Homework 04

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4.1

4.1.1

$$\mathscr{E}_{max} \leq \mathscr{S} \leq \mathscr{N}\mathscr{E}_{max}, \tag{4.1.1}$$

$$\frac{1}{N}\log(\mathscr{E}_{max}) \leq \frac{1}{N}\log(\mathscr{S}) \leq \frac{1}{N}\log(\mathscr{N}\mathscr{E}_{max}), \tag{4.1.2}$$

$$\varphi_{max} \leq \frac{1}{N}\log(\mathscr{S}) \leq \frac{1}{N}\log(\mathscr{N}) + \varphi_{max}. \tag{4.1.3}$$

4.1.2

In the limit as $N \to \infty$, $\mathscr{N} \to N^p$. Hence

$$\lim_{N\to\infty}\frac{1}{N}\log(N^p) = \lim_{N\to\infty}\frac{p}{N}\log(N) = 0. \tag{4.1.4}$$

Therefore,

$$\lim_{N\to\infty}\frac{1}{N}\log(\mathscr{S}) \to \varphi_{max} \leq \lim_{N\to\infty}\frac{1}{N}\log(\mathscr{S}) \leq \varphi_{max} + \lim_{N\to\infty}\frac{1}{N}\log(\mathscr{N}), \tag{4.1.5}$$

$$\varphi_{max} \leq \lim_{N\to\infty}\frac{1}{N}\log(\mathscr{S}) \leq \varphi_{max}, \tag{4.1.6}$$

$$\lim_{N\to\infty}\frac{1}{N}\log(\mathscr{S}) = \varphi_{max}. \tag{4.1.7}$$

4.2

$$\frac{\mathrm{d}p_i}{\mathrm{d}t} = \sum_j \omega_{ij}(p_j - p_i). \tag{4.2.1}$$

$$S = -\sum_i p_i \log(p_i), \tag{4.2.2}$$

$$\frac{\mathrm{d}S}{\mathrm{d}t} = -\sum_i \frac{\mathrm{d}p_i}{\mathrm{d}t}\log(p_i) - \frac{\mathrm{d}}{\mathrm{d}t}\left(\sum_i p_i\right), \tag{4.2.3}$$

$$= -\sum_i \frac{\mathrm{d}p_i}{\mathrm{d}t}\log(p_i), \tag{4.2.4}$$

$$= \sum_{i,j} \omega_{ij}(p_i - p_j)\log(p_i). \tag{4.2.5}$$

If $p_i = p_j$, $\mathrm{d}S/\mathrm{d}t = 0$. Thus,

$$\frac{\mathrm{d}S}{\mathrm{d}t} = \sum_{i,j} \omega_{ij}\frac{1}{2}\Big((p_i - p_j)\log(p_i) - (p_i - p_j)\log\big(p_j\big)\Big), \tag{4.2.6}$$

$$= \sum_{i,j} \frac{\omega_{ij}}{2}(p_i - p_j)\log\left(\frac{p_i}{p_j}\right). \tag{4.2.7}$$

If $p_i > p_j$, then $(p_i - p_j) > 0$ and $\log\left(\frac{p_i}{p_j}\right) > 0$. Lastly, if $p_j > p_i$, then $(p_i - p_j) < 0$ and $\log\left(\frac{p_i}{p_j}\right) < 0$, so their product is positive. Therefore,

$$\frac{\mathrm{d}S}{\mathrm{d}t} \geq 0. \tag{4.2.8}$$

4.3

4.3.1

The definition of the grand partition function is

$$\mathscr{Z} = \sum_{N=0}^{\infty} z^N Z_N, \tag{4.3.1}$$

where $z = e^{\beta\mu}$ is the fugacity, and Z_N is the canonical partition function for the system with N particles.

$$\mathscr{Z}(T,\mu,V) = \sum_{N=0}^{\infty} e^{\beta\mu N}\frac{V^N}{N!(2\pi\hbar)^{3N}}\left(\int \mathrm{d}^3\mathbf{p}\, e^{-\beta\frac{p^2}{2m}}\right)^N, \tag{4.3.2}$$

$$= \sum_{N=0}^{\infty} e^{\beta\mu N}\frac{V^N}{N!}\left(\frac{m}{2\pi\hbar^2\beta}\right)^{3N/2}. \tag{4.3.3}$$

Let

$$l_Q = \sqrt{\frac{2\pi\hbar^2\beta}{m}}. \tag{4.3.4}$$

Then

$$\mathscr{Z}(T,\mu,V) = \sum_{N=0}^{\infty} \frac{e^{\beta\mu N}}{N!}\frac{V^N}{l_Q^{3N}} = \sum_{N=0}^{\infty} \frac{z^N}{N!}\frac{V^N}{l_Q^{3N}} = e^{zV/l_Q^3}. \tag{4.3.5}$$

4.3.2

$$e^{-\beta\mathscr{G}} = \mathscr{Z}, \tag{4.3.6}$$

where $\mathscr{G}$ is the grand potential. Solving for $\mathscr{G}$ gives

$$\mathscr{G}(T,\mu,V) = -\frac{1}{\beta}\log(\mathscr{Z}) = -\frac{e^{\beta\mu}V}{\beta l_Q^3}. \tag{4.3.7}$$

By definition of pressure,

$$P = -\frac{\partial \mathscr{G}}{\partial V}, \tag{4.3.8}$$

$$= \frac{e^{\beta\mu}}{\beta l_Q^3}. \tag{4.3.9}$$

Additionally,

$$N = \langle N \rangle = -\frac{\partial \mathscr{G}}{\partial \mu}, \tag{4.3.10}$$

$$= \frac{e^{\beta\mu}V}{l_Q^3}. \tag{4.3.11}$$

Hence

$$PV = \frac{e^{\beta\mu}}{\beta l_Q^3}\frac{l_Q^3 N}{e^{\beta\mu}}, \tag{4.3.12}$$

$$PV = \frac{N}{\beta}. \qquad \checkmark \tag{4.3.13}$$

4.3.3

The Poisson distribution is defined as

$$P(k) \equiv \frac{\lambda^k e^{-\lambda}}{k!}, \tag{4.3.14}$$

for some random variable, $X = k$, where λ is the expectation value of the random variable. In the case of the problem, the random variable is N, and the expectation value of this variable was found to be $\lambda = \langle N \rangle = zV/l_Q^3$.

To show that the particle number is described by the Poisson distribution, start from the probability of finding N particles in the system:

$$P(N) = \frac{z^N Z_N}{\mathscr{Z}} = \frac{1}{\mathscr{Z}}\frac{(zZ_1)^N}{N!}, \tag{4.3.15}$$

$$= \frac{1}{\mathscr{Z}}\frac{e^{\beta\mu}V}{N! l_Q^3}. \tag{4.3.16}$$

Substituting in 4.3.5 and 4.3.11 gives

$$P(N) = \frac{\langle N \rangle}{N!} e^{-zV/l_Q^3} = \frac{\langle N \rangle\, e^{-\langle N \rangle}}{N!}. \tag{4.3.17}$$

Hence, the distribution of particle numbers is Poissonian.

4.4

4.4.1

The Helmholtz free energy, A is given by

$$A = -\frac{\log Z_N}{\beta}. \tag{4.4.1}$$

The partition function for the system is given by

$$\begin{aligned} Z_N =& \frac{1}{N!(2\pi\hbar)^{6N}} \left(\int e^{-\frac{\beta}{2m}(p_1^2+p_2^2)} e^{-\frac{\beta K}{2}|\mathbf{r}_1-\mathbf{r}_2|^2} \, \mathrm{d}^3 p_1 \, \mathrm{d}^3 p_2 \, \mathrm{d}^3 r_1 \, \mathrm{d}^3 r_2 \right)^N, & (4.4.2) \\ =& \frac{1}{N!(2\pi\hbar)^{3N}} \left(\frac{2\pi m}{\beta} \right)^{3N} \left(\int e^{-\frac{\beta K}{2}|\mathbf{r}_1-\mathbf{r}_2|^2} \, \mathrm{d}^3 r_1 \, \mathrm{d}^3 r_2 \right)^N, & (4.4.3) \\ =& \frac{1}{N! l_Q^{6N}} \left(\int e^{-\frac{\beta K}{2}|\mathbf{r}_1-\mathbf{r}_2|^2} \, \mathrm{d}^3 r_1 \, \mathrm{d}^3 r_2 \right)^N. & (4.4.4) \end{aligned}$$

Let $\mathbf{r} = \mathbf{r}_1 - \mathbf{r}_2$ and $\mathbf{R} = \frac{1}{2}(\mathbf{r}_1 + \mathbf{r}_2)$. Then the integral becomes

$$\begin{aligned} Z_N =& \frac{1}{N! l_Q^{6N}} \left(\int \mathrm{d}^3 R \int e^{-\frac{\beta K}{2}\mathbf{r}^2} \, \mathrm{d}^3 r \right)^N, & (4.4.5) \\ =& \frac{V^N}{N! l_Q^{6N}} \sqrt{\frac{2\pi}{\beta K}}^{3N}. & (4.4.6) \end{aligned}$$

The Helmholtz free energy, then, is

$$A = -\frac{1}{\beta} \log Z_N = -\frac{N}{\beta} \log\left(\frac{V}{N! l_Q^6} \right) - \frac{3N}{2\beta} \log\left(\frac{2\pi}{\beta K} \right) \tag{4.4.7}$$

4.4.2

By the equipartition theorem,

$$C_v = \frac{9}{2} N k_B, \tag{4.4.8}$$

since there are nine different ways to put energy into the molecule:

1. three directions of relative translation,
2. three directions of relative velocities, and
3. three directions of coupled velocity.

4.4.3

The mean square molecular diameter is given by

$$\left\langle |\mathbf{r}_1 - \mathbf{r}_2|^2 \right\rangle = \left\langle r^2 \right\rangle = \frac{\int r^2 e^{-\frac{\beta K}{2} r^2} \, \mathrm{d}^3 r}{\int e^{-\frac{\beta K}{2} r^2} \, \mathrm{d}^3 r}. \tag{4.4.9}$$

One notices that the numerator is given by

$$\int r^2 e^{-\frac{\beta K}{2} r^2}\, \mathrm{d}^3 r = -2\frac{\partial}{\partial(\beta K)}\left(\int r^2 e^{-\frac{\beta K}{2} r^2}\, \mathrm{d}^3 r\right), \tag{4.4.10}$$

$$= -2\frac{\partial}{\partial(\beta K)}\sqrt{\frac{2\pi}{\beta K}}^3, \tag{4.4.11}$$

$$= \frac{3}{2}\sqrt{\frac{(2\pi)^3}{(\beta K)^5}}. \tag{4.4.12}$$

Hence,

$$\langle r^2 \rangle = \frac{3}{2}\sqrt{\frac{(2\pi)^3}{(\beta K)^5}}\sqrt{\frac{\beta K}{2\pi}}^3 = \frac{3}{\beta K}. \tag{4.4.13}$$

4.5

4.5.1

$$\langle \Psi | A | \Psi \rangle = \left(\sum_{\beta,j} C^*_{\beta j} \langle \beta | \otimes \langle j | \right)\left(\sum_{\alpha,i} C_{\alpha i}(A|\alpha\rangle) \otimes |i\rangle\right), \tag{4.5.1}$$

$$= \sum_{\alpha,\beta,i,j} C^*_{\beta j} C_{\alpha i} \langle \beta | A | \alpha \rangle \otimes \langle j | i \rangle, \tag{4.5.2}$$

$$= \sum_{\alpha,\beta,i} C^*_{\beta i} C_{\alpha i} \langle \beta | A | \alpha \rangle, \tag{4.5.3}$$

$$= \sum_{\alpha,\beta} \rho_{\alpha\beta} \langle \beta | A | \alpha \rangle, \tag{4.5.4}$$

$$= \mathrm{Tr}_s (A\rho). \tag{4.5.5}$$

$$\tag{4.5.6}$$

4.5.2

The density operator is Hermitian:

$$\rho^\dagger = \rho^*_{\beta\alpha} = \sum_i C^*_{\beta i} C_{\alpha i}, \tag{4.5.7}$$

$$= \sum_i C_{\alpha i} C^*_{\beta i}, \tag{4.5.8}$$

$$= \rho_{\alpha\beta}. \tag{4.5.9}$$

Since $\rho_{\alpha\beta}$ is hermitian, it can be written as a linear combination of eigenvectors and their respective eigenvalues:

$$\rho_{\alpha\beta} = \langle \alpha | \left(\sum_k \lambda_k |\rho_k\rangle\langle\rho_k|\right) |\beta\rangle, \tag{4.5.10}$$

$$= \sum_k \lambda_k \langle \alpha | \rho_k \rangle \langle \rho_k | \beta \rangle \tag{4.5.11}$$

4.5.3

The eigenvalues all sum to unity:

$$\langle\Psi|\Psi\rangle = \mathrm{Tr}(\rho) = 1 = \sum_n \langle n| \left(\sum_k \lambda_k |\rho_k\rangle\langle\rho_k| \right) |n\rangle , \quad (4.5.12)$$

$$= \sum_n \sum_k \lambda_k \langle n|\rho_k\rangle \langle\rho_k|n\rangle , \quad (4.5.13)$$

$$= \sum_n \sum_k \lambda_k \langle\rho_k|n\rangle \langle n|\rho_k\rangle , \quad (4.5.14)$$

$$= \sum_k \lambda_k \langle\rho_k|\rho_k\rangle , \quad (4.5.15)$$

$$= \sum_k \lambda_k . \quad (4.5.16)$$

The eigenvalues are between zero and one:

$$\forall |\psi\rangle , \langle\psi|\rho|\psi\rangle = \sum_k \lambda_k \big|\langle\psi|\rho_k\rangle\big|^2 \geq 0. \quad (4.5.17)$$

$$\therefore \langle\rho_n|\rho|\rho_n\rangle = \sum_k \lambda_k \big|\langle\rho_n|\rho_k\rangle\big|^2, \quad (4.5.18)$$

$$= \lambda_n \geq 0. \quad (4.5.19)$$

Additionally, since the sum of eigenvalues is equal to unity, all eigenvalues must be less than one.