

Chapter 4 Soft condensed matter

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- (4.1) For each of the following particles, suspended in water,
a) a grain of sand, $100\mu m$ in diameter, density $2200kgm^{-3}$,
b) a polymer particle, $1\mu m$ in diameter, density $1050kgm^{-3}$,
c) a virus particle, $50nm$ in diameter, density $1020kgm^{-3}$,
i.calculate the terminal velocity.

$$F = \zeta v = 6\pi\eta av$$

$$F = m^*g = V\delta\rho g = \frac{4}{3}\pi a^3\delta\rho g$$

$$\Rightarrow \frac{4}{3}\pi a^3\delta\rho g = 6\pi\eta av$$

$$v = \frac{2a^2\delta\rho g}{9\eta} = \frac{[m^2][kgm^{-3}][ms^{-2}]}{[kgm^{-1}s^{-1}]} = [ms^{-1}]$$

$$v = \frac{20a^2\delta\rho}{9 \times 1.002 \times 10^{-3}} = Ca^2\delta\rho, \quad C = 2217.786$$

$$v_a = C(100\mu m)^2(2200 - 1000) = 2.661 \times 10^{-2}ms^{-1}$$

$$v_b = C(1\mu m)^2(1050 - 1000) = 1.108 \times 10^{-7}ms^{-1}$$

$$v_c = C(50nm)^2(1020 - 1000) = 1.108 \times 10^{-10}ms^{-1}$$

- ii.calculate the diffusion constant.

$$T = T_{room}$$

$$D = \frac{k_B T}{\zeta} = \frac{[J][ms^{-1}]}{[N]} = [m^2s^{-1}]$$

$$D = \frac{k_B T}{\zeta} = \frac{k_B T}{6\pi\eta a} = \frac{4.11 \times 10^{-21}}{6\pi \times 1.002 \times 10^{-3}a}$$

$$D = 2.17 \times 10^{-19} \frac{1}{a}$$

$$D_a = 2.17 \times 10^{-19} \frac{1}{100\mu m} = 2.17 \times 10^{-15}m^2s^{-1}$$

$$D_b = 2.17 \times 10^{-19} \frac{1}{1\mu m} = 2.17 \times 10^{-13}m^2s^{-1}$$

$$D_c = 2.17 \times 10^{-19} \frac{1}{50nm} = 4.35 \times 10^{-12}m^2s^{-1}$$

- iii.estimate the time taken for the particle to diffuse a distance equal to its own diameter.

$$\langle R^2 \rangle = 6Dt \rightarrow t = \frac{\langle R^2 \rangle}{6D}$$

$$t_a = \frac{a_a^2}{6D_a} = \frac{(100\mu m)^2}{6 \times 2.17 \times 10^{-15} m^2 s^{-1}} = 7.68 \times 10^5 s$$

$$t_b = \frac{a_b^2}{6D_b} = \frac{(1\mu m)^2}{6 \times 2.17 \times 10^{-13} m^2 s^{-1}} = 7.68 \times 10^{-1} s$$

$$t_c = \frac{a_c^2}{6D_c} = \frac{(50nm)^2}{6 \times 4.35 \times 10^{-12} m^2 s^{-1}} = 9.578 \times 10^{-5} s$$

(4.2) Consider a colloid consisting of particles of mass m and density ρ_c suspended in water.

a. Show that the number density as a function of the height from the bottom of the container, z , $n(z)$, is given by,

$$n(z) = n_0 \exp\left(-\frac{m(\rho_c - \rho_w)gz}{\rho_c k_B T}\right)$$

Boltzman equation:

$$n(z) = n_0 \exp\left(-\frac{U(z)}{k_B T}\right)$$

$$U(z) = m * gz = V \delta \rho g z = \frac{m \delta \rho g}{\rho} = \frac{m(\rho_c - \rho_w)gz}{\rho_c}$$

$$\Rightarrow n(z) = n_0 \exp\left(-\frac{m(\rho_c - \rho_w)gz}{\rho_c k_B T}\right)$$

b. consider a slice of the suspension between heights z and $z + dz$.

i. show that diffusion leads to a net flux of particles J_D into the slice given by

$$J_D = D \frac{m^2 g^2 (\rho_c - \rho_w)^2}{k_B^2 T^2 \rho_c^2} n(z) dz$$

$$J_D = j dz = \frac{I}{A} dz = \frac{\partial n}{\partial t} dz$$

Fick's second law:

$$\frac{\partial n}{\partial t} = D \frac{\partial^2 n}{\partial z^2}$$

$$\frac{\partial n}{\partial z} = -n_0 \frac{m(\rho_c - \rho_w)g}{\rho_c k_B T} \exp\left(-\frac{m(\rho_c - \rho_w)gz}{\rho_c k_B T}\right)$$

$$\frac{\partial^2 n}{\partial z^2} = n_0 \left(\frac{m(\rho_c - \rho_w)g}{\rho_c k_B T}\right)^2 \exp\left(-\frac{m(\rho_c - \rho_w)gz}{\rho_c k_B T}\right) = \left(\frac{m(\rho_c - \rho_w)g}{\rho_c k_B T}\right)^2 n(z)$$

$$J_D = D \left(\frac{m(\rho_c - \rho_w)g}{\rho_c k_B T}\right)^2 n(z) dz = D \frac{m^2 g^2 (\rho_c - \rho_w)^2}{k_B^2 T^2 \rho_c^2} n(z) dz$$

ii. Show that the sedimentation under gravity leads to a net flux of particles out of the slice J_s given by

$$J_s = \frac{m^2 g^2 (\rho_c - \rho_w)^2}{\zeta k_B T \rho_c^2} n(z) dz$$

$$J_s = j dz = \frac{I}{A} dz = \frac{dn}{dt} dz = \frac{\partial n}{\partial z} \frac{dz}{dt} dz = \frac{\partial n}{\partial z} v_z dz$$

$$v_z = \frac{F_{gravity}}{\zeta} = \frac{m^* g}{\zeta} = \frac{mg(\rho_c - \rho_w)}{\zeta \rho_c}$$

$$\frac{\partial n}{\partial z} = -n_0 \frac{m(\rho_c - \rho_w)g}{\rho_c k_B T} \exp\left(-\frac{m(\rho_c - \rho_w)gz}{\rho_c k_B T}\right)$$

$$J_s = -n_0 \frac{m(\rho_c - \rho_w)g}{\rho_c k_B T} \exp\left(-\frac{m(\rho_c - \rho_w)gz}{\rho_c k_B T}\right) \frac{mg(\rho_c - \rho_w)}{\zeta \rho_c}$$

$$J_s = -\frac{m^2 g^2 (\rho_c - \rho_w)^2}{\zeta k_B T \rho_c^2} n(z) dz$$

net flux of particles **out of** the slice:

$$\Rightarrow J_s = \frac{m^2 g^2 (\rho_c - \rho_w)^2}{\zeta k_B T \rho_c^2} n(z) dz$$

iii. Use the Stokes Einstein law to show that the flux into the slice due to diffusion is balanced by the flux out of the slice due to sedimentation.

Stokes Einstein law:

$$D = \frac{k_B T}{\zeta}$$

$$J_D = D \frac{m^2 g^2 (\rho_c - \rho_w)^2}{k_B^2 T^2 \rho_c^2} n(z) dz = \frac{m^2 g^2 (\rho_c - \rho_w)^2}{\zeta k_B T \rho_c^2} n(z) dz = J_s$$

flux into the slice = flux out of the slice

(4.3) Consider the van der Waals interaction between two semi-infinite gold plates interacting across a vacuum.

a. Compare the force per unit area as predicated by the Hamaker approach, taking the value of Hamaker constant $A = 2 \times 10^{-19} J$, with the value of the Casimir force, for values of the plates separation of

i. $1 \mu m$

ii. $100 nm$

iii. $1 nm$.

van der Waals:

$$U_{vdW}(h) = -\frac{A}{12\pi h^2} = -\frac{5.305 \times 10^{-21}}{h^2}$$

$$U_{vdW}(1\mu m) = -\frac{5.305 \times 10^{-21}}{(1\mu m)^2} = -5.305 \times 10^{-9} J$$

$$U_{vdW}(100nm) = -\frac{5.305 \times 10^{-21}}{(100nm)^2} = -5.305 \times 10^{-7} J$$

$$U_{vdW}(1nm) = -\frac{5.305 \times 10^{-21}}{(1nm)^2} = -5.305 \times 10^{-3} J$$

Energy due to Casimir force:

$$E_{Casimir}(h) = -\frac{\hbar c \pi^2}{720 h^3} = -\frac{4.336 \times 10^{-28}}{h^3}$$

$$E_{Casimir}(1\mu m) = -\frac{4.336 \times 10^{-28}}{(1\mu m)^3} = -4.336 \times 10^{-10} J$$

$$E_{Casimir}(100nm) = -\frac{4.336 \times 10^{-28}}{(100nm)^3} = -4.336 \times 10^{-7} J$$

$$E_{Casimir}(1nm) = -\frac{4.336 \times 10^{-28}}{(1nm)^3} = -4.336 \times 10^{-1} J$$

b. At what separation h_x are two forces predicted to be equal?

$$U_{vdW}(h_x) = E_{Casimir}(h_x)$$

$$\frac{5.305 \times 10^{-21}}{h_x^2} = \frac{4.336 \times 10^{-28}}{h_x^3}$$

$$h_x = \frac{4.336 \times 10^{-28}}{5.305 \times 10^{-21}} m = \frac{4.336 \times 10^{-7}}{5.305} m = 8.162 \times 10^{-8} = 81.62 nm$$

c. Which expression is more likely to be accurate for separation greater than h_x , and which is more accurate less than h_x ? Give reason for your answer in each case.

$h < h_x$: Casimir is not accurate enough, because real metals are not perfect conductor and the field would penetrate a certain depth, of order 100nm.

$h > h_x$: Van der Waals force is not accurate enough as it does not consider finite speed of propagation of electromagnetic field.

(4.4) Consider a colloid of charged spheres all of radius $0.1\mu m$ in an aqueous solution of sodium chloride.

a. Calculate the Debye screening length for salt concentration of 10^{-5} , 10^{-4} , 10^{-3} , 10^{-2} .

$$\kappa^{-1} = \left(\frac{K \epsilon_0 k_B T}{e^2 C z^2} \right)^{\frac{1}{2}} = \left(\frac{80(8.85 \times 10^{-12})(4.11 \times 10^{-21})}{(1.6 \times 10^{-19})^2 C' \times 6.63 \times 10^{23} \times 2} \right)^{\frac{1}{2}} = \frac{6.54 \times 10^{-9}}{\sqrt{C'}}$$

$$\kappa_{C=10^{-5}}^{-1} = \frac{6.54 \times 10^{-9}}{\sqrt{10^{-5}}} = 2.07 \times 10^{-6} m = 2.92 \mu m$$

$$\kappa_{C=10^{-4}}^{-1} = \frac{6.54 \times 10^{-9}}{\sqrt{10^{-4}}} = 6.54 \times 10^{-7} m = 925 nm$$

$$\kappa_{C=10^{-3}}^{-1} = \frac{6.54 \times 10^{-9}}{\sqrt{10^{-3}}} = 2.07 \times 10^{-7} m = 292 nm$$

$$\kappa_{C=10^{-2}}^{-1} = \frac{6.54 \times 10^{-9}}{\sqrt{10^{-2}}} = 6.54 \times 10^{-8} m = 92.5 nm$$

b. For each of the salt concentration above, estimate the volume fraction for the transition to an ordered phase. You may assume that the particles may be considered to behave as hard spheres with an effective radius equal to the sum of the physical radius and the Debye screening length.

$$\frac{n_c r_c^3}{n_s r_s^3} = \phi, \quad \frac{n_c (r_c + \kappa^{-1})^3}{n_s r_s^3} = \phi_0 \Rightarrow \phi \left[\frac{r_c + \kappa^{-1}}{r_c} \right]^3 = \phi_0 = 0.67$$

$$\phi \left[1 + \frac{\kappa^{-1}}{r_c} \right]^3 = 0.67 \Rightarrow \phi = 0.67 \left[1 + \frac{\kappa^{-1}}{r_c} \right]^{-3}$$

$$\phi_{C=10^{-5}} = 0.67 \left[1 + \frac{\kappa_{C=10^{-5}}^{-1}}{r_c} \right]^{-3} = 0.67 \left[1 + \frac{2.92 \mu m}{0.1 \mu m} \right]^{-3} = 2.43 \times 10^{-5}$$

$$\phi_{C=10^{-4}} = 0.67 \left[1 + \frac{\kappa_{C=10^{-4}}^{-1}}{r_c} \right]^{-3} = 0.67 \left[1 + \frac{925 nm}{0.1 \mu m} \right]^{-3} = 6.22 \times 10^{-4}$$

$$\phi_{C=10^{-3}} = 0.67 \left[1 + \frac{\kappa_{C=10^{-3}}^{-1}}{r_c} \right]^{-3} = 0.67 \left[1 + \frac{292 nm}{0.1 \mu m} \right]^{-3} = 1.11 \times 10^{-2}$$

$$\phi_{C=10^{-2}} = 0.67 \left[1 + \frac{\kappa_{C=10^{-2}}^{-1}}{r_c} \right]^{-3} = 0.67 \left[1 + \frac{92.5 nm}{0.1 \mu m} \right]^{-3} = 9.39 \times 10^{-2}$$

(4.5) A water-based varnish is composed of a dispersion of polymer spheres with diameters of 200nm. If it is brushed onto a surface as a film of thickness 200 μm , how fast must the brush be moved to achieve an appreciable degree of shear thinning?

$$Pe = 1 \rightarrow \tau_{shear} = \tau_{diffusion} = \frac{6\pi\eta_{water}a^3}{k_B T} = \frac{6\pi \times 1.002 \times 10^{-3} Pa.s \times (200 nm)^3}{4.11 \times 10^{-21} J}$$

$$v = \frac{L}{\tau_{shear}} = \frac{200 \mu m \times 4.11 \times 10^{-21} J}{6\pi \times 1.002 \times 10^{-3} Pa.s \times (200 nm)^3} = \frac{2m \times 4.11 J \times 10^{-25}}{6\pi \times 1.002 Pa.s \times (2m)^3 \times 10^{-24}}$$

$$v = \frac{2 \times 4.11 \times 10^{-1} m}{6\pi \times 1.002 \times 8 s} = 5.44 \times 10^{-3} \frac{m}{s}$$