EXERCISES TO THE LECTURE POLYMER REACTION & COLLOID ENGINEERING

SERIES 1

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Stability of a Colloidal Dispersion under Reaction Limited Cluster Aggregation (RLCA)

In order to examine the stability of a polystyrene latex you obtained from an emulsion polymerization process, you monitored the latex for one day and recorded the evolution of the total number of particules in time. Starting from the information of this experiment, estimate the so-called Fuch's stability ratio W which is defined by equation (7.34) in the lecture notes. and thus is a measure of the ratio between the aggregation rate constant under totally unstable conditions (i.e. diffusion limited aggregation) and the real one. From previous batches you know that W is around 0.5×10^5. To be able to calculate the aggregation rate constant you assume that it is sufficient to track particles up to dimensionless mass of $i = 100$. The latex solution contains 7.5 mM of NaCl. The Fuchs' Stability ratio can be computed according to the DLVO theory by estimating the total potential energy of interaction given by the sum of the attractive and repulsive contributions defined as follows (with $l = r/a$):

$$V_A = -\frac{A_{\mathrm{H}}}{6}\left[\frac{2}{l^2-4} + \frac{2}{l^2} + \ln\left(1 - \frac{4}{l^2}\right)\right]$$

$$V_R = \frac{4\pi\epsilon_0\epsilon_r a\psi_0^2}{l}\ln\left[1 + \exp\left(-\kappa a\left(l-2\right)\right)\right]$$

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a) Start with writing a subfunction that provides the necessary aggregation rate constants for all possible aggregation events for DLCA. Plot the rate constant as a function of the dimensionless mass. To get a three dimensional surface, use the MATLAB command *mesh()*.

b) With the help of a) write your ODE-file for cluster formation up to dimensionless mass $i = 100$.

c) You know that your system is limited by the aggregation. Modify your function written in a) for RLCA. Starting from $W = 0.5 \times 10^5$, try to find W that matches the simulation results with the experimental data. Use the MATLAB command *nlinfit()* to minimize the residual sum of squares (*Hint:* test your program with $i = 10$).

d) Compute the Fuchs stability ratio from equation (7.26). Compare with the result of your fitting.

e) Simulate the particle size distribution at three different times ($1hr$, $4hr$, $8hr$). Can your model be used to predict further coagulation of the latex? Where are the limits?

Additional Information:

$$
\begin{array}{lcll}
T & = & 25 & ^\circ\mathrm{C} \\
\eta & = & 0.89 \times 10^{-3} & \mathrm{Pa\ s} \\
N_\mathrm{p}^0 & = & 1.4 \times 10^{17} & \mathrm{m}^{-3} \\
A_\mathrm{H} & = & 1.5 \times 10^{-20} & \mathrm{J} \\
\epsilon_0 & = & 8.85 \times 10^{-12} & \mathrm{F\ m}^{-1} \\
\epsilon_r & = & 80.1 & - \\
a & = & 100 \times 10^{-9} & \mathrm{m} \\
\psi_0 & = & 25 & \mathrm{mV} \\
d_\mathrm{f} & = & 2.1 & -
\end{array}
$$

Experimental Data:

Time h	N/N_p^0
2	0.89
4	0.79
6	0.67
8	0.59
10	0.51
12	0.46
14	0.43
16	0.35
18	0.32
20	0.28
22	0.27
24	0.21