Solutions to homework assignment 3

2.7 (i) From class (and Pathria, p70) the no. of ways to put energy E into N harmonic oscillators is

$$\Omega(E) = \frac{(j+N-1)!}{j!\,(N-1)!}, \quad j = \frac{E-\frac{N}{2}\hbar\omega}{\hbar\omega}$$

For large j, asymptotically, $(j \gg N)$

$$\ln\frac{(j+N-1)!}{j!} = (j+N-1)\ln(j+N-1) - (j+N-1) - j\ln j + j$$

$$= (j+N-1)[\ln j + \underbrace{\ln(1+\tfrac{N-1}{j})}_{\approx \frac{N-1}{j}}] - N + 1 - j\ln j$$

$$= j\cancel{\ln j} + (N-1)\ln j + \cancel{N-1} - \cancel{N} \cancel{+1} - \cancel{j\ln j} + \frac{(N-1)^2}{j} \to 0$$

$$= (N-1)\ln j$$

So $\Omega(E) \approx \dfrac{j^{N-1}}{(N-1)!}, \quad j \approx \dfrac{E}{\hbar\omega}$

$$\Sigma(E) = \sum_{E' \le E} \Omega(E'), \quad \frac{\Delta\Sigma}{\Delta E} = \frac{\Delta\Sigma}{\Delta j}\frac{\Delta j}{\Delta E} = \frac{\Omega(E)}{\hbar\omega} = \frac{E^{N-1}}{(N-1)!(\hbar\omega)^N}$$

$$\Gamma_{QM} = \frac{\Delta\Sigma}{\Delta E}\Delta = \frac{E^{N-1}\Delta}{(N-1)!(\hbar\omega)^N}$$

(ii) Volume in phase space is

$$\Sigma(E) = \int_{\sum_{i=1}^{N}\left(\frac{kq_i^2}{2} + \frac{p_i^2}{2m}\right) \le E} \prod_{i=1}^{N} dq_i\, dp_i = \frac{(2\pi)^N}{N!}\left(\frac{m}{k}\right)^{\frac{N}{2}} E^N = \frac{\pi^N}{N!}\frac{E^N}{\omega^N}, \quad \omega = \sqrt{\frac{k}{m}}$$

let $x_i^2 = \frac{kq_i^2}{2}$, $y_i^2 = \frac{p_i^2}{2m}$, $R^2 = \sum_1^N (x_i^2 + y_i^2)$

use (7a) in Appendix C.

$$\Gamma_{class} = \frac{d\Sigma}{dE}\Delta = \frac{(2\pi)^N E^{N-1}}{(N-1)!\,\omega^N}. \quad \frac{\Gamma_{class}}{\Gamma_{QM}} = \frac{(\hbar\omega)^N \cdot (2\pi)^N}{\omega^N} = h^N$$

3.14 $\quad AB \rightleftarrows A + B$

$\quad\quad n_{AB} \quad n_A \quad n_B$

$\frac{\partial}{\partial N_A} [N_A (1-\ln N_A)]$

$= -\ln N_A + N_A(-\frac{1}{N_A})$

Derive law of mass action

$$\frac{n_{AB}}{n_A n_B} = V \frac{f_{AB}}{f_A f_B} = K(T)$$

equilibrium const. of reaction

f's are single-particle partition functions $f = Q_1(V,T) = \hat{f}(T)V$

$$Q_{\text{mixture}}(N_A, N_B, N_{AB}, V, T) = \frac{f_A^{N_A} f_B^{N_B} f_{AB}^{N_{AB}}}{N_A!\, N_B!\, N_{AB}!}$$

$$A = -kT \ln Q = -kT\,[\,N_A \ln f_A + N_B \ln f_B + N_{AB} \ln f_{AB} - N_A \ln N_A + N_A - N_B \ln N_B + N_B - N_{AB}\ln N_{AB} + N_{AB}]$$

Maximize under constraints $\quad N_A + N_{AB} = \text{const},\ N_B + N_{AB} = \text{const}.$

Use Lagrange mult.

$$A + \lambda_1 (N_A + N_{AB} - C_A) + \lambda_2 (N_B + N_{AB} - C_B)$$

$$\left.\begin{aligned} \frac{\partial A}{\partial N_A} &= -kT[\ln f_A - \ln N_A] + \lambda_1 = 0 \\ \frac{\partial A}{\partial N_B} &= -kT[\ln f_B - \ln N_B] + \lambda_2 = 0 \end{aligned}\right\} -kT\left[\ln\left(\frac{f_A}{N_A}\frac{f_B}{N_B}\right)\right] + \lambda_1 + \lambda_2 = 0$$

$$\frac{\partial A}{\partial N_{AB}} = -kT[\ln f_{AB} - \ln N_{AB}] + \lambda_1 + \lambda_2 = 0, \quad \lambda_1 + \lambda_2 = kT\left[\ln \frac{f_{AB}}{N_{AB}}\right]$$

$$\frac{\partial A}{\partial \lambda_1} = N_A + N_{AB} - C_A = 0$$

$$\frac{\partial A}{\partial \lambda_2} = N_B + N_{AB} - C_B = 0$$

$n_i = \frac{N_i}{V}, \quad f_i \propto V$

so $\ln \frac{f_{AB}}{N_{AB}} = \ln \frac{f_A f_B}{N_A N_B}$, or $\frac{N_{AB}}{N_A N_B} = \frac{f_{AB}}{f_A f_B}$, or $\frac{V}{V^2}\frac{n_{AB}}{n_A n_B} = \frac{\hat{f}_{AB}}{\hat{f}_A \hat{f}_B V}$

So $\frac{n_{AB}}{n_A n_B} = K(T)$, only

Alternative solution to 3.14

General case $A_1 A_2 \cdots A_r \rightleftarrows B_1 B_2 \cdots B_s$

$n_1 A_1 + n_2 A_2 + \cdots + n_r A_r \rightleftarrows m_1 B_1 + m_2 B_2 + \cdots + m_s B_s$

Chemical notation $[A_i] = A_i \frac{\text{moles}}{\text{unit volume}}$

$$\frac{\prod_1^r [A_i]^{n_i}}{\prod_1^s [B_j]^{m_j}} = K(T) \text{ only}$$

Kinetic equilibrium: As many reactions go $\rightarrow$ as go $\leftarrow$.

To go $\rightarrow$, need multiple collision with $n_1 A_1, n_2 A_2, \ldots$.

Freq. of such collisions is $\propto [A_1]^{n_1} [A_2]^{n_2} \cdots [A_r]^{n_r}$

No. of transitions/unit time has factors of flux that depend on velocities of A_i and hence of T, and a factor dependent on the temperature

$|T|^2$, where $T_{A_1 \cdots A_r \to B_1 \cdots B_s} = T_{B_1 \cdots B_s \to A_1 \cdots A_r}$ due to time (motion) reversal. Detailed balance. The transition amplitudes are ind. of temperature. So

Freq. $\rightarrow$ is $\prod_1^r [A_i]^{n_i} K'(T)$

Freq. $\leftarrow$ is $\prod_1^s [B_j]^{m_j} K''(T)$.

So get law of mass action w. $K(T) = \frac{K''(T)}{K'(T)}$

3.18. We start with eqn. (3.6.2), viz.

$$\frac{\partial U}{\partial \beta} = -\frac{\sum_r E_r^2 e^{-\beta E_r}}{\sum_r e^{-\beta E_r}} + U^2 , \tag{1}$$

and differentiate it with respect to β, keeping the E_r fixed. We get

$$\frac{\partial^2 U}{\partial \beta^2} = \langle E^3 \rangle - \langle E^2 \rangle \langle E \rangle + 2U \frac{\partial U}{\partial \beta} .$$

Substituting for $(\partial U / \partial \beta)$ from eqn. (1), we get

$$\frac{\partial^2 U}{\partial \beta^2} = \langle E^3 \rangle - 3 \langle E^2 \rangle U + 2U^3 ,$$

which is precisely equal to $\langle (E-U)^3 \rangle$. As for $\partial^2 U / \partial \beta^2$, we note that, since

$$\left(\frac{\partial U}{\partial \beta}\right)_{E_r} = -kT^2 \left(\frac{\partial U}{\partial T}\right)_V = -kT^2 C_V ,$$

$$\left(\frac{\partial^2 U}{\partial \beta^2}\right)_{E_r} = -kT^2 \left[\frac{\partial}{\partial T}\left(-kT^2 C_V\right)\right]_V = k^2 T^2 \left[2TC_V + T^2 \left(\frac{\partial C_V}{\partial T}\right)_V\right] .$$

Hence the desired result.

For the ideal classical gas, $U = \frac{3}{2} NkT$ and $C_V = \frac{3}{2} Nk$, which readily yield the stated results.

3.22. Note that a force proportional to q^3 implies a potential energy proportional to q^4. Thus

$$H = \frac{1}{2m} p^2 + cq^4 \qquad (c > 0) .$$

It follows that

$$\left\langle \frac{1}{2m} p^2 \right\rangle = \frac{\int_{-\infty}^{\infty} e^{-\beta p^2/2m} (p^2/2m) dp}{\int_{-\infty}^{\infty} e^{-\beta p^2/2m} dp} = \frac{1}{2\beta} ;$$

for the values of these integrals, see eqns. (13a) of Appendix B. Next,

$$\langle cq^4 \rangle = \frac{\int_{-\infty}^{\infty} e^{-\beta c q^4} (cq^4) dq}{\int_{-\infty}^{\infty} e^{-\beta c q^4} dq} = -\frac{\partial}{\partial \beta} \ln I(\beta) ,$$

where $I(\beta)$ denotes the integral in the denominator. It is straightforward to see that $I(\beta)$ is proportional to $\beta^{-1/4}$, whence $\langle cq^4 \rangle = 1/4\beta$, which proves the desired result.