DLVO theory of colloidal aggregation

Miguel A. Caro

Department of Electrical Engineering and Automation, Aalto University, Finland

Aalto University
4 May 2022

turbogap.fi **miguelcaro.org**

Fundamentals of DLVO theory

Derjaguin
Landau
Verwey
Overbeek

Fundamentals of DLVO theory

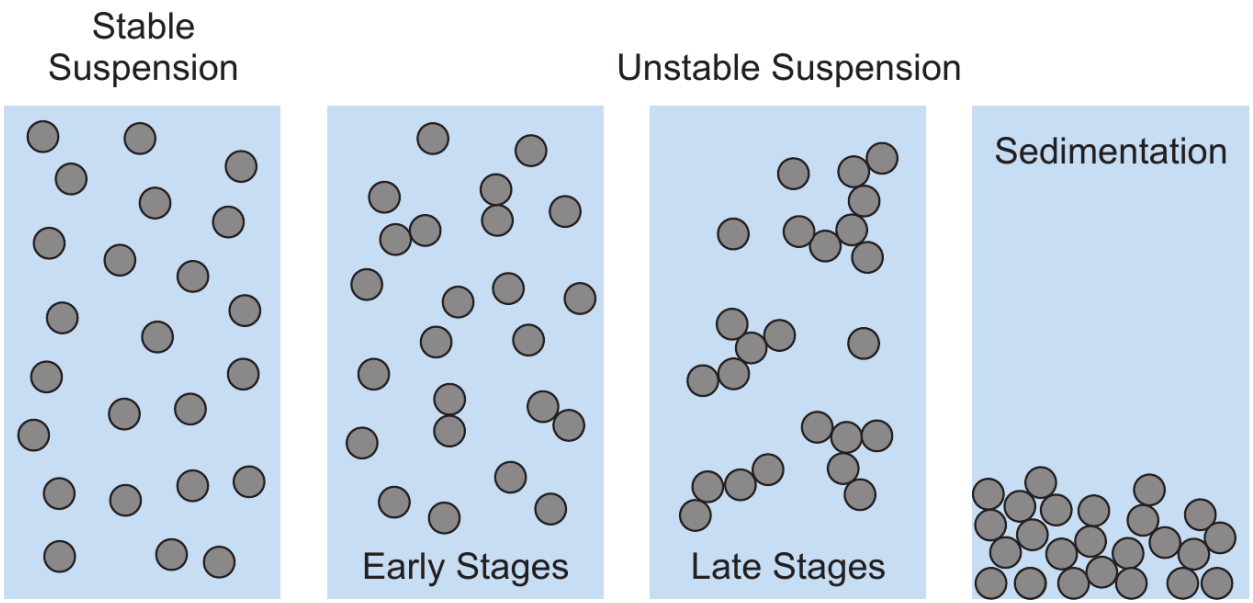
Derjaguin
Landau
Verwey
Overbeek

DLVO theory aims to make quantitative predictions for the aggregation behavior of a colloidal suspension

Fundamentals of DLVO theory

Derjaguin
Landau
Verwey
Overbeek

DLVO theory aims to make quantitative predictions for the aggregation behavior of a colloidal suspension



Credit: Trefalt and Borkovec

Fundamentals of DLVO theory

You will learn:

Fundamentals of DLVO theory

You will learn:

- What is the scope of DLVO theory

Fundamentals of DLVO theory

You will learn:

- What is the scope of DLVO theory
- What are the approximations and basic equations

Fundamentals of DLVO theory

You will learn:

- What is the scope of DLVO theory
- What are the approximations and basic equations
- We will look at homoaggregation (interaction between same type of particles)

Fundamentals of DLVO theory

You will learn:

- What is the scope of DLVO theory
- What are the approximations and basic equations
- We will look at homoaggregation (interaction between same type of particles)
- We will do a computational experiment to examine the connection between DLVO and atomic-scale interactions

Fundamentals of DLVO theory

You will learn:

- What is the scope of DLVO theory
- What are the approximations and basic equations
- We will look at homoaggregation (interaction between same type of particles)
- We will do a computational experiment to examine the connection between DLVO and atomic-scale interactions

You will need:

Fundamentals of DLVO theory

You will learn:

- What is the scope of DLVO theory
- What are the approximations and basic equations
- We will look at homoaggregation (interaction between same type of particles)
- We will do a computational experiment to examine the connection between DLVO and atomic-scale interactions

You will need:

- Basic understanding of electrostatics and classical mechanics

Fundamentals of DLVO theory

You will learn:

- What is the scope of DLVO theory
- What are the approximations and basic equations
- We will look at homoaggregation (interaction between same type of particles)
- We will do a computational experiment to examine the connection between DLVO and atomic-scale interactions

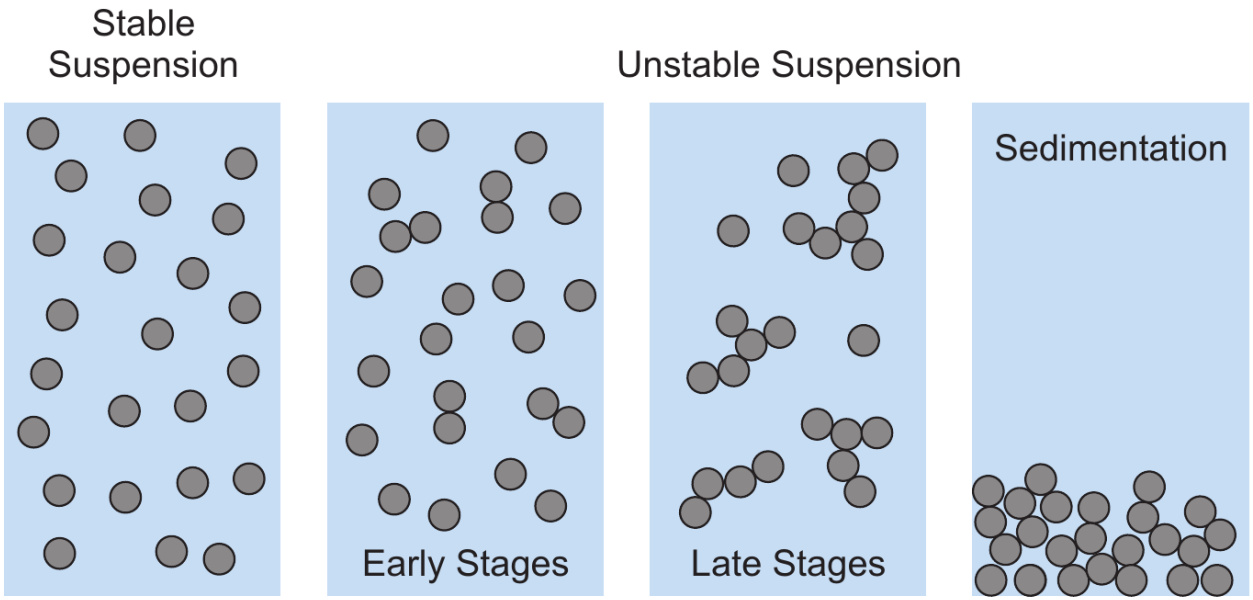
You will need:

- Basic understanding of electrostatics and classical mechanics
- Basic familiarity running a computer program from the command line

Fundamentals of DLVO theory

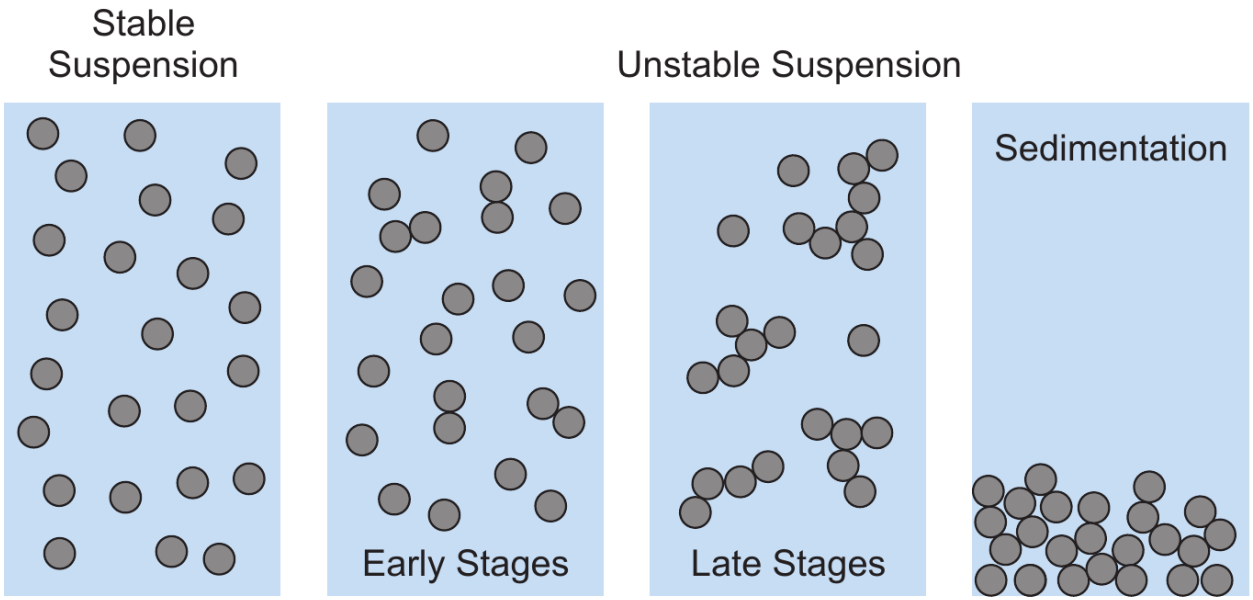
Online resources are available from Github (slides and codes):
`https://github.com/mcaroba/dlvo`

Fundamentals of DLVO theory



Credit: Trefalt and Borkovec

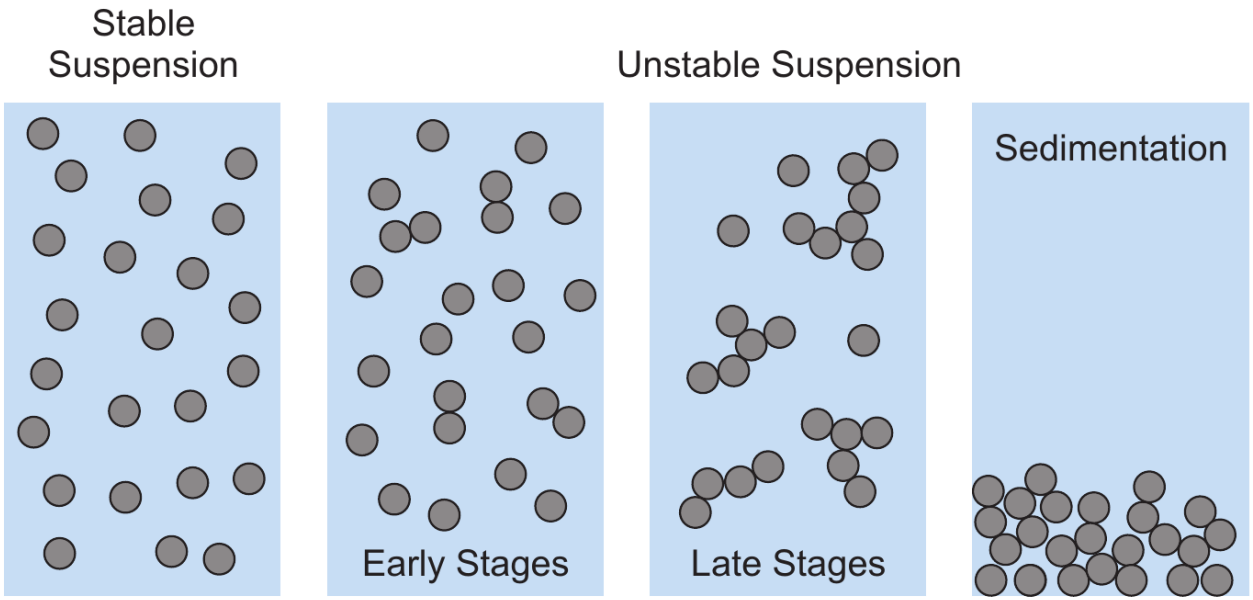
Fundamentals of DLVO theory



Credit: Trefalt and Borkovec

- Colloidal suspension: colloidal (nano)particles plus a (dielectric) medium

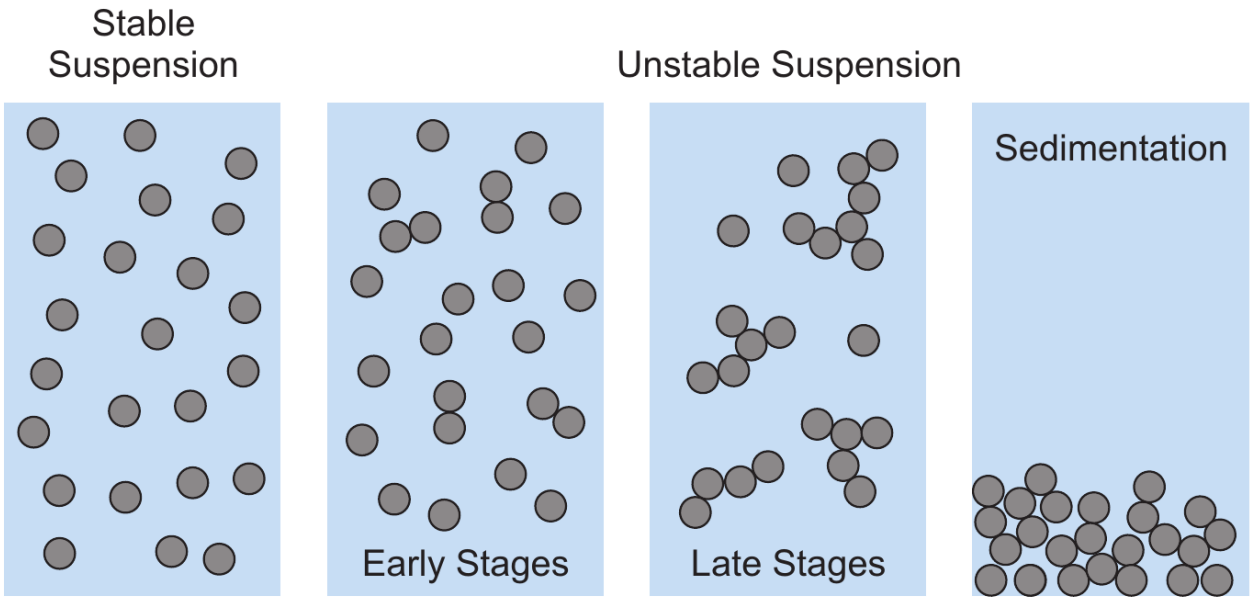
Fundamentals of DLVO theory



Credit: Trefalt and Borkovec

- Colloidal suspension: colloidal (nano)particles plus a (dielectric) medium
- The particles interact through the medium (typically a water-based electrolyte, but not necessarily)

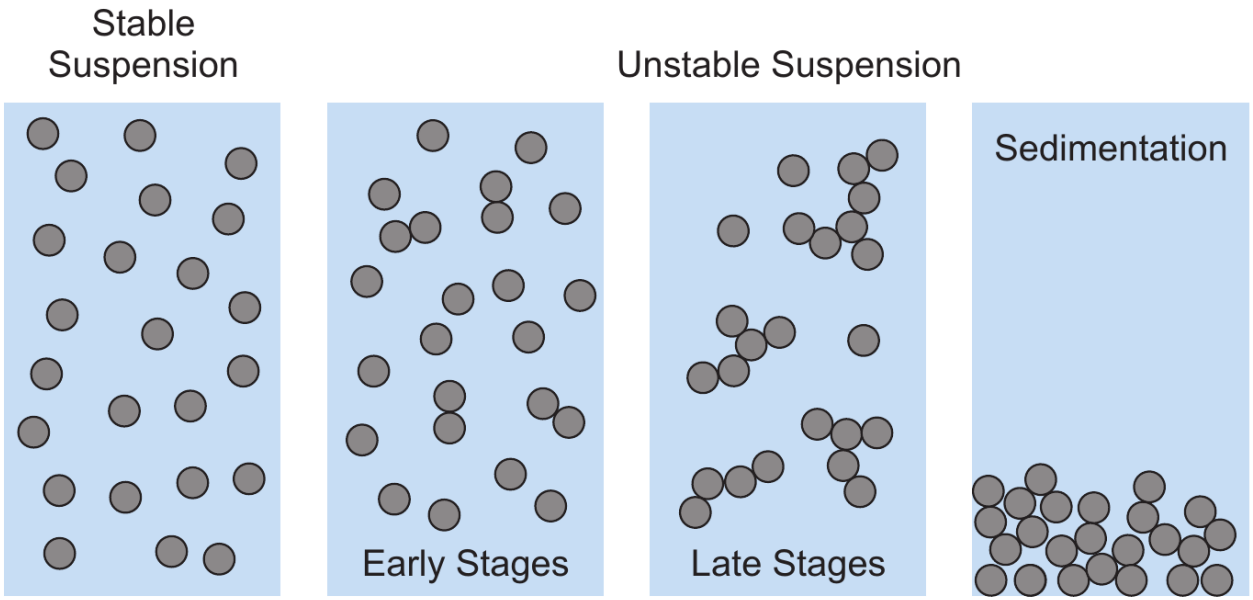
Fundamentals of DLVO theory



Credit: Trefalt and Borkovec

- Colloidal suspension: colloidal (nano)particles plus a (dielectric) medium
- The particles interact through the medium (typically a water-based electrolyte, but not necessarily)
- Question 1: whether the colloidal suspension is stable (i.e., no aggregation)

Fundamentals of DLVO theory



Credit: Trefalt and Borkovec

- Colloidal suspension: colloidal (nano)particles plus a (dielectric) medium
- The particles interact through the medium (typically a water-based electrolyte, but not necessarily)
- Question 1: whether the colloidal suspension is stable (i.e., no aggregation)
- Question 2: for how long does it remain stable (long enough for our experiment?)

Fundamentals of DLVO theory

How do two colloidal particles interact in a dielectric medium?

Fundamentals of DLVO theory

How do two colloidal particles interact in a dielectric medium?

Electrostatics:

$$E_{\text{ele}} = \frac{1}{4\pi\varepsilon\varepsilon_0}\frac{e^2 Z_1 Z_2}{d} \qquad (1)$$

Fundamentals of DLVO theory

How do two colloidal particles interact in a dielectric medium?

Electrostatics:

$$E_{\text{ele}} = \frac{1}{4\pi\varepsilon\varepsilon_0}\frac{e^2 Z_1 Z_2}{d} \qquad (1)$$

Van der Waals (London dispersion approximation):

$$E_{\text{vdW}} = -4\epsilon\left(\frac{\sigma}{d}\right)^6 \qquad (3)$$

Fundamentals of DLVO theory

How do two colloidal particles interact in a dielectric medium?

Electrostatics:

$$E_{\text{ele}} = \frac{1}{4\pi\varepsilon\varepsilon_0}\frac{e^2 Z_1 Z_2}{d} \qquad (1)$$

Van der Waals (London dispersion approximation):

$$E_{\text{vdW}} = -4\epsilon\left(\frac{\sigma}{d}\right)^6 \qquad (3)$$

Valid for point particles!DLVO theory uses the approximation of two interacting surfaces.

Fundamentals of DLVO theory

How do two colloidal particles interact in a dielectric medium?

Electrostatics:

$$E_{\text{ele}} = \frac{1}{4\pi\varepsilon\varepsilon_0}\frac{e^2 Z_1 Z_2}{d} \qquad (1)$$

$$W_{\text{EDL}}(h) = \frac{2\sigma_1\sigma_2}{\varepsilon\varepsilon_0\kappa}\exp\left(-\kappa h\right) \qquad (2)$$

Van der Waals (London dispersion approximation):

$$E_{\text{vdW}} = -4\epsilon\left(\frac{\sigma}{d}\right)^6 \qquad (3)$$

Valid for point particles!DLVO theory uses the approximation of two interacting surfaces.

Fundamentals of DLVO theory

How do two colloidal particles interact in a dielectric medium?

Electrostatics:

$$E_{\text{ele}} = \frac{1}{4\pi\varepsilon\varepsilon_0}\frac{e^2 Z_1 Z_2}{d} \qquad (1)$$

$$W_{\text{EDL}}(h) = \frac{2\sigma_1\sigma_2}{\varepsilon\varepsilon_0\kappa}\exp\left(-\kappa h\right) \qquad (2)$$

Van der Waals (London dispersion approximation):

$$E_{\text{vdW}} = -4\epsilon\left(\frac{\sigma}{d}\right)^6 \qquad (3)$$

$$W_{\text{vdW}}(h) = -\frac{H}{12\pi h^2} \qquad (4)$$

Valid for point particles!DLVO theory uses the approximation of two interacting surfaces.

Fundamentals of DLVO theory

How do two colloidal particles interact in a dielectric medium?

Electrostatics:

$$E_{\text{ele}} = \frac{1}{4\pi\varepsilon\varepsilon_0}\frac{e^2 Z_1 Z_2}{d} \qquad (1) \qquad W_{\text{EDL}}(h) = \frac{2\sigma_1\sigma_2}{\varepsilon\varepsilon_0\kappa}\exp\left(-\kappa h\right) \qquad (2)$$

Van der Waals (London dispersion approximation):

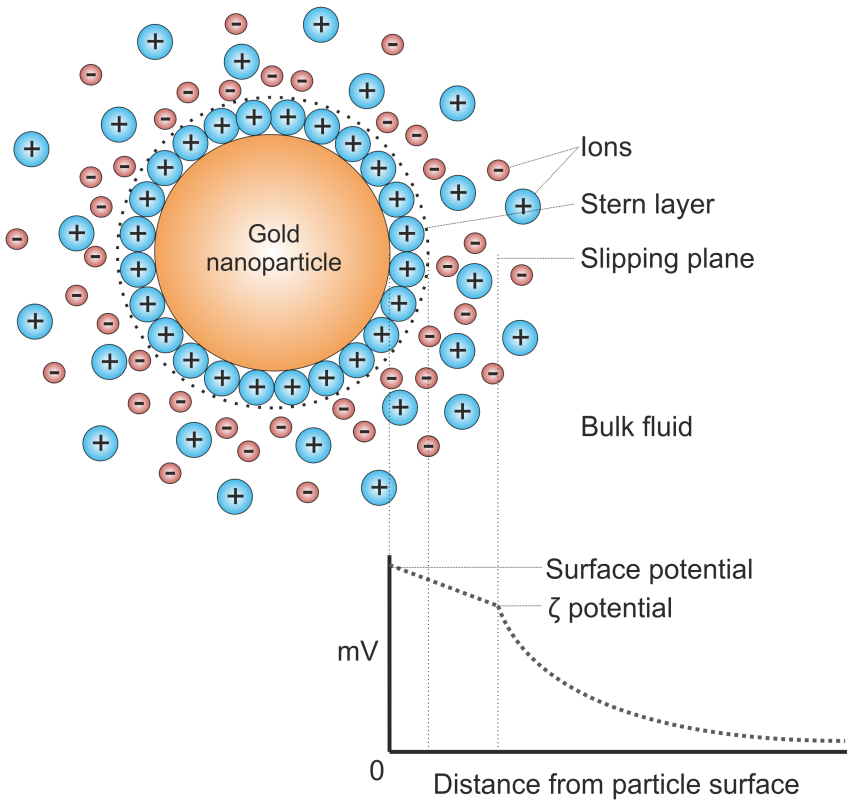
$$E_{\text{vdW}} = -4\epsilon\left(\frac{\sigma}{d}\right)^6 \qquad (3) \qquad W_{\text{vdW}}(h) = -\frac{H}{12\pi h^2} \qquad (4)$$

Valid for point particles!DLVO theory uses the approximation of two interacting surfaces.
h is the separation between the surfaces ($\neq d$); κ is the inverse Debye length; H is Hamaker's constant[1]; W is energy per surface area.

[1] Originally called A in H. C. Hamaker, Physica 4, 1058 (1937).

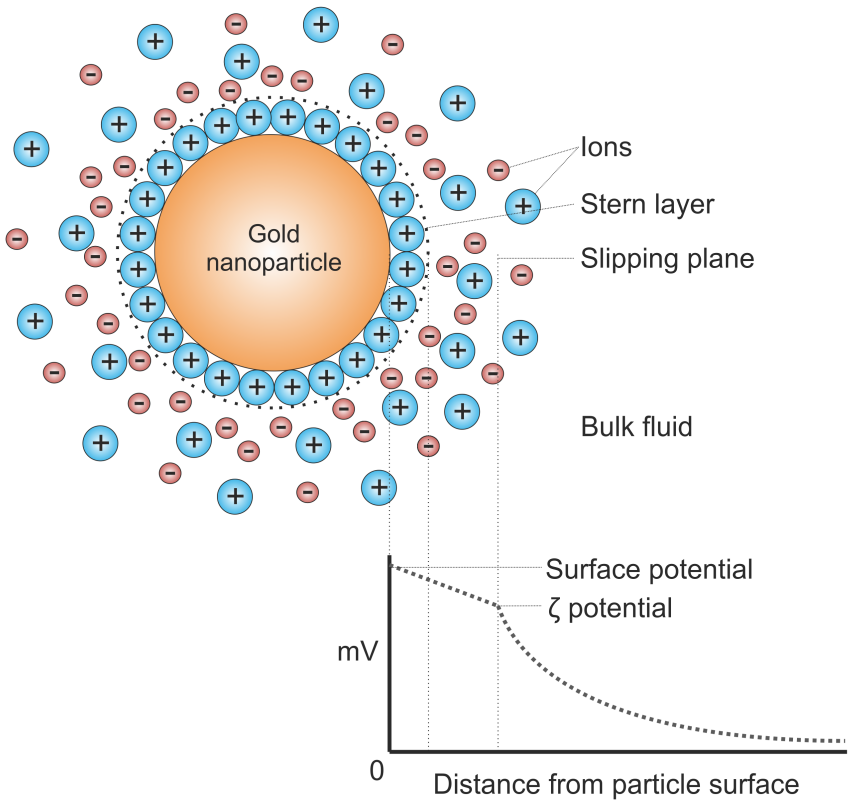
Fundamentals of DLVO theory

The electrical double layer:



Fundamentals of DLVO theory

The electrical double layer:



Due to the EDL the electrostatic potential is screened out. The Debye lenght $1/\kappa$ gives the typical distance over which the decay is significant.

$$W_{\mathrm{EDL}}(h) = \frac{2\sigma_1\sigma_2}{\varepsilon\varepsilon_0\kappa}\exp\left(-\kappa h\right) \quad (5)$$

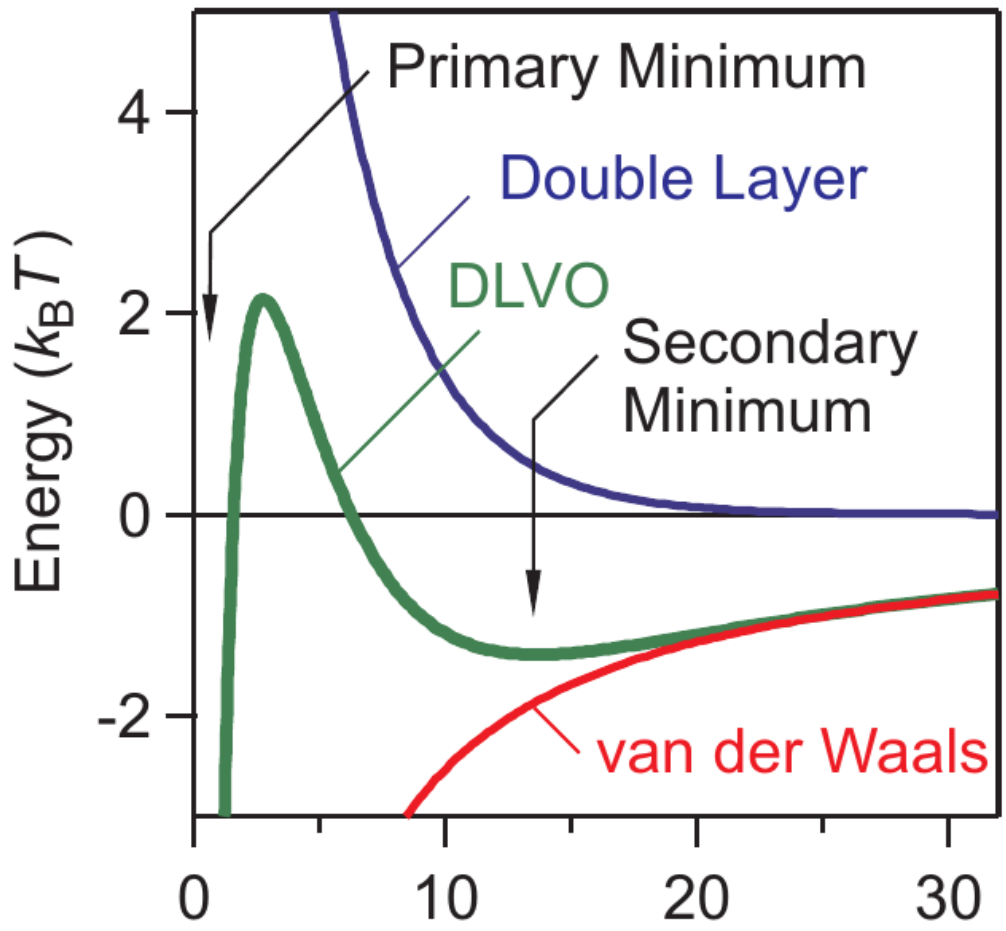
$$\kappa = \sqrt{\frac{2e^2 N_{\mathrm{A}} I}{k_{\mathrm{B}} T \varepsilon\varepsilon_0}} \quad (6)$$

$$I = \frac{1}{2}\sum_i z_i^2 c_i \quad (7)$$

I is the ionic strength of the solution and c_i the concentration of each ion type with charge z_i (units of e)

Fundamentals of DLVO theory

Strength of the DLVO interaction determines aggregation behavior:



Credit: Trefalt and Borkovec

Fundamentals of DLVO theory

A computational experiment:

(8)

(9)

Fundamentals of DLVO theory

A computational experiment:

- Particles with idealized charges and radii

(8)

(9)

Fundamentals of DLVO theory

A computational experiment:

- Particles with idealized charges and radii
- Colloidal particles much bigger than solvent particles

(8)

(9)

Fundamentals of DLVO theory

A computational experiment:

- Particles with idealized charges and radii
- Colloidal particles much bigger than solvent particles
- We consider the following interactions:

(8)

(9)

Fundamentals of DLVO theory

A computational experiment:

- Particles with idealized charges and radii
- Colloidal particles much bigger than solvent particles
- We consider the following interactions:

$$E_{\text{ele}} = \frac{1}{4\pi\varepsilon_0}\frac{e^2 Z_1 Z_2}{d} \tag{8}$$

(9)

Fundamentals of DLVO theory

A computational experiment:

- Particles with idealized charges and radii
- Colloidal particles much bigger than solvent particles
- We consider the following interactions:

$$E_{\text{ele}} = \frac{1}{4\pi\varepsilon_0}\frac{e^2 Z_1 Z_2}{d} \tag{8}$$

$$E_{\text{vdW}} = 4\epsilon\left(\underbrace{\left(\frac{\sigma}{d}\right)^{12}}_{\text{Pauli repulsion}} - \underbrace{\left(\frac{\sigma}{d}\right)^{6}}_{\text{London dispersion}}\right) \tag{9}$$

Fundamentals of DLVO theory

A computational experiment:

- Particles with idealized charges and radii
- Colloidal particles much bigger than solvent particles
- We consider the following interactions:

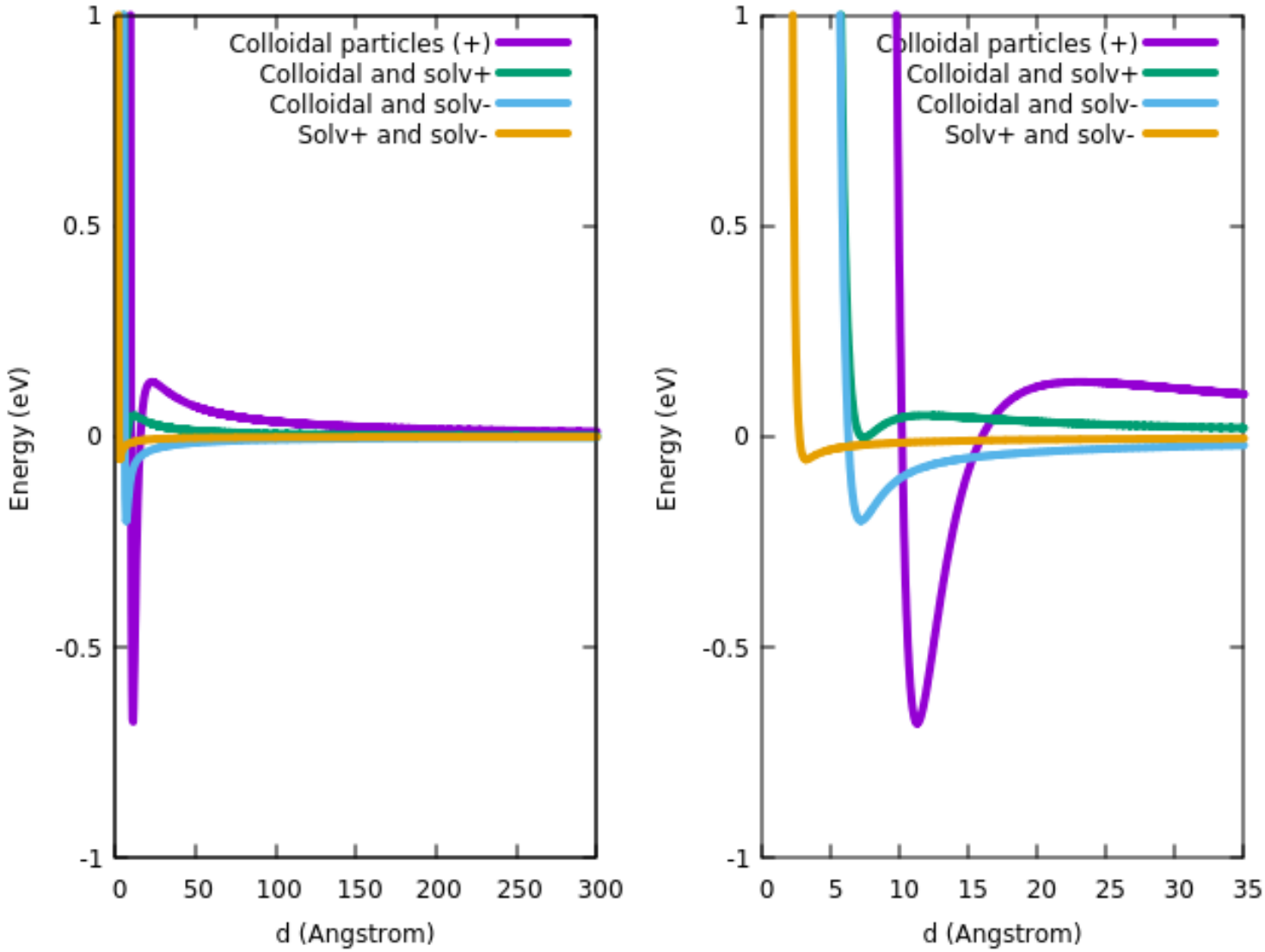
$$E_{\text{ele}} = \frac{1}{4\pi\varepsilon_0}\frac{e^2 Z_1 Z_2}{d} \tag{8}$$

$$E_{\text{vdW}} = 4\epsilon\left(\underbrace{\left(\frac{\sigma}{d}\right)^{12}}_{\text{Pauli repulsion}} - \underbrace{\left(\frac{\sigma}{d}\right)^{6}}_{\text{London dispersion}}\right) \tag{9}$$

`https://github.com/mcaroba/dlvo`

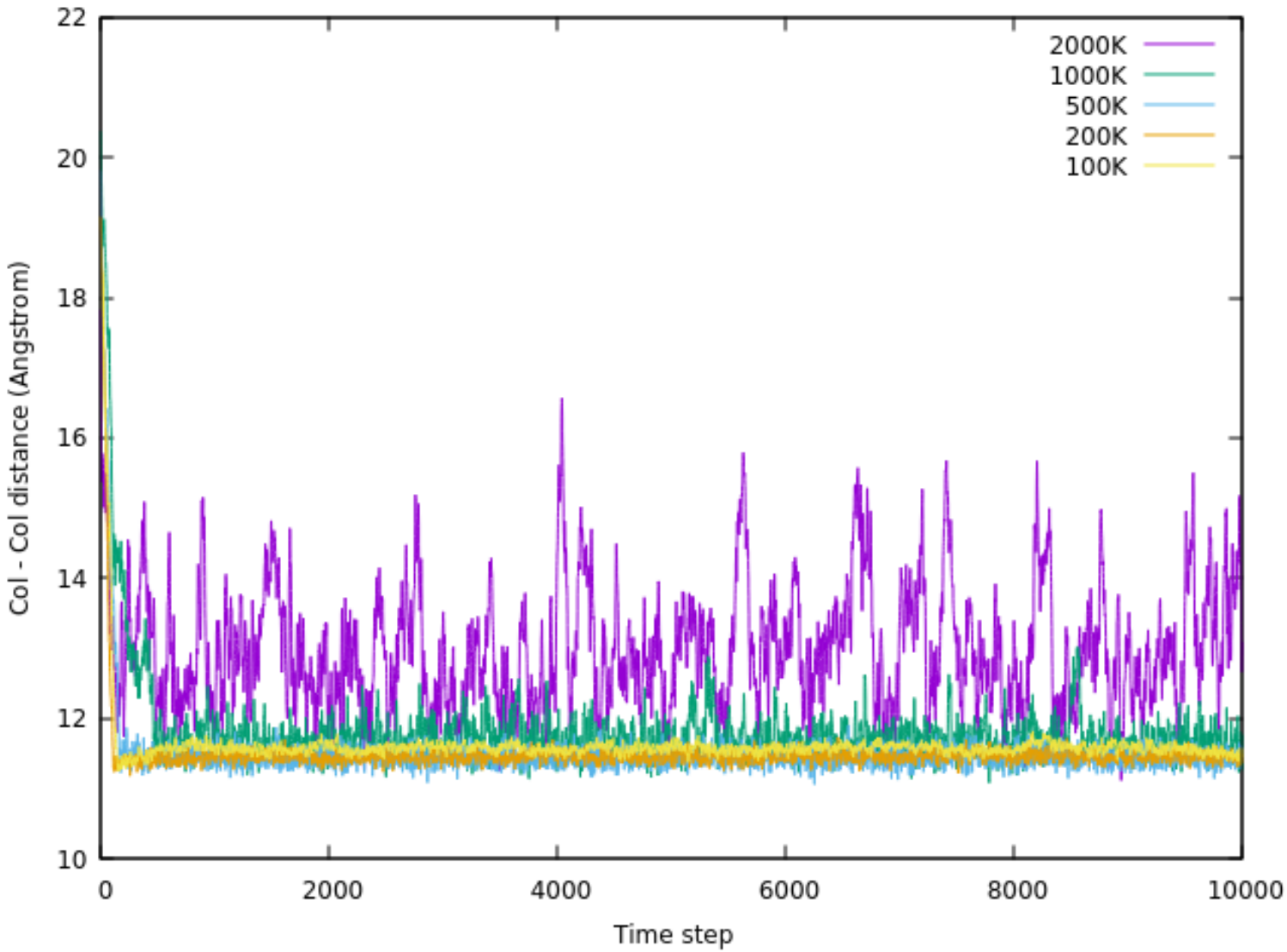
Fundamentals of DLVO theory

Our individual interactions look like this:



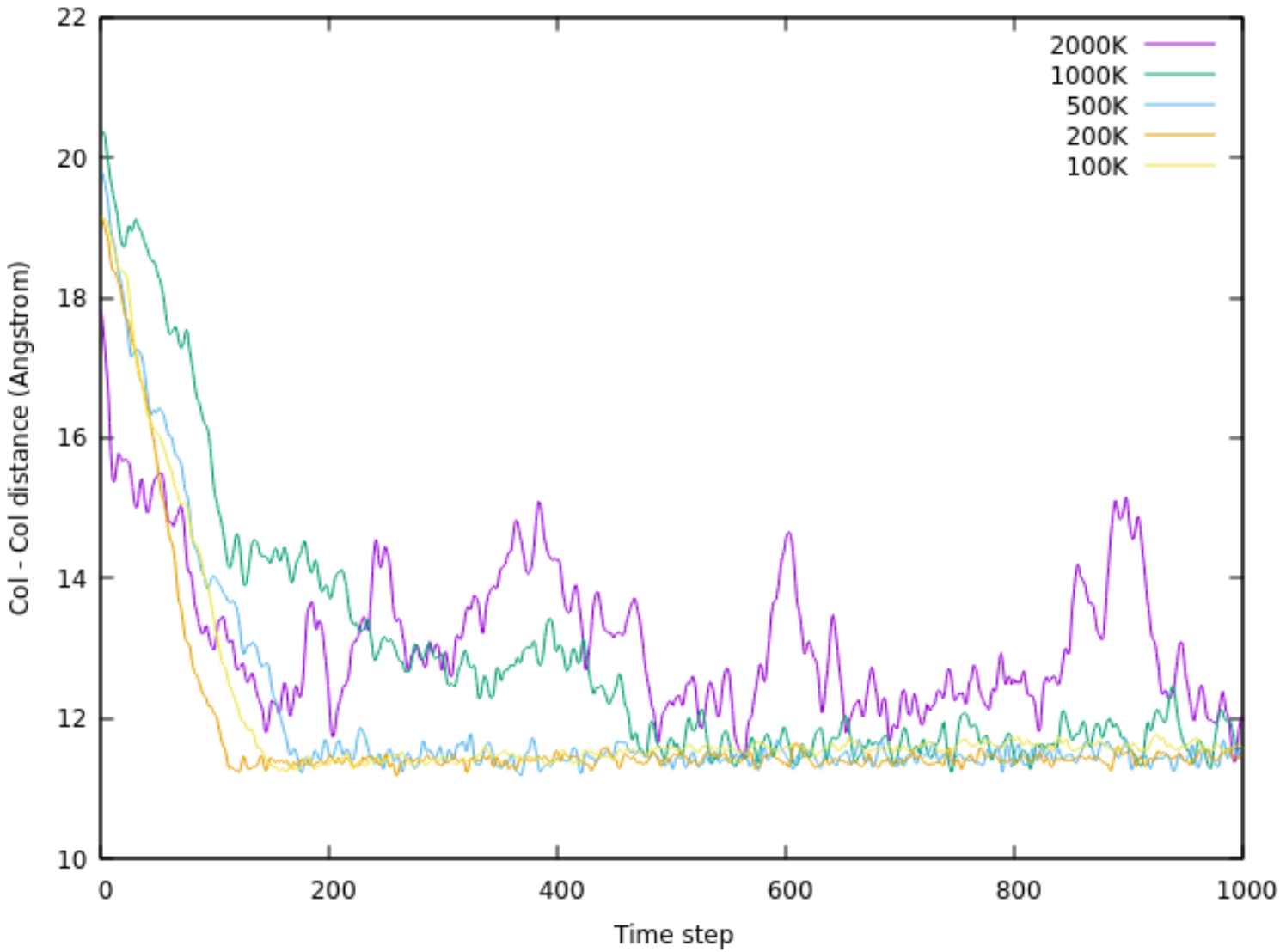
Fundamentals of DLVO theory

The stability of the suspension depends on the temperature:



Fundamentals of DLVO theory

The stability of the suspension depends on the temperature:



Fundamentals of DLVO theory

DLVO theory predicts the following expression for the aggregation rate:

$$k = \frac{2k_B}{3\eta R_{eff}} \left(\int_0^\infty \mathrm{d}h \frac{1 + R_{eff}/h}{(R_1 + R_2 + h)^2} \exp\left(U(h)/(k_B T)\right) \right)^{-1} \tag{10}$$

where $U(h)$ is the energy of the interaction between the colloidal particles according to the DLVO approximation, R_{eff} is the reduced radius ($R/2$ for idential particles) and η is the viscosity of the solvent.

Fundamentals of DLVO theory

DLVO theory predicts the following expression for the aggregation rate:

$$k = \frac{2k_B}{3\eta R_{\text{eff}}} \left(\int_0^\infty \mathrm{d}h \frac{1 + R_{\text{eff}}/h}{(R_1 + R_2 + h)^2} \exp\left(U(h)/(k_B T)\right) \right)^{-1} \tag{10}$$

where $U(h)$ is the energy of the interaction between the colloidal particles according to the DLVO approximation, R_{eff} is the reduced radius ($R/2$ for idential particles) and η is the viscosity of the solvent.

By fine tuning the simulation parameters we can try to estimate this coefficient from the computational experiment and compare to the value obtained analytically by DLVO. Possible project assignment topic!