统计力学第六次作业

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7.1

$\varepsilon = \frac{1}{2m}(\frac{2\pi\hbar}{L})^2 \sum n^2 = aL^{-2} = aV^{-2/3}$, a 为常数 $a = \frac{(2\pi\hbar)^2 \sum n_i^2}{2m}$.
则 $\frac{\partial\varepsilon}{\partial V} = -\frac{2}{3}\varepsilon/V$. 用 l 取代 $\sum n_i^2$. $\frac{\partial\varepsilon}{\partial V} = -\frac{2}{3}\varepsilon/V$
因此 $p = -\sum a_l \frac{\partial\varepsilon_l}{\partial V} = \frac{2}{3}\sum a_l \frac{\varepsilon}{V} = \frac{2}{3}\frac{U}{V}$

7.2

$\varepsilon = c\frac{2\pi\hbar}{L}\sqrt{\sum n^2} = aL^{-1} = aV^{-1/3}$, a 为常数 $a = c2\pi\hbar\sqrt{\sum n^2}$.
则 $\frac{\partial\varepsilon}{\partial V} = -\frac{1}{3}\varepsilon/V$. 用 l 取代 $\sqrt{\sum n^2}$. $\frac{\partial\varepsilon}{\partial V} = -\frac{1}{3}\varepsilon/V$
因此 $p = -\sum a_l \frac{\partial\varepsilon_l}{\partial V} = \frac{1}{3}\sum a_l \frac{\varepsilon}{V} = \frac{1}{3}\frac{U}{V}$

7.4

$$S = Nk(\ln Z_1 - \beta\frac{\partial}{\partial\beta}\ln Z_1)$$

总的 S 为各状态的概率平均:

$$= Nk\sum_s P_s(\ln Z_1 - \beta\frac{\partial}{\partial\beta}(-\beta\varepsilon_s - \ln P_s))$$

$$= \sum_s P_s Nk(\ln Z_1 + \beta\varepsilon_s) = \sum_s P_s Nk(-\beta\varepsilon_s - \ln P_s + \beta\varepsilon_s) = -\sum_s P_s \ln P_s$$

当系统为非定域,

$$S = Nk(\ln Z_1 - \beta\frac{\partial}{\partial\beta}\ln Z_1) - k\ln N! = -\sum_s P_s \ln P_s - k\ln N!$$
$$= -\sum_s P_s \ln P_s - Nk(\ln N - 1)$$

7.5

A 原子共有 Nx 个, 因此 c

$$\Omega = \begin{pmatrix} N \\ Nx \end{pmatrix} = \frac{N!}{(Nx)!(N-Nx)!}$$

又由于定域系统中 $S = k\ln\Omega$.

$$S = k\ln\frac{N!}{(Nx)!(N-Nx)!}$$

利用 $\ln N = N(\ln N - 1)$ 可化简为:

$$S = -Nk[x\ln x + (1-x)\ln(1-x)]$$

7.6

(a)

总的状态数为

$$\Omega = \begin{pmatrix} N \\ n \end{pmatrix}^2 = \left(\frac{N!}{n!(N-n)!}\right)^2$$

又由于定域系统中 $S = k\ln\Omega$.

$$S = 2k\ln\frac{N!}{n!(N-n)!} = 2k(N\ln N - n\ln n - (N-n)\ln(N-n))$$

(b)

平衡态时 F 极小要求 $\frac{\partial F}{\partial n} \to 0 \implies u = T\frac{\partial S}{\partial n}$.

$$\frac{\partial S}{\partial n} = 2k(-\ln n + \ln(N-n)) = 2k\ln(N/n - 1) \approx 2k\ln(N/n)$$

因此

$$\frac{u}{2kT} = \ln(N/n) \implies n = Ne^{-\frac{u}{2kT}}$$

7.7

这种情况由于只有空位没有间隙原子出现, 因此 S 变为 7.5 的表达式, 即

$$S = k\ln\frac{N!}{n!(N-n)!} = k(N\ln N - n\ln n - (N-n)\ln(N-n))$$

同理, 平衡态时 F 极小要求 $\frac{\partial F}{\partial n} \to 0 \implies w = T\frac{\partial S}{\partial n}$.

$$\frac{\partial S}{\partial n} = k(-\ln n + \ln(N-n)) = k\ln(N/n-1) \approx k\ln(N/n)$$

因此

$$\frac{w}{kT} = \ln(N/n) \implies n = Ne^{-\frac{w}{kT}}$$

7.9

当气体没有整体运动时, 最概然分布为:

$$\mathrm{d}N = e^{-\alpha-\frac{\beta}{2m}(p_x^2+p_y^2+p_z^2)}\frac{V\,\mathrm{d}p_x\,\mathrm{d}p_y\,\mathrm{d}p_z}{h^3}$$

使坐标系做沿 $-z$ 方向, 速度为 v_0 的运动, 设此时相对速度变化为 $v_z' = v_z + v_0 \iff p_z' = p_z + p_0$, 分布为:

$$\mathrm{d}N = e^{-\alpha-\frac{\beta}{2m}(p_x^2+p_y^2+p_z'^2)}\frac{V\,\mathrm{d}p_x\,\mathrm{d}p_y\,\mathrm{d}p_z}{h^3}$$

用 p_z 代替 p_z',

$$\mathrm{d}N = e^{-\alpha-\frac{\beta}{2m}(p_x^2+p_y^2+(p_z-p_0)^2)}\frac{V\,\mathrm{d}p_x\,\mathrm{d}p_y\,\mathrm{d}p_z}{h^3}$$

这等价于气体沿 z 方向运动.

7.12

根据速度分布律,

$$f(\vec{v}) = (\frac{m}{2\pi k_BT})^{3/2}\exp(-\frac{mv^2/2}{k_BT}) = C\exp(-\frac{mv^2/2}{k_BT})$$

则某一状态概率为

$$\mathrm{d}W = C^2\exp(-\frac{mv_1^2/2}{k_BT})\exp(-\frac{mv_2^2/2}{k_BT})\,\mathrm{d}\vec{v}_1\mathrm{d}\vec{v}_2$$

修改积分变量 $(\vec{v_1},\vec{v_2})\to(\vec{v_r},\vec{v_e})$. 其中 $v_e=\frac{1}{2}(v_1+v_2), v_r=v_2-v_1$ Jacobi 行列式为

$$\left|\frac{\partial(v_1,v_2)}{\partial(v_e,v_r)}\right|=\begin{vmatrix}1 & 1\\ -\frac{1}{2} & \frac{1}{2}\end{vmatrix}=1$$

此时质量的含义发生变化, 用等效质量替换: $m_e=2m, m_\mu=m/2$,

$$\mathrm{d}W=C_eC_\mu\exp(-\frac{m_ev_e^2/2}{k_BT})\exp(-\frac{m_\mu v_r^2/2}{k_BT})\,\mathrm{d}\vec{v}_e\,\mathrm{d}\vec{v}_r$$

对于相对速度 v_r, 其分布为 $f(v_r)=C_\mu\exp(-\frac{m_\mu v_r^2/2}{k_BT})$

$$\implies f(v_r)=(\frac{m_\mu}{2\pi k_BT})^{3/2}\exp(-\frac{m_\mu v_r^2/2}{k_BT})$$

由于对称性, $|v_r|$ 相同的各个 v_r 的分布是相同的, 因此 $\mathrm{d}|v_r|=4\pi|v_r|^2\,\mathrm{d}v_r$ 速度分布为

$$f(|v_r|)\,\mathrm{d}|v_r|=f(v_r)4\pi|v_r|^2\,\mathrm{d}v_r=(\frac{m_\mu}{2\pi k_BT})^{3/2}\exp(-\frac{m_\mu v_r^2/2}{k_BT})4\pi|v_r|^2\,\mathrm{d}v_r$$

$$\overline{|v|}=\int_0^\infty|v|f(|v|)\,\mathrm{d}|v|$$

$$\begin{aligned}\overline{|v_r|}&=\int_0^\infty|v_r|f(|v_r|)\,\mathrm{d}|v_r|=\int_0^\infty|v_r|(\frac{m_\mu}{2\pi k_BT})^{3/2}\exp(-\frac{m_\mu v_r^2/2}{k_BT})4\pi|v_r|^2\,\mathrm{d}v_r\\&=\int_0^\infty\frac{|v_r|}{\sqrt{2}}\frac{1}{2}(\frac{m}{2\pi k_BT})^{3/2}\exp(-\frac{m(v_r/\sqrt{2})^2/2}{k_BT})4\pi2\times(\frac{|v_r|}{\sqrt{2}})^2\sqrt{2}\,\mathrm{d}\frac{v_r}{\sqrt{2}}\end{aligned}$$

做变量替换 $\frac{v_r}{\sqrt{2}}=v$

$$=\sqrt{2}(\frac{m}{2\pi k_BT})^{3/2}\exp(-\frac{mv^2/2}{k_BT})4\pi|v|^2\,\mathrm{d}v=\sqrt{2}f(|v|)\,\mathrm{d}|v|=\sqrt{2}\overline{|v|}$$

即 $\overline{|v_r|}=\sqrt{2}\overline{|v|}$

7.14

单位时间逃逸的分子数密度为: $\Gamma=\pi n\left(\frac{m}{2\pi kT}\right)^{3/2}\exp(-\frac{mv^2}{2kT})\,\mathrm{d}v$.

分子平均速率为

$$\overline{v}=\frac{\int_0^\infty\Gamma v\,\mathrm{d}v}{\int_0^\infty\Gamma\,\mathrm{d}v}=\frac{\int_0^\infty v^4\exp(-\frac{mv^2}{2kT})\,\mathrm{d}v}{\int_0^\infty v^3\exp(-\frac{mv^2}{2kT})\,\mathrm{d}v}=\sqrt{\frac{9\pi kT}{8m}}$$

方均根速率为

$$\sqrt{\overline{v^2}}=\sqrt{\frac{\int_0^\infty\Gamma v^2\,\mathrm{d}v}{\int_0^\infty\Gamma\,\mathrm{d}v}}=\sqrt{\frac{\int_0^\infty v^5\exp(-\frac{mv^2}{2kT})\,\mathrm{d}v}{\int_0^\infty v^3\exp(-\frac{mv^2}{2kT})\,\mathrm{d}v}}=\sqrt{\frac{4kT}{m}}$$

平均能量为:

$$\overline{E}=\frac{1}{2}m\overline{v^2}=2kT$$

7.18

简谐振动能级为:

$$\varepsilon = (n + \frac{1}{2})\hbar\omega$$

简并度为 1, 则

$$Z_1 = \sum \exp(-\beta(n + \frac{1}{2})\hbar\omega) = \frac{e^{-\frac{1}{2}\beta\hbar\omega}}{1 - e^{-\beta\hbar\omega}}$$

$$\ln Z_1 = -\frac{1}{2}\beta\hbar\omega - \ln(1 - e^{-\beta\hbar\omega})$$

$$S = Nk\left(\ln Z_1 - \beta\frac{\partial}{\partial\beta}\ln Z_1\right)$$

$$= Nk\left(-\frac{1}{2}\beta\hbar\omega - \ln(1 - e^{-\beta\hbar\omega}) - \beta(-\frac{1}{2}\hbar\omega - \frac{1}{1 - e^{-\beta\hbar\omega}}e^{-\beta\hbar\omega}(-\hbar\omega))\right)$$

$$= Nk\left(-\ln(1 - e^{-\beta\hbar\omega}) + \frac{\beta\hbar\omega}{e^{\beta\hbar\omega} - 1}\right)$$

代入 $\theta = T\beta\hbar\omega$,

$$= Nk\left(-\ln(1 - e^{-\theta/T}) + \frac{\theta/T}{e^{\theta/T} - 1}\right)$$

7.21

$$Z_1 = e^{-\beta\varepsilon_1} + e^{-\beta\varepsilon_2}, N = e^{-\alpha-\beta\varepsilon_1} + e^{-\alpha-\beta\varepsilon_2}$$

$$U = -N\frac{\partial}{\partial\beta}\ln Z_1 = -N\frac{\partial}{\partial\beta}\ln(e^{-\beta\varepsilon_1} + e^{-\beta\varepsilon_2})$$

$$= -N(\frac{1}{e^{-\beta\varepsilon_1} + e^{-\beta\varepsilon_2}}(-\varepsilon_1 e^{-\beta\varepsilon_1} - \varepsilon_2 e^{-\beta\varepsilon_2}))$$

$$= N(\frac{1}{e^{-\beta\varepsilon_1} + e^{-\beta\varepsilon_2}}(\varepsilon_1 e^{-\beta\varepsilon_1} + \varepsilon_2 e^{-\beta\varepsilon_2}))$$

$$= N\varepsilon_1 + \frac{N(\varepsilon_2 - \varepsilon_1)}{1 + e^{\beta(\varepsilon_2 - \varepsilon_1)}}$$

$$S = Nk\left(\ln Z_1 - \beta\frac{\partial}{\partial\beta}\ln Z_1\right)$$

$$= Nk\left(-\beta\varepsilon_1 + \ln(1 + e^{-\beta(\varepsilon_2 - \varepsilon_1)}) + \beta\varepsilon_1 + \frac{\beta(\varepsilon_2 - \varepsilon_1)}{1 + e^{\beta(\varepsilon_2 - \varepsilon_1)}}\right)$$

$$= Nk\left(\ln(1 + e^{-\beta(\varepsilon_2 - \varepsilon_1)}) + \frac{\beta(\varepsilon_2 - \varepsilon_1)}{1 + e^{\beta(\varepsilon_2 - \varepsilon_1)}}\right)$$