

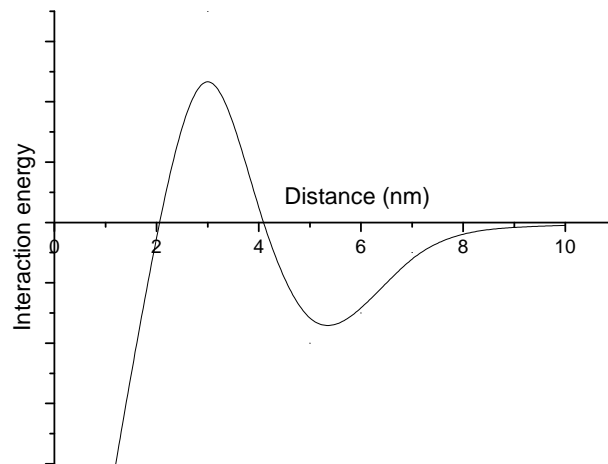
Soft Condensed Matter

Michaelmas 2017

Due: 5pm Thursday Week 5

1. Coagulation

The interaction energy between spherical silica particles in a stable colloidal suspension at pH 7 in an aqueous NaCl solution is shown here.



- (a) Explain the factors that determine the shape of the curve.
- (b) Explain why each of the following actions may lead to coagulation of the silica colloid.
- increasing the NaCl concentration
 - adding a divalent electrolyte
 - adding methanol to the solution (at constant $[\text{NaCl}]$)
 - reducing the pH (note: the isoelectric point of silica is around pH 2)
 - adding a soluble, non-adsorbing polymer, e.g. polyethylene oxide (PEO).

2. Sedimentation

- (a) Calculate the van der Waals interaction between two $1\mu\text{m}$ diameter silica spheres ($A_{11} = 6 \times 10^{-20}$ J) separated by 100 nm in a vacuum and compare this value with the thermal energy of the particles at room temperature. Repeat the calculation for silica in water, where $A_{131} = 0.8 \times 10^{-20}$ J.
- (b) Sufficiently small particles do not sediment under gravity. The barometric height distribution for the particle density n as a function of height is given by

$$n(h) = n(0) \exp(-\Delta\rho Vgh/k_B T),$$

where h is the height of the particle w.r.t. the bottom of the container, g is the acceleration due to gravity, $\Delta\rho$ is the difference in density between the particle and solvent, and V is the volume of the particle. Calculate the decay length (or gravitational length) of the exponential function (i.e. the height at which $n(h)/n(0) = e^{-1}$) for polystyrene particles of diameter $0.1\ \mu\text{m}$, $1\ \mu\text{m}$, and $10\ \mu\text{m}$ in water at 300 K. Comment on the values you obtain. Note that the density of polystyrene is $1.05\ \text{g cm}^{-3}$.

3. Wetting

When octane is placed in a quartz vessel, the octane wets the walls of the vessel. Within a continuum model, the energy, U , per unit area of a film of octane of thickness, D , due to van der Waals interactions is given by,

$$U = -\frac{A}{12\pi D^2},$$

where the Hamaker constant is $A = -7 \times 10^{-21}$ J. The gravitational potential energy per unit area of the film at a height, h above the liquid surface is given by,

$$U = \rho ghD,$$

where ρ is the density of the liquid and $g = 9.81\ \text{m s}^{-2}$ is the acceleration due to gravity.

- (a) Sketch the form of each of these two potentials (for $A < 0$), and of their sum, as a function of D .
- (b) Evaluate the equilibrium thickness of the film at $h = 1\ \text{cm}$ ($\rho = 703\ \text{kg m}^{-3}$). The Hamaker constant for water interacting with itself across a vacuum is $A_{ww} = 3.7 \times 10^{-20}$ J while for a typical hydrocarbon oil, $A_{oo} = 5.1 \times 10^{-20}$ J.
- (c) Estimate the Hamaker constant, A_{wo} , for water interacting with oil across a vacuum.
- (d) Determine the sign of the Hamaker constant for a film of oil on water in air (note the combining relation for medium 1 interacting with medium 2 across medium 3: $A_{123} \approx A_{12} + A_{33} - A_{13} - A_{23}$).
- (e) Hence predict whether oil will spread on water.

4. Van der Waals Interactions

Show that the van der Waals interaction per unit area between two plates of finite thickness T at a separation h can be written as,

$$U = -\frac{A}{12\pi} \left[\frac{1}{h^2} - \frac{2}{(h+T)^2} + \frac{1}{(h+2T)^2} \right].$$

For $h \gg T$ or $T/h \ll 1$ we can expand the above expression. Comment on the resulting $1/h^4$ dependence you obtain.

5. Polymers

A polymer brush is characterised by four parameters:

- N the number of monomers per chain
 - a^3 the volume per monomer
 - L the thickness of the brush
 - $\Gamma (= 1/s^2)$ the number of chains per unit area (s is the mean separation between chains)
- (a) Sketch the polymer brush and indicate the relevant length scales.
 - (b) For random-flight polymers in the semi-dilute regime, the osmotic pressure Π scales as $k_B T \phi^2 / a^3$, where ϕ is the volume fraction of the polymer. Write down an expression for ϕ in terms of N, a, L , and s and hence obtain a scaling expression for Π .
 - (c) The free energy of a single polymer chain is $3k_B T L^2 / 2Na^2$. Calculate the elastic force on a single chain of length L (recall that the force is the negative derivative of the free energy) and hence the force per unit area that resists an increase in L .
 - (d) By balancing the osmotic and stretching pressures on the brush, determine how L scales with N, a and s .
 - (e) Comment on the exponent of N in light of the scaling behaviour in solution.
 - (f) Explain why polymer brushes give rise to a repulsion between two surfaces coated with brushes.

6. Capillaries

- (a) Calculate the capillary rise h of water in a glass capillary with radii of $1 \mu\text{m}$ and 1mm . If the capillary would have been made from gold, what will change?
- (b) What overpressure is needed to force water through Teflon holes of $1 \mu\text{m}$ and 1mm ?
- (c) Consider again a narrow glass capillary in water. Sketch the capillary rise h as a function of the surfactant concentration and explain.

7. Interfaces

Consider a horizontal glass tube, with a diameter of 1 mm, which contains water and mercury forming a water/mercury interface. Water displays complete wetting on the glass, whereas the contact angle between the mercury-air interface and glass is 128° . All interfaces can be described by (part of) a sphere. The interfacial tensions are $\gamma_{\text{H}_2\text{O}/\text{air}} = 73 \text{ mN/m}$, $\gamma_{\text{Hg}/\text{air}} = 472 \text{ mN/m}$ and $\gamma_{\text{Hg}/\text{H}_2\text{O}} = 375 \text{ mN/m}$.

- Draw the water/air and mercury/air interface in the tube.
- Calculate the radius of curvature of the water/mercury interface.
- Draw the water/mercury interface in the tube and indicate its contact angle with the tube.

8. Surface Tension

The surface tension, γ , of the non-ionic surfactant, $\text{C}_{12}\text{H}_{25}(\text{OCH}_2\text{CH}_2)_2\text{OH}$ (known as C_{12}E_2) as a function of concentration, c , at 300 K is given in the table below.

$10^6 c / \text{mol dm}^{-3}$	1.7	3.2	5.6	10	18	32	56	100
$\gamma / \text{mN m}^{-1}$	64	59	52	45	38	31	29.5	29.0

Plot a graph of γ against $\ln c$. Account qualitatively for the shape of this graph and estimate **(i)** the critical micelle concentration (cmc) for C_{12}E_2 and **(ii)** the minimum area per molecule in a monolayer of C_{12}E_2 at the air/water interface.

9. Surfactants

The surface coverage, Γ , at the cmc (or the solubility limit in the case of dodecanol ($m = 0$)) for the family of surfactants C_{12}E_m is given in the table below for various values of m . Comment on these values.

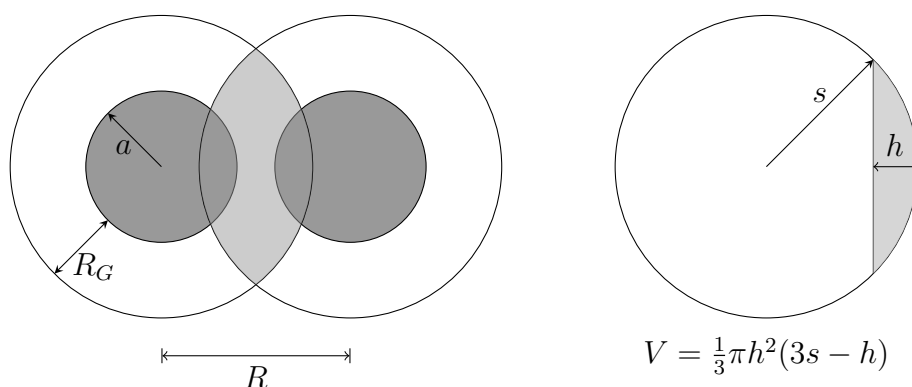
m	0	2	3	4	5	6	8	12
$\Gamma / 10^{-6} \text{ mol m}^{-2}$	7.9	5.3	4.6	3.8	3.3	3	2.7	2.3

- Estimate the area ($\sim \pi Rg^2$) that would be occupied by the head group of $\text{C}_{12}\text{E}_{12}$, treating it as a random flight polymer with segment length, $l = 0.38 \text{ nm}$, and compare this prediction with the experimental value of the area per molecule, $a = (N_A\Gamma)^{-1}$.
- For a liquid alkane near its freezing point, the volume per CH_2 group is 29 \AA^3 and the volume per CH_3 group is $\sim 35 \text{ \AA}^3$. The extended chain length per CH_2 group is 1.27 \AA ; for a CH_3 group one adds $\sim 1.5 \text{ \AA}$ to account for the terminal CH bond. Estimate v and l_c and hence calculate the ratio v/a_0l_c for each value of m above.
- Predict the shape of aggregates in the bulk solution.
- Estimate the aggregation number, N , for micelles of C_{12}E_8 and $\text{C}_{12}\text{E}_{12}$.

- (e) Many members of the family of surfactants $C_{12}E_m$ exhibit a cloud point: on heating, a solution changes from clear to cloudy as a result of the formation of large aggregates with a smectic structure (i.e. parallel bilayers). The microscopic origin is dehydration of the polyethylene glycol head groups with increasing temperature. Explain why this microscopic change causes the observed phase transition.

10. Depletion Interaction

- (a) Derive an expression for the depletion interaction between two spherical particles of radius a , at center-to-center separation R in a sea of polymers with radius of gyration R_G and osmotic pressure Π . See the figure below - the volume of a spherical cap, which you will need, is indicated.



- (b) Calculate the osmotic pressure using van't Hoff's law for a suspension of polymers at a concentration of 5 kg m^{-3} . The polymer's $M_w = 2000 \text{ kg mol}^{-1}$.
- (c) Using your expression and the pressure obtained above calculate the interaction energy at contact ($R = 2a$) when $R_G = a/2, a, 2a$. The colloid's radius is $a = 100 \text{ nm}$. Repeat your calculation, but now at a separation of $R = 2a + R_G$. Compare to the thermal energy and comment on your results.

11. Polymers

Describe ways in which polymers can either stabilise or destabilise suspensions of colloidal particles.

12. Carnahan-Starling Equation

The virial pressure of the hard sphere fluid equals

$$\frac{P}{\rho kT} = 1 + 4\phi + 10\phi^2 + 18.365\phi^3 + 28.24\phi^4 + 39.5\phi^5 + 56.5\phi^6 + \dots \quad (1)$$

Carnahan and Starling noted that this expansion is almost represented by,

$$\frac{P}{\rho kT} = 1 + \sum_{n=0}^{\infty} (n^2 + 3n)\phi^n, \quad (2)$$

which is easy to verify. Using $\sum_{n=0}^{\infty} \phi^n = \frac{1}{1-\phi}$ (differentiate both sides of the equation twice w.r.t. ϕ) show that the above equation can be written as,

$$\frac{P}{\rho kT} = \frac{1 + \phi + \phi^2 - \phi^3}{(1 - \phi)^3}, \quad (3)$$

which is the Carnahan-Starling equation of state. Note that the equation was originally derived via this route.

13. Hard Sphere Crystal

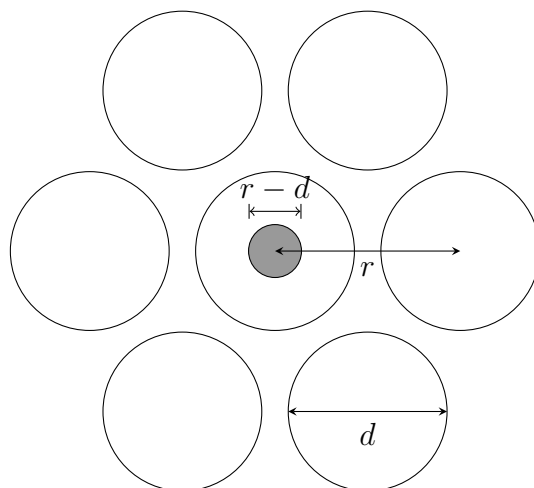
From our Statistical Thermodynamics course we remember that the partition function Q of an ideal gas of N particles can be written as,

$$Q = \frac{1}{N! \lambda^{3N}} V^N, \quad (4)$$

with λ the thermal de Broglie wavelength and V the total volume. Here V is nothing else than the available volume V^* for each particle. In a dense suspension of hard spheres a similar relation holds, but the available volume is much less than V . If we take a hard sphere crystal, it is easy to see that each sphere can roughly rattle around in a cage with volume,

$$V^* = \frac{4\pi}{3}(r - d)^3, \quad (5)$$

which is indeed its available volume.



Although r is in principle a very complicated function, we know that at close packing, where the volume fraction of spheres $\phi \equiv N \frac{\pi}{6} d^3 / V$ is equal to ϕ_{cp} , r will be equal to d . This means that we assume the following scaling relation to be true: $d^3 \phi_{cp} = r^3 \phi$. This provides us with an expression for r and thus for V^* . Writing the partition function in terms of V^* , i.e. $Q = \frac{1}{N! \lambda^{3N}} (V^*)^N$, allows us to calculate the pressure

P . Make use of $F = -kT \ln Q$ and $P = -(\partial F / \partial V)_{T,N}$ to show that

$$\frac{P}{\rho kT} = \frac{1}{1 - (\phi/\phi_{cp})^{1/3}}. \quad (6)$$

We can simplify this result by expanding ϕ around ϕ_{cp} , i.e. write ϕ as $\phi_{cp} - \varepsilon$, with ε a small parameter. Show that this leads to,

$$\frac{P}{\rho kT} = \frac{3}{1 - \phi/\phi_{cp}}, \quad (7)$$

which is indeed a very accurate expression for the pressure of a hard sphere crystal. At which volume fraction does the pressure diverge and does this make sense?

14. Protein Diffusion

- Derive an equation for the time it takes for a spherical colloid of radius a to diffuse over its own diameter. Calculate this time for a colloid with $a = 1 \mu\text{m}$ (assume room-conditions and water as the solvent).
- A spheroidal protein with characteristic radii $a = 500 \text{ nm}$ and $b = 20 \text{ nm}$, is synthesized in the middle of a spherical cell of radius $10 \mu\text{m}$. It need to reach the cell's membrane. How long does this take when the ellipsoid is somehow only moving sideways? And when it is moving lengthways? You may want to look in D & B to obtain the relevant friction coefficients.

15. Diffusion

In this question we will derive an expression for the mean-square displacement in a different manner than shown in lectures. To that end we will follow Langevin's original paper (see the translation by D. S. Lemons and A. Gythiel, *Am. J. Phys.* **65**, 1079 (1997)). We will start with the Langevin equation in only one dimension:

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

Multiply both sides by x and show that this can be written as

$$\frac{m}{2} \frac{d^2x^2}{dt^2} - m \left(\frac{dx}{dt} \right)^2 = -\frac{\xi}{2} \frac{dx^2}{dt} + fx. \quad (9)$$

We now take the ensemble average and apply the equipartition theorem, $m \left\langle \left(\frac{dx}{dt} \right)^2 \right\rangle = kT$,

$$\frac{m}{2} \left\langle \frac{d^2x^2}{dt^2} \right\rangle - kT = -\frac{\xi}{2} \left\langle \frac{dx^2}{dt} \right\rangle. \quad (10)$$

With $z = \langle dx^2/dt \rangle$ the above differential equation can be solved by the method of variation of constants, but more easily by as simple separation of variables. Solve

the equation above to obtain,

$$z = \frac{2kT}{\xi} + x \exp\left(-\frac{\xi t}{m}\right). \quad (11)$$

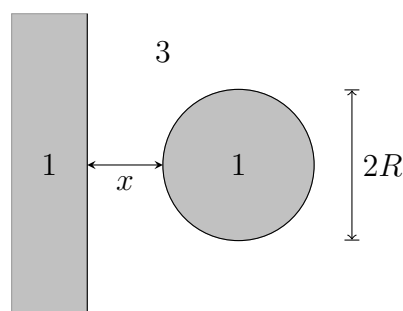
Note that the constant c does not depend on t . For long times, i.e. $t \gg \tau$, the above equation can be solved to obtain the mean square displacement along the x -direction as,

$$\langle x^2 \rangle = \frac{2kT}{\xi} t = 2Dt. \quad (12)$$

Derive the last equation.

16. Colloids (from 2015 Part IB paper)

Consider a spherical colloidal particle of radius R separated by a distance x from a wall made of the same material as the colloidal particle (1), dispersed in a solvent (3).



Relevant parameters are given in the table below.

R / μm	A_{131} / J	η / mPa s	T/K
1.5	5×10^{-20}	1	298

The friction coefficient for a sphere is $\xi = 6\pi\eta R$.

- (a) Show that the time τ_D for a sphere to diffuse over a distance x along one dimension is given by,

$$\tau_D = \frac{3\pi\eta R}{kT} \langle x^2 \rangle. \quad (13)$$

[4]

- (b) Using this expression calculate the time it takes for a colloidal particle to diffuse to the wall, when the initial separation x is equal to $0.5 \mu\text{m}$, ignoring any possible interactions with the wall. [3]

The colloidal particle and the wall interact via the van der Waals interaction, given by,

$$U_{\text{vdW}}(x) = -\frac{A_{131}R}{6x}. \quad (14)$$

- (c) Briefly explain the origin of the van der Waals interaction. Include in your answer a statement about the sign of A_{131} as well as any possible relation between A_{131} and A_{313} . [4]

The van der Waals interaction gives rise to a force F_{vdW} acting on the particle, causing it to move towards the wall. The resulting velocity $v = dx/dt$ of the particle leads to a frictional force, ξv , opposing the van der Waals force.

- (d) Assuming steady-state conditions, such that $|F_{\text{vdW}}| = \xi \frac{dx}{dt}$, show that for an initial separation x , the time τ_{vdW} for the colloidal particle to reach the wall is given by,

$$\tau_{\text{vdW}} = \frac{12\pi\eta x^3}{A_{131}}. \quad (15)$$

[6]

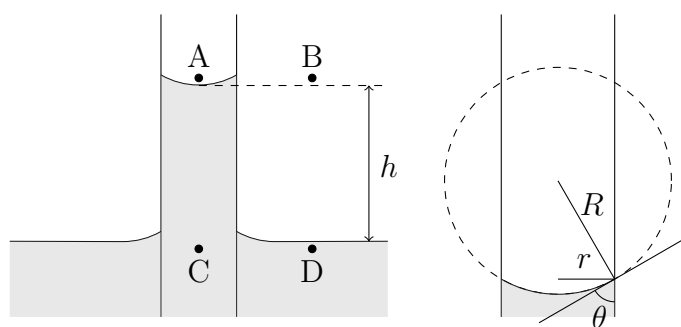
- (e) Calculate τ_{vdW} when $x = 0.5 \mu\text{m}$ and compare to your answer from part (b). Comment on the fact that the particle's diffusion has been ignored in the calculation of part (d). [4]

To modify the interaction between the particle and the wall polymers are grafted onto the surface of the particle.

- (f) Explain how the grafted polymers modify the particle-wall interaction and sketch the resulting overall particle-wall interaction. [4]

17. Interfaces (from 2014 Part IB paper)

A glass tube with radius r is partly immersed in a bath of water as shown in the diagram below. The pressure exerted by the hydrostatic column of height h is ρgh , where ρ is the mass density and g the acceleration due to gravity. The pressure difference across the water-air interface is $2\gamma_{\text{wa}}/R$, with $1/R$ the curvature of the meniscus (see diagram) and γ_{wa} the surface tension between water and air.



- (a) By considering the pressures at points A, B, C, and D in the diagram, construct a pressure balance to derive the following equation for the capillary rise h :

$$h = \frac{2\gamma_{\text{wa}} \cos \theta}{\Delta\rho gr}, \quad (16)$$

where $\Delta\rho$ is the mass density difference between water and air, and θ is the contact angle between water and glass. [7]

- (b) A second glass tube with twice the radius of the first glass tube is also partly immersed in the same water bath. Sketch the relative heights of the menisci in both tubes, explaining your reasoning. [3]
- (c) Given that the height difference between the menisci the two tubes is 1.4 cm, calculate the contact angle, θ , between water and glass. The temperature is 298 K, $\gamma_{\text{wa}} = 72.8 \text{ mN m}^{-1}$, $r = 0.50 \text{ mm}$, $\Delta\rho = 10^3 \text{ kg m}^{-3}$ and $g = 9.81 \text{ m s}^{-2}$. [6]

The relation between the contact angle, θ , and the surface tensions of the glass-air, water-glass, and water-air interfaces (γ_{ga} , γ_{wg} , and γ_{wa}) is given by Young-Dupré's law,

$$\cos\theta = \frac{\gamma_{\text{ga}} - \gamma_{\text{wg}}}{\gamma_{\text{wa}}}. \quad (17)$$

- (c) Use your value for θ from part (c) to calculate the difference in surface tension between the glass-air and water-glass interfaces. If you did not find a value for θ in part (c), then use $\theta = 15^\circ$. [2]
- (d) The temperature dependence of the water-air surface tension is (empirically) described by,

$$\gamma_{\text{wa}} = \gamma_0 \left[1 - \left(\frac{T}{T_C} \right) \right]^{\frac{11}{9}}, \quad (18)$$

where the critical Temperature, T_C , is 647.3 K. Assuming that the γ_{ga} and γ_{wg} do not depend on the temperature, calculate the temperature at which water completely wets the glass. Use the value of γ_{wa} from (c). [7]