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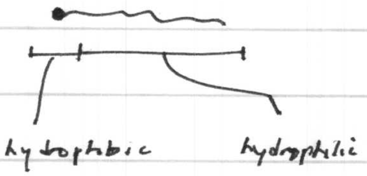
NM – self-assembly in solution

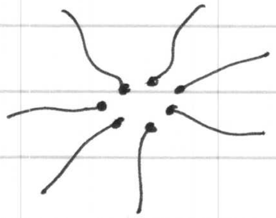
→ formation of aggregates ("micelles")

consider amphiphilic molecules (greek root = "both + friendship")

e.g.,



⇒ will aggregate in solution like



(in H_2O, hydrophobic ends → inward)

so let's consider a solution of amphiphiles, or generally any monomer

(monomer = one part in assembly of many parts)

define X_N = dimensionless molar fraction of components (monomers) in solution as the N^{th} aggregate, so the concentration of the N^{th} aggregate is

$$C_N = \frac{X_N}{N}$$

total molar fraction of monomers in solution:

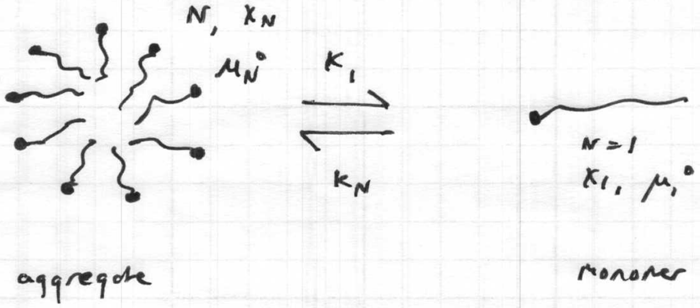
$$c = X_1 + X_2 + X_3 \dots X_N = \sum_{N=1}^{\infty} X_N$$

in solution, assume we have aggregates of 1, 2, .. N monomers each.

the chemical potential (cp) of all components must be equal,

$$\underbrace{\mu}_{\text{mean cp of an aggregation of 'state' } N} = \underbrace{\mu_N^\circ}_{\text{mean interaction energy per molecule in the aggregate}} + \frac{\overset{k_b}{kT}}{N}\ln\left(\frac{X_N}{N}\right) = \text{constant} = \underbrace{\mu_1^\circ + k_bT\ln(X_1)}_{N=1,\ \text{monomers.}}$$

we can derive this from the law of mass action between an aggregate of state N and monomers (state 1)



"reaction" $N \cdot X_1 \longrightarrow \left(\frac{X_N}{N}\right)$

equilibrium constant, $K = \frac{\overset{\text{association}}{k_a}}{\underset{\text{dissociation}}{k_d}} = \exp\left(\frac{-\Delta G}{k_bT}\right) = \exp\left(\frac{-N(\mu_N^\circ - \mu_1^\circ)}{k_bT}\right)$

rate of association $= \overset{X_1^N}{k_1} = k_a X_1^N$

rate of dissociation $= k_N \frac{X_N}{N} = k_d \frac{X_N}{N}$

* see "chemical equilibrium" on wikipedia

reaction rate constant

$nA + mB \rightarrow C + D$

$\frac{d[C]}{dt} = k(T)[A]^n[B]^m$ single-step reaction

$k(T) = Ae^{\underset{\Delta G/k_bT}{-E_a/RT}}$

in equilibrium, rates of association and dissociation must be equal

hence, $k_a X_1^N = k_d \frac{X_N}{N}$

$$\Longrightarrow K = \frac{k_a}{k_d} = \left(\frac{X_N}{N}\right)\frac{1}{X_1^N} = \exp\left(\frac{-N(\mu_N^\circ - \mu_1^\circ)}{k_bT}\right)$$

log of both sides : $\frac{X_N}{N} = X_1^N \exp\left(\frac{-N(\mu_N^\circ - \mu_1^\circ)}{k_bT}\right)$

$$\ln\left(\frac{X_N}{N}\right) = N\ln X_1 + \frac{-N(\mu_N^\circ - \mu_1^\circ)}{k_bT}$$

mistake as initially uploaded

$$\Longrightarrow \underline{\mu_N^\circ + \frac{\frac{1}{N}\ln\left(\frac{X_N}{N}\right)}{(k_bT)^{-1}} = \frac{\ln X_1}{(k_bT)^{-1}} + \mu_1^\circ}$$

same as stated earlier

relates chemical potentials in aggregation states.

generalize between states N and M.

$$\underbrace{\mu_N^\circ + \frac{\ln(X_N/N)}{M(k_bT)^{-1}}}_{\text{aggregation state } N} = \underbrace{\mu_M^\circ + \frac{\ln(X_M/M)}{M(k_bT)^{-1}}}_{\text{aggregation state } M}$$

solve for $X_N = f(X_M)$, relating state N to M.

$$X_N = N\left\{\left(\frac{X_M}{M}\right)\exp\left(M(\mu_M^\circ - \mu_N^\circ)/k_bT\right)\right\}^{N/M}$$

and if $M = 1$

$$X_N = N\left\{X_1 \exp\left((\mu_1^\circ - \mu_N^\circ)/k_bT\right)\right\}^N$$

this plus $C = \sum_1^\infty X_N$

completely defines the aggregation states of the system

using this model, can we tell

when will aggregates form?

when there is a difference in the cohesive energies of the monomers in their dispersed and aggregated states

if all experience the same interaction with their surroundings

↑ molecules in different sized aggregates

$$\mu_1^\circ = \mu_2^\circ \cdots = \mu_N^\circ$$

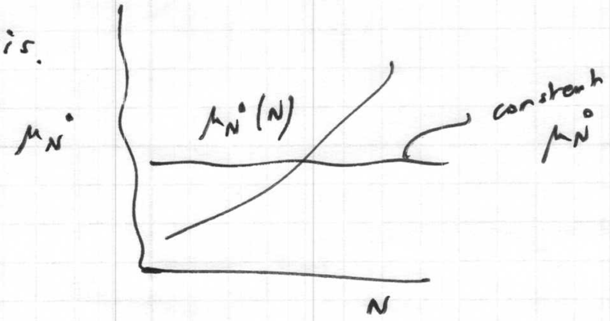
our previous result simplifies to $\underset{\sim\sim\sim\sim}{X_N = N X_1^N}$

since $X_1 < 1$, $X_N << X_1$ $\Rightarrow$ most molecules are monomers, $N = 1$ state

then for large stable aggregates, we need

(*) $\mu_N^\circ < \mu_1^\circ$ for some value of N

if $\mu_N^\circ(N)$ increases with N, vis.



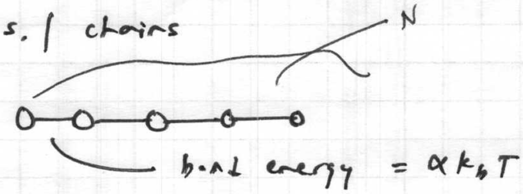
then $X_N <<< X_1$

aggregation is even less probable

$\Rightarrow X_N(N)$ is always a distribution function

let's see what it looks like for some key forms and shapes

(1) rods / chains

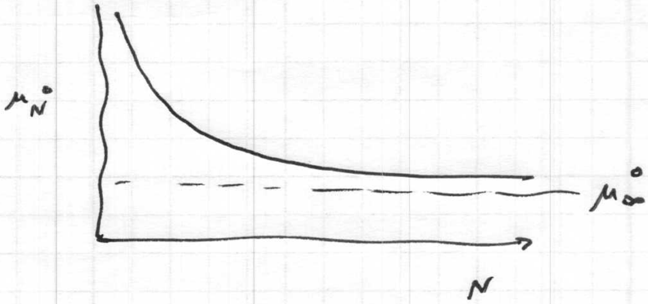


for a N-length chain, $N\mu_N^\circ = -(N-1)\alpha k_b T$

$$\mu_N^\circ = \underbrace{-\alpha k_b T}_{=\mu_\infty^\circ} + \frac{\alpha k_b T}{N}$$

relative state to free molecule w/o bond

$$\Rightarrow \mu_N^\circ = \mu_\infty^\circ + \frac{\alpha k_b T}{N}$$



(2) sheets, $N \propto \pi R^2$

\# of unbonded molecules (on edge) $\propto 2\pi R \propto N^{1/2}$

$$\underline{\Rightarrow \mu_N^\circ = \mu_\infty^\circ + \frac{\alpha k_B T}{N^{1/2}}}$$

(3) spheres, $N \propto R^3$

\# of unbonded molecules $\propto \pi R^2 \propto N^{2/3}$

$$\underline{\Rightarrow \mu_N^\circ = \mu_\infty^\circ + \frac{\alpha k_B T}{N^{2/3}}} \longrightarrow 1/3.$$

$\Big\{$ similar to what we saw for melting, nucleation and growth

example - free energy of a sphere

$N\mu_\infty^\circ + 4\pi R^2\gamma$, recall $N = \frac{4\pi R^3}{3a_v}$

$R = \left(\frac{3Na_v}{4\pi}\right)^{1/3}$

so $N\mu_N^\circ = N\mu_\infty^\circ + 4\pi R^2\gamma$

$$\mu_N^\circ = \mu_\infty^\circ + \frac{4\pi R^2\gamma}{N}$$

$$= \mu_\infty^\circ + 4\pi\gamma\cdot\left(\frac{3Na_v}{4\pi}\right)^{2/3}\cdot\frac{1}{N}$$

$$\boxed{= \mu_\infty^\circ + \frac{\alpha kT}{N^{1/3}}}, \quad \underline{\alpha = \frac{4\pi R^2\gamma}{kT}}$$

at what concentration will aggregates form?

if $\mu_N^\circ = \mu_\infty^\circ + \frac{\alpha k_B T}{N^p}$, p = dimensionality constant

$$X_N = N\left\{X_1 \exp\left(\mu_1^\circ - \mu_N^\circ / k_B T\right)\right\}^N$$

$$\frac{\mu_1^\circ - \mu_N^\circ}{k_B T} = \alpha\left(1 - \frac{1}{N^p}\right) \qquad (*)$$

$\Rightarrow$ relating X_1 to X_N as before, and substituting $(*)$ above,

$$X_N = N\left\{X_1 \exp\left(\alpha\left(1 - \frac{1}{N^p}\right)\right)\right\}^N \approx N\left(X_1 e^\alpha\right)^N$$

if $N^p \gg 1$

e.g. for spheres $X_N = \left[X_1 e^\alpha\right]^N e^{-\alpha N^{2/3}}$

at low X_1 concentrations such that

$X_1 e^\alpha \ll 1$, or more precisely $X_1 e^\alpha < N$

then $X_N < X_{N-1} \ldots < X_2 < \boxed{X_1}$ most molecules are monomers in solution.

and $X_1 \approx C$

when will this change? — well, we can't have

$$X_N > 1$$

we cannot have $X_N > 1$, or $X_1 > 1$ for that matter

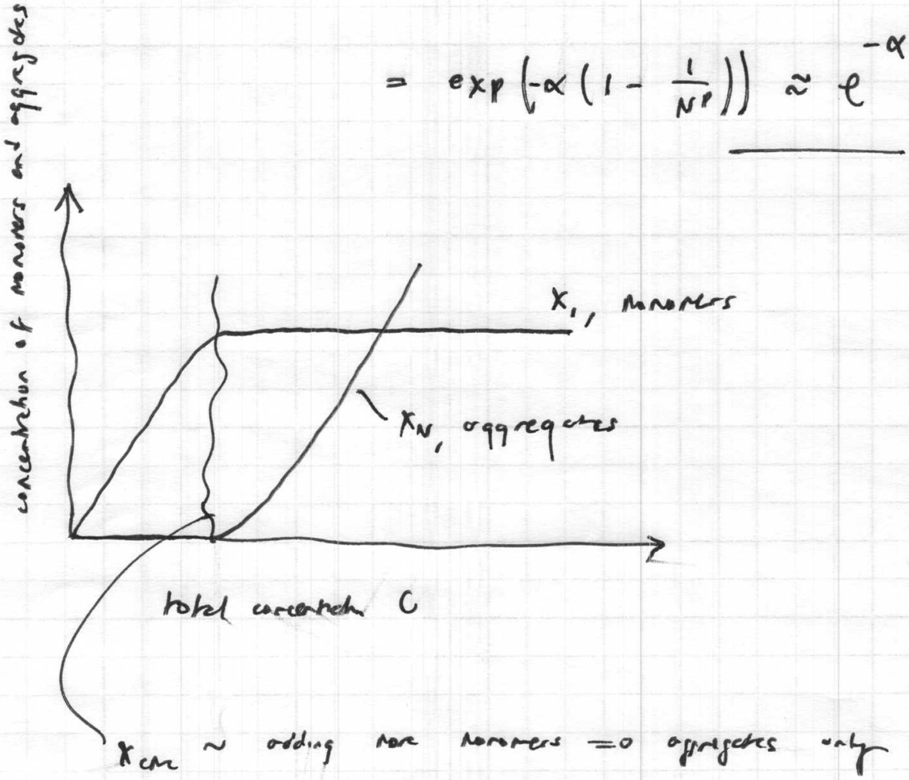
so, returning to X_N as $f(N)$

X_1 cannot exceed $\exp\left(\frac{-(\mu_1^\circ - \mu_N^\circ)}{k_bT}\right)$, else $X_N > 1$

therefore critical micelle concentration, X_{cmc}

$$X_{cmc} = \exp\left(\frac{-(\mu_1^\circ - \mu_N^\circ)}{k_bT}\right)$$

$$= \exp\left(-\alpha\left(1 - \frac{1}{N^p}\right)\right) \approx e^{-\alpha}$$



if spheres, recall $\mu_N^\circ - \mu_1^\circ = \frac{\alpha k_bT}{N^{1/3}} - \alpha k_bT$

$$\mu_1^\circ - \mu_N^\circ = \alpha k_bT\left(1 - \frac{1}{N^{1/3}}\right)$$

$$\mu_1^\circ - \mu_N^\circ = \alpha k_B T \left(1 - \frac{1}{N^{1/3}}\right)$$

$$\Rightarrow X_N = N\left\{X_1 \exp\left(\alpha\left(1 - \frac{1}{N^{1/3}}\right)\right)\right\}^N$$

$$X_N = N X_1^N \cdot e^{\alpha N} e^{-\alpha N^{2/3}}, \quad e^\alpha X_1 \approx 1 \Rightarrow X_N \approx N e^{-\alpha N^{2/3}}$$

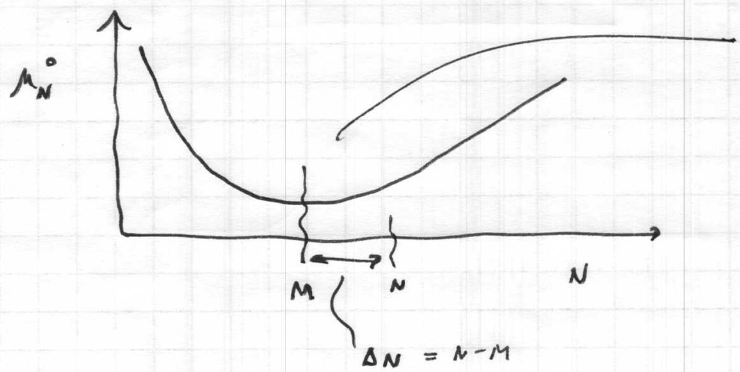
if $\alpha > 0$ then X_N decreases with N below cmc.

$\Rightarrow$ tends to an infinite aggregate in solution, which forms rapidly

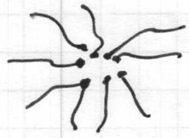
$\Rightarrow$ phase seperation, like oil and water, above the cmc.

however, some systems tend to a particular size distribution rather than simply phase seperating

now, what if



because an aggregate of certain size is stable,



or

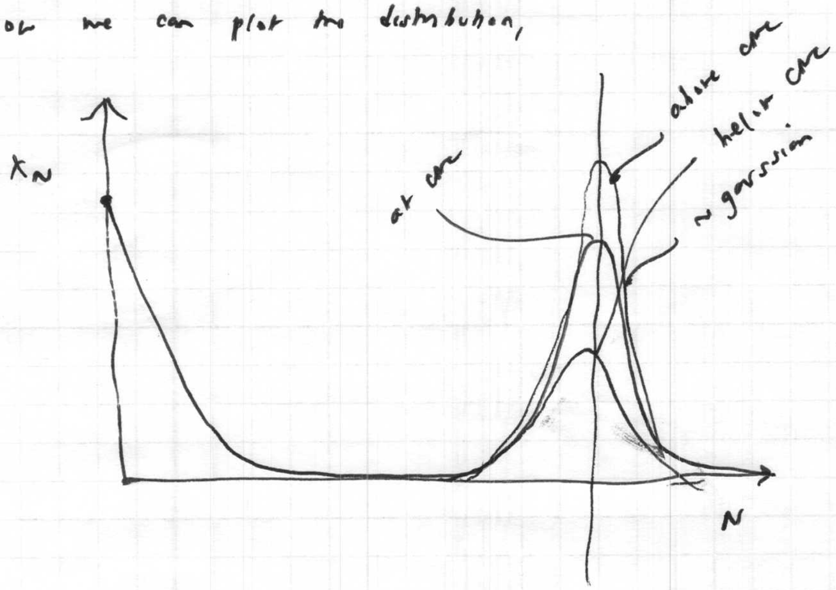
non-symmetric interactions

expand about M: $\mu_N^\circ - \mu_M^\circ = \Lambda(\Delta N)^2$
(parabolic form)

$$\Rightarrow X_N = N\left\{\frac{X_M}{M} \exp\left\{\frac{-M\Lambda(\Delta N)^2 k_B T}{1}\right\}\right\}^{N/M}$$

gaussian distribution is $\propto \exp\left(-\frac{(x-\bar{x})^2}{2\sigma^2}\right)$

now we can plot the distribution,



so using standard gaussian form, $\Delta N = x - \bar{x} = N - M$

$$2\sigma^2 = \frac{k_bT}{M\Lambda}$$

$$\Rightarrow \underline{\sigma = \sqrt{k_bT/2M\Lambda}}$$ ~ st dev of aggregation *

* More shape / curvature effects to be explored later.