Colloids: phase behaviour and self-assembly – Problems Day 1

Exercise: Colloids in external fields

Given that the barometric distribution of colloids as a function of height is described by the Boltzmann distribution

$$\rho = \rho_0 \ e^{-h/l_g}$$

with

$$l_g = \frac{kT}{m_b g}$$

Where ρ is the particle density is the particle density at a height *h* above a reference level with ρ_0.Here $m_b = m - m'$ is the buoyant mass, with *m'* the mass of the fluid displaced by a particle of mass *m.*

a) Show that for colloidal particles dispersed in a liquid, the equilibrium number of particles, *N*, is given by:

$$N = N_0 \exp\left[-\frac{(m-m')g(h-h_0)}{k_b T}\right]$$

Where N_0 is the number of particles at height h_0.

Answer:

Rewrite density into number density

$\rho = \rho_0 \, e^{-h/l_g} \rightarrow N/V = N_0/V \exp\left[-\frac{m_b g \Delta h}{kT}\right] = N_0/V \exp\left[-\frac{(m-m')g\Delta h}{kT}\right]$

Multiple both sides with V

$$N = N_0 \exp\left[-\frac{(m-m')g\Delta h}{kT}\right]$$

Put in the height difference $\Delta h = h - h_0$.

$$N = N_0 \exp\left[-\frac{(m-m')g(h-h_0)}{kT}\right]$$

b) In a tube of height 10 cm spherical colloids with a radius R = 10 nm are dispersed in water (ρ_w = 1.0 g cm^{-3}). The particles have a density of ρ_p = 1.2 g cm^{-3}. What is the ratio between the particle concentration at the top h = 10 cm and the bottom h_0 = 0 cm, after equilibrium has established. Assume the temperature is T = 20 °C.

Answer:

Ratio = $\frac{N}{N_0} = \exp\left[-\frac{(m-m')g(h-h_0)}{kT}\right] = \exp\left[-\frac{V(\rho_p-\rho_w)g(h-h_0)}{kT}\right]$

$$\frac{N}{N_0} = \exp\left[-\frac{4\pi(10^{-9}\mathrm{m})^3 \cdot (1200 - 1000\mathrm{kg/m^3}) \cdot 9.8\mathrm{m/s^2} \cdot (0.1\mathrm{m})}{3 \cdot 4.1 \cdot 10^{-21}}\right] = 0{,}819$$

c) Compute l_g for particles with R = 90 nm using the same densities as above and assess whether the particles will settle in a sample cell of height 10 cm, 1 cm and 100 um.

Answer:

$$l_g = \frac{kT}{m_b g} = \frac{4.1 \cdot 10^{-21}}{6.11 \cdot 10^{-19} \cdot 9.8} = 6{,}85\ \cdot 10^{-4}\mathrm{m}$$

10 cm – yes, 1 cm – yes, and 100 um – no. Thermal motion is high enough to keep particles dispersed over full height of sample cell.

d) Svedverg (1928) gives the following table for the sedimentation equilibrium of a gold sol under gravity.

Height (um)	Number of particles	Height (um)	Number of particles
0	889	600	217
100	692	700	185
200	572	800	152
300	426	900	125
400	357	1000	108
500	253	1100	78

Assume the particles have a radius *R* = 21 nm and density ρ_p = 19.3 g cm^{-3} and the temperature is T = 20 °C. Estimate the Boltzmann constant, k_b, from the equation derived in (a) and then calculate Avogadro's number, N_A, assuming R = 8.31 J K^{-1} mol^{-1}.

Answer:

$$N = N_0 \exp\left[-\frac{(m - m')g(h - h_0)}{kT}\right]$$

$$k = (-\,(m - m')g(h - h_0))/(\ln\left(\frac{N}{N_0}\right)T)$$

For sanity check the units of *k* to be correct!

Determine k for each height:

Height (um)	k	Height (um)	k
0	-	600	1,01024E-23
100	9,47826E-24	700	1,05883E-23

200	1,07693E-23	800	1,07548E-23
300	9,68281E-24	900	1,0893E-23
400	1,041E-23	1000	1,1264E-23
500	9,44695E-24	1100	1,07334E-23

Get the average:

$$\langle k \rangle = 1{,}037 \cdot 10^{-23} \text{J K}^{-1}$$

Calculate N_{av}

$$N_{av} = \frac{R}{k} = \frac{8.31 \text{ J K}^{-1}\text{mol}^{-1}}{1{,}037 \cdot 10^{-23} \text{J K}^{-1}} = 8{,}01 \cdot 10^{-23} \text{mol}^{-1}$$

e) Repeat the calculation with a radius of 22 nm and note how sensitive the answer is to this variable.

Answer:

$$N_{av} = \frac{R}{k} = \frac{8.31 \text{ J K}^{-1}\text{mol}^{-1}}{1{,}19 \cdot 10^{-23} \text{J K}^{-1}} = 6{,}97 \cdot 10^{-23} \text{mol}^{-1}$$

Very sensitive to the exact value of R!