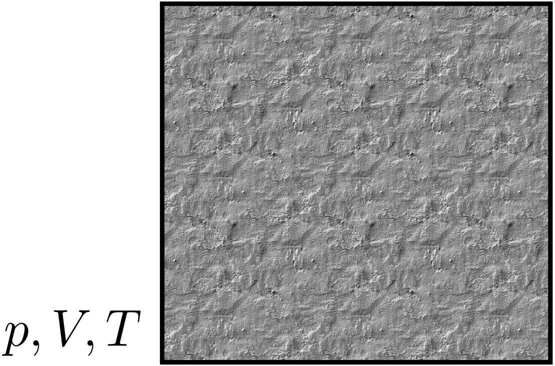
A Statistical Definition of Entropy

MSE 421 - Ceriotti

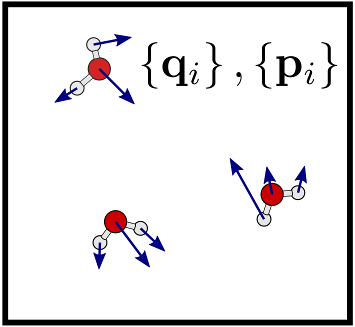
Revisiting macrostates

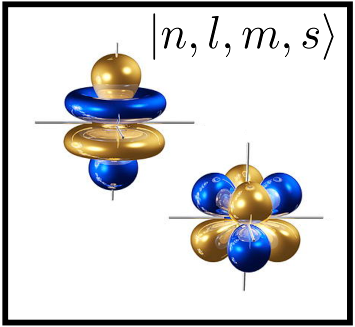
- Remember: it is practically impossible to characterize fully the state of a macroscopic system
- *Equilibrium* systems can be comprehended by a small number of macroscopic observables, e.g. volume V, temperature T, pressure p, molar amounts of components n_i



Defining microstates

- A microstate is a complete characterization of the state of all microscopic components of a system
  - Classically, this involves assigning both positions $\mathbf{q}_i$ and momenta $\mathbf{p}_i$ for all the particles at a given time
  - Quantum mechanically it involves determining quantum numbers $|\nu\rangle$ associated with a *complete set of commuting observables*





Observables and averages

- Imagine we could identify the microstate of the system, and measure it at different times. We could compute the mean of any observable O by summing over the values it takes for the different microstates

$$\langle O\rangle = \frac{1}{N}\sum_{t} O_{\nu(t)}, \quad \text{QM:}\frac{1}{N}\sum_{t}\langle\nu(t)|\,\hat{O}\,|\nu(t)\rangle, \quad \text{CL:}\frac{1}{N}\sum_{t} O(\mathbf{q}(t),\mathbf{p}(t))$$

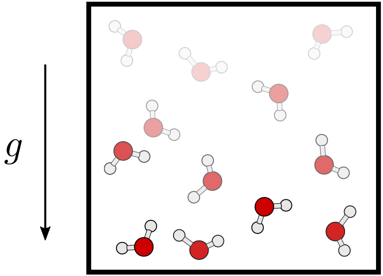
- The assumption here is **ergodicity**, i.e. that within the time of an observation (or given the large size of the observed sample) all representative states will be visited.

Ensemble averages

- We can rewrite the averages looking at how often each state appears, and defining a probability distribution

$$\text{QM:} \sum_{\nu} P(\nu) \langle \nu | \hat{O} | \nu \rangle, \quad \text{CL:} \int d\mathbf{p}d\mathbf{q}\, P(\mathbf{q},\mathbf{p})\, O(\mathbf{q},\mathbf{p})$$

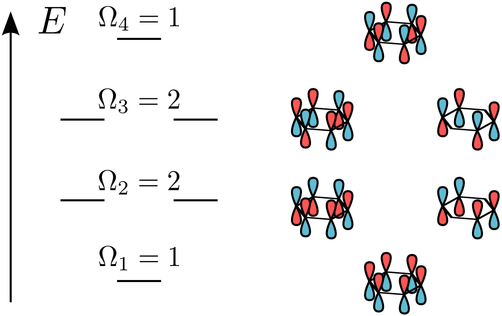
- The probability defines an **ensemble**, i.e. a set of configurations that are consistent with the thermodynamic equilibrium conditions.
- The statistical mechanics approach is to obtain these probability distributions, and to circumvent the need of measuring individual microstates by predicting the average properties of a macroscopic system



Equiprobability axiom

- We need a principle to determine the probability of a state. *For a closed, isolated system, with constant N, V, E, all the microstates that are consistent with these macroscopic observables have the same probability.* [An ensemble with constant NVE is called *microcanonical*]
- Define a counter Ω for the number of states that takes into account the possible degeneracy of energy levels [for large enough quantum systems it is convenient to consider a smooth limit of the discrete Ω, and use a *density of states* as in the classical case]

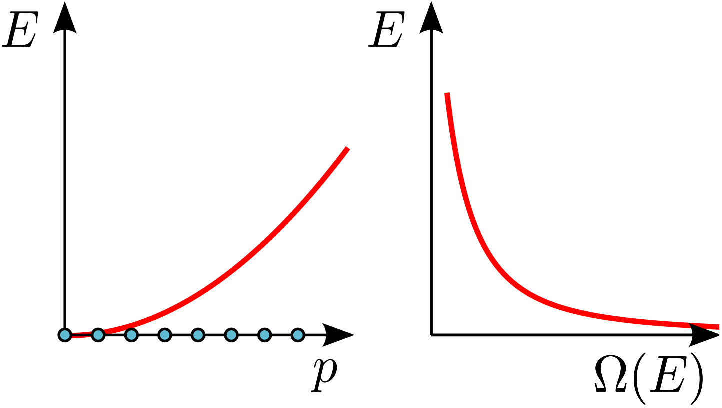
$$\text{QM:}\Omega_E(N,V), \quad \text{CL:}\Omega(N,V,E)\,\mathrm{d}E$$



$$P_{E,\nu} = 1/\Omega_E(N,V)$$

Density of states and dimensionality

- The equiprobability axiom actually involves deep assumptions on the nature of a microstate - namely what is a *complete* determination of one. Think of a system with only kinetic energy, $E = \mathbf{p}^2/2m$
  - 1D: $P(p) \propto 1$ so $\Omega(E) \propto \int \delta\left(E - p^2/2m\right) \mathrm{d}p = \sqrt{m/2E}$
  - 2D: $P(p_x, p_y) \propto 1$ so $\Omega(E) \propto \int \delta\left(E - p^2/2m\right) \mathrm{d}^2\mathbf{p} = 2\pi m$



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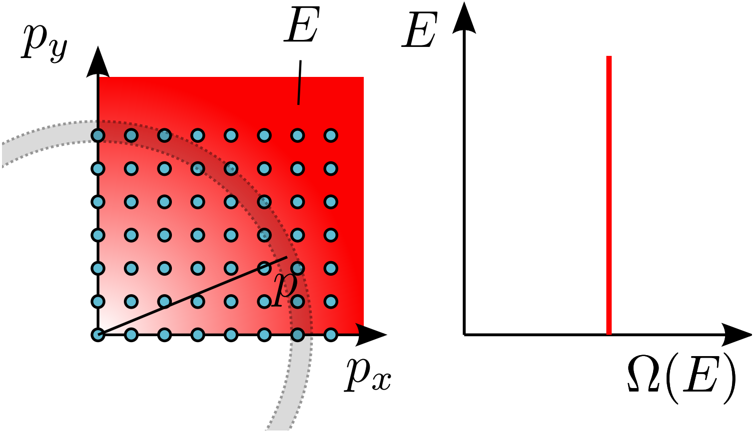
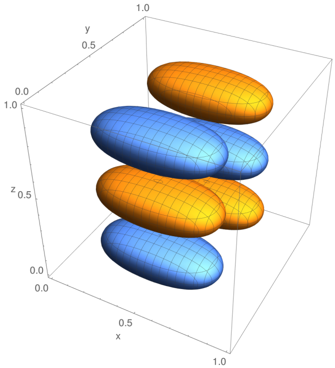


The (3D) Particle in a Box

- Consider a particle in a 3D box of size L. Each state is characterized by 3 quantum numbers $|n_x n_y n_z\rangle$, and has a energy $E \propto \hbar^2 \mathbf{k}^2/2m$ with $k_{x,y,z} = n_{x,y,z}\pi/L$
- 3D: $P(\mathbf{k}) \propto 1\ \Omega(E) \propto \int \delta\left(E - \hbar^2 k^2/2m\right) \mathrm{d}\mathbf{k}$

$$\longrightarrow \mathrm{d}\mathbf{k} = 4\pi k^2 \mathrm{d}k, \qquad \mathrm{d}E = \hbar^2 k m^{-1} \mathrm{d}k, \qquad k = \sqrt{2Em/\hbar^2}$$

$$\longrightarrow \Omega(E) \propto \int \delta\left(\bar{E} - E\right) \sqrt{2Em/\hbar^2} \mathrm{d}E = \sqrt{2Em/\hbar^2}$$



A statistical definition of entropy

$$\boxed{S\left(E,V,N\right)=k_B\ln\Omega\left(E,V,N\right)}$$

- This definitions makes entropy additive [given two non-interacting systems with number of states Ω_1 and Ω_2, the combined number of states is $\Omega=\Omega_1\Omega_2$]

$$S=k_B\ln\Omega_1\Omega_2=k_B\ln\Omega_1+k_B\ln\Omega_2=S_1+S_2$$

- S is consistent with a maximum-entropy principle

$$B\left(E,V,N;const.\right)\subseteq B\left(E,V,N\right)\rightarrow\Omega\left(E,V,N;const.\right)\le\Omega\left(E,V,N\right)$$

$$\rightarrow S\left(E,V,N;const.\right)\le S\left(E,V,N\right)$$

- The condition $\left(\partial S/\partial E\right)_X=1/T>0$ requires [β is often used in lieu of the temperature in a statistical mechanics context]

$$\beta=\frac{1}{k_BT}=\left(\frac{\partial\ln\Omega}{\partial E}\right)_X>0$$

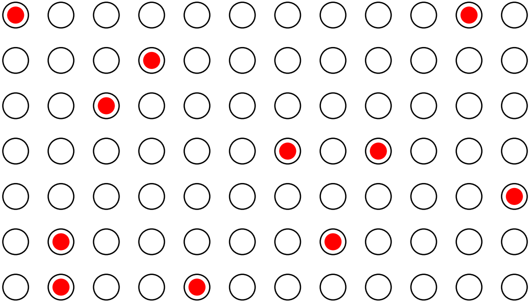
Atoms on a surface/1

- Consider N adsorbed atoms on a surface with M equivalent sites. All the sites are equivalent, and the atoms do not interact with each other, so the energy does not depend on the distribution of the atoms.

$$\Omega(0, M, N) = \frac{M!}{N!\,(M-N)!}$$

- For $N, M \gg 1$, we can use Stirling's approximation to get an estimate of S

$$\frac{S}{k_B} \approx M \ln M - N \ln N - (M-N)\ln(M-N)$$



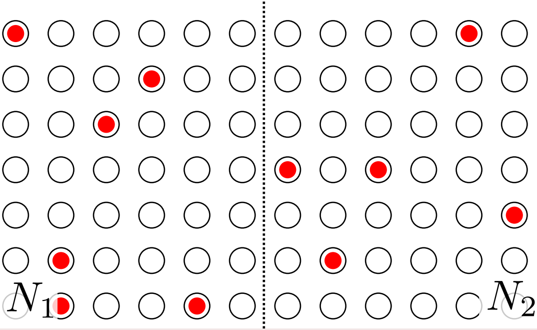
Atoms on a surface/2

- Now partition the surface in half ($2 \times M/2$ sites), and fix N_1 atoms to be in region 1, and N_2 in region 2 [we take $N_1 + N_2 = N$]

$$\Omega_1\left(0, M/2, N_1\right) = \frac{(M/2)!}{N_1!\,(M/2 - N_1)!}, \qquad \Omega_2\left(0, M/2, N_2\right) = \frac{(M/2)!}{N_2!\,(M/2 - N_2)!}$$

- Now, the overall entropy is (with Stirling)

$$\frac{S_1}{k_B} + \frac{S_2}{k_B} \approx \frac{M}{2}\ln\frac{M}{2} - N_1\ln N_1 - \left(\frac{M}{2} - N_1\right)\ln\left(\frac{M}{2} - N_1\right)$$
$$+\frac{M}{2}\ln\frac{M}{2} - (N - N_1)\ln(N - N_1) - \left(\frac{M}{2} - (N - N_1)\right)\ln\left(\frac{M}{2} - (N - N_1)\right)$$



Atoms on a surface/3

- Let's look for the maximum of entropy

$$0 = \frac{1}{k_B}\frac{\partial S\left(\text{cnstr}\right)}{\partial N_1} = -1 - \ln N_1 + 1 + \ln\left(\frac{M}{2} - N_1\right) +$$

$$+1 + \ln\left(N - N_1\right) - 1 - \ln\left(\frac{M}{2} - \left(N - N_1\right)\right)$$

$$\left(\frac{M}{2} - N_1\right)\left(N - N_1\right) = N_1\left(\frac{M}{2} - \left(N - N_1\right)\right) \quad N_1 = \frac{N}{2}$$

- Equilibrium corresponds to equal partitioning of atoms! Now what is the associated entropy?

$$2S\left(M/2, N/2\right) = 2 \times \left(\frac{M}{2}\ln\frac{M}{2} - \frac{N}{2}\ln\frac{N}{2} - \left(\frac{M}{2} - \frac{N}{2}\right)\ln\left(\frac{M}{2} - \frac{N}{2}\right)\right)$$

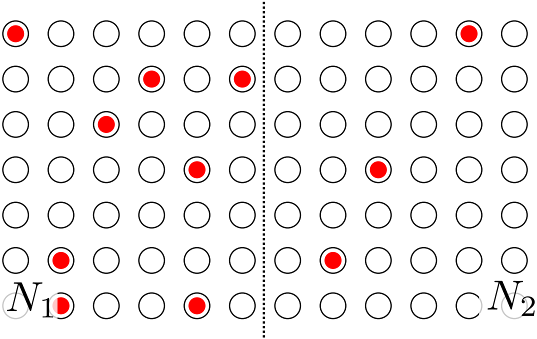
$$= M\left[\ln M - \ln 2\right] - N\left[\ln N - \ln 2\right] - \left(M - N\right)\left[\ln\left(M - N\right) - \ln 2\right] = S\left(M, N\right)$$

Atoms on a surface/4

- BUT, wait a sec... **OOOPS!**

$$[\Omega(0,3,2)]^2 = \left[\frac{3!}{2!1!}\right]^2 = 9, \qquad \Omega(0,6,4) = \frac{6!}{4!2!} = 15$$

- What's happening? Atoms can distribute unevenly between the two subsystems, which is untrue if we set $N_1 = N_2 = N/2$!
  - For nanoscale systems entropy can be non-additive!
  - This can be seen as a "border" effect: a system with twice the size is not the same two independent systems
  - Your first encounter with the magic of the "thermodynamic limit"!



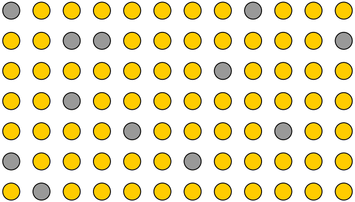
Entropy of mixing

- Consider a system with M sites occupied by two elements, e.g. Au and Ag. Assume the molar fraction of Ag is x. Consider again a non-interacting scenario, so the energy is always zero.

1. Number of states: $\Omega\left(0, M, N = Mx\right) = \frac{M!}{N!(M-N)!}$
2. Entropy (w/Stirling): $S = k_B\left[M \ln M - N \ln N - (M-N)\ln(M-N)\right]$
3. Write as a function of molar concentration

$$S = k_B\left[M \ln M - Mx\left(\ln M + \ln x\right) - (M - Mx)\left[\ln M + \ln(1-x)\right]\right]$$

4. ... Ideal solution model! $S/M = k_B\left[x_{\mathrm{Ag}} \ln x_{\mathrm{Ag}} + x_{\mathrm{Au}} \ln x_{\mathrm{Au}}\right]$



... what is the most stable concentration?