Structure of Matter

Problem Sheet 3 **Answers**

1. $\langle v_x^2 \rangle = \int_{-\infty}^{\infty} v_x^2\, f(v_x)\, \mathrm{d}v_x = 1$

$$= \int_{-\infty}^{\infty} A v_x^2\, \mathrm{e}^{-\alpha v_x^2}\, \mathrm{d}v_x = A \int_{-\infty}^{\infty} v_x^2\, \mathrm{e}^{-\alpha v_x^2}\, \mathrm{d}v_x$$

$$= A\left(\frac{\pi}{2\alpha^3}\right)^{1/2} = \left(\frac{\alpha}{\pi}\right)^{1/2} \frac{1}{2}\left(\frac{\pi}{\alpha^3}\right)^{1/2}$$

$$= \left(\frac{1}{2\alpha}\right) = \left(\frac{k_B T}{m}\right)$$

2. $x_1 = x - (d/2) \quad \rightarrow \quad v_1 = \frac{\mathrm{d}x}{\mathrm{d}t} - \frac{\mathrm{d}(d/2)}{\mathrm{d}t} \quad = v_x - (v/2)$

$$x_2 = x + (d/2) \quad \rightarrow \quad v_2 = \frac{\mathrm{d}x}{\mathrm{d}t} + \frac{\mathrm{d}(d/2)}{\mathrm{d}t} \quad = v_x + (v/2)$$

Total ke $= \frac{1}{2}(m/2)v_1^2 + \frac{1}{2}(m/2)v_2^2$ (each particle has mass m/2)

$$= \frac{m}{4}(v_x - (v/2))^2 + \frac{m}{4}(v_x + (v/2))^2 = 2 \times \frac{m}{4}v_x^2 + 2 \times \frac{m}{4}(v/2)^2$$

$$= \frac{1}{2}mv_x^2 + \frac{1}{2}\left(\frac{m}{4}\right)v^2$$

3. (a) $U(r) = \frac{A}{r^{12}} - \frac{B}{r^6}$

$$\rightarrow \quad \frac{\mathrm{d}U}{\mathrm{d}r} = -12\,\frac{A}{r^{13}} + 6\,\frac{B}{r^7} = 0 \qquad \text{at equilibrium.}$$

$$\rightarrow \quad -12\,\frac{A}{{r_0}^{13}} + 6\,\frac{B}{{r_0}^7} = 0$$

$$\rightarrow \quad 12A = 6B{r_0}^6$$

$$\rightarrow \quad r_0 = (2A/B)^{1/6}$$

(b) $U(r_0) = \frac{A}{r_0^{12}} - \frac{B}{r_0^6} = \frac{AB^2}{4A^2} - \frac{BB}{2A} = -\frac{1}{4}\frac{B^2}{A}$

(c) $-\epsilon = -\frac{1}{4}\frac{B^2}{A} \quad \rightarrow \quad (1) \quad \epsilon = \frac{1}{4}\frac{B^2}{A}$ (using result of part (b))

AND (2) ${r_0}^6 = \frac{2A}{B}$

multiply together (1) and (2), $\quad 2\epsilon {r_0}^6 = B$

and (1) $\times$ (2)^2, $\quad 2\epsilon {r_0}^{12} = A$

So substituting for A and B in the Lennard-Jones expression,

$$U(r) = \epsilon \left\{ \left(\frac{r_0}{r}\right)^{12} - 2\left(\frac{r_0}{r}\right)^{6} \right\}$$

(d) $$\frac{\mathrm{d}^2U}{\mathrm{d}r^2} = \left\{ (12 \times 13\,\epsilon)\,\frac{{r_0}^{12}}{r^{14}} - (12 \times 7\,\epsilon)\,\frac{{r_0}^{6}}{r^{8}} \right\} \times 2$$

(the 2 is because each atom is bounded on either side, so has twice the potential energy)

For $r = r_0$, $\quad \dfrac{\mathrm{d}^2U}{\mathrm{d}r^2} = (12 \times 6\,\epsilon)\,\dfrac{1}{r_0^2} \times 2 = \dfrac{144\epsilon}{{r_0}^2}$

and so $\omega_E = \sqrt{\dfrac{144\epsilon}{m{r_0}^2}}$

and $v_s = \omega\lambda/2\pi = (r_0/2\pi)\sqrt{\dfrac{144\epsilon}{m{r_0}^2}} = \dfrac{1}{2\pi}\sqrt{\dfrac{144\epsilon}{m}}$

(NB Remember to double the potential due to two forces from either side)

4. (a) $U = \dfrac{A}{x^{12}} - \dfrac{B}{x^n}$

$\rightarrow \quad \dfrac{\mathrm{d}U}{\mathrm{d}x} = -12\,\dfrac{A}{x^{13}} + n\,\dfrac{B}{x^{n+1}} = 0 \qquad$ at equilibrium

also at equilibrium $x = 1$, so $-12A + nB = 0$

$\rightarrow \quad B = 12A/n$

So $U(x=1) = -\epsilon = A - B = A - 12A/n$

$\rightarrow \quad \epsilon = A(12/n - 1)$

(b) For $n = 1 \quad \rightarrow \quad \epsilon = A \cdot 11$,
for $n = 6 \quad \rightarrow \quad \epsilon = A$,

Assuming repulsive term is the same in both cases (i.e. value of A is similar), this suggests that the binding potential for the ionic bonding is $11\times$ stronger.

5. (a) Collision just happens if centre of particles is within $2a$ (the radius of both combined) of the other.

$\sigma = 4\pi a^2$

(NB this is different from the expression given in the lectures because a is the radius here, whereas the diameter d was used in lec. 5.)

(b) Volume swept out by this cross-section is $4\pi a^2 l$

Number of particles in this volume $= 4\pi a^2 l n$
(n is number density)

If particles is assumed to not be deflected significantly from its path, this is the number of collisions in this path length too.

(c) So average distance between collisions $\lambda_m = l/4\pi a^2 l n = 1/4\pi a^2 n$

(d) Using $P = nk_B T \quad \rightarrow \quad n = P/k_B T$ and including the extra $\sqrt{2}$

$\rightarrow \quad \lambda_m = k_B T/4\sqrt{2}\pi a^2 P$

(e) $$\lambda_m = \frac{1.38\times10^{-23}\cdot 293}{4\sqrt{2}\pi\,(2\times10^{-10})^2\cdot 1.01\times10^5} = 5.63\times10^{-8}\,\text{m} = 56\text{ nm}$$

(f) mean time between collisions $$\tau_m = \frac{\lambda_m}{\bar{v}} = \frac{5.63\times10^{-8}}{440} = 1.28\times10^{-10}\,\text{s} = 128\text{ ps}$$

6. For monoatomic van der Waal gas, $U = \frac{3}{2}Nk_B T - aN^2/V$

but $$C_V = \left(\frac{\mathrm{d}U}{\mathrm{d}T}\right)_V = \frac{3}{2}Nk_B$$

the same as for an ideal monoatomic gas

7. Volume available to a real gas $= (V - bN)$,

fractional change $= bN$ and % change from ideal gas $= bN/V$

but $b \cong 4V_m$ where V_m is the effective collisional volume of the molecule, i.e. $V_m = \frac{4}{3}\pi a^3$

using the ideal gas eqn. fractional change $a \cong b\,n = \frac{16}{3}\pi a^3 \frac{P}{k_B T}$

$$\rightarrow \quad P = \frac{a\cdot 3k_B T}{16\pi a^3} = \frac{0.01\times 3\times 1.38\times10^{-23}\cdot 293}{16\pi(2\times10^{-10})^3} = 3.02\times10^5\text{ Pa} \approx 3\text{ atm}$$

8. van der Waal's equation: $P = \frac{Nk_BT}{(V - bN)} - \frac{aN^2}{V^2}$

$$\frac{\mathrm{d}P}{\mathrm{d}V} = -\frac{Nk_BT}{(V - bN)^2} + \frac{2aN^2}{V^3} = 0 \qquad \rightarrow \qquad \frac{Nk_BT}{(V - bN)^2} = \frac{2aN^2}{V^3}$$

$$\frac{\mathrm{d}^2P}{\mathrm{d}V^2} = \frac{2Nk_BT}{(V - bN)^3} - \frac{6aN^2}{V^4} = 0 \qquad \rightarrow \qquad \frac{2Nk_BT}{(V - bN)^3} = \frac{6aN^2}{V^4}$$

dividing one expression by the other $(V - bN)/2 = 2V/6$

$$3(V - bN) = 2V \qquad \rightarrow \qquad V_c = 3bN$$

Put this back into the first derivative: $Nk_BT = \frac{2aN^2}{V^3}(V - bN)^2$

$$T = \frac{2aN}{k_B(3bN)^3}\,(2bN)^2$$

$$\rightarrow T_c = \frac{8a}{27k_Bb}$$

and finally in VW equation of state;

$$P_c = \frac{Nk_B 8a}{27k_Bb(2bN)} - \frac{aN^2}{(3bN)^2} = \frac{4a}{27b^2} - \frac{a}{9b^2} = \frac{a}{27b^2}$$