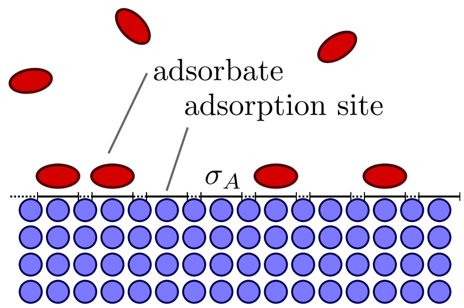
## Exercise 1 Langmuir adsorption isotherm

In 1916, Irving Langmuir presented his model for the adsorption of species onto simple surfaces. Langmuir was awarded the Nobel Prize in 1932 for his work concerning surface chemistry. He hypothesized that a given surface has a certain number of equivalent sites to which a species can "stick", either by physisorption or chemisorption.




In the Langmuir adsorption model, the following assumptions are made for the adsorption of a molecule of one type (A) onto a solid surface:

- The surface containing the adsorbing sites is perfectly flat plane with no corrugations (assume the surface is homogeneous).
- The adsorbing gas adsorbs into an immobile state.
- All adsorption sites are equivalent.
- Each site can hold at most one molecule of A (monolayer coverage only).
- There are no interactions between adsorbate molecules on adjacent sites.

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(a) In the Langmuir model, what is the total number of ways of arranging M identical molecules onto N surface sites? ($M \ll N$)

(b) Can you write down the grand canonical partition function for the Langmuir absorption system with N surface sites? Take the temperature to be T, the absorption energy of each molecule on the surface to be $\epsilon$, and chemical potential to be $\mu$.

(c) In the grand canonical ensemble with temperature T and chemical potential $\mu$, what is the probability of having M molecules absorbed on a surface with N sites?

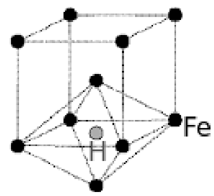
(d) In (c), what is the number of molecules that is most likely to be absorbed on the surface? You may want to use Stirling's approximation, i.e. at large $n$, $\ln(n!) \simeq n\ln(n) - n$ .

(e) We define now the fraction of the surface sites covered as $\theta = \frac{M}{N}$. Taking the chemical potential of the molecules to be equal to that of an ideal gas, i.e. $\exp\frac{\mu}{k_B T} = \frac{P}{P_0}$ (where $P_0$ is constant), what is the surface coverage at constant temperature T and pressure P for the most probable number of adsorbate molecules?

## Exercise 2 Hydrogen embrittlement

Hydrogen embrittlement is the process by which metals such as steel become brittle and fracture due to the introduction and subsequent diffusion of hydrogen into the metal. This is often a result of introduction of hydrogen during metal casting at high temperatures.

As an example, we consider BCC iron with H atoms in the octahedral position in Fe unit cells as shown in the figure below.




(a) If we have a piece of defect-free iron with $M$ atoms, how many arrangements are there to place $N$ ($N \ll M$) hydrogen atoms in the lattice? Ignore the vibration of atoms and just consider the perfect BCC lattice.

(b) In (a), what is the configurational entropy of each H atom absorbed in the lattice? Use Stirling's approximation, i.e. at large $n$, $\ln(n!) \simeq n\ln(n) - n$ .

(c) If the absorption energy of one H atom into the Fe lattice is $\epsilon$, what is the chemical potential $\mu$ of each hydrogen atom as a function of $N$ at temperature $T$ and zero pressure?

(d) During casting, hydrogen atoms from the air can gradually diffuse into the iron until the process reaches thermodynamic equilibrium. Take the chemical potential of an H atom in the air to be $\mu_0$. What is the equilibrium concentration $c = \dfrac{N}{M}$ of hydrogen in iron?

(e) Hydrogen embrittlement can cause metals to crack easily, and therefore the concentration of hydrogen should be lowered as much as possible. Using the expression that you obtained from (d), propose ways to eliminate hygrogen embrittlements.

The End.