- 有相互作用的气体

理想气体：$n \to 0$.

位力展开

$$\frac{P}{k_B T} = n + B_2 n^2 + B_3 n^3 + \cdots \quad [\text{对小量} n \text{展开}]$$

位力系数

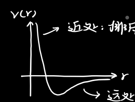
目标：计算位力系数.

$B_2 \to$ 范德瓦耳斯方程！

哈密顿量

$$H = \sum_{i=1}^{N} \frac{\vec{p}_i^{\,2}}{2m} + \sum_{i<j} V(r_{ij})$$

(单原子分子)



近处：排斥

远处：$\frac{1}{r^6}$ 吸引势（源于偶极之间相互作用）

配分函数

$$Z = \frac{1}{N!\, h^{3N}} \int \prod_{i=1}^{N} d^3\vec{p}_i\, d^3\vec{r}_i \cdot \exp\left[\beta\left(\sum_{i=1}^{N} \frac{\vec{p}_i^{\,2}}{2m} + \sum_{i<j} V(r_{ij})\right]\right.$$

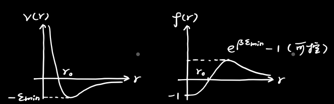
$$= \frac{1}{N!\, \lambda^{3N}} \int \prod_{i=1}^{N} d^3\vec{r}_i \cdot e^{-\beta \sum_{i<j} V(r_{ij})}$$

展开：

$$1 - \beta \sum_{i<j} V(r_{ij}) + \frac{1}{2}\beta^2 \sum_{i<j} \sum_{k<l} V(r_{ij}) V(r_{kl}) + \cdots$$

问题：V_{ij} 在模型中会发散！

Mayer：定义 $f(r_{ij}) = e^{-\beta V(r_{ij})} - 1$.



改写

$$e^{-\beta V(r_{ij})} = 1 + f(r_{ij}) =: 1 + f_{ij}.$$

$$Z = \frac{1}{N!\, \lambda^{3N}} \int \prod_{i=1}^{N} d^3\vec{r}_i \prod_{j<k} (1 + f_{jk}) \quad \left[\text{乘积总项数：} \binom{n}{2}\right]$$

$$= \frac{1}{N!\, \lambda^{3N}} \int \prod_{i=1}^{N} d^3\vec{r}_i \left[1 + \sum_{j<k} f_{jk} + \sum_{j<k} \sum_{l<m} f_{jk} f_{lm} + \cdots\right]$$

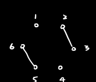
展开总项数：$2^{\binom{N}{2}}$.

图形化表示

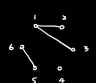
(a) 画N个点，代表N个粒子

(b) $f_{jk} \to$ 在 j 与 k 中间画一条线.

例 $N=6$



$$= \int d^3\vec{r}_1 \cdots d^3\vec{r}_6 \cdot f_{23} f_{56} = \int d^3\vec{r}_1 \cdot \int d^3\vec{r}_2\, d^3\vec{r}_3\, f_{23} \cdot \int d^3\vec{r}_4 \cdot \int d^3\vec{r}_5\, d^3\vec{r}_6\, f_{56}$$



$$= \int d^3\vec{r}_1 \cdots d^3\vec{r}_6 \cdot f_{12} f_{13} f_{56} = \int d^3\vec{r}_1\, d^3\vec{r}_2\, d^3\vec{r}_3\, f_{12} f_{13} \cdot \int d^3\vec{r}_4 \cdot \int d^3\vec{r}_5\, d^3\vec{r}_6\, f_{56}$$

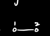
- 积分可以改写为连通子图的乘积！定义有 l 个粒子的子图为一个 l-cluster.

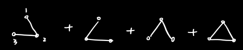
问：如何把N个粒子分成{l-cluster}？

记 l-cluster 数目为 n_l. 限制：$\sum_l l \cdot n_l = N$.

定义 b_l 为 l-cluster 对应的积分数值（对所有可能求和）：

$$b_1 = \int d^3\vec{r}_1 = V.$$

$b_2 =$  $= \int d^3\vec{r}_1\, d^3\vec{r}_2\, f_{12}$

$b_3 =$ 

$$= \int d^3\vec r_1\, d^3\vec r_2\, d^3\vec r_3 \,(f_{12}f_{23} + f_{13}f_{23} + f_{12}f_{13} + f_{12}f_{13}f_{23})$$

$$Z = \frac{1}{N!\,\lambda^{3N}} \int \prod_{i=1}^{N} d^3\vec r_i \prod_{j<k} (1+f_{jk})$$

$$= \frac{1}{N!\,\lambda^{3N}} \cdot {\sum_{\{n_l\}}}' \left[\prod_l (b_l)^{n_l}\right] \cdot W(\{n_l\})$$

相同{n_l}情形下，不同子图的数目.

式中

$$W(\{n_l\}) = \frac{N!}{\prod_l (l!)^{n_l}\, n_l!}$$

n_l个 l-cluster 的排列

l个粒子在每个 l-cluster 内部排列

故

$$Z = \frac{1}{N!\,\lambda^{3N}} {\sum_{\{n_l\}}}' N! \prod_l \frac{(b_l)^{n_l}}{(l!)^{n_l}\, n_l!}$$

对{n_l}的求和有限制：$\sum_l l\cdot n_l = N$. 如何解除？

考虑巨配分函数

$$Q = \sum_{N=0}^{\infty} e^{\beta\mu N} \cdot Z(N)$$

$$= \sum_{N=0}^{\infty} \underline{\underline{\left(\frac{e^{\beta\mu}}{\lambda^3}\right)^N}} \cdot {\sum_{\{n_l\}}}' \prod_l \frac{(b_l)^{n_l}}{(l!)^{n_l}\, n_l!}$$

限制：$N = \sum_l l\cdot n_l$

$$= \sum_{N=0}^{\infty} \prod_l \left(\frac{e^{\beta\mu}}{\lambda^3}\right)^{l\cdot n_l} \cdot {\sum_{\{n_l\}}}' \prod_l \frac{(b_l)^{n_l}}{(l!)^{n_l}\, n_l!}$$

$$= \underbrace{\sum_{N=0}^{\infty} {\sum_{\{n_l\}}}'}_{} \prod_l \frac{1}{n_l!} \cdot \left(\frac{e^{\beta\mu l}\, b_l}{\lambda^{3l}\, l!}\right)^{n_l}$$

N求和 + 对N限制 = 无限制求和！

$$= \sum_{\{n_l\}} \prod_{l=1}^{|\{n_l\}|} \frac{1}{n_l!} \cdot \left(\frac{e^{\beta\mu l}\, b_l}{\lambda^{3l}\, l!}\right)^{n_l}$$

$$= \prod_{l=1}^{\infty} \sum_{n_l=0}^{\infty} \frac{1}{n_l!} \cdot \left(\frac{e^{\beta\mu l}\, b_l}{\lambda^{3l}\, l!}\right)^{n_l}$$

$$= \prod_{l=1}^{\infty} \exp\left(\frac{e^{\beta\mu l}\, b_l}{\lambda^{3l}\, l!}\right) = \exp \sum_l \frac{e^{\beta\mu l}\, b_l}{\lambda^{3l}\, l!}.$$

这里应该从下向上推.

$$\prod_{l=1}^{\infty} \sum_{n_l=0}^{\infty} f(l,n_l)$$

$$= [f(1,0) + f(1,1) + f(1,2) + \cdots]$$ (注意 $f(l,0)=1$)

$$\times [f(2,0) + f(2,1) + f(2,2) + \cdots]$$

$$\times \cdots$$

$$= [f(1,0)\cdot f(2,1)\cdot f(3,0)\cdot f(4,?),\cdots] + [f(1,?)\cdot f(2,?)\cdot f(3,?)\cdots] + \cdots$$

$$= \prod_{l=1}^{|\{n_l\}_1|} f(l,n_l) + \prod_{l=1}^{|\{n_l\}_2|} f(l,n_l) + \cdots$$

$$= \sum_{\{n_l\}} \prod_l f(l,n_l)$$

$$pV = \frac{1}{\beta}\ln Q = \frac{1}{\beta}\cdot \sum_{l=1}^{\infty} \left(\frac{z}{\lambda^3}\right)^l \cdot \frac{b_l}{l!}.$$

$$N = \frac{\partial}{\partial(\beta\mu)} \ln Q = \sum_{l=1}^{\infty} l\cdot \left(\frac{z}{\lambda^3}\right)^l \cdot \frac{b_l}{l!} = \sum_{l=1}^{\infty} \left(\frac{z}{\lambda^3}\right) \cdot \frac{b_l}{(l-1)!}.$$

* 方法：把连通的图放到指数上 → 生成了连通的图.

为什么没有出现体积？实际上，$b_l \propto V$.

例：

$$b_1 = \int d^3r = V.$$

$$b_2 = \int d^3r_1\, d^3r_2\, f_{12}$$ 

$$= \int d^3r_1 \cdot \int d^3r_{12}\, f_{12} \propto V.$$ (取一个粒子为标准，用相对距离 r_{12})

对于 b_l 同理：$b_l \propto V$.

可以定义 $b_l = V\cdot \bar b_l \Rightarrow \frac{P}{k_BT} = \sum_{l=1}^{\infty} \left(\frac{z}{\lambda^3}\right)^l \cdot \frac{\bar b_l}{l!}$, $\quad n = \sum_{l=1}^{\infty} \left(\frac{z}{\lambda^3}\right)^l \cdot \frac{\bar b_l}{(l-1)!}$

令 $x = \frac{z}{\lambda^3}$. 尝试把z用n展开：

$$n = x + x^2 \bar b_2 + \frac{x^3 \bar b_3}{2} + \cdots$$

$$\Rightarrow x = n - \bar b_2 x^2 - \frac{\bar b_3 x^3}{2} + \cdots$$

(1) 领头阶：$x = n + O(n^2)$.

(2) $O(n^2)$：$x = n - \bar b_2 n^2 + O(n^3)$.

(3) $O(n^3)$：$x = n - \bar b_2 (n - \bar b_2 n^2)^2 - \frac{\bar b_3 n^3}{2} + O(n^4)$

$$= n - \bar b_2 n^2 + (2\bar b_2^2 - \tfrac{1}{2}\bar b_3) n^3 + O(n^4).$$

$$\frac{P}{k_BT} = x + \frac{1}{2}\bar b_2 x^2 + \frac{1}{6}\bar b_3 x^3 + \cdots$$

$$= [n - \bar b_2 n^2 + (2\bar b_2^2 - \tfrac{1}{2}\bar b_3) n^3] + \frac{1}{2}\bar b_2 [n - \bar b_2 n^2]^2 + \frac{1}{6}\bar b_3 n^3 + O(n^4)$$

$$= n - \frac{1}{2}\bar b_2 n^2 + (\bar b_2^2 - \tfrac{1}{3}\bar b_3) n^3 + O(n^4).$$

这正是位力展开的形式！

对比系数:

$$B_2(T) = -\frac{1}{2}b_2 = -\frac{1}{2}\int d^3r_{12}\,(e^{-\beta V(r_{12})}-1).$$

$$B_3(T) = b_2^2 - \frac{1}{3}b_3$$

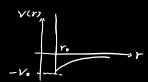
$$= \cancel{\left[\int d^3r\, f(r)\right]^2} - \frac{1}{3}\left[\cancel{3\cdot\int d^3r_1 d^3r_2\, f(r_1) f(r_2)} + \int d^3r_{12}\, d^3r_{13}\, f(r_{12}) f(r_{13}) f(\vec{r}_{12}-\vec{r}_{13})\right]$$

$$= -\frac{1}{3}\int d^3r_{12}\, d^3r_{13}\, f(r_{12}) f(r_{13}) f(r_{23}(r_{12}, r_{13}))$$

- 范德瓦耳斯方程

令

$$V(r) = \begin{cases} \infty, & r<r_0 \\ -V_0\left(\frac{r_0}{r}\right)^6, & r>r_0. \end{cases}$$



计算 $B_2(T)$:

$$B_2(T) = -\frac{1}{2}\int d^3r\,(e^{-\beta V(r)}-1)$$

$$= -2\pi\int dr\cdot r^2(e^{-\beta V(r)}-1)$$

$$= -2\pi\int_0^{r_0} r^2 dr\cdot(-1) - 2\pi\cdot\int_{r_0}^{+\infty} r^2\cdot\left(e^{\beta V_0\left(\frac{r_0}{r}\right)^6}-1\right) dr$$

$$= \frac{2\pi}{3}r_0^3 - 2\pi\cdot\int_{r_0}^{+\infty} r^2\cdot\beta V_0\left(\frac{r_0}{r}\right)^6 dr$$

$$= \frac{2\pi}{3}r_0^3 - 2\pi\beta V_0\cdot\frac{r_0^3}{3} = \frac{2\pi r_0^3}{3}(1-\beta V_0)$$

$$= \frac{\Omega}{2}(1-\beta V_0).$$ Ω: 半径为 r_0 的球体积.

物态方程:

$$\frac{P}{k_BT} = n + \frac{\Omega}{2}\left(1-\frac{V_0}{k_BT}\right)\cdot n^2$$

$$\frac{1}{k_BT}\left(P + \frac{\Omega V_0}{2}\cdot\frac{1}{v^2}\right) = n\left(1+\frac{\Omega}{2}\cdot n\right)$$, $\Omega n \ll 1$. (差不多也是展开成立的条件)

$$\simeq \frac{n}{1-\frac{\Omega}{2}\cdot n} = \frac{1}{v-\frac{\Omega}{2}}$$

$$\Rightarrow \left(P+\frac{\Omega V_0}{2}\cdot\frac{1}{v^2}\right)\cdot\left(v-\frac{\Omega}{2}\right) = k_BT.$$

范氏方程: $\left(P+\frac{a}{v^2}\right)(v-b) = k_BT. \Rightarrow a = \frac{\Omega V_0}{2}.\quad b = \frac{\Omega}{2}.$

— a 与吸引势相关.

— b 与粒子占据的体积相关.