

2661

**SECOND PUBLIC EXAMINATION**

**Honour School of Physics Part A: 3 and 4 Year Courses**

**Honour School of Physics and Philosophy Part A**

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**A1: THERMAL PHYSICS**

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**TRINITY TERM 2011**

**Wednesday, 22 June, 9.30 am – 12.30 pm**

*Answer all of Section A and three questions from Section B.*

*For Section A start the answer to each question on a fresh page.  
For Section B start the answer to each question in a fresh book.*

*A list of physical constants and conversion factors accompanies this paper.*

*The numbers in the margin indicate the weight that the Examiners expect to assign to each part of the question.*

**Do NOT turn over until told that you may do so.**



## Section A

1. An engine is operated between a body of heat capacity  $C_1$  and temperature  $T_1$  and a second body of heat capacity  $C_2$  and temperature  $T_2$ , in order to extract work. You may assume that  $C_1$  and  $C_2$  are independent of temperature and that  $T_1 > T_2$ . Assume also that the engine produces the maximum possible amount of work.

Derive expressions for the final temperature  $T_f$  of the bodies and for the work performed by the engine. [7]

2. A thin-walled container of volume  $10^{-3} \text{ m}^3$  is evacuated to a pressure of  $10^{-7} \text{ mbar}$ . The vessel is surrounded by air at 1 bar and 290 K. If a small hole of area  $10^{-17} \text{ m}^2$  is made in the wall of the container, how long does it take the pressure inside to rise to  $10^{-6} \text{ mbar}$ ?

[1 bar =  $10^5 \text{ Pa}$ ; 1 mbar =  $10^{-3} \text{ bar}$ . You may assume that the mean speed of molecules in a gas at temperature  $T$  is  $(8k_B T / \pi m)^{1/2}$ , where  $m$  is the molecular mass.] [8]

3. The temperature inside a house is 290 K. The owner turns the central heating up so that the temperature becomes 291 K. What is the increase in the total energy of the air inside the house following this change of temperature? [4]

4. Estimate the energy density of thermal radiation in equilibrium inside a container whose walls are held at a temperature of 300 K. [4]

5. The energy levels of a system consist of a ground state level (energy  $E = 0$ ) and a triply-degenerate excited state (energy  $E = \Delta$ ). Derive expressions for  $\langle E \rangle$  and  $\text{Var} E = \langle E^2 \rangle - \langle E \rangle^2$  when in equilibrium with a reservoir at temperature  $T$  and show how your expressions behave in the limits  $T \rightarrow 0$  and  $T \rightarrow \infty$ . [9]

6. The gradient of the melting line of water on a  $p$ - $T$  diagram close to  $0^\circ\text{C}$  is  $-1.4 \times 10^7 \text{ Pa K}^{-1}$ . At  $0^\circ\text{C}$ , the specific volume of water is  $1.00 \times 10^{-3} \text{ m}^3 \text{ kg}^{-1}$  and of ice is  $1.09 \times 10^{-3} \text{ m}^3 \text{ kg}^{-1}$ . Using this information, deduce the latent heat of fusion of ice, expressing your result in  $\text{MJ kg}^{-1}$ . [4]

7. The functions  $f_n(x)$ , where  $n$  is any non-negative integer, satisfy the differential equation

$$\frac{d}{dx} \left( x e^{-x} \frac{df_n}{dx} \right) + n e^{-x} f_n = 0 \quad \text{for } 0 \leq x < \infty.$$

Each  $f_n$  and its derivative is bounded at  $x = 0$  and as  $x \rightarrow \infty$ . Show that, if  $m$  is a non-negative integer not equal to  $n$ , then

$$\int_0^\infty e^{-x} f_n(x) f_m(x) dx = 0.$$

[4]



## Section B

8. In a Joule expansion, a gas in volume  $V_1$  at temperature  $T_1$  undergoes free expansion to a larger volume  $V_2$  and final temperature  $T_2$ . The whole process takes place under thermally isolated conditions. Show that in such a process the internal energy  $U$  of the gas is conserved. [3]

Show that the Joule coefficient is

$$\left(\frac{\partial T}{\partial V}\right)_U = -\frac{1}{C_V} \left[ T \left(\frac{\partial p}{\partial T}\right)_V - p \right].$$

[5]

The equation of state for one mole of a van der Waals gas is

$$p + \frac{a}{V^2} = \frac{RT}{V-b}.$$

Derive an expression for the cooling  $\Delta T = T_1 - T_2$  for a van der Waals gas undergoing a Joule expansion from volume  $V_1$  to  $V_2$ . [You may assume that  $C_V$  is independent of temperature.] Consider the limits (i)  $a = 0$ ,  $b \neq 0$  and (ii)  $b = 0$ ,  $a \neq 0$ , and discuss the physical reasons for the value of  $\Delta T$  in each case. [7]

Explain why the Joule expansion is not a practical cooling mechanism for liquefying gases, and outline the principles of a gas liquefier based upon an alternative mechanism. [5]

9. The energy  $E$  of a three-dimensional harmonic oscillator is given by

$$E = \left(n_x + \frac{1}{2}\right) \hbar\omega + \left(n_y + \frac{1}{2}\right) \hbar\omega + \left(n_z + \frac{1}{2}\right) \hbar\omega.$$

Show that the partition function  $Z$  of this system is given by  $Z = Z_{\text{SHO}}^3$ , where

$$Z_{\text{SHO}} = \frac{e^{-\frac{1}{2}\beta\hbar\omega}}{1 - e^{-\beta\hbar\omega}},$$

and  $\beta = 1/(k_B T)$ . Show that the Helmholtz function of this oscillator is given by

$$F = \frac{3}{2} \hbar\omega + 3k_B T \ln(1 - e^{-\beta\hbar\omega}),$$

and find expressions for the entropy, the internal energy and the heat capacity. [11]

Show that the heat capacity tends to a constant value at high temperature and show that this is in agreement with the equipartition theorem. [4]

[Turn over]



10. Derive an expression for the partition function of a classical gas of  $N$  spinless indistinguishable particles of mass  $m$  in a volume  $V$  at temperature  $T$ . [5]

Show that for such a gas the entropy  $S$  is given by

$$S = Nk_B \left[ \alpha - \ln \left( \frac{N}{V} \lambda(T)^3 \right) \right],$$

where  $\alpha$  is a numerical constant and  $\lambda(T)$  is a function of temperature, both of which you should find. Use the expression for  $S$  to show that for an ideal monatomic gas under adiabatic conditions the pressure  $p$  obeys the law

$$pV^{5/3} = \text{constant}. \quad [8]$$

Two equal volumes of ideal gases at the same temperature and pressure are mixed. Find the entropy change (a) when the gases are identical and (b) when they are different. Comment on your answer. [7]

11. The Fourier transform  $\tilde{f}(k)$  of the function  $f(x)$  is defined by

$$\tilde{f}(k) = \int_{-\infty}^{\infty} dx e^{-ikx} f(x).$$

Write down the inverse Fourier transform. Show that

- (a) the Fourier transform of  $df/dx$  is  $ik\tilde{f}$
- (b) the Fourier transform of  $e^{iqx}$  is  $2\pi\delta(k - q)$

Find an expression for the Fourier transform  $\tilde{y}(k)$  of the function  $y(x) = \cos(qx)$ . [10]

The thermal diffusion equation is given by

$$\frac{\partial T}{\partial t} = D \frac{\partial^2 T}{\partial x^2}.$$

By Fourier transforming this equation, show that the solution is given by

$$\tilde{T}(k, t) = \tilde{T}(k, 0) e^{-Dk^2 t},$$

and hence find  $T(x, t)$  for the initial condition

$$T(x, 0) = T_0 + \sum_{m=1}^{\infty} T_m \cos\left(\frac{m\pi x}{L}\right),$$

where  $T_m$  ( $m = 0, 1, 2, \dots$ ) are constants. Show that for  $t \gg L^2/D$  the solution is approximately given by

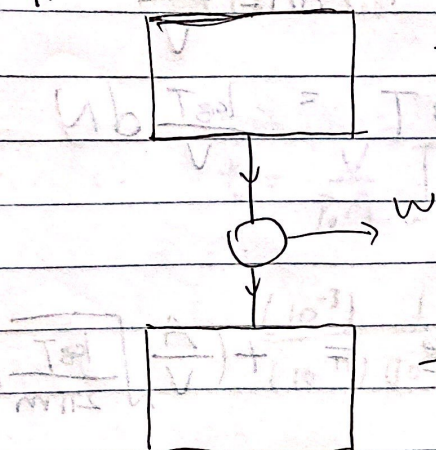
$$T(x, t) = T_0 + T_1 e^{-D\pi^2 t/L^2} \cos\left(\frac{\pi x}{L}\right). \quad [10]$$



A1 2011

First Attempt

1.



maximum possible work

→ most efficient

→ reversible  $dS_{univ} = 0$

→ Carnot efficiency

$$\therefore 0 = dS = C_1 \frac{dT_1}{T_1} + C_2 \frac{dT_2}{T_2}$$

$$\rightarrow 0 = \Delta S = C_1 \int_{T_1}^{T_f} \frac{dT_1'}{T_1'} + C_2 \int_{T_2}^{T_f} \frac{dT_2'}{T_2'} = C_1 \ln\left(\frac{T_f}{T_1}\right) + C_2 \ln\left(\frac{T_f}{T_2}\right)$$

$$0 = \ln \left[ \left(\frac{T_f}{T_1}\right)^{C_1} \left(\frac{T_f}{T_2}\right)^{C_2} \right]$$

$$\rightarrow \frac{T_f^{C_1+C_2}}{T_1^{C_1} T_2^{C_2}} = 1 \rightarrow T_f = (T_1^{C_1} T_2^{C_2})^{\frac{1}{C_1+C_2}}$$

2. Flux of effusing particles (particles coming out of the hole per area per time) is

$$\Phi = \frac{1}{4} n \langle v \rangle = \frac{1}{4} n \sqrt{\frac{8k_B T}{\pi m}} \quad \text{ideal gas } n = \frac{P_0}{k_B T}$$

$$\therefore \Phi = \frac{1}{4} \frac{P_0}{k_B T} \sqrt{\frac{8k_B T}{\pi m}} = \frac{P_0}{\sqrt{2\pi m k_B T}}$$

In time  $dt$ , number of particles coming out is  $\Phi A dt = dN$



$$V, T \text{ is constant} \quad n = \frac{N}{V} \quad \therefore dn = \frac{dN}{V}$$

$$p = n k_B T \quad \therefore dp = dn k_B T = \frac{k_B T}{V} dN$$

$$\therefore dp = + \frac{k_B T}{V} \Phi A dt$$

$$dp = + \frac{k_B T}{V} A \frac{P_0}{\sqrt{2\pi m k_B T}} dt = + \left( \frac{A}{V} \sqrt{\frac{k_B T}{2\pi m}} \right) P_0 dt$$

$$\int_{P_0}^{P_1} \frac{dp}{p} = \int_0^t \frac{A}{V} \sqrt{\frac{k_B T}{2\pi m}} dt'$$

$$\therefore \ln\left(\frac{P_1}{P_0}\right) = - \frac{A}{V} \sqrt{\frac{k_B T}{2\pi m}} t$$

$$\therefore P_1 = P_0 \exp\left(- \frac{A}{V} \sqrt{\frac{k_B T}{2\pi m}} t\right)$$

$$\rightarrow t = \frac{V}{A} \sqrt{\frac{2\pi m}{k_B T}} \ln\left(\frac{P_0}{P_1}\right)$$

$$V = 10^{-3} \text{ m}^3 \quad A = 10^{-17} \text{ m}^2 \quad T = 290 \text{ K}$$

$$P_1 = 10^{-7} \text{ mbar} = 10^{-7} \times 10^{-3} \times 10^5 \text{ Pa} = 10^{-5} \text{ Pa}$$

$$P_0 = 10^5 \text{ Pa}, \quad P_2 = 10^{-4} \text{ Pa}, \quad m = 28 \text{ mp}$$

$$\therefore t = \frac{(10^{-3})}{(10^{-17})} \left( \frac{2\pi \times 28 \times 1.67 \times 10^{-27}}{1.38 \times 10^{-23} \times 290} \right)^{\frac{1}{2}} \ln\left(\frac{10^{-4}}{10^{-5}}\right)$$

pressure



$$\rightarrow (P_2 - P_1) = \frac{FV}{P_0 A} \sqrt{\frac{k_B T}{2\pi m}} t$$

$$\therefore t = \frac{V}{P_0 A} \sqrt{\frac{2\pi m}{k_B T}} (P_2 - P_1)$$

$$V_{69-267} = \frac{(10^{-3})}{(10^{-17}) (10^5)} \frac{1}{1.38 \times 10^{-23} \times 290} \sqrt{2\pi \times 28 \times 1.67 \times 10^{-27}} (10^{-4} - 10^{-5})$$

$$t \approx \underline{\underline{77 \mu s}}$$

3.  $\rightarrow$  The room is not completely sealed ~~enough~~  
 (at least allow some ~~air~~ exchange of gas  
 particles with the surrounding) unless the  
 owner is crazy.

$\rightarrow$  pressure is ~~the~~ the same as pressure  
 outside no matter how temperature  
 in the room varies

$$\rightarrow P = \frac{2U}{3V} = \frac{2}{3} u \quad (U = \text{internal energy,}$$

$V = \text{volume, } u = \text{energy density})$

$\rightarrow P, \text{ constant, } V \text{ constant}$

$\therefore U \text{ is constant}$



4. Energy density  $u = \frac{U}{V}$

$$\therefore U = uV \quad \therefore \left(\frac{\partial U}{\partial V}\right)_T = u \left(\frac{\partial V}{\partial V}\right)_T + V \left(\frac{\partial u}{\partial V}\right)_T$$

Assuming  $u$  independent of  $V$

$$\rightarrow u = \left(\frac{\partial U}{\partial V}\right)_T \quad \therefore dU = Tds - PdV$$

$$\therefore u = \left(\frac{\partial U}{\partial V}\right)_T \quad \therefore u = T \left(\frac{\partial s}{\partial V}\right)_T - P$$

$$= T \left(\frac{\partial P}{\partial T}\right)_V - P$$

Maxwell

For (photon) (ultrarelativistic gas)  $u = \frac{P}{3}$

$$P = \frac{u}{3} \quad \therefore u = \frac{1}{3} T \left(\frac{\partial u}{\partial T}\right)_V - \frac{u}{3}$$

$$4u = T \left(\frac{\partial u}{\partial T}\right)_V$$

$V$  is constant

$$\therefore \frac{du}{dT} = \left(\frac{\partial u}{\partial T}\right)_V \quad \therefore 4u = T \frac{du}{dT}$$

$$\therefore 4 \frac{dT}{T} = \frac{du}{u} \quad \rightarrow \quad u = AT^4 = \frac{4\sigma}{c} T^4$$

$$\rightarrow u = \frac{4 \times 5.67 \times 10^{-8}}{3 \times 10^8} (300)^4 = 6.1 \times 10^{-6} \text{ W}$$



$$5. \quad Z = 1 + 3e^{-\beta\Delta} \quad P_\alpha = \frac{e^{-\beta E_\alpha}}{Z}$$

$$\langle E \rangle = \sum_\alpha P_\alpha E_\alpha = \frac{1}{Z} \sum_\alpha E_\alpha e^{-\beta E_\alpha} = -\frac{1}{Z} \frac{\partial Z}{\partial \beta}$$

$$\langle E^2 \rangle = \sum_\alpha P_\alpha E_\alpha^2 = \frac{1}{Z} \sum_\alpha E_\alpha^2 e^{-\beta E_\alpha} = \frac{1}{Z} \frac{\partial^2 Z}{\partial \beta^2}$$

$$\frac{\partial Z}{\partial \beta} = -3\Delta e^{-\beta\Delta} \quad \frac{\partial^2 Z}{\partial \beta^2} = 3\Delta^2 e^{-\beta\Delta}$$

$$\therefore \langle E \rangle = \frac{3\Delta e^{-\beta\Delta}}{1 + 3e^{-\beta\Delta}} = \frac{3\Delta}{3 + e^{\beta\Delta}}$$

$$\langle E^2 \rangle = \frac{3\Delta^2 e^{-\beta\Delta}}{(1 + 3e^{-\beta\Delta})^2} = \frac{3\Delta^2 e^{\beta\Delta}}{(3 + e^{\beta\Delta})^2}$$

$$\text{Var}(E) = \frac{3\Delta^2 e^{\beta\Delta}}{(3 + e^{\beta\Delta})^2} - \langle E \rangle^2$$

$$= \frac{3\Delta^2 (3 + e^{\beta\Delta}) - 9\Delta^2}{(3 + e^{\beta\Delta})^2} = \frac{3\Delta^2 e^{\beta\Delta}}{(3 + e^{\beta\Delta})^2}$$

$$\langle E \rangle: \quad T \rightarrow 0 \quad \beta \rightarrow \infty \quad \langle E \rangle \rightarrow 0$$

$$T \rightarrow \infty \quad \beta \rightarrow 0 \quad \langle E \rangle \rightarrow \frac{3}{4} \Delta$$

$$\text{Var}(E): \quad T \rightarrow 0 \quad \beta \rightarrow \infty \quad \text{Var}(E) \rightarrow 0$$

$$T \rightarrow \infty \quad \beta \rightarrow 0 \quad \text{Var}(E) \rightarrow \frac{3}{16} \Delta^2$$



6. Clausius - Clapeyron equation

$$\frac{dP}{dT} = \frac{L}{T \Delta V}$$

$$\therefore L = \left( \frac{dP}{dT} \right) T \Delta V$$

$$= (-1.4 \times 10^7 \text{ Pa/K}) (273 \text{ K}) \left( \frac{1.00}{1.09 \times 10^3} \right) \text{ m}^3/\text{kg}^{-1}$$

$$= 3.44 \times 10^5 \text{ J/kg}$$

$$= 0.34 \text{ MJ/kg}$$

7. Consider ~~two~~ two integers  $m, n$  such that  $m \neq n$

$$\frac{d}{dx} \left( x e^{-x} \frac{df_n}{dx} \right) + n e^{-x} f_n = 0$$

$$\int_0^{\infty} f_m \frac{d}{dx} \left( x e^{-x} \frac{df_n}{dx} \right) dx + n \int_0^{\infty} e^{-x} f_n f_m dx = 0$$

$$\rightarrow \left[ f_m x e^{-x} \frac{df_n}{dx} \right]_0^{\infty} - \int_0^{\infty} x e^{-x} \frac{df_n}{dx} \frac{df_m}{dx} dx$$

$$+ n \int_0^{\infty} e^{-x} f_n f_m dx = 0$$

Similarly



$$-\int_0^{\infty} x e^{-x} \frac{df_n}{dx} \frac{df_m}{dx} dx + m \int_0^{\infty} e^{-x} f_n f_m dx = 0$$

If we ~~is~~ multiply  $f_n$  to the equation of  $f_m$  and integrate

$$\therefore \text{we get } (m-n) \int_0^{\infty} e^{-x} f_n(x) f_m(x) dx$$

$$\because m \neq n \therefore \int_0^{\infty} e^{-x} f_n(x) f_m(x) dx = 0$$

8.  ~~$\Delta U = \Delta Q + \Delta W$~~   $\Delta U = \Delta Q + \Delta W$

thermally isolated  $\Delta Q = 0$

free expansion  $\Delta W = 0$

$$\therefore \Delta U = 0 \rightarrow U \text{ is constant}$$

$$\left(\frac{\partial T}{\partial V}\right)_U = - \left(\frac{\partial T}{\partial U}\right)_V \left(\frac{\partial U}{\partial V}\right)_T$$

$$\left(\frac{\partial T}{\partial V}\right)_U = \frac{1}{\left(\frac{\partial U}{\partial T}\right)_V} = \frac{1}{C_V}$$

$$\frac{\partial U}{\partial V} = T dS - P dV \rightarrow \left(\frac{\partial U}{\partial V}\right)_T = T \left(\frac{\partial S}{\partial V}\right)_T - P$$

$$\therefore \left(\frac{\partial T}{\partial V}\right)_U = \frac{1}{C_V} \left[ T \left(\frac{\partial S}{\partial V}\right)_T - P \right] = - \frac{1}{C_V} \left[ T \left(\frac{\partial P}{\partial T}\right)_V - P \right]$$

~~$\left(\frac{\partial T}{\partial V}\right)_U = \frac{1}{C_V}$~~  For van der Waal's gas:

$$P + \frac{a}{V^2} = \frac{RT}{V-b}$$



$$\therefore \left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{V-b}$$

$$\therefore \frac{TR}{V-b} = P + \frac{a}{V^2} \quad T\left(\frac{\partial P}{\partial T}\right)_V = \frac{TR}{V-b} = P + \frac{a}{V^2}$$

$$\therefore \left(\frac{\partial T}{\partial V}\right)_U = -\frac{1}{C_V} \left[ P + \frac{a}{V^2} - P \right] = -\frac{a}{C_V V^2}$$

For Joule expansion  $\frac{dT}{dV} = \left(\frac{\partial T}{\partial V}\right)_U$

$$\rightarrow \frac{dT}{dV} = -\frac{a}{C_V V^2}$$

$$\int_{T_2}^{T_1} dT = -\frac{a}{C_V} \int_{V_2}^{V_1} \frac{dV}{V^2} = \frac{a}{C_V} \left[ \frac{1}{V} \right]_{V_2}^{V_1}$$

$$\rightarrow \Delta T = \frac{a}{C_V} \left[ \frac{1}{V_1} - \frac{1}{V_2} \right]$$

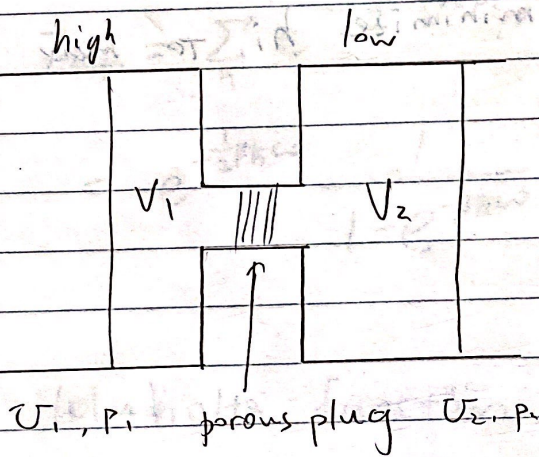
(i)  $a=0, b \neq 0 \rightarrow \Delta T = 0$  = No ~~inter molecular~~ inter molecular forces  
 but finite size of particles  $\rightarrow$  No potential energy  $\rightarrow$  if  $U = \text{constant}$ ,  $T$  doesn't change with  $V$

(ii)  $a \neq 0, b = 0 \rightarrow \Delta T \neq 0$  ~~particle~~ particle has zero size but non-zero intermolecular force  
 $\rightarrow$  gas expands  $V$  increases  $\rightarrow$  potential energy increase  $\rightarrow$  kinetic energy decreases because  $U$  stays the same  $\rightarrow$  gas cools.



Joule expansion ~~has~~ has little practical use because gas cools ~~only~~ when volume increases and the cooling goes like  $\frac{1}{V}$ . Hence to achieve significant cooling we need a very large vacuum for gas to expand ~~to~~ into.

→ use an alternative mechanism ~~for~~ called the Joule-Kelvin expansion.



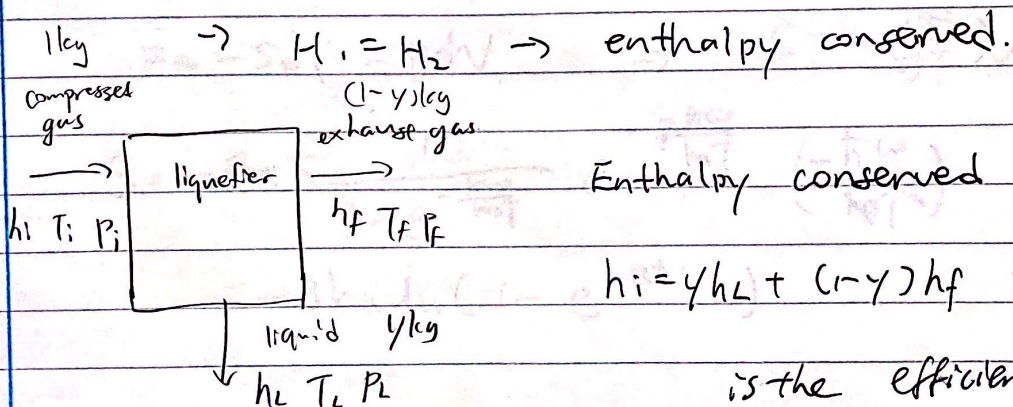
→ steady flow process in which gas at high pressure  $P_1$  is forced through a porous plug to a lower pressure  $P_2$

→ System thermally isolated  $Q = 0$

$$\therefore \Delta U = \Delta W \rightarrow U_2 - U_1 = -P_1 V_1 - (-P_2 V_2)$$

$$-P_2 V_2 - (-P_1 V_1)$$

$$\rightarrow U_1 + P_1 V_1 = U_2 + P_2 V_2$$





$\therefore P_f = P_{atm}$   $T_i$  and  $T_f$  are kept constant  
~~and same~~ and equal  
to  $T_L$

$V_L$  is constant for liquid

$\therefore (P_f, T_f)$  and  $(T_L, V_L)$  are all known  
to be constant

$h_f, h_L$  are constant

$\rightarrow$  we only minimize  $h_i$  to max  $y$

$\rightarrow$  System thermally isolated  $Q = 0$

$\therefore \Delta U = \Delta W$   
 $-P_f \Delta V_f - P_L \Delta V_L = P_i \Delta V_i$

$\rightarrow U_i + P_i V_i = U_f + P_f V_f$

$H_i = H_f$

enthalpy conserved

$h_i = h_f + (c_p - c_v) \Delta T$

enthalpy



9. partition function is  $Z = \sum_{\underline{n}} e^{-\beta E_{\underline{n}}}$

$$\therefore Z = \sum_{n_x, n_y, n_z} e^{-\beta \hbar \omega (n_x + n_y + n_z + \frac{3}{2})}$$

$$= \sum_{n_x} e^{-\beta \hbar \omega (n_x + \frac{1}{2})} \sum_{n_y} e^{-\beta \hbar \omega (n_y + \frac{1}{2})} \sum_{n_z} e^{-\beta \hbar \omega (n_z + \frac{1}{2})}$$

$$= \left( \sum_n e^{-\beta \hbar \omega (n + \frac{1}{2})} \right)^3 = Z_{SHO}^3$$

$$Z_{SHO} = \sum_n e^{-\beta \hbar \omega (n + \frac{1}{2})} = e^{-\frac{1}{2} \beta \hbar \omega} (1 + e^{-\beta \hbar \omega} + e^{-2\beta \hbar \omega} + \dots)$$

$$= e^{-\frac{1}{2} \beta \hbar \omega} \frac{1}{1 - e^{-\beta \hbar \omega}} = \frac{e^{-\frac{1}{2} \beta \hbar \omega}}{1 - e^{-\beta \hbar \omega}} \quad \left( \beta = \frac{1}{k_B T} \right)$$

Helmholtz function

$$F = -k_B T \ln Z = -3k_B T \left[ \ln \left( e^{-\frac{1}{2} \beta \hbar \omega} \right) - \ln \left( 1 - e^{-\beta \hbar \omega} \right) \right]$$

$$= \frac{3}{2} \beta k_B T \hbar \omega + 3k_B T \ln \left( 1 - e^{-\beta \hbar \omega} \right)$$

$$= \frac{3}{2} \hbar \omega + 3k_B T \ln \left( 1 - e^{-\beta \hbar \omega} \right)$$

$$F = -SdT - pdV \quad \rightarrow \quad S = - \left( \frac{\partial F}{\partial T} \right)_V$$

$$S = -3k_B T \frac{1}{1 - e^{-\frac{\hbar \omega}{k_B T}}} e^{-\frac{\hbar \omega}{k_B T}} \left( -\frac{\hbar \omega}{k_B T^2} \right)$$

$$+ 3k_B \ln \left( 1 - e^{-\beta \hbar \omega} \right)$$



$$\rightarrow S = + \frac{3\hbar\omega}{T} \frac{1}{e^{\frac{\hbar\omega}{k_B T}} - 1} - 3k_B \ln(1 - e^{-\frac{\hbar\omega}{k_B T}})$$

$$F = U - TS \quad \rightarrow \quad U = -k_B T \ln Z$$

$$U = \frac{3}{2}\hbar\omega + 3k_B T \ln(1 - e^{-\frac{\hbar\omega}{k_B T}})$$

~~$$U = \frac{3}{2}\hbar\omega + 3k_B T \ln(1 - e^{-\frac{\hbar\omega}{k_B T}})$$~~

$$= \frac{3}{2}\hbar\omega + \frac{3\hbar\omega}{e^{\frac{\hbar\omega}{k_B T}} - 1}$$

Heat Capacity

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V = - \frac{3\hbar\omega}{(e^{\frac{\hbar\omega}{k_B T}} - 1)^2} e^{\frac{\hbar\omega}{k_B T}} \left(-\frac{\hbar\omega}{k_B T^2}\right)$$

$$= \frac{3k_B \left(\frac{\hbar\omega}{k_B T}\right)^2}{(e^{\frac{\hbar\omega}{k_B T}} - 1)^2} e^{\frac{\hbar\omega}{k_B T}}$$

As  $T \rightarrow \infty$   $e^{\frac{\hbar\omega}{k_B T}} \rightarrow 1 + \frac{\hbar\omega}{k_B T}$

$$\therefore C_V \approx 3k_B \left(\frac{\hbar\omega}{k_B T}\right) \frac{1}{(1 - \frac{\hbar\omega}{k_B T})^2}$$

$$\left(\approx 3k_B \left(\frac{\hbar\omega}{k_B T}\right) \left(\frac{k_B T}{\hbar\omega}\right)^2\right) \approx 3k_B$$

Equipartition theorem: d.o.f =  $n = 6 \rightarrow$  (3 potential, 3 kinetic)

$$C_V = \frac{n}{2} k_B = \frac{6}{2} k_B = 3k_B$$

$\rightarrow$  ~~const~~ consistent.



(10.1) 3-D density of states  $g(k) dk = \frac{V}{2\pi^2} k^2 dk$

partition function (single particle)  $Z_1$

$$Z_1 = \int d^3k g(k) e^{-\beta \epsilon(k)}$$

$$= \frac{V}{2\pi^2} \int_0^\infty dk \cdot k^2 \exp\left(-\frac{\beta \hbar^2}{2m} k^2\right)$$

$$\left\{ \begin{array}{l} x = \sqrt{\frac{\beta \hbar^2}{2m}} k \\ dk = \sqrt{\frac{2m}{\beta \hbar^2}} dx \end{array} \right.$$

$$= \frac{V}{2\pi^2} \left(\frac{2m}{\beta \hbar^2}\right)^{3/2} \int_0^\infty dx x^2 e^{-x^2}$$

$$= \frac{V}{2\pi^2} \cdot \frac{\sqrt{\pi}}{4} \left(\frac{2m k_B T}{\hbar^2}\right)^{3/2}$$

$$= \frac{V}{\pi^{3/2}} \frac{1}{4^{3/2}} \left(\frac{2m k_B T}{\hbar^2}\right)^{3/2} = V \left(\frac{m k_B T}{2\pi \hbar^2}\right)^{3/2}$$

$$= \frac{V}{\lambda(T)^3} \quad \text{if} \quad \lambda(T) = \hbar \sqrt{\frac{2\pi}{m k_B T}}$$

For  $N$  identical particles

$$Z_N = \frac{1}{N!} Z_1^N$$

indistinguishability, divide by the ~~overall~~ over counting factor  $N!$



$$F = -k_B T \ln Z = -k_B T [N \ln V - N \ln(\lambda^3)] - k_B T N$$

$$= -k_B T N \ln V + k_B T N \ln(\lambda^3) - \cancel{N k_B T} - \cancel{k_B T N}$$

Sterling formula  $\nearrow$   
 $\frac{4}{3} \pi r^3$   $\nearrow$   
 length  $\nearrow$

$$= -N k_B T [1 - \ln(\lambda^3)]$$

$$= -k_B T [N \ln V - N \ln(\lambda^3) - N \ln N + N]$$

$$= -k_B T N - N k_B T [\ln V - \ln \lambda^3 - \ln N + 1]$$

$$= -N k_B T [1 + \ln(\frac{V \lambda^3}{N})] = -N k_B T [1 - \ln(\frac{N \lambda^3}{V})]$$

$$S = -(\frac{\partial F}{\partial T})_V = N k_B [1 - \ln(\frac{N \lambda^3}{V})]$$

$$+ N k_B T \left( -\frac{1}{N \lambda^3} \frac{N}{\lambda^3} \left( \frac{3}{2} \frac{1}{T} \right) \right)$$

$$= N k_B \left( \frac{5}{2} - \ln(\frac{N \lambda^3}{V}) \right)$$

$$\alpha = \frac{5}{2}$$

Adiabatic: Adiabatic  $S \rightarrow \text{const}$

$\therefore N$  constant,  $\frac{\lambda^3}{V} \rightarrow \text{constant}$



$$\rightarrow VT^{3/2} = \text{constant}$$

$$P = -\left(\frac{\partial F}{\partial V}\right)_T = Nk_B T \frac{1}{V}$$

$$\rightarrow PV = Nk_B T \quad \therefore \frac{PV}{T} = \text{const.}$$

$$\therefore V(PV)^{3/2} = \text{constant}$$

$$\left(\frac{PV}{T}\right)^{3/2} \frac{1}{PV} = \text{constant} = \frac{3/2 - 1/2}{T} = \frac{1}{T}$$

$$\therefore PV^{5/3} = \text{constant}$$

→ For identical particles

$$S_1 = Nk_B \left[ \frac{5}{2} - \ln\left(\frac{N\lambda}{V}\right) \right]$$

$$S_2 = 2Nk_B \left[ \frac{5}{2} - \ln\left(\frac{2N\lambda}{2V}\right) \right]$$

$$\therefore \Delta S = S_2 - 2S_1 = 0$$

~~For distinguishable particles.~~

→ ~~Z~~ For different gases.

the mixed gas is not a completely indistinguishable gas so we cannot use the formula for  $S$  we derived.

We need to sum the entropy from the expansion of 2 gases.



$$S_1 = Nk_B \left[ \frac{5}{2} - \ln \left( \frac{N\lambda}{V} \right) \right]$$

$$S_2 = 2 \times Nk_B \left[ \frac{5}{2} - \ln \left( \frac{N\lambda}{2V} \right) \right]$$

↓  
 $V \rightarrow 2V$  but  $N$  stays  
is during expansion

$$\Delta S = S_2 - S_1 = 2Nk_B \left[ \ln \left( \frac{N\lambda}{V} \right) - \ln \left( \frac{N\lambda}{2V} \right) \right]$$

$$= \underline{2Nk_B \ln 2}$$

Comment: When gases are same there is

no difference between the initial and final systems

→ entropy must not change

When gases are different, the system

becomes more disordered when gases are mixed

So entropy increases

When one gas expands each particles can  
have 2 ways to be placed

$N$  particles has  $\Omega = 2^N$  ways

If 2 gases →  $\Omega = 2^{2N}$  ways

$$\therefore \Delta S = k_B \ln \Omega = \underline{2Nk_B \ln 2}$$



$$\tilde{f}(k) = \int_{-\infty}^{\infty} dx e^{-ikx} f(x)$$

~~(a)~~ Inverse transform  $f(x) = \frac{1}{2\pi} \int_{-\infty}^{\infty} dx dk e^{+ikx} \tilde{f}(k)$

(a)  $\frac{d\tilde{f}}{dk} = \int_{-\infty}^{\infty} \left(\frac{df}{dx} dx\right) e^{-ikx} = \left[ f e^{-ikx} \right]_{-\infty}^{\infty} - \int_{-\infty}^{\infty} (-ik) f(x) e^{-ikx} dx$

$$= ik \tilde{f}$$

(b) inverse transform  $2\pi \delta(k-2)$

$$f(x) = \frac{1}{2\pi} \int_{-\infty}^{\infty} 2\pi \delta(k-2) e^{+ikx} dx = e^{i2x}$$

~~\therefore we have~~

$\rightarrow$  the Fourier transform of  $e^{i2x}$  is  $2\pi \delta(k-2)$

$$\tilde{f}(k) = \int_{-\infty}^{\infty} dx e^{-ikx} \cos(2x) = \frac{1}{2} \int_{-\infty}^{\infty} dx e^{-ikx} e^{i2x} + \frac{1}{2} \int_{-\infty}^{\infty} dx e^{-ikx} e^{-i2x}$$

$$= \pi \delta(k-2) + \pi \delta(k+2)$$



$$\frac{\partial T}{\partial t} = D \frac{\partial^2 T}{\partial x^2} \quad (\rightarrow \text{fourier transform}) \rightarrow \frac{\partial \tilde{T}(k,t)}{\partial t} = -Dk^2 \tilde{T}(k,t)$$

for constant  $k$   $\frac{d\tilde{T}}{dt} = -Dk^2 \tilde{T}$

$$\rightarrow \tilde{T}(k,t) = \tilde{T}(k,0) e^{-Dk^2 t}$$

if  $t=0$ ,  $\tilde{T} = \tilde{T}(k,0) \rightarrow$  ~~correct~~ consistent.

initial condition  $T(x,0) = T_0 + \sum_{m=1}^{\infty} T_m \cos\left(\frac{m\pi x}{L}\right)$

Fourier transform this gives

$$\tilde{T}(k,0) = \int_{-\infty}^{\infty} e^{-ikx} \left[ T_0 + \sum_{m=1}^{\infty} T_m \cos\left(\frac{m\pi x}{L}\right) \right]$$

$$= 2\pi T_0 \delta(k) + \pi \sum_{m=1}^{\infty} T_m \left[ \delta\left(k - \frac{m\pi}{L}\right) + \delta\left(k + \frac{m\pi}{L}\right) \right]$$

$$= 2\pi T_0 \delta(k) + \pi \sum_{m=1}^{\infty} T_m \left[ \delta\left(k - \frac{m\pi}{L}\right) + \delta\left(k + \frac{m\pi}{L}\right) \right]$$

$$= 2\pi T_0 \delta(k) + \pi \sum_{m=1}^{\infty} T_m \left( \delta\left(k - \frac{m\pi}{L}\right) + \delta\left(k + \frac{m\pi}{L}\right) \right)$$

$$\therefore \tilde{T}(k,t) = \left[ 2\pi T_0 \delta(k) + \pi \sum_{m=1}^{\infty} T_m \left( \delta\left(k - \frac{m\pi}{L}\right) + \delta\left(k + \frac{m\pi}{L}\right) \right) \right] e^{-Dk^2 t}$$

$$T(x,t) = \frac{1}{2\pi} \int_{-\infty}^{\infty} \tilde{T}(k,t) e^{ikx} dk$$

$$= \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{ikx} e^{-Dk^2 t} \left[ 2\pi T_0 \delta(k) + \pi \sum_{m=1}^{\infty} T_m \left( \delta\left(k - \frac{m\pi}{L}\right) + \delta\left(k + \frac{m\pi}{L}\right) \right) \right] dk$$



$$= \frac{1}{2\pi} \left[ 2\pi T_0 + \pi \sum_{m=1}^{\infty} \cancel{4} e^{-D(\frac{m\pi}{L})^2 t} \right]$$

$$\pi \sum_{m=1}^{\infty} e^{-D(\frac{m\pi}{L})^2 t} \left[ e^{i(\frac{m\pi}{L})x} + e^{-i(\frac{m\pi}{L})x} \right]$$

$$= T_0 + \sum_{m=1}^{\infty} T_m e^{-D(\frac{m\pi}{L})^2 t} \cos\left(\frac{m\pi x}{L}\right)$$

For  $t \gg L^2/D$ , all  $m > 1$  terms  
has negligible contribution

$$\rightarrow T(x,t) \approx T_0 + T_1 e^{-D\pi^2 t/L^2} \cos\left(\frac{\pi x}{L}\right)$$