SOLUTIONS TO 4A9 Molecular Thermodynamics 2021

Examiners' comments:

Q1. Most candidates did very well on this question, showing a thorough grasp of the MFP model, and tackling the Sutherland model part of the question very competently.

Q2. The least popular question, but most of those that attempted it negotiated the derivation of Maxwell's Equations of Change very well, and gave good interpretations of the resulting viscous stress terms in the momentum equation. Most marks were lost at the end of part (c) in showing that h_0 is constant.

Q3. Most students easily determined the degeneracy in 3a, while a few omitted to provide the energy level. Reducing the partition function of a single molecule to the expression given in 3b using the binomial expansion formula was among the most challenging aspects of the exam. A minority of students receiving less than full marks as a result of either an inability to formulate the partition function correctly or as a result of errors in identifying the analogous terms in the given formula. The expression of the specific heat capacity was found by most students in 3c, despite a few missing the simplification found by taking the limit at high temperatures. Most students identified the contributions of vibrational potential and kinetic energy components to the equipartition theorem.

Q4. All but a few students were able to determine the constraint in 4ai. There was a mix of valid approaches in deriving the maximum entropy for three microstates in 4aii, either by finding the maximum from a derivative or by use of Lagrangian multipliers. Most were able to show that *S'* was extensive for 4aiii, while a few mistakenly demonstrated that *S''* was extensive as done in the notes. Almost all students were able to determine the P_i and *S'* values for an isolated system in 4aiv. A large majority of students were able to use Gibbs' relation to correctly find the derivatives to determine the variance in value for 4bi. Nearly half the cohort were able to determine the numerical value for the normalized volume fluctuation with a few students not identifying that helium could be treated as a perfect gas.

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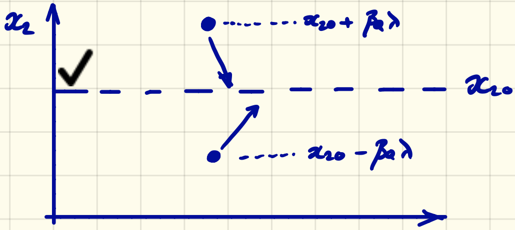
Q2.

(a)



Net upward flux, $F_Q = \frac{n\bar{C}}{4}\left(\bar{Q}(x_{20}) - \beta_Q\lambda\frac{d\bar{Q}}{dx_2}\right) - \frac{n\bar{C}}{4}\left(\bar{Q}(x_{20}) + \beta_Q\lambda\frac{d\bar{Q}}{dx_2}\right)$

$$F_Q = -\frac{n\bar{C}}{2}\beta_Q\lambda\frac{d\bar{Q}}{dx_2}$$

$$\therefore \quad D_Q = \frac{n\bar{C}}{2}\beta_Q\lambda$$

[5]

(b) Molecules with higher kinetic energy tend, on average, to come from further away, hence $\beta_K > \beta_\mu$.

For x_1-momentum, $\bar{Q} = mu_1$

$$\tau = \mu\frac{du_1}{dx_2} = -F_Q = \frac{n\bar{C}}{2}\beta_\mu\lambda m\frac{du_1}{dx_2} \Rightarrow \mu = \frac{\rho\bar{C}}{2}\lambda$$

For thermal kinetic energy $\bar{Q} = \frac{m\bar{C}^2}{2} = mc_vT$

$$\therefore \quad q = -k\frac{dT}{dx_2} = \frac{n\bar{C}}{2}\beta_K\lambda mc_v\frac{dT}{dx_2} \Rightarrow k = \frac{5}{4}\rho\bar{C}\lambda c_v$$

$$P_r = \frac{\mu c_p}{k} = \cancel{\frac{\rho\bar{C}}{2}\lambda} \times \gamma c_v \times \frac{\cancel{4}\,2}{5\cancel{\rho\bar{C}\lambda} c_v} = \frac{2\gamma}{5}$$

For He, $\gamma = 5/3$, $\therefore$ $P_r = \frac{2}{5}\times\frac{5}{3} = \frac{2}{3}$

[6]

(c) $$\frac{\mu_2}{\mu_1} = \frac{n_2 m \lambda_2 \bar{c}_2}{n_1 m \lambda_1 \bar{c}_1}$$

Here we have to note that $\lambda \sim 1/n$. For example, the simple "test molecule" model gives that

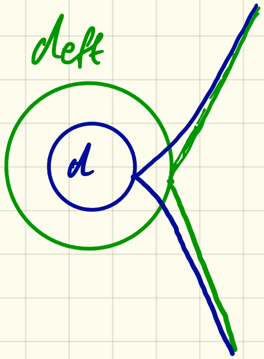
$$n \pi d^2 \lambda = 1 \quad \text{where } d = \text{molecular diameter.}$$

Thus $$\frac{\mu_2}{\mu_1} = \frac{\bar{c}_2}{\bar{c}_1} = \sqrt{\frac{T_2}{T_1}}$$

[3]

$$\therefore \mu_2 = \mu_1 \times \sqrt{\frac{600}{300}} = 19.9 \times 10^{-6} \times \sqrt{2} \simeq \underline{\underline{28.1 \times 10^{-6}\ \mathrm{kg\,m^{-1}\,s^{-1}}}}$$

(d)



$$d_{\text{eff}}^2 = d^2 (1 + \chi/T)$$

Attractive forces make the effective diameter larger, hence $\chi > 0$.

This means that deff decreases with temperature. This is because the attractive forces have less impact on the trajectory when molecules have high kinetic energy.

We note that $\lambda \sim \frac{1}{n d_{\text{eff}}^2}$ so $$\frac{\mu_2}{\mu_1} = \frac{\bar{c}_2}{\bar{c}_1} \cdot \frac{d_{\text{eff}_1}^2}{d_{\text{eff}_2}^2} = \left(\frac{T_2}{T_1}\right)^{1/2} \frac{1 + \chi/T_1}{1 + \chi/T_2}$$

$$\therefore \mu_2 = 19.9 \times 10^{-6} \times \left(\frac{600}{300}\right)^{1/2} \times \frac{1 + 101/300}{1 + 101/600} \simeq \underline{\underline{32.2 \times 10^{-6}\ \mathrm{kg\,m^{-1}\,s^{-1}}}}$$

[6]

Q1. f is defined such that $f(t, x_i, c_i)\,dc_1 dc_2 dc_3 = f\,dV_c$

(a) is the number of molecules per unit volume in the velocity range c_i to $c_i + dc_i$ $(i = 1, 2, 3)$ at point (x_i, t)

(i) $$\rho = \int_{-\infty}^{\infty} m f\, dV_c = nm$$ (m = molecular mass, n = molecules per unit vol.)

(ii) $$u_i = \frac{1}{n}\int_{-\infty}^{\infty} c_i f\, dV_c$$

(iii) $\frac{3}{2} kT = \frac{1}{2} m \overline{C^2}$ where C_i is the peculiar velocity

$C^2 = C_1^2 + C_2^2 + C_3^2$ ← BIG C's

$$\therefore T = \frac{m}{3k}\left\{\frac{1}{n}\int_{-\infty}^{\infty} c^2 f\, dV_c - u^2\right\}$$

LITTLE c's

$\boxed{5}$

(b) Multiply Boltzmann equation by Q and integrate over all velocities:

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

Noting that x_j, t & c_j are independent:

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

Put $Q = mc_i = m(u_i + C_i)$

$$\Rightarrow \frac{\partial}{\partial t}(\rho u_i) + \frac{\partial}{\partial x_j}\left(\rho\overline{(u_j + C_j)(u_i + C_i)}\right) = 0$$

Because momentum is conserved during collisions

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

The terms on the RHS correspond to the divergence of the stress components i.e., RHS $= \frac{\partial}{\partial x_j}\sigma_{ij}$ where $\sigma_{ij} = -\rho\overline{C_iC_j}$

For $i \neq j$, σ_{ij} are the viscous shear stesses, whereas the normal components $(i=j)$ include the pressure. Thus:

$$\tau_{ij} = -\left(\rho\overline{C_iC_j} - p\,\delta_{ij}\right) \quad \text{where} \quad p = \tfrac{1}{3}\rho\left(\overline{C_1^2} + \overline{C_2^2} + \overline{C_3^2}\right)$$ [8]

(c) Starting from:

$$\cancel{\frac{\partial}{\partial t}\left\{\frac{\rho}{2}\left(u^2 + \overline{C^2}\right)\right\}} + \frac{\partial}{\partial x_j}\left\{\frac{\rho u_j}{2}\left(u^2 + \overline{C^2}\right)\right\} = -\frac{\partial}{\partial x_j}\left\{\rho u_k\overline{C_jC_k} + \cancel{\frac{\rho\overline{C_jC^2}}{2}}\right\}$$

For steady flow, all the $\frac{\partial}{\partial t}$ terms go, and for a Maxwellian velocity distribution (which is symmetric in C_1, C_2 & C_3) the only terms on the RHS which remain are due to the pressure, when $j=k$. Note also that the specific internal energy is $e = \overline{C^2}/2$

Thus $$\frac{\partial}{\partial x_j}\left\{\rho u_j\left(e + \frac{u^2}{2}\right)\right\} = -\frac{\partial}{\partial x_j}\left(u_j p\right)$$

$\therefore$ $$\frac{\partial}{\partial x_j}\left\{\rho u_j\left(e + \frac{u^2}{2} + p/\rho\right)\right\} = 0$$

or $$\frac{\partial}{\partial x_j}\left\{\rho u_j h_0\right\} = h_0\cancel{\frac{\partial}{\partial x_j}\left(\rho u_j\right)} + \rho u_j\frac{\partial h_0}{\partial x_j} = 0$$

The first term is zero due to mass continuity $(\nabla\cdot\rho\underline{u} = 0)$
The second term implies h_0 is constant along a s/l

i.e., $$\underline{u}\cdot\nabla h_0 = 0$$ [7]

Q3 (AJW CRIB) $\varepsilon_j = (n_1 + n_2 + n_3 \cdots + n_\omega + \frac{\omega}{2}) h\nu$

(a) $= jh\nu + \frac{\omega h\nu}{2}$

g_j is given as the number ways j balls can be distributed between ω boxes. This is found by finding the number of distinct arrangements of j balls and $\omega - 1$ partitions.

$\bullet \; \bullet \, | \, \bullet \, | \, | \, \bullet \; \bullet$ etc

No. of possible arrangements if balls and partitions are distinguishable

$$= (\omega + j - 1)!$$

This needs to be divided by $j!$ because the balls are not distinguishable, and by $(\omega-1)!$ because neither are the partitions.

$$\therefore \quad g_j = \frac{(\omega+j-1)!}{(\omega-1)!\, j!}$$

[6]

(b) The vibrational partition function for a single molecule is given by:

$$Z = \sum_0^\infty g_j e^{-\varepsilon_j / kT}$$

NOTE the $e^{-\omega h\nu/kT}$ is a constant and does not affect Z.

$$= \sum_0^\infty \frac{(\omega+j-1)!}{(\omega-1)!\, j!} \phi^j$$

where $\phi = e^{-\theta/T}$

$$\text{cf.} \quad (x+y)^{-\omega} = \sum_{j=0}^\infty \frac{(\omega+j-1)!}{(\omega-1)!\, j!} (-1)^j x^j y^{-(\omega+j)}$$

These are the same if $x = -\phi$ and $y = 1$

$$\therefore \quad Z_{(\omega)} = (1-\phi)^{-\omega} = \frac{1}{\left(1-e^{-\theta_v/T}\right)^{\omega}}$$

Alter. $Z_1 = 1 + e^{-\theta_v/T} + e^{-2\theta_v/T} + \cdots$ no degeneracy for $\omega = 1$

$$= \sum_{j=0}^{\infty} \phi^j = \frac{1}{1-\phi}$$

$$\therefore Z_\omega = Z_1^{\omega} = \left(1-e^{-\theta_v/T}\right)^{-\omega}$$ because modes are distinguishable.

(c) $U = kT^2 \frac{\partial}{\partial T}(\ln Q)_{N,V}$ where $Q = \frac{Z_1^{\omega N}}{N!}$

$$\therefore U = N\omega kT^2 \frac{\partial}{\partial T} \ln Z_1 = N\omega k\cancel{T^2} \frac{\theta_v}{\cancel{T^2}} \frac{e^{-\theta_v/T}}{1-e^{-\theta_v/T}}$$

$$u = \frac{U}{NM} = \frac{\omega R\theta_v}{e^{\theta_v/T}-1}$$

$$c_v = \left(\frac{\partial u}{\partial T}\right)_v = \frac{-\omega R\theta_v}{\left(e^{\theta_v/T}-1\right)^2} e^{\theta_v/T}\left(-\frac{\theta_v}{T^2}\right)$$

$$c_v = R\omega\left(\frac{\theta_v}{T}\right)^2 \frac{e^{\theta_v/T}}{\left(e^{\theta_v/T}-1\right)^2}$$

Let $x = \frac{\theta_v}{T}$, so $T \gg \theta_v \Rightarrow x \to 0$

$$c_v = \lim_{x\to 0} R\omega \cancel{x^2} \frac{(1+x+\cdots)}{\cancel{x^2}+\text{HOT}} = \underline{\underline{R\omega}}$$

This is consistent with $\frac{R}{2}$ per "squared term" since there are two squared terms for each mode (PE & KE)

Q4 (a) $S' = -k \sum p_i \ln p_i$ [1]

(i) $\sum p_i = 1$ (the system must be in one of its possible microstates)

(ii) Let $p_1 = p$, $p_2 = 1-p$

$\Rightarrow -S'/k = p \ln p + (1-p)\ln(1-p)$

$\Rightarrow -\frac{1}{k}\frac{dS'}{dp} = \cancel{p \times 1/p} + \ln p + \cancel{(1-p)\times\frac{1}{1-p}} - \ln(1-p)$

$= \ln\left(\frac{p}{1-p}\right) = 0$ at S'_{max}

$\Rightarrow p = 1-p \Rightarrow p = 1/2$; $(1-p) = 1/2 \Rightarrow$ $\underline{\underline{S' = k \ln 2}}$ [~~3~~]

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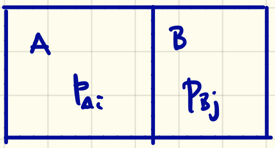
(iii) Consider two subsystems A & B



Probability A is in state i and B is in state j $\quad P_{ij} = P_{Ai} P_{Bj}$

$$S' = -k \sum_i \sum_j P_i P_j \ln P_i P_j = -k \sum_i \sum_j P_i P_j (\ln P_i + \ln P_j)$$

$$= -k \sum_i P_i \sum_j P_j \ln P_j - k \sum_j P_j \sum_i P_i \ln P_i$$

because $\sum P_i = \sum P_j = 1$

$$= -k \sum_j P_j \ln P_j - k \sum P_i \ln P_i$$ [4]

$$= \underline{S'_A + S'_B}$$ (i.e., S' is extensive) [~~3~~]

(iv) All microstates are equally probable for an isolated system at equilibrium

$\therefore P_i = \frac{1}{\Omega} \Rightarrow S' = -k \sum \frac{1}{\Omega} \ln\left(\frac{1}{\Omega}\right) = \underline{\underline{k \ln \Omega}}$ [2]

(6) (i) $\sigma_V^2 = kT\left\{\left(\frac{\partial^2 U}{\partial V^2}\right)_T - T\left(\frac{\partial^2 S}{\partial V^2}\right)_T\right\}^{-1}$

$T\,dS = dU + p\,dV$

$\therefore\ T\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial U}{\partial V}\right)_T + p \Rightarrow T\left(\frac{\partial^2 S}{\partial V^2}\right) = \left(\frac{\partial^2 U}{\partial V^2}\right)_T + \left(\frac{\partial p}{\partial V}\right)_T$

$\therefore\ \sigma_V^2 = kT\left\{\cancel{\frac{\partial^2 U}{\partial V^2}} - \cancel{\frac{\partial^2 U}{\partial V^2}} - \left(\frac{\partial p}{\partial V}\right)_T\right\}^{-1} = \underline{\underline{-kT\left(\frac{\partial V}{\partial p}\right)_T}}$ [4]

(ii) For He – assume perfect gas

$\therefore\ V = \frac{mRT}{p} \Rightarrow \left(\frac{\partial V}{\partial p}\right)_T = -\frac{mRT}{p^2} = -\frac{V}{p} =$

$\therefore\ \sigma_V^2 = \frac{mRT^2k}{p^2}$ now $V_0 = \frac{mRT}{p}$

$\therefore\ \left(\frac{\sigma_V}{V}\right)^2 = \frac{\cancel{m}R\cancel{T^2}k\cancel{p^2}}{\cancel{p^2}m^2R^2\cancel{T^2}} = \frac{k}{mR}$ $R = k/m$ mol. mass.

$\therefore\ \left(\frac{\sigma_V}{V}\right)^2 = \frac{1}{N} \Rightarrow \frac{\sigma_V}{V} = \frac{1}{\sqrt{N}}$

$N = \frac{0.1}{4.0} \times 6.023 \times 10^{+23} \Rightarrow \underline{\underline{\frac{\sigma_V}{V} \approx 8.15 \times 10^{-12}}}$ [5]

4A9 Q4 (a) (ii) – additional crib

$$\phi = -S'/k = \sum p_i \ln p_i = p\ln p + q\ln q + (1-p-q)\ln(1-p-q)$$

$$\frac{\partial \phi}{\partial p} = \cancel{1} + \ln p - \cancel{1} - \ln(1-p-q) = 0$$

$$\Rightarrow \quad p = 1-p-q$$

Similarly, $\quad q = 1-p-q$

$$\therefore \quad \underline{p = q = 1/3} \quad \Rightarrow \quad S' = -3 \times k \times 1/3 \times \ln 1/3$$

$$\underline{S' = k\ln 3}$$

[4]