Lecture 3. Combinatorics, Probability and Multiplicity (Ch. 2)

- Combinatorics and probability

- 2-state paramagnet and Einstein solid

- Multiplicity of a macrostate

  – Concept of Entropy (next lec.)

- Directionality of thermal processes (irreversibility)

  – Overwhelmingly probable

Combinatorics and probability

Combinatorics is the branch of mathematics studying the enumeration, combination, and permutation of sets of elements and the mathematical relations that characterize their properties.

Examples: random walk, two-state systems, …

Probability is the branch of mathematics that studies the possible outcomes of given events together with the outcomes' relative likelihoods and distributions. In common usage, the word "probability" is used to mean the chance that a particular event (or set of events) will occur.

Math 104 - Elementary Combinatorics and Probability

Probability

An event (very loosely defined) – any possible outcome of some measurement.
An event is a statistical (random) quantity if the probability of its occurrence, **P**, in the process of measurement is < 1.

The "sum" of two events: in the process of measurement, we observe either one of the events. **Addition rule** for independent events: $P(i \text{ or } j) = P(i) + P(j)$

(independent events – one event does not change the probability for the occurrence of the other).

The "product" of two events: in the process of measurement, we observe both events.

Multiplication rule for independent events: $P(i \text{ and } j) = P(i) \times P(j)$

Example: What is the probability of the same face appearing on two successive throws of a dice?

The probability of any specific combination, e.g., (1,1): 1/6x1/6=1/36   (multiplication rule) . Hence, by addition rule, P(same face) = $P(1,1) + P(2,2) +...+ P(6,6) = 6 \times 1/36 = 1/6$

Expectation value of a macroscopic observable **A:**
(averaged over all accessible microstates)

$$\langle A \rangle = \sum_{\{\sigma\}} P(\sigma_1,...,\sigma_N) A(\sigma_1,...,\sigma_N)$$

Two model systems with fixed positions of particles and discrete energy levels

- the models are attractive because they can be described in terms of discrete microstates which can be easily counted (for a continuum of microstates, as in the example with a freely moving particle, we still need to learn how to do this). This **simplifies calculation of** Ω. On the other hand, the results will be applicable to many other, more complicated models.

Despite the simplicity of the models, they describe a number of experimental systems in a surprisingly precise manner.
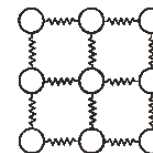
- two-state paramagnet   ↑↓↓↑↓↑↑↓↓↓↑↓↑**....**

("limited" energy spectrum)

- the Einstein model of a solid

("unlimited" energy spectrum)

The Two-State Paramagnet

- a system of non-interacting magnetic dipoles in an external magnetic field **B**, each dipole can have only two possible orientations along the field, either parallel or any-parallel to this axis (e.g., a particle with spin ½). No "quadratic" degrees of freedom (unlike in an ideal gas, where the kinetic energies of molecules are unlimited), the energy spectrum of the particles is *confined within a finite interval of E* (just two allowed energy levels).

$\vec{B}$

E

$E_2 = + \mu B$

an arbitrary choice of zero energy $\longrightarrow$ **0**

$E_1 = - \mu B$
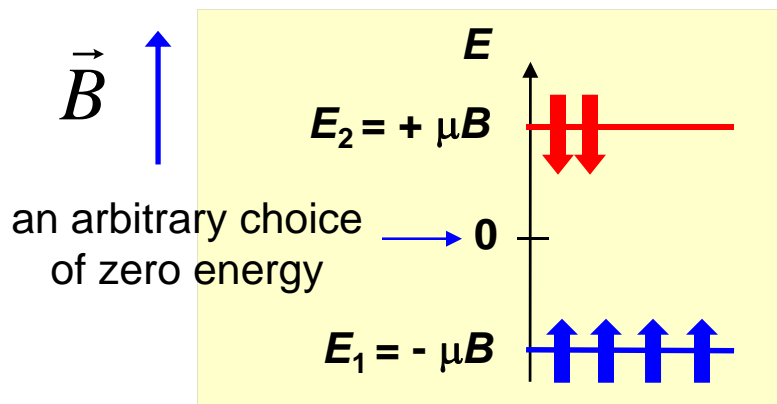
A particular *microstate* ($\uparrow\downarrow\downarrow\uparrow\downarrow\uparrow\uparrow\downarrow\downarrow\downarrow\uparrow\downarrow\uparrow$....) is specified if the directions of all spins are specified. A *macrostate* is specified by the total # of dipoles that point "up", $N_\uparrow$ (the # of dipoles that point "down", $N_\downarrow = N - N_\uparrow$).

$$N = N_\downarrow + N_\uparrow$$

$N_\uparrow$ - the number of "up" spins

$N_\downarrow$ - the number of "down" spins

μ - the magnetic moment of an individual dipole (spin)

The total magnetic moment:
(a macroscopic observable)

$$\vec{M} = \vec{\mu}\left(N_\uparrow - N_\downarrow\right) = \left[N_\downarrow = N - N_\uparrow\right] = \vec{\mu}\left(2N_\uparrow - N\right)$$

The energy of a single dipole in the external magnetic field:

$$\varepsilon_i = -\vec{\mu}_i \cdot \vec{B} \qquad \begin{cases} -\mu B \text{ for } \mu \text{ parallel to } \textbf{\textit{B}}, \\ +\mu B \text{ for } \mu \text{ anti-parallel to } \textbf{\textit{B}} \end{cases}$$

The energy of a macrostate:

$$U = -\vec{M} \cdot \vec{B} = \mu B\left(N_\downarrow - N_\uparrow\right) = \mu B\left(N - 2N_\uparrow\right)$$

Example

Consider two spins. There are four possible configurations of microstates:

↑↑   ↑↓   ↓↑   ↓↓

$M =$ 2μ 0 0 -2μ

In zero field, all these microstates have the same energy (degeneracy). Note that the two microstates with M=0 have the same energy even when $B \neq 0$: they belong to the same macrostate, which has multiplicity Ω=2. The macrostates can be classified by their moment M and multiplicity Ω:

$M =$ 2μ 0 -2μ

$\Omega =$ 1 2 1

For three spins: ↑↑↑   ↑↑↓   ↑↓↑   ↓↑↑   ↑↓↓   ↓↑↓   ↓↓↑   ↓↓↓

$M =$ 3μ μ μ μ $-\mu$ $-\mu$ $-\mu$ -3μ

macrostates:

$M =$ 3μ μ $-\mu$ -3μ

$\Omega =$ 1 3 3 1

The Multiplicity of Two-State Paramagnet

Each of the microstates is characterized by N numbers, the number of equally probable microstates – 2^N, the probability to be in a particular microstate – $1/2^N$.

For a two-state paramagnet in zero field, the energy of all macrostates is the same (0). A macrostate is specified by $(N, N_\uparrow)$. Its multiplicity - the number of ways of choosing $N_\uparrow$ objects out of $\mathbf{N}$:

$$\Omega\,(N,0)=1 \qquad \Omega\,(N,1)=N \qquad \Omega\,(N,2)=\frac{N\times(N-1)}{2} \qquad \Omega\,(N,3)=\frac{N\times(N-1)\times(N-2)}{3\times 2}$$

$$\Omega\,(N,n)=\frac{N\times(N-1)\times...\times[N-(n-1)]}{n\times...\times 3\times 2\times 1}=\frac{N!}{n!(N-n)!}$$

$$=\binom{N}{n}$$

$n\,! \equiv$ **n factorial = 1·2·.....·n**

$\mathbf{0\,! \equiv 1}$ (exactly one way to arrange zero objects)

The multiplicity of a macrostate of a two-state paramagnet with $(N, N_\uparrow)$:

$$\Omega\,(N,N_\uparrow)=\frac{N!}{N_\uparrow!\,N_\downarrow!}=\frac{N!}{N_\uparrow!\,(N-N_\uparrow)!}$$

Stirling's Approximation for *N*! (*N*>>1)

Multiplicity depends on *N*!, and we need an approximation for ln(*N*!):

$$\ln N! = \ln 1 + \ln 2 + \ln 3 + \cdots + \ln N \approx \int_1^N \ln(x)\,dx = \left[x \ln x - x \right]_1^N \approx N \ln N - N$$

$$\boxed{\ln N! \approx N \ln N - N} \qquad \text{or} \qquad \boxed{N! \approx \left(\frac{N}{e} \right)^N}$$

More accurately:

$$\boxed{N! \approx N^N e^{-N} \sqrt{2\pi N} = \left(\frac{N}{e} \right)^N \sqrt{2\pi N}}$$

Check:

$$\ln(N!) = N \ln(N) - N + \frac{1}{2} \ln N + \frac{1}{2} \ln 2\pi \approx N \ln(N) - N$$

because ln *N* << *N* for large *N*

The Probability of Macrostates of a Two-State PM (*B*=0)
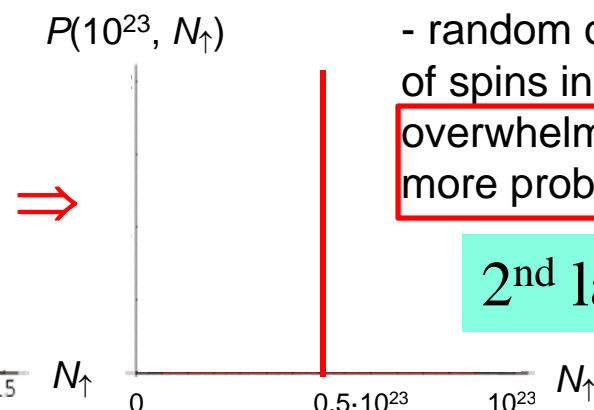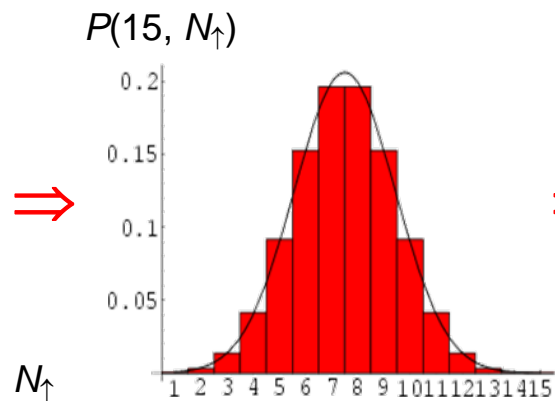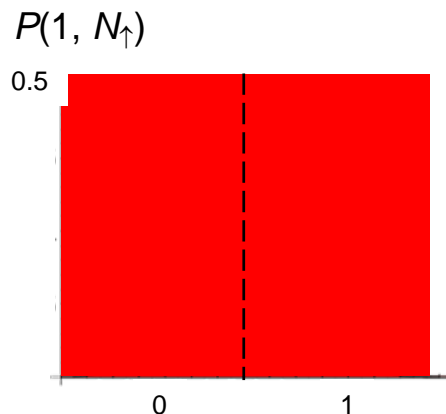
$$P(N, N_\uparrow) = \frac{\Omega(N, N_\uparrow)}{\# \text{ of all microstates}} = \frac{\Omega(N, N_\uparrow)}{\Omega(N, \text{all } N_\uparrow)} = \frac{\Omega(N, N_\uparrow)}{2^N}$$

$$P(N, N_\uparrow) = \frac{N!}{N_\uparrow!(N-N_\uparrow)!2^N} \approx \frac{N^N e^{-N}}{N_\uparrow^{N_\uparrow} e^{-N_\uparrow}(N-N_\uparrow)^{(N-N_\uparrow)} e^{-(N-N_\uparrow)} 2^N}$$

$$= \frac{N^N}{N_\uparrow^{N_\uparrow}(N-N_\uparrow)^{(N-N_\uparrow)} 2^N}$$

- as the system becomes larger, the $P(N,N_\uparrow)$ graph becomes more sharply peaked:

$N = 1 \Rightarrow \Omega(1, N_\uparrow) = 1$, $2^N = 2$, $P(1, N_\uparrow) = 0.5$

$P(1, N_\uparrow)$

$P(15, N_\uparrow)$

$P(10^{23}, N_\uparrow)$

- random orientation of spins in *B*=0 is overwhelmingly more probable

2nd law!

(http://stat-www.berkeley.edu/~stark/Java/Html/BinHist.htm)

Multiplicity (Entropy) and Disorder

In general, we can say that small multiplicity implies "order", while large multiplicity implies "disorder". An arrangement with large Ω could be achieved by a random process with much greater probability than an arrangement with small Ω.
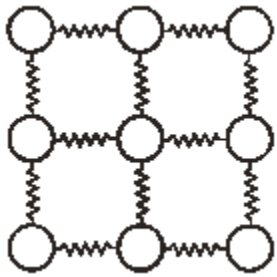
↑↑↑↑↑↑↑↑↑↑↑↑   ↑↓↓↑↓↑↑↓↓↓↑↓↑

small Ω large Ω

The Einstein Model of a Solid

In 1907, Einstein proposed a model that reasonably predicted the thermal behavior of crystalline solids (a 3D bed-spring model):

a crystalline solid containing **N** atoms behaves as if it contained **3N** identical independent quantum harmonic oscillators, each of which can store an integer number n_i of energy units $\varepsilon = \hbar\omega$.

We can treat a 3D *harmonic* oscillator as if it were oscillating independently in 1D along each of the three axes:

classic:
$$E = \frac{1}{2}mv^2 + \frac{1}{2}k\,r^2 = \left(\frac{1}{2}mv_x^2 + \frac{1}{2}k\,x^2\right) + \left(\frac{1}{2}mv_y^2 + \frac{1}{2}k\,y^2\right) + \left(\frac{1}{2}mv_z^2 + \frac{1}{2}k\,z^2\right)$$

quantum:
$$E_i = \hbar\omega\left(n_{i,x} + \frac{1}{2}\right) + \hbar\omega\left(n_{i,y} + \frac{1}{2}\right) + \hbar\omega\left(n_{i,z} + \frac{1}{2}\right) = \sum_{i=1}^{3}\varepsilon\left(n_i + \frac{1}{2}\right)$$
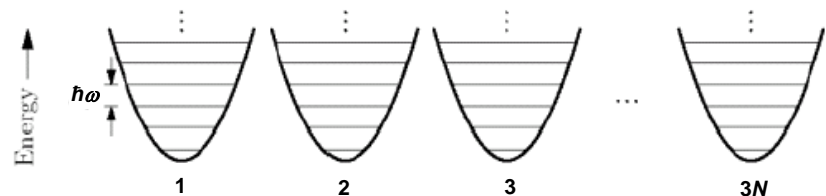
the solid's internal energy:
$$U = \sum_{i=1}^{3N}\varepsilon\left(n_i + \frac{1}{2}\right) = \sum_{i=1}^{3N}\varepsilon\,n_i + \sum_{i=1}^{3N}\frac{1}{2}\varepsilon = \sum_{i=1}^{3N}\varepsilon\,n_i + \frac{3N}{2}\varepsilon$$
the zero-point energy

the effective internal energy:
$$U = \sum_{i=1}^{3N}\varepsilon\,n_i$$

all oscillators are identical, the energy quanta are the same

The Einstein Model of a Solid (cont.)

At high $k_B T \gg \hbar\omega$ (the classical limit of large n_i):

$$U = \sum_{i=1}^{3N} \varepsilon\, n_i = 3N(2)\frac{1}{2}k_B T = 3Nk_B T \quad \Rightarrow \quad \frac{dU}{dT} = 3Nk_B$$

Dulong-Petit's rule $\Rightarrow$ $24.9 \; \text{J/K} \cdot \text{mole}$

To describe a macrostate of an Einstein solid, we have to specify **N** and **U**, a microstate – n_i for **3N** oscillators.

solid	dU/dT, J/K·mole
Lead	26.4
Gold	25.4
Silver	25.4
Copper	24.5
Iron	25.0
Aluminum	26.4

Example: the "macrostates" of an Einstein Model with only one atom

The Multiplicity of Einstein Solid

The multiplicity of a state of **N** oscillators (**N**/3 atoms) with **q** energy quanta distributed among these oscillators:

$$\Omega\,(N,q) = \frac{(q+N-1)!}{q!(N-1)!} = \binom{q+N-1}{q}$$

Proof: let's consider N oscillators, schematically represented as follows:
● | ●● | | ●●● | ●● - **q** dots and **N-1** lines, total **q+N-1** symbols. For given **q** and **N**, the multiplicity is the number of ways of choosing **n** of the symbols to be dots, q.e.d.

In terms of the total internal energy **U =qε**:

$$\Omega\,(N,U) = \frac{(U\,/\,\varepsilon + N - 1)!}{(U\,/\,\varepsilon)!(N-1)!}$$

Example: The multiplicity of an Einstein solid with three atoms and eight units of energy shared among them

$$\Omega\,(9,\,8) = \frac{(8+9-1)!}{(8)!(9-1)!}$$ ⟹ 12,870

Multiplicity of a Large Einstein Solid ($k_BT \gg \varepsilon$)

$q = U/\varepsilon = \beta N$ - the total # of energy quanta in a solid.

$\beta = U/(\varepsilon N)$ - the average # of quanta (microstates) available for *each* molecule

$$\ln\Omega(N,q) = \ln\left[\frac{(q+N-1)!}{(q)!(N-1)!}\right] \approx \ln\left[\frac{(q+N)!}{(q)!N!}\right] = \ln\left[(q+N)!\right] - \ln[q!] - \ln[N!]$$

Stirling approxmation: $\ln(N!) \approx N\ln N - N$

$$\approx (q+N)\ln(q+N) - (q+N) - q\ln q + q - N\ln N + N$$

$$= (q+N)\ln(q+N) - q\ln(q) - N\ln N$$

High temperature limit: $k_B T \gg \varepsilon \Leftrightarrow q \gg N$

$$
\text{Dulong-Petit's rule: } \left.\begin{array}{l} U = q\cdot\varepsilon \\ U = Nk_BT \end{array}\right\} \Rightarrow q\cdot\varepsilon = Nk_BT \left.\begin{array}{l} \\ q\cdot\varepsilon \gg N\varepsilon \Rightarrow q \gg N \\ k_BT \gg \varepsilon \Rightarrow Nk_BT \gg N\varepsilon \end{array}\right\}
$$

Multiplicity of a Large Einstein Solid ($k_B T \gg \varepsilon$)

$q = U/\varepsilon = \beta N$ - the total # of energy quanta in a solid.

$\beta = U/(\varepsilon N)$ - the average # of quanta (microstates) available for *each* molecule

high temperatures:
$(k_B T \gg \varepsilon, \beta \gg 1, q \gg N)$

$$\ln(q+N) = \ln\left[q\left(1+\frac{N}{q}\right)\right] \approx \ln q + \frac{N}{q}$$

$$\ln\Omega(N,q) = (q+N)\left[\ln q + \frac{N}{q}\right] - q\ln(q) - N\ln N$$

$$= N\ln q + N + \frac{N^2}{q} - N\ln N \approx N\ln\frac{q}{N} + N$$

$$\boxed{\Omega(N,q) \approx e^{N\ln\frac{q}{N}}e^N = \left(\frac{eq}{N}\right)^N = (e\beta)^N} \quad \boxed{\Omega(U,N) \approx \left(\frac{eU}{N\varepsilon}\right)^N = f(N)\,U^N}$$
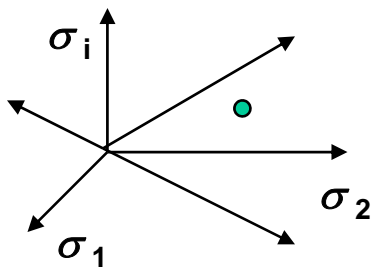
Einstein solid:
(2*N* degrees
of freedom)

General statement: for any system with **N** "quadratic" degrees of freedom
("unlimited" spectrum), the multiplicity is proportional to **$U^{N/2}$**.

Multiplicity of a Large Einstein Solid ($k_B T \ll \varepsilon$)

low temperatures:
($k_B T \ll \varepsilon$, $\beta \ll 1$, $q \ll N$)

$$\Omega(N, q) = \left(\frac{eN}{q} \right)^q = \left(\frac{e}{\beta} \right)^{N\beta}$$

(*Pr.* 2.17)

Microstates of a system (e.g. ideal gas)

The evolution of a system can be represented by a trajectory in the multidimensional (configuration, phase) space of micro-parameters. Each point in this space represents a microstate.

During its evolution, the system will only pass through **accessible** microstates – the ones that do not violate the conservation laws: e.g., for an **isolated** system, the total internal energy must be conserved.

Microstate: the state of a system specified by describing the quantum state of each molecule in the system. For a classical particle – **6** parameters (x_i, y_i, z_i, p_{xi}, p_{yi}, p_{zi}), for a macro system – **6N** parameters.
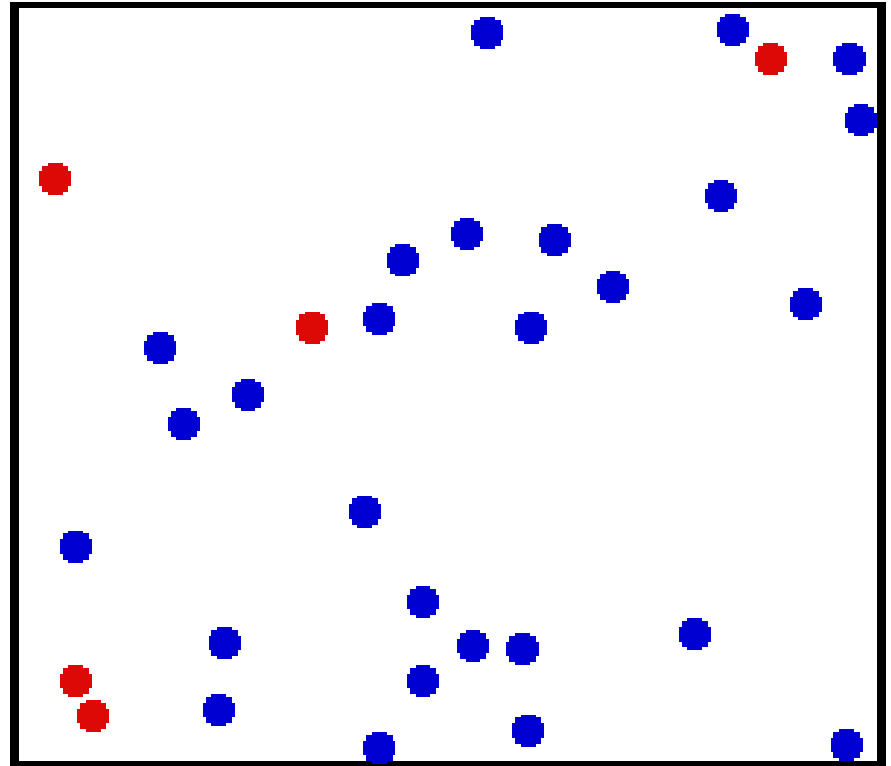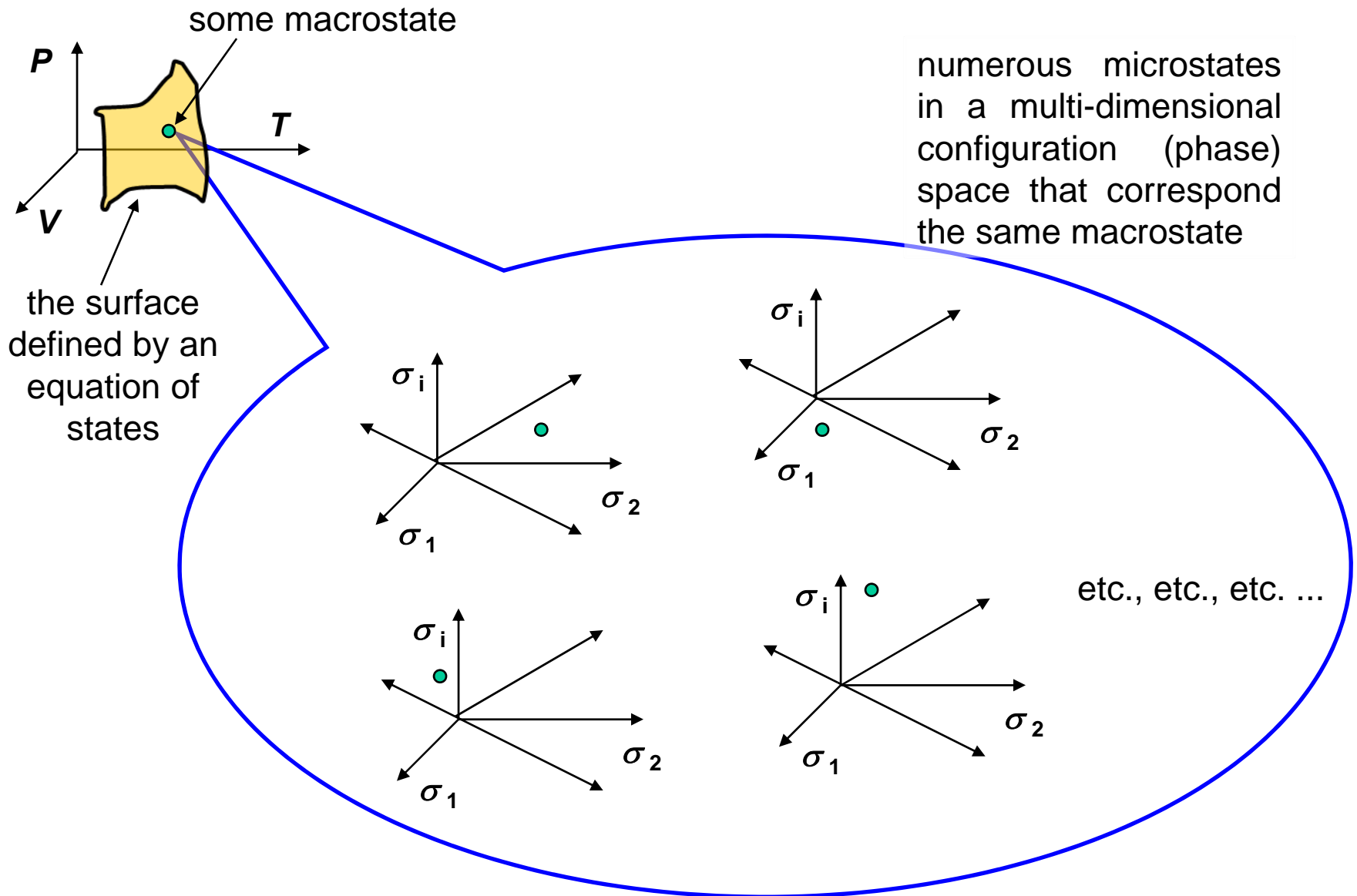
Statistics → Probabilities of Macrostates

The statistical approach: to connect the macroscopic observables (averages) to the probability for a certain microstate to appear along the system's trajectory in configuration space, $P(\sigma_1, \sigma_2,...,\sigma_N)$.
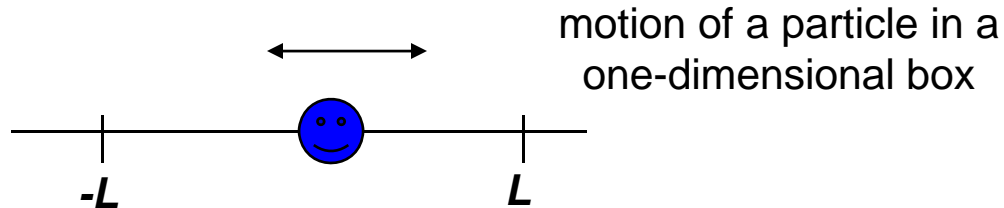
Macrostate: the state of a macro system specified by its macroscopic parameters. Two systems with the same values of macroscopic parameters are thermodynamically indistinguishable. A macrostate tells us nothing about a state of an individual particle.

For a given set of constraints (conservation laws), a system can be in many macrostates.

The Phase Space vs. the Space of Macroparameters

some macrostate

P

T

V

the surface defined by an equation of states

numerous microstates in a multi-dimensional configuration (phase) space that correspond the same macrostate

σ_i

σ_2

σ_1

σ_i

σ_1

σ_2

σ_i

σ_1

σ_2

σ_i

σ_1

σ_2

etc., etc., etc. ...

Examples: Two-Dimensional Configuration Space

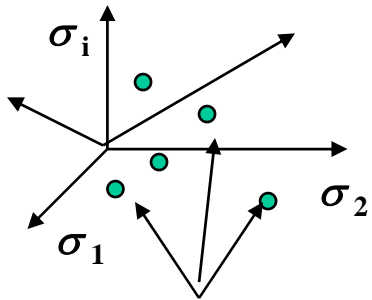motion of a particle in a one-dimensional box

$-L$ L

$K=K_0$

0 K

"Macrostates" are characterized by a single parameter: the kinetic energy K_0

Another example: one-dimensional harmonic oscillator

$U(r)$

$K + U =const$

x p_x

p_x

$-L$ L x

$-p_x$
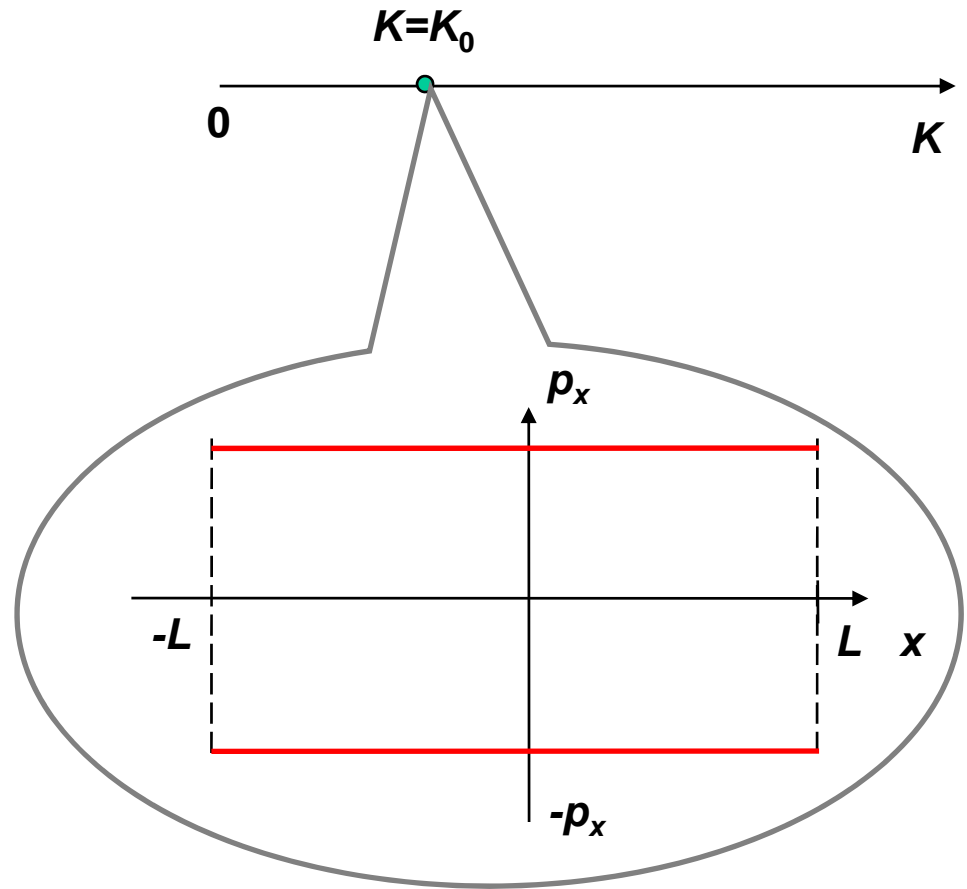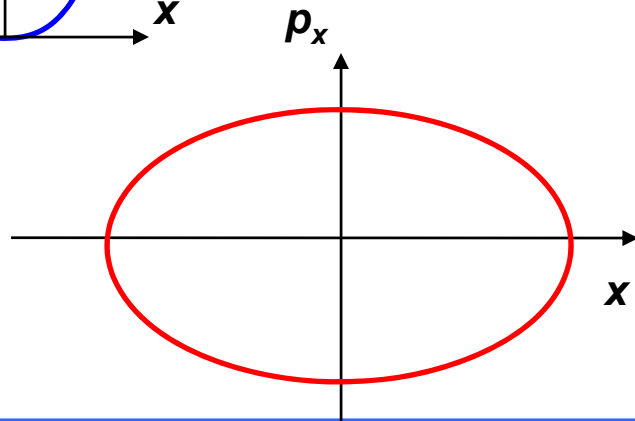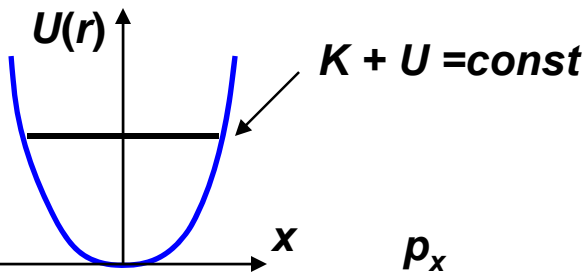
Each "macrostate" corresponds to a continuum of microstates, which are characterized by specifying the position and momentum

microstates which correspond to the same energy

The ergodic hypothesis: an ┃*isolated*┃ system in an equilibrium state, evolving in time, will pass through all the ***accessible*** microstates at the same recurrence rate, i.e. **all *accessible* microstates are ┃*equally probable*┃**.

The ensemble of all equi-energetic states
⇒ *a microcanonical ensemble*.

The average over long times will equal the average over the ensemble of all equi-energetic microstates: if we take a snapshot of a system with N microstates, we will find the system in ***any*** of these microstates with the ***same*** probability.

Probability for a stationary system

→ many identical measurements on a single system

→ a single measurement on many copies of the system

Probability of a Macrostate, Multiplicity

Probability of a particular microstate of a microcanonical ensemble

$$= \frac{1}{\text{\# of all accessible microstates}}$$

The probability of a certain macrostate is determined by how many microstates correspond to this macrostate – **the multiplicity of a given macrostate** Ω .

Probability of a particular macrostate $=$

$$= \frac{\Omega \left(\text{\# of microstates that correspond to a given macrostate} \right)}{\text{\# of all accessible microstates}}$$

This approach will help us to understand why some of the macrostates are more probable than the other, and, eventually, by considering the interacting systems, we will understand **irreversibility** of processes in macroscopic systems.

Concepts of Statistical Mechanics

1. **The macrostate** is specified by a sufficient number of macroscopically measurable parameters (for an Einstein solid – *N* and *U*).

2. **The microstate** is specified by the quantum state of each particle in a system (for an Einstein solid – # of the quanta of energy for each of *N* oscillators)

3. **The multiplicity** is the number of microstates in a macrostate. For each macrostate, there is an extremely large number of possible microstates that are macroscopically indistinguishable.

4. **The Fundamental Assumption: for an isolated system, all accessible microstate are equally likely.**

5. **The probability of a macrostate** is proportional to its multiplicity. This will be sufficient to explain irreversibility.