

Soft Matter

①

$$u(D) = - \frac{A_{132} R}{6D}$$

vdw mls.

a). vdw interaction originates from $u \sim -\frac{c}{r^6}$ interactions between the molecules & then by pairwise addition of all these molecular interactions, the 'vdw interaction between macroscopic bodies arises.

A_{132} means, the Hamaker constant for a body of material 1 interacting with a body of material 2, immersed in medium 3. A_{132} may be < 0 or > 0 .
determines sign of u

b). $A_{132} = 1.19 \cdot 10^{-20} \text{ J}$, $D = 0.1 \mu\text{m}$ $R = 1 \cdot 10^{-6} \text{ m}$.

$$u(D = 0.1 \cdot 10^{-6}) = - \frac{1.19 \cdot 10^{-20} \cdot 10^{-6}}{6 \cdot 0.1 \cdot 10^{-6}} = -2.0 \cdot 10^{-20} \text{ J}$$

$u_{\text{air}} \approx 4.1 \cdot 10^{-21} \text{ J}$, so attraction much stronger \rightarrow sticky.

$$F = - \frac{du}{dD} = - \frac{d}{dD} \left(- \frac{A_{132} R}{6D} \right) = \frac{A_{132} R}{6} \frac{d}{dD} (D^{-1}) = - \frac{A_{132} R}{6D^2}$$

$$F = - \frac{1.19 \cdot 10^{-20} \cdot 10^{-6}}{6 \cdot (0.1 \cdot 10^{-6})^2} = -2.0 \cdot 10^{-13} \text{ N} \quad (\text{smaller than } pN).$$

c). $A_{132} \rightarrow A_{131} \Rightarrow A_{131} = A_{11} + A_{33} - A_{13} - A_{13}$
 $= A_{11} + A_{33} - 2A_{13}$
 $= A_{11} + A_{33} - 2\sqrt{A_{11} A_{33}}$

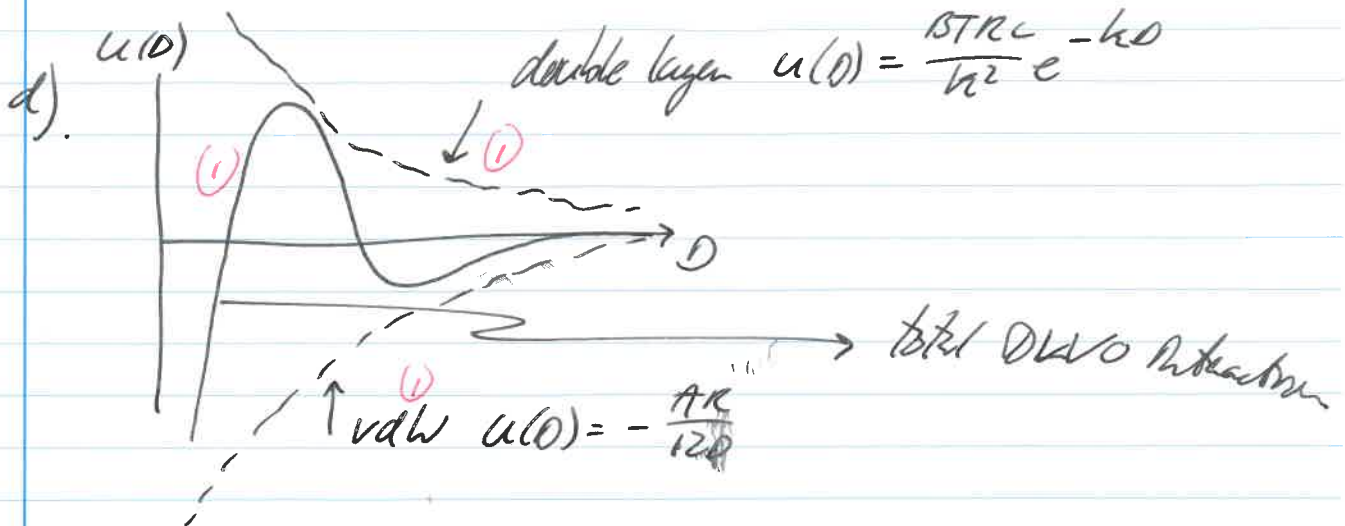
$$\Rightarrow A_{131} = \left(\sqrt{A_{11}} - \sqrt{A_{33}} \right)^2 \quad (= A_{11} + A_{33} - 2\sqrt{A_{11} A_{33}})$$

> 0

as $A_{131} > 0$, $u(D) < 0$ $(u(D) = - \frac{A_{131} R}{6D})$

So the vdw interactions for like objects (in a medium) is always attractive.

$$u(D) = \frac{BTRC}{k^2} e^{-kD} - \frac{AR}{12D}$$



- increasing the salt concentration leads to a reduction of the double layer separation, as $k^{-1} \sim \frac{1}{\sqrt{c_{\text{salt}}}}$. $c \uparrow \rightarrow k^{-1} \downarrow$
- so, both the range (via e^{-kD}) decreases (1) → $k \uparrow$ and the "amplitude" (via $\frac{1}{k^2}$) decrease,
- and the barrier for stabilization of particles ~~is~~ reduces, which may lead to aggregation.

e) $u(D) = \frac{BTRC_0}{k^2} e^{-kD} - \frac{AR}{12D} = 0 \rightarrow \boxed{\frac{AR}{12D} = \frac{BTRC_0}{k^2} e^{-kD}}$

$$F(D) = -\frac{du}{dD} = \frac{BTRC_0}{k^2} e^{-kD} \cdot +k - \frac{AR}{12D^2} = 0$$

Subst: $\frac{BTRC_0}{k^2} e^{-kD} - \frac{1}{D} \cdot \left(\frac{BTRC_0}{k^2} e^{-kD} \right) = 0$

$$\frac{BTRC_0}{k^2} e^{-kD} \left(k - \frac{1}{D} \right) = 0 \rightarrow k - \frac{1}{D} = 0 \rightarrow kD = 1$$

$$\Rightarrow D = \frac{1}{k} = k^{-1} \text{ (2)}$$

this makes sense as k^{-1} is the "thickness" of double layer; @ k^{-1} the charges are screened, which may lead to aggregation. (1)
 & beyond

Soft Matter Sample Exam – Answers

Problem 2

- a) In a mixture of colloids with nonadsorbing polymers, the polymers cannot get closer with their center of mass to the surface of the colloids than the polymer radius. This creates a depletion zone around the colloids from which polymers are absent (depleted). If two depletion zones overlap, the osmotic pressure from polymers surrounding the colloids is no longer balanced and the colloids are pushed together. The overlap volume is the volume of the overlapping depletion zones. The depletion energy is directly proportional to the overlap volume (and the osmotic pressure).
- b) Maximum overlap volume for $h = 0$.

$$V_{\text{ov}} = \frac{\pi}{6} (2R_p)^2 (3a + 2R_p)$$

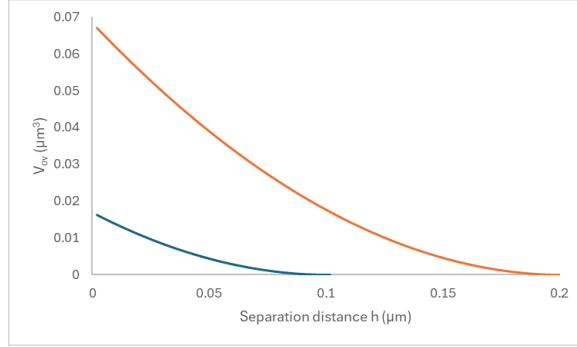
For $R_p = 50$ nm, $V_{\text{ov}} = 0.00838 \mu\text{m}^3$

For $R_p = 100$ nm, $V_{\text{ov}} = 0.0356 \mu\text{m}^3$

The range of the depletion interaction is $2R_p$ (from $V_{\text{ov}} = 0$ at $h = 2R_p$, to maximum overlap volume at $h = 0$).

For $R_p = 50$ nm, range is 100 nm

For $R_p = 100$ nm, range is 200 nm



- c) Per monomer: $F_{\text{int}} = k_B T b^3 n = k_B T b^3 \frac{N}{R^3}$ Per chain: $F_{\text{int}} = k_B T b^3 \frac{N^2}{R^3}$ Stretching free energy: $F_{\text{ent}} = k_B T \frac{R^2}{N b^2}$ Sum: $F = F_{\text{int}} + F_{\text{ent}}$ Equilibrium size of polymer chain: $R = R_F$ if $\frac{\partial F}{\partial R} = 0$.

$$\frac{\partial F}{\partial R} = -3k_B T b^3 N^2 \frac{1}{R^4} + 2k_B T \frac{R}{N b^2} = 0$$

$$3k_B T b^3 N^2 \frac{1}{R_F^4} = 2k_B T \frac{R_F}{N b^2}$$

$$R_F^5 \approx b^5 N^3 \quad R_F \approx b N^{3/5}$$

- d) The overlap volume fraction is given by the volume of all monomers (Nb^3) divided by the volume of the entire chain ($4/3\pi R_F^3$):

$$\phi^* = \frac{Nb^3}{(4/3)\pi R_F^3} = \frac{3Nb^3}{4\pi b^3 N^{9/5}} = \frac{3}{4\pi} N^{-4/5} \sim N^{1-3\nu}$$

The expression for the osmotic pressure used in the question is that of an ideal solution (ideal gas law), in which particles do not interact. This is only valid far below the overlap concentration, because polymer chains strongly interact above the overlap concentration.

- e) The colloids are stabilized by charges; counterion osmotic pressure keeps them apart. Strong enough depletion attraction can cause the colloids to aggregate. The polymers in a good solvent have larger (swollen) size and therefore a larger overlap volume than the polymers in a theta solvent. Therefore, the depletion energy (attractive potential at zero separation) is also larger for polymers in a good solvent. In addition, the range of the depletion interaction is equal to the polymer size. For polymers in a good solvent, the colloids will be attracted already at larger separations. This could result in a net abolishing of the charge stabilization by polymers in a good solvent, but still weak stabilization by polymers in theta solvent. (Drawing of the interaction potential could help!)

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a). Brownian motion is caused by the continuous bombardment of the colloidal particles by the solvent molecules. As these collisions are random & more balanced, this gives rise to Brownian motion via this random fluctuating random force $f(t)$.
 $\langle f(t) \rangle = 0$
 \rightarrow as $f(t)$ is random, this force averaged over long time is zero.

b) i) $\mu(x) = \mu^0 + kT \ln \frac{c}{c^0}$

$F = - \frac{d\mu(x)}{dx} = - \frac{2}{2x} (\mu^0 + kT \ln \frac{c}{c^0}) = \frac{2\mu^0}{2x} + kT \frac{2 \ln c}{2x} - kT \frac{2 \ln c^0}{2x}$
 $= -kT \frac{2 \ln c}{2x}$

from Langevin: $m \frac{dv(t)}{dt} = F - \zeta v(t) + f(t)$

Steady-state $\rightarrow v(t) = \langle v \rangle$ [$\langle v \rangle$ depends on x , depends on μ of $c(x)$]

$\frac{dv(t)}{dt}$ no acceleration & $\langle f(t) \rangle = 0$

$\therefore 0 = F - \zeta \langle v \rangle \rightarrow \langle v \rangle = \frac{F}{\zeta} = \frac{-kT}{\zeta} \frac{d \ln c}{dx}$

$\therefore \langle v \rangle = - \frac{kT}{\zeta c} \frac{dc}{dx}$

ii) $J = c \langle v \rangle = - \frac{kT}{\zeta} \frac{dc}{dx} = -D \frac{dc}{dx}$

\Rightarrow cancel $\frac{dc}{dx} \rightarrow D = \frac{kT}{\zeta}$

c) $r_m = \left(\frac{V_p}{\phi}\right)^{1/3}$ $\langle v^2 \rangle = 6Dt$ $D = \frac{kT}{\zeta}$

set $\langle v^2 \rangle = \langle v_m^2 \rangle = \left(\frac{V_p}{\phi}\right)^{2/3} = 6Dt_m = 6 \frac{kT}{\zeta} t_m$

$\Rightarrow t_m = \frac{1}{6D} \left(\frac{V_p}{\phi}\right)^{2/3} \Rightarrow t_m \sim \phi^{-2/3}$

$t_m = \frac{6\pi\eta R}{6kT} \cdot \left(\frac{4}{3}\pi R^3\right)^{2/3} \cdot \phi^{-2/3} =$
 $\phi = 0.3$
 $R = 10^{-6} \text{ m}$
 $\eta = 0.89 \cdot 10^{-3}$
 $= \frac{\pi\eta R^3}{kT} \left(\frac{4}{3}\pi\right)^{2/3} \cdot \phi^{-2/3} = \frac{\pi \cdot 0.89 \cdot 10^{-3} \cdot (10^{-6})^3}{1.38 \cdot 10^{-23} \cdot 298} \cdot \left(\frac{4}{3}\pi\right)^{2/3} \cdot 0.3^{-2/3}$
 $= 3.94 \text{ s}$

d) $\tau \ll \tau_m$: particles will not really encounter any other particles at these time scales, so $D(\phi)$ will be comparable/similar to single particle D :

$$D(\phi) = D. \quad (1)$$

$\tau \gg \tau_m$: particles will be encountering many other particles at the longer time scales (relative to τ_m), they will effectively be moving in a sea of other particles \rightarrow much slower.

$$D(\phi) \ll D. \quad (1)$$

e) $\langle x(t') x(t) \rangle = \frac{k_B T}{\zeta} e^{-\Delta t / \tau}$

$$\text{MSD} = \langle (x(t') - x(t))^2 \rangle = \langle x^2(t') \rangle + \langle x^2(t) \rangle - 2 \langle x(t') x(t) \rangle \quad (1)$$

$$\langle x^2(t') \rangle = \langle x^2(t) \rangle = \frac{k_B T}{\zeta} \quad (\text{doesn't matter which time it is.})$$

$$\text{MSD} = \frac{k_B T}{\zeta} + \frac{k_B T}{\zeta} - 2 \cdot \frac{k_B T}{\zeta} e^{-\Delta t / \tau} =$$

$$= \frac{2k_B T}{\zeta} (1 - e^{-\Delta t / \tau}) \quad (1)$$

(i). for $\Delta t \gg \tau$: $\text{MSD} = \frac{2k_B T}{\zeta}$ as $e^{-\Delta t / \tau} \rightarrow 0$.

so MSD plateaus @ long times and from plateau value $\rightarrow k_B T$. (1)



(for $\Delta t \ll \tau$ $e^{-\Delta t / \tau} \approx 1 - \frac{\Delta t}{\tau}$ &)

$$\text{MSD} = \frac{2k_B T}{\zeta} \left(1 - \left(1 - \frac{\Delta t}{\tau} \right) \right) = \frac{2k_B T \cdot \Delta t}{\zeta \cdot \tau} \quad \left(\tau = \frac{\zeta}{k} \right)$$

$$= \frac{2k_B T \cdot \Delta t}{\zeta} = \frac{2k_B T}{\zeta} \cdot \Delta t \Rightarrow \text{MSD} = 2D \cdot t$$

diffusion

Problem 4

- a) A heterogeneous surface (different wettabilities, because of different surface energy or different roughness)
- b) Laplace pressure top: $\Delta p_L = \frac{2\gamma \cos \theta_1}{R}$ Laplace pressure bottom: $\Delta p_L = \frac{2\gamma \cos \theta_2}{R}$ Hydrostatic pressure difference: $\Delta p_h = \rho g h$ Stable if:

$$\frac{2\gamma \cos \theta_1}{R} > \frac{2\gamma \cos \theta_2}{R} + \rho g h$$

$$\cos \theta_1 - \cos \theta_2 > \frac{\rho g h R}{2\gamma}$$

- c) The surface energy change per unit length upon a small movement dx of the contact line:

$$dU/L = -r\gamma_{SV}dx + r\gamma_{SL}dx + \gamma_{LV} \cos \theta^* dx$$

$$dU/dx = 0$$

$$r\gamma_{SV} - r\gamma_{SL} = \gamma_{LV} \cos \theta^*$$

$$\cos \theta^* = r \left(\frac{\gamma_{SV} - \gamma_{SL}}{\gamma_{LV}} \right) = r \cos \theta$$

- d) Roughness will make the cosine of both contact angles a factor r larger (Wenzels law), so the contact angle hysteresis $\cos \theta_1 - \cos \theta_2$ will also be larger by a factor r , and therefore, the height h will be larger by a factor r .
- e) $\cos \theta_1$ cannot become larger than 1; this would be complete wetting. If r increases further, $\cos \theta_2$ will still increase, and the contact angle hysteresis and maximum height h decrease again.