Chapter 4 Non-Interacting (Ideal) Systems

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4.1

$$
\begin{aligned}
\frac{\partial \langle n_i \rangle}{\partial(-\beta\varepsilon_j)} =& \frac{\partial}{\partial(-\beta\varepsilon_j)} \left(\frac{\sum_{n_1,n_2,\cdots} n_i \exp[-\beta(n_1\varepsilon_1 + n_2\varepsilon_2 + \cdots + n_i\varepsilon_i + \cdots)]}{Q} \right) \\
=& - \frac{\partial Q}{\partial(-\beta\varepsilon_j)} \left(\frac{\sum_{n_1,n_2,\cdots} n_i \exp[-\beta(n_1\varepsilon_1 + n_2\varepsilon_2 + \cdots + n_i\varepsilon_i + \cdots)]}{Q^2} \right) \\
& + \frac{1}{Q} \frac{\partial}{\partial(-\beta\varepsilon_j)} \left(\sum_{n_1,n_2,\cdots} n_i \exp[-\beta(n_1\varepsilon_1 + n_2\varepsilon_2 + \cdots + n_i\varepsilon_i + \cdots)] \right) \\
=& - \frac{\partial \ln Q}{\partial(-\beta\varepsilon_j)} \langle n_i \rangle + \frac{1}{Q} \sum_{n_1,n_2,\cdots} n_j n_i \exp[-\beta(n_1\varepsilon_1 + n_2\varepsilon_2 + \cdots + n_i\varepsilon_i + \cdots)] \\
=& - \langle n_j \rangle \langle n_i \rangle + \langle n_j n_i \rangle \\
=& \langle \delta n_i \delta n_j \rangle
\end{aligned} \tag{1}
$$

Thus if $i \neq j$,

$$
\langle \delta n_i \delta n_j \rangle = \frac{\partial \langle n_i \rangle}{\partial(-\beta\varepsilon_j)} = \frac{\partial}{\partial(-\beta\varepsilon_j)} \frac{1}{e^{\beta\varepsilon_i} - 1} = 0. \tag{2}
$$

That is, there is no correlation between occupation numbers of two different single particle states.

If $j = i$,

$$
\langle (\delta n_i)^2 \rangle = \frac{\partial \langle n_i \rangle}{\partial(-\beta\varepsilon_i)} = \frac{\partial}{\partial(-\beta\varepsilon_i)} \frac{1}{e^{\beta\varepsilon_i} - 1} = \frac{e^{\beta\varepsilon_i}}{(e^{\beta\varepsilon_i} - 1)^2} = \frac{1}{2\cosh(\beta\varepsilon_i) - 2}. \tag{3}
$$

4.2

Since the distribution of free ideal photon gas is

$$
\langle n(\varepsilon) \rangle = \frac{1}{e^{\beta\varepsilon} - 1}, \tag{4}
$$

That is to say, at temperature β, the number of photons at energy ε is $\langle n_i \rangle$.

Here, ε is the energy of a single photon out of many kinds. From relativity, we know that

$$
\varepsilon = pc = c\sqrt{p_x^2 + p_y^2 + p_z^2} \tag{5}
$$

The volume of the phase space

$$g(\varepsilon)d\varepsilon = 2\cdot\int_{\varepsilon<c\sqrt{p_x^2+p_y^2+p_z^2}<\varepsilon+d\varepsilon}\frac{1}{h^3}d^3qd^3p = \frac{L^3\varepsilon^2}{\pi^2\hbar^3c^3}d\varepsilon \tag{6}$$

where h^3 is the unit volume of the phase space for 3D system, and the factor 2 stands for two polarizations (spin states) of the photon. Then the total energy is

$$E = \int_0^\infty d\varepsilon g(\varepsilon)\langle n(\varepsilon)\rangle\varepsilon = \int_0^\infty d\varepsilon\frac{L^3\varepsilon^2}{\pi^2\hbar^3c^3}\frac{1}{e^{\beta\varepsilon}-1}d\varepsilon = \frac{L^3}{\pi^2\hbar^3c^3}\frac{\pi^4}{15\beta^4} \tag{7}$$

Thus

$$\frac{E}{V} = \frac{\pi^2k_B^4}{15\hbar^3c^3}T^4. \tag{8}$$

4.3

Since

$$Q = \prod_{\alpha=1}^{DN}\left(\sum_n \exp\left[-\beta\left(\frac{1}{2}+n\right)\hbar\omega_\alpha\right]\right) \tag{9}$$

$$\begin{aligned}
\ln Q &= \sum_{\alpha=1}^{DN}\ln\left[\exp\left(-\frac{1}{2}\beta\hbar\omega_\alpha\right)\sum_n\exp\left(-\beta n\hbar\omega_\alpha\right)\right]\\
&= \sum_{\alpha=1}^{DN}\ln\left[\exp\left(-\frac{1}{2}\beta\hbar\omega_\alpha\right)\frac{1}{1-e^{-\beta\hbar\omega_\alpha}}\right]\\
&= \sum_{\alpha=1}^{DN}\ln\left[\frac{1}{e^{\frac{1}{2}\beta\hbar\omega_\alpha}-e^{-\frac{1}{2}\beta\hbar\omega_\alpha}}\right]\\
&= -\sum_{\alpha=1}^{DN}\ln\left(e^{\frac{1}{2}\beta\hbar\omega_\alpha}-e^{-\frac{1}{2}\beta\hbar\omega_\alpha}\right)
\end{aligned} \tag{10}$$

4.4

If for N particles

$$g(\omega) = N\delta(\omega-\omega_0) \tag{11}$$

$$\beta A = \int_0^\infty d\omega g(\omega)\ln\left(e^{\beta\hbar\omega/2}-e^{-\beta\hbar\omega/2}\right) = N\ln\left(2\sinh(\beta\hbar\omega_0/2)\right) \tag{12}$$

$$E = \left(\frac{\partial\beta A}{\partial\beta}\right)_{V,N} = \frac{N\hbar\omega_0}{2}\coth(\beta\hbar\omega_0/2) \tag{13}$$

$$-k_BT^2C_V = \left(\frac{\partial E}{\partial\beta}\right)_{N,V} = -\frac{N\hbar^2\omega_0^2}{4}\operatorname{csch}^2(\beta\hbar\omega_0/2) \tag{14}$$

$$\therefore C_V/k_B = \frac{N\beta^2\hbar^2\omega_0^2}{4}\operatorname{csch}^2(\beta\hbar\omega_0/2) \tag{15}$$

When $T\to 0$, $\beta\to+\infty$, $C_V\to 0$, which is an important feature of the Einstein model.

4.5

Given

$$g(\omega)=\begin{cases}\frac{9N}{\omega_0^3}\omega^2, & \omega<\omega_0\\ 0, & \omega>\omega_0\end{cases} \tag{16}$$

$$\beta A=\int_0^\infty d\omega g(\omega)\ln\left(e^{\beta\hbar\omega/2}-e^{-\beta\hbar\omega/2}\right)=\frac{9N}{\omega_0^3}\int_0^{\omega_0}d\omega\omega^2\ln\left(2\sinh(\beta\hbar\omega/2)\right) \tag{17}$$

$$E=\left(\frac{\partial\beta A}{\partial\beta}\right)_{V,N}=\frac{9N}{\omega_0^3}\int_0^{\omega_0}d\omega\omega^2\coth(\beta\hbar\omega/2)\frac{\hbar\omega}{2} \tag{18}$$

$$-k_BT^2C_V=\left(\frac{\partial E}{\partial\beta}\right)_{N,V}=-\frac{9N\hbar^2}{4\omega_0^3}\int_0^{\omega_0}d\omega\omega^4\text{csch}^2(\beta\hbar\omega/2) \tag{19}$$

$$\begin{aligned}\therefore C_V/k_B=&\frac{9N\beta^2\hbar^2}{4\omega_0^3}\int_0^{\omega_0}d\omega\omega^4\text{csch}^2(\beta\hbar\omega/2)\\ =&\frac{9N}{4\beta^3\hbar^3\omega_0^3}\int_0^{\beta\hbar\omega_0}dx\frac{4x^4e^x}{(e^x-1)^2}\\ =&9N\left(\frac{T}{T_D}\right)^3\int_0^{T_D/T}\frac{x^4e^xdx}{(e^x-1)^2}\end{aligned} \tag{20}$$

where $T_D=\dfrac{\hbar\omega_0}{k_B}$ is the Debye temperature. When $T\to0$, $T_D/T\to\infty$,

$$C_V/k_B\to9N\left(\frac{T}{T_D}\right)^3\frac{4\pi^4}{15}=\frac{12}{5}N\left(\frac{T}{T_D}\right)^3. \tag{21}$$

4.6

$$\langle n_in_j\rangle=1\cdot P(n_in_j=1)=P(n_i=1,n_j=1)=P(\text{a particle is in state } i \text{ and a particle is in state } j) \tag{22}$$

Let a_{pi} be 1 if particle p is in state i and 0 if not. Then

$$\begin{aligned}\langle n_i\rangle\delta_{ij}=P(n_i=1)P(a_{pj}=1|a_{pi}=1)=&P(\text{a particle is in state } i)P(\text{a particle is in state } j \text{ if it is in state } i)\\ =&P(\text{a particle is in state } i \text{ and it is in state } j)\end{aligned} \tag{23}$$

Thus

$$\begin{aligned}g_{ij}=\langle n_in_j\rangle-\langle n_i\rangle\delta_{ij}=&P(\text{a particle is in state } i \text{ but it is not in state } j\text{, and a particle is in state } j)\\ =&P(\text{a particle is in state } i \text{ and another particle is in state } j)\end{aligned} \tag{24}$$

4.7

For ideal identical fermion gas,

$$\begin{aligned}\langle n_in_j\rangle=&\sum_v n_i^{(v)}n_j^{(v)}P_v=\frac{1}{\Xi}\sum_v n_i^{(v)}\frac{\partial\exp[-\beta\sum_k n_k(\varepsilon_k-\mu)]}{\partial(-\beta\varepsilon_j)}=\frac{1}{\Xi}\frac{\partial^2\sum_v\exp[-\beta\sum_k n_k(\varepsilon_k-\mu)]}{\partial(-\beta\varepsilon_j)\partial(-\beta\varepsilon_i)}\\ =&\frac{1}{\Xi}\frac{\partial^2\Xi}{\partial(-\beta\varepsilon_i)\partial(-\beta\varepsilon_j)}\end{aligned} \tag{25}$$

If $j \neq i$,

$$\langle n_i n_j \rangle = \frac{1}{(1+e^{\beta(\varepsilon_i - \mu)})(1+e^{\beta(\varepsilon_j-\mu)})} = \langle n_i \rangle \langle n_j \rangle. \tag{26}$$

If $j = i$,

$$\langle n_i n_j \rangle = \langle n_i n_i \rangle = \langle n_i \rangle. \tag{27}$$

In summary,

$$\langle n_i n_j \rangle = \langle n_i \rangle \delta_{ij} + \langle n_i \rangle \langle n_j \rangle (1 - \delta_{ij}). \tag{28}$$

Therefore

$$g_{ij} = \langle n_i n_j \rangle - \langle n_i \rangle \delta_{ij} = \langle n_i \rangle \langle n_j \rangle (1 - \delta_{ij}). \tag{29}$$

4.8

By definition, the Euler-Maclaurin formula is

$$\sum_{i=m}^{n} f(i) - \int_m^n f(x)dx = \frac{f(m)+f(n)}{2} + \frac{1}{6}\frac{f'(n)-f'(m)}{2!} - \frac{1}{30}\frac{f'''(n)-f'''(m)}{4!} + \cdots \tag{30}$$

$$\Delta = \sum_{n_x=0}\sum_{n_y=0}\sum_{n_z=0} F(\varepsilon_{\vec{n}}) - \int_0^\infty dn_x \int_0^\infty dn_y \int_0^\infty dn_z F(\varepsilon_{\vec{n}}) \approx \frac{1}{2}F(\varepsilon_0) = \frac{1}{2}\frac{1}{e^{\beta(\varepsilon_0-\mu)}+1} \tag{31}$$

The ground state of the free electron is

$$\varepsilon_0 = \frac{\hbar^2\pi^2}{2mL^2} = \frac{\hbar^2\pi^2}{2mV^{2/3}} \tag{32}$$

When $V \to \infty$, $\Delta \to \frac{1}{2e^{-\beta\mu}+2}$. However, we know that

$$\langle N \rangle \simeq \int_0^\infty dn_x \int_0^\infty dn_y \int_0^\infty dn_z F(\varepsilon_{\vec{n}}) \approx \frac{1}{2}F(\varepsilon_0) = \frac{2V}{(2\pi)^3}\int d^3k F(\varepsilon(k)) \tag{33}$$

which means

$$\frac{\Delta}{\langle N \rangle} \propto \frac{1}{V}. \tag{34}$$

Therefore when $V \to \infty$, the error of using integral instead of summation can be ignored.

4.9

$$k_F = \left(\frac{3N\pi^2}{V}\right)^{\frac{1}{3}} = \left(\frac{3\pi^2 N_A m_{Cu}}{VM_{Cu}}\right)^{\frac{1}{3}} = \left(\frac{3\pi^2 N_A \rho_{Cu}}{M_{Cu}}\right)^{\frac{1}{3}} \tag{35}$$

$$\mu_0/k_B = \frac{\hbar^2 k_F^2}{2m_e k_B} = \frac{\hbar^2}{2m_e k_B}\left(\frac{3\pi^2 N_A \rho_{Cu}}{M_{Cu}}\right)^{\frac{2}{3}} \tag{36}$$

Given $\rho_{Cu} = 9 \times 10^3\,\mathrm{kg\,m^{-3}}$, $M_{Cu} = 63.5 \times 10^{-3}\,\mathrm{kg\,mol^{-1}}$, it can be calculated that

$$\mu_0/k_B = 8.203 \times 10^4\,\mathrm{K}. \tag{37}$$

4.10

Start from

$$\langle E\rangle = \sum_{m=0}^{\infty} E_m \tag{38}$$

where

$$E_m = -\frac{1}{m!}\left(\frac{d^m\Phi}{d\varepsilon^m}\right)_{\varepsilon=\mu_0}\int_0^\infty \frac{dF}{d\varepsilon}(\varepsilon-\mu_0)^m d\varepsilon \tag{39}$$

and

$$F = \frac{1}{e^{\beta(\varepsilon-\mu)}+1}, \qquad \frac{dF}{d\varepsilon} = -\frac{\beta e^{\beta(\varepsilon-\mu)}}{(e^{\beta(\varepsilon-\mu)}+1)^2}. \tag{40}$$

For simplicity we denote $C_m = \frac{1}{m!}\frac{d^m\Phi}{d\varepsilon^m}\Big|_{\varepsilon=\mu_0}$. C_m is explicitly independent of temperature.

We use the approximation

$$\int_0^\infty \frac{dF}{d\varepsilon}f(\varepsilon)d\varepsilon \approx \int_{\mu_0-k_BT}^{\mu_0+k_BT}\frac{dF}{d\varepsilon}\Big|_{\mu=\mu_0} f(\varepsilon)d\varepsilon. \tag{41}$$

$$E_0 = -C_0\int_0^\infty \frac{dF}{d\varepsilon}d\varepsilon = -\Phi(\mu_0)[F(\infty)-F(0)] = C_0\frac{1}{e^{-\beta\mu}+1}. \tag{42}$$

$$\begin{aligned} E_{2n+1} \approx & C_{2n+1}\int_{\mu_0-k_BT}^{\mu_0+k_BT}\frac{\beta e^{\beta(\varepsilon-\mu_0)}}{\left(e^{\beta(\varepsilon-\mu_0)}+1\right)^2}(\varepsilon-\mu_0)^{2n+1}d\varepsilon \\ = & C_{2n+1}\frac{1}{\beta^{2n+1}}\int_{-1}^{1}\frac{x^{2n+1}e^x}{(e^x+1)^2}dx \\ = & C_{2n+1}\frac{1}{\beta^{2n+1}}\int_{-1}^{1}\frac{x^{2n+1}}{e^x+e^{-x}+2}dx = 0. \end{aligned} \tag{43}$$

$$E_2 \approx C_2\int_{\mu_0-k_BT}^{\mu_0+k_BT}\frac{\beta e^{\beta(\varepsilon-\mu_0)}}{\left(e^{\beta(\varepsilon-\mu_0)+1}\right)^2}(\varepsilon-\mu_0)^2 d\varepsilon = C_2\frac{1}{\beta^2}\int_{-1}^{1}\frac{x^2}{e^x+e^{-x}+2}dx = C_2A_2\frac{1}{\beta^2} \tag{44}$$

where

$$A_2 = \int_{-1}^{1}\frac{x^2}{e^x+e^{-x}+2}dx \approx 0.144 \tag{45}$$

Thus

$$\langle E\rangle \approx C_0A_0 + C_2A_2(k_BT)^2 + O(T^4). \tag{46}$$

where $\frac{1}{e^{-\beta\mu}+1} \to A_0$ when $\beta \to +\infty$.

4.11

The series can not have infinitive terms, because as the quantum number n goes to infinity, the average distance from the nucleus to the electron goes to infinity. Then it is impossible to say that the hydrogen atoms are not correlated, because the total space is after all finite.

4.12

(i) The original Schrödinger's equation for the total system is

$$[K_n(R) + K_e(r) + U_{ee}(r) + U_{nn}(R) + U_{ne}(r,R)]\psi(r,R) = E\psi(r,R) \tag{47}$$

where $\Psi(r,R)$ is the total wave function.

In the Born-Oppenheimer approximation, the total wave function is

$$\psi(r,R) = \Phi(r;R)\chi(R) \tag{48}$$

Form the procedure, we have

$$[K_e(r) + U_{ee}(r) + U_{nn}(R) + U_{ne}(r,R)]\Phi(r;R) = E_{BO}(R)\Phi(r;R) \tag{49}$$

where $E_{BO}(R)$ is the Born-Oppenheimer energy that does not include the kinetic energy of the nuclei, or the effective potential for nuclei.

$$[K_n(R) + E_{BO}(R)]\chi(R) = E\chi(R) \tag{50}$$

The equation (47) then becomes

$$\begin{aligned}
&[K_n(R) + K_e(r) + U_{ee}(r) + U_{nn}(R) + U_{ne}(r,R)]\psi(r,R)\\
=&[K_n(R) + K_e(r) + U_{ee}(r) + U_{nn}(R) + U_{ne}(r,R)]\Phi(r;R)\chi(R)\\
=&\Phi(r;R)K_n(R)\chi(R) + [K_e(r) + U_{ee}(r) + U_{nn}(R) + U_{ne}(r,R)]\Phi(r;R)\chi(R)\\
=&\Phi(r;R)K_n(R)\chi(R) + \Phi(r;R)E_{BO}(R)\chi(R)\\
=&\Phi(r;R)\chi(R)E = E\psi(r,R).
\end{aligned} \tag{51}$$

(ii) Around the point of the crossing point of the excited energy surfaces, the off-diagonal elements in the total Hamiltonian is as significant as the energy difference of the two states, and no more can be ignored. Instead, it requires a full decomposition or diagonalization of the total Hamiltonian. This way gives the "avoided crossing" of the energy surfaces.

4.13

$$\begin{aligned}
q_{\text{vib}}(T) =&\sum_{v=0}^{\infty} \exp\left[-\left(\frac{1}{2}+v\right)\beta\hbar\omega_0\right]\\
=&e^{-\beta\hbar\omega_0/2}\sum_{v=0}^{\infty}\left(e^{-\beta\hbar\omega_0}\right)^v\\
=&e^{-\beta\hbar\omega_0/2}\frac{1}{1-e^{-\beta\hbar\omega_0}}\\
=&\frac{1}{e^{\beta\hbar\omega_0/2} - e^{-\beta\hbar\omega_0/2}}.
\end{aligned} \tag{52}$$

4.14

By definition, the Euler-Maclaurin formula is

$$\sum_{i=m}^{n} f(i) - \int_m^n f(x)dx = \frac{f(m)+f(n)}{2} + \frac{1}{6}\frac{f'(n)-f'(m)}{2!} - \frac{1}{30}\frac{f'''(n)-f'''(m)}{4!} + \cdots \tag{53}$$

In this Exercise,

$$f(J) = (2J+1)\exp[-J(J+1)\theta_{\text{rot}}/T], \qquad J = 0,1,2,\cdots \tag{54}$$

Then correspondingly

$$f(x) = (2x+1)\exp[-x(x+1)\beta\hbar^2/2I_0], \quad x \in [0,\infty). \tag{55}$$

$$f'(x) = e^{-x(x+1)\theta_{\rm rot}/T}\left[2-(2x+1)^2\theta_{\rm rot}/T\right]. \tag{56}$$

$$f''(x) = e^{-x(x+1)\theta_{\rm rot}/T}\left[-6(2x+1)\theta_{\rm rot}/T+(2x+1)^3\theta_{\rm rot}/T\right]. \tag{57}$$

$$f'''(x) = e^{-x(x+1)\theta_{\rm rot}/T}\left[-12\theta_{\rm rot}/T+12(2x+1)^2\theta_{\rm rot}^2/T^2-(2x+1)^4\theta_{\rm rot}^3/T^3\right]. \tag{58}$$

$$\begin{aligned} q_{\rm rot} =& \sum_{J=0}^{\infty} f(J) \approx \int_0^\infty f(x)dx + \frac{f(\infty)+f(0)}{2} + \frac{f'(\infty)-f'(0)}{12} - \frac{f'''(\infty)-f'''(0)}{720} \\ =& \frac{T}{\theta_{\rm rot}} + \frac{1}{2} + \frac{1}{12}\left(\frac{\theta_{\rm rot}}{T}-2\right) + \frac{1}{720}\left(-12\frac{\theta_{\rm rot}}{T} + 12\frac{\theta_{\rm rot}^2}{T^2} - \frac{\theta_{\rm rot}^3}{T^3}\right) \\ =& \frac{T}{\theta_{\rm rot}}\left[1+\frac{1}{3}\left(\frac{\theta_{\rm rot}}{T}\right)+\frac{1}{15}\left(\frac{\theta_{\rm rot}}{T}\right)^2+\cdots\right]. \end{aligned} \tag{59}$$

4.15

For dilute multi-component gas with fixed N_A and N_B, which are decided by the chemical equilibrium, the canonical partition function is

$$Q = \frac{q_A^{N_A}}{N_A!}\frac{q_B^{N_B}}{N_B!} \tag{60}$$

where

$$q_A = g_A e^{-\beta\varepsilon_A}, \qquad q_B = g_B e^{-\beta\varepsilon_B} \tag{61}$$

$$\begin{aligned} \beta A =& -\ln Q = -\left(N_A \ln q_A + N_B \ln q_B - \ln N_A! - \ln N_B!\right) \\ \approx& -N_A \ln q_A - N_B \ln q_B + N_A \ln N_A + N_B \ln N_B - N_A - N_B \end{aligned} \tag{62}$$

$$dA = -SdT - pdV + \mu_A dN_A + \mu_B dN_B \tag{63}$$

$$\therefore \ \beta\mu_A = \left(\frac{\partial \beta A}{\partial N_A}\right)_{T,V,N_B} = -\ln q_A + \ln N_A, \tag{64}$$

$$\beta\mu_B = \left(\frac{\partial \beta A}{\partial N_B}\right)_{T,V,N_A} = -\ln q_B + \ln N_B. \tag{65}$$

$$\because \ \mu_A = \mu_B \tag{66}$$

$$\therefore \ -\ln q_A + \ln N_A = -\ln q_B + \ln N_B \tag{67}$$

Therefore

$$\frac{N_A}{N_B} = \frac{q_A}{q_B} = \frac{g_A e^{-\beta\varepsilon_A}}{g_B e^{-\beta\varepsilon_B}} = \frac{g_A}{g_B}e^{-\beta\Delta\varepsilon} \tag{68}$$

where $\Delta\varepsilon = \varepsilon_A - \varepsilon_B$.

4.16

(a)

$$q = q_A + q_B \tag{69}$$

$$q^N = (q_A + q_B)^N = \sum_{N_A=0}^{N} \binom{N}{N_A} q_A^{N_A} q_B^{N-N_A} = \sum_{N_A=0}^{N} \frac{N!}{(N-N_A)!N_A!} q_A^{N_A} q_B^{N-N_A} = N! \sum_{N_A=0}^{N} \frac{q_A^{N_A} q_B^{N_B}}{N_A!N_B!} \tag{70}$$

Then

$$Q = \frac{q^N}{N!} = \sum_{N_A=0}^{N} \frac{q_A^{N_A} q_B^{N_B}}{N_A!N_B!} \tag{71}$$

By the definition given in the question,

$$-\beta A(N_A, N_B) = \ln\left(\frac{q_A^{N_A} q_B^{N_B}}{N_A!N_B!}\right) \tag{72}$$

$$Q = \sum_{N_A=0}^{N} \exp[-\beta A(N_A, N_B)]. \tag{73}$$

(b)

$$\mu_A = \left(\frac{\partial A}{\partial \langle N_A \rangle}\right)_{T,V,\langle N_B \rangle}, \qquad \mu_B = \left(\frac{\partial A}{\partial \langle N_B \rangle}\right)_{T,V,\langle N_A \rangle} \tag{74}$$

$$\because \ \mu_A = \mu_B, \tag{75}$$

$$\therefore \ \left(\frac{\partial A}{\partial \langle N_A \rangle}\right)_{T,V,N_B} = \left(\frac{\partial A}{\partial \langle N_B \rangle}\right)_{T,V,N_A} \tag{76}$$

$$\because \ \langle N_A \rangle = N - \langle N_B \rangle, \tag{77}$$

$$\therefore \ \left(\frac{\partial A}{\partial \langle N_A \rangle}\right)_{T,V,N_B} = -\left(\frac{\partial A}{\partial \langle N_B \rangle}\right)_{T,V,N_A} \tag{78}$$

Therefore

$$\left(\frac{\partial A}{\partial \langle N_A \rangle}\right)_{T,V,N_B} = \left(\frac{\partial A}{\partial \langle N_B \rangle}\right)_{T,V,N_A} = 0. \tag{79}$$

4.17

(i)

$$Q = \sum_{N_A=0}^{N} \frac{q_A^{N_A} q_B^{N_B}}{N_A!N_B!} = \frac{(q_A + q_B)^N}{N!} \tag{80}$$

$$\langle N_A \rangle = \frac{1}{Q} \sum_{N_A=0}^{N} N_A \frac{q_A^{N_A} q_B^{N_B}}{N_A!N_B!} = \frac{1}{Q} \sum_{N_A=0}^{N} q_A \left(\frac{\partial}{\partial q_A} \frac{q_A^{N_A} q_B^{N_B}}{N_A!N_B!}\right)_{q_B,N} = q_A \left(\frac{\partial}{\partial q_A} \ln Q\right)_{q_B,N} = \frac{q_A N}{q_A + q_B}. \tag{81}$$

Similarly,

$$\langle N_B \rangle = \frac{q_B N}{q_A + q_B}. \tag{82}$$

Thus

$$\frac{\langle N_A \rangle}{\langle N_B \rangle} = \frac{q_A}{q_B}. \tag{83}$$

(ii)

$$\begin{aligned}
\langle N_A^2 \rangle =& \frac{1}{Q} \sum_{N_A=0}^{N} N_A^2 \frac{q_A^{N_A} q_B^{N_B}}{N_A! N_B!} = \frac{1}{Q} \sum_{N_A=0}^{N} q_A \left[\frac{\partial}{\partial q_A} q_A \left(\frac{\partial}{\partial q_A} \frac{q_A^{N_A} q_B^{N_B}}{N_A! N_B!} \right)_{q_B,N} \right]_{q_B,N} \\
=& \frac{1}{Q} q_A \left(\frac{\partial}{\partial q_A} q_A \frac{\partial Q}{\partial q_A} \right)_{q_B,N} = \frac{1}{Q} q_A \left(\frac{\partial}{\partial q_A} Q q_A \frac{\partial \ln Q}{\partial q_A} \right)_{q_B,N} \\
=& \frac{1}{Q} q_A \left(\frac{\partial}{\partial q_A} (Q \langle N_A \rangle) \right)_{q_B,N} \\
=& \frac{1}{Q} q_A \left(\langle N_A \rangle \frac{\partial Q}{\partial q_A} + Q \frac{\partial \langle N_A \rangle}{\partial q_A} \right)_{q_B,N} \\
=& \langle N_A \rangle q_A \left(\frac{\partial \ln Q}{\partial q_A} \right)_{q_B,N} + q_A \left(\frac{\partial \langle N_A \rangle}{\partial q_A} \right)_{q_B,N} \\
=& \langle N_A \rangle^2 + q_A \left(\frac{\partial \langle N_A \rangle}{\partial q_A} \right)_{q_B,N}.
\end{aligned} \tag{84}$$

$$\therefore\ \langle [N_A - \langle N_A \rangle]^2 \rangle = \langle N_A^2 \rangle - \langle N_A \rangle^2 = q_A \left(\frac{\partial \langle N_A \rangle}{\partial q_A} \right)_{q_B,N}. \tag{85}$$

$$\because\ \langle N_A \rangle = \frac{q_A N}{q_A + q_B} \tag{86}$$

$$\therefore\ \left(\frac{\partial \langle N_A \rangle}{\partial q_A} \right)_{q_B,N} = \frac{N}{q_A + q_B} - \frac{q_A N}{(q_A + q_B)^2} = \frac{q_B N}{(q_A + q_B)^2} \tag{87}$$

$$\therefore\ \langle [N_A - \langle N_A \rangle]^2 \rangle = \frac{q_A q_B N}{(q_A + q_B)^2} = \frac{1}{N} \langle N_A \rangle \langle N_B \rangle. \tag{88}$$

4.18

(a) (i)

$$\Xi = \prod_j \left(1 + e^{-\beta(\varepsilon_j - \mu)} \right) \tag{89}$$

Let

$$\lambda = \sqrt{2\pi\beta\hbar^2/m}, \quad z = e^{\beta\mu}, \tag{90}$$

then

$$\beta\varepsilon_j = \beta \frac{\hbar^2 k_j^2}{2m} = \frac{\lambda^2 k_j^2}{4\pi}. \tag{91}$$

$$\begin{aligned}
\beta p V =& \ln \Xi = \sum_j \ln \left[1 + e^{\beta(\mu - \varepsilon_j)} \right] \\
=& \sum_j \ln \left[1 + z e^{-\beta\varepsilon_j} \right] = \sum_j \ln \left[1 + z e^{-\lambda^2 k_j^2 / 4\pi} \right] \\
\approx& \frac{V}{(2\pi)^3} \int d^3k \ln \left[1 + z e^{-\lambda^2 k^2 / 4\pi} \right] \\
=& \frac{V}{(2\pi)^3} \int_0^\infty 4\pi k^2 dk \ln \left[1 + z e^{-\lambda^2 k^2 / 4\pi} \right] \\
=& \frac{V}{2\pi^2} \int_0^\infty dk\ k^2 \ln \left(1 + z e^{-\lambda^2 k^2 / 4\pi} \right)
\end{aligned} \tag{92}$$

Let $x = \frac{\lambda k}{2\sqrt{\pi}}$,

$$\beta p V = \frac{V}{2\pi^2}\left(\frac{2\sqrt{\pi}}{\lambda}\right)^3 \int_0^\infty dx\ x^2 \ln\left(1 + ze^{-x^2}\right) = \frac{V}{\lambda^3}\frac{4}{\sqrt{\pi}}\int_0^\infty dx\ x^2 \ln\left(1 + ze^{-x^2}\right) = \frac{V}{\lambda^3} f_{5/2}(z). \tag{93}$$

$$\therefore\ \beta p = \frac{1}{\lambda^3} f_{5/2}(z). \tag{94}$$

(ii)

$$\rho = \frac{\langle N\rangle}{V} = \frac{1}{V}\left(\frac{\partial \ln \Xi}{\partial \beta\mu}\right)_{\beta,V} = \left(\frac{\partial \beta p}{\partial \beta\mu}\right)_{\beta,V} = \frac{1}{\lambda^3}\frac{df_{5/2}}{dz}\left(\frac{\partial z}{\partial \beta\mu}\right)_{\beta,V} = \frac{1}{\lambda^3}\frac{df_{5/2}}{dz} z \tag{95}$$

$$\because\ \frac{df_{5/2}}{dz} z = z\frac{d}{dz}\sum_{l=1}^{\infty}(-1)^{l+1}\frac{z^l}{l^{5/2}} = z\sum_{l=1}^{\infty}(-1)^{l+1}\frac{lz^{l-1}}{l^{5/2}} = \sum_{l=1}^{\infty}(-1)^{l+1}\frac{z^l}{l^{3/2}} = f_{3/2}(z) \tag{96}$$

$$\therefore\ \rho\lambda^3 = f_{3/2}(z). \tag{97}$$

(b)

$$\langle E\rangle = -\left(\frac{\partial \ln \Xi}{\partial \beta}\right)_{\beta\mu,V} = -\left(\frac{\partial \beta p V}{\partial \beta}\right)_{z,V} = -\left(\frac{\partial}{\partial \beta}\frac{1}{\lambda^3}\right) f_{5/2}(z) V \tag{98}$$

$$\because\ \frac{\partial}{\partial \beta}\frac{1}{\lambda^3} = -\frac{3}{\lambda^4}\frac{\partial \lambda}{\partial \beta} = -\frac{3}{\lambda^4}\left(\frac{2\pi\hbar^2}{m}\right)^{\frac{1}{2}}\frac{1}{2}\beta^{-\frac{1}{2}} = -\frac{3}{2}\frac{1}{\lambda^3\beta} \tag{99}$$

$$\therefore\ \langle E\rangle = \frac{3}{2}\frac{1}{\lambda^3\beta} f_{5/2}(z) V = \frac{3}{2} pV. \tag{100}$$

4.19

(a) Because $\rho\lambda \ll 1$, $z \ll 1$.

$$\rho\lambda^3 = z - \frac{z^2}{2^{3/2}} + \frac{z^3}{3^{3/2}} + \cdots \tag{101}$$

$$(\rho\lambda^3)^2 = z^2 - 2\frac{z^3}{2^{3/2}} + \left(\frac{2}{3^{3/2}} + \frac{1}{2^3}\right) z^4 + \cdots \tag{102}$$

$$\tag{103}$$

Thus

$$z = \rho\lambda^3 + \frac{1}{2^{3/2}}(\rho\lambda^3)^2 + \cdots . \tag{104}$$

(b)

$$\langle n_p\rangle = \frac{1}{1 + ze^{-\beta\varepsilon_p}} \approx \frac{1}{1 + (\rho\lambda^3)e^{-\beta\varepsilon_p}} \approx (\rho\lambda^3)e^{-\beta\varepsilon_p}. \tag{105}$$

(c)

$$\langle |p|\rangle = \frac{V}{h^3}\int_0^\infty 4\pi p^2 dp\ p\langle n_p\rangle = \frac{4\pi V}{h^3}\int_0^\infty dp\ p^3(\rho\lambda^3)e^{-\beta p^2/2m} = \frac{4\pi V}{h^3}\rho\lambda^3\frac{m^2}{\beta^2} = \frac{\rho V h}{\pi\lambda}. \tag{106}$$

Thus

$$\lambda = \frac{\rho V}{\pi}\frac{h}{\langle |p|\rangle}. \tag{107}$$

(d)

$$\begin{aligned}\frac{\beta p}{\rho} =&\frac{1}{\rho\lambda^3} f_{5/2}(z) = \frac{1}{\rho\lambda^3}\left(z - \frac{z^2}{2^{5/2}} + O(z^3)\right)\\ =&\frac{1}{\rho\lambda^3}\left(\rho\lambda^3 + \frac{(\rho\lambda^3)^2}{2^{3/2}} + O[(\rho\lambda^3)^3] - \frac{\rho\lambda^3}{2^{5/2}} + O[(\rho\lambda)^3]\right)\\ =&1 + \frac{\rho\lambda^3}{2^{5/2}} + O[(\rho\lambda^3)^2]. \end{aligned} \tag{108}$$

$\rho\lambda^3$ lead to deviations from the classical idea gas law because the fermions interact with each other abide by the Pauli's principle. When $\rho\lambda^3 \to 0$, the distance between any two fermions become large and the exchange correlation can be ignored.

4.20

(a)

$$\begin{aligned} f_{3/2}(z) =&\frac{4}{\sqrt{\pi}}\int_0^\infty dx\ x^2(z^{-1}e^{x^2}+1)^{-1}\\ =&\frac{4}{\sqrt{\pi}}\int_0^\infty \frac{1}{2}y^{1/2}dy\frac{1}{z^{-1}e^y+1}\\ =&\frac{4}{\sqrt{\pi}}\int_0^\infty \frac{1}{2}y^{1/2}dy\frac{1}{e^{y-\ln z}+1} \end{aligned} \tag{109}$$

We notice that the function $\dfrac{1}{e^{y-a}+1}$ is a logistic function. When $a \gg 1$, the function can be seen as a step function, starting from 1 at $y=0$, sharply dropping to 0 at $y=a$. The integral becomes

$$f_{3/2}(z) \approx \frac{4}{\sqrt{\pi}}\int_0^{\ln z}\frac{1}{2}y^{1/2}dy = \frac{4}{3\sqrt{\pi}}(\ln z)^{3/2}. \tag{110}$$

Thus

$$\ln z = \left(\frac{3\sqrt{\pi}}{4}\rho\lambda^3\right)^{\frac{2}{3}} \tag{111}$$

Let $z = e^{\beta\varepsilon_F}$,

$$\varepsilon_F = \beta^{-1}\left(\frac{3\sqrt{\pi}}{4}\rho\right)^{\frac{2}{3}}\lambda^2 = \left(\frac{3\sqrt{\pi}}{4}\rho\right)^{\frac{2}{3}}\frac{2\pi\hbar^2}{m} = \frac{\hbar^2}{2m}(6\pi^2\rho)^{2/3}. \tag{112}$$

(b)

$$z\frac{df_{5/2}}{dz} = f_{3/2}(z) \tag{113}$$

Higher accuracy of $f_{3/2}(z)$ is needed. Around $y = \ln z$ the logistic function is expand as $\dfrac{1}{2} - \dfrac{1}{4}(y-\ln z)$. Thus we can make an estimate

$$\Delta \sim \int_{\ln z-2}^{\ln z}\frac{1}{2}y^{1/2}\left[\frac{1}{2}+\frac{1}{4}(y-\ln z)\right]dy + \int_{\ln z}^{\ln z+2}\frac{1}{2}y^{1/2}\left[-\frac{1}{2}+\frac{1}{4}(y-\ln z)\right]dy \sim O[(\ln z)^{-1/2}] \tag{114}$$

Thus

$$\begin{aligned} f_{5/2}(z) \approx& \int_1^z\frac{1}{z}\left[f_{3/2}(z)+O[(\ln z)^{-1/2}]\right]dz = \frac{4}{3\sqrt{\pi}}\int_1^z(\ln z)^{3/2}d\ln z + O[(\ln z)^{1/2}]\\ =&\frac{4}{3\sqrt{\pi}}\frac{2}{5}(\ln z)^{5/2} + O[(\ln z)^{1/2}] \end{aligned} \tag{115}$$

$$
\begin{aligned}
\beta p =& \frac{1}{\lambda^3}\left[\frac{8}{15\sqrt{\pi}}(\beta\varepsilon_F)^{5/2} + O[(\ln z)^{1/2}]\right] = \frac{6\pi^2\rho}{(4\pi\beta\varepsilon_F)^{3/2}}\left[\frac{8}{15\sqrt{\pi}}(\beta\varepsilon_F)^{5/2} + O[(\beta\varepsilon_F)^{1/2}]\right] \\
=& \frac{2}{5}\varepsilon_F\rho\beta\left[1 + O[(1/\beta\varepsilon_F)^2]\right]
\end{aligned} \tag{116}
$$

Thus

$$
p = \frac{2}{5}\varepsilon_F\rho\{1 + O[(1/\beta\varepsilon_F)^2]\}. \tag{117}
$$

The non-zero pressure at $T = 0$ is caused by the exchange correlation and is purely a quantum effect.

4.21

(a) Non-conducting electrons:

$$
\rho_n = 2 \times \rho_s\langle n(\varepsilon)\rangle = \frac{2\rho_s}{1 + e^{\beta(-\varepsilon-\mu)}} = \frac{2\rho_s}{1 + e^{-\beta(\varepsilon-\varepsilon_F)}} \tag{118}
$$

Free electrons:

$$
\rho_c = \frac{2}{(2\pi)^3}\int d^3k\frac{1}{1 + e^{\beta(\varepsilon_k-\mu)}} = \frac{2}{(2\pi)^3}\int d^3k\frac{1}{1 + e^{\beta(\varepsilon_k+\varepsilon_F)}} \tag{119}
$$

$$
\therefore\ \rho = 2\rho_s[1 + e^{-\beta(\varepsilon-\varepsilon_F)}] + \frac{2}{(2\pi)^3}\int d^3k[1 + e^{\beta(\varepsilon_k+\varepsilon_F)}] \tag{120}
$$

(b)

$$
p = 2\rho_s - \rho_n = 2\rho_s\frac{1}{e^{\beta(\varepsilon-\varepsilon_F)} + 1} \approx 2\rho_s e^{-\beta\varepsilon+\beta\varepsilon_F} \tag{121}
$$

$$
\begin{aligned}
n =& \frac{2}{(2\pi)^3}\int d^3k\frac{1}{e^{\beta(\varepsilon_k+\varepsilon_F)} + 1} \\
=& \frac{2\cdot 4\pi}{(2\pi)^3}\int_0^\infty k^2dk\frac{1}{e^{\beta\hbar^2k^2/2m+\beta\varepsilon_F} + 1} \\
=& \frac{1}{\pi^2}\left(\frac{2\sqrt{\pi}}{\lambda}\right)^3\int_0^\infty dx\frac{x^2}{e^{x^2+\beta\varepsilon_F} + 1} \\
=& \frac{8}{\pi^{1/2}\lambda^3}\left(-\frac{\pi^{1/2}}{4}\right)f_{3/2}(-e^{-\beta\varepsilon_F}) \\
\approx& \frac{8}{\pi^{1/2}\lambda^3}\left(-\frac{\pi^{1/2}}{4}\right)(-e^{-\beta\varepsilon_F}) \\
=& \frac{2}{\lambda^3}e^{-\beta\varepsilon_F}
\end{aligned} \tag{122}
$$

$$
pn = 2\rho_s e^{-\beta\varepsilon+\beta\varepsilon_F}\cdot\frac{2}{\lambda^3}e^{-\beta\varepsilon_F} = \frac{4\rho_s}{\lambda^3}e^{-\beta\varepsilon}. \tag{123}
$$

4.22

Adsorbed atoms:

$$
\rho_{ad} = \rho_s\langle n(\varepsilon)\rangle = \rho_s e^{-\beta(-\varepsilon-\mu)} \tag{124}
$$

The chemical potential for the gas:

$$\begin{aligned}\beta\mu =& \ln N - \ln \sum_j e^{-\beta\varepsilon_j} \\ =& \ln N - \ln \frac{V}{(2\pi)^3} \int d^3k e^{-\beta\hbar^2 k^2/2m} \\ =& \ln N - \ln \left[\frac{V}{(2\pi)^3} 4\pi \int_0^\infty k^2 dk e^{-\lambda^2 k^2/4\pi}\right] \\ =& \ln N - \ln \left[\frac{V}{(2\pi)^3} 4\pi \left(\frac{2\pi^{1/2}}{\lambda}\right)^3 \int_0^\infty dx\ x^2 e^{-x^2}\right] \\ =& \ln N - \ln \left[\frac{V}{(2\pi)^3} 4\pi \left(\frac{2\pi^{1/2}}{\lambda}\right)^3 \frac{\pi^{1/2}}{4}\right] \\ =& \ln N - \ln \left(\frac{V}{\lambda^3}\right) \\ =& \ln \rho_g \lambda^3 \end{aligned} \tag{125}$$

Thus for free atoms:

$$\rho_g = \lambda^{-3} e^{\beta\mu} \tag{126}$$

Thus

$$\frac{\rho_{ad}}{\rho_g} = \lambda^3 \rho_s e^{\beta\varepsilon} \tag{127}$$

The results are similar because the models are both a problem of gas-lattice equilibrium.

4.23

(a) Because by definition

$$C_V/k_B = \beta^2 \langle (\Delta E)^2 \rangle = -\beta^2 \left(\frac{\partial \langle E \rangle}{\partial \beta}\right)_{N,V} = \beta^2 \left(\frac{\partial^2 \ln Q}{\partial \beta^2}\right)_{N,V} \tag{128}$$

If the energy eigenvalues of a system can be written as

$$E = E_A + E_B + E_C \tag{129}$$

$$\begin{aligned} Q =& \sum_v e^{-\beta E^{(v)}} = \sum_v e^{-\beta E_A^{(v)}} e^{-\beta E_B^{(v)}} e^{-\beta E_C^{(v)}} \\ =& \left(\sum_v e^{-\beta E_A^{(v)}}\right) \left(\sum_v e^{-\beta E_B^{(v)}}\right) \left(\sum_v e^{-\beta E_C^{(v)}}\right) \\ =& Q_A Q_B Q_C \end{aligned} \tag{130}$$

$$\ln Q = \ln Q_A + \ln Q_B + \ln Q_C \tag{131}$$

Thus

$$\begin{aligned} C_V/k_B =& \beta^2 \left(\frac{\partial^2 \ln Q_A}{\partial \beta^2}\right)_{N,V} + \beta^2 \left(\frac{\partial^2 \ln Q_B}{\partial \beta^2}\right)_{N,V} + \beta^2 \left(\frac{\partial^2 \ln Q_C}{\partial \beta^2}\right)_{N,V} \\ =& C_V^{(A)}/k_B + C_V^{(B)}/k_B + C_V^{(C)}/k_B. \end{aligned} \tag{132}$$

Because for zero point energy $\langle(\Delta E)^2\rangle = 0$, $C_V^{ZP}/k_B = 0$.
(b) Since the zero point energy does not effect the heat capacity, we can select the ground state energy as a reference.

$$q_{\text{ele}} = g_0 + g_1 e^{-\beta\varepsilon_1'} + g_2 e^{-\beta\varepsilon_2'} \tag{133}$$

$$\begin{aligned} C_V^{(\text{ele})}/k_B =& \beta^2 \left(\frac{\partial^2 \ln Q}{\partial \beta^2}\right)_{N,V} = N\beta^2 \left(\frac{\partial^2 \ln q}{\partial \beta^2}\right)_{N,V} = \frac{N\beta^2}{q}\left[\frac{\partial^2 q}{\partial \beta^2} - \frac{1}{q}\left(\frac{\partial q}{\partial \beta}\right)^2\right] \\ =& \frac{N\beta^2}{q}\left[\left(g_1 {\varepsilon_1'}^2 e^{-\beta\varepsilon_1'} + g_2 {\varepsilon_2'}^2 e^{-\beta\varepsilon_2'}\right) - \frac{1}{q}\left(g_1\varepsilon_1' e^{-\beta\varepsilon_1'} + g_2\varepsilon_2' e^{-\beta\varepsilon_2'}\right)^2\right] \end{aligned} \tag{134}$$

(c) neglect the second excited state, and select the ground state as a reference.

$$e^{-\beta\varepsilon_1'} \sim e^{-50000/300} = e^{-166} \approx 10^{-72} \tag{135}$$

$$q_{\text{ele}} \approx g_0, \tag{136}$$

$$C_V^{(\text{ele})}/Nk_B \approx \frac{\beta^2}{g_0}\left(g_1\varepsilon_1' e^{-\beta\varepsilon_1'}\right) \sim \beta\frac{g_1}{g_0}10^{-70} \tag{137}$$

Therefore can be neglected. Neglect all the excited states gives $C_V^{(\text{ele})} = 0$. (d) The excited energy states are hardly populated, thus will not effect the entropy much. Suppose electrons only populate on the ground state.

$$S_{\text{ele}} = \frac{E_{\text{ele}} - A_{\text{ele}}}{T} = \frac{\varepsilon_0 + (\ln g_0 - \beta\varepsilon_0)/\beta}{T} = k_B \ln g_0 \tag{138}$$

This result is quite reasonable because the electronic ground state provide $\Omega_{\text{ele}} = g_0$.

4.24

$$q = q_{\text{trans}} \cdot q_{\text{rot}} \cdot q_{\text{vib}} \cdot g_0 e^{-\beta\varepsilon_0} \cdot g_n \tag{139}$$

$$C_V/Nk_B = C_V^{(\text{trans})}/Nk_B + C_V^{(\text{rot})}/Nk_B + C_V^{(\text{vib})}/Nk_B \tag{140}$$

$$C_V^{(\text{trans})}/Nk_B = \frac{3}{2} \tag{141}$$

$$q_{\text{rot}} = \frac{T}{\theta_{\text{rot}}}, \quad \theta_{\text{rot}} = \frac{\hbar^2}{2I_0 k_B} \tag{142}$$

$$C_V^{(\text{rot})}/Nk_B = \beta^2\left(\frac{\partial^2 \ln q_{\text{rot}}}{\partial\beta^2}\right)_{N,V} = -\beta^2\frac{\partial^2 \ln\beta}{\partial\beta^2} = 1. \tag{143}$$

$$q_{\text{vib}} = [\exp(\beta\hbar\omega_0/2) - \exp(-\beta\hbar\omega_0/2)]^{-1} \tag{144}$$

$$C_V^{(\text{vib})}/Nk_B = \beta^2\left(\frac{\partial^2 \ln q_{\text{vib}}}{\partial\beta^2}\right)_{N,V} = \left(\frac{\beta\hbar\omega_0}{2}\right)^2 \frac{1}{e^{\beta\hbar\omega_0/2} - e^{-\beta\hbar\omega_0/2}} \tag{145}$$

$$C_V^{(\text{vib})}/Nk_B \approx 0.0798 \tag{146}$$

Because for non-interacting gas particles,

$$C_p - C_V = Nk_B \tag{147}$$

$$C_p/Nk_B = \frac{3}{2} + 1 + 1 + 0.00798 = 3.50798 \tag{148}$$

$$c_p = 29.167\,\text{J}\,\text{mol}^{-1}\,\text{K}^{-1} = 6.968\,\text{cal}\,\text{mol}^{-1}\,\text{K}^{-1}. \tag{149}$$

4.25

For the chemical reaction $I_2(g)=2\,I(g)$, Denote I_2 by 1 and I by 2.

$$K=\left(\frac{q_1^{(\mathrm{int})}}{\lambda_1^3}\right)^{-1}\left(\frac{q_2^{(\mathrm{int})}}{\lambda_2^3}\right)^2=\frac{q_2^{(\mathrm{int})2}}{q_1^{(\mathrm{int})}}\left(\frac{\lambda_1}{\lambda_2^2}\right)^3 \tag{150}$$

$$q_1^{(\mathrm{int})}=g_0e^{-\beta\varepsilon_0}(2I_I+1)^2q_{\mathrm{rot}}q_{\mathrm{vib}}/2 \tag{151}$$

$$q_{\mathrm{rot}}=\frac{T}{\theta_{\mathrm{rot}}},\qquad q_{\mathrm{vib}}=\frac{e^{-\theta_{\mathrm{vib}}/2T}}{1+e^{-\theta_{\mathrm{vib}}/T}} \tag{152}$$

$$q_2^{(\mathrm{int})}=g_0'e^{-\beta\varepsilon_0'}(2I_I+1) \tag{153}$$

$\theta_{rot}=0.054\,\mathrm{K}$, $\theta_{\mathrm{vib}}=310\,\mathrm{K}$, $\lambda_2^2/\lambda_1=\sqrt{\frac{4\pi\beta\hbar^2}{m_I}}$, $M_I=127\times10^{-3}\,\mathrm{kg/mol}$, $\Delta E=151\,\mathrm{kJ/mol}$. $g_0=1$, $g_0'=2$.

$$\begin{aligned}\frac{q_2^{(\mathrm{int})2}}{q_1^{(\mathrm{int})}}&=\frac{2{g_0'}^2}{g_0}e^{-\beta(2\varepsilon_0'-\varepsilon_0)}\frac{\theta_{\mathrm{rot}}}{T}2\cosh\left(\frac{\theta_{\mathrm{vib}}}{2T}\right)=\frac{4g_0'}{g_0}e^{-\frac{\Delta E}{RT}}\frac{\theta_{\mathrm{rot}}}{T}\cosh\left(\frac{\theta_{\mathrm{vib}}}{2T}\right)\\&=1.132\times10^{-11}\end{aligned} \tag{154}$$

$$\frac{\lambda_2^2}{\lambda_1}=\sqrt{\frac{4\pi\beta\hbar^2}{m_I}}=6.928\times10^{-12}\,\mathrm{m} \tag{155}$$

$$K=3.404\times10^{22}\,\mathrm{m}^{-3} \tag{156}$$

$$K^{\ominus}=\frac{K}{c^{\ominus}}=\frac{K}{N_A/(1\times10^{-3}\,\mathrm{m}^3)}=5.653\times10^{-5}. \tag{157}$$

4.26

(a)

$$\begin{aligned}\Xi&=\sum_v e^{-\beta E^{(v)}+\beta\mu N^{(v)}}=\sum_N e^{\beta\mu N}\sum_{v,\langle N^{(v)}\rangle=N}e^{-\beta E^{(v)}}\\&=\sum_N e^{\beta\mu N}Q_N=\sum_N e^{\beta\mu N}\frac{1}{N!}q^N=\sum_N\frac{1}{N!}(zq)^N=e^{zq}\end{aligned} \tag{158}$$

where $z=e^{\mu\beta}$ and

$$q=\sum_j e^{-\beta\varepsilon_j}=\frac{V}{(2\pi)^3}\int d^3k e^{-\beta\hbar^2k^2/2m}=\frac{V}{\lambda^3} \tag{159}$$

Therefore

$$\Xi=\exp\left(\frac{zV}{\lambda^3}\right) \tag{160}$$

(b)

$$\beta pV=\ln\Xi=\frac{zV}{\lambda^3} \tag{161}$$

$$\langle N\rangle=\left(\frac{\partial\ln\Xi}{\partial\beta\mu}\right)_{V,T}=\frac{zV}{\lambda^3} \tag{162}$$

Therefore

$$p=\frac{z}{\beta\lambda^3}=\frac{\langle N\rangle}{\beta V}=\frac{\rho}{\beta}. \tag{163}$$

(c)

$$\langle(\delta N)^2\rangle = \left(\frac{\partial\langle N\rangle}{\partial\beta\mu}\right)_{V,T} = \frac{zV}{\lambda^3} = \langle N\rangle \tag{164}$$

$$\therefore\ \frac{\sqrt{\langle(\delta\rho)^2\rangle}}{\rho} = \frac{\sqrt{\langle(\delta N)^2\rangle}}{\langle N\rangle} = \frac{1}{\langle N\rangle^{1/2}}. \tag{165}$$

For 1cc ($V = 1\times10^{-6}\,\mathrm{m}^3$) gas at STP ($T = 273.15\,\mathrm{K}$, $p = 1\times10^5\,\mathrm{Pa}$), $N = 2.65\times10^{19}$.

$$\frac{\sqrt{\langle(\delta\rho)^2\rangle}}{\langle\rho\rangle} = 1.94\times10^{-10}. \tag{166}$$

(d) Suppose in the observation, the density is normally distributed, $\dfrac{\rho-\langle\rho\rangle}{\langle\rho\rangle} \sim N[0,(1.94\times10^{-10})^2]$.

For $X \sim N(0,1)$,

$$P(|X|>x) = 2[1-\Phi(x)] = 1-\mathrm{erf}\left(\frac{x}{\sqrt{2}}\right) \tag{167}$$

The expansion when $x\to\infty$ is

$$P(|X|>x) \approx \sqrt{\frac{2}{\pi}}\frac{1}{x}e^{-x^2/2} \tag{168}$$

Then the probability of observing a spontaneous fluctuation for which the instantaneous density differs from the mean by $1/10^6$ is

$$P(|X|>1\times10^{-6}/1.94\times10^{-10}) \approx 10^{-5.76\times10^6} \tag{169}$$

which means very unlikely.