Advanced Physical Chemistry (SK-MPC3) / Fysische Chemie 3 (SK-BFYC3)

Partial Exam on March 8, 2017 – 17:00-19:30 in Educatorium Beta

Instructions

- This exam has 4 pages and consists of 2 parts: “Statistical Thermodynamics” (pp. 2-3) and “Colloids & Polymers” (p. 4).
- A maximum of 100 points can be obtained per part. The maximum number of points per question is given between square brackets.

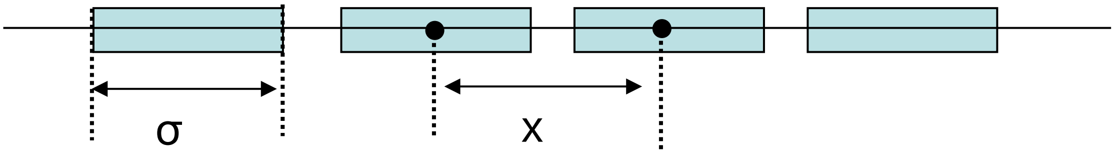
- Provide your answers in English or Dutch.
- Show how you arrive at your answers, and in the case of calculations, do not forget to give the units.

- You are not allowed to use any other tools than a calculator (with an empty memory) and a pen.
- Notes, books, electronic devices, or other sources of information are not allowed to be used.

- Hand in your answers to **Parts 1 and 2 on separate sheets of paper.**
- Please show your personal identification when you hand in your answers (for instance: student card, passport, driver’s license).

Statistical Thermodynamics

1. Consider a 1-dimensional fluid of N 'rods' of hard-core 'diameter' σ in a length L (L being the 1- dimensional equivalent of volume V) as schematically depicted below. The separation between the midpoints of two neighboring rods is x. The rods have an infinite repulsion upon overlap: $\phi(x< \sigma)=\infty$ and a weak interaction at larger distance with a potential energy of interaction $\phi(x)$.



a. [20] Show that the equation of state of the hard-core part is exactly given by $p_{HC} = \dfrac{kT\rho}{1-\sigma\rho}$, with $\rho=N/L$.

b. [10] When the weak interaction at larger distance is given by:

$$\phi(x) = -\varepsilon \ln\left(1 + A\mathrm{e}^{-|x|/a}\right) \qquad (|x| > \sigma)$$

calculate the second virial coefficient for the 1-dimensional fluid for $T = \varepsilon / k$.

c. [10] In the 3-dimensional equivalent of the hard-core equation of state above one should substitute $\sigma=4\upsilon_0$ for low densities, with υ_0 the volume of a hard sphere. Is that equation of state also exact at higher densities? Why, or why not?

d. [10] Make a sketch of the 3-dimensional radial distribution function for hard spheres at low density and at liquid density. Explain and justify your sketch in words and/or by making drawings.

2. **a.** [10] In a harmonic oscillator the energy levels are equally spaced (with energy steps $h\nu$; neglect the zero-point energy). Show that the partition function is given by $z = \left(1 - e^{-h\nu/kT}\right)^{-1}$ in this case.

b. [10] The vibrational frequency in Br_2 is given by a wavenumber $\tilde{\nu} = 323\ \mathrm{cm}^{-1}$ (with wavenumber $\tilde{\nu} \equiv \nu / c$). Calculate the percentage of molecules in the ground state at room temperature (20^{o}C).

c. [10] Starting from the expression in part a. give a derivation that the heat capacity per mole is expressed by the formula: $C_V = R\left(\dfrac{h\nu / kT}{e^{\frac{1}{2}h\nu/kT} - e^{-\frac{1}{2}h\nu/kT}}\right)^2$.

d. [10] Show mathematically that $C_V \to 0$ when $T \to 0$. Explain physically why this is the case considering the Boltzmann distribution over the energy levels.

e. [10] When it is given that the number density of (harmonic) elastic vibrations per frequency unit in a solid is proportional to ν^2 at low ν, show that this implies that C_V is proportional to T^3 when $T \to 0$.

Equations and constants for statistical thermodynamics

Taylor series: exponent: $e^x \approx 1 + x$ x<<1

logarithm: $\ln(1+x) \approx x$ x<<1

Geometric series: $\dfrac{1}{1-x} = 1 + x + x^2 + x^3 + \ldots$ x<1.

Derivative: $\dfrac{dx^n}{dx} = nx^{n-1}$

Stirling approximation: $\ln N! \approx N \ln N - N$ (N>>1)

$$A = U - TS = -kT \ln Z$$

$$U = -\left[\frac{\partial \ln Z}{\partial (1/kT)}\right]_{V,N}$$

Independent particles

Distinguishable: $Z = z^N$

Indistinguishable: $Z = z^N / N!$

$$z = \sum_i e^{-\varepsilon_i / kT}$$

Fundamental constants

Planck's constant *h* = 6.63 10^{-34} J s

Boltzmann's constant *k* =1.38 10^{-23} J K^{-1}

Speed of light *c* = 3.00 10^{8} m s^{-1}

Colloids & Polymers

3. Nanoparticles of iron oxide (spheres 5.0 nm in radius, 5.2 g/cm^3) are sterically stabilized in water (18.0 g/mol, 1.0 g/cm^3, viscosity 1.0×10^{-3} Pas) by a 3.0 nm thick layer of poly(ethylene glycol) attached to the iron oxide surface ("PEG", 5000 g/mol, 114 segments per molecule, 1.1 g/cm^3). The Flory-Huggins interaction parameter χ is 0.43 at a temperature of 300 K and the PEG concentration in the polymer layer is 0.10 g/cm^3.

a. [20] Explain the sterical stabilization in a few sentences. Illustrate your words by drawing two particles at a given distance from each other and by also drawing two total interaction potentials: in the cases of a good and a bad solvent. Refer to the interparticle distance and layer thickness in both drawings.

b. [20] Calculate the osmotic pressure in the polymer layer.

c. [20] Assuming that the exchange energy does not depend on temperature, calculate in what temperature range you expect water to be a good solvent for PEG.

d. [20] Calculate the expected sedimentation rate of single nanoparticles, temporarily neglecting back-diffusion. Do take into account that friction acts on the entire particle, including its attached polymer layer.

e. [20] Describe the concentration profile expected at sedimentation-diffusion equilibrium in good solvent at relatively low concentrations and calculate the characteristic length scale of the height dependence of the concentration.

Equations and constants for colloids & polymers

$\Pi V = nRT$ $\chi = w/(RT)$ $\chi_c = \left(1+\sqrt{r}\right)^2/2r$ $\phi_c = \left(1+\sqrt{r}\right)^{-1}$

$\Delta G = \left(n_1 + rn_2\right)RT\chi\phi_1\phi_2 + RT\left[n_1 \ln\phi_1 + n_2 \ln\phi_2\right]$ $\Pi = \frac{RT}{M_2}c_2 + \frac{RT}{\rho_2{}^2 v_1}\left(\frac{1}{2} - \chi\right)c_2{}^2$

$\chi_c = \left(1+\sqrt{r}\right)^2/2r$ $\phi_c = \left(1+\sqrt{r}\right)^{-1}$ $\mu_1 = \mu_1{}^0 + k_B T\left[\ln\left(1-\phi\right) + \left(1 - \frac{1}{r}\right)\phi + \chi\phi^2\right]$

$R = 8.314$ JK^{-1}mol^{-1} $g = 9.8$ m/s^2 $k_B \approx 1.38\times10^{-23}$ JK^{-1} 1 atm = 101325 Pa

$\mu = \mu^0 + k_B T\ln(c)$ $P = \rho gh$ $F = \Delta mg$ $E = \Delta mgh$ $F = 6\pi\eta au$

$\eta = (F/A)/(V/h)$ $D = k_B T/(6\pi\eta a)$ $V = (4/3)\pi a^3$ $f = f_0 \exp[-U/(kT)]$

Tentamen fysische chemie 3 / advanced physical chemistry, 08 March 2017

Answers to STD

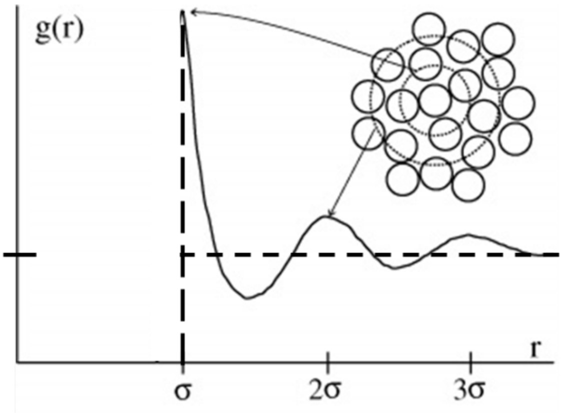
1a. In a 1D system, the length available for the centers of the rods is *L-Nσ* (removing the internal part of a particle does not change anything in the interactions but restricts the available length). This is to be the length used in the ideal gas equation of state : $p_{id} = \dfrac{NkT}{L - N\sigma}$. Dividing both numerator and denominator by L immediately leads to the p_{HC} in 1D.

1b. In 1D the definition of the second virial coefficient is given by $B = \int_0^\infty \left(1 - \mathrm{e}^{-\phi(x)/kT}\right)dx$ in complete analogy with the 3D case (NB here we do not multiply by ½ but restrict the integration to x>0 to avoid double counting). Use $\mathrm{e}^{-\phi(x)/kT} = \mathrm{e}^{\ln(1+A\mathrm{e}^{-x/a})} = 1 + A\mathrm{e}^{-x/a}$, so that:

$$B = \sigma + \int_\sigma^\infty \left(-A\mathrm{e}^{-x/a}\right)dx = \sigma + \left[Aa\mathrm{e}^{-x/a}\right]_{x=\sigma}^{\infty} = \sigma - Aa\mathrm{e}^{-\sigma/a}$$

1c. NO, in 3D and at high number densities, the available volume is NOT $(V - N4\upsilon_0)$ with υ_0 the volume of a particle. The situation is complicated because of the overlap of excluded volumes when more than 2 particles are close to each other and there is NO exact equation of state in 3D hard-core particles.

1d.



At low densities the dashed line jumps to 1, at high densities you observe a shell-like structure.

2.a. Calculate the molecular partition function starting at energy level n=0:

$$z = \sum_{n=0}^{\infty} e^{-nh\nu/kT} = \sum_{n=0}^{\infty}\left(e^{-h\nu/kT}\right)^n \overset{\text{geometric series}}{=} \frac{1}{1 - e^{-h\nu/kT}} = \left(1 - e^{-h\nu/kT}\right)^{-1}.$$

2b. The (normalized) Boltzmann distribution for n=0 is given by:

$P_{n=0} = e^{-(n=0)h\nu/kT}/z = e^{0}\left(1-e^{-h\nu/kT}\right) = 1-e^{-h\nu/kT}$ which gives **80% in the ground state** considering that:

$$\frac{h\nu}{kT} = \frac{hc\tilde{\nu}}{kT} = \frac{6.63\,10^{-34}\;3.00\,10^{8}\;32300}{1.38\,10^{-23}\;293} = 1.59$$

2c. Using $U = -\left(\frac{\partial \ln Z}{\partial 1/kT}\right)_{V,N}$ and substituting $Z = \frac{1}{N!}z^{N}$, (where z is given in a.) gives per mole:

$$U_{\text{molar}} = -N_A\left(\frac{\partial \ln z}{\partial 1/kT}\right)_V \overset{x=\frac{1}{kT}}{=} N_A\left(\frac{d\ln\left(1-e^{-h\nu x}\right)}{dx}\right)_V = N_A\frac{h\nu e^{-h\nu x}}{\left(1-e^{-h\nu x}\right)} = \frac{N_A h\nu}{\left(e^{h\nu/kT}-1\right)}$$

The change of this energy with temperature gives the molar heat capacity:

$$C_V = \frac{dU_{\text{molar}}}{dT} = N_A h\nu\frac{d\left(e^{h\nu/kT}-1\right)^{-1}}{dT} = -N_A h\nu\left(e^{h\nu/kT}-1\right)^{-2}e^{h\nu/kT}\,\frac{d(h\nu/kT)}{dT}$$

$$= (N_A k)\left(\frac{e^{h\nu/2kT}h\nu/kT}{e^{h\nu/kT}-1}\right)^{2} = R\left(\frac{h\nu/kT}{e^{h\nu/2kT}-e^{-h\nu/2kT}}\right)^{2}$$

2d. The first term in the denominator becomes dominant at small *T*, so that $C_V \approx R\left(\frac{h\nu/kT}{e^{h\nu/2kT}-0}\right)^{2} \approx R\left(h\nu/kT\right)^{2}e^{-h\nu/kT} \to 0 \quad \text{for} \quad T \to 0$, because of the exponential function going to zero (much faster than $T^{-2} \to \infty$).

Physically this means that the system cannot take up any heat at low temperature because all the molecules are in the ground state and remain so upon a small temperature change.

2e. With the expression given in c. and a quadratic dependence on ν we can write:

$$C_V \propto \int_{\nu=0}^{\nu_{\max}}\left(\frac{h\nu/kT}{e^{\frac{1}{2}h\nu/kT}-e^{-\frac{1}{2}h\nu/kT}}\right)^{2}\underbrace{\nu^{2}d\nu}_{\substack{\propto\text{ number}\\ \text{of modes}}}$$

Substituting $x = h\nu/kT$ so that $d\nu = (kT/h)dx$ gives:

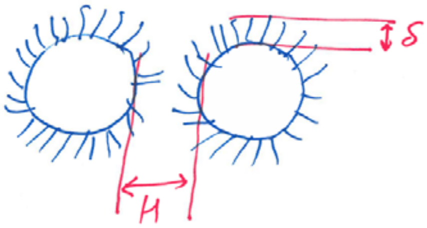
$$C_V \propto (kT/h)^{3}\int_{\nu=0}^{\frac{h\nu_{\max}}{kT}}\left(\frac{x}{e^{\frac{1}{2}x}-e^{-\frac{1}{2}x}}\right)^{2}x^{2}dx$$

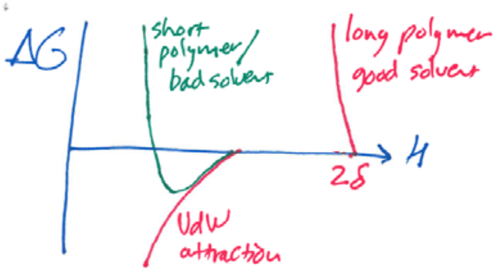
For small *T* the integral extends to large values of x (where the integrand goes to zero) and therefore just gives a numerical value (becoming independent of *T*), from which follows:

$$C_V \propto T^{3}$$

Answers to colloids & polymers

3.a. The thickness δ of the polymer layer on each particle determines the distance 2δ between the iron oxide surfaces at which the polymer layers start to overlap. In a good solvent, stability depends on whether the resulting sterical repulsion (enhanced osmotic pressure in the overlap volume) starts at sufficiently large distance that the shorter ranged attractions (Van der Waals, magnetic) do not yet dominate. As the polymers overlap, if the repulsion increases to many times the thermal energy kT, this is sufficient for colloidal stability. In bad solvent, attractions between the colloidal particles are no longer prevented from dominating at short interparticle distances.
The polymers even become attractive to each other, is the prediction from Flory-Huggins theory.





3.b. Enough information is given to use the Flory-Huggins formula:

$$\Pi = \frac{RT}{M_2} c_2 + \frac{RT}{\rho_2^{\,2} v_1}\left(\frac{1}{2} - \chi\right) c_2^{\,2}$$

Recognition of the meaning of the parameters and correct handling of units are essential here (a partially correct calculation will be evaluated with part of the maximum possible number of points):

$$\Pi = \frac{\left(8.314\ \mathrm{JK^{-1}mol^{-1}}\right)\left(300\ \mathrm{K}\right)}{\left(5.000\ \mathrm{kg/mol}\right)}\left(\frac{0.10\times10^{-3}\ \mathrm{kg}}{(0.01\ \mathrm{m})^3}\right)$$

$$+\frac{\left(8.314\ \mathrm{JK^{-1}mol^{-1}}\right)\left(300\ \mathrm{K}\right)}{\left(\frac{1.1\times10^{-3}\ \mathrm{kg}}{(0.01\ \mathrm{m})^3}\right)^2\left(\frac{18.0\times10^{-3}\ \mathrm{kg}}{\mathrm{mol}}\ \frac{(0.01\ \mathrm{m})^3}{1.0\times10^{-3}\ \mathrm{kg}}\right)}\left(\frac{1}{2}-0.43\right)\left(\frac{0.10\times10^{-3}\ \mathrm{kg}}{(0.01\ \mathrm{m})^3}\right)^2$$

The final outcome is:

$$\Pi = 0.50\times10^5\ \mathrm{Pa} + 0.80\times10^5\ \mathrm{Pa} = 1.30\times10^5\ \mathrm{Pa} = 1.28\ \mathrm{atm}$$

3.c. The solvent is good as long as $\chi < 1/2$. From $\chi = w/(RT)$, the exchange energy is $w = \chi RT = 0.43(8.314\ \mathrm{JK^{-1}mol^{-1}})(300\ \mathrm{K}) = 1073$ J/mol.

The temperature at which $\chi = ½$ is given by $T = w/(\chi R) = 1073\ \mathrm{J/mol} / (½\times 8.314\ \mathrm{JK^{-1}mol^{-1}}) = 258$ K, well below the normal freezing point of water.

From our assumptions we expect that solvent quality will increase at temperatures above the θ temperature. We thus expect that water is a good solvent for PEG across the entire stability range of liquid water (at 1 atm pressure), from freezing point to boiling point.

3.d. The force of gravity acts on the buoyant mass of the particles (the mass corrected for the mass of displaced solvent; a complicating detail is that the polymer does not match the density of the solvent and is present only at 0.1 g/cm^3 concentration in the layer—neglecting the buoyant mass of the layer leads to practically the same answer):

$$\Delta m = \frac{4}{3}\pi \cdot \left(5.0 \times 10^{-9}\ \mathrm{m}\right)^3 \left(5200 - 1000\ \frac{\mathrm{kg}}{\mathrm{m}^3}\right)$$

$$+ \frac{4}{3}\pi\left(8.0^3 - 5.0^3\right)\left(10^{-9}\ \mathrm{m}\right)^3 \left[\frac{100\ \mathrm{kg\,PEG} + \left(1\ \mathrm{m}^3 - \frac{100\ \mathrm{kg}}{1100\ \frac{\mathrm{kg}}{\mathrm{m}^3}}\right)\cdot 1000\ \frac{\mathrm{kg}}{\mathrm{m}^3}\ \mathrm{H_2O}}{\mathrm{m}^3} - 1000\ \frac{\mathrm{kg}}{\mathrm{m}^3}\right]$$

$$= 2.20 \times 10^{-21}\ \mathrm{kg} + 1.5 \times 10^{-23}\ \mathrm{kg} = 2.214 \times 10^{-21}\ \mathrm{kg}$$

The force of friction acts on the entire particle, whose radius includes the polymer layer. To calculate the sedimentation rate, we put the forces of gravity and friction equal to each other: $\Delta mg = 6\pi\eta a_H u$.

The sedimentation rate is then:

$$u = \frac{\Delta mg}{6\pi\eta a_H} = \frac{\left(2.21 \times 10^{-21}\ \mathrm{kg}\right)\left(9.8\ \mathrm{ms^{-2}}\right)}{6\pi\left(1.0 \times 10^{-3}\ \mathrm{Pa.s}\right)\left(8.0 \times 10^{-9}\ \mathrm{m}\right)} = 1.44 \times 10^{-10}\ \mathrm{m/s}$$

3.e. A barometric distribution is expected here, with the concentration c depending on concentration c_0 at height h=0 and on altitude h and buoyant mass Δm:

$c = c_0 \exp[-\Delta mgh/(kT)]$

The characteristic length scale is the height difference that causes the concentration to change by a factor of e, the barometric length:

$$L_g = \frac{kT}{\Delta mg} = \frac{\left(1.38 \times 10^{-23}\ \mathrm{J/K}\right)\left(300\ \mathrm{K}\right)}{\left(2.21 \times 10^{-21}\ \mathrm{kg}\right)\left(9.8\ \mathrm{ms^{-2}}\right)} = 0.19\ \mathrm{m} = 19\ \mathrm{cm}$$

where the buoyant mass was calculated in problem d (depending on the clarity of the answer, a wrong answer for Δm in problem d may not be counted wrong a second time in problem e).

Partial exam 2 Fysische Chemie 3/ Advanced Physical Chemistry, **12 April 2017**

Statistical Thermodynamics

1a. [20] The grand probability distribution is:

$$P_{n_0,n_1,n_2,\dots} = \Xi^{-1} e^{-E(n_0,n_1,n_2,\cdots)/kT} e^{\mu N/kT}.$$

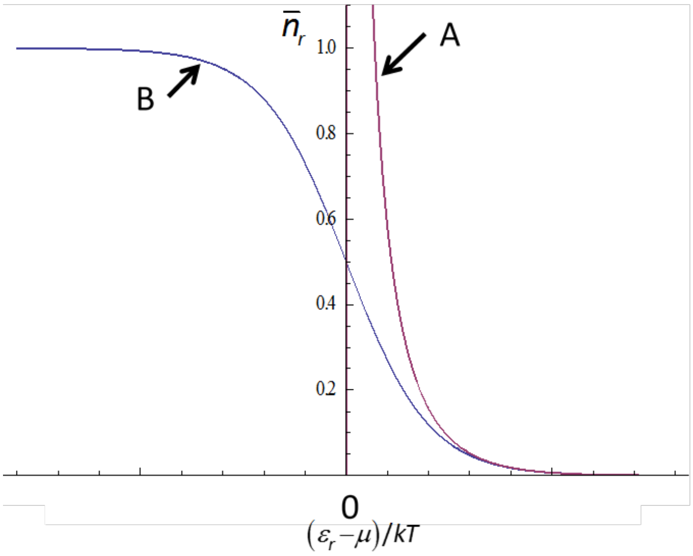
Use this to show that the probability to find n_r particles in a given state r is given by

$$p_r(n_r) = \frac{e^{-n_r(\varepsilon_r-\mu)/kT}}{\sum_n e^{-n(\varepsilon_r-\mu)/kT}}.$$

1b. [20] Starting from the probability above, show that the average occupation number of particles in a single-particle state with energy ε_r in Fermi-Dirac (FD) statistics is given by

$$\bar{n}_r = \frac{1}{\exp\left((\varepsilon_r-\mu)/kT\right)+1}.$$

1c. [10] Which of the following curves corresponds to FD statistics? Indicate why you say so and explain the crucial difference with the other curve which corresponds to Bose-Einstein statistics.



1d. [10] Under which circumstances does the FD distribution reduce to a Boltzmann distribution? How does the mean distance between the particles compare to the thermal wavelength Λ in that case?

1e. [20] Give a value for the thermal wavelength of electrons at room temperature and explain why this implies that occupation numbers of electron energy levels in a metal very suddenly drop to 0 (at a value of the energy called the Fermi energy ε_F).

1f. [20] Given that the density of states $\omega(\varepsilon)$ is proportional to $\sqrt{\varepsilon}$, express the average energy $\overline{\varepsilon}$ of electrons in terms of their Fermi energy.

Equations and constants for statistical thermodynamics

Taylor series: exponent: $e^x \approx 1+x+\frac{x^2}{2}$ x<<1

logarithm: $\ln(1+x) \approx x-\frac{x^2}{2}$ x<<1

Geometric series: $\frac{1}{1-x}=1+x+x^2+x^3+\ldots$ x<1.

Standard integrals $\int_0^y x^n dx=\frac{y^{n+1}}{n+1}$

Stirling approximation: $\ln N! \approx N\ln N - N$ (N>>1)

$$A=U-TS=-kT\ln Z$$

$$\Lambda \equiv \frac{h}{\sqrt{2\pi mkT}}$$

$$\Xi=\sum_{N=0}^{\infty} e^{N\mu/kT} Z(N,T,V); \qquad <N>=kT\left(\frac{\partial \ln \Xi}{\partial \mu}\right)_{T,V}$$

Independent particles

Distinguishable: $Z=z^N$

Indistinguishable: $Z=z^N/N!$

$$z=\sum_i e^{-\varepsilon_i/kT}$$

Fundamental constants

Planck's constant *h* = 6.63 10^{-34} J s

Boltzmann's constant *k* =1.38 10^{-23} J K^{-1}

Speed of light *c* = 3.00 10^{8} m s^{-1}

Electron mass m_e = 9.11 10^{-31} kg

Solutions *Partial exam 2 FC3/ APC,* **12 April 2017** *Statistical Thermodynamics*

1a. [20] Substitute $E(n_0,n_1,n_2,\cdots)=\sum_r n_r\varepsilon_r$ and $N=\sum_r n_r$ into the expression for $P_{n_0,n_1,n_2,\dots}$ and arrive at $P_{n_0,n_1,n_2,\dots}=\Xi^{-1}\prod_r e^{-n_r(\varepsilon_r-\mu)/kT}$. Ξ is the normalizing factor which sums the numerator over all (in the grand canonical case, independent) values of each n_r, which means $\Xi=\prod_r\sum_n e^{-n(\varepsilon_r-\mu)/kT}$ This implies $P_{n_0,n_1,n_2,\dots}$ is made up of the product of independent one-state probabilities: $p_r(n_r)=\dfrac{e^{-n_r(\varepsilon_r-\mu)/kT}}{\sum_n e^{-n(\varepsilon_r-\mu)/kT}}$.

1b. [20]

Use the definition of $\bar{n}_r=\sum_{n_r} n_r p_r(n_r)=\dfrac{\sum_n ne^{-n(\varepsilon_r-\mu)/kT}}{\sum_n e^{-n(\varepsilon_r-\mu)/kT}}$ and realise that for FD statistics *n* only takes the values 0 and 1, so that: $\bar{n}_r=\dfrac{0+1e^{-(\varepsilon_r-\mu)/kT}}{e^0+e^{-(\varepsilon_r-\mu)/kT}}=\dfrac{1}{e^{(\varepsilon_r-\mu)/kT}+1}$. Alternatively use the method of Windom pp. 148-149.

1c. [10] **B** corresponds to FD statistics since the formula calculated in **b** levels off at $\dfrac{1}{0+1}=1$ at the left (for large values of μ). The crucial difference with curve **A** which corresponds to Bose-Einstein statistics is that the latter goes to infinity if $\mu\to(-)0$ (the difference is due to the fact that the number of particles per energy state is limited to 1 in FD statistics but unlimited in BE statistics).

1d. [10] Under the condition that $e^{(\varepsilon_r-\mu)/kT}$ is large (implying $e^{\mu/kT}$ is small) the FD distribution reduces to a Boltzmann distribution (where curves **A** and **B** merge). The mean distance between the particles is much larger than the thermal wavelength Λ in that case.

1e. [20] The thermal wavelength of electrons at room temperature can be estimated as:

$$\Lambda\equiv\frac{h}{\sqrt{2\pi mkT}}=\frac{6.63\;10^{-34}\,\mathrm{J\;s}}{\sqrt{2\pi\;9.11\;10^{-31}\mathrm{kg}\;1.38\;10^{-23}\mathrm{J\;K^{-1}}\;298\;\mathrm{K}}}\approx 4\;\mathrm{nm}.$$

Since the density of electrons in a metal is much higher than 1/(4 nm)^3 electrons obey FD statistics. This means that they fill up the energy states completely until an energy value ε where $\varepsilon=\mu\,(=\varepsilon_F)$. At even higher ε the occupation $\dfrac{1}{e^{(\varepsilon-\mu)/kT}+1}$ suddenly drops to 0 (as seen from curve **B**).

1f. [20] Since the density of states $\omega(\varepsilon)$ is proportional to $\sqrt{\varepsilon}$, the average energy is:

$$\bar{\varepsilon}=\int_0^{\varepsilon_F}\varepsilon\omega(\varepsilon)d\varepsilon\Big/\int_0^{\varepsilon_F}\omega(\varepsilon)d\varepsilon\overset{\omega(\varepsilon)=c\sqrt{\varepsilon}}{=}\int_0^{\varepsilon_F}\varepsilon^{3/2}d\varepsilon\Big/\int_0^{\varepsilon_F}\varepsilon^{1/2}d\varepsilon=\frac{2}{5}\varepsilon_F^{5/2}\Big/\frac{2}{3}\varepsilon_F^{5/2}=\frac{3}{5}\varepsilon_F$$

Fysische chemie 3 / advanced physical chemistry
April 2017
grensvlakken / interfaces

Problem 1 [1+1+1=3 points]

The variation of the Helmholtz free energy of a bulk phase *b* is written as

$$dA^b = -S^b dT + \sum_i \mu_i dn_i^b - PdV^b \qquad (1)$$

while that for a surface σ is

$$dA^\sigma = -S^\sigma dT + \sum_i \mu_i dn_i^\sigma + \gamma\, d\sigma \qquad (2)$$

- Why some quantities (e.g., S^σ or S^b) have superscript σ or *b* while some other (e.g., *T*) do not?
- How the number of molecules n_i^σ at the interface is defined for solutions?
- Explain the difference in the sign of the last term in Eqs. (1) and (2) [$-PdV^b$ versus $+\gamma\, d\sigma$].

Problem 2 [2+2=4 points]

The table below gives the dependence of the critical micelle concentration (c.m.c.) of sodium dodecylsulphate on the concentration of sodium chloride added to the solution.

[NaCl] [mol/dm^3]	0	0.01	0.03	0.3
c.m.c. [mmol/dm^3]	8.1	5.6	3.1	0.7

- Calculate the change of the standard chemical potential $\Delta\mu$ during micelle formation for these four cases.
- Explain the change of c.m.c. Is it $(\Delta\mu)_{\text{head}}$ or $(\Delta\mu)_{\text{tail}}$ that depends on the salt concentration?

Problem 3 [2+1=3 points]

- Describe what happens when a drop of hexanol $H(CH_2)_6OH$ (h) is applied to a clean water (w) / air (a) interface, given γ_{wh} = 6.8 mN/m, γ_{ha} = 24.8 mN/m, γ_{wa} = 72.8 mN/m for a clean water surface and γ_{wa} = 28.5 mN/m for a saturated hexanol solution in water.
- Using Gibbs adsorption equation explain why the water/air interfacial tension reduces when a small amount of hexanol dissolves in water?

Possibly useful formulas

The Gibbs adsorption equation $d\gamma = -\sum_{i>1} \Gamma_i^{(1)} d\mu_i$.

Chemical potential of a solute in a dilute solution $\mu_i = \mu_i^\circ + RT \ln c_i$

Critical micelle concentration $x_{\text{cmc}} = \exp\left(\frac{\mu_n - n\mu_1}{(n-1)RT} \right) = \exp\left(\frac{\Delta\mu}{RT} \right)$.

Young's law $\gamma_{SG} = \gamma_{SL} + \gamma_{LG} \cos\theta$

Adsorption energy at an oil-water interface $\Delta U_{\text{ad}} = -\frac{\pi}{4} d^2 \gamma_{\text{ow}} \left(1 \mp \cos\theta\right)^2$ where d the particle diameter, θ the contact angle and γ_{ow} the oil-water surface tension.

Area of a circle with diameter D: $A_{\text{circle}} = (\pi / 4) D^2$

Surface area of a sphere with diameter D: $A_{\text{sphere}} = \pi D^2$

Volume of a sphere $V_{\text{sphere}} = (\pi / 6) D^3$

Avogadro number N_{av} = 6 10^{23} mol^{-1}.

Boltzmann constant $k_B = 1.38 \times 10^{-23}$ J/K.

Ideal gas constant R = $k_B N_{\text{av}}$ = 8.31 J mol^{-1} K^{-1}.

ANSWERS

Problem 1

- Some quantities (e.g., S^σ or S^b) represent the contribution of the bulk phase b or of the interface σ to the that of the whole system (e.g., the total entropy). The quantities as temperature T, on the other hand, have to be the same in the whole system at equilibrium.
- The number of molecules n_i^σ at the interface is defined for solutions with respect to the Gibbs dividing plane. By definition, the surface excess number of the solvent molecules is set to zero ($n_1^\sigma = 0$). Solutes can adsorb positively ($n_i^\sigma > 0$) or negatively ($n_i^\sigma < 0$) at the interface.
- To shrink a bulk system ($dV < 0$) one has to do work against the internal pressure P. The free energy of the system will *always* increase for $dV < 0$;
  P cannot be negative.
  To create more surface ($d\sigma > 0$), one also has to do work as the surface costs energy. Thus, the free energy of the system will *always* increase for $d\sigma > 0$;
  γ cannot be negative.

In other words, any thermodynamic system likes to expand and to reduce the interface area. More volume is “good”; more surface is “bad”.

Problem 2

- We need to calculate the corresponding x_{cmc} relative to water (55 mol/dm^3), which can then be used to calculate $\Delta\mu = RT \ln x_{\mathrm{cmc}}$. Numerical data are given in the table below.

[NaCl] [mol/dm^3]	0	0.01	0.03	0.3
c.m.c. [mmol/dm^3]	8.1	5.6	3.1	0.7
x_{cmc}	1.5 10^{-4}	1.0 10^{-4}	5.6 10^{-5}	1.3 10^{-5}
ln x_{cmc}	-8.82	-9.19	-9.78	-11.27
$\Delta\mu$ [kJ/mol]	-21.5	-22.4	-23.8	-27.4

- Salt ions are able to screen Coulomb repulsion between negatively charged head groups. This makes $(\Delta\mu)_{\mathrm{head}}$ smaller (less positive).

Problem 3

- A droplet of hexanol will initially spread over the water surface since it is energetically favorable to replace the water/air interface (γ_{wa} = 72.8 mN/m) with water/hexanol and hexanol/air interfaces ($\gamma_{\mathrm{wh}} + \gamma_{\mathrm{ha}} = 6.8 + 24.8 = 31.6 < 72.8$ mN/m). However, in equilibrium hexanol will partially dissolve in water. This will significantly reduce the water/air interfacial tension and the spreading coefficient will become negative: $S = 28.5 - (24.8 + 6.8) = -3.1$ mN/m. The droplet will therefore stay on the water surface in a form of a thin “lens”.
- Water and hexanol do not mix and only a small amount of hexanol can be dissolved in water. This is an indication that the interactions between hexanol and water molecules are not favorable. Some of the hexanol molecules dissolved in water apparently find a solution at the interface. The significant reduction of the interfacial tension is a signature of strong adsorption. It is not surprising since the hexanol molecules have a hydrophilic OH group on one side and a hydrophobic tail on the other side. We can therefore expect positive adsorption of hexanol, $\Gamma^{(1)}_{\mathrm{hexanol}} > 0$. According to the Gibbs adsorption equation, hexanol can therefore reduce surface tension γ.

Course description for SK-BFYC3 / SK-MPC3 "Fysische Chemie 3" / “Advanced Physical Chemistry” in 2017

Content p.

Course name and code in Osiris	bachelor students: Fysische Chemie 3 SK-BFYC3 master students: Advanced Physical Chemistry SK-MPC3
Coordinator	Dr. Ben Erné B.H.Erne@uu.nl
Teachers	"*statistical thermodynamics*" lecturer: Dr. Gert Jan Vroege G.J.Vroege@uu.nl problem classes: Faranaaz Rogier, MSc F.Rogier@uu.nl “*interfaces”* Dr. Andrei Petoukhov A.Petoukhov@uu.nl "*colloids and polymers”* Dr. Ben Erné B.H.Erne@uu.nl
ECTS credits	7.5 EC
Level	3
Block	3
Time slot	Wednesdays 15:15-19:00, Fridays 9:00-12:45, see page 3 for details
Format	Lectures, problem classes, self-study
Examination	Two partial exams, see pages 3 and 4 for details
Course materials	(1) The following e-book, to be downloaded for free via the UU library: *B. Widom, “Statistical Mechanics” (Cambridge Univ. Press, 2002)*. The following link should work: http://aleph.library.uu.nl/F?func=direct&doc_number=002806329 In the first “full text” link (to Cambridge Univ. press), you can choose “select all” followed by “download pdf (zip)” or other options to download the book. The book can also be found via: https://www.uu.nl/en/university-library Under “quick links” select “catalogue” and search for “Widom statistical mechanics” (option “search in all fields”). Feel free to buy a paper copy (€ 50 at bol.com, 1-2 months delivery time). (2) The lecture notes for *Interfaces*, edition 2017: Copies will be on sale (about € 4) via Proton, the association for chemistry students, offices on the 2nd floor of the Koningsberger building. (3) The following book will be on loan for free: *D. H. Everett, "Basic Principles of Colloid Science" (Royal Society of Chemistry, 1988)*. Feel free to buy a paper copy (€ 25 at bol.com, 1-2 weeks delivery time). (4) The manual/lecture notes for *Colloids*, edition 2017: Electronic version: see BlackBoard. Paper version: provided for free at the first lecture on colloids. (5) Blackboard: http://uu.blackboard.com/: (a) course description (the present document) (b) lectures notes, manuals, and other electronic texts (c) powerpoint slides (d) past exams

Required background

Participation in this course implies that you have background knowledge on the following topics:

- Classical thermodynamics (state functions, chemical potential, Gibbs-Duhem, Maxwell relations…).
- Basic concepts of statistical thermodynamics (Boltzmann distribution, thermodynamic ensembles, partition function, Nernst heat theorem).
- Basic mathematical skills (integration, differentiation).
- Basic concepts in physical chemistry (Van der Waals fluids, regular solutions, interfacial tension, electrical screening in electrolyte solutions).

Our local Chemistry students have acquired this knowledge by following the 2nd year bachelor course on physical chemistry (SK-BFYCH, “Fysische Chemie 2”).

If you are in doubt whether you have the proper background knowledge, feel free to contact the course coordinator, who may for instance show you the course materials. If you wish to meet the coordinator in person, please send an e-mail that indicates several options of dates and times when you are available.

Introduction to the content of the course

This “advanced level” course builds on the aforementioned background knowledge, going into further depth on topics of statistical thermodynamics and interfacial physical chemistry and providing a first introduction to the physical chemistry of colloids and polymers.

The lectures on statistical thermodynamics deal with nonideal gases, liquids, solids, and quantum gasses (Fermi-Dirac and Bose-Einstein statistics). The lectures on interfaces discuss wetting, adsorption, surface-active substances, charged interfaces, and experimental methods for studying interfaces. The lectures on colloids and polymers give an introduction to basic colloidal concepts (colloidal synthesis, Brownian motion, diffusion, sedimentation, interaction between colloidal particles, colloidal stability) and Flory-Huggins theory of polymer solutions.

Learning objectives

At the end of the course, students will be better equipped for the independent study and application of scientific literature on statistical thermodynamics, interfaces, polymers, and colloids. This course also forms a bridge towards even more specialized master courses, such as “Colloid Science” (SK-MCS) and “Soft Condensed Matter Theory” (NS-T453M).

Planning of the teaching sessions

- Each week, there will be two sessions of 4 hours, on Wednesdays starting at 15:15 and on Fridays starting at 9:00.
- Each session of 4 hours will start with 2 hours of lecture, after which there will be 2 hours to work on practice problems in the presence of a teacher.
- Students are recommended to attend all lectures to study the reading materials, and not to fall behind with their work on the practice problems.
- There are two blocks of 4 weeks, each followed by a week in which an examination is scheduled, pertaining to the subjects that have been treated in the preceding 4 weeks. 2.5 hours are scheduled for each exam.

The table below provides the schedule of the sessions, with topics Thermo1…Thermo6, Colloids1…Colloids4, and Interfaces1…Interfaces5. The rooms and times are subject to change in Osiris. DdW = David de Wied building; BBG = Buys Ballot building; Educ = Educatorium building.

Week	Date, time	Room	Topics
6	Wed. Feb. 8, 15:15-19:00	DdW 1.30	**Thermo1:** Review of statistical thermodynamics and ideal gases (Widom: chapters 1, 2, 5)
	Friday Feb. 10, 9:00-12:45	BBG 061	**Colloids1**: Colloids: what they are and how they are made (Everett: chapters 1-5, 9, 10)
7	Wed. Feb. 15, 15:15-19:00	DdW 1.30	**Thermo2:** Solids (Widom: chapter 4)
	Friday Feb. 17, 9:00-12:45	BBG 061	**Colloids2**: Colloids in motion, field-induced and Brownian (Everett: chapters 6-8)
8	Wed. Feb 22, 15:15-19:00	DdW 1.30	**Thermo3:** Non-ideal gases (Widom: chapter 6)
	Friday Feb. 24, 9:00-12:45	BBG 061	**Colloids3**: Flory-Huggins theory of single polymer solutions (lecture notes in the manual for the Colloids part of the course)
9	Wed. March 1, 15:15-19:00	DdW 1.30	**Thermo4:** Liquids (Widom: chapter 7.1 and 7.2)
	Friday March 3, 9:00-12:45	BBG 061	**Colloids4**: Polymer effects on colloidal stability (Everett: pages 45-50, 137-141, 220-221, Ch. 9)
10	Wed. March 8, 17:00-19:30	Educ Beta	**Partial exam 1**, on topics **Thermo1-Thermo4** and **Colloids1-Colloids4**
11	Wed. March 15, 15:15-19:00	DdW 1.30	**Thermo5:** quantum gases (Widom: chapter 8)
	Friday March 17, 9:00-12:45	BBG 061	**Interfaces1:** Introduction, Gibbs dividing plane & Gibbs adsorption equation
12	Wed. March 22, 15:15-19:00	**BBG061; DdW1.30**	**Thermo6:** quantum gases – continued (Widom: chapter 8 – continued)
	Friday March 24, 9:00-12:45	BBG 061	**Interfaces2:** Soaps and Debye theory of micelle formation
13	Wed. March 29, 15:15-19:00	DdW 1.30	**Interfaces3:** Wetting
	Friday March 31, 9:00-12:45	BBG 061	**Interfaces4:** Nanoparticles adsorption, Pickering emulsions, effects of shape, gravity and curvature
14	Wed. April 5, 15:15-19:00	DdW 1.30	**Interfaces5:** Experimental approaches, short summary of the Interfaces part
	Friday April 7, 9:00-12:45	BBG 061	*Extra time slot, in case one of the earlier sessions cannot take place.*
15	Wed. April 12, 17:00-19:30	Educ Theatron	**Partial exam 2**, on topics **Thermo5-Thermo6** and **Interfaces1-Interfaces5**

Friday July 7, 13:30-16:00 in BBG 001	Retake exam, for those who did not pass one or both of the partial exams. See page 4 and be sure to check Osiris, as retake exams are often rescheduled.

Examination

The final grade of the course will be determined as follows, giving equal weight to each of the three general subjects:

Grade[Final] = 1/3 Grade[Thermo] + 1/3 Grade[Colloids] + 1/3 Grade[Interfaces]

where Grade[Final] = the final grade
Grade[Thermo] = the grade for statistical thermodynamics, 2/3 of which is determined by the questions on Thermo1-Thermo4 at Partial exam 1, and 1/3 of which is determined by the questions on Thermo5-Thermo6 at Partial exam 2.
Grade[Colloids] = the grade for the Colloids1-Colloids4 questions (Partial exam 1)
Grade[Interfaces] = the grade for the Interfaces1-Interfaces5 questions (Partial exam 2)

To pass the course, the final grade must be at least 5.5. Final grades of 5.5 to 5.9 will be rounded off to 6.0, whereas grades from 5.0 to 5.4 are rounded off to 5.0. In the latter case, the course has not been passed. Students with at least a 4.0 and at most 5.4 (before it is rounded off to 5) are allowed to participate in the retake exam. On the retake exam, students have to do at least all the questions that pertain to the subjects for which the grade was below 5.0, the grades Grade[Thermo], Grade[Colloids], and Grade[Interfaces]; students are then also allowed to do the questions pertaining to subjects for which they received a grade of 5.0 or higher. If the final grade is below 4.0, the student is not allowed to take the retake exam and is invited to follow the course again one year later. If the final grade is 5.5 (which is rounded off to 6) or higher, the student is not allowed to participate in the retake exam either, since the Science Faculty forbids retake exams for students who have a passing grade (exceptions are possible via the board of examination and the faculty's student advisor). The retake exam is 2.5 hours and consists of three parts, pertaining to each of the three parts of the course.

The examinations are not open book exams. The use of books, notes, mobile phones, or other sources of information of any type, paper or electronic, constitute fraud. However, it is required to bring a calculator to the exams, provided that no information is stored in its memory.

Students who did not get a passing grade for one or more of the three main general subjects are invited to make an appointment with the corresponding teachers via e-mail. Please provide several possible dates and times for a meeting, from which the teacher can choose.