

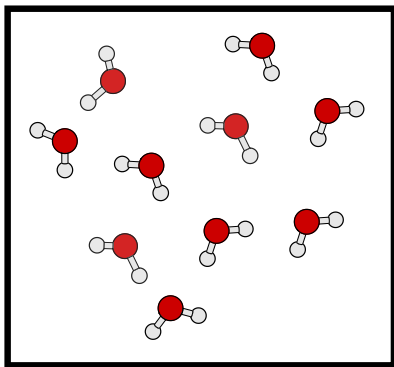
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# A Statistical Definition of Entropy

MSE 421 - Ceriotti

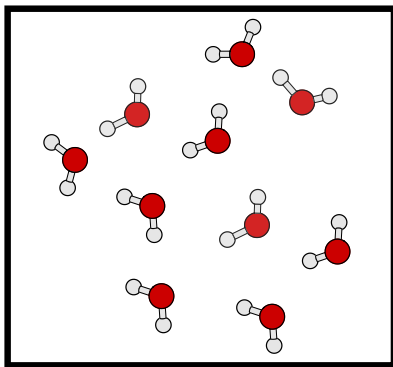
# Revisiting macrostates

- 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  $n_i$



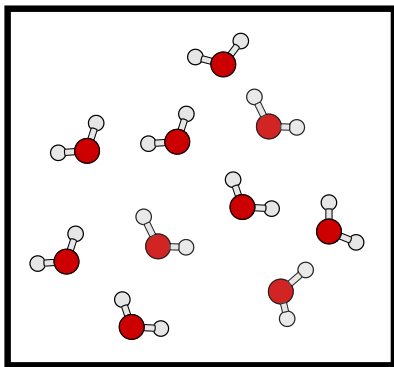
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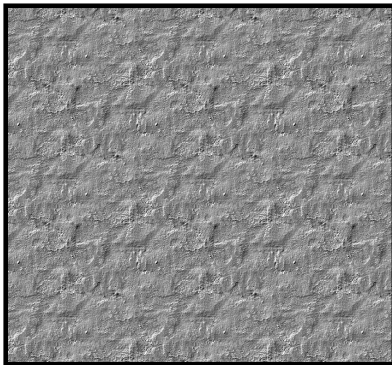
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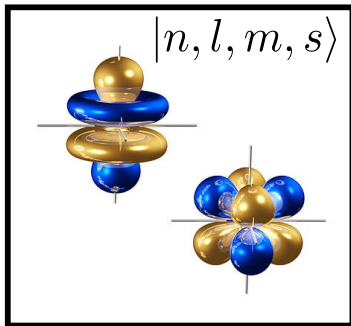
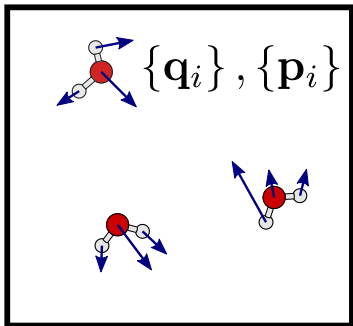
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$p, V, T$



# 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

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

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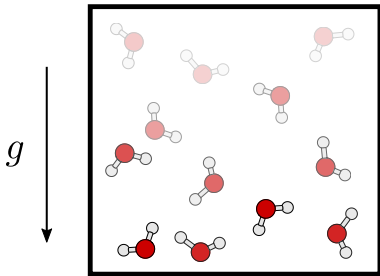


# Ensemble averages

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

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

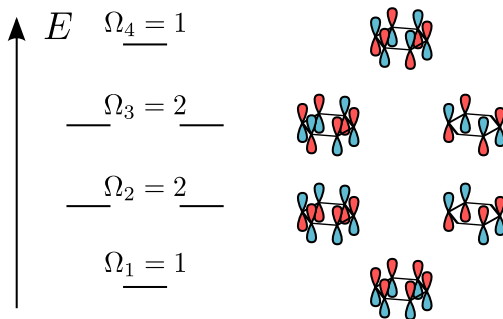
- The probability defines an **ensemble**, i.e. a set of configurations that are consistent with the thermodynamic equilibrium conditions.
- The statistical mechanics approach is to obtain these probability distributions, and to circumvent the need of measuring individual microstates by predicting the 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  $\Omega$  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  $\Omega$ , and use a *density of states* as in the classical case]

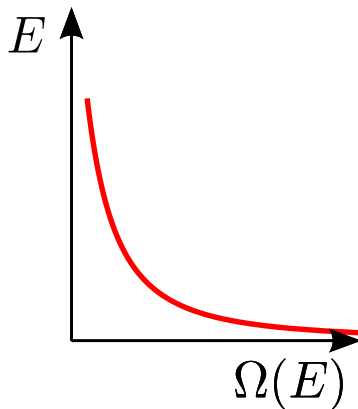
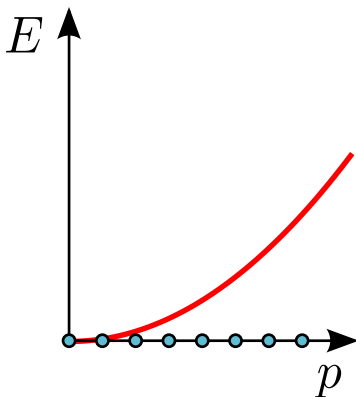
$$\text{QM: } \Omega_E(N, V), \quad \text{CL: } \Omega(N, V, E) dE$$



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

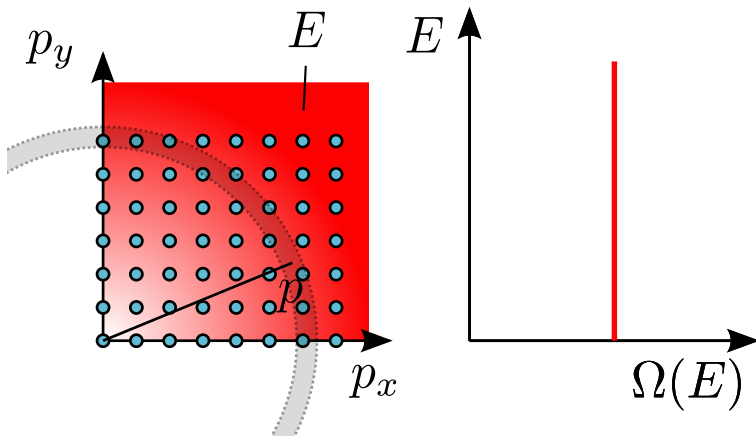
# Density of states and dimensionality

- 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  $\Omega(E) \propto \int \delta(E - p^2/2m) dp = \sqrt{m/2E}$
  - 2D:  $P(p_x, p_y) \propto 1$  so  $\Omega(E) \propto \int \delta(E - p^2/2m) d^2\mathbf{p} = 2\pi m$



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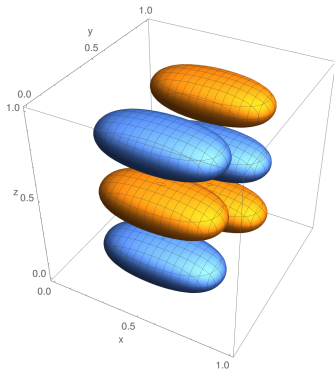
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# The (3D) Particle in a Box

- 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:  $P(\mathbf{k}) \propto 1$   $\Omega(E) \propto \int \delta(E - \hbar^2 k^2 / 2m) d\mathbf{k}$

$$\begin{aligned} \longrightarrow d\mathbf{k} &= 4\pi k^2 dk, & dE &= \hbar^2 k m^{-1} dk, & k &= \sqrt{2Em/\hbar^2} \\ \longrightarrow \Omega(E) &\propto \int \delta(\bar{E} - E) \sqrt{2Em/\hbar^2} dE = \sqrt{2Em/\hbar^2} \end{aligned}$$



# A statistical definition of entropy

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

- This definition makes entropy additive [given two non-interacting systems with number of states  $\Omega_1$  and  $\Omega_2$ , 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

$$\begin{aligned} B(E, V, N; \text{const.}) \subseteq B(E, V, N) &\rightarrow \Omega(E, V, N; \text{const.}) \leq \Omega(E, V, N) \\ &\rightarrow S(E, V, N; \text{const.}) \leq S(E, V, N) \end{aligned}$$

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

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

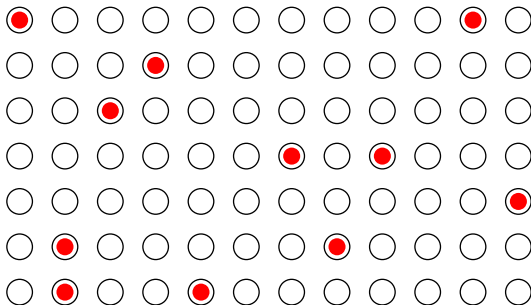
# Atoms on a surface/1

- 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  $S$

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



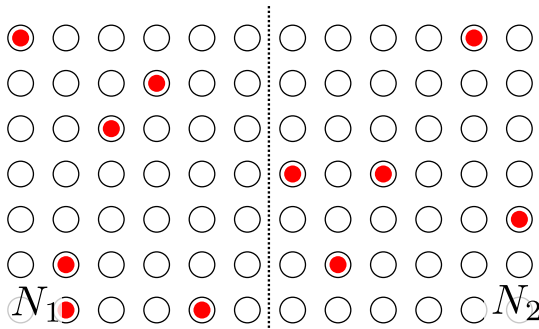
# Atoms on a surface/2

- 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  $N_1 + N_2 = N$ ]

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

- Now, the overall entropy is (with Stirling)

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





# Atoms on a surface/3

- Let's look for the maximum of entropy

$$\begin{aligned} 0 &= \frac{1}{k_B} \frac{\partial S(\text{cnstr})}{\partial N_1} = -1 - \ln N_1 + 1 + \ln \left( \frac{M}{2} - N_1 \right) + \\ &\quad + 1 + \ln (N - N_1) - 1 - \ln \left( \frac{M}{2} - (N - N_1) \right) \\ \left( \frac{M}{2} - N_1 \right) (N - N_1) &= N_1 \left( \frac{M}{2} - (N - N_1) \right) \quad N_1 = \frac{N}{2} \end{aligned}$$

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

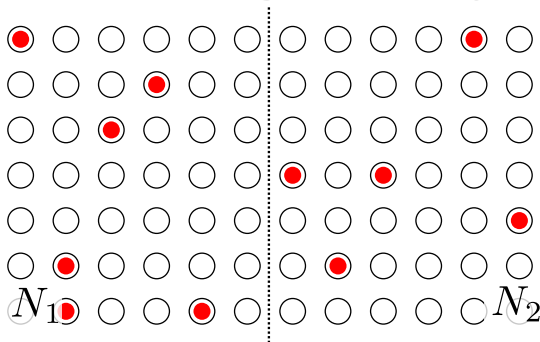
$$\begin{aligned} 2S(M/2, N/2) &= 2 \times \left( \frac{M}{2} \ln \frac{M}{2} - \frac{N}{2} \ln \frac{N}{2} - \left( \frac{M}{2} - \frac{N}{2} \right) \ln \left( \frac{M}{2} - \frac{N}{2} \right) \right) \\ &= M [\ln M - \ln 2] - N [\ln N - \ln 2] - (M - N) [\ln (M - N) - \ln 2] = S(M, N) \end{aligned}$$

# Atoms on a surface/4

- BUT, wait a sec...

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

- 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”!

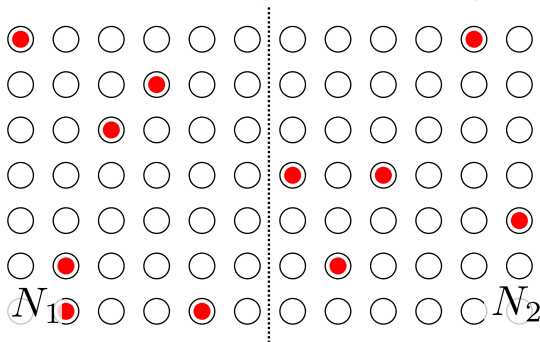


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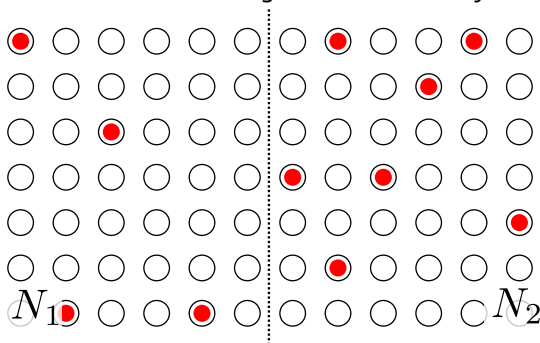


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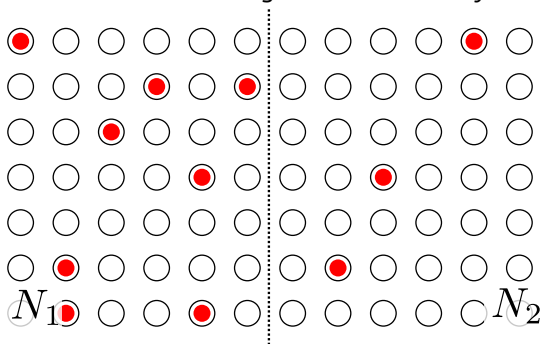


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# Entropy of mixing

- 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.

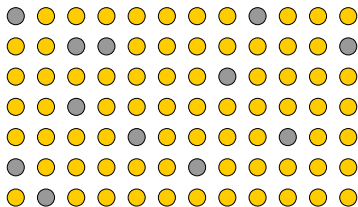
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2 Entropy (w/Stirling):  $S = k_B [M \ln M - N \ln N - (M - N) \ln (M - N)]$

3 Write as a function of molar concentration

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

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



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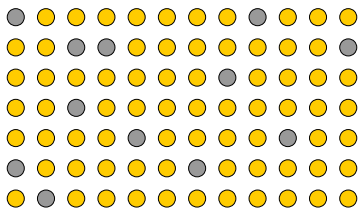
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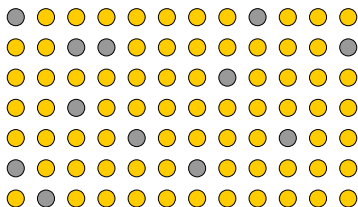
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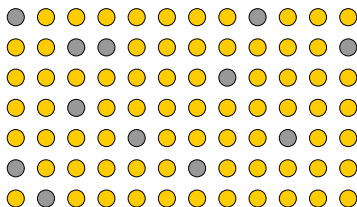
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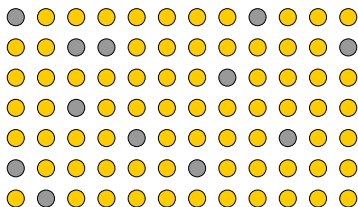
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