

# Classical Thermodynamics

## Ideal gases

- **Assumptions**
  - **Identical** particles in **random** motion.
  - **Small solid spheres** – occupy **negligible volume**.
  - **Elastic** collisions.
  - **No long range forces** – only forces **during collisions** → **only energy is KE**,  $\frac{1}{2}mv^2$  per particle.
- **Results**
  - Pressure is given by  $p = \frac{1}{3}nm\langle v^2 \rangle$ .
  - Flux is given by  $J = \frac{1}{4}n\langle v \rangle$ .
- The **Maxwell-Boltzmann Distribution**
  - $P(v) = \left(\frac{m}{2\pi kT}\right)^{3/2} 4\pi v^2 \exp(-mv^2/2kT)$
  - This gives
 
$$\langle v \rangle = \sqrt{\frac{8kT}{\pi m}}$$

$$\langle v^2 \rangle = \frac{3kT}{m}$$
- Energy...
  - $U = \frac{3}{2}RT = \frac{3}{2}N_A kT$

## Definitions

- A **system** is in **Thermal Equilibrium** when **all its macroscopic observables have ceased to change with time**.
- A **function of state** is any **physics quantity** that has a **well-defined value** for **each equilibrium state of the system**. They are represented by **exact differentials**.
- **Functions of state** can be **either**
  - **Extensive** (proportional to system size) – eg: volume.
  - **Intensive** (independent of system size) – eg: pressure.
  - Intensive and extensive variables form **conjugate pairs**, the product of which is **energy**.

- The **heat capacity** is the amount of heat we need to supply to raise the temperature by  $dT$ . This can be measured at **constant volume** or at **constant pressure**, so

$$C_V = \left( \frac{dQ}{dT} \right)_V \quad C_p = \left( \frac{dQ}{dT} \right)_p$$

- For an **ideal gas**

$$pV = nRT$$

- **Stirling's Approximation**

$$\ln N! \approx N \ln N - N$$

## The First Law

- The **First Law of Thermodynamics** states that

*Energy is conserved, and heat and work  
are both forms of energy*

$$\Delta U = \Delta Q + \Delta W$$

- Convention:

*$\Delta Q$  and  $\Delta W$  are **POSITIVE** when  
energy is given **TO** the system*

- For a **differential change**

$$dU = \delta Q + \delta W$$

- The **work done compressing a gas** is given by

$$\delta W = -pdV$$

And so **for a gas**, the first law can be written

$$dU = \delta Q - pdV$$

## Heat Capacities

- In general, the **internal energy** will be a function of **temperature** and **volume**, so

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

- Using the form of the **first law** for a **gas**, above, we can write

$$\delta Q = dU + pdV$$

$$\delta Q = \left( \frac{\partial U}{\partial T} \right)_V dT + \left[ \left( \frac{\partial U}{\partial V} \right)_T + p \right] dV$$

And dividing by  $dT$ :

$$\frac{\delta Q}{dT} = \left(\frac{\partial U}{\partial T}\right)_V + \left[\left(\frac{\partial U}{\partial V}\right)_T + p\right] \frac{dV}{dT}$$

- By taking the equation above at constant volume and constant pressure (only the  $dV/dT$  term will matter), we obtain

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

$$C_p = C_V + \left[\left(\frac{\partial U}{\partial V}\right)_T + p\right] \left(\frac{\partial V}{\partial T}\right)_p$$

- For an ideal gas:

$$C_p = C_V + R$$

- We define

$$\boxed{\gamma = \frac{C_p}{C_V}}$$

## Reversibility

- A change is **reversible** if an **infinitesimal change in external conditions** would **reverse the direction of the change**.
- Reversible changes are typically **very slow** and **quasi-static**.
- They are also **frictionless** – no **viscosity, turbulence, etc...**

## Isothermal expansions

- When an expansion is **isothermal**, the **temperature of the system does not change**. Therefore, the **internal energy** of the system does not change, and

$$\delta W = -\delta Q$$

- Therefore, when a gas is **expanded isothermally** from  $V_1$  to  $V_2$  at a temperature  $T$ , the **heat absorbed by the gas** is given by

$$\begin{aligned} \Delta Q &= \int \delta Q \\ &= -\int \delta W \\ &= \int_{V_1}^{V_2} p \, dV \\ &= \int_{V_1}^{V_2} \underbrace{p}_{=RT/V} \, dV \\ &= RT \int_{V_1}^{V_2} \frac{1}{V} \, dV \end{aligned}$$

$$\boxed{\Delta Q = RT \ln \frac{V_2}{V_1}}$$

- An **adiabatic** process is both **adiathermal** (no flow of heat) and **reversible**, so

$$\delta Q = 0$$

And

$$dU = \delta W$$

However, for an ideal gas

$$dU = C_V dT$$

Therefore

$$C_V dT = \delta W$$

$$C_V dT = -p dV$$

$$C_V dT = -\frac{RT}{V} dV$$

$$\frac{dT}{T} = -\frac{R}{C_V} \frac{dV}{V}$$

$$\frac{dT}{T} = \overbrace{\left(1 - \gamma\right)}^{\text{Obvious from def}^n \text{ of } \gamma} \frac{dV}{V}$$

$$\boxed{TV^{\gamma-1} = \text{constant}}$$

Other versions can easily be generated using  $pV \propto T$ .

## The Second Law

- The **Second Law of Thermodynamics** can be stated in **two different ways**

### The Clausius Formulation

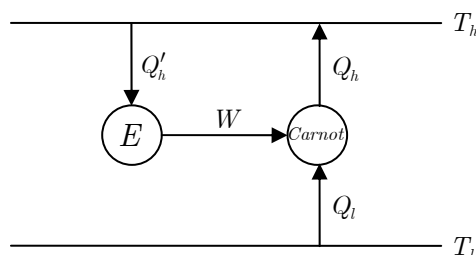
No process is possible whose sole result is the transfer of heat from a hotter to a cooler body.

### The Kelvin Formulation

No process is possible whose sole result is the complete conversion of heat into work.

- The **equivalence** of these two formulations can be shown in two steps
  - Violating Kelvin  $\rightarrow$  Violating Clausius

Consider a “**Kelvin-violator**”  $E$  connected to a **Carnot engine**:



We then have

$$Q'_h = W$$

$$Q_h = W + Q_l$$

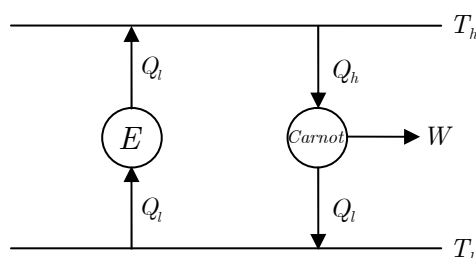
But the **total heat dumped at  $T_h$**  is given by

$$Q_h - Q'_h = W + Q_l - W = Q_l$$

Thus, the **net effect** is to **transfer heat from  $T_l$  to  $T_h$**  – this **violates Clausius’ Formulation**.

○ **Violating Clausius → Violating Kelvin**

Consider a “**Clausius violator**”  $E$  running next to a **Carnot engine**:



Overall, **no heat** is being **dumped** at  $T_l$ , but a heat  $Q_h - Q_l$  is **drawn** from  $T_h$ . Furthermore, by the **First Law**

$$W = Q_h - Q_l$$

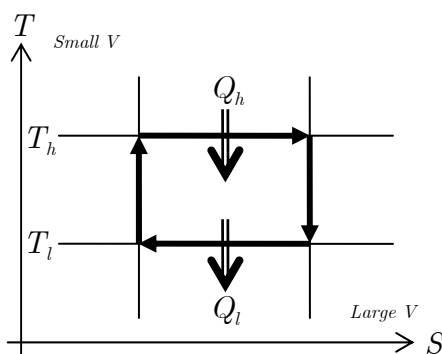
Which means that the **net effect** of this engine is to **convert heat  $Q_h - Q_l$  into work** which **Violates Kelvin’s Formulation**.

## Engines

- **Engines** are **systems** operating **cyclic processes** that **convert heat** into **work**.
- The **Carnot Engine** is based on the **Carnot Cycle**:
  - **Isothermal expansion** – heat  $Q_h$  absorbed.

- **Adiabatic expansion** – no heat flow.
- **Isothermal compression** – heat  $Q_l$  given out.
- **Adiabatic compression** – no heat flow

A **schematic** is as follows:



Where  $S$  is some quantity proportional to  $pV^\gamma$ , constant during an **adiabatic change**.

- By the **First Law**, the **work output** must be

$$W = \oint p \, dV = Q_h - Q_l$$

- The **efficiency** of an engine is defined as

$$\eta = \frac{\text{What we want}}{\text{What we gave for it}} = \frac{\text{Work done by engine}}{\text{Heat put in}} = \frac{Q_h - Q_l}{Q_h} = 1 - \frac{Q_l}{Q_h}$$

- For a **Carnot Cycle**, we can show, using the formulae derived above for isotherms and adiabats, that

$$\frac{Q_h}{Q_l} = \frac{T_h}{T_l} \Rightarrow \eta = 1 - \frac{T_l}{T_h}$$

- Note, crucially, that this implies that the quantity  $Q/T$  is always the same in a reversible Carnot Cycle, so, for a **Carnot Cycle**

$$\oint \frac{\delta Q}{T} = 0$$

Furthermore, for any *other* sort of engine,  $\eta_{\text{Engine}} \leq \eta_{\text{Carnot}}$ , so

$$1 - \frac{Q_l}{Q_h} \leq 1 - \frac{T_l}{T_h} \Rightarrow \frac{Q_h}{T_h} \leq \frac{Q_l}{T_l}$$

$$\boxed{\oint \frac{\delta Q}{T} \leq 0}$$

We can show that this is true for *any* cycle – **Clausius’ Theorem** (see below).

- An **engine** can be run in **reverse** in two ways:
  - **Refrigerator**

- In this case, the desired aim is the **removal of heat from a cold reservoir**, and this is done by the **provision of work**

- Therefore, the **efficiency** is given by

$$\eta = \frac{Q_l}{W}$$

- High efficiency can be achieved if  $T_2 \approx T_1$ .

○ **Heat pump**

- In this case, the desired aim is the **dumping of heat at a hot reservoir**, and this is done by the **provision of work**.

- Therefore, the efficiency is given by

$$\eta = \frac{Q_h}{W}$$

- This is always greater than 1, because **all work** is converted to heat (eg: like in an electric heater), but **more** is also added, from the **cold reservoir!**

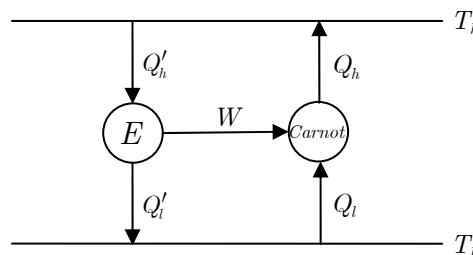
## Carnot's Theorem

- **Carnot's Theorem** states that

*Carnot's Theorem*

**Of all the heat engines working between two given temperatures, none is more efficient than a Carnot engine**

*Proof*



Consider an engine  $E$  that is **more efficient** than a Carnot Engine (ie:  $\eta_E > \eta_{Carnot}$ ), whose **produced work** is used to drive a **Carnot engine in reverse**. We then have

$$\eta_E > \eta_{Carnot}$$

$$\frac{W}{Q'_h} > \frac{W}{Q_h}$$

$$Q_h > Q'_h$$

$$Q_h - Q'_h > 0$$

The **First Law** further implies that

$$W = Q'_h - Q'_l = Q_h - Q_l$$

And therefore

$$Q_h - Q'_h = Q_l - Q'_l > 0$$

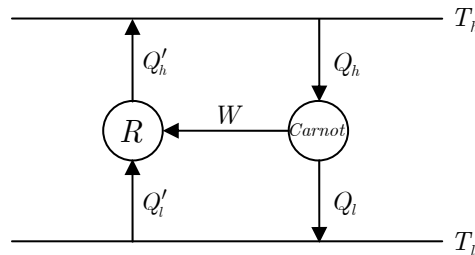
This means that the **net effect** of these engines is to **transfer energy from  $T_l$  to  $T_h$**  – this **violates the Clausius Formulation**.

- A **corollary** is that

*Corollary to Carnot's Theorem*

All reversible engines have the same efficiency as a Carnot engine,  $\eta_{Carnot}$

*Proof*



We now imagine a **reversible engine  $R$** , with  $\eta_R < \eta_{Carnot}$  and drive it **backwards**, using the work from a **Carnot Engine**. The overall result will be to **transfer heat from  $T_l$  to  $T_h$** , in **violation of Clausius' Formulation**. Thus, since the **efficiency** of any engine has to be **both  $\leq$  and  $\geq$**  that of a **Carnot engine**, it must be **equal**.

### Clausius' Theorem

- Consider **any cycle** that
  - Absorbs **heats  $dQ_i$**  at various points  $i$  which have **temperature  $T_i$** .
  - **Releases**, overall, work  $\Delta W$ , which, by the **First Law**, must be

$$\Delta W = \sum_{\text{cycle}} dQ_i$$



- Further imagine that each of these heats,  $\delta Q_i$ , are being provided by **Carnot Engines**, operating from a **single reservoir** at  $T_0$  and produce work  $\delta W_i$  each time. From the discussions above, we know that

$$\frac{\delta Q_i}{T_i} = \frac{\delta Q_i - \delta W_i}{T}$$

$$\delta W_i = \delta Q_i \left( \frac{T}{T_i} - 1 \right)$$

- [Note that no assumptions has been made about the *sign* of  $\delta Q_i$ , so heat could have been released as well].
- In any case, it looks, at the moment, like all the system is doing is **absorbing heat** and **producing work**. This violates **Kelvin's Statement**. To remedy to this, we must have

$$\text{total work produced per cycle} = \Delta W + \sum_{\text{cycle}} \delta W_i \leq 0$$

$$T \sum_{\text{cycle}} \frac{\delta Q}{T_i} \leq 0$$

Since  $T > 0$ , we must therefore have

$$\oint \frac{\delta Q}{T_i} \leq 0$$

- If the cycle was **reversible**, we could have run it backwards (with  $\delta Q'_i = -\delta Q_i$ ), and obtained the result with the inequality sign flipped. So, **Clausius' Theorem** is that

$$\boxed{\oint \frac{\delta Q}{T_i} \leq 0}$$

For any closed cycle, with equality when the cycle is reversible.

## Entropy

- We saw that for a **reversible cycle**,  $\int_{\text{cycle}} \delta Q_{\text{rev}} / T = 0$ , which means that the **integral**  $\int_A^B \delta Q_{\text{rev}} / T = 0$  is **path independent**. As such, the quantity  $\delta Q_{\text{rev}} / T$  is an **exact differential**, and we can write a new **state function**, **entropy**,  $S$ , which we **define** by

$$\boxed{dS = \frac{\delta Q_{\text{rev}}}{T}}$$

- Now, consider going **from A → B reversibly**, and then **returning from B → A irreversibly**. We then have

$$\oint_{A \rightarrow B \rightarrow A} \frac{\delta Q}{T} \leq 0$$

$$\oint_{A \rightarrow B} \frac{\delta Q_{rev}}{T} + \oint_{B \rightarrow A} \frac{\delta Q}{T} \leq 0$$

$$\oint_{B \rightarrow A} \frac{\delta Q}{T} \leq \oint_{\substack{B \rightarrow A \\ \text{Note} \\ \text{change}}} \frac{\delta Q_{rev}}{T}$$

$$\oint_{B \rightarrow A} \frac{\delta Q}{T} \leq dS$$

This is true **however close A and B get to each other**, so

$$dS \geq \frac{\delta Q_{irreversible}}{T}$$

- However, for a **thermally isolated system**,  $\delta Q = 0$  for **any process**. Therefore, assuming that the **universe is thermally isolated**:

$$dS_{universe} \geq 0$$

- We can **re-write the First Law** as follows:

$$dU = \delta Q + \delta W$$

But for a **reversible change** in a **gas**, we can write

$$dU = TdS - pdV$$

However, all the quantities in this equation are **equations of state** – therefore, this holds for **any change**, reversible or irreversible.

- This implies that **U** changes when either **S** or **V** change – in other words, **S** and **V** are the **natural variables** of **U**, and they are both **extensive** – they depend on the size of the system. **T** and **p**, by contrast, are variables that are **intensive**, and that tell us how each of these extensive variables **affect U**. In fact:

$$T = \left( \frac{\partial U}{\partial S} \right)_V$$

$$p = - \left( \frac{\partial U}{\partial V} \right)_S$$

## Pot-Pourri of facts

- It is interesting to note that for an **adiabatic** (reversible adiathermic) change,  $\delta Q_{rev} = 0$ , and so  $dS = 0$ .
- **Body of heat capacity C**, from  $T_1 \rightarrow T_2$ :

$$\Delta S = \int_{T_1}^{T_2} \frac{\delta Q}{T} = \int_{T_1}^{T_2} \frac{C}{T} dT = C \ln \left( \frac{T_2}{T_1} \right)$$

- **Reservoir** at temperature **T** absorbing heat **q**

$$\Delta S = \frac{q}{T}$$

[Note:  $q$  is always reversible for a reservoir, because the heat content is so large that any small change can reverse the direction of flow].

- For a **ideal gas**, we can write

$$dU = TdS - pdV$$

$$\underbrace{C_V dT}_{\text{Only for gas}} = TdS - pdV$$

$$dS = C_V \frac{dT}{T} + p \frac{dV}{T}$$

$$dS = C_V \frac{dT}{T} + \overbrace{R \frac{dV}{V}}^{\text{Ideal gas law}}$$

$$\boxed{S = C_V \ln T + R \ln V + S_0}$$

This gives the **Entropy of an Ideal Gas**, from which we can work out the **Entropy of mixing**.

This expression, however, has an **intrinsic problem** – **S** is **extensive**, but **V** is **also** extensive in the expression above ( $T$  is not).

- **Joule Expansion** from  $V \rightarrow nV$  – can be worked out either using the expression for **S** for a gas, or using the fact that **S** is a **state function**, and that  $\Delta S$  will therefore be the same than for an **isothermal expansion** from  $V$  to  $nV$ . It turns out it's

$$\Delta S = R \ln n$$

- This is a **generally** very **useful** principle – we can use a **reversible change** between the **same two steps** to find the change in entropy in an **irreversible change**.
- The **latent heat** is the **amount of heat needed to convert unit mass/mole** from **one phase to another**;

$$L = \Delta Q = T(S_2 - S_1)$$

- We can also express **heat capacities** in terms of **entropy**

$$C_V = \left( \frac{\delta Q}{dT} \right)_V = T \left( \frac{\partial S}{\partial T} \right)_V$$

$$C_p = \left( \frac{\delta Q}{dT} \right)_p = T \left( \frac{\partial S}{\partial T} \right)_p$$

- The **work** that can be gotten out of a **system** through some **change** is given by (note the **change in signs** due to the fact we're **extracting** energy)

$$\delta W = \delta Q - dU \geq TdS - dU$$

Clearly, the **maximum work** can be extracted when the **equality** holds – ie: when the process is **reversible**. **Increase in entropy (ie: irreversibility)** corresponds to **conversion of energy into a less useful form than work**.

## Statistics

- We note that  $dU = TdS - pdV$  implies that

$$T = \left( \frac{\partial U}{\partial S} \right)_V$$

$$\frac{1}{T} = \left( \frac{\partial S}{\partial U} \right)_V$$

If we compare this with the definition of temperature, below

$$\frac{1}{k_B T} = \frac{d \ln \Omega}{dE}$$

We find good justification to say

$$\boxed{S = k_B \ln \Omega}$$

This is an expression for a system that is in a **particular macrostate** (ie: fixed energy) with an associated number of **microstates**. This is the **microcanonical ensemble**. However...

- ... we can also consider the **canonical ensemble**, a system which can be in **any number of macrostates of energy**  $\epsilon_i$  (ie: any energy – for example, by allowing it to **exchange** energy with a **reservoir**) each of which have  $n_i$  **indistinguishable microstates** associated with them, where the **total number of microstates** is, necessarily,  $N = \sum n_i$ .

The **number of ways of rearranging the system** is

$$\Omega = \frac{N!}{\prod_i n_i!}$$

And this means that the **entropy** is given by

$$\begin{aligned} S &= k \left[ \ln N! - \sum_i n_i! \right] \\ &\approx k \left[ N \ln N \overset{\text{Insignificant}}{\cancel{-N}} - \sum_i n_i \ln n_i \overset{\text{Insignificant}}{\cancel{-n_i}} \right] \\ &\approx k \left[ N \ln N - \sum_i n_i \ln n_i \right] \\ &= k \left[ \sum_i n_i \ln N - \sum_i n_i \ln n_i \right] \\ &= k \left[ \sum_i n_i (\ln N - \ln n_i) \right] \\ &= -kM \left[ \sum_i \frac{n_i}{N} \ln \left( \frac{n_i}{N} \right) \right] \\ &= -kM \sum_i P_i \ln P_i \end{aligned}$$

Where  $P_i$  is the **probability** of finding the system in **macrostate**  $i$ . And therefore, the **entropy** in any **one microstate** (ie: **actual state of existence**) of the system is

$$S = -k \sum_i P_i \ln P_i$$

- We can use this to **elegantly** derive the **Boltzmann Distribution**. What we effectively want to do is to **maximise**  $S/k$  (for tidiness) **subject to**

$$\sum_i P_i = 1 \quad \text{and} \quad \sum_i P_i \epsilon_i = U$$

So, consider:

$$L = \sum_i -P_i \ln P_i - \alpha (P_i - 1) - \beta (P_i \epsilon_i - U)$$

Choose one of the probabilities  $P_j$ :

$$\boxed{\frac{\partial L}{\partial P_j} = 0}$$

$$\frac{\partial L}{\partial P_j} = -[\ln P_j + 1] - \alpha - \beta \epsilon_j = 0$$

$$\Rightarrow P_j = \frac{e^{-\beta \epsilon_j}}{Z}$$

To find  $\beta$ , we note that

$$\begin{aligned} S &= -k \sum_i \frac{e^{-\beta \varepsilon_i}}{Z} \ln \frac{e^{-\beta \varepsilon_i}}{Z} \\ &= -k \left[ \sum_i \frac{e^{-\beta \varepsilon_i}}{Z} \ln e^{-\beta \varepsilon_i} - k \ln Z \sum_i \frac{e^{-\beta \varepsilon_i}}{Z} \right] \\ &= k \left[ \beta \sum_i P_i \varepsilon_i + k \ln Z \right] \\ &= k\beta U + k^2 \ln Z \end{aligned}$$

Therefore:

$$k\beta = \left( \frac{\partial S}{\partial U} \right) = \frac{1}{T}$$
$$\boxed{\beta = \frac{1}{kT}}$$

As, indeed, expected.

# Analytical Thermodynamics

## Thermodynamics Potentials

- We can **make** a number of other **functions of state** by **adding to  $U$**  various other **combinations** of the **functions of state  $p$ ,  $V$ ,  $T$  and  $S$**  such that the resulting quantity has **energy dimensions**.

- Most, however, are **not very useful**. A number, however, **are**.

- **INTERNAL ENERGY** –  $\boxed{dU = TdS - pdV}$

For processes at a **constant volume (isochoric)**, we have

$$dU = TdS = \delta Q_{\text{rev}} = C_V dT$$

As such, if a process involves going **from  $T_1$  to  $T_2$**  at **constant  $V$** :

$$\Delta U = \int_{T_1}^{T_2} C_V dT$$

- **ENTHALPY** –  $\boxed{H = U + PV}$   $\Rightarrow dH = TdS + Vdp$

- The **natural variables** are now **entropy** and **pressure**.

- For **isobaric processes** (at **constant pressure**)

$$dH = TdS = \delta Q_{\text{rev}} = C_p dT$$

As such, if a process involves going **from  $T_1$  to  $T_2$**  at **constant  $p$** :

$$\Delta H = \int_{T_1}^{T_2} C_p dT$$

- Also

$$T = \left( \frac{\partial H}{\partial S} \right)_p \quad V = \left( \frac{\partial H}{\partial p} \right)_S$$

- Also, in a flow process, if a **fluid** comes **in** at **pressure  $p_1$**  and **volume  $V_1$**  with **energy  $U_1$**  and **leaves** at **pressure  $p_2$**  and **volume  $V_2$**  with **energy  $U_2$** , then it is **enthalpy** that is conserved.

- **HELMHOLTZ FREE ENERGY** –  $\boxed{F = U - TS}$   $\Rightarrow dF = -SdT - pdV$

- The **natural variables** are now **temperature** and **volume**.

- For **isothermal processes** between  **$V_1$  and  $V_2$** :

$$\Delta F = - \int_{V_1}^{V_2} p dV$$

- **GIBBS FREE ENERGY** –  $\boxed{G = H - TS}$   $\Rightarrow dG = -SdT + Vdp$

- The **natural variables** are now **pressure** and **temperature**.

- If **both**  $T$  and  $p$  are **constant** for a process,  $G$  is conserved.
- Consider a **system** in **contact** with surroundings at  $T_0$  and  $p_0$ . Let's transfer **energy**  $dU$  and **volume**  $dV$  **from surroundings**  $\rightarrow$  **system**. Consider the **internal energy of the surroundings**,  $dU_0$ :

$$dU_0 = T_0 dS_0 - p_0(-dV) = -dU$$

$$dS_0 = -\frac{dU + p_0 dV}{T_0}$$

And now, let's assume that as a result of the change, the **entropy of the system** has changed by  $dS$  – then, assuming that the process **does occur**:

$$dS_{\text{tot}} = dS_0 + dS \stackrel{\text{2}^{\text{nd}} \text{law}}{\geq} 0$$

$$\Rightarrow dU + p_0 dV - T_0 dS \leq 0$$

If we define  $A = U + p_0 V - T_0 S$ , then this means that

$$dA \leq 0$$

So  $A$  **always decreases** for a process that occurs, at tends to a **minimum** at **equilibrium**.

It turns out that  $dA$  can be **identified** with the **potentials** above, whenever their **natural variables** are **constant**.

- The **Gibbs-Helmholtz Equations** can be derived by writing any one potential as the sum of others – for example, to obtain one for  $H$  in terms of  $F$ , write  $H = F + pV + TS$ , and convert the  $p$  and the  $S$  into forms involving  $F$ , using the differentials.

## Maxwell Relations

- Derive them **directly** from the potentials.
- However, remember that
  - The **BOTTOM BITS** of the equation are the **NATURAL VARIABLES** of the potential they're from.
  - The **TOP BITS** are the **OTHER VARIABLES** of the potential they're from.

## Strategy for these problems



- **Write down a function of state in terms of particular variables.** These can be “**non-natural variables**” by **expressing one of the differentials as a differential itself...** eg:

$$\begin{aligned} df &= \left(\frac{\partial f}{\partial x}\right)_z dx + \left(\frac{\partial f}{\partial z}\right)_x dz \\ &= \left(\frac{\partial f}{\partial x}\right)_z dx + \left(\frac{\partial f}{\partial z}\right)_x \left[ \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy \right] \\ &= \underbrace{\left[ \left(\frac{\partial f}{\partial x}\right)_z + \left(\frac{\partial f}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y \right]}_{(\partial f / \partial x)_y} dx + \underbrace{\left(\frac{\partial f}{\partial z}\right)_x \left(\frac{\partial z}{\partial y}\right)_x}_{(\partial f / \partial y)_x} dy \end{aligned}$$

- **Use Maxwell’s relations to transform to easier partial differentials**
- **Use one of the following Theorems**

$$\left(\frac{\partial f}{\partial y}\right)_x = \left(\frac{\partial f}{\partial z}\right)_x \left(\frac{\partial z}{\partial y}\right)_x \quad (\text{chain rule})$$

$$\left(\frac{\partial x}{\partial z}\right)_y = \frac{1}{(\partial z / \partial x)_y} \quad (\text{reciprocal theorem})$$

$$\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y = -1 \quad (\text{reciprocity})$$

$$\left(\frac{\partial x}{\partial y}\right)_z = -\left(\frac{\partial x}{\partial z}\right)_y \left(\frac{\partial z}{\partial y}\right)_x \quad (\text{corollary of reciprocity})$$

- **Identify a heat capacity**
- **Identify a generalised susceptibility**

This **quantifies** how much a **particular variable changes** when a **generalised force** (the differential of  $U$  w.r.t. some other parameter) **is applied**. For example, **compressibilities** (isothermal and adiabatic) are

$$\kappa_T = -\frac{1}{V} \left(\frac{\partial V}{\partial p}\right)_T \qquad \kappa_S = -\frac{1}{V} \left(\frac{\partial V}{\partial p}\right)_S$$

We can show that  $\kappa_T / \kappa_S = \gamma > 1$ , which implies that **adiabats** are **steeper** than **isotherms**.

# Statistical Thermodynamics

## Basic Ideas

- A multi-particle system can be defined as a set of quantum states.
- A particular configuration (quantum state) is called a **microstate**
  - Each microstate is **equally likely** to occur
  - The internal dynamics of the system are such that it can make **transitions** between microstates.
  - Given **enough time**, the system will **explore all** possible microstates and spend an **equal time in each of them** (the **ergodic hypothesis**).

Taken together, these three facts imply that **a system will appear to choose a macroscopic configuration which maximizes the number of microstates.**

- Measurements concern a **property** of the **macrostate** of the system, comprising of many different microstates, each with the same macroscopic property.
- The number of microstates making up a macrostates is given the symbol  $\Omega$ .
- It is possible to find  $\Omega$  as a function of some variable of the system around  $\Omega_0$ , the **maximum**, and it is usually found that it **peaks extremely sharply** at that point – the highest probability configuration gives the macroscopic state to a **high** degree of accuracy.

## Temperature

- The 0<sup>th</sup> Law of Thermodynamics stated that

**Two systems, each separately in thermal  
equilibrium with a third, are also in thermal  
equilibrium with each other**

This allows a definition of temperature as “*the property which systems in thermal equilibrium have in common*”.

In a way this law states that “**thermometers work**”, because it allows us to measure the **temperature** of **one body** by placing it in **contact** with **another body** which displays a **property** that has **well-known dependence on temperature**.

- Consider two systems in thermal contact with each other
  - With energy (a property of the **macrostate**)  $E_1$  and  $E_2$
  - With each of these energy macrostates corresponding to  $\Omega(E)$  microstates.
  - With total energy  $E = E_1 + E_2 \Rightarrow dE_2/dE_1 = -1$ .
- The **whole system** can therefore be in any one of  $\Omega(E_1)\Omega(E_2)$  **microstates**.
- If those two systems have come to **Thermal Equilibrium**, the number of microstates the whole system is in must be at a maximum. So, maximising the expression with respect to  $E_i$ :

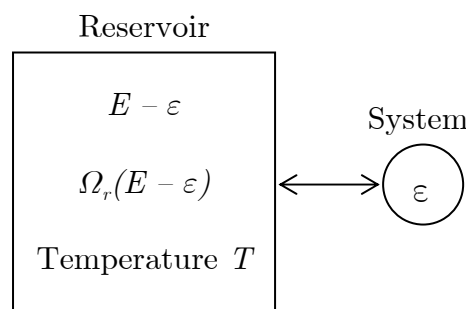
$$\begin{aligned} \frac{d}{dE_1} [\Omega(E_1)\Omega(E_2)] &= 0 \\ \frac{1}{\Omega_1} \frac{d\Omega_1}{dE_1} &= \frac{1}{\Omega_2} \frac{d\Omega_2}{dE_2} \\ \frac{d \ln \Omega_1}{dE_1} &= \frac{d \ln \Omega_2}{dE_2} \end{aligned}$$

- So we see that the function  $d \ln \Omega / dE$  must be a **constant** of the system, and must therefore be a function of **temperature**. We define:

$$\boxed{\boxed{\frac{1}{k_B T} = \frac{d \ln \Omega}{dE}}}$$

## The Boltzmann Distribution – Canonical Ensembles

- Consider a **system** in **equilibrium** with a **reservoir** at temperature  $T$ .



And, consider that

- The **total energy** is  $E$ , and the energy of the system is  $\varepsilon$ , which leaves  $E - \varepsilon$  to the reservoir.
- The **temperature** of the reservoir is **constant**, as long as  $\varepsilon$  is small.
- The number of **microstates** of the **reservoir** corresponding to energy  $E - \varepsilon$  is  $\Omega_r(E - \varepsilon)$ , and the number of microstates of the **system** corresponding to energy  $\varepsilon$  is  $\Omega_s(\varepsilon)$ .

This is known as the **canonical ensemble**.

- We can view a **gas**, for example, as a **canonical example**, where **one molecule** is the system, and the rest of the gas is the **reservoir**.
- The number of **microstates** the system can be in is therefore

$$\Omega_{total}(\text{system has energy } \varepsilon) = \Omega_r(E - \varepsilon)\Omega_s(\varepsilon)$$

- But since  $\varepsilon$  is small, we can perform a Taylor Expansion:

$$\ln[\Omega_r(E - \varepsilon)] = \ln[\Omega(E)] - \frac{d\ln[\Omega(E)]}{dE}\varepsilon + \underbrace{\frac{d^2\ln[\Omega(E)]}{dE^2}}_{\propto \frac{dT}{dE}=0, \text{ because of assumptions}}\varepsilon^2 + \dots$$

And using our definition of temperature:

$$\ln[\Omega_r(E - \varepsilon)] = \ln[\Omega(E)] - \frac{\varepsilon}{k_B T}$$

$$\Omega_r(E - \varepsilon) = \Omega(E)e^{-\varepsilon/k_B T}$$

- Combining this with the above, we get

$$\Omega_{total} \propto \Omega_s(\varepsilon)e^{-\varepsilon/k_B T}$$

- Now, we said above that the **probability** of a given **macrostate** is proportional to the number of microstates that make it up. So, normalising:

$$P(\text{system in energy } \varepsilon) = \frac{\Omega_s(\varepsilon)e^{-\varepsilon/k_B T}}{\sum_{\forall \varepsilon} \Omega_s(\varepsilon)e^{-\varepsilon/k_B T}}$$

This is the **Boltzmann Distribution**.

- In a way, the reason why the probability falls as  $\varepsilon$  increases is because the degeneracy of the reservoir decreases exponentially with  $\varepsilon$ .

## The Boltzmann Distribution – Other Derivation

- Consider  $N$  **distinguishable particles** and a set of **energy levels**  $\varepsilon_j$ , each with degeneracy  $g_j$  and population  $N_j$ . Consider further that the whole system has energy  $U$ . We can write

$$N = \sum_{\forall j} N_j$$

$$U = \sum_{\forall j} N_j \varepsilon_j$$

- The number of ways of choosing  $N_1$  particles to be in the state  $\varepsilon_1$  is (taking degeneracy into account)

$$\Omega_1 = \frac{N!}{\underbrace{(N - N_1)!}_{\substack{\text{Number of ways} \\ \text{of choosing } N_1 \\ \text{from } N}}} \cdot \frac{1}{\underbrace{N_1!}_{\substack{\text{Remove all repeat} \\ \text{counts - we deal with} \\ \text{degeneracy later}}}} \cdot \underbrace{g_1^{N_1}}_{\substack{\text{Degeneracy} \\ \text{factor}}} = \frac{N!}{N_1!(N - N_1)!} g_1^{N_1}$$

The number of ways of choosing  $N_2$  of the remaining ones is

$$\Omega_2 = \frac{(N - N_1)!}{N_2!(N - N_1 - N_2)!} g_2^{N_2}$$

Note that when multiplied together, some cancelling occurs. Therefore, the total number of configurations is

$$\Omega = \prod_{\forall j} \Omega_j = N! \prod_{\forall j} \frac{g_j^{N_j}}{N_j!}$$

Notes:

- We considered the particles to be **distinguishable** – we considered that there was **more than one way** for  $N_i$  particle to exist in the state  $\varepsilon_i$ . More on this later.
  - We assumed that the degeneracy factor was  $g_i^N$ . This is true **only if**
- Now, we “simply” need to minimise  $\ln \Omega$  with respect to the  $N_i$ , subject to the two constraints. The steps are roughly as follows:

- Take the logarithm. Simplify logarithms using Stirling’s Formula:

$$\ln N! = N \ln N - N$$

- Add the Lagrange undetermined multipliers  $a$  and  $b$  using the two constraints defined above.
  - Differentiate with respect to an arbitrary  $N_i$ , and set to 0 – most components of each sum will come out of the wash, because

they'll involve other terms than  $N_i$ . (Remember to use the product rule for the double sum).

- The result will now be something like

$$N_i = g_i \exp(a + b\varepsilon_i)$$

- To find  $b$ , feed this expression back into the expression for  $\ln \Omega$ , and obtain something like

$$\ln \Omega = C - bU \Rightarrow \frac{\partial \ln \Omega}{\partial U} = -b$$

And note that from our statistical definition of temperature

$$\frac{1}{kT} = \frac{\partial \ln \Omega}{\partial U}$$

Which simply gives

$$b = -\frac{1}{kT}$$

- The rest is simple manipulation, and taking a constant out.

## Fermi-Dirac Statistics

- In this case, we consider the statistics of **indistinguishable particles** like **fermions**, where **no two particles can occupy the same quantum state**.
- In such a case
  - The **number** of ways of getting  $N_i$  **particles** into the  $i^{\text{th}}$  level is **1** – all particles are **identical**, and so there's only **one way** of getting a **certain number** in.
  - Within the  $i^{\text{th}}$  level, the number of particles we have **must** be  $\leq$  the **degeneracy** of the level ( $g_i$ ), because no two particles can be in the same state. So  $N_i \leq g_i$ .
  - So  $\Omega_i$  is the number of ways of arranging the  $g_i$  levels amongst the  $N_i$  particles:

$$\Omega_i = \frac{g_i!}{N_i!(g_i - N_i)!}$$

- The **total** number of **microstates** is therefore

$$\Omega = \prod_i \frac{g_i!}{N_i!(g_i - N_i)!}$$

- Solve as above (the constant  $a$  in the exponential is usually written  $a = \mu/kT$ , where  $\mu$  is the chemical potential). This gives:

$$N_i = \frac{g_i}{e^{(\varepsilon_i - \mu)/kT} + 1}$$

Notes:

- At **low temperature**,  $\mu \gg kT$ , states for  $\varepsilon_i < \mu$  are essentially **fully filled** (ie:  $N_i \approx g_i$ ), whereas those for  $\varepsilon_i > \mu$  are **essentially empty**. As  $T \rightarrow 0$ , the distribution approaches a **step function**, with  $\mu$  being the **Fermi energy** – the **lowest energy** up to which the states must be **filled to accommodate** all the particles.
- At **high temperature**  $\mu \ll kT$ , the chemical potential effectively has **no effect**.

## Bose-Einstein Statistics

- In this case, we consider the statistics of **indistinguishable particles** like **fermions**, where **two particles can occupy the same quantum state**.
- In such a case
  - Once again, the **number** of ways of getting  $N_i$  **particles** into the  $i^{\text{th}}$  **level** is **1**.
  - The number of ways of getting the  $N_i$  particles in the  $g_i$  different states is equivalent to having  $N_j + g_j - 1$  symbols in a line,  $g_j - 1$  of each are “|”, and asking “how many different ways can they be shuffled”.
  - This is given by

$$\Omega_j = \frac{1}{N_j!} \frac{(N_j + g_j - 1)!}{(g_j - 1)!}$$

- Once again, calculations follow and we obtain (making the assumption that  $g_i \gg 1$ , to remove a “-1” from the denominator):

$$N_i = \frac{g_i}{e^{(\varepsilon_i - \mu)/kT} - 1}$$

Notes:

- At high temperature,  $\mu \ll kT$ , this behaves like the Fermi-Dirac distribution.
- As  $T \rightarrow 0$ , the population becomes very small, expect for  $\varepsilon_i$  *just* above  $\mu$  – this is **Bose-Einstein Condensation**.

## The Equipartition Theorem

- Let the energy,  $E$  of a particular system be given by

$$E = \alpha x^2$$

Assuming that  $x$  can take any value, the mean energy is given by

$$\begin{aligned} \langle E \rangle &= \int_{-\infty}^{\infty} EP(x) dx \\ &= \frac{\int_{-\infty}^{\infty} \alpha x^2 e^{-\beta \alpha x^2} dx}{\int_{-\infty}^{\infty} e^{-\beta \alpha x^2} dx} \\ &= \frac{1}{2\beta} \\ &= \frac{1}{2} k_B T \end{aligned}$$

This result (the whole proof's a bit longer!) implies that **each quadratic energy dependence** of the **system** (**mode** of the system) has an energy  $\frac{1}{2}k_B T$  associated with it. This is the **Equipartition Theorem**.

- There are, however, two assumptions involved in the derivation of this result:
  - That the wells are **quadratic** (the **Harmonic Approximation**).
  - That the parameter  $x$  can take **any** value, and that the variables could be **integrated continuously**. This is **dubious** for **quantum** systems with **quantised** values.

**The Equipartition Theorem is only valid at high temperatures so that the thermal energy is larger than the energy gap between quantised energy levels.**

## The Partition Function

- The **partition function** is the **sum over all states** of the **Boltzmann Factor**:

$$Z = \sum_{\forall \alpha} e^{-\beta E_{\alpha}}$$

However, since the point from which we measure energy is **arbitrary**,  $Z$  is defined **up to an arbitrary multiplicative constant**.



- The partition functions **only refers to a single particle** in the system. It may well be coupled to a **reservoir** of other particles, but it's a **single one**.
- $Z$  contains, “zipped up within it”, full information about every property of the system
  - **The internal energy**

The **internal energy** is given by

$$U = \frac{\sum_i E_i e^{-\beta E_i}}{\sum_i e^{-\beta E_i}} = \frac{-dZ/d\beta}{Z} = -\frac{d \ln Z}{d\beta}$$

- **The Entropy**

We know that  $P_j = e^{-\beta E_j} / Z$ , and so using **Gibbs' Expression for Entropy**, we have

$$\begin{aligned} S &= -k \sum_i P_i \ln P_i \\ &= k \sum_i P_i (\beta E_i + \ln Z) \\ &= k (\beta \langle E \rangle + \ln Z) \\ &= k (\beta U + \ln Z) \end{aligned}$$

$$\boxed{S = \frac{U}{T} + k \ln Z}$$

- **The Helmholtz Energy**

We know that  $F = U - TS$ , so

$$\boxed{F = -kT \ln Z}$$

$$Z = e^{-\beta F}$$

- **The rest can then easily be worked out as follows...**

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

$$p = -\left(\frac{\partial F}{\partial V}\right)_T$$

$$H = U + pV$$

$$G = F + pV = H - TS$$

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V = T \left(\frac{\partial S}{\partial T}\right)_V$$

- If the **energy** of a particular system depends on **various independent contributions**,  $E_{i,j} = E_i^{(a)} + E_j^{(b)}$ , then the **combined Partition Function** is given by

$$Z = \sum_i \sum_j e^{-\beta(E_i^a + E_j^b)} = \sum_i \sum_j e^{-\beta E_i^a} e^{-\beta E_j^b} = \sum_i e^{-\beta E_i^a} \sum_j e^{-\beta E_j^b} = Z_a Z_b$$

So partition functions can be combined by **multiplication**.

## The Ideal Monoatomic Gas

- Consider a gas in a cubic box of side  $L$ .
  - The **wavefunction** of each atom must be

$$\psi(x) = A \sin(k_x x) \sin(k_y y) \sin(k_z z)$$

Where

$$k_i = \frac{n_i \pi}{L}$$

And the  $n_i$  are **integers** (due to the boundary conditions).

- In  $k$ -space, each state (distinct combination of  $n$ s) occupies a volume

$$\frac{\pi^3}{L^3}$$

- The number of states with  $k$  in the range  $k + dk$  is therefore equal to the number of states in the relevant **octant** in  $k$ -space

$$g(k) dk = \frac{1}{8} \times 4\pi k^2 dk \times \frac{1}{\pi^3 / L^3} = \frac{V k^2}{2\pi^2} dk$$

- If  $m$  is the **mass** of an atom, then the **kinetic energy** of the atom is given by

$$E = \frac{\hbar^2 |\mathbf{k}|^2}{2m} = \frac{\hbar^2 \pi^2}{2mL^2} (n_x^2 + n_y^2 + n_z^2)$$

- The **partition function** for a **single molecule** of our ideal gas is therefore

$$\begin{aligned} \sum_i g(E_i) e^{-\beta E_i} &= \int_0^\infty e^{-\beta E(k)} g(k) dk \\ &= \int_0^\infty e^{-\beta \hbar^2 k^2 / 2m} \frac{V k^2}{2\pi^2} dk \\ &= \frac{V}{\hbar^3} \left( \frac{mk_B T}{2\pi} \right)^{3/2} \end{aligned}$$

For a gas of **more than 1 indistinguishable molecule**, the partition function is

$$Z_N = \frac{Z^N}{N!}$$

This is because we can **combine** the **energies** as we did in the previous section, but we must make sure we do not **overcount states**. If we assume that the gas is **dilute** and that **no more than 1 particle occupies each state**, then we have **overcounted** by **exactly  $N!$**  This explains the denominator above.

- We can derive a number of properties for the partition function, all of which turn out to be as expected classically.
- We can also work out an expression for **entropy**

$$S = \frac{3}{2} Nk_B \ln T + Nk_B \ln\left(\frac{V}{N}\right) + \frac{3}{2} Nk_B \ln\left(\frac{mk_B}{2\pi\hbar^2}\right) + \frac{5}{2} Nk_B$$

This is called the **Sackur-Tetrode Equation**, and it could not have been obtained using classical thermodynamics. It can also be used to demonstrate the **Gibbs Paradox**:

- The **Sackur-Tetrode Equation** correctly predicts the **entropy change** of a **Joule expansion** to be  $\Delta S = Nk_B \ln 2$ .
- However, if a vessel is divided into **two**, with an **identical gas** on each side, the **entropy change** when the **partition is removed** becomes  $\Delta S = 0$ .
- However, one could argue that the gas on **each side** of the partition has itself undergone a **Joule expansion!**
- This demonstrates the importance of realising that **indistinguishable** particles really are **indistinguishable** – no **information** can be **lost** when removing the partition in that example.
- **Adiabatic changes**
  - Consider **reversibly compressing** a gas, keeping the **relative populations** of the **energy levels** fixed – ie: **adiabatically compress it**.
  - The **energies** are proportional to  $V^{-2/3}$ , so they'll **increase**, and  $U \propto V^{-2/3}$ .
  - However,  $U = \frac{3}{2} kT$ .
  - Therefore,  $TV^{3/2} = \text{constant}$ , as expected for an adiabatic expansion.

- **Heat and work** – we can also consider a **general** change in the **internal energy**

$$dU = N \sum p_i d\varepsilon_i + \varepsilon_i dp_i$$

This includes two terms

- The first involves **changing energy levels** but **keeping populations fixed** – this is an **adiabatic change**, and can be interpreted as the **reversible work**  $dW = -p dV$ .
- The second involves **keeping the energy levels fixed** but **changing the populations** and therefore the **entropy**. This can be interpreted as the **reversible heat**  $dQ = T dS$ .

## The Ideal Diatomic Gas

- If the gas is now **diatomic**, we have two additional terms in the energy

$$E = \underbrace{\frac{\hbar^2 \pi^2}{2mL^2} (n_x^2 + n_y^2 + n_z^2)}_{\text{translational E}} + \underbrace{\frac{\ell(\ell + 1)\hbar^2}{2I}}_{\text{rotational E}} + \underbrace{(n + \frac{1}{2})\hbar\omega}_{\text{vibrational E}}$$

- We need to take **products** to find the combined partition functions (see above) and the new contributions to the potentials are therefore **additive**.
- The actual contributions can be found by writing the **expressions** for the **rotational** and **vibrational partition functions**. Notes:
  - The **degeneracy** of each **rotational energy** is  $2\ell + 1$ .
  - The **degeneracy** of each **vibrational energy** is 1.
- In each case, the limits  $T \rightarrow 0, \infty$  need to be considered, because the general case is rather difficult to evaluate.

## Paramagnetism

- Atoms in **crystals** may have **permanent magnetic dipole moments**. These are linked to their **angular momentum** (orbital or spin).
- In **QM**, **angular momentum** is **quantised** along **any given axis** as  $J_z = m\hbar$  where  $m$  takes **integer spaced values** from  $J$  to  $-J$ , where  $J$  is the **total angular momentum quantum number** of the atom.

- The upshot of this is that the ***z*-component** of **magnetic moment** is also quantised, according to

$$\mu_z = g\mu_B m$$

Where  $\mu_B = e\hbar/2m_e$  is the **Bohr Magnetron** and  $g$  is the “**Landé *g* factor**”, which is **O(1)**.

- The **energy** of such a dipole in a **magnetic field  $B$  along the *z*-axis** is  $\mu_z B$ .
- The calculations reveal a number of interesting things (note that  $\mu$  is the **magnitude** of the dipole moment)
  - **Curie’s Law** – as  $T \rightarrow \infty$ ,  $\langle \mu_z \rangle \rightarrow \mu^2 B / kT$ .
  - As  $T \rightarrow 0$ ,  $\langle \mu_z \rangle \rightarrow \mu$  (ie: **all magnetic dipoles aligned with the field**).
- We can obtain the **magnetisation**,  $M$  and **magnetic susceptibility**,  $\chi$  of the magnet, given by

$$M = n \langle \mu_z \rangle$$

$$\chi = \frac{M}{H} \approx \frac{\mu_0 M}{B}$$

## Photons, etc...

### Introduction

- Consider an **evacuated** box of **volume**  $V$  at **temperature**  $T$  – a **cavity**. It contains **electromagnetic radiation**.
- In **thermodynamics**, we can treat this as a **gas of photons** which is constantly being **emitted/absorbed/reflected** at the walls.

### Spectral Energy Density

- It is relatively simple to work out that if the **photon gas** contains  $n$  **photons per unit volume**, the **total energy per unit volume** in the cavity is

$$u = n \langle \hbar\omega \rangle$$

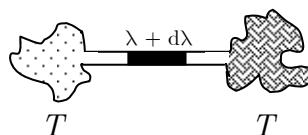
- However, one might ask which **frequency ranges** this energy is stored in. We therefore introduce the **spectral energy density**,  $u_\lambda$ , such that **the energy stored in wavelengths of range  $\lambda$  to  $\lambda + d\lambda$**  is

$$u_\lambda d\lambda$$

The **total** energy density is then

$$u = \int u_\lambda d\lambda$$

- We can show that this spectrum is **totally independent** of the **kind of cavity** (shape/size/material) and is a **universal function of  $\lambda$  and  $T$**  by considering **two cavities**, each kept at  $T$  by a **heat bath**, and connected by a **tube** containing a **filter** that only allows **wavelength in the range  $[\lambda, \lambda + d\lambda]$**  **though:**



By the **second law**, **no heat** can flow along the tube (equal temperatures). Therefore, any **energy flux** from **right to left** must be **balanced** by a **flux** from **left to right**. Bearing in mind our expression for  $P$  (**power absorbed per unit area**) below, we find that  $P_{left} = P_{right}$ , and therefore that  $u_{l,left} = u_{l,right}$ .

## Banalities

- First, we note that if the **photons** are moving in **completely arbitrary directions**, then the **fraction** of them moving at angles  $\theta$  to  $\theta + d\theta$  to **any particular direction** is

$$\frac{d\Omega}{4\pi} = \frac{1}{\underbrace{4\pi}_{\text{Total solid angles}}} \underbrace{2\pi \sin \theta d\theta}_{\text{Solid angle } d\Omega \text{ subtended by photons moving in the said directions}} = \frac{1}{2} \sin \theta d\theta$$

Therefore, the **number of molecules per unit volume** that are:

- Travelling with a **speed  $v$  to  $v + dv$** .
- Travelling at **angles  $\theta$  to  $\theta + d\theta$  to a certain direction**.

Is given by

$$\frac{1}{2} n f(v) \sin \theta dv d\theta = \frac{1}{2} \underbrace{n \sin \theta d\theta}_{\substack{\text{In the photon case,} \\ \text{where } v=c}}$$

Now, if we consider this “**certain direction**” to be perpendicular to a wall, and if we consider particles:

- Travelling with a **speed  $v$** .
- Travelling at an **angle  $\theta$  to the wall**.

Then only those particles **closer than  $v \cos \theta dt$**  to the wall will **hit** it in **time  $dt$** . In other words, those particles in a volume  **$v \cos \theta dt$** . The **number** of such particles is therefore (from above)

$$\underbrace{v \cos \theta dt}_{\substack{\text{Volume} \\ \text{concerned}}} \underbrace{\frac{1}{2} n f(v) \sin \theta dv d\theta}_{\substack{\text{Particles per unit volume}}} = \frac{1}{2} n v f(v) \cos \theta \sin \theta dv d\theta dt$$

$$= \frac{1}{2} \underbrace{nc \cos \theta \sin \theta d\theta}_{\substack{\text{For a photon gas, and for} \\ \text{unit time}}}$$

To find, therefore, the **total flux of photons** hitting **unit surface area** in **unit time**, we integrate this over **all angles** [Note: in this context, “all angles” means  $0 \rightarrow \pi/2$ , because of the way we defined solid angles above – the range  $-\pi/2 \rightarrow 0$  is implicitly included]:

$$\Phi = \frac{1}{2} \int_0^{\pi/2} nc \cos \theta \sin \theta d\theta$$

$$\boxed{\Phi = \frac{1}{4} nc}$$

Since each **photon** has energy  $\langle \hbar\omega \rangle$ , we can also write the **average power incident per unit area of wall** as

$$P = \hbar\omega\Phi = \frac{1}{4}uc$$

(See next section for definition of  $u$ ).

- We saw above that the **number of photons** travelling at angles  $[\theta, \theta + d\theta]$ , in a photon gas, hitting **unit area** of a wall in **unit time** was

$$\frac{1}{2}nc \cos\theta \sin\theta d\theta$$

Now, if instead of the number of photons,  $n$ , we are interested in the “**momentum change perpendicular to the wall at each collision and reflection**”, then we must replace  $n$

$$n \rightarrow \int_{\forall \varepsilon} \underbrace{2}_{\substack{\text{Double the momentum,} \\ \text{because we're recoiling}}} \underbrace{\frac{u_\varepsilon}{c}}_{\substack{\text{Momentum is} \\ \text{energy}/c}} \underbrace{\cos\theta}_{\substack{\text{Perpendicular} \\ \text{to wall}}} \underbrace{d\varepsilon}_{\substack{\text{Integrate over} \\ \text{all energies}}} = \frac{2u \cos\theta}{c}$$

And we now get that the “**momentum change per unit area per unit time = pressure**” is

$$\begin{aligned} p &= \int_0^{\pi/2} \frac{2u \cos\theta}{c} \frac{1}{2}c \cos\theta \sin\theta d\theta \\ &= \int_0^{\pi/2} u \cos^2\theta \sin\theta d\theta \\ &= \frac{1}{3}u \end{aligned}$$

## The Stefan-Boltzmann Law

- Consider the **First Law of Thermodynamics** –  $dU = TdS - pdV$ . Differentiating w.r.t  $V$  at constant  $T$ :

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

However,  $(\partial U / \partial V)_T = u$  [by definition, but this can also be proved by noting that since  $U = uV$ ,  $(\partial U / \partial V)_T = u + V(\partial u / \partial V)_T = u$ ], so:

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

But we have shown that  $p = \frac{1}{3}u$ , so



$$u = \frac{1}{3} \left[ T \frac{du}{dT} - u \right] \Rightarrow \frac{du}{u} = 4 \frac{dT}{T}$$

$$\Downarrow$$

$$u = AT^4$$

Feeding this into our expression for **power incident per unit area**:

$$P = \frac{1}{4} uc = \left( \frac{1}{4} Ac \right) T^4 = \sigma T^4$$

- Note, also, that if the **cavity** is in **equilibrium**, “**power incident = power emitted**”, so the above also gives an expression for the power emitted.

### Kirchhoff’s Law

- We wish to discuss how **well** particular **surfaces** of a **cavity** will **absorb** or **emit electromagnetic radiation** of a particular **wavelength**. We therefore define:

- The **spectral absorptivity**  $\alpha_\lambda$  is the **fraction of incident radiation absorbed** at  $\lambda$ .
- The **spectral emissive power**  $e_\lambda$  is a function such that the **power emitted per unit area** of the **surface** having **wavelength** in the range  $[\lambda, \lambda + d\lambda]$  is

$$e_\lambda d\lambda$$

- Now, in equilibrium, the **power absorbed** is equal to the **power emitted**, so using our expression for the **power incident** above, we have that in the range  $[\lambda, \lambda + d\lambda]$ :

$$\left( \frac{1}{4} u_\lambda d\lambda c \right) \alpha_\lambda = e_\lambda d\lambda$$

$$\boxed{\frac{e_\lambda}{\alpha_\lambda} = \frac{c}{4} u_\lambda}$$

This is **Kirchhoff’s Law** – it states that  $e_\lambda / \alpha_\lambda$  is a **universal function** of  $\lambda$  and  $T$ . Therefore, if we **fix**  $T$ , then  $e_\lambda \propto \alpha_\lambda$ . This means that “**good absorbers are good emitters**” and **vice versa**.

- For a **perfect black body**,  $\alpha_\lambda = 1$  for **all**  $\lambda$ , which also means that the black body is the **best possible emitters**.
- A **cavity** whose walls have  $\alpha_\lambda = 1$  is known as a **black body cavity**.

## Statistical Mechanics

- The **black body spectrum** can be derived in the usual ways (see QM course).
- To **convert** the spectrum from one kind of measurement (eg: **wavelength**) to another (eg: **frequency**), write (for example)

$$u_\lambda d\lambda = u_\nu d\nu$$

- This can be **integrated** to give

$$u = \frac{\hbar}{\pi^2 c^3} \int_0^\infty \frac{\omega^3}{e^{\beta\hbar\omega} - 1} d\omega = \frac{k^4 \pi^2}{15 \hbar^3 c^3} T^4$$

The **Stefan-Boltzmann Law**. We have therefore obtained

$$\sigma = \frac{\pi^2 k_B^4}{60 c^2 \hbar^3}$$