习题 VII

截止时间：2021. 4. 20（周二）

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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：

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

其中

$$\begin{aligned}
b_l(V,T)=&\frac{1}{Vl!}\int\prod_{i=1}^{l}\mathrm{d}^3\vec{r}_i\sum_{\text{all }l\text{-cluster}}\left(\prod f_{ij}\right), &(2)\\
b_1(V,T)=&\frac{1}{V}\int\mathrm{d}^3\vec{r}=1, &(3)\\
b_2(V,T)=&\frac{1}{2!V}\int\mathrm{d}^3\vec{r}_1\vec{r}_2\,f_{12}, &(4)\\
b_3(V,T)=&\frac{1}{3!V}\int\mathrm{d}^3\vec{r}_1\mathrm{d}^3\vec{r}_2\mathrm{d}^3\vec{r}_3\,(f_{12}f_{13}+f_{12}f_{23}+f_{13}f_{23}+f_{12}f_{13}f_{23})=\frac{1}{3!V}\int\mathrm{d}\vec{r}_1\mathrm{d}\vec{r}_2\mathrm{d}\vec{r}_3\,(3f_{12}f_{13}+f_{12}f_{13}f_{23}), &(5)\\
&\cdots &(6)
\end{aligned}$$

故

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

□

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}

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

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

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

根据 Mayer 第一定理，

$$\begin{aligned}
\frac{P}{kT}=&\sum_{l=1}^{\infty}b_ly^l=b_1y+b_2y^2+b_3y^3+O(y^4), &(11)\\
\rho=&y\frac{\partial\left(\frac{P}{kT}\right)}{\partial y}=b_1y+2b_2y^2+3b_3y^3+O(y^4), &(12)
\end{aligned}$$

其中一维情况下

$$
\begin{aligned}
b_l(V,T)=&\frac{1}{l!L}\int\prod_{i=1}^{l}\mathrm{d}x_i\sum_{\text{all }l\text{-clusters}}\left(\prod f_{ij}\right), && (13)\\
b_1(V,T)=&\frac{1}{L}\int\mathrm{d}x_1=1, && (14)\\
b_2(V,T)=&\frac{1}{2!L}\int\mathrm{d}x_1\mathrm{d}x_2\,f_{12}=\frac{1}{2!L}\int\mathrm{d}x_1\int_{-d}^{d}\mathrm{d}x_{12}\,f_{12}(x_{12})=-d, && (15)\\
b_3(V,T)=&\frac{1}{3!L}\int\mathrm{d}x_1\mathrm{d}x_2\mathrm{d}x_3\,(3f_{12}f_{13}+f_{21}f_{13}f_{23})\\
=&\frac{1}{3!L}\int\mathrm{d}x_1\int_{-d}^{d}\mathrm{d}x_{12}\int_{-d}^{d}\mathrm{d}x_{13}\,(3f_{12}(x_{12})f_{13}(x_1-x_3)+f_{21}(x_{12})f_{13}(x_{13})f_{23}(|x_{12}-x_{13}|))=\frac{3d^2}{2},
\end{aligned}
$$

由式 (12) 得

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

将上式代入式 (11) 中得

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

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

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

其中

$$
\begin{aligned}
\beta_1=&2b_2=-2d, && (20)\\
\beta_2=&3(b_3-2b_2^2)=-\frac{3d^2}{2}. && (21)
\end{aligned}
$$

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

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

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

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

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

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

其中 virial 系数

$$\beta_1=2b_2,\tag{27}$$

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

而

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

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

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

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

从而

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

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

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

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

$\square$