**ENGINEERING TRIPOS PART IIB 2024**
**MODULE 4A9 – Molecular Thermodynamics**

**Solutions**

**Examiners' comments:**

Q1 *Six-group velocity distribution and intermolecular forces*. This question was done well with most candidates able to determine the gas temperature and work out the various components of molecular energy. The manipulations associated with the Lennard-Jones potential were also handled well.

Q2 *Moments of the Boltzmann equation.* Candidates knew how to derive these moments (starting from the given Boltzmann equation) and apply them to conservation of mass and momentum, correctly identifying viscous stresses and pressure terms in most cases. The last part (on decomposing the molecular kinetic energy flux into four terms and relating these to physical quantities) was perhaps not quite so well done.

Q3 *De Broglie wavelength.* All students were able to show de Broglie wavelength as a function of energy (3a) and most students were able to answer when quantised effects were important (3b). Almost all identified that the length scale to de Broglie ratio gave an indication of the scale of quantum effects (3ci). Less than half of students could transition from the quantized sum to an integral by properly identifying that the energy spacing was close and arrive at the appropriate relationship for the partition function (3cii) and most struggled with fully identifying the number of degrees of freedom for entropy to compare the two methods of calculating entropy (3ciii).

Q4 *State space for 2D system.* All students were able to describe the momentum and wave function terms (4a), but several did not appropriately identify the units. Almost all students could write down the appropriate wave equation partial differential equation (4b) and identify the boundary conditions (4ci). A few students missed the final solution. Students had mixed results in identifying the number of state spaces and the gradient of state space with molecular speed (4cii). Likewise, many students had the right approach to the number of state spaces below the RMS speed, but made calculation mistakes or had minor errors (4d).

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Q1 (a) (i) Average (bulk) velocity $\underline{u} = \frac{1}{6}\sum \underline{c}_j = (23, 40, -10)$

$\therefore$ Peculiar velocity is $C = \pm 525$ in each coordinate direction.

i.e., Molecular speed $= 525\ \mathrm{ms^{-1}}$

$\therefore \quad \frac{3}{2}kT = m\frac{C^2}{2} \Rightarrow T = \frac{C^2}{3R} = \frac{525^2}{3\times 8314/28} = \underline{309.4\ K}$ [4]

(ii) Assume P/G with rotational modes excited (but not vibrational modes)

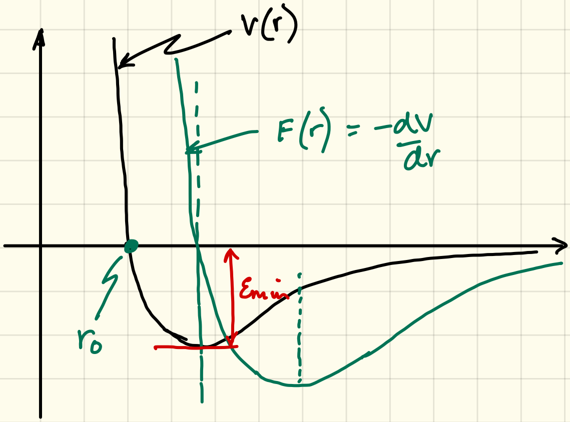
Per unit mass:-

BULK KE $= \frac{1}{2}u^2 = \frac{1}{2}(23^2 + 40^2 + 10^2) \simeq \underline{1.115\ \mathrm{kJ/kg}}$

THERMAL TRANSLATIONAL KE $= \frac{1}{2}C^2 = \underline{137.8\ \mathrm{kJ/kg}}$

INTERNAL ROTATIONAL KE $= RT = \underline{91.88\ \mathrm{kJ/kg}}$ [5]

(b) (i)




[3]

(ii) $V = A(x^{12} - x^6)$ where $x = r_0/r$

$F = 0$ when $-\frac{dV}{dr} = 0 \Rightarrow \frac{dV}{dx} = 0$

$\therefore \quad 12x^{11} = 6x^5 \Rightarrow \frac{1}{x} = \frac{r}{r_0} = 2^{1/6} \quad \therefore r = 2^{1/6} r_0 \simeq \underline{0.418\ \mathrm{nm}}$ [2]

(iii) $T_{CRIT} \sim |\varepsilon_{min}|/k$

$\varepsilon_{min}$ occurs at $F = 0$, when $x^6 = 1/2$

$\therefore \quad \varepsilon_{min} = A\left(\frac{1}{2^2} - \frac{1}{2}\right) = -A/4$

$\therefore \quad T_{CRIT} \sim \frac{A}{4k} \simeq \frac{5.3\times 10^{-21}}{4\times 1.38\times 10^{-23}} \simeq \underline{96.2\ K}$ [3]

(iv) To obtain estimate, assume each molecule occupies a cube of side $a$. Thus,

$$pV = NkT \Rightarrow pa^3 = 1 \times kT \Rightarrow a = \sqrt[3]{kT/p}$$

@ 100 bar & 309.4K, $a = \sqrt[3]{\dfrac{1.38\times10^{-23} \times 309.4}{2\times10^{7}}} \approx 0.6$ nm

Considering only closest neighbours, each pair has a potential energy of $\sim -A\left(\frac{r_0}{a}\right)^6$. Each molecule has six close neighbour, so the potential energy associated with each molecule $\sim -3A\left(\frac{r_0}{a}\right)^6 = \varepsilon_p \sim -9.23\times10^{-22}$ J

Other internal energy $= \frac{5}{2}kT \sim 1.07\times10^{-20}$ J

Thus, fraction of (thermodynamic) energy associated with potential interaction $\sim \dfrac{9.23\times10^{-22}}{1.07\times10^{-20} - 9.23\times10^{-22}}$

$\sim \underline{\underline{10\ \%}}$

THIS IS VERY APROXIMATE AND IS LIKELY TO BE A SIGNIFICANT UNDERESTIMATE DUE TO CONTRIBUTIONS FROM OTHER NEARBY MOLECULES, BUT NONETHELESS SHOWS SIGNIFICANT DEPARTURE FROM IDEAL GAS BEHAVIOUR. [3]

② (a)

$$\frac{\partial f}{\partial t} + c_j \frac{\partial f}{\partial x_j} = \left[\frac{\partial f}{\partial t}\right]_{coll.}$$

(i) $f$ defined s.t. $f(c_1, c_2, c_3)\, dc_1\, dc_2\, dc_3$ is the number of molecules per unit volume with velocity components in the ranges $c_1$ to $c_1 + dc_1$ ; $c_2$ to $c_2 + dc_2$ etc (or similar) [2]

(ii) Multiply B-E by Q and integrate over all velocity space:

$$\int_{-\infty}^{\infty} Q \frac{\partial f}{\partial t} dV_c + \int_{-\infty}^{\infty} Q c_j \frac{\partial f}{\partial x_j} dV_c = \int_{-\infty}^{\infty} Q \left[\frac{\partial f}{\partial t}\right]_{coll} dV_c$$

Noting $t$, $x_j$ and $c_j$ are independent:

$$\frac{\partial}{\partial t}\int_{-\infty}^{\infty} Q f\, dV_c + \frac{\partial}{\partial x_j}\int_{-\infty}^{\infty} Q c_j f\, dV_c = \int_{-\infty}^{\infty} Q \left[\frac{\partial f}{\partial t}\right]_{coll} dV_c$$

$$\therefore \quad \frac{\partial}{\partial t}(n\bar{Q}) + \frac{\partial}{\partial x_j}(n\,\overline{c_j Q}) = \underline{\int_{-\infty}^{\infty} Q \left[\frac{\partial f}{\partial t}\right]_{coll} dV_c}$$ [4]

(iii) For mass continuity, put $Q = m$ (molecular mass). Note $\rho = nm$

$$\therefore \quad \frac{\partial}{\partial t}(nm) + \frac{\partial}{\partial x_j}(nm\bar{c}_j) = 0$$

RHS is 0 because mass conserved in collisions.

$$\Rightarrow \quad \frac{\partial \rho}{\partial t} + \frac{\partial}{\partial x_j}(\rho u_j) = 0 \qquad \left[\text{or } \frac{\partial \rho}{\partial t} + \nabla\cdot(\rho \underline{u}) = 0\right]$$

For momentum conservation, put $Q = mc_i$

$$\therefore \quad \frac{\partial}{\partial t}(nm\bar{c}_i) + \frac{\partial}{\partial x_j}(nm\overline{c_j c_i}) = 0$$

RHS is 0 because momentum is conserved during collisions.

$$\therefore \quad \frac{\partial}{\partial t}(\rho u_i) + \frac{\partial}{\partial x_j}\left(\rho \overline{c_i c_j}\right) = 0$$

Now write $c_i = u_i + C_i$ etc.

$$\overline{c_i c_j} = \overline{(u_i + C_i)(u_j + C_j)} = u_i u_j + \overline{C_i C_j}$$

$$\therefore \quad \frac{\partial}{\partial t}(\rho u_i) + \frac{\partial}{\partial x_j}(\rho u_i u_j) = -\frac{\partial}{\partial x_j}\left(\rho \overline{C_i C_j}\right)$$

DEFINE $p = \frac{1}{3}\rho \overline{C^2}$ (-ve of average normal stress)

$$\tau_{ij} = -\left(\rho \overline{C_i C_j} - p\,\delta_{ij}\right)$$

$$\therefore \quad \boxed{\frac{\partial(\rho u_i)}{\partial t} + \frac{\partial}{\partial x_j}(\rho u_i u_j) = \frac{\partial \tau_{ij}}{\partial x_j} - \frac{\partial p}{\partial x_i}}$$

[8]

(c) $F_j = \rho\, \overline{c_j\,(c^2/2)}$ = the net flux of KE in the $x_j$ direction

$$F_j = \tfrac{1}{2}\rho \left\{ \overline{(u_j + C_j)(u_i + C_i)(u_i + C_i)} \right.$$

$$= \tfrac{1}{2}\rho\, \overline{(u_j + C_j)(u_i^2 + C_i^2 + 2u_i C_i)}$$

$$= \tfrac{1}{2}\rho \left\{ \overline{u_j(u_i^2 + C_i^2 + \cancel{2u_i C_i}) + C_j(\cancel{u_i^2} + C_i^2 + 2u_i C_i)} \right\}$$

$$= \rho u_j \frac{u^2}{2} + \rho u_j \frac{\overline{C^2}}{2} + \rho \frac{\overline{C_j C^2}}{2} + \rho u_i \overline{C_i C_j}$$

$= u_i\,(p\delta_{ij} - \tau_{ij})$

[6]

BULK KE CONVECTED BY BULK FLOW

RANDOM THERMAL KE CONVECTED BY BULK FLOW

HEAT FLUX $q_j$

RATE OF WORK DONE AGAINST VISCOUS STRESSES (PLUS FLOW WORK)

Q3 (a) $\lambda = \frac{h}{p} = \frac{h}{mu}$

$\varepsilon = \frac{1}{2}mu^2 \Rightarrow mu = \sqrt{2m\varepsilon}$

$\therefore \lambda = \frac{h}{\sqrt{2m\varepsilon}}$ [2]

NOTE $\varepsilon = \frac{3kT}{2}$ is ALSO OK, BUT $\varepsilon = \frac{1}{2}kT$ is the average KE associated with motion in one direction.

(b) (i) $m \sim 2000$ kg ; $v \sim 30\ ms^{-1}$

$\therefore \lambda = 6.626\times10^{-34}/(2000\times30) \sim \underline{1.1\times10^{-38}\ m}$

(ii) $\varepsilon = \frac{kT}{2} \Rightarrow \lambda = \frac{6.626\times10^{-34}}{\sqrt{2\times4\times\frac{1}{2}\times1.38\times10^{-23}\times300/6.023\times10^{26}}} \simeq \underline{1.26\times10^{-10}\ m}$

(iii) $\varepsilon = V\times e \Rightarrow \lambda = \frac{h}{\sqrt{2m_e eV}} = \frac{6.626\times10^{-34}}{\sqrt{2\times9.11\times10^{-31}\times1.6\times10^{-19}\times100}}$

$= \underline{1.23\times10^{-10}\ m}$

All very small lengths, but relative importance depends on the size of the system — eg. quantum effects entirely negligible for the car. [4]

(c) (i) $\lambda$ may be interpreted as an effective spatial resolution with which the location of a particle is known. $\Pi = a/\lambda$ thus quantifies the relative importance of quantum effects (the larger $\Pi$, the less important quantum effects are) [2]

(ii) $Z = \sum_i e^{-\varepsilon_i/kT} = \sum_{n_1=1}^{\infty}\sum_{n_2=1}^{\infty}\sum_{n_3=1}^{\infty} e^{-\tau^2(n_1^2+n_2^2+n_3^2)} \times 1\times1\times1$ $\Delta n_1$ etc.

where $\tau^2 = h^2/(8mV^{2/3}kT)$ BUT $kT = m\overline{c_1^2} = m\overline{c_2^2}$ etc.

$\therefore \tau^2 = \frac{h^2}{8m^2\overline{c_1^2}a^2} = \frac{1}{8}\left(\frac{\lambda}{a}\right)^2 \Rightarrow \tau = \frac{1}{2\sqrt{2}}\frac{1}{\Pi}$

Provided $\tau \ll 1$ (i.e., $\Pi \gg 1$) $Z \simeq \left(\int_0^\infty e^{-\tau^2n^2}dn\right)^3 = \frac{\pi^{3/2}}{2^3\tau^3} = 2\sqrt{2}\,\pi^{3/2}\,\Pi^3$

$\Rightarrow \underline{\alpha = 2\sqrt{2}\,\pi^{3/2} \text{ and } q = 3}$

[NOTE DIFFERENT VALUE of $\alpha$ also possible — see note above re. $\varepsilon = \frac{1}{2}kT$]

$\Pi \gg 1$ means quantum states are v. closely spaced compared to $\bar{\varepsilon}$ for a molecule. i.e., classical (or high-temperature) limit. [6]

(iii) For $N$ molecules with 3 degrees of freedom $d = 3N$

$$S = k \ln \Omega = Nk \ln \Pi^3 = 3Nk \ln \Pi$$

$$\Pi = \frac{a}{\lambda} = \frac{a\sqrt{mkT}}{h} \Rightarrow \Pi^3 = VT^{3/2} \times \left(\frac{mk}{h^2}\right)^{3/2}$$

Thus $$S = Nk\left(\ln V + \frac{3}{2}\ln T\right) + \frac{3Nk}{2}\ln\left(\frac{mk}{h^2}\right)$$

$$Q = \frac{Z^N}{N!} = \frac{\alpha^N \Pi^{3N}}{N!} \Rightarrow \ln Q = N\ln\alpha + 3N\ln\Pi - \ln N!$$

Now $$S = k\frac{\partial}{\partial T}\left(T\ln Q\right)_{V,N} = k\ln Q + kT\frac{\partial}{\partial T}\ln Q$$

$$\therefore \quad S = 3Nk\ln\Pi + \underbrace{Nk\ln\alpha - k\ln N! + 3NkT\frac{d}{dT}\left(\tfrac{1}{2}k\ln T\right)}$$

This difference is independent of $T$ & $V$ so only affects the datum of entropy.

$\boxed{6}$

Q4 (a) $p_i$ is the momentum of the particle in the $x_i$ direction. Units $kg\,ms^{-1}$

$\psi$ is the wave function defined such that $|\psi|^2 dV$ is the probability of finding the particle in the volume $dV$. Thus $\psi$ must have units of $m^{-3/2}$ [3]

(b) $$\frac{d^2\psi}{dx^2} + \omega^2\psi = 0 \Rightarrow \psi = A\cos\omega x + B\sin\omega x$$

or $$\underline{\psi_1 = A\cos\left(\frac{2\pi p_1}{h}x_1\right) + B\sin\left(\frac{2\pi p_1}{h}x_1\right)}$$ [3]

(c) (i) $\psi_i(0) = \psi_i(L) = 0, \quad i = 1,2$

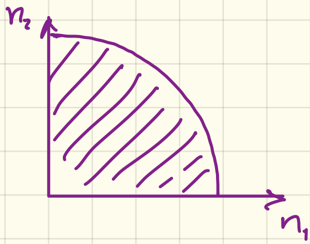
$\psi_i(0) = 0 \Rightarrow A_i = 0$

$\psi_i(L) = 0 \Rightarrow \frac{2\pi p_i}{h}L = n_i\pi \quad \therefore \; p_i = \frac{n_i h}{2L}$

$$\therefore \; \varepsilon_k = \tfrac{1}{2}m(u_1^2 + u_2^2) = \frac{1}{2m}(p_1^2 + p_2^2) = \underline{\frac{h^2}{8mL^2}(n_1^2 + n_2^2)}$$ [4]

(ii) Start with $\Gamma(\varepsilon)$, the number of states with energy $< \varepsilon$.

For large $n_1$ & $n_2$ (i.e., large $\varepsilon$




$$\Gamma(\varepsilon) = \tfrac{1}{4}\text{ Area of circle} = \tfrac{1}{4}\pi(n_1^2 + n_2^2)$$

$$= 2\pi mL^2\varepsilon / h^2$$

$$= \pi\left(\frac{mL}{h}\right)^2 c^2$$

$$\underline{g(c) = \frac{d\Gamma}{dc} = 2\pi\left(\frac{mL}{h}\right)^2 c}$$ [6]

(d) There are only two degrees of freedom so $\tfrac{1}{2}m\overline{c^2} = kT \Rightarrow m\overline{c^2} = 2kT$

$$\therefore \; \Gamma(\varepsilon) = \pi\frac{mA\,2kT}{h^2}$$

$$= \pi \times \frac{40}{6.023\times10^{26}} \times \frac{0.01}{(6.626\times10^{-34})^2} \times 2\times300\times 1.38\times10^{-23}$$

$$= \underline{3.94\times10^{19} \text{ STATES}}$$ [4]