I   Review of relevant parts of Statistical Physics

Statistical physics: study of macroscopic systems with $N \gtrsim 10^{23}$ particles

system is characterized by a <u>microstate</u> and a <u>macrostate</u>

microstate : defined by the location and momenta of all N
particles (classical systems) or the N-body wave
function (quantum mechanical systems)

macrostate : characterizes system by a few macroscopic observables
like energy (E), volume (V), pressure (P), temperature (T),...

- Microstate is practically impossible to determine.

- Even if we would know this state, how can we solve $N \sim 10^{23}$
coupled different equations and extract useful information?

- Microstate changes all the time due to interaction processes
with environment. These interactions are usually weak enough
such that only the microstate changes, but the macrostate
remains the same

- basic idea of statistical physics:

Consider <u>all</u> microstates at the same time that are consistent
with certain values of <u>macro</u> observables. $\Rightarrow$ ensembles

ensemble : a large number of virtual copies of a system,
where each copy represents a possible microstate
the system can be in

phase space (in classical physics) : consider one particle in 1 dim

harmonic oscillator : $x(t) = x_0 \cos(\omega t)$

$p(t) = -m x_0 \omega \sin(\omega t)$
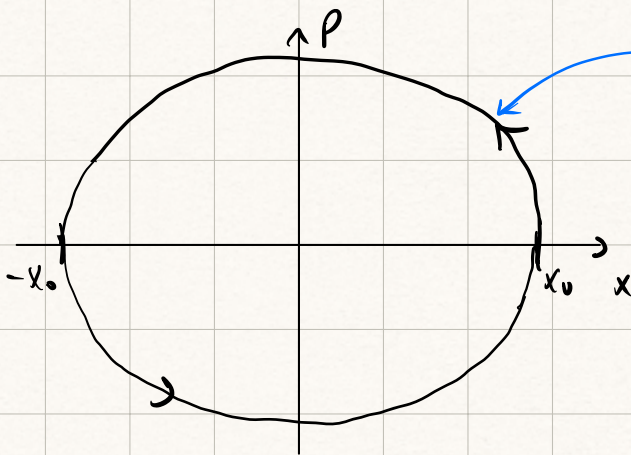
phase space trajectory corresponds to a fixed __energy__ of the system

$$E = \frac{p^2}{2m} + \frac{1}{2} m x^2 \omega^2$$

$$= \frac{1}{2} m x_0^2 \omega^2$$

— state of system at a given time is a point in a 2d phase space

— for N particles in 3d phase space has 6N dimensions

— __MANY__ different points (microstates) correspond to a macrostate of a given energy

— introduce __probability distribution__ in phase space

$$\rho(x, p, t)\, dx\, dp = \rho(x_1, x_2, \dots, x_{3N}, p_1, p_2, \dots, p_{3N}, t) \prod_{i=1}^{3N} dx_i\, dp_i$$

conservation law : $\dfrac{\partial \rho}{\partial t} = - \nabla \cdot v \rho$ (Liouville equation)

Microcanonical ensemble and partition function

consider isolated macroscopic system
with N particles, volume V
and energy E

$$\boxed{N, V, E}$$

in reality the total energy is given by a
range $[E-\Delta E, E]$

↙ macroscopic ↓ microscopic (e.g. fluctuations due to interactions
                                 with environment)

Fundamental postulate of statistical physics

All microstates with energy in range $[E-\Delta E, E]$
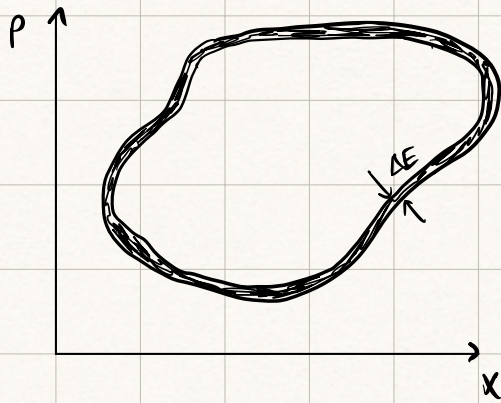have the <u>same</u> probability (density):

$$\rho_{mc} = \begin{cases} \dfrac{1}{Z_{mc}} & \text{for } E-\Delta E \leq H(p,x) \leq E \quad ((E-\Delta E)(n) \leq H(n) \leq E(n)) \\ 0 & \text{else} \end{cases}$$

Z_{mc} is a phase space volume in classical physics and
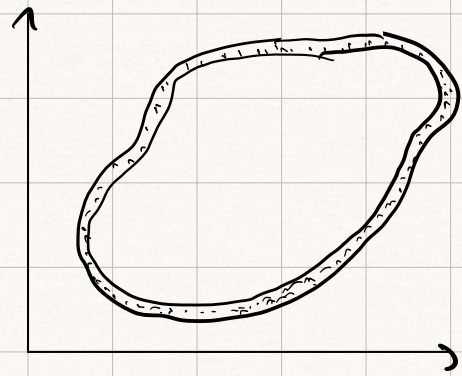a discrete number of states in Qm.

microcanonical partition function:

$$Z_{mc} = \text{Tr} \left[\Theta(E-H) - \Theta(H - (E-\Delta E)) \right]$$

classical   Qm

One can show that Z_{mc} is basically independent of ΔE
since the phase space increases VERY rapidly with energy: $Z_{mc} \sim E^N$
$\Rightarrow$ For $N \approx 10^{23}$ the entire phase space is dominated by
the upper limit of the energy shell
                                          $\rightarrow$ exercise

density matrix, entropy and expectation values

Consider QM system in a microstate $|\psi_i\rangle$ with probability ρ_i

$\Rightarrow$ then the density matrix is defined by

$$\rho = \sum_i \rho_i \, |\psi_i\rangle\langle\psi_i|$$

$\qquad\qquad\qquad\qquad \rightarrow$ contains inherent Qm uncertainties

$\qquad\qquad\qquad$ describes statistical uncertainties (ensembles)

$\Rightarrow$ expectation value of operator A :

$$\langle A \rangle = \sum_i \rho_i \, \langle\psi_i|A|\psi_i\rangle$$

$$= \sum_i \rho_i \sum_n \langle\psi_i|n\rangle\langle n|A|\psi_i\rangle$$

$$= \sum_i \rho_i \sum_n \langle n | A | \psi_i \rangle \langle \psi_i | n \rangle$$

$$= \sum_n \langle n | A \rho | n \rangle$$

$$= \sum_n \langle n | \rho A | n \rangle = \text{Tr} (\rho \cdot A)$$

$\vdash$ short hand notation for sum over complete set of N-body states

$$\text{Tr} = \int \frac{d^{3N}x \, d^{3N}p}{h^{3N} N!}$$

semiclassical approx. for N identical particles

microcanonical density matrix:

$$\rho_{mc} = \sum_n \rho_{mc}(E_n) \, |n\rangle\langle n| = \sum_n \frac{1}{Z_{mc}(E_n)} |n\rangle\langle n|$$

$$\text{Tr} \, \rho_{mc} = 1 \qquad (\text{normalization of total probability})$$

Definition of entropy (general):

$$S = - k_B \, \text{Tr} \left(\rho \log \rho \right) = - k_B \langle \log \rho \rangle$$

for the microcanonical ensemble:

$$S_{mc} = - k_B \sum_n \rho(E_n) \log(\rho(E_n))$$

$$= - k_B \sum_n Z_{mc}^{-1}(E_n) \log \left[Z_{mc}^{-1}(E_n) \right]$$

$$= + k_B \log Z_{mc}(E_n)$$

$\hookrightarrow$ Boltzmann entropy

Temperature

consider a system consisting of two subsystems,
total system __isolated__

energy
exchange

V_1, N_1, E_1 V_2, N_2, E_2

Hamiltonian: $H = H_1 + H_2 + W$
↑
Small correction to
total energy of system,
but allows __energy exchange__
between subsystems
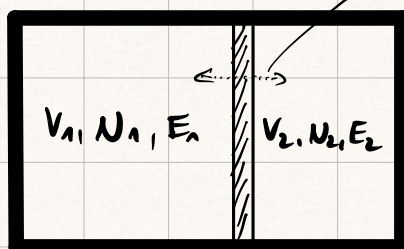
probability of microstates of system 1+2 with energy $E = E_1 + E_2$

$$
P_{mc}(E) = \begin{cases} \dfrac{1}{Z_{mc}(E)} & \text{for} \quad E - \Delta E \leq H_1 + H_2 + W \leq E \\ & \left((E - \Delta E)|n\rangle \leq (H_1 + H_2 + W)|n\rangle \leq E|n\rangle \right) \\ \\ 0 & \text{else} \end{cases}
$$

probability for subsystem 1 to have energy in range $\left[E_1 - \Delta E_1, E_1 \right]$,
and hence subsystem 2 to have energy in range $\left[E_2 - \Delta E_2, E_2 \right]$:

$$
\rho(E_1) = \text{Tr}'_{E_1} \, \rho_{mc}^{(1+2)}(E) \equiv \text{Tr} \, \rho_{mc}^{(1+2)}(E) \, \delta_{E_1, H_1}
$$

↓
restricted trace

↓
consider only those states
for which subsystem 1 has
energy in given range

$$\Rightarrow \rho(E_1) = Tr \; \S_{mc}^{(1+2)}(E) \; \delta_{E_1 H_1}$$

$$= Tr \; \frac{1}{Z_{mc}^{(1+2)}(E)} \; \delta_{E_1 H_1 + H_2} \; \delta_{E_1 H_1}$$

$$= Tr_1 \; Tr_2 \; \frac{1}{Z_{mc}^{(1+2)}(E)} \; \delta_{E_1 H_1} \; \delta_{E - E_1, H_2}$$

$$= \frac{Z_{mc}^{(1)}(E_1) \; Z_{mc}^{(2)}(E - E_1)}{Z_{mc}^{(1+2)}(E)}$$

determine the most probable energy $\bar{E}_1$: $\left. \dfrac{d\rho(E_1)}{dE_1} \right|_{E_1 = \bar{E}_1} = 0$

$$\Rightarrow \left. \frac{\partial Z_{mc}^{(1)}(E_1)}{\partial E_1} \right|_{E_1 = \bar{E}_1} Z_{mc}^{(2)}(E - E_1) + Z_{mc}^{(1)}(E_1) \left. \frac{\partial Z_{mc}^{(2)}(E - E_1)}{\partial E_1} \right|_{E_1 = \bar{E}_1} = 0$$

$$\Rightarrow \underbrace{\left. \frac{\partial \log Z_{mc}^{(1)}(E_1)}{\partial E_1} \right|_{E_1 = \bar{E}_1}}_{\dfrac{\partial S_1(E_1)}{\partial E_1} = T_1^{-1}} = \underbrace{\left. \frac{\partial \log Z_{mc}^{(2)}(E_2)}{\partial E_2} \right|_{E_2 = E - \breve{E}_1}}_{\dfrac{\partial S_2(E_2)}{\partial E_2} = T_2^{-1}}$$

$$\boxed{\begin{array}{c} \text{Definition of temperature :} \\[2mm] T^{-1} = \dfrac{\partial S(E)}{\partial E} \end{array}}$$