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Applied Theoretical Physics
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Project 4 for '*Computational Physics - Material Science*', SoSe 2025

Project title: Simulating Colloidal Flocculation with Langevin Dynamics

Goal: Colloid stability and clustering are crucial for self-assembly, as they determine the formation of ordered structures, leading to the fabrication of advanced materials with tailored architectures and functionalities. The objectives of the project are to (i) implement a Langevin Dynamics (LD) simulation code to model colloid stability and clustering using the DLVO theory, and (ii) recover flocculation with increasing the salt concentration.

Langevin dynamics is a stochastic simulation method, extending Newton's MD to include friction and fluctuations (modeling an implicit solvent). It can also be used as thermostat. The trajectory in one dimension of interacting particles is then described by the stochastic equation of motion

$$m\ddot{x}_i + \xi\dot{x} = F_{x,i} + R_i(t) \tag{1}$$

where m is the mass of an individual ion, $x_i(t)$ is the x-coordinate of the ion i, ξ is the friction coefficient, T is the temperature, R_i is a random force presents due to solvent kicks following a Gaussian distribution with mean $\mu_R = 0$ and a non-zero variance $\langle R_i(t)R_i(t')\rangle = 2\xi k_B T\delta(t-t')$, and $F_{x,i}$ is the force acting on ion i due to the other ions. The characteristic time scale unit, τ_{LD} is set to

$$\tau_{LD} = \frac{\sigma^2}{k_B T}\xi$$

where σ is a unit of length, and k_BT is a unit of energy.

The stochastic equation of motion can be integrated numerically using the following algorithm using a time step Δt:

Algorithm 1: Algorithm to integrate the Langevin equation of motion.

Input: at $t = 0$, Initialize $x[0]$ and $v[0]$
for $t \leftarrow 0$ **to** $n\Delta t$ **do**
  calculate $F_x(t)$
  generate a random number, $\zeta(t)$, following a Gaussian distribution with $\mu_\zeta = 0$ and variance $\chi_\zeta = 1$
  calculate acceleration at t: $a_x(t) = (F_x(t) - \xi v(t))/m$
  update velocity at $t + \Delta t$: $v(t + \Delta t) = v(t) + a(t)\Delta t + \frac{\sqrt{2k_BT\xi}}{m}\zeta(t)\sqrt{\Delta t}$
  update position at $t + \Delta t$: $x(t + \Delta t) = x(t) + v(t)\Delta t$
end

The DLVO type of interaction is characterized by the occurrence of a primary and a secondary well (energy minimum) separated by a energy barrier, and the magnitude of the barrier depends on the salt concentration. The effective interaction between two charged colloids is given as a sum of effective van der Waals (vdW) and electrostatic potentials, V_{vdW} and V_{elec} which write as

$$V_{DLVO}(r) = \begin{cases} V_{vdw}(r) + V_{elec}(r) & \text{if } r > \sigma + \delta \\ 8k_BT\left(\left(\frac{0.6}{r}\right)^{12} - \left(\frac{0.6}{r}\right)^{6}\right) & \text{otherwise} \end{cases} \tag{2}$$

where

$$V_{vdW}(r) = -\frac{A}{24}\frac{\sigma}{r-\sigma} \text{ and } V_{elec}(r) = Z'^2\frac{\lambda_B}{r}e^{-\kappa_D r} \tag{3}$$

with $Z' = Z\frac{\exp[\kappa_D\sigma/2]}{1+\kappa_D\sigma/2}$, $A = 0.1k_BT$, $\kappa_D = \sqrt{8\pi\lambda_B C_s}$ and $\lambda_B = \frac{e^2}{4\pi\epsilon_0\epsilon k_B T} = \frac{\sigma}{100}$. In the above equation, r is the centre-to-centre distance, σ is the colloid diameter, and C_s is the salt concentration.

The objective of the project is to simulate colloid stability and clustering using the DLVO theory. The project is build up in successive tasks. Students are encouraged to follow the time schedule given in Fig 1.

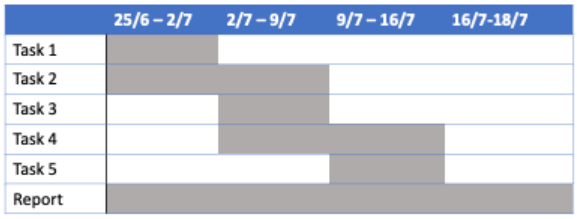

Abbildung 1: Workplan for a successful completion of the project.

Task 1. Implementation

Implement a Langevin Dynamics code with the following functionalities:

- a 3D simulation box of size L^3 with N charged colloids corresponding to a density ρ, and periodic boundary conditions along x, y, and z,
- DLVO interaction according to Eq. (2),
- integration scheme according to Algo. 1 with the random forces being uncorrelated in x, y, and z,
- save the colloids' position coordinates with a frequency N_{save}

Task 2. Validation of the LD integration scheme

Switch off the interactions between colloids, and simulate the trajectory of $N = 256$ colloids with $\rho = 0.5\sigma^3$ for $200000\Delta t$ with $\Delta t = 10^{-3}\tau_{LD}$ and $N_{save} = 10\Delta t$. Calculate and plot the Mean Squared Displacement (MSD) according to

$$\left\langle r^2(t)\right\rangle = \frac{1}{N}\sum_{i=1}^{N}\frac{1}{t_{max}}\sum_{t'=0}^{t_{max-1}}|\mathbf{r}_i(t'+t) - \mathbf{r}_i(t')|^2 \tag{4}$$

with t_{max} being half of the number of the saved snapshots. What are the different regimes you are observing on the MSD plot, and can you estimate the long time diffusion? How does it compare to the Einstein-Smoluchowski relation $D = k_BT/\xi$? Conclude on the validity of the implementation of your LD simulation code. (Another, optional, validation would be to simulate the density profile of the ideal gas in an external field as in exercise sheet 4.)

Task 3. Simulation

Simulate the trajectories of a system containing $N = 343$ colloids of diameter σ and density $\rho = 0.05\sigma^{-3}$ in a volume of dimension L^3 for $200000\Delta t$ with $\Delta t = 10^{-2}\tau_{LD}$ with $C_s \in (10, 100, 333, 666, 1000)\sigma^{-3}$. The last $100000\Delta t$ are for the production run. The parameters for

the DLVO potential are $A = 0.1k_BT$, $Z = 50$, and $\delta = 10^{-2}\sigma$. Save the trajectory every $N_{save} = 10\Delta t$.

Task 4. Analysis

Using the trajectories obtained in Task 4, analyse, plot and interpret:

a) the radial distribution function $g(r)$ when considering r as the colloid-colloid distance. Do you observe colloid flocculation (and clustering) when increasing the salt concentration? Plot peak height and coordination number versus salt concentration. Is the cluster size increasing with salt concentration? Does it change with simulation time? If yes, why?

b) the structure factor, $S(k)$ can be derived directly from $g(r)$ as Fourier transform

$$S(k) = 1 + 4\pi\rho \int_{0^+}^{\infty} dr(g(r) - 1)r^2 \frac{\sin(kr)}{kr} \tag{5}$$

with k being the magnitude of the wave vector. What is the magnitude of the isothermal compressibility and how does it change with salt concentration?

c) Optional: for colloids interacting through the DLVO potential and low salt concentration, how does the MSD compare to the theoretical MSD of a free particle with diffusion constant $D = k_BT/\xi$? Discuss. Hypothesise what happens at high colloid density and high salt concentration.

Task 5. Real world context and play around.

- Check literature, what are examples of DLVO parameters (Hamaker constant and charges) for real application? Check in the simulation or hypothesize what happens when you play with these parameters. For what type of length scales and systems is the DLVO theory typically used for? How do the specific choice of materials tune the parameters?
- Check the literature to find the differences between Agglomeration, Coagulation, and Flocculation. What are the applications, e.g. in medical diagnostics or other important fields?