IB Physics Notes: Thermodynamics

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Thermodynamics is like cooking, you get the ingredients and know how to (rules) combine them together (math) to create delicious dishes.

1 Laws of Thermodynamics

1.1 Conservation of particles, energy and entropy

Very useful rules.

1.2 Zeroth law of thermodynamics (special case of 2nd law)

Thermal equilibrium defined by state of system with temperature as a state variable marker for thermal equilibrium.

Statement: if system A is in thermal equilibrium with system C, and if system C is separately in thermal equilibrium with system B, then system A and B will be in thermal equilibrium. It is an empirical law.

Thermal equilibrium: when two systems are in thermal contact and there is no net heat flow.

Consequences: imply there must be something about a system that is due to the state it is in which will determine whether heat flows from it to another. To quantify this, we introduce a state variable called <u>temperature</u>.

1.2.1 Measuring temperature

Based on Boyle's law and Charles's law:

$$\lim_{P\to 0} pV = \text{constant} \quad \text{(Boyle's law)},$$

$$\frac{V_{100\,^\circ C} - V_{0\,^\circ C}}{V_{0\,^\circ C}} = \text{constant} \quad \text{(Charles' law)}$$

for all gases, provided pressure is low and not near liquefaction temperature of gas.

Charles' law: fractional change in volume between two fixed temperatures same for all gases

Temperature scales (Celsius scale & Absolute scale)

$$T_{\text{Celsius}} = 100\frac{(pV)_T - (pV)_{mpt}}{(pV)_{bpt} - (pV)_{mpt}}$$

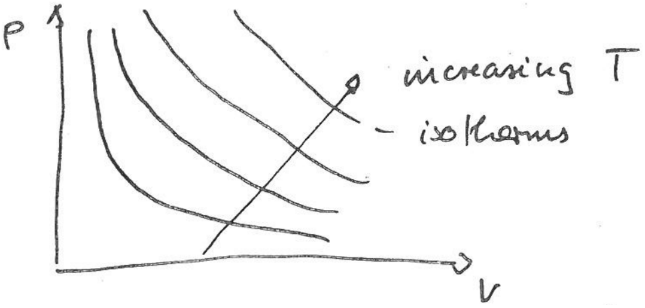
$$T_{\text{Kelvin}} = 273.16\frac{(pV)_T}{(pV)_{\text{triple pt}}}$$

1.3 Equation of state

State variables are quantities that do not depend on history of the system, but on its configuration at the present. State variables include p, V, T, U and S, but exclude path dependent quantities like Q and WD. Equation of state relates these path independent quantities. An important one is the ideal gas equation:

$$\boxed{pV = nRT \quad \text{or} \quad pV = NK_BT}$$

Extra note: singular points in these equations denote phase transitions.



For 1 mole, putting in differential form:

$$dT = \frac{1}{R}(p\,dV + V\,dp)$$

1.4 First law of thermodynamics

States conservation of energy, when heat is taken into account.

$$\boxed{\begin{gathered} dU = dQ_{\text{in}} + dW_{\text{on}} \\ dU = TdS - pdV \end{gathered}}$$

State variables: path independent, only depend on current state.
Mechanical work done (W) or heat transfer (Q): path dependent.

Internal energy

$$\boxed{U = \frac{3}{2}nRT}$$

Can be involved with conservation of energy.

Heat is mechanical energy (PE and KE) stored in the internal motions/positions of the constituent particles in matter.

Work: is done on a system whenever it responds to the change in some external constraint ('force').

$$\boxed{dW_{\text{on}} = -pdV} \quad \text{(for gas)}$$

provided pressure is constant, which is possible for slow enough movement of piston.

Other types of work: $dW = \underbrace{Fdx}_{\text{extension}} = \underbrace{\gamma dA}_{\text{surface tension}} = \underbrace{-PdE}_{\text{Electrostatic energy}} = \underbrace{-VdQ}_{\text{Electrochemical}}$

1.4.1 Heat capacity, C

$$dQ_{\text{in}} = dU + pdV$$

At constant V, all heat go into increasing the internal energy.
At constant p, extra heat must be supplied for gas to push back its surrounding and expand. So, $C_p > C_V$.

Constant volume, C_V

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

$$\boxed{C_{V,m} = \frac{\text{degrees of freedom}}{2}R}$$

Example:
1. Monoatomic ideal gas has 3 translational degrees of freedom. So, $C_{V,m} = \frac{3}{2}R$.
2. Diatomic gas has 3 translational and 2 rotational degrees of freedom. So, $C_{V,m} = \frac{5}{2}R$.

Constant pressure, C_p

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

Derivation to link C_p and C_V
Use:

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

Then, divide by dT and specify a path with constant p. The LHS is C_p.

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

For an ideal gas, there is no intermolecular forces, meaning internal energy is purely kinetic and has no potential energy contribution, so U is independent of volume $\Rightarrow \frac{\partial U}{\partial V} = 0$.

Alternative derivation
Start from enthalpy H:

$$H = U + pV \Rightarrow dH = dU + d(nRT)$$

$$C_p dT = C_V dT + nRdT$$

$$\Rightarrow C_p = C_V + R$$

$$\boxed{C_{p,m} = C_{V,m} + R} \quad \text{and} \quad \boxed{dQ = C_V dT + pdV}$$

C_m is intensive heat capacity. (per mole, per volume, per mass)

1.4.2 Reversibility

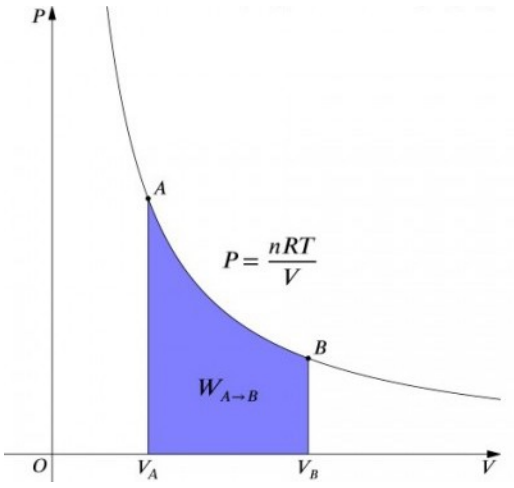
A reversible process is one that proceeds in infinitesimal steps from one equilibrium to another, such that the change in the system is smaller than random fluctuations. The system cannot 'know' that this change is not just another random fluctuation.

1.4.3 Isothermal and Adiabatic expansions

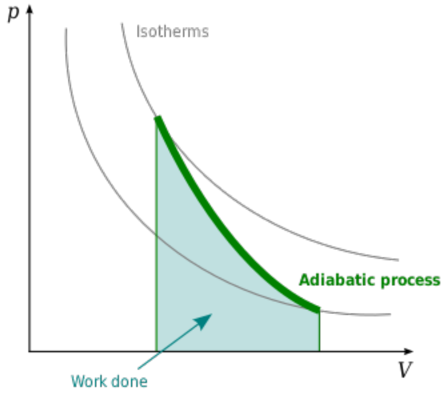
Isothermal expansion (T = constant)
Internal energy stays the same, so heat must be supplied equal to the work done.

To be reversible, it needs to be **slow**: each time a molecule hits the moving (away) wall, its velocity is, on average, reduced, and the gas cools. To keep temperature constant, heat must flow in from the walls so the expansion must be very slow for this to happen reversibly.

$$\boxed{pV = \text{constant}}$$



(a) Isotherm



(b) Adiabat

Adiabatic expansions ($dQ = 0$)
Reversible ($dS = 0$, isentropic), no matter speed of expansion.
No heat flow. Work done converted to internal energy:

$$dU = -pdV = C_V dT$$

Substitute $pdV + Vdp = RdT$ from ideal gas law and noting $C_p = C_V + R$. We obtain:

$$\frac{dp}{p} + \gamma \frac{dV}{V} = 0$$

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

$$\boxed{PV^\gamma = \text{constant}}$$

Using PV = RT, equivalently:

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

$$T^\gamma p^{1-\gamma} = \text{constant}$$

Real gas expansion
Mean free path of molecules in real gases at r.t.p. $\approx 70\,nm$, so most molecules never get anywhere near the moving wall. What happens is the molecules bounce off their neighbours. If the gas is expanding, molecules are, on average, moving away from each other and behave on average like a wall moving away.

Nugget for thought: for cooling to actually happen, the atom molecules has to hit its neighbours.

1.5 Second law of thermodynamics

Based on irreversibility of natural processes, establishes a new state variable to quantify irreversible progress, entropy. It is empirical.

The direction of an irreversible process is determined by the states of the system.

Statement: NO process is possible whose only effect is:

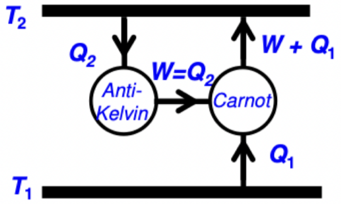
1. to transfer heat from a colder to hotter body. (Clausius)
   i.e. heat flows from hot to cold unless you do work to push it back.
2. the complete conversion of heat to work. (Kelvin)
   i.e. you can't undo dissipation

1.6 Heat engines

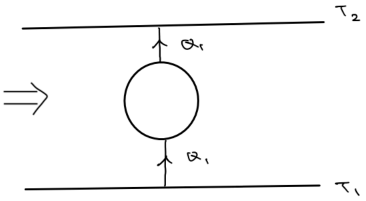
A heat engine is a device that converts thermal energy to work, by moving energy from hot reservoir to a cold reservoir, extracting a fraction of energy as useful work.

1.6.1 Proof that Clausius's and Kelvin's statement are equivalent

1. Suppose that we have an anti-kelvin engine that completely converts heat to work.

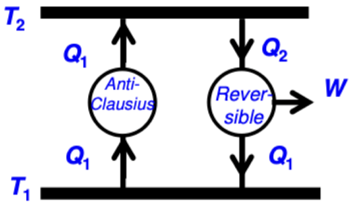


$\Longrightarrow$

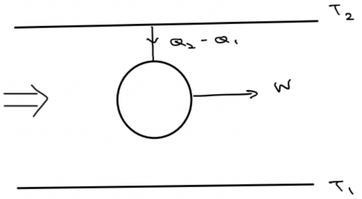


   Connect it to a Carnot engine that uses its work to pump heat from T_1 to T_2. Net effect is the transfer of heat from T_1 to T_2, violating Clausius's statement.

2. Suppose we have an anti-clausius engine that brings heat from cold to hot.

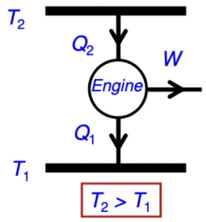


$\Longrightarrow$



   Run it in tandem with a Carnot engine that rejects the same amount of heat as drawn by the anti-clausius engine.
   Net effect is the complete conversion of heat to work, violating Kelvin's statement.

1.6.2 Carnot engine



Assumption: temperature of reservoirs is unchanged as heat is transferred in and out.

Key points from Carnot:

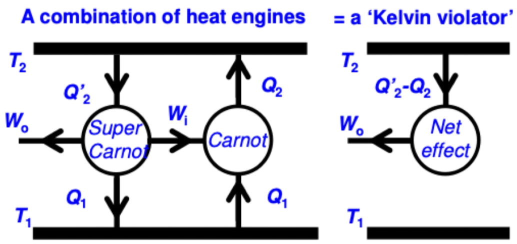
- work could only be generated if heat flowed from a hot to a cold reservoir
- the greater the temperature difference, the more work you get out of the engine
- the most efficient heat engines must be reversible

Carnot's theorem:

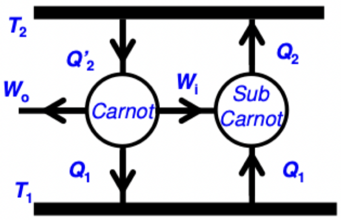
(1) Statement: Of all the heat engines working between two given temperatures, none is more efficient than a Carnot engine.

(2) Corollary: All reversible engines have the same efficiency η_{Carnot}.

Proof by contradiction **(1)**: suppose there exist a super-Carnot engine,

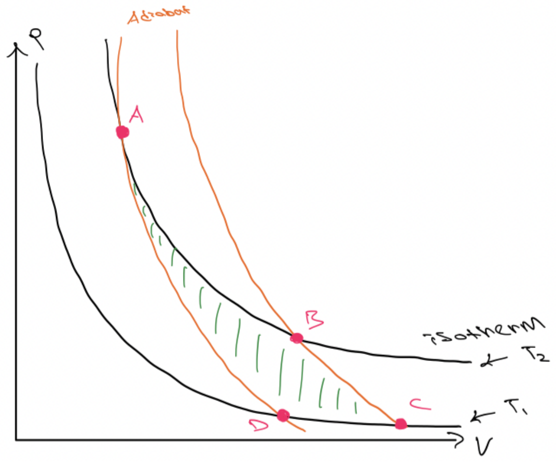


Proof by contradiction **(2)**: suppose there exist a reversible sub-Carnot engine,



Net effect is a Kelvin violator.

Carnot cycle: a theoretical thermodynamic cycle that consists of 4 reversible processes: two isothermal and two adiabatic processes. Basically, it takes heat from the hot reservoir and reject it into the cold one, producing work in the process.



A → B: isothermal expansion. Absorbs Q_2 from hot T_2 reservoir.
B → C: adiabatic expansion. Cools to T_1.
C → D: isothermal compression. Releases Q_1 to cold T_1 reservoir.
D → A: adiabatic compression. Warms to T_2.

Work done is area enclosed by loop:

$$\boxed{W = Q_2 - Q_1} = \oint p\,dV$$

Efficiency:

$$\boxed{\eta = \frac{\text{useful/net work done}}{\text{heat absorbed}}}$$

For all reversible heat engines:

$$\boxed{\frac{Q_1}{T_1} = \frac{Q_2}{T_2}}$$

Derivations:

Along isotherm,

$$Q_2 = \int_{V_A}^{V_B} pdV = \int_{V_A}^{V_B} \frac{RT_2}{V} dV = RT_2 \ln \left(\frac{V_B}{V_A} \right)$$

Likewise for $Q_1 = RT_1 \ln \left(\frac{V_C}{V_D} \right)$.

Along adiabat,

$$T_2 V_B^{\gamma-1} = T_1 V_C^{\gamma-1} \quad \text{and} \quad T_2 V_A^{\gamma-1} = T_1 V_D^{\gamma-1}$$

$$\Rightarrow \frac{V_B}{V_A} = \frac{V_C}{V_D}$$

Hence,

$$\frac{Q_1}{T_1} = \frac{Q_2}{T_2}$$

Using this result, we can obtain the **efficiency of Carnot engine** between two heat reservoirs:

$$\eta = \frac{W}{Q_2} = 1 - \frac{Q_1}{Q_2} = 1 - \frac{T_C}{T_H}$$

Refrigerator

$$\eta = \frac{Q_1}{W} = \frac{Q_1}{Q_2 - Q_1} = \frac{T_1}{T_2 - T_1}$$

Heat pump

$$\eta = \frac{Q_2}{W} = \frac{Q_2}{Q_2 - Q_1} = \frac{T_2}{T_2 - T_1} > 1$$

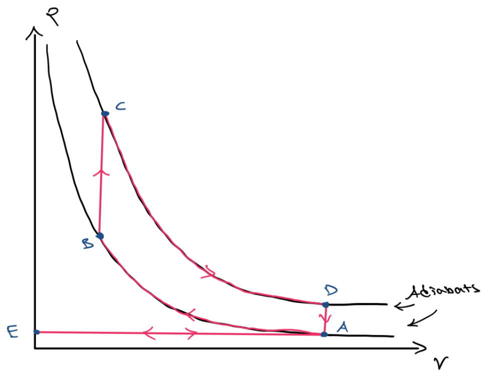
where Q_2 is heat dumped to hot reservoir and Q_1 is heat extracted from cold reservoir.

1.6.3 Real heat engines

Real heat engines are not reversible.

1. Losses of heat through thermal conduction
2. Friction, turbulence are irreversible processes
3. Design flaws
4. May not operate between fixed temperatures
5. Approximated by 'Air standard' cycles, where air is taken as working substance assumed to be ideal gas

Otto cycle (internal combustion engine)



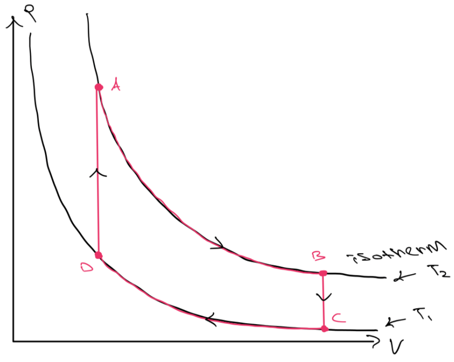
E → A: intake stroke, drawing fuel + air into cylinder
A → B: compression stroke (adiabatic)
B → C: ignition, combustion of fuel generates heat
C → D: power stroke, adiabatic gas expansion
D → A → E: open exhaust valve and expel remaining gas

Efficiency (can be derived using $TV^{\gamma-1}$ = constant):

$$\boxed{\eta = 1 - r^{1-\gamma}}$$

with r = $\frac{V_A}{V_B}$ (compression ratio)

Stirling cycle (external combustion engine)



A → B: isothermal expansion of compressed gas in hot cylinder. $dQ_{2,in} = dW_{by} > 0$
B → C: gas is cooled and move to cool cylinder. Q_{cooling}
C → D: isothermal compression in cold cylinder. $dQ_{1,in} = dW_{by} < 0$
D → A: gas is heated and move to hot cylinder. Q_{heating}

Efficiency (can be derived):

$$\eta = \frac{Q_2 + Q_{\text{cooling}} + Q_1 + Q_{\text{heating}}}{Q_2 + Q_{\text{heating}}}$$

1.7 Entropy

1.7.1 Clausius' theorem

For any closed cycle,

$$\boxed{\oint \frac{dQ}{T} \leq 0}$$

with equality only for reversible cycle.

Proof using Carnot's theorem:

$$\text{Carnot cycle: } \frac{Q_2}{Q_1} = \frac{T_2}{T_1}$$

Suppose the engine takes heat from T_2 and reject it at T_1, we can define a reversible heat transfer to the system with $Q_{rev,2} = Q_2$ and $Q_{rev,1} = -Q_1$, thus:

$$\frac{Q_{rev,2}}{T_2} = -\frac{Q_{rev,1}}{T_1} \Rightarrow \frac{Q_{rev,2}}{T_2} + \frac{Q_{rev,1}}{T_1} = 0 \quad \text{or} \quad \oint \frac{dQ_{rev}}{T} dT = 0$$

For any cycle operating between T_1 and T_2, Carnot's theorem say $\eta \leq \eta_{rev}$ so for a given heat absorbed Q_2, more heat is rejected $|Q_{irrev,1}| \geq |Q_{rev,1}|$:

$$\frac{Q_{irrev,1}}{T_1} \leq \frac{Q_{rev,1}}{T_1} \Rightarrow \oint \frac{dQ}{T} \leq 0$$

It is path independent,

$$\oint \frac{dQ_{\text{rev}}}{T} = \int_{\text{A, path 1}}^{B} \frac{dQ_{\text{rev}}}{T} + \int_{\text{B, path 2}}^{A} \frac{dQ_{\text{rev}}}{T} = 0$$

$$\Rightarrow \int_{\text{A, path 1}}^{B} \frac{dQ_{\text{rev}}}{T} = \int_{\text{A, path 2}}^{B} \frac{dQ_{\text{rev}}}{T}$$

Hence, dQ_{rev}/T must be the derivative of a function of state, that we call entropy S (JK^{-1}).

$$\boxed{dS \geq \frac{dQ}{T}}$$

with equality for reversible process.

$$\boxed{dQ_{\text{rev}} = TdS}$$

1.7.2 Law of increase of entropy

For an isolated system, $dQ = 0$.

$$\boxed{\sum_i dS_i \geq 0}$$

Total entropy of an isolated system cannot decrease, but remains constant **(conservation of entropy)** for reversible change and increase for irreversible ones.

1.7.3 Temperature

$$\boxed{\frac{1}{T} = \left(\frac{\partial S}{\partial Q}\right)_{\mathrm{rev}}}$$

Temperature is the reciprocal of the rate of entropy change with reversible heat transfer to a system. Lower temperature → higher rate of entropy change with heat transfer.

The condition for thermal equilibrium is that the rate of change of entropy with heat transfer must be the same for both i.e. for a particular transfer of heat, entropy drop of heat source must equal entropy increase of heat sink.

1.7.4 Change in entropy

$$\boxed{\Delta S = \int_{T_i}^{T_f} \frac{dQ}{T}} = C \ln\left(\frac{T_f}{T_i}\right)$$

For irreversible process, the entropy change is determined by finding an equivalent set of reversible steps. Example:

1. Joule expansion → calculate ΔS from equivalent isothermal expansion
2. Heat transfer from hot to cold body → $\Delta S = \int dQ/T$

1.8 Master equation

Combining 0^{th} law (T), 1^{st} law ($dU = dQ - pdV$) and 2^{nd} law ($TdS = dQ$), and that a single component p-V system is defined by its V, U and N.

$$\boxed{dU = T dS - p\,dV + \mu\,dN}$$

where $\mu = \left(\frac{\partial U}{\partial N}\right)_{V,S}$ (chemical potential)

Rearranging,

$$dS = \frac{1}{T}dU + \frac{p}{T}dV - \frac{\mu}{T}dN$$

Interpretation:

1. 1/T: how fast entropy change when we change the energy
2. p/T: how fast entropy change when we change volume
3. μ/T: how fast entropy change when we change N

1.9 More entropy

1.9.1 Entropy of ideal gas

Using $dU = C_V dT = TdS - pdV$ and $pV = nRT$:

$$dS = \frac{C_V dT}{T} + \frac{nR\,dV}{V}$$

Integrate along (T,V) path,

$$S = C_V \ln T + nR \ln V + S_0(n)$$

The term $nR\ln V$ is not extensive, doubling n and V gives extra term, $2nR\ln 2$. Make extensive by $S_0(n) \to nS_0' - nR\ln n$

$$S = n\,C_{V,m} \ln T + nR\ln V + nS_0' - nR\ln n$$

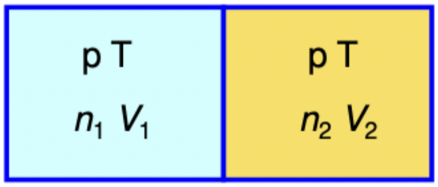
$$\boxed{S = \underbrace{n\,C_{V,m} \ln T}_{\text{heat component}} + \underbrace{nR\ln\left(\frac{V}{n}\right)}_{\text{configuration component}} + nS_0'}$$

For 1 mole,

$$\boxed{S = C_{V,m} \ln T + R\ln V + S_0'}$$

$$\Rightarrow \Delta S = C_{V,m} \ln\left(\frac{T_f}{T_i}\right) + R\ln\left(\frac{V_f}{V_i}\right)$$

1.9.2 Entropy of mixing



$$\Delta S = n_1 R \ln\left(\frac{V_1 + V_2}{V_1}\right) + n_2 R \ln\left(\frac{V_1 + V_2}{V_2}\right) > 0$$

Gibbs' paradox: if the two gases is the same, ΔS should be 0, which contradicts the above result. The resolution lies in the subtlety of treating distinguishable and indistinguishable particles differently.

Discontinuity: there is a step change in the expression for entropy when when you suddenly go from treating the particles as distinguishable to indistinguishable.

2 Analytical Thermodynamics

Motivation: how a system changes when connected to the outside world. Our primary interest is in the system.

Assume the surrounding is a reservoir: it is so large that their **intensive** (independent of N) variables T, p, μ do not change when heat, volume or particles are transferred to and from them.

2.1 Definitions

1. **Thermally isolated**: no heat flow, any change will be adiabatic.
2. **Thermal contact**: imply thermal equilibrium.
3. **Open system**: particles and energy can move between the system and its surroundings. Extensive variables of system match those of the surrounding.
4. ***Closed system**: particles do not flow between the system and its surrounding, but energy can (fixed N).
5. **Isolated system**: no energy or particles can flow between the system and its surroundings.

2.2 Useful Math

Reciprocity theorem

$$\left(\frac{\partial X}{\partial Z}\right)_Y \left(\frac{\partial Y}{\partial X}\right)_Z \left(\frac{\partial Z}{\partial Y}\right)_X = -1$$

Maxwell's relations
Derived below

2.3 Thermodynamic potentials

Motivation: S and V are not always the most convenient variables, hence, we want to derive other functions that contain the same information but in terms of other variables that will prove more useful in certain circumstances.

Assume fixed N.

Assume only do pV work, means we are not pushing the system around, leaving it to do where the internal flux takes it to find equilibrium by itself.

Always comes in intensive-extensive pairs (conjugates): μdN / TdS / pdV.

2.3.1 Internal energy $U(S, V)$

$$\boxed{\begin{gathered} dU = TdS - pdV \\ dU = \left(\frac{\partial U}{\partial S}\right)_V dS + \left(\frac{\partial U}{\partial V}\right)_S dV \end{gathered}}$$

Comparing terms, hence:

$$T = \left(\frac{\partial U}{\partial S}\right)_V \quad \text{and} \quad p = -\left(\frac{\partial U}{\partial V}\right)_S$$

$U(S, V)$ gives complete thermodynamic information about the system and variables. S and V are the natural variables for U.

$$\boxed{\text{At constant V, dU = dQ}}$$

$$\boxed{\text{At constant S, dU = dW}}$$

2.3.2 Enthalpy $H(S, p)$

$$\boxed{\begin{gathered} H = U + pV \\ dH = TdS + Vdp \\ dH = \left(\frac{\partial H}{\partial S}\right)_p dS + \left(\frac{\partial H}{\partial p}\right)_S dp \end{gathered}}$$

Derivation:

$$dH = dU + pdV + Vdp = (TdS - pdV) + pdV + Vdp = TdS + Vdp$$

Uses:

1. **dH is the dQ at constant p**.

$$\boxed{\text{At constant pressure, dQ = dH}}$$

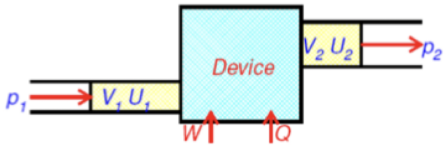
$$\boxed{C_p = \left(\frac{dH}{dT}\right)_p = T\left(\frac{dS}{dT}\right)_p}$$

2. Chemical energetics: enthalpy is the heat given out when a reaction occurs at constant pressure.

3. Flow processes: H is conserved if no external heat or work input.

$$\boxed{\Delta H = Q + W \text{ (energy in)}}$$

Proof:



For steady state and by conservation of energy:

$$U_1 + p_1V_1 + Q + W = U_2 + p_2V_2$$

$$H_2 - H_1 = \Delta H = Q + W$$

2.3.3 Helmholtz free energy $F(T, V)$

$$\boxed{\begin{gathered} F = U - TS \\ dF = -SdT - pdV \\ dF = \left(\frac{\partial F}{\partial T}\right)_V dT + \left(\frac{\partial F}{\partial V}\right)_T dV \end{gathered}}$$

Derivation:

$$dF = (TdS - pdV) - TdS - SdT = -SdT - pdV$$

Uses:

1. At constant temperature, the maximum amount of energy that is free for a system to convert to work is dF.

   $$\boxed{\text{At constant temperature, } dF = dW_{by} = pdV \text{ (}dF\text{ is max work obtainable)}}$$

2. For constant T and V, relates to total entropy change:

   $$\boxed{dS_{tot} = dS_{res} + dS_{sys} = -\frac{dF}{T}}$$

   $dF < 0$ for irreversible steps.

2.3.4 Gibbs free energy $G(T, p)$

$$\boxed{\begin{gathered} G = H - TS = U + pV - TS \\ dG = -SdT + Vdp \\ dG = \left(\frac{\partial G}{\partial T}\right)_p dT + \left(\frac{\partial G}{\partial p}\right)_T dp \end{gathered}}$$

Derivation:

$$dG = (TdS - pdV) + (pdV + Vdp) - (TdS + SdT) = Vdp - SdT$$

Uses:

1. At constant T and p, dG gives the maximum non-pV work done by the system.

   $$dU = dQ + dW_{pV} + dW_e = dQ - pdV + \underbrace{\sum X_i da_i}_{\text{Non-pV work (on)}}$$

   $$dG = dQ - pdV + \sum X_i da_i + pdV + Vdp - TdS - SdT$$

   For constant T and p, and for max work, $dQ = dQ_{rev} = TdS$

   $$dG = \sum X_i da_i = dW_e \quad \boxed{(dG \text{ gives max non-}pV\text{ work})}$$

   Significance: pV work is done during changes in volume at a fixed pressure. In many cases, the pV work is not useful work that can be harnessed, and is lost as heat. In (electrochemical) reactions (cathode and anode), we are more interested in the amount of non-pV work which is the work we can actually extract.

2. At constant T and p, relates to total entropy change:

   $$\boxed{dG = -TdS_{tot} = -T(dS_{rev} + dS_{sys})}$$

   where heat loss ↔ negative entropy. TdS ($= dH = dQ$), is essentially heat change.

   $dG = 0$ at equilibrium. (useful for phase equilibrium where both phases are at the same T and p)

   In a reversible change, a system can decrease its entropy $dG_{sys} < 0$.

3. Flow processes: if the transport process is reversible ($\Delta S = 0$), at constant T and without external work done, G is conserved ($\Delta G = 0$).

   $$\Delta G = -T\Delta S$$

4. Chemical potential is the Gibbs free energy per particle. It is the energy that can be absorbed or released due to a change in the number of particles.

   $$\boxed{\mu = \frac{G}{N}}$$

Remembering the 4 thermodynamic potentials

Ingredients:
1. S dependence: add **TdS**
2. V dependence: add **-pdV**
3. T dependence: add **-SdT**
4. p dependence: add **Vdp**

So,

$$U(S,V) \Rightarrow dU = TdS - pdV$$

$$H(S,p) \Rightarrow dH = Tds + Vdp$$

$$F(T,V) \Rightarrow dF = -SdT - pdV$$

$$G(T,p) \Rightarrow dG = -SdT + Vdp$$

Also,

$$H = U + pV$$

$$F = U - TS$$

$$G = U + pV - TS$$

2.4 Chemical potential

Isothermal atmosphere
μ is the same at all heights as the particles are in dynamic equilibrium and no work is being done.

Driving force: (1) Density gradient causing atoms to diffuse upwards. (2) Gravitational potential gradient makes atom tend to diffuse downwards.

With:

$$\mu = \frac{G}{n} = \frac{1}{n}(U + pV - TS)$$

Substituting:

$$U = nC_{V,m}T + nm_R gh$$

$$S = nC_{V,m}\ln T + nR\ln(V/n) + nS_0'$$

$$pV = nRT$$

Equate chemical potential at different heights:

$$p = p_0 e^{-\frac{m_r gh}{RT}}$$

Contact potential

Electrons in different materials have different chemical potentials, so when two conductors are placed in electrical conduct, there will be a net diffusion of electrons from one with the higher electron chemical potential μ_1 to the lower one μ_2.

$$dG = dn(\mu_1 - \mu_2) \leq 0$$

Flow of electrons sets up a charge imbalance and hence an electrostatic potential gradient called contact potential.

$$\mu_2 - \mu_1 = e(\phi_2 - \phi_1)$$

2.5 Gibbs Helmholtz equation

$$\boxed{U = F + TS = F - T\left(\frac{\partial F}{\partial T}\right)_V = -T^2\left(\frac{\partial}{\partial T}\frac{F}{T}\right)_V}$$

Similar expressions can be written for G and H:

$$G = F + pV$$

$$H = F + pV + TS$$

Rationale: F is the easiest thermodynamics potential to evaluate. It is convenient to write the other thermodynamics (U, G, H) variable in terms of F.

2.6 Maxwell relations

Example:

$$\left(\frac{\partial^2 U}{\partial S \partial V}\right)_{V,S} = \left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial p}{\partial S}\right)_V$$

Likewise for H, F and G.

You can invert them when needed as well:

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

2.7 Applications

2.7.1 Heat capacities

Start with:

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

Divide by dT at fixed p, multiply by T, and use Maxwell's relations to eliminate S,

$$C_p - C_V = T\left(\frac{\partial p}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_p$$

Using reciprocity theorem to find an expression for $\left(\frac{\partial p}{\partial T}\right)_V$, we obtain:

$$\boxed{C_p - C_V = \frac{TV\beta_p^2}{\kappa_T}}$$

Isobaric expansivity (β_T): fractional increase in volume per unit change in temperature, at constant pressure.

$$\beta_T = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p$$

Isothermal compressibility (κ_T): fractional change in volume per unit change in pressure, at constant temperature.

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

2.7.2 Compressibility

Adiabatic compressibility (κ_S): fractional change in volume per unit change in pressure, at constant entropy.

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

Using reciprocity theorem:

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

2.7.3 Joule's law

Statement: no change of temperature in a free expansion a.k.a Joule expansion.
Proof:

$$\text{Joule coefficient: } \left(\frac{\partial T}{\partial V}\right)_U = 0 = -\underbrace{\left(\frac{\partial T}{\partial U}\right)_V}_{1/C_V}\left(\frac{\partial U}{\partial V}\right)_T$$

$$\Rightarrow \left(\frac{\partial U}{\partial V}\right)_T = 0$$

$$\Rightarrow U = U(T)$$

The internal energy of an ideal gas depends on temperature only. The joule coefficient is a measure of how non-ideal a gas can be. For ideal gas, joule coefficient is zero.

2.7.4 Elastic wire

$$dW = Fdx$$

So,

$$dU = TdS + Fdx$$

$$H = U - Fx$$

$$F = U - TS$$

$$G = U - Fx - TS$$

2.7.5 Surface tension

Surface energy
Work done to increase area is:

$$dW = \gamma \underbrace{\delta l \delta x}_{\delta A}$$

where γ is surface tension. So,

$$dU = TdS + \gamma \delta A$$

Surface tension and surface energy are not identical because there is an entropy change when you create more surface. For $\Delta S_{\text{universe}} = 0$, heat must be exchanged with the surroundings (isothermal) or the liquid must change temperature (adiabatic) to compensate for the change in entropy due to the creation of more surface.

After some mathematical massaging, one can obtain:

$$u(T) = \left(\frac{\partial U}{\partial A}\right)_T = \gamma - T\frac{d\gamma}{dT}$$

Laplace pressure The curved surface of a small droplet/bubble produces and increase in internal pressure:

$$\Delta p = \frac{2\gamma}{R}$$

3 Phase Transitions

Real gases:

1. **Finite molecular size**: hit the walls sooner and more often, increasing the pressure if n/V is high.
2. **Finite long-range intermolecular attraction**: spend longer in each others vicinity and pull back molecules heading for the walls, reducing collisions with the wall and speed of hitting wall, reduce pressure.

Theorem of corresponding states:
All fluids have approximately the same compressibility factor, Z, when the pressure and temperature are expressed in reduced units (as fractions of the the fluid's critical temperature and pressure)

$$\boxed{Z = \frac{pV}{nRT}}$$

Boyle's law:
Virial expansion (in p),

$$pV = A_0 + A_1 p + A_2 p^2 + A_3 p^3 + ...$$

At sufficiently low p, Boyle's law holds well. Could also be expanded in 1/V.

Boyle temperature, T_B is the temperature where $A_1 = 0$, at which Boyle's law is the most closely obeyed. Physically, the long-range attraction cancels the short-range repulsion between 'real' molecules.

3.1 Van der Waal's equation

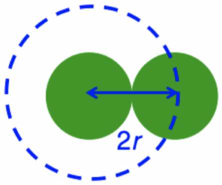
$$\boxed{\left(p + n^2 \frac{a}{V^2}\right)(V - nb) = nRT}$$

1. Modified volume - finite molecular size

   $$V \rightarrow V - b$$

   where b is to account for the finite molecular size. Volume is reduced as there are regions of space with radius 2r that cannot be occupied.

   It can be estimated using a hard sphere model with radius r.



For one mole,

$$b = \frac{4}{3}\pi(2r)^3 \cdot \left(\frac{1}{2}N_A\right)$$

where the 1/2 arises due to the consideration of a pair of atoms.

2. Modified pressure - intermolecular forces

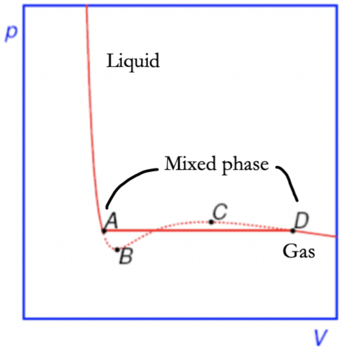
$$p \to p + \frac{a}{V^2}$$

where a is to correct for intermolecular forces. Molecules hitting the wall are slowed down due to attractive forces from molecules in the bulk of the gas. Hence, slight pressure reduction at the walls.
Note: (p + correction) is experienced pressure with p being measured pressure.

Modelling pressure reduction:
1. rate of molecules hitting wall $\propto \rho$
2. number of molecules pulling them back $\propto \rho$

$$\Rightarrow \delta p \propto \rho^2 \propto \frac{1}{V^2}$$

Van der Waal's isotherm



A real gas proceeds at constant p from $D \to A$ as the gas liquefies, both phases coexist in equilibrium. Only volume change.

Maxwell area rule: same area below and above the dashed and solid line.

3.1.1 Liquid/gas transition

1. Nucleation sites (e.g. impurities) typically needed to induce phase change ($A \leftrightarrow D$).

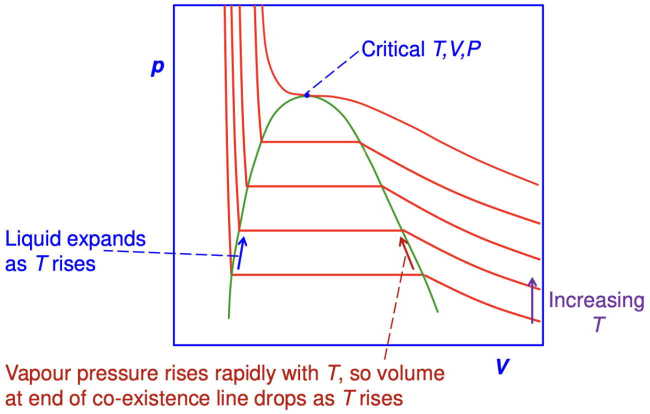
For very pure/clean substances, can exist in metastable states at regions of −ve slope:
2. $A \to B$: super-heated liquid
3. $D \to C$: super-cooled vapour. E.g. cloud chamber
4. $B \to C$: unphysical/unstable (+ve slope on $p - V$ diagram)

3.1.2 Critical point

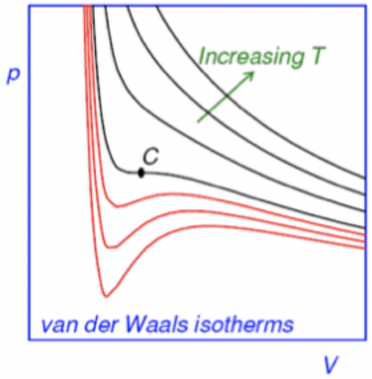
Critical point is where different phases of the material cannot be distinguished. It is where unstable behaviour ensues so will not be observed. For example for a gas, it is a region beyond which pressure increase with increasing volume. It is the **horizontal point of inflection** on a p-V plot.

$$\boxed{\left(\frac{\partial p}{\partial V}\right)_T = 0 \quad \text{and} \quad \left(\frac{\partial^2 p}{\partial V^2}\right)_T = 0}$$

Van der Waal's isotherm



(a) inverted parabola of phase segregation



(b) Below T_c, the system phase segregates

Critical temperature, T_c
T_c is the highest temperature at which liquid and vapour can coexist.

Critical volume, V_c
Make p the subject in Van der Waal's. Differentiate wrt V. Eliminate T to find V:

$$\boxed{V_c = 3b}$$

Substitute back to also find T_c, p_c and a dimensionless quantity $Z_c = \frac{p_c V_c}{n T_c}$.

3.2 Liquefaction of gas

Trick: expand a gas from high pressure and above inversion temperature to below the inversion temperature using Joule-Thomson expansion valve.

Expansion of gas → temperature change.

- Below inversion temperature, the attractive force dominate and the gas cools.
- Above the inversion temperature, weak attractive forces becomes not so important and high pressure, short range repulsive forces dominate and the gas warms up.

Equivalent to a flow process with no energy input, H is conserved.

$$\Delta H = 0$$

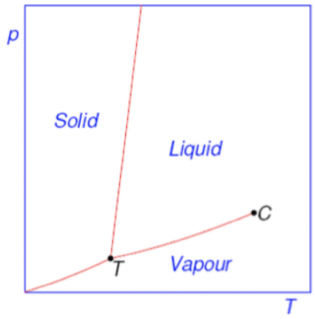
3.3 Phase transitions

Two phases can coexist with a flux of particles between the two phases. At any given temperature, there will be some pressure called the **vapour pressure** where liquid ↔ gas transition are in dynamic equilibrium in a closed system.

Liquid → gas: some molecule in a liquid close to the surface might have sufficient energy to escape the intermolecular forces of its neighbour, and enter the gas phase.

Gas → liquid: gas molecules may hit the surface and stick.

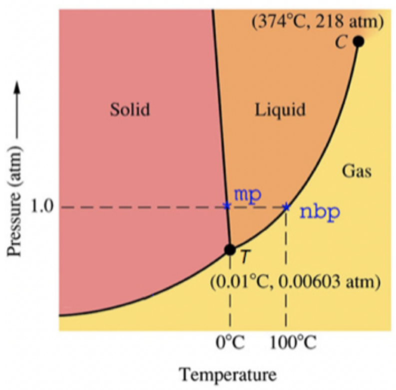
3.3.1 Phase diagram



T = triple point: all 3 phases coexist
C = critical point

Lines generally have positive slope:
1. Volume generally increase as you go through a phase transition by increasing the temperature.
2. Le Chaterlier's principle indicates that as you increase the pressure, the system will react to reduce its volume, so it will tend to go to the more dense phase, and you need a higher temperature for it to melt.

3.3.2 Example 1: water



Key features:
1. S-L boundary has negative slope as water expand on freezing.
2. The L-G boundary terminates at critical point, beyond which there is no distinction between liquid and vapour. Also, the associated phase transition is second order and there is no latent heat.
3. At the triple point, all three phases co-exist in equilibrium.

3.3.3 Example 2: tin pest

Tin has 2 allotropic form:

1. White beta tin (normal): stable tetragonal crystal structure and metal.

   Beyond T = 13.2°C, it becomes

2. Grey alpha tin: cubic, diamond structure and a semiconductor. Greater volume.

3.3.4 Clausius-Clapeyron equation (phase transition)

During phase transition, there is entropy change (change of order). For S_{universe} to remain constant, need transfer of heat where latent heat $L = T\Delta S$. Accompanied by volume change ΔV as well.

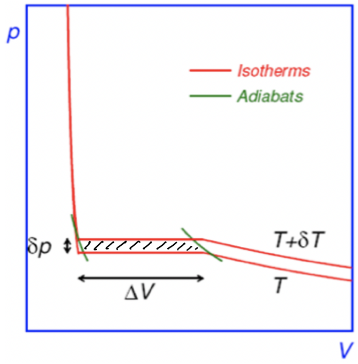
First-order phase transition (discontinuity in S):

$$\boxed{\frac{dp}{dT} = \frac{\Delta S}{\Delta V} = \frac{L}{T\Delta V}}$$

Note for second order phase transition - discontinuity in $T(\partial S/\partial T)$.

Derivation:

1. <u>Using temperature differential</u>
   Consider 2 isotherms T and $T + \delta T$ on p-V diagram, where the temperature differential is just enough to straddle the phase transition, so a finite amount of latent heat is needed to achieve an infinitesimal temperature difference.



Connect them with two adiabats, forming a Carnot cycle with efficiency:

$$\eta = \frac{W}{Q} = \frac{\delta T}{T}$$

Q is latent heat. W is area of cycle.

$$\frac{\delta T}{T} = \frac{\delta p}{T}\frac{\Delta V}{\Delta S}$$

Taking limit as $\delta T \to 0$

$$\frac{dp}{dT} = \frac{\Delta S}{\Delta V} = \frac{L/T}{\Delta V}$$

2. Using chemical potential/Gibbs energy
   Suppose we have 2 phases, with N_1 and N_2 particles in each and μ_1 and μ_2 chemical potential respectively.

   $$G = N_1\mu_1 + N_2\mu_2$$

   At equilibrium,

   $$dG = 0 = dN_1\mu_1 + dN_2\mu_2 \tag{1}$$

   Since $N_1 + N_2 =$ constant, $dN_1 + dN_2 = 0$.

   $$\Rightarrow \mu_1 = \mu_2$$

   The **chemical potentials for the two phases are equal** as you go along the phase boundaries for a particular change in temperature.

   Consider 2 points along the phase boundary and using one mole, $G = \mu$:

   $$\begin{aligned} d\mu_1 &= d\mu_2 \\ -S_1\,dT + V_1\,dp &= -S_2\,dT + V_2\,dp \qquad (2) \\ (S_2 - S_1)\,dT &= (V_2 - V_1)\,dp \\ \frac{dp}{dT} &= \frac{\Delta S}{\Delta V} \end{aligned}$$

Combining (1) and (2) more generally, we get the Gibbs-Duhem equation,

$$\boxed{dG = \sum_i dN_i\ \mu_i = -SdT + Vdp}$$

Integration of Clausius-Clapeyron equation

Example, transition to vapour:

1. **Calculate ΔV**

   $$\boxed{\Delta V \approx V_{\text{vap}}} \text{ (for any transition to gas)}$$

   Can use ideal gas law if pressure is sufficiently low,

   $$\Delta V = \frac{RT}{p}$$

   Hence,

   $$\frac{dp}{dT} = \frac{L}{T\Delta V} = \frac{Lp}{RT^2}$$

2. For small temperature intervals, can approximate $L \approx$ constant.

   $$\int \frac{dp}{p} = \frac{L}{R} \int \frac{dT}{T^2}$$

   $$\ln p = -\frac{L}{RT} + c$$

Could also be transition between solid and liquid. Use the more general Clapeyron equation:

$$\frac{dp}{dT} = \frac{\Delta H}{T\Delta V}$$

where ΔH and ΔV is the molar change in enthalpy and volume.
Boiling point: when vapour pressure = ambient atmospheric pressure.

3.4 Examples

1. Problem sheet Qn 17: state functions
   State variables are path-independent, only depends on initial and final states. So, can take different paths for the same initial and final states.

   1) Enthalpy same:
   $$C_\alpha \, \Delta T = \Delta H_1 + C_\gamma \, \Delta T - \Delta H_2$$

   2) Entropy same:
   $$C_\alpha \ln \frac{T_2}{T_1} = \Delta S_1 + C_\gamma \ln \frac{T_2}{T_1} - \Delta S_2$$

   where $\Delta S_1 = \frac{\Delta H_1}{T}$

2. Problem sheet Qn 18: configurations and heat component of entropy

   Change in volume: configuration (decrease V, decrease S)
   $$\Delta S_{sys} = R \ln \frac{V_f}{V_i}$$

   If $V_f < V_i$, the decrease in entropy of the system is compensated for by expending work W which is converted to heat and dissipated into the environment increasing its entropy.
   $$W = -T \Delta S_{sys}$$

   Change in temperature: heat

Important note:

1.
$$\frac{d}{dT} = \left(\frac{\partial}{\partial T} \right)_p + \frac{dp}{dT} \left(\frac{\partial}{\partial p} \right)_T$$

4 Statistical Thermodynamics

4.1 Macro and micro states

2nd law: thermodynamics can be deduced from the properties of the system states without considering how you get from one state of another. Fundamentally, it is a result of time reversibility symmetry of the laws of nature.

4.1.1 Quantum states $\longrightarrow$ classical states

A 'proper' microstate is defined by quantum mechanics, and is an eigenfunction of the time development operator, $\hat{\boldsymbol{H}}$:

$$\text{Eigenstates of the Hamiltonian: } \Psi_j(\mathbf{r},t) = \psi_j(\mathbf{r})e^{-i\omega_j t}$$

Energy is the expectation value of the time development operator, and is conserved because the eigenfunctions of this operator, by definition, do not change with time.

If we can approximate the motion of the constituent particles with classical mechanics, then we can use states that are 'small boxes' in a 6 dimensional combined $\mathbf{x}$ and $\mathbf{v}$ space. The boxes are made so small that no measurable property depends on the box size.

Principle of equal a priori probability (PEAP)
All microstates are equally likely $\Rightarrow$ the probability that a system at equilibrium is in a certain macrostate is proportional to the number of microstates that correspond to the macrostate.

4.1.2 Counting microstates

Isolated system: the system can move from one microstate to another (flux), whilst keeping the same energy and no. of particles.

Consider splitting an isolated system **(fixed E and fixed N)** into 2 sub-systems in thermal contact. For a particular macrostate in which sub-systems have energy E_1 and E_2, there are many different configurations of atoms and energy, Ω_1 & Ω_2 (degeneracy).

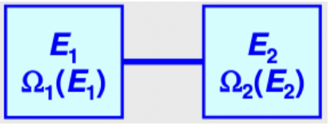


Figure 5: Total number of microstates of whole system: $\boxed{\Omega = \Omega_1 \times \Omega_2}$

For M boxes (# of energy levels) and N quanta (# of particles), treat as (M-1) walls and N quanta:

$$\boxed{\Omega = \frac{(N+M-1)!}{N!(M-1)!}}$$

The most likely macrostate is the one with the most corresponding microstates i.e. maximum value of $\Omega = \Omega_A\Omega_B$.

Thus, is the condition when $T_A = T_B$ (0^{th} law)

Note: the most likely macrostate may not be the average one.

Consider:

$$\frac{d\left(\Omega_A(E_A)\Omega_B(E - E_A)\right)}{dE_A} = 0$$

After differentiating, Will get:

$$\frac{\Omega_A^{'}}{\Omega_A} = \frac{\Omega_B^{'}}{\Omega_B} \Rightarrow \frac{d(\ln\Omega_A)}{dE_A} = \frac{d(\ln\Omega_B)}{dE_B}$$

Hence, the relation between Ω and E must relate to classical thermodynamics concept of temperature:

$$\boxed{\beta(T) = \frac{d(\ln\Omega)}{dE}}$$

4.1.3 Real systems

Have a myriad of finely spaced energy levels, characterised by:

$$\text{Density of states: } g(E) = \frac{dN}{dE}$$

$$\delta N = g(E)\ \delta E$$

$$\Rightarrow \boxed{\Omega(E) = g(E)\ \delta_E}$$

The spread in energy, δ_E, is related to the time a system spends in a state by the time-energy uncertainty principle ($\Delta E\Delta t \geq \frac{\hbar}{2}$).

Similar expression for β (**temperature function**) expressed in terms of a system's energy density of states:

$$\boxed{\beta = \frac{d(\ln g)}{dE}}$$

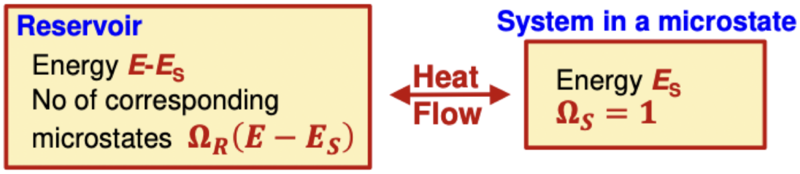
4.2 Boltzmann distribution - connecting β and T

Boltzmann distribution states that the probability of a state with energy E being occupied is given by:

$$P(E_i) = \frac{e^{-\frac{E_i}{k_B T}}}{Z}$$

where $Z = \sum_i e^{-E_i/k_B T}$ is the partition function to normalise the Boltzmann distribution.

4.2.1 Derivation



Total energy is E. The probability that the system will be in an 'excited' microstate of energy E_s (i.e. energy E_s taken out of reservoir) is:

$$P_r(E_s) = \frac{\Omega_R(E - E_s)}{\Omega_R(E)}$$

i.e. how Ω_R varies as you take energy out of reservoir. Ground state energy $E_s = 0$ has relative probability 1.

Given that $E_s \ll E_R$ (small compared to energy of reservoir), use Taylor expansion:

$$\begin{aligned} \ln \Omega_R(E_R) &= \ln \Omega_R(E - E_s) \\ &\approx \ln \Omega_R(E) - E_s \frac{d \ln \Omega_R}{dE} \\ &= \ln \Omega_R(E) - E_s \beta \end{aligned}$$

$$\Rightarrow \boxed{P_r(E_s) = e^{-\beta E_s} = e^{-\frac{E_s}{k_B T}}}$$

To establish a connection between β and T, we need a temperature dependent property derived using both statistical and classical thermodynamics. Consider kinetic energy of ideal monoatomic gas:

From classical thermodynamics: $KE = \frac{3}{2} k_B T$
From statistical thermodynamics: $KE = \frac{3}{2\beta}$

Hence,

$$\boxed{\beta = \frac{1}{k_B T}}$$

4.2.2 Understanding β

Applies to a system in contact with a heat reservoir (condition: so big that T remains unchanged as you take heat out) and gives the chance of that the system is in a particular microstate relative to the chance that the system is in a ground microstate.

As you transfer heat out of the reservoir, the number of microstates available to the reservoir drops. The Boltzmann factor measures the drop in the number of states in the reservoir as you take energy out.

$$\boxed{\text{The temperature of the reservoir is defined in terms of the \textbf{rate} at which its accessible microstates changes as heat is transferred out of the reservoir.}}$$

The most likely system microstate is the ground state, where all energy is in the reservoir.

4.2.3 Normalizing Boltzmann distribution

$$\text{P(microstate r)} = \frac{e^{-\frac{E_r}{k_B T}}}{\sum_i e^{-\frac{E_i}{k_b T}}}$$

where $\boxed{Z = \sum_i e^{-E_i/k_B T}}$ is the **partition function**.

$1/Z$ gives probability of system in ground state.

Degeneracy, g, of a macrostate is the number of microstates (Ω) in the macrostate.

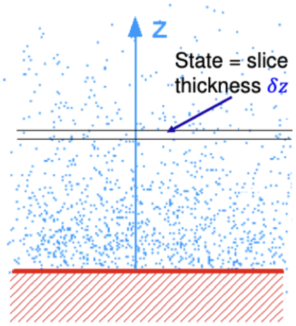
$$\text{P(macrostate q)} = \frac{g_q e^{-E_q/kT}}{\sum_i g_i e^{-E_i/kT}}$$

Average energy:

$$\boxed{\langle E \rangle = \sum_i E_i \times P(E_i)}$$

Example: isothermal atmosphere

Consider molecule in an ideal gas at temperature T in the presence of gravity. Microstates are horizontal 'slices' of uniform infinitesimally small width, δz, all equally likely:



Can treat one molecule as system and the rest of the atmosphere as the reservoir.

Probability of molecule of mass m being at height z is:

$$P(z) \propto e^{-mgz/k_B T}$$

$$\text{Number density: } N(z) = N(0)e^{-mgz/k_B T}$$

Compare with pressure:

$$p(z) = p_0 e^{-mgz/k_B T}$$

4.2.4 Planck formula

Redefining internal energy

Internal energy is found by summing the contribution for all the system microstates:

$$\begin{aligned} U_{sys} &= \sum_i p_i E_i \\ &= \frac{\sum E_i e^{-\beta E_i}}{Z} = \frac{-\frac{\partial}{\partial \beta}\sum e^{-\beta E_i}}{Z} = \boxed{-\frac{1}{Z}\frac{\partial Z}{\partial \beta} = -\frac{d(\ln Z)}{d\beta}} \end{aligned}$$

Energy of simple harmonic oscillator - Planck formula

Excess energy above ground state energy: $E_n = n\hbar\omega$:

$$Z = \sum_{n=0}^{\infty} e^{-\frac{n\hbar\omega}{kT}} = 1 + e^{-\frac{\hbar\omega}{kT}} + \left(e^{-\frac{\hbar\omega}{kT}}\right)^2 + ... = \frac{1}{1 - e^{-\hbar\omega\beta}}$$

$$\frac{\partial Z}{\partial \beta} = -\frac{\hbar\omega e^{-\hbar\omega\beta}}{(1 - e^{-\hbar\omega\beta})}$$

$$\boxed{\therefore\ U = -\frac{1}{Z}\frac{\partial Z}{\partial \beta} = \frac{\hbar\omega}{e^{\hbar\omega\beta} - 1} \quad \text{(Planck formula)}}$$

1. Low temperature ($kT \ll \hbar\omega$)

   $$U \approx \hbar\omega e^{-\hbar\omega\beta}$$

   Small chance of being in the first excited state.

2. High temperature ($kT \gg \hbar\omega$)
   Trick: at hight T convert summation to integral.

   $$U \approx \frac{\hbar\omega}{1+\hbar\omega\beta-1} = kT$$

   We have moved over to classical dynamics where the energy level spacing is too small to have an effect and equipartition of energy holds, $KE = PE = \frac{1}{2}kT$.

Heat capacity of simple harmonic oscillator

$$C = N\frac{dU}{dT} = N\left(\frac{\hbar\omega}{kT}\right)^2 \frac{ke^{\hbar\omega/kT}}{\left(e^{\hbar\omega/kT}-1\right)^2}$$

$C \to 0$ for low T and $C \to k$ for high T.

Q: why $C \to k_B$ at high T?
A: $\Rightarrow$ $k_B = 2 \times \frac{k_B}{2}$, hows that the system has 2 quadratic terms/2 degrees of freedom.

4.2.5 Equipartition of Energy

Each quadratic coordinate term in the energy contributes $1/2\ kT$ of energy (provided we can ignore QM meaning the spacing of the energy levels is small compared to kT)

Examples for which the energy is a **quadratic** function of u ($E = \alpha u^2$).

u	**E**
x	$1/2\ kx^2$
v	$1/2\ mv^2$
ω	$1/2\ I\omega^2$

Proof using Boltzmann distribution:

$$U = \frac{\sum \delta N \alpha u^2 e^{-\alpha u^2 \beta}}{\sum \delta N e^{-\alpha u^2 \beta}}$$

where $\delta N = \delta u/\epsilon$ is the number of states in the interval $u \to u + \delta u$. Convert to integral. Use substitution $x = \alpha u^2$ so $dx = 2udu$:

$$\boxed{U = \frac{\int_{\infty}^{\infty} \alpha u^2 e^{-\alpha u^2 \beta} du}{\int_{\infty}^{\infty} e^{-\alpha u^2 \beta} du} = \text{...integrate by parts...} = \frac{1}{2}k_B T}$$

The above expression for U works if expression for total energy separates into addition of separate terms that depend quadratically on a coordinate so that the integral separates.

Example: for 1D SHO, a state is a box of size ϵ_x and ϵ_v in x and v spaces respectively. Number of microstates is $\delta x \delta v / \epsilon_x \epsilon_v$.

$$\begin{aligned}
U =& \frac{\sum(\frac{1}{2}kx^2 + \frac{1}{2}mv^2)e^{-\left(\frac{1}{2}kx^2+\frac{1}{2}mv^2\right)/kT}\delta N}{\sum e^{-\left(\frac{1}{2}kx^2+\frac{1}{2}mv^2\right)/kT}\delta N} \\
=& \frac{\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}(\frac{1}{2}kx^2 + \frac{1}{2}mv^2)e^{-\left(\frac{1}{2}kx^2+\frac{1}{2}mv^2\right)/kT}dxdv/\epsilon_x\epsilon_v}{\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}e^{-\left(\frac{1}{2}kx^2+\frac{1}{2}mv^2\right)/kT}dxdv/\epsilon_x\epsilon_v} \\
=& \ldots \\
=& \frac{\int_{-\infty}^{\infty}\frac{1}{2}kx^2 e^{-\frac{1}{2}kx^2/kT}dx}{\int_{-\infty}^{\infty}e^{-\frac{1}{2}kx^2/kT}dx} + \frac{\int_{-\infty}^{\infty}\frac{1}{2}mv^2 e^{-\frac{1}{2}mv^2/kT}dx}{\int_{-\infty}^{\infty}e^{-\frac{1}{2}mv^2/kT}dx} \\
=& \frac{1}{2}kT + \frac{1}{2}kT \\
=& kT
\end{aligned}$$

We know that the **mean energy per quadratic degree of freedom** is:

$$U = \frac{1}{2\beta}$$

For 3D ideal gas, with 3 quadratic degrees of freedom $E = \frac{1}{2}mv_x^2 + \frac{1}{2}mv_y^2 + \frac{1}{2}mv_z^2$,

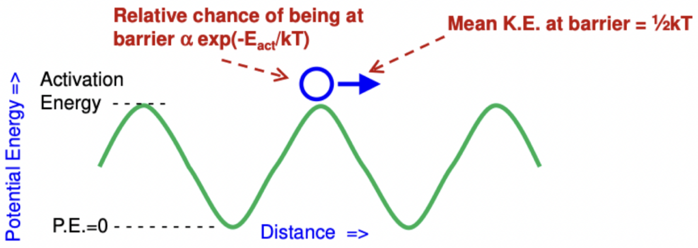
$$U = \frac{3}{2\beta} = \frac{3}{2}kT$$

Consequences

The notion of KE as a measure of T is irrespective of state ⇒ mean speed and K.E. same for solids, liquids and gases at the same T.

Even for particles moving in a varying potential energy, at any point, the mean KE, velocity (and velocity distribution) are the same.

Activated processes



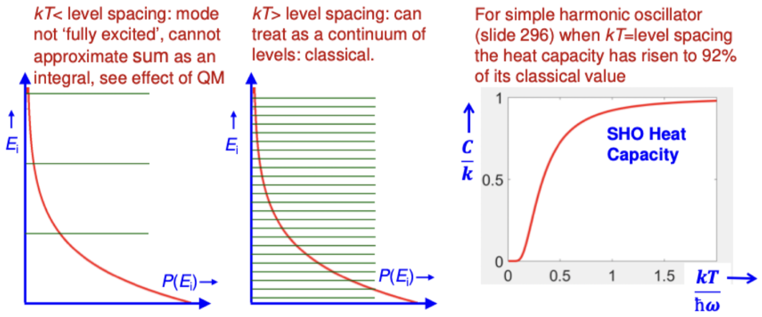
Activation energy: is the minimum energy required to overcome energy barrier.

Useful in deriving a theory of ’activated processes’ such as chemical reaction/diffusion, since the rate of barrier crossings depend on the 1) number density at the barrier, and 2) their velocity at the barrier.

4.2.6 Boundary between QM and CM

k_BT is the total energy available for the system to distribute among the energy levels. Energy level spacing v.s. k_BT:

1. If they are small (less than kT): can replace sum as an integral and equipartition of energy holds. Classical regime.
2. If they are large (equal or greater than kT), have to consider effects of quantum mechanics.



Heat capacity of gas

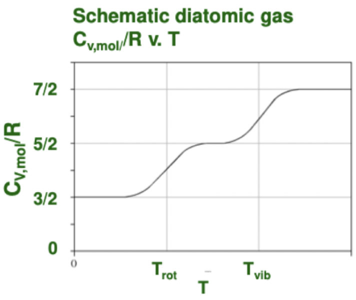
Diatomic gas has **3 translational**, **2 rotational**, **1 vibrational** degrees of freedom.

Transnational and rotational contribute $1/2k$ per degree of freedom. Vibrational has both kinetic and spring energies, contribute k per degree of freedom.

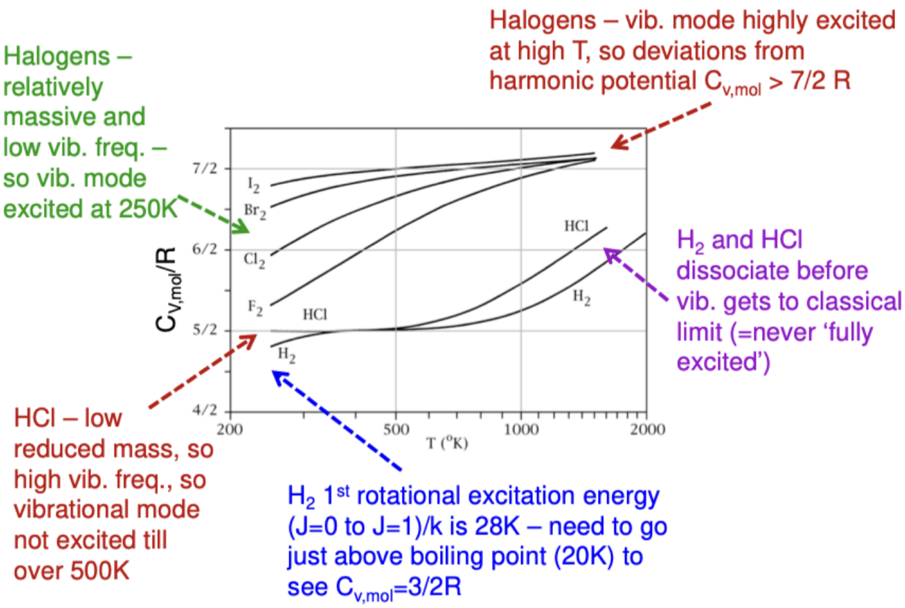
Vibration is more localised than rotation which is more localised than translation. Hence, energy level spacing decrease in this order.

So, heat capacity:

$$C_m = \frac{3}{2}R \text{ (low T)} = \frac{5}{2}R \text{ (intermediate T)} = \frac{7}{2}R \text{ (high T)}$$



Increasing the temperature allows higher modes to be excited (switched on)



Halogens – relatively massive and low vib. freq. – so vib. mode excited at 250K

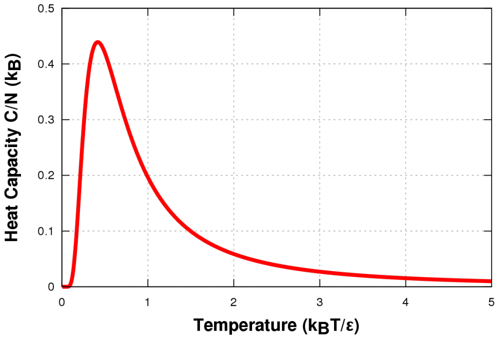
Halogens – vib. mode highly excited at high T, so deviations from harmonic potential $C_{v,mol}$ > 7/2 R

H_2 and HCl dissociate before vib. gets to classical limit (=never 'fully excited')

HCl – low reduced mass, so high vib. freq., so vibrational mode not excited till over 500K

H_2 1st rotational excitation energy (J=0 to J=1)/k is 28K – need to go just above boiling point (20K) to see $C_{v,mol}$=3/2R

For finite level systems (2 level systems),



Low T ($T \to 0K$): perfect order. $C \sim e^{-\frac{E}{k_BT}} \to 0$.
High T ($T \to \infty$): perfect disorder, all energy levels equally occupied. $C \to 0$.

$$\boxed{\text{Temperature is a measure of disorder}}$$

4.3 Deep dive into entropy

Entropy is defined as a concept in classical thermodynamics in terms of reversible heat transfer i.e. for a system in continuous contact with a reservoir:

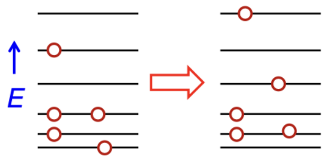
$$dS = \frac{dQ_{\text{reversible}}}{T}$$

4.3.1 New look at internal energy

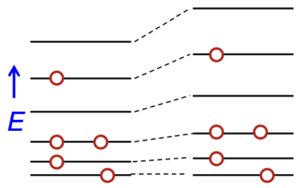
$$U = \sum p_i E_i$$

$$\boxed{dU = \underbrace{\sum E_i dp_i}_{dQ} + \underbrace{\sum p_i dE_i}_{dW}} = dQ + dW$$

For reversible processes,



(a) dQ



(b) dW

1. Heat transfer changes the <u>probabilities</u> of occupying the microstates.
2. Work done changes the <u>energies</u> of the microstates.

Example of work
Slow change, morphs from one state to the other.
Fast change, weighted linear combination of all possible new wavefunctions of the new system.

Consider a monatomic gas in a cubic box of side length L,

$$k \propto \frac{1}{L} \quad \text{and} \quad KE = \frac{\hbar^2 k^2}{2m} \propto \frac{1}{L^2}$$

$$U = KE \propto \frac{1}{L^2} \propto \boxed{V^{-\frac{2}{3}}}$$

Compare with T-V relationship for adiabatic expansion, $TV^{\gamma-1} = \text{const}$, with $\gamma = \frac{C_p}{C_v} = \frac{R+C_v}{C_v} = \frac{5}{3}$. So,

$$U \propto T \propto V^{1-\gamma} \propto V^{-\frac{2}{3}}$$

It agrees!

Effect of work done on temperature
When an external constraint is changed, the quantum states change in energy. As the box size decrease, the energy levels becomes wider spaced. Temperature increase as the whole energy distribution is roughly scaled to larger energies.

4.3.2 Entropy

For slow change,

$$dS = \frac{\sum E_i dp_i}{T} \quad \text{and} \quad p_i = \frac{e^{-\frac{E_i}{kT}}}{Z} \Rightarrow \ln p_i = -\frac{E_i}{kT} - \ln Z$$

Substitute: $\frac{E_i}{T} = -k \ln p_i - k \ln Z$

$$dS = -\sum k \ln p_i dp_i - k \ln Z \underbrace{\sum dp_i}_{0}$$

$$\begin{aligned} S &= -\sum k \int \ln p_i \, dp_i \\ &= -\, k \sum (p_i \ln p_i - p_i) + \text{constant} \\ &= -\, k \sum p_i \ln p_i + \text{constant} \end{aligned}$$

So,

$$\boxed{S_{\text{Gibbs}} = -k \sum p_i \ln p_i}$$

4.3.3 Connecting Ω and S (Boltzmann expression for entropy)

$$\text{Comparing} \quad \frac{dE}{T} = d(k \ln \Omega) \quad \text{and} \quad dS = \frac{dQ_{rev}}{T}$$

Most important entropy formula:

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

$$\Delta S = k_B \ln \left(\frac{\Omega_{\text{final}}}{\Omega_{\text{initial}}} \right)$$

Linking together with $\Delta Q = T \Delta S$.

The formula is only valid for an **isolated system at equilibrium**, where all microstates have the same probability $p_i = {}^1\!/_\Omega$. Proof:

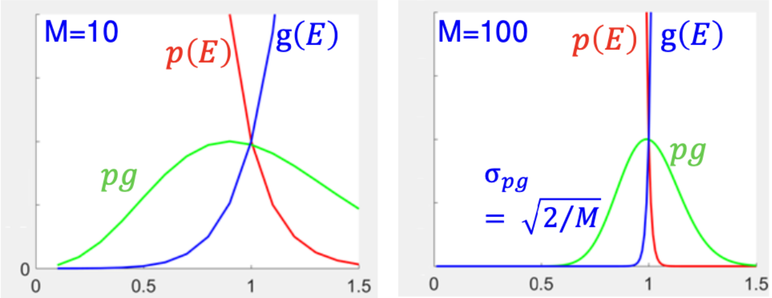
$$S = -k \sum p_i \ln p_i = k \sum \frac{1}{\Omega_i} \ln \Omega = k \ln \Omega$$

In practice, real systems do not have perfectly degenerate energy states, but have a permitted uncertainty δ_E in their energy i.e. $\Omega = g(E)\, \delta_E$. It is good to write S in terms of $g(E)$:

$$\boxed{S \approx k \ln(g(E))}$$

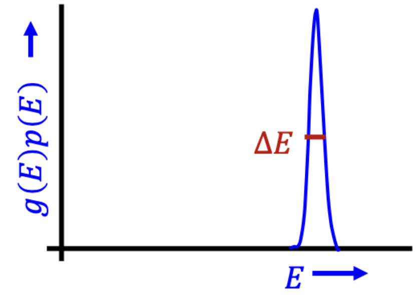
More properly,

$$S = -k \int \ln p(E) \underbrace{g(E)\, p(E)\, dE}_{\substack{\text{chance of being} \\ \text{in macrostate} \\ \text{between } E \text{ to } E+dE}} = -k \langle \ln p(E) \rangle = \boxed{-k \langle \ln p(E_{avg}) \rangle}$$



Width of $g(E)p(E) \propto \frac{1}{\sqrt{M}}$. Peaks sharply at E_{avg}

The larger the system, the more sharply peaked it is.



$$S = k \ln \omega = k \ln g(E_{avg}) + k \ln \Delta E$$

where ΔE is the spread in system energy due to random heat transfers to and from the reservoir.

Boltzmann expression is not strictly extensive, because when two isolated systems are in contact, energy can flow between them and there will be additional states with the same total energy but a different distribution of energy:

$$\Omega_{\text{combined}} > \Omega_1 \Omega_2$$

4.3.4 Time averaged geometric mean (TAGM) probability

$$p_T = \prod p_i^{np_i} = p_{\text{TAGM}}^n$$

Taking ln on both sides and cancelling n,

$$\boxed{\ln p_{\text{TAGM}} = \sum p_i \ln p_i}$$

So,

$$\boxed{S = -k \ln p_{\text{TAGM}}}$$

1. $\ln p_{\text{TAGM}} \geq \frac{1}{n}$ (average probability) Can use method of Lagrange multipliers to prove that the minimum of p_{TAGM} is p_{AM}.

> As irreversible change progress towards thermal equilibrium, the microstate probabilities converge to their mean values and p_{TAGM} is minimised, so the entropy is maximised.

2. $\boxed{1/p_{\text{TAGM}}}$ tells you the **effective number of states** involved.

   The power of Gibbs entropy is that it handles all the questions of which microstate to include in the entropy and with what weight. If states are not occupied then they will not contribute.

3. Monotonic increase in entropy. Proof:

   Compare two probabilities, $p_1 > p_2$, change in $\ln p_{\text{TAGM}}$,

$$\begin{aligned} d(p_{\text{TAGM}}) &= d(p_1 \ln p_1) + d(p_2 \ln p_2) \\ &= (1 + \ln p_1) dp_1 + (1 + \ln p_2) dp_2 \\ &= -(1 + \ln p_1) dp + (1 + \ln p_2) dp \\ &= (\ln p_2 - \ln p_1) dp < 0 \end{aligned}$$

   Hence, entropy rises.

4. S_{Gibb} is extensive. Depends on quantity of matter. Proof:
   Consider two independent subsystems connected to a reservoir,

$$\begin{aligned} S = -k \sum_{i,j} p_i f_j \ln(p_i f_j) &= -k \sum_{i,j} p_i f_j [\ln(p_i) + \ln(f_j)] \\ &= -k \sum_i p_i \ln p_i - k \sum_j f_j \ln f_j \\ &= S_A + S_B \end{aligned}$$

4.4 Measurement

Measurement is an irreversible process. Anything that has a well defined result is irreversible. Collapse of wavefunction results in dissipation of heat/energy.

5 3rd Law of Thermodynamics

Statement:

[Nernst] Near absolute zero, all reactions in a system in internal equilibrium take place with no change in entropy.

$$dS \to 0 \text{ as } T \to 0$$

[Planck] The entropy of all systems in internal equilibrium is the same at absolute zero and may be taken as zero .

$$S = 0 \text{ at } T = 0$$

5.1 Motivation for and origin of 3rd Law

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

$$\Rightarrow \left(\frac{\partial S}{\partial T}\right)_p = \frac{C_p}{T}$$

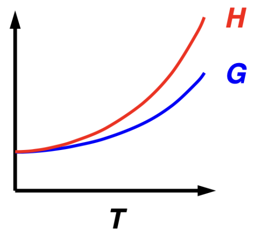
$$S(T) = S(T=0) + \int_o^T \left(\frac{\partial S}{\partial T}\right)_p dT = S(0) + \int_0^T \frac{C_p}{T} dT$$

This requires the value of entropy at absolute zero.

Aside: at phase transitions, entropy jumps by discrete amount:

$$\Delta S = \frac{L}{T} \quad \left(\frac{\text{heat}}{\text{temperature}}\right)$$

- Step 1: we know that $\Delta S \to 0$ as $T \to 0$ from $\Delta G = \Delta H - T\Delta S$ and that ΔH and ΔG approach each other asymptotically.



- Step 2: As absolute zero is approached, if the system is in equilibrium (capable of moving from microstate to microstate), it will all drop into the ground energy state with $\Omega = 1$. $S = -k \cdot 1 \ln 1 = 0$.

However, in practice the dropping to ground state cannot be achieved as equilibrium can't be reached at low temperatures. Atomic rearrangements require activation energy. They would just end up in some higher entropy non-equilibrium state.

5.2 Consequences

Any quantity with dependence on ΔS goes to zero at absolute zero.

1. **All heat capacities to go zero at absolute zero**.
   Why: at low T, only the first excited state has significant probability of occupation other than the ground state. Essentially, it becomes a 2-state system.

2. Isobaric thermal expansion coefficient:

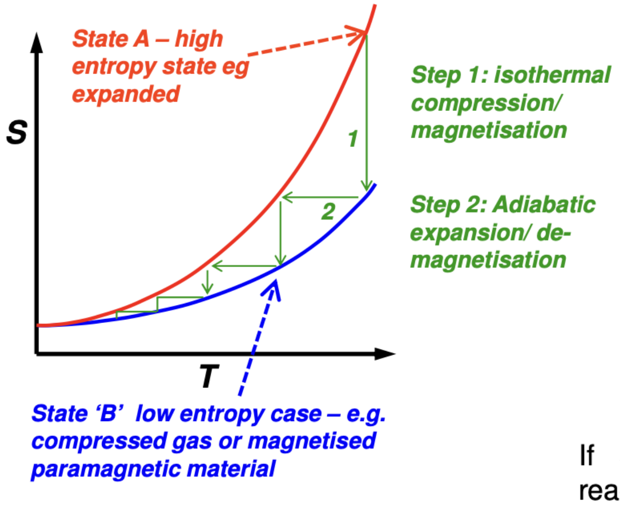
$$\beta_p = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p = -\frac{1}{V}\left(\frac{\partial S}{\partial p}\right)_T \to 0 \quad \text{(Maxwell's relations)}$$

3. Clausius-Clapeyron:

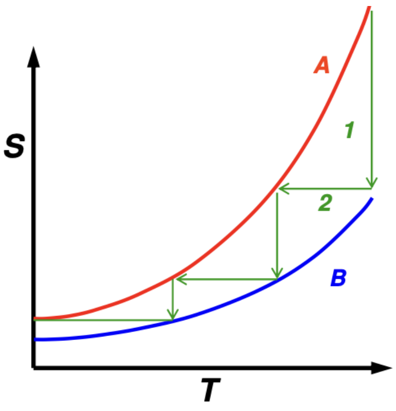
$$\frac{dp}{dT} = \frac{\Delta S}{\Delta V} \to 0$$

5.3 Absolute zero is unattainable

Unattainability of absolute zero:
It is impossible by any procedure, no matter how idealized, to reduce the temperature of any system to zero temperature in a finite number of finite operations.



Actual case: 3rd law dictates both systems have same entropy at 0K, hence infinite number of steps needed to attain 0K.



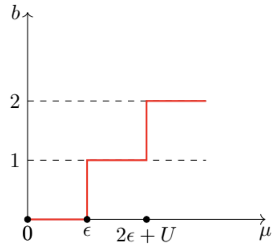
If $S_A \neq S_B$ at 0K then 0K can be reached in a finite number of steps.

5.4 Tripos Q & A

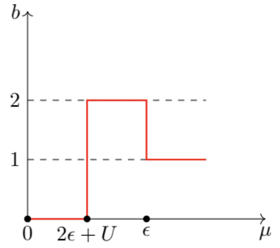
Q1: (2018 P2 A5) A defect in a material produces an electronic spin state which has energy ϵ. The state may be unoccupied, occupied by a spin up electron, occupied by a spin down electron or occupied by two electrons. The interaction energy of two electrons occupying the state is U, which can be positive or negative. **Sketch** the occupancy of the level as a function of the electronic chemical potential.

A1: The chemical potential is defined as the energy at which the probability of occupancy is half.

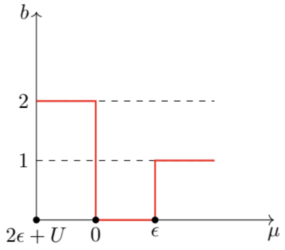
There are 4 states:
1. Unoccupied E $= 0$ occupancy $= 0$
2. One spin up E $= \epsilon$ occupancy $= 1$
3. One spin down E $= \epsilon$ occupancy $= 1$
4. Doubly occupied E $= 2\epsilon + U$ occupancy $= 2$



$U > -\epsilon$



$-2\epsilon < U < -\epsilon$



$U < -2\epsilon$

6 Thermodynamics of Radiation

Consider electromagnetic radiation in a cavity, which can be thought of as photon gas. QM: walls continually emit, absorb and reflect photons. Classical: superposition of standing EM waves.

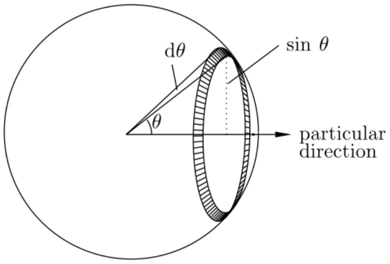
Key characteristics:
1. Number (N) of photons not fixed. Wall can freely emit or absorb photons to keep energy density constant.
2. All photons have same speed.
3. If we expand the cavity at fixed T, the total energy will increase by creating more photons, not by changing their energy density.

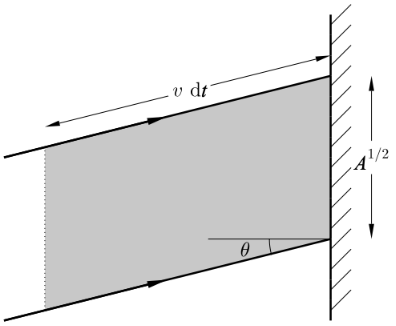
Black-body radiation: A black body is a body that perfectly absorbs radiation ($\alpha_\lambda = 1$ for all λ). Black body radiation is the radiation emitted by a black body at a particular temperature. It obeys Stefan Boltzmann Law.

6.1 Radiation pressure

Derivation

1. Number of photons per unit volume with energy range $[\epsilon, \epsilon + d\epsilon]$ is $\boldsymbol{n_\epsilon \, d\epsilon}$
2. If all molecules are equally likely to be travelling in any direction, the fraction whose trajectories lie in elemental solid angle is $\boldsymbol{\frac{d\Omega}{4\pi}}$.





Fraction of particles between θ to $\theta + d\theta$ direction:

$$\begin{aligned}\text{Fraction} &= \frac{\text{area of annulus}}{4\pi r^2} \\ &= \frac{2\pi(r\sin\theta) r d\theta}{4\pi r^2} \\ &= \frac{1}{2}\sin\theta d\theta\end{aligned}$$

Hence, number of molecules per unit volume between energy $[\epsilon, \epsilon + d\epsilon]$ travelling between $[\theta, \theta + d\theta]$ is $\boldsymbol{n_\epsilon d\epsilon \cdot \frac{1}{2}\sin\theta d\theta}$.

3. Hitting the wall: in time dt, photons in volume $\boldsymbol{c\cos\theta}$ will hit the wall of unit area.

So, the number of molecules hitting a unit area of wall per unit time is:

$$dN = c\cos\theta \cdot n_\epsilon d\epsilon \cdot \frac{1}{2}\sin\theta d\theta$$

On hitting wall, Δ(momentum of single photon) $= 2 \times \frac{\epsilon}{c}\cos\theta$ (for perfectly reflecting). For perfectly absorbing surface, the surface must be radiating the same energy as it absorbs, so expression still holds.

$$p = \frac{\Delta(\text{momentum})}{\Delta t} = \int_{\epsilon=0}^{\infty}\int_{\theta=0}^{\pi/2} \frac{2\epsilon\cos\theta}{c} \cdot c\cos\theta \cdot n_\epsilon d\epsilon \cdot \frac{1}{2}\sin\theta\, d\theta$$

$$\boxed{p = \frac{1}{3}u}$$

6.2 Kirchhoff's Law

Kirchhoff's Law: states that the ratio $\frac{e_\lambda}{\alpha_\lambda}$ is a universal function of λ and T.
In other words, 'good absorbers are good emitters' and 'bad absorbers are bad emitters'.

$\boldsymbol{\alpha_\lambda}$ **(spectral absorptivity)**: is the fraction of the incident radiation which is absorbed at wavelength λ.

$\boldsymbol{e_\lambda(\lambda, T)}$ **(spectral emissive power)**: is a function of wavelength and temperature such that $e_\lambda d\lambda$ is the power emitted per unit area by the EM radiation having wavelengths between λ and $\lambda + d\lambda$ at temperature T.

Derivation

Flux of photons hitting wall (number of photons striking per unit area per unit time):

$$\Phi = \int c\cos\theta \cdot n \cdot \frac{1}{2}\sin\theta d\theta = \frac{1}{4}nc$$

where n can be $n_\epsilon d\epsilon$ or $n_\lambda d\lambda$.

Consider power per unit area absorbed and emitted by a surface for an energy interval $d\epsilon$,

$$\text{Energy hitting surface} = \frac{1}{4}(u_\epsilon\, d\epsilon)c = \frac{1}{4}(u_\lambda\, d\lambda)c$$

$$\text{Power per unit area absorbed} = \frac{1}{4}(u_\lambda d\lambda)\, c \cdot \alpha_\lambda$$

$$\text{Power per unit area emitted} = e_\lambda d\lambda$$

At equilibrium, power absorbed and emitted are equal. Equating, we obtain Kirchhoff's Law:

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

For non-black body, $e_\lambda = \boldsymbol{\epsilon_\lambda}\, e_\lambda^{BB}$ where ϵ_λ is the emissivity.

6.3 Stefan-Boltzmann Law

$$u = AT^4$$

For power emitted per unit area from a black-body:

$$\frac{P}{A} = \sigma T^4$$

where σ is the Stefan-Boltzmann constant.

Derivation

$$dU = TdS - pdV \Rightarrow \left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial T}{\partial V}\right)_T - p$$

$$\Rightarrow u = T \underbrace{\left(\frac{\partial p}{\partial T}\right)_V}_{\substack{\text{Helmholtz's}\\ \text{Maxwell}}} - p$$

Using $p = \frac{1}{3}u$,

$$\begin{aligned} u &= \frac{1}{3}T\left(\frac{\partial u}{\partial T}\right)_V - \frac{1}{3}u \\ 4u &= T\frac{\partial u}{\partial T} \\ 4\frac{dT}{T} &= \frac{du}{u} \end{aligned}$$

Integrating, we obtain Stefan-Boltzmann Law:

$$u = AT^4$$

To relate to emission from black-body, consider energy emitted per unit area per unit time:

$$\int e_\lambda d\lambda = \int \frac{1}{4}u_\lambda c\, d\lambda = \frac{1}{4}u(T)c = \frac{1}{4}AcT^4 = \sigma T^4$$

6.4 Photon gas

The photons inside the cavity are in thermal equilibrium with the cavity walls, and form electromagnetic standing waves.

Gibbs free energy per photon/chemical potential (μ) is zero.

Derive from $G = U + pV - TS$ and get s by integrating $\frac{dq}{T}$.

Because photons are created on the wall, so do not have to take it from the reservoir. No entropy hit to reservoir for creating any photons, dN can change with no penalty. So, chemical potential is zero.

6.5 Density of states

In k-space:

$$\mathbf{k} = \frac{\pi}{L}(n_x, n_y, n_z)$$

Similar to what is being done in Condensed Matter Physics:

$$\delta N = g(k)dk = \frac{2 \cdot \frac{4\pi k^2 \delta k}{8}}{\frac{\pi^3}{L^3}} = \frac{Vk^2}{\pi^2}\delta k$$

$$g(k) = \frac{Vk^2}{\pi^2}$$

Then using $\epsilon = \hbar kc$,

$$g(\epsilon) = g(k)\frac{dk}{d\epsilon} = \frac{V\epsilon^2}{\hbar^3 c^3 \pi^2}$$

Or using $k = \frac{2\pi}{\lambda}$,

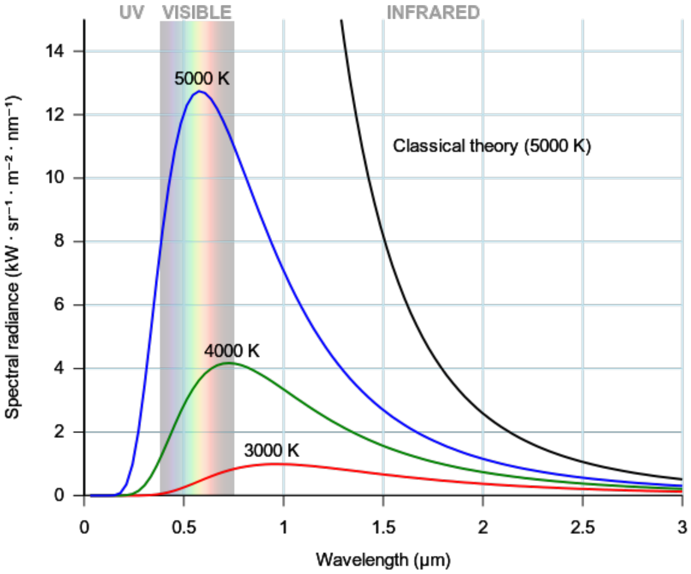
$$g(\lambda) = g(k)\frac{dk}{d\lambda} = \frac{8\pi V}{\lambda^4}$$

Or using $c = \frac{\omega}{k}$,

$$g(\omega) = g(k)\frac{dk}{d\omega} = \frac{Vk^2}{\pi^2 c}$$

6.6 Ultraviolet Catastrophe

Energy density diverges as $\lambda \to 0$,



$$u_\lambda = \frac{du}{d\lambda} = \boxed{\frac{k_B T}{V}\frac{dN}{d\lambda} = \frac{k_B T}{V} \cdot g(\lambda)} \quad \text{(Rayleign-Jeans Law)}$$

6.7 Planck's Law (revisited)

To resolve the ultraviolet catastrophe, Planck proposed that energy was transferred in quanta of $\hbar\omega$, the mean energy per mode is the same as that for the simple harmonic oscillator:

$$\bar{U} = -\frac{1}{Z}\frac{dZ}{d\beta} = \frac{\hbar\omega}{e^{\hbar\omega\beta} - 1}$$

$$g(\omega) = g(\epsilon)\frac{d\epsilon}{d\omega} = \frac{V\omega^2}{c^3\pi^2}$$

Energy density $u(\omega, T)\, d\omega$ is the energy per unit volume between ω and $\omega + d\omega$, this is the **Planck black-body distribution**:

$$\boxed{u(\omega, T) = \frac{g(\omega) \cdot \bar{U}}{V} = \frac{\hbar\omega^3}{\pi^2 c^3 \left(e^{\frac{\hbar\omega}{k_B T}} - 1\right)}}$$

Total energy density is obtained by integration w.r.t. ω. Use substitution $x = \hbar\omega\beta$:

$$\begin{aligned} u(T) &= \frac{\hbar}{\pi^2 c^3} \int_0^\infty \frac{\omega^3}{e^{\hbar\omega\beta} - 1} d\omega \\ &= \frac{\hbar}{\pi^2 c^3} \left(\frac{k_B T}{\hbar}\right)^4 \int_0^\infty \frac{x^3 dx}{e^x - 1} \end{aligned}$$

$$\Rightarrow \boxed{u(T) = \frac{k_B^4 \pi^2}{15\hbar^3 c^3} T^4 \propto T^4} \quad \textbf{(Stefan-Boltzmann Law)}$$

6.8 Wien's Displacement Law

Writing the Planck distribution in terms of wavelength, we get the **Wien's Distribution Law**:

$$\boxed{u(\lambda, T) = \frac{f(\lambda T)}{\lambda^{\mathbf{5}}}}$$

Differentiating w.r.t. λ, obtain the Wien's Displacement Law:

$$\boxed{\lambda_{max} T = \text{constant}}$$

Peak wavelength of black-body radiation goes inversely with temperature.

7 Kinetic Gas Theory

Assumptions:

1. Dilute monoatomic gas (size of particle $\ll$ average distance between them)
2. Non-interacting (no potential energy), neglect rotational and internal vibration contributions to total energy. The only energy present is the kinetic energy.

$$\frac{1}{2}mv^2 = \frac{1}{2}mv_x^2 + \frac{1}{2}mv_y^2 + \frac{1}{2}mv_z^2$$

3. Particles only exchange energy during collisions. Every particle behaves as a small system connected to heat reservoir at temperature T, where the heat reservoir is all other particles of the gas. So, we can say that the probability that a particle is in a given microstate is given by the Boltzmann factor.

7.1 Maxwell Boltzmann Distribution

Gives the distribution of speeds in an ideal gas:

$$f(v) \propto v^2 e^{-mv^2/2k_BT}$$

7.1.1 1D Velocity Distribution

$$\delta P_r = \underbrace{e^{-\frac{1}{2}mv_x^2/k_BT}}_{\text{Boltzmann factor}} \cdot \underbrace{\delta v_x/\epsilon_v}_{\substack{\text{number of states}\\\text{in the interval}}} \propto f_{1D}(v_x)\delta v_x$$

where ϵ_v is the velocity state width.

$$\Rightarrow \boxed{f_{1D}(v_x) \propto e^{-\frac{1}{2}mv_x^2/k_BT}}$$

With a probability distribution function, it is natural to use it to find expectation values of v_x and v_x^2:

$$\langle v_x \rangle = \int_{-\infty}^{\infty} v_x f_{1D}(v_x) dv_x = 0 \quad \text{(even function)}$$

Instead,

$$\langle |v_x| \rangle = 2\int_0^{\infty} ... = \sqrt{\frac{2k_BT}{\pi m}}$$

and

$$\boxed{\langle v_x^2 \rangle = \frac{k_BT}{m}}$$

Since $\frac{1}{2}mv^2 = \frac{1}{2}k_BT$ (equipartition theory).

7.1.2 3D Velocity Distribution

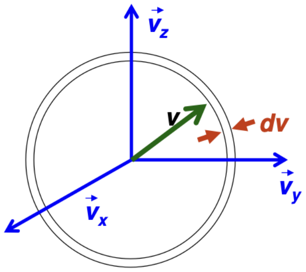
The three coordinates are independent of each other.

$$\begin{aligned} f_{3D}(v)dv &= f_{1D}(v_x)dv_x \cdot f_{1D}(v_y)dv_y \cdot f_{1D}(v_z)dv_z \\ &= Ae^{-mv^2/2k_BT}dv_xdv_ydv_z \end{aligned}$$

It is a 3D Gaussian centred at $\tilde{v} = (0, 0, 0)$

7.1.3 Speed distribution

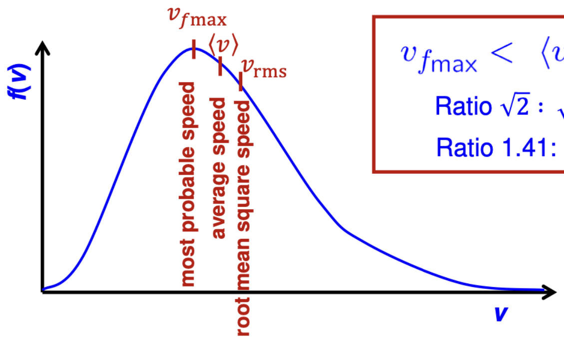
Speed is a shell in v-space. The number of speed states is proportional to v^2.



$$\boxed{f(v) \propto \boldsymbol{v^2} \underbrace{e^{-mv^2/2k_BT}}_{\text{Boltzmann factor}}}$$

It can be normalised by integrating from 0 to ∞.
You can also use it to find $\langle v \rangle$, $\langle v^2 \rangle$ and v_{max}.

Picture to remember



$v_{f\text{max}} < \langle v \rangle < v_{\text{rms}}$

Ratio $\sqrt{2} : \sqrt{8/\pi} : \sqrt{3}$

Ratio 1.41: 1.60 : 1.73

Key points:

1. Relative position of those speeds. Mean speed is in the middle.
2. If you need $\langle v \rangle$, can just use the v_{rms} since it is easier to find, but remember the % diff between them.

7.2 Pressure

7.2.1 Quick derivation

$$\langle \text{force on wall} \rangle = \text{impulse} \times \text{collision rate}$$

$$\text{Impulse } = 2mu_x$$

$$\text{Collision rate} = \frac{1}{2}Au_x(N/V)$$

where factor of 1/2 is because half the molecules within a the particular volume will be moving towards the wall.

$$\langle F \rangle = mu_x^2 \cdot A\frac{N}{V}$$

$$\langle p \rangle = mu_x^2\frac{N}{V}$$

with $u_x^2 = \frac{1}{3}\bar{u}^2$,

$$\Rightarrow pV = \frac{1}{3}Nm\bar{u}^2 = nRT \quad \text{(ideal gas equation)}$$

For monoatomic gas, the internal energy is stored as translational kinetic energy:

$$\boxed{U = \frac{1}{2}m\bar{u}^2 \cdot N = \frac{3}{2}nRT}$$

7.2.2 More formal derivation

dN is the number of particles hitting a unit area of wall in unit time and having speeds between v and $v + dv$ travelling at angles θ and $\theta + d\theta$:

$$\boxed{dN = v\cos\theta \cdot nf(v)dv \cdot \frac{1}{2}\sin\theta d\theta}$$

$$p = \text{(momentum change)} \times dN$$

$$\begin{aligned} p &= \int_0^\infty \int_0^{\frac{\pi}{2}} (2mv\cos\theta) \cdot \left(v\cos\theta \cdot nf(v)dv \cdot \frac{1}{2}\sin\theta d\theta\right) \\ &= ... \\ p &= \boxed{\frac{1}{3}mn\langle v^2 \rangle} \end{aligned}$$

From $\frac{1}{2}m\langle v^2 \rangle = \frac{3}{2}k_BT$, we can obtain:

$$\text{Ideal gas equation: } \boxed{pV = Nk_BT} \quad \text{or} \quad p = nk_BT$$

7.2.3 Dalton's Law

In mixtures of gases, the total pressure is given by sum of pressure caused by separate components.

$$\boxed{p = \sum_i p_i = k_B T \sum_i n_i}$$

where p_i is the partial pressure of the i^{th} species and n_i is the number density of the i^{th} species.

7.3 Effusion and flux

Effusion: a process by which a gas escapes from a hole so small that a molecule or atom can pass without colliding with another.

$$\boxed{\text{rate of effusion} \propto nAv_{rms} \propto nA\sqrt{\frac{T}{m}}}$$

Flux: number of molecules **per unit area per second**.

$$\Phi = \frac{\text{number of molecules}}{\text{area} \times \text{time}}$$

$$\Phi = \int_0^\infty \int_0^{\frac{\pi}{2}} v\cos\theta \cdot nf(v)dv \cdot \frac{1}{2}\sin\theta d\theta = \boxed{\frac{1}{4}n\langle v\rangle}$$

Also using $p = nk_BT$ and expression for average speed $\langle v\rangle = \sqrt{\frac{8k_Bt}{\pi m}}$,

$$\Phi = \frac{p}{\sqrt{2\pi m k_B T}}$$

Effusion rate

$$\boxed{\text{Effusion rate} = \Phi \times A}$$

which counts the number of molecules hitting a hole of cross-sectional area A.

Note: Effusing molecules do not have Maxwellian speed distribution.

$$dN = Av\cos\theta dt \cdot nf(v)dv \cdot \frac{1}{2}\sin\theta d\theta$$

where $f(v) \propto v^2 e^{-mv^2/2k_BT}$

Thus, the distribution of molecules effusing through a hole is proportional to:

$$\boxed{\boldsymbol{v^3}}\ e^{-mv^2/2k_BT}$$

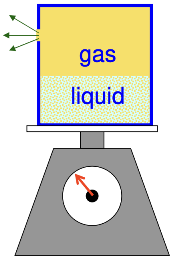
7.3.1 Graham's law

At equal pressure, the effusion speed of different gases is inverse proportional to the square root of their densities.
Used to separate isotopes in gas.

7.3.2 Measuring vapour pressure

The effusion rate at equilibrium is:

$$\Phi A = \frac{pA}{\sqrt{2\pi m k_B T}}$$



Measure rate of change of mass:

$$\boxed{\frac{dM}{dt} = -m\Phi A}$$

which can be rearranged to obtain an expression for p.

7.4 Mean free path

$$\lambda = \langle v\rangle \tau = \frac{\langle v\rangle}{n\sigma\langle v_r\rangle} = \frac{1}{\sqrt{2}n\sigma} = \frac{k_B T}{\sqrt{2}p\sigma}$$

where $\langle v_r\rangle$ is the mean relative speed of the molecules in the gas. The last equality is obtained via ideal gas law, and $\langle v_r\rangle = \sqrt{2}\langle v\rangle$.

Quick derivation:
A volume of diameter $d = 2a$ defines a cylinder of volume $v = \pi d^2 \lambda$,

$$pV = Nk_B T \Rightarrow pN\pi d^2\lambda = Nk_B T$$

$$\boxed{\lambda = \frac{k_B T}{\pi p d^2}}$$

Factor of $\sqrt{2} \to \pi$.

7.4.1 Ingredient 1: mean collision time

Consider a freeze frame which only one particle is moving at speed v. If the particle has **collision cross-section**, σ, then in time δt, it will sweep out volume of $\boldsymbol{\sigma v \delta t}$. If another molecule happen to lie inside this volume, there will be a collision.

$$\boxed{\text{probability of hitting a molecule} = n\sigma v\,\delta t}$$

Let $P(t)$ be probability that a molecule survives without colliding up to a time t.

$$P(t+\delta t) = P(t) + \frac{dP}{dt}\delta t$$

So probability that molecule survives without collisions until time $t+\delta t$ given that it survived until time t is:

$$\frac{P(t+\delta t)}{P(t)} = 1 + \frac{1}{P(t)}\frac{dP}{dt}\delta t = 1 - n\sigma v\delta t$$

$$\Rightarrow \frac{dP}{dt} = -nv\sigma$$

So,

$$\boxed{P(t) = e^{-n\sigma v t}}$$

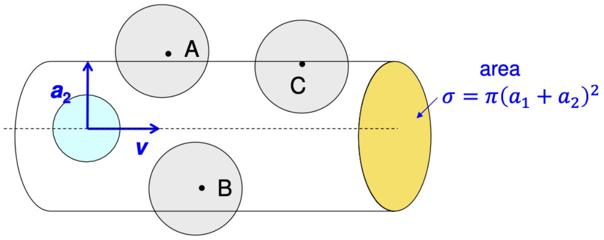
Probability fo molecule surviving until time t and colliding in the next δt is:

$$\text{Probability of finally colliding} = e^{-n\sigma v t} n\sigma v dt$$

Now, we can find the average time between collision:

$$\boxed{\tau = \int_0^\infty t e^{-n\sigma v t} n\sigma v dt = ... = \frac{1}{n\sigma v}}$$

7.4.2 Ingredient 2: collision cross-section



A collision will take place when the centres of the larger molecule fall within a tube of radius $a_1 + a_2$. So, collision cross-section is:

$$\boxed{\sigma = \pi(a_1 + a_2)^2}$$

7.4.3 Ingredient 3: mean relative speed

We have assumed so far only a single particle moving in an array of fixed particles. In reality, other particles are moving as well. So you do an average of the vector sum of velocities.

$$\vec{v}_r = \vec{v}_1 - \vec{v}_2$$

$$v_r^2 = v_1^2 + v_2^2 - 2\vec{v}_1 \cdot \vec{v}_2$$

Averaging over all v_1 and v_2:

$$\langle v_r^2 \rangle = \langle v_1^2 \rangle + \langle v_2^2 \rangle = 2\langle v \rangle$$

$$\langle v_r \rangle \approx \sqrt{2}\langle v \rangle$$

7.5 Mean kinetic energy of molecules hitting wall

$$\boxed{\text{Mean KE per particle at wall} = \frac{\text{Energy flux}}{\text{Particle flux}} = 2k_BT}$$

Derivation

$$\begin{aligned}\text{Energy flux } &= \int_0^\infty \int_0^{\frac{\pi}{2}} (\frac{1}{2}mv^2) \cdot \left(v\cos\theta \cdot nf(v)dv \cdot \frac{1}{2}\sin\theta d\theta \right) \\ &= \frac{1}{8}mn\langle v^3 \rangle\end{aligned}$$

$$\text{Particle flux } = \int_0^\infty \int_0^{\frac{\pi}{2}} v\cos\theta \cdot nf(v)dv \cdot \frac{1}{2}\sin\theta d\theta$$

Do the ratio of energy flux over particle flux, do integration by parts, and something will cancel out:

$$\langle v^3 \rangle = ... = \frac{4k_BT}{m}\langle v \rangle$$

So,

$$\langle KE \rangle = \frac{\frac{1}{8}mn \cdot \frac{4k_BT}{m}\langle v \rangle}{\frac{1}{4}n\langle v \rangle} = 2k_BT$$

7.6 3D v.s. 2D

<u>3D</u>
Flux:

$$\Phi = \frac{1}{4}n\langle v \rangle$$

<u>2D</u>

$$\Phi = \frac{1}{\pi}n\langle v \rangle$$

Q: Two identical large vessels containing argon initially at temperature T_0 and pressure p_0 are connected by a hole of diameter much less than the mean free path. One vessel is then heated to T_1 while the other remains at T_0. Under steady-state conditions, what pressure difference is then established between the two vessels?
A:

1. Equal mass flow:
$$\frac{1}{4}n_A\bar{v}_A = \frac{1}{4}n_B\bar{v}_B$$

2. Ideal gas equation
$$p_A = n_A k_B T_A \quad \text{and} \quad p_B = n_B k_B T_B \quad \text{and} \quad p_0 = n_0 k_B T_0$$

3. Conservation of particles:
$$n_A + n_B = 2n_0$$

$$\begin{aligned}
\Delta p &= p_B - p_A \\
&= n_B k_B T_B - n_A k_B T_A \\
&= n_B k_B T_B \left(1 - \frac{n_A T_A}{n_B T_B}\right) \\
&= n_B k_B T_B \left(1 - \frac{\bar{v}_B T_A}{\bar{v}_A T_B}\right) \\
&= n_B k_B T_B \left(1 - \sqrt{\frac{T_A}{T_B}}\right) \\
&= n_B k_B T_0 \left(1 - \sqrt{\frac{T_1}{T_0}}\right)
\end{aligned}$$

And

$$\begin{aligned}
n_A + n_B &= 2n_0 \\
n_B\left(\frac{\bar{v}_B}{\bar{v}_A} + 1\right) &= 2\frac{p_0}{k_B T_0} \\
\Rightarrow n_B k_B T_0 &= \frac{2p_0}{\sqrt{\frac{T_B}{T_A}} + 1}
\end{aligned}$$

Hence,

$$\Delta p = 2p_0 \frac{1 - \sqrt{\frac{T_1}{T_0}}}{1 + \sqrt{\frac{T_1}{T_0}}}$$

8 Transport Phenomena

8.1 Momentum transport - Viscosity

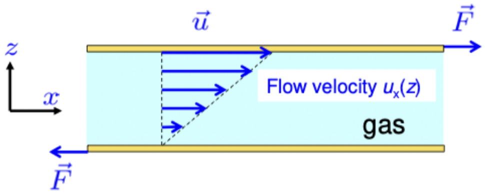
Viscosity is a measure of the resistance of the fluid to be deformed by shear stress τ_{ij}.

$$\boxed{\tau_{xz} = \frac{F}{A} = \eta \frac{d\langle v_x \rangle}{dz}}$$

where units of η is $Pas = Nm^{-2}s$.

Molecules travelling in the $+z$ direction move from a layer in which $\langle u_x \rangle$ is smaller to one in which $\langle u_x \rangle$ is larger, and hence they transfer net momentum to that layer in the $-x$ direction. Hence, the shear stress τ_{xz} is equal to the transverse momentum transported across each square metre per second, which is the flux of momentum:

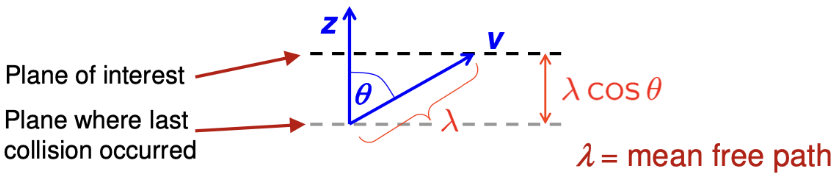
$$\text{Momentum flux: } \sqcap_z = -\eta \frac{d\langle v_x \rangle}{dz}$$



Top plate is transferring momentum *F* per second to the gas, across which it diffuses and arrives on bottom plate.

Boundary conditions:
1. Top plate: $\langle v_x \rangle = \vec{u}$
2. Bottom plate: $\langle v_x \rangle = 0$

Deriving viscosity of gas



$$dN = v\cos\theta \cdot nf(v)dv \cdot \frac{1}{2}\sin\theta d\theta$$

Find the mean extra momentum per molecule:

$$p = -m\left(\frac{\partial\langle u_x \rangle}{\partial z}\right)\lambda\cos\theta$$

Hence, the net momentum brought to the plane per unit area is:

$$\begin{aligned}\sqcap_z &= \int_0^{\infty}\int_0^{\pi} v\cos\theta \cdot nf(v)dv \cdot \frac{1}{2}\sin\theta d\theta \cdot m\left(-\frac{\partial\langle u_x\rangle}{\partial z}\right)\lambda\cos\theta \\ &= \ldots \\ &= -\underbrace{\frac{1}{3}nm\lambda\langle v\rangle}_{\text{viscosity}} \cdot \frac{\partial\langle u_x\rangle}{\partial z}\end{aligned}$$

Finally, we have the expression for dynamic viscosity:

$$\boxed{\eta = \frac{1}{3}mn\lambda\langle v\rangle = \frac{1}{3}\rho\langle v\rangle\lambda}$$

1. **Independent of pressure** since $\lambda \propto n^{-1}$
2. $\boldsymbol{\eta \propto \sqrt{T}}$ since λn is constant and $\langle v\rangle \propto \sqrt{T}$.
3. $\boldsymbol{\eta \propto d^{-2}\sqrt{m}}$

Substituting expression for $\lambda \approx \frac{1}{\sqrt{2}n\sigma}$ and $\langle v\rangle = \sqrt{\frac{8k_BT}{\pi m}}$, we have in full:

$$\eta = \frac{2}{3\sigma}\sqrt{\frac{mk_BT}{\pi}}$$

Many assumptions are made:

$$\boxed{L \gg \lambda \gg d}$$

1. $\lambda \gg d$ (pressure not too high): so that we can neglect collisions involving more than two particles
2. $\lambda \ll L$ (pressure not too low): so that molecules mainly collide with each other and not with the container walls.
3. Factor of $\frac{1}{3}$ not correct. Model assumed uniform velocity distribution, but velocity distribution is different in different layers (because of the shear stress applied).

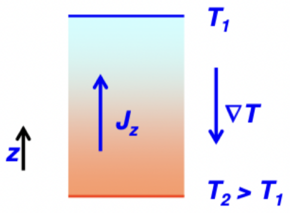
8.2 Energy transport - Thermal conductivity

Heat is "energy in transit". It quantifies the transfer of energy in response to a temperature gradient.

Define heat flux, **J** which flows against the temperature gradient from hot to cold (heat flows downhill):

$$\boxed{J_z - \kappa\left(\frac{\partial T}{\partial z}\right)} \quad \text{or} \quad \mathbf{J} = -\kappa\nabla T$$

Units: $Js^{-1}m^{-2}$ or Wm^{-2}.



Deriving thermal conductivity

$$dN = v\cos\theta \cdot nf(v)dv \cdot \frac{1}{2}\sin\theta d\theta$$

Find the excess heat brought by a molecule to a plane perpendicular to z:

$$H = C_{\text{molecule}} \times \Delta T = C_{\text{molecule}} \left(\frac{\partial T}{\partial z}\right) \lambda \cos\theta$$

Hence, the total thermal energy transported per unit area per unit time is (heat flux):

$$\begin{aligned} J_z &= \int_0^\infty \int_0^\pi v\cos\theta \cdot nf(v)dv \cdot \frac{1}{2}\sin\theta d\theta \cdot \left(-C_{\text{molecule}}\left(\frac{\partial T}{\partial z}\right)\lambda\cos\theta\right) \\ &= \ldots \\ &= -\underbrace{\frac{1}{3}nC_{\text{molecule}}\lambda\langle v\rangle}_{\text{conductivity}} \cdot \frac{\partial\langle T\rangle}{\partial z} \end{aligned}$$

where $C_V = nC_{\text{molecule}}$ and it is the heat capacity per unit volume.

Finally, we have the expression for conductivity:

$$\boxed{\kappa = \frac{1}{3}C_V\langle v\rangle\lambda}$$

"One-third C c l".

1. κ is **independent of pressure**.
2. $\boldsymbol{\kappa \propto \sqrt{T}}$
3. Using $\lambda \approx \frac{1}{\sqrt{2}n\sigma}$ and $\langle v\rangle = \sqrt{\frac{8k_BT}{\pi m}}$:

$$\kappa = \frac{2}{3\sigma}C_{\text{molecule}}\sqrt{\frac{k_BT}{\pi m}}$$

So, $\boldsymbol{\kappa \propto \frac{1}{d^2\sqrt{m}}}$

So, (remembering this kind of ratios is IMPT)

$$\boxed{\frac{\kappa}{\eta} = \frac{C_{\text{molecule}}}{m} = C_{V,s}}$$

where $C_{V,s}$ is the specific heat capacity per unit volume.

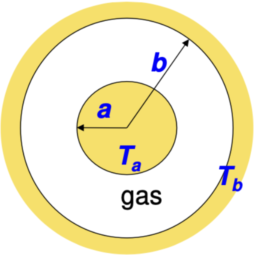
8.2.1 Refining the formula for thermal conductivity

After accounting for heat stored in translational, rotational and vibrational degrees of freedom:

$$\text{Eucken's formula: } \kappa = \frac{1}{4}(9\gamma - 5)\eta C_{V,s}$$

8.2.2 Measuring heat conductivity

Use coaxial cylinder method.



- Gas of interest is filled between 2 coaxial cylinders.
- Temperature of outer cylinder is fixed to T_b by temperature bath.
- Inner cylinder is heated at rate Q per unit length (Wm^{-1}) until it reaches T_a.

$$Q = 2\pi r J_z = 2\pi r \left(-\kappa \frac{\partial T}{\partial r}\right)$$

Integration gives an expression for κ:

$$Q \int_a^b \frac{dr}{r} = -2\pi\kappa \int_{T_a}^{T_b} dT$$

8.3 Particle transport - Diffusion

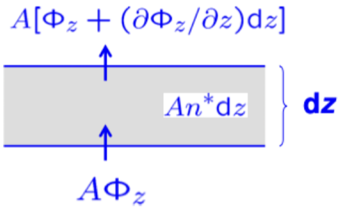
Fick's Law gives the flux of labelled molecules in the z-direction:

$$\boxed{\Phi_z = -D\left(\frac{\partial n^*}{\partial z}\right)} \quad \text{or} \quad \mathbf{\Phi} = -D\boldsymbol{\nabla} n^*$$

where $n^*(z)$ is the number density of labelled molecules and D is the coefficient of self-diffusion. Units of Φ_z is $m^{-2}s^{-1}$.

Deriving self diffusing coefficient

Consider a thin layer of gas of thickness dz and area A.



Flux in is $A\Phi_z$. Flux out is $A[\Phi_z + \frac{\partial \Phi_z}{\partial z} dz]$. The net flux is equal to the time-dependent changes in the number of labelled particles inside the layer:

$$\frac{\partial}{\partial t}(n^* A dz) = -A\frac{\partial \Phi_z}{\partial z} dz$$

Hence, the excess labelled molecules hitting per unit area per unit time is:

$$\begin{aligned}\Phi_z &= \int_0^\infty \int_0^\pi v\cos\theta \cdot nf(v)dv \cdot \frac{1}{2}\sin\theta d\theta \cdot \left(-\frac{\partial n^*}{\partial z}\lambda\cos\theta\right)\\ &= \ldots\\ &= \underbrace{\frac{1}{3}\lambda\langle v\rangle}_{\substack{\text{diffusing}\\ \text{coefficient}}} \frac{\partial n^*}{\partial z}\end{aligned}$$

Finally, we have the expression for the diffusing coefficient:

$$\boxed{D = \frac{1}{3}\langle v\rangle\lambda} = \frac{2}{3n\sigma}\sqrt{\frac{k_B T}{\pi m}}$$

We see that:
1. $\boldsymbol{D \propto p^{-1}}$
2. $\boldsymbol{D \propto T^{3/2}}$
3. $\boldsymbol{Dmn = D\rho = \eta}$
4. $\boldsymbol{D \propto \frac{1}{d^2\sqrt{m}}}$

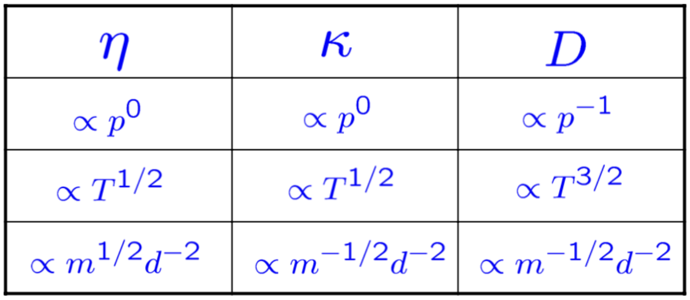
For mixture of two different type of molecules of mass m_1 and m_2, diameter d_1 and d_2:
1. Replace collision cross section, σ with:

$$\sigma = \pi\left[\frac{d_1 + d_2}{2}\right]^2$$

2. Replace m with reduced mass:

$$\mu = \frac{2m_1 m_2}{m_1 + m_2}$$

Summary of dependencies



η	κ	D
$\propto p^0$	$\propto p^0$	$\propto p^{-1}$
$\propto T^{1/2}$	$\propto T^{1/2}$	$\propto T^{3/2}$
$\propto m^{1/2}d^{-2}$	$\propto m^{-1/2}d^{-2}$	$\propto m^{-1/2}d^{-2}$

Applications

1. Large electricity generators have rotating electromagnet that is cooled by hydrogen gas.
    - Hydrogen: light mass and higher heat capacity compared with noble gas → excellent thermal conductivity. Also has low viscosity.
    - Both are independent of pressure → so one can increase the pressure to increase the thermal capacity of the gas.
    - However, H_2 has to be quite pure (97%).
2. Halogen light bulbs filled with high pressure Xe gas
    - Why high pressure: at such high temperatures, the tungsten atoms would sublime and escape. Liquids would boil then its vapour pressure exceeds the ambient pressure. So high pressure of surrounding halogen suppress the escape of tungsten atoms.
    - Xenon: high density, huge atoms → reduce diffusion rate of Tungsten → retain good lifetime
    - Also, low heat capacity, slow atomic velocities and short mean free path of Xe → low thermal conductivity → reduce conductive heat loss from the bulb.

8.4 Thermal diffusion equation

$$\text{heat } \mathbf{J} = -\kappa \nabla T \quad , \quad \text{particle } \mathbf{\Phi} = -D \nabla n^* \quad , \quad \text{current } \boldsymbol{J}_e = -\sigma \nabla \phi$$

Feynman: the same equation have the same solution.

By conservation of particles and using divergence theorem, we obtain the **3D diffusion equation**:

$$\boxed{\frac{\partial n^*}{\partial t} = D \nabla^2 n^*}$$

Derivation:
The total number of labelled particles that flow out of a closed surface must be balanced by the rate of decrease of labelled particles inside the volume V which is surrounded by S:

$$\int_S \mathbf{\Phi} \cdot d\mathbf{S} = -\frac{\partial}{\partial t} \int_V n^* dV$$

$$\text{Applying divergence theorem: } \int_V \nabla \cdot \mathbf{\Phi} \, dV = -\frac{\partial}{\partial t} \int_V n^* dV$$

$$\nabla \cdot \mathbf{\Phi} = -\frac{\partial n^*}{\partial t}$$

$$\Rightarrow \frac{\partial n^*}{\partial t} = D \nabla^2 n^*$$

Thermal diffusion equation

Derivation:
Consider a volume V. The total heat flow out of V through a closed surface S is equal to rate of heat loss by body:

$$\int_S \mathbf{J} \cdot d\mathbf{S} = -\int_V C_V \frac{\partial T}{\partial t} dV = \int_V \nabla \cdot \mathbf{J} \, dV$$

where C is the heat capacity per unit volume.

$$\Rightarrow \nabla \cdot \mathbf{J} = -C_V \frac{\partial T}{\partial t}$$

Knowing that $\mathbf{J} = -\kappa \nabla T$,

$$\boxed{\frac{\partial T}{\partial t} = D \nabla^2 T}$$

where $\boxed{D = \frac{\kappa}{C_V}}$

Solving thermal diffusion equation

Step 1: consider separable solution:

$$T(\mathbf{r},t) = R(\mathbf{r})\tau(t)$$

Thermal diffusion equation becomes:

$$\frac{\tau'(t)}{\tau(t)} = \frac{D\nabla^2 R(\mathbf{r})}{R(\mathbf{r})} = -\alpha$$

Step 2: Solve.
For the t dependence part:

$$\ln(\tau) = -\alpha t + C_1 \Rightarrow \tau(t) = \boxed{Ae^{-\alpha t}}$$

For the spatial part:

$$\nabla^2 R(\mathbf{r}) = -\frac{\alpha}{D}R(\mathbf{r})$$

Try solution $R_k(\mathbf{r}) = R_{0,k}e^{i\mathbf{k}\cdot\mathbf{r}}$, so:

$$-k^2 R_k(\mathbf{r}) = -\frac{\alpha}{D}R_k(\mathbf{r}) \Rightarrow \boxed{\alpha = k^2 D}$$

Step 3: Form general solution by linear combinations

$$\boxed{T(\mathbf{r},t) = \sum_k R_{0,k}e^{i\mathbf{k}\cdot\mathbf{r}}\underbrace{e^{-k^2 Dt}}_{\text{decay}}}$$

or Fourier transform could be used by converting summation to integral:

$$T(\mathbf{r},t) = \int R_0(\mathbf{k})e^{i\mathbf{k}\cdot\mathbf{r}}e^{-k^2 Dt}d\mathbf{k}$$

where $R_0(\mathbf{k})$ is the Fourier Transform of the initial temperature profile:

$$R_0\mathbf{k} = \frac{1}{(2\pi)^n}\int T(\mathbf{r},0)e^{-i\mathbf{k}\cdot\mathbf{r}}d\mathbf{k}$$

Step 4: investigations.

1. Different Fourier components have different time dependence, short k ones decay faster. Characteristic time:

$$\boxed{\tau = \frac{1}{k^2 D} = \frac{\lambda^2}{4\pi^2 D}}$$

   Interpretation: for long time, **longest wavelength** dominate as they have the longest time constants. The short ones would have decayed away. For example, time for center of egg to reach temperature is related to square of its radius.

2. Boundary condition problem: relaxation of temperature profile

   (a) Oscillating boundary condition

Look for periodic solutions in the temporal part:

$$-i\omega = -Dk^2 \Rightarrow k^2 = \frac{i\omega}{D}$$

$$\boxed{\therefore k = \pm(1+i)\sqrt{\frac{\omega}{2D}}}$$

Avoiding divergence as $x \to \infty$,

$$\begin{aligned} T(x,t) &= \sum_{\omega} A(\omega) e^{-i\omega t} e^{\left((i-1)\sqrt{\frac{\omega}{2D}}\right)x} \\ &= \sum_{\omega} A(\omega) e^{-x/\delta} e^{-i(\omega t - x/\delta)} \end{aligned}$$

Then substitute the relevant boundary conditions to solve.
Relevant quantities:

$$\boxed{\text{Skin depth: } \delta = \sqrt{\frac{2D}{\omega}}}$$

Key features:
1. T falls off exponentially as $e^{-x/\delta}$
2. There is a phase shift of $\frac{x}{\delta}$ rads in the oscillations.
3. $\delta \propto \omega^{-1/2}$ so faster oscillations fall off faster.

Solving steady state (Laplace equation)

No time dependence:

$$\nabla^2 T = 0$$

Spherical symmetry:

$$\nabla^2 T = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 \frac{\partial T}{\partial r}\right) + \frac{1}{r^2 \sin\theta}\frac{\partial}{\partial \theta}\left(\sin\theta \frac{\partial T}{\partial \theta}\right) + \frac{1}{r^2 \sin^2\theta}\frac{\partial^2 T}{\partial \phi^2} = 0$$

For a spherical object that conducts heat isotropically in all directions, so T is only a function of r:

$$\nabla^2 T = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 \frac{\partial T}{\partial r}\right)$$

General solution:

$$T = A + \frac{B}{r}$$

Problem solving tips

1. To find minimum temperature, find stationary points (differentiate) instead of observing the cos since there is an exponential envelope.

~ End of Notes ~