高等热力学与统计物理
PHYS2110
2020-2021学年第二学期

习题 VII

截止时间：2021. 4. 20（周二）

姓名：陈 稼 霖
学号：45875852
成绩：_____

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：

$$\mathcal{Q} = \prod_l e^{Vb_l y^l}, \tag{1}$$

其中

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

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

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

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

$$\cdots \tag{6}$$

故

$$\begin{aligned}
\mathcal{Q} &= e^{Vb_1y} \times e^{Vb_2y^2} \times e^{Vb_3y^3} \times \cdots = e^{Vy} \times e^{Vb_2y^2} \times e^{Vb_3y^3} \times \cdots \\
&= \left[1 + Vy + \frac{1}{2}(Vy)^2 + \frac{1}{3!}(Vy)^3 + \cdots \right] \times \left[1 + Vb_2y^2 + \cdots \right] \times \left[1 + Vb_3y^3 + \cdots \right] \times \cdots \\
&= 1 + Vy + \left(\frac{1}{2}V^2 + Vb_2 \right)y^2 + \left(\frac{1}{3!}V^3 + V^2b_2 + Vb_3 \right)y^3 + O(y^4).
\end{aligned} \tag{7}$$

$\square$

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}

$$u_{ij} = \begin{cases} \infty, & |x_{ij}| \le d \\ 0, & |x_{ij}| > d \end{cases} \tag{8}$$

计算这系统的前两个 virial 系数，并同准确的状态方程

$$\frac{P}{kT} = \frac{\rho}{1 - \rho d} \tag{9}$$

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

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

根据 Mayer 第一定理，

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

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

其中一维情况下

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

$$b_1(V,T) = \frac{1}{L} \int \mathrm{d}x_1 = 1, \tag{14}$$

$$b_2(V,T) = \frac{1}{2!L} \int \mathrm{d}x_1 \mathrm{d}x_2 \, f_{12} = \frac{1}{2!L} \int \mathrm{d}x_1 \int_{-d}^{d} \mathrm{d}x_{12} \, f_{12}(x_{12}) = -d, \tag{15}$$

$$b_3(V,T) = \frac{1}{3!L} \int \mathrm{d}x_1 \mathrm{d}x_2 \mathrm{d}x_3 \, (3f_{12}f_{13} + f_{21}f_{13}f_{23})$$

$$= \frac{1}{3!L} \int \mathrm{d}x_1 \int_{-d}^{d} \mathrm{d}x_{12} \int_{-d}^{d} \mathrm{d}x_{13} \, (3f_{12}(x_{12})f_{13}(x_1 - x_3) + f_{21}(x_{12})f_{13}(x_{13})f_{23}(|x_{12} - x_{13}|)) = \frac{3d^2}{2},$$

由式 (12) 得

$$y = \rho - 2b_2 y^2 - 3b_3 y^3 + O(y^4). \tag{16}$$

将上式代入式 (11) 中得

$$\frac{P}{kT} = \rho - b_2 y^2 - 2b_3 y^3 + O(y^4). \tag{17}$$

将式 (16) 代入式 (16) 并近似到 2 阶得

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

将上式代入式 (17) 中可得

$$\frac{P}{kT} = \rho - b_2(\rho - 2b_2\rho^2)^2 - 2b_3(\rho - 2b_2\rho^2)^3 + O(\rho^4) = \rho - b_2\rho^2 + (4b_2^2 - 2b_3)\rho^3 + O(\rho^4)$$

$$= \rho \left[1 - \frac{1}{2}\beta_1\rho - \frac{2}{3}\beta_2\rho^2 + O(\rho^3) \right], \tag{19}$$

其中

$$\beta_1 = 2b_2 = -2d, \tag{20}$$

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

由准确的状态方程出发，有

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

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

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

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

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

从而

$$f_{ij} = e^{-\beta u_{ij}} - 1 = \begin{cases} -1, & r \le d \\ 0, & r > d \end{cases} \tag{25}$$

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

$$\frac{P}{kT} = \rho \left[1 - \frac{1}{2}\beta_1\rho - \frac{2}{3}\beta_2\rho^2 + O(\rho^3) \right], \tag{26}$$

其中 virial 系数

$$\beta_1 = 2b_2, \tag{27}$$
$$\beta_2 = 3(b_3 - 2b_2^2), \tag{28}$$

而

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

$$b_3 = \frac{1}{3!V} \int \mathrm{d}^3\vec{r}_3 \int \mathrm{d}^3\vec{r}_2 \int \mathrm{d}^3\vec{r}_1\, \left[3f_{12}(|\vec{r}_1 - \vec{r}_2|)f_{13}(|\vec{r}_1 - \vec{r}_3|) - f_{12}(|\vec{r}_1 - \vec{r}_2|)f_{13}(|\vec{r}_1 - \vec{r}_3|)f_{23}(|\vec{r}_2 - \vec{r}_3|) \right]$$

$$= 8\pi^2 \int_0^d \mathrm{d}r_{12}\, r_{12}^2 f(r_{12}) \int_0^d \mathrm{d}r_{13}\, r_{13}^2 f(r_{13}) - \frac{1}{6} \int \mathrm{d}^3\vec{r}_{12} \int \mathrm{d}^3\vec{r}_{13}\, f_{12}(r_{12})f_{13}(r_{13})f_{23}(|\vec{r}_{12} - \vec{r}_{13}|)$$

$$= \frac{8\pi^2 d^6}{9} - \frac{1}{6} \int \mathrm{d}^3\vec{r}_{12} \int \mathrm{d}^3\vec{r}_{13}\, f_{12}(r_{12})f_{13}(r_{13})f_{23}(|\vec{r}_{12} - \vec{r}_{13}|). \tag{30}$$

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

$$-\int \mathrm{d}^3\vec{r}_{13}\, f_{12}(r_{12})f_{13}(r_{13})f_{23}(|\vec{r}_{12} - \vec{r}_{13}|) = 2\int_0^{d - \frac{r_{12}}{2}} \pi[d^2 - (d-x)^2]\,\mathrm{d}x$$

$$= \frac{\pi}{12}(16d^3 - 12d^2 r_{12} + r_{12}^3). \tag{31}$$

从而

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

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

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

$$P(V - Nb) = NkT, \tag{34}$$

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

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

$$b = \frac{2\pi}{3}d^3. \tag{36}$$

$\square$