SoM: Problem Sheet 3, Answers

1. $$\langle v_x^2 \rangle = \int_{-\infty}^{+\infty} v_x^2 f(v_x)\, dv_x = A \int_{-\infty}^{+\infty} v_x^2 e^{-\alpha v_x^2} dv_x$$

$$\int_{-\infty}^{+\infty} v_x^2 e^{-\alpha v_x^2} dv_x = \frac{1}{2}\left(\frac{\pi}{\alpha^3}\right)^{1/2}$$

$$= \left(\frac{m}{2\pi k_B T}\right)^{1/2} \frac{1}{2} \pi^{1/2} \left(\frac{2k_B T}{m}\right)^{3/2} = \frac{k_B T}{m}$$

---

2. $$v_{x1} = \frac{dx_1}{dt} = \frac{d}{dt}\left\{x - \frac{1}{2}(d_0 + \xi)\right\} = \frac{dx}{dt} - \frac{1}{2}\frac{d\xi}{dt}$$ (since d_0 is ind of t)

$$= v_x - \frac{1}{2}v \qquad \text{Sim'ly} \quad v_{x2} = v_x + \frac{1}{2}v$$

$$ke = \frac{1}{2}\left(\frac{m}{2}\right)v_{x1}^2 + \frac{1}{2}\left(\frac{m}{2}\right)v_{x2}^2$$ (each atom has mass $m/2$).

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

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

---

3. In eqm $\dfrac{dU}{dr} = 0$

$$\therefore \epsilon\left\{\frac{-12 r_0^{12}}{r^{13}} + \frac{2\times 6\, r_0^6}{r^7}\right\} = 0 \rightarrow \frac{r_0^{12}}{r^{13}} = \frac{r_0^6}{r^7} \rightarrow r^6 = r_0^6 \rightarrow r = r_0$$

Binding energy = U at bottom of poten. well

i.e. $U(r_0) = \epsilon\{1-2\} = -\epsilon$

---

4 (a) $U = \frac{A}{x^{12}} - \frac{B}{x^n} = \frac{A r_0^{12}}{r^{12}} - \frac{B r_0^n}{r^n}$

$\frac{dU}{dr} = -\frac{12 A r_0^{12}}{r^{13}} + \frac{n B r_0^n}{r^{n+1}} = 0$ at eqm $(r=r_0)$

∴ $-\frac{12A}{r_0} + \frac{nB}{r_0} = 0 \rightarrow B = \frac{12A}{n}$

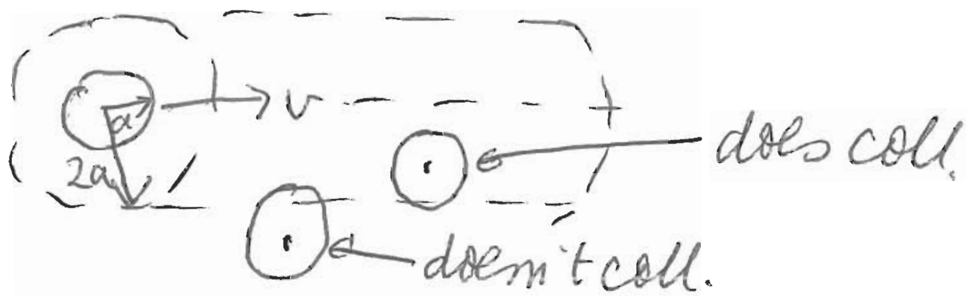
∴ $U = A\left(\frac{1}{x^{12}} - \frac{12}{n x^n}\right)$. At $x=1$ $(r=r_0)$ $U=-\epsilon$

∴ $-\epsilon = A\left(1-\frac{12}{n}\right) \rightarrow \epsilon = A\left(\frac{12}{n}-1\right)$

(b) VW: $n=6 \rightarrow \epsilon = A$
ionic: $n=1 \rightarrow \epsilon = 11A$
i.e. ionic potn well is 11× deeper
→ ionic bond is much stronger.

---

5 (a) Coll's occur with mol's whose centres are within cylinder of radius 2a.



i.e. $\sigma = \pi (2a)^2$

(b) Vol swept out travelling distance l is $4\pi a^2 l$

∴ average no of coll's = no of mol's with centres in this vol.

$$= \underbrace{\left(\frac{N}{V}\right)}_{\text{no density}} \times 4\pi a^2 l$$

(c) Average distance travelled before 1 coll given by.

$$1 = \frac{4\pi N a^2 \lambda}{V} \rightarrow \lambda = \frac{V}{4\pi N a^2}.$$

(d) motion of other mol's $\rightarrow \lambda = \dfrac{V}{4\sqrt{2}\pi N a^2}$

$$\text{IG: } \frac{V}{N} = \frac{k_B T}{P} \rightarrow \lambda = \frac{k_B T}{4\sqrt{2}\pi a^2 P}$$

(e) $\lambda = \dfrac{1.38\times10^{-23}\times 293}{4\sqrt{2}\pi\,(2\times10^{-10})^2\times 1.01\times10^{5}} = 5.63\times10^{-8}\,m$

(f) τ = average time between coll's

$$= \frac{\lambda}{\langle v \rangle} = 1.28\times10^{-10}\,s \quad \text{i.e. } \sim 10^{10} \text{ colls/s.}$$

---

6 VW gas $U = \dfrac{3}{2} N k_B T - \dfrac{aN^2}{V}$

keep V fixed, increase T by dT

$\rightarrow$ U increases by $dU = \dfrac{3}{2} N k_B \, dT$

1st Law: $dQ = dU - dW = \dfrac{3}{2} N k_B \, dT + \underbrace{\cancel{P\,dV}}_{V = \text{const}}$

$\rightarrow C_V = \dfrac{3}{2} N k_B = C_V$ for MIG

---

7 $Nb \geq \frac{1}{100} V \leftarrow \frac{Nk_BT}{P}$

i.e. $b \geq \frac{k_BT}{100P} \rightarrow P \geq \frac{k_BT}{100b}$

$b = \frac{4}{3}\pi \times (2.0\times 10^{-10})^3 = 3.35\times 10^{-29}\, m^3$

$P \geq 1.21\times 10^6\, Nm^{-2} \simeq 12$ atmospheres

---

8 At $T = T_C$, VW eq $\Rightarrow P = \frac{Nk_BT_C}{(V-bN)} - \frac{aN^2}{V^2}$

$\frac{dP}{dV} = -\frac{Nk_BT_C}{(V-bN)^2} + \frac{2aN^2}{V^3} = 0 \rightarrow \frac{k_BT_C}{(V_C-bN)^2} = \frac{2aN}{V_C^3}$ ①

$\frac{d^2P}{dV^2} = \frac{2Nk_BT_C}{(V-bN)^3} - \frac{6aN^2}{V^4} = 0 \Rightarrow \frac{k_BT_C}{(V_C-bN)^3} = \frac{3aN}{V_C^4}$ ②

sub ① into ② $\rightarrow \frac{2aN}{V_C^3(V-bN)} = \frac{3aN}{V_C^4} \rightarrow 2V_C = 3(V_C - bN)$

$\rightarrow \boxed{V_C = 3bN}$

① $\rightarrow T_C = \frac{2aN}{V_C^3}\frac{(V_C-bN)^2}{k_B} = \frac{2aN}{27b^3N^3}\frac{4b^2N^2}{k_B}$

$\rightarrow \boxed{T_C = \frac{8a}{27k_Bb}}$
