

### 2.3.2 Effusion

Suppose now that we open a small hole of dimension  $d \ll \lambda_{mfp}$  (the typical distance travelled by a given particle, as we will see later) in the side of the container. Then, flux of particles escaping through the hole or *effusing* is simply given by

$$\begin{aligned}\Phi(\underline{v}) &= \int d\Phi(\underline{v}) \\ &= n \int_0^{2\pi} d\phi \int_0^{\pi/2} d\theta \sin\theta \cos\theta \int_0^\infty dv v^3 f(\underline{v}) \\ &= \frac{1}{4} n \langle v \rangle\end{aligned}$$

Using the fact that  $p = nk_B T$  and assuming that the distribution is Maxwellian, we can arrive at the expression

$$\boxed{\Phi = \frac{p}{\sqrt{2\pi m k_B T}}} \quad (2.10)$$

Once again, the distribution of effusing particles has the properties outlined in Section (2.3); faster particles, and those that make small angles with the normal, are more likely to effuse. We have derived this expression assuming that *all* incident angles are possible. Suppose instead that we wanted to find the flux of particles that effuse into a particular solid angle. Then, instead of integrating  $\theta$  over the interval  $[0, \pi/2]$ , we would integrate up to the corresponding solid angle.

Effusion can be used experimentally as a way of measuring internal properties of the distribution without modifying the distribution itself. For example, we can find the vapour pressure of a gas inside a container by measuring the rate of change of mass inside that container. Suppose that the particles effuse through a hole of area  $A$ . Then the rate of change of mass is

$$\begin{aligned}\frac{dM}{dt} &= -m \Phi A \\ &= -p A \sqrt{\frac{m}{2k_B \pi T}} \\ p &= \sqrt{\frac{2k_B \pi T}{m}} \frac{1}{A} \frac{dM}{dt}\end{aligned}$$

*A closed vessel is partially filled with liquid mercury; there is a hole of area  $A = 10^7 \text{ m}^2$  above the liquid level. The vessel is placed in a region of high vacuum at  $T = 273 \text{ K}$  and after 30 days is found to be lighter by  $\Delta M = 2.4 \times 10^5 \text{ kg}$ . Estimate the vapour pressure of mercury at 273 K. (The relative molecular mass of mercury is 200.59)*

We have already derived the appropriate expression, it is just a matter of putting the information together.

$$\begin{aligned}\frac{\Delta M}{\Delta t} &\approx 9.26 \times 10^{-12} \text{ kgs}^{-1} \\ m &= \frac{\text{Relative Atomic Mass}}{N_a} \\ &\approx 3.3 \times 10^{-25} \text{ kg} \\ \rightarrow p &\approx 0.0247 \text{ Nm}^{-2}\end{aligned}$$

This is the approximate vapour pressure of mercury, assuming that the system is at equilibrium.

### Conditions for Equilibrium

Suppose that we have two containers joined by a hole of radius  $a$ . What are the conditions for now flow between the containers? This will actually depend on the size of the hole.

- $a \gg \lambda_{mfp}$  - In this case, we require that the pressures balance, namely

$$\boxed{n_1 T_1 = n_2 T_2} \quad (2.11)$$

- $a \ll \lambda_{mfp}$  - This is the effusive case. Evidently, we require that the effusive flux is the same in both directions, namely

$$\boxed{n_1 \sqrt{T_1} = n_2 \sqrt{T_2}} \quad (2.12)$$

Remember that in both cases, total number density  $n = n_1 + n_2$  must be conserved.

### Some results of Effusion

Suppose that we have a container with a small hole of area  $A$ . We can use the expression for particle flux, under the effusion condition, to find the rate of change of some quantities inside the container.

- Number Density - The rate of particles escaping from the container is evidently

$$\frac{dN}{dt} = -\Phi A = -\frac{1}{4} A \langle v \rangle n$$

Dividing through by the volume in the container, we find that the differential equation for the number density is given by

$$\boxed{\frac{dn}{dt} = -\frac{1}{4} \frac{A}{V} \langle v \rangle n} \quad (2.13)$$

If the temperature of the vessel remains constant, this can simply be solved to find  $n(t)$  and consequently  $p(t)$ .

- Energy - We need to calculate the energy flux  $J$

$$\begin{aligned} dJ &= d\Phi(v) \cdot \frac{1}{2} m v^2 \\ J &= \frac{1}{8} n m \langle v^3 \rangle \end{aligned}$$

This means that we can write the rate of change of the internal energy as

$$\boxed{\frac{dU}{dt} = -JA} \quad (2.14)$$

Recalling (2.9), we find that  $U = U(n, T)$ . Assuming that neither  $n$  or  $T$  remain constant (such as for an isolated container), we can obtain a set of coupled equations for these variables from the above equation, which we can then solve for their time evolution.

We require that  $c_2 = 0$  for the solution to be properly bounded. Let  $c_1 = \tilde{T}(0, \omega)$ .

$$\begin{aligned} i\omega &= -\alpha k^2 \\ k^2 &= -\frac{i\omega}{\alpha} \\ k &= (-1 + i)\sqrt{\frac{\omega}{2\alpha}} = \frac{1}{\delta_\omega}(-1 + i) \end{aligned}$$

Thus, the final solution is of the form

$$T(x, t) = \sum_w \tilde{T}(0, \omega) e^{-x/\delta_\omega} e^{i(\omega t - x/\delta_\omega)} \quad (2.28)$$

$\delta_\omega$  is known as the *skin depth*, and is a measure of the attenuation of the propagating wave. Calculating the FT of the initial condition:

$$\begin{aligned} \tilde{T}(0, \omega) &= T_o + \int_{-\infty}^{\infty} dt e^{-i\omega t} \sum_n T_n \cos(nt) \\ &= T_o + \frac{1}{2} \sum_n T_n \int_{-\infty}^{\infty} dt e^{-i\omega t} (e^{int} + e^{-int}) \\ &= T_o + \frac{1}{2} \sum_n T_n \int_{-\infty}^{\infty} dt e^{-i(\omega - n)t} + e^{-i(\omega + n)t} \\ &= T_o + \frac{1}{2} \sum_n T_n \cdot (\delta(\omega - n) + \delta(\omega + n)) \end{aligned}$$

Substituting this result back into (2.28), we find that

$$T(x, t) = T_o + \sum_n T_n e^{-x/\delta_n} \cos\left(nt - \frac{x}{\delta_n}\right)$$

- The interior of the material is subject to a space-dependant sinusoidal temperature variation given by

$$T(x, 0) = T_o + \sum_n T_n \cos(nx)$$

Suppose that the solution is of the form

$$T(x, t) = \sum_k \tilde{T}(k, t) e^{ikx}$$

Taking the FT of both sides of the heat equation:

$$\begin{aligned} \int_{-\infty}^{\infty} dk e^{-ikx} \frac{\partial T}{\partial t} &= \int_{-\infty}^{\infty} dk e^{-ikx} \frac{\partial^2 T}{\partial x^2} \\ \frac{\partial}{\partial t} \int_{-\infty}^{\infty} dk e^{-ikx} T &= \alpha (ik)^2 \tilde{T} \end{aligned}$$

$$\frac{\partial \tilde{T}}{\partial t} = -\alpha k^2 \tilde{T}$$

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

This means that we obtain the *Kinetic Equation*

$$\boxed{\frac{\partial F}{\partial t} + \underline{v} \cdot \nabla F = C[F]} \quad (2.31)$$

where  $\underline{v}$  is the velocity of the particles, and  $C[F]$  is known as the *collision operator*. We know that  $C[F]$  needs to satisfy the following properties:

- The local Maxwellian must be a fixed point

$$C[F_M] = 0$$

That is, the collision will not change the local Maxwellian

- Relaxation to the local Maxwellian must happen on a time-scale  $\sim \tau_c$
- Conservation laws must be satisfied.

The simplest model that satisfies this is:

$$\boxed{C[F] = -\frac{F - F_M}{\tau_c} = -\frac{1}{\tau_c} \delta F} \quad (2.32)$$

This is known as *Krook's Collision Operator*.

## 2.6.2 Conservation Laws

Now that we have an equation for the evolution of the local distributions, we can use it to derive some local conservation equations for the gas. We assume that there is some mean flow  $\underline{u} = u_x \hat{x}$ , and define  $\underline{w}$  as the *peculiar velocity* (the difference between the velocity of the particle and the mean flow).

- Number Density

$$\begin{aligned} \frac{\partial n}{\partial t} &= \frac{\partial}{\partial t} \int d^3 \underline{v} F \\ &= \int d^3 \underline{w} \left( -v_z \frac{\partial F}{\partial z} + C[F] \right) \\ &= \underbrace{-\frac{\partial}{\partial z} \int d^3 \underline{v} v_z F}_{\text{no mean velocity in } z \text{ direction}} + \underbrace{\int d^3 \underline{v} C[F]}_{\text{collisions do not change particle no.}} \end{aligned}$$

This means we obtain the expected result of

$$\frac{\partial n}{\partial t} = 0 \quad \longrightarrow \quad n = \text{const}$$

- Momentum Density

$$\begin{aligned} \frac{\partial}{\partial t} (m n u_x) &= \frac{\partial}{\partial t} \int d^3 \underline{v} m v_x F \\ &= \int d^3 \underline{v} m v_x \left( -v_z \frac{\partial F}{\partial z} + C[F] \right) \\ &= \underbrace{-\frac{\partial}{\partial z} \int d^3 \underline{v} m v_x v_z F}_{= \text{total } \Pi_{zx} \text{ by definition}} + \underbrace{\int d^3 \underline{v} m v_x C[F]}_{\text{momentum is conserved}} \end{aligned}$$

Again, we obtain the expected result of

$$\frac{\partial}{\partial t} (m n u_x) + \frac{\partial \Pi_{zx}}{\partial z} = 0$$

### 3. *Statistical Mechanics*

This chapter aims to cover the basics of Statistical Mechanics, including:

- Basic Principles
- The Canonical Ensemble
- The Ideal Gas
- The Grand Canonical Ensemble
- Quantum Gases
- The Photon Gas

Arguably, Statistical Mechanics is one of the most powerful pieces of physics that one learns as an undergraduate. Evidently, Quantum Mechanics will always give the correct answer, but it will become increasingly difficult - and almost impossible - to compute the required problem. Statistical Mechanics provides an elegant solution to this, allowing one to treat a large variety of relatively complex systems without much thought actually being given to the small details of the problem. The author certainly enjoyed this course immensely, and hopes that this is reflected in these notes.

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Taking the first and second derivatives:

$$\begin{aligned}\frac{\partial f}{\partial x} &= \frac{N}{x} - 1 \\ \frac{\partial^2 f}{\partial x^2} &= -\frac{N}{x^2}\end{aligned}$$

This means that the maximum of the integrand will occur at  $x = N$ . We can thus Taylor expand the integrand as

$$\begin{aligned}N! &= \int_0^\infty dx e^{f(x)} \\ &= e^{N \log N - N} \int_0^\infty dx e^{-\frac{1}{2N}(x-N)^2 + \dots} \\ &\sim e^{N \log N - N} \sqrt{2\pi N}\end{aligned}$$

where we have used the fact that we can extend the integral range to  $[-\infty, \infty]$  as the contribution from the negative part of the integral becomes vanishingly small for large  $N$  (width scales as  $\sqrt{N}$ ). It follows that

$$\log N! \sim N \log N - N + \frac{1}{2} \log(2\pi N)$$

If  $N$  is sufficiently large, we can ignore the last term, as it scales as  $\log N$  rather than as  $N$ . We thus arrive the result quoted above.

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As entropy is additive, the entropy of the total system is the sum of the entropy of the individual systems; that is:

$$S = \sum_i S_i$$

Note that  $S_i$  can only depend on the internal energy of the sub-system, as the total energy of the total system is conserved. This means that  $S_i = S_i(U_i, V_i)$ , where  $U_i$  is the internal energy of the system (the difference between the total and kinetic energy).

We thus want to maximise the total entropy with respect to the following conservation laws:

$$\begin{aligned} \delta \left( \sum_i \varepsilon_i - \varepsilon \right) &= 0 \\ \underline{a} \cdot \left( \sum_i m_i \underline{u}_i - \underline{p} \right) &= 0 \\ \underline{b} \cdot \left( \sum_i m_i \underline{r}_i \times \underline{u}_i - \underline{L} \right) &= 0 \\ \sigma \left( \sum_i V_i - V \right) &= 0 \end{aligned}$$

We are not going to try and assign any significance to the Lagrange multipliers used, as they are completely arbitrary, with  $\delta = k_B \beta$  being the notable exception.

## Equilibria

Maximising the expression for entropy and requiring that all of the individual constraints are zero allows us to obtain relationships between the quantities in each of our subsystems.

- Thermal Equilibrium:

$$\frac{\partial S_i}{\partial \varepsilon_i} = \frac{\partial S_i}{\partial U_i} = \frac{1}{T_i} \longrightarrow \frac{1}{T_i} = \delta = \frac{1}{T}$$

This means that the condition for the subsystems to be in thermal equilibrium is if their *temperatures are the same*, as anticipated by the Zeroth Law of Thermodynamics

- Mechanical Equilibrium:

$$\frac{\partial S_i}{\partial V_i} = \frac{p_i}{T_i} \longrightarrow p_i = \frac{\sigma}{\delta}$$

This means that the condition for the subsystems to be in mechanical equilibrium is if the *pressures within them are the same*, meaning that the pressures are balanced at the boundaries

- Dynamical Equilibrium:

$$\frac{\partial S}{\partial \underline{u}_i} = \frac{\partial S}{\partial U_i} \frac{\partial U_i}{\partial \underline{u}_i} = -m_i \underline{u}_i \frac{1}{T_i} \longrightarrow m_i \delta \underline{u}_i = -m_i (\underline{a} + \underline{b} \times \underline{r}_i)$$

This means that we can write  $\underline{u}_i = \underline{u} + \underline{\Omega} \times \underline{r}_i$ , where  $\underline{u}$  represents constant translational motion, while  $\underline{\Omega} \times \underline{r}_i$  represents rigid rotation.

This means that in equilibrium, we cannot have any gradients of temperature, pressure, or velocity inside the total system, as we could have anticipated.

The quantity we are most often interested in with the spin- $\frac{1}{2}$  paramagnet is its heat capacity  $C_V$ . Using (3.9):

$$U = -N\mu_B B \tanh(\beta\mu_B B) = -\frac{1}{2}Nk_B\Theta_B \tanh\left(\frac{\Theta_B}{2T}\right)$$

where we have defined  $\Theta_B = \frac{2\mu_B B}{k_B}$ , which is the excitation temperature for the paramagnetic effects. From the definition of heat capacity, we find that

$$C_B = \left(\frac{\partial U}{\partial T}\right)_B = Nk_B \left(\frac{\Theta_B}{T}\right)^2 \frac{e^{\Theta_B/T}}{(e^{\Theta_B/T} + 1)^2}$$

Let us look at some limits of this expression.

- High Temperature Limit ( $T \gg \Theta_B$ ):

$$e^{\Theta_B/T} \sim 1 \longrightarrow c_B \propto \frac{1}{T^2}$$

- High Temperature Limit ( $T \ll \Theta_B$ ):

$$e^{\Theta_B/T} \gg 1 \longrightarrow c_B \propto \frac{1}{T^2} e^{-\Theta/T}$$

As  $C_B$  tends to zero in both limits, this means that there must be some maximum temperature for which the magnetic heat capacity of the system is maximised. This turns out to be around  $\sim 5.6K$ .

For the magnetisation, we need our expression for the Helmholtz free energy as

$$F = U - TS - m \cdot B$$

where  $m = MV$  is the magnetic moment. This means that the magnetisation can be easily obtained as

$$M = -\frac{1}{V} \left(\frac{\partial F}{\partial B}\right)_T = \frac{N\mu_B}{V} \tanh\left(\frac{\mu_B B}{k_B T}\right)$$

This once again behaves sensibly; we re-obtain Curie's Law in the high temperature limit, and find that the magnetisation is constant in the low temperature limit.

### The Harmonic Oscillator

We know from Quantum Mechanics that the energy levels of a 1-D harmonic oscillator are

$$E_n = \left(n + \frac{1}{2}\right) \hbar\omega$$

This means that the partition function is given by

$$Z_1(\beta) = \sum_{\alpha} e^{-\beta E_{\alpha}} = \sum_{n=0}^{\infty} e^{-(n+\frac{1}{2})\beta\hbar\omega} = e^{-\frac{1}{2}\beta\hbar\omega} \sum_{n=0}^{\infty} e^{-n\beta\hbar\omega}$$

We can sum the last term as an infinite geometric series to obtain

$$\boxed{Z_1(\beta) = \frac{e^{-\frac{1}{2}\beta\hbar\omega}}{1 - e^{-\beta\hbar\omega}}} \quad (3.14)$$

### 3.4 The Ideal Gas

We will first treat the Ideal Gas using the Canonical Ensemble. If we treat the ideal gas classically, it's energy levels are given by

$$\varepsilon_k = \frac{\hbar^2 k^2}{2m}$$

Theoretically, we could just plug this expression into (3.7) and obtain the partition function. However, the problem that we encounter is that sums of this type are very difficult to calculate; it is much easier to calculate an equivalent integral. Suppose that our system is a box with side lengths  $L_x, L_y, L_z$ . Then, we are restricted to the wavenumbers that satisfy

$$\underline{k} = \left( \frac{2\pi}{L_x} i_x, \frac{2\pi}{L_y} i_y, \frac{2\pi}{L_z} i_z \right)$$

for integers  $i_x, i_y, i_z$  in order to fulfil appropriate (periodic) boundary conditions at the extremities of the box. This means that  $\Delta k_{x,y,z} = (2\pi)/(L_{x,y,z})$  represents the mesh-size (spacing between discrete grid points) in phase-space. Then, we can approximate the desired sum by an integral:

$$Z_1 = \sum_{\underline{k}} e^{-\beta\varepsilon_k} = \sum_{\underline{k}} \underbrace{\frac{L_x L_y L_z}{(2\pi)^3}}_{\frac{V}{(2\pi)^3}} \underbrace{\frac{2\pi}{L_x}}_{\Delta k_x} \underbrace{\frac{2\pi}{L_y}}_{\Delta k_y} \underbrace{\frac{2\pi}{L_z}}_{\Delta k_z} e^{-\beta\varepsilon_k} \sim \frac{V}{(2\pi)^3} \int d^3 \underline{k} e^{-\beta\hbar^2 k^2 / 2m}$$

Assuming that the system is isotropic, we can transform to spherical coordinates:

$$\frac{V}{(2\pi)^3} \int d^3 \underline{k} e^{-\beta\hbar^2 k^2 / 2m} = \frac{V}{(2\pi)^3} \int_0^\infty dk 4\pi k^2 e^{-\beta\hbar^2 k^2 / 2m} = \int_0^\infty dk g(k) e^{-\beta\hbar^2 k^2 / 2m}$$

The quantity  $g(k) = (V k^2)/(2\pi^2)$  is known as the *density of states*, which tells us the number of microstates  $\alpha$  per  $k$  (or, by appropriate substitution) per  $\varepsilon$ . From the calculation above, it is clear that the density of states depends on the dimensionality of the space; this means that the behaviour of the 3-D Ideal Gas (as described in the following sections) will be altered if we assume different dimensions for the space.

Evaluating this integral, we obtain the single particle partition function

$$Z_1 = \frac{V}{\lambda_{th}^3} \quad \text{for} \quad \lambda_{th} = \hbar \sqrt{\frac{2\pi}{mk_B T}} \quad (3.25)$$

It is clear that  $\lambda_{th}$  has dimensions of length in order to allow  $Z_1$  to remain dimensionless. This means that this expression *must* hold in the relativistic case, except with a different definition of  $\lambda_{th}$  (it is left as an exercise to the reader to find out exactly the definition is modified).

#### 3.4.1 Distinguishability

If we were to assume that the particles were distinguishable, we could use (3.12) to calculate the partition function for the entire system. However, if we were to calculate the entropy, we would find that it is not additive, even though it has to be additive by definition. This is a result of the fact that we have determinate momenta for the particles, but indeterminate position; this essentially means that every particle is everywhere, and so we

### Classical Limit

The Correspondence Principle tells us that any results we derive in a quantum mechanical system must hold in the classical limit. We now ask the question *what is the classical limit for quantum gases?* In general, the classical limit will occur where the gas is hot ( $T \rightarrow \infty$ ) and dilute ( $n \rightarrow 0$ ). In this limit,  $e^{-\beta\mu} \gg 1$ . Then:

$$f(\beta, \mu) = \frac{2}{\sqrt{\pi}} \int_0^\infty dx \frac{\sqrt{x}}{e^{x-\beta\mu} \pm 1} \sim \frac{2}{\sqrt{\pi}} \int_0^\infty dx \sqrt{x} e^{-x} e^{\beta\mu} = e^{\beta\mu}$$

Using the definition of  $f(\beta, \mu)$ , this means that the condition for the classical limit of a quantum gas is

$$\boxed{\frac{n}{n_Q} \ll 1} \quad (3.42)$$

again for appropriate definitions of  $n_Q$ . This is in fact the same condition that we found in Section (3.4.1). This result can be used to show that the mean occupation numbers  $\bar{n}_i$  for Fermi-Dirac and Bose-Einstein statistics reduce to a Maxwellian concentration in the classical limit.

### Degeneration

In this context, *degeneration* occurs when the number of quantum states available to a single particle becomes comparable to the number of particles in the system. Physically, we can interpret our quantum concentration  $n_Q$  as 'concentration' of quantum states for the system, coming from the density of states. This means that we would expect degeneration appear when  $n$  is on the order of  $n_Q$ , namely that

$$\frac{n}{n_Q} \sim 1$$

By writing  $n_Q$  explicitly, and  $n$  in terms of the pressure  $p$ , we can show that air at STP is safely non-degenerate ( $n/n_Q \sim 10^{-6}$ ), whereas electrons in metals are very much degenerate ( $n/n_Q \sim 10^4$ ) under everyday conditions. This means that we cannot describe the properties of electrons in metals via classical models; we require Fermi-Dirac statistics in the degenerate limit. The following two sections will examine how Fermi and Bose gases behave when they become degenerate.

#### 3.5.4 Degenerate Fermi Gas

Consider a Fermi gas for which  $T \rightarrow 0$  so  $\beta \rightarrow \infty$ . Then, considering carefully the behaviour of the exponential factor, the mean occupation numbers will behave according to

$$\bar{n}_i = \frac{1}{e^{\beta(\varepsilon_i - \mu)} + 1} \rightarrow \begin{cases} 1 & \text{for } \varepsilon_i < \mu(T=0) \\ 0 & \text{for } \varepsilon_i > \mu(T=0) \end{cases}$$

This is shown in Figure (3.2). The consequence of this is that when Fermi gases become degenerate, the electrons will begin to 'stack up' and occupy all the available single-particle states from the lowest-energy one to maximum energy equal to the value of the chemical potential at  $T = 0$

$$\varepsilon_F = \mu(T = 0)$$

This quantity  $\varepsilon_F$  is known as the *Fermi energy*, and tells us what the maximum energy per particle is at  $T = 0$ . Let us find an expression for the Fermi energy, remembering that in this state the occupation number has become a step-function.

### 3.6 The Photon Gas

Thermal radiation can be modelled as a gas of photons with energy per particle  $\hbar\omega$ , with chemical potential  $\mu = 0$ , and which has an energy density profile that is only dependent on temperature (black body radiation). It follows that for a gas of  $N$  particles that the energy density is given by

$$u = u(T) = n\hbar\omega$$

From Kinetic Theory, we know that the particle flux is  $\Phi = nc/4$ , meaning that the energy flux is given by  $P = uc/4$ . Lastly, by analogy to (2.8), we can write the pressure of the photon as  $p = u/3$ . With this set-up, let us derive some further properties of the gas from both Thermodynamics, and the theory of Quantum Gases.

#### 3.6.1 Thermodynamically

Starting from (3.17), it quickly follows that for a gas with the above properties

$$dU = TdS - \frac{u}{3}dV \longrightarrow \left(\frac{\partial U}{\partial V}\right)_T = T \left(\frac{\partial S}{\partial V}\right)_T - \frac{u}{3}$$

However, we know that

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

as  $u$  cannot depend on the size of the system by the definition of energy density. Recalling (1.31):

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V = \frac{1}{3} \frac{du}{dT}$$

We thus obtain the differential equation

$$u = \frac{1}{3}T \frac{du}{dT} - \frac{u}{3} \longrightarrow 4u = T \frac{du}{dT}$$

that we can solve to obtain  $u \propto T^4$ . This means that *incident power per unit area* is given by

$$P = \frac{1}{4}uc = \sigma T^4 \quad (3.53)$$

for some constant of proportionality  $\sigma$  that is known as the *Stefan-Boltzmann constant*. However, to find the actual value of the constant, we have to treat the photon gas using the theory of Section (3.5).

#### 3.6.2 As a Quantum Gas

Photons are bosons, where their spin can take the values  $s = \pm 1$ . We want to calculate the number density of photons with frequencies in the range  $[\omega, \omega + d\omega]$ . The density of states for such a system is given by

$$g(k) dk = \underbrace{2}_{\text{polarisation states}} \frac{V}{(2\pi)^3} 4\pi k^2 dk = \frac{V k^2}{\pi^2} dk$$

## 4.1 Real Gases

For most of the Thermodynamics that we have been doing with gases, we have merely dealt with the Ideal Gas, as this is the simplest way to model gases. However, evidently most gases are non-ideal, and so it would be useful to develop other ways of describing the behaviour of gases, as we will do so in the following sections. Before we do so, let us derive a useful result for the energy of a gas. Consider  $U = U(T, V)$ :

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV$$

From (3.17), assuming a closed system ( $dN = 0$ ):

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

where we have made use of (1.31). Putting these together, this gives

$$\boxed{dU = C_V dT + \left[T \left(\frac{\partial p}{\partial T}\right)_V - p\right] dV} \quad (4.1)$$

This can be used to show, for example, that  $U$  is only a function of temperature for certain gases (the second term is zero for an ideal gas, and certain other equations of state). It is also a relation that one is commonly asked to derive, so it is well worth having in the memory bank.

Let us also recap some important notation. We will use  $n_m = N/N_A$  to refer to the number of moles of a substance. Recall the gas constant  $pV = N_A k_B$ . This means that we can write the simple relation

$$Nk_B = n_m R \quad (4.2)$$

that allows us to convert between (typically) Statistical Mechanics and Kinetic Theory expressions (involving  $k_B$ ) and Thermodynamic expressions (involving  $R$ ), though they are of course equivalent.

### 4.1.1 Virial Expansion

The equations describing real gases include some corrections for the fact that intermolecular forces, that we have neglected with the Ideal Gas, exist. This often means that they will reduce to the case of the Ideal Gas in some limit, and so we can write them as a *virial expansion* in their density:

$$\boxed{\frac{pV}{n_m RT} = 1 + \frac{n_m B}{V} + \frac{n_m^2 C}{V^2} + \dots} \quad (4.3)$$

where  $B$  and  $C$  are the (possibly) temperature dependent coefficients, and  $n_m$  is the number of moles of the gas.

The *Boyle temperature* is defined as the temperature that satisfies  $B(T_b) = 0$ ; that is, the temperature that means that the gas behaves like an ideal gas to first order in  $n_m$ . It is so called because it will thus obey Boyle's empirical law.

### 4.1.2 Van-der-Waals Gas

This is the one of the most common real gas approximations. The equation of state can be derived through a Statistical Mechanics approach by making a mean-field approximation, but it is much easier to quote the equation and explain the origin of the various terms. The *Van-der-Waals* equation of state is as follows:

$$\left( p + \frac{a n_m^2}{V^2} \right) (V - b n_m) = n_m R T \quad (4.4)$$

where  $a$  and  $b$  are coefficients that depend on the nature of the gas being examined. This has been written in molar form as this allows easier comparison with (4.3), but it can also be written in terms of particle number  $N$ . There are some key features to note:

- The number of nearest neighbours to a particular particle is proportional to  $n_m/V$ , and so attractive intermolecular interactions lower the total potential energy by an amount proportional the number of atoms multiplied by the number of nearest neighbours. This means that we can write the potential change as  $(a n_m)/V$  which gives rise to an energy change  $-(a n_m^2 dV)/V^2$ . This can be thought of as an effective pressure causing the energy change, giving rise to the extra term shown
- The term  $b n_m$  comes from considering the particles to have a finite size (instead of point particles), meaning that we must exclude this volume in the equation of state

It is evident that this equation reduces to the Ideal Gas equation in the low density limit  $n_m/V \ll 1$ . It is also under this limit that we can write this equation as a virial expansion:

$$\frac{pV}{n_m R T} = \left( 1 - \frac{b n_m}{V} \right)^{-1} - \frac{a n_m}{R T V} \sim 1 + \left( \frac{a}{R T} \right) \frac{n_m}{V} + \left( \frac{b n_m}{V} \right)^2 + \dots$$

This means that the Boyle temperature for a Van der Waals gas is  $T_b = a/(bR)$ .

### 4.1.3 Dieterici Gas

An alternative equation of state is that of the *Dieterici gas*, which is as follows:

$$p(V - b n_m) = n_m R T \exp\left(-\frac{a n_m}{R T V}\right) \quad (4.5)$$

Once again, the  $b n_m$  comes from the requirement of excluding the finite volume of the particles from the calculation, and the exponential term regulates the strength of the inter-particle interaction. This description of real gases can prove more accurate than that of the Van der Waals model, but not by a significant margin. Once again, this can also be written as a virial expansion in the low density limit:

$$\frac{pV}{n_m R T} = \frac{e^{-(a n_m)/(R T V)}}{1 - (b n_m)/V} \sim 1 + \left( b - \frac{a}{R T} \right) \frac{n_m}{V} + \left( b^2 + \frac{a^2}{2 R^2 T^2} - \frac{a b}{R T} \right) \left( \frac{n_m}{V} \right)^2 + \dots$$

This means that the Boyle temperature for a Dieterici gas is actually the same as that of the Van der Waals gas.

### 4.1.4 Critical Points

In Thermodynamics, *phases* are *regions of a system throughout which all physical properties of a material are essentially uniform*; this is often used to refer to different states of a particular substance that exist within the one system, such as a 'liquid phase' and 'gas

### The Joule Expansion

We have already met this expansion in Section (1.4.5). To recap, this involves two chambers with adiabatic walls, so no heat is exchanged with the surroundings - the gas is allowed to expand freely when the piston is drawn back, so no work is done. The change in internal energy is therefore zero. We are thus interested in whether this results in a change in temperature, and so we define the *Joule coefficient*  $\mu_J$  as

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

Making use of (1.31), this becomes

$$\mu_J = - \frac{1}{C_V} \left[ T \left( \frac{\partial p}{\partial T} \right)_V - p \right] \quad (4.8)$$

We can find the change in temperature by the simple integration of this coefficient over the change in volume. As we have seen,  $\mu_J = 0$  for an Ideal Gas, meaning that we observe no change in temperature. However, for a Van der Waals gas, we find that  $\mu_J = -(an_m^2)/(C_V V^2)$ , meaning that there is in fact cooling of the gas upon expansion. This we would expect, as for real gases the potential energy is raised by forcing the molecules apart against intermolecular forces upon expansion, which lowers the kinetic energy, and thus temperature.

### The Joule-Kelvin Expansion

The Joule-Kelvin expansion involves the steady flow of gas through a porous plug that imposes the condition of quasi-stasis. The position between the two chambers, as well as the rate of flow, are kept constant using pistons. The chambers are again have adiabatic walls, and so there is no heat exchange with the surroundings.

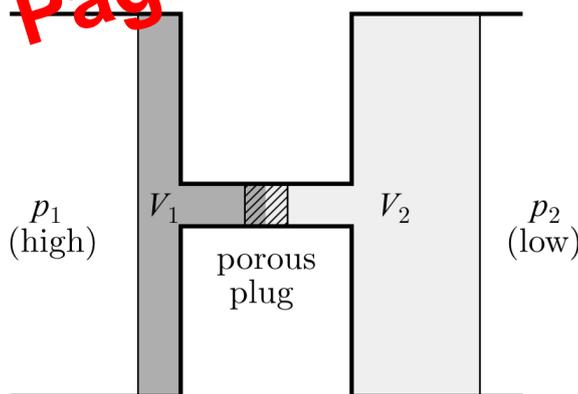


Figure 4.2: A schematic of the Joule-Kelvin Expansion

Suppose that after some time, the gas occupies a volume  $V_1$  in the higher pressure chamber, and a volume  $V_2$  in the lower pressure. This means that we can write the energy change as

$$U_2 - U_1 = \underbrace{p_1 V_1}_{\text{work done by } p_1} - \underbrace{p_2 V_2}_{\text{work against } p_2} \rightarrow \underbrace{U_1 + p_1 V_1}_{H_1} = \underbrace{U_2 + p_2 V_2}_{H_2}$$

It is clear that the the enthalpy  $H$  is conserved in the process. This means that we are interested in temperature changes at constant  $H$ . We thus define (you guessed it), the *Joule-Kelvin coefficient*

$$\mu_{JK} = \left( \frac{\partial T}{\partial p} \right)_H = - \left( \frac{\partial T}{\partial H} \right)_p \left( \frac{\partial H}{\partial p} \right)_T$$

Recalling that  $dH = TdS + Vdp$ , we have that

$$\left( \frac{\partial H}{\partial T} \right)_p = T \left( \frac{\partial S}{\partial T} \right)_p = C_p \quad \text{and} \quad \left( \frac{\partial H}{\partial p} \right)_T = T \left( \frac{\partial S}{\partial p} \right)_T + V$$

Putting this together, we can write the Joule-Kelvin coefficient as

$$\boxed{\mu_{JK} = \frac{1}{C_p} \left[ T \left( \frac{\partial V}{\partial T} \right)_p - V \right]} \quad (4.9)$$

We can thus find the change in temperature by integrating  $\mu_{JK}$  over the change in pressure. This is evidently again zero for the ideal gas. However, for real gases,  $\mu_{JK}$  can either be positive (cooling) or negative (heating), meaning that we have a cross-over *inversion curve* that is defined by the equation  $\mu_{JK} = 0$ , or rather

$$\left( \frac{\partial V}{\partial T} \right)_p = \frac{V}{T}$$

Using the reciprocity relation (1.22), this can be written in the more convenient form

$$\boxed{T \left( \frac{\partial p}{\partial T} \right)_V + V \left( \frac{\partial p}{\partial V} \right)_T = 0} \quad (4.10)$$

From this, we can also define the *maximum inversion temperature* below which the Joule-Kelvin process results in cooling.

## 4.2 Phase Transitions and Equilibria

We are now going to look at the details of *phase transitions*; that is, the Thermodynamic processes where-by a substance changes from one phase to another. A very typical example is that of the boiling of water; the phase transition is quite rapid, as it is only when the boiling point is reached that the liquid phase becomes thermodynamically unstable, and the gas phase thermodynamically stable.

### 4.2.1 Latent Heat

Usually to change from one phase, at entropy  $S_1$ , to another phase at entropy  $S_2$ , we require some additional heat supply. This is known as the *latent heat* (of evaporation, melting, etc.) given by

$$L = \Delta Q_{rev} = T(S_2 - S_1) \quad (4.11)$$

where  $T$  is used to refer to the temperature at which the phase transition occurs; the change in entropy occurs instantaneously at this temperature. As we are interested in changes at constant temperature, we will be making use of the Gibbs Free Energy.

Ehrenfest's method of classifying phase transitions is that the *order* of a phase transition is the order of the derivative of  $G$  or  $\mu$  that is discontinuous. First-order phase transitions have discontinuous entropy and volume, and so they exhibit a latent heat. Second-order phase transitions have no latent heat but may have discontinuous heat capacities or compressibility ( $2^{nd}$  derivatives of  $G$ ). When no latent heat is exhibited (continuous entropy), we have a continuous phase change. In Van der Waals gas, we can have either continuous or discontinuous phase changes depending on whether we go 'directly across' the phase boundary or around the critical point, as outlined in Section (4.1.4).

### 4.2.2 The Clausius-Clapeyron Equation

Recall from (3.18) that  $G = \mu N$ . This means that we obtain the two differential forms for  $G$ :

$$dG = Vdp - SdT \quad \text{and} \quad dG = \mu dN + Nd\mu$$

Assuming that total particle number is conserved, we find that the differential form of  $\mu$  can be written as

$$d\mu = -\frac{S}{N}dT + \frac{V}{N}dp = -sdT + vdp$$

where  $s$  and  $v$  are the entropy per particle and volume per particle respectively. From Section (3.3.1), we know that  $\mu_1 = \mu_2$  for the phases to coexist in equilibrium, and so we know that along the  $p$ - $T$  boundary for the two phases

$$\begin{aligned} d\mu_1 &= d\mu_2 \\ -s_1 + v_1 \frac{dp}{dT} &= -s_2 + v_2 \frac{dp}{dT} \\ \frac{dp}{dT} &= \frac{s_1 - s_2}{v_1 - v_2} \end{aligned}$$

Substituting in our expression for latent heat, we obtain the *Clausius-Clapeyron equation*

$$\frac{dp}{dT} = \frac{L}{T(V_2 - V_1)} \quad (4.12)$$

Depending on the type of transition, we can use this to derive different  $p$ - $T$  curves for the phase boundaries.

### Solid-Liquid Boundary

The Clausius-Clapeyron equation can be simply re-arranged to give

$$dp = \frac{LdT}{T\Delta V}$$

where  $\Delta V = V_2 - V_1$ . Assuming that both  $\Delta V$  and  $L$  are temperature independent, then this equation can be integrated to yield

$$p = p_0 + \frac{L}{\Delta V} \log \left( \frac{T}{T_0} \right) \quad (4.13)$$

The constants  $p_0$  and  $T_0$  are chosen such that  $p = p_0$  and  $T = T_0$  on the boundary. The volume change  $\Delta V$  on melting is relatively small, so that the gradient of the phase boundary in the  $p$ - $T$  plane is very steep.

*When lead is melted at atmospheric pressure the melting point is  $327.0^\circ\text{C}$ , the density decreases from  $11.01 \times 10^3$  to  $10.65 \times 10^3 \text{ kg m}^3$  and the latent heat is  $24.5 \text{ kJ kg}^{-1}$ . Estimate the melting point of lead at a pressure of 100 atm.*

We can use the above equation to write that

$$\Delta p = \frac{L}{\Delta V} \log \left( \frac{T_2}{T_1} \right) \rightarrow T_2 = T_1 e^{\frac{\Delta p \Delta V}{L}}$$

We are already given that  $\Delta p = 99 \text{ atm}$ . Suppose that there is a mass  $M$  of lead. Then the change in the specific volume (volume per unit mass) is given by

$$\Delta V = v_{\text{liquid}} - v_{\text{solid}} = \frac{1}{\rho_{\text{liquid}}} - \frac{1}{\rho_{\text{solid}}} = 0.07 \times 10^{-6} \text{ m}^3 \text{ kg}^{-1}$$

Recalling that  $L$  is a specific, per unit mass quantity, we can then simply plug everything into our expression for  $T_2$  and find  $327.75^\circ\text{C}$ , which is a very small change in temperature.

### Liquid-Gas Boundary

Let us initially treat this boundary assuming that  $V_{\text{gas}} = V \gg V_{\text{liquid}}$ , the resultant gas is ideal, and  $L$  is temperature independent. The former of these assumptions is not particularly assumptive, as most incompressible fluids undergo a large expansion when moving to their gaseous phase. Then, according to the Clausius-Clapeyron equation:

$$\frac{dp}{dT} = \frac{L}{TV} = \frac{pL}{n_m RT^2}$$

where we have used the ideal gas equation in the second equality. This equation can be integrated to give

$$p = p_0 \exp \left( -\frac{L}{n_m RT} \right) \quad (4.14)$$

As  $R = N_A k_B$ , the exponential factor is roughly Boltzmann. This equation can be used to solve that annoyingly typical example about boiling a cup of tea on the top of a mountain; it is evident that the British simply cannot get away from their tea.