



Cryocourse 2011 – Chichilianne

Introduction to Statistical Thermodynamics

Henri GODFRIN

CNRS Institut Néel Grenoble

<http://neel.cnrs.fr/>

Josiah Willard Gibbs worked on statistical mechanics, laying a foundation and providing a mathematical framework for quantum theory and for Maxwell's theories. He wrote classic textbooks on statistical mechanics, which Yale published in 1902.

Recognition was slow in coming, in part because Gibbs published mainly in the *Transactions of the Connecticut Academy of Sciences* *. At first, only a few European theoretical physicists and chemists, such as the Scot James Clerk Maxwell, paid any attention to his work. Only when Gibbs's papers were translated into German (then the leading language for chemistry) by Wilhelm Ostwald in 1892, and into French by Henri Louis le Chatelier in 1899, did his ideas receive wide currency in Europe.

* *In modern language: a low Impact factor journal...*

I) General introduction

1) Study of a system with a very large number of particles N .

Examples: solids, liquids, gases, plasmas, magnetic systems, chemical and biological systems...

Even if the interaction potentials are known, it is impossible to solve the problem for large N

Statistical mechanics allows to predict the behaviour of such systems

2) Definitions:

a) **Microscopic system: atomic dimensions (\sim nm)**

b) **Macroscopic system: contains a large number of particles N (size $\gg 1$ nm). It is characterised by macroscopic parameters (P , V , κ_{th} , C_v , etc...). If these parameters do not vary in time, the system is "in equilibrium".**

3) History of Statistical Thermodynamics (http://en.wikipedia.org/wiki/Statistical_thermodynamics)

In 1738, Swiss physicist and mathematician [Daniel Bernoulli](#) published *Hydrodynamica* which laid the basis for the [kinetic theory of gases](#). In this work, Bernoulli positioned the argument, still used to this day, that gases consist of great numbers of molecules moving in all directions, that their impact on a surface causes the gas pressure that we feel, and that what we experience as [heat](#) is simply the kinetic energy of their motion.

In 1859, after reading a paper on the diffusion of molecules by [Rudolf Clausius](#), Scottish physicist [James Clerk Maxwell](#) formulated the [Maxwell distribution](#) of molecular velocities, which gave the proportion of molecules having a certain velocity in a specific range. This was the first-ever statistical law in physics. Five years later, in 1864, [Ludwig Boltzmann](#), a young student in Vienna, came across Maxwell's paper and was so inspired by it that he spent much of his long and distinguished life developing the subject further.

Hence, the foundations of statistical thermodynamics were laid down in the late 1800s by those such as [James Maxwell](#), [Ludwig Boltzmann](#), [Max Planck](#), [Rudolf Clausius](#), and [Willard Gibbs](#) who began to apply statistical and quantum atomic theory to ideal gas bodies. Predominantly, however, it was Maxwell and Boltzmann, working independently, who reached similar conclusions as to the statistical nature of gaseous bodies. Yet, most consider Boltzmann to be the "father" of statistical thermodynamics with his 1875 derivation of the relationship between entropy S and multiplicity Ω , the number of microscopic arrangements (microstates) producing the same macroscopic state (macrostate) for a particular system.

4) Thermodynamics or Statistical Mechanics?

- Systems in equilibrium
 - Thermodynamics: general results, but not many!
 - Statistical Physics: all these results, plus detailed description.
- Systems out of equilibrium
 - Irreversible Thermodynamics: limited!
 - Statistical Physics: kinetic theory, powerful, complex!

Statistical Mechanics allows calculating with an excellent accuracy the properties of systems containing 10^{23} atoms!

II) Introduction to the methods of Statistical Mechanics

1) Definitions:

An experiment is said to be stochastic if it can be repeated N times in apparently identical conditions. If the experiment consists in determining a magnitude X , it is impossible to foresee the exact value x_i that X will have.

We define the probability $P(x_i)$ to get the value x_i empirically: in N experiments we obtain N_i time the value x_i , and observe that N_i/N tends to a finite value, defined as $P(x_i)$, when N tends to infinity.

$$\text{Therefore, } P(x_i) \geq 0 \text{ and } \sum_i P(x_i) = 1$$

When x_i is a numerical value, it is called “stochastic variable”.

- Discrete stochastic variable: x_i with $i = 1, 2, 3, \dots$
 Example : for a dice, $x_i = 1, 2, 3, 4, 5, 6$ (“event”, or “result of the measurement”)



- Continuous stochastic variable: x can take an infinite set of values in an interval (finite or infinite). In this case we define the probability for x to fall in an elementary interval,

$$dP(x_0; x_0 + dx)$$

We assume that dP is proportional to dx , then $dP(x_0 < x < x_0 + dx) = \rho(x_0) \cdot |dx|$

- $\rho(x_0)$ is the “probability density”, or “distribution function”. It is NOT a probability!!!!
- $\rho(x_0) \geq 0$ and $\int_{x_0}^{x_1} \rho(x) dx = 1$ Note that $\rho(x) dx$ is a probability !
- The probability to find x in an interval $(x_0 < x < x_1)$ is $P(x_0; x_1) = \int_{x_0}^{x_1} \rho(x) dx = 1$



Examples : - angle made by a stick falling on the floor,



- angle of the needle of a broken clock

if random.... !

2) Mean or average values

- Discrete stochastic variable: over N measurements, we observe N_i times the value x_i .

$$\bar{X} = \frac{1}{N} \sum_i N_i x_i = \sum_i P_i x_i$$

- Continuous stochastic variable: $\bar{X} = \int_{-\infty}^{+\infty} \rho(x) x dx$

- Function of a stochastic variable $\bar{Y} = \overline{f(x)} = \int_{-\infty}^{+\infty} \rho(x) f(x) dx$

- Fluctuation: $\Delta x = x - \bar{x}$

- $\overline{(\Delta x)^2} = \overline{x^2} - \bar{x}^2$

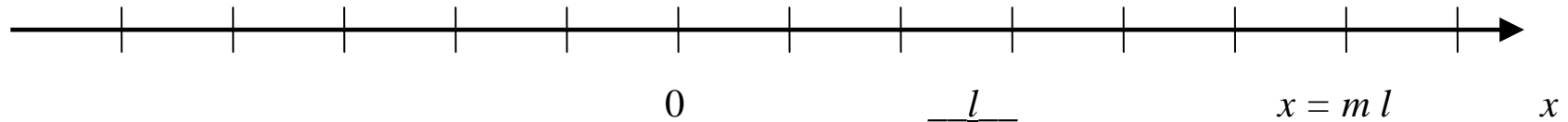
Correlation functions: systems with many stochastic variables

$$\overline{xy} = \iint \rho(x, y) x y dx dy$$



3) Random walk

- in one dimension:



Probability to make one step to the right = p

Probability to make one step to the left = q

$$p + q = 1$$

Probability to reach $x = m.l$ after N steps?

Statistics: ensemble of many systems, or ensemble of several experiments

Number of steps to the right = n_1

Number of steps to the left = n_2

$$n_1 + n_2 = N$$

$$m = n_1 - n_2 = 2 n_1 - N$$

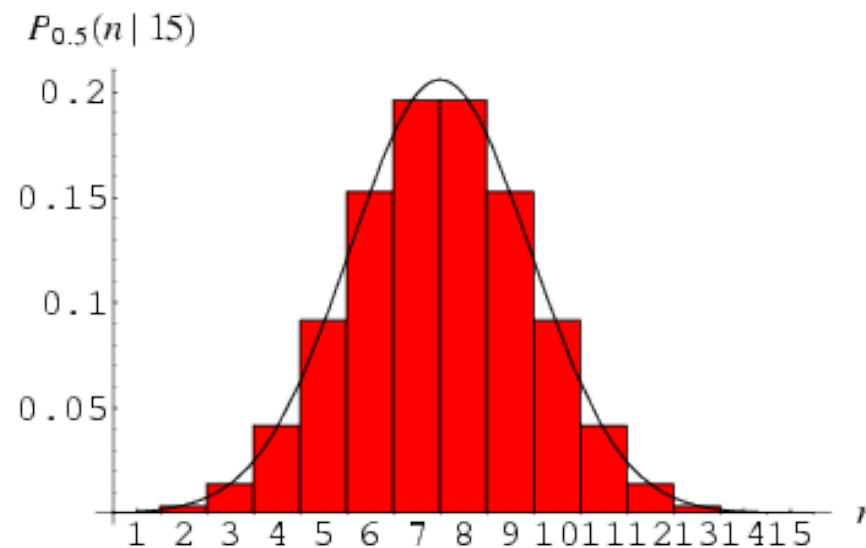
Binomial distribution:

$$W_N(n_1) = \frac{N!}{n_1! n_2!} p^{n_1} q^{n_2}$$

$$\text{Since } P_N(m) = W_N(n_1)$$

We get

$$P_N(m) = \frac{N!}{\left(\frac{N+m}{2}\right)! \left(\frac{N-m}{2}\right)!} p^{\frac{N+m}{2}} (1-p)^{\frac{N-m}{2}}$$



We can check that this distribution function has all the expected properties: it is normalised to 1, the average displacements are $\bar{n}_1 = N p$ $\bar{m} = N(p - q)$ etc....

We can calculate also $\overline{(\Delta m)^2} = 4 \overline{(\Delta n_1)^2} = 4 N p q$

The variance σ of m is therefore $\sigma = \sqrt{\overline{(\Delta m)^2}} = 2\sqrt{N p q}$

If $p = q = 1/2$, then $\sigma = \sqrt{N}$

Probability distribution for large N:

It can be shown that the binomial distribution tends to the Gaussian distribution

$$W_N(n_1) = \frac{1}{\sqrt{2\pi} \sigma} \exp\left(-\frac{(n_1 - \bar{n}_1)^2}{2\sigma^2}\right) \quad \text{with} \quad \bar{n}_1 = N p \quad \sigma = \sqrt{N p q}$$

Continuous distribution: Gaussian

$$P(x) dx = \frac{1}{\sqrt{2\pi} \sigma} \exp\left(-\frac{(x - \mu)^2}{2\sigma^2}\right) dx \quad \text{with} \quad \mu = Nl(p - q) \quad \sigma = 2\sqrt{Npq}l$$

One can show that $\bar{x} = \mu$ $\overline{(x - \mu)^2} = \sigma^2$

Large N limit for $p \ll 1$: Poisson distribution (mathworld.wolfram.com/NormalDistribution.html)

The probability of obtaining exactly n successes in N trials is given by the limit of the binomial distribution

Viewing the distribution as a function of the expected number of successes $\nu \equiv Np$ instead of N or fixed p ,

$$P_{\nu/N}(n | N) = \frac{N!}{n! (N - n)!} \left(\frac{\nu}{N}\right)^n \left(1 - \frac{\nu}{N}\right)^{N-n},$$

$$\frac{\nu^n e^{-\nu}}{n!},$$

Letting the [sample size](#) N become large, the distribution then approaches

which is known as the Poisson distribution

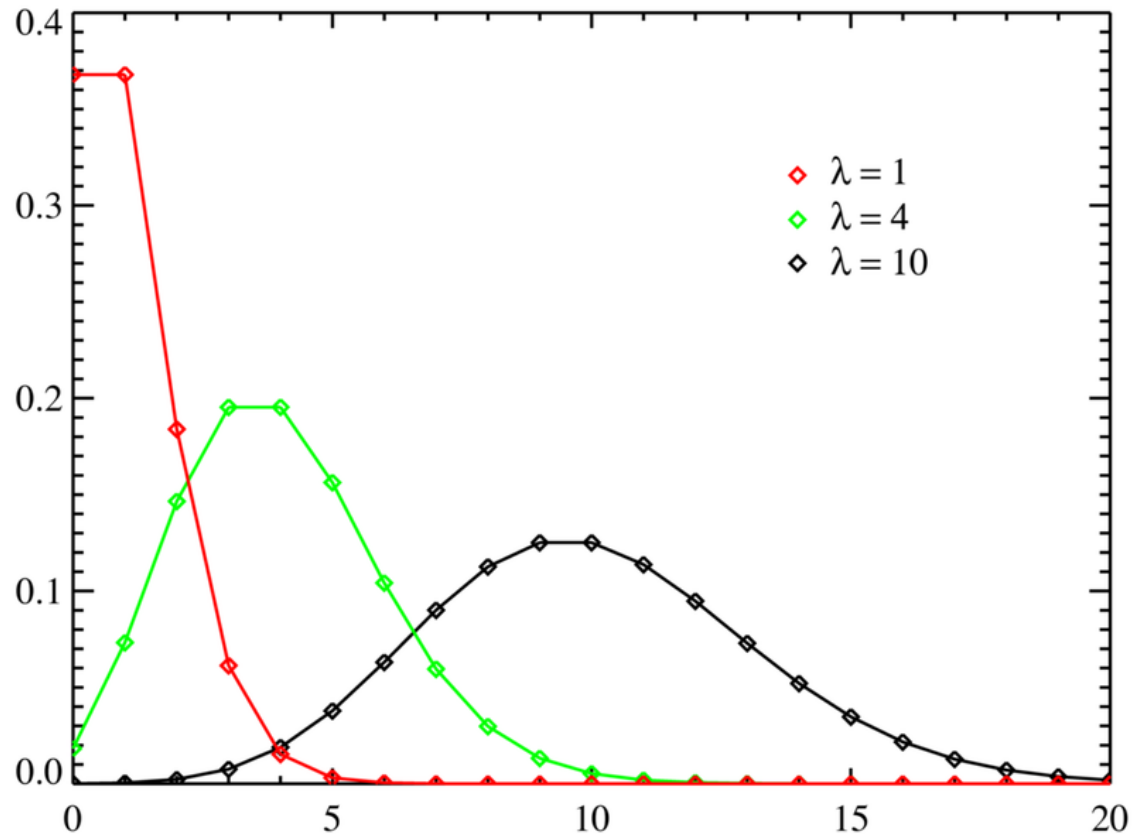
Note that the N has completely dropped out of the probability function, which has the same functional form for all values of ν .

The Poisson distribution is implemented in [Mathematica](#) as [PoissonDistribution](#)[μ].

As expected, the Poisson distribution is normalized so that the sum of probabilities equals 1.

Poisson distribution: If the expected number of occurrences in this interval is λ , then the probability that there are exactly x occurrences (x being a non-negative integer) is equal to

$$f(x; \lambda) = \frac{\lambda^x e^{-\lambda}}{x!},$$

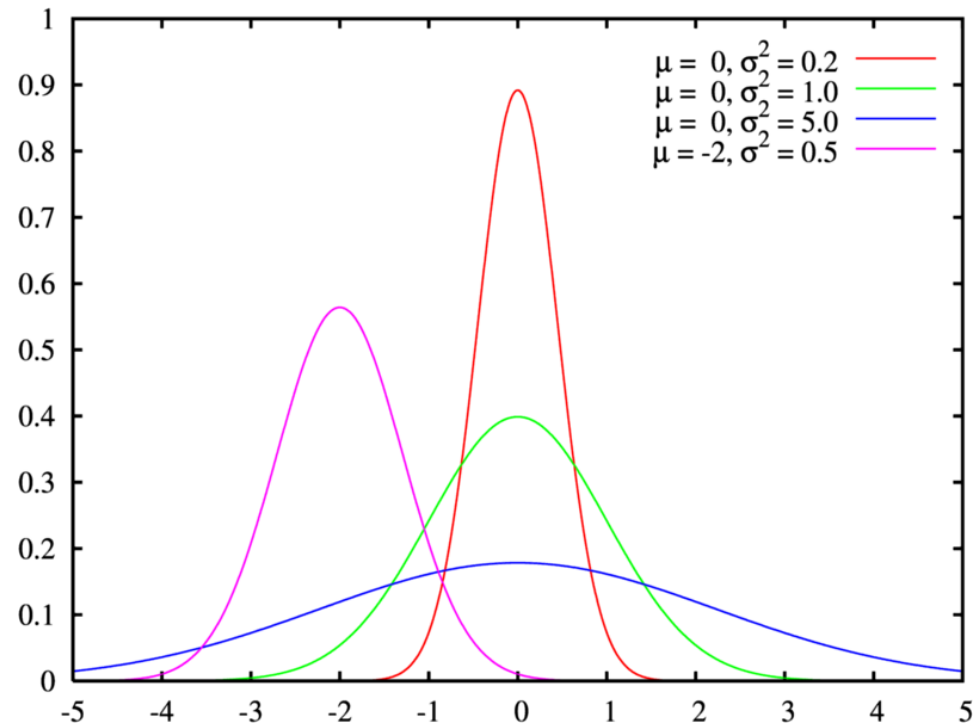


en.wikipedia.org/?title=Poisson_distribution

Central limit theorem

The Central Limit Theorem states that if the sum of the variables has a finite variance, then it will be approximately following a normal or Gaussian distribution.

Since many real processes yield distributions with finite variance, this explains the ubiquity of the normal probability distribution.



From Wikipedia

III) Many particles systems

Statistics + laws of the mechanics of particles

Example : 10 dice; the analysis involves several points:

- Description of the states accessible to the system
- Statistical ensemble: we consider several experiments (throwing the 10 dices)
- We calculate the probability to get a particular “result”, but this requires some information and postulates:

“The probability to get any face of the dice is the same”

This can come from symmetry arguments, but has to be checked experimentally

- We apply then the methods of Statistics.
-

1) Description of the states accessible to the system

We consider a many particle system. Its behaviour is described by Quantum Mechanics.

The wave function $\Psi(q_1, \dots, q_f)$ provides a complete description of the system; the q_i are generalised coordinates, and f is the number of degrees of freedom of the system.

The “state” of a system is determined by the values of an ensemble of quantum numbers.

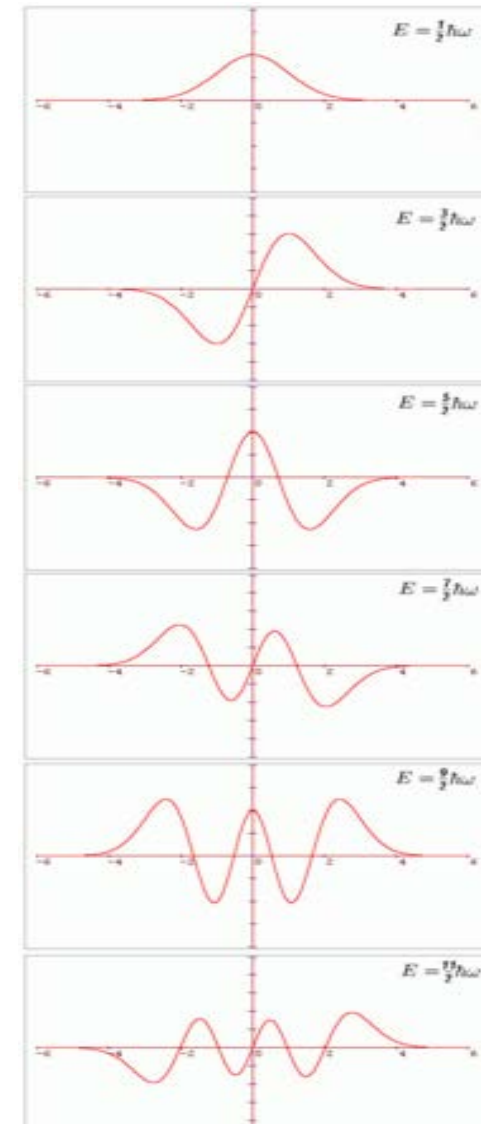
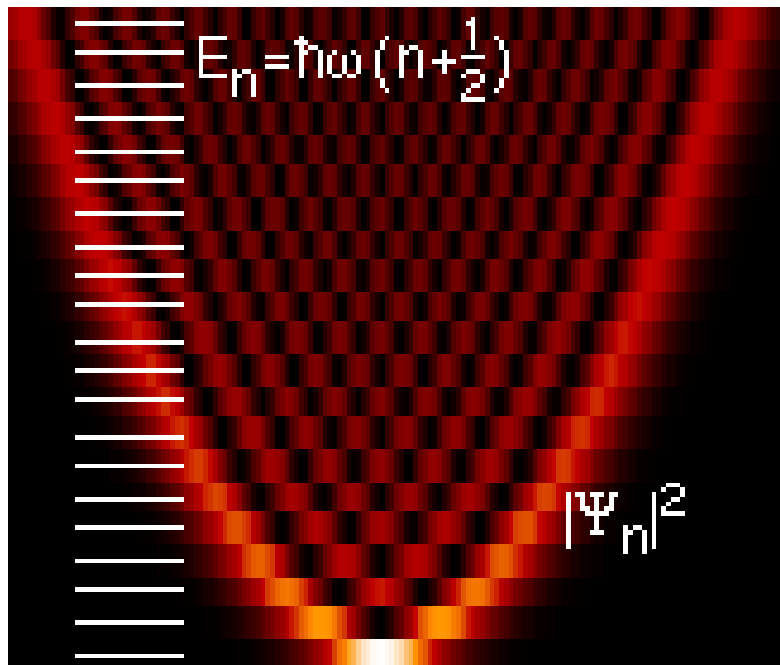
Examples:

a) **N particles with spin 1/2**. The quantum number m can take two values for each particle ($-1/2$ or $+1/2$).

The state of the system is determined by the set $\{m_1, m_2, \dots, m_N\}$.



b) for one **Harmonic oscillator**, the possible states are described by a quantum number n , the energy of these states is $E_n = (n + 1/2) \hbar\omega$, with $n = 0, 1, 2, \dots$



For $n = 0$ the system is in the ground state. Note that $\langle x^2 \rangle \neq 0$!

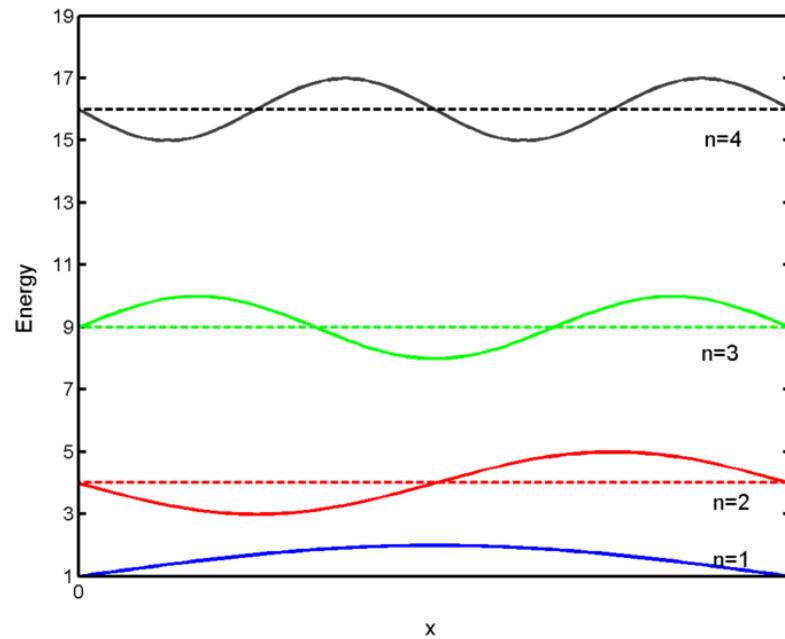
Pictures from Wikipedia

For **N Harmonic oscillators (solids!)** : The possible states are described by the set $\{n_1, n_2, \dots, n_N\}$

d) The states of a particle in a box in 3D are given by

$$\psi_{n_x, n_y, n_z} = \sqrt{\frac{8}{L_x L_y L_z}} \sin\left(\frac{n_x \pi x}{L_x}\right) \sin\left(\frac{n_y \pi y}{L_y}\right) \sin\left(\frac{n_z \pi z}{L_z}\right)$$

with $n_i = 1, 2, 3, \dots$



from Wikipedia

And their energies are

$$E_{n_x, n_y, n_z} = \frac{\hbar^2 \pi^2}{2m} \left[\left(\frac{n_x}{L_x}\right)^2 + \left(\frac{n_y}{L_y}\right)^2 + \left(\frac{n_z}{L_z}\right)^2 \right]$$

2) Statistical ensemble

Example: consider a system of three spins $\frac{1}{2}$ in a magnetic field H . What are the states of this system? Which states have a magnetisation equal to μ (magnetic moment of 1 spin)? 3 states over 8 !

Accessible states: Constraints may cause that some theoretical states are not accessible to the system. This reduces the “phase space”.

Example: with the system considered before, find the states accessible if the total magnetisation is fixed at the value μ . Three states are possible, but we ignore which one will be selected, or their probabilities...

Knowing some of the properties of the system, we can often readily build the ensemble of accessible states!

3) Fundamental postulate

To progress in the study of these systems, we need to make some assumptions, i.e., reasonable postulates based on our knowledge of the system.

- a) We assume that the system is *isolated* from the surroundings.
The Energy is conserved. This reduces remarkably the number of accessible states.
- b) We assume that the system is *in equilibrium*.
This means that the probability of finding the system in a given state does not change with time.
The macroscopic parameters, hence, do not depend on time.

Fundamental Postulate: An isolated system in equilibrium has the same probability to be found in any of its accessible states.

- One can show that this probability does not evolve with time.
- This leads to results that agree remarkably well with experiments.
- Equilibrium is achieved through “small interactions” that induce transitions between these states.
(notion of “relaxation time”...)

4) Calculation of probabilities

Isolated system in equilibrium: the energy is conserved, i.e., in a small interval $[E ; E + \delta E]$

Note that we consider a statistical ensemble of these systems!

We define as $\Omega(E)$ the number of accessible states (their energy is in $[E ; E + \delta E]$)

Calculating mean values of physical parameters:

Among all these states, many of them have the property that a physical parameter has a specific value, for instance Y has the value Y_k .

We call $\Omega(E, Y_k)$ the corresponding number of accessible states.

The equiprobability of all accessible states allows us to write $P(Y_k) = \frac{\Omega(E, Y_k)}{\Omega(E)}$

and the average value of Y is therefore $\bar{Y} = \sum_k Y_k P(Y_k) = \sum_k \frac{\Omega(E, Y_k) Y_k}{\Omega(E)}$

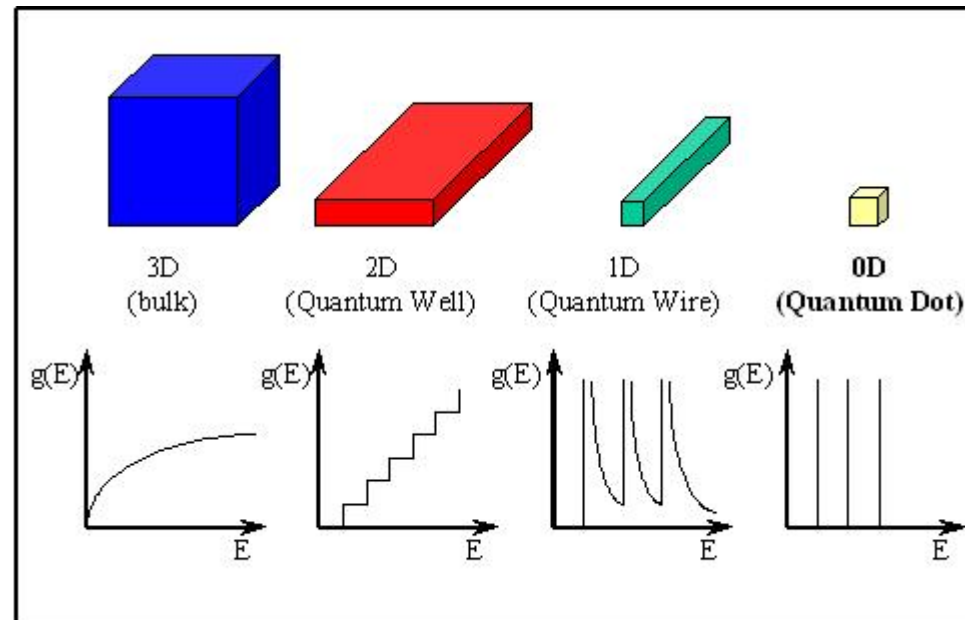
The calculations are often very simple, the main difficulty resides in identifying the interesting states among all the possible states.

5) Density of states

We consider a macroscopic system, of energy E , and δE the accuracy with which we determine E . The number of states, even for a small interval $[E ; E + \delta E]$, is VERY large.

It is convenient to define a “density of states” $\omega(\mathbf{E})$, such that $\Omega(\mathbf{E}) = \omega(\mathbf{E}) \delta E$ (number of states per unit of energy)

How does the density of states of a body depend on the Energy?



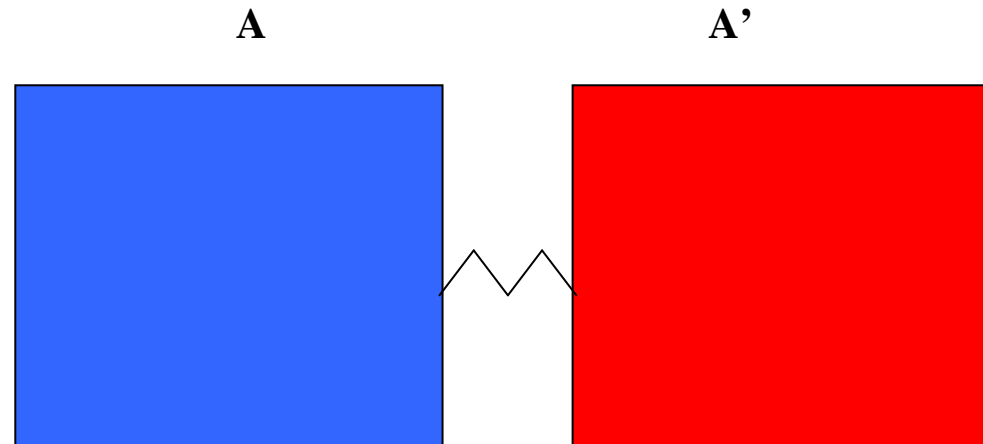
6) Thermal and Mechanical interaction

The quantum energy-levels of the system depend on the EXTERNAL PARAMETERS x_i .

$E_r = E_r(x_1, x_2, \dots, x_n)$ The values of the x_i must be given to determine the accessible states.

We construct then the ensemble of the accessible states.

7) Interaction of two macroscopic systems:



The total Energy is constant (isolated system A+A')

a) If the parameters x_i do NOT vary with the interaction, the energy levels do NOT move.

Definition: THERMAL INTERACTION

b) If the parameters x_i vary with the interaction, the energy levels will move.

Definition: MECHANICAL INTERACTION

Heat:

Let us consider a collection of similar systems $A + A'$.

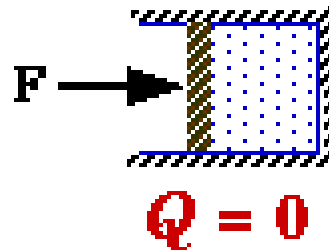
The energy transferred has an average value $\overline{\Delta E}$

We call “**heat**” the energy transferred in a thermal interaction process: $Q \equiv \overline{\Delta E}$

It can be > 0 or < 0 !!! Since the total energy is conserved, the heat given by a system is equal to that it receives, with a minus sign. Q is defined here as “the energy received by the system”.

Work:

Systems which are thermally insulated can exchange energy by a change of the external parameters



We consider again the interaction of a collection of systems $A+A'$, but now we calculate the change in energy due to the variation of the external parameters.

$\Delta_x \bar{E} + \Delta_x \bar{E}' = 0$ where this indicates the change of the average energy due to the change of one external parameter x .

The work done on the system A is defined as $W' = \Delta_x \bar{E}$

The work made by the system A is defined as $W = -W' = \Delta_x \bar{E}$

Heat or Work?

Work is associated with the change of the average Energy with the displacement of the quantum levels.
Heat corresponds to the change in energy due to the probability of occupation of levels.

8) General case: Heat and Work

The external parameters are NOT fixed, and the system is NOT thermally insulated.

We write: $\Delta \bar{E} = \Delta_x \bar{E} + Q$

Q is therefore defined as $Q = \Delta \bar{E} + W$ W is the work done by the system, Q the heat received...

Case of the infinitesimal change of energy: 8) General case: Heat and Work

Note that the symbols δQ and δW indicate that Q and W are infinitesimal. This does not correspond to the “variation” of any “function” Q or W . There is no heat “after” or “before” the interaction. There is heat and work associated to the process of interaction, not to the initial and final states.

9) Quasi-static processes: in equilibrium at all stages of the process.

During such processes, the probability of occupying the quantum levels are well defined, and we can thus calculate all the averages (see the definition of heat and work).

For example, if the external parameter is the volume V :

- a change in V will change the energy of the states (see “particle in a box” example!). Different

states will react differently, but the average gives $\delta W = \overline{P} dV$

(see demonstration in textbooks)

The work done in a transformation from a state A of volume V1 to a state B of volume V2 is

therefore $W = \int_A^B \delta W = \int_A^B \overline{P} dV$ which depends on the path followed in the P,V plane.

If the system is thermally **isolated**, $Q = \Delta \overline{E} + W = 0$ and hence $\Delta \overline{E} = -W$: the work done is independent on the path.

If the system is mechanically **isolated**, $Q = \Delta \overline{E}$ and the heat received is independent on the path of the transformation.

In these limits, the “ δ ” become “exact differentials”

Note that we have demonstrated here the “**First principle of Thermodynamics**”

III) Statistical Thermodynamics

1) Conditions of equilibrium and constraints

Suppression a constraint increases the number of accessible states. The resulting state is of very small probability. The system evolves, until all states are equally probable.

Example : probability to find all the molecules of a gas in the left half of a box? $(1/2)^N$...!!!
Calculate for one mole...

The system evolves towards the most probable configuration, i.e., that for which $\Omega(E)$ is maximum. This happens for a set of parameters Y_k . These characterise the equilibrium.

2) Reversible and irreversible processes

If we restore the constraints (for instance put back the wall partitioning the big box), the number of accessible states does not change, it is still much larger than the initial value (gas on the left side).

- If $\Omega(E)$ final $>$ $\Omega(E)$ initial, the process is called irreversible.
- If $\Omega(E)$ final = $\Omega(E)$ initial, the process is called reversible.

3) Thermal interaction between two macroscopic systems

Consider the two systems A and A'. Since the total energy is conserved, the only variable is E, the energy of the system A. So Ω^0 , the number of states available to A+A', depends only on E.

Simple arguments of counting states of A and A', together with the postulate that all states are equally probable, lead to the demonstration that the equilibrium is achieved for the values \hat{E} and \hat{E}' satisfying the condition

$$\frac{\partial \ln \Omega(E)}{\partial E} = \frac{\partial \ln \Omega'(E')}{\partial E'}$$

We now define

$$\beta(E) \equiv \frac{\partial \ln \Omega}{\partial E}$$

hence the equilibrium corresponds to $\beta(\hat{E}) = \beta(\hat{E}')$

We define the temperature T by the expression

$$kT \equiv \frac{1}{\beta(E)}$$

(k is a constant that sets the unit of T)

Hence the equilibrium corresponds to

$$T = T'$$

We define now the Entropy of the system as

$$S(E) = k \ln \Omega(E)$$

And therefore

$$\frac{1}{T} = \frac{\partial S(E, V)}{\partial E}$$

N.B. : The condition of a maximum of Ω^0 is equivalent to a maximum of the total entropy S^0

4) Thermal bath, very small systems

One can show that if the system A' ("bath") is much larger than A,

$$\Delta S' = \frac{Q'}{T'}$$

The entropy change of the bath is the heat it receives, divided by its temperature. Note that the bath is, by definition, always in equilibrium...

If the heat exchanged is small ($\delta Q \ll E$) then

$$\ln \Omega(E + \delta Q) - \ln \Omega(E) = \frac{\partial \ln \Omega}{\partial E} \delta Q = \beta \delta Q = \frac{\delta Q}{T} \quad \text{and hence}$$

$$dS = \frac{\delta Q}{T}$$

(for a thermal process, but see later!)

5) Equilibrium conditions in the general case of Thermal + Mechanical interaction

Again, one considers the total system, A+A', and looks at the accessible states.

In this case, the number of states depends also on the “external” variables x : $\Omega(E, x)$

$\Omega^0(E, x)$ has a huge maximum for some values of the parameters, $E = E_{max}$ and $x = x_{max}$ (remember that E is the energy of system A, not A+A' !!!).

We define a « generalised force » X conjugated to x by the expression $\overline{X} = -\frac{\overline{\partial E_r}}{\partial x}$
(sensitivity of the energy of the microscopic states to an external parameter)

One can show (not very difficult, but cumbersome!), that the averaged values satisfy the relation

$$\beta \overline{X} = \frac{\partial \ln \Omega}{\partial x} \quad \text{with} \quad \beta \equiv \frac{1}{kT}$$

For infinitesimal **quasi-static processes**, one can show that $d \ln \Omega = \beta (d\overline{E} + \delta W) \equiv \beta \delta Q$

$$dS = \frac{\delta Q}{T}$$

Note that we have demonstrated here the “**Second principle of Thermodynamics**”....

Let's go further in the study of the equilibrium, for the case when x is the volume V .

Since $\Omega^0(E, V) = \Omega(E, V)\Omega'(E', V')$ where $E' = E^0 - E$

Then $\ln \Omega^0(E, V) = \ln \Omega(E, V) + \ln \Omega'(E', V')$ and $S = S + S'$

The maximum of Ω^0 is obtained when $d \ln \Omega^0(E, V) = d \ln \Omega(E, V) + d \ln \Omega'(E', V') = 0$
for arbitrary variations dE and dV

One can show that this leads to the equation $(\beta - \beta')dE + (\beta\bar{P} - \beta'\bar{P}')dV = 0$

the solution is $\beta = \beta' \quad \bar{P} = \bar{P}'$

$$T = T'$$

$$\bar{P} = \bar{P}'$$

equilibrium condition

6) Properties of the Entropy

a) δQ is NOT an exact differential, but $dS = \frac{\delta Q}{T}$ yes! The Entropy, as the Energy, is a State Function.

The difference in entropy between two states is $S_f - S_i = \int_{i \text{ equil}}^f dS = \int_{i \text{ equil}}^f \frac{\delta Q}{T}$
in a quasi static process, so that T is well defined.

The integral $\int_{i \text{ equil}}^f \frac{\delta Q}{T}$ is therefore independent on the path.

c) When the temperature tends to the absolute zero, the Energy is close to E_0 , the “ground state” of a quantum mechanical system. The number of accessible states is very small (of order 1!).

Since $S(E) = k \ln \Omega(E)$, clearly **S tends to zero as T tends to zero**

Note that we have demonstrated here the “Third principle of Thermodynamics”

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