

ENGINEERING TRIPOS PART IIB 2012
MODULE 4A9 – MOLECULAR THERMODYNAMICS
SOLUTIONS

1. (a) The four flow regimes are :

Continuum flow ($Kn < \sim 0.01$). N-S equation with no-slip wall boundary condition is valid.

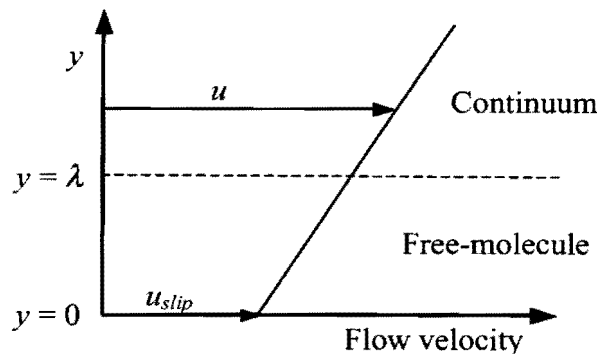
Slip flow ($\sim 0.01 < Kn < \sim 0.1$). N-S equation with a slip wall boundary condition is valid.

Transition flow ($\sim 0.1 < Kn < \sim 5$). N-S equation not valid.

Free-molecule flow ($\sim 5 < Kn$). N-S equation not valid.

[20 %]

(b)



[10 %]

Assume molecules make their last collision before striking the wall at $y = \lambda$. The velocity gradient is continued through the free-molecule region to the wall, thus defining u_{slip} .

$$\text{Flux of } x\text{-momentum carried to the wall by the incident molecules} = \frac{\rho \bar{C}}{4} \left(u_{slip} + \lambda \frac{du}{dy} \right) \quad [5 \%$$

For diffuse reflection, the flux of x -momentum carried by the reflected molecules is zero. In the continuum region the net x -momentum flux to the wall equals the shear stress τ . Hence,

$$\tau = \mu \frac{du}{dy} = \frac{\rho \bar{C} \lambda}{2} \frac{du}{dy} \quad [5 \%$$

Equating the two expressions for the flux of x -momentum gives,

$$\frac{\rho \bar{C}}{4} \left(u_{slip} + \lambda \frac{du}{dy} \right) = \frac{\rho \bar{C} \lambda}{2} \frac{du}{dy} \quad \rightarrow \quad u_{slip} = \lambda \left(\frac{du}{dy} \right)_{y=0} \quad [5 \%$$

(c) Applying the force-momentum principle to the control volume shown gives,

$$2\pi r \tau \delta x - \pi r^2 \frac{dp}{dx} \delta x = 0 \quad \rightarrow \quad \tau = \frac{r}{2} \frac{dp}{dx} \quad [5\%]$$

This is valid irrespective of the flow regime. In the central, Navier-Stokes, region we have,

$$\tau = \mu \frac{du}{dr} = \frac{r}{2} \frac{dp}{dx} \quad [5\%]$$

This is valid across the tube if we apply the slip boundary condition (compensating for the free-molecule layer near the wall). Integrating with respect to r subject to $u = u_{slip}$ at $r = R$,

$$u = u_{slip} + \left(\frac{R^2 - r^2}{4\mu} \right) \left(-\frac{dp}{dx} \right) \quad [10\%]$$

From part (b), noting that $y = R - r$,

$$u_{slip} = \lambda \left(\frac{du}{dy} \right)_{y=0} = -\lambda \left(\frac{du}{dr} \right)_{r=R} = \lambda \frac{R}{2\mu} \left(-\frac{dp}{dx} \right) \quad [5\%]$$

Thus,

$$u = \left[\frac{\lambda R}{2\mu} + \frac{(R^2 - r^2)}{4\mu} \right] \left(-\frac{dp}{dx} \right) \quad [5\%]$$

Noting that $Kn = \lambda/2R$ we obtain the velocity profile,

$$u = \left[\frac{(1 + 4Kn)R^2 - r^2}{4\mu} \right] \left(-\frac{dp}{dx} \right) \quad [5\%]$$

(d) If ρ is the density, the mass flowrate is,

$$\begin{aligned} \dot{m} &= \int_0^R 2\pi r \rho u \, dr = \frac{2\pi\rho}{4\mu} \left(-\frac{dp}{dx} \right) \int_0^R [(1 + 4Kn)R^2 r - r^3] \, dr \\ &= \frac{\pi\rho}{2\mu} \left(-\frac{dp}{dx} \right) \left[\frac{(1 + 4Kn)R^4}{2} - \frac{R^4}{4} \right] = (1 + 8Kn) \frac{\rho\pi R^4}{8\mu} \left(-\frac{dp}{dx} \right) \end{aligned} \quad [15\%]$$

The continuum result is obtained by setting $Kn = 0$. Hence,

$$\frac{\dot{m}}{\dot{m}_{cont}} = (1 + 8Kn) \quad [5\%]$$

Examiners' note:

In the first (descriptive) part of the question, many candidates had only a hazy idea about the characteristics of the different non-continuum regimes although all were able to derive the expression for the slip velocity at a solid boundary. Quite a large proportion then managed to work successfully through calculating the velocity profile and mass flowrate in pipeflow in the slip regime.

2. (a) (i) The kinetic temperature T_K of a monatomic gas is defined by the relation,

$$\text{Mean translational KE of a molecule} = \frac{m\overline{C^2}}{2} = \frac{3kT_K}{2} \quad \left(\text{or} \quad \frac{\overline{C^2}}{2} = \frac{3RT_K}{2} \right) \quad [5 \%]$$

(ii) The kinetic temperature of a diatomic molecule is defined in precisely the same way. The rotational and vibrational energies do not enter into the definition of temperature. [5 %]

(b) (i) The mixture is at equilibrium. By the principle of the 'equipartition of energy' the mean translational KE of the N_2 and He molecules are the same. Hence,

$$\frac{m_{N_2}\overline{C_{N_2}^2}}{2} = \frac{m_{He}\overline{C_{He}^2}}{2} = \frac{3kT}{2} \quad \rightarrow \quad \frac{M_{N_2}\overline{C_{N_2}^2}}{2} = \frac{M_{He}\overline{C_{He}^2}}{2} = \frac{3RT}{2}$$

where m is the mass of a molecule and M is the molar mass. Hence,

$$\overline{C_{He}^2} = \frac{M_{N_2}}{M_{He}} \overline{C_{N_2}^2} = \frac{28}{4} \times 500^2 \quad \rightarrow \quad (C_{He})_{RMS} = 1323 \text{ m.s}^{-1} \quad [15 \%]$$

(ii) The initial temperature of the mixture is given by,

$$T_I = \frac{M_{N_2}\overline{C_{N_2}^2}}{3R} = \frac{28 \times 500^2}{3 \times 8.3143 \times 1000} = 280.6 \text{ K} \quad [5 \%]$$

At 280.6 K the rotational but not the vibrational states of the N_2 are activated.

Hence, by the principle of the equipartition of energy, the constant volume molar heat capacities of the two gases are,

$$\overline{C_{v,N_2}} = \left(\frac{3}{2} + \frac{2}{2} \right) \overline{R} = \frac{5}{2} \overline{R}, \quad \overline{C_{v,He}} = \frac{3}{2} \overline{R} \quad [10 \%]$$

The constant volume molar heat capacity for the mixture is,

$$\overline{C_v} = \frac{0.01\overline{C_{v,N_2}} + 0.03\overline{C_{v,He}}}{0.04} = \frac{0.01 \times 5/2 + 0.03 \times 3/2}{0.04} \overline{R} = \frac{7}{4} \times 8.3143 \text{ kJ/kmol.K} \quad [10 \%]$$

The rise in temperature, and the final temperature, of the mixture are,

$$\Delta T = \frac{Q}{0.04\overline{C_v}} = \frac{50}{0.04 \times (7/4) \times 8.3143} = 85.9 \text{ }^\circ\text{C} \quad \rightarrow \quad T_F = 280.6 + 85.9 = 366.5 \text{ K} \quad [5 \%]$$

Note that the final temperature is such that the vibrational states of the N_2 remain inactive so that the above theory is valid. Finally, the rms velocity of the helium molecules is,

$$(C_{\text{He}})_{\text{RMS}} = \left(\frac{3\bar{RT}_F}{M_{\text{He}}} \right)^{1/2} = \left(\frac{3 \times 8.3143 \times 1000 \times 366.5}{4} \right)^{1/2} = 1512 \text{ m/s} \quad [5 \%]$$

(c) As the gas is monatomic the only form of energy is translational kinetic energy,

$$E = \frac{m(C_1^2 + C_2^2 + C_3^2)}{2}$$

where m is the mass of a molecule. To prove the principle of the equipartition of energy we take $Q = mC_1^2/2$ in order to find the x_1 component of the mean translational kinetic energy of a molecule (and then $Q = mC_2^2/2$ and $Q = mC_3^2/2$). Thus,

$$\bar{E}_1 = \frac{1}{n} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \frac{mC_1^2}{2} \frac{n}{(2\pi RT)^{3/2}} \exp\left(-\frac{C_1^2}{2RT}\right) \exp\left(-\frac{C_2^2}{2RT}\right) \exp\left(-\frac{C_3^2}{2RT}\right) dC_1 dC_2 dC_3 \quad [10 \%]$$

To simplify, we define $x_1 = C_1/\sqrt{2RT}$, $x_2 = C_2/\sqrt{2RT}$, $x_3 = C_3/\sqrt{2RT}$ and hence $dx_1 = dC_1/\sqrt{2RT}$, $dx_2 = dC_2/\sqrt{2RT}$, $dx_3 = dC_3/\sqrt{2RT}$. Substituting, we obtain,

$$\begin{aligned} \bar{E}_1 &= \frac{mRT}{\pi^{3/2}} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} x_1^2 e^{-x_1^2} e^{-x_2^2} e^{-x_3^2} dx_1 dx_2 dx_3 \\ &= \frac{mRT}{\pi^{3/2}} \int_{-\infty}^{\infty} e^{-x_3^2} dx_3 \int_{-\infty}^{\infty} e^{-x_2^2} dx_2 \int_{-\infty}^{\infty} x_1^2 e^{-x_1^2} dx_1 \end{aligned} \quad [10 \%]$$

Using the given integrals and $k = mR$ (where k is Boltzmann's constant) we find,

$$\bar{E}_1 = \frac{mRT}{\pi^{3/2}} \times \pi^{1/2} \times \pi^{1/2} \times \frac{\pi^{1/2}}{2} = \frac{mRT}{2} = \frac{kT}{2} \quad [15 \%]$$

Hence, the x_1 component of the mean translational kinetic energy of a molecule is $kT/2$.

Clearly, the same result will be obtained for the x_2 and x_3 components.

The total mean translational kinetic energy of a molecule is therefore $3kT/2$ as expected.

This proves the principle of the equipartition of energy for a monatomic gas at equilibrium. [5 %]

Examiners' note:

All the candidates could recite the definition of kinetic temperature for a monatomic gas and very few fell into trap of thinking that it was defined differently for a diatomic gas. However, many had difficulty with calculating the effect of heat addition. The last part on the equipartition principle was done quite well, with most candidates coping with the tricky triple integral.

3. (a) The wave function must be single-valued and therefore have the same value when $\phi = \phi_0, \phi_0 + 2\pi, \phi_0 + 4\pi \dots$. This is only possible if:

$$\left(\frac{8\pi^2 I \epsilon}{h^2} \right)^{1/2} = n \quad \text{where } n = 1, 2, 3, \dots \text{ (not zero)}$$

$$\therefore \epsilon = \frac{n^2 h^2}{8\pi^2 I} \quad [20 \%]$$

(b) (i) σ is a symmetry factor which is 1 for hetero-nuclear and 2 for homo-nuclear molecules.

$$\begin{aligned} \text{(ii)} \quad Z_{rot} &= \sum_{m=0}^{\infty} g_m \exp(-\epsilon_m / kT) \\ &= \sum_{m=0}^{\infty} \frac{1}{\sigma} (2m+1) \exp\left(-\frac{(m^2 + m)h^2}{8\pi^2 I kT}\right) \\ &= \sum_{m=0}^{\infty} \frac{1}{\sigma} (2m+1) \exp\left(-\frac{(m^2 + m)\theta_{rot}}{T}\right) \end{aligned}$$

$$\text{(iii)} \quad \theta_{rot} = \frac{h^2}{8\pi^2 I k} \text{ by inspection.} \quad [20 \%]$$

(c) For $\theta_{rot} \ll T$, the summation may be replaced by an integral.

$$\begin{aligned} Z_{rot} &\approx \int_0^{\infty} \frac{1}{\sigma} (2m+1) \exp(-\{m^2 + m\}\theta_{rot} / T) dm \\ \therefore &= -\frac{1}{\sigma} \left[\frac{T}{\theta_{rot}} \exp(-\{m^2 + m\}\theta_{rot} / T) \right]_0^{\infty} \\ &= \frac{T}{\sigma \theta_{rot}} \end{aligned}$$

Now $U = NkT^2 \frac{\partial}{\partial T} (Z_{other} \times Z_{rot}) = U_{other} + U_{rot}$

$$\therefore U_{rot} = NkT^2 \times \frac{1}{T} = NkT$$

$$\Rightarrow u_{rot} = \frac{U_{rot}}{Nm} = \frac{k}{m} T = RT \quad [\text{where } m \text{ is mass of a molecule here}]$$

i.e., rotational modes contribute R to c_v . [60 %]

(i) accurate for N_2 ; (ii) not so accurate for H_2 . This is because, due to the low moment of inertia, the characteristic temperature of rotation for hydrogen is quite high (about 87 K), whereas for nitrogen it is less than 3 K.

Examiners' note:

The first two parts of this question were, in general, done well. Most marks were lost in the last section on the rotational partition function since many students failed to realise that the summation expression can be written as an integral in the high temperature limit.

4. (a) (i) True. The entropy increases since the temperature is constant but the volume increases. The number of microstates therefore also increases. [Explanations in terms of the number density of translational energy states increasing with volume would also be acceptable.] [10 %]

(iii) False. Each 'squared term' for the molecular energy states contributes $R/2$ to c_v and there are 3 translational terms of this type. At sufficiently high temperature, electronic excitation contributes nothing to c_v since all molecules will be in the excited state ($Z_{el} = 1$). The correct statement is therefore that at sufficiently high temperature $c_v = 3R/2$. [15 %]

(b) $\phi = -S'/k = x \ln x + y \ln y + z \ln z$
 where x, y, z are the probabilities of the three microstates. We wish to minimize ϕ subject to the constraint:

$$x + y + z = 1 \quad \text{or} \quad dz = -(dx + dy) \quad (\text{A})$$

Thus,

$$\begin{aligned} d\phi &= (1 + \ln x)dx + (1 + \ln y)dy + (1 + \ln z)dz \\ &= \ln(x)dx + \ln(y)dy - \ln(1 - x - y)(dx + dy) \\ &= \ln\left(\frac{x}{1 - x - y}\right)dx + \ln\left(\frac{y}{1 - x - y}\right)dy \end{aligned}$$

Since dx and dy are independent and arbitrary, $d\phi$ is only zero if the two log terms are simultaneously zero. Thus,

$$x = 1 - x - y \quad (\text{B})$$

$$y = 1 - x - y \quad (\text{C})$$

Simultaneous solution of A, B and C gives $x = y = z = 1/3$, and so

$$S' = -k \times \sum_{i=1}^3 (1/3) \times \ln(1/3) = k \ln 3 \quad [40 \%]$$

[Alternatively, this can be shown more succinctly and generally using Lagrange multipliers, as in the notes.]

$$(c) \quad U = \bar{E} = \sum P_i E_i$$

$$\therefore dU = \sum E_i dP_i + \sum P_i dE_i = \delta Q - \delta W$$

$$\text{Now} \quad S' = -k \sum P_i \ln P_i$$

$$\therefore dS' = -k \sum (1 + \ln P_i) dP_i = -k \sum (1 - E_i / kT - \ln Q) dP_i \quad [35 \%]$$

$$\Rightarrow \underline{dS' = \frac{1}{T} \sum E_i dP_i = \frac{\delta Q}{T}} \quad (\text{since } \sum dP_i = 0)$$

Examiners' note:

First part: most students recognised that the entropy (and hence the number of available microstates) increases for a gas undergoing isothermal expansion, though some took "reversible" to imply isentropic. The equipartition principle, however, was misapplied, so that most thought that electronic excitation would contribute $R/2$ to c_v . Second part: it seems that students have responded to the examiners' note in the 2010 crib, and most applied Lagrange multipliers correctly in this section and thereby obtained full marks. Third part: this concerned the statistical interpretation of heat and work transfer in terms of energy levels and their probabilities. Many students went off at a tangent, despite a very similar analysis in the notes. Some provided near-perfect solutions, however.

AJW / JBY