

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

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

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

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

$$= (j+N-1) \left[\ln j + \ln \left(1 + \frac{N-1}{j}\right) \right] - N + 1 - j \ln j$$

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

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

$$\text{So } \Omega(E) \approx \frac{j^{N-1}}{(N-1)!}, \quad j \approx \frac{E}{h\omega}$$

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

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

(ii) Volume in phase space is

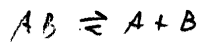
$$\Sigma(E) = \int \prod_{i=1}^N \pi \, d p_i \, d q_i = \frac{(2\pi)^N}{N!} \left(\frac{m}{k}\right)^{\frac{N}{2}} E^N = \frac{\pi^N}{N!} \frac{E^N}{\omega^N}, \quad \omega = \sqrt{\frac{k}{m}}$$

$$\sum_{i=1}^N \left(\frac{m \dot{q}_i^2}{2} + \frac{k q_i^2}{2} \right) \leq E \quad \text{let } x_i^2 = \frac{k q_i^2}{2}, \quad y_i^2 = \frac{m \dot{q}_i^2}{2}, \quad R^2 = \sum_{i=1}^N (x_i^2 + y_i^2)$$

use (7a) in Appendix C.

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

3.14



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

$$\frac{\partial}{\partial N_A} (N_A | 1 - \ln N_A V$$

$$= \gamma \ln N_A + N_A \left(\frac{\gamma}{N_A} \right)$$

Derive law of mass action

$$\frac{n_{AB}}{n_A n_B} = V \frac{f_{AB}}{f_A f_B} = K(T) \quad \text{equilibrium const. of reaction}$$

f's are single-particle

$$\text{partition function } f = \frac{Q_i(V, T)}{h^3} = \hat{f}(T) V$$

$$Q_{\text{structure}}(N_A, N_B, N_{AB}, V, T) =$$

$$\frac{f_A^{N_A} f_B^{N_B} f_{AB}^{N_{AB}}}{N_A! N_B! N_{AB}!}$$

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

Maximize under constraints

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

Use Lagrange mult.

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

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

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

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

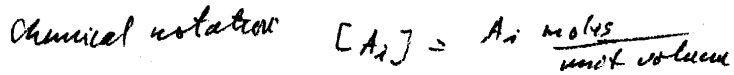
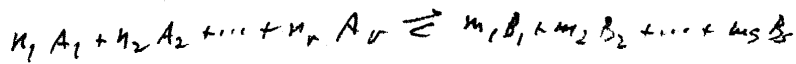
$$\frac{\partial A}{\partial \lambda_2} = N_B + N_{AB} - C_B = 0$$

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

$$\text{so } \ln \frac{f_{AB}}{N_{AB}} = \ln \frac{f_A f_B}{N_A N_B}, \quad \text{or } \frac{N_{AB}}{N_A N_B} = \frac{f_{AB}}{f_A f_B}, \quad \text{or } V^2 \frac{n_{AB}}{n_A n_B} = \frac{f_{AB}}{f_A f_B}$$

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

Alternative solution to 3.14



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

Kinetic equilibrium: As many reactions $g_0 \rightarrow$ as $g_0 \leftarrow$

To $g_0 \rightarrow$, need multiple collisions with $n_1 A_1, n_2 A_2, \dots$

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

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

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

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

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

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

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

$$\frac{\partial U}{\partial \beta} = - \frac{\sum E_r^2 e^{-\beta E_r}}{\sum e^{-\beta E_r}} + U^2, \quad (1)$$

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

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

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

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

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

It follows that

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

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

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

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.