec{x}_1 - \vec{x}_2|) = \frac{N^2}{V^2} g(|\vec{x}_1 - \vec{x}_2|) \quad g(|\vec{x}_1 - \vec{x}_2|): \text{对分布函数 PDF}$$

通过光的散射,

$$\text{结构因子 } S(\vec{q}) - 1 = \frac{N}{V} \int d^3\vec{r} [g(\vec{r}) - 1] e^{-i\vec{q} \cdot \vec{r}}$$

$$I \propto |S(\vec{q})|^2$$

$h(\vec{r}) = g(\vec{r}) - 1$  对关联函数.

$$\int d^3\vec{r} [g(\vec{r}) - 1] = \frac{V^2}{N^2} \int d^3\vec{r} (n_2(\vec{x}_1, \vec{x}_2) - \frac{N^2}{V^2})$$

$$= -\frac{V}{N} + V \frac{\langle 4N^2 \rangle}{N^2} \quad \text{--- 1 + 4k_B T K_T}$$

$$\Rightarrow N \int d^3\vec{r} [g(\vec{r}) - 1] = -1 + 4k_B T K_T. \quad \text{压缩物态方程.}$$

位力定理.

$$pV = Nk_B T \left[ 1 - \frac{n}{6k_B T} \int d^3r (\vec{r} \cdot \nabla V(r)) g(r) \right]$$

★如何得到 PDF  $g(r)$ ?

$$N(r) \rightarrow n_2(\vec{x}_1, \vec{x}_2) \rightarrow n_3(\vec{x}_1, \vec{x}_2, \vec{x}_3) \rightarrow \dots$$

BBGKY hierarchy.

要严格得到  $g(r)$ , 最终需要得到  $N$  体 Hamiltonian.



分子动力学模拟...

(稀薄)

等离子体的统计性描述.

集团展开不收敛.

设 Plasma 完全为整体电中性, 离子电荷  $ze$

当  $n \ll (\frac{k_B T}{z^2 e^2})^3$  时, 称为稀薄等离子体.

动能主要来自于电势能.

$$n_{i0} = \frac{N_i}{V}$$

(平均).

$$U = \frac{1}{2} \sum_i (ze) n_{i0} \Phi_i$$

第  $i$  种离子感受到其他离子在其位置上产生的电势.

$$n_i(r) = n_{i0} \exp\left(-\frac{ze\Phi(r)}{k_B T}\right) \approx n_{i0} - \frac{n_{i0} ze}{k_B T} \Phi(r) \quad \text{Boltzmann distribution}$$

$$\text{由电动力学 } \nabla^2 \Phi(r) = -4\pi \sum_i (ze) n_i(r).$$

$$\Rightarrow \nabla^2 \Phi(r) = -K \Phi(r)$$

$$K = \frac{4\pi e^2}{k_B T} \sum_i n_{i0} z_i^2$$

$$\Rightarrow \Phi(r) = ze \left( \frac{e^{-Kr}}{r} \right)$$

$$\phi_i = K z_i e$$

或: Debye length  $\epsilon_0 = \frac{1}{K}$

$$\Rightarrow \Phi(r) = ze \left( e^{-r/\epsilon_0} / r \right) = \frac{ze}{r} \left[ \frac{ze}{-r} (Kr) \right]$$

$$\Rightarrow U_{int} = - \sqrt{\frac{\pi}{N k_B T}} \left( \sum_i N_i z_i^2 e^z \right)^{3/2}$$

$$U = - \frac{\partial \ln Z}{\partial \beta} \propto \ln Z$$

$$F = -k_B T \ln Z \Rightarrow F = F_0 - \frac{2e^3}{3} \sqrt{\frac{\pi}{N k_B T}} \left( \sum_i N_i z_i^2 \right)^{3/2}$$

$$\Rightarrow p = - \frac{\partial F}{\partial V} = \frac{N k_B T}{V} - \frac{e^3}{2 V^{3/2}} \sqrt{\frac{\pi}{N k_B T}} \left( \sum_i N_i z_i^2 \right)^{3/2}$$

$$G = F + PV = F_0 - \frac{\sqrt{\pi}}{\sqrt{N k_B T}} \left( \sum_i N_i z_i^2 e^z \right)^{3/2} = \sum_i N_i (g_i + k_B T \ln x_i) - \frac{V k_B T}{\lambda^3} \left( \sum_i N_i z_i^2 e^z \right)^{3/2}$$

~~$= \sum_i N_i (g_i + k_B T \ln x_i)$~~       理想溶液  $\mu$ :

修正后的化学势

$$\mu_i = g_i + k_B T (\ln x_i + \ln \gamma_i)$$

$\gamma_i$ : 活度系数,

以双离子溶液为例

$$M_{2+}^+ M_{2-}^- \Rightarrow 2+z_+ + 2-z_- = 0$$

$$\ln \gamma_{\pm} = - \frac{e^2 (2+z_+^2 + 2-z_-^2)}{8\pi \epsilon k_B T}$$



# CH 8 二组分相变 及其平均场理论

## 自旋模型 (Ising 模型)

Hamiltonian  $H = H\{S_i\}$

由粒子全同性 带来交换相互作用, 量子效应.

$\Psi(r_1, r_2) = \phi_{\sigma_1}(r_1) \phi_{\sigma_2}(r_2) \otimes \chi_{S_1, S_2}$

triplet  $\left\{ \begin{array}{l} \chi_{1,2} = |\uparrow\uparrow\rangle \\ \chi_{1,2} = \frac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle) \\ \chi_{1,2} = |\downarrow\downarrow\rangle \end{array} \right\} S=1$

单态  $\chi_{1,2} = \frac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle) S=0$

对称部分  $\Psi^{(S)}(r_1, r_2)$ , 反对称  $\Psi^{(A)}(r_1, r_2)$

$\Psi^{(S)}(r_1, r_2) \cdot \chi^{(A)} \Rightarrow$  反对称

$\Psi^{(A)}(r_1, r_2) \cdot \chi^{(S)} \Rightarrow$  反对称

$H_2 \begin{cases} k-J & \text{三重态} \\ k+J & \text{单态} \end{cases}$

称  $J$  为交换积分.

$\Rightarrow H_{ex} = -J \vec{S}_1 \cdot \vec{S}_2$  (Heisenberg model)

## Ising model

对于一简单晶格, 在每个格点定义一自旋变量  $\sigma_i = \pm 1$

则  $H = -J \sum_{\langle i,j \rangle} \sigma_i \sigma_j$

加外磁场

$H = -J \sum_{\langle i,j \rangle} \sigma_i \sigma_j - H \sum_i \sigma_i$

$\left\{ \begin{array}{l} \text{自旋平均值 } \langle \sigma_i \rangle = 0 \Rightarrow \text{para} \\ \langle \sigma_i \rangle \neq 0 \Rightarrow \text{ferro} \end{array} \right.$

recall ~~Landau~~ Landau theory

$$m = \langle \sigma_i \rangle$$

$$H = -J \sum_{\langle ij \rangle} \sigma_i \sigma_j - \sum_i H \sigma_i$$

外场.

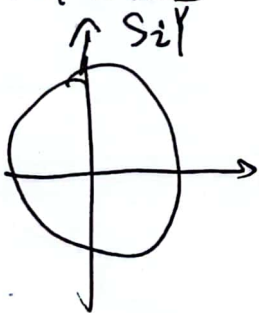
$$Z = \sum_{\{\sigma_i\}} e^{-\beta H(\{\sigma_i\})} = \sum_{\sigma_1=\pm 1} \sum_{\sigma_2=\pm 1} \cdots \sum_{\sigma_N=\pm 1} e^{-\beta H(\{\sigma_i\})}$$

In practice 直接严格求解是不可能

对称性.

考虑 连续变化的自旋

XY 模型



$$\vec{S}_i = (S_i^x, S_i^y)$$

$$S_i^{x^2} + S_i^{y^2} = 1$$

$$H = -J \sum_{\langle ij \rangle} \vec{S}_i \cdot \vec{S}_j$$

H 具有  $O(2)$  旋转不变性.  $\rightarrow$  Abelian 群

五维情况 (Heisenberg 模型)  
 $\vec{S}_i = (S_i^x, S_i^y, S_i^z), |\vec{S}_i|^2 = 1.$

H 具有  $O(3)$  转动不变性  $\rightarrow$  非 Abelian 群  $\xrightarrow{\text{推广到 n 维}} O(n) - \text{sigma model}.$

Ising model: 对称群  $\mathbb{Z}_2 = \{-1, 1\}$  - 分立对称性.

Ising model 的求解方法. 1. 2 维可直接精确求解

0) 严格解

3 维 Ising 模型无解析解.

1) 平均场近似.

优: 物理图像清晰, 求解简洁

缺: 不一定对.

2) ~~高维展开~~ 高温展开

优: 精确得到系统离临界点较远时的性质

缺: 在临界点附近收敛性差.

3) 重整化群.

优: 在临界区域 ~~效果~~ 效果好

缺: 必须深入临界区域.

往往需结合其他近似方法.

4) monte-carlo.



平均场近似

$$H(\{\sigma_i\}) = -J \sum_{\langle ij \rangle} \sigma_i \sigma_j - H \sum_i \sigma_i$$

对某固定格点:

$$- \sigma_i (H + J \sum_{j \in \langle i \rangle} \sigma_j)$$

随机度量, 有涨落

↓ 平均场近似

$$H_{\text{eff}} = \langle J \sum_{j \in \langle i \rangle} \sigma_j \rangle$$

$$= J \sum_{j \in \langle i \rangle} \langle \sigma_j \rangle = qJ \langle \sigma_i \rangle \text{ where } q \text{ 为配位数}$$

$$\Rightarrow - \sigma_i (H + H_{\text{eff}})$$

Weiss 分子场

$$\begin{cases} H^{\text{(mean field)}}[\{\sigma_i\}] = - \sum_i \sigma_i (H + H_{\text{eff}}) \\ H_{\text{eff}} = \langle J \sum_{j \in \langle i \rangle} \sigma_j \rangle \end{cases}$$

$$Z = \sum_{\{\sigma_i\}} e^{-\beta H^{\text{(MF)}}} = \sum_{\{\sigma_i\}} e^{-\beta (H + H_{\text{eff}}) \sum_i \sigma_i} = \sum_{\{\sigma_i\}} \prod_i e^{-\beta (H + H_{\text{eff}}) \sigma_i}$$

$$= \prod_i \sum_{\sigma_i} e^{-\beta (H + H_{\text{eff}}) \sigma_i}$$

$$= \prod_i (e^{\beta (H + H_{\text{eff}})} + e^{-\beta (H + H_{\text{eff}})})$$

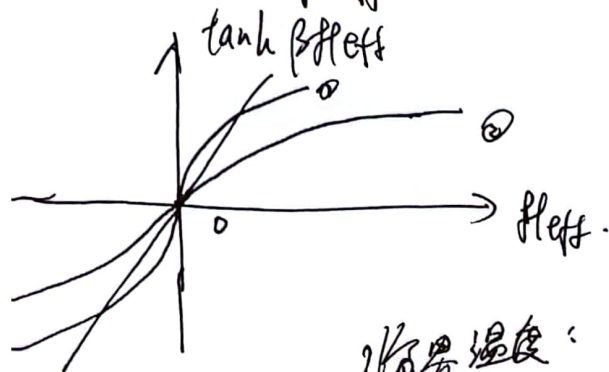
$$= [e^{\beta (H + H_{\text{eff}})} + e^{-\beta (H + H_{\text{eff}})}]^N$$

计算  $H_{\text{eff}}$ :

$$H_{\text{eff}} = qJ \langle \sigma_i \rangle = qJ \frac{1}{\beta} \frac{\partial \ln Z}{\partial H} = qJ \tanh[\beta (H + H_{\text{eff}})]$$

无外场时:

$$H_{\text{eff}} = qJ \tanh \beta H_{\text{eff}}$$



①: 自发磁化

②: 无自发磁化

临界温度:  $\frac{qJ}{k_B T_c} = 1 \Rightarrow T_c = \frac{qJ}{k_B}$

矛盾: 二维三角晶格  $q=6$

三维立方晶格  $q=6$

$\Rightarrow T_c$  相等? NO!

序参量  $m = \langle \sigma_i \rangle = \frac{H_{\text{eff}}}{qJ}$

由  $x \rightarrow 0$  时  $\tanh x = x - \frac{x^3}{3} + \dots$

当  $T \rightarrow T_c$  时

$$m = \langle \sigma_i \rangle \approx \sqrt{3} (1 - \frac{T}{T_c})^{1/2}$$

$$m \sim \begin{cases} 0 & T > T_c \\ (T_c - T)^{1/2} & T \leq T_c \end{cases}$$

总存在外场时,

$$m = \tanh[\beta(H + qJm)] \xrightarrow{H \rightarrow 0, T \rightarrow T_c} \beta(H + qJm)$$

$$\Rightarrow \chi_T = \left( \frac{\partial m}{\partial H} \right)_{T, H \rightarrow 0} = \frac{1}{[T - T_c]^\gamma} \quad \gamma \geq 1$$

$T = T_c$  时

$$m = \beta(H + qJm) - \frac{1}{3} \beta^3 (H + qJm)^3 + \dots$$

$$= m + \beta H - \frac{1}{3} \beta^3 m^3 + \dots$$

$$\Rightarrow H \propto m^3, \quad \delta = 3$$

还可证明,  $\chi_T = \begin{cases} 3Nk_B/2 \cdot (T - T_c)^{-1} & T \rightarrow T_c^- \\ 0 & T \rightarrow T_c^+ \end{cases}$

Bragg-Williams 近似

$$H = -J \sum_{\langle ij \rangle} \sigma_i \sigma_j - H \sum_i \sigma_i$$

假设: 各格点上  $\sigma_i$  统计独立.

$$\Rightarrow \langle \sigma_i \sigma_j \rangle \approx \langle \sigma_i \rangle \langle \sigma_j \rangle$$

注意到  $\langle \sigma_i \rangle$  与位置无关.

$$m = \langle \sigma_i \rangle$$

$$\sigma_i = \begin{cases} +1, & \text{概率 } p_+ \\ -1, & \text{概率 } p_- \end{cases}$$

$$\langle \sigma_i \rangle = p_+ - p_-$$

在 B-W 近似下,

$$U = \langle H \rangle = -J \sum_{\langle ij \rangle} \langle \sigma_i \rangle \langle \sigma_j \rangle - H \sum_i \langle \sigma_i \rangle$$

$$= -\frac{1}{2} q J N m^2 - N \mu H m$$

$$S = k_B \ln \Omega$$

$$\text{where } \Omega = \frac{N!}{N_+! N_-!} = \frac{N!}{(N p_+)! (N p_-)!}$$

$$\Rightarrow S = k_B \left( N \ln N - N p_+ \ln N p_+ - N p_- \ln N p_- \right)$$

$$= k_B N \ln N (p_+ \ln p_+ + p_- \ln p_-)$$

$$\text{注意: } p_{\pm} = \frac{1 \pm m}{2}$$

$$\text{故 } S = N k_B \left( -\frac{1+m}{2} \ln \frac{1+m}{2} - \frac{1-m}{2} \ln \frac{1-m}{2} \right)$$

$$\Rightarrow F = U - TS = N f$$

$$f = -\frac{qJ}{2} m^2 - \mu H m - k_B T \left[ -\frac{1+m}{2} \ln \frac{1+m}{2} - \frac{1-m}{2} \ln \frac{1-m}{2} \right]$$



磁场的真实状态:  $\frac{\partial F}{\partial m} = 0$

$$-qJm - \mu + \frac{k_B T}{2} \ln \left( \frac{1+m}{1-m} \right) = 0$$

$$\Rightarrow m = \tanh \left[ \beta (qJm + \mu) \right]$$

这与平均场近似完全等价

$$F: \text{将 } f = -\frac{qJ}{2} m^2 - m\mu - k_B T \left[ \left( \frac{1+m}{2} \right) \ln \frac{1+m}{2} + \left( \frac{1-m}{2} \right) \ln \frac{1-m}{2} \right]$$

在临界点附近展开, 则

$$f(m) = f_0 - m\mu + \frac{m^2}{2} (k_B T - qJ) + \frac{k_B T}{12} m^4 + \dots$$

这与 Landau 理论的假设一致.

recall that in Landau theory:

$$a(\tau) = k_B T - qJ = k_B (\tau - \tau_c)$$

$$b(\tau) = \frac{k_B T}{3}$$

临界点附近的涨落与关联.

$$\langle \sigma_i \rangle \sim m$$

考虑空间分布

$$m \rightarrow m_i \rightarrow m(\vec{r})$$

$$\text{则 } F[m(\vec{r})] = \int d^3r f(\vec{r}) = \int d^3r \left[ f_0(\tau) + \frac{a(\tau)}{2} m^2(\vec{r}) + \frac{b(\tau)}{4} m^4(\vec{r}) + \dots \right] + \frac{d(\tau)}{2} (\nabla m(\vec{r}))^2$$

求  $F[m(\vec{r})]$  极值

$$m(\vec{r}) = \langle m(\vec{r}) \rangle + \delta m(\vec{r})$$

$$= \bar{m} + \delta m(\vec{r})$$

与  $\vec{r}$  无关

$$m^2 = \begin{cases} -a(\tau)/b(\tau), & \tau < \tau_c \\ 0, & \tau > \tau_c \end{cases}$$

$$C(\vec{r}_1, \vec{r}_2) = \langle (m(\vec{r}_1) - \langle m(\vec{r}_1) \rangle) (m(\vec{r}_2) - \langle m(\vec{r}_2) \rangle) \rangle$$

平移不变体系,  $C(\vec{r}_1, \vec{r}_2) = C(\vec{r}_1 - \vec{r}_2)$

Pourier 展开.

$$\delta m(\vec{r}) = m(\vec{r}) - \bar{m} = \frac{1}{V} \sum_{\vec{k}} \tilde{m}_{\vec{k}} e^{i\vec{k} \cdot \vec{r}}$$

逆变换

$$\int d^3r \delta m(\vec{r}) e^{-i\vec{p} \cdot \vec{r}} = \sum_{\vec{k}} \tilde{m}_{\vec{k}} \int_V e^{i(\vec{k}-\vec{p}) \cdot \vec{r}} \frac{d^3r}{V} = \tilde{m}_{\vec{p}}$$

代入  $C(\vec{r}_1, \vec{r}_2)$ , 得

$$C(\vec{r}_1, \vec{r}_2) = \frac{1}{V^2} \sum_{\vec{k}_1, \vec{k}_2} \langle \tilde{m}_{\vec{k}_1} \tilde{m}_{\vec{k}_2} \rangle e^{i\vec{k}_1 \cdot \vec{r}_1 + i\vec{k}_2 \cdot \vec{r}_2}$$

$$= \frac{1}{V^2} \sum_{\vec{k}_1, \vec{k}_2} \langle \tilde{m}_{\vec{k}_1} \tilde{m}_{\vec{k}_2} \rangle e^{i\vec{k}_1 \cdot \vec{r}} e^{i\vec{k}_2 \cdot \vec{r}}$$

由 ~~平移~~ 不变性

$$C(\vec{r}_1 - \vec{r}_2) = \frac{1}{V} \int d^3r_2 C(\vec{r}_1, \vec{r}_2)$$

$$= \frac{1}{V^2} \sum_{\vec{k}_1, \vec{k}_2} \langle \tilde{m}_{\vec{k}_1} \tilde{m}_{\vec{k}_2} \rangle e^{i\vec{k}_1 \cdot \vec{r}} \delta_{\vec{k}_1 + \vec{k}_2, 0}$$

$$= \frac{1}{V^2} \sum_{\vec{k}} \langle m_{\vec{k}} m_{-\vec{k}} \rangle e^{i\vec{k} \cdot \vec{r}}$$

$$\Rightarrow C(\vec{r}) = \frac{1}{V} \sum_{\vec{k}} \langle m_{\vec{k}} m_{-\vec{k}} \rangle e^{i\vec{k} \cdot \vec{r}}$$

由 ~~涨落~~ 涨落-耗散理论,

$$W \propto \exp\left(-\frac{\Delta F}{k_B T}\right).$$

$$\Delta F = \int d^3r \left[ \frac{a(T)}{2} (\delta m(\vec{r}))^2 + \frac{b(T)}{2} (\nabla \delta m(\vec{r}))^2 + \frac{c(T)}{4} (\bar{m} + \delta m(\vec{r}))^4 + \dots \right]$$

$$\text{where } \Delta F = \frac{a(T)}{2} \int d^3r (\delta m(\vec{r}))^2 + \frac{b(T)}{2} \int d^3r (\nabla \delta m(\vec{r}))^2 + \frac{c(T)}{4} \int d^3r (\bar{m} + \delta m(\vec{r}))^4 + \dots$$

$$\Rightarrow \Delta F = \frac{1}{V} \sum_{\vec{k}} [a(T) + b(T) k^2] |m_{\vec{k}}|^2$$

$$\Rightarrow W \propto \frac{1}{k} \exp\left(-\frac{[a(T)d(T)]k^2}{2V k_B T}\right)$$

$$\Rightarrow \langle |\tilde{m}_{\vec{k}}|^2 \rangle = \frac{V k_B T}{a(T) + d(T)k^2}$$

$$\Rightarrow C(\vec{r}) = \frac{k_B T}{4\pi d(T)} \frac{1}{V} \sum_{\vec{k}} \left( \frac{4\pi}{a(T)/d(T) + k^2} \right) e^{i\vec{k} \cdot \vec{r}}$$

$V \rightarrow \infty, \sum \rightarrow \int$

$$C(\vec{r}) = \frac{k_B T}{4\pi d(T)} \frac{1}{V} \int d^3k \frac{4\pi}{a(T)/d(T) + k^2} e^{i\vec{k} \cdot \vec{r}}$$

$$= \frac{k_B T}{4\pi d(T)} \frac{e^{-r/\xi}}{r}, \quad \text{where } \xi = \frac{1}{\sqrt{a(T)/d(T)}} \sim |T - T_c|^{-\frac{1}{2}} \text{ — 关联长度}$$

$T \sim T_c$  时  $\xi$  发散

对于D维空间的标度模型,

关联函数在相变点的r行为是

$$\langle F \rangle \sim r^{-D+2-\eta} \quad (r \rightarrow \infty)$$

$$\int \frac{4\pi}{k_0^2 + k^2} = \frac{e^{-k_0 r}}{r}$$

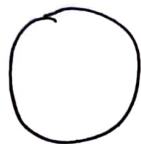


1-D Ising model 严格解.

$N$  格点.

$$H = -J \sum_i \sigma_i \sigma_{i+1} - \frac{H}{2} \sum_i (\sigma_i + \sigma_{i+1})$$

引入周期性边界条件.  $\sigma_{N+1} = \sigma_1$ .



$$Z = \sum_{\{\sigma_i\}} e^{-\beta H}$$

$$= \sum_{\{\sigma_i\}} \prod_i \exp \left\{ \beta \left[ J \sigma_i \sigma_{i+1} + \frac{H}{2} (\sigma_i + \sigma_{i+1}) \right] \right\}$$

写成矩阵形式

引入 transfer matrix

$$T = \begin{pmatrix} T_{11} & T_{1,-1} \\ T_{-1,1} & T_{-1,-1} \end{pmatrix} = \begin{pmatrix} e^{\beta(J+H)} & e^{-\beta J} \\ e^{-\beta J} & e^{\beta(J-H)} \end{pmatrix}$$

$$Z = \sum_{\{\sigma_i\}} \prod_{i=1}^N T_{\sigma_i \sigma_{i+1}} = \text{Tr}(T^N)$$

将  $T$  对角化 (得本征值), 则

$$Z = \text{Tr}(T^N) = \lambda_1^N + \lambda_2^N \xrightarrow{\lambda_1 > \lambda_2, N \sim 10^{23}} \lambda_1^N$$

$$\begin{vmatrix} e^{\beta(J+H)} - \lambda & e^{-\beta J} \\ e^{-\beta J} & e^{\beta(J-H)} - \lambda \end{vmatrix} = \lambda^2 - (e^{\beta(J+H)} + e^{\beta(J-H)}) \lambda + e^{2\beta J}$$

$$\Rightarrow \lambda_{1,2} = e^{\beta J} \cosh(\beta H) \pm \sqrt{e^{2\beta J} \sinh^2(\beta H) + e^{2\beta J}}$$

$$Z = \lambda_1^N = \left[ e^{\beta J} \cosh(\beta H) + \sqrt{e^{2\beta J} \sinh^2(\beta H) + e^{-4\beta J}} \right]^N$$

$$F = -k_B T \ln Z = -N k_B T \ln \left( e^{\beta J} \cosh(\beta H) + \sqrt{e^{2\beta J} \sinh^2(\beta H) + e^{-4\beta J}} \right)$$

$$m = -\frac{1}{\beta} \frac{\partial F}{\partial H} = \frac{\sinh(\beta H)}{\sqrt{\sinh^2(\beta H) + e^{-4\beta J}}}$$

发现:  $H=0$  时  $m=0$ , 无自发磁化.

矩阵元

$$C(i,j) \triangleq \langle \sigma_i \sigma_j \rangle$$

$$C(i,j) = \langle \sigma_i \sigma_j \rangle$$

$$H = 0$$

$$H = -J \sum_i \sigma_i \sigma_{i+1}$$

$$\Rightarrow Z = \sum_{\{\sigma_i\}} \prod_i \exp\{\beta J \sigma_i \sigma_{i+1}\}$$

$$\text{令 } T^{(i)} = \begin{pmatrix} e^{\beta J_i} & e^{-\beta J_i} \\ e^{-\beta J_i} & e^{\beta J_i} \end{pmatrix}$$

$$Z = \sum_{\{\sigma_i\}} \prod_i T^{(i)} = \text{Tr} \left( \prod_{i=1}^N T^{(i)} \right) = \text{Tr} \left( \prod_{i=1}^N T^{(i)} \right)$$

$$\text{将 } T^{(i)} \text{ 写作 } e^{\beta J_i} + e^{-\beta J_i} \tau \quad \text{where } \tau = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$$

$$\text{有投影算子 } P_{\pm} = \frac{1 \pm \tau}{2}, \quad \text{性质: } \begin{cases} P_+^n = P_+, \quad n=1,2,\dots \\ P_+ P_- = P_- P_+ = 0 \end{cases}$$

$$\Rightarrow T^{(i)} = 2 [\cosh(\beta J_i) P_+ + \sinh(\beta J_i) P_-]$$

$$\begin{aligned} \Rightarrow Z &= \text{Tr} \left( 2^N \left\{ \prod_i \cosh \beta J_i P_+ + \prod_i \sinh \beta J_i P_- \right\} \right) \\ &= 2^{N-1} \left( \prod_i \cosh \beta J_i + \prod_i \sinh \beta J_i \right) \end{aligned}$$

$$\text{链式} \quad \frac{\partial \ln Z}{\partial J} = \frac{1}{Z} \sum_{\sigma} \sigma_1 \sigma_2 \dots \sigma_N \frac{\partial \ln Z}{\partial J} = \frac{1}{Z} \sum_{\sigma} \sigma_1 \sigma_2 \dots \sigma_N \frac{\partial \ln Z}{\partial J}$$

解得

$$C_j = \langle \sigma_i \sigma_j \rangle = \frac{\tanh^{j-1}(\beta J) + \tanh^{N-j+1}(\beta J)}{1 + \tanh^N(\beta J)}$$

$\tanh(\beta J) < 1 \Rightarrow$  略去  $N$  项。

$$C_j = \tanh^{j-1}(\beta J) \propto e^{-j/\xi} \quad \text{where } \xi \text{ 是关联长度}$$

$$\xi = -\frac{1}{\ln \tanh(\beta J)} \approx \frac{1}{2\beta J} \quad \text{低温}$$

$\rightarrow$  1-D Ising model 的关联长度不收敛 对临界状态无法做研究

2-D Ising model 的高温展开和对偶性。

二维晶格, 无外场 Ising model.

$$H = -J \sum_{\langle i,j \rangle} \sigma_i \sigma_j$$

周期边界条件。

$$\text{易证 } e^{\beta J \sigma_i \sigma_j} = \cosh \beta J + \sigma_i \sigma_j \sinh \beta J = \cosh \beta J [1 + \sigma_i \sigma_j \tanh \beta J]$$

$$Z = \sum_{\{\sigma_i\}} \prod_{\langle i,j \rangle} e^{\beta J \sigma_i \sigma_j} = [\cosh \beta J]^N \sum_{\{\sigma_i\}} \prod_{\langle i,j \rangle} [1 + \sigma_i \sigma_j \tanh \beta J]$$

$$T \gg T_c \text{ 时, } \tanh \beta J \sim \beta J \ll 1$$

$$Z \approx [\cosh \beta J]^N \sum_{\{\sigma_i\}} \prod_{\langle i,j \rangle} (1 + \underbrace{\sigma_i \sigma_j \beta J}_{f_{ij} \ll 1})$$

$\downarrow$   
Mayer 集团展开



注意到  $f_{ij} \neq 0$  的格点不同时,

$\sum$  使得  $z \equiv 0$ .

所以

不为零的项来自一定单自闭合回路:

只有“小方块”会贡献  $z$ .



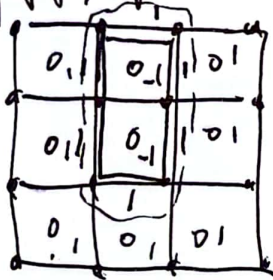
$$Z = (\cosh \beta J)^{2N} \sum_{\{f_{ij}\}} \prod_i (1 + \tanh \beta J)$$

$$= (\cosh \beta J)^{2N} \sum_{\Gamma} (\tanh \beta J)^{L(\Gamma)}$$

$\Gamma$  为集团类型 (闭合回路).

$L(\Gamma)$  为集团长度.

换一种求和方式



正立方格  $\longleftrightarrow$  对偶晶格 (0).

以格点间的 link 计数

$$n_l = \begin{cases} 1, & \text{link 在回路上} \\ 0, & \text{否} \end{cases}$$

以格点间的 link 计数

$$n_l = \begin{cases} 1, & \text{link 在回路上} \\ 0, & \text{否} \end{cases}$$

$$\text{故 } Z = [\cosh \beta J]^{2N} \sum_{\{n_l\}} [\tanh \beta J]^{\sum n_l}$$

$$P = \sum_l n_l = \sum_{\langle ab \rangle} \frac{1 - \tau_a \tau_b}{2}$$

$\tau_a, \tau_b$   $\begin{cases} \text{同号, 相邻回路 link 两侧} \\ \text{异号, 闭合回路 link 两侧} \end{cases}$

则在对称性上,

$$Z = \sum_{\{a_b\}} e^{\tilde{\beta} J \sum_{\langle ab \rangle} T_{ab}}.$$

定义  $\beta$  的对偶温度  $\tilde{\beta}$  为  $e^{-2\tilde{\beta}J} \triangleq \tanh \beta$ .

$$\begin{aligned} \text{则 } \sinh(2\tilde{\beta}J) &= \frac{1}{2}(e^{2\tilde{\beta}J} - e^{-2\tilde{\beta}J}) \\ &= \frac{1}{2}\left(\frac{\cosh \beta}{\sinh \beta} - \frac{\sinh \beta}{\cosh \beta}\right) \\ &= \frac{1}{2\sinh \beta \cosh \beta} = \frac{1}{\sinh 2\beta} \end{aligned}$$

$$\text{或 } \sinh 2\beta \sinh 2\tilde{\beta}J = 1.$$

$$\text{则 } Z(\beta) = [\sinh(2\beta J)]^N Z(\tilde{\beta}).$$

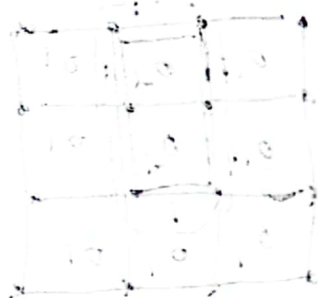
$$\Rightarrow \frac{F(\beta)}{N} = \frac{1}{N} \ln \sinh 2\beta J = \frac{F(\tilde{\beta})}{N}$$

$N \rightarrow \infty$ , 二级相变.  
 $F(\beta) = F(\tilde{\beta})$  奇点.

$$\beta = \tilde{\beta} = \beta_c$$

$$\Rightarrow \sinh(2\beta_c J) = 1$$

$$\Rightarrow \beta_c = \frac{1}{2} \ln(1 + \sqrt{2}) = 0.44068.$$



Ising model 对称性.  $Z_2 = \{1, -1\}$ .

铁磁相:  $\langle \sigma_i \rangle \neq 0$

$$\langle \sigma_i \rangle = \frac{1}{Z} \sum_{\{\sigma_i\}} \sigma_i e^{\beta \sum_{\langle ij \rangle} \sigma_i \sigma_j}$$

$$\sigma_i \rightarrow -\sigma_i \Rightarrow \langle \sigma_i \rangle = -\langle \sigma_i \rangle \Rightarrow \langle \sigma_i \rangle = 0.$$

如何表现相变?

Hamiltonian 具某种对称性

但低温下系统基态不遵守该对称性.

How about (3)?

Heisenberg model.

$$H = -J \sum_{\langle ij \rangle} \vec{S}_i \cdot \vec{S}_j - \sum_i \vec{S}_i \cdot \vec{H}$$

↓ mean field  $H_{\text{eff}} = qJ \langle S_z \rangle$

$$\text{则 } H^{(\text{MF})} = - \sum_i S_{iz} (H_{\text{eff}} + H)$$

$$\text{解得 } m_z = \langle S_z \rangle = \left( \coth(\beta(H_{\text{eff}} + H)) - \frac{1}{\beta(H_{\text{eff}} + H)} \right)$$

$\beta(H_{\text{eff}} + H)$  很小时,

$$T_c \sim \frac{qJ}{3k_B}$$



连续对称性 \$S^z\$ 的对称性的区别

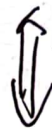
考虑无外场 Heisenberg 模型

它具有 \$O(3)\$ 转动不变性 (无 \$H\_z\$)

$$O(3) \rightarrow O(2)$$

铁磁相变

\$\langle S^z \rangle \neq 0\$, 在 \$z\$ 轴转动方向有对称性



$$\text{Ising } \{-1, 1\} \rightarrow \{1\}$$

Heisenberg model 的 Landau 模型

$$F[\vec{m}(r)] = \int d^3r \left[ \frac{a}{2} \vec{m}(r) \cdot \vec{m}(r) + \frac{c}{2} (\nabla \vec{m}(r))^2 + \frac{b}{4} (\vec{m}(r) \cdot \vec{m}(r))^2 + \dots \right]$$

$$\text{有 } \vec{m}^2 = \begin{cases} -aT/bT, & T < T_c \text{ 破缺相 (铁磁相)} \\ 0, & \text{铁磁相 (对称相)}$$

where \$\vec{m} = m \vec{n}\$ 随空间不变

$$\begin{aligned} \vec{n}(r) &= \vec{m} + \vec{\phi}(r) \\ &= m \vec{n} + \vec{\phi}(r) \end{aligned}$$

$$\text{故 } F[\vec{m}(r)] = f(m) + \frac{\delta F}{\delta m} \Big|_{m=m} \vec{\phi} + \frac{1}{2} \frac{\delta^2 F}{\delta m \delta m} \vec{\phi} \cdot \vec{\phi}$$

$$\left. \begin{aligned} &\text{对称相 } m=0 \\ &\text{破缺相 } m \neq 0 \end{aligned} \right\}$$

代入 \$F[\vec{m}(r)]\$ 表达式得

$$(\text{对称 } \nabla m(r) = \nabla [m \vec{n} + \vec{\phi}(r)] = \nabla \vec{\phi}(r)$$

$$\textcircled{2} (\vec{m}(r))^2 = m^2 + 2m(\vec{n} \cdot \vec{\phi}(r)) + (\vec{\phi}(r))^2 \quad (\times \frac{a}{2})$$

$$\textcircled{3} (\vec{m}(r))^4 = m^4 + 4m^3(\vec{n} \cdot \vec{\phi}) + 4m^2(\vec{n} \cdot \vec{\phi})^2 + 2m^2\vec{\phi}^2 \quad (\times \frac{b}{4})$$

$$\Rightarrow F^{(2)}(\vec{\phi}(\vec{r})) = \int d^3r \left\{ \frac{1}{2} \vec{\phi}(\vec{r})^2 + \frac{1}{4} m^2 [2\phi^2 + 4(\vec{n} \cdot \vec{\phi})] + \frac{d}{2} (\nabla \phi)^2 \right\}$$

忽略  $F^{(4>2)}$  的贡献

$$\vec{\phi}(\vec{r}) = \vec{n} \sigma(\vec{r}) + \vec{\phi}_T(\vec{r})$$

$$\text{Then } (\nabla \vec{\phi})^2 = (\nabla \sigma)^2 + \nabla \vec{\phi}_T \cdot \nabla \vec{\phi}_T$$

$$\Rightarrow F^{(2)}[\sigma, \vec{\phi}_T] = \int d^3r \left[ \frac{d}{2} (\nabla \vec{\phi}_T)^2 + (\nabla \sigma)^2 + \mu(\sigma) \right]$$

$$F^{(2)}(\delta m(\vec{r})) = \int d^3r \left[ \frac{d}{2} (\nabla \delta m(\vec{r}))^2 + \frac{a}{2} (\delta m(\vec{r}))^2 \right]$$

$$\delta m(\vec{r}) = \frac{1}{V} \sum_{\vec{k}} \tilde{m}_{\vec{k}} e^{i\vec{k} \cdot \vec{r}}$$

$$C(\vec{r}) = \langle \delta m(\vec{r}) \delta m(\vec{0}) \rangle = \langle \tilde{m}_{\vec{k}} \rangle^2$$

$\Rightarrow$  ①  $\sigma$  的涨落

$$C(\vec{r}) = \langle \sigma(\vec{r}) \sigma(\vec{0}) \rangle = \frac{k_B T}{4\pi d(r)} e^{-\frac{r}{\xi}}$$

$$\text{where } \xi = \sqrt{\frac{d(r)}{2|a(r)|}}$$

$$\text{② } \vec{\phi}_T \text{ 的涨落 } C_T(\vec{r}) = \langle \phi_T^\alpha(\vec{r}) \phi_T^\beta(\vec{0}) \rangle$$

$$= \langle \delta^{\alpha\beta} - n^\alpha n^\beta \rangle \frac{k_B T}{4\pi d(r)} \left( \frac{1}{r} \right)$$

$p^{\alpha\beta} \phi^\beta = \phi^\alpha$

— 长德斯通模式

长德斯通定理

$O(3) \xrightarrow{\text{破缺}} O(2)$ , 2个生成元破缺  $\rightarrow$  涨落方向  
3个生成元 1个生成元

对称性自发破缺与 universality.

二级相变: 两相对称性不同

高温 - 较高对称性  $G$

$$G \supset H$$

低温 - 较低对称性  $H$

体系在参数变化下 对称性自发破缺

群  $\left\{ \begin{array}{l} \text{分立群} \\ \text{连续群} \end{array} \right.$

$H(\{\phi_i\})$  具有完整对称性

但系统基态 不具有对称性