Fast Algorithm for Quasi-2D Coulomb Systems

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Introduction: MD simulation and electrostatic interaction

Molecular Dynamics (MD) Simulation

- Molecular dynamics (MD) simulation is a powerful tool to study the structure and dynamics of complex systems, by calculating the motion of molecules by solving Newton's equations of motion.
- The accuracy and efficiency of MD simulation are determined by the interaction model and the numerical method.

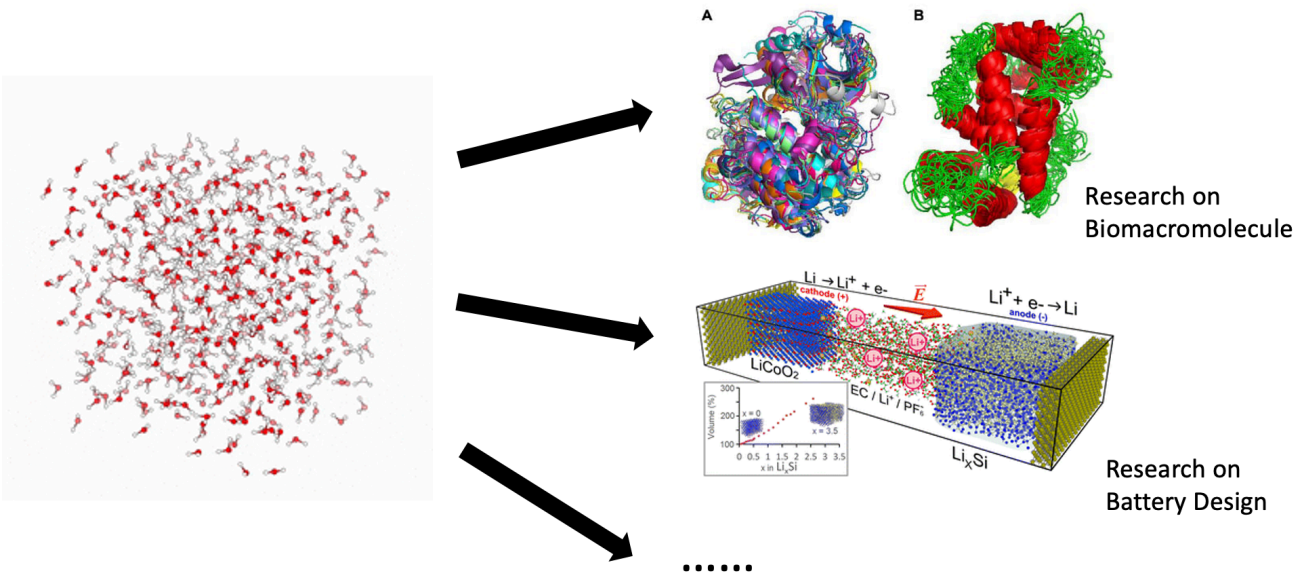
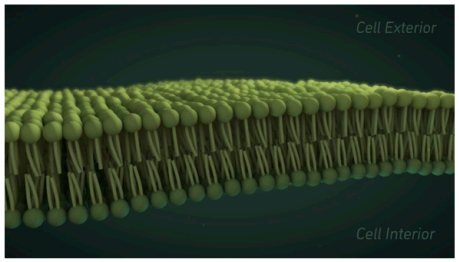


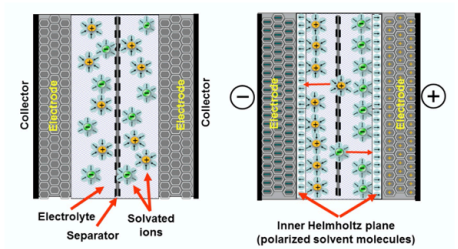
Figure: Molecular Dynamics Simulation

Quasi-2D Systems

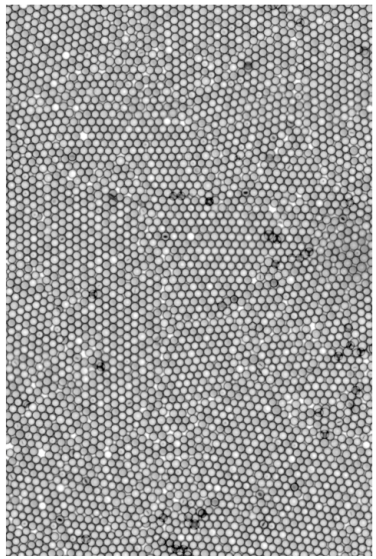
- The Quasi-2D (Q2D) systems are macroscopic in the xy direction, while are microscopic in the z direction, so that is always modeled to be *doubly periodic*.



Membranes



Electric capacitors



Colloidal monolayer

Figure: Quasi-2D Systems

Long Range Coulomb Interaction

For quasi-2D systems with charged particles, the electrostatic interaction is governed by the Poisson's equation

$$\boldsymbol{\nabla}^2\phi(\boldsymbol{r}) = -4\pi\sum_{i=1}^{N}\sum_{\boldsymbol{n}} q_i\delta(\boldsymbol{r}_i + \boldsymbol{n}\circ\boldsymbol{L})\ . \tag{1}$$

with the infinite boundary condition in z

$$\lim_{z\to\infty}\phi(\boldsymbol{r}) = 0\ . \tag{2}$$

Long Range Coulomb Interaction

- The Coulomb interaction between charged particles is long-range, which decays as $1/r$ in 3D space.
- The total electrostatic interaction energy is given by

$$U = \frac{1}{2}\sum_{i,j}{}' \sum_{\boldsymbol{n}} \frac{q_i q_j}{|\boldsymbol{r}_{ij} + \boldsymbol{n} \circ \boldsymbol{L}|} \ . \tag{3}$$

- The Coulomb interaction can be the most time-consuming part in the simulation of charged systems, the complexity of direct computation is of $O(N^2/\sqrt{\epsilon})$.

Ewald2D Summation Revisit

To handle the long range nature of the Coulomb interaction, the Ewald summation method is widely used in MD simulation, where the charge distribution is split as:

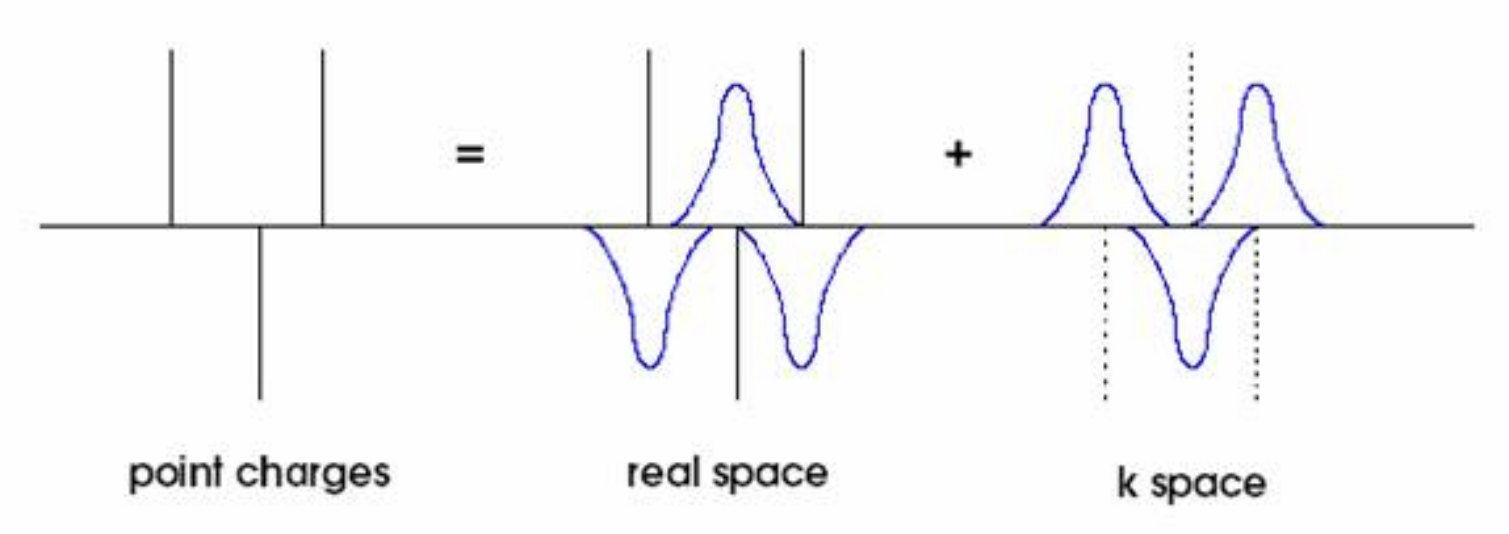


Figure: The Ewald splitting on charge distribution

$$\delta(\boldsymbol{r}) = \left(\delta(\boldsymbol{r}) - C_\alpha e^{-r^2\alpha^2}\right) + C_\alpha e^{-r^2\alpha^2} \ . \tag{4}$$

Ewald2D Summation Revisit

Using the Ewald splitting, the Coulomb interaction can be written as:

$$\begin{aligned}\frac{1}{r} &= \overbrace{\frac{\operatorname{erfc}(\alpha r)}{r}}^{\text{short range}} + \overbrace{\frac{1}{r} - \frac{\operatorname{erfc}(\alpha r)}{r}}^{l\text{ong range}} \\ &= \frac{\operatorname{erfc}(\alpha r)}{r} + \frac{\operatorname{erf}(\alpha r)}{r}\,,\end{aligned} \tag{5}$$

where $\operatorname{erfc}(x)$ is the complementary error function, and α is a parameter that controls the convergence of the Ewald summation.

Ewald2D Summation Revisit

The short range part is singular at $r = 0$, but decay rapidly as r increases. Thus the summation of the short range part can be done in real space via cell list method.

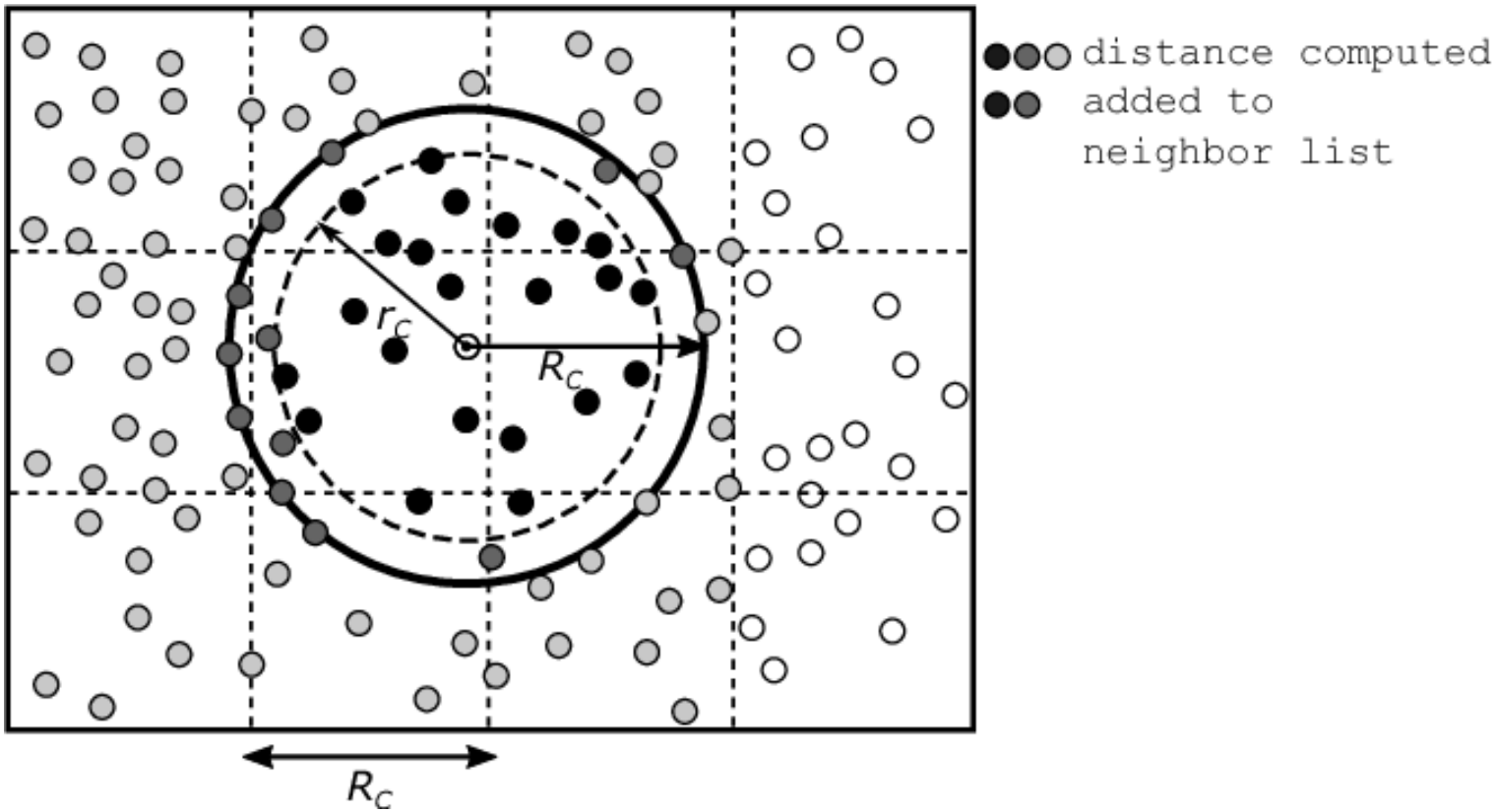


Figure: Short range interaction via cell list

Ewald2D Summation Revisit

The long range part is smooth, so that it can be computed in Fourier space, the summation of the long range part in Fourier space is given by:

$$U_l = \frac{\pi}{L_x L_y} \sum_{i,j=1}^{N} \sum_{k_x,k_y} q_i q_j \frac{e^{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{\rho}_{ij}}}{k} e^{\pm k z_{ij}} \operatorname{erfc}\left(\frac{k}{2\alpha} \pm \alpha z_{ij}\right) , \tag{6}$$

where $\boldsymbol{\rho}_{ij} = (x_i - x_j, y_i - y_j)$, $z_{ij} = |z_i - z_j|$.
The summation in Fourier space decay as $e^{-k^2/4\alpha}$, so that the summation can be truncated at a cutoff $k_{\max}$. Finally, the complexity of the Ewald2D summation is given by $O(N^2 \log \epsilon^{-1})$

Numerical Method: SOE and FGT

Sum-of-exponentials (SOE) Approximation

For a given precision ε, the objective of an SOE[1] approximation is to find suitable weights w_l and exponents s_l such that $\forall x \in \mathbb{R}$, the following inequality holds:

$$\left| f(x) - \sum_{l=1}^{M} w_l e^{-s_l |x|} \right| \leq \varepsilon, \tag{7}$$

where M is the number of exponentials.

[1] Zixuan Gao, Jiuyang Liang, and Zhenli Xu. "A kernel-independent sum-of-exponentials method". In: *J. Sci. Comput.* 93.2 (2022), p. 40. DOI: 10.1007/s10915-022-01999-1.

Sum-of-exponentials (SOE) Approximation

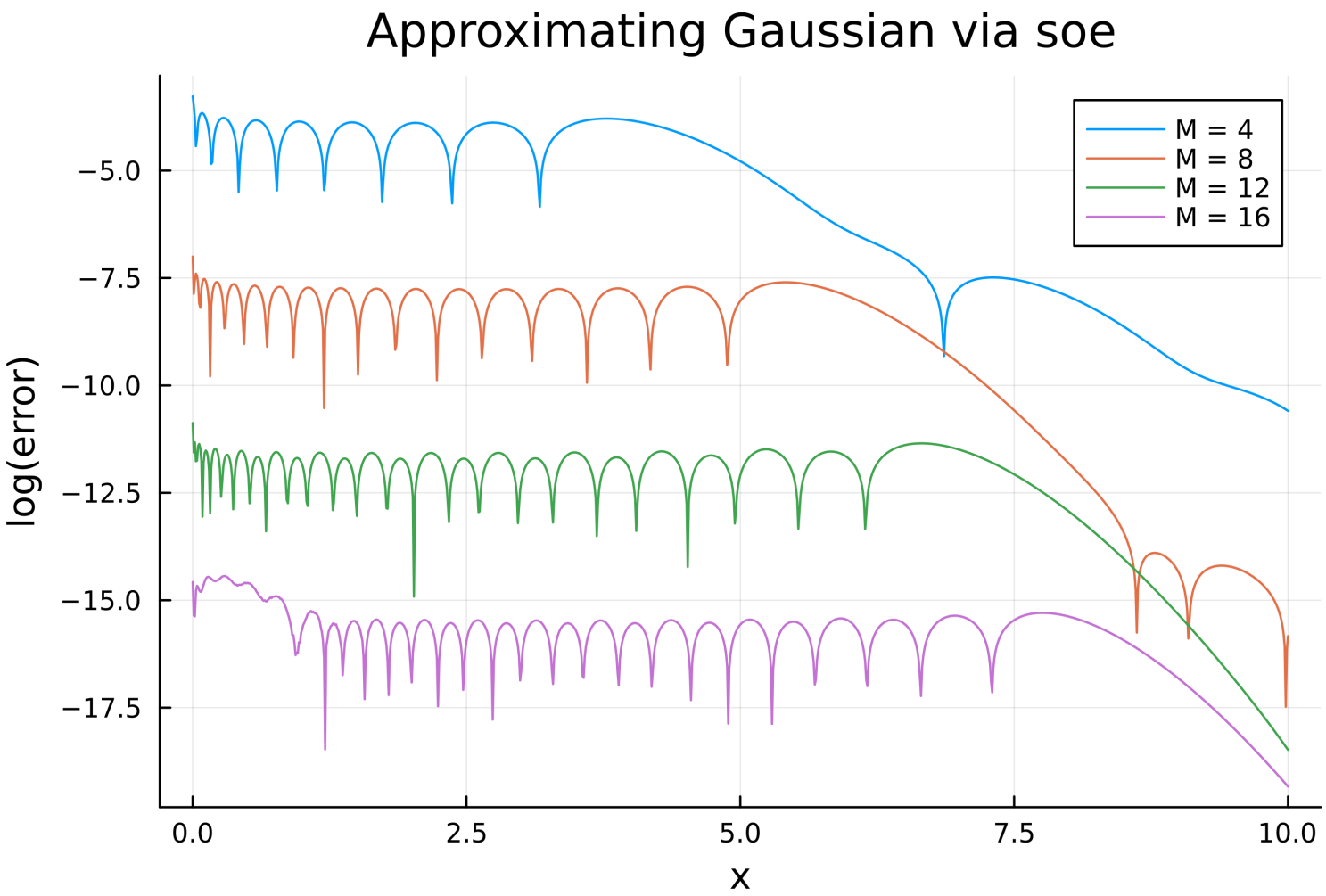


Figure: SOE approximation by the VPMR method

Fast Gauss Transform (FGT) via SOE Approximation

Consider the following summation

$$S = \sum_{i \neq j} q_i q_j e^{-(z_i - z_j)^2} , \tag{8}$$

where $z_i \in [0, 1]$ and $i, j \in [1, N] \cap \mathbb{Z}$. Calculating the summation directly leads to $O(N^2)$ cost.
Applying the SOE on the Gaussian[2] leads to

$$S \approx S^* = \sum_{i \neq j} \sum_{l=1}^{M} q_i q_j w_l e^{-s_l |z_i - z_j|} . \tag{9}$$

[2] Shidong Jiang and Leslie Greengard. "Approximating the Gaussian as a sum of exponentials and its applications to the fast Gauss transform". In: *Commun. Comput. Phys.* 31.1 (2022), pp. 1–26. ISSN: 1991-7120. DOI: https://doi.org/10.4208/cicp.OA-2021-0031.

Fast Gauss Transform (FGT) via SOE Approximation

Then by sorting, we make

$$z_1 < z_2 < ... < z_N \ , \tag{10}$$

the summation can be reformulated as

$$\begin{aligned} S^* &= 2\sum_{i<j}\sum_{l=1}^{M} q_i q_j w_l e^{-s_l(z_j - z_i)} \\ &= 2\sum_{l=1}^{M} w_l \sum_{i=1}^{N-1} q_i e^{s_l z_i} \sum_{j=i+1}^{N} q_j e^{-s_l z_j} \ , \end{aligned} \tag{11}$$

where the summation over j is irrelevant to i and can be calculated iteratively, thus the complexity is reduced to $O(N)$.

Fast Gauss Transform (FGT) via SOE Approximation

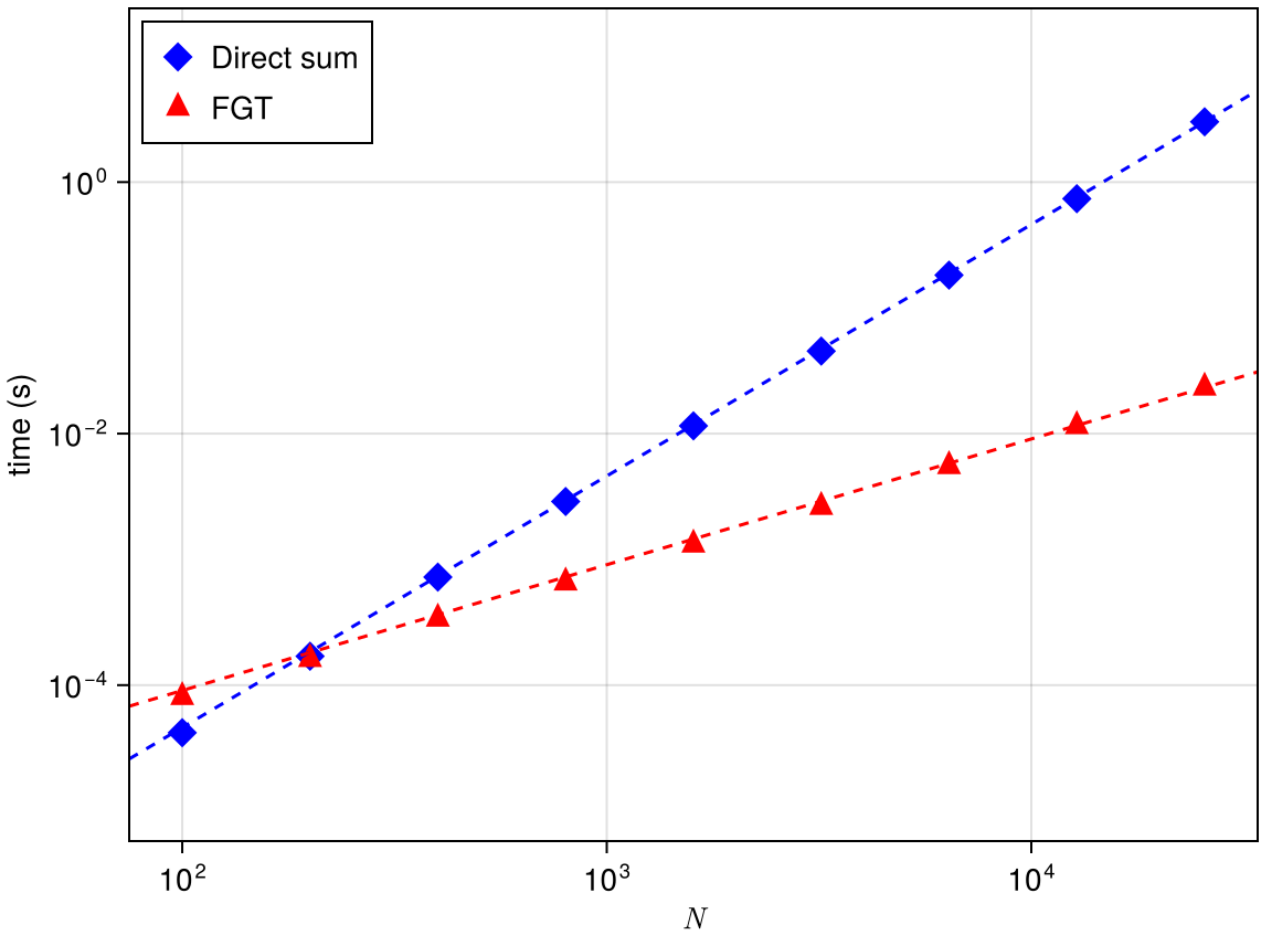


Figure: Comparing the complexity of direct sum and FGT.

Sum-of-exponentials Ewald2D (SOEwald2D)[3] method

To reduce the complexity of the Ewald2D summation, we applied the SOE approximation. Notice that:

$$e^{\pm kz_{ij}}\operatorname{erfc}\left(\frac{k}{2\alpha}\pm\alpha z_{ij}\right)=\frac{2\alpha}{\sqrt{\pi}}e^{-k^2/(4\alpha^2)}e^{\pm kz}\int_{\pm z}^{\infty}e^{-\alpha^2t^2-kt}dt\,, \tag{12}$$

which can be approximated by

$$\frac{2\alpha}{\sqrt{\pi}}e^{-k^2/(4\alpha^2)}e^{\pm kz}\int_{\pm z}^{\infty}\sum_{l=1}^{M}w_le^{-s_l\alpha|t|}e^{-kt}dt=\frac{2\alpha}{\sqrt{\pi}}e^{-k^2/(4\alpha^2)}\sum_{l=1}^{M}w_l\frac{e^{-\alpha s_lz}}{\alpha s_l+k}\,, \tag{13}$$

so that the summation is reformulated as

$$\sum_{1\le j<i\le N}q_iq_je^{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{\rho}_{ij}}e^{-\beta z_{ij}}\,, \tag{14}$$

which can be solved in $O(N)$ time via the FGT.

[3] Zecheng Gan et al. *Fast Algorithm for Quasi-2D Coulomb Systems*. 2024. arXiv: 2403.01521 [math.NA]. URL: https://arxiv.org/abs/2403.01521.

Sum-of-exponentials Ewald2D (SOEwald2D) method

To analyze the complexity, we first define ρ_s and ρ_ℓ by the average densities in the real and Fourier spaces

$$\rho_s = \frac{N}{L_x L_y L_z}, \quad \text{and} \quad \rho_\ell = \frac{L_x L_y}{(2\pi)^2}, \tag{15}$$

respectively. Thus, the short range and long range cost is given by

$$C_s = \frac{4\pi}{3} r_c^3 \rho_s N = \frac{4\pi s^3 N^2}{3\alpha^3 L_x L_y L_z}, \; C_\ell = \pi k_c^2 \rho_\ell M N = \frac{1}{\pi} s^2 \alpha^2 L_x L_y M N \; . \tag{16}$$

To balance C_s and C_ℓ, one takes

$$\alpha \sim \frac{N^{1/5}}{L_x^{2/5} L_y^{2/5} L_z^{1/5}}, \tag{17}$$

leading to the optimal complexity

$$C_s = C_\ell \sim \mathcal{O}(\log \epsilon^{-1} N^{7/5}). \tag{18}$$

Random batch SOEwald2D (RBSE2D) method

To further reduce the complexity, we applied the importance sampling technique, similar to that used in the random batch Ewald (RBE)[4] method, where the summation over the reciprocal space is replaced via an importance sampling.

$$\sum_{\boldsymbol{k}\neq\mathbf{0}} e^{-k^2/(4\alpha^2)} f(\boldsymbol{k}) \approx \frac{H}{P} \sum_{\eta=1}^{P} f(\boldsymbol{k}_\eta) \,, \tag{19}$$

where $f(k)$ represents the double summation above, P is an $O(1)$ constant, k_η are k are sampled Fourier modes according to

$$h(\boldsymbol{k}) := \frac{e^{-k^2/(4\alpha^2)}}{H} \quad \text{with} \quad H := \sum_{\boldsymbol{k}\neq\mathbf{0}} e^{-k^2/(4\alpha^2)}, \tag{20}$$

where H serves as a normalization factor.

[4] Shi Jin et al. "A random batch Ewald method for particle systems with Coulomb interactions". In: *SIAM J. Sci. Comput.* 43.4 (2021), B937–B960. DOI: 10.1137/20M1371385.

Random batch SOEwald2D (RBSE2D) method

Similar to the strategy in some FFT-based solvers, one may choose α such that the time cost in real space is cheap and the computation in the Fourier space is accelerated. More precisely, one chooses

$$\alpha \sim \frac{N^{1/3}}{L_x^{1/3} L_y^{1/3} L_z^{1/3}} \tag{21}$$

so that the complexity for the real space part and recirpocal space part is

$$C_s \sim \mathcal{O}(N),\ C_l \sim \mathcal{O}(PN)\ . \tag{22}$$

Thus the overall complexity of the RBSE2D is $\mathcal{O}(N)$ for all quasi-2D system setups.

Numerical Results

Numerical Error

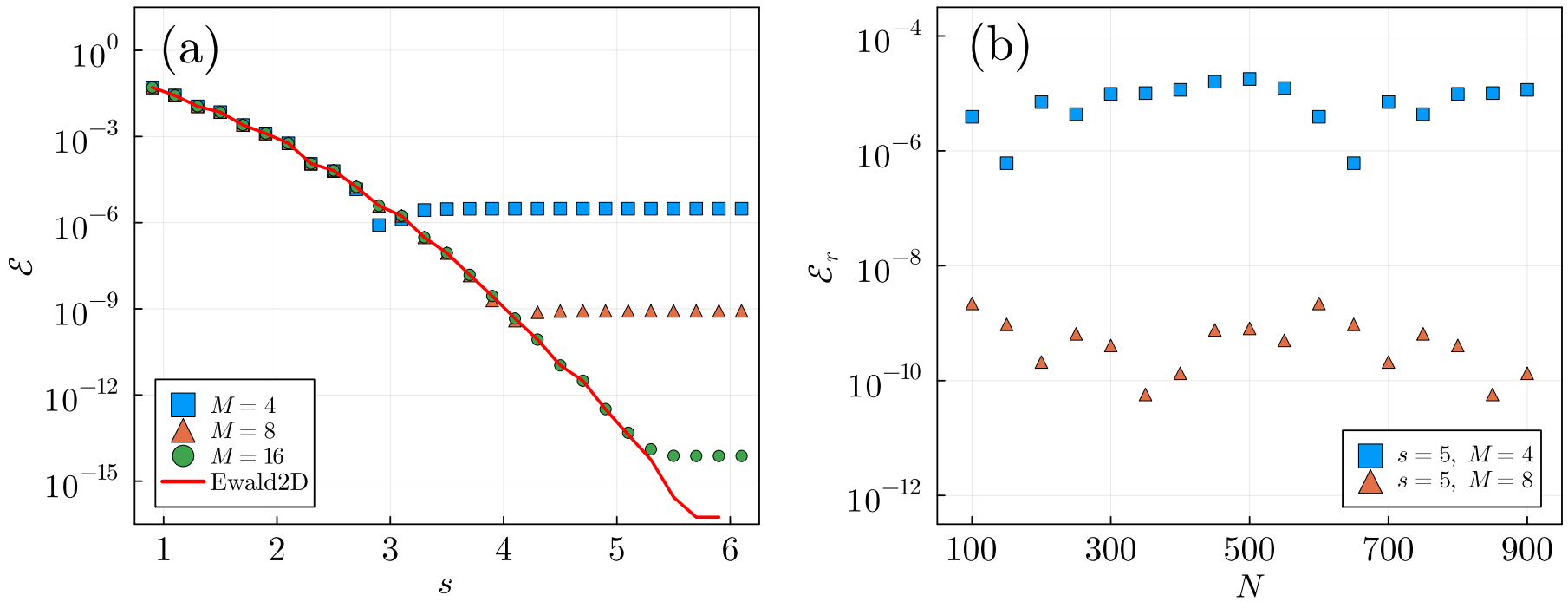


Figure: Accuracy in the electrostatic energy by the SOEwald2D method. (a): absolute error as a function of s; (b): relative error as a function of total number of ions N with fixed ion density ρ_s. Results with different number of exponentials M are considered.

Numerical Error

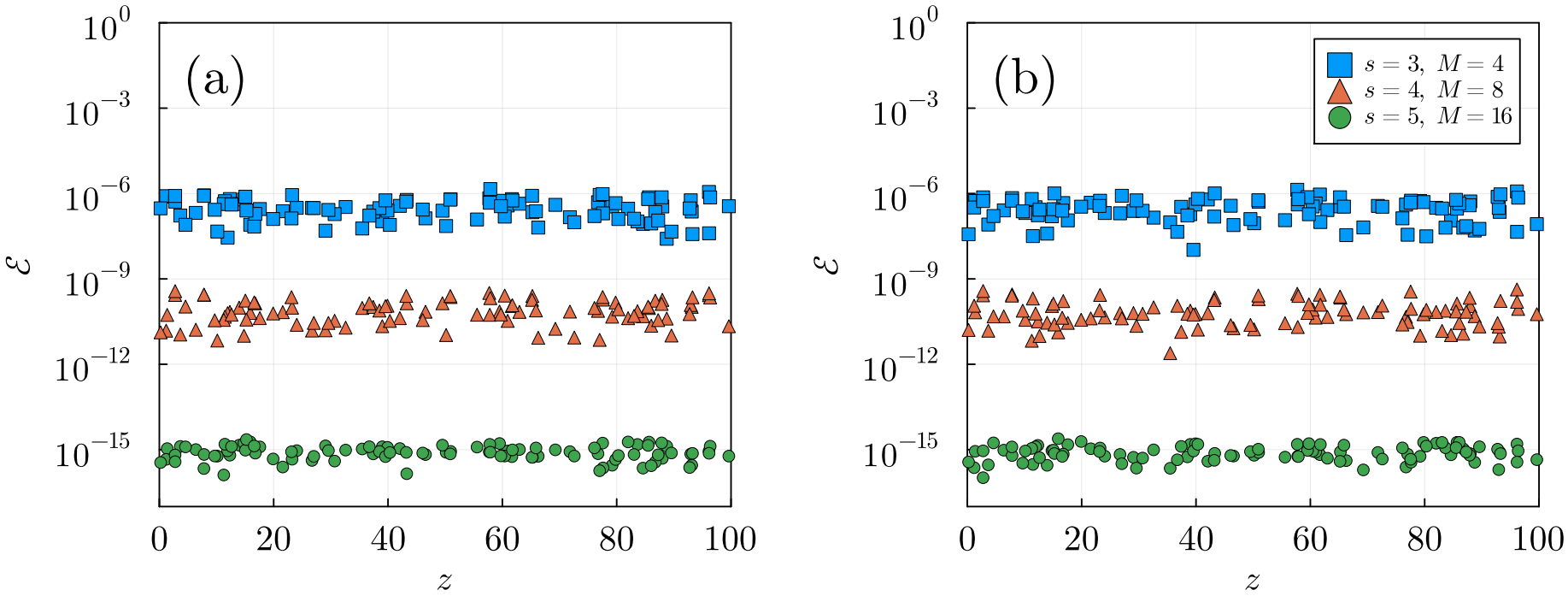


Figure: The absolute error in the pointwise electrostatic forces calculated using the SOEwald2D versus particles' z-coordinates. Two different scenarios are considered: (a) uniformly distributed 50 anions and 50 cations and (b) uniformly distributed 100 cations with surface charge densities $\sigma_{\text{top}} = \sigma_{\text{bot}} = -0.005$.

Numerical Error

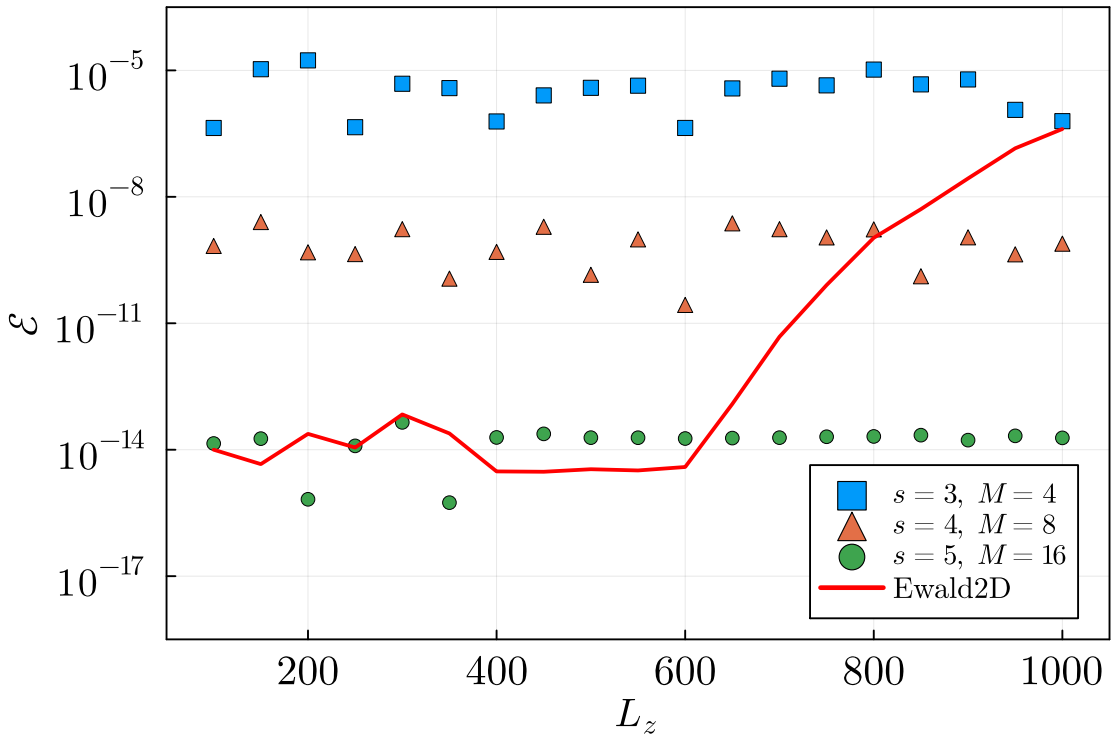


Figure: The absolute error in electrostatic energy is evaluated for the SOEwald2D method using three sets of parameters, as well as for the Ewald2D method with $s = 5$, as a function of the system's thickness L_z.

MD simulations

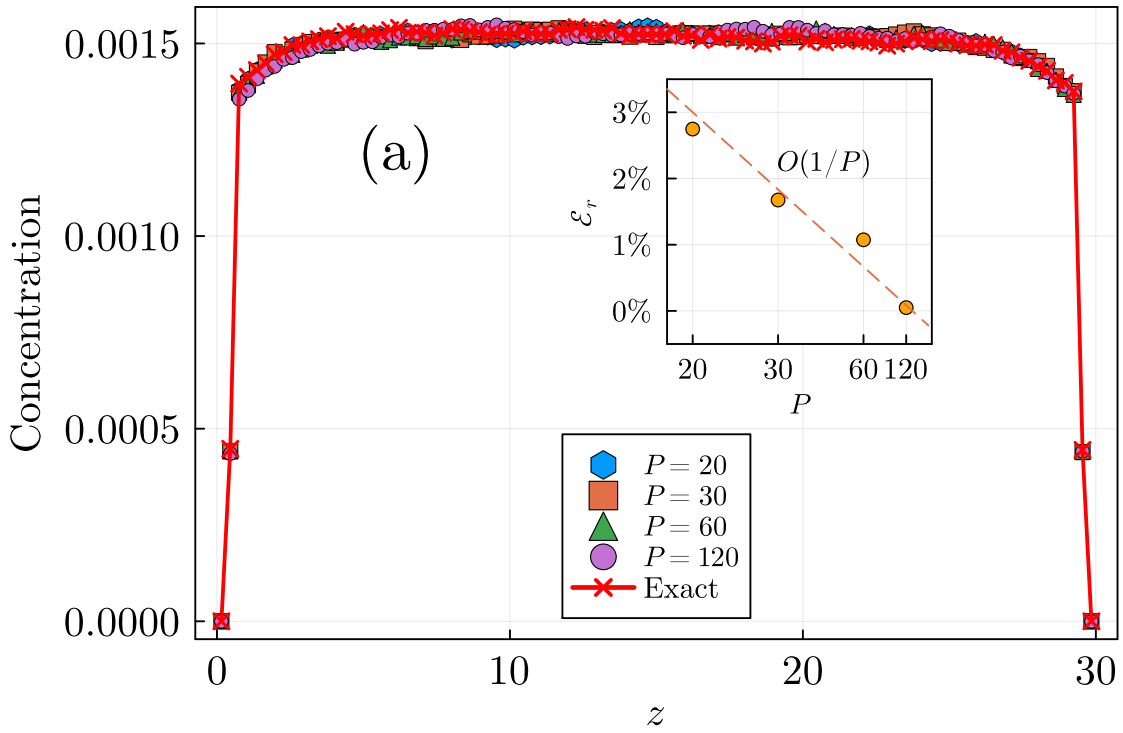


Figure: (a) The concentration of cations along z for a $1:1$ electrolyte confined by neutral slabs, with subplot indicating the convergence in the relative error of the average electrostatic energy as a function of batch size P; Results by using different batch sizes $P = 20, 30, 60, 120$ are shown.

MD simulations

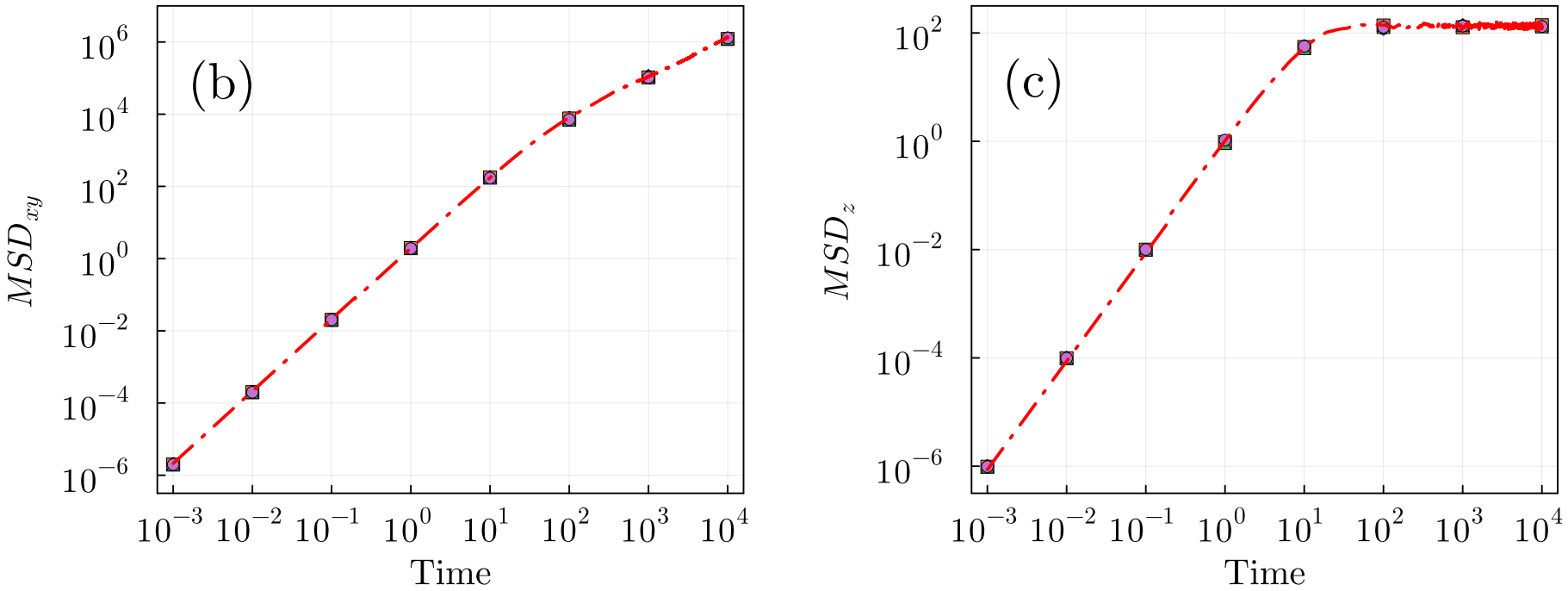


Figure: (b) and (c) the MSD profiles in xy and z against time for a $1:1$ electrolyte confined by neutral slabs. Results by using different batch sizes $P = 20, 30, 60, 120$ are shown.

MD simulations

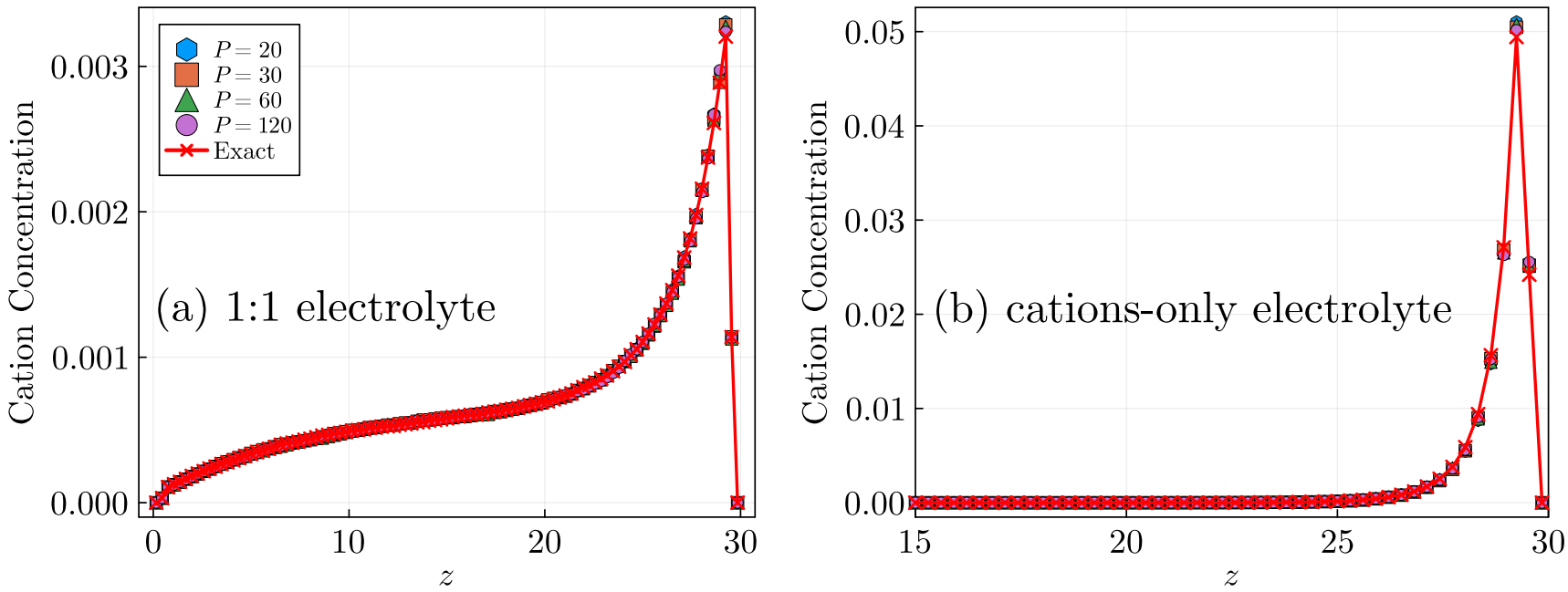


Figure: Concentration of cations in z for (a) a $1:1$ electrolyte confined between two charged slabs and (b) a cations-only system confined between two slabs, one of which is charged to neutralize the system.

Computational Complexity

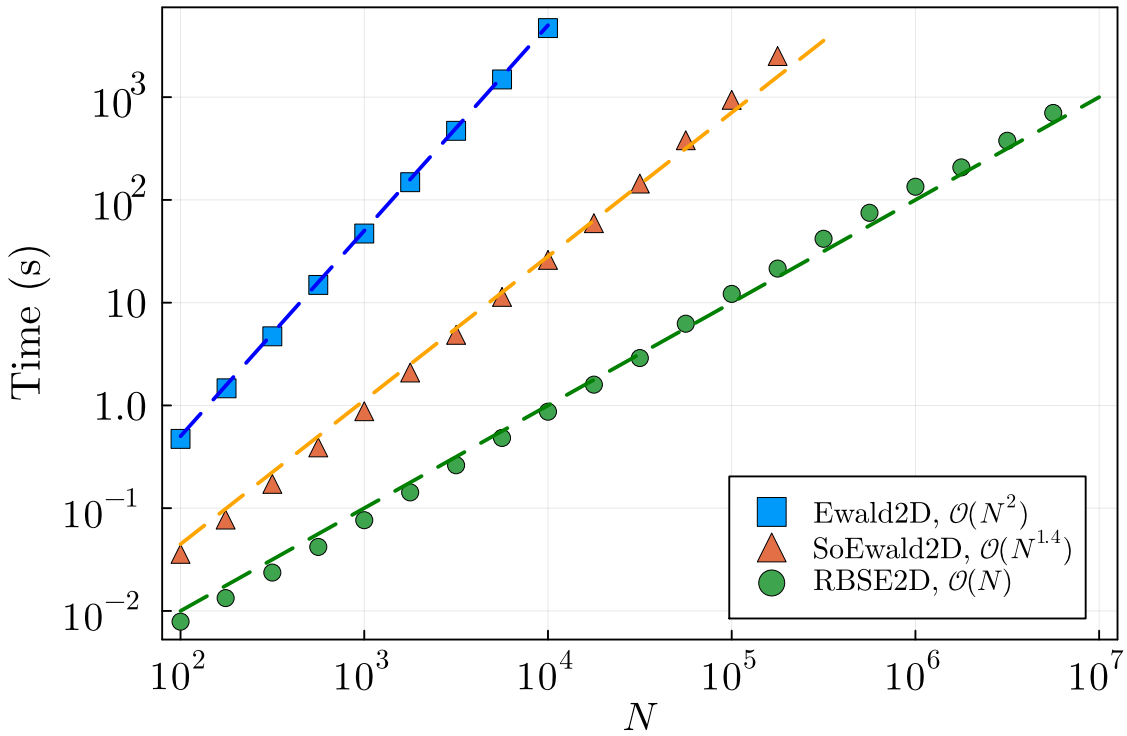


Figure: The CPU time cost for the Ewald2D, SOEwald2D, and RBSE2D methods versus the number of particles N, with fixed particle density ρ_s.

Conslusion

Conclusion

- A novel algorithm framework for calculating electrostatic interaction in a quasi-2D geometry, based on SOE kernel approximation and random batch sampling method.
- Achieving linear computational complexity with small prefactor, handles the anisotropy of quasi-2D systems without any loss of efficiency.
- A speedup of $2 \sim 3$ orders of magnitude comparing with Ewald2D method, enabling molecular dynamics (MD) simulations with up to 10^6 particles on a single core.
- Our method is mesh-free, and can be flexibly extended to other partially-periodic lattice kernel summations, with broad applications in material science, hydrodynamics and many other fields.

Conclusion

Figure: QR code to visit github repo for SoEwald2D.jl (left) and EwaldSummations.jl (right).

References

[1] Zixuan Gao, Jiuyang Liang, and Zhenli Xu. "A kernel-independent sum-of-exponentials method". In: *J. Sci. Comput.* 93.2 (2022), p. 40. DOI: 10.1007/s10915-022-01999-1.

[2] Shidong Jiang and Leslie Greengard. "Approximating the Gaussian as a sum of exponentials and its applications to the fast Gauss transform". In: *Commun. Comput. Phys.* 31.1 (2022), pp. 1–26. ISSN: 1991-7120. DOI: https://doi.org/10.4208/cicp.OA-2021-0031.

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