高等热力学与统计物理第六次作业

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1 计算 Maxwell 分布下的最可几速度，平均速度和速度分布的宽度，即

$$\Delta v \equiv \sqrt{\langle (v-\langle v\rangle)^2\rangle}$$

将结果用绝对温度和分子质量表达。并算出氢气和氧气以上各量在室温下的数值。

Maxwell 速度分布为:

$$f(\vec{v}) = \left(\frac{m}{2\pi kT}\right)^{3/2} 4\pi v^2 e^{-\frac{mv^2}{2kT}}.$$

求导可得:

$$\frac{df}{dv} = \left(\frac{m}{2\pi kT}\right)^{3/2} 4\pi v e^{-\frac{mv^2}{2kT}} \left(2-\frac{mv^2}{kT}\right).$$

令 $\frac{df}{dv}=0$，可以解得最可几速度为:

$$v_1 = \sqrt{\frac{2kT}{m}}.$$

平均速度为:

$$\langle v\rangle = \int_0^\infty v f(\vec{v})\, dv = \left(\frac{m}{2\pi kT}\right)^{3/2} 4\pi \int_0^\infty v^3 e^{-\frac{mv^2}{2kT}}\, dv = 4\pi \left(\frac{m}{2\pi kT}\right)^{3/2} 2\left(\frac{kT}{m}\right)^2 = \sqrt{\frac{8kT}{\pi m}}.$$

速度平方的平均值为:

$$\langle v^2\rangle = \int_0^\infty v^2 f(v)\, dv = \left(\frac{m}{2\pi kT}\right)^{3/2} 4\pi \int_0^\infty v^4 e^{-\frac{mv^2}{2kT}}\, dv = \frac{3kT}{m}.$$

则速度分布的宽度为:

$$\Delta v = \sqrt{\langle v^2\rangle - \langle v\rangle^2} = \sqrt{\left(3-\frac{8}{\pi}\right)\frac{kT}{m}}.$$

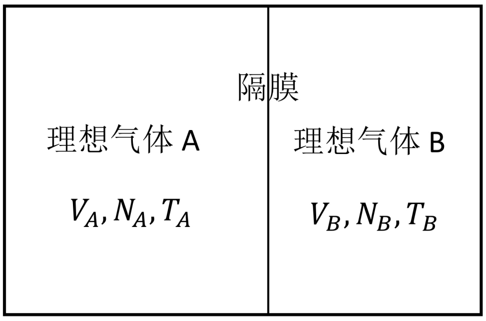
在室温下 $T=300K$，氢气分子质量为: $m_{H_2}=3.32\times 10^{-24}g$，氧气分子质量为: $m_{O_2}=5.32\times 10^{-23}g$，代入数据可得，对于氢气有:

$$v_1 = 1.58\times 10^3 m/s;\ \langle v\rangle = 1.782\times 10^3 m/s;\ \Delta v = 752 m/s.$$

对于氧气有:

$$v_1 = 395 m/s;\ \langle v\rangle = 445 m/s;\ \Delta v = 188 m/s.$$

2 由同一种分子组成的理想气体被隔膜分成两部分。每部分的体积，粒子数和温度如图所示。假设隔膜左右温度相同但密度不同，且系统与外界热绝缘。证明隔膜撤掉后气体的熵增加。



由于气体为理想气体，则初态的熵为:

$$S_A = \frac{3}{2}N_A k \ln \frac{2\pi mkT}{\hbar^2} + N_A k \ln \frac{V_A}{N_A} + \frac{5}{2}N_A k,$$
$$S_B = \frac{3}{2}N_B k \ln \frac{2\pi mkT}{\hbar^2} + N_B k \ln \frac{V_B}{N_B} + \frac{5}{2}N_B k.$$

则初态系统的熵为:

$$S_0 = S_A + S_B = \frac{3}{2}(N_A + N_B)k \ln \frac{2\pi mkT}{\hbar^2} + \frac{5}{2}(N_A + N_B)k + N_A k \ln \frac{V_A}{N_A} + N_B k \ln \frac{V_B}{N_B}.$$

隔膜撤掉后，气体分子总数为：$N = N_A + N_B$，温度为：T，体积为：$V = V_A + V_B$ 则气体的熵为:

$$S_1 = \frac{3}{2}(N_A + N_B)k \ln \frac{2\pi mkT}{\hbar^2} + \frac{5}{2}(N_A + N_B)k + (N_A + N_B)k \ln \frac{V_A + V_B}{N_A + N_B}.$$

则熵变化量为:

$$\Delta S = S_1 - S_0 = (N_A + N_B)k \ln \frac{V_A + V_B}{N_A + N_B} - \left(N_A k \ln \frac{V_A}{N_A} + N_B k \ln \frac{V_B}{N_B}\right)$$

令 $x_1 = \frac{V_A}{N_A}$，$x_2 = \frac{V_B}{N_B}$，$\alpha = \frac{N_A}{N_A+N_B}$，$f(x) = \ln x$，则可以计算:

$$\frac{d^2 f(x)}{dx^2} = -\frac{1}{x^2} < 0.$$

即 $f(x)$ 为凹函数 (上凸)。则有对于任意的 $\alpha \in (0,1)$，满足

$$f(\alpha x_1 + (1-\alpha)x_2) > \alpha f(x_1) + (1-\alpha)f(x_2).$$

注意到熵的变化量为:

$$\Delta S = (N_A + N_B)k(f(\alpha x_1 + (1-\alpha)x_2) - \alpha f(x_1) + (1-\alpha)f(x_2)) > 0.$$

则隔膜撤掉后气体的熵增加。

3 在高温条件下，即

$$\epsilon \equiv \frac{\hbar^2}{2IkT} << 1$$

证明双原子气体的转动配分函数

$$q_r = \omega \left[\frac{1}{\epsilon} + \frac{1}{3} + \frac{1}{15}\epsilon + \mathcal{O}(\epsilon^2)\right]$$

和每个分子平均转动动能

$$u_r = kT \left[1 - \frac{1}{3}\epsilon - \frac{1}{45}\epsilon^2 + \mathcal{O}(\epsilon^3)\right]$$

其中 ω 为核自旋的简并度

$$\omega = \begin{cases} (2s_A+1)(2s_B+1), & AB \\ \frac{1}{2}(2s_A+1)^2, & AA \end{cases}$$

提示：可用 Euler-Maclaurin 公式计算修正项

令 $f(j) = (2j+1)e^{-\epsilon(j^2+j)}$，则有:

$$\int_0^\infty f(j)\,dj = -\frac{1}{\epsilon}e^{-\epsilon(j^2+j)}\bigg|_0^\infty = \frac{1}{\epsilon}.$$

$$f(0) = 1,\ f(\infty) = 0.$$

$$\frac{df}{dj} = 2e^{-\epsilon(j^2+j)} - \epsilon(2j+1)^2 e^{-\epsilon(j^2+j)}$$

$$f^{(1)}(0) = 2 - \epsilon,\ f^{(1)}(\infty) = 0.$$

$$f^{(2)}(j) = \epsilon^2(2j+1)^3 e^{-\epsilon(j^2+j)} - 6\epsilon(2j+1)e^{-\epsilon(j^2+j)}.$$

$$f^{(3)}(j) = \left(-\epsilon^3(2j+1)^4 + 12\epsilon^2(2j+1)^2 - 12\epsilon\right)e^{-\epsilon(j^2+j)}.$$

$$f^{(3)}(0) = (-\epsilon^3 + 12\epsilon^2 - 12\epsilon),\ f^{(3)}(\infty) = 0.$$

则有:

$$\begin{aligned}\sum_0^\infty f(j) =& \frac{1}{\epsilon} + \frac{1}{2} - \frac{1}{12}(2-\epsilon) + \frac{1}{720}(-\epsilon^3 + 12\epsilon^2 - 12\epsilon) \\ =& \frac{1}{\epsilon} + \frac{1}{3} + \frac{1}{15}\epsilon + \mathcal{O}(\epsilon^2).\end{aligned}$$

对于 AB 型分子，$\Delta j = 1$，则有:

$$\begin{aligned}q_r =& (2s_A+1)(2s_B+1)\sum_{j=0}^\infty (2j+1)e^{-\epsilon j(j+1)}\Delta j \\ =& (2s_A+1)(2s_B+1)\left[\frac{1}{\epsilon} + \frac{1}{3} + \frac{1}{15}\epsilon + \mathcal{O}(\epsilon^2)\right].\end{aligned}$$

对于 AA 型分子，$\Delta j = 2$，当 j 为偶数时则有:

$$\begin{aligned}q_r =& (2s_A+1)^2 \sum_{j,\Delta j=2} (2j+1)e^{-\epsilon j(j+1)}\frac{\Delta j}{2} \\ =& \frac{1}{2}(2s_A+1)^2 \sum_{i=0}^\infty (8i+2)e^{-\epsilon(4i^2+2i)}\end{aligned}$$

其中 $i=j/2$。令 $g(i)=(8i+2)e^{-\epsilon(4i^2+2i)}$，则可以计算:

$$\int_0^\infty g(i)\,di=-\frac{1}{\epsilon}e^{-\epsilon(4i^2+2i)}\Big|_0^\infty=\frac{1}{\epsilon}.$$

$$g(0)=2,\ g(\infty)=0.$$

$$g^{(1)}=(8-\epsilon(8i+2)^2)e^{-\epsilon(4i^2+2i)}.$$

$$g^{(1)}(0)=8-4\epsilon,\ g^{(1)}(\infty)=0.$$

$$g^{(3)}=\left(-\epsilon^3(8i+2)^4+24\epsilon^2(8i+2)^2-192\epsilon\right)e^{-\epsilon(4i^2+2i)}$$

$$g^{(3)}(0)=-\epsilon^3+24\epsilon^2-192\epsilon,\ g^{(3)}(\infty)=0.$$

则有:

$$\begin{aligned}\sum_{i=1}^\infty g(i)=&\frac{1}{\epsilon}+1-\frac{1}{12}(8-4\epsilon)+\frac{1}{720}(-\epsilon^3+24\epsilon^2-192\epsilon)\\=&\frac{1}{\epsilon}+\frac{1}{3}+\frac{1}{15}\epsilon+\mathcal{O}(\epsilon^2).\end{aligned}$$

同理可知，当 j 为奇数时，令 $k=(j-1)/2$，可以计算得相同结果。则有双原子气体的转动配分函数为:

$$q_r=\omega\left[\frac{1}{\epsilon}+\frac{1}{3}+\frac{1}{15}\epsilon+\mathcal{O}(\epsilon^2)\right].$$

其中核自旋简并度为:

$$\omega=\begin{cases}(2s_A+1)(2s_B+1), & AB\\ \frac{1}{2}(2s_A+1)^2, & AA\end{cases}$$

则每个分子的平均转动动能为:

$$u_r=-\frac{\partial\ln q_r}{\partial\beta}=-\frac{\hbar^2}{2I}\frac{\partial\ln q_r}{\partial\epsilon}$$

可以计算:

$$\ln q_r=\ln\omega-\ln\epsilon+\ln\left(1+\frac{\epsilon}{3}+\frac{\epsilon^2}{15}+\mathcal{O}(\epsilon^3)\right)=\ln\omega-\ln\epsilon+\frac{\epsilon}{3}+\frac{\epsilon^2}{90}+\mathcal{O}(\epsilon^3).$$

则平均转动动能为:

$$u_r=\epsilon kT\left(\frac{1}{\epsilon}-\frac{1}{3}-\frac{1}{45}\epsilon+\mathcal{O}(\epsilon^2)\right)=kT\left(1-\frac{1}{3}\epsilon-\frac{1}{45}\epsilon^2+\mathcal{O}(\epsilon^3)\right).$$