Colloid Science Exam Part II June 30, 2021 **Maximum total points: 120**

1. During the initial stage of fast flocculation, the number density *c* of monomeric colloids decreases with time *t* as

$dc/dt = -\,k_{11}\,c^2$; k_{11} = rate constant of monodisperse colloids

a) Explain why the initial flocculation kinetics is of second order in concentration.[4]

b) If we decrease the size of the colloids, how does that modify the flocculation kinetics? [7]

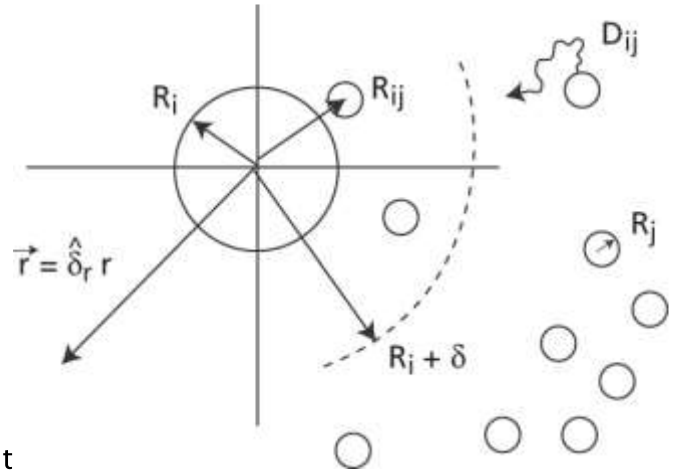
c) Defend or criticize the following statement: “the above given differential equation strictly speaking only holds for colloids that are spherical”. [7]

d) Colloidal spheres with radius $R_1 = 500\ \mathrm{nm}$ and volume fraction $\phi_1 = 0.01$ are mixed in a dispersion with small nano-particles with radius $R_2 = 10\ \mathrm{nm}$ and volume fraction $\phi_2 = 0.05$. Calculate the Brownian encounter frequency between small spheres and big spheres. [13]

e) Write down Fick’s first diffusion law for the total diffusion flux $J(j \rightarrow i)$ of *j*-particles, through a shell area $4\pi r^2$, in the direction of particle *i* at the origin (see BM Figure 9.2). Show how integration of this law leads to the stationary diffusion flux $J(j \rightarrow i) = 4\pi D_{ij} R_{ij} c_{j,\infty}$. Specify boundary conditions – and meaning of symbols. [14]

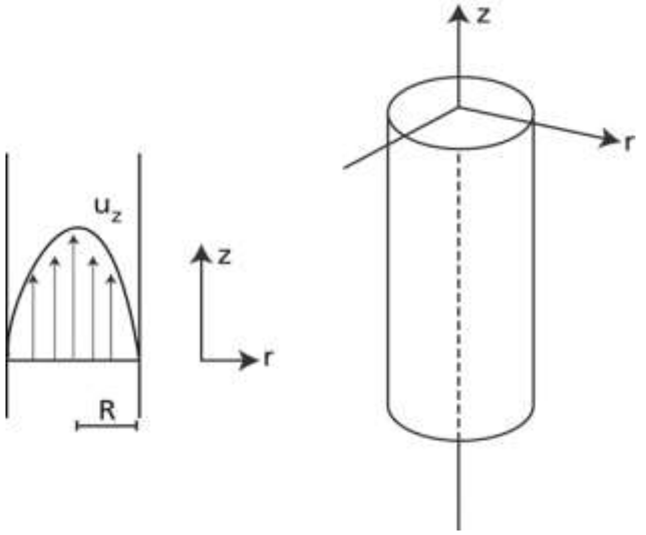
f) BM Equation (9.34) is the time dependence[1] of the (number) concentration c_α of flocs containing α monomers (singlet colloids). Show how (9.33) leads to equation (9.36) for the *total* number density, c_{tot} of monomers and flocs. Demonstrate that the half-life of that total number is $t_{1/2} = 2/k_{11}c_0$. [15]

[1] Assuming all rate constants k_{ij} equal k_{11}



g) t

BM Figure 9.2. Spheres *j* diffuse from a bulk (with number concentration $c_{j,\infty}$) at a distance $R_i + \delta$ towards a diffusing tracer sphere with radius R_i which acts as an infinite sink from which no *j*-sphere can escape.



BM Figure 8.2. Axial flow in a straight tube; the velocity profile is given by BM eq. (8.15); the radial co-ordinate runs from $r = 0$ in the center to the tube radius $r = R$. The flow is driven by a pressure gradient $dp/dz = \Delta P / L$, where ΔP is the total pressure drop over a tube length L.

2. The flow of blood through veins of a human being is an example of the flow of a viscous colloidal dispersion in a tube. Assume an axial flow in a straight tube with radius *R* and length *L* (BM Figure 8.2) in the z direction as a model for the vein. The dispersion's Newtonian viscosity[2] equals $\eta = 1 \text{ mPa sec.}$

a) Calculate the average blood speed $<u>$ in a tube with radius $R = 1\,\mu\text{m}$ and a blood pressure gradient of 0.3 bar m^{-1}.[8]

b) Evaluate the Reynolds number for the flow in a), for a blood mass density $\delta = 1 \text{ g mL}^{-1}$. Conclusion? [8]

c) Show how the viscous stress σ_{zr} depends on radial position *r* in the vein, and sketch the stress profile; assuming no-slip boundary conditions, i.e. u(r = R) = 0. [12]

d) Derive the total viscous force , F_{vis}, on the inner wall of the tube. Explain why your result for F_{vis} must be correct. [14]

e) Calculate the magnitude of the liquid permeability k (defined by Darcy's law $< u >= k\Delta P / \eta L$) of the tube with radius $R = 1\mu\text{m}$.[9]

f) What is a pure-slip boundary condition, and what can you say about flow in a tube when a pure-slip condition would be present ? Do you expect the geometry of the flow channel still to be relevant under pure-slip conditions? [9]

[2] Blood is actually a non-Newtonian fluid, but its shear-thinning viscosity is close to that of water.

Answers CS Exam Part II June 30, 2021.

1 a) Kinetics is proportional to concentration squared as initially there only encounters between two monomers ; in a later stage also aggregation of dimers, trimers etc occurs.

b) It depends: if the colloid size decreases for a given number density, the kinetics will hardly change because $k \propto D \times \text{size}$ and $D \propto 1/\text{size}$ so k is size independent. However, if we fix the colloid volume fraction (or weight concentration), than a size decrease enhances the colloid number density so the kinetics will speed up.

c) Colloid shape is hidden in the rate constants; shape does not affect the form of the differential equation for dc/dt.

d)

Frequency $f = k_{12}c_1c_2$ (BM eq. 9.24) ; $k_{12} = 4\pi D_{12}R_{12}$ (BM eq. 9.26). Since $R_1 \gg R_2$ we put $D_{12} \approx D_2$ and $R_{12} \approx R_1$: $\Rightarrow k_{12} \approx \dfrac{4\pi kT}{6\pi\eta R_2} R_1 = 1.54\times10^{-16}\,\text{m}^3\text{s}^{-1}$, taking $\dfrac{kT}{\eta} = 4.63\times10^{-18}\,\text{m}^3\text{s}^{-1}$ for water at 25 ^{0}C.

Volume fraction $\phi_1 = c_1(4\pi/3)R_1^3 \Rightarrow c_1 = 1.91\times10^{16}\,\text{m}^{-3}$; $c_2 = 1.19\times10^{22}\,\text{m}^{-3}$ $\Rightarrow f = 3.5\times10^{22}\,\text{m}^{-3}\text{s}^{-1}$

e) $J(j\to i) = 4\pi r^2 D_{ij}\dfrac{dc_j}{dr}$; $J(j\to i)$ independent of r (stationary state)

$$\Rightarrow J(j\to i)\int_{\infty}^{R_{ij}} \frac{dr}{r^2} = 4\pi D_{ij}\int_{c_{j,\infty}}^{0} dc_j$$

$$\Rightarrow J(j\to i) = 4\pi D_{ij}R_{ij}c_{j,\infty} \quad (\text{sec}^{-1})$$

Note that we do not need to know the concentration profile $c_j(r)$ (that follows from Fick's second diffusion law) to obtain this stationary flux.

f) $$\frac{dc_\alpha}{dt} \approx \frac{1}{2}k_{11}\sum_{i=1}^{\alpha-1} c_i c_j \; - \; c_\alpha k_{11}\sum_{i=1}^{\infty} c_i \; ; \quad c_{\text{tot}} = \sum_{\alpha=1}^{\infty} c_\alpha$$

$$\Rightarrow \frac{dc_{\text{tot}}}{dt} = \frac{1}{2}k_{11}\sum_{\alpha=1}^{\infty}\sum_{i=1}^{\alpha-1} c_i c_j - k_{11}\sum_{\alpha=1}^{\infty} c_\alpha \sum_{i=1}^{\infty} c_i = \frac{1}{2}k_{11}\sum_{\alpha=1}^{\infty}\sum_{i=1}^{\alpha-1} c_i c_j - k_{11}c^2{}_{\text{tot}}$$

Writing out the double summation for α=1, 2, 3 ....

it turns out to equal : $\frac{1}{2}c_1 c_{\text{tot}} + \frac{1}{2}c_2 c_{\text{tot}} + \frac{1}{2}c_3 c_{\text{tot}} + ... = \frac{1}{2}c_{\text{tot}}\sum_{j=1}^{\infty} c_j = \frac{1}{2}c^2{}_{\text{tot}}$

$$\Rightarrow \frac{dc_{\text{tot}}}{dt} = \frac{1}{2}k_{11}c_{\text{tot}}^2 \; - k_{11}c_{\text{tot}}^2 = -\frac{1}{2}k_{11}c_{\text{tot}}^2 \quad \Rightarrow c(t) = \frac{c_0}{1 + c_0(k/2)t} \quad \Rightarrow t_{1/2} = \frac{2}{k_{11}c_0}$$

2 a) $$< u > = \frac{R^2}{8\eta}\frac{\Delta P}{L} = \frac{(1\times 10^{-6}\,\text{m})^2 \times (0.3\text{ bar m}^{-1})}{8\times 10^{-3}\text{ Pa sec}} = 3.8\ \mu\text{m s}^{-1}$$

b) $$\text{Re} = \delta\frac{< u > R}{\eta} = \frac{(10^3\text{ kg m}^{-3})\times(3.8\ 10^{-6}\text{ m s}^{-1})\times(10^{-6}\text{m})}{10^{-3}\text{ Pa s}} = 3.8\times 10^{-6}\,\frac{\text{kg m}}{\text{N s}^2} = 3.8\times 10^{-6}$$

Since Re <<1, the blood flow is purely viscous Stokes flow.

c) The velocity gradient in the tube is

$$\frac{du_z}{dr} = \frac{1}{2\eta}\frac{dp}{dz}r + \text{zero} \quad \text{(BM eq. 8.12)}$$

Substitution in Newton's viscosity law

$$\sigma_{\text{zr}} = -\eta\frac{du_z}{dr} \qquad \text{(BM eq. 8.13)}$$

yields

$$\sigma_{\text{zr}} = -\frac{1}{2}\frac{dp}{dz}r \quad (= \text{positive constant} \times r)$$

So the viscous stress increases linearly from

$\sigma = 0$ at $r = 0$ to its value $\sigma = (r = R)$ at the (no-slip boundary) wall.

d) Stress at the wall: $\sigma(r=R) = -\frac{1}{2}R\frac{dp}{dz}$ [N m^{-2}]

Integrate along $z: -\frac{1}{2}R\int_0^L \frac{dp}{dz}dz = -\frac{1}{2}R\int_{P+\Delta P}^{P} dp = \frac{1}{2}R\,\Delta P$ [N m^{-1}]

Multiplication by the circumference $2\pi R$ gives the total viscous force:

$F_{\mathrm{vis}} = \frac{1}{2}R\,\Delta P \times 2\pi R = \Delta P \pi R^2$

The flow is driven by a net pressure force $\Delta P \pi R^2$, exerted on the inlet and outlet tube cross-sectional area πR^2. In the stationary state of constant flow speeds, this external force must be balanced by the total viscous force (equal in magnitude but opposite in direction).

e) Comparing Darcy's law $<u> = k\Delta P / \eta L$ with $<u> = \frac{R^2}{8\eta}\frac{\Delta P}{L}$ it follows that

$k = \frac{R^2}{8} = \frac{1}{8}\ (\mu\mathrm{m})^2$

f) Under pure-slip conditions there are no viscous forces so fluid moves everywhere at the same speed; a speed that cannot reach a steady, stationary state – which requires that viscous forces balance the driving pressure force. For parallel walls the geometry is not relevant; a fluid cannot distinguish one perfect-slip wall from another. (More complex geometries might offer resistance to fluid flow in the form of pressure forces – as occurs in the flow along a pure-slip sphere surface; no points will be distracted, however, if a student does not mention this option as in the course we only studied parallel geometries..)