

Entropy lecture

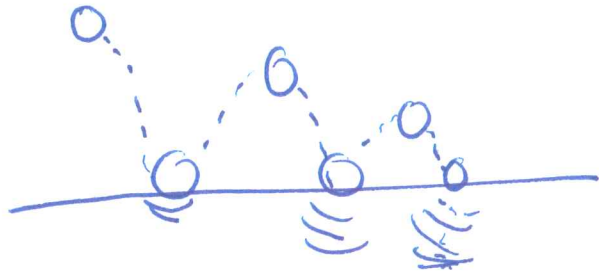
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Sources: Atking: Physical Chemistry
Reichl: A Modern Course in
Statistical Physics
Pathria and Beale: Statistical
Mechanics

- some things happen "naturally": spontaneously
 - examples: gas expands to fill container, chemical reaction proceeds in one direction, hot body cools to temperature of surroundings
 - to oppose spontaneity: need to expend energy, do work
 - what determines direction of spontaneity?
- 1st law of thermodynamics: energy is conserved
- does not offer too much insight into question of direction of spontaneous change $\rightarrow$ total energy remains constant

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- possible explanation: distribution of energy
 - total energy remains constant, but it is parcelled out in different ways

example: ball bouncing on floor $\rightarrow$ tends to damp



1.) never bounces back to initial height

2.) energy is dissipated to the floor, air, etc.
surroundings

- reverse process (stationary ball starts to bounce) has never been observed

- how could this occur? - energy in the floor should localize under the ball and launch it

tendency of spontaneous process: to go from orderly (energy localized) to disorderly (delocalized)

- it is spontaneous to go from localized, orderly towards chaotic disorderly

- cool object will not warm up spontaneously
- gas will not spontaneously contract inside container

1st law of thermodynamics: $dE = dQ + dW$ (3)

E - state function $\Rightarrow E_f - E_i$ depends only on the initial and final states of the system

valid thermodynamic processes $\Rightarrow$ conserve energy

2nd law of thermodynamics

- introduces new state function: entropy S
- allows assessment of direction of spontaneous change

$$dS_{\text{tot}} \geq 0$$

- irreversible processes:
 - accompanied by increase in entropy
- reversible processes:
 - balanced at each step
(system is always in equilibrium with surroundings)
 - do not generate entropy

- statistical definition of entropy: $S = k_B \ln \Omega(E)$

Ω - number of different arrangements of the system with energy E

Second Law: Heat flows spontaneously from High Temperatures to Low Temperatures

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three equivalent statements of this law:

- 1.) The spontaneous tendency of a system to go toward thermodynamic equilibrium cannot be reversed without at the same time changing some organized energy, work, into disorganized energy, heat.
 - 2.) In a cyclic process, it is not possible to convert heat from a hot reservoir without at the same time transferring some heat to a colder reservoir.
 - 3.) The entropy change of any system and its surroundings, considered together, is positive and approaches zero for any process which approaches reversibility.
- second law allows assessment of efficiency of heat engines
 - second law leads to introduction of entropy
 - link between reversible - irreversible
 - stability of equilibrium states

analysis of heat engine:

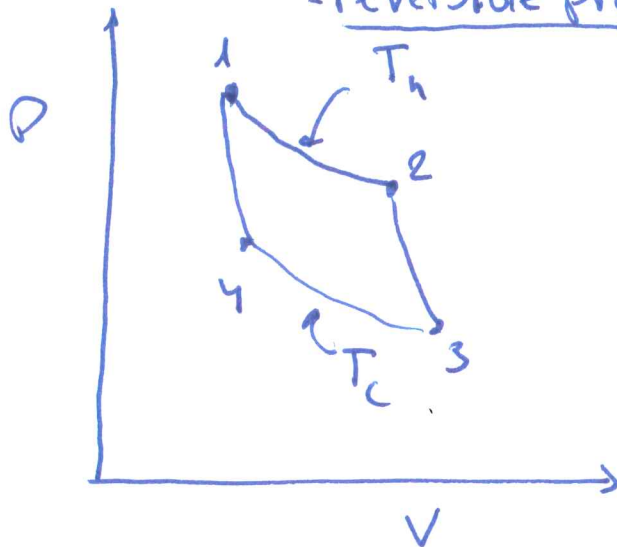
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- heat engine: if heat is allowed to flow from hot reservoir to cold reservoir, some of that heat can be converted into work

- BUT: temperature differences can also disappear spontaneously without producing work (observation of Carnot)

- ideal engine: Carnot cycle - hot and cold reservoirs

- reversible processes: T_h T_c



(1→2) Isothermal absorption of heat ΔQ_{12} from hot reservoir

(2→3) Adiabatic ($\Delta Q=0$) cooling to temperature T_c

(3→4) Isothermal expulsion of heat ΔQ_{43} into reservoir at temperature T_c

(4→1) Adiabatic return to original state

- efficiency: $\eta = \frac{\Delta W_{\text{tot}}}{\Delta Q_{12}}$ work divided by heat extracted

1st law: $\Delta U = 0$ (cyclic process)

$$\Delta U = \Delta Q_{\text{tot}} - \Delta W_{\text{tot}} = \Delta Q_{12} + \Delta Q_{34} - \Delta W_{\text{tot}} = 0$$

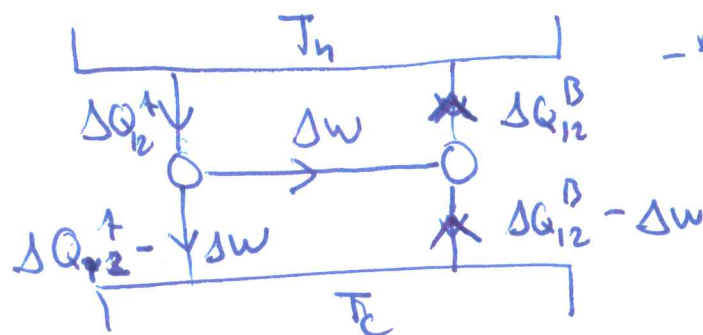
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$$\Rightarrow \eta = 1 - \frac{\Delta Q_{43}}{\Delta Q_{12}}$$

- Carnot engine: based only on reversible processes

$\Rightarrow$ most efficient engine operating between two reservoirs

- to show this: couple two engines running between the two reservoirs together, but run one as a refrigerator $\Rightarrow$ turns heat + work into heat
assume $\eta_A > \eta_B$ (will lead to contradiction)



- fix system so that ΔW is the same

$$\eta_A > \eta_B \Rightarrow \frac{\Delta W}{\Delta Q_{12}^A} > \frac{\Delta W}{\Delta Q_{12}^B}$$

$$\Delta Q_{12}^B \text{ or } > \Delta Q_{12}^A$$

$$\text{if } \Delta Q_{12}^B > \Delta Q_{12}^A \Rightarrow$$

net heat flow from cold reservoir to hot reservoir

$$\Delta Q_{12}^B - \Delta W - (\Delta Q_{12}^A - \Delta W) = \Delta Q_{12}^B - \Delta Q_{12}^A > 0$$

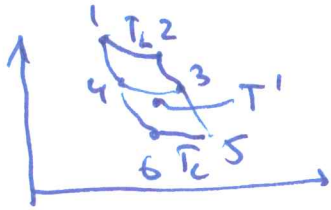
violates second law

heat cannot flow from cold to hot

- Carnot engine is independent of variables P, V , etc. ⑦
only depends on T_c, T_h

$$\Rightarrow \frac{\Delta Q_{43}}{\Delta Q_{12}} = f(T_h, T_c)$$

- we can consider two Carnot engines running between T_h, T' and T', T_c



$$\frac{\Delta Q_{43}}{\Delta Q_{12}} = f(T_h, T')$$

$$\frac{\Delta Q_{65}}{\Delta Q_{43}} = f(T', T_c)$$

$$\frac{\Delta Q_{65}}{\Delta Q_{12}} = f(T_h, T_c) = f(T_h, T') f(T', T_c)$$

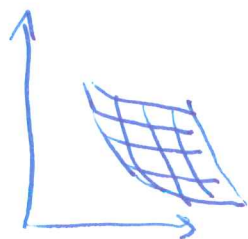
- $\Rightarrow$ allows definition of temperature scale

$$\rightarrow f(T_h, T_c) = \frac{T_c}{T_h}$$

$$\frac{\Delta Q_{43}}{\Delta Q_{12}} = \frac{T_c}{T_h} \Rightarrow \frac{\Delta Q_{43}}{T_c} - \frac{\Delta Q_{12}}{T_h} = 0$$

$$\frac{\Delta Q_{12}}{T_h} + \frac{\Delta Q_{34}}{T_c} = 0$$

- can also consider a sum of many infinitesimal Carnot cycles:



$$\Rightarrow \oint \frac{dQ}{T} = 0$$

$$\text{define entropy } dS = \frac{dQ}{T}$$

entropy $dS = \frac{dQ}{T} \Rightarrow$ state function since (8)
 $\oint dS = 0$

- for engines not running reversibly between
reservoirs T_c, T_h

$$\Rightarrow \frac{\Delta Q_{43}}{\Delta Q_{12}} > \frac{T_c}{T_h}$$

$$\rightarrow \frac{\Delta Q_{43}}{T_c} - \frac{\Delta Q_{12}}{T_h} > 0$$

$$\Rightarrow \oint \frac{dQ}{T} < 0 \Rightarrow \frac{dQ}{T} \text{ no longer exact differential}$$

- entropy for an irreversible process?

- process runs between state i and state f

- to calculate entropy, construct a
hypothetical reversible path between
i and f

$$\int_i^f dS = \int_i^f \frac{dQ}{T}_{\text{rev}}$$

since $\int_{\text{ir-rev}} \frac{dQ}{T} < \int_{\text{rev}} \frac{dQ}{T} \Rightarrow \int_{\text{irrev}} \frac{dQ}{T}$ does not
include all
entropy contri-
butions

$\Rightarrow$ entropy production due to spontaneous

processes: $dS = \frac{dQ}{T} + d\tilde{S} \Rightarrow \boxed{d\tilde{S} \geq 0}$

$d\tilde{S} \geq 0 \Rightarrow$ equality - reversible process

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$\Rightarrow$ equilibrium state: stable against spontaneous changes $\Rightarrow$ equilibrium state is a maximum entropy state

Entropy from the Microscopic Point of View

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- easiest to start with quantum mechanical picture: system is in a particular state i

$$H|\Psi_i\rangle = E_i|\Psi_i\rangle$$

H - Hamiltonian ~~the~~ $|\Psi_i\rangle$ - wavefunction
 E_i - energy of state i

$\Omega(E_i)$ - number of states with energy E_i

- more generally $\Omega(N, E, V)$ - number of states with N particles, volume V , energy E

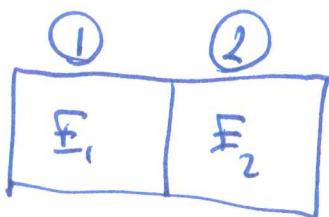
- extension to classical mechanics $\Rightarrow$ states become configurations in the space $\vec{p}_1, \dots, \vec{p}_N, \vec{r}_1, \dots, \vec{r}_N$
($\vec{p}_i$ - momenta of particles, $\vec{r}_i$ - positions of particles)

- basic assumption: a system with $\Omega(N, E, V)$ states is equally likely to be in any one of the states $\Omega(N, E, V)$

connection to microscopic thermodynamics

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- consider quantity $\ln \Omega(N, E, V)$ (will turn out to be the entropy)
- consider also two systems which can exchange energy with each other
(can not exchange particles/volume)



~~system~~	number of configurations
system 1	$\Omega_1(E_1)$
system 2	$\Omega_2(E_2)$

- if the compound system (system 1 + system 2) is isolated then $E_1 + E_2$ is a constant

$$E = E_1 + E_2$$

- number of configurations of the compound system: $\Omega(E) = \Omega_1(E_1) \Omega_2(E_2)$

$$\ln \Omega(E) = \ln \Omega_1(E_1) + \ln \Omega_2(E_2)$$

$\Omega(E)$ - maximum if

$$\frac{\partial \ln \Omega_1(E_1)}{\partial E_1} + \frac{\partial \ln \Omega_2(E_2)}{\partial E_1} = 0$$

$$\frac{\partial \ln \Omega_1(E_1)}{\partial E_1} - \frac{\partial \ln \Omega_2(E_2)}{\partial E_2} = 0$$

$$\text{Since } E_2 = E - E_1$$

- if two systems are in thermal equilibrium: (12)

their temperatures are equal

can we associate $\frac{\partial \ln \Omega(E)}{\partial E}$ with temperature?

let's try: $\frac{1}{k_B T_1} = \frac{\partial \ln \Omega(E_1)}{\partial E_1}$

$$\frac{1}{k_B T_2} = \frac{\partial \ln \Omega(E_2)}{\partial E_2}$$

$$\Rightarrow \frac{1}{T} = \frac{\partial}{\partial E} [k_B \ln \Omega(E)]$$

(k_B - Boltzmann constant)

1st law of thermodynamics for reversible case:

$$dE = dQ + dW \quad (\text{using } dQ = \frac{dS}{T})$$

$$dE = T ds + dW$$

$$\stackrel{!}{dS} = \frac{dE}{T} - dW$$

$$\Rightarrow \frac{1}{T} = \left(\frac{\partial E}{\partial S} \quad \frac{\partial S}{\partial E} \right)_{\text{other variables fixed}}$$

$$\stackrel{!}{S} = k_B \ln \Omega(E) \quad \left. \begin{array}{l} S = k_B \ln \Omega(E) \\ \frac{1}{T} = \frac{\partial k_B \ln \Omega(E)}{\partial E} \end{array} \right\} \begin{array}{l} \text{consistent with} \\ \text{1st law} \\ \text{of thermodynamics} \end{array}$$

$\Rightarrow$ we managed to relate macroscopic thermodynamics to microscopic (statistical) description