# Electrostatics in doubly periodic geometries

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# Steps

Doubly periodic problems with smooth forcing

Ewald splitting for point-like charges

Dielectric boundaries (walls)

Results

# Doubly periodic geometry

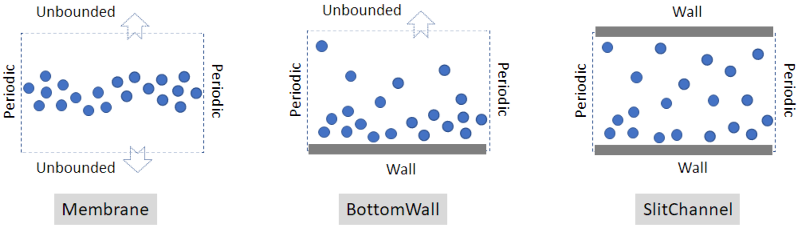
Poisson's equation for electrostatic potential

$$\epsilon \Delta \phi = -f$$

*doubly periodic* in $(x, y) \in [-L, L]$. Unbounded in $z$. Assuming electroneutral domain

$$\nabla \phi(x, y, z \to \pm\infty) \to 0$$

For now, assume $f$ is a smooth function



# Fourier approach

$$\epsilon \Delta \phi = -f$$

In our applications, $f$ is compactly supported in $[-L, L]^2 \times [0, H]$.

$$\rightarrow \epsilon \Delta \phi = 0 \quad z < 0 \text{ or } z > H$$

*Harmonic solve* in $xy$ Fourier space $k^2 = k_x^2 + k_y^2$

$$\epsilon \left( \widehat{\phi}_{zz} - k^2 \widehat{\phi} \right) = 0$$

$$\rightarrow \widehat{\phi}(k, z) = \begin{cases} Ae^{-kz} & z > H \\ Be^{kz} & z < 0 \end{cases}$$

This implies the boundary conditions

$$\widehat{\phi}_z(k, H) + k\widehat{\phi}(k, H) = 0$$

$$\underbrace{\widehat{\phi}_z(k, 0) - k\widehat{\phi}(k, 0) = 0}_{\text{Dirichlet to Neumann map!}}$$

Boundaries arbitrary $\rightarrow$ same BCs hold for *interior* $\widehat{\phi}$

# Finite problem to solve

$$\epsilon \Delta \phi = -f$$

Periodic BCs $\rightarrow$ FFT $\rightarrow$ 2 point BVP for each $k^2 = k_x^2 + k_y^2$

$$\epsilon \left( \widehat{\phi}_{zz} - k^2 \widehat{\phi} \right) = -\widehat{f}(k, z)$$
$$\widehat{\phi}_z(x, y, H) + k\phi(k, H) = 0$$
$$\widehat{\phi}_z(x, y, 0) - k\widehat{\phi}(x, y, 0) = 0$$

Solve this BVP using spectral integration matrix (Greengard 1991)

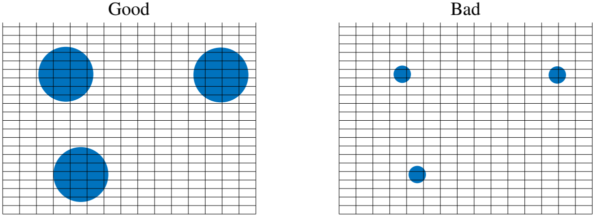
- Lay down Chebyshev grid
- Solve for $\hat{\phi}_{zz}$ on the Cheb grid: $\epsilon \left( \boldsymbol{I} - k^2 \boldsymbol{S} \right) \widehat{\phi}_{zz} = -\widehat{f}(k, z)$
- Obtain $\hat{\phi}$ by integration

Greengard. *SIAM J. Numer. Anal.* 28 (4), 1991.

# Smoothness of $f$

$$f(\boldsymbol{x}) = \sum_{i=1}^{N} \frac{q_i}{(2\pi g_w^2)^{3/2}} \exp\left(-\frac{\|\boldsymbol{x} - \boldsymbol{z}_i\|^2}{2g_w^2}\right)$$

- $f$ is the charge density due to collection of Gaussian charges
- How large can $g_w$ be?
- Can a grid-based method work? Only if $h \sim g_w$.




- Need alternative strategy for small charges

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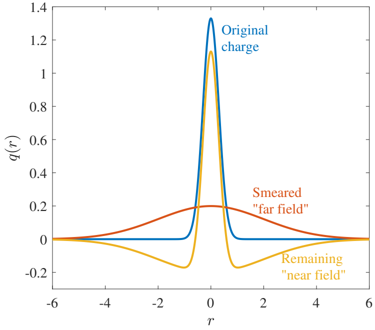
# Ewald splitting

- Introduce Gaussian splitting function

$$\gamma(r;\xi) \propto e^{-r^2\xi^2}$$

- *Splitting parameter* $\xi$ has units 1/length optimized for speed
- Split charge = smeared charge + "dipole"

$$f = \underbrace{f * \gamma}_{\text{far field}} + \underbrace{f * (1-\gamma)}_{\text{near field}}$$



# Why does Ewald help?

- Near field $\epsilon\Delta\phi^{(n)} = (1-\gamma) * f$ has net zero charge
  - Exponentially-decaying near field Green's function
  - Free space BC $\rightarrow$ analytical solution
  - Can be made nonzero at $\mathcal{O}(1)$ neighbors per point
  - Cost of near field $= \mathcal{O}(N)$
- Far field $\epsilon\Delta\phi^{(f)} = \gamma * f$ is wider and smoother
  - Grid-based solver works
  - Spread charge density to grid by convolving $f * \gamma^{1/2}$
  - Solve $\epsilon\Delta\psi = (f * \gamma^{1/2})$ on grid
  - Interpolate grid $\gamma^{1/2} * \psi$ to get $\phi^{(f)} = \epsilon^{-1}\Delta^{-1}(f * \gamma)$ at charges.

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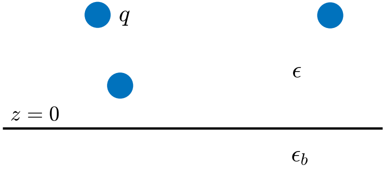
# Permittivity jump - single wall

BCs for the potential $\phi$ at a dielectric interface: continuity of potential and displacement

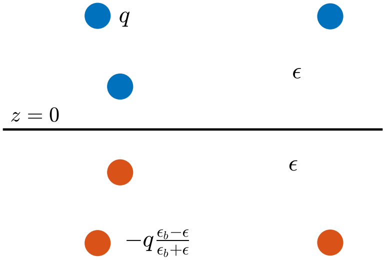
$$\phi(x, y, 0^+) = \phi(x, y, 0^-)$$

$$\epsilon \phi_z(x, y, 0^+) = \epsilon_b \phi_z(x, y, 0^-)$$



# Image construction - single wall

Solution on $z > 0$ same as with uniform permittivity and set of *image charges*



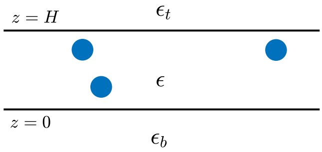

Use DP solver + Ewald splitting on the problem with images

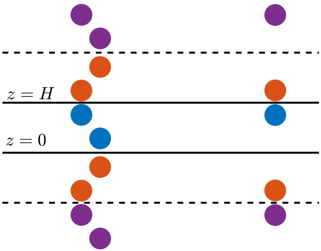
# Complications for slab geometry

- Three different permittivities
- New BCs at $z = H$

$$\phi(x, y, H^+) = \phi(x, y, H^-)$$

$$\epsilon \phi_z(x, y, H^-) = \epsilon_t \phi_z(x, y, H^+)$$



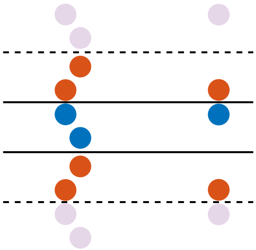




- Infinitely many images! Back to an infinite problem

# Ewald splitting for slab geometries

Near field is easy

- Choose $\xi$ s.t. only one set of images interact with slab
- Image construction satisfies BCs
- Still $\mathcal{O}(N)$



# Ewald splitting: far field

Far field more involved

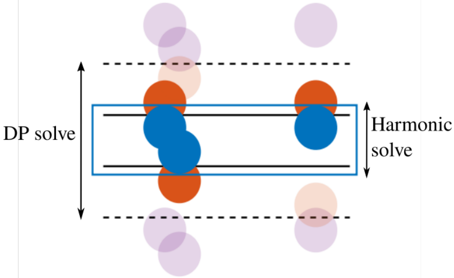
$$\epsilon\Delta\phi^{(f)} = -\gamma * \left(f^{(\text{charges})} + f^{(\text{img})}\right) = -\gamma * \left(f^{(\text{charges})} + f^{(\text{img, }1)} + f^{(\text{img, }2)}\right)$$

- Spread to grid = smear charges
- Identify interpolation domain
- Find images that overlap domain
- Do initial solve with *only* these images (BCs *not* satisfied)

$$\epsilon\Delta\tilde{\phi}^{(f)} = -\gamma * \left(f^{(\text{charges})} + f^{(\text{img, }1)}\right)$$

- But remaining images have $f^{(\text{img})} = 0$ in interp domain

$$\epsilon\Delta\left(\phi^{(f)} - \tilde{\phi}^{(f)}\right) = -\gamma * f^{(\text{img, }2)} = 0$$



# Charged walls

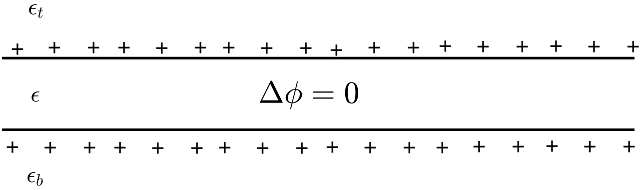
- Assume no charges (superposition)
- Harmonic solve with continuity BCs and

$$\epsilon\phi_z(x,y,0^+) - \epsilon_b\phi_z(x,y,0^-) = -\sigma_b(x,y)$$
$$\epsilon\phi_z(x,y,H^-) - \epsilon_t\phi_z(x,y,H^+) = \sigma_t(x,y)$$

- 2D FFT to get $\widehat{\sigma}_b(k)$, $\widehat{\sigma}_t(k)$
- Solve 2 pt BVP

$$\widehat{\phi}_{zz} - k^2\widehat{\phi} = 0$$

  with BCs above ($(x,y) \to k$)
- Can be combined with prior harmonic solve if desired



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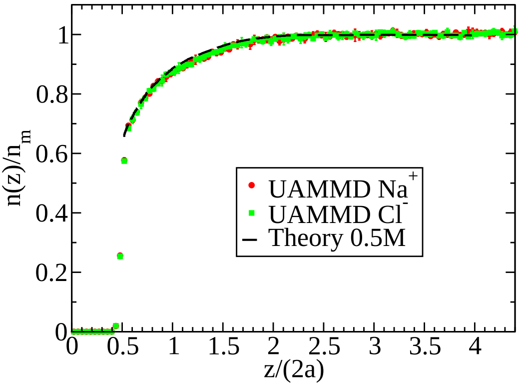
# Salt water electrolyte

$Na^+$ and $Cl^-$ ions (soft spheres of radius $a$) in water ($\epsilon \approx 78$) confined by glass wall ($\epsilon_{\text{out}} \approx 1$, really $2-5$)

- $q^* = -q\frac{\epsilon_{\text{out}}-\epsilon}{\epsilon_{\text{out}}+\epsilon} \approx 0.9q$, images repelled by each other



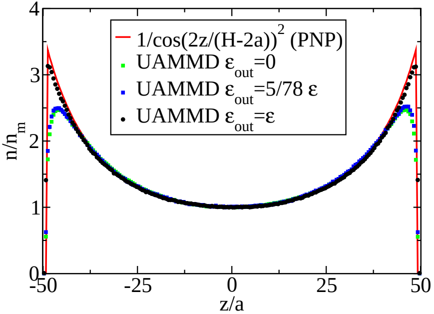

UAMMD = Brownian dynamics GPU code by Raul P.

Croxton et. al. *Can. J. Chem* 59 (13), 1981.

## Charged walls

Positively-charged wall with negatively charged ions

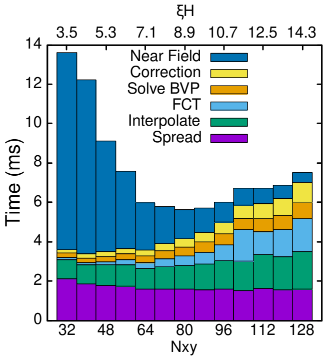
- $\epsilon_{\text{out}} = \epsilon \rightarrow$ no images, matches analytical solution of PNP equations (macroscopic theory, no $\epsilon_{\text{out}}$)
- $\epsilon_{\text{out}} = 5/78\epsilon \approx 0.06\epsilon \rightarrow$ Images repelled by each other
- $\epsilon_{\text{out}} = 0 \rightarrow$ field outside irrelevant, close to glass
- Density of charges drops near wall



# Speed on the GPU

Splitting parameter $\xi$ chosen to optimize speed

- Smaller $\xi$: slow near $e^{-r^2\xi^2}$ decay, fast Fourier $e^{-k^2/\xi^2}$ decay
  - Near field eats up entire cost
- Larger $\xi$: faster near field decay, slower Fourier decay
  - Finer grid, far field (spread & interpolate, FFT) cost more




- 20K charges = 6 ms per time step!