

Thermostatistics: a different point of view ①

- entropy can also be introduced in a different way
- in previous notes entropy is introduced based on noticing that the Carnot cycle gives rise to an auxiliary state variable which characterizes the heat transfer associated with a cyclic process
- one can also introduce entropy through comparing microstates with macrostates, noticing that there are a large number of microstates consistent with any given macrostate \rightarrow ~~and~~ this necessitates the introduction of probability \Rightarrow thus the existence of an entropy function with certain properties is postulated
- this path will be pursued in the following
- this path is similar to "information theory" the science of guessing probability distributions ~~from~~ from incomplete data

Thermodynamic equilibrium

②

microscopic and Macroscopic Descriptions

stat. mech. describes LARGE systems

number of particles $N \sim 10^{23}$

- they move!!!

- suppose they are classical

- can we follow their dynamics?

- in principle yes, in practice no

* 10^{23} too large (10^{23} positions + momenta)

* numerical method would be MD (molecular dynamics), which suffers from chaos problem

- suppose they are ~~classical~~ quantum

- can we follow dynamics of system?

- in principle yes, in practice no

* no exact solution exists for such large systems

- assume that system is susceptible to a microscopic description

microscopic description: - positions and momenta (3)

of all particles in classical case

- wavefunction in the

quantum case

⇓ ⇓ ⇓
system has been attributed a microstate

from microstate to macrostate

example: density as a macroscopic variable

$$n(\vec{R}) = \frac{1}{\Delta V} \int_{\Delta V} d\vec{r} \sum_{i=1}^N \delta(\vec{r} - \vec{r}_i(t))$$

\vec{R} → macroscopic (or at least mesoscopic)
length scale

\vec{r} → microscopic length scale

ΔV → small unit of volume - infinitesimal
by macroscopic "standards" - large by
microscopic "standards"

(average over time is also necessary)

- microscopic length scale → nanometer and smaller
- macroscopic length scale → micrometer and larger

⇓ ⇓
macroscopic quantities arise from summing
(integration) over microscopic variables

⇒ exception is entropy

- from a macroscopic point of view ④
⇒ macrostates - defined by thermodynamic variables

- One macrostate is compatible with a large number of microstates

⇓ ⇓
- the question is the probability distribution associated with the microstates corresponding to the particular macrostate

- distribution is defined by use of entropy

Walls

example of macroscopic variable ⇒ energy

$$E = \underbrace{\sum_i \frac{\vec{p}_i^2}{2m}}_{\text{kinetic}} + \underbrace{V(\vec{r}_1, \dots, \vec{r}_N)}_{\text{potential}}$$

energy of an isolated system is conserved

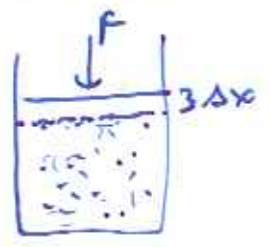
- also applies to quantum system (quantities replaced by operators)

- if system is not isolated \rightarrow we can change its energy (5)

- example: compress a spring (change length)
spring acquires energy stored as elastic potential energy

* force applied through distance
 $F \rightarrow dx$
 \Rightarrow work is done on the system

- example: supply energy to a gas by compressing piston (change volume)



\Rightarrow work done on the system

- in both cases: external parameters (parameters which are under direct control of experimentalist) are modified in a known way

\Downarrow
WORK

- other way to transfer energy: heat
object can heat up, in this case no change in external parameters

HEAT: energy transfer in the form of heat leaves external parameters of the system and of the external medium unchanged (6)

work: measurable from mechanical considerations

- by measuring the changes in the external parameters of the system (length, volume)
- or by measuring the change in the parameters of the associated external medium
- or both

energy change is not known with precision unless exchange of energy between system and surroundings ~~can be eliminated~~ in the form of heat can be eliminated

- achieved by walls

* adiabatic wall: no exchange of ~~energy~~ ^{heat} (heat transfer) between system and surroundings

* diathermic wall: allows heat exchange

* rigid wall: eliminates energy exchange in the form of work

- isolated systems: no exchange of energy between system and surroundings

thermodynamic description depends ⑦
 crucially on existence of such walls
work, heat, internal energy

quantitative development: distinguish
 different ways of supplying energy

- there are different ways of supplying work

$$W_{A \rightarrow B} = \int_{x_A}^{x_B} dx F(x)$$

$F(x)$ - generalized force

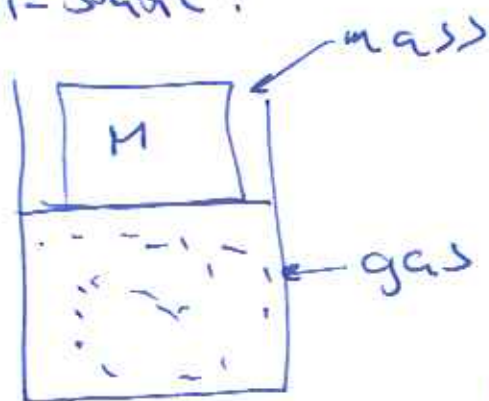
x - generalized displacement

$$dW = F(x) dx$$

- quasi-static transformation

work supplied in such a way that
 the system is always at equilibrium

- example of a transformation which is not
 quasi-static:



\Rightarrow mass suddenly

removed

\downarrow

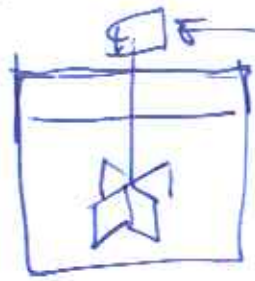
gas will expand against

external pressure ~~$- P_{ext} \Delta V$~~

work $- P_{ext} \Delta V$

volume change not controlled

- another example:



motor \Rightarrow rotate motor
work is done, energy of system will change

- examine energy transfer between states of system: A, B two states

internal energy: U_A, U_B

take U_A as reference energy \Rightarrow consider going from $A \rightarrow B$ i.e. $U_A \rightarrow U_B$ doing only work

- empirical observation:

if states A and B have the same volume

$V_A = V_B$ then we can go from U_A to U_B if $U_B > U_A$
 (for example like this)

if $V_A \neq V_B \rightarrow$ adiabatic expansion or compression $A \rightarrow A'$

$V_A \rightarrow V_{A'} = V_B$
 if $U_{A'} < U_B$ work can be done to arrive at state B

- if transformation is then performed in some other manner, but work is known

we can say $\Rightarrow U_B - U_A = Q_{A \rightarrow B} + W_{A \rightarrow B}$ (9)

\Rightarrow 1st law of thermodynamics

or $dU = dQ + dW$

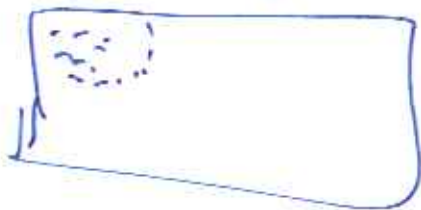
(here we are doing work on system
so W is positive)

$dW = \vec{F} \cdot d\vec{l}$ if $\vec{\nabla} \times \vec{F} \neq 0 \Rightarrow$ work
not an exact differential

Thermal equilibrium

experience tells us that if we wait long
enough system will equilibrate

example \swarrow initial state of gas



equilibrium state
of gas

some times (depending on relaxation)