Speeding Electrostatic Calculation for Ferroelectric

Qingsong Zhang, Tahir Cagin and William A. Goddard, III

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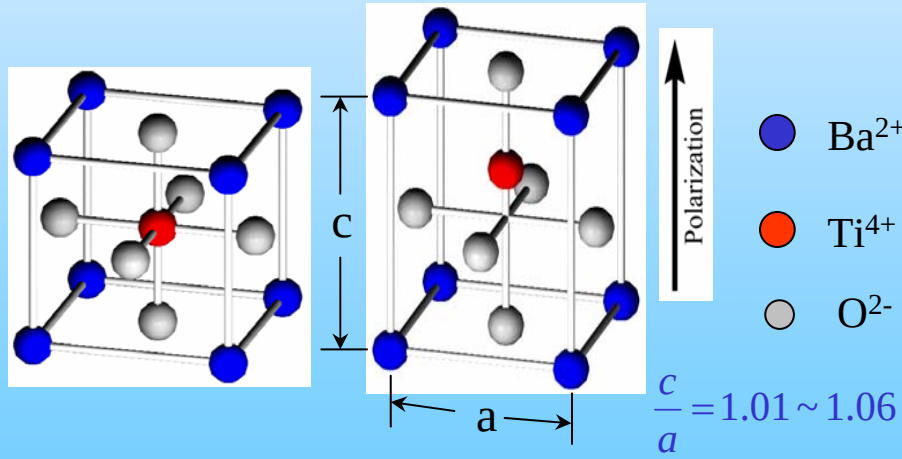
$BaTiO_3$

<111> polarized rhombohedral(**R**) | <110> polarized orthorhombic(**O**) | <100> polarized tetragonal(**T**) | Non-polar cubic(**C**)

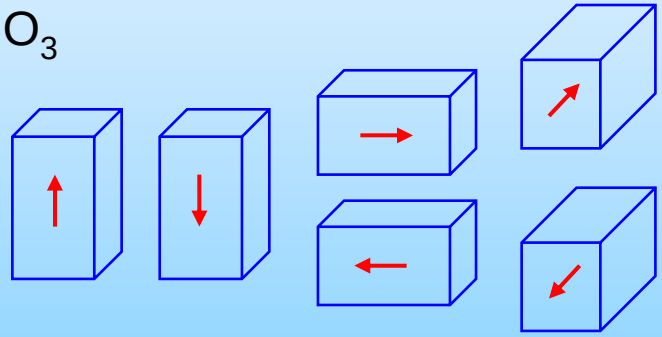
-90°C | 5°C | 120°C | Temperature

Different phases of $BaTiO_3$

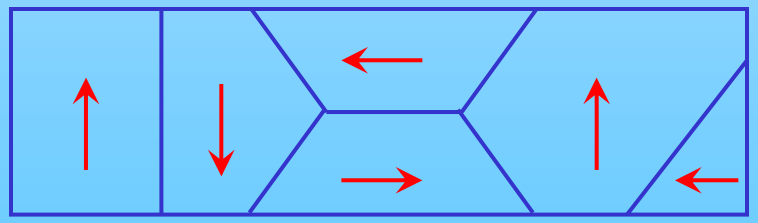


Non-polar cubic above Tc

<100> tetragonal below Tc



Six variants at room temperature



Domains separated by domain walls

Multi-scale Simulation of domain wall

DFT/GGA/PW

- Equation of State
- Minimized structure
- Hessian
- Dielectric Matrices

Force Field

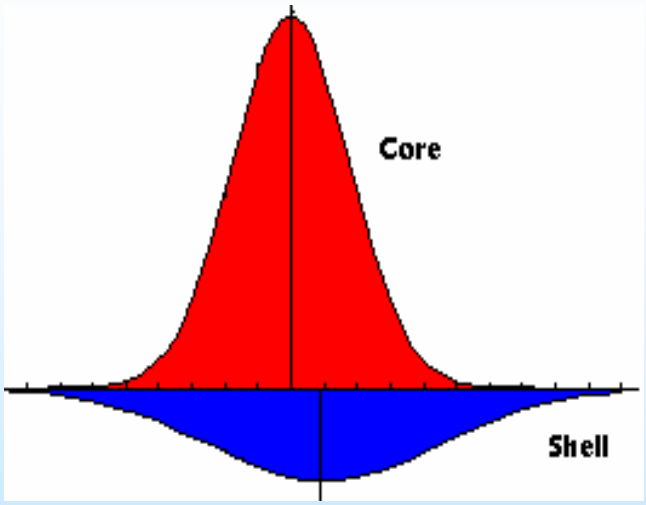
- Polarization
- Charge Transfer
- Efficient for million atom simulation

Application

- Phase structure
- Domain structure
- Oxygen Vacancies

P-QEq – Self-consistent Charge Transfer and Electronic Polarization

Electrostatic Interactions:



Proper description of Electrostatics is critical

- Core/Shell Separation
- Gaussians Distribution

  Shielding Effect
- Fixed core charge
- Variable shell charge

  Charge Transfer
- Shell move w.r.t. its core

  Electronic Polarization

$$\rho_{ic}(\vec{r}) = \left(\frac{\alpha_{ic}}{\pi}\right)^{3/2} q_{ic} \exp(-\alpha_{ic} \cdot |\vec{r} - \vec{r}_{ic}|^2)$$

$$\rho_{is}(\vec{r}) = \left(\frac{\alpha_{is}}{\pi}\right)^{3/2} q_{is} \exp(-\alpha_{is} \cdot |\vec{r} - \vec{r}_{is}|^2)$$

Part I: Long range interaction summation

Long Range Coulomb Interaction

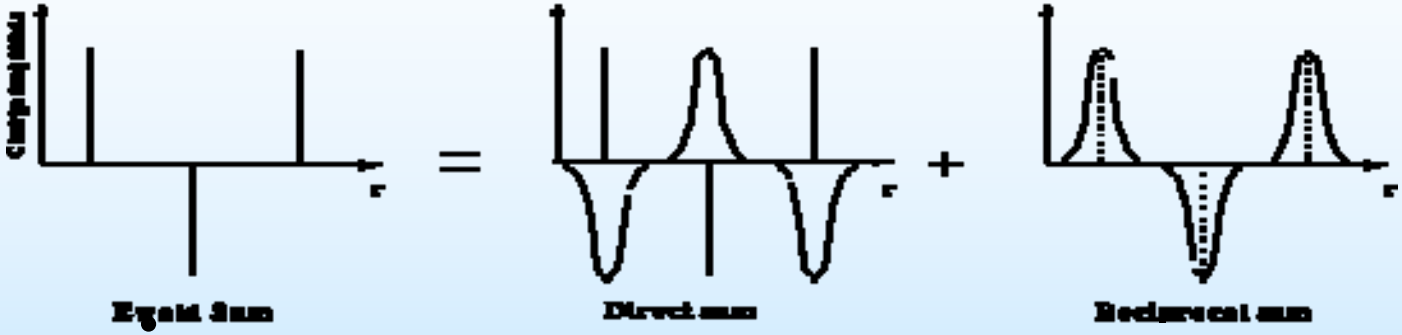
$$U = \frac{1}{2}{\sum_{\mathbf{n}}}' \sum_{i=1}^{N} \sum_{j=1}^{N} \frac{q_i q_j}{r_{ij,\mathbf{n}}}$$

$$\mathbf{n} = (n_1, n_2, n_3) = n_1 \mathbf{L}_x + n_2 \mathbf{L}_y + n_1 \mathbf{L}_z$$

$$r_{ij,n} = \left| \mathbf{r}_{jn} - \mathbf{r}_i \right| = \left| \mathbf{r}_i - \mathbf{r}_j + \mathbf{nL} \right|$$

Ewald Summation

Idea: Separation of Potential into direct sum and reciprocal sum



$$U_{Ewald} = U^r + U^m + U^o$$

1. Real part, $U^r = \frac{1}{2}\sum_{i,j}^{N'}\sum_{n} q_i q_j \frac{erfc(\alpha r_{ij,n})}{r_{ij,n}}$ ⟶ O(N)

2. Reciprocal part, $U^m = \frac{1}{2\pi V}\sum_{i,j}^{N} q_i q_j \sum_{m\neq 0} \frac{\exp(-(\pi m/\alpha)^2 + 2\pi i \mathbf{m}\cdot(\mathbf{r}_i - \mathbf{r}_j))}{m^2}$ ⟶ $O(N^3)$!!!

3. Self energy correction, $U^o = \frac{-\alpha}{\sqrt{\pi}}\sum_{i-1}^{N} q_i^2$ ⟶ O(N)

1. P. Ewald, Ann. Phys. Commun. 87 (1995) 375

2. S. De Leeuw, J. Perram and E. Smith, Proc. Roy. Soc London A 373 (1980) 27

Standard Ewald Summation Methods

1. Reciprocal Space : double loops to single loop by structure factor

$$U^m = \frac{1}{2\pi V}\sum_{m\neq 0}\frac{1}{m^2}\exp\left(-\left(\frac{\pi m}{\alpha}\right)^2\right)\sum_{i,j}^{N} q_i q_j \exp\left(2\pi i\mathbf{m}\cdot(\mathbf{r}_i-\mathbf{r}_j)\right)$$

$O(N^3)$ to $O(N^2)$

$$U^m = \frac{1}{2\pi V}\sum_{m\neq 0}\frac{1}{m^2}\exp\left(-\left(\frac{\pi m}{\alpha}\right)^2\right)S(\mathbf{m})S(-\mathbf{m})$$

$$= \frac{1}{2\pi V}\sum_{m\neq 0}\frac{1}{m^2}\exp\left(-\left(\frac{\pi m}{\alpha}\right)^2\right)\left|S(\mathbf{m})\right|^2$$

where $S(m) = \sum_{k=1}^{N} q_k \exp(i\cdot 2\pi\cdot m\cdot r_k)$

Standard Ewald Summation Method

2. Balance calculation cost in real space and reciprocal space

$$T_r = O(N)$$
$$T_m = O(N^2)$$

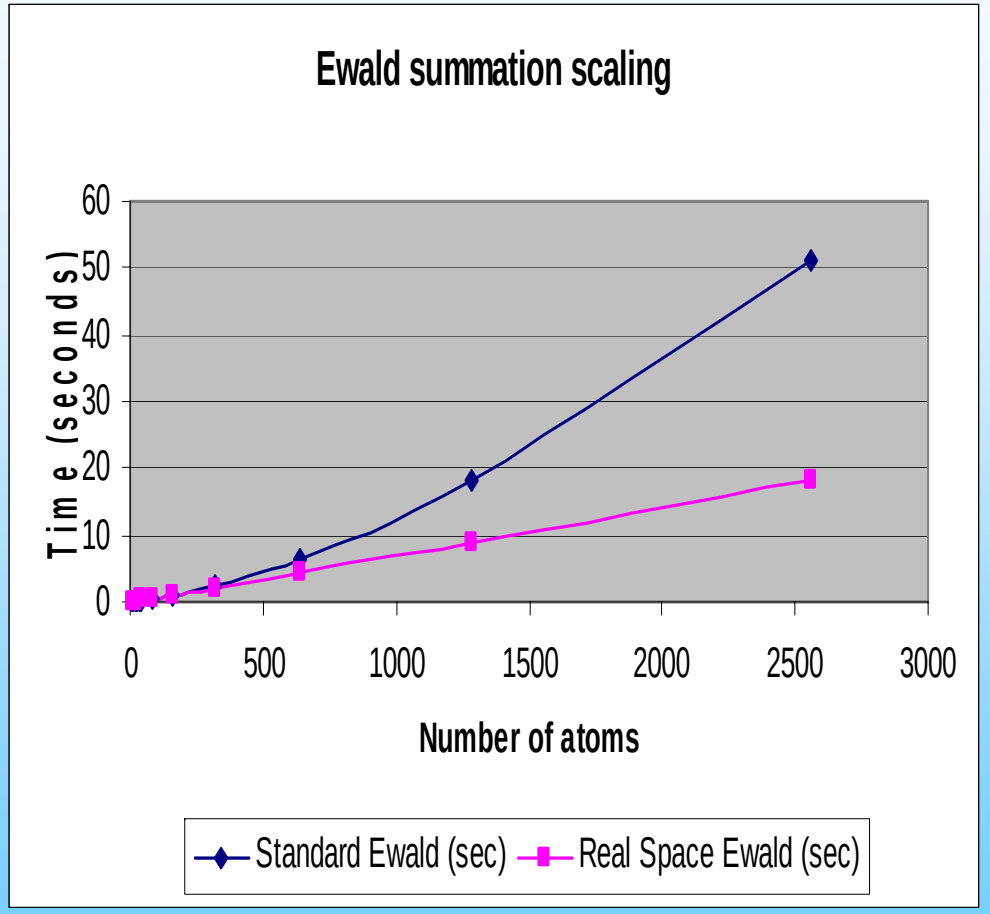
↓ Optimize a

$$T_r + T_m = O(N^{3/2})$$

3. Real space Ewald

By choosing very small alpha, contribution from reciprocal space can be ignored.

$$T = T_r = O(N)$$



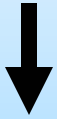
Part II: Charge Transfer

Electrostatic energy

$$E^{ES} = E^{ES}\left(q_{1s}, q_{2s} \cdots q_{Ns}\right)$$

Charge Equilibration

$$\begin{cases} \chi = \frac{\partial}{\partial q_1^s} E^{el} = \frac{\partial}{\partial q_2^s} E^{el} = \ldots = \frac{\partial}{\partial q_N^s} E^{el} \\ \sum_{i=1}^{N} q_i^s = q_{total} - \sum_{i=1}^{N} q_i^c \end{cases}$$



$$q_1^s, q_2^s \ldots q_N^s$$

- Energy
- First Derivatives (Force & Stress)
- Second Derivatives (Hessian & Elastic Constant)

Exact Solution of Charge Equilibration

$$\begin{pmatrix} J_{1s,1s}+J_1^o & J_{1s,2s} & \dots & J_{1s,Ns} & -1 \\ J_{2s,1s} & J_{2s,2s}+J_2^o & \dots & J_{2s,Ns} & -1 \\ \dots & \dots & \dots & \dots & \dots \\ J_{Ns,1s} & J_{Ns,2s} & \dots & J_{Ns,Ns}+J_N^o & -1 \\ -1 & -1 & \dots & -1 & 0 \end{pmatrix} \cdot \begin{pmatrix} q_{1s} \\ q_{2s} \\ \dots \\ q_{Ns} \\ \chi \end{pmatrix} = \begin{pmatrix} -\sum_j (J_{1s,jc}+\delta_{1j}J_1^o)q_{jc} - \chi_1^o + j_{1c,1s}^o q_{1c} \\ -\sum_j (J_{2s,jc}+\delta_{2j}J_2^o)q_{jc} - \chi_2^o + j_{2c,2s}^o q_{2c} \\ \dots \\ -\sum_j (J_{Ns,jc}+\delta_{Nj}J_N^o)q_{jc} - \chi_N^o + j_{Nc,Ns}^o q_{Nc} \\ \sum_j q_{jc} - Q_{tot} \end{pmatrix}$$

Memory scales with N^2;Time scales with N^3

Compuation Time (seconds)

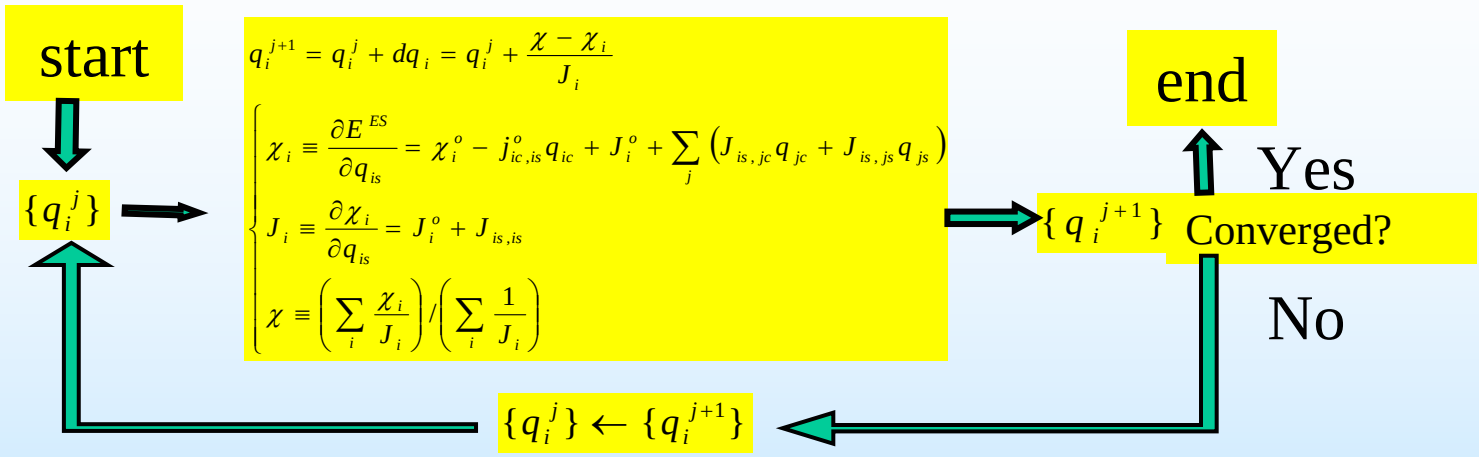
Test

Number of	Qeq/Exact
80	0.156
160	0.48
320	2.059
640	10.804
1280	69.245
2560	478.1
...	...

Estimate

10,000	8 hour
100,000	1 year
1,000,000	1000 year

Self consistent field charge equilibration



Compuation Time (seconds)

Number of	Qeq/Exact	Qeq/SCF
80	0.156	0.54
160	0.48	1.04
320	2.059	2.14
640	10.804	4.29
1280	69.245	8.81
2560	478.1	17.75
…	…	…
10,000	8 hour	1.2 min
100,000	1 year	12 min
1,000,000	1000 year	2 hour

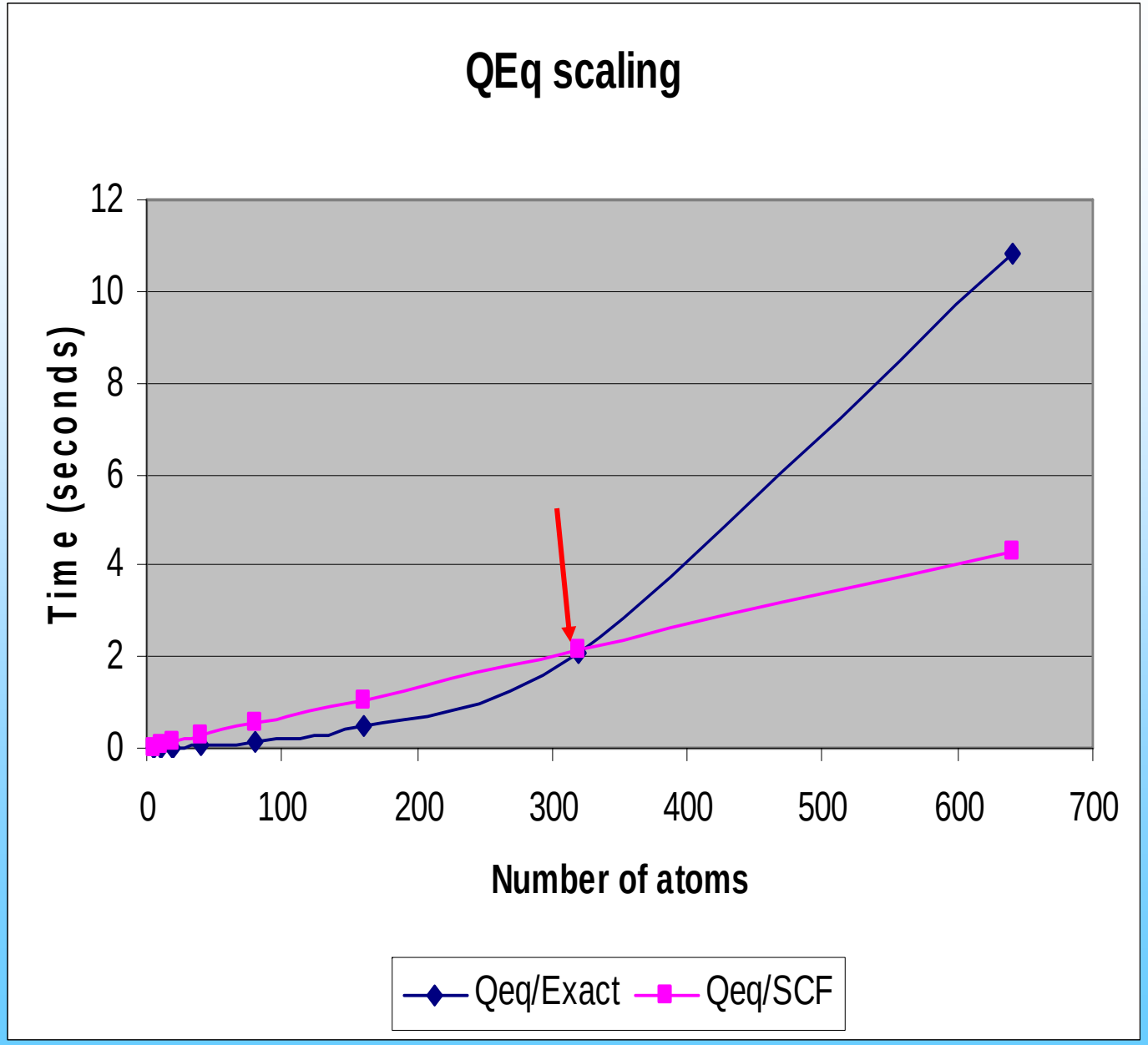
Test

Estimate

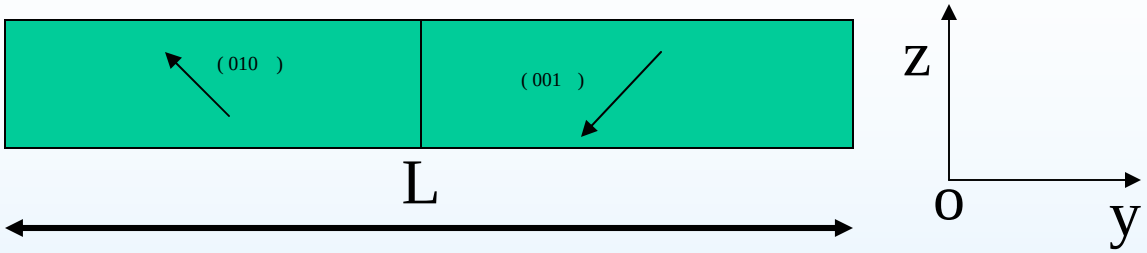
Memory scales with N;

Time scales with N

QEq/Exact vs. QEq/SCF



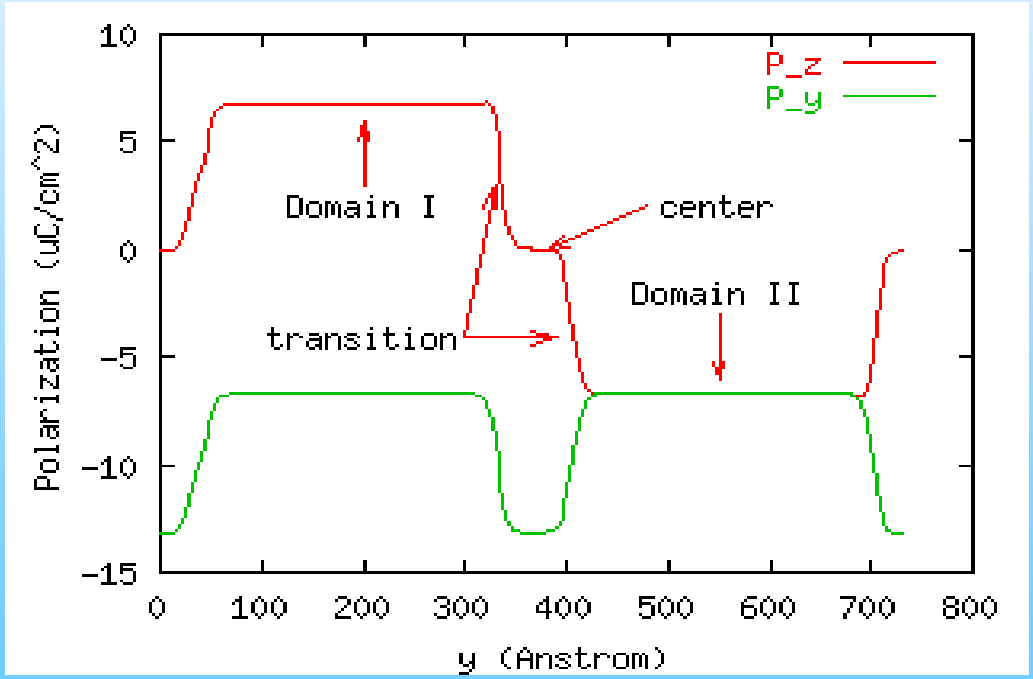
90° Domain Wall of BaTiO3

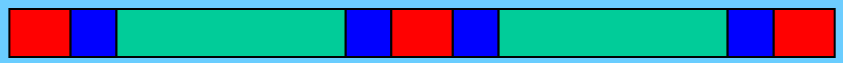


$$2 \times \sqrt{2}N \times 2\sqrt{2}$$

with N=128

8 Å x 724 Å x 11 Å (5160 atoms)





- Wall energy is 0.68 erg/cm^2
- Only stable for L>=362 Å (N>=64)

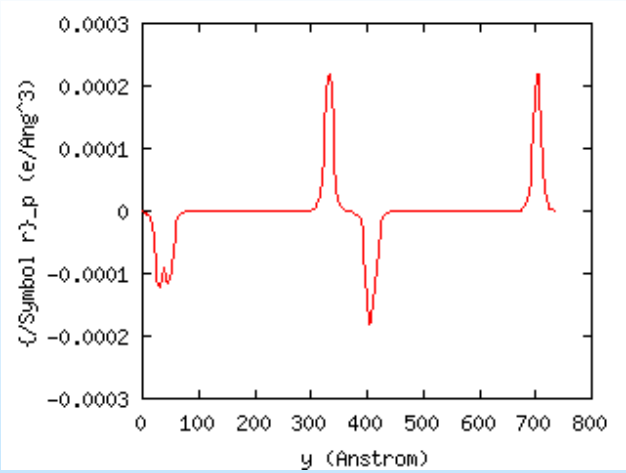
Wall center

Transition Layer

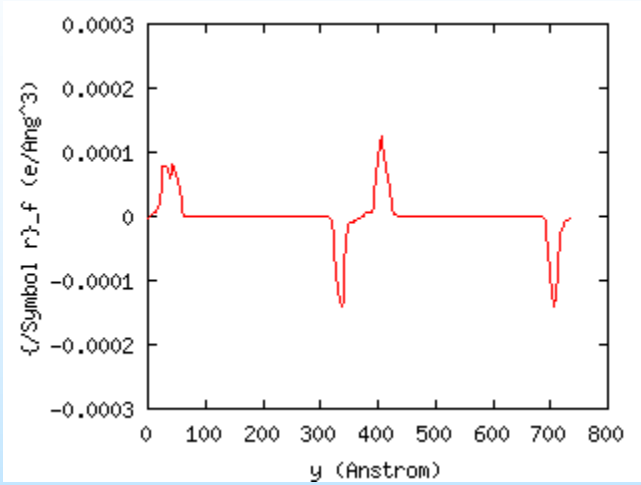
Domain Structure

90° Domain Wall of BaTiO3

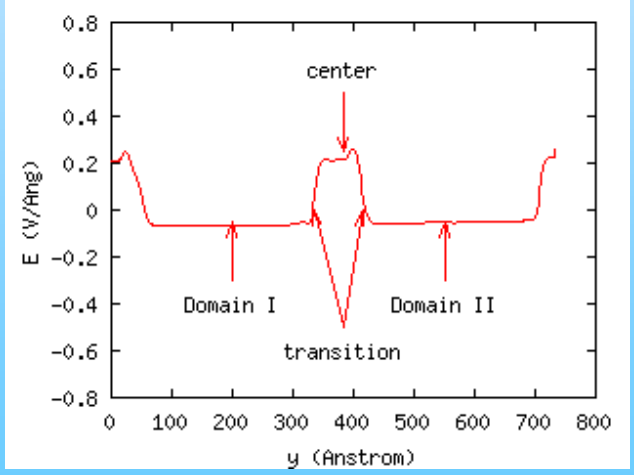
Polarization Charge Density



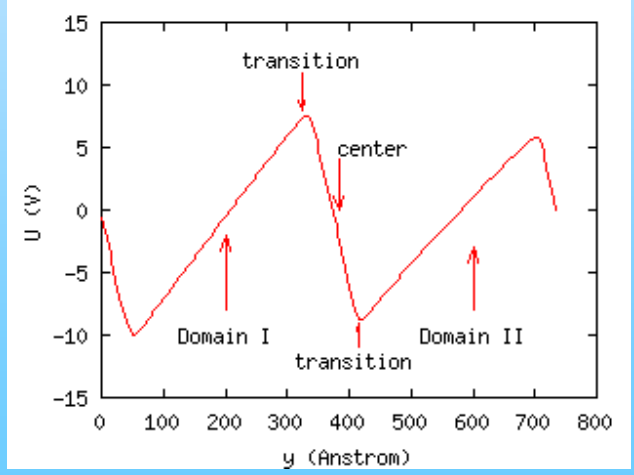
Free Charge Density



Electric Field



Electric Potential



Conclusion:

1. Linear Scaling of Electrostatic Interaction Summation
2. Linear Scaling of Charge Transfer Calculation
3. 90 degree domain wall structure