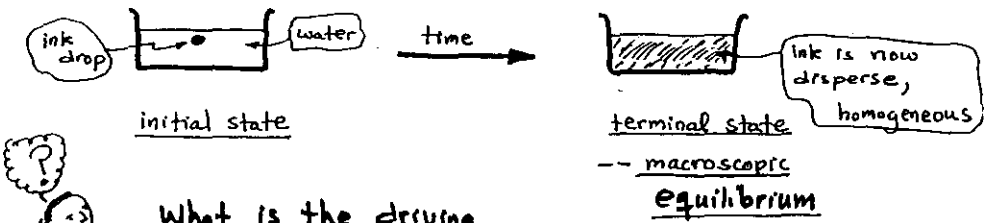


Physical Chemistry Lecture Notes ¹

Chem 120B. Prof. David Chandler

Principles of Macroscopic Systems

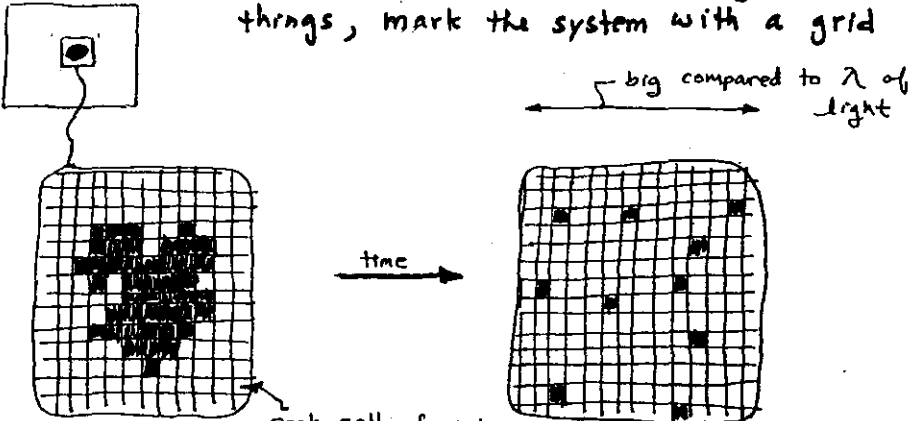
First, a simple experiment



What is the driving force? It has something to do with fluctuations, statistics and chaos.

You can do this experiment with system totally isolated -- i.e., insulated, at constant energy.

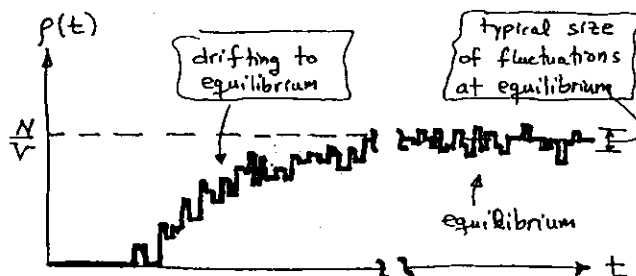
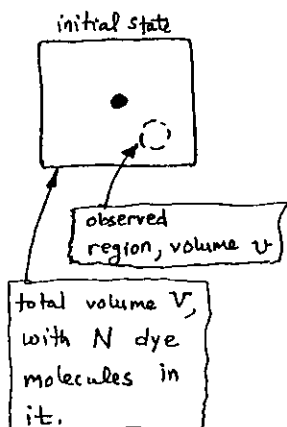
To think about it, consider an enlargement, and for the purpose of keeping track of things, mark the system with a grid



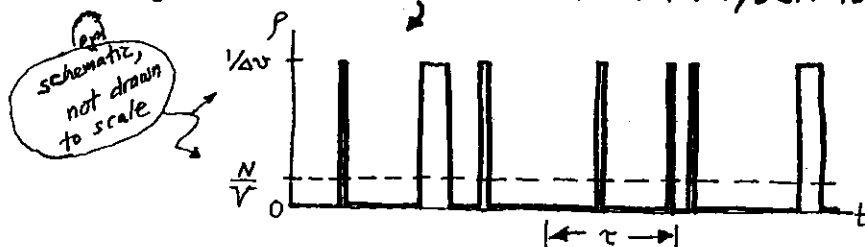
each cell of volume Δv ; black cells are those containing dye molecules. Δv is very little -- so small that no more than 1 dye molecule can fit in it.

With light (through scattering or absorption) we can observe or measure

ρ = concentration of dye molecules in observed region of volume v
 -- #molecules/ v .



Even at equilibrium, fluctuations never stop. These microscopic fluctuations are a consequence of molecular motions. The relative size of the fluctuations in ρ depends upon the size of the observed system -- the size of v . For $v = \Delta v =$ microscopic volume \sim size of a molecule, ρ looks like this when the total system is at equilibrium



If observations are made over short periods of time and over short distance scales, the system will always look chaotic. On the other hand, observations over long times or over long length scales will be easy to characterize -- so ordinary and self evident at macroscopic equilibrium they seem almost boring.

How long is "long" -- long enough so that in effect, one observation corresponds to many statistically independent measurements.

Observation over a long time, \mathcal{T} :

$$\begin{aligned} \langle p \rangle &= \frac{1}{\mathcal{T}} \int_0^{\mathcal{T}} dt p(t) \quad \leftarrow \text{a time average} \\ &\stackrel{\mathcal{T} = n\tau}{=} \frac{1}{n} \sum_{n=1}^n \frac{1}{\tau} \int_{(n-1)\tau}^{n\tau} dt p(t) \\ &= \frac{1}{n} \sum_{n=1}^n [p]_{n\text{th observation}} \end{aligned}$$

If \mathcal{T} is long enough and if the system is at equilibrium, $\langle p \rangle$ will be a "constant" -- i.e., we'll get the "same" value every time we do the experiment.

Observation over a large region of volume v .

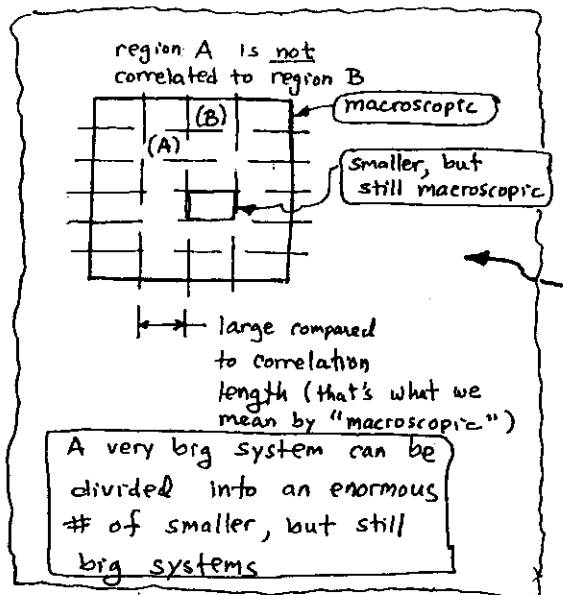
$$\langle p \rangle = \frac{1}{M} \sum_{j=1}^M [\text{\# molecules in cell } j] / \Delta v$$

$M \Delta v = v$

$$= \frac{1}{M} \sum_{j=1}^M [p]_{j\text{th cell}}$$

If M is large enough and if system is at macroscopic equilibrium, this $\langle p \rangle$ is also a constant, and should have the same value as $\langle p \rangle$ corresponding to a time average.

Range or length of correlations -- distance over



which a disturbance or fluctuation has an effect.

Usually, this distance is very short -- microscopic

The very big system is an ensemble of subsystems

Observation of whole system corresponds to an ensemble average

What does it mean to be correlated? Here's an example,

$P(f_A, f_B)$ = joint probability that subsystem A has density f_A and that subsystem B has density f_B . It's a normalized histogram built up from many measurements.

Clearly

$$\langle f_A f_B \rangle = \sum_{f_A} \sum_{f_B} P(f_A, f_B) f_A f_B$$

But if subsystems are uncorrelated,

$$P(f_A, f_B) = \underbrace{P_A(f_A) P_B(f_B)}_{\substack{\text{histogram from observations} \\ \text{of B ignoring A.}}}$$

Thus

$$\begin{aligned} \langle f_A f_B \rangle_{\text{uncorrelated}} &= \sum_{f_A} \sum_{f_B} P_A(f_A) P_B(f_B) f_A f_B \\ &= \left(\sum_{f_A} P_A(f_A) f_A \right) \left(\sum_{f_B} P_B(f_B) f_B \right) \\ &= \langle f_A \rangle \langle f_B \rangle \end{aligned}$$

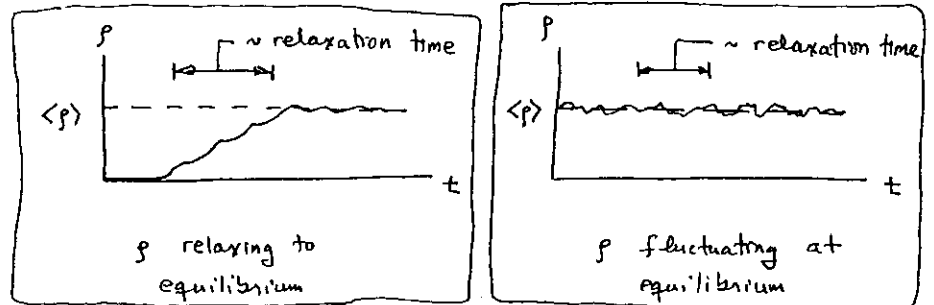
Therefore, $\langle f_A f_B \rangle - \langle f_A \rangle \langle f_B \rangle = \langle (f_A - \langle f_A \rangle)(f_B - \langle f_B \rangle) \rangle$

is a measure of correlations. When

$$\langle (f_A - \langle f_A \rangle)(f_B - \langle f_B \rangle) \rangle \neq 0$$

the two subsystems are correlated

Relaxation time -- time for system to forget a particular fluctuation or disturbance (example, time τ on page 2)

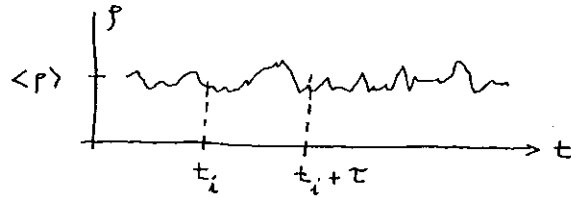


macroscopic systems are at equilibrium if they have been prepared and controlled over times long compared to relaxation time.

$$\langle p \rangle = \text{observed } p = \begin{cases} \text{either} \\ \text{time average of } p \\ \text{or} \\ \text{ensemble average of } p \end{cases}$$

The assumed equivalence of the two averages is called the ergodic assumption -- if you believe it, it means you believe in relaxation (loss of memory and chaos) and finite correlation lengths; and you are thinking about experiments performed over long times +/or large spatial scales.

What does it mean to be uncorrelated at different times? Consider the "time line" for f in an equilibrium system



For every time t_i , look also at $t_i + \tau$, and average $f(t_i)f(t_i + \tau)$ over many many t_i 's. The averaging gives a function of τ :

$$C(\tau) = \frac{1}{N} \sum_{i=1}^N f(t_i)f(t_i + \tau)$$

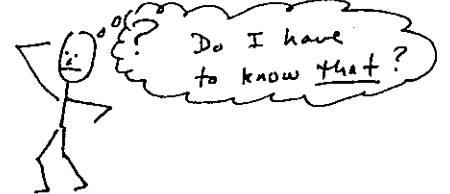
$$= \langle f(0)f(\tau) \rangle$$

zero time refers to the initial time that is averaged over

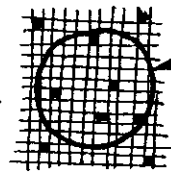
If τ is larger than the relaxation time,

$$C(\tau) \rightarrow \langle f(0) \rangle \langle f(\tau) \rangle = \langle f \rangle \langle f \rangle$$

↳ time correlations, a sophisticated concept!



Fluctuations, large numbers, extensive and intensive



observe
this region
with M
cells

How many particles (e.g.,
dye molecules in a solution, or
air molecules in air) will
we find in an observed volume
 $M \Delta v = V$?

Let

$$n_i = 1, \text{ if a molecule is in cell } i,$$

$$= 0, \text{ if no molecule is in cell } i.$$

We'll be assuming low concentrations and very small Δv , so $n_i > 1$ is "impossible."

Total number of particles in system at
a particular instant is

$$N = \sum_{i=1}^M n_i$$

At equilibrium

on the average, each
cell is the same

Thus, $\langle N \rangle = \sum_{i=1}^M \langle n_i \rangle = M \langle n \rangle.$

Here,

$\langle n \rangle =$ average of n_i for any one
cell.

$=$ probability that one particular
cell is occupied.

At low concentrations,

$$\langle n \rangle \ll 1 \text{ (i.e., } \frac{\langle N \rangle}{V} \Delta v \text{ is small)}$$

Notice that $\langle N \rangle$ scales linearly with M , the size of the system. Thus, $\langle N \rangle$ is called an EXTENSIVE property.

On the other hand, $\langle n \rangle$ appears to be independent of the system size. As such, $\langle n \rangle$ is called an INTENSIVE property.

Examples of intensive properties:

pressure, average concentrations, ...

Examples of extensive properties of large systems

volume, total average energy, ...

Is $\langle N \rangle$ a meaningful estimate of an instantaneously observed N ? To see, let's estimate the size of typical fluctuations:

$$\delta N = N - \langle N \rangle$$

$$\begin{aligned} \langle (\delta N)^2 \rangle &= \langle N^2 - 2N\langle N \rangle + \langle N \rangle^2 \rangle \\ &= \langle N^2 \rangle - \langle N \rangle^2 \end{aligned}$$

Now write both $\langle N^2 \rangle$ and $\langle N \rangle^2$ in terms of averages involving the "occupation" numbers, the n_i 's:

$$\begin{aligned} \langle (\delta N)^2 \rangle &= \left\langle \sum_{i=1}^M \sum_{j=1}^M n_i n_j \right\rangle - \left\langle \sum_{i=1}^M n_i \right\rangle \left\langle \sum_{j=1}^M n_j \right\rangle \\ &= \sum_{i,j=1}^M \left[\langle n_i n_j \rangle - \langle n_i \rangle \langle n_j \rangle \right] \end{aligned}$$

non zero, only if n_i is correlated to n_j

At low concentrations, n_i 's of different cells are uncorrelated. So,

$$\begin{aligned} \langle (\delta N)^2 \rangle &= \sum_{i=1}^M \left[\langle n_i^2 \rangle - \langle n_i \rangle^2 \right] \\ &= M(\langle n \rangle - \langle n \rangle^2) = M\langle n \rangle (1 - \langle n \rangle) \\ &\approx M\langle n \rangle = \langle N \rangle \end{aligned}$$

Note, $n_i^2 = n_i$

Thus, particle fluctuations for a gas or solution of uncorrelated particles obeys

$$\boxed{\langle (\delta N)^2 \rangle = \langle N \rangle}$$

Things to notice:

(1) $\langle (\delta N)^2 \rangle$ is extensive

(2) Relative size of fluctuations,

$$\frac{\sqrt{\langle (\delta N)^2 \rangle}}{\langle N \rangle} = \frac{1}{\langle N \rangle^{1/2}} = \frac{1}{(\langle n \rangle M)^{1/2}},$$

are small for big systems and large for little systems.

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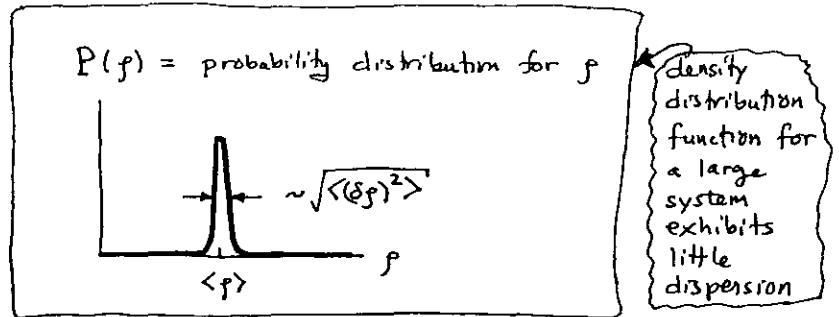
Equivalently, if we observe concentrations or densities, $\rho = N/V$, then

$$\langle \rho \rangle = \langle n \rangle / \Delta V$$

and

$$\langle (\delta \rho)^2 \rangle = \frac{\langle N^2 \rangle - \langle N \rangle^2}{V^2} = \frac{\langle N \rangle}{V^2} = \langle \rho \rangle \frac{1}{M \Delta V}$$

For M large, fluctuations in the intensive property ρ become negligible.



Principle of equal weights -- statistical characterization of macroscopic equilibrium

Think about the ink dye experiment. It seems to illustrate that terminal stationary states are the most random or chaotic macroscopic states -- i.e., all possible microscopic states are equally likely.

In other words, all fluctuations consistent with the constraints that define the system occur with the same probability.

As we will see shortly, the Second Law of Thermodynamics follows from this principle.

But what's the First Law?



For example, consider an isolated system of fixed size.



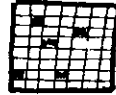
System is totally insulated from its surroundings. No particles can come in or out, no energy can be transmitted through the boundaries.

N and V is fixed, and from conservation of total energy, E , the energy is fixed too. These are the constraints defining this system -- fixed N , V and E .

Let

$\Omega(N, V, E)$ = total number of states, microscopic states that is, consistent with fixed N, V and E .

Oh! That's like the degeneracy of the macroscopic system



How many ways can you put $N=5$ particles in the available boxes?

At macroscopic equilibrium, the principle of equal weights implies that for each of these microscopic states, the probability is

$$P = \frac{1}{\Omega(N, V, E)}, \text{ with } N, V, E \text{ fixed.}$$

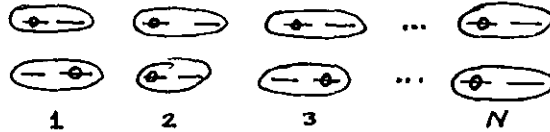
A related quantity is the ENTROPY, S , which we define as

$$S(N, V, E) \equiv k_B \ln \Omega(N, V, E)$$

This is, at this point, an arbitrary constant. We call it Boltzmann's constant

Expectation is that S is extensive.

Example: N identical particles, each one can exist in one of two degenerate states



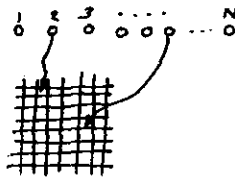
two different microscopic states of the total N particle system

In this case, there are a total of 2^N states, i.e.,

$$\Omega = 2^N \Rightarrow S = k_B \ln \Omega = N k_B \ln 2$$

it is extensive!

Another example: N uncorrelated and indistinguishable particles in a volume composed of M cells.



particle 1 has M places to go

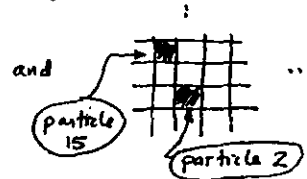
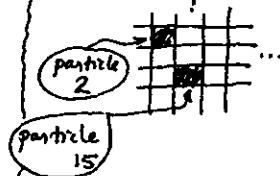
particle 2 has M places to go

⋮

particle N has M places to go

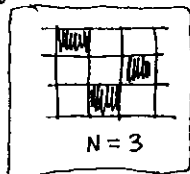
seems to suggest $\Omega = M^N$

But due to indistinguishability,

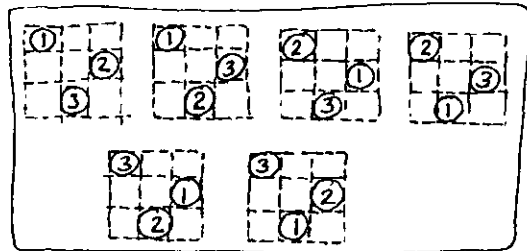


are the same macroscopic state.

The number of equivalent configurations is the number of ways to relabel the indistinguishable particles, and that number is $N! = \# \text{ permutations of } N \text{ things}$.



1 state with 3 indistinguishable particles



$3 \times 2 \times 1 = 6$ states with 3 distinguishable particles

Thus, $\Omega = M^N$ over counts the number of different states by a factor of $N!$. Hence

$$\Omega = \frac{1}{N!} M^N$$

As a result, in this case

$$S/k_B = N \ln M - \ln N!$$

For N large, Stirling's formula is

$$\ln N! = N \ln N - N$$

Thus, finally,

$$\begin{aligned} S/k_B &= N \ln M - N \ln N + N \\ &= N \left[\ln(M/N) + 1 \right] \end{aligned}$$

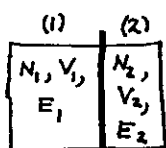
extensive

$\frac{1}{\langle n \rangle}$

The Second Law and the meaning of temperature

$\Omega(N, V, E)$ = number of all possible microscopic states (i.e., instantaneous fluctuations) with N, V, E fixed

Consider a subset of all these fluctuations which can be realized through internal constraints



"internal constraint"

Divide system into two subsystems such that

$$N = N_1 + N_2$$

$$V = V_1 + V_2$$

$$E = E_1 + E_2$$

If internal constraint was impermeable, then it could be used to enforce an inhomogeneous distribution of particles in the system. If it was insulating and rigid, it could enforce a partitioning of energy that was inconsistent with the partitioning at equilibrium without the constraint.

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Let

$\Omega'(N, V, E)$ = total # of microscopic states
with internal constraint
applied.

Since the constraint reduces the total number
of possible fluctuations,

$$\Omega'(N, V, E) < \Omega(N, V, E)$$

or

$$S'(N, V, E) < S(N, V, E)$$

But macroscopic states accessed through the
application of internal constraints correspond
to nonequilibrium macroscopic states
without those constraints. Thus,

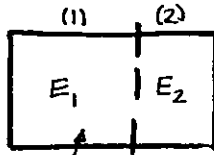
S is max. at equilibrium

$\Rightarrow S$ increases for all natural processes

This idea is the essence of the 2nd
Law of Thermodynamics.

To see what this law can predict,
consider the following question:

At equilibrium, how is the total
energy of a system partitioned?

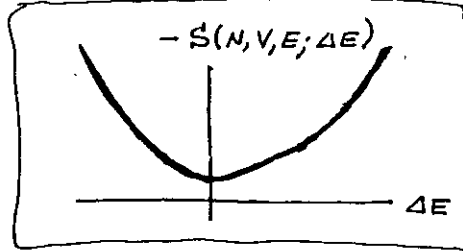


at equilibrium
 $E_1 = E_1^{(eq)}$

$$E = E_1 + E_2 \quad \leftarrow \text{Since energy is extensive}$$

$$E_1 = E_1^{(eq)} + \Delta E \quad \leftarrow \Delta E \text{ is the fluctuation in energy}$$

$$E_2 = E_2^{(eq)} - \Delta E$$



$$\frac{\partial(-S)}{\partial \Delta E} = \frac{\partial(-S_1)}{\partial \Delta E} + \frac{\partial(-S_2)}{\partial \Delta E}$$

Since S is extensive,
 $S = S_1 + S_2$

Define temperature, T , by

$$\frac{1}{T} \equiv \left(\frac{\partial S}{\partial E} \right)_{N, V}$$

Since both E and S are extensive,
 T must be intensive

Thus,
$$\frac{\partial(-S)}{\partial \Delta E} = -\frac{1}{T_1} + \frac{1}{T_2}$$

$\Rightarrow T_1 = T_2$ at thermal equilibrium,
 and ΔE flows from "hot"
 (high T) to "cold" (low T).

$$\left[\frac{\partial(-S)}{\partial \Delta E} \right] = \left(\frac{\partial(-S_1)}{\partial E_1} \right)_{N_1, V_1} \frac{\partial E_1}{\partial \Delta E} = \left(-\frac{1}{T_1} \right) (1)$$

$$\left[\frac{\partial(-S_2)}{\partial \Delta E} \right] = \left(\frac{\partial(-S_2)}{\partial E_2} \right)_{N_2, V_2} \frac{\partial E_2}{\partial \Delta E} = \left(+\frac{1}{T_2} \right) (-1)$$

The chain rule!
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