

**MODULE 4A9 – MOLECULAR THERMODYNAMICS  
SOLUTIONS 2018**

1. (a) Kinetic temperature  $T_K$  is defined as proportional to the average thermal (i.e., random) translational kinetic energy of molecules, with the constant of proportionality such that:

$$\frac{1}{2}m\overline{C^2} = \frac{3}{2}kT$$

where  $k$  is Boltzmann's constant (i.e., an average molecular energy of  $kT/2$  per mode). Thus,

$$T = \frac{1}{3} \frac{m}{k} \overline{C^2} = \frac{\overline{C^2}}{3R} = \frac{1250^2}{3 \times 2078.5} = 250.6 \text{ K}$$

$T_K$  is equal to the thermodynamic temperature  $T$  under equilibrium conditions. (Unlike  $T$ , the kinetic temperature is well-defined for non-equilibrium situations.) [3]

(b) (i) Putting  $Q = mc_i$  in the expression for  $F_Q$  gives:

$$\begin{aligned} F_M &= \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} (mc_i)c_j \, dc_3 \, dc_2 \, dc_1 = n\overline{mc_i c_j} = \rho \overline{c_i c_j} \\ &= \rho(u_i + C_i)(u_j + C_j) \\ &= \rho u_i u_j + \rho \overline{C_i C_j} \end{aligned} \quad (1)$$

The first term represents the convection  $x_i$ -momentum due to bulk motion of the gas, whereas the second term is the negative of the stress  $\sigma_{ij}$  and is due to the transport of momentum by random molecular motion. [3]

(ii) For a Maxwellian velocity distribution, the peculiar velocity components are uncorrelated (this is clear from the distribution given in the question paper), so

$$\overline{C_i^n C_j^m} = \begin{cases} \overline{C_i^n} \times \overline{C_j^m} & \text{for } i \neq j \\ \overline{C_i^{n+m}} & \text{for } i = j \end{cases}$$

Since the Maxwellian distribution is an even function in each of the  $C_i$ , the averaged quantity is zero if  $n$  or  $m$  is odd for  $i \neq j$  or if  $n+m$  is odd for  $i = j$ . [2]

(iii) Shear stresses are given by

$$\tau_{ij} = -\rho \overline{C_i C_j} \quad \text{for } i \neq j$$

which according to (iii) would be identically zero in a Maxwellian distribution. Since at least some of the shear stresses are non-zero in a laminar boundary layer it follows that the velocity distribution is not Maxwellian – some of the peculiar velocity components must be correlated. [1]

(iv) The pressure is the negative of the average normal stress, so:

$$p = -\frac{1}{3}(\sigma_{11} + \sigma_{22} + \sigma_{33}) = +\frac{\rho}{3}(\overline{C_1^2} + \overline{C_2^2} + \overline{C_3^2}) = \frac{2}{3}n\left(\frac{m}{2}\overline{C^2}\right) = \frac{2}{3}E_{tr} \quad [2]$$

(c) The flux of energy in the  $x_j$  direction ( $F_Q$  with  $Q = mc^2/2$ ) is :

$$F_E = \frac{\rho}{2}\overline{(c_i c_i c_j)} = \frac{\rho}{2}\overline{(c_1^2 + c_2^2 + c_3^2)c_j}$$

Choosing the streamwise direction as  $x_1$  gives

$$F_E = \frac{\rho}{2}\overline{\{(V + C_1)^2 + C_2^2 + C_3^2\}(V + C_1)} = \frac{\rho}{2}\overline{\{V^2 + 2VC_1 + C_1^2 + C_2^2 + C_3^2\}(V + C_1)}$$

Along the nozzle centre line (out of the boundary layer) the velocity distribution will be Maxwellian, so use can be made of the results of part (b) (ii). Thus,

$$F_E = \frac{\rho}{2}\left\{V^3 + \overline{(C_1^2 + C_2^2 + C_3^2)}V + 2V\overline{C_1^2}\right\} = \rho V\left\{\frac{V^2}{2} + \frac{1}{2}(\overline{C_1^2} + \overline{C_2^2} + \overline{C_3^2}) + \overline{C_1^2}\right\}$$

each squared term involving  $C_i$  inside the brackets contribute  $RT/2$  (from the definition of kinetic temperature, and since there is no preferred direction for the peculiar velocity components. Hence,

$$F_E = \rho V\left\{\frac{V^2}{2} + \frac{3}{2}RT + RT\right\} \quad \text{so } \underline{B = 5/2}$$

The additional  $RT$  equates to  $p/\rho$  and is due to the flow work. [9]

Examiner's note:

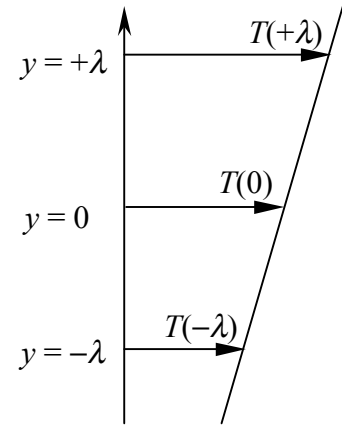
*This was the least popular question. Many of those that attempted it failed to spot the link in part (b) between the integral expression for  $F_M$  (see eq. 1 above) and the averaged values (RHS of eq. 1) and hence got bogged down in difficult integrals (which in any case would only be valid for equilibrium distributions). Remarkably, a few students correctly evaluated these integrals in part (c).*

2. (a)

Assume molecules make their last collision one mean free path above or below the plane  $y = 0$ .

$$\text{Flux of KE from below} = \frac{\rho \bar{C}}{4} c_v \left[ T(0) - \lambda \frac{dT}{dy} \right]$$

$$\text{Flux of KE from above} = \frac{\rho \bar{C}}{4} c_v \left[ T(0) + \lambda \frac{dT}{dy} \right]$$



$$\text{Net flux of KE in positive } y\text{-direction} = \text{heat flux} = q = -\frac{\rho \bar{C} \lambda c_v}{2} \frac{dT}{dy}$$

$$\text{Thermal conductivity } k \text{ is defined by } q = -k \frac{dT}{dy} \text{ and hence, } k = \frac{\rho \bar{C} \lambda c_v}{2} = \frac{1}{2} \rho \bar{C} \lambda \frac{3}{2} R.$$

Thus  $\beta = 3/4$ .

More detailed solutions of the Boltzmann equation increase  $\beta$  (by a factor of  $5/2$ ). This is because molecules with higher velocity (and therefore higher KE) tend to come from further away and this correlation is not accounted for in the simpler mean-free-path theories. [7]

(b) The mean free path can be estimated by considering the average volume swept out between collisions and assuming this to contain one molecule, thus

$$\lambda \pi d^2 n \sim 1 \quad \Rightarrow \quad \lambda \sim \frac{1}{\pi n d^2} = \frac{m}{\pi \rho d^2}$$

where  $d$  is the effective diameter of a molecule and  $m$  is its mass. Thus,

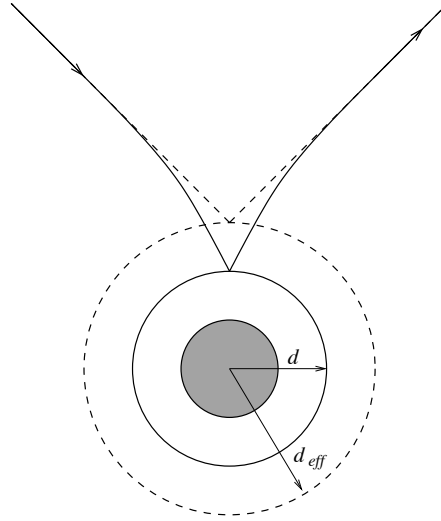
$$k = \frac{3}{4} \rho \bar{C} \lambda R = \frac{3}{4} \rho \sqrt{\alpha T} \times \frac{m}{\pi \rho d^2} R = AT^{1/2}$$

i.e.,  $k$  is independent of pressure and scales as the square root of  $T$ . Hence

$$k_{400} = k_{300} \times \sqrt{(4/3)} = 0.0178 \times 1.155 = \underline{0.0206 \text{ Wm}^{-1}\text{K}^{-1}} \text{ (to 3 SF)}$$

[4]

(c) The attractive intermolecular forces ‘soften’ the molecule such that its effective ‘target’ diameter is bigger:



The effective diameter  $d_{eff}$  would be expected to fall with increasing molecular speed, so that the  $\lambda$  would be expected to *increase* with  $T$ , and hence  $k$  will increase faster than  $T^{1/2}$ . Thus the real value of  $k$  is likely to be higher than  $0.021 \text{ Wm}^{-1}\text{K}^{-1}$ . [3]

(d) Conditions are in the continuum regime ( $\text{Kn}=0.001$ ) so,

$$(i) \quad q = k_{400} \frac{\Delta T}{H} = 0.02055 \times \frac{200}{0.001} = \underline{4.11 \text{ kWm}^{-2}} \quad [2]$$

$$(ii) \quad q = -k \frac{dT}{dy} = -AT^{1/2} \frac{dT}{dy} = \text{const.}$$

$$\therefore \quad q \int dy = -A \int_{T_1}^{T_2} T^{1/2} dT$$

$$\Rightarrow \quad qH = \frac{2}{3} [AT_2^{3/2} - AT_1^{3/2}] = \frac{2}{3} [k_{500} \times 500 - k_{300} \times 300]$$

where  $k_{500} = k_{300} (500/300)^{1/2} = 0.02298 \text{ Wm}^{-1}\text{K}^{-1}$ .

$$\therefore \quad q = \frac{2}{3} [0.02298 \times 500 - 0.0178 \times 300] / 0.001 = \underline{4.10 \text{ kWm}^{-2}} \quad [4]$$

i.e., only  $\sim 0.25\%$  error

*Examiner's note: Part (a) was done very well by nearly all who attempted this question, as might be expected (MFP models have appeared many times), but performance on the rest of the question was 'mixed'. There were, however, several perfect or near-perfect solutions.*

3 a)

$$F = U - TS \quad U = Q_H - W$$

PHYSICS  
2018

$$dF = dU - Tds - SdT \quad dU = Tds - pdV$$

$$dF = Tds - pdV - Tds - SdT \quad (\text{Chemical potential omitted})$$

$$S = - \left( \frac{dF}{dT} \right)_{V=\text{const}}$$

b)  $F = -kT \ln Q$

$$U = F + TS = F + T \left( \frac{-dF}{dT} \right) \quad \text{from a}$$

$$F = -kT \ln Q \quad \frac{dF}{dT} = -k \left( \ln Q + T \frac{d(\ln Q)}{dT} \right)$$

$$U = -kT \ln Q - T \left( -k \ln Q - kT \frac{d(\ln Q)}{dT} \right)$$

$$U = kT^2 \frac{d(\ln Q)}{dT}$$

alternative b)

$$U = \sum_i \epsilon_i P_i = \sum_i \epsilon_i \frac{e^{-\epsilon_i/kT}}{Q}$$

$$\frac{d e^{-\epsilon_i/kT}}{dT} = \frac{+\epsilon_i}{kT^2} e^{-\epsilon_i/kT} \quad \therefore e^{-\epsilon_i/kT} = \frac{kT^2}{\epsilon_i} \frac{d e^{-\epsilon_i/kT}}{dT}$$

sub into

$$U = \frac{kT^2}{Q} \sum_i \frac{\epsilon_i}{\epsilon_i} \frac{d e^{-\epsilon_i/kT}}{dT} = \frac{kT^2}{Q} \frac{d}{dT} \underbrace{\sum_i e^{-\epsilon_i/kT}}_Q = \frac{kT^2}{Q} \frac{dQ}{dT}$$

Recognize that  $\frac{d \ln Q}{dT} = \frac{1}{Q} \frac{dQ}{dT}$

$$U = kT^2 \frac{d(\ln Q)}{dT}$$

$$3c \quad Q = \frac{Z^N}{N!} \quad \omega / N=1 \quad \therefore Q = Z = g_0 + g_1 e^{-\epsilon/kT}$$

$$i) \quad S = - \left( \frac{\partial F}{\partial T} \right)_V \quad \omega / F = -kT \ln Q$$

$$S = k \frac{\partial}{\partial T} (T \ln(g_0 + g_1 e^{-\epsilon/kT}))$$

$$S = k \left( \ln(g_0 + g_1 e^{-\epsilon/kT}) + \frac{T(\epsilon/kT^2) g_1 e^{-\epsilon/kT}}{g_0 + g_1 e^{-\epsilon/kT}} \right)$$

$$\boxed{S = k \ln(g_0 + g_1 e^{-\epsilon/kT}) + \frac{\epsilon g_1 e^{-\epsilon/kT}}{T(g_0 + g_1 e^{-\epsilon/kT})}}$$

alternative i)

$$S' = -k \sum_{i \text{ states}} P_i \ln P_i \neq -k \sum_{j \text{ levels}} P_j \ln P_j$$

Be careful with states versus levels!

$$P_i = \frac{e^{-\epsilon_i/kT}}{Q} \quad \text{where } Q = \sum_{i \text{ states}} e^{-\epsilon_i/kT} = \sum_{j \text{ levels}} g_j e^{-\epsilon_j/kT}$$

$$S' = -k (g_0 P_0 \ln P_0 + g_1 P_1 \ln P_1) = -k \left( g_0 \frac{1}{Q} \ln \frac{1}{Q} + g_1 \frac{e^{-\epsilon_1/kT}}{Q} \ln \frac{e^{-\epsilon_1/kT}}{Q} \right)$$

$$= +k \left( \frac{g_0 \ln Q}{Q} + \frac{g_1 e^{-\epsilon_1/kT}}{Q} (+\epsilon_1/kT + \ln Q) \right)$$

$$= k \frac{g_0 + g_1 e^{-\epsilon_1/kT}}{Q} \ln Q + \frac{g_1 \epsilon_1 e^{-\epsilon_1/kT}}{T Q}$$

$$\boxed{S' = k \ln(g_0 + g_1 e^{-\epsilon/kT}) + \frac{\epsilon g_1 e^{-\epsilon/kT}}{T(g_0 + g_1 e^{-\epsilon/kT})}}$$

Same as above

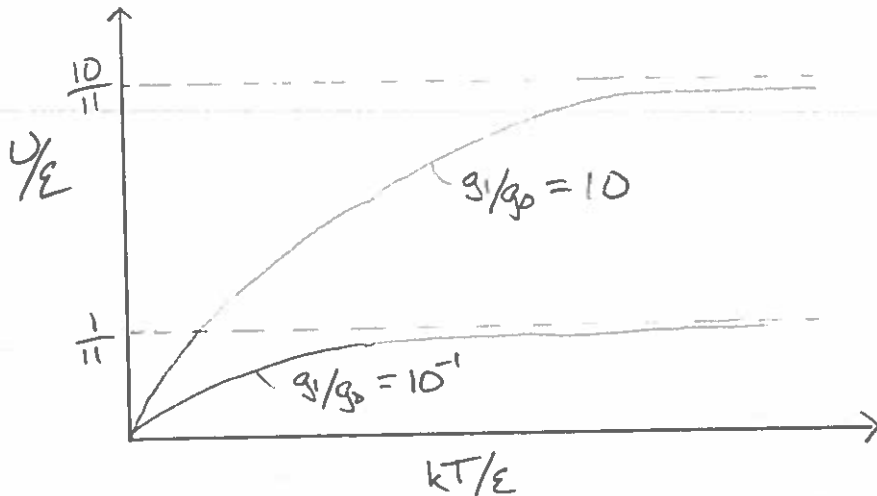
Examiner's comment: This was the second most popular question and was done very well by most students. Parts (a) & (b) were correctly completed by nearly all. Student performance in (c) was distinguished by ability to identify the proper roles of degeneracies and sketch the bounds of the solution.

$$3 \text{ cii) } U = kT^2 \frac{\partial(\ln Q)}{\partial T} = kT^2 \frac{\partial}{\partial T} (\ln(g_0 + g_1 e^{-\epsilon/kT}))$$

$$U = \cancel{kT^2} \frac{g_1 e^{-\epsilon/kT} (\epsilon/kT^2)}{g_0 + g_1 e^{-\epsilon/kT}} = \epsilon \frac{g_1 e^{-\epsilon/kT}}{g_0 + g_1 e^{-\epsilon/kT}}$$

$$\boxed{U/\epsilon = \frac{1}{1 + g_0/g_1 e^{\epsilon/kT}}}$$

for  $x = kT/\epsilon \quad \epsilon = kT/x \quad \therefore \frac{U}{\epsilon} = \frac{1}{1 + \frac{g_0}{g_1} e^{1/x}}$

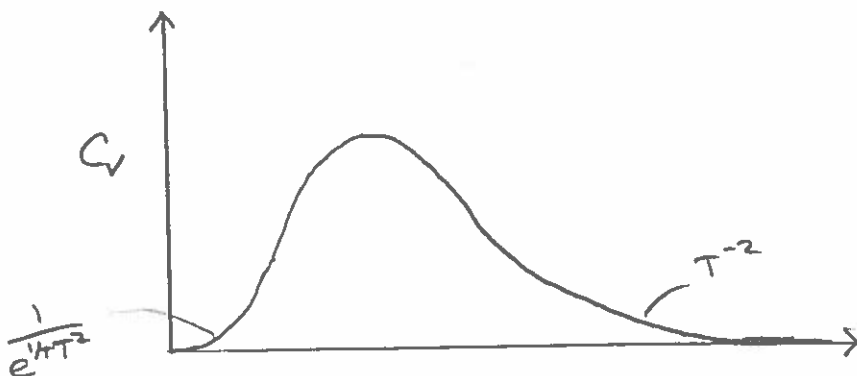


$$\text{ciii) } C_V = \left(\frac{\partial U}{\partial T}\right)_V = \epsilon \frac{\partial}{\partial T} \left(\frac{1}{1 + g_0/g_1 e^{\epsilon/kT}}\right)$$

$$C_V = -\epsilon \frac{g_0/g_1 e^{\epsilon/kT} (-\epsilon/kT^2)}{(1 + g_0/g_1 e^{\epsilon/kT})^2} = \frac{\epsilon^2}{kT^2} \frac{g_0/g_1 e^{\epsilon/kT}}{(1 + g_0/g_1 e^{\epsilon/kT})^2}$$

$$\lim_{T \rightarrow 0} C_V = \frac{1}{T^2} \frac{e^{1/T}}{(e^{1/T})^2} = \frac{1}{T^2 e^{1/T}} \text{ which goes to } 0$$

$$\lim_{T \rightarrow \infty} C_V = \frac{1}{T^2} \text{ which goes to } 0$$



4 (a)

$$i) S = -k \sum P_i \ln P_i$$

$$\frac{S_A}{k} = \frac{1}{2} \ln 2 + \frac{2}{12} \ln 12 + \frac{1}{3} \ln 3 = 1.127$$

$$\frac{S_B}{k} = 0$$

$$\frac{S_C}{k} = \frac{2}{4} \ln 4 + \frac{1}{2} \ln 2 = 1.04$$

$$\frac{S_D}{k} = \frac{3}{10} \ln 10 + \frac{10}{7} \ln \frac{7}{10} = 0.94$$

$$\therefore S_A > S_C > S_D > S_B$$

$$ii) S_E = k \ln N = S_A$$

$$\therefore \ln N \approx 1.127$$

$$N = 3.09 \approx \underline{3}$$

$$b) F = U - TS = \sum P_i E_i + kT \sum P_i \ln P_i$$

$$G = \sum P_i - 1 = 0$$

$$\mathcal{L} : \nabla F + \lambda \nabla G = 0$$

$$\frac{\partial F}{\partial P_i} + \lambda \frac{\partial G}{\partial P_i} = 0$$

$$\Rightarrow \boxed{E_i + kT(1 + \ln P_i) + \lambda = 0}$$

$$\ln P_i = \frac{-E_i - \lambda}{kT} - 1 \Rightarrow \boxed{P_i = A e^{-E_i/kT}}$$

where  $A = \frac{1}{Q}$  — Partition Function



$$H(c) \quad \sum P_i E_i = \frac{6\epsilon}{5} \quad \sum P_i = 1$$

$$i) \quad P_1 = P_2 = A e^{-\epsilon/kT} \quad P_3 = P_4 = P_5 = A e^{-2\epsilon/kT}$$

$$2P_1 \epsilon + 3P_3 2\epsilon = 6\epsilon/5 \quad w/ \quad 3P_3 = 1 - 2P_1$$

$$2P_1 + 2(1 - 2P_1) = \frac{6}{5}$$

from  $\sum P_i = 1$

$$\boxed{P_1 = 2/5 = P_2} \quad \text{and} \quad \boxed{P_3 = \frac{1 - 2P_1}{3} = \frac{1}{15} = P_4 = P_5}$$

Shown schematically (not req'd)

Microstate	# within each microstate	$\sum H$
1 Energy	2 2 2 3 3 3 1 1 1 4 4 4 0 0 0	30
2 $\epsilon$	2 2 2 1 1 1 3 3 3 0 0 0 4 4 4	30
3	1 - - 1 - - 1 - - 1 - - 1 - -	5
4 $2\epsilon$	- 1 - - 1 - - 1 - - 1 - - 1 - -	5
5	- - 1 - - 1 - - 1 - - 1 - - 1 - -	5

$$\bar{U} = \frac{6\epsilon}{5}$$

$$P_1 = P_2 = \frac{30}{75} = \frac{2}{5} \quad P_3 = P_4 = P_5 = \frac{5}{75} = \frac{1}{15}$$

Total 75

$$[1] \quad P_1 = \frac{2}{5} = A e^{-\epsilon/kT}$$

$$[2] \quad P_3 = \frac{1}{15} = A e^{-2\epsilon/kT}$$

$$[1] / [2] \Rightarrow \frac{2 \cdot 15}{5} = e^{\epsilon/kT}$$

to elim. A

$$\therefore \boxed{T = \frac{\epsilon}{k \ln 6}}$$

$$ii) \quad \text{RMS}^2 = \sum P_i E_i^2 - \bar{U}^2 = \sigma_E^2 = 2 \frac{2}{5} \epsilon^2 + 3 \frac{1}{15} 4\epsilon^2 - \frac{36}{25} \epsilon^2$$

$$\therefore \sigma_E^2 = \frac{4}{25} \epsilon^2 \Rightarrow \sigma_E = \frac{2}{5} \epsilon$$

$$\frac{\sigma_E}{\bar{U}} = \frac{2/5 \epsilon}{6/5 \epsilon} = \boxed{\frac{1}{3}}$$

33%

This fluctuation is large relative to typical systems as it is small with only 5 particles.

Examiner's comment:-

Over  $2/3$  of students attempted this. Part (a) was trivial for most, and in part (b) the majority correctly applied Lagrange multipliers. Fewer students were able to find the correct probabilities for each state and get the correct temperature in the final part.

AJW/AMB May 2018.