第八章　系综法

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8.1 引言

- Coarse graining
  宏观物理量是微观量在大空间、长时间下的平均 ⇔ 在一段时间内对系统多次测量的平均 ⇔ 多个具有相同宏观性质但是微观状态不同的假想系统的平均
- 系综
  假想系统的集合，这些系统具有相同的宏观态，但是可以处于不同的微观态上
- 微观态
  - 量子力学：系统态 $|\psi(t)\rangle$

    $$i\hbar\partial_t|\psi(t)\rangle = \hat{\mathcal{H}}|\psi(t)\rangle$$

  - 经典力学：系统相空间 Γ 中的一个点，$\boldsymbol{r}_1, \boldsymbol{p}_1, \boldsymbol{r}_2, \boldsymbol{p}_2, \cdots$

    $$\dot{\boldsymbol{r}}_i = \boldsymbol{\nabla}_{\boldsymbol{p}_i} H(\boldsymbol{r}_i, \boldsymbol{p}_i) \qquad \dot{\boldsymbol{p}}_i = -\boldsymbol{\nabla}_{\boldsymbol{r}_i} H(\boldsymbol{r}_i, \boldsymbol{p}_i)$$

- 宏观态：(E, N, V)；(T, N, V)；(T, μ, V)；$\cdots$
- 等几率假设
  由孤立系统组成的系综里的系统处于不同微观态的几率相同

8.2 经典系综理论

微观描述

- N 个粒子在 d 维空间里运动
  微观态 $\Leftrightarrow$ Γ 空间（相空间）里的一个点 ☞代表点
  $\boldsymbol{r}_1, \boldsymbol{p}_1, \boldsymbol{r}_2, \boldsymbol{p}_2, \cdots, \boldsymbol{r}_N, \boldsymbol{p}_N$ 简记为 $\{\boldsymbol{r}, \boldsymbol{p}\}$
- 状态演化：正则方程

$$\dot{\boldsymbol{r}}_i = \nabla_{\boldsymbol{p}_i}\mathcal{H} \qquad \dot{\boldsymbol{p}}_i = -\nabla_{\boldsymbol{r}_i}\mathcal{H}$$

☞系统态随时间变化 $\Leftrightarrow$ 代表点在 Γ 空间移动的曲线/轨道

- 物理量：$O = O(t) = O[\boldsymbol{r}(t), \boldsymbol{p}(t)]$

$$\dot{O} = \frac{dO}{dt} = \sum_i \frac{\partial O}{\partial \boldsymbol{r}_i}\dot{\boldsymbol{r}}_i + \frac{\partial O}{\partial \boldsymbol{p}_i}\dot{\boldsymbol{p}}_i$$

$$= \sum_i \frac{\partial O}{\partial \boldsymbol{r}_i}\frac{\partial \mathcal{H}}{\partial \boldsymbol{p}_i} - \frac{\partial O}{\partial \boldsymbol{p}_i}\frac{\partial \mathcal{H}}{\partial \boldsymbol{r}_i} = \{O, \mathcal{H}\}$$

☞守恒量：$\dot{O} = 0$，例如：保守系里的能量 $\mathcal{H}$，粒子数等

系综

- 宏观态：由总能量，粒子数，体积等宏观参量描述
- 系综：具有系统宏观态，但是不同微观态的假想系统集合
  假设系综里有 M 个系统，t 时刻，l-th 系统的态为 $\boldsymbol{r}^l, \boldsymbol{p}^l$
  - ☞ 系综状态 ⇔ 相空间中代表点的集合
  - ☞ 系统 vs 系综：质点 vs 流体
- 系综平均：

$$O = \frac{1}{M}\sum_{l=1}^{M} O[\boldsymbol{r}^l(t), \boldsymbol{p}^l(t)] = \sum_{\boldsymbol{r},\boldsymbol{p}} \Delta\boldsymbol{r}\Delta\boldsymbol{p}\frac{\Delta n(\boldsymbol{r},\boldsymbol{p},t)}{M\Delta\boldsymbol{r}\Delta\boldsymbol{p}} O(\boldsymbol{r},\boldsymbol{p})$$

$\Delta n(\boldsymbol{r},\boldsymbol{p},t)$ 为 $\boldsymbol{r} - \boldsymbol{r}+\Delta\boldsymbol{r}, \boldsymbol{p} - \boldsymbol{p}+\Delta\boldsymbol{p}$ 之间的系统数目

$$= \int d\boldsymbol{r}\, d\boldsymbol{p}\, \rho(\boldsymbol{r},\boldsymbol{p},t) O(\boldsymbol{r},\boldsymbol{p})$$

几率密度

- 几率密度：$\rho(\boldsymbol{r}, \boldsymbol{p}, t)$

$$\rho(\boldsymbol{r}, \boldsymbol{p}, t)\Delta\boldsymbol{r}\Delta\boldsymbol{p} = \frac{1}{M}\Delta n(\boldsymbol{r}, \boldsymbol{p}, t) = \frac{1}{M}\sum_{\substack{\{l|\boldsymbol{r}<\boldsymbol{r}^l(t)<\boldsymbol{r}+\Delta\boldsymbol{r},\\ \boldsymbol{p}<\boldsymbol{p}^l(t)<\boldsymbol{p}+\Delta\boldsymbol{p}\}}} 1$$

☞ t 时刻系统处于 $\boldsymbol{r}-\boldsymbol{r}+\Delta\boldsymbol{r}, \boldsymbol{p}-\boldsymbol{p}+\Delta\boldsymbol{p}$ 的几率 $=\rho(\boldsymbol{r}, \boldsymbol{p}, t)\Delta\boldsymbol{r}\Delta\boldsymbol{p}$
⇔ 相空间中代表点的密度 ⇔ 相空间中“流体”的密度

- 正定：$\rho \geq 0$
- 归一

$$\int \rho d\boldsymbol{r} d\boldsymbol{p} = \frac{1}{M}\int d\boldsymbol{r} d\boldsymbol{p} \sum_{\{l|\boldsymbol{r}<\boldsymbol{r}^l(t)<\boldsymbol{r}+d\boldsymbol{r}, \boldsymbol{p}<\boldsymbol{p}^l(t)<\boldsymbol{p}+d\boldsymbol{p}\}} 1$$

$$= \frac{1}{M}M = 1$$

Liouville 定理

- 物理量随时间的变化

$$\frac{dO}{dt} = \int d\boldsymbol{r} d\boldsymbol{p} \, \frac{\partial \rho}{\partial t} O(\boldsymbol{r}, \boldsymbol{p})$$

☞ 相空间代表点密度改变导致系综平均改变

- Liouville 定理
  系综里的系统不会凭空消失或者凭空增加 ⇔ 相空间中代表点守恒 ⇔ 代表点密度改变仅由从体积元表面进出决定

$$\begin{aligned}
0 &= \frac{\partial \rho}{\partial t} + \sum_i [\partial_{\boldsymbol{r}_i}(\rho \dot{\boldsymbol{r}}_i) + \partial_{\boldsymbol{p}_i}(\rho \dot{\boldsymbol{p}}_i)] \\
&= \frac{\partial \rho}{\partial t} + \sum_i [(\partial_{\boldsymbol{r}_i}\rho)\dot{\boldsymbol{r}}_i + (\partial_{\boldsymbol{p}_i}\rho)\dot{\boldsymbol{p}}_i + \rho(\partial_{\boldsymbol{r}_i}\dot{\boldsymbol{r}}_i + \partial_{\boldsymbol{p}_i}\dot{\boldsymbol{p}}_i)] \\
&= \frac{\partial \rho}{\partial t} + \sum_i [(\partial_{\boldsymbol{r}_i}\rho)(\partial_{\boldsymbol{p}_i}\mathcal{H}) - (\partial_{\boldsymbol{p}_i}\rho)(\partial_{\boldsymbol{r}_i}\mathcal{H})] \\
&\quad + \rho \sum_i [\partial_{\boldsymbol{r}_i}\partial_{\boldsymbol{p}_i}\mathcal{H} - \partial_{\boldsymbol{p}_i}\partial_{\boldsymbol{r}_i}\mathcal{H}]
\end{aligned}$$

Liouville 定理

$$0 = \frac{\partial \rho}{\partial t} + \sum_i (\partial_{\boldsymbol{r}_i} \rho)(\partial_{\boldsymbol{p}_i} \mathcal{H}) - \sum_i (\partial_{\boldsymbol{p}_i} \rho)(\partial_{\boldsymbol{r}_i} \mathcal{H})$$

$$= \frac{\partial \rho}{\partial t} + \{\rho, \mathcal{H}\}$$

$$\frac{d\rho}{dt} = \frac{\partial \rho}{\partial t} + \sum_i [(\partial_{\boldsymbol{r}_i} \rho)\dot{\boldsymbol{r}}_i + (\partial_{\boldsymbol{p}_i} \rho)\dot{\boldsymbol{p}}_i]$$

$$= \frac{\partial \rho}{\partial t} + \sum_i (\partial_{\boldsymbol{r}_i} \rho)(\partial_{\boldsymbol{p}_i} \mathcal{H}) - \sum_i (\partial_{\boldsymbol{p}_i} \rho)(\partial_{\boldsymbol{r}_i} \mathcal{H}) = 0$$

- ☞ 跟随某个代表点运动时，其周围代表点密度不变
  ⇒ 系综是不可压缩“流体”
- ☞ 跟随系综里某个系统，与其状态相似的系统数不随时间变化
- ☞ 代表点占据的总体积不变

定态系综

$$0 = \frac{\partial \rho}{\partial t} = \{\mathcal{H}, \rho\}$$

- 平衡态 $\Leftarrow$ 物理量不随时间变化 $\Leftarrow$ 几率密度不随时间变化（定态）
- 定态系综的几率密度是守恒量的函数 $\rho = \rho(A, B, \cdots)$
- 系综主要反映系统的宏观性质，因此只应该这些守恒量也应该是体现宏观性质的物理量
- 常见的宏观守恒量：保守系里的 Hamiltonian $\mathcal{H}$，粒子数 N，$\cdots \Rightarrow$ $\rho = \rho(\mathcal{H}, N, \cdots)$
  - 微正则系综：$\rho(\boldsymbol{r}, \boldsymbol{p}) = \frac{1}{\Omega}\delta(E - \mathcal{H}(\boldsymbol{r}, \boldsymbol{p})]$
  - 正则系综：$\rho(\boldsymbol{r}, \boldsymbol{p}) = \frac{1}{Z}e^{-\beta\mathcal{H}(\boldsymbol{r}, \boldsymbol{p})}$
  - 巨正则系综：$\rho(\boldsymbol{r}_N, \boldsymbol{p}_N) = \frac{1}{\Xi}e^{-\beta[\mathcal{H}(\boldsymbol{r}_N, \boldsymbol{p}_N)_N - \mu N]}$

8.3 量子系综理论

微观描述

- 微观描述：系统的波函数 $|\psi(t)\rangle$

$$i\hbar\partial_t|\psi(t)\rangle = \hat{\mathcal{H}}|\psi(t)\rangle$$

- 基展开：正交完备基 $\{|\sigma\rangle\}$：$\langle\sigma|\sigma'\rangle = \delta_{\sigma\sigma'}$　　$\sum_\sigma |\sigma\rangle\langle\sigma| = 1$

$$|\psi(t)\rangle = \sum_\sigma |\sigma\rangle\langle\sigma|\psi(t)\rangle = \sum_\sigma c_\sigma(t)|\sigma\rangle$$

$c_\sigma(t) = \langle\sigma|\psi(t)\rangle$：向量

$$1 = \langle\psi(t)|\psi(t)\rangle = \sum_\sigma \langle\psi(t)|\sigma\rangle\langle\sigma|\psi(t)\rangle = \sum_\sigma |c_\sigma(t)|^2$$

$|c_\sigma(t)|^2$ = 系统处于 $|\sigma\rangle$ 的几率

$$\hat{O} = \sum_{\sigma\sigma'} = |\sigma\rangle\langle\sigma|\hat{O}|\sigma'\rangle\langle\sigma'| = \sum_{\sigma\sigma'} O_{\sigma\sigma'}|\sigma\rangle\langle\sigma'|$$

矩阵

$$\overline{O}(t) = \langle\psi(t)|\hat{O}|\psi(t)\rangle = \sum_{\sigma\sigma'} \langle\psi(t)|\sigma\rangle\langle\sigma|\hat{O}|\sigma'\rangle\langle\sigma'|\psi(t)\rangle$$

$$= \sum_{\sigma\sigma'} \langle\sigma|\hat{O}|\sigma'\rangle\langle\sigma'|\psi(t)\rangle\langle\psi(t)|\sigma\rangle = \sum_{\sigma\sigma'} O_{\sigma\sigma'}\rho_{\sigma'\sigma}(t) = Tr\{\hat{O}\hat{\rho}(t)\}$$

密度矩阵：$\hat{\rho}(t) = |\psi(t)\rangle\langle\psi(t)|$

$$\rho^{\dagger}(t) = |\psi(t)\rangle\langle\psi(t)| = \rho(t)$$

$$\rho_{\sigma\sigma'}(t) = \langle\sigma|\psi(t)\rangle\langle|\psi(t)|\sigma'\rangle = c_{\sigma}(t)c^{*}_{\sigma'}(t)$$

$$\rho_{\sigma\sigma}(t) = |c_{\sigma}(t)|^2$$

对角元：处于 $|\sigma\rangle$ 态的几率

$$Tr\{\rho(t)\} = \sum_{\sigma}\rho_{\sigma\sigma}(t) = \sum_{\sigma}|c_{\sigma}(t)|^2 = 1$$

$$\rho^2(t) = |\psi(t)\rangle\langle\psi(t)|\psi(t)\rangle\langle\psi(t)| = |\psi(t)\rangle \times 1 \times \langle\psi(t)| = \rho(t)$$

$$i\hbar\partial_t\hat{\rho} = [i\hbar\partial_t|\psi(t)\rangle]\langle\psi(t)| + |\psi(t)\rangle[i\hbar\partial_t\langle\psi(t)|]$$

$= [-i\hbar\partial_t|\psi(t)\rangle]^{\dagger}$

$$= \hat{\mathcal{H}}|\psi(t)\rangle\langle\psi(t)| - |\psi(t)\rangle\langle\psi(t)|\hat{\mathcal{H}} = \hat{\mathcal{H}}\hat{\rho}(t) - \hat{\rho}(t)\hat{\mathcal{H}}$$

$$i\hbar\partial_t\hat{\rho}(t) = [\hat{\mathcal{H}}, \hat{\rho}(t)]$$

☞可以用密度矩阵 $\hat{\rho}$ 来代替波函数

系综

- 有 M 个假想系统，t 时刻，l-th 个系统处于态 $|\psi_l(t)\rangle$

$$i\hbar\partial_t|\psi_l(t)\rangle = \hat{\mathcal{H}}|\psi_l(t)\rangle$$

- 物理量 = 系综平均

$$\overline{O}(t) = \frac{1}{M}\sum_{l=1}^{M}\langle\psi_l(t)|\hat{O}|\psi_l(t)\rangle = \frac{1}{M}\sum_{l=1}^{M}Tr\{\hat{O}\hat{\rho}_l(t)\}$$

$$= Tr\{\hat{O}\frac{1}{M}\sum_{l=1}^{M}\hat{\rho}_l(t)\} = Tr\{\hat{O}\hat{\rho}(t)\}$$

系综

- 系综密度矩阵 $\hat{\rho} = \frac{1}{M}\sum_l \hat{\rho}_l(t)$

$$\rho_{\sigma\sigma'}(t) = \langle\sigma|\hat{\rho}(t)|\sigma'\rangle = \frac{1}{M}\sum_l \langle\sigma|\psi_l(t)\rangle\langle\psi_l(t)|\sigma'\rangle$$

$$= \frac{1}{M}\sum_l c_{l\sigma}(t)c^*_{l\sigma'}(t)$$

$$\rho_{\sigma\sigma}(t) = \frac{1}{M}\sum_{l=1}^{M} |c_{l\sigma}(t)|^2$$

处于 $|\sigma\rangle$ 上的几率

- 量子 Liouville 方程

$$i\hbar\partial_t\hat{\rho}(t) = \frac{1}{M}\sum_l i\hbar\partial_t\hat{\rho}_l(t) = \frac{1}{M}\sum_l [\hat{\mathcal{H}}, \hat{\rho}_l(t)] = [\hat{\mathcal{H}}, \frac{1}{M}\sum_l \hat{\rho}_l(t)]$$

$$i\hbar\partial_t\hat{\rho}(t) = [\hat{\mathcal{H}}, \hat{\rho}(t)]$$

☞ 利用密度矩阵，系综理论的结果和纯粹量子力学的结果形式上完全相同

纯态密度矩阵和混合态密度矩阵

$$\rho_p = |\psi\rangle\langle\psi|$$ 纯态密度矩阵

$$\rho_p^2 = |\psi\rangle\langle\psi|\psi\rangle\langle\psi| = |\psi\rangle\langle\psi| = \rho_p$$

$$\rho_m = \frac{1}{M}\sum_l |\psi_l\rangle\langle\psi_l|$$ 混合态密度矩阵

$$\rho_m^2 = \frac{1}{M^2}\sum_{ll'}(\langle\psi_l|\psi_{l'}\rangle)|\psi_l\rangle\langle\psi_{l'}| \neq \rho_m$$

例子

$$|\psi\rangle = \frac{1}{\sqrt{2}}(|0\rangle + |1\rangle) \Rightarrow \hat{\rho}_p = \frac{1}{2}\begin{pmatrix}1 & 1\\ 1 & 1\end{pmatrix}$$

$$|\psi_1\rangle = \frac{1}{\sqrt{2}}(|0\rangle + |1\rangle) \qquad |\psi_2\rangle = \frac{1}{\sqrt{2}}(|0\rangle - |1\rangle)$$

$$\Rightarrow \hat{\rho}_m = \frac{1}{4}\left[\begin{pmatrix}1 & 1\\ 1 & 1\end{pmatrix} + \begin{pmatrix}1 & -1\\ -1 & 1\end{pmatrix}\right] = \frac{1}{2}\begin{pmatrix}1 & 0\\ 0 & 1\end{pmatrix}$$

纯态密度矩阵和混合态密度矩阵

$$0 = \rho_p - \rho_p^2 = \rho_p(1 - \rho_p) \Rightarrow \lambda_p = 0/1$$

- ☞ 纯态密度矩阵：ρ_p 的特征值为零或者一
- ☞ $Tr\{\rho_p\} = 1 \Rightarrow$ 特征值中有一个为一，其余为零
- ☞ 混合态密度矩阵的特征值介乎零和一之间

密度矩阵的含义

- 对角元 $\rho_{\sigma\sigma}(t)$ 表示（系综里的）系统处于 $|\sigma\rangle$ 态的几率
- 归一性：$1 = Tr\{\rho\} = \sum_\sigma \rho_{\sigma\sigma}(t)$
- 非对角元 $\rho_{\sigma'\sigma}(t)$ 描述 $|\sigma\rangle$ 和 $|\sigma'\rangle$ 态之间的关联

定态系综

$$\hat{O}(t) = Tr\{\hat{\rho}(t)\hat{O}\}$$

平衡态：达到平衡，系统状态不随时间变化；
$\Leftarrow$ 定态：$\hat{O}$ 不随时间变化 $\Leftarrow$ 密度矩阵不随时间改变

$$0 = i\hbar\partial_t\hat{\rho} = [\hat{\mathcal{H}}, \hat{\rho}] \Rightarrow [\hat{\mathcal{H}}, \hat{\rho}] = 0$$

- 定态系综中 ρ 是宏观守恒量的函数
  $\hat{\rho} = \hat{\rho}(\hat{A}, \hat{B}, \cdots)$
- 常见宏观守恒量有能量 $\hat{\mathcal{H}}$，粒子数 $\hat{N}$，$\cdots$
  $\hat{\rho} = \hat{\rho}(\hat{\mathcal{H}}, \hat{N}, \cdots)$
  - 微正则系综：$\hat{\rho} = \frac{1}{\Omega}\delta(E - \hat{\mathcal{H}})$
  - 正则系综：$\hat{\rho} = \frac{1}{Z}e^{-\beta\hat{\mathcal{H}}}$
  - 巨正则系综：$\hat{\rho} = \frac{1}{\Xi}e^{-\beta(\mathcal{H}-\mu\hat{N})}$

8.4 微正则系综

- 微正则系综：由孤立系统组成的系综
  系综里所有的系统具有相同的能量、粒子数和体积（外界参数）
- 等几率假设：系综里系统等几率处于各种可能的微观态上
  - 经典系综

$$\rho(\boldsymbol{r},\boldsymbol{p}) = \frac{1}{\Omega(E,N,V)}\delta[E-\mathcal{H}(\boldsymbol{r},\boldsymbol{p})]\ \boxed{\text{系统能量严格为 } E}$$

$$\rho(\boldsymbol{r},\boldsymbol{p}) = \frac{1}{C}\Theta(E+\Delta-\mathcal{H})\Theta(\mathcal{H}-E)\ \boxed{\text{系统能量在 } E - E+\Delta E \text{ 之间}}$$

$$C \simeq \Omega\Delta E$$

  - 量子系综

$$\hat{\rho} = \frac{1}{\Omega(E,N,V)}\delta_{E,\hat{\mathcal{H}}}$$

$$\hat{\rho} = \frac{1}{C}\Theta(E+\Delta-\mathcal{H})\Theta(\mathcal{H}-E) \qquad C \simeq \Omega\Delta E$$

量子微正则系综

$$\hat{\rho}_{\sigma\sigma'} = \langle\sigma|\hat{\rho}|\sigma'\rangle$$

$\rho_{\sigma\sigma}$ 对角元：系统处于 $|\sigma\rangle$ 态上的几率

$\rho_{\sigma\sigma'}$ 非对角元：关联

能量本征态：$\hat{\mathcal{H}}|s\rangle = E_s|s\rangle$

量子微正则系综

定态系综：量子 Liouville 方程 $i\hbar\partial_t\rho = [\hat{\mathcal{H}}, \hat{\rho}] = 0$

$$0 = \langle s|[\hat{\mathcal{H}}, \hat{\rho}]|s'\rangle = \langle s|\hat{\mathcal{H}}\hat{\rho} - \hat{\rho}\hat{\mathcal{H}}|s'\rangle = (E_s - E_{s'})\rho_{ss'}$$

$$\Rightarrow \rho_{ss'} = \begin{cases} 0 & E_s \neq E_{s'} \\ ? & E_s = E_{s'} \end{cases}$$

$$\rho_{ss'} = \frac{1}{M}\sum_l \langle s|\Psi_l(t)\rangle\langle\Psi_l(t)|s'\rangle$$

$$= \frac{1}{M}\sum_l e^{-i(E_s - E_s')t/\hbar + i(\theta_s^l - \theta_{s'}^l)}|c_s^l(0)||c_{s'}^l(0)|$$

$$\rho_{ss} = \frac{1}{M}\sum_l |c_s^l|^2$$

系统处于 $|s\rangle$ 态上的几率

无规相近似，Random phase approximation：假设不同系统相位无关

$$\rho_{ss'} = \frac{1}{M}\sum_l e^{i(\theta_s^l - \theta_{s'}^l)}|c_s^l(0)c_{s'}^l(0)| \simeq 0 \qquad s \neq s'$$

量子微正则系综

等几率假设 + 无规相近似 $\Rightarrow$

$$\rho_{ss'} = \langle s|\rho|s'\rangle = \frac{1}{C}\delta_{E,E_s}\delta_{ss'}$$

$$1 = Tr\{\hat{\rho}\} = \sum_s \rho_{ss} = \frac{1}{C}\sum_s \delta_{E,E_s} = \frac{\Omega}{C}$$

$\Omega = \Omega(E,N,V) =$ 系统能量为 E 时的简并度;
$=$ 系统能量为 E 的微观状态数

$$\hat{\rho} = \frac{1}{\Omega(E,N,V)}\delta_{E,\hat{\mathcal{H}}}$$

经典极限

在 d 维空间运动的 N 个粒子

- 体积为 h^{Nd} 的相空间体积元 $\Leftrightarrow$ 一个量子态

$$E_s = \mathcal{H}(\boldsymbol{r}, \boldsymbol{p})$$

- 几率密度
  - 定域性，非全同粒子

$$\rho(\boldsymbol{r}, \boldsymbol{p}) d\boldsymbol{r} d\boldsymbol{p} = \frac{1}{\Omega(E, N, V)} \delta[E - \mathcal{H}(\boldsymbol{r}, \boldsymbol{p})] \frac{d\boldsymbol{r}\, d\boldsymbol{p}}{h^{Nd}}$$

  - 非定域性，全同粒子

$$\rho(\boldsymbol{r}, \boldsymbol{p}) d\boldsymbol{r} d\boldsymbol{p} = \frac{1}{N!\Omega(E, N, V)} \delta[E - \mathcal{H}(\boldsymbol{r}, \boldsymbol{p})] \frac{d\boldsymbol{r}\, d\boldsymbol{p}}{h^{Nd}}$$

- 归一化

$$\Omega(E, N, V) = \begin{cases} \int \delta(E - \mathcal{H}) \frac{d\boldsymbol{r} d\boldsymbol{p}}{h^{Nd}} & \boxed{\text{定域}} \\ \frac{1}{N!} \int \delta(E - \mathcal{H}) \frac{d\boldsymbol{r} d\boldsymbol{p}}{h^{Nd}} & \boxed{\text{非定域}} \end{cases}$$

热力学量

$$U = Tr\{\mathcal{H}\hat{\rho}\} = \frac{1}{\Omega}Tr\{\mathcal{H}\delta_{E,\mathcal{H}}\} = \frac{1}{\Omega}E\Omega = E$$

$$S = S(E,N,V) = k_B \ln \Omega(E,N,V)$$

Boltzmann 关系

$$dS = \frac{dE}{T} + \frac{p}{T}dV - \frac{\mu}{T}dN$$

$$d\ln\Omega = dS/k_B = \beta dE + \beta p dV - \beta\mu dN$$

$$\frac{1}{T} = \left(\frac{\partial S}{\partial E}\right)_{NV} \qquad \frac{p}{T} = \left(\frac{\partial S}{\partial V}\right)_{EN} \qquad -\frac{\mu}{T} = \left(\frac{\partial S}{\partial N}\right)_{EV}$$

Gibbs 熵

$$S = -k_B Tr\{\hat{\rho}\ln\hat{\rho}\} = -k_B\sum_s \langle s|\hat{\rho}\ln\hat{\rho}|s\rangle = -k_B\sum_s \rho_{ss}\ln\rho_{ss}$$

$$= -k_B\sum_s p_s \ln p_s$$

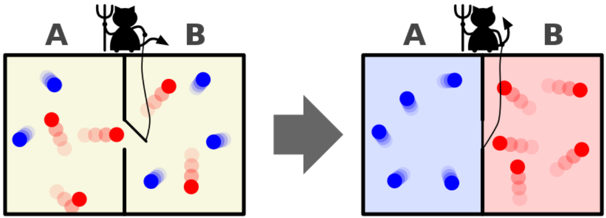
Shannon 熵： p_s 处在 s 态上的几率

$$= -k_B \sum_{\{s|E_s=E\}} \frac{1}{\Omega}\ln\frac{1}{\Omega} = k_B \sum_{\{s|E_s=E\}} \frac{1}{\Omega}\ln\Omega = k_B\ln\Omega$$

各种各样的熵

- Boltzmann 熵： $S = k_B \ln \Omega$
- Gibbs 熵、von Neumann 熵： $S = -k_B Tr\{\hat{\rho} \ln \hat{\rho}\}$
- Shannon 熵 / 信息熵： $S = -\sum_s p_s \ln p_s$
  ☞Shannon 熵和 Gibbs 熵基本相同，相差一个 k_B
- Rényi 熵： $S_\alpha = \frac{1}{1-\alpha} \ln Tr\{\hat{\rho}\}^\alpha = \frac{1}{1-\alpha} \ln \sum_s p_s^\alpha$
  ☞$S_{\alpha=1}$ =Shannon 熵
- Tsallis 熵： $S_q = \frac{1}{1-q} [Tr\{\rho^q\} - 1]$
  ☞$S_{q=1}$ =Shannon 熵

Maxwell's Demon



- Maxwell 设想的一种小生物（finite being），可以把快慢分子/原子分开来，这样可以自发的创造温度差，违背热力学第二定律。
- Kelvin 把这个“生物”称为 Maxwell's demon
  The defination of a “demon” according to the use of this word by Maxwell, is an intelligent being endowed with free will, and fine enough tactile and perceptive organsation to give him the faculty of observing and influencing individual molecules of matter.

“The Sorting Demon of Maxwell”, Kelvin, Nature **20**, 126 (1879)

THE word “demon” which originally in Greek meant a supernatural being, has never been properly used to signify a real or ideal personification of malignity.

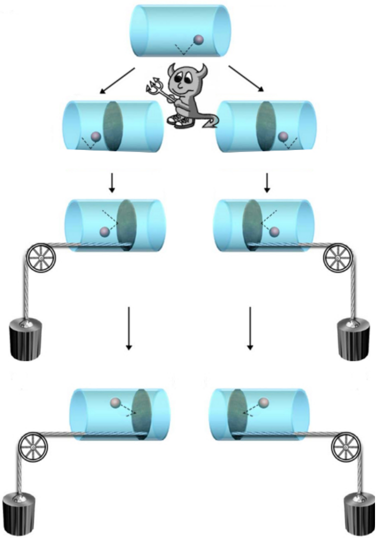
Clerk Maxwell’s “demon” is a creature of imagination having certain perfectly well-defined powers of action, purely mechanical in their character, invented to help us fo understand the “Dissipation of Energy” in nature.

He is a being with no preternatural qualities, and differs from real living animals only in extreme smallness and agility. He can at pleasure stop, or strike, or push, or pull any single atom of matter, and so moderate its natural course of motion. Endowed ideally with arms and hands and fingers—two hands and ten fingers suffice —he can do as much for atoms as a pianoforte player can do for the keys of the piano—just a little more, he can push or pull each atom in any direction.

Thermodynamic Exorcism

- Maxwell 本人并不认为这是个大问题，只是揭示了如果能够在原子 / 分子层面操控系统的话，就可以规避热力学第二定律。
- Smoluchowski 等人（1912 年）认为如果这个 demon 也服从物理定律的话，那么要么热涨落会让 demon 失效，要么 demon 运作过程需要消耗能量，导致整个宇宙熵。
- Szilard（1929 年）认为获得 / 测量分子运动速度信息需要消耗能量。这些工作首次揭示了信息处理与熵的关系。
- von Neumann （1949 年）和 Brillouin（1962 年）认为处理一个 bit 的信息需要消耗 $k_B T \ln 2$ 的能量。
- Landauer （1961 年）发现可逆的测量 / 获得信息不需要消耗能量，但是删除一个 bit 的信息需要消耗 $k_B T \ln 2$ 的能量。
- 信息熵和热力学熵没有区别，可以通过消耗信息熵来做功。

Szilard Engine：信息 ⇒ 做功



- 单原子热机，和热源 T 接触
- 如果知道原子位置（在左边或者右边），那么可以构造相应热机
- 初态信息熵：知道粒子位置信息
  $S = -1\ln 1 - 0\ln 0 = 0$
- 热机做功

$$W = Q = \int_{V/2}^{V} p dv$$

$$= \int_{V/2}^{V} \frac{k_B T}{V} dv = k_B T \ln 2$$

- 末态信息熵：丢失粒子位置信息
  $S = -\frac{1}{2}\ln\frac{1}{2} - \frac{1}{2}\ln\frac{1}{2} = \ln 2$

Fantastic beasts in physics and where to find them

- Zeno's tortoise
- Lapalace's demon
- Maxwell's demon
- Boltzmann's brain
- Schrödinger's cat

微正则系综的例子

顺磁系统：磁场 H 中 N 个无相互作用的自旋 1/2 粒子

$$\mathcal{H} = -\sum_i g\mu_B H\hat{s}_{iz}$$

- 几率法：两能级系统

$$\hat{h} = -g\mu_B H s_z \qquad \hat{h}|\uparrow\rangle = -g\mu_B H \qquad \hat{h}|\downarrow\rangle = g\mu H$$

$$z = \sum_s e^{-\beta\varepsilon_s} = e^{\beta g\mu_B H} + e^{-\beta g\mu_B H}$$

$$U = -N\left(\frac{\partial \ln z}{\partial\beta}\right) = -Ng\mu_B H\frac{e^{\beta g\mu_B H} - e^{-\beta g\mu_B H}}{e^{\beta g\mu_B H} + e^{-\beta g\mu_B H}}$$

$$= -Ng\mu_B H\frac{\sinh\beta g\mu_B H}{\cosh\beta g\mu_B H}$$

微正则系综的例子

顺磁系统：磁场 H 中 N 个无相互作用的自旋 1/2 粒子

$$\mathcal{H} = -\sum_i g\mu_B H \hat{s}_{iz}$$

- 微正则系综 $|s\rangle = \{|\uparrow\uparrow\cdots\rangle, |\downarrow\uparrow\cdots\rangle, |\uparrow\downarrow\cdots\rangle, |\downarrow\downarrow\cdots\rangle, \cdots\}$: 2^N 个可能

$$\hat{\mathcal{H}}|\uparrow\downarrow\cdots\rangle = [-g\mu_B H + g\mu_B H + \cdots]|\uparrow\downarrow\cdots\rangle$$

$$= -g\mu_B H(N_\uparrow - N_\downarrow)|\uparrow\downarrow\cdots\rangle$$

$$E_s = -g\mu_B H(N_\uparrow - N_\downarrow \boxed{= N - N_\uparrow}) = (N - 2N_\uparrow) g\mu_B H$$

$$\Rightarrow N_\uparrow = \frac{N}{2} - \frac{E_s}{2g\mu_B H}$$

$$\Omega(E, N) = C_N^{N_\uparrow} = \frac{N!}{N_\uparrow! N_\downarrow!}$$

$$S = k_B \ln \Omega = k_B[\ln N! - \ln N_\uparrow! - \ln N_\downarrow!]$$

微正则系综的例子

- 微正则系综

$$
\begin{aligned}
S &= k_B[N\ln N - N_\uparrow \ln N_\uparrow - N_\downarrow \ln N_\downarrow] \\
&= k_B\left[N\ln N - \left(\frac{N}{2} - \frac{E}{2g\mu_B H}\right)\ln\left(\frac{N}{2} - \frac{E}{2g\mu_B H}\right)\right. \\
&\left. - \left(\frac{N}{2} + \frac{E}{2g\mu_B H}\right)\ln\left(\frac{N}{2} + \frac{E}{2g\mu_B H}\right)\right] \\
\beta &= \frac{1}{k_B T} = \left(\frac{\partial S/k_B}{\partial E}\right)_N \\
&= \frac{1}{2g\mu_B H}\ln\left(\frac{N}{2} - \frac{E}{2g\mu_B H}\right) - \frac{1}{2g\mu_B H}\ln\left(\frac{N}{2} + \frac{E}{2g\mu_B H}\right) \\
&= \frac{1}{2g\mu_B H}\ln\frac{N - E/(g\mu_B H)}{N + E/(g\mu_B H)} \Rightarrow \frac{N - E/(g\mu_B H)}{N + E/(g\mu_B H)} = e^{2\beta g\mu_B H} \Rightarrow \\
E &= N g\mu_B H \frac{1 - e^{2\beta g\mu_B H}}{1 + e^{2\beta g\mu_B H}} = -N g\mu_B H \frac{\sinh \beta g\mu_B H}{\cosh \beta g\mu_B H}
\end{aligned}
$$

8.5 正则系综

- 正则系综：由和热源有热接触的系统组成的系综；系综里所有系统的温度、粒子数和体积相同
- 密度矩阵：可以从微正则系综理论中推导出来

$$\hat{\rho} = \frac{1}{Z} e^{-\beta \hat{\mathcal{H}}} \qquad Tr\{\hat{\rho}\} = 1 \Rightarrow Z = Tr\{e^{-\beta \hat{\mathcal{H}}}\}$$

系统配分函数

能量本征态 $\hat{\mathcal{H}}|s\rangle = E_s|s\rangle$

$$p_s = \rho_{ss} = \langle s|\hat{\rho}|s\rangle = \frac{1}{Z} e^{-\beta E_s}$$

系统处于 $|s\rangle$ 态的几率

- 处于 $|s\rangle$ 态的几率 $\propto$ Boltzmann 因子 $e^{-\beta E_s}$
  ☞能量越小的态，出现的几率越大；系统基态出现几率最大
- 能量为 E 的态出现的几率 $\propto \Omega(E, N, V) e^{-\beta E}$

$$p(E) = \frac{1}{Z} \sum_{\{s|E_s=E\}} e^{-\beta E_s} = \frac{1}{Z} \Omega(E, N, V) e^{-\beta E}$$

☞并非能量越低出现几率越大

$\Rightarrow$ 出现几率最大的能量 $E_m = \overline{E} = U$

配分函数

$$Z = Tr\{e^{-\beta\hat{\mathcal{H}}}\} = \sum_s \langle s|e^{-\beta\mathcal{H}}|s\rangle = \sum_s e^{-\beta E_s}$$

$$= \sum_{E_l} \sum_{\{s|E_s=E_l\}} e^{-\beta E_s} = \sum_{E_l} \Omega(E_l, N, V) e^{-\beta E_l}$$

☞ 可以把正则系综看成不同能量的微正则系综的集合，能量为 E 的微正则系综的权重为 $e^{-\beta E}$

- 物理量

$$\overline{O} = Tr\{\hat{O}\hat{\rho}\} = \sum_s \langle s|\hat{O}\frac{1}{Z}e^{-\beta\hat{\mathcal{H}}}|s\rangle = \frac{1}{Z}\sum_{ss'}\langle s|O|s'\rangle\langle s'|e^{-\beta\hat{\mathcal{H}}}|s\rangle$$

$$= \frac{1}{Z}\sum_s O_{ss'} e^{-\beta E_s}\delta_{ss'} = \frac{1}{Z}\sum_s O_{ss} e^{-\beta E_s}$$

物理量

- 内能

$$U = \overline{E} = Tr\{\hat{\mathcal{H}}\hat{\rho}\} = \frac{1}{Z}\sum_s E_s e^{-\beta E_s} = \frac{1}{Z}\sum_s \left(\frac{-\partial}{\partial\beta} e^{-\beta E_s}\right)_{N,V}$$

$$= -\frac{1}{Z}\frac{\partial}{\partial\beta}\left(\sum_s e^{-\beta E_s}\right)_{NV} = -\frac{1}{Z}\left(\frac{\partial Z}{\partial\beta}\right)_{NV} = -\left(\frac{\partial \ln Z}{\partial\beta}\right)_{NV}$$

$$= k_B T^2 \left(\frac{\partial \ln Z}{\partial T}\right)_{NV}$$

形式化推导

$$U = Tr\{\hat{\mathcal{H}}\hat{\rho}\} = \frac{1}{Z} Tr\{\hat{\mathcal{H}} e^{-\beta\hat{\mathcal{H}}}\}$$

$$= \frac{1}{Tr\{e^{-\beta\hat{\mathcal{H}}}\}} Tr\{-\partial_\beta e^{-\beta\hat{\mathcal{H}}}\} = \frac{1}{Tr\{e^{-\beta\hat{\mathcal{H}}}\}} (-\partial_\beta) Tr\{e^{-\beta\hat{\mathcal{H}}}\}$$

$$= -\partial_\beta \ln Tr\{e^{-\beta\hat{\mathcal{H}}}\} = -\left(\frac{\partial \ln Z}{\partial\beta}\right)_{NV}$$

物理量

- 压强

$$
\begin{aligned}
p &= \left\langle -\frac{\partial \mathcal{H}}{\partial V} \right\rangle = -Tr\left\{ \frac{\partial \mathcal{H}}{\partial V} \hat{\rho} \right\} = -Tr\left\{ \frac{\partial \mathcal{H}}{\partial V} \frac{1}{Z} e^{-\beta \mathcal{H}} \right\} \\
&= -\frac{1}{Tr\{e^{-\beta \mathcal{H}}\}} Tr\left\{ \frac{\partial \mathcal{H}}{\partial V} e^{-\beta \mathcal{H}} \right\} = \frac{1}{Z} Tr\left\{ \frac{\partial}{\beta \partial V} e^{-\beta \mathcal{H}} \right\}_{\beta N} \\
&= \frac{1}{Z} \frac{1}{\beta \partial V} Tr\left\{ e^{-\beta \mathcal{H}} \right\}_{\beta N} = \frac{1}{\beta} \frac{1}{Z} \left(\frac{\partial Z}{\partial V} \right)_{\beta N} = \frac{1}{\beta} \left(\frac{\partial \ln Z}{\partial V} \right)_{\beta N} \\
&= -\frac{1}{Z} \sum_s \left(\frac{\partial E_s}{\partial V} \right) e^{-\beta E_s} = \frac{1}{Z} \sum_s \frac{1}{\beta} \left(\frac{\partial}{\partial V} e^{-\beta E_s} \right)_{\beta N} \\
&= \frac{1}{Z} \frac{1}{\beta} \left(\frac{\partial}{\partial V} \sum_s e^{-\beta E_s} \right)_{\beta N} = \frac{1}{\beta Z} \left(\frac{\partial Z}{\partial V} \right)_{\beta N} = \frac{1}{\beta} \left(\frac{\partial \ln Z}{\partial V} \right)_{\beta N} \\
&= k_B T \left(\frac{\partial \ln Z}{\partial V} \right)_{TN}
\end{aligned}
$$

熵

$$dS = \frac{dU}{T} + \frac{p}{T}dV = d\frac{U}{T} - Ud\frac{1}{T} + \frac{p}{T}dV$$

$$\frac{dS}{k_B} = d(\beta U) - Ud\beta + \beta p dV = d(\beta U) + \left(\frac{\partial \ln Z}{\partial \beta}\right)_V d\beta + \left(\frac{\partial \ln Z}{\partial V}\right)_\beta dV$$

$$= d(\beta U + \ln Z)$$

$$S = k_B(\ln Z + \beta U) = k_B \ln Z + \frac{U}{T}$$

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

Gibbs 熵

$$S = -k_B Tr\{\hat{\rho} \ln \hat{\rho}\} = -k_B \sum_s p_s \ln p_s$$

$$= -k_B Tr\left\{\hat{\rho} \ln\left(\frac{1}{Z} e^{-\beta \hat{H}}\right)\right\}$$

$$= -k_B Tr\left\{\hat{\rho}(-\ln Z - \beta\hat{\mathcal{H}})\right\} = k_B[\ln Z\, Tr\{\hat{\rho}\} + \beta Tr\{\hat{\rho}\hat{\mathcal{H}}\}]$$

$$= k_B(\ln Z + \beta U)$$

☞ 我们在几率法中得到相同的表达式

正则系综和微正则系综

- 微正则系综：等几率假设 $p_s = \rho_{ss} = \frac{1}{\Omega}\delta_{E,E_s}$
  ☞系综里的系统都是孤立系统
- 正则系综：由和热源接触的系统组成
  总系统 = 系统 + 热源 ⇒ 孤立系统 ☞ 微正则系综

$$\hat{\mathcal{H}}_T = \mathcal{H} + \mathcal{H}_R + H_i \simeq \mathcal{H} + \mathcal{H}_R$$

$$|T\rangle = |s\rangle|R\rangle \Rightarrow \hat{\mathcal{H}}_T|T\rangle = \hat{\mathcal{H}}|s\rangle|R\rangle + |s\rangle\hat{\mathcal{H}}_R|R\rangle$$

$$= (E_s + E_R)|s\rangle|R\rangle = E_T|s\rangle|R\rangle$$

$$\hat{\rho}_T = \frac{1}{\Omega_T(E_T)}\delta_{E_T,\hat{\mathcal{H}}_T}$$

$\Omega_T(E_T)$：总系统的简并度

系统物理量 O（只和系统有关，和热源无关）

$$\overline{O} = Tr\{\hat{O}\hat{\rho}_T\} = \frac{1}{\Omega_T}\sum_T \langle T|\hat{O}\delta_{E_T,\hat{\mathcal{H}}}|T\rangle = \frac{1}{\Omega_T}\sum_{sR}\langle s|\langle R|\hat{O}\delta_{E_T,E_s+E_R}|s\rangle|R\rangle$$

$$= \sum_s O_{ss}\frac{1}{\Omega_T}\sum_R \delta_{E_T,E_s+E_R} = \sum_s O_{ss}\frac{\Omega_R(E_R = E_T - E_s)}{\Omega_T(E_T)} = \sum_s O_{ss}p_s$$

正则系综和微正则系综

- 正则系综：由和热源接触的系统组成

  态 $|s\rangle$ 出现的几率：

$$p_s = \frac{\Omega_R(E_R = E_T - E_s)}{\Omega_T(E_T)}$$

$\Omega_R(E_R)$ 为热源的简并度

$$p_s = \frac{1}{\Omega_T} e^{\ln \Omega_R (E_T - E_s)} = \frac{1}{\Omega_T} e^{S_R(E_T - E_s)/k_B}$$

Boltzmann 关系

$$= \frac{1}{\Omega_T} \exp\left\{ \frac{1}{k_B} S_R[E_T - \overline{E}_s - (E_s - \overline{E}_s)] \right\}$$

$\overline{E}_s = \langle E_s \rangle$

$$= \frac{1}{\Omega_T} \exp\left\{ \frac{1}{k_B} \left[S_R(\overline{E}_R) - \frac{\partial S_R}{\partial \overline{E}_R}(E_s - \overline{E}_s) + \frac{1}{2}\frac{\partial^2 S_R}{\partial \overline{E}_R^2}(E_s - \overline{E}_s)^2 + \cdots \right] \right\}$$

$$= \frac{1}{\Omega_T} \exp\left\{ \frac{\overline{S}_R}{k_B} - \frac{(E_s - \overline{E}_S)}{k_B T} + \frac{1}{2k_B}\frac{\partial(1/T)}{\partial \overline{E}_R}(E_s - \overline{E}_s)^2 + \cdots \right\}$$

$$= \frac{1}{\Omega_T} \exp\left\{ \frac{\overline{S}_R}{k_B} - \frac{(E_s - \overline{E}_S)}{k_B T} - \frac{(E_s - \overline{E}_s)^2}{2k_B T^2 C_R} + \cdots \right\} = C \exp\left\{ -\frac{E_s}{k_B T} \right\}$$

热源热容 $C_R \to \infty \Rightarrow p_s \propto e^{-\beta E_s}$ ☞正则系综

Reduced density matrix

从整体（宇宙）密度矩阵 ρ^T 获得部分（研究系统）密度矩阵的方法：物理量 O 只和系统有关，和外界无关

$$\overline{O} = Tr\{\hat{O}\hat{\rho}^T\} = \sum_{sR}\langle sR|\hat{O}\hat{\rho}^T|sR\rangle = \sum_{sR;s'R'}\langle sR|\hat{O}|s'R'\rangle\langle s'R'|\hat{\rho}^T|sR\rangle$$

$$= \sum_{sR;s'R'} O_{ss'}\delta_{RR'}\rho^T_{s'R',sR} = \sum_{ss'} O_{ss'}\sum_{R}\rho^T_{s'R,sR} = \sum_{ss'} O_{ss'}\rho_{s's}$$

$$= Tr\{\hat{O}\hat{\rho}\}$$

Reduced density matrix

$$\rho_{s's} = \langle s'|\hat{\rho}|s\rangle = \sum_{R}\rho^T_{s'R,sR}$$

$$\hat{\rho} = Tr_R\{\rho^T\} = \frac{1}{Z}e^{-\beta\hat{\mathcal{H}}}$$

Canonical typicality

- 等几率假设：微正则系综 $\Rightarrow$ 正则系综 $\hat{\rho} = e^{-\beta\hat{\mathcal{H}}}/Z$
- 正则典型性：总系统 = 环境 + 系统，总系统处于一个典型的量子力学态，系统对应的 reduced density matrix 和正则系综的 density matrix 相同

$$\hat{\mathcal{H}}_T = \hat{\mathcal{H}} + \hat{\mathcal{H}}_R + \hat{\mathcal{H}}_I \qquad \hat{\rho}_T = |T\rangle\langle T|$$

$$S_T = -k_B Tr\{\hat{\rho}_T \ln \hat{\rho}_T\} = 0$$ 总系统的熵为零

$$\hat{\rho} = Tr_R\{\hat{\rho}_T\} \propto e^{-\beta\hat{H}}$$

$$S = -k_B Tr\{\hat{\rho} \ln \hat{\rho}\} \neq 0$$ 系统的熵非零

- "Canonical Typicality", Goldstein *et al*, PRL **96**, 050403 (2006)
- "The foundations of statistical mechanics from entanglement: Individual states vs. averages", Popescu *et al*, Nature Physics **2**, 754 (2006)

☞ 利用 Canonical Typicality 可以避免等几率假设。

正则系综里的能量分布

- 把热源（环境）平均掉之后，得到正则系综
- 系综里系统能量不再是确定量
- 能量分布

$$p(E) = \sum_{\{s|E_s=E\}} p_s = \frac{1}{Z}\sum_{\{s|E_s=E\}} e^{-\beta E_s} = \frac{\Omega(E)}{Z}e^{-\beta E} = \frac{1}{Z}e^{\ln\Omega(E)-\beta E}$$

$$= \frac{1}{Z}\exp\left\{\frac{S(E)}{k_B} - \frac{E}{k_B T}\right\} = \frac{1}{Z}\exp\left\{\frac{S(U+E-U)}{k_B} - \frac{E-U}{k_B T} - \frac{U \boxed{= \overline{E}}}{k_B T}\right\}$$

$$= \frac{1}{Z}\exp\left\{\frac{TS(U)-U}{k_B T} + \frac{E-U}{k_B}\frac{\partial S}{\partial U} + \frac{(E-U)^2}{2k_B}\frac{\partial^2 S}{\partial U^2} + \cdots - \frac{E-U}{k_B T}\right\}$$

$$= \frac{1}{Z}\exp\left\{-\frac{F}{k_B T} + \frac{E-U}{k_B T} + \frac{(E-U)^2}{2k_B}\frac{\partial(1/T)}{\partial U} + \cdots - \frac{E-U}{k_B T}\right\}$$

$$= \exp\left\{-\frac{(E-U)^2}{2k_B T^2 C_V} + \cdots\right\}$$

$$p(E) = (1/Z)e^{\ln\Omega-\beta E} = e^{[-k_B T\ln Z + TS(E) - E]/(k_B T)}$$

$$= e^{-(F-\overline{F})/(k_B T)} = e^{-\Delta F/(k_B T)}$$

把自由能定义扩展到非平衡态

正则系综里的能量分布

平衡时自由能极小，一阶导数为零 ⇒ 高斯分布

- 能量分布： $p(E) = \exp[-(F - \bar{F})/k_B T]$

$$p(E) \propto \exp\left\{-\frac{(E-U)^2}{2k_B T^2 C_V}\right\}$$

$$E_m = \overline{E} = U$$

最可几值 = 平均值 = 热力学量

- 能量涨落

$$\overline{\Delta E^2} = \overline{(E-U)^2} = \frac{\int_{-\infty}^{\infty} e^{-(E-U)^2/(2k_B T^2 C_V)}(E-U)^2 dE}{\int_{-\infty}^{\infty} e^{-(E-U)^2/(2k_B T^2 C_V)} dE}$$

$$= k_B T^2 C_V$$

$$\frac{\overline{\Delta E}}{\overline{E}} = \frac{\sqrt{k_B T^2 C_V}}{U} \propto \frac{1}{\sqrt{N}}$$

☞ 正则系综里系统能量基本上在平均值附近，只有极少数偏离平均值 ⇒ 在热力学极限下用正则系综和微正则系综得到的热力学量是相同的

正则系综里的能量分布

- 能量涨落的系综求法

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

$$\overline{E^2} = Tr\{\hat{\mathcal{H}}^2\hat{\rho}\} = \frac{1}{Z}\sum_s E_s^2 e^{-\beta E_s} = \frac{1}{Z}\sum_s \frac{\partial^2}{\partial\beta^2} e^{-\beta E_s}$$

$$= \frac{1}{Z}\frac{\partial^2}{\partial\beta^2}\sum_s e^{-\beta E_s} = \frac{1}{Z}\frac{\partial^2 Z}{\partial\beta^2}$$

$$= \frac{\partial}{\partial\beta}\left(\frac{1}{Z}\frac{\partial Z}{\partial\beta}\right) - \frac{\partial(1/Z)}{\partial\beta}\frac{\partial Z}{\partial\beta} = \frac{\partial^2 \ln Z}{\partial\beta^2} + \frac{1}{Z^2}\left(\frac{\partial Z}{\partial\beta}\right)^2$$

$$= \frac{\partial^2 \ln Z}{\partial\beta^2} + \left(-\frac{\partial \ln Z}{\partial\beta}\right)^2 \boxed{= \overline{E}^2}$$

$$\Delta E^2 = \overline{(E-\overline{E})^2} = \frac{\partial^2 \ln Z}{\partial\beta^2} = -\left(\frac{\partial U}{\partial\beta}\right)_{NV} = k_B T^2\left(\frac{\partial U}{\partial T}\right)_{NV} = k_B T^2 C_V$$

经典极限

$$Z_{cl} = \int \frac{d\boldsymbol{r}\, d\boldsymbol{p}}{h^{Nd}} e^{-\beta\mathcal{H}}$$

定域系；非全同粒子

$$Z_{cl} = \frac{1}{N!} \int \frac{d\boldsymbol{r}\, d\boldsymbol{p}}{h^{Nd}} e^{-\beta\mathcal{H}}$$

非定域系；全同粒子

8.6 巨正则系综

由开放系统组成的系综，系综里的系统和温度为 T 的热源以及化学势为 μ 的粒子源接触。

- 密度矩阵：和正则系综类似，可以从微正则系综推导出来

$$\hat{\rho} = \frac{1}{\Xi} e^{-\beta(\hat{\mathcal{H}}-\mu\hat{N})} \qquad \Xi = Tr\{e^{-\beta(\hat{\mathcal{H}}-\mu\hat{N})}\}$$

巨配分函数

$$\hat{\mathcal{H}}|s\rangle = E_s|s\rangle \qquad \hat{N}|s\rangle = N_s|s\rangle$$

取 $\hat{\mathcal{H}}$ 和 $\hat{N}$ 的共同本征态

$$\rho_{ss'} = \frac{1}{\Xi} e^{-\beta(E_s-\mu N_s)}\delta_{ss'}$$

$$p_s = \frac{1}{\Xi} e^{-\beta(E_s-\mu N_s)}$$

系统处于 $|s\rangle$ 的几率 $\propto$ Gibbs 因子

$$\Xi = \Xi(\beta,\mu,V) = \sum_s e^{-\beta(E_s-\mu N_s)} = \sum_N \sum_{E_l} \sum_{\{s|E_s=E_l,N_s=N\}} e^{-\beta E_s+\beta\mu N_s}$$

$$= \sum_N e^{\beta\mu N} \sum_{E_l} e^{-\beta E_l}\Omega(E_l,N,V) = \sum_N e^{\beta\mu N} Z(\beta,N,V)$$

☞ 可以看成是权重为 $e^{\beta\mu N}$ 的正则系综的集合

经典极限

$$\rho(\boldsymbol{r}_N, \boldsymbol{p}_N) d\boldsymbol{r}_N d\boldsymbol{p}_N = \frac{1}{\Xi}\frac{1}{N!} e^{-\beta[\mathcal{H}(\boldsymbol{r}_N,\boldsymbol{p}_N)-\mu N]} \frac{d\boldsymbol{r}_N d\boldsymbol{p}_N}{h^{Nd}}$$

$$\Xi = \sum_{N=0}^{\infty} \frac{1}{N!} e^{\beta\mu N} \int e^{-\beta\mathcal{H}(\boldsymbol{r}_N,\boldsymbol{p}_N)} \frac{d\boldsymbol{r}_N d\boldsymbol{p}_N}{h^{Nd}}$$

☞定域性则没有 $1/N!$ 因子

热力学量

- 一般物理量

$$\overline{O} = Tr\{\hat{O}\hat{\rho}\} = \sum_s O_{ss}\rho_{ss} = \frac{1}{\Xi}\sum_s O_{ss}e^{-\beta(E_s-\mu N_s)}$$

- 粒子数 N

$$N = Tr\{\hat{N}\hat{\rho}\} = \frac{1}{\Xi}\sum_s N_s e^{-\beta E_s+\beta\mu N_s} = \frac{1}{\Xi}\sum_s \left(\frac{\partial}{\partial\beta\mu}e^{-\beta E_s+\beta\mu N_s}\right)_{\beta,V}$$

$$= \frac{1}{\Xi}\left(\frac{\partial}{\partial\beta\mu}\sum_s e^{-\beta E_s+\beta\mu N_s}\right)_{\beta,V} = \frac{1}{\Xi}\left(\frac{\partial\Xi}{\partial\beta\mu}\right)_{\beta V} = \left(\frac{\partial\ln\Xi}{\partial\beta\mu}\right)_{\beta V}$$

形式化计算

$$N = \frac{1}{\Xi}Tr\{\hat{N}e^{-\beta\hat{H}+\beta\mu\hat{N}}\} = \frac{1}{\Xi}Tr\left\{\left(\frac{\partial}{\partial\beta\mu}e^{-\beta\hat{\mathcal{H}}+\beta\mu\hat{N}}\right)_{\beta V}\right\}$$

$$= \frac{1}{\Xi}\left(\frac{\partial}{\partial\beta\mu}Tr\left\{e^{-\beta\hat{\mathcal{H}}+\beta\mu\hat{N}}\right\}\right)_{\beta V} = \frac{1}{\Xi}\left(\frac{\partial\Xi}{\partial\beta\mu}\right)_{\beta V} = \left(\frac{\partial\ln\Xi}{\partial\beta\mu}\right)_{\beta V}$$

热力学量

- 内能

$$U=\overline{\hat{\mathcal{H}}}=Tr\{\hat{\mathcal{H}}\hat{\rho}\}=\frac{1}{\Xi}Tr\{\hat{\mathcal{H}}e^{-\beta\hat{\mathcal{H}}+\beta\mu\hat{N}}\}$$

形式化计算

$$=\frac{1}{\Xi}Tr\left\{-\left(\frac{\partial}{\partial\beta}e^{-\beta\hat{\mathcal{H}}+\beta\mu\hat{N}}\right)_{\beta\mu,V}\right\}=-\frac{1}{\Xi}\left(\frac{\partial}{\partial\beta}Tr\left\{e^{-\beta\hat{\mathcal{H}}+\beta\mu\hat{N}}\right\}\right)_{\beta\mu,V}$$

$$=-\frac{1}{\Xi}\left(\frac{\partial\Xi}{\partial\beta}\right)_{\beta\mu,V}=-\left(\frac{\partial\ln\Xi}{\partial\beta}\right)_{\beta\mu,V}$$

基展开

$$=\frac{1}{\Xi}\sum_s E_s e^{-\beta E_s+\beta\mu N_s}=\frac{1}{\Xi}\sum_s(-)\left(\frac{\partial}{\partial\beta}e^{-\beta E_s+\beta\mu N_s}\right)_{\beta\mu,V}$$

$$=-\frac{1}{\Xi}\left(\frac{\partial}{\partial\beta}\sum_s e^{-\beta E_s+\beta\mu N_s}\right)_{\beta\mu,V}=-\frac{1}{\Xi}\left(\frac{\partial\Xi}{\partial\beta}\right)_{\beta\mu,V}=-\left(\frac{\partial\ln\Xi}{\partial\beta}\right)_{\beta\mu,V}$$

热力学量

- 压强

$$p = \frac{1}{\Xi} Tr\left\{-\left(\frac{\partial \mathcal{H}}{\partial V}\right) e^{-\beta\hat{\mathcal{H}}+\beta\mu\hat{N}}\right)\right\} = \frac{1}{\Xi} Tr\left\{\left(\frac{\partial}{\partial \beta V} e^{-\beta\hat{\mathcal{H}}+\beta\mu\hat{N}}\right)_{\beta,\beta\mu}\right\}$$

$$= \frac{1}{\Xi}\left(\frac{\partial}{\partial \beta V} Tr\left\{e^{-\beta\hat{\mathcal{H}}+\beta\mu\hat{N}}\right\}\right)_{\beta,\beta\mu} = \frac{1}{\Xi}\left(\frac{\partial \Xi}{\partial \beta V}\right)_{\beta,\beta\mu} = \frac{1}{\beta}\left(\frac{\partial \ln \Xi}{\partial V}\right)_{\beta,\mu}$$

- 熵

$$dS = \frac{dU}{T} + \frac{p}{T} dV - \frac{\mu}{T} dN$$

$$d(S/k_B) = \beta dU + \beta p dV - \beta\mu dN$$

$$= d(\beta U - \beta\mu N) - U d\beta + \beta p dV + N d(\beta\mu)$$

$$= d(\beta U - \beta\mu N) + \left(\frac{\partial \ln \Xi}{\partial \beta}\right)_{\beta\mu V} d\beta + \left(\frac{\partial \ln \Xi}{\partial V}\right)_{\beta\beta\mu} dV + \left(\frac{\partial \ln \Xi}{\partial \beta\mu}\right)_{\beta V} d(\beta\mu)$$

$$= d(\beta U - \beta\mu N + \ln \Xi)$$

$$S = k_B \ln \Xi + \frac{U}{T} - \frac{\mu N}{T}$$

热力学量

- Gibbs 熵

$$
\begin{aligned}
S &= k_B \ln \Xi + \frac{U}{T} - \frac{\mu N}{T} \\
&= -k_B Tr\{\hat{\rho} \ln \hat{\rho}\} \qquad = -k_B \sum_s p_s \ln p_s \\
&= -k_B Tr\left\{\hat{\rho} \ln\left(\frac{1}{\Xi} e^{-\beta\hat{\mathcal{H}}+\beta\mu\hat{N}}\right)\right\} \\
&= -k_B Tr\left\{\hat{\rho}(-\ln \Xi - \beta\hat{\mathcal{H}} + \beta\mu\hat{N})\right\} \\
&= k_B[\ln \Xi \, Tr\{\hat{\rho}\} + \beta \, Tr\{\hat{\rho}\hat{\mathcal{H}}\} - \beta\mu \, Tr\{\hat{\rho}\hat{N}\}] \\
&= k_B(\ln \Xi + \beta U - \beta\mu N)
\end{aligned}
$$

$$
J = F - \mu N = U - TS - \mu N = -k_B T \ln \Xi \qquad \boxed{\text{巨势}}
$$

☞ 同样，相同的表达式我们在几率法中已经得到

粒子涨落

$$\Delta N^2 = \overline{(N-\overline{N})^2} = \overline{N^2} - \overline{N}^2$$

$$\overline{N^2} = Tr\{\hat{N}^2\hat{\rho}\} = \frac{1}{\Xi}Tr\{\hat{N}^2 e^{-\beta\hat{\mathcal{H}}+\beta\mu\hat{N}}\}$$

$$= \frac{1}{\Xi}Tr\left\{\left(\frac{\partial^2}{\partial(\beta\mu)^2}e^{-\beta\hat{\mathcal{H}}+\beta\mu\hat{N}}\right)_{\beta,V}\right\} = \frac{1}{\Xi}\left(\frac{\partial^2}{\partial(\beta\mu)^2}Tr\{e^{-\beta\hat{\mathcal{H}}+\beta\mu\hat{N}}\}\right)_{\beta,V}$$

$$= \frac{1}{\Xi}\frac{\partial^2\Xi}{\partial(\beta\mu)^2} = \frac{\partial}{\partial\beta\mu}\left(\frac{1}{\Xi}\frac{\partial\Xi}{\partial\beta\mu}\right) - \frac{\partial(1/\Xi)}{\partial\beta\mu}\frac{\partial\Xi}{\partial\beta\mu} = \left(\frac{\partial^2\ln\Xi}{\partial(\beta\mu)^2}\right) + \left(\frac{\partial\ln\Xi}{\partial\beta\mu}\right)^2$$

$$\Delta N^2 = \left(\frac{\partial^2\ln\Xi}{\partial(\beta\mu)^2}\right) = \left(\frac{\partial N}{\partial\beta\mu}\right)_{\beta V} = k_B T\left(\frac{\partial N}{\partial\mu}\right)_{TV}$$

粒子涨落

$$\Delta N^2 = k_B T \left(\frac{\partial N}{\partial \mu}\right)_{TV}$$

$$d\mu = -sdT + vdp$$ Gibbs-Duhem 关系，$v = V/N$

$$df = -sdT - pdv \qquad \mu = f + pv$$

$$\left(\frac{\partial N}{\partial \mu}\right)_T V = V\left(\frac{\partial N/V}{\partial \mu}\right)_{TV} = V\left(\frac{\partial 1/v}{\partial \mu}\right)_T = -\frac{V}{v^2}\left(\frac{\partial v}{\partial \mu}\right)_T = -\frac{N^2}{V} / \left(\frac{\partial \mu}{\partial v}\right)_T$$

$$\left(\frac{\partial \mu}{\partial v}\right)_T = \left(\frac{\partial (f+pv)}{\partial v}\right)_T = \left(\frac{\partial f}{\partial v}\right)_T + p + v\left(\frac{\partial p}{\partial v}\right)_T$$

$$= -p + p - \frac{1}{-\frac{1}{v}\left(\frac{\partial v}{\partial p}\right)_T} = -\frac{1}{\kappa_T}$$

$$\Delta N^2 = k_B T N^2 \kappa_T / V \propto O(N^1)$$

$$\frac{\Delta N}{N} = \sqrt{\frac{k_B T \kappa_T}{V}} = \sqrt{\frac{k_B T \kappa_T}{N v}} \propto \frac{1}{\sqrt{N}}$$

能量涨落

$$\Delta E^2 = \overline{E^2} - \overline{E}^2 = \frac{\partial^2 \ln \Xi}{\partial \beta^2} = -\left(\frac{\partial U}{\partial \beta}\right)_{\beta\mu, V} = -\frac{\partial(U, \beta\mu)}{\partial(\beta, \beta\mu)}$$

$$= -\frac{\partial(U, \beta\mu)}{\partial(\beta, N)} \frac{\partial(\beta, N)}{\partial(\beta, \beta\mu)}$$

$$= -\left[\left(\frac{\partial U}{\partial \beta}\right)_N - \left(\frac{\partial U}{\partial N}\right)_\beta \left(\frac{\partial \beta\mu}{\partial \beta}\right)_N \left(\frac{\partial N}{\partial \beta\mu}\right)_\beta\right]$$

$$d \ln \Xi = \left(\frac{\partial \ln \Xi}{\partial \beta}\right)_{\beta\mu} d\beta + \left(\frac{\partial \ln \Xi}{\partial \beta\mu}\right)_\beta d(\beta\mu) = -U d\beta + N d(\beta\mu)$$

$$d(\ln \Xi - N\beta\mu) = -U d\beta - \beta\mu dN \Rightarrow \left(\frac{\partial \beta\mu}{\partial \beta}\right)_N = \left(\frac{\partial U}{\partial N}\right)_\beta$$

$$\Delta E^2 = -\left(\frac{\partial U}{\partial \beta}\right)_N + \left(\frac{\partial U}{\partial N}\right)_\beta^2 \left(\frac{\partial N}{\partial \beta\mu}\right)_\beta = k_B T^2 \left(\frac{\partial U}{\partial T}\right)_{NV} + \left(\frac{\partial U}{\partial N}\right)_{TV}^2 \Delta N^2$$

$$= k_B T^2 C_V + \left(\frac{\partial U}{\partial N}\right)_{TV}^2 \Delta N^2$$

$$= \boxed{\text{保持 NTV 不变时的能量涨落 + 粒子数涨落导致的能量变动}}$$

能量涨落

$$dF = -SdT - pdV + \mu dN \qquad U = F + TS$$

$$\left(\frac{\partial U}{\partial N}\right)_{TV} = \left(\frac{\partial F}{\partial N}\right)_{TV} + T\left(\frac{\partial S}{\partial N}\right)_{TV} = \mu - T\left(\frac{\partial \mu}{\partial T}\right)_{NV} = \mu - T\left(\frac{\partial \mu}{\partial T}\right)_{v}$$

$$\boxed{\mu = \mu(T, N, V) = \mu(T, \frac{V}{N}) = \mu(T, v) \qquad d\mu = -sdT + vdp}$$

$$\left(\frac{\partial U}{\partial N}\right)_{TV} = \mu - T\left[-s + v\left(\frac{\partial p}{\partial T}\right)_v\right] = \mu + TS - pv + v\left[p - T\left(\frac{\partial p}{\partial T}\right)_v\right]$$

$$= u + v\left[p - T\left(\frac{\partial p}{\partial T}\right)_v\right]$$

$$\Delta^2 E = k_B T^2 C_V + \left[u + v\left(p - T\left(\frac{\partial p}{\partial T}\right)_v\right)\right]^2 \Delta N^2$$

- 经典理想气体: $p = nk_BT$,

$$\Delta E^2 = k_B T^2 C_V + u^2 \Delta N^2$$

- 强简并 Fermion

$$\Delta E^2 \simeq k_B T^2 C_V + \varepsilon_F^2 \Delta N^2 \simeq \Delta N^2 \varepsilon_F^2$$

能量涨落和粒子数涨落的关联

$$\overline{\Delta N \Delta E} = \overline{(N-\overline{N})(E-\overline{E})} = \overline{NE} - \overline{N}\overline{E}$$

$$\overline{NE} = Tr\{\hat{N}\hat{\mathcal{H}}\hat{\rho}\} = \frac{1}{\Xi}Tr\{\hat{N}\hat{\mathcal{H}}e^{-\beta\hat{\mathcal{H}}+\beta\mu\hat{N}}\} = -\frac{1}{\Xi}\frac{\partial^2}{\partial\beta\partial(\beta\mu)}Tr\{e^{-\beta\hat{\mathcal{H}}+\beta\mu\hat{N}}\}$$

$$= -\frac{1}{\Xi}\frac{\partial^2 \Xi}{\partial\beta\partial(\beta\mu)} = -\frac{\partial}{\partial\beta}\left[\frac{1}{\Xi}\frac{\partial\Xi}{\partial(\beta\mu)}\right] + \left(\frac{\partial(1/\Xi)}{\partial\beta}\right)_{\beta\mu}\left(\frac{\partial\Xi}{\partial\beta\mu}\right)_{\beta}$$

$$= -\frac{\partial}{\partial\beta}\left[\frac{1}{\Xi}\frac{\partial\Xi}{\partial(\beta\mu)}\right] - \frac{1}{\Xi^2}\left(\frac{\partial\Xi}{\partial\beta}\right)_{\beta\mu}\left(\frac{\partial\Xi}{\partial\beta\mu}\right)_{\beta}$$

$$= -\frac{\partial^2 \ln\Xi}{\partial\beta\partial(\beta\mu)} - \left(\frac{\partial\ln\Xi}{\partial\beta}\right)_{\beta\mu}\left(\frac{\partial\ln\Xi}{\partial\beta\mu}\right)_{\beta}$$

$$= -\frac{\partial^2 \ln\Xi}{\partial\beta\partial(\beta\mu)} + \overline{N}\overline{E}$$

$$\overline{\Delta N \Delta E} = -\frac{\partial^2 \ln\Xi}{\partial\beta\partial(\beta\mu)} = -\left(\frac{\partial N}{\partial\beta}\right)_{\beta\mu V} = \left(\frac{\partial U}{\partial\beta\mu}\right)_{\beta V} = k_B T\left(\frac{\partial U}{\partial\mu}\right)_{TV}$$

$$= k_B T\left(\frac{\partial U}{\partial N}\right)_{TV}\left(\frac{\partial N}{\partial\mu}\right)_{TV} = \left(\frac{\partial U}{\partial N}\right)_{TV}\overline{\Delta N^2}$$

能量和粒子数分布

$$p(E,N)=\sum_s p_s=\frac{1}{\Xi}\sum_{\{s|E_s=E,N_s=N\}}e^{-\beta E_s+\beta\mu N_s}=\frac{1}{\Xi}\Omega(E,N,V)e^{-\beta E+\beta\mu N}$$

$$=\frac{1}{\Xi}e^{\ln\Omega(E,N,V)-\beta E+\beta\mu N}=\frac{1}{\Xi}e^{S(E,N,V)/k_B-\beta E+\beta\mu N}$$

$$=e^{(k_BT\ln\Xi+TS-E+\mu N)/(k_BT)}=e^{(-\overline{J}+J)/(k_BT)}=e^{-\Delta J/(k_BT)}$$

$$J=J(T,\mu,V|E,N,V)=E-TS(E,N,V)-\mu N$$ 广义的巨势

$$\overline{J}=J(T,\mu,V)=\overline{E}-TS(\overline{E},\overline{N},V)-\mu\overline{N}$$ 热力学平衡态时的巨势

$$-\Delta J/T=[S(E,N)-S(\overline{E},\overline{N})]-(E-\overline{E})/T+\mu(N-\overline{N})/T$$

$$=\left[\left(\frac{\partial S}{\partial E}\right)_N\Delta E+\left(\frac{\partial S}{\partial N}\right)_E\Delta N\right]+(-\Delta E+\mu\Delta N)/T$$ $dS=\frac{dU}{T}-\frac{\mu}{T}dN$

$$+\frac{1}{2}\frac{\partial^2 S}{\partial U^2}\Delta E^2+\frac{1}{2}\frac{\partial^2 S}{\partial N^2}\Delta N^2+\frac{\partial^2 S}{\partial U\partial N}\Delta N\Delta E+\cdots$$

$$=\frac{1}{2}\left(\frac{\partial(1/T)}{\partial U}\right)_N\Delta E^2+\frac{1}{2}\left(\frac{\partial(\mu/T)}{\partial N}\right)_U\Delta N^2+\left(\frac{\partial(1/T)}{\partial N}\right)_U\Delta N\Delta E$$

能量和粒子数分布

$$p(E,N) = e^{-\Delta J/(k_B T)}$$

$$= \frac{1}{C}\exp\left\{\frac{1}{2k_B}\left(\frac{\partial(1/T)}{\partial U}\right)_N \Delta E^2 + \frac{1}{2k_B}\left(\frac{\partial(\mu/T)}{\partial N}\right)_U \Delta N^2 + \frac{1}{k_B}\left(\frac{\partial(1/T)}{\partial N}\right)_U \Delta N \Delta E\right\}$$

$$= \frac{1}{C}\exp\left\{-\frac{\Delta E^2}{2k_B T^2 C_V} - \frac{\Delta N^2}{2k_B T N^2 \kappa_T/V} - \frac{\Delta N \Delta E}{2k_B T N^2 (\partial U/\partial N)_{TV} \kappa_T/V}\right\}$$

- ☞ 在正常情况下，我们同样得到了 Gauss 分布：
  热力学量 = 系综平均 = 最可几值
- ☞ 类似的，我们用这个结果得到能量、粒子数涨落，以及能量和粒子数之间的关联

$$\Delta N^2 = \frac{k_B T N^2 \kappa_T}{V} \Rightarrow \Delta\rho^2 = \frac{\Delta N^2}{V^2} = \frac{k_B T N^2}{V^3}\kappa_T = \frac{k_B T \rho^2}{V}\kappa_T$$

$$\Delta E^2 = k_B T^2 C_V + \left(\left(\frac{\partial U}{\partial N}\right)_{TV}\right)^2 \Delta N^2$$

- ☞ 在临界点附近，κ_T、C_V 等物理量发散，不再服从 Gauss 分布
  $\Rightarrow$ 平衡态热力学结果失效

8.7 近独立粒子组成系统的系综理论

Boltzmann 统计

考虑无相互作用的，非全同的粒子组成的系统

$$\hat{\mathcal{H}} = \sum_{i=1}^{N} \hat{h}_i \qquad \hat{h}|s\rangle = \varepsilon_s|s\rangle = \varepsilon_l|l\alpha\rangle \qquad \alpha = 1, 2, \cdots, \omega_l$$

$$|S\rangle = |s_1 s_2 \cdots s_N\rangle \qquad \hat{\mathcal{H}}|S\rangle = (\varepsilon_{s_1} + \varepsilon_{s_2} + \cdots + \varepsilon_{s_N})|S\rangle = E_s|S\rangle$$

$$Z = Tr\{e^{-\beta\hat{\mathcal{H}}}\} = \sum_S e^{-\beta E_S}$$

正则系综：配分函数

$$= \sum_{s_1, s_2, \cdots, s_N} e^{-\beta(\varepsilon_{s_1}+\varepsilon_{s_2}+\cdots+\varepsilon_{s_N})} = \sum_{s_1, s_2, \cdots, s_N} e^{-\beta\varepsilon_{s_1}} e^{-\beta\varepsilon_{s_2}} \ldots e^{-\beta\varepsilon_{s_N}}$$

$$= \sum_{s_1} e^{-\beta\varepsilon_{s_1}} \sum_{s_2} e^{-\beta\varepsilon_{s_2}} \ldots \sum_{s_N} e^{-\beta\varepsilon_{s_N}}$$

$$= z^N$$

$z = \sum_s e^{-\beta\varepsilon_s}$：单粒子配分函数

Boltzmann 分布

第 l 个单粒子能级上的分布 a_l

$$E_s = \sum_{i=1}^{N} \varepsilon_{s_i} = \sum_s a_s \varepsilon_s = \sum_l a_l \varepsilon_l \qquad \sum_s a_s = \sum_l a_l \equiv N$$

$$Z = \sum_S e^{-\beta E_s} = \sum_E \sum_{\{S|E_S=E\}} e^{-\beta E_s} = \sum_E \Omega(E,N,V) e^{-\beta E}$$

$$= \sum_E \sum_{\{a_l|\sum_l a_l = N; \sum_l a_l \varepsilon_l = E\}} \frac{N!}{\prod_l a_l!} \prod_l \omega_l^{a_l} e^{-\beta E}$$

$$= \sum_{\{a_l|\sum_l a_l = N\}} \frac{N!}{\prod_l a_l!} (\prod_l \omega_l^{a_l}) e^{-\beta \sum_l a_l \varepsilon_l} = \boxed{= \prod_l (\omega_l e^{-\beta \varepsilon_l})^{a_l}}$$

$$= (\sum_l \omega_l e^{-\beta \varepsilon_l})^N = z^N$$

Boltzmann 分布

第 l 个单粒子能级上的分布 a_l

$$\overline{a_l} = \frac{1}{Z}\sum_S a_l e^{-\beta E_S} = \frac{1}{Z}\sum_{\{a_j|\sum_j a_j=N\}} a_l \frac{N!}{\prod_j a_j!}\prod_j (\omega_j^{a_j} e^{-\beta\varepsilon_j a_j})$$

$$= \frac{1}{Z}\sum_{\{a_j|\sum_j a_j=N\}} \frac{\partial}{\partial(-\beta\varepsilon_l)}\prod_j (\omega_j e^{-\beta\varepsilon_j})^{a_j} = -\frac{1}{Z}\frac{\partial}{\partial\beta\varepsilon_l}Z = -\left(\frac{\partial \ln Z}{\partial\beta\varepsilon_l}\right)$$

$$= -\left(\frac{\partial \ln z^N}{\partial\beta\varepsilon_l}\right) = -\frac{N}{z}\frac{\partial}{\partial\beta\varepsilon_l}\left(\sum_j \omega_j e^{-\beta\varepsilon_j}\right)$$

$$= \frac{N}{z}\omega_l e^{-\beta\varepsilon_l}$$

$$\overline{a}_s = \frac{N}{z}e^{-\beta\varepsilon_s}$$ 单粒子态上的分布

☞无须假设 $\omega_l, a_l \gg 1$

分布函数的涨落

$$\delta a_s^2 = \overline{(a_s - \overline{a}_s)^2} = \frac{\partial^2 \ln Z}{\partial(\beta\varepsilon_s)^2}$$

$$= -\frac{\partial a_s}{\partial(\beta\varepsilon_s)} = \frac{N}{z}e^{-\beta\varepsilon_s} - \frac{N}{z^2}e^{-2\beta\varepsilon_s}$$

$$= a_s - a_s^2/N = a_s(1 - a_s/N)$$

Fermi/Bose 统计

由于全同性，没有相互作用的粒子组成的系统态可以用单粒子态占据数表示 $|S\rangle = |a_1 a_2 \cdots\rangle = |\{a_s\}\rangle$，利用巨正则系综

$$\Xi = Tr\{e^{-\beta\hat{\mathcal{H}}+\beta\mu\hat{N}}\} = \sum_S e^{-\beta E_s+\beta\mu N_s} = \sum_{\{a_s\}} e^{-\beta\sum_s a_s\varepsilon_s+\beta\mu\sum_s a_s}$$

$$= \sum_{\{a_s\}}\prod_s e^{-\beta a_s\varepsilon_s+\beta\mu a_s} = \prod_s\sum_{a_s}(e^{-\beta\varepsilon_s+\beta\mu})^{a_s}$$

利用不同的 a_s 取值独立

$$= \prod_s \begin{cases} 1+e^{-\beta\varepsilon_s+\beta\mu} & a_s = 0,1 \quad \textit{Fermion} \\ 1+e^{-\beta(\varepsilon_s-\mu)}+e^{-2\beta(\varepsilon_s-\mu)}+\cdots & a_s = 0,1,2,\cdots \quad \textit{Boson} \end{cases}$$

$$= \prod_s[1\pm e^{-\beta(\varepsilon_s-\mu)}]^{\pm} = \prod_l[1\pm e^{-\beta(\varepsilon_l-\mu)}]^{\pm\omega_l}$$

☞无须 $a_s, a_l, \omega_l \gg 1$ 的条件

Fermi/Bose 统计

$$\Xi = Tr\{e^{-\beta\hat{\mathcal{H}}+\beta\mu\hat{N}}\} = \sum_S e^{-\beta E_S+\beta\mu N_S}$$

$$= \sum_N \sum_E \sum_{\{a_l|\sum_l a_l=N;\sum_l a_l\varepsilon_l=E\}} \Omega(\{a_l\})e^{-\beta\sum_l a_l\varepsilon_l+\beta\mu\sum_l a_l}$$

$$= \sum_N \sum_E \sum_{\{a_l|\sum_l a_l=N;\sum_l a_l\varepsilon_l=E\}} \prod_l \gamma(a_l,\omega_l)(e^{-\beta\varepsilon_l+\beta\mu})^{a_l}$$

$$\gamma(a_l,\omega_l) = \begin{cases} C_{\omega_l}^{a_l} = \frac{\omega_l!}{a_l!(\omega_l-a_l)!} & \text{Fermion} \\ C_{a_l+\omega_l-1}^{a_l} = \frac{(a_l+\omega_l-1)!}{a_l!(\omega_l-1)!} & \text{Boson} \end{cases}$$

$$= \sum_{\{a_l\}} \prod_l \gamma(a_l,\omega_l)e^{-\beta(\varepsilon_l-\mu)a_l} = \prod_l \sum_{a_l=0}^{\infty} \gamma(a_l,\omega_l)e^{-\beta(\varepsilon_l-\mu)a_l}$$

$$= \prod_l [1 \pm e^{-\beta(\varepsilon_l-\mu)}]^{\pm\omega_l}$$

Fermi/Bose 统计

第 i 个单粒子态上的平均分布

$$\overline{a}_i = \frac{1}{\Xi}\sum_{\{a_s\}} a_i e^{-\sum_s \beta(\varepsilon_s-\mu)a_s} = \frac{1}{\Xi}\sum_{\{a_s\}} \frac{-1}{\beta}\frac{\partial}{\partial\varepsilon_i} e^{-\sum_s \beta(\varepsilon_s-\mu)a_s}$$

$$= -\frac{1}{\beta\Xi}\frac{\partial}{\partial\varepsilon_i}\sum_{\{a_s\}} e^{-\sum_s \beta(\varepsilon_s-\mu)a_s} = -\frac{1}{\beta\Xi}\frac{\partial\Xi}{\partial\varepsilon_i} = -\frac{1}{\beta}\left(\frac{\partial\ln\Xi}{\partial\varepsilon_i}\right)$$

$$= -\frac{1}{\beta}\frac{\partial}{\partial\varepsilon_i}\sum_s(\pm)\ln[1\pm e^{-\beta(\varepsilon_s-\mu)}] = \frac{e^{-\beta(\varepsilon_i-\mu)}}{1\pm e^{-\beta(\varepsilon_i-\mu)}}$$

$$= \frac{1}{e^{\beta(\varepsilon_i-\mu)}\pm 1}$$

$$a_l = \sum_{\varepsilon_i=\varepsilon_l} a_i = \frac{\omega_l}{e^{\beta(\varepsilon_l-\mu)}\pm 1}$$

☞同样无须 $a_l, \omega_l \gg 1$ 等条件

分布函数的涨落

$$\Delta a_s^2 = \overline{a_s^2} - \overline{a_s}^2 = \frac{\partial^2 \ln \Xi}{\partial(\beta\varepsilon_s)^2} = -\frac{1}{\beta}\frac{\partial}{\partial\varepsilon_s}\frac{1}{e^{\beta(\varepsilon_s-\mu)} \pm 1} = \frac{e^{\beta(\varepsilon_s-\mu)}}{[e^{\beta(\varepsilon_s-\mu)} \pm 1]^2}$$

$$= \frac{e^{\beta(\varepsilon_s-\mu)} \pm 1 \mp 1}{[e^{\beta(\varepsilon_s-\mu)} \pm 1]^2} = a_s \mp a_s^2 = a_s(1 \mp a_s)$$

- $\varepsilon_s \gg \mu$ 时， $a_s \ll 1$， $\Delta a_s^2 \simeq a_s$
- 强简并 Fermion， $\varepsilon_s \ll \mu$， $a_s \simeq 1$， $\Delta a_s^2 \simeq 1 - a_s \ll 1$；
  $\varepsilon_s \gg \mu$， $a_s \simeq 0$， $1 - a_s \simeq 1$， $\Delta a_s^2 \simeq a_s \ll 1$
- 强简并 Boson， $\Delta a_g^2 \simeq a_g^2 \sim N^2$

☞ 一般情况下，广延量的涨落 $\sqrt{N}$。用巨正则系综计算表明：发生 BEC 时，基态上的粒子数涨落很大，达到 N 的量级。

总粒子数涨落：

$$\Delta N^2 = \overline{(\sum_s (a_s - \overline{a_s})^2} = \sum_s \overline{(a_s - \overline{a_s})^2} + \sum_{s \neq s'} \overline{(a_s - \overline{a_s})(a_{s'} - \overline{a_{s'}})}$$

$$= \sum_s \Delta a_s^2$$

不同系综的结果比较

$$d\ln\Omega = \alpha dN + \beta dE$$
$$d\ln Z = d(\ln\Omega - \beta E) = \alpha dN - E d\beta$$
$$d\ln\Xi = d(\ln\Omega - \beta E - \alpha N) = d(\ln Z - \alpha N) = -N d\alpha - E d\beta$$

- 在 N 和 E 很大时（热力学极限），可以把它们当成是连续的实数，不同系综数学上可以通过 Legendre 变换相互转换，因此得到的热力学量是相同的。
- 在 N 和 E 有限大时，用不同系综得到热力学量稍有差别，这个差别随着 N 和 E 增大消失。
- 但是在计算非热力学量时，不同系综结果可以不同。比如微正则系综 $\Delta E^2 = 0, \Delta N^2 = 0$；正则系综 $\Delta E^2 \neq 0, \Delta N^2 = 0$；巨正则系综 $\Delta E^2 \neq 0, \Delta N^2 \neq 0$。正则和巨正则系综给出的能量涨落也不同。

不同系综的结果比较

- 一般情况下，不同系综计算结果没有可观测的差别，因此采用哪种系综计算纯粹是从计算简便角度出发。
- 一个典型的例外是，我们前面的计算表明发生 BEC 时凝聚相的粒子数有很大涨落，涨落大小 $\Delta a_g \simeq a_g \sim N$。如果这个结论是对的话，那么即便控制相同的外界条件，不同实验观测到的凝聚相上的粒子数也会有巨大的差别。但实验表明发生 BEC 时，凝聚相上的粒子数很稳定，和计算结果没有区别。
- 导致这个差别的原因是我们利用了巨正则系综，粒子数本身不守恒。如果采用正则系综，可以得到正确结果。但是计算非常复杂。

  "Bose–Einstein condensation, fluctuations, and recurrence relations in statistical mechanics", W. J. Mullin and J. P. Fernández, American Journal of Physics **71**, 661 (2003).

8.8 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 $\Rightarrow$ 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

$H = 0$

$$M = N\mu_B \tanh \beta g\mu_B H = 0$$ 顺磁相，无自发磁矩

$H \to 0$， $M = \chi(T)H$

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

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

$$\Rightarrow \chi(T) = \frac{Ng\mu_B^2/k_B}{T} = \frac{C}{T}$$ Curier's law

热容

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

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

一维 Ising model 的严格解

N 个格点，周期性边界条件

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

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

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

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

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

Transfer matrix

Transfer Matrix

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

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

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

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

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

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

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

$$\xrightarrow{H\to 0} 0$$

☞ 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

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

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

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

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

- 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

$$C(r)=\frac{1}{Z}\mathrm{Tr}\left\{\begin{pmatrix}\lambda_+^{N-l} & \\ & \lambda_-^{N-l}\end{pmatrix}\begin{pmatrix} & 1\\ 1 & \end{pmatrix}\begin{pmatrix}\lambda_+^{l} & \\ & \lambda_-^{l}\end{pmatrix}\begin{pmatrix} & 1\\ 1 & \end{pmatrix}\right\}$$

$r=(k-j)a=la$

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

$$\xrightarrow{N\to\infty}\left(\frac{\lambda_-}{\lambda_+}\right)^l=(\tanh\beta J)^{r/a}=e^{-r/\xi}$$

关联长度

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

- ☞ 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

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

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

$$= -J/2 \sum_{\langle ij\rangle} (\overline{\sigma} + \delta\sigma_i)(\overline{\sigma} + \delta\sigma_j) - g\mu_B H \sum_i \sigma_i$$

$$= -J/2 \sum_{\langle ij\rangle} [\overline{\sigma}^2 + \overline{\sigma}\delta\sigma_i + \overline{\sigma}\delta\sigma_j + \delta\sigma_i\delta\sigma_j \boxed{\text{涨落高阶项}}] - g\mu_B H \sum_i \sigma_i$$

$$\simeq -J/2 \sum_i z \boxed{\text{最近邻格点数}} \times [\overline{\sigma}^2 + 2\overline{\sigma}\delta\sigma_i] - g\mu_B H \sum_i \sigma_i$$

$$= -J/2 \sum_i z[\overline{\sigma}^2 + 2\overline{\sigma}(\sigma_i - \overline{\sigma})] \boxed{= [2\overline{\sigma}\sigma_i - \overline{\sigma}^2]} - g\mu_B H \sum_i \sigma_i$$

$$= -Jz\overline{\sigma} \sum_i \sigma_i - g\mu_B H \sum_i \sigma_i + NJz\overline{\sigma}^2/2$$

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

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： $\tanh(x) = x - x^3/3 + \cdots$

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

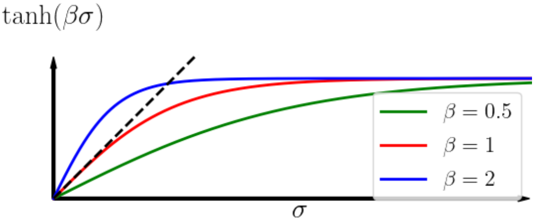
$$\Rightarrow \beta_c Jz = 1 \Rightarrow T_c = \frac{Jz}{k_B}$$

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

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

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

$$\overline{\sigma} = \frac{Jz}{k_B T}\overline{\sigma} - \left(\frac{Jz}{k_B T}\right)^3\overline{\sigma}^3 + \cdots$$

$$= \frac{T_c}{T}\overline{\sigma} - \left(\frac{T_c}{T}\right)^3\overline{\sigma}^3 + \cdots$$

$$\overline{\sigma}^2 \simeq (T_c/T - 1) \Rightarrow \overline{\sigma} \propto |T_c/T - 1|^{1/2} \Rightarrow \beta = 1/2$$

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

$$\overline{\sigma} \simeq \frac{g\mu_B H}{k_B T} + \frac{Jz\overline{\sigma}}{k_B T} = \frac{g\mu_B H}{k_B T} + \frac{T_c}{T}\overline{\sigma}$$

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

$$M = N\mu_B\overline{\sigma} = \frac{Ng\mu_B^2/k_B}{T - T_c}H \Rightarrow \chi(T) = \frac{Ng\mu_B^2/k_B}{T - T_c}$$

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 $\Rightarrow$ 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

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

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

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

$$H_i^{eff} = H_i + \frac{J}{g\mu_B}\sum_{j\in\langle ij\rangle}\overline{\sigma}_j$$

$$Z = Z(\{H_i\}) = \sum_{\{\sigma_i\}} e^{-\beta E(\{\sigma_i\})} = e^{-\beta E_0}\prod_i\Big[2\cosh\beta g\mu_B H_i^{eff}\Big]$$

关联函数

$$\overline{\sigma}_j = \frac{1}{Z}\sum_{\{\sigma_i\}} \sigma_j e^{-\beta E(\{\sigma_i\})} = \frac{1}{Z}\frac{\partial}{\partial(\beta g\mu_B H_j)}\sum_{\{\sigma_i\}} e^{-\beta E(\{\sigma_i\})}$$

$$= \frac{\partial \ln Z}{\partial(\beta g\mu_B H_j)} = \tanh(\beta g\mu_B H_j^{eff}) \simeq (\beta g\mu_B H_j^{eff}) - \frac{1}{3}(\beta g\mu_B H_j^{eff})^3$$

$$\simeq \beta g\mu_B H_j + \beta J \sum_{l\in\langle jl\rangle} \overline{\sigma}_l + \frac{(\beta J)^3}{3}(\sum_{l\in\langle jl\rangle} \overline{\sigma}_l)^3$$

$$C_{jk} = \langle(\sigma_j - \bar{\sigma}_j)(\sigma_k - \bar{\sigma}_k)\rangle = \langle\sigma_j\sigma_k\rangle - \bar{\sigma}_j\bar{\sigma}_k$$

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

$$= \frac{1}{Z}\frac{\partial}{\partial(\beta g\mu_B H_j)}\frac{\partial}{\partial(\beta g\mu_B H_k)}\sum_{\{\sigma_i\}} e^{-\beta E(\{\sigma_i\})} - \bar{\sigma}_j\bar{\sigma}_k$$

$$= \frac{\partial^2 \ln Z}{\partial(\beta g\mu_B H_j)\partial(\beta g\mu_B H_k)} = \frac{\partial\overline{\sigma}_k}{\partial(\beta g\mu_B H_j)}$$

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

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

$$= \sum_k \delta_{jk} e^{-i\boldsymbol{k}\cdot(\boldsymbol{r}_k - \boldsymbol{r}_j)} + \sum_k \beta J[1 + (\beta J z\overline{\sigma})^2] \sum_{l\in\langle kl\rangle} C_{jl} e^{-i\boldsymbol{k}\cdot(\boldsymbol{r}_k - \boldsymbol{r}_j)}$$

$$= 1 + \beta J[1 + (\beta J z\overline{\sigma})^2] \sum_l C_{jl} e^{-i\boldsymbol{k}\cdot(\boldsymbol{r}_l - \boldsymbol{r}_j)} \sum_{k\in\langle kl\rangle} e^{-i\boldsymbol{k}\cdot(\boldsymbol{r}_k - \boldsymbol{r}_l)}$$

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

$$\boxed{\gamma(\boldsymbol{k}) = \textstyle\sum_{\boldsymbol{r}_s\in nn} e^{-i\boldsymbol{k}\cdot\boldsymbol{r}_s}}$$

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

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

方格子

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

$$\xi \propto |T - T_c|^{-\nu}$$

平均场理论中： $\nu = 1/2$ $\eta = 0$

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

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

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

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

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

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

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

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

8.9 非理想气体的状态方程

气体状态方程

- 理想气体

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

- van der Waals 方程

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

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

- Onnes 方程

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

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

$\rho = N/V$ 粒子数密度

相互作用势

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

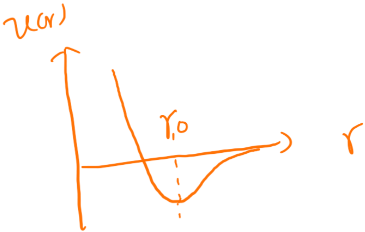
$$= \sum_{i=1}^{N}\left[\frac{\boldsymbol{p}_i^2}{2m} + V(\boldsymbol{r}_i)\right] + \sum_{1\le i<j\le N} u(|\boldsymbol{r}_i - \boldsymbol{r}_j|)$$

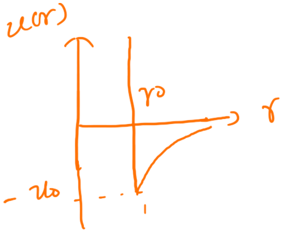
$$= \sum_{i=1}^{N}\left[\frac{\boldsymbol{p}_i^2}{2m} + V(\boldsymbol{r}_i)\right] + \sum_{1\le i<j\le N} u_{ij}$$

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

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

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

$$Q_N = \int_V e^{-\beta \sum_{i<j} u_{ij}} \prod_i d\boldsymbol{r}_i$$

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

- 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

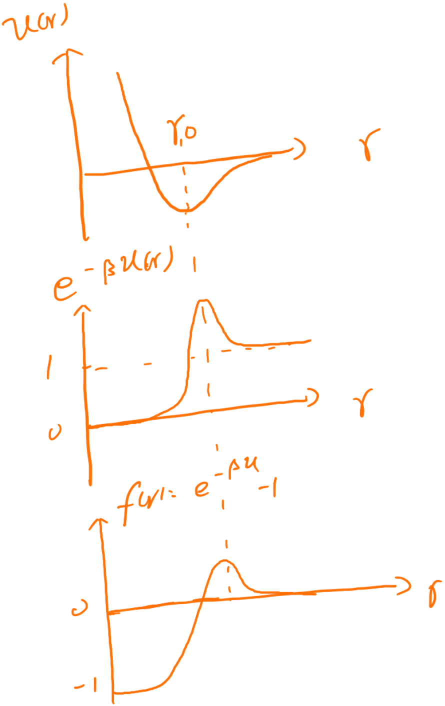
$$Q_N = \int_V \prod_{1\le i<j\le N} e^{-\beta u_{ij}} d\boldsymbol{r}$$

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

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

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

- $e^{-\beta u}$ 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

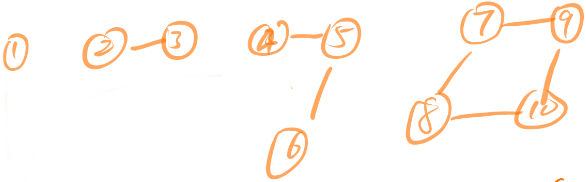
$$Q_N = \int \prod_{i<j} (1 + f_{ij}) d\boldsymbol{r} = \int (1 + f_{12})(1 + f_{13}) \cdots (1 + f_{23})(1 + f_{24}) \cdots d\boldsymbol{r}$$

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

$\sum'_{i_1<j_1; i_2<j_2; \cdots}$ 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



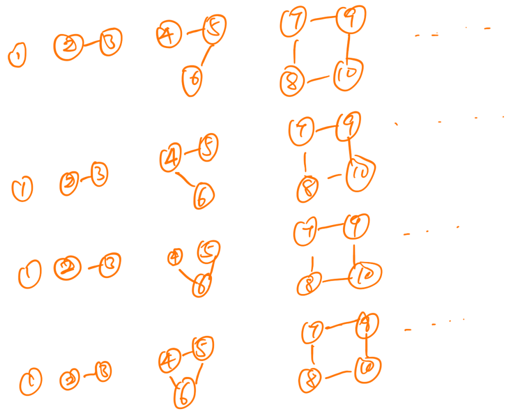
$$= \int f_{23} f_{45} f_{56} f_{78} f_{79} f_{8,10} f_{9,10}$$

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

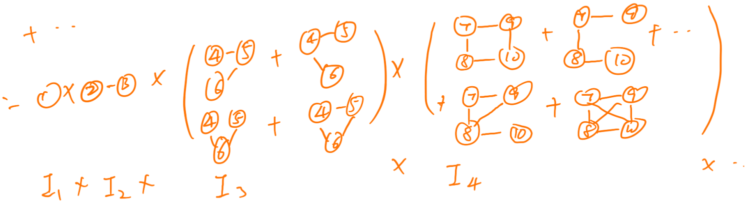
$$\times \int f_{78} f_{79} f_{8,10} f_{9,10}\, dr_7\, dr_8\, dr_9\, dr_{10} \times \cdots$$

- 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



Cluster expansion

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

$$N(\{m_l\}) = C_N^1 C_{N-1}^1 \cdots C_{N-m_1+1}^1 \times \frac{1}{m_1!}$$

$$\times C_{N-m_1}^2 C_{N-m_1-2}^2 \cdots C_{N-m_1-2m_2+2}^2 \times \frac{1}{m_2!}$$

$$C_{N-m_1-2m_2}^3 \cdots \times \frac{1}{m_3!} C_{N-\sum_{i=1}^{l-1} im_i}^l \cdots \times \frac{1}{m_l!} \cdots$$

$$= \frac{N!}{1!^{m_1} 2!^{m_2} \cdots l!^{m_l} \cdots} \frac{1}{m_1! m_2! \cdots m_l! \cdots}$$

$$= \frac{N!}{\prod_l (l!^{m_l} m_l!)}$$

$$Q_N = \sum_{\{m_l | \sum_l l m_l = N\}} \frac{N!}{\prod_l (l!^{m_l} m_l!)} \prod_l I_l^{m_l}$$

$$= N! \sum_{\{m_l | \sum_l l m_l = N\}} \prod_l \frac{1}{m_l!} \left(\frac{I_l}{l!}\right)^{m_l}$$

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

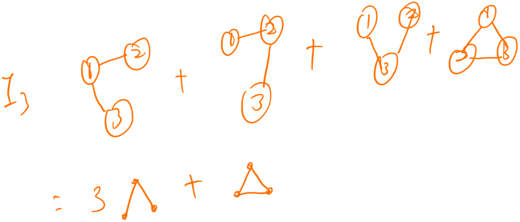
$$I_3 = \int_V [f_{12}f_{13} + f_{12}f_{23} + f_{13}f_{23} + f_{12}f_{13}f_{23}]d\boldsymbol{r}_1 d\boldsymbol{r}_2 d\boldsymbol{r}_3$$

$$= 3\int_V f_{12}f_{13}\, d\boldsymbol{r}_1 d\boldsymbol{r}_2 d\boldsymbol{r}_3 + \int_V f_{12}f_{13}f_{23}\, d\boldsymbol{r}_1 d\boldsymbol{r}_2 d\boldsymbol{r}_3$$

$$= 3\int_V f_{21}f_{31}\, d\boldsymbol{r}_{21} d\boldsymbol{r}_{31} d\boldsymbol{r}_1 + \int_V f_{21}f_{31}f(|\boldsymbol{r}_{31} - \boldsymbol{r}_{21}|)\, d\boldsymbol{r}_{21} d\boldsymbol{r}_{31} d\boldsymbol{r}_1$$

$$\simeq 3\int_V d\boldsymbol{r}_1 \int_V f_{21} d\boldsymbol{r}_{21} \int_V f_{31} d\boldsymbol{r}_{31} + \int_V d\boldsymbol{r}_1 \int f_{21}f_{31}f(|\boldsymbol{r}_{31} - \boldsymbol{r}_{21}|)\, d\boldsymbol{r}_{31} d\boldsymbol{r}_2$$

$$= 3V\beta_1^2 + 2V\beta_2$$

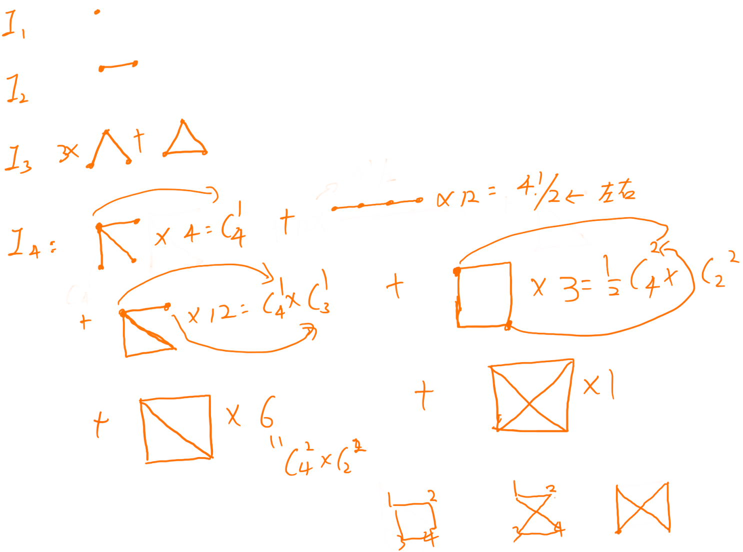


$$b_3(T) = \frac{I_3}{3!V} = \frac{\beta_1^2}{2} + \frac{\beta_2}{3}$$

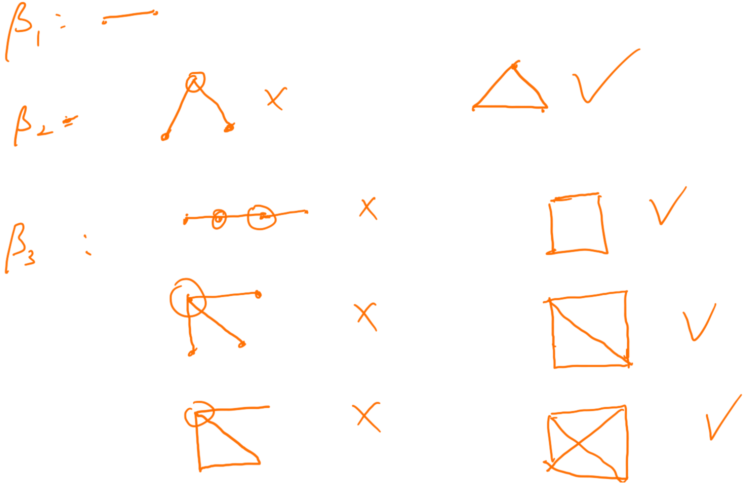
$V \to \infty$ 时 b_3 和 β_2 都和体积无关

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

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

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

$$b_l = \lim_{V\to\infty} \frac{I_l(T,V)}{V l!} = b_l(T)$$

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

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

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

β_ν 只包含不可约图

硬球势的结果

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

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

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

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

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

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

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

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，

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

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

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

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

- 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。
- 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

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

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

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

$V \to \infty$ 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。