4A9 - MOLECULAR THERMODYNAMICS

SOLUTIONS TO TRIPOS 2023

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NOTE EXAMINERS' COMMENT ON LAST PAGE.

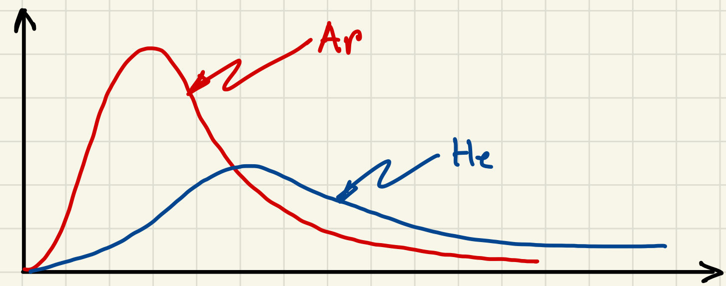
Q1 (a) The speed distn is defined such that $g_e(c)\,dC = f_e(c)\,dV_c$, but the "volume" containing molecules in speed range $C \to C+dC$ is $dV_c = 4\pi C^2 dC$ (i.e., a thin spherical shell). Thus $g_e(c)\,dC = f_e(c)\cdot 4\pi C^2 dC$

$$\therefore \quad g_e(c) = \frac{4\pi n c^2}{(2\pi RT)^{3/2}} \exp\left(-\frac{c^2}{2RT}\right)$$

Modal velocity given by maximum in $g_e(c)$

$$\therefore \frac{dg_e}{dC} = 0 \Rightarrow 2\cancel{C} - C^2 \times \frac{2\cancel{C}}{2RT} = 0 \quad \Rightarrow \quad C_m = \sqrt{2RT}$$ [4]

(b) (i)



[2]

(ii) Flux $= \int_0^{\infty}\iint_{-\infty}^{\infty} (mC_1)\, C_1\, f_e(C_i)\, dC_3\, dC_2\, dC_1 = \tfrac{1}{2} n m \overline{C_1^2} = p_{He}/2$

[NOTE: It is possible to evaluate this using the integrals, with much more work]

$= \underline{\underline{0.25 \text{ bar}}}$ [5]

(iii) Let $\psi(C_1)\,dC_1$ be the fraction of He molecules with x_1 velocity in range $C_1 \to C_1 + dC_1$. From the form of f_e this must be of the form $\psi(C_1) = A\exp(-C_1^2/2RT)$

Thus:

$$\bar{C}_1 = \frac{\int_0^{\infty} C_1\,\psi(C_1)\,dC_1}{\int_0^{\infty} \psi(C_1)\,dC_1} = \frac{\int_0^{\infty} A C_1^2 e^{-C_1/2RT}\,dC_1}{\int_0^{\infty} A\, e^{-C_1^2/2RT}\,dC_1}$$

Now put $x = \frac{C_1}{\beta}$ where $\beta = \sqrt{2RT}$:

$$\bar{C}_1 = \frac{\beta^2 I_1}{\beta I_0} = \sqrt{2RT} \times \frac{1/2}{\sqrt{\pi}/2} = \sqrt{\frac{2RT}{\pi}} = \sqrt{\frac{2 \times 8314 \times 200}{4\pi}} = \underline{\underline{630 \text{ m/s}}}$$ [5]

R

[NOTE: It is also possible to deduce this value on the basis of the one-sided molecular flux being $F_+ = n\bar{C}/4 \Rightarrow \bar{C}_1 = \bar{C}/2$ but noting that only $\frac{n}{2}$ molecules move in the +ve C_1 dirn]

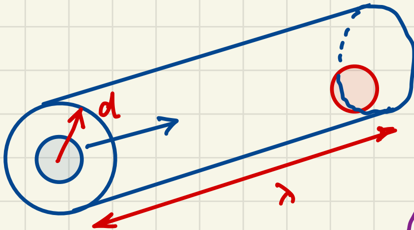
(c) The fraction of molecules with $c_1 > c_0$ is given by: $1 - \dfrac{\int_0^{c_0} A \exp(-c_1^2/2RT)\, dc_1}{\int_0^{\infty} A \exp(-c_1^2/2RT)\, dc_1}$

$$= 1 - \operatorname{erf}(x_0)$$

where $x_0 = \dfrac{c_0}{\sqrt{2RT_0}} = \dfrac{670}{\sqrt{2 \times 8314 \times 300/4}} = 0.6$

Thus fraction with $c_1 > 670 = 1 - \operatorname{erf}(0.6) = \underline{\underline{0.3961}}$ [4]

Q2. (a) Volume of influence swept out by molecule over λ contains, on average, one other molecule:



[Note: Full credit given if $\sqrt{2}$ not included]

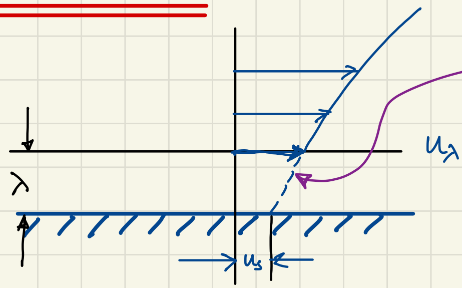
$$\therefore \quad \pi d^2 \lambda n \approx 1 \quad \Rightarrow \quad \lambda = \frac{1}{\sqrt{2}\, n \pi d^2}$$

(i) $$\mu = \frac{\rho \bar{c} \lambda}{2} = \frac{\cancel{n} m \bar{c}}{2\sqrt{2}\,\cancel{n} \pi d^2}$$ (depends on T only) [2]

(ii) $$d^2 \approx \frac{m \bar{c}}{2\sqrt{2}\,\pi \mu} = \frac{28 \sqrt{8 \times 297 \times 300/\pi}}{6.023 \times 10^{26} \times 2\sqrt{2} \times \pi \times 1.79 \times 10^{-5}}$$

$$\Rightarrow \quad d \approx 3.73 \times 10^{-10}\ \text{m}$$ [3]

(b) (i)



velocity profile extrapolated over distance λ.

Incident flux of momentum on surface $= \frac{\rho \bar{c}}{4} u_\lambda = \frac{\rho \bar{c}}{4}\left(u_s + \lambda \left.\frac{du}{dr}\right|_R\right)$

Reflected flux of momentum $= 0$ (diffuse)

$\therefore$ Net flux of momentum $= \frac{\rho \bar{c}}{4}\left(u_s + \lambda \left.\frac{du}{dr}\right|_R\right) = \tau_w$

$= \mu \left(\frac{du}{dr}\right)_R = \frac{\rho \bar{c} \lambda}{2} \left.\frac{du}{dr}\right|_R .$

$$\therefore \quad u_s = \lambda \left(\frac{du}{dr}\right)_R$$ [6]

(ii) The axial force must be independent or radius (otherwise there would be net force on a fluid element between two radii). Thus $r\tau$ = const.

This is purely a dynamic relation and does not depend on any assumption about continuum or non-continuum flow.

Thus $$\frac{du}{dr} = \frac{a}{r} \Rightarrow u(r) = a\ln r + b$$

B/C's
$$u(R) = a\ln R + b = u_s = \lambda \left.\frac{du}{dr}\right|_R = \frac{\lambda a}{R} \qquad (1)$$
$$u(2R) = a\ln 2R + b = V - \frac{\lambda a}{2R} \qquad (2)$$

SLIP ON OUTER CYLINDER

$$\therefore (2)-(1): \quad a\ln 2 = V - \frac{3\lambda a}{2R} \Rightarrow a = \frac{V}{\ln 2 + \frac{3\lambda}{2R}}$$

Thus $$u(r) = \left(\frac{V}{\ln 2 + \frac{3\lambda}{2R}}\right)\left[\ln\left(\frac{r}{R}\right) + \frac{\lambda}{R}\right]$$

[6]

(iii) The force F is proportional to $\left.\frac{du}{dr}\right|_{2R} \propto a$

$\frac{1}{a}$ in continuum limit

$$\therefore \frac{F}{F_0} = \frac{\cancel{V}}{\ln 2 + \frac{3}{2}Kn} \times \frac{\ln 2}{\cancel{V}} \equiv \frac{1}{1 + B\,Kn}$$

[3]

$$\Rightarrow B = \frac{3}{2\ln 2}$$

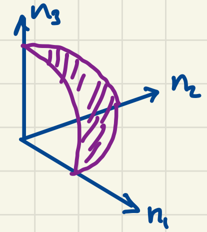
Q3 (a) Degeneracy g_j is the number of states having the same energy.

For $g_j > 3$; n_1, n_2 & n_3 must be different.

Lowest energy level is thus with quantum numbers 1, 2 & 3 and has degeneracy.

$$\varepsilon_{TR} = \frac{h^2 N_A}{8 \times M \times 0.001^2} \times (1+4+9) = \underline{\underline{1.156 \times 10^{-34}\ J}}$$ [4]

(b) $\Gamma(\varepsilon) = 1/8 \times$ volume of sphere



[Because each state occupies unit vol.]

$$= 1/8 \times \frac{4\pi}{3} n^3$$

But $n^2 = (n_1^2 + n_2^2 + n_3^2) = \frac{8mV^{2/3}\varepsilon}{h^2} \Rightarrow n = \frac{2V^{1/3}}{h}(2m\varepsilon)^{1/2}$

$$\Rightarrow \Gamma(\varepsilon) = \frac{\pi}{6} \times \frac{8V}{h^3}(2m\varepsilon)^{3/2} = \underline{\underline{\frac{4\pi}{3}\frac{V}{h^3}(2m\varepsilon)^{3/2}}}$$

Average energy of molecules, $\bar{\varepsilon} = \frac{3kT}{2}$

$$\therefore \Gamma(\bar{\varepsilon}) = \frac{4\pi}{3} \times \frac{10^{-9}}{h^3}\left(\frac{\cancel{2} \times 4}{N_A} \times \frac{3 \times k \times 300}{\cancel{2}}\right)^{3/2} = \underline{\underline{1.08 \times 10^{22}\ \text{STATES}}}$$ [5]

(c) $g(c)\,dc = \frac{d\Gamma}{d\varepsilon} d\varepsilon$; $\varepsilon = \frac{1}{2}mc^2 \Rightarrow d\varepsilon = mc\,dc$

$$\therefore g(c) = mc \frac{d\Gamma}{d\varepsilon} = mc \times \frac{4\pi}{\cancel{3}}\frac{V}{h^3} \times \frac{\cancel{3}}{\cancel{2}} \times \cancel{2}m \times (2m\varepsilon)^{1/2}$$

$$= mc \times \frac{4\pi V}{h^3} \times m \times mc = \underline{\underline{\frac{m^3 c^2 4\pi V}{h^3}}}$$ [5]

(d) $\frac{\delta N_j}{N} = \zeta(c)\,dc \quad \frac{g_j e^{-\varepsilon_j/kT}}{Z} \doteq \frac{g(c)\,dc\; e^{-mc^2/2kT}}{Z}$

$$\therefore \zeta(c) = \frac{m^3 c^2 4\pi \cancel{V}}{\cancel{h^3}} \times \frac{\cancel{h^3}}{\cancel{V}} \frac{1}{(2\pi mkT)^{3/2}} e^{-(c^2/2kT)}$$

$$\zeta_1(c) = \frac{4\pi c^2}{(2\pi RT)^{3/2}} e^{-(c^2/2RT)}$$

[6]

Q4 (a) (i) $S' = -k \sum_{i=1}^{\Omega} P_i \ln P_i$

k = Boltzmann's constant

Ω = number of system microstates

P_i = probability of system being in its i-th microstate. [2]

(ii) Consider two subsystems A & B

$$S'_A = -k \sum_{i=1}^{\Omega_A} P_i \ln P_i \qquad S'_B = -k \sum_{j=1}^{\Omega_B} P_j \ln P_j$$

The combined prob. that system A is in state i and system B is in state is $P_{ij} = P_i \times P_j$ [because the states are independent]

$$\therefore -\frac{S'_{AB}}{k} = \sum_i \sum_j P_i P_j (\ln P_i + \ln P_j) = \sum_i P_i \sum P_j (\ln P_i + \ln P_j)$$

$$= \sum_i P_i \left(\ln P_i + \sum P_j \ln P_j\right) = \sum_i P_i \ln P_i + \sum_j P_j \ln P_j \quad \left[\sum P_i = \sum P_j = 1\right]$$

$$\therefore S'_{AB} = S_A + S_B$$ [5]

(iii) We wish to maximise S' subject to $G = \sum P_i - 1 = 0$

Method of Lagrange multipliers $\Rightarrow \frac{\partial S'}{\partial P_i} + \lambda \frac{\partial G}{\partial P_i} = 0$

$$\therefore -k\left(P_i \times \frac{1}{P_i} + \ln P_i\right) + \lambda \times 1 = 0$$

$$\Rightarrow \ln P_i = \frac{\lambda}{k} - 1 \Rightarrow P_i = \text{const} = \frac{1}{\Omega} \quad \left[\text{since } \sum P_i = 1\right]$$

Thus $S'_{max} = -k \sum_{i=1}^{\Omega} \frac{1}{\Omega} \ln \frac{1}{\Omega} = \underline{\underline{k \ln \Omega}}$

For an isolated system at eq^{m}. the fundamental postulate states that all microstates are equally probable, and this is precisely the condition that maximises S'. In classical thermodynamics, the entropy of an isolated system reaches a maximum at equilibrium. [5]

(b) Need to calculate $\sigma_E^2 = \overline{E_i^2} - U^2$

But $\overline{E_i^2} = \sum E_i^2 P_i = \frac{1}{Q}\sum E_i^2 e^{-E_i/kT}$

Now $U = \sum E_i P_i = \frac{1}{Q}\sum E_i e^{-E_i/kT}$

$\therefore \quad QU = \sum E_i e^{-E_i/kT}$

$\Rightarrow \quad \frac{\partial}{\partial T}\left(QU\right)_{N,V} = \sum \frac{E_i^2}{kT} e^{-E_i/kT} = \frac{Q}{kT^2}\overline{E_i^2}$

$\therefore \quad \overline{E_i^2} = \frac{kT^2}{Q}\frac{\partial}{\partial T}\left(QU\right) = kT^2\left\{\frac{\partial U}{\partial T} + \frac{U}{Q}\frac{\partial Q}{\partial T}\right\}$

$= kT^2\frac{\partial U}{\partial T} + U^2$

$\Rightarrow \quad \sigma_E^2 = kT^2\frac{\partial U}{\partial T} = kT^2 C_v M = kT^2 C_v M$

$\therefore \quad \left(\frac{\sigma_E}{U}\right)^2 = \frac{k\cancel{T^2}\cancel{C_v}\cancel{M}}{M^{\cancel{2}}C_v^{\cancel{2}}\cancel{T^2}} = \frac{k}{NmC_v} = \frac{R}{NC_v} = \frac{\gamma-1}{N}$

$\Rightarrow \quad N = \frac{\gamma-1}{(\sigma_E/U)^2} = \underline{\underline{0.4\times10^{10} \text{ molecules}}}$ [8]

Examiners' Comment

Q1. *Maxwellian velocity distribution, fluxes and averages*. Part (a) on obtaining the equilibrium speed distribution and calculating the modal speed was done well. Most also sketched the speed distributions for argon and helium acceptably well. In calculating the momentum flux, no-one saw that this was easily related to pressure so candidates got bogged down in long integrals. There were nonetheless several near-perfect answers.

Q2. *Viscosity and non-continuum (slip) flow in an annular channel.* Candidates knew how to relate mean-free path to other properties and estimate molecular diameter from the viscosity. The flux matching model was also handled well. However, very few correctly derived the shear stress distribution for the annular control volume (really 1B material) so did not obtain the right velocity distribution.

Q3. *Translational energy modes and the Maxwell-Boltzmann distribution.* Most students efficiently calculated the density of translational energy states and correctly defined degeneracy. Many struggled to determine the energy distribution from the density of translational states and fewer were able to determine the molecular speed distribution. Several students saw the relationship between the density of states and distribution of speeds, thus providing efficient answers.

Q4. *Statistical analogue of entropy fluctuations.* The identification of variables and proof of entropy's extensive nature were readily completed by nearly all students who attempted it. Most students were able to show that entropy is a maximum via Lagrange multipliers or by setting the derivative to zero and identifying the point as a maximum. However, few students were able to calculate the RMS fluctuations or provide a viable path to the answer despite this being the approach explicitly shown in one of the lectures. Nonetheless, this was the most popular question with many doing well and several giving perfect answers.

Dr A.J. White & Prof. A.M. Boies
8th May 2023