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Depletion Forces

Force & function at the nanoscale

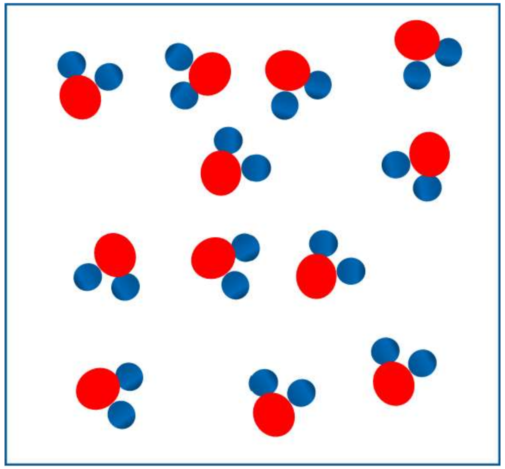
Macrostates and Microstates

A “macrostate” is the collection of all possible configurations of a system

A “microstate” is one possible configuration of a macrostate

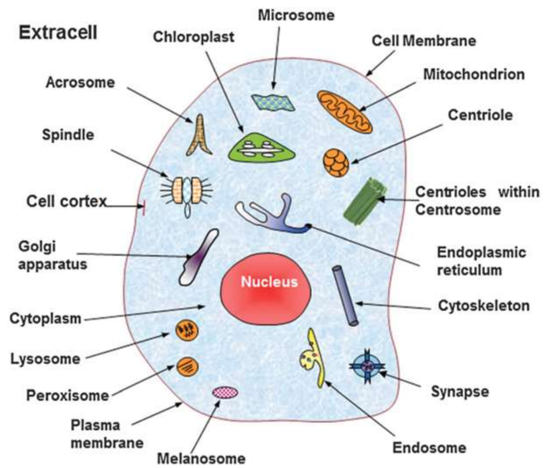
Drafts on a chess board

Water molecules in a box



Multi-component systems

In many real systems there are often many different components in the same liquid volume.

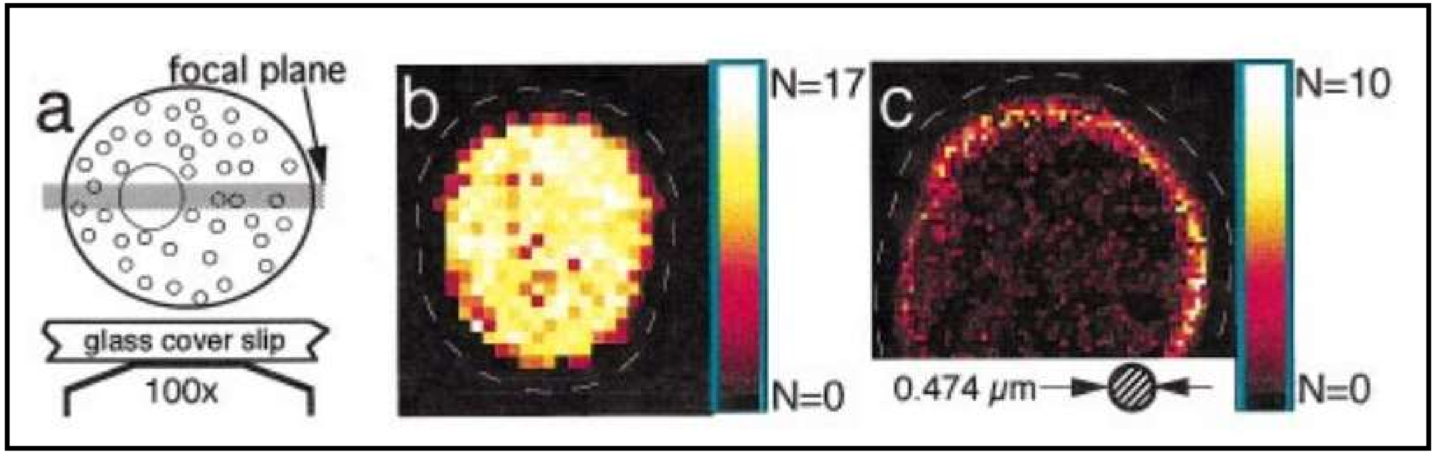


Consider for example a biological cell with many different sized proteins or a paint with large latex particles and small pigment particles.

How does the presence of non-adsorbing small particles affect the stability of larger objects?

The Depletion Force

The depletion force can be observed directly from the motion of a single large sphere diffusing inside a container.



[Dinsmore et al PRL 1998]

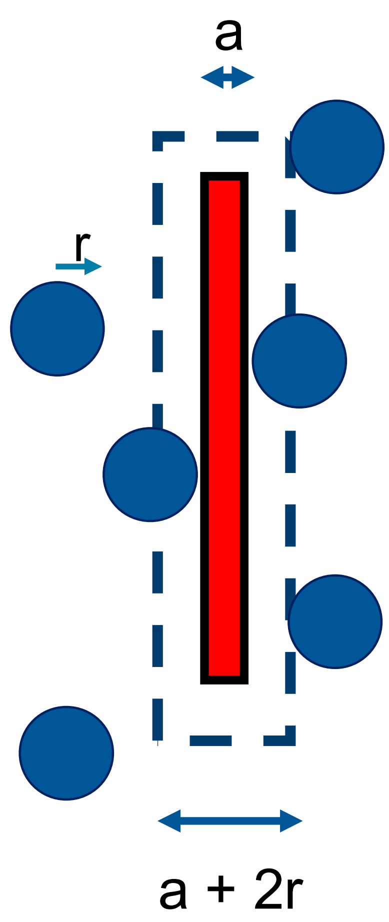
b) <u>Without</u> small spheres: it diffuses freely throughout the whole volume.
c) <u>With</u> small spheres: The sphere is trapped against the edge by an attractive depletion force.

Excluded Volume

Key insight: *Small particles are excluded / depleted from a volume around any larger object in solution.*

The volume they are excluded from is larger than the physical volume of the large object and is related to the combined size of the object and the small particle.

The centre of each particle cannot enter the excluded volume shown as a dash

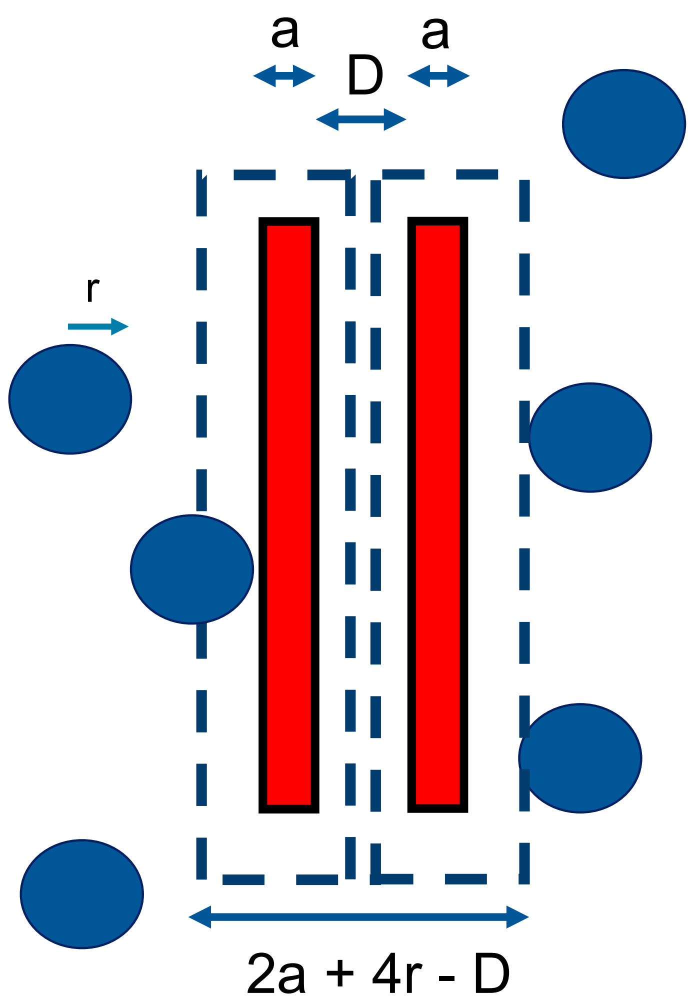


Depletion Forces and Excluded Volume

How is the excluded volume affected as two surfaces approach one another?

The excluded volumes around each object overlap. The total excluded volume actually decreases as the objects are separated by D < 2r.

This means the volume available to the small particles increases



Depletion Force: 2 plates

2 cases:

$D > 2r \longrightarrow \Delta V_p = 0$

$D < 2r \longrightarrow \Delta V_p = [2r - D]A$

So the number of microstates accessible to the small spheres increases when the plates come close together leading to an increase in entropy.

An increase in entropy with decreasing distance, results in an attractive force.

$$\boxed{\mathrm{F} = \mathrm{T}\frac{d\Delta S}{dD}}$$

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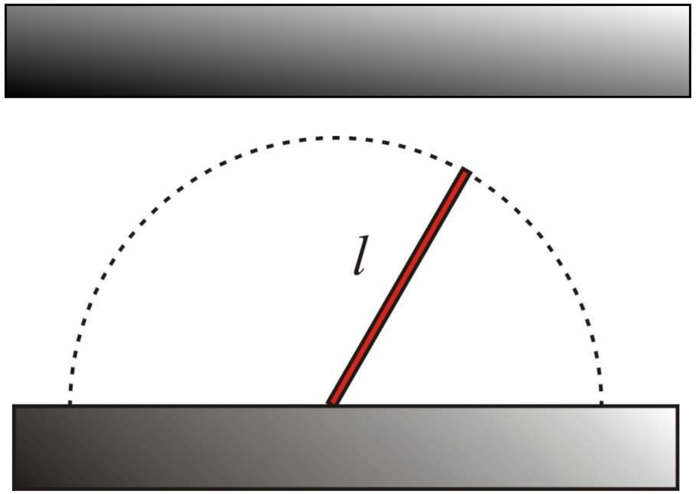
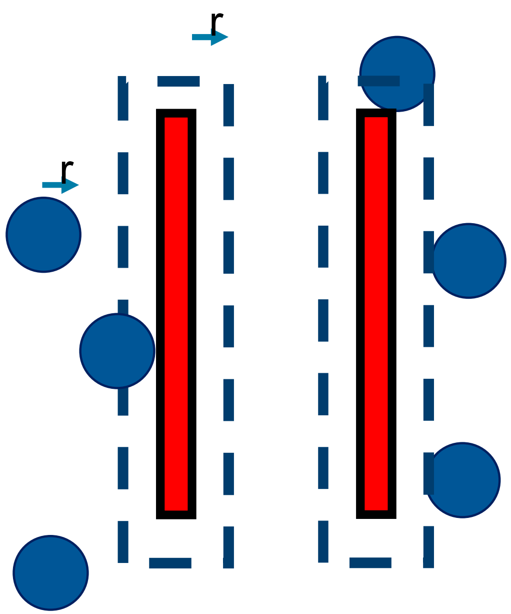
Problem: Entropy

Entropy is a measure of the number of possible microstates consistent with the current macrostate.

$$\boxed{S = k_B ln\mathrm{w}}$$



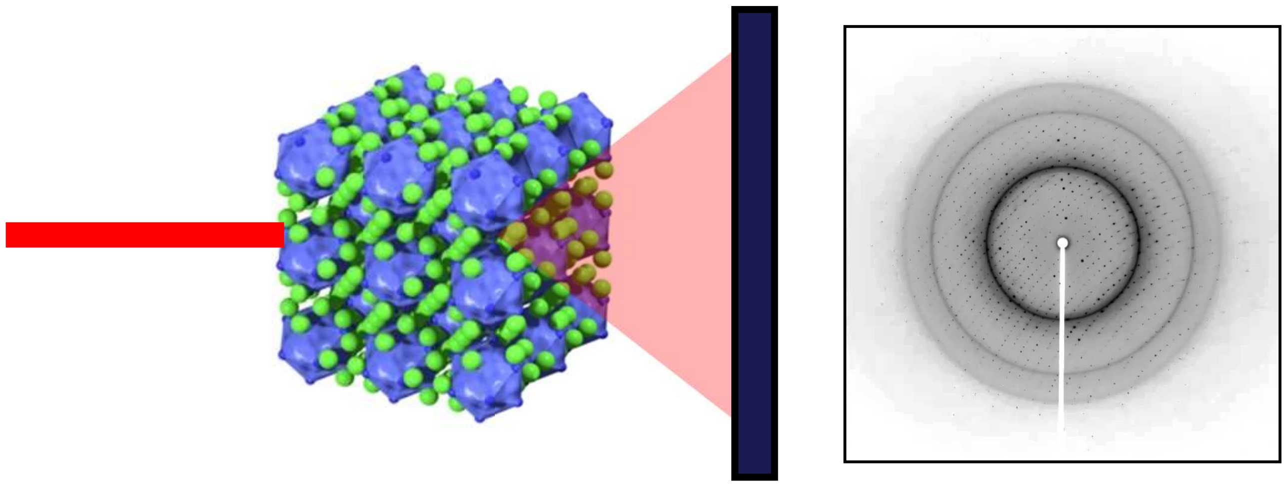


Depletion Force: 2 Spheres

Crystallizing Proteins

Medical / Pharmaceutical advances often depend on understanding the structure function relationship of various important proteins. The main method to measure their structure is through xray diffraction experiments on a single crystal. However, many proteins are difficult to crystallize.

The addition of high concentrations of small polymers (PEG) is a common route to help crystallization and works due to the depletion force.



14.1 Derivation: Entropic Force v Osmotic Pressure

The Depletion force can be described in 2 different but equivalent ways:

1. It arises due to the increasing entropy of the small spheres due to the increased volume as the plates move together.

2. It is an osmotic pressure difference acting on the plates due to the different concentration of small particles in between and outside the plates.

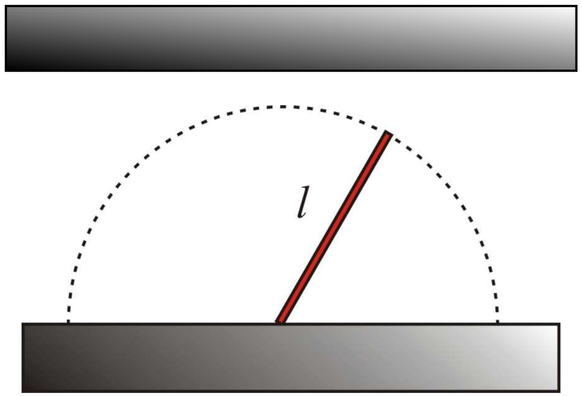
$$\boxed{\Delta U = P_{osm} \Delta V_{excl}}$$

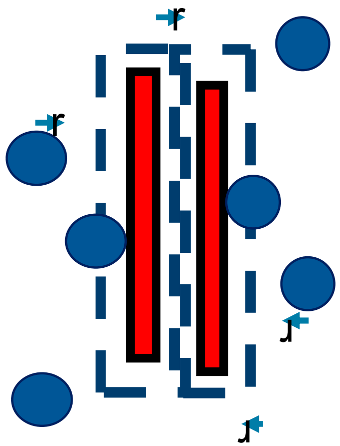
Problem: Entropy and Osmotic pressure

Osmotic pressure – a pressure that arises from differences in concentration

$$\Pi = nk_BT$$

Explain these two phenomena using the language of osmotic pressure.



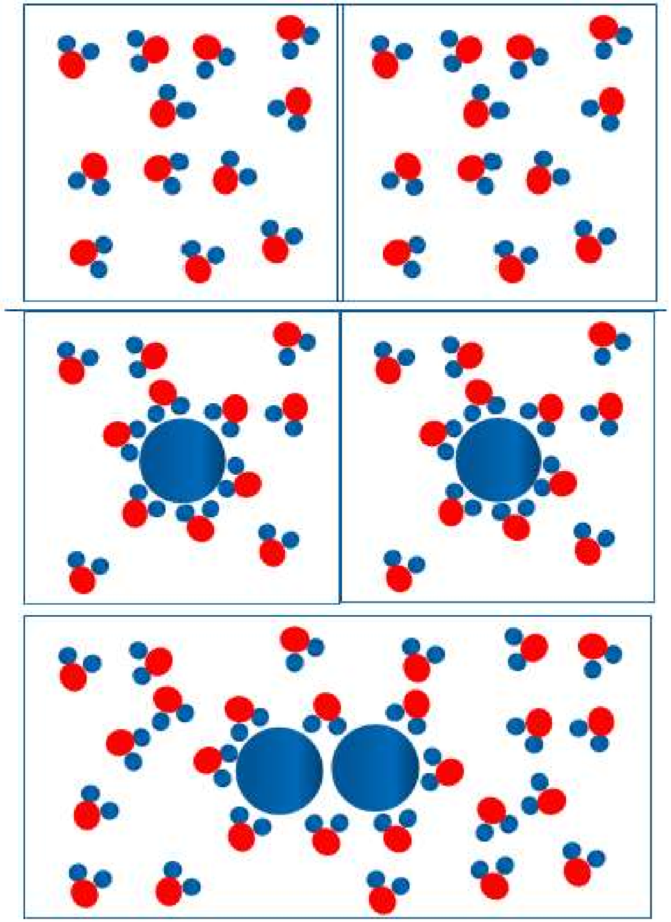


14.2 Problem - Hydrophobic Effect Revisited

A

B

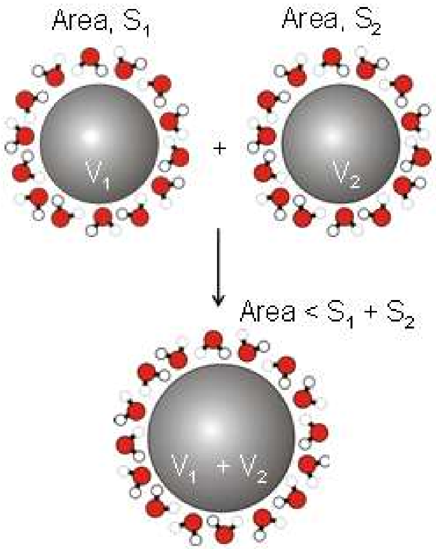
C



What happens to the number of microstates when you put a non-polar molecule in water? Why?

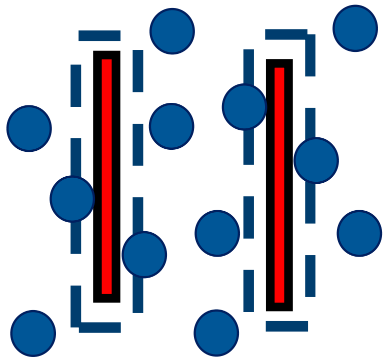
How is the number of microstates different when 2 non-polar molecules are separate or together?

Hence explain the force.



Summary of key concepts

Small spheres near walls or larger objects are excluded from the neighbouring volume



This excluded volume can be reduced as walls or large objects come closer together. This increases the entropy and leads to an attractive force.

The entropic force can also be understood as an osmotic pressure due to the different concentrations of small spheres inside and outside the gap between the large objects.

$$\Delta U = P_{osm} \Delta V_{excl}$$