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PHYS3009: Force and Function at the Nanoscale

Week 26 – 10:00am Tuesday – 14 March 2023

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Entropic forces

Force & function at the nanoscale

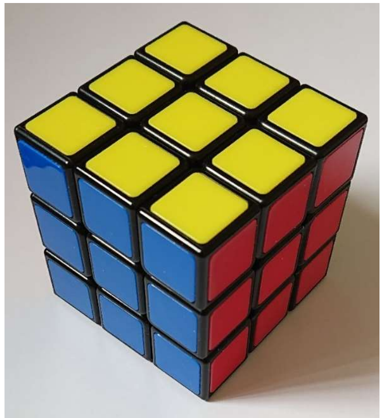
Simple mixing experiment

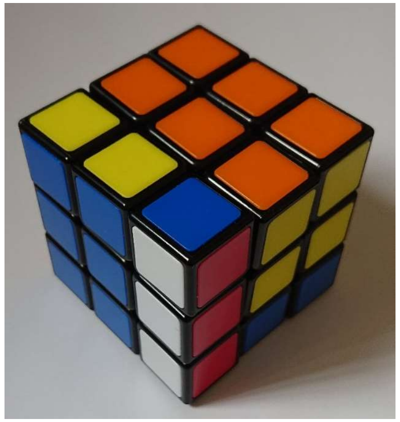
Why does a droplet of one miscible liquid spread out uniformly in the other?

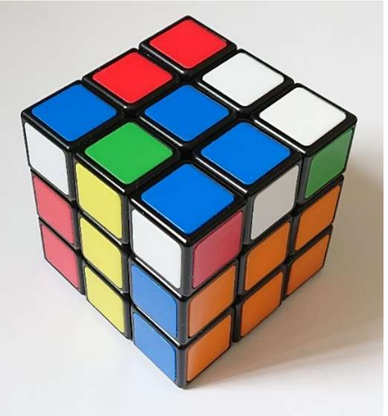
We know that the force is:
$F=-dU/dr$

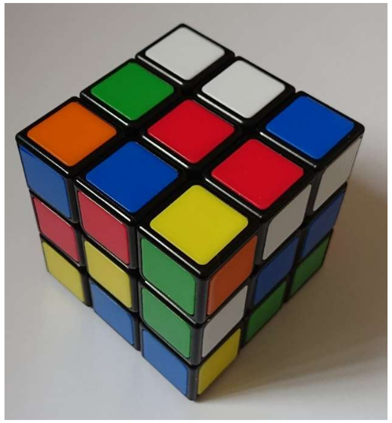
But the interactions are the same whether all the red molecules stay on the rhs of the glass or spread out to fill the whole.

Why is a Rubik's cube so annoying!









1 possible configuration

43 252 003 274 489 total configurations

Playing Poker

Pattern	Microstates
royal flush	4
straight flush	$(13-4)\times 4 = 36$
four of a kind	$13 \times 24 = 624$
full house	$\binom{4}{2} \times \binom{4}{3} \times 13 \times 12 = 3,744$
flush	$4 \times \binom{13}{5} - 4 - 36 = 5,108$
straight	$10 \times 4^5 - 40 = 10,200$
any three of a kind	$13 \times \binom{4}{3} \times \binom{12}{2} \times \binom{4}{1}^2 - 3,744 = 51,168$
two pairs	$\binom{4}{2}^2 \times 13 \times 12 \times 2 \times 11 = 123,552$
any two of a kind	$\binom{4}{2} \times 13 \times \binom{12}{3} \times 4^3 = 1,098,240$

Macrostates and microstates

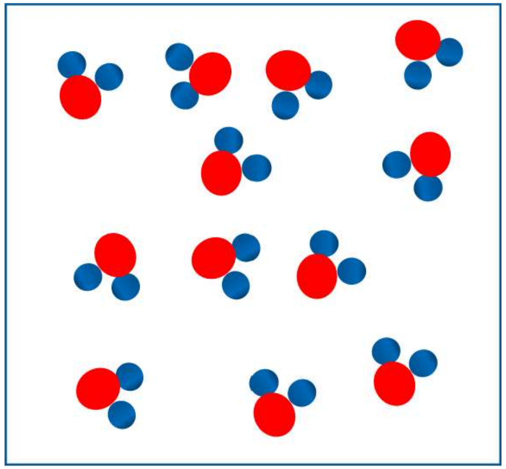
Macrostate	Microstate
The Rubik's cube	One possible arrangement of squares on a Rubik's cube
The set of cards	The particular hand you are dealt
The glass of squash	The arrangement of molecules in the liquid.

13.1 Problem - Macrostates and Microstates

Chat with person next to you and decide what the macrostate and microstate of these two systems would be.

Drafts on a chess board

Water molecules in a box



Boltzmann form of Entropy

Boltzmann derived a statistical form of the entropy of a system, S, such that

$$\boxed{S = k_B \ln W}$$

where W is the number of available (micro) states corresponding to a given macrostate and k_B is Boltzmann's constant (JK^{-1}).

Equilibrium

“When an isolated system is left long enough, it evolves to thermal equilibrium. Equilibrium is not one particular microstate. Rather it’s that probability distribution of microstates having the greatest disorder allowed by physical constraints on the system.

Nelson, Biological Physics

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Changes in entropy produce a force

$$F = -\frac{dU}{dD}$$

$$U = \cancel{\Delta H} - T\Delta S$$

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

In earlier lectures we have considered how the energy change from different interactions give rise to a force.

A more complete statement would be the expression for the free energy. This depends on the formation of bonds (e.g covalent, dipole interactions etc). This is the enthalpic contribution (ΔH).

However, it also depends on the entropy of a system.

How does entropy produce a force?

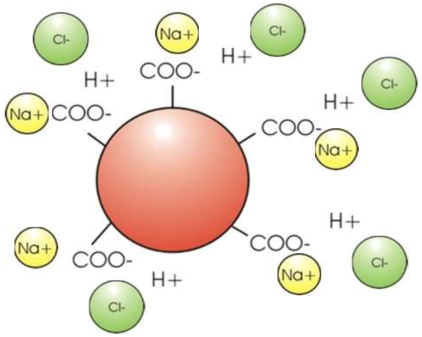
$$\boxed{U = \Delta H - T\Delta S}$$

In earlier lectures we have considered how this interaction energy depends on the formation of bonds (e.g covalent, dipole interactions etc). This is the enthalpic contribution (ΔH).

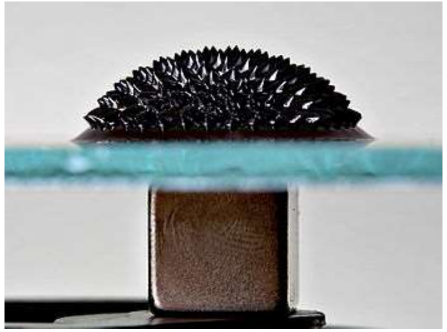
$$\boxed{F = -\frac{dU}{dD}}$$

Colloidal stability

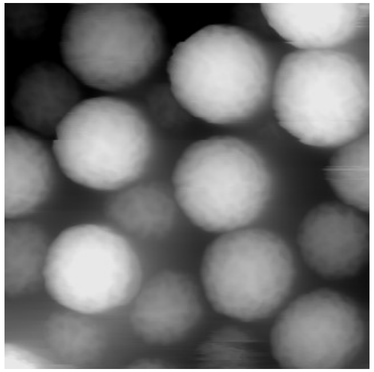
It is sometimes not possible to use charges to keep particles and surfaces apart in solution



This is true when using organic solvents as the suspending medium (e.g. in ferrofluids), as ionic solids (electrolytes) are often poorly soluble in these solvents



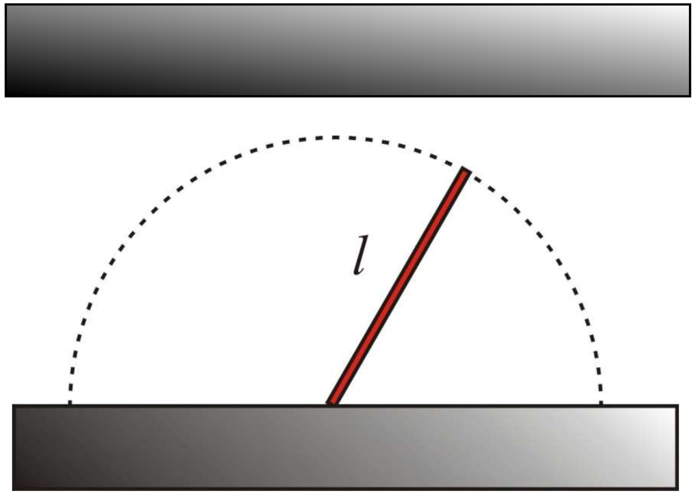
An alternative route to stabilisation is to use Steric (or entropic) repulsion effects between surfaces



Steric / Entropic Forces

Surfaces can be decorated with long molecules (e.g. polymers)

Molecules are tethered to a surface by one end and can wave around freely in solution. As a result they have a large number of **configurations** (directions in which they can point)



When two surfaces come close together, the number of configurations that the molecules can adopt is reduced. The number of available configurations is related to the **entropy** (or measure of disorder).

The system resists this reduction in entropy by generating a repulsive force…

Key points

A system can have many configurations known as microstates.

The number of equivalent microstates defines the entropy

Systems sample nearby microstates due to thermal fluctuations and will move towards configurations with high entropy.

Surfaces can be prevented from sticking together by tethering molecules on the surface.

The force between the surfaces is repulsive and related to the separation

$$\boxed{F = \frac{k_B T}{D}}$$