Bridging to the Continuum Scale for Ferroelectric Applications

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Background: Characteristics of Ferroelectric Materials

- Ceramic materials
  - BaTiO₃, PZT, PLZT, etc.

- Polarization

- Electromechanical response

- Extensive applications
  - sensors, actuators, high frequency microwave, etc.
Background: Designability of the material

- **Material composition**
  - PZT solid solution: \( \text{PbTiO}_3 / \text{PbZrO}_3 \)
  - Various composition: PZT-4, PZT-5, PZT-5A, PZT-5H, etc

- **Temperature effect** (Merz, 77)

- **Frequency sensitivity**

- **Pressure sensitivity**

- **Grain size effect**
  (McNeal, 97)


**Background:** Complexity of the problem

- Polycrystals of material
- Complicate domain structure within a grain
- Multiple states of material
- Complicate geometry of problem
- Unclear mobility of domain wall
- Highly incompatible front of domain wall

*Jaffe, 1971*

*Merz, 1954*
**Multiscale Modeling: Enabling Technology for System-Level Material Design**

**Force Fields and MD**
- Dielectric constant for various nanostructures
- Dielectric loss mechanism
- Domain wall and interface mobility
- Interaction with substrate
- Normal modes – soft modes

**ab initio QM**
- EoS of various phases
- Transition barriers
- Vibrational frequencies
- Normal modes

**Mesoscale**
- Electromechanical constitutive laws of single crystal
- Domain switching dynamics
- Response to high frequent loading
- Role of grain size
- Effect of temperature

**Finite Element (Macro Scale)**
- Polycrystals
- Complex geometry of thin film
- Complicate applied loading
- Large scale simulation

**Direct Problem**

**Inverse Problem**

**Sensitivity Analysis**
Model linking from QM/FF/MD to continuum

- dielectric constants
- polarization and spontaneous strain
- transition barriers
- domain wall mobility

ab initio QM

FF and MD

Meso Scale

Finite Element

Applications as continuum

Inverse problem

• geometry
• constraints
• grain structures
• loadings

• local constitutive
• local polarization
QM/FF/MD: Nanostructure-property relationship

Ti positions in each region as a function of time

- **2x2x8 cell**
- **T=300 K** (near the transition temperature for this force field)
- **Ti hopping indicates the motion of the domain wall**

- **c/a=1.01**
  - Non-polar

- **c/a=1.03**
  - Polar

- **c/a=1.05**
  - Polar with mobile walls
Nanostructure-property relationship: polarization

- **Strain can be used to control the ferroelectric phase transition** (change the transition temperature)
- **An appropriately chosen substrate can be used to tune the dielectric response**

**Polarization vs. time – T=300 K**

- **c/a in the range 1-1.01**
  - Non-polar: small polarization fluctuations
  - → low dielectric constant

- **c/a in the range 1.02-1.03**
  - Ferroelectric transition: large fluctuations & easy switching → good MW properties

- **c/a 1.5**
  - Ferroelectric: large fluctuations & switching is harder → domain wall mobility
Tests against canonical systems: MD

Role of local strain on dielectric relaxation frequency

MD simulations, BaTiO₃
P-QEq force field (Caltech)

- Simulations capture increase in relaxation frequency from tetragonal to cubic BaTiO3
- Higher relaxation frequency in MD simulations is due to sample size

Experiment: McNeal et al. JAP 1998

- Fine grain sample (FGBT) is pseudo-cubic due to internal stresses
- Coarse grain sample (CGBT) is tetragonal
Predicted response to electric field: Meso

- $\sigma = 0$
- Transition temperature

$\varepsilon$ vs. $E$

$D$ vs. $E$

180° switching

90° switching
Tests against canonical systems: Meso

- Pressing force applied parallel to the electrical field.
- Simulations capture the change of butterfly loops of $\varepsilon$ vs. $E$ with the increase of applied force.
- Simulations agree well with experiments in $P$ vs. $E$ loop at a range of applied force.

Experiments are from E. Baucsu, etc., JMPS, 52, 2004
• Stable hysteresis loop at low frequency
• Complete loss of response to the change of applied electrical field at extremely high frequency.
• Lagging movement of domain-wall behind the change of applied field increase the energy loss.
• The sensitivity to domain-wall mobility is the slope of individual curves at specific frequency of applied field.

• As expected it is very low when the frequency is low but very high when it makes the loss close to \( \tan(\delta_{\text{max}}) \).
Simulations demonstrate the double hysterisis loop near Curie temperature, which agrees well with experimental findings.

The rationality is due to the equal stability of cubic phase and tetragonal phase near Curie temperature $T_c$.

Right figures show the presence of cubic phase during domain switching process at $T_c$, but not found at temperature $T<<T_c$.

(experiment from W.J. Merz, Phys. Rev., 91, 1953, 513-517)
• Grain size significantly affect the domain-switching in a single-grain lattice.

• Small grain size makes it easy to nucleate new domains and to complete a cycle of domain switching.

• Energy loss in left figure indicates the lattice with small size responds well to high frequently cyclic electrical field.

Variation of energy loss with the frequency when the sinusoidal electrical fields apply on grain with different size.
Macroscale: From mesoscale to continuum

Within each element:
- Material is homogeneous
- Constitutive law follows the prediction by mesoscale model

Between elements
- Material may be different
- Grain boundary
- Local interaction
- Compatibility

Capability
- Complicate geometry
- Heterogeneous material
- Complex constraints and loading conditions
- Local interaction
Example of applications: mechanically driven polarization

- ARBITRARY GEOMETRIES
- GENERAL B.C.
- 2D and 3D PROBLEMS

Initial condition

Load

Undeformed

Deformed

- Complex nucleation and propagation of domain switching
- Most flexible in matching real conditions

Front of domain switching
Simulation results: switched domains

Domains switched

Red (1) = full switched;
blue (0) = no switched.
Simulation results: mechanical

\[ \sigma_{xx} \]

\[ \sigma_{yy} \]

\[ \tau_{xy} \]
Simulation results: electrical

Potential

$E_x$

$E_y$
**Inverse problem**: Sensitivity analysis

**Goal:**
- Understand how small changes at the microscale affect macroscopic behavior
- Quantify the precision of the simulations
- Critical tool for the design of new materials

**Sensitivity analysis**: take derivatives across scales

Calculate the change in dielectric loss with local strain \( \varepsilon = \frac{c}{a} \)
(ratio between \( c \) and \( a \) lattice parameters)

\[
\frac{\partial \text{Loss}}{\partial \varepsilon} = \frac{\partial \text{Loss}}{\partial u_{\text{wall}}} \cdot \frac{\partial u_{\text{wall}}}{\partial \varepsilon}
\]

- Dielectric loss
- Domain wall mobility
- Local strain (\( \varepsilon = \frac{c}{a} \))

From mesoscale simulations

From atomistic simulations
Sensitivity analysis

From MD simulations

From meso-scale simulations
Sensitivity analysis @work

Dielectric loss

\[
\frac{\partial \text{Loss}}{\partial \epsilon} = \frac{\partial \text{Loss}}{\partial u_{\text{wall}}} \cdot \frac{\partial u_{\text{wall}}}{\partial \epsilon}
\]

Domain wall mobility

Local strain (\(\epsilon = c/a\))

From mesoscale simulations

\[
\left. \frac{\partial \text{Loss}}{\partial u_{\text{wall}}} \right|_{f=10\, \text{GHz}, \ u_{\text{wall}}=100\, \text{m/s/Pa}} = -\frac{100\%}{10\%}
\]

From atomistic simulations

Dielectric Loss increases by 10% per 1% decrease in wall mobility

\[
\left. \frac{\partial \text{Loss}}{\partial \epsilon} \right|_{c/a=1.85} = -\frac{130\%}{2.77\%}
\]

Wall mobility increases by 47% per 1% decrease in c/a

\[
\frac{\partial \text{Loss}}{\partial \epsilon} = 469
\]
Conclusions

- Test against canonical systems indicates the approach at each particular level is appropriate.
- Dielectric constants, polarization & spontaneous strain, transition energy barriers, and domain wall mobility play the roles to bridge QM/MD to Meso/Macro scale models.
- Constraint elements in finite element link the mesoscale to macroscale model in dealing with complicating geometry, various constraints, and heterogeneous materials.
- Sensitivity analysis supplies a tool to do material design by optimize either a particular parameter or a group of factors.