In normal stars, thermal effects dominate.

At the microscopic level, this amounts to fluctuations in electron energy levels in which e^- can freely move up or down.

As the matter is highly compressed, electrons get closer.

↘ Cooling

The resulting white dwarf does not house any thermonuclear reaction. It is not hot enough compared to the sun's core. Despite this inferior temperature, the white dwarf can still hold itself against gravity.

The internal energy of the white dwarf comes not from thermal pressure but electron degeneracy pressure!

The insides of the White dwarf consists of matter in the Plasma State. The electrons do not interact with nuclei due to high T. They are ionised.

In the quantum model, the insides can be seen as a gas of free electrons.

Particle in a Box Model

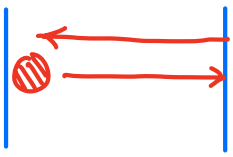
Small particles have wave-like properties and can thus be described by Wave Equations.

↘ De Broglie Hypothesis.

From the Wave equations, we can find the energy. ⟶ Energy of Standing Waves.

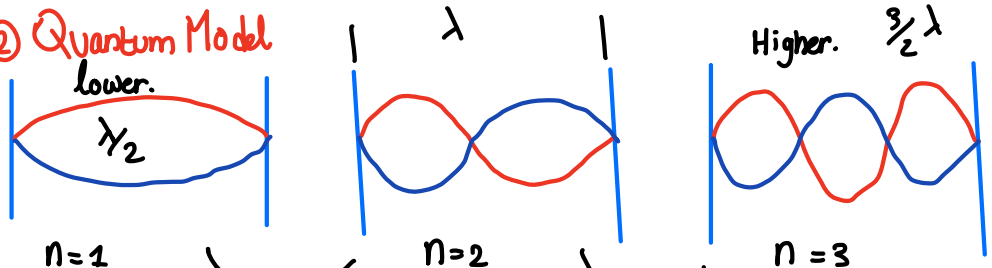
Models

① Newtonian Model



To/fro motion

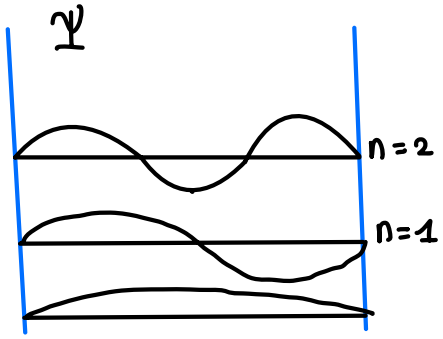
② Quantum Model



Different Energy levels.

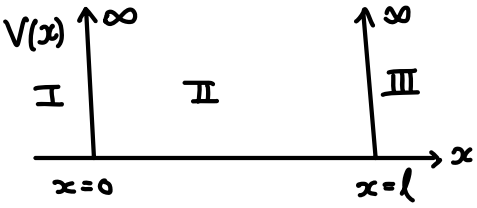
More wavelength ⇒ Higher Energy

When confined in a box, the electrons are allowed only certain energy levels



Ψ^2 corresponds to the probability of finding a particle within a certain space.

Particle in a 1D box. : Solve time independant S.E for a particle in a 1D box.



Classical Mechanics applies only to Macroscopic particles. [Originally, when Clausius derived entropy, it was only a mathematical object which appeared to satisfy certain conditions.] To better understand entropy, we need to look at "microscopic mechanics": Quantum Mechanics.

↳ Quanta - Small.

Schrödinger Equation. (Time independant)

$H\psi = E\psi$ ← Wave function.

↑ Hamiltonian (T+V)

↖ Energy Eigen Value

$$E\psi = -\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + V(x)\psi$$

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} = (E-\infty)\psi$$

↘ $-\infty$

Neglecting E in comparison to ∞,

$$\frac{d^2\psi}{dx^2} = \infty\psi \Rightarrow \psi = \frac{1}{\infty}\frac{d^2\psi}{dx^2} \Rightarrow \psi_I, \psi_{III} = 0 \text{ (Outside box)}$$

For region II, x between 0 & l, V = 0

$$\Rightarrow -\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} = (E-0)\psi_{II}$$

$$\frac{d^2\psi}{dx^2} = -\frac{2m}{\hbar^2}E\psi_{II}$$

$$\boxed{\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2}E\psi_{II} = 0}$$

Solving ODE,

$$\psi_{II} = C_1 e^{i(2mE)^{1/2}x/\hbar} + C_2 e^{-i(2mE)^{1/2}x/\hbar}$$

$$\text{let } \theta = \frac{(2mE)^{1/2}x}{\hbar} \Rightarrow \psi_{II} = C_1 e^{i\theta} + C_2 e^{-i\theta}$$

$$e^{i\theta} = \cos\theta + i\sin\theta \quad e^{-i\theta} = \cos\theta - i\sin\theta$$

$$\Rightarrow C_1\cos\theta + iC_1\sin\theta + C_2\cos\theta - iC_2\sin\theta$$
$$= (C_1+C_2)\cos\theta + (iC_1 - iC_2)\sin\theta$$

$= A\cos\theta + B\sin\theta$ (A & B are new Constants)

$$\psi_{II} = A\cos\left[\hbar^{-1}(2mE)^{1/2}x\right] + B\sin\left[\hbar^{-1}(2mE)^{1/2}x\right]$$

Find A & B by applying boundry conditions.

We assume function is continuous.

If ψ is to be continuous at the point $x = 0$, then ψ_1 and ψ_2 must approach the same value at $x = 0$.

$$\lim_{x\to 0}\psi_1 = \lim_{x\to 0}\psi_2$$

$$0 = \lim_{x\to 0}\left[\left[A\cos\left[\hbar^{-1}(2mE)^{1/2}x\right] + B\sin\left[\hbar^{-1}(2mE)^{1/2}x\right]\right]\right]$$

$$0 = A$$ How?!

$\Rightarrow$ With $A=0$ Eqn becomes

$$\psi_{II} = B\sin\left[\left(\frac{2\pi}{h}\right)(2mE)^{1/2}x\right]$$

x can be equal to l.

Applying continuity condition at $x = l$, we get (0 at l and l is a Sdn)

$$B\sin\left[\left(\frac{2\pi}{h}\right)(2mE)^{1/2}l\right] = 0$$

$\sin = 0$ at $0, \pm\pi, \pm 2\pi, \ldots, \pm n\pi$

$$\Rightarrow \frac{2\pi}{h}(2mE)^{1/2}l = \pm n\pi$$

$n = 0$ corresponds to $E = 0 \ldots n = 0$ is not allowed.

$$\Rightarrow E = \frac{n^2h^2}{8ml^2} \qquad n = 1, 2, 3, \ldots$$

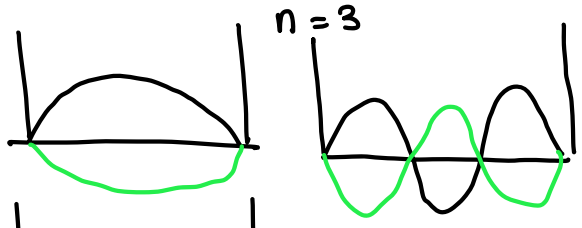
These Satisfy cont. at $x = l$

l: length of the box

Each harmonics

$$\psi_i = \left(\frac{2}{l}\right)^{1/2}\sin\left(\frac{n_i\pi x}{l}\right)$$

Expressed in terms of E-levels.



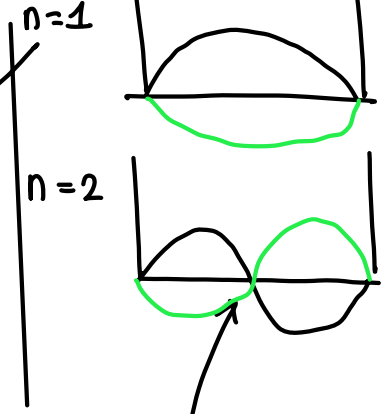
More maths

$$\psi_{II} = \left(\frac{2}{l}\right)^{1/2}\sin\left(\frac{n\pi x}{l}\right) \qquad n = 1, 2, 3, \ldots$$

Argument of the term

n: Quantum number.

(Stationary State Wave eqn)



As $n \to \infty$ $\Rightarrow$ Classic Uniform P. distribution.

Tunneling.

Eigenvalues

Operators...

How can $P = 0$ here.
↳ The particle "jumps" in the box

Two identical particles in a box.

In the classical case, the particles can be labelled but in Q.M, we can only predict the prob. that the particle is in region dx, about x_1, and same for x_2. This affects both the allowed energies and the wave function.

Classical Energy in box is: $\frac{p_1^2}{2m} + \frac{p_2^2}{2m} = E$

Energy is sum of independant energies : $E = \varepsilon_1 + \varepsilon_2$

Why not independant?
↳ The particles affect each other.

The wave function will depend on the positions x_1 and x_2 : $\psi(x_1, x_2)$

↳ for the particles.

↳ Wavefunction for one particle or the system of 2?

↳ // We are looking at total Energy.

We have 4 B.C.

$$\left.\begin{aligned} \psi(0, x_2) &= 0 \\ \psi(x_1, 0) &= 0 \\ \psi(L, x_2) &= 0 \\ \psi(x_1, L) &= 0 \end{aligned}\right\} P(\text{particle present at extremities (nodes)} = 0)$$

Allowed values of ε_1 & ε_2. $\varepsilon_{n_1} = \frac{\hbar^2 \pi^2}{2mL^2} n_1^2 \qquad \varepsilon_{n_2} = \frac{\hbar^2 \pi^2}{2mL^2} n_2^2$

$\Rightarrow$ Allowed values of the total energy

$= E_{n_1 n_2} = \frac{\hbar^2 \pi^2}{2mL^2}(n_1^2 + n_2^2)$

Each particle get an independant integer for enumerating the energy levels n_1 & n_2.
(The particles 1 & 2 are in their respective E. level n_1 & n_2)

Like for a single particle in a 2D box, we might expect the wave function to be a product.

$$\psi_{n_1 n_2}(x_1, x_2) = \psi_{n_1}(x_1)\,\psi_{n_2}(x_2)$$

Property of Sys. at x_1 = $P(A \text{ at } x_1)$ consists of A & B $\times$ $P(B \text{ at } x_1)$ AND.

$$\left(\psi_n(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right)\right) - \text{for 1 particle.}$$

n_1 : E level for particle 1
x_1 : Posn of particle 1

Problems | If the particles are identical, how do we know which to assign E-level n_1; could be either particle 1 or 2. Total Energy would not change.

The Product above specifies assigning n_1 to particle 1 and so on...

The second problem is that the product says $\psi_{n_1 n_2}(x,x) \neq 0$. Particles can sit onto each other!

Eigen / Hamil.
Gas in a 1D box
Boltzmann-Distribution
Fermi-Dirac Dist..
Entropy...
φ...

1st Problem

We include the 2 possible product form.

ie. $\psi_{n_1}(x_1)\psi_{n_2}(x_2)$ $\psi_{n_2}(x_1)\psi_{n_1}(x_2)$

We can put them together to get

$$\psi_{n_1 n_2}(x_1, x_2) = \frac{1}{\sqrt{2}} \left[\psi_{n_1}(x_1)\psi_{n_2}(x_2) \pm \psi_{n_2}(x_1)\psi_{n_1}(x_2) \right]$$

↑ Normalizing factor.

first form: $\psi_{n_1 n_2}(x_1, x_2) = \frac{1}{\sqrt{2}} \left[\psi_{n_1}(x_1)\psi_{n_2}(x_2) + \psi_{n_2}(x_1)\psi_{n_1}(x_2) \right]$

Second form: $\psi_{n_1 n_2}(x_1, x_2) = \frac{1}{\sqrt{2}} \left[\psi_{n_1}(x_1)\psi_{n_2}(x_2) - \psi_{n_2}(x_1)\psi_{n_1}(x_2) \right]$

The 2 particles cannot be in same space. ←

for $\psi_{n_1 n_2}(x,x)$ we have $\frac{1}{\sqrt{2}} \left[\psi_{n_1}(x)\psi_{n_2}(x) - \psi_{n_2}(x)\psi_{n_1}(x) \right]$ → 0

$Pr(\text{Same space}) = 0$

also $\psi_{nn}(x_1, x_2) = \frac{1}{\sqrt{2}} \left[\psi_n(x_1)\psi_n(x_2) - \psi_n(x_1)\psi_n(x_2) \right]$ → 0

↳ The 2 particles cannot be at same E-level.

(Pauli Exclusion Principle)

↳ 2 fermions, e^-, p, n, nuclei, atoms cannot be in same quantum state

orbital defined by: n, m_l, l, s ↖ Spin flip.

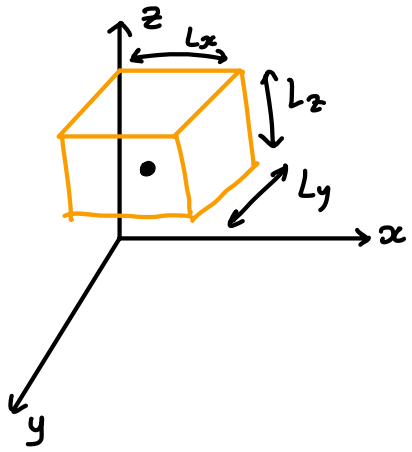
same for e^- in one orbital

Particle in a 3D box.

Expansion of the 1D box problem to 3D!

3 lengths - L_x, L_y, L_z

No force acts on the particles inside the box!



Potential for the particle inside the box:

$$V(\vec{r}) = 0$$

$\vec{r}$ is a vector with all 3 components along the axes:

$$\vec{r} = L_x\hat{x} + L_y\hat{y} + L_z\hat{z}$$

$0 \leq x \leq L_x$ $\quad L_x < x < 0$

$0 \leq y \leq L_y$ $\quad L_y < y < 0$

$0 \leq z \leq L_z$ $\quad L_z < z < 0$

↖ meaning of this?

When p·Energy is infinite, Wave function = 0.
When p·E is 0, the wave function obeys the Time independant SE.

$$-\frac{\hbar^2}{2m}\nabla^2\psi(r) + V(r)\psi(r) = E\psi(r)$$

We are dealing with 3D figure. We need to add 3 axes to SE.

$$-\frac{\hbar^2}{2m}\left(\frac{d^2\psi(r)}{dx^2} + \frac{d^2\psi(r)}{dy^2} + \frac{d^2\psi(r)}{dz^2}\right) = E\psi(r) \quad -③$$

Consider x AND y AND z ↑

To solve this p.d.e, let wavefunction be a <u>product</u> of individual function for each indep. Variable

$$\psi(x,y,z) = X(x)Y(y)Z(z) \quad -④$$

Each function has its own Variable
$X(x)$ is a function of Var x only.

Sub ④ in ③ and divide it by xyz product

e.g. Heat Equation

$\frac{\partial u}{\partial t} - \alpha\frac{\partial^2 u}{\partial x^2} = 0$ Let $u(x,t) = X(x)T(t)$ Sub u back in first eqn & Product Rule.

$\frac{\partial}{\partial t}X(x)T(t)$ $\quad \frac{\partial}{\partial t}X(x)T(t) - \alpha\frac{\partial^2}{\partial x^2}X(x)T(t) = 0$

$X(x)T'(t) - \alpha X''(x)T(t) = 0$

RHS depends only on x and LHS only on t, both sides are equal to some constant value $-\lambda$

$X(x)T'(t) = \alpha X''(x)T(t)$

↖ Eigen Value of both differential operators

$\Rightarrow \frac{T'(t)}{\alpha T(t)} = \frac{X''(x)}{X(x)}$

TISE in 1D $-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\psi(x) + V(x)\psi(x) = E\psi(x)$

$\hbar = \frac{h}{2\pi} \Rightarrow h = \hbar 2\pi$

The term $-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\psi(x)$ can be identified with the E_K $\frac{p_x^2}{2m} = \frac{\hbar^2 k_x^2}{2m}$

$\frac{p}{h} = \frac{1}{\lambda}$ (De Broglie's Relation)

$\frac{p}{2\pi\hbar} = \frac{1}{\lambda}$ Wave number (K)

$\frac{p}{\hbar} = \frac{2\pi}{\lambda}$

$\Rightarrow p = k\hbar$

In 3D $E_K = \frac{p_x^2 + p_y^2 + p_z^2}{2m}$

$E_K = \frac{p^2}{2m}$

$E_K = \frac{1}{2}mv^2$ ↘ Vel. is a vector.

∴ net disp.

$= |\vec{V}| = (v_x^2 + v_y^2 + v_z^2)^{1/2}$

$= v^2 = v_x^2 + v_y^2 + v_z^2$

$\Rightarrow mv^2 = mv_x^2 + mv_y^2 + mv_z^2$

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

$\frac{1}{2}mv^2 \xrightarrow{\times m} \frac{1}{2}m^2v^2 \rightarrow \frac{p^2}{2} \xrightarrow{\text{div. } m} \frac{p^2}{2m}$

$\times m$ ↘

$mE_K = \frac{1}{2}m^2v^2 = \frac{1}{2}m^2v_x^2 + \frac{1}{2}m^2v_y^2 + \frac{1}{2}m^2v_z^2$

div. m ↘

$= \frac{1}{2m}m^2v^2 = \frac{1}{2m}m^2v_x^2 + \frac{1}{2m}m^2v_y^2 + \frac{1}{2m}m^2v_z^2$

$E_K = \frac{p^2}{2m} = \frac{p_x^2}{2m} + \frac{p_y^2}{2m} + \frac{p_z^2}{2m}$

$p_{NET} = \sqrt{p_x^2 + p_y^2 + p_z^2}$

$p_{NET}^2 = p_x^2 + p_y^2 + p_z^2$

$\psi = e^{i(kx - \omega t)}$

$\frac{d^2\psi}{dx^2} = -k^2\psi \qquad k = \frac{p}{\hbar}$

$= -\frac{p^2}{\hbar^2}\psi$

$-\hbar^2\frac{d^2\psi}{dx^2} = p^2\psi \Rightarrow \boxed{-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} = p^2\psi}$

In 3D

Grad = Collection of Partial der. in all directions. (Net sum) ↗

$-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2}\psi(x,y,z) + \frac{\partial^2}{\partial y^2}\psi(x,y,z) + \frac{\partial^2}{\partial z^2}\psi(x,y,z)\right) + V(x,y,z)\psi(x,y,z) = E\psi(x,y,z)$

Inside box, $V(x,y,z) = 0$, $V(x,y,z) = \infty$ at walls.

Use Separation of Variable to Solve p.d.e (3D SE)

Let $\psi(x,y,z) = X(x)Y(y)Z(z)$, Sub. this in 3D SE., $V(x,y,z) = 0$

$$\Rightarrow -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2}X(x)Y(y)Z(z) + \frac{\partial^2}{\partial y^2}X(x)Y(y)Z(z) + \frac{\partial^2}{\partial z^2}X(x)Y(y)Z(z)\right) = EX(x)Y(y)Z(z)$$

$$= -\frac{\hbar^2}{2m}\left(Y(y)Z(z)\frac{d^2X}{dx^2} + X(x)Z(z)\frac{d^2Y}{dy^2} + X(x)Y(y)\frac{d^2Z}{dz^2}\right) = EX(x)Y(y)Z(z)$$

X is a function of x only. p. der disapp. as X is a function of one variable. (X, Y and Z)

Divide both sides by $-\frac{\hbar^2}{2m}X(x)Y(y)Z(z)$

$$\Rightarrow \left(\frac{1}{X}\frac{d^2X}{dx^2} + \frac{1}{Y}\frac{d^2Y}{dy^2} + \frac{1}{Z}\frac{d^2Z}{dz^2}\right) = -\frac{2mE}{\hbar^2} \quad (1)$$

$\frac{dy}{dx} = k$

$\int dy = \int k\,dx$

$y = kx$ * Possible Soln

$x = 1 \quad y = k$

$x = 2 \quad y = 2k$

* for a given Soln, E is a constant.

ie. $\varepsilon_x + \varepsilon_y + \varepsilon_z = E_{Total}$ of 1 Soln (x,y,z)

(ε_x: x value of Soln; ε_y: y value of Soln; ε_z: z value of Soln)

Each part contributes ε amount of Energy to E_{Tot}

$\Rightarrow$ If $\frac{1}{X}\frac{d^2X}{dx^2} = -\frac{2m}{\hbar^2}\varepsilon_x$ — (11)

$+ \frac{1}{Y}\frac{d^2Y}{dy^2} = -\frac{2m}{\hbar^2}\varepsilon_y$

$+ \frac{1}{Z}\frac{d^2Z}{dz^2} = -\frac{2m}{\hbar^2}\varepsilon_z$

$$\frac{1}{X}\frac{d^2X}{dx^2} + \frac{1}{Y}\frac{d^2Y}{dy^2} + \frac{1}{Z}\frac{d^2Z}{dz^2} = -\frac{2m}{\hbar^2}\underbrace{(\varepsilon_x + \varepsilon_y + \varepsilon_z)}_{E}$$

Consider (11)

$$\frac{1}{X}\frac{d^2X}{dx^2} = -\frac{2m\varepsilon_x}{\hbar^2} \Rightarrow \frac{d^2X}{dx^2} = -\frac{2m\varepsilon_x}{\hbar^2}X \Rightarrow \frac{d^2X}{dx^2} + \frac{2m\varepsilon_x}{\hbar^2}X = 0$$

↖ Like 1D Particle in a box.

$$\Rightarrow \frac{d^2X}{dx^2} + \frac{2m\varepsilon_x}{\hbar^2}X = 0$$

$$\frac{d^2Y}{dy^2} + \frac{2m\varepsilon_y}{\hbar^2}Y = 0$$

$$\frac{d^2Z}{dz^2} + \frac{2m\varepsilon_z}{\hbar^2} = 0$$

3 1D box problems!

$$\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2}E\psi = 0 \xrightarrow{\text{Soln}} \psi = B\sin\left(\frac{2\pi}{\hbar}(2mE)^{1/2}l\right)$$

$$\varepsilon_x + \varepsilon_y + \varepsilon_z = E$$

$$\hbar = \frac{h}{2\pi} \Rightarrow \hbar^2 = \frac{h^2}{4\pi^2}$$

$$E_n = \frac{n^2h^2}{8ml^2} = \frac{n^2\hbar^2\pi^2}{2ml^2}$$

$$\Rightarrow \varepsilon_{nx} = \frac{n_x^2h^2}{8ml_x^2}$$

$$\vdots$$

$$E_{n_x n_y n_z} = \varepsilon_{nx} + \varepsilon_{ny} + \varepsilon_{nz} = \frac{h^2}{8m}\left(\left(\frac{n_x}{l_x}\right)^2 + \left(\frac{n_y}{l_y}\right)^2 + \left(\frac{n_z}{l_z}\right)^2\right)$$

Stationary wave eqns:

$$\psi = B\sin\left(\frac{2\pi}{\hbar}(2mE)^{1/2}l\right)$$

Also:

$$\psi_{(x)} = \left(\frac{2}{l}\right)^{1/2}\sin\left(\frac{n\pi x}{l}\right)$$ Stationary wave eqn.

$$X = A_x\sin\left(\frac{2\pi}{\hbar}(2m\varepsilon_x)^{1/2}L_x\right)$$

$$\Rightarrow X_{(x)} = \left(\frac{2}{L_x}\right)^{1/2}\sin\left(\frac{n_x\pi x}{L_x}\right)$$

$$\psi(x,y,z) = X(x)\,Y(y)\,Z(z)$$

$$\Rightarrow \psi_{n_x n_y n_z}(x,y,z) = A\sin\left(\frac{n_x\pi x}{L_x}\right)\sin\left(\frac{n_y\pi y}{L_y}\right)\sin\left(\frac{n_z\pi z}{L_z}\right)$$

$$E_{n_x n_y n_z} = \frac{h^2}{8m}\left(\left(\frac{n_x}{l_x}\right)^2 + \left(\frac{n_y}{l_y}\right)^2 + \left(\frac{n_z}{l_z}\right)^2\right)$$

G.S. Energy is $E_{111} = \frac{h^2}{8m}\left(\frac{1}{L_x^2} + \frac{1}{L_y^2} + \frac{1}{L_z^2}\right)$

↖ l is the length of the box. l in that case is the total length occupied by the wave/e⁻.

If box is a cube $L_x = L_y = L_z = L$

$$E_{n_x n_y n_z} = \frac{h^2}{8m}\left(\frac{n_x^2}{L^2} + \frac{n_y^2}{L^2} + \frac{n_z^2}{L^2}\right) = \frac{h^2}{8mL^2}\left(n_x^2 + n_y^2 + n_z^2\right)$$

$\frac{\hbar^2}{8m} \cdot \frac{1}{L^2} \cdot (n_x^2 + n_y^2 + n_z^2)$

$$\therefore \text{G·S Energy} = E_{111} = \frac{3\hbar^2\pi^2}{2mL^2} = \frac{3h^2}{8mL^2}$$

$h = \hbar 2\pi$

$\frac{3(\hbar^2 4\pi^2)}{8mL^2}$

2

Degeneracy.

For the next higher level, 3 states have the same Energy

Same L, cube $\frac{\hbar^2}{8mL^2}(n_x^2 + n_y^2 + n_z^2) = \psi_{121}, \psi_{211}, \psi_{112}$

Different states. as probability densities are different

$\Rightarrow$ Same Energy Different States.

$$|\psi_{211}| = |A|^2 \sin^2\left(\frac{2\pi x}{L}\right)\sin^2\left(\frac{\pi y}{L}\right)\sin^2\left(\frac{\pi z}{L}\right) \neq |A|^2 \sin^2\left(\frac{\pi x}{L}\right)\sin^2\left(\frac{2\pi y}{L}\right)\sin\left(\frac{\pi z}{L}\right)$$

$$\neq |\psi_{121}|^2$$

This is called degeneracy

In the case of the cube, the next lowest E-level is three fold degenerate

$$E_{211} = E_{121} = E_{112} = \frac{3\hbar^2\pi^2}{mL^2}$$

G·S is non-degenerate. Threefold degeneracy of the first excited state is removed $L_x \neq L_y \neq L_z$

Degeneracy is intimately connected to symmetry. The greater the symmetry the higher the degeneracy of the quantum states.

Carnot Cycle

System is ideal as transformation involved would usually increase entropy state variable.

It is a theoretical ideal thermodynamic cycle.

↳ Processes that involve transfer of heat and work in/out of the system while varying P, T, ..., state var. within the system and that eventually returns the system to initial state.

It provides an upper limit on the efficiency that any classical thermodynamic engine can achieve during conversion of heat into work. It is a theoretical construct.

Setup: There are 2 heat reservoirs; hot and cold at temperatures T_h and T_c respectively.
Their thermal capacity is very large and is unaffected by 1 cycle.
Since the cycle is reversible, entropy is conserved.

During cycle some ΔS is extracted from hot reservoir and deposited into cold.

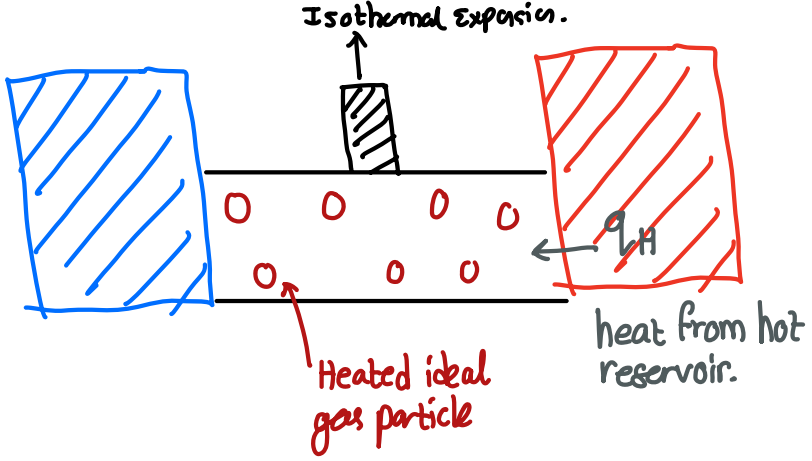
Since no volume change in either reservoir, NO work is done.

The energy $T_h \Delta S$ extracted from hot and a smaller amount deposited into cold. ($T_c < T_h$)

The difference in 2 energies $(T_h - T_c)\Delta S$ is the work done by engine.

STEPS

① Isothermal Expansion



Heat is released from the hot reservoir and absorbed by the gas particles in the system.

Thus, the temperature of the system rises.

This causes the gas to expand, doing work against atmosphere (surroundings) (push piston up)

Although the pressure of the gas drops during expansion, this causes NO change in temperature as the gas is in contact with the hot reservoir.

$\Rightarrow$ Isothermal

Heat Q_1 is absorbed by the gas from the hot reservoir

ΔS (entropy) increases in gas by amount Q_1/T_h ← gas is at temperature T_h

② Isentropic (reversible adiabatic) expansion of the gas

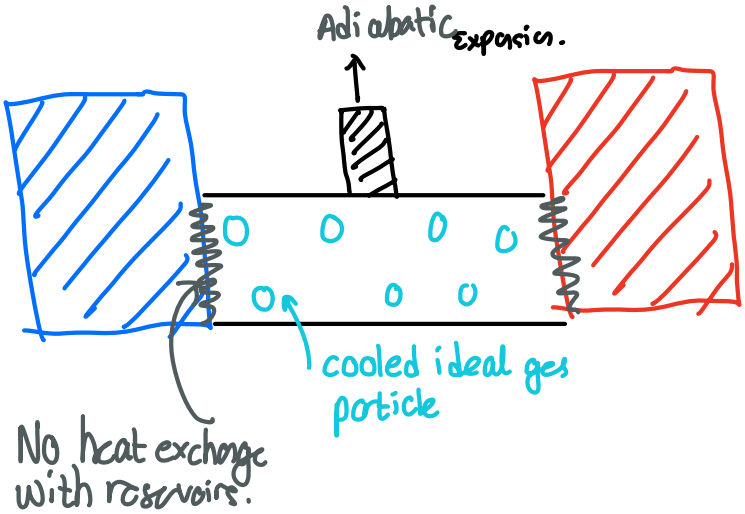
The heat reservoirs from step ① are disconnected

While the gas continues its expansion.

This time, as expansion continues and pressure inside is reduced, the loss of internal energy equals work done.

The gas starts to cool down.

It does so until it reaches (a certain temperature, T_c.)



Entropy does not change despite cooling effect. ← Why??

③ Isothermal Compression

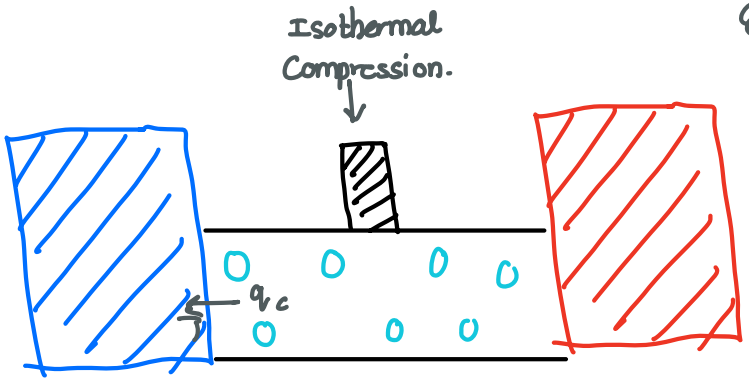
Sys. in contact with cold res.

Heat transferred reversibly to Very cold reservoir at constant temperature T_c.

The surroundings do work on the gas, pushing the piston down. Causing amount of heat Q_2 to leave system to the low temperature reservoir.

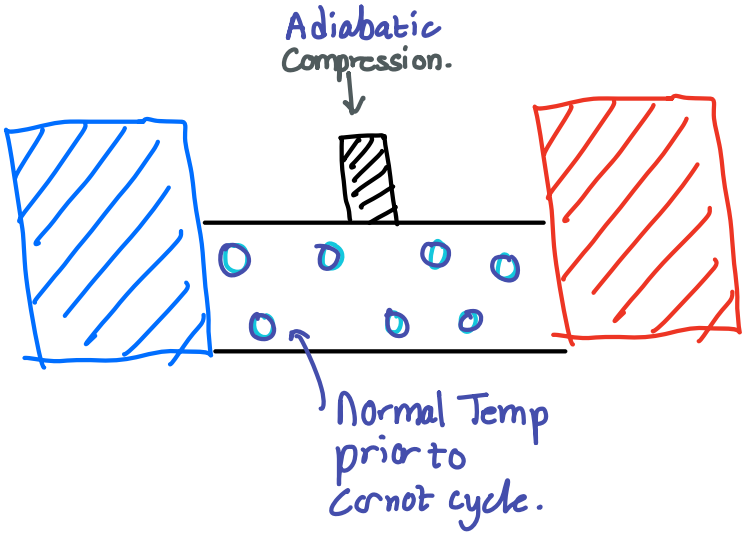
The entropy of the system decreases by the same amount. $\Delta S_2 = \frac{Q_2}{T_c}$

↳ Same amount of Entropy absorbed.



① Carnot Cycle Microscopic.
② Classical Entropy.
③ 2nd Law of Thermodynamics.

④ Adiabatic Reversible Compression.



Once again, the gas is insulated from the hot and cold reservoirs.
(Assume Engine is frictionless - reversible)

- The surroundings do work on the gas, pushing the piston down.

Internal Energy increases and compression causes temperature to rise back to T_h due solely to the work added to the system.

(Entropy unchanged)

Gas is in same state as start of step 1.

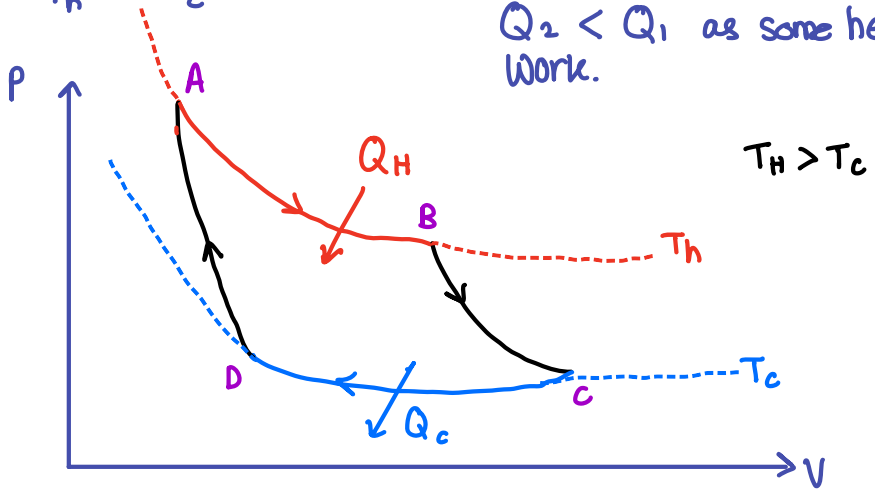
In this case,

$\Delta S_1 = \Delta S_2$

$\frac{Q_1}{T_h} = \frac{Q_2}{T_c}$ (Same ratio)

Q_2 and T_c are both lower than Q_1 & T_h.

$Q_2 < Q_1$ as some heat was converted into work.



$T_H > T_c$

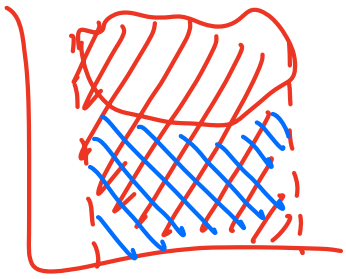
Area in Cycle = Work done in 1 Cycle

$\Rightarrow W.D = Q_H - Q_c$

A - B : Isothermal Expansion
Hot reservoir provides heat to system (+ IE as Heat) due to (from res.)
: + S

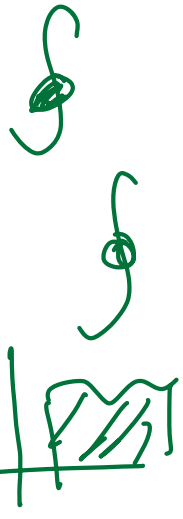
$W.D = \oint P.dV$

B - C : Adiabatic Expansion (Reversible)
Reservoir shut off
Expansion continues at cost of internal energy (- IE as Work)
Gas cools.
: S = Constant.



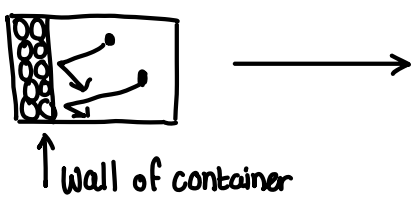
C - D : Isothermal Compression
Surroundings do work on gas
Gas cools down due to heat rejection in cold reservoir (- IE as heat)
: - S

D - A : Adiabatic Compression (Reversible)
Reservoirs shut off.
Surroundings compress gas, heating it up (+ IE as Work) from Surr.
Gas Ends up in same state prior to cycle
: S = Constant

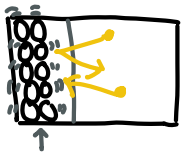


Heat vs Work (Classical)

Wall is moving slowly. Collision of gas molecule with know momentum & angle is predictable.



Molecular collision is less predictable. (random)



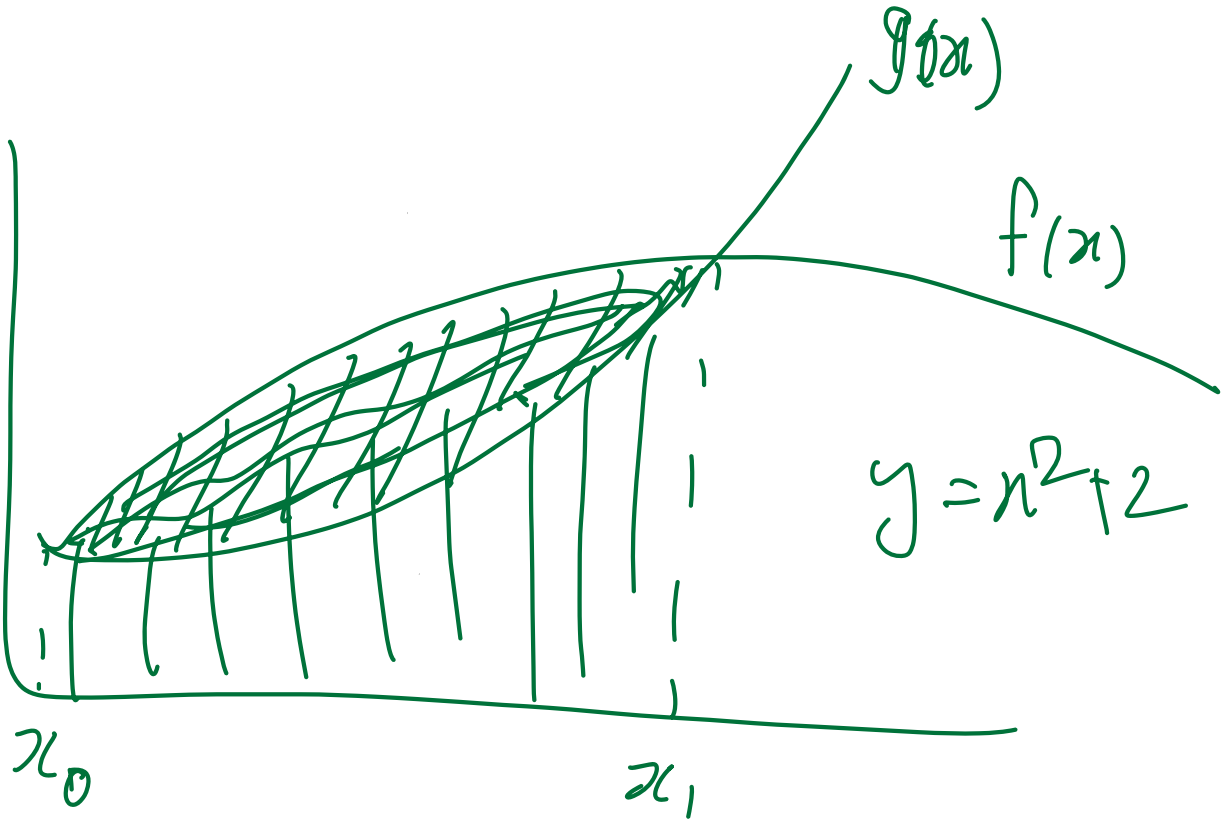
Most molecules in similar states (p, θ°) will behave similarly.
i.e. 2 molecules with same coordinate & momentum will end up with same parameters after collision.

2 molecules with same coord. & p may not end up in same state after collision. (Although Vel. increased).

We DO NOT kNOW ATOMS EXIST!!!

Gas Overview

Reversible Heat Transfers



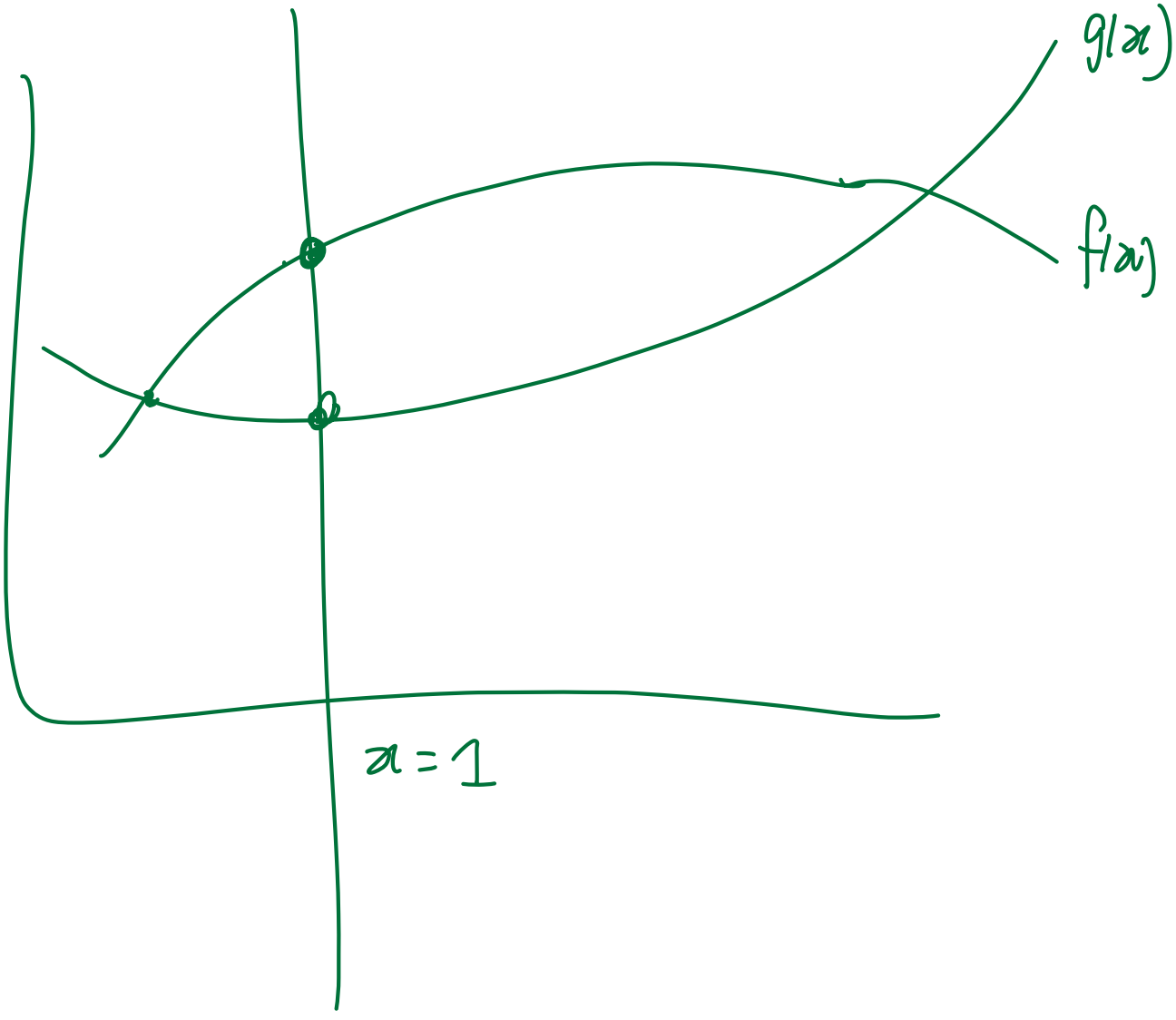
$$\int_{x_0}^{x_1} f(x) - g(x)\, dx$$

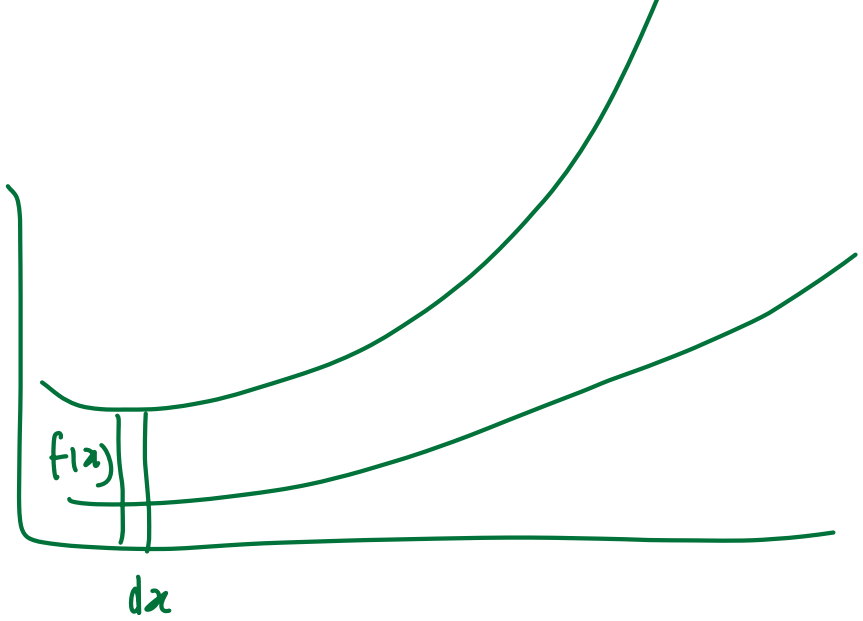
$$- 2x^2 - \cdots -$$

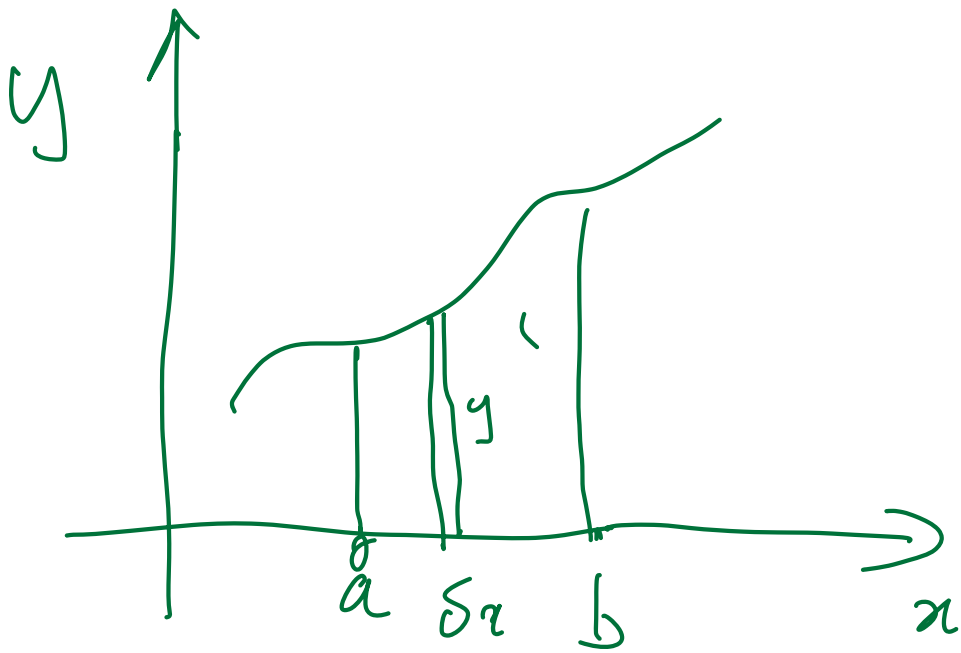
$f(x)$: $x^2 + 2x$

$g(x)$: $3x^2 - 5$

$$\int_{x_0}^{x_1} x^2 + 2x - 3x^2 + 5 \, dx$$



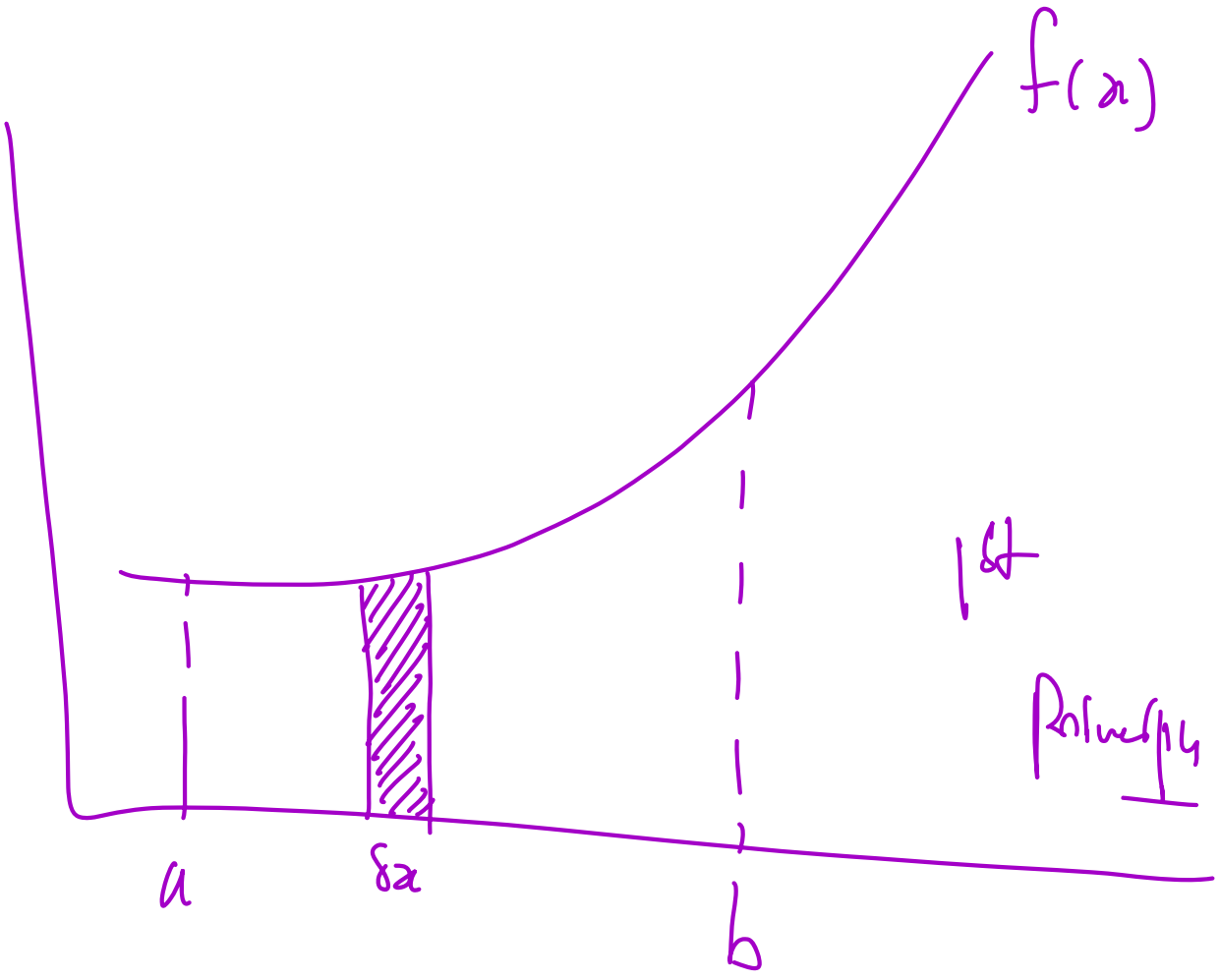




$A = y\,\delta x$.

$\text{Area} = \int_a^b y\,\delta x = \int_a^b y\,dx$.

$=$

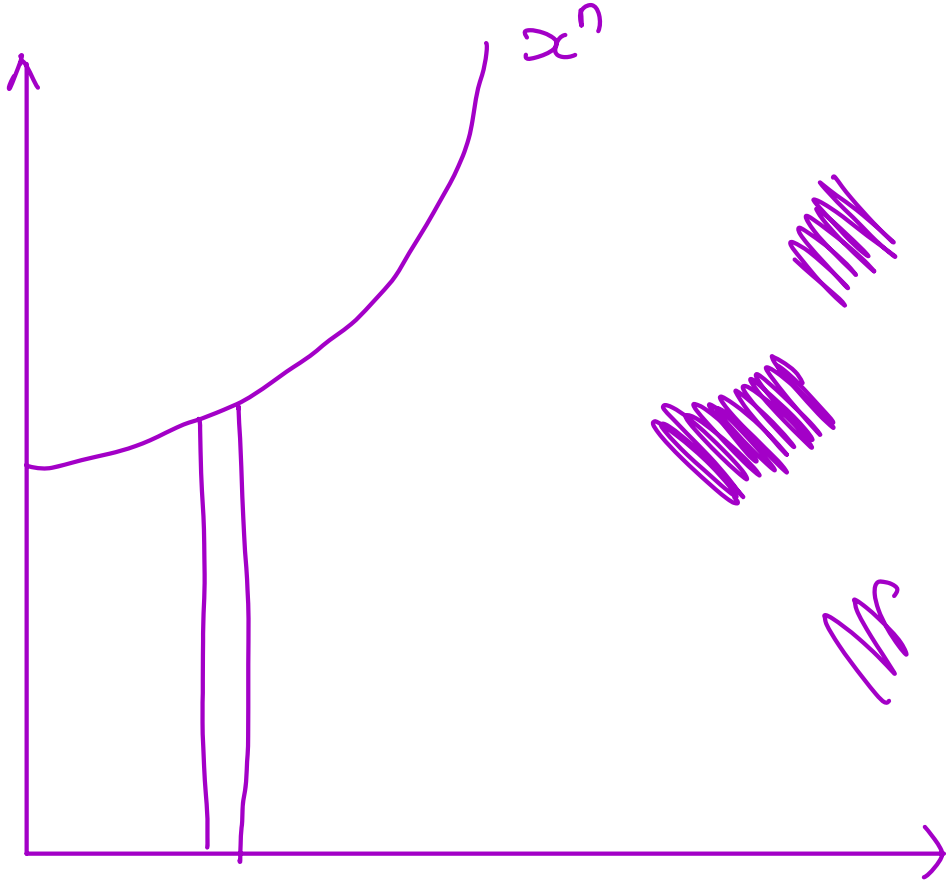


$$A = \delta x f(a) \times (b-a)$$

$$\delta y = x^2 + 2$$

$$\int \delta y = \int x^2 + 2$$

$$A = \int_a^b \delta y \, \delta x =$$



$y = x^n$

Q/T represents how many times the average energy we have gained or loss.

If we gained more, then we increased the number of ways we can permute the energies.

More value
⇒ More ways to get same T!

Suppose we have 2 bodies at $T_h > T_c$
T represent the average energy per molecule in each system.
ΔQ represent the heat exchanged with each system.

Let's consider T_c
Consider Q/T_c. This represents the number of times

We can change the average energy of the molecules in the system.
e.g. If $\Delta Q/T_c = 5$, We can increase T_c with $+5T_c$

This heat transfer represent more ways we can permute the energies from its original state

$T_c < T_h \Rightarrow T_c$ has more permutations $\Rightarrow \uparrow S$

Why more permutation represent more disorder
Does it not mean more spreading
⇒ less clustering about a single microstate ?

NO!

If Energies is more dispersed,
⇒ There are more ways to get a microstate
Consider : less dispersed : All molecules are at $\varepsilon = 2$
$4 = (2+2)$ ✓
More dispersed
$4 = (1+3)(2+2)$ ✓

Single Macrostate but single microstate.

Single Macrostate : Multiple Possible microstates

$Q = nT$??

1 mol
$PV = RT$
PVRT

Not from higher disorder to lower disorder entropy,
But the process must increase disorder.

$PV = kT$

What does this come from? → $PV = \frac{3}{2}U$

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

$U = k'T$

S

Also $PV = nRT$

$T \propto \frac{1}{n}$ Less n ⇒ Higher T

same Q ← Higher T ⇒ Less n

More spread out but lower Energy. ← If we have 3J of Energy, but many molecules, each Molecule will get a small amount of energy ⇒ lower average ⇒ lower T.

If less Molecule ⇒ each get large amount ⇒ ↑T.
↳ Less spread out but higher ε.

Suppose we have (3) (3) (3)

$T = 3$

First Law : Internal Energy is a function of Temperature & Volume

$U = f(T, V)$

Changed by Q ↑ ← Changed by W

$\Delta W = P\Delta V$

$\Delta Q = mc\Delta T$

$\gamma = \frac{C_p}{C_v}$ ↑ Isentropic expansion factor.

$\Delta Q = mc\Delta T$
C_v at const. Vol. ⇒ No Work
C_p at const. P ⇒ Work possible

$n = \frac{\text{Mass}}{mr}$

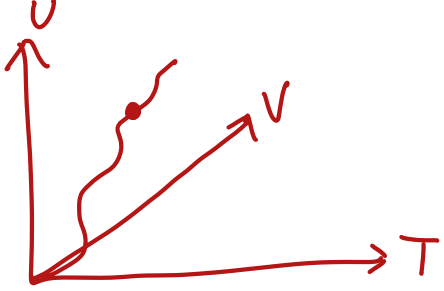
nN_a = No. of particles

$N = \frac{\text{Mass}}{mr} \times N_a$

Mr =

like any function

U can result from effect of both T & V



Sometimes change in T

Causes a change in V which leads to a value of U.

Already has a shape.

Suppose we have a plot for $U = f(T, V)$ (All 3 variables)

We know U depends on T & V

But Is T & V independent ?

The graph represents a plane

Must look carefully.

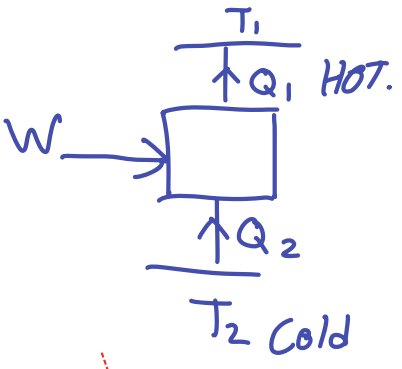
↳ Isothermal expansion / compression.

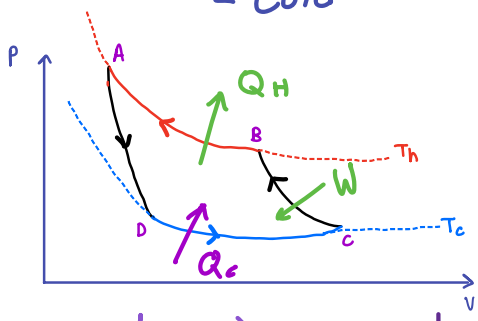
Quasi-static - Reversible

↳ Always Near Equilibrium

Refrigerator Cycle

Reverse of CARNOT CYCLE





Start at C (lower T)

(1)' C to B
Adiabatic Compression
$\Delta Q = 0$
$\Rightarrow \Delta U = -P\Delta V$
Temperature of coolant rises
no heat exchange $\Rightarrow$ Isentropic

E_K only
for ideal gas U is function of T only
V becomes important when considering E_P (Squeeze together $\Rightarrow \uparrow E_P$)
$(U = \frac{3}{2} nRT)$

(2)' B to A
Isothermal Compression
$\Delta T = 0 \Rightarrow \Delta U = 0$
$\Rightarrow \Delta Q = \Delta W$
Temperature remains constant
U gained by compression work is equal to U lost as Q (rejected heat)
S decreases in System.

(3)' A to D
Adiabatic Expansion
$\Delta Q = 0$, $\Delta U = -P\Delta V$ $U = \frac{3}{2} nRT$
Gas expands paid by decrease in U
T coolant drops below refrigerator
no heat exchanged $\Rightarrow$ Isentropic

(4)' D to C
Isothermal Expansion
$\Delta T = 0 \Rightarrow \Delta U = 0 \Rightarrow \Delta Q = -P\Delta V$
Gas expands w/o decrease in T/U.
Q is injected from refrigerator
S increases in System.

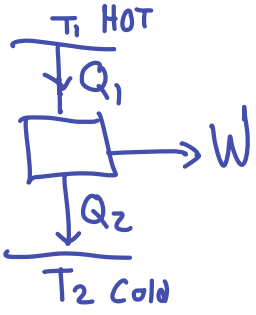
Temp. represents U.
Temp is affected by Q & W.

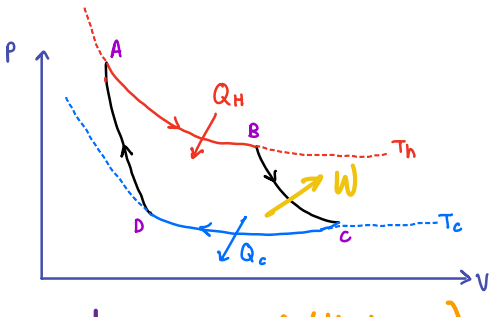
Temp. is average E_K not total.

More heat loss than what is collected (friction)!

Heat Engine Cycle

CARNOT CYCLE





Start at A (Higher T)

(1) A to B
Isothermal Expansion
$\Delta T = 0 \Rightarrow \Delta U = 0 \Rightarrow \Delta Q = -P\Delta V$
Heat Q from hot reservoir cause work via gas expansion.
Temperature does not change ($\Delta U = 0$)
S increases in system

(2) B to C
Adiabatic Expansion
$\Delta Q = 0 \Rightarrow \Delta U = -P\Delta V$
Expansion against atmosphere is paid by U.
T decreases
No heat transfer $\Rightarrow$ Isentropic

(3) C to D
Isothermal Compression
$\Delta T = 0 \Rightarrow \Delta U = 0 \Rightarrow \Delta Q = -P\Delta V$
U gained by compression work equals to U lost as Q rejected in cold reservoir
S decreases in system.

(4) D to A
Adiabatic Compression
$\Delta Q = 0 \Rightarrow \Delta U = -P\Delta V$ (Expansion cause U to increase)
Temperature rises
No heat exchanged $\Rightarrow$ Isentropic

Adiabatic & Isothermal Processes

A - B : Isothermal Expansion
Hot reservoir provides heat to System (+ IE as Heat) due to (from res.)
: + S

B - C : Adiabatic Expansion (Reversible)
Reservoir shut off
Expansion continues at cost of internal energy (- IE as Work)
Gas cools.
: S = Constant.

C - D : Isothermal Compression
Surroundings do work on gas
Gas cools down due to heat rejection in cold reservoir (- IE as heat)
: - S

D - A : Adiabatic Compression (Reversible)
Reservoirs shut off.
Surroundings compress gas, heating it up (+ IE as Work) from Surr.
Gas Ends up in same state prior to cycle
: S = Constant

Let us look at some cases where we might at first object

We might think that the decrease in S for surroundings violates the 2nd law, but we remember that the law talks for the whole universe. $dS_{univ} = dS_{sys} + dS_{surr}$
Since magnitude of entropy gain by glass offsets magnitude of loss in surroundings, $dS_{univ} > 0$!

↳ Temperature (T) is the average energy per particle and measures hotness or coldness.

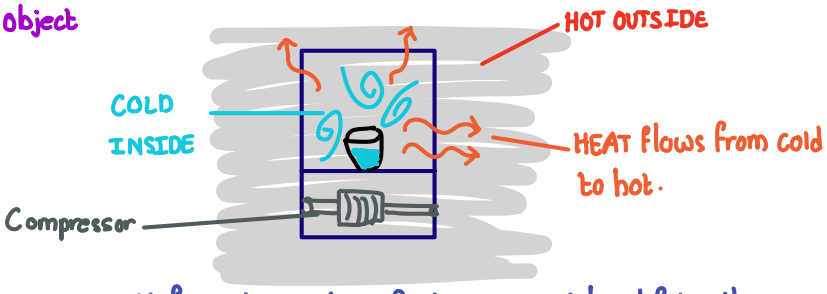
If we transfer heat Q to a cold body at temp. T_c, the ratio Q/T_c represents how many multiples of the average energy T_c we got from the heat added.

For $T_H > T_c$, we get less multiples of T_H from heat Q.

Higher multiples means more way to permute Energy. (Review)

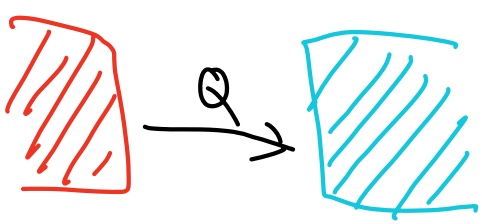
For HOT → COLD $\Delta S = -\frac{Q}{T_H} + \frac{Q}{T_c} \geq 0$

For Cold → HOT $\Delta S = -\frac{Q}{T_c} + \frac{Q}{T_H} < 0$ ✗



At first glance the refrigirator would be defying the 2nd Law! It moves heat from cold to hot which would lead to think that it is operating despite decreasing Entropy.
We however notice that there is a compressor present. It inputs work by compressing a coolant (tetrafluoroethane/CFC). After a series of steps, heat flows from refrigerator to coolant which

$$\Delta S = -\frac{\Delta H}{T}$$



Q : Random microscopic Energy Transfer

T : Average level of internal Energy U in ideal gas

Q/T : factor of average increase in random Energy

2nd law suggests that S↑

H to C

C has lower T ⇒ Can get more random Energy increments from 1Q transfered.

Transfer to C indukes more disturbace

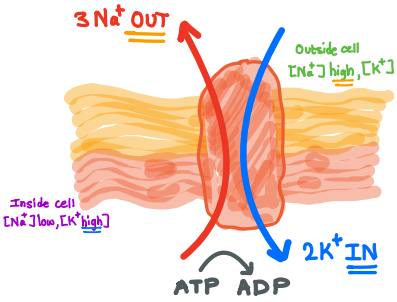
must know U_C, U_H are state variable only for their respective system

Movement of Q to H would result in smaller increment

& Too big decrease in C.

Active Transport (Na^+/K^+ Pump)

This little device is present in the membranes of all animal cell. One function is to maintain cell voltage.



As we can see, it is organising the ions into their respective compartments. It opposes the 'spreading' of the molecules and seems to violate the law of Entropy!

But this process is active. Energy is being input as ATP. The mechanism occurs in a very precise and ordered manner.

The second law does not forbid the opposition to Entropy with help from work. It just says that decrease in Entropy does not occur by itself.

We know the extent of this process. It occurs in all animals. How can the universe allow for the system to decrease Entropy? Somehow the increase in ΔS_{surr} must offset the decrease by the system!

$\Delta S = \frac{\Delta Q}{T}$ + T

↑ Disorder term.

↘ same disorder independent of system T!

Interpretation of the ratio $\frac{\Delta Q}{T}$.

Terms: ΔQ (Heat transf.) - A form of Energy with a certain randomness.

: T (Temperature) - The average (Internal) energy in an ideal gas.

Suppose I transfer a parcel of energy ΔQ to a system at temp. T. The ratio $\frac{\Delta Q}{T}$ tells me how many times the prior internal Energy I added. A colder System will receive more times its internal energy compared to a hotter system (higher ratio). Remember, this Energy is associated with randomness. So, the same heat ΔQ will cause many times more randomness in a colder body compared to a hotter one! Or, the magnitude of decrease in randomness when ΔQ leaves hot body is less than the gain in cold one. $\Delta S_{univ} \geq 0$ from HOT to COLD.

↘ HEAT ITSELF MUST ACT ON A BODY TO CAUSE DISORDER!!

Entropy wished to destroy ↑ single-handed.

→ Talking in a room full of loud people creates less disorder than talking in a quiet room.

Effectiveness of shouting & passing a message! ← Talking in a quiet room (library) creates more disorder (in that room) compared to a room full of loud people (market).

①

Why MUST Carnot Cycle Reject Heat?

Why does generation of Work Produce heat.

↘ IRREversible Work in Most cases.

↳ Refer to Entropy or heat?

Why Carnot cycle has isotherm

↳ No Energy required to raise U (T = Constant)

All heat conv. to work.

① If heat is so widely available (escapes everytime), why not use it as a source to do work

② Explain nature of heat.

③ Carnot cycle Rejecting heat (or include it with refrigerator example?)

④ What happens at heat death!

Say heat escapes as friction

Process not reversible

∴ $\Delta S = 0$ for reversible part but inefficiencies cause additional heat → friction!

Why heat needs to go from hot to cold!

① Heat vs Work (again)

HEAT

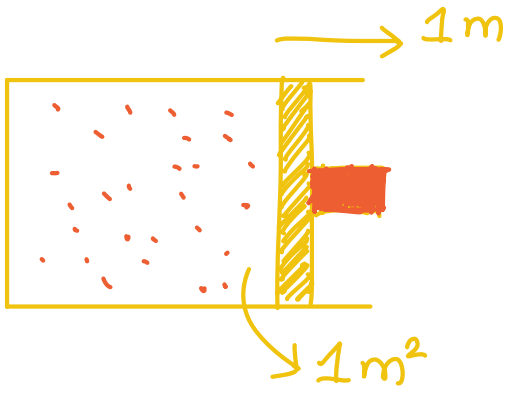
ΔQ 

↳ Disorder in energy distribution

large dispersion

↗ (many possible combinations to get 1J)

$1J = 0.3J, 0.2J, 0.05J, 0.1J, 0.35J$



To get 1J of work, all the molecules must collide with the walls simultaneously.

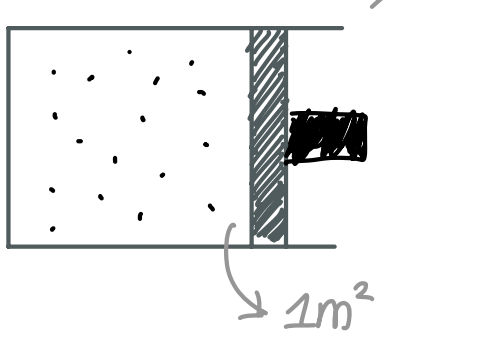
Else, from random collisions of the numerous gas molecules, Work will never get done.

Move once with 0.05 J after 1 year, 0.003 J...

TO INFINITY

Work

$\Delta W = -P\Delta V$ 



T?

↑

All molecules are at $\frac{x}{N}$ J of Energy (5 molecules for 1J ⇒ 0.2J per molecule).

Even if collisions are random, all possess the same amount of Energy!

Work is done in finite time!

Now a usual system consists of both kind of Energy: High grade (Work) & low grade (Heat)

Heat & Work are modes of transfer of Energy.

Heat transfers low grade while Work high-grade

$$\Delta Q - \Delta W = \Delta U$$

↑ Add heat to add low grade.

↑ do work to add high grade E

↑ To change the Energy of a system

$$\boxed{T\,dS - P\,dV = dU}$$

Now temperature tells the average Energy of a Sys.

$\uparrow \Delta S = \frac{\Delta Q}{\downarrow T}$: If S cause more dispersion T decreases

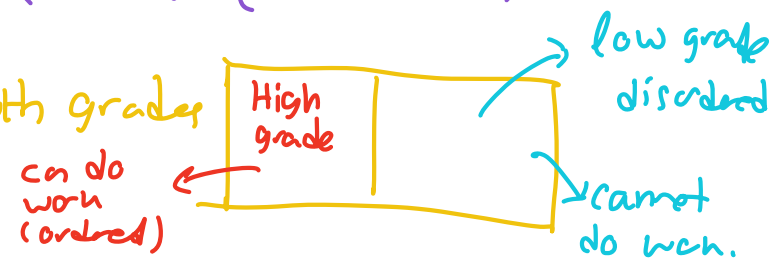
(Normal distribution)

mean - Even distribution at little Energy

NOW, What happens in an isothermal process?

$\Delta T = 0 \Rightarrow \Delta U = 0 \Rightarrow \Delta Q = \Delta W \; (= -P\Delta V)$

Usually a system consists of both grades



Note: This happens in a concerted fashion but still:

Internal Energy U decreases to do work (Expansion) (paid for)

To keep average Energy (T) constant, System draws Energy albeit a low grade one (Heat).

This brings disorder (ΔS) with it.

The ordered portion of energy was expended to do work & it was replaced by a low grade one!

NOW, during isothermal compression, Work is done on system & ordered portion increases.

To keep temperature constant, (average molecular Energy) (must not increase) (Isothermal!)

The system rejects the low-grade Energy (heat)

The disorder associated with the system decreases ($\downarrow \Delta S$)

↳ Now like heating is random, cooling is too.

Cooling is just our system heating up another body!

Since processes are random, we can think for a

large no of molecules, Statistics apply & heating & cooling add or remove the disorder of each other They cancel due to statistics, same randomness & large numbers!

Let's Jump to adiabatic processes!

$\Delta Q = 0 \Rightarrow$ lagging $\Rightarrow \Delta U = -P\Delta V$

Internal Energy pays for Work done in adiabatic Expansion.

$\Delta Q = 0 \rightarrow$ NO heat Enters or leaves the system

↑ No gain of random Energy

↑ No loss of random Energy

No loss or gain of U (IE) due to low grade E

Only Work portion considered!

[What about only heat considered??

Adiabatic Expansion is the expenditure of the useful part of Energy (high grade) only to do Work.

Adiabatic compression is the gain of useful ordered Energy!

Note: Since friction is present, Cycle is non-reversible, More heat here disorder enters $\Delta S_H \neq \Delta S_{cold}$

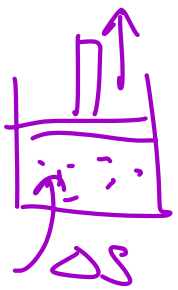
$\Delta S_H - \Delta S_c \neq 0$!? valid??

① Isothermal Expansion $\Delta W = \Delta Q$ (high grade going being replaced by low grade.

W.D, High grade ↓
low grade ↑ ΔS ↑

② Adiabadic expansion
Extract least amount of high grade present.

Simply heating a gas



ΔS

Both Q & W involved
- No restrictions on either.

Review More!

Both heat & Work can change temprature.

{ Going down a gradient generates Entropy!

Gradient exists because diffeent conc.

Grad = 0 when equilibrium

at eq. ⇒ max Entropy

Gradient follow involves some kind of spreading (dispersion).

Work must be done to go against gradient. ←

{ this minimises dispersion.

↳ No process is ideal/reversible

↳ doing work to go back generates heat too.

↳ Ends with death.

Life is work.

different forms of death.

know when to flow & when to oppose (Human)

AS LONG AS ± DRAW BREATH, I SHALL TRULY LIVE.

On this Earth, starting as a human & to my great destiny which I will work for. For the latter is living itself.

How will the general heat flow lead to Equilibrium?

Friction generates heat

↓ Lose at heat

↓ ΔS_{surr} ↑

↓

Explain via linking chain

how ΔS_{univ} will increase!

↓ Consequences.

↓ Cannot do work

Energy in all system

tend to low grade!

↓

To put high grade energy back in system at Universal thermodynamic Equilibrium outside source needed to transfer work!

↙

① ATP Synthase mitochondria (life)

② Gravitational fields & bowling balls (Entropy)

③ Electric Wires (Electric energy & magnetic energy)

④ Computation (Propose time crystals)

③ Electric Wires

Apply V → flow down gradient → Generate Entropy

↓

$W = qV$

$U = qV$

↓ Higher Entropy

more $W = qV$ (higher V)

needed to make electrons move

in desired direction.

max Entropy (NO Work can overcome disordered particles)

But where does the potential difference originate?

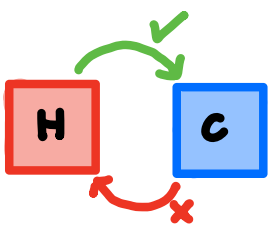
How is it related to thermodynamics

and does increasing Entropy affects it?

↳ Interpretation of the ratio $\Delta Q/T$.

Terms: ΔQ (Heat transf.) - A form of Energy with a certain randomness.

: T (Temperature) - The average (Internal) energy in an ideal gas.



T does not change in isothermal

Suppose I transfer a parcel of energy ΔQ to a system at temp. T. The ratio $\Delta Q/T$ tells me how many times the prior internal Energy I added. A colder system will receive more times its internal energy compared to a hotter system (higher ratio).

Remember, this Energy is associated with randomness. So, the same heat ΔQ will cause many times more randomness in a colder body compared to a hotter one! Or, the magnitude of decrease in randomness when ΔQ leaves hot body is less than the gain in cold one. $\Delta S_{univ} > 0$ from HOT to COLD.

We notice the presence of a compressor! It does work on the coolant by compressing it. This cause T to rise in coolant. Later, this energy is rejected as heat causing T of coolant to drop below refrigerator temp, drawing heat from the latter. The cycle keeps repeating to keep the inside cool!

The 2nd law does not forbid Work from accomplishing this. It just says heat by itself does not flow from hot to cold. As for the feasibility of this set up, heat is given off to surrounding by rejection in cycle, friction, vibration and heat in cables.
$\Rightarrow \Delta S_{univ} \geq 0$ ✓✓ (ΔS_{surr} offsets ΔS_{sys})

At first glance the refrigirator would be defying the 2nd Law! It moves heat from cold to hot which would lead to think that it is operating despite decreasing Entropy.

$$R = R_{ref}\left(1 + \alpha\left(T - T_{ref}\right)\right)$$

$$R = R_{ref} + \alpha\left(T - T_{ref}\right)$$

$$R - R_{ref} = \alpha\left(T - T_{ref}\right)$$

$$\Delta R \propto \Delta T \rightarrow \uparrow T \Rightarrow \uparrow R$$