F. Looking Deeper into the Postulate†

[Ideas behind microcanonical ensemble]

Phase Space

e.g. 1D harmonic oscillator (one oscillator)

$$E = \frac{p_x^2}{2m} + \frac{1}{2}m\omega^2 x^2$$ Classical Mechanics

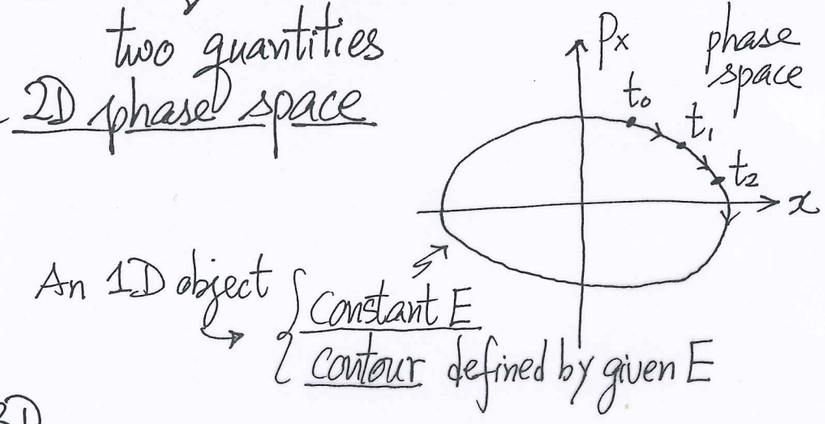
A state of the oscillator is specified by

(x, p_x) ("")

position, momentum

two quantities

Need a 2D phase space



An 1D object → { constant E contour defined by given E

A Particle in 3D

⇒ a 6D phase space [μ-space]

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† This section is a bit abstract and requires a level of maturity in physics on the part of the students. But it gives a qualitative discussion on the ideas (philosophy) behind Stat. Mech. However, students find it too abstract may jump to Sec. 6. One can still apply Statistical Mechanics to many problems and appreciate its usefulness!

Γ-space

e.g. a gas of N particles (atoms/molecules)

A state is specified by (a state of the N-particle system)

$$(x_1, y_1, z_1, p_{x1}, p_{y1}, p_{z1}; \cdots; x_N, y_N, z_N, p_{xN}, p_{yN}, p_{zN})$$

6N variables (6N degrees of freedom)

- We need a phase space of 6N dimensions ($N \sim 10^{23}$)!

called Γ-space → (hard to draw!)

[6×10^{23} Dimensions!]

- One point in the Γ-space specifies a state (microstate)

$$H_N = H(\vec{p}_1, \cdots \vec{p}_N; \vec{r}_1, \cdots \vec{r}_N)$$ N-particle Hamiltonian

$$= \sum_{i=1}^{N} \frac{\vec{p}_i^{\,2}}{2m} + \frac{1}{2}\sum_{\substack{i,j \\ (i\neq j)}} U(\vec{r}_i - \vec{r}_j)$$

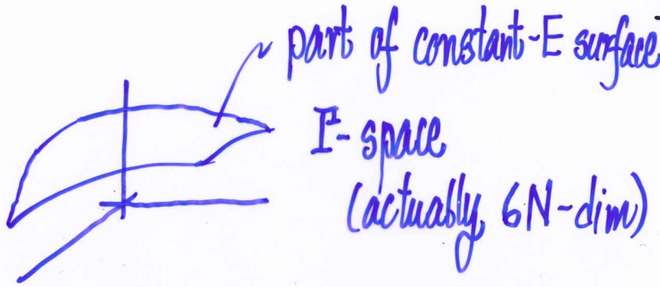
k.e. p.e. due to inter-particle interactions

If only conservative force is involved, then energy is a constant of the motion.

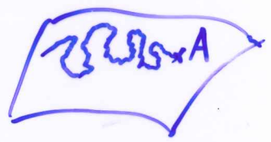
Given E (macrostate), the microstates are those on a (6N-1)-dimensional constant energy "surface".

(i.e. E defines a constant-E surface)

Schematically,



- If at time t_0, the system is in a state A, what† will happen at a later time?



The system will change from one state to another, due to interactions.

But all these states must be on the constant-E surface! i.e. as system evolves, it tracks a trajectory in Γ-space on the constant-E surface.

- Postulate of equal a priori probabilities:

for an isolated system in equilibrium, the system visits all states with equal probabilities [if we wait long enough! How long? Long enough for many collisions (interactions) to occur so that the system can sample the constant-E surface evenly.]

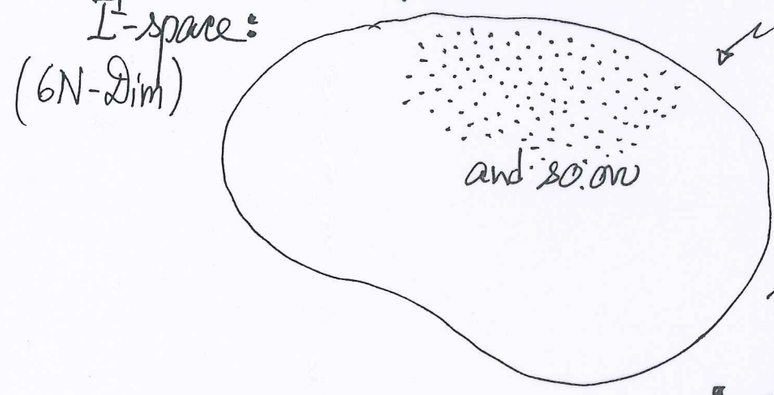
⇒ trajectory will fill the surface evenly

† Let's consider classical mechanics. But within QM, the idea is basically the same, except we need to take care of what the uncertainty principle implies.

Pictorially, (6N-1)-dim constant-E surface, think about the system leaving a footprint every time it visits a microstate.

Equal a priori probabilities

⇒ after long time, system spends equal time in every accessible microstate (ergodic hypothesis)†



Postulate

- dots are of equal darkness
- uniform density of dots

† Rigorous proof of the idea can be carried out for some systems, but not all. Recall that the Hamilton's equations actually tell us how a system evolves. [Or the Liouville equation governs how a collection of systems evolve.] But it is easier to take "equal a priori probabilities" as an assumption. The theory works because the results are right!

Taking averages:

- Practically, thermodynamic measurements

  time of measurement → Many collisions + during that time
  [electrons in metal ~10^{14} collisions in one second!]

- One way to think about measurements:

  Follow one system in time and take Time Average

  visits all accessible states evenly (after long time approached equilibrium)

  Measure Quantity A

  Value of A may be different in different microstates
  (they have same E)

  [Microstates: #1, #2, ···, #W
  Value of A: $A_1, A_2, \cdots, A_W$]

  In principle, $\langle A \rangle = \frac{1}{T}\int_0^T A(t)\,dt$

  (T: follow system from 0 to T; $A(t)$: value of A at time t, depends on which state the system is at t)

  $$\langle A \rangle = \sum_i p_i A_i$$

  ($\langle A \rangle$: quantity measured in exp'ts; p_i: prob. of system being in state i)

  $$= \sum_i \frac{1}{W} A_i$$ ← (equal a-priori probabilities) [isolated, equilibrium]
  (thus time spent at state i in a long time window)

+ On one hand, we like non-interacting systems for their simplicity. On the other hand, we like interactions for their help in taking a system to equilibrium.

Interpreting the average differently

- Ensemble average [Here enters "ensemble"!]

[Recall: we are concerned with isolated system in equilibrium here, i.e. fixed (E, V, N)]

- An ensemble: a collection (Many, infinitely many) of identical copies of the system SUITABLY CHOSEN+ so that we can replace a time average following one system BY an average over the ensemble of systems (at one time) for the condition (isolated? equil. with heat bath? equil. with heat and particle bath?) under consideration.

i.e. Replace "time average" by an "ensemble average", but must construct the ensemble carefully!

+ "Suitably chosen" is important here and it means one needs to learn physics and statistical physics in particular!

Properly choosing the members in an ensemble

- Isolated system in equilibrium: Microcanonical Ensemble

  $(E,V,N) \rightarrow 1, \cdots, W$ accessable microstates

  (for simplicity, let's say a finite number of microstates)

- Choose a collection of

  $\mathcal{N}$ copies of the systems

  (all with (E,V,N))

  - $\mathcal{N}\frac{1}{W}$ of them in microstate #1
  - $\mathcal{N}\frac{1}{W}$ of them in microstate #2
  - ⋮
  - $\mathcal{N}\frac{1}{W}$ of them in microstate #W

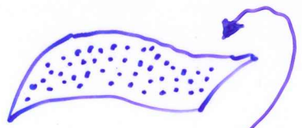
  reflects equal a priori probabilities

  $[\mathcal{N}\frac{1}{W} \gg 1]$ $(\mathcal{N} \gg W)$

then average over this ensemble gives the same result as a time average

i.e.

Pictorially,



• = a copy in an ensemble

collection of copies = many dots

equal a-priori probabilities

= density of dots on constant-E surface ρ is a constant

- For an isolated system in equilibrium,

  i.e. fixed (E,V,N),

  such an ensemble is called the

  Microcanonical Ensemble (微正則系綜)

With these averaging processes in mind, we can ask questions about averaged quantities.

e.g. For the example in Sec. C (see distributions on p.III-⑨ and III-⑩), what is the averaged number of particles in each level?

[This is called the averaged distribution]

Summary

- Imagine an ensemble consisting one copy of each of the $W(E,V,N)$ microstates. they form the microcanonical ensemble.
- Thus, each microstate carries the same $\frac{1}{W}$ weight
- Average over members in an ensemble gives physical quantities