

Norwegian University of
Science and Technology,
Department of Physics

Contact during the exam:
Rita de Sousa Dias
Phone 47155399

EXAM I COURSE
TFY4310 MOLECULAR BIOPHYSICS

Friday, 30 November 2018
Time: kl. 09.00 - 13.00

All questions have the same weight. None of the questions require lengthy answers so answer as precisely and concisely as possible. Good luck!

Exercise 1.

Justify **six** (6) of the following correct sentences:

1. A triple bond between carbon atoms ($\text{HC} \equiv \text{CH}$) consists of one sigma and two pi molecular orbitals occupied with electrons.
2. Absorption of a polymer to a nanoparticle decreases the conformational entropy of the polymer.
3. When performing molecular modeling of concentrated systems it is desirable to use periodic boundary conditions.
4. Both Raman scattering and IR spectroscopy probe the vibrational states of molecules. In Raman scattering however, one typically illuminates the sample with a laser beam and does not need to scan all frequencies in the IR spectra to obtain a spectrum.
5. In a common transient electric birefringence set-up the analyser is oriented 90° relatively to the polariser.
6. Spin-spin (T_2) relaxation does not involve the flipping of spins between levels.
7. The ^1H -NMR spectrum of $\text{CH}_3\text{--CH}_2\text{--Br}$ possesses a quadruplet (intensities of 1:3:3:1) and a triplet (intensities of 1:2:1) at the chemical shifts of 3.5 and 1.7 ppm (in relation to TMS), respectively.
8. In the most usual configuration for light scattering, the incident and scattered beams lie in the xy -plane, which is horizontal, and the incident beam is provided by a laser source which is vertically polarized.

Exercise 2. Cationic surfactant X has 14 carbon atoms, $\text{X}^+(\text{CH}_2)_{13}\text{--CH}_3 \text{ Cl}^-$, in the alkyl chain and forms spherical micelles in aqueous solution above the critical micellar concentration. Assume that the bare radius of the headgroup is 0.32 nm.

1. What is the hybridization of the carbons in the surfactant alkyl chain? Justify.
2. What is the driving force for micelle formation?
3. Calculate the radius of the micelle.
4. Calculate the root-mean-square (rms) of the end-to-end distance of the surfactant assuming that the hydrophobic tail behaves as an ideal freely jointed chain. Assume that the Kuhn length is 1 nm, corresponding to 7 CH₂ units. Ignore the contribution from the headgroup.
5. Draw a schematic representation of a spherical micelle. Discuss the results obtained in questions 3 and 4 and consider them in your drawing.
6. Increasing the salt concentration of the solution leads to a change in the shape of the micelle. Which shape do you predict it will form and why?
7. Calculate the potential energy between the headgroup of the surfactant and a water molecule for the shorter possible separation. Assume a conformation that maximizes the interaction. Consider water to be a dipole with a radius of 0.14 nm and a dipole moment of 1.85 D (1 D = 3.336×10^{-30} Cm). Due to the proximity between water and headgroup assume that $\epsilon = 1$.
8. Is this interaction strong enough to orient the water molecule at room temperature (T=20 °C)?
9. To learn more about the surfactant aqueous solution you performed dynamic light scattering experiments were using light with a wavelength of 500 nm and a scattering angle of 40° at 20 °C. Plotting the results as $\ln[g^{(2)}(q, \tau) - 1]$ as a function of τ gives a straight line with a slope equal to $-14,423 \text{ s}^{-1}$.

Calculate the hydrodynamic radius of the micelle. Comment the result taking into account your previous answers.

Exercise 3.

Consider a mixture of two proteins of molecular weight $M_1 = 20,000 \text{ g/mol}$ and $M_2 = 200,000 \text{ g/mol}$ in water. Assume that both are unhydrated and have the same partial specific volume of $0.74 \text{ cm}^3/\text{g}$. Consider that the average viscosity of the medium is $\eta = 1.5 \times 10^{-3} \text{ kg m}^{-1}\text{s}^{-1}$ and the density 1.05 g/cm^3 .

1. Show that, for a unhydrated mixture of proteins, the following relation is valid: $s_2/s_1 = (M_2/M_1)^{2/3}$.
2. Calculate the ratio of the sedimentation coefficients of the proteins.
3. Consider a sedimentation experiment where the two proteins are placed on top of a centrifuge tube filled with aqueous buffer containing a linear sucrose gradient from 5% to 20%, and then the tube is spun. The top of the tube is 4 cm from center, the bottom is 8 cm from the center. When the larger protein has sedimented a distance of 3 cm, how far has the smaller protein traveled (neglect any changes in viscosity and density associated with the sucrose gradient)? Is this a good method to separate the proteins?

4. Calculate the diffusion coefficients for each of the two proteins at 298 K. Note that a simple relation between D_i and M_i should also be valid in this case.
5. As the proteins sediment, the concentrated layer of protein will spread out due to diffusion. If the distance over which the molecules spread is larger than the distance separating the two proteins, then it will not be possible to use this method to separate the two proteins, because they will overlap. Calculate the average (root-mean-square) distance the two proteins move due to diffusion at 298 K if the experiment lasts 12 hours. Is this spreading distance due to diffusion significant, compared to the separation of the two proteins due to sedimentation?

The following formulas and data may or may not be of use in answering the preceding questions. You do not need to derive any of the formulas but all parameters must be defined, if used.

Electron charge: $e = 1.602 \times 10^{-19} \text{ C}$

Avogadro constant: $N_{\text{Av}} = 6.022 \times 10^{23} \text{ mol}^{-1}$

Boltzmann constant: $k_{\text{B}} = 1.380 \times 10^{-23} \text{ JK}^{-1}$

Permittivity in vacuum: $\epsilon_0 = 8.854 \times 10^{-12} \text{ C V}^{-1} \text{ m}^{-1}$

Relative dielectric permittivity of air: $\epsilon = 1.0$

Properties of water at 20 °C: $\epsilon = 78.4$; $\eta = 1.0 \times 10^{-3} \text{ kg m}^{-1}\text{s}^{-1}$; $\rho = 1.02 \text{ g/cm}^3$

Properties of polyethylene: Kuhn length: $14 \text{ \AA}$; $\theta = 110^\circ$; $\langle \cos \phi \rangle = 0.26$

Temperature: $[\text{K}] = [^\circ\text{C}] + 273.15$

Atomic orbitals: H: $1s^1$; C: $1s^2 2s^2 2p_x^1 2p_y^1$; O: $1s^2 2s^2 2p_x^2 2p_y^1 2p_z^1$

Atomic weights: $A_r(\text{H}) = 1.0$; $A_r(\text{C}) = 12.0$

Thermodynamics $\Delta G = \Delta H - T\Delta S$ $S = k_{\text{B}} \ln W$

$$\mu_1 - \mu_1^0 = N_{\text{Av}} \left(\frac{\partial \Delta G}{\partial n_1} \right)_{T,P} \quad \Pi = \frac{\mu_1 - \mu_1^0}{V_1^{(M)}}$$

Potential energies

$$V(r) = \frac{z_1 z_2 e^2}{4\pi\epsilon_0\epsilon r} \quad V(r) = \frac{z_1 z_2 e^2}{4\pi\epsilon_0\epsilon r} \exp\left(-\frac{r}{\lambda_D}\right) \quad V(r, \theta) = -\frac{(ze)u \cos \theta}{4\pi\epsilon_0\epsilon r^2}$$

$$V(r, \theta_1, \theta_2, \phi) = -\frac{u_1 u_2}{4\pi\epsilon_0\epsilon r^3} [2 \cos \theta_1 \cos \theta_2 - \sin \theta_1 \sin \theta_2 \cos \phi]$$

$$V(r) = -\frac{(ze)^2 u^2}{6(4\pi\epsilon_0\epsilon)^2 k_B T r^4} \quad \text{for } k_B T > \frac{Qu}{4\pi\epsilon_0\epsilon r^2}$$

$$V(r) = -\frac{u_1^2 u_2^2}{3(4\pi\epsilon_0\epsilon)^2 k_B T r^6} \quad \text{for } k_B T > \frac{u_1 u_2}{4\pi\epsilon_0\epsilon r^3}$$

$$\lambda_D^2 = \frac{\varepsilon_0 \varepsilon k_B T}{\sum_i (eZ_i)^2 n_{i\infty}}$$

$$u = ql = zel$$

$$\text{CPP} = v/a_0 l_c$$

$$l_c \leq l_{\max} \approx (0.154 + 0.1265n) \quad [\text{nm}]$$

$$v \approx (27.4 + 26.9n) \times 10^{-3} \quad [\text{nm}^3]$$

$$\text{Statistical chain molecules } \langle R_{\text{ee}}^2 \rangle = C_n Q^2 n$$

$$C_n = 1 ; C_n = \frac{1 - \cos \theta}{1 + \cos \theta} ; C_n = \frac{1 - \cos \theta}{1 + \cos \theta} \frac{1 + \langle \cos \phi \rangle}{1 - \langle \cos \phi \rangle}$$

$$\text{Scaling} \quad \langle R_{\text{ee}}^2 \rangle^{1/2} \sim Q n^\alpha ; \alpha = 1/2 ; \alpha = 3/5$$

$$\text{For ideal chains} \quad \langle R_{\text{ee}}^2 \rangle = 6 \langle R_G^2 \rangle$$

$$\text{Overlap concentration (in molar concentration of monomers)}$$

$$C^\star = \frac{3N_p}{4\pi N_{\text{Av}}} \frac{10^{-3}}{R_G^3}$$

$$\text{Polymer molecular weights}$$

$$\langle M \rangle_n = \frac{\sum_i N_i M_i}{\sum_i N_i}$$

$$\langle M \rangle_w = \frac{\sum_i N_i M_i^2}{\sum_i N_i M_i}$$

$$\text{Regular solution model}$$

$$\frac{\Delta G_{\text{mix}}}{N} = B x_1 x_2 + R T (x_1 \ln x_1 + x_2 \ln x_2)$$

$$\text{Flory-Huggins theory}$$

$$\frac{\Delta G_{\text{mix}}}{N} = R T \left(v_1 \ln v_1 + \frac{v_2}{x} \ln v_2 + \chi v_1 v_2 \right)$$

$$\text{For dilute solutions: } W_2 = \left(\frac{Z-1}{n} \right)^{n_2(x-1)} \frac{n!}{(n-n_2 x)! n_2!}$$

$$\text{Critical composition, temperature and interaction } (\chi) \text{ parameter}$$

$$v_{1,c} = \frac{\sqrt{x}}{1+\sqrt{x}} \quad \Rightarrow \quad v_{2,c} = \frac{1}{1+\sqrt{x}}$$

$$T_c \sim \frac{1}{R \chi_c}$$

$$\chi_c = \chi_s(v_1 = v_{1,c}) = \frac{1}{2} + \frac{1}{2x} + \frac{1}{\sqrt{x}}$$

Swelling of networks

$$\Delta G = k_{\text{B}}T \left[(n_1 \ln v_1 + \chi n_1 v_2) + \frac{3}{2}n(v_2^{-2/3} - 1 + \frac{1}{3} \ln v_2) \right]$$

Equilibrium swelling ratio

$$q_m \cong \left[\frac{V_0}{n} \frac{1/2 - \chi}{V_1^{(\text{M})}} \right]^{3/5}$$

Swelling of charged networks

$$\Pi_{\text{tot}} = -RT \left[\frac{1}{V_1^{(\text{M})}} (\ln(1 - v_2) + v_2 + \chi v_2^2) + (n/V_0)(v_2^{1/3} - v_2/2) - \Delta C \right]$$

$$\Delta C = \sum_i (c_{i,\text{n}} - c_{i,\text{l}})$$

Planck's law

$$E = h\nu = \frac{hc}{\lambda} = hc\tilde{\nu}$$

Particle distribution in therm. equil.

$$\frac{n_{\text{A}}}{n_{\text{B}}} = \exp \left[-\frac{\Delta E_{\text{AB}}}{k_{\text{B}}T} \right]$$

Beer-Lambert law

$$A(\lambda) = \varepsilon(\lambda)cl$$

IR spectroscopy

$$\boldsymbol{\mu}_{\mathbf{10}} = \sum_i \left(\frac{\partial \hat{\boldsymbol{\mu}}}{\partial q_i} \right)_{q_i=0} \int N_1^* q_i N_0 \, \text{d}\tau_{\text{n}}$$

Raman scattering

$$P = \alpha_0 E_0 \cos 2\pi\nu_0 t + \frac{1}{2} \left(\frac{\partial \alpha}{\partial q_i} \right)_0 q_{i0} [\cos(2\pi(\nu_0 + \nu_m)t) + \cos(2\pi(\nu_0 - \nu_m)t)]$$

Nuclear spin

$$\vec{m} = \gamma \vec{L}, \quad (\vec{m})^2 = \gamma^2 \hbar^2 \ell(\ell + 1), \quad m_z = m_\ell \gamma \hbar$$

Gyromagnetic ratio

Nucleus	¹ H	² H	¹³ C	¹⁴ N	¹⁹ F	³¹ P
$\gamma \left(10^7 \frac{\text{rad/s}}{\text{T}} \right)$	26.753	4.107	6.728	1.934	25.179	10.840

Larmor frequency

$$\omega = \frac{\gamma}{2\pi} B_0$$

Pulses

$$\beta = \omega_1 \tau_{\text{rf}}$$

Local magnetic field

$$B_{\text{local}} = B_0(1 - \sigma)$$

Friction coefficients

$$\vec{F} = -f\vec{v}, \quad \vec{M} = -\xi\vec{\omega}$$

Stokes formula

$$f = 6\pi\eta R_h, \quad \xi = 8\pi\eta R_h^3$$

Hydrodynamic volume

$$v_{\text{h},1} = \left(\overline{V}_1^{(S)} + \delta \overline{V}_0^{(S)} \right) \frac{M_1}{N_{\text{Av}}}$$

Specific volume (per mass) $\bar{V}_1^{(S)} = v_1 \left(\frac{N_{\text{Av}}}{M_1} \right)$

Fick's laws $\frac{\partial c}{\partial t} = -\vec{\nabla} \cdot \vec{J}, \quad \vec{J} = -D_{\text{T}} \vec{\nabla} c, \quad \frac{\partial c}{\partial t} = D_{\text{T}} \frac{\partial^2 c}{\partial x^2}$

Nernst-Einstein relations $f D_{\text{T}} = k_{\text{B}} T, \quad \xi D_{\text{R}} = k_{\text{B}} T$

Diffusion $\langle r^2 \rangle^{1/2} = \sqrt{2 D_{\text{T}} t}$

Lamm-equation $\frac{\partial c(r, t)}{\partial t} = D_{\text{T}} \left(\frac{\partial^2 c(r, t)}{\partial r^2} + \frac{1}{r} \frac{\partial c(r, t)}{\partial r} \right) - s \omega^2 \left(r \frac{\partial c(r, t)}{\partial r} + 2c(r, t) \right)$

Sedimentation centrifugation: $s = \frac{\ln(c_0/c_{\text{p}}(t))}{2\omega^2 t}; \quad s = \frac{\ln(r_2/r_1)}{\omega^2(t_2 - t_1)}$

Svedberg equation $s = \left(1 - \bar{V}_1^{(S)} \rho \right) \frac{M_1}{N_{\text{Av}} f}$

Equilibrium centrifugation: $m_1(r) = m_1(r_{\text{m}}) \exp \left\{ \frac{M_1 (1 - \bar{V}_1^{(S)} \rho) \omega^2 (r^2 - r_{\text{m}}^2)}{2RT} \right\}$

Electrically-induce birefringence $I(t) = \frac{I_0}{4} \delta_0^2 \exp(-12 D_{\text{R}} t)$

Raman spectroscopy $P = \alpha_0 E_0 \cos 2\pi \nu_0 t + \frac{1}{2} \left(\frac{\partial \alpha}{\partial q_i} \right)_0 q_{i0} [\cos(2\pi(\nu_0 + \nu_m)t) + \cos(2\pi(\nu_0 - \nu_m)t)]$

Nuclear spin $\vec{m} = \gamma \vec{L}, \quad (\vec{m})^2 = \gamma^2 \hbar^2 \ell(\ell + 1), \quad m_z = m_{\ell} \gamma \hbar$

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Larmor frequency $\nu = \frac{\gamma}{2\pi} B_0$

Scattering $\langle I_{\text{S}}(q) \rangle = \frac{E_0^2}{R^2} \left\langle \sum_{j=1}^N \sum_{k=1}^N b_j(\mathbf{q}) b_k^*(\mathbf{q}) \exp[-i\mathbf{q} \cdot (\mathbf{R}_j - \mathbf{R}_k)] \right\rangle$

$$E'_x = \frac{E_x(t) \alpha k^2 \sin \theta_1}{4\pi \varepsilon \varepsilon_0 R}$$

$$q = \frac{4\pi}{\lambda} \sin\left(\frac{\theta}{2}\right), \quad \lambda = \frac{\lambda_0}{n_0}, \quad \xi = 2\pi R_s/\lambda$$

Identical particles $\langle I_s(q) \rangle = N b^2(0) P(q) S(q)$

Guinier approximation $I_s(q) = I_0 \exp\left(-\frac{1}{3} q^2 R_G^2\right)$

RGD regime ($\xi \ll 1$) $\frac{\langle I_s(q) \rangle}{I_0} R^2 = c M \kappa,$

For larger particles $\frac{\kappa c}{R_\theta} = \frac{1}{M} \left[1 + \frac{16\pi^2}{3\lambda^2} R_G^2 \sin^2 \frac{\theta}{2} \right] \cdot [1 + 2B_2c],$

Incoming light direction of polarization	Rayleigh ratio	Optical constant
x-direction	$R_\theta = \frac{\langle I_s(q) \rangle}{I_0 \cos^2 \theta} R^2$	$\kappa = \frac{1}{N_{Av}} \frac{4\pi^2 n_0^2}{\lambda_0^4} \left(\frac{dn_0}{dc} \right)^2$
z-direction	$R_\theta = \frac{\langle I_s(q) \rangle}{I_0} R^2$	$\kappa = \frac{1}{N_{Av}} \frac{4\pi^2 n_0^2}{\lambda_0^4} \left(\frac{dn_0}{dc} \right)^2$
unpolarized	$R_\theta = \frac{\langle I_s(q) \rangle}{I_0 (1 + \cos^2 \theta)} R^2$	$\kappa = \frac{1}{N_{Av}} \frac{2\pi^2 n_0^2}{\lambda_0^4} \left(\frac{dn_0}{dc} \right)^2$

Dynamic light scattering
Siegert relation $g^{(2)}(q, \tau) = 1 + [g^{(1)}(q, \tau)]^2$
 $g^{(1)}(q, \tau) = \exp(-q^2 D_T \tau)$

Scattering length density

Substance	H ₂ O	D ₂ O	proteins	nucleic acids	lipids
$\rho \text{ (} 10^{-4} \text{ nm}^{-2} \text{)}$	-0.55	6.36	3.11	4.44	-0.01