Problem set 2 - soft matter

(5) 1 mM NaCl → $k^{-1} = 10\cdot10^{-9}$ m, $D = 20\cdot10^{-9}$ m, $A_{131} = 6.7\cdot10^{-20}$ J/m², $\psi_0 = 22\cdot10^{-3}$

a). $\Pi_A = -\frac{du}{dD}$; $u = -\frac{A}{12\pi D^2}$

so: $\Pi_A = -\frac{du}{dD} = +\frac{A}{12\pi}\cdot\frac{-2}{D^3} = -\frac{A_{131}}{6\pi D^3} = -\frac{6.7\cdot10^{-20}}{6\pi\cdot(20\cdot10^{-9})^3} = -444$ Pa.

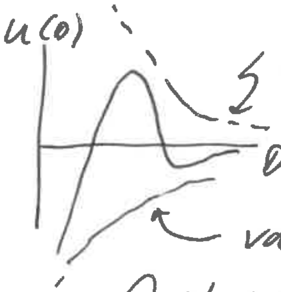
b). repulsive pressure → due to double layer repulsion:

$\Pi = \frac{2\sigma^2}{\varepsilon\varepsilon_0} e^{-kD}$ $\sigma = 1.5\cdot10^{-3}$ C/m² $\varepsilon = 78$ $\varepsilon_0 = 8.85\cdot10^{-12} \frac{C^2}{Nm^2}$

$\Pi_R = \frac{2\cdot(1.5\cdot10^{-3})^2}{78\cdot8.85\cdot10^{-12}} \exp\left(-\frac{20\cdot10^{-9}}{10\cdot10^{-9}}\right) = 882$ Pa

$\Pi_R \gtrsim \Pi_A$ → so double layer repulsion can indeed prevent sticking due to attractive vdWaals interactions.

c).



double layer repulsion $u(D) = \frac{2\sigma^2}{\varepsilon\varepsilon_0 k} e^{-kD}$

vdWaals attraction $u(D) = \frac{-A}{12\pi D^2}$ (plate-plate expressions).

@ short D: algebraic ~~ded~~decay $\underset{\text{vdW}}{\downarrow}$ wins over exponential dependence $\underset{\text{double layer}}{\downarrow}$

d).

- increasing salt conc: → decreases Debye length ($k^{-1} \sim \frac{1}{\sqrt{n_0}}$) and therefore reduces strength and range of double layer repulsion.

$u(D) = \frac{2\sigma^2}{\varepsilon\varepsilon_0 k} e^{-kD}$ → may lead to aggregation.

- divalent electrolyte
  ↳ see above, same as increasing salt conc.

- adding methanol: change of ε ($\varepsilon_{MeOH} = 32$ cf $\varepsilon_{water} = 78$)
  → decrease of ε changes strength double layer repulsion, and also ~~na~~ $k^{-1} \sim \sqrt{\varepsilon}$: so k^{-1} decrease → aggregation

- pH reduction: decreases surface charge as pH → isoelectric point: aggregation.

(6) $m\frac{dv}{dt} = F - \xi v + f(t)$

a). Continuous random collisions of solvent molecules with colloidal particle gives rise to random Brownian motion (as the momenta of all collisions will never be balanced).
→ this leads to randomly fluctuating force $f(t)$.
However, averaged over long times this random force is zero $\langle f(t) \rangle = 0$

b). $F = -\frac{d\mu}{dx}$ & $\mu = \mu^{\ominus} + k_BT \ln \frac{c}{c^{\ominus}}$

$$F = -\frac{d}{dx}\left(\mu^{\ominus} + k_BT \ln \frac{c}{c^{\ominus}}\right) = \cancel{-\frac{d\mu^{\ominus}}{dx}}^{\,0} - kT\frac{d\ln c}{dx} + kT \cancel{\frac{d\ln c^{\ominus}}{dx}}^{\,0}$$

$$F = -kT\frac{d\ln c}{dx} = -k_BT\frac{1}{c}\frac{dc}{dx}.$$

Langevin @ "long-time" steady-state: $m\cancel{\frac{dv}{dt}}^{\,0 \text{ (no acceleration; } v = \text{cst)}} = F - \xi\langle v\rangle + \cancel{\langle f(t)\rangle}^{\,0}$

$$\therefore\ 0 = F - \xi\langle v\rangle \rightarrow \langle v\rangle = \frac{F}{\xi} = -\frac{k_BT}{\xi c}\frac{dc}{dx}.$$

c). $[J] = \frac{mol}{m^2 s} = ? \times \langle v\rangle = ? \cdot \frac{m}{s}$ → so unit $[?] = \frac{mol}{m^3}$ → c!

$$\therefore J = c\cdot\langle v\rangle = -\frac{k_BT}{\xi}\frac{dc}{dx}$$

Fick's 1st law: $J = -D\frac{dc}{dx}$

$$\left.\begin{aligned} J &= -\frac{k_BT}{\xi}\frac{dc}{dx} \\ J &= -D\frac{dc}{dx}\end{aligned}\right\}\ -\frac{k_BT}{\xi}\frac{dc}{dx} = -D\frac{dc}{dx}$$

$$\Rightarrow D = \frac{k_BT}{\xi}.$$

d). $\langle r^2\rangle = 6Dt = \frac{\cancel{6}kT}{\cancel{6}\pi\eta R}\cdot t$

diffuse distance ~ diameter: $\underset{\uparrow t = t_B}{\langle r^2\rangle = (2R)^2}$ $\Bigg\}$ $\cancel{t_B}$ $(2R)^2 = \frac{kT}{\pi\eta R}\cdot t_B$

$$t_B = \frac{4R^2\cdot\pi\eta R}{k_BT} = \frac{4\pi\eta R^3}{k_BT} = \frac{4\cdot\pi\cdot 0.89\cdot 10^{-3}\cdot(1\cdot 10^{-6})^3}{1.38\cdot 10^{-23}\cdot 298} = 2.7\ s.$$

$t_B \sim R^3 \rightarrow$ 80 particle 10x larger $t_B \sim 3000$ s.

e). 1st: find mean distance between N particles in volume V:

$$r_m = \left(\frac{V}{N}\right)^{1/3} = \left(\frac{1}{\rho}\right)^{1/3} \underset{\uparrow \phi = \rho V_p}{=} \left(\frac{V_p}{\phi}\right)^{1/3}$$

$\Rightarrow \langle r^2\rangle = 6D\cdot t \quad \rightarrow$ set $\langle r^2\rangle = r_m^2$ at $t = \tau$

$$r_m^2 = 6D\cdot\tau \quad\longrightarrow\quad \left(\frac{V_p}{\phi}\right)^{2/3} = 6\cdot D\cdot\tau \quad\rightarrow \tau\sim\phi^{-2/3}.$$

$\phi = 0.3$

$D = \frac{kT}{6\pi\eta R}$

$$\tau = \frac{1}{6D}\cdot\left(\frac{V_p}{\phi}\right)^{2/3} = \frac{\cancel{6}\pi\eta R}{\cancel{6}kT}\cdot\left(\frac{4}{3}\pi R^3\right)^{2/3}\phi^{-2/3}$$

$$\tau = \frac{\pi\eta R^3}{kT}\left(\frac{4\pi}{3}\right)^{2/3}\cdot\phi^{-2/3}$$

$$= \frac{\pi\cdot 0.89\cdot 10^{-3}\cdot(1\cdot 10^{-6})^3}{1.38\cdot 10^{-22}\cdot 298}\left(\frac{4\pi}{3}\right)^{2/3}\cdot(0.3)^{-2/3}$$

$$= 3.9\ s.$$

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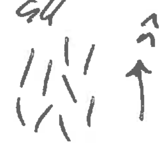
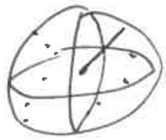
a). • Isotropic phase: both positions & orientations of the ~~rod~~ rods are "liquid-like", i.e. disordered.

• nematic phase: positions of the rods are still liquid-like, but the orientations are not → they roughly all orient in the same direction:



b). $S = k \ln \Omega \rightarrow \Delta S = S_N - S_I = k_B \ln \frac{\Omega_N}{\Omega_I}$

Isotropic phase:  $\Omega_I \sim 4\pi$ Nematic:  $\Omega_N \sim 1$

$$\Rightarrow \Delta S \simeq k_B \ln \frac{1}{4\pi} \simeq -k_B \ln 4\pi \underset{\substack{\uparrow \\ \text{roughly.}}}{\sim} -k_B \quad \text{(entropy loss)}$$

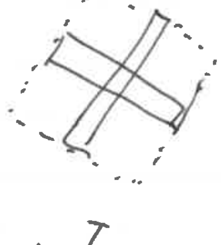
c). $\left.\begin{array}{l} N d\mu = -S dT \rightarrow \frac{S}{N} = -\frac{d\mu}{dT} \\ \mu = \mu_0 - kT \ln \frac{V_i}{V} \end{array}\right\} \frac{S_{excl}}{N} = -\frac{d}{dT}\left(\mu_0 - kT \ln \frac{V_i}{V}\right)$

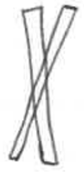
$$\Rightarrow \frac{S_{excl}}{N} = k_B \ln \frac{V_i}{V} = k_B \ln \left(\frac{V - V_{excl}}{V}\right) = k_B \ln \left(1 - \frac{V_{excl}}{V}\right)$$

as $V \gg V_{excl}$: Taylor-expansion of $\ln(1-x) \simeq -x$

$$\Rightarrow \frac{S_{excl}}{N} \simeq -k_B \ln \frac{V_{excl}}{V}.$$

d). isotropic phase: nematic phase:





$V_{excl}^{I} \sim L^2 D \quad \underset{\substack{\uparrow \\ L \gg D!}}{\gg} \quad V_{excl}^{N} \sim D^2 L$

$(V_{excl}^{I} \gg V_{excl}^{N})$.

e). $\frac{\Delta S_{excl}}{N} = \frac{S^{N}_{excl}}{N} - \frac{S^{I}_{excl}}{N} = -k_B \frac{V^{N}_{excl}}{V} + k_B \frac{V^{I}_{excl}}{V}$

$$= \cancel{\frac{k_B}{V}\left(\frac{V^{I}_{excl}}{V}\right)} = \frac{k_B}{V}\left(V^{I}_{excl} - V^{N}_{excl}\right) \approx \frac{k_B V^{I}_{excl}}{V}$$

$V^{I}_{excl} \gg V^{N}_{excl}$ (see d).

$\Rightarrow \Delta S_{excl} = k_B \frac{N}{V} \cdot L^2 D = k_B \rho L^2 D.$ (entropy gain).

f). I-N transition: $\Delta S_{or} + \Delta S_{excl} = 0$ at the transition! (ρ^*)

$$-k_B + k_B \rho^* L^2 D = 0$$

$$\Rightarrow \rho^* L^2 D = 1 \longrightarrow \rho^* = \frac{1}{L^2 D}$$

$\Rightarrow$ in volume fraction: $\phi^* = \rho^* V_p = \rho^* \cdot D^2 \cdot L$

$$= \frac{1}{L^2 D} \cdot D^2 \cdot L$$

$$\phi^* = \frac{D}{L}.$$

e.g. $\frac{L}{D} = 10 \rightarrow \phi^* = 0.10$ (only 10% of total volume needs to be occupied by rods for the nematic phase to form).

$\rightarrow$ this goes further down as $\frac{L}{D}$ becomes larger (so longer & thinner rods).

8 $$m\frac{d^2x}{dt^2} = F - \xi\frac{dx}{dt} + f(t)$$

a). * $$\underbrace{mx\frac{d^2x}{dt^2}}_{A} = Fx - \xi\underbrace{x\frac{dx}{dt}}_{B} + xf(t)$$

A: $$\frac{d^2x^2}{dt^2} = \frac{d}{dt}\left(\frac{dx^2}{dt}\right) \overset{*}{=} \frac{d}{dt}\left(2x\frac{dx}{dt}\right) = 2\left[x\frac{d^2x}{dt^2} + \left(\frac{dx}{dt}\right)^2\right].$$

$$\therefore\ x\frac{d^2x}{dt^2} = \frac{1}{2}\frac{d^2x^2}{dt^2} - \left(\frac{dx}{dt}\right)^2$$

B: $$x\frac{dx}{dt} \overset{*}{=} \frac{1}{2}\frac{dx^2}{dt}$$ *(as $\frac{dx^2}{dx} = 2x \rightarrow \frac{1}{2}\frac{dx^2}{dx} = x \rightarrow 2x\,dx = dx^2$)

$\therefore$ ~~sub~~ sub in A & B in Langevin Eq:

$$\Rightarrow m\left[\frac{1}{2}\frac{d^2x^2}{dt^2} - \left(\frac{dx}{dt}\right)^2\right] = Fx - \xi\frac{1}{2}\frac{dx^2}{dt} + xf(t)$$

$$\frac{m}{2}\frac{d^2x^2}{dt^2} - m\left(\frac{dx}{dt}\right)^2 = Fx - \frac{\xi}{2}\frac{dx^2}{dt} + xf(t)$$ as required.

b). i: $F=0$ ii: $\langle\ \rangle$ & iii: $m\langle(\frac{dx}{dt})^2\rangle = k_BT$ (in 10).

$$\Rightarrow \frac{m}{2}\left\langle\frac{d^2x^2}{dt^2}\right\rangle - \underbrace{m\left\langle\left(\frac{dx}{dt}\right)^2\right\rangle}_{k_BT} = \cancelto{0}{\langle Fx\rangle} - \frac{\xi}{2}\left\langle\frac{dx^2}{dt}\right\rangle + \cancelto{0}{\langle xf(t)\rangle}$$

$$\langle x\rangle\cancelto{0}{\langle f(t)\rangle}$$

$$\therefore\ \frac{m}{2}\left\langle\frac{d^2x^2}{dt^2}\right\rangle - k_BT = -\frac{\xi}{2}\left\langle\frac{dx^2}{dt}\right\rangle$$

c). $z = \left\langle\frac{dx^2}{dt}\right\rangle$ & $\left\langle\frac{d^2x^2}{dt^2}\right\rangle = \frac{d}{dt}\left\langle\frac{dx^2}{dt}\right\rangle = \frac{dz}{dt}$

$$\Rightarrow \frac{m}{2}\frac{dz}{dt} + \frac{\xi}{2}z = k_BT$$ p.T.O.

$$\frac{dz}{dt} + \frac{\xi}{m} z = \frac{2k_BT}{m} \xrightarrow{\cdot -\frac{m}{\xi}} -\frac{m}{\xi}\frac{dz}{dt} = z - \frac{2kT}{\xi}$$

$$\Rightarrow \frac{dz}{\left(z - \frac{2kT}{\xi}\right)} = -\frac{\xi}{m} dt \quad \rightarrow \text{integrate}$$

$$\int \frac{dz}{\left(z - \frac{2kT}{\xi}\right)} = \int -\frac{\xi}{m} dt \rightarrow \ln\left(z - \frac{2kT}{\xi}\right) = -\frac{\xi}{m} t + \overset{\substack{\text{constant}\\ \downarrow}}{C}$$

$$\Rightarrow z = \frac{2kT}{\xi} + \exp\left(-\frac{\xi}{m}t\right)\cdot A \qquad \left(\overset{\text{constant}}{A} = \exp(C)\right)$$

d). $t \gg m/\xi \rightarrow \exp\left(-\frac{\xi}{m}\cdot t\right) \rightarrow 0$

$$z = \left\langle \frac{dx^2}{dt} \right\rangle = \frac{d}{dt}\langle x^2 \rangle \quad \Rightarrow \frac{d}{dt}\langle x^2 \rangle = \frac{2kT}{\xi}$$

$$\int_{\langle x^2(0)\rangle = 0}^{\langle x^2(t)\rangle} d\langle x^2 \rangle = \frac{2k_BT}{\xi}\int_0^t dt$$

$$\Rightarrow \langle x^2 \rangle = \frac{2k_BT}{\xi} t = 2Dt \quad \text{(in 1D)}.$$