第十章　有相互作用系统的统计物理

10.1　铁磁系统的平均场理论
10.2　非理想气体的状态方程
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10.1 铁磁系统的平均场理论

晶格里每个格点上有一个自旋 $\boldsymbol{S}$，外场 $\boldsymbol{H}$ 下的 Heisenberg model

$$\hat{\mathcal{H}} = -\frac{1}{2}\sum_{ij} J_{ij}\hat{\mathbf{S}}_i\cdot\hat{\mathbf{S}}_j \boxed{\text{相互作用}} - \sum_i g\mu_B \boldsymbol{H}\cdot\hat{\mathbf{S}}_i \boxed{\text{磁场贡献}}$$

$$\Rightarrow -\frac{1}{2}\sum_{ij} J_{ij}\hat{S}_{iz}\hat{S}_{jz} - \sum_i g\mu_B H\hat{S}_{iz} \qquad \text{单轴磁系统}$$

$$\Rightarrow -\frac{1}{2}\sum_{\langle ij\rangle} J\hat{S}_{iz}\hat{S}_{j}jz - \sum_i g\mu_B H S_{iz} \qquad \text{最近邻近似}$$

$$\Rightarrow -\frac{J}{2}\sum_{\langle ij\rangle} \hat{\sigma}_i\hat{\sigma}_j - g\mu_B H\sum_i \hat{\sigma}_i \qquad \text{Ising model, } \sigma_i = \pm 1\text{，自旋 } 1/2$$

- 交换项 $J_{ij} = J(|\boldsymbol{R}_i - \boldsymbol{R}_j|)$ 代表第 i 个和第 j 个格点上自旋的相互作用强度，和电子波函数交叠有关。一般是短程作用。
- $J > 0$ 自旋平行的时候能量小，反平行的时候能量大 ⇒ 铁磁作用

正则配分函数

系统本征态 $|S\rangle = |\uparrow,\downarrow,\cdots\rangle = |+,-,\cdots,\rangle = |\{\sigma_i\}\rangle$

$$\hat{H}|\{\sigma_i\}\rangle = E(\{\sigma_i\})|\{\sigma_i\}\rangle = -\Big(J/2\sum_{\langle ij\rangle}\sigma_i\sigma_j + g\mu_B H\sum_i \sigma_i\Big)|\{\sigma_i\}\rangle$$

格点数为 N 时，本征态数目为 2^N

$$Z = \sum_S e^{-\beta E_S} = \sum_{\{\sigma_i\}} e^{\beta J/2\sum_{\langle ij\rangle}\sigma_i\sigma_j + \beta g\mu_B H\sum_i\sigma_i}$$

无相互作用极限 $J = 0$

$$Z = \sum_{\{\sigma_i\}} e^{\beta g\mu_B H\sum_i\sigma_i} = \sum_{\{\sigma_i\}}\prod_i e^{\beta g\mu_B H\sigma_i} = \prod_i\sum_{\sigma_i=\pm} e^{\beta g\mu_B H\sigma_i}$$

$$= [2\cosh(\beta g\mu_B H)]^N$$

$$M = Tr\Big\{\sum_i(\sigma_i)\mu_B\hat{\rho}\Big\} = \frac{1}{\beta g}\frac{\partial \ln Z}{\partial H} = N\mu_B\frac{\sinh\beta g\mu_B H}{\cosh\beta g\mu_B H}$$

$$= N\mu_B\tanh\beta g\mu_B H$$

$J = 0 \Rightarrow$ 顺磁相

$H = 0$

$$M = N\mu_B \tanh \beta g \mu_B H = 0$$

$\boxed{\text{顺磁相，无自发磁矩}}$

$H \to 0$， $M = \chi(T) H$

$$\tanh x = x - x^3/3 + \cdots$$

$$M \simeq N\mu_B \beta g \mu_B H = \frac{N g \mu_B^2 / k_B}{T} H$$

$$\Rightarrow \chi(T) = \frac{N g \mu_B^2 / k_B}{T} = \frac{C}{T}$$

$\boxed{\text{Curier's law}}$

热容

$$U = -\left(\frac{\partial \ln Z}{\partial \beta}\right) = -N\left(\frac{\partial \ln \cosh[\beta g \mu_B H]}{\partial \beta}\right) = -N g \mu_B H \tanh(\beta g \mu_B H)$$

$$C_H = \left(\frac{\partial U}{\partial T}\right)_H = \frac{N(g\mu_B H)^2}{k_B T^2} \frac{1}{\cosh^2(\beta g \mu_B H)}$$

一维 Ising model 的严格解

N 个格点，周期性边界条件

$$E(\{\sigma_i\}) = -J[\sigma_1\sigma_2 + \sigma_2\sigma_3 + \cdots + \sigma_{N-1}\sigma_N + \sigma_N\sigma_1] - g\mu_B H \sum_i \sigma_i$$

$$= -J\sum_{i=1}^{M} \sigma_i\sigma_{i+1} - g\mu_B H \sum_{i=1}^{N} \sigma_i = -\sum_{i=1}^{M} [J\sigma_i\sigma_{i+1} + g\mu_B H(\sigma_i + \sigma_{i+1})/2]$$

$$Z = \sum_{\{\sigma_i\}} e^{-\beta E(\{\sigma_i\})} = \sum_{\{\sigma_i\}} \prod_i e^{\beta J\sigma_i\sigma_{i+1} + \beta g\mu_B H(\sigma_i + \sigma_{i+1})/2} = \sum_{\{\sigma_i\}} \prod_i T_{\sigma_i\sigma_{i+}}$$

$$= \sum_{\{\sigma_i\}} T_{\sigma_1\sigma_2} T_{\sigma_2\sigma_3} \cdots T_{\sigma_i\sigma_{i+1}} T_{\sigma_{i+1}\sigma_{i+2}} \cdots T_{\sigma_{N-1}\sigma_N} T_{\sigma_N\sigma_1} = Tr\{T^N\}$$

$$T = \begin{pmatrix} T_{++} & T_{+-} \\ T_{-+} & T_{--} \end{pmatrix} = \begin{pmatrix} e^{\beta J + \beta g\mu_B H} & e^{-\beta J} \\ e^{-\beta J} & e^{\beta J - \beta g\mu_B H} \end{pmatrix}$$

Transfer matrix

Transfer Matrix

$$T=\begin{pmatrix} e^{\beta J+\beta g\mu_B H} & e^{-\beta J} \\ e^{-\beta J} & e^{\beta J-\beta g\mu_B H}\end{pmatrix} \xRightarrow{\text{对角化}} U^{\dagger}TU=\Lambda\begin{pmatrix}\lambda_+ & \\ & \lambda_-\end{pmatrix}$$

$$0=|T-\lambda I|=\lambda^2-\lambda e^{\beta J}\left(e^{\beta g\mu_B H}+e^{-\beta g\mu_B H}\right)+e^{2\beta J}-e^{-2\beta J}$$

$$=\lambda^2-2\lambda e^{\beta J}\cosh\beta g\mu_B H+2\sinh 2\beta J=(\lambda-\lambda_+)(\lambda-\lambda_-)$$

$$\lambda_\pm=e^{\beta J}\cosh\beta g\mu_B H\pm\sqrt{e^{2\beta J}\cosh^2\beta g\mu_B H-2\sinh 2\beta J}$$

$$Z=\lambda_+^N+\lambda_-^N\xRightarrow{N\to\infty}=\lambda_+^N$$

$$M=\frac{1}{\beta g}\frac{\partial\ln Z}{\partial H}=\frac{N}{\beta g\lambda_+}\frac{\partial\lambda_+}{\partial H}$$

$$=N\mu_B\frac{e^{\beta J}\sinh\beta g\mu_B H+\dfrac{e^{2\beta J}\cosh\beta g\mu_B H\sinh\beta g\mu_B H}{\sqrt{e^{2\beta J}\cosh^2\beta g\mu_B H-2\sinh 2\beta J}}}{e^{\beta J}\cosh\beta g\mu_B H+\sqrt{e^{2\beta J}\cosh^2\beta g\mu_B H-2\sinh 2\beta J}}$$

$$\xRightarrow{H\to 0} 0$$

☞ 温度不为零，外场趋于零，平均磁场始终为零，无相变

关联函数

$$C_{jk} = \langle\sigma_j\sigma_k\rangle - \langle\sigma_j\rangle\langle\sigma_k\rangle = \frac{1}{Z}\sum_{\{\sigma_i\}} e^{-\beta E(\{\sigma_i\})}\sigma_j\sigma_k - \bar{\sigma}_j\bar{\sigma}_k$$

$$= \frac{1}{Z}\sum_{\{\sigma_i\}} T_{\sigma_1\sigma_2}\cdots T_{\sigma_{j-1}\sigma_j}\sigma_j T_{\sigma_j\sigma_{j+1}}\cdots T_{\sigma_{k-1}\sigma_k}\sigma_k T_{\sigma_k\sigma_{k+1}}\cdots T_{\sigma_N\sigma_1} - \bar{\sigma}_j$$

$$= \frac{1}{Z}\mathtt{Tr}\{T^j\sigma_z T^{k-j}\sigma_z T^{N-k}\} - \bar{\sigma}_j\bar{\sigma}_k = \frac{1}{Z}\mathtt{Tr}\{T^{N-(k-j)}\sigma_z T^{k-j}\sigma_z\} - \bar{\sigma}_j\bar{\sigma}_k$$

$$= \frac{1}{\mathtt{Tr}\{\Lambda^N\}}\mathtt{Tr}\{\Lambda^{N-(k-j)}U^\dagger\sigma_z U\Lambda^{(k-j)}U^\dagger\sigma_z U\} - \bar{\sigma}_j\bar{\sigma}_k$$

- 关联函数只和相对距离有关系：

  $C_{jk} = C_{k-j,0} = C_l = C(r = la), \qquad l = k - j$
- 一般情况下比较复杂，外磁场为零时：

$$T = \begin{pmatrix} e^{\beta J} & e^{-\beta J} \\ e^{-\beta J} & e^{\beta J} \end{pmatrix} \qquad U = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 & 1 \\ 1 & -1 \end{pmatrix} \Rightarrow \Lambda = \begin{pmatrix} 2\cosh\beta J & \\ & 2\sinh\beta J \end{pmatrix}$$

$$U^\dagger\sigma_z U = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} = \sigma_x$$

关联长度

$$C(r)=\frac{1}{Z}\mathtt{Tr}\left\{\begin{pmatrix}\lambda_+^{N-l} & \\ & \lambda_-^{N-l}\end{pmatrix}\begin{pmatrix} & 1\\ 1 & \end{pmatrix}\begin{pmatrix}\lambda_+^{l} & \\ & \lambda_-^{l}\end{pmatrix}\begin{pmatrix} & 1\\ 1 & \end{pmatrix}\right\} \quad \boxed{r=(k-j)a=la}$$

$$=\frac{1}{\lambda_+^N+\lambda_-^N}\mathtt{Tr}\left\{\begin{pmatrix}\lambda_+^{N-l}\lambda_-^{l} & \\ & \lambda_-^{N-l}\lambda_+^{l}\end{pmatrix}\right\}=\frac{\lambda_+^{N-l}\lambda_-^{l}+\lambda_-^{N-l}\lambda_+^{l}}{\lambda_+^N+\lambda_-^N}$$

$$\xRightarrow{N\to\infty}\left(\frac{\lambda_-}{\lambda_+}\right)^l=(\tanh\beta J)^{r/a}=e^{-r/\xi} \qquad \boxed{\text{关联长度}}$$

$$\xi=\frac{a}{-\ln(\tanh\beta J)}=\begin{cases}\dfrac{a}{-\ln(\beta J)}\to 0 & \beta J\to 0\\[2ex] \dfrac{a}{2}e^{2\beta J}\to\infty & \beta J\to\infty\end{cases}$$

- ☞ 一维 Ising model 在有限温度下没有相变，在 $T=0$ 时为铁磁相
- ☞ 在高温下，关联长度趋于零，体系只有短程序。$T\to 0$ 时，关联长度变得无穷大，体现出长程序的特点。

Ising model

- 用平均场理论，任意维度的磁性系统都可以发生铁磁/顺磁相变
- Lenz（Lenz 矢量）提出 Ising model，让他的博士生 Ernst Ising 用这个模型研究铁磁系统的相变
- Ising 得到一维系统的严格解，发现一维系统在 $T \neq 0$ 时都是顺磁相，不会发生相变；他推广认为高维系统同样不会发生相变
- 其它物理学家认为 Ising 过分简化了问题，Heisenberg 进一步提出 X-Y model，Heisenberg model 希望量子效应可以导致铁磁相，但都没有结果
- 1936 年 Peierls 得到二维 Ising model 高温无长程序，低温存在长程序，因此有相变
- 1941 年 Kramers 和 Wannier 得到二维 Ising model 的相变温度
- 1944 年 Onsager 得到了二维 Ising model 的严格解，发现存在相变，这是第一个有非平凡结果的严格解模型
- 可以应用于其它领域，例如格点气体模型、合金

二维 Ising model 的严格解

$$\mathcal{H} = -\sum_{i=1}^{L_x}\sum_{j=1}^{L_y}\left[J_x\sigma_{j,k}\sigma_{j+1,k} + J_y\sigma_{j,k}\sigma_{j,k+1}\right]$$

- 临界点 $T_c, H_c = 0$： $\sinh\frac{2J_x}{k_BT_c}\sin\frac{2J_y}{k_BT_c} = 1$
- 临界点附近热容： $C \sim A_c \ln|T - T_c|$
- 临界点自发磁矩： $M \sim M_c|T - T_c|^{1/8}$

$$M = \left[1 - \left(\sinh\frac{2J_x}{k_BT}\sinh\frac{2J_y}{k_BT}\right)^{-2}\right]^{1/8}$$

- 临界点磁化率： $\chi(T) \sim A_\pm|T - T_c|^{-7/4}$

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399th solution of the Ising model

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Abstract. We show that the nearest-neighbour correlations of the honeycomb, triangular and square Ising models can be obtained by using *only* the star-triangle relations and simple assumptions concerning the thermodynamic limit and differentiability. This gives the internal energy, and hence the free energy and specific heat.

1. Introduction

Since the original solution of the two-dimensional Ising model by Onsager (1944), many alternative derivations have been given. Onsager diagonalised the transfer matrix by looking for irreducible representations of a related matrix algebra; Kaufman (1949) simplified this derivation by using spinor operators; Schultz *et al* (1964), and Thompson (1965), further simplified it by using fermion operators.

平均场理论

$$\sigma_i = \overline{\sigma}_i + \sigma_i - \overline{\sigma}_i = \overline{\sigma}_i \boxed{\text{平均值}} + \delta\sigma_i \boxed{\text{涨落}} = \overline{\sigma} + \delta\sigma_i \qquad \boxed{\text{平移不变性}}$$

$$\begin{aligned}
E(\{\sigma_i\}) &= -J/2 \sum_{\langle ij \rangle} \sigma_i \sigma_j - g\mu_B H \sum_i \sigma_i \\
&= -J/2 \sum_{\langle ij \rangle} (\overline{\sigma} + \delta\sigma_i)(\overline{\sigma} + \delta\sigma_j) - g\mu_B H \sum_i \sigma_i \\
&= -J/2 \sum_{\langle ij \rangle} [\overline{\sigma}^2 + \overline{\sigma}\delta\sigma_i + \overline{\sigma}\delta\sigma_j + \delta\sigma_i\delta\sigma_j \boxed{\text{涨落高阶项}}] - g\mu_B H \sum_i \sigma_i \\
&\simeq -J/2 \sum_i z \boxed{\text{最近邻格点数}} \times [\overline{\sigma}^2 + 2\overline{\sigma}\delta\sigma_i] - g\mu_B H \sum_i \sigma_i \\
&= -J/2 \sum_i z[\overline{\sigma}^2 + 2\overline{\sigma}(\sigma_i - \overline{\sigma})] \boxed{= [2\overline{\sigma}\sigma_i - \overline{\sigma}^2]} - g\mu_B H \sum_i \sigma_i \\
&= -Jz\overline{\sigma} \sum_i \sigma_i - g\mu_B H \sum_i \sigma_i + NJz\overline{\sigma}^2/2 \\
&= -g\mu_B H_{eff} \sum_i \sigma_i + NJz\overline{\sigma}^2/2
\end{aligned}$$

平均场理论

$$E(\{\sigma_i\}) = -g\mu_B H_{eff} \sum_i \sigma_i + NJz\overline{\sigma}^2/2$$

$$H_{eff} = H + Jz\overline{\sigma}/(g\mu_B)$$

外场 + 分子场

$$M = N\mu_B\overline{\sigma} = N\mu_B \tanh \beta g\mu_B H_{eff}$$

$$\overline{\sigma} = \tanh\{\beta g\mu_B[H + Jz\overline{\sigma}/(g\mu_B)]\} = \tanh(\beta g\mu_B H + \beta Jz\overline{\sigma})$$

外场为零时的自发极化：$\tanh(x) = x - x^3/3 + \cdots$

$$\overline{\sigma} = \tanh(\beta Jz\overline{\sigma}) = \beta Jz\overline{\sigma} - (Jz\overline{\sigma})^3/3 + \cdots$$

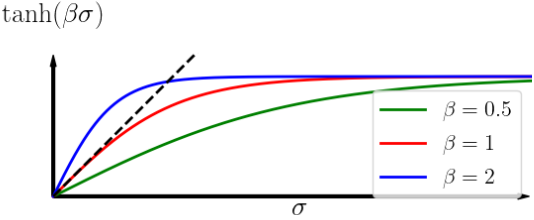
$$\Rightarrow \beta_c Jz = 1 \Rightarrow T_c = \frac{Jz}{k_B}$$

$T > T_c \Rightarrow \overline{\sigma} = 0$

无自发磁矩，顺磁相

$T < T_c \Rightarrow \overline{\sigma} \neq 0$

有自发磁矩，铁磁相



临界指数

$$H = 0, T \leq T_c\,,\quad M = N\mu_B\overline{\sigma} \propto |T - T_c|^{\beta}$$

$$\begin{aligned}\overline{\sigma} &= \frac{Jz}{k_BT}\overline{\sigma} - \left(\frac{Jz}{k_BT}\right)^3\overline{\sigma}^3 + \cdots \\ &= \frac{T_c}{T}\overline{\sigma} - \left(\frac{T_c}{T}\right)^3\overline{\sigma}^3 + \cdots \\ \overline{\sigma}^2 &\simeq (T_c/T - 1) \Rightarrow \overline{\sigma} \propto |T_c/T - 1|^{1/2} \Rightarrow \beta = 1/2\end{aligned}$$

$$T > T_c\,,\quad H \to 0,\quad M = \chi(T)H,\quad \chi(T) \propto |T - T_c|^{-\gamma}$$

$$\overline{\sigma} \simeq \frac{g\mu_BH}{k_BT} + \frac{Jz\overline{\sigma}}{k_BT} = \frac{g\mu_BH}{k_BT} + \frac{T_c}{T}\overline{\sigma}$$

$$\overline{\sigma} = \frac{g\mu_BH/(k_BT)}{1 - T_c/T} = \frac{g\mu_B/k_B}{T - T_c}H$$

$$M = N\mu_B\overline{\sigma} = \frac{Ng\mu_B^2/k_B}{T - T_c}H \Rightarrow \chi(T) = \frac{Ng\mu_B^2/k_B}{T - T_c} \qquad \boxed{\text{Curier's law}}$$

$$\Rightarrow \gamma = 1$$

临界指数

$H = 0$, $C_H \propto |T - T_c|^{-\alpha}$

$$U = -NJz\overline{\sigma}^2/2 = \begin{cases} -NJz(T_c/T - 1)/2 & T < T_c \\ 0 & T > T_c \end{cases}$$

$$C_H = \left(\frac{\partial U}{\partial T}\right)_{H=0} = \frac{NJzT_c}{2T^2} = \frac{Nk_BT_c^2}{2T^2} \simeq \frac{Nk_B}{2} \qquad T < T_c$$

$$C_H = 0 \qquad T > T_c$$

$$\Rightarrow \alpha = 0$$

$T = T_c$, $H \to 0$, $M \propto H^{1/\delta}$

$$\overline{\sigma} = \tanh(\beta g\mu_B H + T_c\overline{\sigma}/T) = \tanh(\beta_c g\mu_B H + \overline{\sigma})$$

$$= \beta_c g\mu_B H + \overline{\sigma} - (\beta_c g\mu_B H + \overline{\sigma})^3/3 + \cdots$$

$$\Rightarrow 0 \simeq \beta_c g\mu_B H - \overline{\sigma}^3/3 \Rightarrow \delta = 3$$

☞平均场结果和 Landau 理论完全相同

自发对称破缺

$$\bar{\sigma} = \frac{N_+ - N_-}{N} = \frac{2N_+ - N}{N} \qquad N_+ + N_- = N \qquad N_+ = \frac{N}{2}(1+\bar{\sigma})$$

$$p(\bar{\sigma}) = \frac{\Omega(N_+, N_-)}{Z} e^{-\beta E(\bar{\sigma})} = \frac{1}{Z} C_N^{N_+} \exp[\beta g \mu_B H_{eff} N \bar{\sigma} - \beta N J z \bar{\sigma}^2/2]$$

$$= \frac{1}{Z} \exp[\ln \frac{N!}{(N/2 - N\bar{\sigma}/2)!(N/2 + N\bar{\sigma}/2)!} + \beta g \mu_B H_{eff} N \bar{\sigma} - \beta N J z \bar{\sigma}^2/2$$

$$\xRightarrow{H=0} \frac{1}{Z} \exp[N \ln N - (N/2 - N\bar{\sigma}/2) \ln(N/2 - N\bar{\sigma}/2)$$

$$- (N/2 + N\bar{\sigma}/2) \ln(N/2 + N\bar{\sigma}/2) + \beta N J z \bar{\sigma}^2/2]$$

$$= \frac{1}{C} \exp[-\frac{N\bar{\sigma}^2}{2} - \frac{N}{24}\bar{\sigma}^4 + \frac{T_c}{2T} N \bar{\sigma}^2]$$

$$= \frac{1}{C} \exp\left[-\left(1 - \frac{T_c}{T}\right) N \bar{\sigma}^2/2 - \frac{N}{24}\bar{\sigma}^4\right] = \frac{1}{C} \exp[-\Delta G/(k_B T)]$$

- 体系自旋为 $\bar{\sigma}$ 或者 $-\bar{\sigma}$ 几率相同，但实际只能取其中一个 ⇒ 自发对称破缺。
- 在临界点附近不服从 Gauss 分布，具有很大的涨落。
- 临界点附近平均值和最可几值不同。

关联函数

$$\mathcal{H} = -\frac{J}{2}\sum_{\langle ij\rangle}\hat{\sigma}_i\hat{\sigma}_j - g\mu_B\sum_i H_i\hat{\sigma}_i \qquad \boxed{H_i \equiv H}$$

$$\sigma_i = \overline{\sigma}_i + \delta\sigma_i \boxed{\text{无平移不变性}}$$

$$\begin{aligned}
E(\{\sigma_i\}) &= -J/2\sum_{\langle ij\rangle}\sigma_i\sigma_j - g\mu_B\sum_i H_i\sigma_i \\
&= -J\sum_i\Big[\sum_{j\in\langle ij\rangle}\overline{\sigma_j}\Big]\sigma_i - g\mu_B\sum_i H_i\sigma_i + \frac{J}{2}\sum_{\langle ij\rangle}\bar{\sigma}_i\bar{\sigma}_j \\
&= -g\mu_B\sum_i H_i^{eff}\sigma_i + \frac{J}{2}\sum_{\langle ij\rangle}\bar{\sigma}_i\bar{\sigma}_j = -g\mu_B\sum_i H_i^{eff}\sigma_i - E_0 \\
H_i^{eff} &= H_i + \frac{J}{g\mu_B}\sum_{j\in\langle ij\rangle}\overline{\sigma}_j \\
Z = Z(\{H_i\}) &= \sum_{\{\sigma_i\}} e^{-\beta E(\{\sigma_i\})} = e^{-\beta E_0}\prod_i\Big[2\cosh\beta g\mu_B H_i^{eff}\Big]
\end{aligned}$$

关联函数

$$
\begin{aligned}
\overline{\sigma}_j &= \frac{1}{Z}\sum_{\{\sigma_i\}} \sigma_j e^{-\beta E(\{\sigma_i\})} = \frac{1}{Z}\frac{\partial}{\partial(\beta g\mu_B H_j)}\sum_{\{\sigma_i\}} e^{-\beta E(\{\sigma_i\})} \\
&= \frac{\partial \ln Z}{\partial(\beta g\mu_B H_j)} = \tanh(\beta g\mu_B H_j^{eff}) \simeq (\beta g\mu_B H_j^{eff}) - \frac{1}{3}(\beta g\mu_B H_j^{eff})^3 \\
&\simeq \beta g\mu_B H_j + \beta J\sum_{l\in\langle jl\rangle}\overline{\sigma}_l + \frac{(\beta J)^3}{3}\Big(\sum_{l\in\langle jl\rangle}\overline{\sigma}_l\Big)^3 \\
C_{jk} &= \langle(\sigma_j - \bar{\sigma}_j)(\sigma_k - \bar{\sigma}_k)\rangle = \langle\sigma_j\sigma_k\rangle - \bar{\sigma}_j\bar{\sigma}_k \\
&= \frac{1}{Z}\sum_{\{\sigma_i\}}\sigma_j\sigma_k e^{-\beta E(\{\sigma_i\})} - \bar{\sigma}_j\bar{\sigma}_k \\
&= \frac{1}{Z}\frac{\partial}{\partial(\beta g\mu_B H_j)}\frac{\partial}{\partial(\beta g\mu_B H_k)}\sum_{\{\sigma_i\}} e^{-\beta E(\{\sigma_i\})} - \bar{\sigma}_j\bar{\sigma}_k \\
&= \frac{\partial^2 \ln Z}{\partial(\beta g\mu_B H_j)\partial(\beta g\mu_B H_k)} = \frac{\partial\overline{\sigma}_k}{\partial(\beta g\mu_B H_j)}
\end{aligned}
$$

关联长度

$$C_{jk} = \frac{\partial}{\partial(\beta g\mu_B H_j)}\left[g\mu_B H_k + \beta J \sum_{l\in\langle kl\rangle} \overline{\sigma}_l + \frac{(\beta J)^3}{3}\Big(\sum_{l\in\langle kl\rangle} \overline{\sigma}_l\Big)^3\right]$$

$$= \delta_{jk} + \beta J \sum_{l\in\langle jl\rangle} C_{jl} + (\beta J)^3\Big(\sum_{l\in\langle jl\rangle} \overline{\sigma}_l\Big)^2 \sum_{l\in\langle kl\rangle} C_{jl}$$

$$= \delta_{jk} + \beta J\left[1 + (\beta J)^2\Big(\sum_{l\in\langle jl\rangle} \overline{\sigma}_l\Big)^2\right] \sum_{l\in\langle kl\rangle} C_{jl}$$

$$H_i \Rightarrow H \to 0 \qquad \overline{\sigma}_i \Rightarrow \overline{\sigma}$$

$$C_{jk} = \delta_{jk} + \beta J[1 + (\beta J z\overline{\sigma})^2] \sum_{l\in\langle kl\rangle} C_{jl}$$

$$C_{jk} = C(\boldsymbol{r}_k - \boldsymbol{r}_j) = \sum_{\boldsymbol{k}} e^{i\boldsymbol{k}\cdot(\boldsymbol{r}_k - \boldsymbol{r}_j)} C(\boldsymbol{k})$$

Fourier 变换

关联函数

$$
\begin{aligned}
C(\boldsymbol{k}) &= \sum_{k} C_{jk} e^{-i\boldsymbol{k}\cdot(\boldsymbol{r}_k-\boldsymbol{r}_j)} \\
&= \sum_{k} \delta_{jk} e^{-i\boldsymbol{k}\cdot(\boldsymbol{r}_k-\boldsymbol{r}_j)} + \sum_{k} \beta J[1+(\beta J z\overline{\sigma})^2] \sum_{l\in\langle kl\rangle} C_{jl} e^{-i\boldsymbol{k}\cdot(\boldsymbol{r}_k-\boldsymbol{r}_j)} \\
&= 1 + \beta J[1+(\beta J z\overline{\sigma})^2] \sum_{l} C_{jl} e^{-i\boldsymbol{k}\cdot(\boldsymbol{r}_l-\boldsymbol{r}_j)} \sum_{k\in\langle kl\rangle} e^{-i\boldsymbol{k}\cdot(\boldsymbol{r}_k-\boldsymbol{r}_l)} \\
&= 1 + \beta J[1+(\beta J z\overline{\sigma})^2]\gamma(\boldsymbol{k})C(\boldsymbol{k}) \qquad \boxed{\gamma(\boldsymbol{k}) = \textstyle\sum_{\boldsymbol{r}_s\in nn} e^{-i\boldsymbol{k}\cdot\boldsymbol{r}_s}}
\end{aligned}
$$

$$
C(\boldsymbol{k}) = \frac{1}{1-\beta J[1+(\beta J z\overline{\sigma})^2]\gamma(\boldsymbol{k})}
$$

$$
\gamma(\boldsymbol{k}) = \sum_{\boldsymbol{r}_s\in nn} e^{-i\boldsymbol{k}\cdot\boldsymbol{r}_s} = 2(\cos k_x a + \cos k_y a + \cdots] \qquad \boxed{\text{方格子}}
$$

$$
C(\boldsymbol{r}) = \int C(\boldsymbol{k}) e^{i\boldsymbol{k}\cdot\boldsymbol{r}} d\boldsymbol{k} = \left(\frac{a}{|\boldsymbol{r}|}\right)^{d-2+\eta} e^{-|\boldsymbol{r}|/\xi}
$$

$$
\xi \propto |T-T_c|^{-\nu} \qquad \boxed{\text{平均场理论中：} \nu = 1/2 \qquad \eta = 0}
$$

Ising model 的结果

指数	二维	三维	四维	平均场
α	0	0.11008	0	0
β	1/8	0.326419	1/2	1/2
γ	7/4	1.237075	1	1
δ	15	4.78984	3	3
ν	1	0.63	1/2	1/2
η	1/8	0.04	0	0

- 空间维度 $d \geq 4$ 时，得到的结果和平均场相同
- 维度越低，涨落越大，越偏离平均场

实空间重整化方法

$$E(\{\sigma_i\}) = -J\sum_i \sigma_i\sigma_{i+1} - Hg\mu_B\sum_i \sigma_i + \sum_i \epsilon_0$$

$$= -J\sum_i \sigma_i\sigma_{i+1} - \frac{hg\mu_B}{2}(\sigma_i + \sigma_{i+1}) + \sum_i \epsilon_0$$

$$T_{\sigma_i\sigma_{i+1}} = e^{\beta J\sigma_i\sigma_{i+1}+(\beta Hg\mu_B)/2(\sigma_i+\sigma_{i+1}+\beta\varepsilon_0}$$

$$= e^{K\sigma_i\sigma_{i+1}+h(\sigma_i+\sigma_{i+1})/2+\epsilon}$$

$$T = \begin{pmatrix} e^{K+h+\epsilon} & e^{-K+\epsilon} \\ e^{-K+\epsilon} & e^{K-h+\epsilon} \end{pmatrix} = e^{\epsilon}\begin{pmatrix} e^{K+h} & e^{-K} \\ e^{-K} & e^{K-h} \end{pmatrix}$$

$$T^2 = e^{\tilde{\epsilon}}\begin{pmatrix} e^{\tilde{K}+\tilde{h}} & e^{-\tilde{K}} \\ e^{-\tilde{K}} & e^{\tilde{K}-\tilde{h}} \end{pmatrix} = e^{2\epsilon}\begin{pmatrix} e^{2K+2h} + e^{-2K} & e^{h} + e^{-h} \\ e^{h} + e^{-h} & e^{2K-2h} + e^{-2K} \end{pmatrix}$$

$$= e^{2\epsilon}\begin{pmatrix} 2e^{h}\cosh(2K+h) & 2\cosh h \\ 2\cosh h & 2e^{-h}\cosh(2K-h) \end{pmatrix}$$

参数的重整化

$$e^{4\tilde{\epsilon}} = 2^4 e^{8\epsilon} \cosh^2 h \cosh(2K+h)\cosh(2K-h) \boxed{= T_{++}T_{+-}T_{-+}T_{--}}$$

$$\tilde{\epsilon} = 2\epsilon + \ln 2 + \frac{1}{4}\ln[\cosh^2 h \cosh(2K+h)\cosh(2K-h)]$$

$$e^{2\tilde{h}} = e^{2h}\frac{\cosh(2K+h)}{\cosh(2K-h)} \qquad \boxed{= T_{++}/T_{--}}$$

$$\tilde{h} = h + \frac{1}{2}\ln\left[\frac{\cosh(2K+h)}{\cosh(2K-h)}\right]$$

$$e^{2\tilde{K}} = e^{-2\tilde{\epsilon}}\cosh(2K+h)\cosh(2K-h) \boxed{= T_{++}T_{--}/e^{2\tilde{\epsilon}}}$$

$$= [\cosh(2K+h)\cosh(2K-h)/\cosh^2 h]^{1/2}$$

$$\tilde{K} = \frac{1}{4}\ln\left[\frac{\cosh(2K+h)\cosh(2K-h)}{\cosh^2 h}\right]$$

10.2 非理想气体的状态方程

气体状态方程

- 理想气体

$$pV = nRT = Nk_BT \qquad \Rightarrow \qquad \frac{p}{k_BT} = \frac{N}{V} = \rho$$

- van der Waals 方程

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

$$p = \frac{Nk_BT}{V - Nb} - \frac{aN^2}{V^2} = k_BT\frac{\rho}{1 - \rho b} - a\rho^2$$

- Onnes 方程

$$p = \frac{Nk_BT}{V} + \frac{a_2(T)N^2}{V^2} + \frac{a_3(T)N^3}{V^3} + \cdots$$

$$= \rho k_BT + a_2(T)\rho^2 + a_3(T)\rho^3 + \cdots$$

$\boxed{\rho = N/V \text{ 粒子数密度}}$

相互作用势

$$\mathcal{H}_N = \sum_{i=1}^{N}\left[\frac{\boldsymbol{p}_i^2}{2m} + V(\boldsymbol{r}_i)\boxed{\text{容器势}}\right] + \frac{1}{2}\sum_{i\neq j} u(|\boldsymbol{r}_i - \boldsymbol{r}_j|)$$

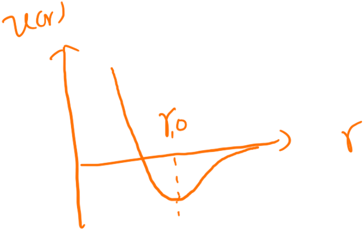
$$= \sum_{i=1}^{N}\left[\frac{\boldsymbol{p}_i^2}{2m} + V(\boldsymbol{r}_i)\right] + \sum_{1\le i<j\le N} u(|\boldsymbol{r}_i - \boldsymbol{r}_j|)$$

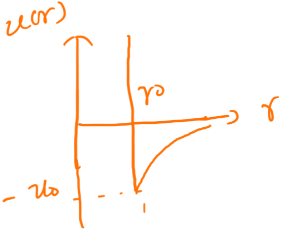
$$= \sum_{i=1}^{N}\left[\frac{\boldsymbol{p}_i^2}{2m} + V(\boldsymbol{r}_i)\right] + \sum_{1\le i<j\le N} u_{ij}$$

$$Z(T,N,V) = \frac{1}{N!}\int e^{-\beta H_N}\frac{d\boldsymbol{r}\,d\boldsymbol{p}}{h^{3N}}$$

$$\Xi(T,\mu,V) = \sum_{N} e^{\beta\mu N} Z(T,N,V)$$

相互作用势





- 近距离排斥，远距离吸引 ($\propto 1/r^6$)
- LJ 势能

$$u(r) = \frac{a}{r^{12}} - \frac{b}{r^6}$$

- Hard ball

$$u(r) = \begin{cases} \infty & r < r_0 \\ -u_0\left(\frac{r_0}{r}\right)^6 & \end{cases}$$

配分函数

$$Z = \frac{1}{N!h^{3N}} \int e^{-\sum_i \boldsymbol{p}_i^2/(2mk_BT)} \prod_i d\boldsymbol{p}_i \int e^{-\beta \sum_{i<j} u_{ij}} \prod_i d\boldsymbol{r}_i$$

$$= \frac{1}{N!h^{3N}} \prod_i \int e^{-\boldsymbol{p}_i^2/(2mk_BT)} d\boldsymbol{p}_i \boxed{= (2\pi mk_BT)^{3/2}} \int e^{-\beta \sum_{i<j} u_{ij}} \prod_i d\boldsymbol{r}_i$$

$$= \frac{\lambda_D^{-3N}}{N!} \int e^{-\beta \sum_{i<j} u_{ij}} \prod_i d\boldsymbol{r}_i \qquad \boxed{\lambda_D = (2\pi mk_BT/h^2)^{-1/2}}$$

$$Q_N = \int_V e^{-\beta \sum_{i<j} u_{ij}} \prod_i d\boldsymbol{r}_i \qquad \boxed{\text{位型积分}}$$

位形积分：cumulant expansion

- ☞ 位形积分包含了所以相互作用的信息
- ☞ cumulant expansion：
  如果 βu_{ij} 比较小的话，可以做 Taylor 展开

$$
\begin{aligned}
Q_N &= \int_V e^{-\beta \sum_{i<j} u_{ij}} \prod_i d\boldsymbol{r}_i \\
&= \int_V [1 - \beta \sum_{i<j} u_{ij} + \frac{\beta^2}{2} \sum_{i<j,k<l} u_{ij} u_{kl} + \cdots] \prod_i d\boldsymbol{r}_i
\end{aligned}
$$

- ☞ 这种方法是处理高温体系时常见方法，比如高温的 Ising model 等。但在处理非理想气体时存在一个严重问题：无法处理近程强烈的排斥作用。

位型积分：Mayer f 函数

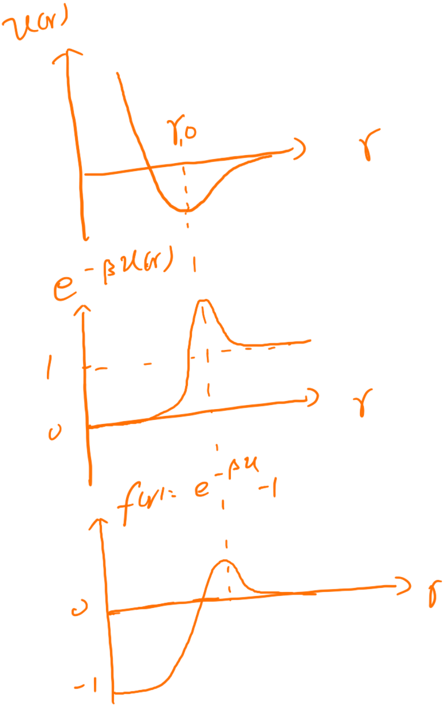
$$Q_N = \int_V \prod_{1 \le i < j \le N} e^{-\beta u_{ij}} d\boldsymbol{r}$$

$$= \int_V \prod_{1 \le i < j \le N} (1 + f_{ij}) d\boldsymbol{r}$$

$$f_{ij} = f(|\boldsymbol{r}_i - \boldsymbol{r}_j|) = e^{-\beta u_{ij}} - 1$$

$$= e^{-\beta u(|\boldsymbol{r}_i - \boldsymbol{r}_j|)} - 1$$

- $e^{-\beta u}$ 力程外接近一
- f 力程外接近零，
  力程内非零
- 只要考虑原子接近时的情况
  ☞cluster expansion
  分子团展开



Mayer’s cluster expansion

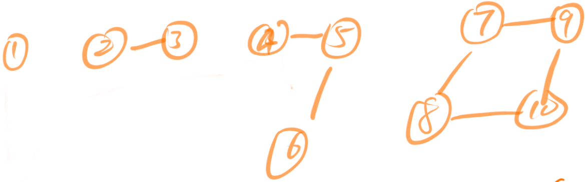
$$Q_N = \int \prod_{i<j}(1+f_{ij})\,d\boldsymbol{r} = \int (1+f_{12})(1+f_{13})\cdots(1+f_{23})(1+f_{24})\cdots d\boldsymbol{r}$$

$$= \int \Big[1 + \sum_{i<j} f_{ij} + \sideset{}{'}\sum_{i_1<j_1;i_2<j_2} f_{i_1j_1}f_{i_2j_2} + \sideset{}{'}\sum_{i_1<j_1;i_2<j_2;i_3<j_3} f_{i_1j_1}f_{i_2j_2}f_{i_3j_3} + \cdots\Big]\,d\boldsymbol{r}$$

$\sideset{}{'}\sum_{i_1<j_1;i_2<j_2;\cdots}$ 表示求和里任何一对 $(i_p j_p) \neq (i_q j_q)$

☞ 共有 $2^{N(N-1)/2}$ 项，需要寻找合适的方法来求和

Mayer’s cluster expansion



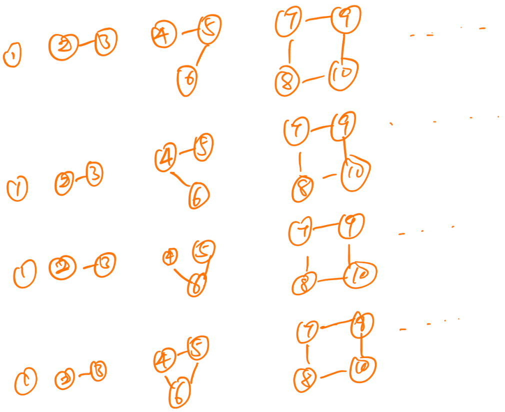
$$= \int f_{23} f_{45} f_{56} f_{78} f_{79} f_{8,10} f_{9.10}$$

$$= \int dr_1 \int f_{23}\, dr_2 dr_3 \int f_{45} f_{56}\, dr_4 dr_5 dr_6$$

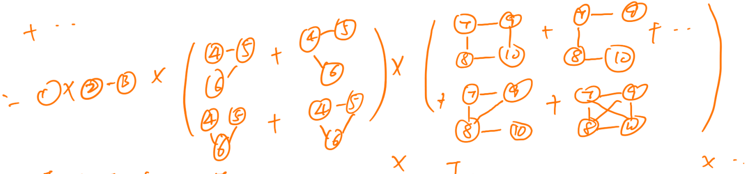
$$\times \int f_{78} f_{79} f_{8.10} f_{9,10}\, dr_7 dr_8 dr_9 dr_{10} \times \cdots$$

- 积分 ⇔ 图表示
- 不相连的图积分 = 相连子图积分的乘积
  $I(G = \sum g) = \prod_g I(g)$

Mayer’s cluster expansion



- 可把相同原子组成的不同 cluster 组合在一起
  $I(C=\sum c)=\prod_c I(c)$
  $I(c)=\sum_{g\in c} I(g)$
- 相同类型的图积分数值相同, 和标号无关 ☞ Cluster 积分只和 cluster 里的分/原子数有关: $I(c)=I_c$
  $Q_N=\sum_c N_c I_c$, N_c 表示具有相同 cluster 组合的图的数目



$I_1 + I_2 + \quad I_3 \quad \times \quad I_4 \quad \times \cdots$

Cluster expansion

- $\{m_l\}$ 个 l 阶相连图：$\sum_l m_l l = N$

$$
\begin{aligned}
N(\{m_l\}) &= C_N^1 C_{N-1}^1 \cdots C_{N-m_1+1}^1 \times \frac{1}{m_1!} \\
&\times C_{N-m_1}^2 C_{N-m_1-2}^2 \cdots C_{N-m_1-2m_2+2}^2 \times \frac{1}{m_2!} \\
&C_{N-m_1-2m_2}^3 \cdots \times \frac{1}{m_3!} C_{N-\sum_{i=1}^{l-1} i m_i}^l \cdots \times \frac{1}{m_l!} \cdots \\
&= \frac{N!}{1!^{m_1} 2!^{m_2} \cdots l!^{m_l} \cdots} \frac{1}{m_1! m_2! \cdots m_l! \cdots} \\
&= \frac{N!}{\prod_l (l!^{m_l} m_l!)} \\
Q_N &= \sum_{\{m_l | \sum_l l m_l = N\}} \frac{N!}{\prod_l (l!^{m_l} m_l!)} \prod_l I_l^{m_l} \\
&= N! \sum_{\{m_l | \sum_l l m_l = N\}} \prod_l \frac{1}{m_l!} \left(\frac{I_l}{l!}\right)^{m_l}
\end{aligned}
$$

巨配分函数

$$Z = \frac{\lambda_D^{-3N}}{N!} Q_N = \lambda_D^{-3N} \sum_{\{m_l \mid \sum_l l m_l = N\}} \prod_l \frac{1}{m_l!} \left(\frac{I_l}{l!} \right)^{m_l}$$

$$\Xi = \sum_N e^{\beta \mu N} \lambda_D^{-3N} \sum_{\{m_l \mid \sum_l l m_l = N\}} \prod_l \frac{1}{m_l!} \left(\frac{I_l}{l!} \right)^{m_l}$$

$$= \sum_N \sum_{\{m_l \mid \sum_l l m_l = N\}} (e^{\beta\mu} \lambda_D^{-3})^{\sum_l l m_l} \prod_l \frac{1}{m_l!} \left(\frac{I_l}{l!} \right)^{m_l} \qquad \boxed{z = e^{\beta\mu} \lambda_D^{-3}}$$

$$= \sum_{\{m_l\}} \prod_l \frac{1}{m_l!} \left(\frac{I_l z^l}{l!} \right)^{m_l} = \prod_l \sum_{m_l=0}^{\infty} \frac{1}{m_l!} \left(\frac{I_l z^l}{l!} \right)^{m_l} = \prod_l e^{I_l z^l / l!}$$

$$= e^{\sum_l I_l z^l / l!} = e^{\sum_l V b_l z^l} \qquad b_l = I_l / (V l!)$$

$$\ln \Xi = \sum_l V b_l z^l$$

单粒子可约图和不可约图

$$I_1 = \int_V d\boldsymbol{r} = V = Vb_1$$

I_1

$$b_1 = \frac{I_1}{1!V} = 1$$

I_2

$$I_2 = \int_V f_{12} d\boldsymbol{r}_1 d\boldsymbol{r}_2 = \int_V f(|\boldsymbol{r}_2 - \boldsymbol{r}_1|) d(\boldsymbol{r}_2 - \boldsymbol{r}_1) d\boldsymbol{r}_1$$

$$= \int_V d\boldsymbol{r}_1 \int_{V \cap V + \boldsymbol{r}_1} f(|\boldsymbol{r}_{21}|) d\boldsymbol{r}_{21} \simeq \int_V d\boldsymbol{r}_1 \int_V f(r) d\boldsymbol{r}$$

$$= V\beta_1(T)$$

忽略边界的影响

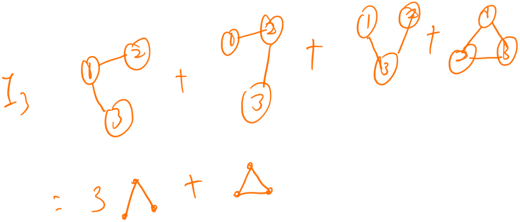
$$b_2 = \frac{I_2}{2!V} = \frac{\beta_1}{2} = b_2(T)$$

与体积无关

$$\beta_1(T) = \int_V f(r) d\boldsymbol{r}$$

单粒子可约图和不可约图

$$
\begin{aligned}
I_3 &= \int_V [f_{12}f_{13} + f_{12}f_{23} + f_{13}f_{23} + f_{12}f_{13}f_{23}]\, d\boldsymbol{r}_1 d\boldsymbol{r}_2 d\boldsymbol{r}_3 \\
&= 3\int_V f_{12}f_{13}\, d\boldsymbol{r}_1 d\boldsymbol{r}_2 d\boldsymbol{r}_3 + \int_V f_{12}f_{13}f_{23}\, d\boldsymbol{r}_1 d\boldsymbol{r}_2 d\boldsymbol{r}_3 \\
&= 3\int_V f_{21}f_{31}\, d\boldsymbol{r}_{21} d\boldsymbol{r}_{31} d\boldsymbol{r}_1 + \int_V f_{21}f_{31} f(|\boldsymbol{r}_{31} - \boldsymbol{r}_{21}|)\, d\boldsymbol{r}_{21} d\boldsymbol{r}_{31} d\boldsymbol{r}_1 \\
&\simeq 3\int_V d\boldsymbol{r}_1 \int_V f_{21} d\boldsymbol{r}_{21} \int_V f_{31} d\boldsymbol{r}_{31} + \int_V d\boldsymbol{r}_1 \int f_{21}f_{31} f(|\boldsymbol{r}_{31} - \boldsymbol{r}_{21}|)\, d\boldsymbol{r}_{31} d\boldsymbol{r} \\
&= 3V\beta_1^2 + 2V\beta_2
\end{aligned}
$$

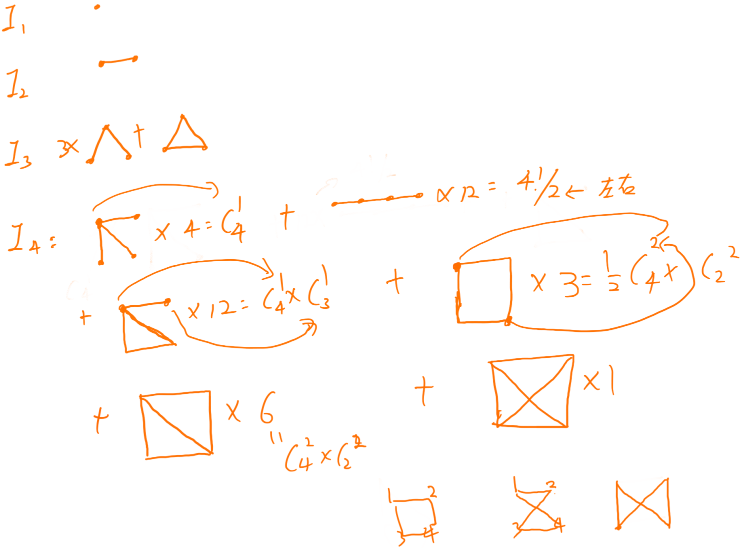


$$
b_3(T) = \frac{I_3}{3!V} = \frac{\beta_1^2}{2} + \frac{\beta_2}{3}
$$

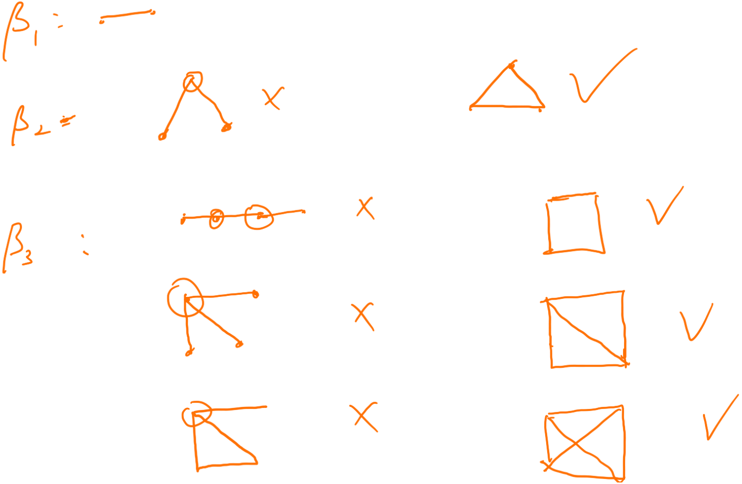
$\boxed{V \to \infty \text{ 时 } b_3 \text{ 和 } \beta_2 \text{ 都和体积无关}}$

$$
\beta_2(T) = \frac{1}{2}\int f(r) f(r') f(|\boldsymbol{r} - \boldsymbol{r}'|)\, d\boldsymbol{r} d\boldsymbol{r}'
$$

单粒子可约图和不可约图



单粒子可约图和不可约图



- ☞可约图的积分可以进一步化简为不可约图的乘积

$$\int f_{12}f_{13}f_{14}f_{34}d1d2d3d4 = \int d\boldsymbol{r}_1 \times \int f(r_{21})d\boldsymbol{r}_{21}$$

$$\times \int f(r_{31})f(r_{41})f(|\boldsymbol{r}_{41}-\boldsymbol{r}_{31})d\boldsymbol{r}_{31}d\boldsymbol{r}_{41} = V\beta_1\beta_2$$

状态方程

$$\ln \Xi = \sum_l V b_l z^l \qquad z = z(T,\mu) = e^{\beta\mu}\lambda_D^{-3} = e^{\beta\mu}(2\pi m k_B T/h^2)^{3/2}$$

$$b_l = \lim_{V\to\infty} \frac{I_l(T,V)}{Vl!} = b_l(T) \qquad \boxed{\text{与体积无关}}$$

$$N = \left(\frac{\partial \ln \Xi}{\partial \beta\mu}\right)_{\beta V} = V\sum_l l b_l z^l$$

$$\rho = \frac{N}{V} = \sum_l l b_l z^l = b_1 z + 2b_2 z^2 + 3b_3 z^3 + \cdots$$

$$p = \frac{1}{\beta}\left(\frac{\partial \ln \Xi}{\partial V}\right)_{\beta,\mu} = k_B T \sum_l b_l z^l$$

$$= k_B T\left[b_1 z + b_2 z^2 + b_3 z^3 + \cdots\right]$$

状态方程

$$\rho = \frac{N}{V} = \sum_l l b_l z^l = b_1 z + 2b_2 z^2 + 3b_3 z^3 + \cdots$$

$$z = c_1\rho + c_2\rho^2 + c_3\rho^3 + \cdots$$

待定系数法

$$\rho = b_1(c_1\rho + c_2\rho^2 + c_3\rho^3 + \cdots) + 2b_2\rho^2(c_1 + c_2\rho + c_2\rho^2 + \cdots)^2 + 3b_3\rho^3(c_1 + c_2\rho + c_2\rho^2 + \cdots)^3 + \cdots$$

$$\rho^1 :\Longrightarrow 1 = b_1 c_1 \Rightarrow c_1 = 1/b_1 = 1$$

$$\rho^2 :\Longrightarrow 0 = b_1 c_2 + 2b_2 c_1^2 \Rightarrow c_2 = -2b_2 c_1^2/b_1 = -2b_2$$

$$\rho^3 :\Longrightarrow 0 = b_1 c_3 + 2b_2 \times 2c_1 c_2 + 3b_3 c_1^3$$

$$\Rightarrow c_3 = (-4b_2 c_1 c_2 - 3b_3 c_1^3)/b_1 = 8b_2^2 - 3b_3$$

状态方程

$$\begin{aligned} z &= c_1\rho + c_2\rho^2 + c_3\rho^3 + \cdots \\ &= \rho - 2b_2\rho^2 + (8b_2 - 3b_3)\rho^3 + \cdots \end{aligned}$$

$$\begin{aligned} \frac{p}{k_BT} &= b_1 z + b_2 z^2 + b_3 z^3 + \cdots \\ &= b_1(c_1\rho + c_2\rho^2 + c_3\rho^3 + \cdots) + b_2\rho^2(c_1 + c_2\rho + c_3\rho^2 + \cdots)^2 \\ &\quad + b_3\rho^3(c_1 + c_2\rho + c_3\rho^2 + \cdots)^3 + \cdots \\ &= b_1c_1\rho + (b_2c_2 + b_2c_1^2)\rho^2 + (b_1c_3 + 2b_2c_1c_2 + b_3c_1^3)\rho^3 + \cdots \\ &= \rho + (-2b_2 + b_2)\rho^2 + (8b_2^2 - 3b_3 - 4b_2^2 + b_3)\rho^3 + \cdots \\ &= \rho - b_2\rho^2 + (4b_2^2 - 2b_3)\rho^3 + \cdots \\ &= \rho - \frac{\beta_1}{2}\rho^2 + [4(-\beta_1/2)^2 - 2(\beta_1^2/2 + \beta_2/3)]\rho^3 + \cdots \\ &= \rho - \frac{\beta_1}{2}\rho^2 - \frac{2\beta_2}{3}\rho^3 + \cdots = \rho - \sum_{\nu} \frac{\nu\beta_\nu}{\nu+1}\rho^{\nu+1} \end{aligned}$$

β_ν 只包含不可约图

硬球势的结果

$$u(r) = \begin{cases} \infty & r < r_0 \\ \\ -u_0(r_0/r)^6 & r > r_0 \end{cases}$$

$$\beta_1 = \int f(r) d\boldsymbol{r} = \int [e^{-\beta u(r)} - 1] r^2 dr \sin\theta d\theta d\phi$$

$$= 4\pi \int_0^{r_0} (-1) r^2 dr + 4\pi \int_{r_0}^{\infty} [e^{-(u_0/k_B T)(r_0/r)^6} - 1] r^2 dr$$

$$\simeq -\frac{4\pi}{3} r_0^3 + 4\pi \int_{r_0}^{\infty} \frac{u_0}{k_B T} \frac{r_0^6}{r^4} dr$$

$$= -\frac{4\pi}{3} r_0^3 \boxed{\text{排斥作用}} + \frac{4\pi}{3} r_0^3 \frac{u_0}{k_B T} \boxed{\text{吸引作用}} = -v_0 + v_0 u_0/(k_B T)$$

$$\frac{p}{k_B T} \simeq \rho - \frac{1}{2}\beta_1 \rho^2 = \rho + v_0\rho^2 - v_0 u_0 \rho^2/(k_B T)$$

$$\frac{p + v_0 u_0 \rho^2}{k_B T} = \rho(1 + v_0\rho) \simeq \frac{\rho}{1 - v_0\rho}$$ ☞ $\boxed{\text{van der Waals: } a = v_0 u_0\,, \quad b = v_0}$

β_2

$$f(\boldsymbol{k}) = \int e^{i\boldsymbol{k}\cdot\boldsymbol{r}} f(r) d\boldsymbol{r} = \int e^{ikr\cos\theta} f(r) r^2 dr \sin\theta d\theta d\phi$$

$$= 2\pi \int_0^\infty f(r) r^2 dr \int_{-1}^{1} e^{ikrt} dt \qquad \boxed{t = \cos\theta}$$

$$= 2\pi \int_0^\infty f(r) r^2 \frac{e^{ikr} - e^{-ikr}}{ikr} dr = \frac{4\pi}{k} \int_0^\infty f(r) r \sin kr \, dr = \tilde{f}(k)$$

$$\beta_2 = \int f(r) f(r') f(|\boldsymbol{r} - \boldsymbol{r}'|) d\boldsymbol{r} d\boldsymbol{r}'$$

$$= \frac{1}{(2\pi)^9} \int \tilde{f}(k_1) \tilde{f}(k_2) \tilde{f}(k_3) e^{-i\boldsymbol{k}_1\cdot\boldsymbol{r} - i\boldsymbol{k}_2\cdot\boldsymbol{r}' - i\boldsymbol{k}_3\cdot(\boldsymbol{r}-\boldsymbol{r}')} d\boldsymbol{k}_1 d\boldsymbol{k}_2 d\boldsymbol{k}_3 \, d\boldsymbol{r} d\boldsymbol{r}'$$

$$= \int \frac{d\boldsymbol{k}_1 d\boldsymbol{k}_2 d\boldsymbol{k}_3}{(2\pi)^9} \tilde{f}(k_1) \tilde{f}(k_2) \tilde{f}(k_3) \int e^{-i(\boldsymbol{k}_1+\boldsymbol{k}_3)\cdot\boldsymbol{r}} d\boldsymbol{r} \int e^{-i(\boldsymbol{k}_2-\boldsymbol{k}_3)\cdot\boldsymbol{r}'} d\boldsymbol{r}'$$

$$= \int \frac{d\boldsymbol{k}}{(2\pi)^3} \tilde{f}^3(k)$$

热力学极限和相变

在推导状态方程时，我们假设了 b_l 和体积无关，

$$\ln\Xi = \sum_l \frac{I_l(T,V)z^l}{l!} = V\sum_l \frac{I_l(T,V)}{l!\,V}z^l$$

$$\xRightarrow{V\infty} V\sum_l b_l(T,V)z^l \qquad b_l(T,V) = \lim_{V\to\infty}\frac{I_l(T,V)}{l!V} \equiv b_l(T)$$

$$\rho = \frac{N}{V} = \lim_{V\to\infty} z\frac{\partial}{\partial z}\frac{1}{V}\ln\Xi \boxed{= \textstyle\sum_l l b_z z^l}$$

$$\frac{p}{k_BT} = \lim_{V\to\infty}\left(\frac{\partial\ln\Xi}{\partial V}\right) = \lim_{V\to\infty}\frac{\ln\Xi}{V} = \sum_l b_l z^l \boxed{= \rho - \textstyle\sum_{\nu=2}^{\infty}\dfrac{\nu\beta_l}{\nu+1}\rho^\nu}$$

- 方框里结果是交换 $V\to\infty$ 和 $z\partial/\partial z$ 次序得到的。
- l 很大时，b_l 可以和体积有关系，因此交换次序可能会出问题。例如取硬球势时，当 $l\times(4\pi/3)r_0^3 > V$ 时，$b_l(T,V) = 0$。
- 凝聚相下，ρ 比较大，按照 ρ 级数展开可能发散。

热力学极限和相变

硬球势下，有限体积 V，最多能容纳 M 个粒子，$N > M$ 时，$Q_N = \int e^{-\beta\sum_{i<j}u_{ij}} = 0$，因此

$$\Xi(z,T,V) = 1 + zQ_1(T,V) + z^2Q_2(T,V) + \cdots z^M Q_M(T,V)$$

$$\frac{p}{k_BT} = \lim_{V\to\infty}\frac{\ln\Xi}{V}$$

$$\rho = \lim_{V\to\infty} V^{-1}z\left(\frac{\partial\ln\Xi}{\partial z}\right)$$

$V \to \infty$ 和 $z\partial/\partial z$ 不能随便交换位置。
杨振宁和李正道证明相变由巨配分函数 $\Xi(z)$ 的零点在 z 为复数空间上的分布决定：

$$F_\infty(z) = \lim_{V\to\infty}\frac{1}{V}\ln\Xi$$

R 是包含正实轴的的 z 复数空间，如果 R 不包含 $\Xi(z)$ 的零点，那么 F_∞ 均匀收敛，可以交换 $V \to \infty$ 和 $z\partial/\partial z$ 顺序。这种情况下只有一个相，不会发生相变。否则可以发生相变。

热力学极限和相变

相变只能在热力学极限下发生。例如如果

$$\frac{p}{\rho k_B T} = N^{-1} \ln[a^N z^N + a^N b^{-N} z^{2N}]$$

这个函数在有限 N 下，对 z 变化是连续的，没有相变。但是在保持 $\rho = N/V$ 不变，同时取 $N \to \infty$，$V \to V$ 时，

$$\frac{p}{\rho k_B T} \xRightarrow{N\to\infty} \ln(ab) + \ln(z/b) \qquad z < b$$
$$\frac{p}{\rho k_B T} \xRightarrow{N\to\infty} \ln(ab) + 2\ln(z/b) \qquad z > b$$

有相变。

Summary

- 统计基本假设：等几率假设（孤立系统、微正则系综）+ 测量量是平均值
- 几率法：平衡态是最可几态。无相互作用系统中可以直接从单粒子态构造出系统态。利用等几率假设得到孤立系统的最可几态。然后利用 Legendre 变化得到 Boltzmann 统计（非全同）或者 Bose、Fermi 统计（全同）。
- 宏观量和微观量之间的对易关系得到能量、功和热的形式，从而给出了各个物理量的表达式，以及熵的 Boltzmann 关系 $S = k_B \ln \Omega$。
- 系综理论：从 Liouville 定理构造出定态系综密度矩阵满足的形式。加上等几率假设以及无规相假设（量子系综）得到微正则密度矩阵表达式。利用 Boltzmann 关系得到温度、压强等物理量。
- 从微正则系综可以构造出正则、巨正则系综，乃至更一般的广义系综。由此可以计算各种物理量以及物理量的涨落。