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Aggregation &
Self-assembly
Force & function at the nanoscale

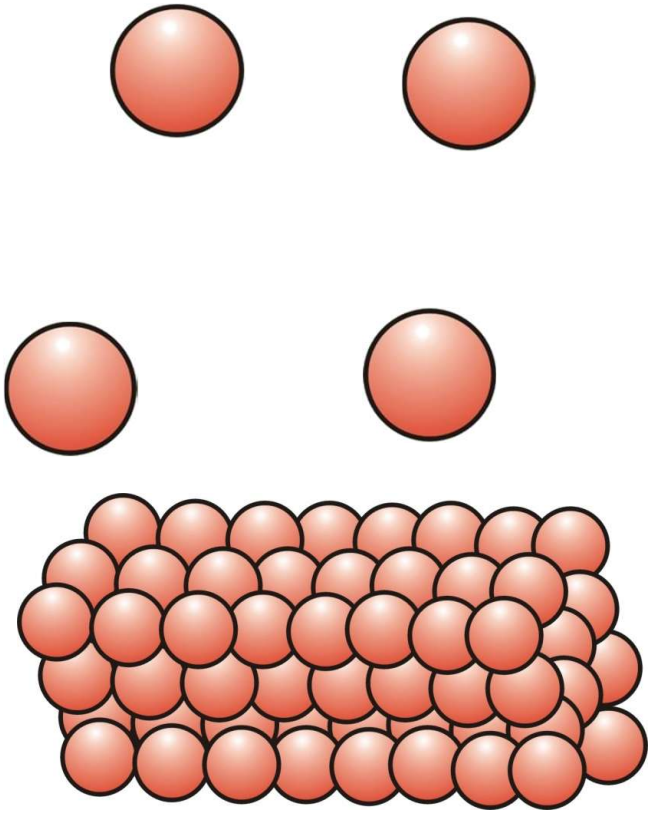
Aggregation / crystallization

We have seen that particles and surfaces can interact via many different physical interactions.

The subtle balance between these interactions determines whether the particles/surfaces will remain separated in solution.

When the interactions between particles favour the attraction of particles, they will tend to aggregate.

A crystal is an aggregate where the packing of the particles / molecules has a regular, repeating order.



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Scrambling an egg

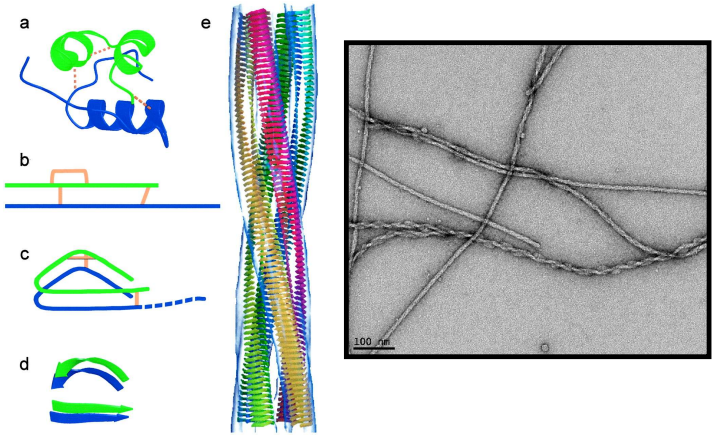
Questions about scrambling an egg

1. Why do I need to apply heat?
2. Why do we observe a long waiting time before aggregates start to form?
3. Why does aggregate form first on the edge of saucepan and end of spoon?
4. Why am I stirring?
5. Why once aggregates start to form is the rest of the process quite quick in comparison to the initial waiting time?

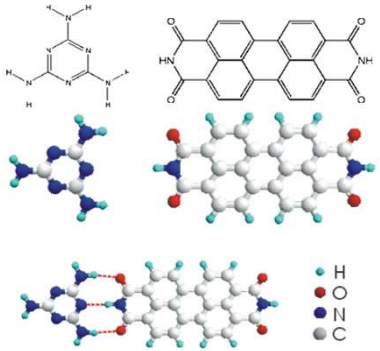
The shape of aggregates

The shape / dimensionality of an aggregate composed of many molecules will depend on the nature of the molecular interactions.

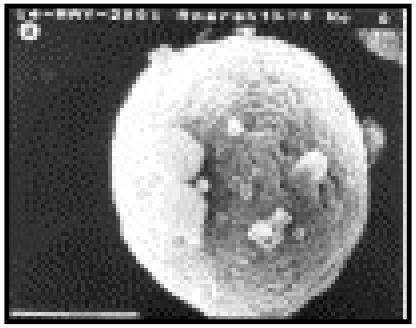
"Amyloid Fibrils"



Molecules on a surface



Spherical Starch aggregate



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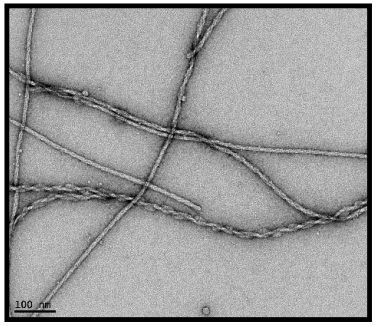
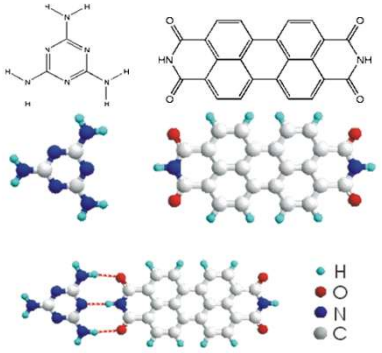
Why do aggregates form?

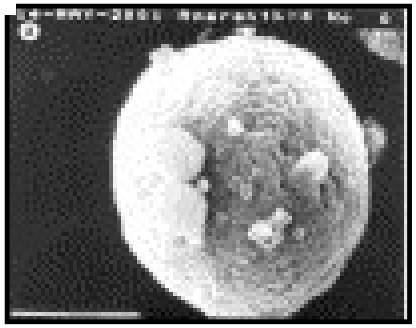
Aggregates will form when the change in free energy dU, upon addition of a molecule or particle is negative.

As we will see the chemical potential (μ) depends upon the shape of the aggregates and the number of particles in the aggregate (N)

$$\mu = \frac{dU}{dN}$$







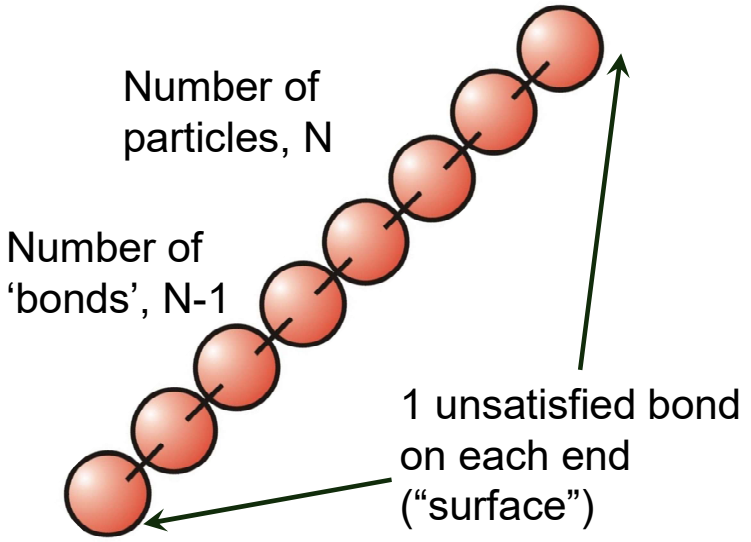
1 Dimensional aggregates (rods)

Consider a linear aggregate where all the N particles/molecules are joined together in a line.

$$\boldsymbol{U_{bulk}} = -N\mu_{Bulk}$$

Free energy change due to 2 bonds or a "bulk" atom

$$\boldsymbol{U_{surface}} = \gamma = \mu_{Bulk}$$



$$\boldsymbol{U_{tot}} = \boldsymbol{U_{bulk}} + \boldsymbol{U_{surface}}$$

$$\boldsymbol{U_{tot}} = -\mathrm{N}\mu_{Bulk} + \mu_{Bulk} = -(N-1)\mu_{Bulk}$$

$$\frac{dU}{dN} = -\mu_{Bulk}$$

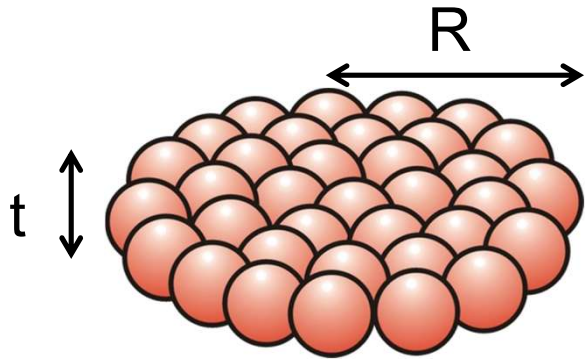
Always energetically favourable for aggregates to grow.

2D aggregation

The case of 2D aggregation is slightly more complicated.

As a disk-like aggregate grows the area of the surface on which the particles attach increases with radius of the disk. The production of this excess surface area has an energy penalty associated with it.

A consideration of the bulk and surface contributions of the energy per molecule gives



Number of particles, N

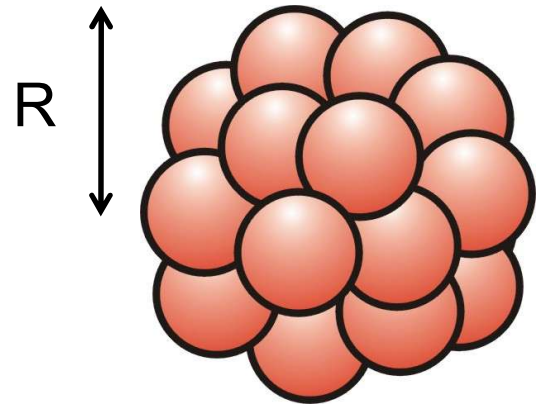
$$\frac{dU}{dN} = -\mu_{Bulk} + \frac{\gamma(\pi v t)^{1/2}}{N^{1/2}}$$

v is molecular/particle volume and γ is excess surface energy of unbonded particles around circumference

3D aggregation

Similarly for 3D aggregation we consider bulk and surface terms and we obtain:

$$\frac{dU}{dN} = -\mu_{Bulk} + \left(\frac{3v}{4\pi}\right)^{2/3} \frac{8\pi\gamma}{3N^{1/3}}$$



Number of particles, N

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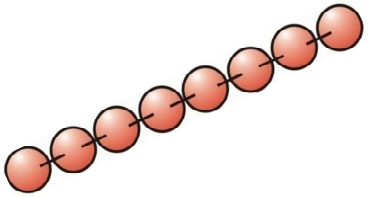
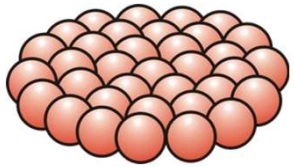
What happens as the aggregation number increases?

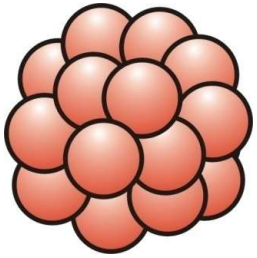
Rods $\frac{dU}{dN} = -\mu_{Bulk}$



Discs $\frac{dU}{dN} = -\mu_{Bulk} + \frac{(v\pi t)^{1/2}\gamma}{N^{1/2}}$



Spheres/droplets $\frac{dU}{dN} = -\mu_{Bulk} + \left(\frac{3v}{4\pi}\right)^{2/3} \frac{8\pi\gamma}{3N^{1/3}}$



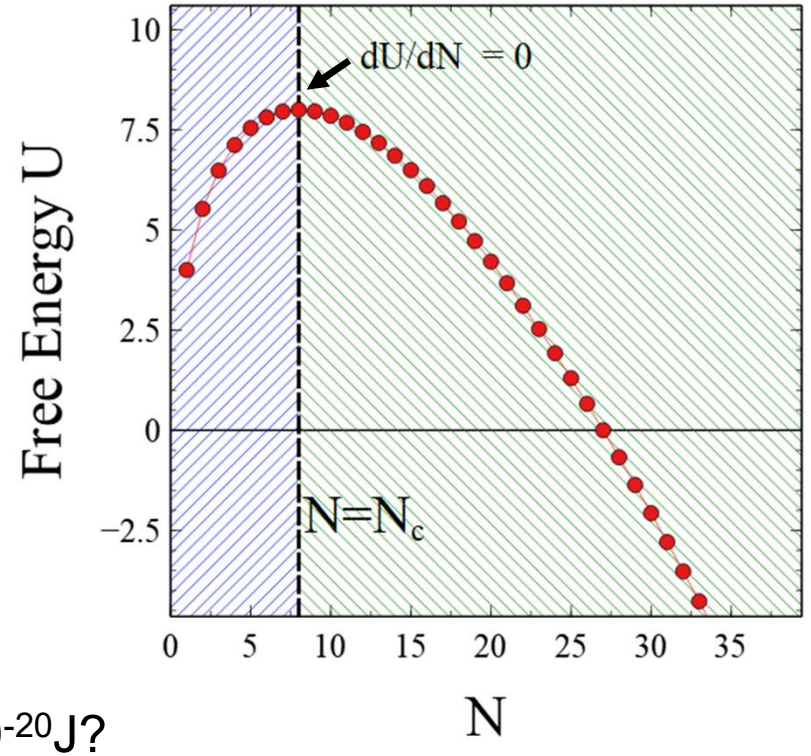
For 1D μ is always <0 → Aggregates will grow.

For 2 and 3D there is a critical value of N = Nc above which μ is < 0 but below which μ >0

15.2 Critical aggregate number

Find an expression for the critical aggregation number Nc of a 2D disc-like aggregate.

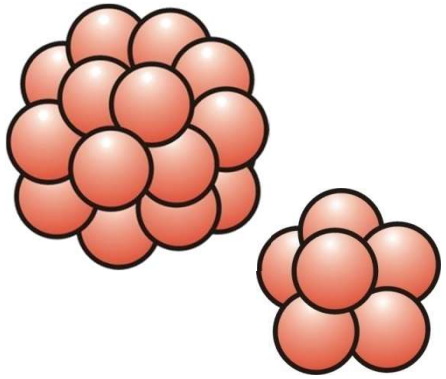
$$\frac{dU}{dN} = -\mu_{Bulk} + \frac{(v\pi t)^{1/2}\gamma}{N^{1/2}}$$



How many molecules does this critical aggregate contain if v=1nm^3,t=0.1nm, γ=50mJm^{-2} & μ_{Bulk}=10^{-20}J?

So how do aggregates start growing?

In order for it to be favourable for an aggregate to grow the free energy change must be negative, however we have seen that below N=Nc this is not the case. So how do 2 and 3D aggregates ever start growing?



Homogeneous nucleation: Fluctuations mean the probability of producing a stable nucleus by chance is:

$$P(N = Nc) \propto e^{-U_c/k_B T}$$

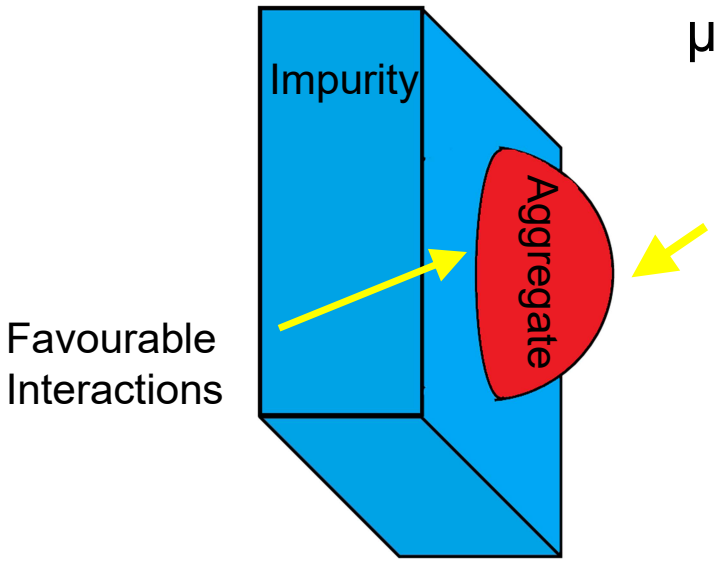
$$Uc = \mu_B N_C \qquad (2D)$$

$$Uc = \frac{\mu_B N_C}{2} \qquad (3D)$$

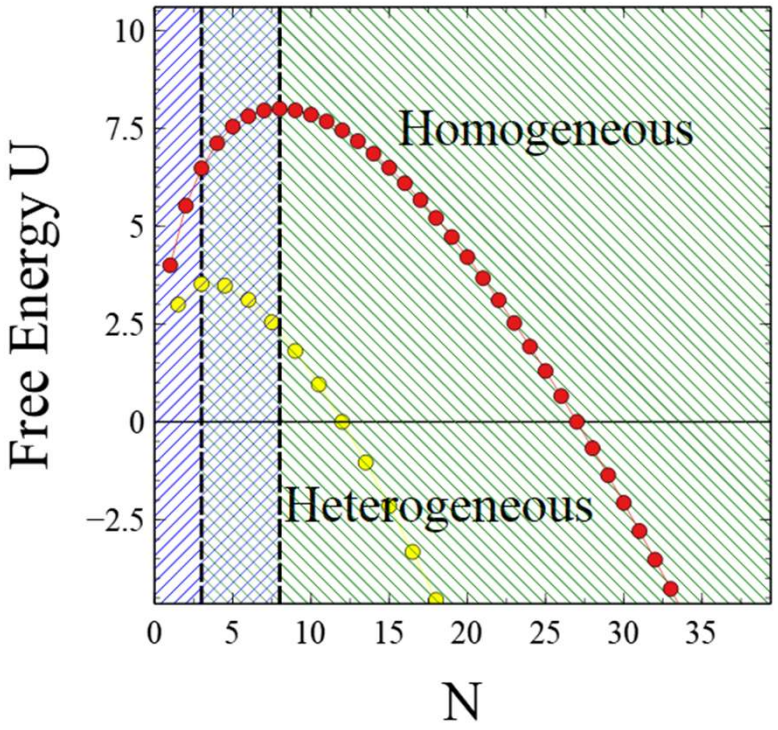
Heterogeneous nucleation

Heterogeneous nucleation: Impurities can act as nucleation sites, lowering the energy barrier Uc to nucleation.

$$U = U_{Bulk} + U_{surface}$$



$$\mu = -\mu_{bulk} + k\gamma/N^{1/3}$$



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