

第 1 题 得分：_____. 根据集团积分的定义和图形展开的规则验证 Mayer 第一定理至 y^3 项.

证: Mayer 第一定理:

$$\mathcal{Q} = \prod_l e^{V b_l y^l}, \quad (1)$$

其中

$$b_l(V, T) = \frac{1}{V l!} \int \prod_{i=1}^l d^3 \vec{r}_i \sum_{\text{all } l\text{-cluster}} (\prod f_{ij}), \quad (2)$$

$$b_1(V, T) = \frac{1}{V} \int d^3 \vec{r} = 1, \quad (3)$$

$$b_2(V, T) = \frac{1}{2!V} \int d^3 \vec{r}_1 d^3 \vec{r}_2 f_{12}, \quad (4)$$

$$b_3(V, T) = \frac{1}{3!V} \int d^3 \vec{r}_1 d^3 \vec{r}_2 d^3 \vec{r}_3 (f_{12}f_{13} + f_{12}f_{23} + f_{13}f_{23} + f_{12}f_{13}f_{23}) = \frac{1}{3!V} \int d\vec{r}_1 d\vec{r}_2 d\vec{r}_3 (3f_{12}f_{13} + f_{12}f_{13}f_{23}), \quad (5)$$

$$\dots \quad (6)$$

故

$$\begin{aligned} \mathcal{Q} &= e^{V b_1 y} \times e^{V b_2 y^2} \times e^{V b_3 y^3} \times \dots = e^{V y} \times e^{V b_2 y^2} \times e^{V b_3 y^3} \times \dots \\ &= \left[1 + V y + \frac{1}{2} (V y)^2 + \frac{1}{3!} (V y)^3 + \dots \right] \times [1 + V b_2 y^2 + \dots] \times [1 + V b_3 y^3 + \dots] \times \dots \\ &= 1 + V y + \left(\frac{1}{2} V^2 + V b_2 \right) y^2 + \left(\frac{1}{3!} V^3 + V^2 b_2 + V b_3 \right) y^3 + O(y^4). \end{aligned} \quad (7)$$

□

第 2 题 得分：_____. 考虑在长度为 L 的一维线性匣子内的气体系统. 两原子的相互作用能量是 u_{ij}

$$u_{ij} = \begin{cases} \infty, & |x_{ij}| \leq d \\ 0, & |x_{ij}| > d \end{cases} \quad (8)$$

计算这系统的前两个 virial 系数, 并同准确的状态方程

$$\frac{P}{kT} = \frac{\rho}{1 - \rho d} \quad (9)$$

相比较. 其中线密度 $\rho = N/L$.

解: 根据两原子的相互作用能量 u_{ij} 的表达式, 有

$$f_{ij} = e^{-\beta u_{ij}} - 1 = \begin{cases} -1, & |x_{ij}| \leq d \\ 0, & |x_{ij}| > d \end{cases} \quad (10)$$

根据 Mayer 第一定理,

$$\frac{P}{kT} = \sum_{l=1}^{\infty} b_l y^l = b_1 y + b_2 y^2 + b_3 y^3 + O(y^4), \quad (11)$$

$$\rho = y \frac{\partial (\frac{P}{kT})}{\partial y} = b_1 y + 2b_2 y^2 + 3b_3 y^3 + O(y^4), \quad (12)$$

其中一维情况下

$$b_l(V, T) = \frac{1}{l!L} \int \prod_{i=1}^l dx_i \sum_{\text{all } l\text{-clusters}} \left(\prod f_{ij} \right), \quad (13)$$

$$b_1(V, T) = \frac{1}{L} \int dx_1 = 1, \quad (14)$$

$$b_2(V, T) = \frac{1}{2!L} \int dx_1 dx_2 f_{12} = \frac{1}{2!L} \int dx_1 \int_{-d}^d dx_{12} f_{12}(x_{12}) = -d, \quad (15)$$

$$\begin{aligned} b_3(V, T) &= \frac{1}{3!L} \int dx_1 dx_2 dx_3 (3f_{12}f_{13} + f_{21}f_{13}f_{23}) \\ &= \frac{1}{3!L} \int dx_1 \int_{-d}^d dx_{12} \int_{-d}^d dx_{13} (3f_{12}(x_{12})f_{13}(x_1 - x_3) + f_{21}(x_{12})f_{13}(x_{13})f_{23}(|x_{12} - x_{13}|)) = \frac{3d^2}{2}, \end{aligned}$$

由式 (12) 得

$$y = \rho - 2b_2y^2 - 3b_3y^3 + O(y^4). \quad (16)$$

将上式代入式 (11) 中得

$$\frac{P}{kT} = \rho - b_2y^2 - 2b_3y^3 + O(y^4). \quad (17)$$

将式 (16) 代入式 (16) 并近似到 2 阶得

$$y = \rho - 2b_2\rho^2 + O(\rho^3). \quad (18)$$

将上式代入式 (17) 中可得

$$\begin{aligned} \frac{P}{kT} &= \rho - b_2(\rho - 2b_2\rho^2)^2 - 2b_3(\rho - 2b_2\rho^2)^3 + O(\rho^4) = \rho - b_2\rho^2 + (4b_2^2 - 2b_3)\rho^3 + O(\rho^4) \\ &= \rho \left[1 - \frac{1}{2}\beta_1\rho - \frac{2}{3}\beta_2\rho^2 + O(\rho^3) \right], \end{aligned} \quad (19)$$

其中

$$\beta_1 = 2b_2 = -2d, \quad (20)$$

$$\beta_2 = 3(b_3 - 2b_2^2) = -\frac{3d^2}{2}. \quad (21)$$

由准确的状态方程出发, 有

$$\frac{P}{kT} = \frac{\rho}{1 - \rho d} = \rho [1 + \rho d + (\rho d)^2 + O(\rho^3)] = \rho \left[1 - \frac{1}{2}\beta_1\rho - \frac{2}{3}\beta_2\rho^2 + O(\rho^3) \right]. \quad (22)$$

其中的 virial 系数与前一种方法得到的 virial 系数相同. □

第 3 题 得分: _____. 证明直径为 d 的硬球的三维经典气体的状态方程是

$$\frac{P}{kT} = \rho \left[1 + \frac{2}{3}\pi\rho d^3 + \frac{5}{18}\pi^2(\rho d^3)^2 + O(\rho^3 d^9) \right] \quad (23)$$

试比较同一系统由 Van der Waals 方程给出的 $(\rho d^3)^2$ 的系数.

证: 直径为 d 的硬球的三维经典气体的原子间相互作用能量为

$$u_{ij} = \begin{cases} \infty, & r \leq d \\ 0, & r > d \end{cases}, \quad (24)$$

从而

$$f_{ij} = e^{-\beta u_{ij}} - 1 = \begin{cases} -1, & r \leq d \\ 0, & r > d \end{cases} \quad (25)$$

利用 Mayer 第一定理对 $\frac{P}{kT}$ 按 ρ 的幂级数展开, 有

$$\frac{P}{kT} = \rho \left[1 - \frac{1}{2}\beta_2\rho - \frac{2}{3}\beta_2\rho^2 + O(\rho^3) \right], \quad (26)$$

其中 virial 系数

$$\beta_1 = 2b_2, \quad (27)$$

$$\beta_2 = 3(b_3 - 2b_2^2), \quad (28)$$

而

$$b_2 = \frac{1}{2!V} \int d^3\vec{r}_2 \int d^3r_1 f_{12}(|\vec{r}_1 - \vec{r}_2|) = 2\pi \int_0^d dr_{12} r_{12}^2 f_{12}(r_{12}) = -\frac{2\pi d^3}{3}, \quad (29)$$

$$\begin{aligned} b_3 &= \frac{1}{3!V} \int d^3\vec{r}_3 \int d^3\vec{r}_2 \int d^3\vec{r}_1 [3f_{12}(|\vec{r}_1 - \vec{r}_2|)f_{13}(|\vec{r}_1 - \vec{r}_3|) - f_{12}(|\vec{r}_1 - \vec{r}_2|)f_{13}(|\vec{r}_1 - \vec{r}_3|)f_{23}(|\vec{r}_2 - \vec{r}_3|)] \\ &= 8\pi^2 \int_0^d dr_{12} r_{12}^2 f(r_{12}) \int_0^d dr_{13} r_{13}^2 f(r_{13}) - \frac{1}{6} \int d^3\vec{r}_{12} \int d^3\vec{r}_{13} f_{12}(r_{12})f_{13}(r_{13})f_{23}(|\vec{r}_{12} - \vec{r}_{13}|) \\ &= \frac{8\pi^2 d^6}{9} - \frac{1}{6} \int d^3\vec{r}_{12} \int d^3\vec{r}_{13} f_{12}(r_{12})f_{13}(r_{13})f_{23}(|\vec{r}_{12} - \vec{r}_{13}|). \end{aligned} \quad (30)$$

其中 $-\int d^3\vec{r}_{13} f_{12}(r_{12})f_{13}(r_{13})f_{23}(|\vec{r}_{12} - \vec{r}_{13}|)$ 等价于两个直径 d , 球心相距 r_{12} 的球的重叠部分体积, 即

$$\begin{aligned} - \int d^3\vec{r}_{13} f_{12}(r_{12})f_{13}(r_{13})f_{23}(|\vec{r}_{12} - \vec{r}_{13}|) &= 2 \int_0^{d-\frac{r_{12}}{2}} \pi[d^2 - (d-x)^2] dx \\ &= \frac{\pi}{12}(16d^3 - 12d^2 r_{12} + r_{12}^3). \end{aligned} \quad (31)$$

从而

$$b_3 = \frac{8\pi^2 d^6}{9} + \frac{\pi^2}{18} \int_0^d dr_{12} r_{12}^2 (16d^3 - 12d^2 r_{12} + r_{12}^3) = \frac{8\pi^2 d^6}{9} + \frac{5\pi^2 d^6}{36}, \quad (32)$$

$$\Rightarrow \frac{P}{kT} = \rho \left[1 + \frac{2\pi}{3}\rho d^3 + \frac{5}{18}\pi^2(\rho d^3)^2 + O(\rho^3 d^9) \right]. \quad (33)$$

由于将分子作为相互之间无吸引力的硬球处理, 该系统的 Van der Waals 方程为

$$P(V - Nb) = NkT, \quad (34)$$

$$\Rightarrow \frac{P}{kT} = \frac{N}{V - Nb} = \frac{\rho}{1 - b\rho} = \rho + b\rho^2 + b^2\rho^3 + O(\rho^4), \quad (35)$$

两种方式得到的 $(\rho d^3)^2$ 的系数均不依赖于温度. 比较得

$$b = \frac{2\pi}{3}d^3. \quad (36)$$

□