Incorporating surface polarization effects into massively parallel coarse-grained Molecular Dynamics simulations

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Introduction

Polarization effects due to dielectric mismatch between two media are known to influence the spatial distribution of the charged particles in the vicinity of the interface. Few open-source software packages support coarse-grained models with surface polarization effects.

We implement and extend three methods for incorporating surface polarization effects into LAMMPS: the boundary element method (BEM) for solving the Poisson's equation, the image charge computation (ICC*) method, and the direct optimization of an energy functional of induced charge density. Our implementation is complementary to COPPS and works seamlessly with SSAGES.

Methods and Algorithms

Gauss's law: $\nabla \cdot \mathbf{E}(\mathbf{r}) = \frac{\rho_f(\mathbf{r})}{\epsilon_0 \epsilon}$

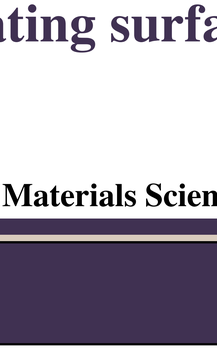
Displacement equation:

$$\rho_f(\mathbf{r}) = \epsilon_0 \nabla \cdot [\epsilon(\mathbf{r})\mathbf{E}(\mathbf{r})] = \nabla \cdot \mathbf{D}(\mathbf{r})$$

Reduction to interface:

$$\epsilon_0[\epsilon_2 \mathbf{E}^{(2)}(\mathbf{s}) - \epsilon_1 \mathbf{E}^{(1)}(\mathbf{s})] \cdot \mathbf{n}(\mathbf{s}) = \sigma_f(\mathbf{s})$$

$$\epsilon_0[\mathbf{E}^{(2)}(\mathbf{s}) - \mathbf{E}^{(1)}(\mathbf{s})] \cdot \mathbf{n}(\mathbf{s}) = \sigma_f(\mathbf{s}) + \sigma_b(\mathbf{s})$$



$$\bar{\epsilon} = (\epsilon_1 + \epsilon_2)/2$$

$$\Delta\epsilon = \epsilon_2 - \epsilon_1$$

1. Boundary element method (BEM) – COPPS

$$\bar{\epsilon}\sigma_b + \epsilon_0(\Delta\epsilon)\mathbf{E}_b \cdot \mathbf{n} = (1-\bar{\epsilon})\sigma_f - \epsilon_0(\Delta\epsilon)\mathbf{E}_f \cdot \mathbf{n}$$

- GMRES to solve a set of linear equations iteratively for σ_b

2. Image charge computation (ICC*) – Holm et al.

$$\sigma_b^{(m+1)} = (1-\omega)\sigma_b^{(m)} + \omega\left[\frac{1-\bar{\epsilon}}{\bar{\epsilon}}\sigma_f(\mathbf{s}) - \epsilon_0\frac{\Delta\epsilon}{\bar{\epsilon}}\mathbf{E}^{(m)} \cdot \mathbf{n}\right]$$

- SOR to solve a set of linear equations for σ_b

3. Optimization of an energy functional of induced surface charge density – Olvera et al.

$$I[\rho_f;\sigma_b] = \frac{1}{2}\iint \rho_f(\mathbf{r})R_{\rho\rho}(\mathbf{r},\mathbf{r}')\rho_f(\mathbf{r}')d\mathbf{r}d\mathbf{r}' + \frac{1}{2}\iint \rho(\mathbf{r})R_{\rho\sigma}(\mathbf{r},\mathbf{s})\sigma_b(\mathbf{s})d\mathbf{r}d\mathbf{s} + \frac{1}{2}\iint \sigma_b(\mathbf{s})R_{\sigma\sigma}(\mathbf{s},\mathbf{s}')\sigma_b(\mathbf{s}')d\mathbf{s}d\mathbf{s}'$$

- Matrix inversion to solve a set of linear equations for σ_b

Implementation and Validation

A new user package in LAMMPS: USER-DIELECTRIC

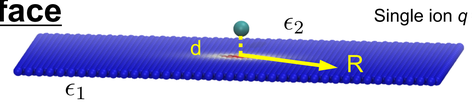
- new atom style: **AtomVecDielectric**
- new *pair* and *kspace* styles for per-atom electrical fields
- new *fixes*: **FixPolarizeBEM**, **FixPolarizeICC**, **FixPolarizeFunctional**

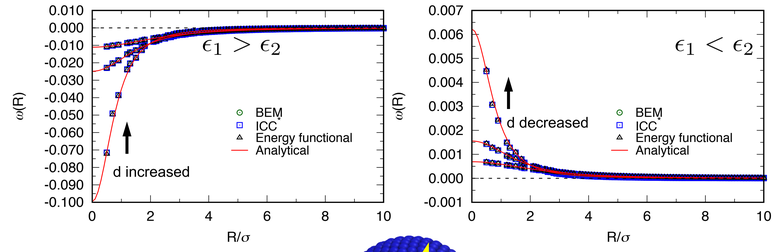
Advantages:

- Compatible with existing functionalities in LAMMPS including molecular, rigid bodies, time integrators, long-range electrostatics solvers (PPPM and MSM), and built-in analysis
- Support moving and/or flexible interfaces
- Compatible with SSAGES out of the box

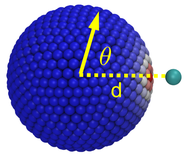
Planar interface

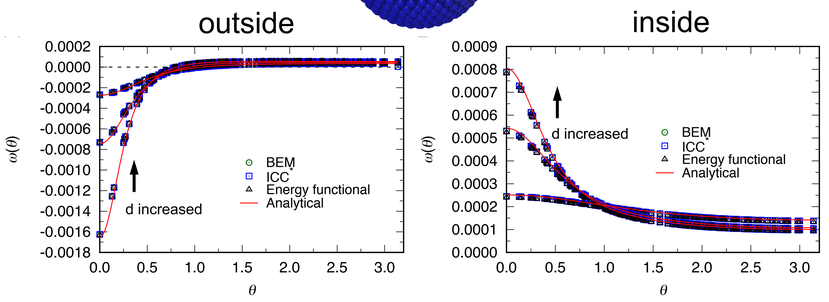
Single ion q = +1 (reduced unit)



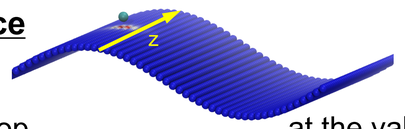


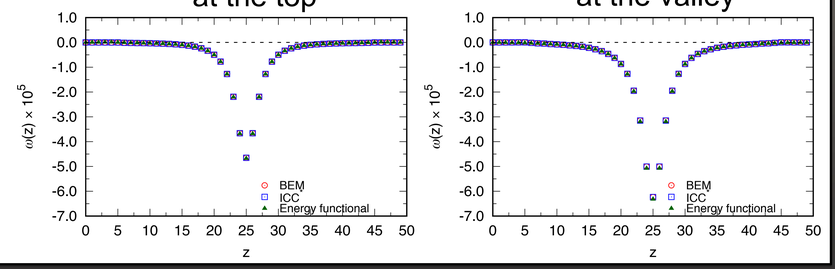
Spherical interface





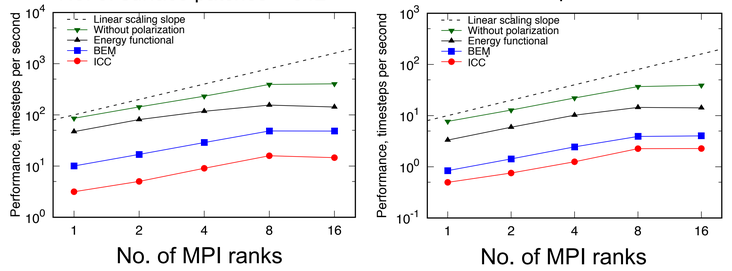
Sinusoidal interface





Simulation Performance

Benchmark system: Confined polyelectrolyte in a spherical cavity



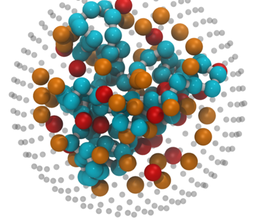
Strong scaling on a single node: built with LAMMPS version 16Mar18

Case study: Confined Polyelectrolyte

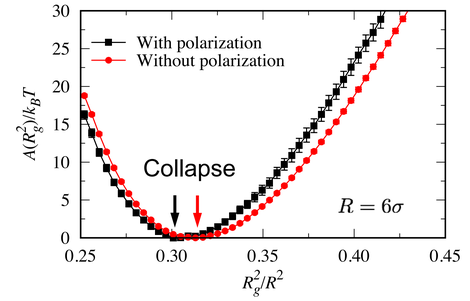
Free energy profile of the polyelectrolyte radius of gyration using umbrella sampling with SSAGES

$l_B/\sigma = 4.0 \quad \epsilon_{in}/\epsilon_{out} = 10$

100-mer + 30 trivalent counterions + 10 monovalent ions



100-mer polyelectrolyte (cyan)
M trivalent counterions (red)
N monovalent counterions (orange)
spherical interface: induced charges (gray)

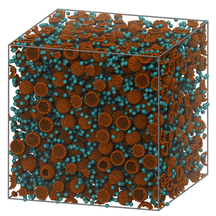


Key findings:

- Polarization effects leads to more compact conformation in the collapse state.
- Trivalent counterions increase the free energy barrier between collapse and coil states.

Ongoing and future work

- Validation with COPPS
- Collaboration with Juan de Pablo and Whitmer groups using SSAGES for efficient sampling and free energy calculations
- Collaboration with Talapin group for nanoparticle assembly studies
- Application to other case studies including polyelectrolytes, salt-doped block copolymers, and proteins



Metallic/Dielectric particle assembly

References and Acknowledgements

Acknowledgments: SSAGES for umbrella sampling; WHAM code by Alan Grossfield (U Rochester)

References

- Luijten *et al. Phys. Rev. Lett.* **2014**, 113, 017801 (BEM); Holm *et al. J. Chem. Phys.* **2010**, 132, 154112 (ICC*); Olvera de la Cruz *et al. Phys. Rev. Lett.* **2017**, 119, 138002. (Energy functional)

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