MIXING

* consider two different gases m_1, m_2 in two different compartments, V_1, V_2 and with different numbers of particles N_1, N_2 separated by a barrier, but with $P_1 = P_2 = P$, $T_1 = T_2 = T$
* lift barrier ⇒ what is the entropy change after equilibration?

$$S_1 = kN_1\left[\ln\frac{V_1}{N_1} + \frac{3}{2}\ln\left(\frac{2\pi m_1 kT}{h^2}\right) + \frac{5}{2}\right]$$

$$S_2 = kN_2\left[\ln\frac{V_2}{N_2} + \frac{3}{2}\ln\left(\frac{2\pi m_2 kT}{h^2}\right) + \frac{5}{2}\right]$$

$$S_{initial} = S_1 + S_2$$

$$S_1' = kN_1\left[\ln\frac{V}{N_1} + \frac{3}{2}\ln\left(\frac{2\pi m_1 kT}{h^2}\right) + \frac{5}{2}\right]$$

$$S_2' = kN_2\left[\ln\frac{V}{N_2} + \frac{3}{2}\ln\left(\frac{2\pi m_2 kT}{h^2}\right) + \frac{5}{2}\right]$$

$$S_{final} = S_1' + S_2'$$

$$\Delta S = S_{final} - S_{initial} = kN_1\ln\frac{V}{V_1} + kN_2\ln\frac{V}{V_2} > 0$$

occurs spontaneously

once mixed, gases will not return to initial state spontaneously

For two identical gases:

$$S_1 = k N_1 \left[\ln \frac{V_1}{N_1} + \dots \right]$$

$$S_2 = k N_2 \left[\ln \frac{V_2}{N_2} + \dots \right]$$

$$S_{initial} = k N_1 \ln \frac{V_1}{N_1} + k N_2 \ln \frac{V_2}{N_2} + \dots$$

$$\cancel{S_f = k N \ln \frac{V}{N}}$$

$$S_{final} = k N \ln \frac{V}{N}$$

$$\Delta S = k N_1 \ln \frac{V N_1}{N V_1} + k N_2 \ln \frac{V N_2}{N V_2}$$

$$\text{if } \frac{N}{V} = \frac{N_1}{V_1} = \frac{N_2}{V_2} \Rightarrow \underline{\Delta S = 0}$$

Pressure and Chemical Potential

$$dW = \mathrm{Tr}\, D_B\, dH = \sum_i \left(\mathrm{Tr}\, D_B \frac{\partial H}{\partial x_i} \right) dx_i$$

$$= \sum_i X_i\, dx_i$$

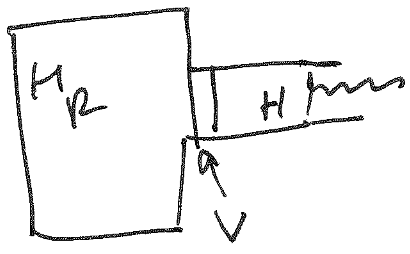
$$X_i = \left\langle \frac{\partial H}{\partial x_i} \right\rangle$$

p = generalised force

$-V$ = generalised displacement

$$p = \frac{1}{\beta} \frac{\partial \ln Z}{\partial V}$$

consider again a system like



but now V allows particles to pass between system and reservoir

$\bar{N} = \mathrm{Tr}\, D_B N \rightarrow$ average particle number known $\Rightarrow D_B = \frac{e^{-\beta\hat{H} + \mu\hat{N}}}{Z}$

$dS_B = -k \mathrm{Tr}\, dD_B (\ln D_B + 1)$

$dS_B = -k \mathrm{Tr}\, dD_B (-\beta H + \overset{\alpha}{\cancel{\beta\mu}} \hat{N})$

in this case associating Boltzmann entropy with thermodynamic entropy

$\beta = \frac{1}{kT}$

$\Rightarrow \quad \alpha = \frac{\mu}{kT}$

Irreversibility, growth of entropy

* classical mechanics ⇒ equations of motion are time-reversible
  * if we send $t \to -t$, path from where system came will be retraced exactly
* also true for quantum mechanics

$$i\hbar \frac{\partial \Psi}{\partial t} = H(t)\,\Psi(t)$$

$$t \to -t \Rightarrow -i\hbar \frac{\partial \Psi}{\partial t} = \cancel{H(t)\,\Psi(t)}\ H(t)\,\Psi(-t)$$

in QM ⇒ measurement theory brings some issues, but for a closed, isolated system time-reversibility holds

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MICROSCOPIC REVERSIBILITY

Newton:
$$m\ddot{x}(t) = F(x(t))$$

if $x(t) = y(-t)$

still we have

$$m\ddot{y}(\cancel{t}) = F(y(-t))$$

(2nd order equation)

- if there is a 1^{st} order term (friction) 14

* $m\ddot{x}(t) + \gamma\dot{x}(t) + m\omega^2 x(t) = 0$

no longer true ⇒ but friction is an "artificial" term ⇒ not the true microscopic description of system, only an approximation

* everyday phenomena are not reversible!!!
  - example: one can cook an egg, it will become an omelette, but one can not take an omelette and turn it into an egg

MACROSCOPIC IRREVERSIBILITY!!!

- is this a paradox?
- according to microscopic dynamics (reversible) it should be possible to turn omelette into an egg

- even microscopically there is a physical basis of irreversibility
- can argue in microcanonical framework

$$\Omega(E) = \frac{1}{N!\, h^{3N}} \int_{E \le E_r \le E + \Delta E} \prod_{i=1}^{N} d\vec{r}_i \, d\vec{p}_i$$

phase space volume

$$S(E) = k \ln \Omega(E)$$

- example: consider a gas which is initially in the left half of container, separated from right half by a barrier
- pierce the barrier, make a small hole
- eventually atoms diffuse through hole and distribution will be equal

configurations consistent with initial constraint compared to configurations consistent with final equilibrium state

$\frac{1}{2^N}$ ⇒ many more confs. in the final state than initial one (VASTLY more)

there are vastly more ways of being an omelette than an egg

⇒ irreversibility appears as the time asymmetry of number of accessible configurations ⇒ increase in entropy

⇒ ENTROPY: THERMODYNAMIC ARROW OF TIME

* possible counterarguments:

- Poincaré recurrences: according to this scheme all ~~particles~~ trajectories return to their starting point (actually will pass arbitrarily close to their starting point) in some finite amount of time

- but this occurs after very long times for systems with a large number of particles

- Loschmidt paradox: if we take a configuration of gas atoms which are in equilibrium after piercing ⇒ and reverse time $t \to -t$ ⇒ particles should return to original configuration and be in the left compartment

- but this numerical experiment is not possible ⇒ small errors in trajectories (unavoidable) will propagate exponentially (chaos) and particles will not return to original state

Summary:

* irreversibility arises due to probabilistic arguments: number of microstates available to final state is much larger than for initial state
* for this argument to hold a very large number of degrees of freedom are needed
* probability of initial macrostate is negligible after equilibration
* chaotic dynamics ⇒ not important quantitatively, but important quantitatively

in information theoretical terms: loss of information / growth of entropy $\Rightarrow$ IRREVERSIBILITY

* consider system in canonical ensemble
* equivalence between thermodynamic and information entropy only holds at equilibrium
  - start with equilibrium state $\Rightarrow$

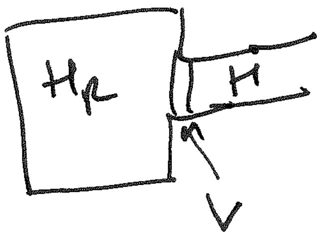
    $$-\mathrm{Tr}\, D \ln D = -\mathrm{Tr}\, D_B \ln D_B \quad \rightarrow D = D_B$$

    - D_B - fixed by constraints on initial equilibrium state

    $$A_i = \mathrm{Tr}\, \hat{D} \hat{A}_i \Rightarrow \hat{D}_B = \frac{e^{-\sum_i \lambda_i \hat{A}_i}}{\mathrm{Tr}\, \hat{D}_B}$$

  - imagine process in which system plus reservoir is at first uncoupled

    $V = 0$ initially



  - slowly we allow interaction

    $$V(t) = \Theta(t)\left(1 - e^{-t/\tau}\right) \sum_{\alpha\gamma} V(r_\alpha - r_\gamma)$$

as time goes on system + reservoir interact

- Hamiltonian evolution $\Rightarrow$ information entropy does not change (19)

$$D(t_i) = D(t_f)$$

$$\Rightarrow S_{info}^{(initial)} = S_B^{(initial)} = S_{info}^{(final)}$$

- however this does not need to hold for Boltzmann entropy

$\Rightarrow$ Boltzmann entropy fixed by constraints on final state: $A_i^{(final)} = \mathrm{Tr}\, \hat{D}_B \hat{A}_i$

$\Rightarrow$ since Boltzmann entropy is a maximum for a given set of constraints it must hold that

$$-\mathrm{Tr}\, D_B^{(final)} \ln D_B^{(final)} \geq \mathrm{Tr}\, D^{(final)} \ln D^{(final)}$$

$\Rightarrow$ entropy increase $\Leftrightarrow$ loss of information