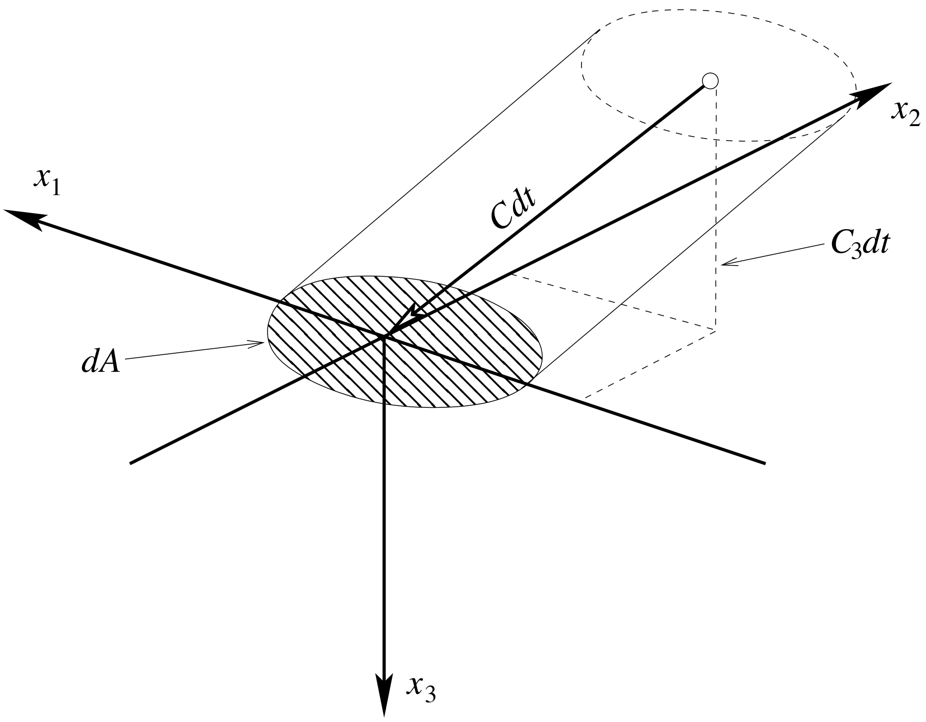
MODULE 4A9 – MOLECULAR THERMODYNAMICS
SOLUTIONS

1. (a)



No. of class C_i molecules incident on dA in time $dt = f(C_1, C_2, C_3)\, dC_1\, dC_2\, dC_3\, (C_3\, dt\, dA)$
Each molecule carries Q, but only molecules with $C_3 > 0$ contribute to the one-sided flux.
Thus total flux in +ve x_3 direction is

$$F_3^+(Q) = \int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{0}^{\infty} Q\, C_3\, f(C_1, C_2, C_3)\, dC_3\, dC_2\, dC_1$$ [6]

(b) The speed and velocity distributions must be related by $g(C)\,dC = f(C)\,dV_C$, but molecules in the speed range C to $C+dC$ are contained within a spherical shell in velocity space of volume $dV_c = 4\pi C^2\, dC$. Thus $g(C)\,dC = f(C)\,4\pi C^2\, dC$. [1]

(c) For spherical polar velocity space, $dV_c = (C\sin\theta\, d\phi)\times(C\, d\theta)\times dC = C^2\sin\theta\, d\theta\, d\phi$ and $C_3 = C\cos\theta$. Thus with $Q = m$ and noting the range of θ for positive C_3

$$F_3^+(m) = m\int_0^{\pi/2}\int_0^{2\pi}\int_0^{\infty} C\cos\theta\, f(C)\, C^2 \sin\theta\, dC\, d\phi\, d\theta$$

$$= \frac{m}{4\pi}\int_0^{\infty} C\, g(C)\, dC \times \int_0^{2\pi} d\phi \times \int_0^{\pi/2} \sin\theta\cos\theta\, d\theta$$

$$= \frac{nm}{4\pi}\,\overline{C} \times 2\pi \times \frac{1}{2} = \frac{\rho\overline{C}}{4}$$ [6]

(d) Since the pressure outside the box is zero, the net force on the box is given by the total outward flux of momentum due to the escaping molecules. Thus, with $Q = mC_3$

$$
\begin{aligned}
F_3^+(mC_3) &= m\int_0^{\pi/2}\int_0^{2\pi}\int_0^{\infty} C^2\cos^2\theta\, f(C)\, C^2\sin\theta\, dC\, d\phi\, d\theta \\
&= \frac{m}{4\pi}\int_0^{\infty} C^2\, g(C)\, dC \times \int_0^{2\pi} d\phi \times \int_0^{\pi/2} \sin\theta\cos^2\theta\, d\theta \\
&= \frac{nm}{4\pi}\,\overline{C^2} \times 2\pi \times \frac{1}{3} = \frac{\rho\overline{C^2}}{6}
\end{aligned}
$$

but at equilibrium $\dfrac{C^2}{2} = \dfrac{3RT}{2}$ (equipartition of KE) and thus the force is

$$
\begin{aligned}
F &= A \times \frac{\rho \times 3RT}{6} = \frac{pA}{2} \\
&= \frac{10^5 \times 10^{-5}}{2} = 0.05 \text{ N}
\end{aligned}
$$

Thus $\quad a = \dfrac{F}{M} = \dfrac{0.05}{0.5} = 0.1 \text{ ms}^{-2}$ [7]

<u>Examiner's note</u>: Parts (a), (b) and (c) were done well, including the transformation to polar coordinates. Most candidates tackled part (d) approximately by computing the mass flux and multiplying by the mean molecular speed, rather than computing the one-sided flux of momentum.

Q2 (a) To estimate λ, note that the volume swept out by a 'test molecule' over one mean free path contains on average one other molecule. Thus,

$$\pi d^2 \lambda n = 1$$

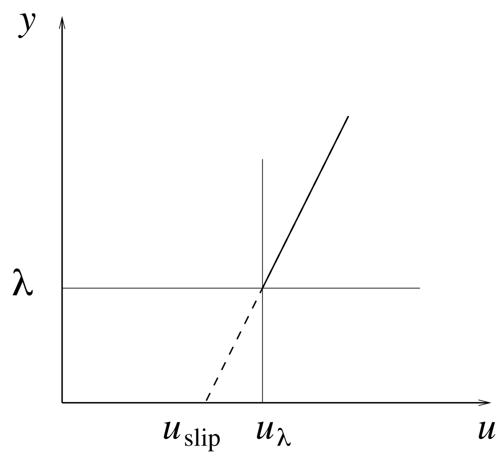
$$\therefore \qquad \text{Kn} = \frac{\lambda}{h} = \frac{1}{n\pi d^2 h} = \frac{kT}{\pi d^2 p h}$$

$$\therefore \qquad p = \frac{kT}{\pi d^2 h\ \text{Kn}} = \frac{1.38\times10^{-23}\times300}{\pi\times(0.26\times10^{-9})^2\times10^{-4}\ \text{Kn}} \approx \frac{200}{\text{Kn}}$$

Slip regime for $0.01 < \text{Kn} < 0.1$ => <u>0.02 bar < p < 0.2 bar</u> [4]

[Note some leeway is given – e.g., more precise expression for λ or slightly different range of Kn.]

(b)



Free-molecule regime:

Momentum flux to wall $= \dfrac{\rho\overline{C}}{4}u_\lambda$

Momentum flux from wall $= 0$ (diffuse reflection)

Net downward momentum flux $= \dfrac{\rho\overline{C}}{4}u_\lambda$

Continuum regime:

Net momentum flux (shear stress) $= \mu\left(\dfrac{du}{dy}\right)_0 = \dfrac{\rho\overline{C}\lambda}{2}\left(\dfrac{du}{dy}\right)_0$

Equating two fluxes:

$$\frac{\rho\overline{C}\lambda}{2}\left(\frac{du}{dy}\right)_0 = \frac{\rho\overline{C}}{4}\left\{u_{\text{slip}} + \lambda\left(\frac{du}{dy}\right)_0\right\}$$

$$\therefore \qquad \underline{u_{\text{slip}} = \lambda\left(\frac{du}{dy}\right)_0} \qquad [6]$$

(c) Application of force-momentum principle to a simple CV ($dy \times dx$) gives

$$\frac{d\tau}{dy} = \frac{dp}{dx} = -\frac{\Delta p}{L}$$

$$\therefore \qquad \tau = \mu\frac{du}{dy} = -\frac{\Delta p}{L}y + \text{const.}$$

This applies across entire flow, but with slip boundary conditions. Integrating gives,

$$u = -\frac{\Delta p}{2\mu L}y^2 + Ay + B \quad \text{with } u = u_{\text{slip}} \text{ at } \quad y = 0, h$$

$$\therefore \qquad u - u_{\text{slip}} = \frac{\Delta p}{2\mu L}y(h-y)$$

But $\qquad u_{\text{slip}} = \lambda\left(\frac{du}{dy}\right)_0 = \lambda\frac{\Delta p}{2\mu L}h$

$$\therefore \qquad \underline{u = \frac{\Delta p h^2}{2\mu L}\left\{\frac{y}{h} - \frac{y^2}{h^2} + \frac{\lambda}{h}\right\} = \frac{\Delta p h^2}{2\mu L}\left\{z - z^2 + \text{Kn}\right\}} \quad \text{where} \quad z = y/h$$

Mass flow: $\dot{m} = \int_0^h \rho u\, dy = \rho\frac{\Delta p h^3}{2\mu L}\int_0^1\left\{z - z^2 + \text{Kn}\right\}dz = \rho\frac{\Delta p h^3}{2\mu L}\left\{\frac{1}{6} + \text{Kn}\right\}$

For fixed mass flow:

$$\Delta p \propto \frac{1}{1/6 + \text{Kn}}$$

$$\therefore \qquad \frac{\Delta p}{\Delta p_{\text{cont}}} \propto \frac{1/6}{1/6 + \text{Kn}} = \underline{\frac{1}{1 + 6\text{Kn}}} \qquad [10]$$

<u>*Examiner's note:*</u> *Part (a) was done well. Parts (b) and (c) were done reasonably well, though quite a few candidates had difficulty deriving the force-momentum equation.*

3. (a)

(i) For an isolated system at equilibrium, each of the Ω microstates compatible with the fixed energy E of a system are equally probable.

(ii) Microcanonical systems have a fixed number of molecules N, volume V and internal energy U. Canonical systems have fixed number of molecules N, volume V and temperature T.

(iii) Internal modes become fully excited in the order (1) rotational, (2) vibrational and then (3) electrical.

(iv) Heat addition changes the number of particles within each energy level, whereas work done changes the spacing of the energy levels.

(b)

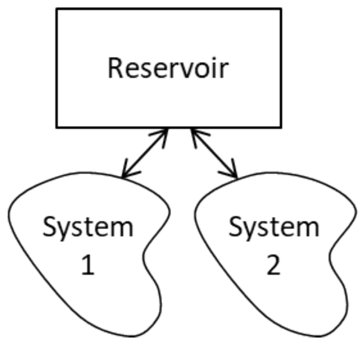


Figure 1: Schematic of systems in contact with thermal reservoir.

The probability P of each system being having a given energy E is each $P_i = f_1(E_i)$ and $P_j = f_2(E_j)$.

The joint probability $P_{ij} = P_i P_j$, thus $P_{ij} = f_1(E_i) f_2(E_j) = f_{12}(E_i + E_j)$. The function that has these properties is $P(E_i) = C \exp^{\beta E_i}$ where C and β.

β must be related to temperature because it is the only property shared between System 1 and System 2.

(c)

$$Q_{int} = Z_{rot}^N / N!$$

$$U_{rot} = kT^2\ \partial(\ln(Z_{rot}^N/N!))/\partial T = kT^2 \partial(N \ln(Z_{rot}) - \ln(N!))/\partial T$$

$$U_{rot} = NkT^2 \partial(\ln(Z_{rot}))/\partial T$$

$Z_{rot} = \sum_{n=0}^{\infty}(2n+1)e\hat{}(-n(n+1)\tau)$, where $\tau = \theta_r/T$ and $\partial\tau/\partial T = -\theta_r/T^2$.

$$Z_{rot} = 1 + 3e^{-2\tau} + 5e^{-6\tau} + 7e^{-12\tau} + 9e^{-20\tau} + ...$$

Check: the first two terms of the infinite sum allow for correct calculation to six significant figures.

$$U_{rot} = NkT^2 \, \frac{\partial \tau}{\partial T} \frac{\partial}{\partial T} (\ln(1 + 3e^{-2\tau}))$$

$$U_{rot} = NkT^2(-\theta_r/T^2) \cdot (-6e^{-2\tau})/(1 + 3e^{-2\tau})$$

For $T = 40$ K and $\theta_r = 80$ K gives $\tau = 2$.

$$U_{rot} = Nk\theta_r \cdot (6e^{-4})/(1 + 3e^{-4}) = 8.314 \cdot 80 \cdot 0.1 \text{ J}$$

$$U_{rot} = 66.5 \text{ J}$$

(d)

$$\sigma_E^2 = \frac{\partial U}{\partial \beta}, \ \beta = \frac{-1}{kT} \Rightarrow \ T = \frac{-1}{k\beta}$$

$$\sigma_E^2 = \frac{\partial U}{\partial T} \frac{\partial T}{\partial \beta} \text{ where } \frac{\partial T}{\partial \beta} = \frac{1}{k\beta^2} = \frac{1}{k(-1/kT)^2} = kT^2$$

$$\sigma_E^2 = kT^2 C_v, \text{ where } C_v = (0.8 + 1.5)Nk = 2.3Nk$$

$$\sigma_E = \sqrt{kT^2 C_v} = kT\sqrt{2.3N}$$

$$dU = C_v dT \ \Rightarrow \ \sigma_E = C_v \sigma_T$$

$$\sigma_T = \frac{\sqrt{kC_v}}{C_v} T = \frac{T}{\sqrt{2.3N}} = 3.4 \cdot 10^{-11} \text{ K}$$

$$\sigma_T = 3.4 \cdot 10^{-11} \text{ K}$$

Examiner's note: Most students were able to provide general definitions and explain the functional form of the probability of energy using a canonical framework. Many of those attempting the second part did not distinguish the individual particle and system partition functions, and several incorrectly assumed that the energy level spacing was small.

4. (a)

$$\delta Q - \delta W = dU$$

$$\delta Q = TdS, \ \delta W = p_s dA$$

$$dU = TdS - p_s dA$$

$$F \equiv U - TS \Rightarrow \ dF = dU - TdS - SdT$$

$$dF = -p_s dA - SdT$$

(b)

$$E(n_x, n_y) = \frac{h^2 2\pi}{m} \left(\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} \right)$$

$$Z_{tr} = \sum_{i=1}^{\infty} e^{-E_i/(kT)} = \sum_{n_x=1}^{\infty} e^{-E_{ix}/(kT)} \sum_{n_y=1}^{\infty} e^{-E_{iy}/(kT)}$$

For small energy spacing

$$Z_{tr}^{x} = \int_1^{\infty} e^{-\tau_x^2 n_x^2} dn_x \simeq \int_0^{\infty} e^{-\tau_x^2 n_x^2} dn_x = \frac{\sqrt{\pi}}{2\tau_x}, \text{ where } \tau_x^2 = \frac{h^2 2\pi}{mkTL_x^2}$$

$$Z_{tr} = Z_{tr}^{x} Z_{tr}^{y} = \frac{\pi}{4}(\tau_x \tau_y)^{-1} = \frac{\pi}{4}\frac{mkTL_xL_y}{2\pi h^2}$$

$$Z_{tr} = \frac{mkTA}{8h^2}$$

(c)
From (a)

$$S = \frac{-\partial F}{\partial T} - p_s \frac{\partial A}{\partial T} \Rightarrow S = -\left(\frac{\partial F}{\partial T}\right)_A$$

$$F = -kT \ln Q = -kT \ln\left(\frac{Z_{tr}^N}{N!}\right)$$

$$S = -\frac{\partial}{\partial T}\left(-kT \ln\left(\left(\frac{mkTA}{8h^2}\right)^N /N!\right)\right)$$

$$S = k\frac{\partial}{\partial T}\left(T\left(N \ln T + N \ln\left(\frac{mkA}{8h^2}\right) - \ln N!\right)\right)$$

$$S = k\left(N \ln T + N \ln\left(\frac{mkA}{8h^2}\right) - \ln N! + N\right)$$

$$S = Nk\left(\ln T + \ln\left(\frac{mkA}{8h^2}\right) - \ln N!/N + 1\right)$$

$$S = Nk\left(\ln\left(\frac{mkAT}{8h^2}\right) - \ln N!/N + 1\right)$$

(d)

$$S_2 = Nk\left(\ln T_2 + \ln A_2 + \ln\left(\frac{mk}{8h^2}\right) - \ln N!/N + 1\right)$$
$$S_1 = Nk\left(\ln T_1 + \ln A_1 + \ln\left(\frac{mk}{8h^2}\right) - \ln N!/N + 1\right)$$
$$\Delta S_{1\to 2} = Nk(\ln(T_2/T_1) + \ln(A_2/A_1))$$

For isothermal

$$\Delta S_{1\to 2} = Nk \ln(A_2/A_1) \text{ and from statistical definition } \Delta S_{1\to 2} = k \ln(\Omega_2/\Omega_1)$$

$$\Omega_2/\Omega_1 = (A_2/A_1)^N$$

$$\Omega_2/\Omega_1 = (A_2/A_1)^N = 2^{6.022\cdot 10^{23}} \simeq 2^{\cdot 10^{23}}, \text{ very large increase.}$$

<u>*Examiner's note:*</u> *Almost all candidates managed part (a) well but many made mistakes with the calculus in part (b). Candidates clearly found the derivation of entropy from the Helmholtz function more challenging, but part (d) was done well.*