EXAM COVER PAGE

COURSE: Colloid Science
COURSE CODE: SK-MCS
EXAM: Final exam
TIME: 09-11-2017 from 17.00h to 19.30h
LENGTH: 2h30m (plus 25m extra time=2h55m)
PLACE: Educatorium Megaron

IMPORTANT

- PLACE YOUR ID CARD (WITH PHOTO) ON THE TABLE – Show your ID when you hand in the exam.
- WRITE YOUR NAME AND STUDENT NUMBER ON EVERY ANSWER SHEET
- WHEN YOU HAND IN YOUR EXAM, YOU CAN TAKE THE QUESTIONS AND SCRATCH PAPER HOME

EXAM SPECIFICS

- This exam counts for 100% of the final grade.
- The minimum score of this exam needs to be at least 5.5 to prevent a re-exam. In order to be allowed to take a re-exam, the final grade for the course needs to be at least 4.0 and at most 5.4.
- Points per question are distributed as follows: questions 1-6 have equal weight.
- When answering the questions, please take the following into account: answer either in English or in Dutch and write legibly.

PERMITTED EQUIPMENT

A calculator is permitted, but no other electronic devices, no books, no notes of any kind

SUCCESS!

Examinators: Prof. Albert Philipse, Dr. Ben Erné

GENERAL EXAMINATION RULES

- You are not allowed to leave the exam room in the first 30 minutes. Latecomers are allowed in up to 30 minutes after the start time.
- All electronic equipment needs to be switched off (including mobile phones), with the exception of electronic equipment allowed by the examiner.
- Your coat and closed bag are placed on the ground.
- Raise your hand when you need to go to the bathroom. 1 person at a time. Place your mobile phone visibly on your table just before you go.
- Raise your hand if you have a question about the exam, or need extra paper, etc.
- Not following the instructions of the examiner or surveillant can lead to exclusion from the exam.
- When fraud is suspected the exam will be confiscated immediately. The examiner will act according to the Education and Exam Regulations and will inform the Exam Committee and the Education Manager in writing within one work day.
- Upon receiving your result you can request the examiner for access to your graded exam.

Exam Colloid Science, November 9, 2017.

1. A) Show for a colloidal cube of side *d* (in water) that the Gibbs energy of formation of a critical nucleus is given by: $\Delta G^* = (1/3)A^*\gamma$. Here A^* is the surface area of a critical nucleus and γ the silica-water surface tension.

   B) Why is ΔG^* smaller than the energy needed to form the surface of the nucleus?

   C) Discuss whether or not the result $\Delta G^* = (1/3)A^*\gamma$ is typical for a cube.

2. Consider the Donnan equilibrium between a solution of colloids and a very large salt reservoir solution (with constant salt concentration) separated by a semi-permeable membrane (see figure on page 3).

   A) Formulate the equilibrium condition for the ions involved, and the condition of electro-neutrality for the compartment *L* containing the colloids.

   B) Show that the chloride-ion number density ρ_- in *L* is given by:

$$\frac{\rho_-}{\rho_{\text{salt}}} = -y + \sqrt{1+y^2} \quad ; \; y = \frac{z\rho_{\text{colloid}}}{2\rho_{\text{salt}}}$$

   C) Show that the chloride concentration in L is always lower than in the reservoir solution R. Can you explain in words why that should be the case?

   D) What should we do to minimize the chloride concentration in *L* – or even drive it to zero ? Explain the measure(s) that you would take.

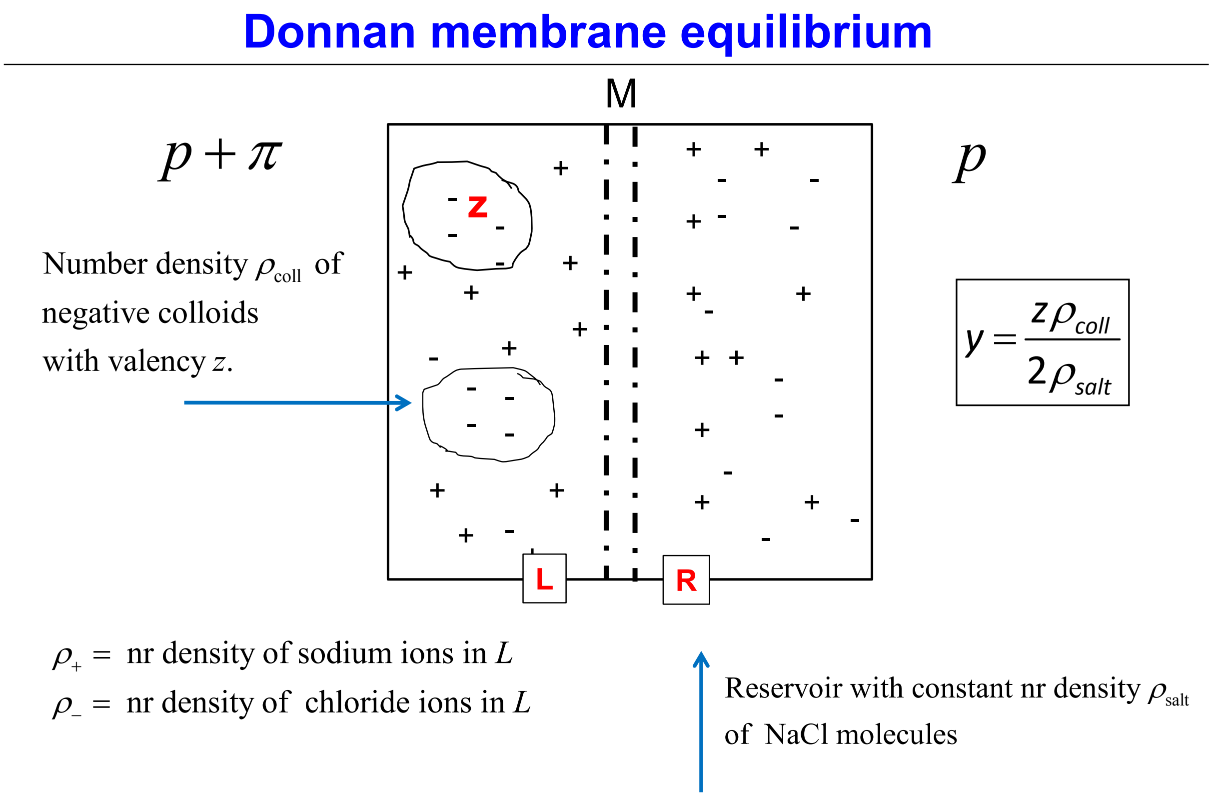
3. A) Provide a derivation that shows that the mean-square displacement $<x^2>$ of a single, free Brownian particle, diffusing in the x-direction, grows linearly in time:

$$<x^2> \ = \ \text{constant} \ \times t$$

B) Does this scaling apply all the way down to time $t \to 0$? If not, why not?

C) Suppose we charge-up the Brownian particle such that it is surrounded by an electrical double-layer. Argue whether or not this will affect the proportionality $<x^2> \propto t$.

<u>Figure to question 2</u>



Solution of the quadratic $ax^2 + bx + c = 0$ is : $x_{1,2} = \dfrac{-b \pm \sqrt{b^2 - 4ac}}{2a}$

For questions 4-6, formulas are present on page 6.

4. Silica particles with a radius of 100 nm in an aqueous solution of 1.0 mM NaCl have an electrophoretic velocity of 100 µm/s in an external electric field of 30 V/cm.
   - A) Calculate κa at 300 K.
   - B) Calculate the approximate zeta potential. What is the physical significance of the zeta potential? Why is it a relevant property to be characterized?
   - C) Assume that the electrophoresis instrument switches the field direction every 0.05 s. Calculate the minimum electric field required for electrophoretic motion of the particles to dominate over Brownian motion on this time scale.

5. The aqueous serum from a hospital patient freezes at –0.60 °C.
   - A) Derive an expression that allows calculation of the osmotic pressure from the lowering of the freezing point. Explain the steps and define the symbols.
   - B) Calculate the osmotic pressure due to dissolved or dispersed species.
   - C) Decreased health may lead to aggregation of dispersed species. Explain what effect of aggregation you expect on the osmotic pressure.

<u>Physical properties of water, silica, and NaCl</u>

In the absence of further information, the temperature is 300 K and one may assume that the values are approximately temperature-independent.

Water

molar mass	18.0 g/mol
density	1.00 g/cm^3
viscosity	0.0009 Pa.s
surface tension	0.071 N/m
dielectric constant	78
vapor pressure	3600 Pa
melting point	0 °C
melting enthalpy at 0 °C	6.0 kJ/mol
melting entropy at 0 °C	22 JK^{-1}mol^{-1}
boiling point (at 1 atm)	100 °C
vaporization enthalpy at 100 °C and 1 atm	40.7 kJ/mol
vaporization entropy at 100 °C and 1 atm	109 JK^{-1}mol^{-1}

Silica

density	2 g/cm^3
dielectric constant	4

NaCl

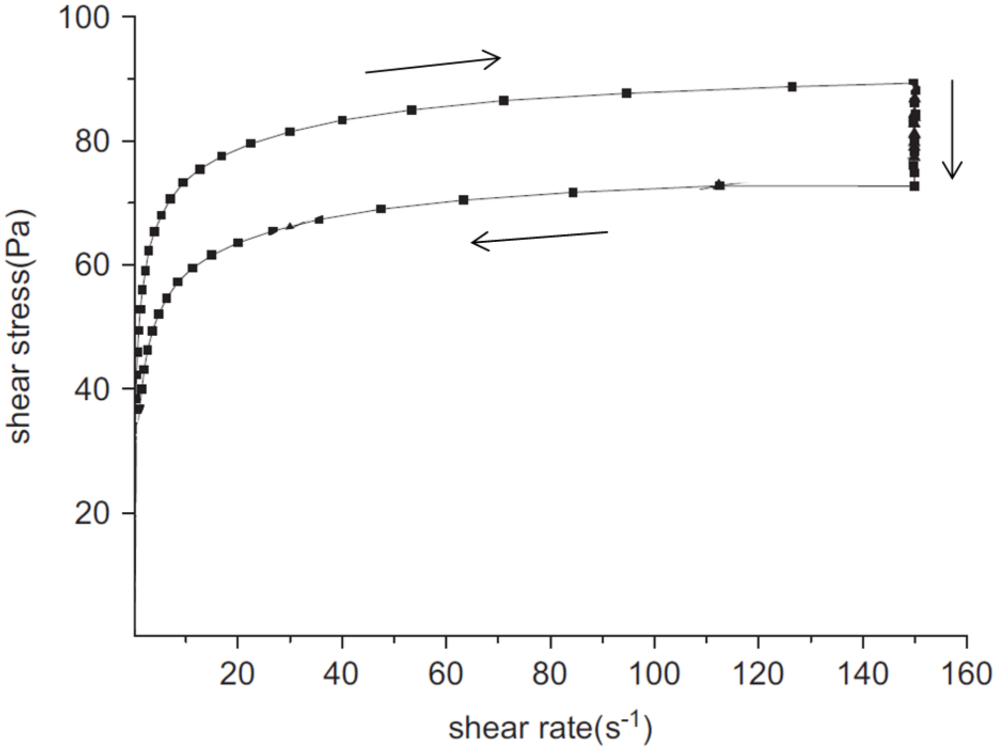
molar mass	58.4 g/mol
density	2.16 g/cm^3
refractive index	1.54
Na^+ ion radius from crystallography	0.102 nm
Cl^- ion radius from crystallography	0.181 nm
Na^+ mobility in water	5×10^{-8} ^{2}s^{-1}V^{-1}
Cl^- mobility in water	8×10^{-8} ^{2}s^{-1}V^{-1}

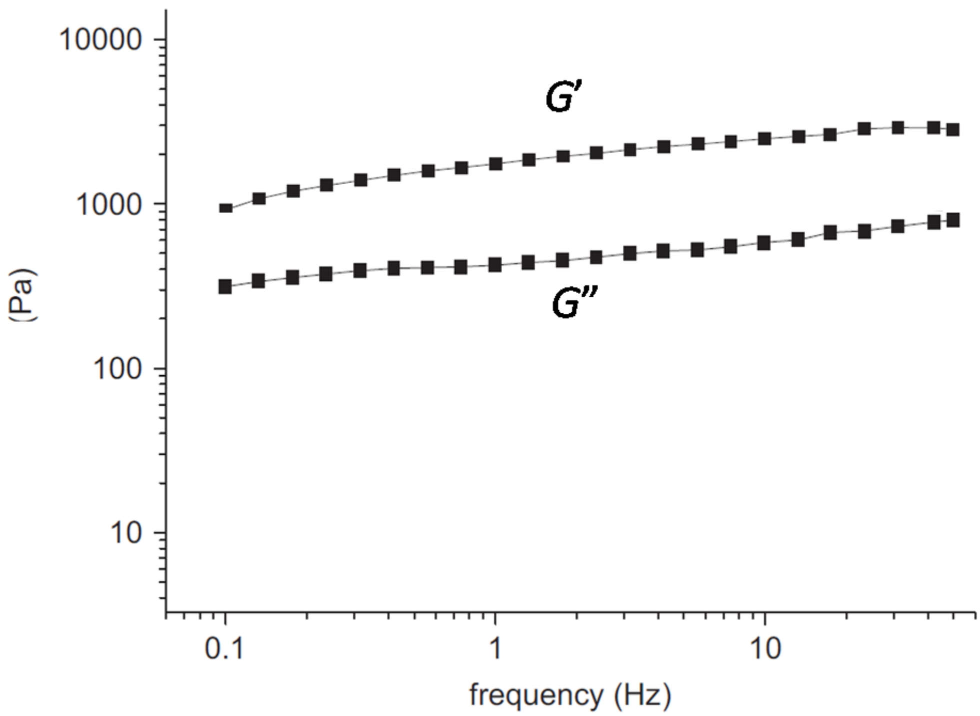
6. Experimental results of a rheological study on mayonnaise (an emulsion of closely packed oil droplets in water) are shown in the figures below:

   A) Explain what is plotted along the *x*- and *y*-axes in the upper figure.

   B) The curves in the upper figure show hysteresis and do not go through the origin (positive shear stress at zero shear rate). Interpret these observations.

   C) What evidence indicates that mayonnaise is not purely viscous but viscoelastic?





Formula Sheet:

Equations and Constants relating to *Colloidal Analysis Techniques*

Colloid Science (SK-MCS)

Constants

$k_B = 1.38\times10^{-23}$ J/K $R = 8.314$ JK^{-1}mol^{-1} $N_{Av} = 6.0\times10^{23}$ mol^{-1}

$e = 1.6\times10^{-19}$ C $F = 96485$ C/mol

$\varepsilon_0 = 9\times10^{-12}$ CV^{-1}m^{-1}

1 atm = 101325 Pa = 1.01325 bar

Light Scattering

$$\left(\frac{I}{I_0}\right)_V = \frac{16\pi^2}{r^2\lambda^4}\left(\frac{\alpha}{4\pi\varepsilon_0}\right)^2 \qquad \alpha = 3\varepsilon_0\left(\frac{n^2-1}{n^2+2}\right)V$$

$$P(Q)=\frac{I(Q)}{I(Q\to 0)}=1-\frac{1}{3}(QR_g)^2+\ldots \text{ for } QR_g \ll 1 \qquad Q=\frac{4\pi}{\lambda}\sin\left(\frac{\theta}{2}\right) \qquad R_g=\sqrt{3/5}a$$

$$\frac{I(Qa)}{I(Qa\to 0)}=\left[\frac{3\{\sin(Qa)-(Qa)\cos(Qa)\}}{(Qa)^3}\right]^2 \qquad g_2(\tau)=\frac{\langle I(t)\cdot I(t+\tau)\rangle}{\langle I(t)\rangle^2}$$

$$g_2(\tau)-1=|g_1(\tau)|^2 \qquad g_1(\tau)=\exp\left(-\frac{\tau}{\tau_c}\right) \qquad \tau_c=\frac{1}{Q^2D} \qquad D=\frac{k_BT}{6\pi\eta a_H}$$

Electrophoresis

$$u=\frac{v}{E} \qquad u=\frac{2}{3}\frac{\varepsilon_0\varepsilon_r}{\eta}\zeta \text{ for } \kappa a<0.1 \qquad u=\frac{\varepsilon_0\varepsilon_r}{\eta}\zeta \text{ for } \kappa a>100$$

$$q=4\pi a^2\sigma=4\pi a^2\left[-\varepsilon\frac{d}{dr}\left(\psi_0\frac{a}{r}\exp(-\kappa(r-a))\right)\right]=4\pi\varepsilon a(1+\kappa a)\psi_0$$

$$\psi=\psi_0\frac{a}{r}\exp[-\kappa(r-a)] \qquad \frac{1}{\kappa}=\sqrt{\frac{\varepsilon_0\varepsilon_r k_BT}{e^2\sum_i n_iz_i^2}} \qquad \zeta\approx\psi_0\approx\frac{q}{4\pi\varepsilon_0\varepsilon_r a}$$

Osmometry

$$\Pi=\rho k_BT(1+B_2\rho) \qquad \Pi=\frac{-RT\ln(a_1)}{v_1} \qquad \Pi=-\frac{RT}{v_1}\ln\frac{P_1}{P_1^0} \qquad \Pi=-\frac{\Delta_m s_1^0}{v_1}\left(T_m-T_m^0\right)$$

$$\Delta T_m=-\frac{R\left(T_m^0\right)^2}{\Delta_m H}x_2 \qquad d\Pi=-\rho(h)\cdot\Delta m\cdot g\cdot dh \qquad P(h)=P(h=0)\cdot\exp\left(-\frac{h}{L_g}\right)$$

$$\mu_1^B=\mu_1^0+RT\ln(a_1) \qquad \mu_1(vap)=\mu_1^0(vap)+RT\ln\frac{P_1}{1\,\text{atm}} \qquad \frac{\partial\mu_1^0(solid)}{\partial T}=-s_1^0(solid)$$

Conductivity and interfacial potentials

$$V=IR \qquad R=\frac{d}{A}\rho \qquad \sigma=1/\rho=\sum_i c_i\lambda_i \qquad \lambda_i=z_iF\cdot u_i \quad \lambda_i=\frac{F^2z_i^2}{RT}D_i \qquad f_i=\frac{k_BT}{D_i}$$

$$u_i=\frac{v_i}{E}=\frac{z_ieD_i}{k_BT}=\frac{z_iFD_i}{RT} \qquad \Lambda=\Lambda_0+Ac^{1/2} \qquad \Delta\psi_{\alpha\to\beta}=-\frac{RT}{F}\sum_i\int_\alpha^\beta\frac{t_i}{z_i}d\ln c_i$$

$$\Delta\psi_{\alpha\to\beta}=-\frac{RT}{F}\sum_i\frac{|z_i|u_i\left(c_i^\beta-c_i^\alpha\right)}{z_i\sum_j|z_j|u_j\left(c_j^\beta-c_j^\alpha\right)}\ln\frac{\sum_j|z_j|u_jc_j^\beta}{\sum_j|z_j|u_jc_j^\alpha} \qquad \psi^\beta-\psi^\alpha=\frac{RT}{F}\frac{Xc_x^\beta}{2c_+^\beta}$$

Rheology

$$E=\frac{\tau}{\Delta d/d} \qquad \tau=F/A \qquad \gamma=\Delta x/h \qquad G=\frac{\tau}{\gamma} \qquad \eta=\frac{\tau}{d\gamma/dt}$$

$$\frac{d\gamma}{dt}=\frac{1}{G}\frac{d\tau}{dt}+\frac{1}{\eta}\tau \qquad \tau=\tau_i\exp\left[-\frac{t}{\eta/G}\right]$$

$$\frac{d\tilde{\gamma}}{dt}=\frac{1}{G}\frac{d\tilde{\tau}}{dt}+\frac{1}{\eta}\tilde{\tau} \qquad \tilde{\gamma}=\gamma_0\cos(\omega t)=\gamma_0\exp(i\omega t)$$

$$\tilde{\tau}=\tau_0\cos(\omega t-\theta)=\gamma_0\exp[i(\omega t-\theta)]$$

$$\tilde{G}=G'+iG'' \qquad G'=G\frac{\omega^2(t_{rel})^2}{1+\omega^2(t_{rel})^2} \qquad G''=G\frac{\omega(t_{rel})}{1+\omega^2(t_{rel})^2}$$