Universität Freiburg – Institut für Physik
Applied Theoretical Physics
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Exercise 8 for '*Computational Physics - Material Science*', SoSe 2021
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Please provide a well documented submission of your solution. Your submission should include

- A pdf file containing the solution to the questions with the corresponding equations that are implemented in your codes. Figures must contain axis titles with corresponding units and a caption.
- The source code should be commented, and the equations given in the pdf file have to be referenced in the source code.
- There is no need to provide the trajectory files.
- In case your code is not working properly, please provide a description of the debugging attempts you did.
- to avoid any performance issue, students are encouraged to use the numba implementation of the NH thermostat available on Ilias.

**Exercise 8.1: Poisson-Boltzmann equation in planar geometry: Application to the counter-ions only**

In molecular simulations, electrostatic interactions are essential, and their evaluation is one of the most computationally demanding tasks. One solution to reduce the computational cost when handling the electrostatic interaction is to treat the Coulombic interactions with an approximative short-range, spherically truncated, charge-neutralized, damped, and shifted pair potential. Thus, the pair-potential between the ion $i$ with charge $q_i$ and position $\boldsymbol{r}_i$ and the ion $j$ with charge $q_j$ and position $\boldsymbol{r}_j$ separated by a distance $r_{ij} = |\boldsymbol{r}_i - \boldsymbol{r}_j| < R_c$ is

$$V_{q_iq_j}(r_{ij}) = \frac{q_iq_j}{4\pi\epsilon_0}\left[\frac{\mathrm{erfc}(\alpha r_{ij})}{r_{ij}} - \frac{\mathrm{erfc}(\alpha R_c)}{R_c} + \left(\frac{\mathrm{erfc}(\alpha R_c}{R_c^2} + \frac{2\pi}{\alpha}\frac{\exp(-\alpha^2 R_c^2)}{2}\right)(r_{ij} - R_c)\right]$$

where $\alpha$ is the damping parameter, and erfc() is the complementary error-function.

a) Consider two equally planar charged surfaces located at $\pm L_z/2$, each of them having a charge density $\sigma_{surf} < 0$ immersed in solution, and assume that only monovalent counter-ions in solution neutralize the surfaces ($-L_z/2 \leq z \leq L_z/2$). Using the Poisson-Boltzmann equation and the boundary condition $\phi'(z=0) = 0$ and $\phi'(z = \pm L/2) = \frac{4\pi}{\epsilon}\sigma_{surf}$, demonstrate that the density distribution of the ions, $n(z)$, along the direction normal to the charged surfaces, $z$, can be written in the form $n(z) = \frac{n_m}{\cos^2(\kappa z)}$. $n_m$ is the value of the density at the mid-plane ($z = 0$), and $1/\kappa$ is a new length scale of the problem defined by $\kappa^2 = \frac{2\pi e^2}{\epsilon k_B T} n_m$ (the general solution of the PB equation is in the form $\Phi(z) = \frac{k_B T}{e}\ln(\cos^2(\kappa z))$). Derive a relation between $\kappa$, $L_z$ and $\sigma_{surf}$ using the boundary condition at $z = \pm L_z/2$.

b) Starting from the geometrical setup of the fluid confined between two walls (sheet #4) combined with the NH thermostat (sheet #5), add the following in your code:

- assign a partial charge, $q$, to each of the $N$ LJ atoms (the LJ atom with charge $q$ will be referred to as counter-ions),
- implement the electrostatic force, $\boldsymbol{F}_{q_i q_j} = -\nabla V_{q_i q_j}(r_{ij})$, acting on the counter-ion $i$ with charge $q_i$ due to the presence of a counter-ion $j$ with charge $q_j$.

c) Build a configuration such that $N = 250$ counter-ions, with density $\rho = 0.05\sigma^{-3}$, are uniformly distributed in a volume $V = L_x L_y L_z$ with $L_z = 2L_x = 2L_y$. The planar surfaces, modeled using the 9-3 potential, are set at $\pm L_z/2$. Using a surface charge $\sigma_{surf} = 0.005$ e/Å$^2$, what is the partial charge assigned to the counter-ions to electroneutralize the system? Using $R_c = 5\sigma$ and $\alpha = 1/R_c$, equilibrate the system at 300K using the NH thermostat during 10000 time steps. Once equilibrated, generate the counter-ions trajectory for 50000 times steps. Calculate and plot $n(z)$ versus $z$ averaged over the whole production run. What is the magnitude of $n_m$ as defined in (a). What is the corresponding inverse screening length $\kappa$? What is the magnitude of $\kappa$ obtained by fitting $n(z)$ versus $z$ using the functional form derived in (a). How does it compare with the theoretical prediction?

d) Using the same simulation setup as in (c), perform similar calculations and analysis with $\sigma_{surf} \in (0.001, 0.00375, 0.0075, 0.01)$ eÅ$^2$. Plot $\kappa$ versus $n_m$, and compare with the corresponding equation given in (a). Plot $\kappa$ versus $\sigma_{surf}$, and compare with the analytical expression derived in (a).

e) Build $N_s = 100$ discrete points on the surface planes, uniformly distributed on a square lattice, with partial charge $q_s$ on each surface such that $2N_s q_s = Nq$. Calculate now also the electrostatic force between counter-ion $i$ of charge $q$ and the discrete points from the surface of charge $q_s$. Perform the same calculation as in (b). Plot $n(z)$ versus $z$ averaged over the whole production run. How does it differ from the one obtain in (b). Comment and interpret the results, in particular the influence of the different surface models in our simulation. Which model is more realistic?

*Numerical values of quantities to be used:*

| quantity | value (units) |
|---|---|
| $k_B$ | $1.38 \times 10^{-23}$ (m$^2$ kg s$^{-2}$ K$^{-1}$) |
| $\epsilon = \epsilon_w$ | $0.1\ k_B T_d$ |
| $\sigma = \sigma_w$ | $2.55\times10^{-10}$ (m) |
| $T_d$ | 300 (K) |
| mass | $105.52\times10^{-27}$ (kg) |
| $\Delta t$ | $10^{-15}$ (s) |
| $t_c$ | 50 $\Delta t$ (s) |
| $\rho$ | 0.05 ($\sigma^{-3}$) |
| $r_{cut}^{LJ} = r_{cut}^{w}$ | $5\sigma$ |
| $R_c$ | $5\sigma$ |