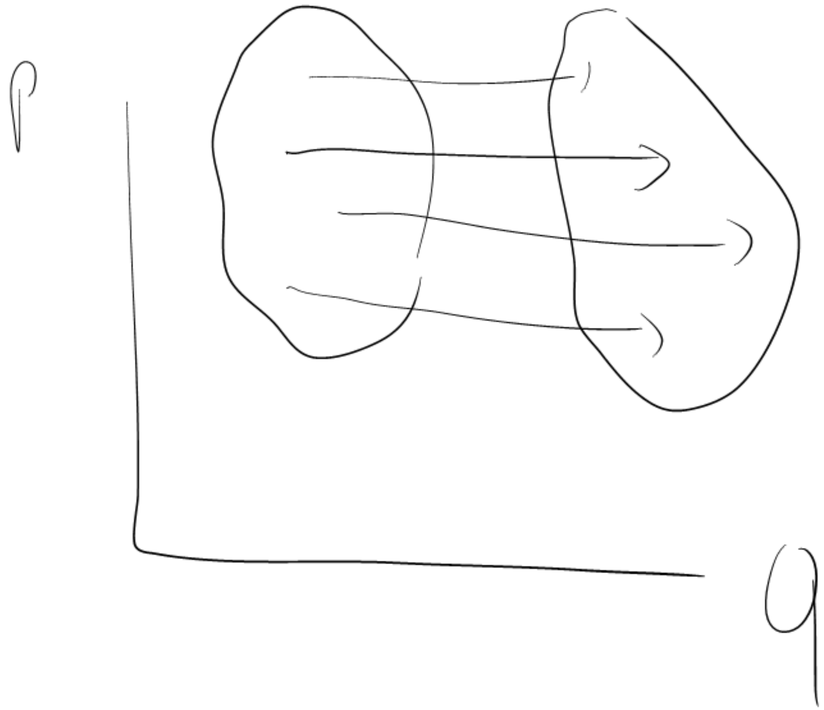
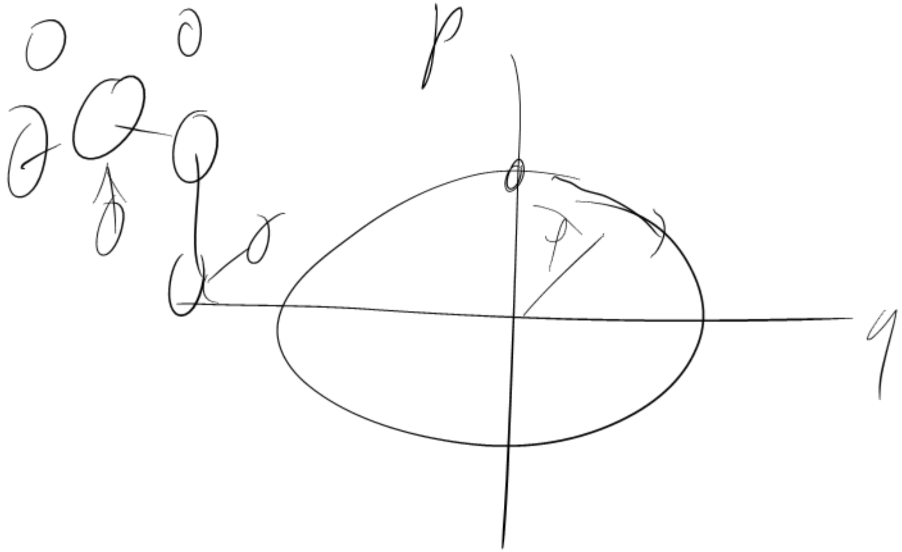
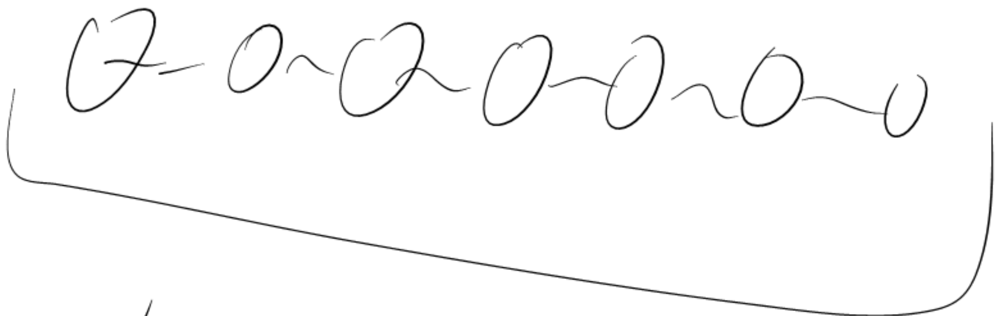
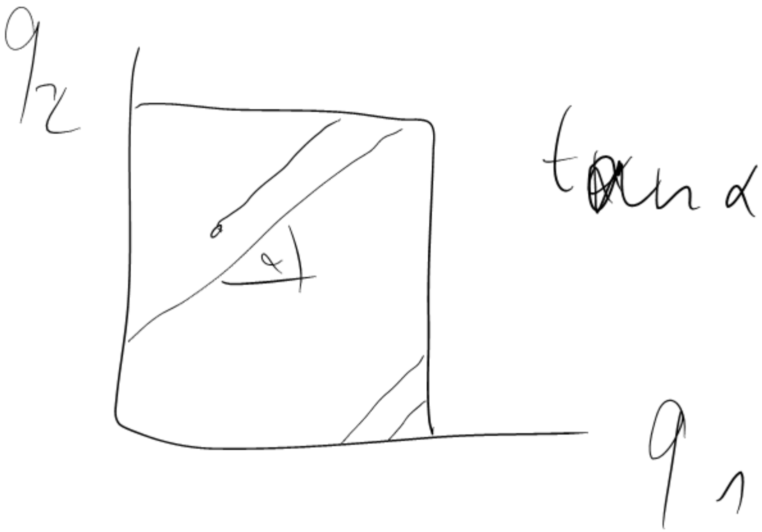


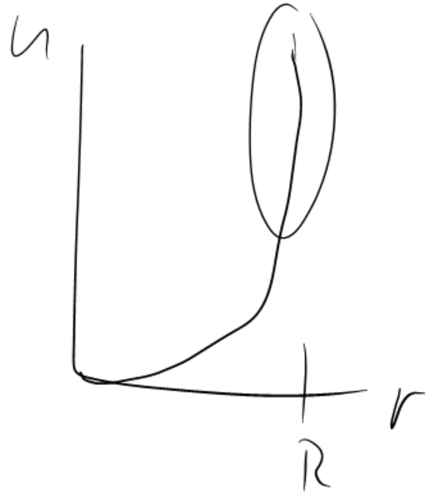






tan α = rational

ergodicity



Introduction to Statistical Physics

Systems with MANY ($N \gg 1$)

Degrees of Freedom

<u>Mechanics</u> "Molecular Dynamics":

Solve Newton's eqs. of motion for an N-particle system ($10^3 \lesssim N \lesssim 10^6$)

trajectory $\longrightarrow$ SO WHAT???

Statistics / probability theory: NEED

ASSUMPTION about the underlying probabilities

What IS a reasonable assumption??

We assume: Each state of the system has the SAME probability.

What IS the state of the system?

What are the ACCESSIBLE States?

($\rightarrow$ boundary conditions?) $\longrightarrow$ ensemble

→ Relation to DYNAMICS?

Mechanics (quantum mechanics) + statistics →

STATISTICAL PHYSICS

(statistical mechanics, statistical thermodynamics)

Statements about observables:

- mean value
- fluctuations
- distributions

New concepts:

- entropy
- temperature
- pressure
- chemical potential
- thermodynamic potentials
- partition functions

"thermodynamic limit" $N \to \infty$

fluctuations average out

$\longrightarrow$ Thermodynamics (fluctuations are ignored)

- thermodynamic potentials
- relations between thermodynamic quantities

Example for illustration:

Gas (air) in the lecture hall

$V = 100\,m^3$, room temperature $300\,K$

$$k_B T = 1.380657 \cdot 10^{-23} \frac{J}{K} \cdot 300\,K \simeq 4 \cdot 10^{-21}\,J$$

New unit system: $k_B = 1$ (temperature is measured in energy units); $T(\text{lecture}) = k_B T(\text{conv. lit.})$

atmospheric pressure: $p = 10^5\,Pa$

eq. of state of an ideal gas: $pV = NT$

$$\Rightarrow N = \frac{10^5 \cdot 10^2}{4 \cdot 10^{-21}} = 0.25 \cdot 10^{28} \text{ particles}$$

How large is the probability that all air particles assemble in one corner ($V = 1\,\ell = 10^{-3}\,m^3$)

assumptions: - every subvolume is equally likely
- particles are statistically independent

one particle: probability: $\frac{10^{-3}\,m^3}{10^2\,m^3} = 10^{-5}$

total prob: $\left(10^{-5}\right)^{0.25 \cdot 10^{28}}$

n: # particles in the sub-volume

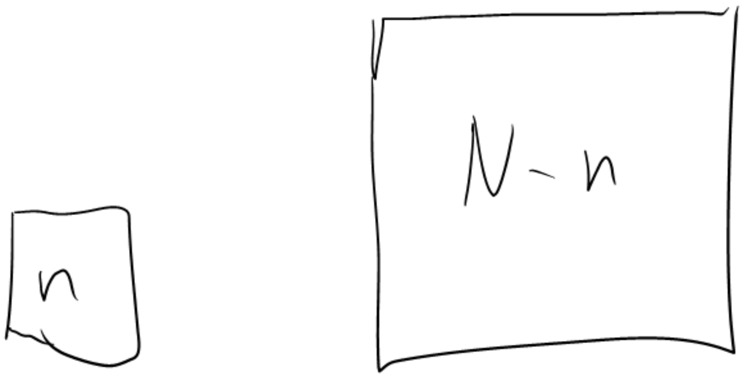
$\langle n \rangle$: MEAN VALUE of n

$$\langle n \rangle = 10^{-5} \cdot 0.25 \cdot 10^{28} = 0.25 \cdot 10^{23}$$

fluctuations?

single-particle prob.:

$1-q$



prob.: $q = 10^{-5}$

probab. for a filling with n:

$$p(n) = \underbrace{q^n (1-q)^{N-n}}_{\text{prob. for one particular subset of size } n} \underbrace{\frac{N!}{n!\,(N-n)!}}_{\#\text{ of subsets of size } n \quad {}^N C_n}$$

binomial distribution

$$\Omega(n) = \binom{N}{n} = \frac{N!}{n!\,(N-n)!}$$

$$\underbrace{\sum_n p(n)} = \sum_{n=0}^{N} \binom{N}{n} q^n (1-q)^{N-n} \overset{\text{binomial theorem}}{=}$$

$$\left[q + (1-q)\right]^N = 1^N = 1 \quad \checkmark$$

$$\langle n \rangle = \sum_n n\, p(n) = ?$$

observation: $n q^n = q\, n\, q^{n-1} = q \frac{d}{dq} q^n$

<u>define:</u> $f(n) = \binom{N}{n} q^n r^{N-n} \Rightarrow p(n) = f(n)\Big|_{r=1-q}$

$$\sum_n f(n) = (q+r)^N$$

$$\langle n \rangle = \sum_n n\, p(n) = \sum_n n\, f(n) \Big|_{r=1-q} = \sum_n q \frac{d}{dq} f(n) \Big|_{r=1-q} =$$

$$= q \frac{d}{dq} \sum_n f(n) \Big|_{r=1-q} = q \frac{d}{dq} (q+r)^N \Big|_{r=1-q} =$$

$$= q\, N (q+r)^{N-1} \Big|_{r=1-q} = qN$$

$$\langle n^2 \rangle = \sum_n n^2 p(n) = \sum_n n^2 f(n) \Big|_{r=1-q} =$$

$$= q \frac{d}{dq}\, q \frac{d}{dq} (q+r)^N \Big|_{r=1-q} = q \frac{d}{dq}\, q N (q+r)^{N-1} =$$

$$= qN \left\{ (q+r)^{N-1} + q(N-1)(q+r)^{N-2} \right\} \Big|_{r=1-q} =$$

$$= qN \{ 1 + q(N-1) \} = qN + q^2 N^2 - q^2 N =$$

$$= \langle n \rangle + \langle n \rangle^2 - q \langle n \rangle = \langle n^2 \rangle$$

$$\underbrace{\langle n^2 \rangle - \langle n \rangle^2}_{= \langle (n - \langle n \rangle)^2 \rangle} = \langle n \rangle (1-q)$$

$$\Downarrow$$

$$\langle \Delta n^2 \rangle = \langle n \rangle (1-q)$$

$$\frac{\langle \Delta n^2 \rangle}{\langle n \rangle^2} = \frac{1-q}{\langle n \rangle} \qquad \frac{\Delta n}{n} = \sqrt{\frac{\langle \Delta n^2 \rangle}{\langle n \rangle^2}} = \frac{\overset{\simeq 1}{\overset{\uparrow}{\sqrt{1-q}}}}{\sqrt{\langle n \rangle}}$$

$$\boxed{\frac{\Delta n}{n} = \frac{1}{\sqrt{n}}} \simeq 6 \cdot 10^{-12}$$

$\uparrow$
$n = 10^{23}$

generally: for independent degrees of freedom:

$$\underbrace{\frac{\Delta A}{A}}_{\text{rel. error of observable } A} \propto N^{-1/2}$$

N: # of degrees of freedom involved in A

BUT: This considerations rest on the assumption of independent particles (≡ weakly interacting)

What about water, polymers, liquid helium, iron, butter, ... ???

Solution, part 1

Subsystem, size >> range of interaction

Sub-systems only interact via the interface

$\rightarrow$ quasi-statistically independent

Study so-called EXTENSIVE Observables (volume-additive)

$$A(\text{total system}) = \sum_{\text{subsystems}} A(\text{subsystem})$$

<u>Ex:</u> Mass, particle number, energy, magnetization, ...

Let $N = \#$ subsystems

$$A_{tot} = \sum_i A_i \qquad \langle A_i \rangle = \langle A_{subs} \rangle$$

$$\Rightarrow \langle A_{tot} \rangle = N \langle A_{subs} \rangle$$

$$\langle A_{tot}^2 \rangle = \sum_{ij} \langle A_i A_j \rangle = \sum_i \langle A_i^2 \rangle + \sum_{i \neq j} \langle A_i A_j \rangle =$$

$$= N \langle A_{subs}^2 \rangle + N(N-1) \langle A_{subs} \rangle^2$$

$$\langle A_{tot}^2 \rangle - \langle A_{tot} \rangle^2 = N \langle A_{subs}^2 \rangle + (N^2 - N) \langle A_{subs} \rangle^2$$

$$- N^2 \langle A_{subs} \rangle^2 =$$

$$= N \left[\langle A_{subs}^2 \rangle - \langle A_{subs} \rangle^2 \right]$$

$$\frac{\sqrt{\langle A_{tot}^2\rangle - \langle A_{tot}\rangle^2}}{\langle A_{tot}\rangle} \propto \frac{\sqrt{N}}{N} \propto \frac{1}{\sqrt{N}}$$

$\uparrow$ works also for subsystems!

<u>BUT</u>: We do <u>not</u> know $\underbrace{\langle A_{subs}\rangle, \langle A_{subs}^2\rangle}_{\text{where from?}}$

solution, part 2 (Gibbs)

Idea: Do NOT consider the particles (or degrees of freedom) as the objects to do statistics on, but *rather* the **state points of the total system!!!** Assume that *these* are statistically equivalent. $\longrightarrow$ Hamiltonian dynamics!