Beyond piezoelectrics: First-principles theory and calculations of flexoelectricity

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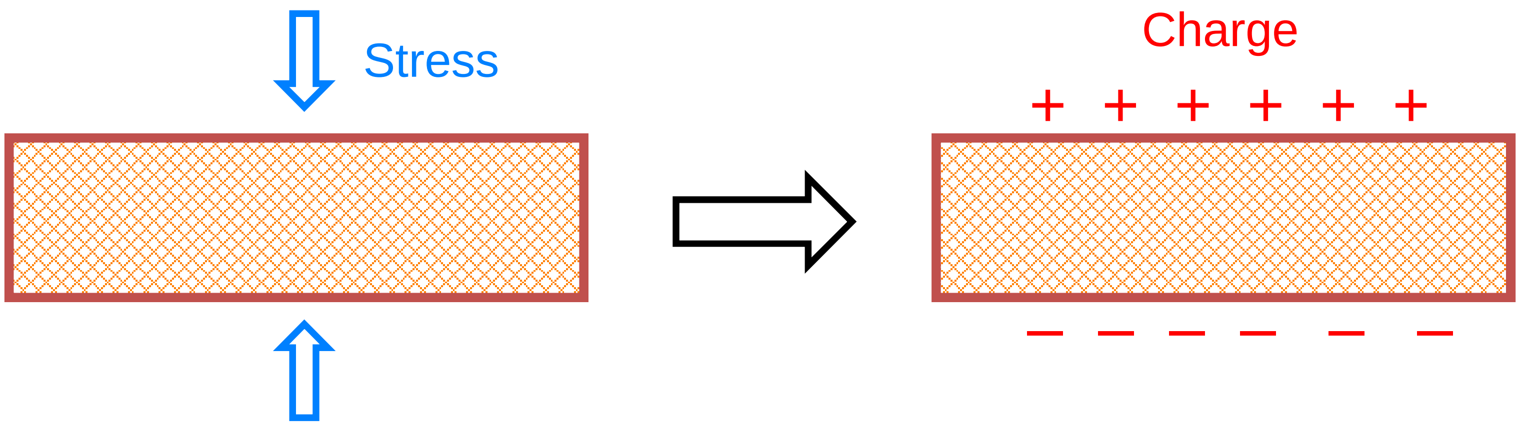
Outline

- Introduction
- First-principles theory of flexoelectricity
- First-principles calculation of flexoelectricity
- Summary

Piezoelectricity

Coupling between **strain** and polarization

$$P_i = e_{ijk}\,\eta_{jk}$$

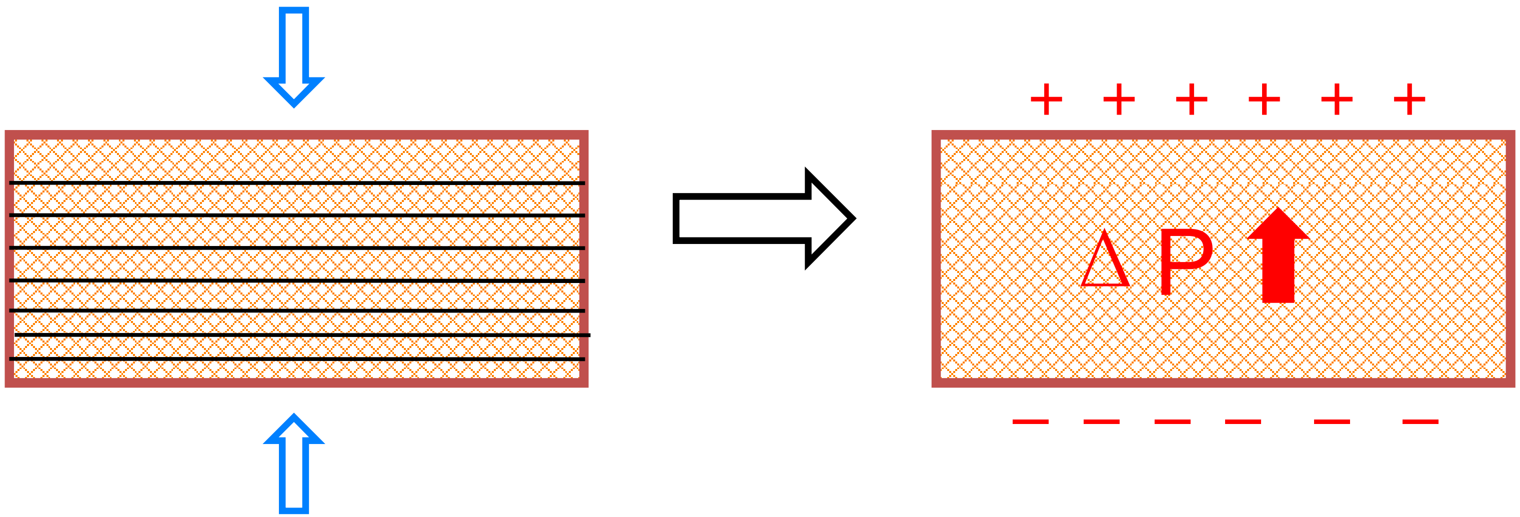


Only exists in **non-centrosymmetric** materials

Flexoelectricity

Linear coupling between **strain gradient** and polarization.

Flexo $$P_i = \mu_{ijkl} \frac{\partial \eta_{jk}}{\partial x_l}$$



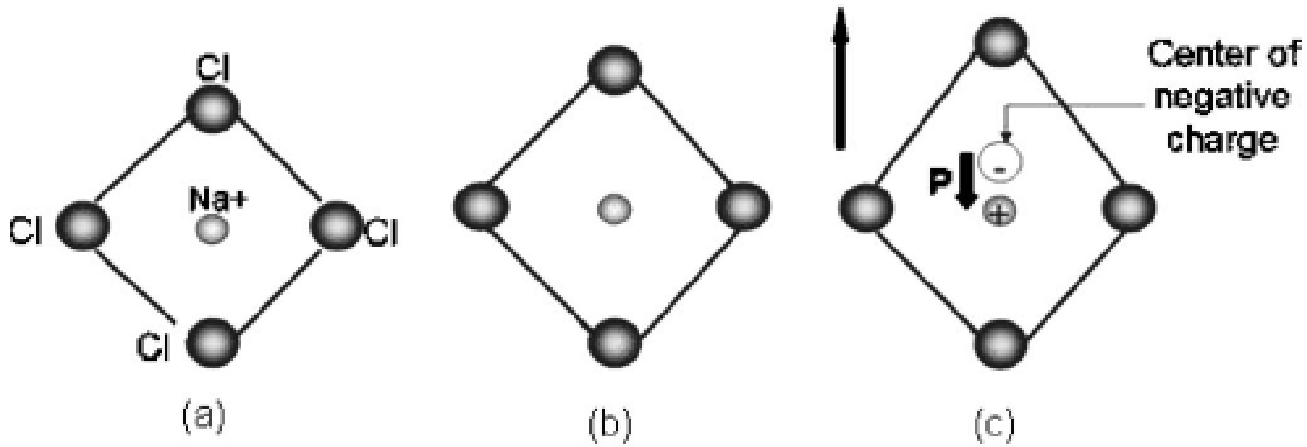
Similarly:

Can exist in **ALL** insulators

Flexoelectricity

Centrosymmetric crystal:

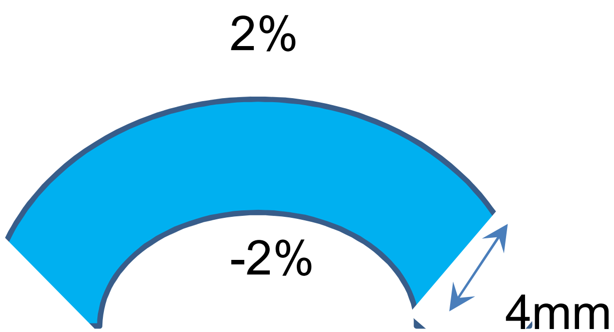
No strain	uniform strain	**Strain gradient**
No dipole	No dipole	**Dipole!!**



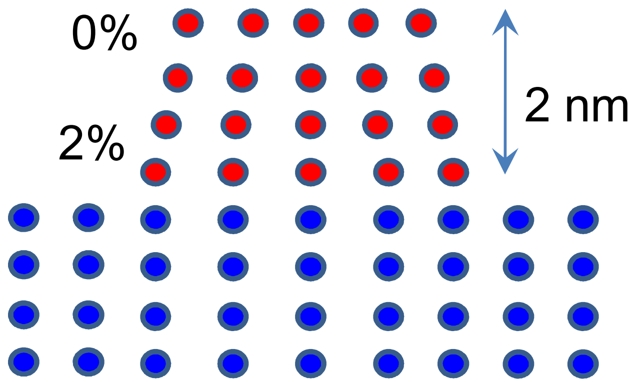
Sodium chloride

Flexoelectricity

Large effect on properties at nanoscale: strain gradients may be huge



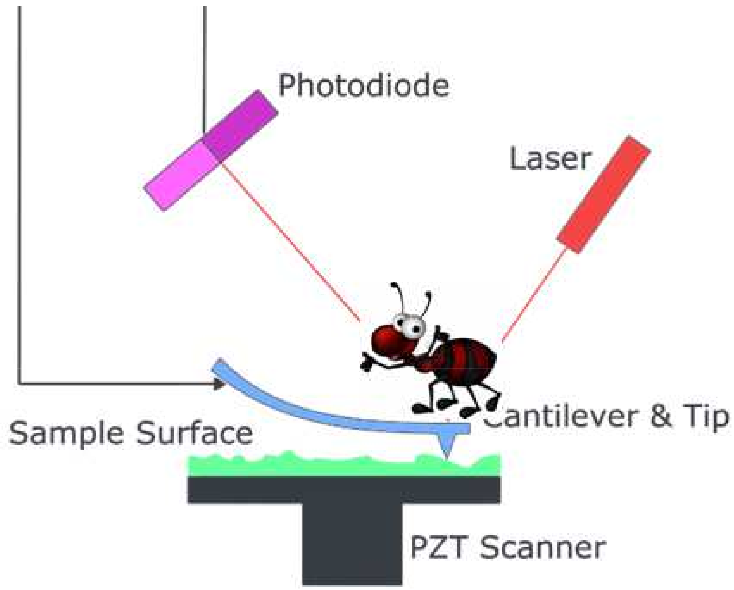
Macrosopic
$\nu = 10^{3}$/m



nanoscale
$\nu = 10^{9}$/m

Huge!

Stress under AFM tip

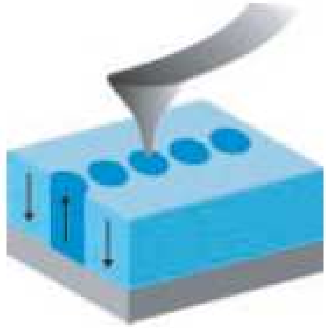


~ 1 GPa

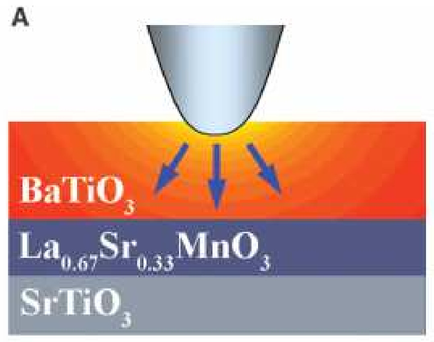
Figures courtesy of G. Catalan and J.Kreisel

Large stress and stress gradient around AFM tip

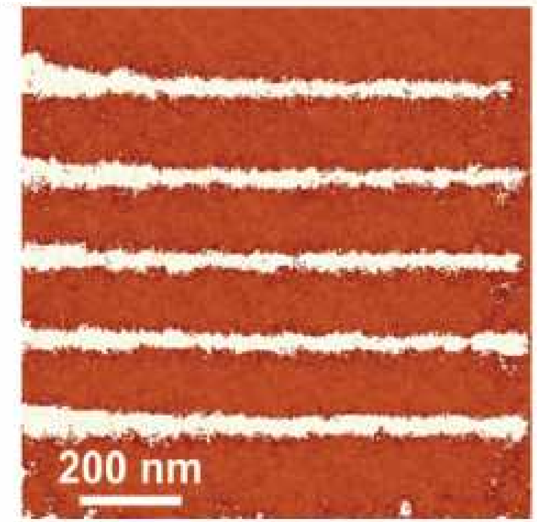
Flexoelectrically written domains



C.H. Ahn et al, Science, 303, 488 (2004)



Epitaxial $BaTiO_3$ film on STO



Flexo written domain dots (30nm in size) , high-density data storage application.

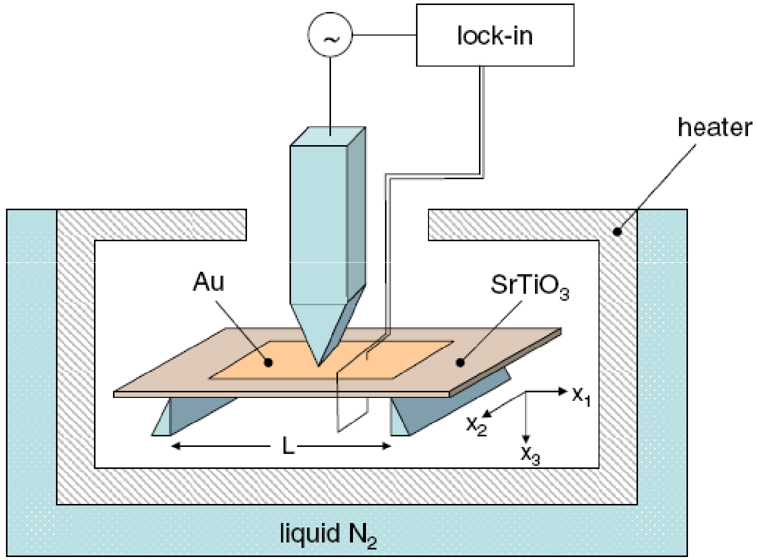
H. Lu et al, Science, 336, 59 (2012)

Measurement of FEC

$$P_i = \mu_{ijkl} \frac{\partial \eta_{jk}}{\partial x_l}$$

Ma and Cross,
(2001, 2002, 2003,
2005,2006)

P. Zubko et al
(2007)



P. Zubko et al (2007)

Can’t measure the full FEC tensor

Theoretical flexo study

- Martin, 1972
  - Long-wave analysis of piezoelectricity
- Tagantsev, 1986, 1991
  - Rigid-ion model of flexoelectricity
- Maranganti and Sharma, 2009
  - Lattice-dynamical approach
- Resta, 2010
  - First-principles; electronic only; elements only
- Hong and Vanderbilt, 2011
  - Generalized theory of electronic part
- Ponomareva, Tagantsev and Bellaiche, 2012
  - Lattice part generalized to finite T simulations
- Massimiliano Stengel (unpublished)
  - density-functional perturbation theory

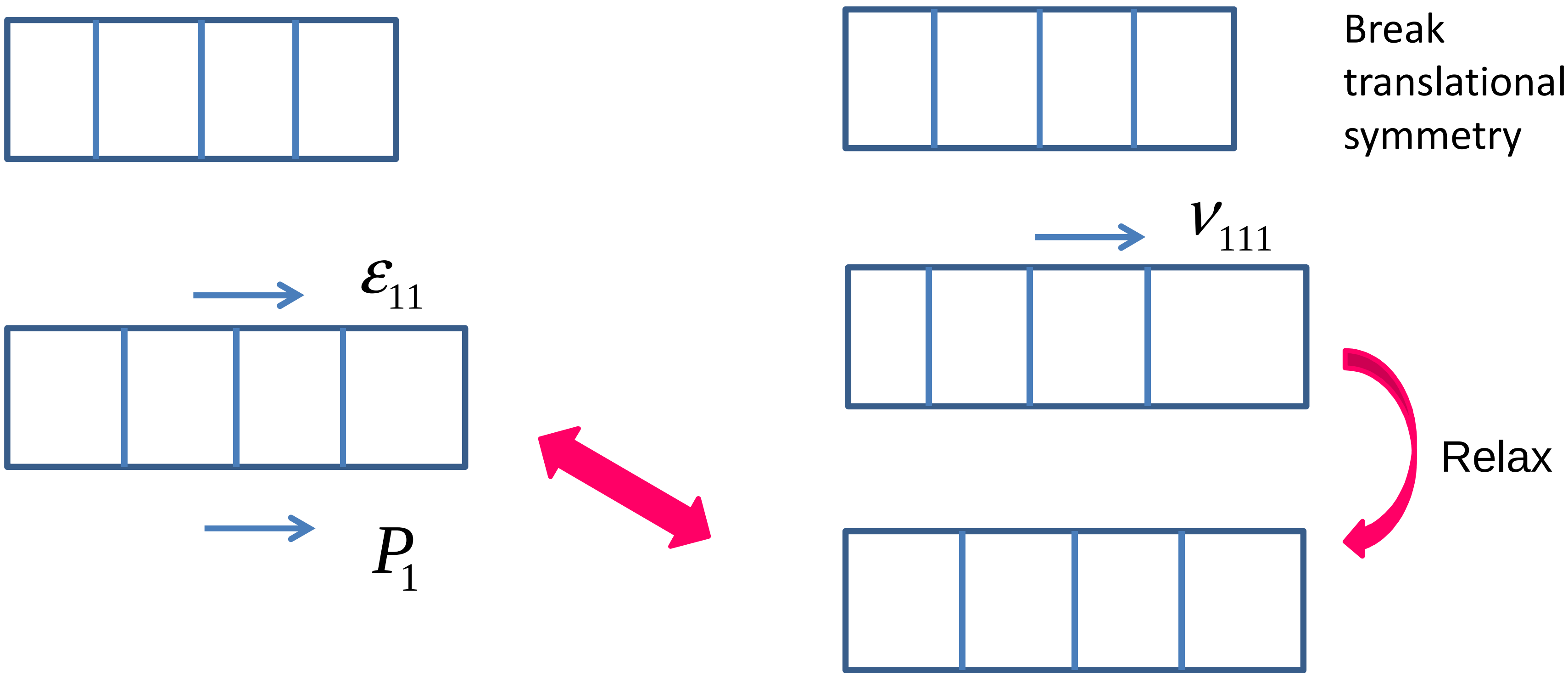
Lattice contribution (Tagantsev; Maranganti and Sharma)

Electronic contribution (Resta; Hong and Vanderbilt)

Difficulties in FEC calculation

$$P_i = e_{ijk}\varepsilon_{jk}$$

$$P_i = \mu_{ijkl}\nu_{jkl}$$



Strain gradient not kept

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  - **Derivation of flexoelectricity**
  - Longitudinal vs. transverse
  - Force pattern dependence
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Strategy of the derivation

PHYSICAL REVIEW B VOLUME 5, NUMBER 4 15 FEBRUARY 1972

Piezoelectricity

Richard M. Martin
Xerox Palo Alto Research Center, Palo Alto, California 94304

Piezoelectricity theory based on the density of local **dipoles** and **quadrupoles** induced by a long-wave deformation

$$Q^{(1)},\ Q^{(2)} \qquad \mathbf{u}_{lI} = (\mathbf{u}^{(0)} + \mathbf{u}_I^{(1)})\, e^{i\mathbf{k}\cdot\mathbf{R}_{lI}}$$

Using Linear-response and Berry-phase methods to calculate piezo response.

Derived from Bloch's theorem which needs periodic boundary condition.

Strain gradient breaks periodic BC.

$$Q^{(1)},\ Q^{(2)},\ Q^{(3)} \qquad \mathbf{u}_{lI} = (\mathbf{u}^{(0)} + \mathbf{u}_I^{(1)} + \mathbf{u}_I^{(2)})\, e^{i\mathbf{k}\cdot\mathbf{R}_{lI}}$$

Derivation: Flexoelectricity

Let

$P_\alpha(\mathbf{r})$ be a local dipole density

$Q_{\alpha\beta}(\mathbf{r})$ be a local quadrupole density

$\mathcal{O}_{\alpha\beta\gamma}(\mathbf{r})$ be a local octupole density

Then the resulting effective charge density is

$$\rho^{(\text{eff})}(\mathbf{r}) = -\partial_\alpha P_\alpha(\mathbf{r}) + \frac{1}{2}\partial_\alpha\partial_\beta Q_{\alpha\beta}(\mathbf{r}) - \frac{1}{6}\partial_\alpha\partial_\beta\partial_\gamma \mathcal{O}_{\alpha\beta\gamma}(\mathbf{r}) + \ldots$$

But Poisson's equation is

$$\rho^{(\text{eff})}(\mathbf{r}) = -\partial_\alpha P_\alpha^{(\text{eff})}(\mathbf{r})$$

so alternatively we can write

$$P_\alpha^{(\text{eff})}(\mathbf{r}) = P_\alpha(\mathbf{r}) - \frac{1}{2}\partial_\beta Q_{\alpha\beta}(\mathbf{r}) + \frac{1}{6}\partial_\beta\partial_\gamma \mathcal{O}_{\alpha\beta\gamma}(\mathbf{r}) + \ldots$$

Derivation: Flexoelectricity

Define

$$u_{\mathbf{R}I\tau} = \text{displacement of atom } I \text{ in direction } \tau \text{ in cell } \mathbf{R}$$

and let

$$u_{\mathbf{R}I\tau} = g(\mathbf{R})\, u_{I\tau} \quad , \quad g(\mathbf{R}) \text{ slowly varying.}$$

Then the induced dipole, quadrupole, and octupole densities are

$$P_\alpha = \frac{1}{V_c} \sum_I Q^{(1)}_{I,\alpha\tau}\, u_{I\tau}$$

$$Q_{\alpha\beta} = \frac{1}{V_c} \sum_I Q^{(2)}_{I,\alpha\tau\beta}\, u_{I\tau}$$

$$\mathcal{O}_{\alpha\beta\gamma} = \frac{1}{V_c} \sum_I Q^{(3)}_{I,\alpha\tau\beta\gamma}\, u_{I\tau}$$

$$Q^{(1)}_{I,\alpha\tau} = \int d\mathbf{r}\, r_\alpha\, f_{I\tau}(\mathbf{r})$$ (Dynam. Z*)

$$Q^{(2)}_{I,\alpha\tau\beta} = \int d\mathbf{r}\, r_\alpha\, f_{I\tau}(\mathbf{r})\, r_\beta$$

$$Q^{(3)}_{I,\alpha\tau\beta\gamma} = \int d\mathbf{r}\, r_\alpha\, f_{I\tau}(\mathbf{r})\, r_\beta\, r_\gamma$$

where

$$f_{I\tau}(\mathbf{r} - \mathbf{R} - \mathbf{r}_I) = \frac{\partial \rho(\mathbf{r})}{\partial u_{\mathbf{R}I\tau}}$$

Derivation: Flexoelectricity

$$P_\alpha^{(\mathrm{eff})}(\mathbf{r}) = P_\alpha(\mathbf{r}) - \frac{1}{2}\partial_\beta Q_{\alpha\beta}(\mathbf{r}) + \frac{1}{6}\partial_\beta\partial_\gamma \mathcal{O}_{\alpha\beta\gamma}(\mathbf{r}) + \ldots$$

$$P_\alpha^{(\mathrm{eff})}(\mathbf{r}) = \frac{1}{V_\mathrm{c}}\sum_I \left[Q^{(1)}_{I,\alpha\tau}\, g(\mathbf{r}) - \frac{1}{2} Q^{(2)}_{I,\alpha\tau\beta}\, \partial_\beta\, g(\mathbf{r}) + \frac{1}{6} Q^{(3)}_{I,\alpha\tau\beta\gamma}\, \partial_\beta\partial_\gamma\, g(\mathbf{r}) \right] u_{I\tau}$$

So, for a long-wavelength mode of the form

$$g(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}}$$

the local polarization is

$$P_\alpha = \frac{1}{V_\mathrm{c}}\sum_I \left[Q^{(1)}_{I,\alpha\tau} - \frac{i}{2} Q^{(2)}_{I,\alpha\tau\beta}\, k_\beta - \frac{1}{6} Q^{(3)}_{I,\alpha\tau\beta\gamma}\, k_\beta k_\gamma \right] u_{I\tau}$$

Derivation: Flexoelectricity

Define the *unsymmetrized* strain and strain gradient tensors

$$\eta_{\alpha\beta} = \frac{\partial u_\alpha}{\partial r_\beta}$$

$$\nu_{\alpha\beta\gamma} = \frac{\partial \eta_{\alpha\beta}}{\partial r_\gamma} = \frac{\partial u_\alpha}{\partial r_\beta r_\gamma}$$

Let

$$\Gamma_{I\tau\beta\gamma} = \frac{du_{I\tau}}{d\eta_{\beta\gamma}} \qquad \text{“internal strain response tensor”}$$

$$N_{I\tau\beta\gamma\delta} = \frac{du_{I\tau}}{d\nu_{\beta\gamma\delta}} \qquad \text{“internal strain-gradient response tensor”}$$

Then

$$u_{I\tau} = u_\tau + \Gamma_{I\tau\beta\gamma}\,\eta_{\beta\gamma} + N_{I\tau\beta\gamma\delta}\,\nu_{\beta\gamma\delta}$$

Derivation: Flexoelectricity

Then, for the long-wavelength acoustic mode, we have a

Displacement	$u_\beta(\mathbf{r}) = u_{0\beta}\, e^{i\mathbf{k}\cdot\mathbf{r}}$
Strain	$\eta_{\beta\gamma}(\mathbf{r}) = iu_{0\beta}\, k_\gamma\, e^{i\mathbf{k}\cdot\mathbf{r}}$
Strain gradient	$\nu_{\beta\gamma\delta}(\mathbf{r}) = -u_{0\beta}\, k_\gamma\, k_\delta\, e^{i\mathbf{k}\cdot\mathbf{r}}$

or

$$u_{I\tau} = [\delta_{\tau\beta} + i\Gamma_{I\tau\beta\gamma}\, k_\gamma - N_{I\tau\beta\gamma\delta}\, k_\gamma k_\delta]\, u_{0\beta}$$

Thus

$$P_\alpha = \frac{1}{V_c}\sum_I \left[Q^{(1)}_{I,\alpha\tau} - \frac{i}{2}Q^{(2)}_{I,\alpha\tau\beta}\, k_\beta - \frac{1}{6}Q^{(3)}_{I,\alpha\tau\beta\gamma}\, k_\beta k_\gamma\right] \times \left[\delta_{\tau\beta} + i\Gamma_{I\tau\beta\gamma}\, k_\gamma - N_{I\tau\beta\gamma\delta}\, k_\gamma k_\delta\right] u_{0\beta}$$

Derivation: Flexoelectricity

Finally, we define the *unsymmetrized*

Piezo tensor: $e_{\alpha\beta\gamma} = \frac{\partial P_\alpha}{\partial \eta_{\beta\gamma}}$

Flexo tensor: $\mu_{\alpha\beta\gamma\delta} = \frac{\partial P_\alpha}{\partial \nu_{\beta\gamma\delta}}$

so that

$$P_\alpha = e_{\alpha\beta\gamma}\, \eta_{\beta\gamma} + \mu_{\alpha\beta\gamma\delta}\, \nu_{\beta\gamma\delta} + \dots$$

or, for the acoustic wave in question,

$$\boxed{P_\alpha = i\, e_{\alpha\beta\gamma}\, k_\gamma\, u_{0\beta} - \mu_{\alpha\beta\gamma\delta}\, k_\gamma k_\delta\, u_{0\beta} + \dots}$$

Derivation: Flexoelectricity

$$P_\alpha = \frac{1}{V_c}\sum_I \left[Q^{(1)}_{I,\alpha\tau} - \frac{i}{2}Q^{(2)}_{I,\alpha\tau\beta}\,k_\beta - \frac{1}{6}Q^{(3)}_{I,\alpha\tau\beta\gamma}\,k_\beta k_\gamma\right] \times \left[\delta_{\tau\beta} + i\Gamma_{I\tau\beta\gamma}\,k_\gamma - N_{I\tau\beta\gamma\delta}\,k_\gamma k_\delta\right] u_{0\beta}$$

$$P_\alpha = i\,e_{\alpha\beta\gamma}\,k_\gamma\,u_{0\beta} - \mu_{\alpha\beta\gamma\delta}\,k_\gamma k_\delta\,u_{0\beta} + \ldots$$

Comparing powers of k, we find

Piezo $$e_{\alpha\beta\gamma} = \frac{1}{V_c}\sum_I \left[Q^{(1)}_{I\alpha\tau}\,\Gamma_{I\tau\beta\gamma} - \frac{1}{2}\,Q^{(2)}_{I\alpha\beta\gamma}\right]$$

Flexo $$\mu_{\alpha\beta\gamma\delta} = \frac{1}{V_c}\sum_I \left[Q^{(1)}_{I\alpha\tau}\,N_{I\tau\beta\gamma\delta} - \frac{1}{2}\,Q^{(2)}_{I\alpha\tau\delta}\,\Gamma_{I\tau\beta\gamma} + \frac{1}{6}\,Q^{(3)}_{I\alpha\beta\gamma\delta}\right]$$

Piezoelectric tensor

Lattice

Electronic

$$e_{\alpha\beta\gamma} = \frac{1}{V_c} \sum_I \left[Q^{(1)}_{I\alpha\tau} \Gamma_{I\tau\beta\gamma} - \frac{1}{2} Q^{(2)}_{I\alpha\beta\gamma} \right]$$

Dynamic dipole (Z*)

Displacement induced by strain

Dynamic quadrupole

Flexoelectric tensor

Lattice — Electronic

$$\mu_{\alpha\beta\gamma\delta} = \frac{1}{V_\mathrm{c}} \sum_I \left[Q^{(1)}_{I\alpha\tau} N_{I\tau\beta\gamma\delta} - \frac{1}{2} Q^{(2)}_{I\alpha\tau\delta} \Gamma_{I\tau\beta\gamma} + \frac{1}{6} Q^{(3)}_{I\alpha\beta\gamma\delta} \right]$$

- Dynamic dipole (Z*)
- Displacement induced by strain gradient
- Dynamic quadrupole
- Displacement induced by strain
- Dynamic octupole

Displacement-response tensors

Internal strain and strain-gradient response tensors:

$$\Gamma_{I\tau\beta\gamma} = \frac{du_{I\tau}}{d\eta_{\beta\gamma}} = \sum_{I'\tau'} \frac{du_{I\tau}}{dF_{I'\tau'}} \frac{dF_{I'\tau'}}{d\eta_{\beta\gamma}}$$

$$\frac{dF_{I'\tau'}}{d\eta_{\beta\gamma}} = \Lambda_{I'\tau'\beta\gamma}$$

$$N_{I\tau\beta\gamma\delta} = \frac{du_{I\tau}}{d\nu_{\beta\gamma\delta}} = \sum_{I'\tau'} \frac{du_{I\tau}}{dF_{I'\tau'}} \frac{dF_{I'\tau'}}{d\nu_{\beta\gamma\delta}}$$

$$\frac{dF_{I'\tau'}}{d\nu_{\beta\gamma\delta}} = T_{I'\tau'\beta\gamma\delta}$$

$$\frac{du_{I\tau}}{dF_{I'\tau'}} = -(K^{-1})_{I\tau,I'\tau'}$$

Then

$$\Gamma = (K^{-1}) \cdot \Lambda \qquad \text{and} \qquad N = (K^{-1}) \cdot T$$

Displacement-response tensors

These can be obtained as moments of the full force-constant matrix

$$K_{\mathbf{R}I\tau,\mathbf{R}'I'\tau'} = -\frac{dF_{\mathbf{R}I\tau}}{du_{\mathbf{R}'I'\tau'}}$$

as

$$K_{I\tau,I'\tau'} = \sum_{\mathbf{R}'} K_{\mathbf{0}I\tau,\mathbf{R}'I'\tau'}$$

$$\Lambda_{I\tau\beta\gamma} = -\sum_{\mathbf{R}'} K_{\mathbf{0}I\tau,\mathbf{R}'I'\beta}\,(\mathbf{R}' + \mathbf{r}_{I'} - \mathbf{r}_I)_\gamma$$

$$T_{I\tau\beta\gamma\delta} = -\frac{1}{2}\sum_{\mathbf{R}'} K_{\mathbf{0}I\tau,\mathbf{R}'I'\beta}\,(\mathbf{R}' + \mathbf{r}_{I'} - \mathbf{r}_I)_\gamma\,(\mathbf{R}' + \mathbf{r}_{I'} - \mathbf{r}_I)_\delta$$

0^{th} moment

1^{st} moment

2^{nd} moment

First-principles ingredients

$$f_{I\tau}(\mathbf{r}-\mathbf{R}-\mathbf{r}_I) = \frac{\partial \rho(\mathbf{r})}{\partial u_{\mathbf{R}I\tau}}$$

$$K_{\mathbf{R}I\tau,\mathbf{R}'I'\tau'} = -\frac{\partial F_{\mathbf{R}I\tau}}{\partial u_{\mathbf{R}'I'\tau'}}$$

1st moment: $Q^{(1)}$

2nd moment: $Q^{(2)}$

3rd moment: $Q^{(3)}$

0th moment: K

1st moment: Λ

2nd moment: T

$\Gamma = (K)^{-1} \cdot \Lambda$

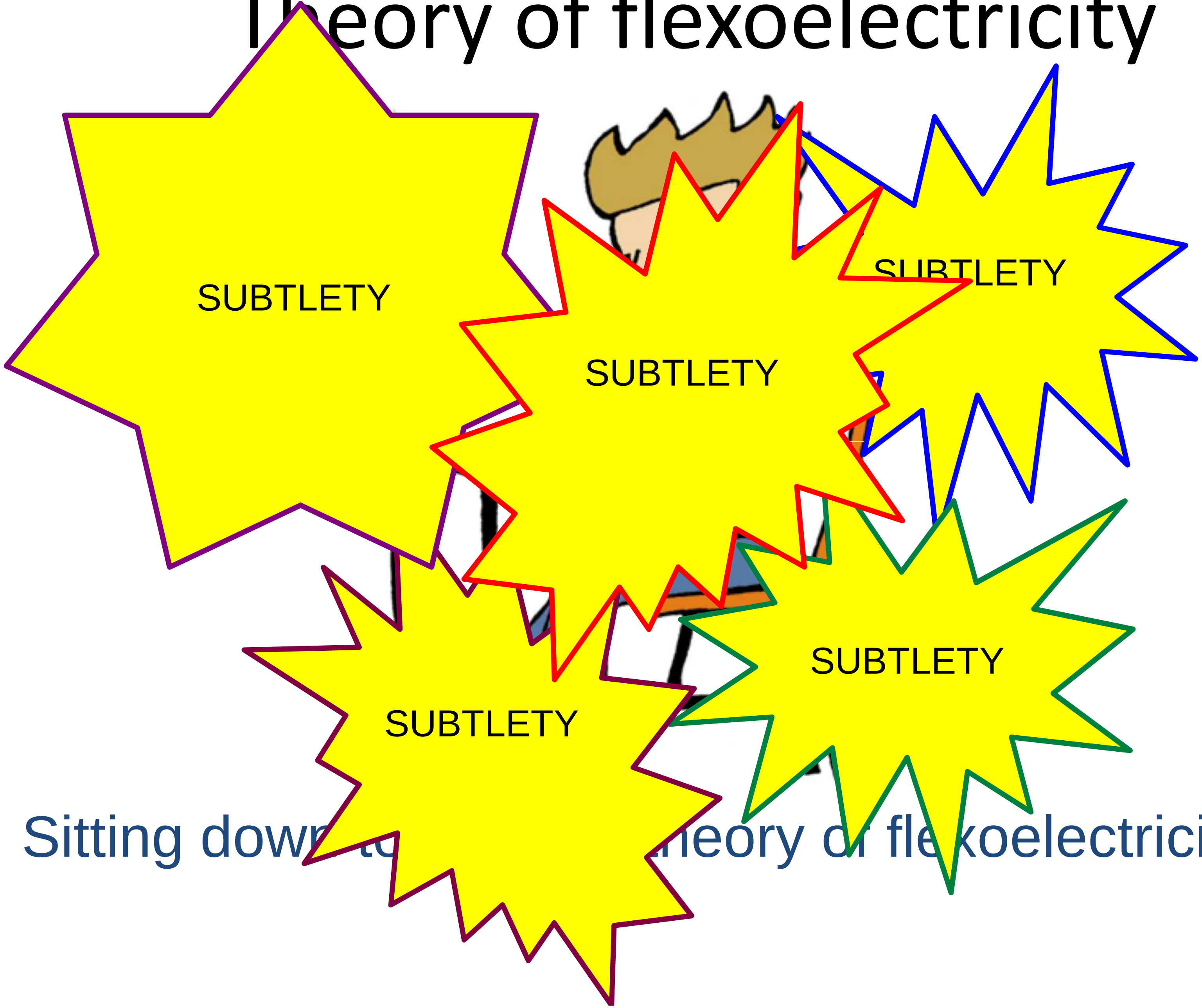
$N = (K)^{-1} \cdot T$

$$\mu_{\alpha\beta\gamma\delta} = \frac{1}{V_c}\sum_I \left[Q^{(1)}_{I\alpha\tau} N_{I\tau\beta\gamma\delta} - \frac{1}{2} Q^{(2)}_{I\alpha\tau\delta} \Gamma_{I\tau\beta\gamma} + \frac{1}{6} Q^{(3)}_{I\alpha\beta\gamma\delta} \right]$$

Vanishes in high-symmetry crystals (e.g., cubic)

Are we done?

Theory of flexoelectricity



Sitting down to [...] theory of flexoelectricity…

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  - **Longitudinal vs. transverse**
  - Force pattern dependence
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Longitudinal vs. transverse flexo

$$\mu_{\alpha\beta\gamma\delta} = \frac{1}{V_c} \sum_I \left[Q^{(1)}_{I\alpha\tau} N_{I\tau\beta\gamma\delta} + \frac{1}{6} Q^{(3)}_{I\alpha\beta\gamma\delta} \right]$$

symmetric under interchanges

(3 x 3 x 6 = 54 components)

(3 x 10 = 30 components)

Not enough!

Example: Cubic material

$$\mu_{1111},\ \mu_{1221},\ \mu_{1122} \qquad \text{vs.} \qquad Q^{(3)}_{1111},\ Q^{(3)}_{1122}$$

Longitudinal vs. transverse: Cubic material

Define

$$\mu_{\mathrm{L1}} = \mu_{1111}$$

$$\mu_{\mathrm{L2}} = \mu_{1111} + 2\mu_{1221}$$

$$\mu_{\mathrm{T}} = \mu_{1122} - \mu_{1221}$$

Then

$$\mu_{\mathrm{L1}}^{\mathrm{el}} = \frac{1}{6V_{\mathrm{c}}} \sum_{I} Q_{I,1111}^{(3)}$$

$$\mu_{\mathrm{L2}}^{\mathrm{el}} = \frac{1}{6V_{\mathrm{c}}} \sum_{I} (Q_{I,1111}^{(3)} + 2Q_{I,1122}^{(3)})$$

$$\mu_{\mathrm{T}}^{\mathrm{el}} = \text{?}$$

Longitudinal vs. transverse flexo

- Our theory was based on charge density
- But charge density is only induced by longitudinal part of flexo response

Charge density is

$$-\rho = \partial_\alpha P_\alpha = \partial_\alpha \, \mu_{\alpha\beta\gamma\delta} \, \nu_{\beta\gamma\delta} = \mu_{\alpha\beta\gamma\delta} \, \sigma_{\beta\alpha\gamma\delta}$$

where

$$\eta_{\alpha\beta} = \frac{\partial u_\alpha}{\partial r_\beta} \, , \qquad \nu_{\alpha\beta\gamma} = \frac{\partial^2 u_\alpha}{\partial r_\beta \partial r_\gamma} \, , \qquad \sigma_{\alpha\beta\gamma\delta} = \frac{\partial^3 u_\alpha}{\partial r_\beta \partial r_\gamma \partial r_\delta}$$

Longitudinal vs. transverse flexo

- Our theory was based on charge density
- But charge density is only induced by longitudinal part of flexo response

Cubic material:

$$-\rho = \mu_{\mathrm{L1}}(\sigma_{1111} + \sigma_{2222} + \sigma_{3333}) + \mu_{\mathrm{L2}}(\sigma_{1122} + \sigma_{2211} + \sigma_{1133} + \sigma_{3311} + \sigma_{2233} + \sigma_{3322})$$

independent of μ_T !

Need *current* response tensors

Induced *charge* response tensors:

$$Q^{(1)}_{I,\alpha\tau} = \int d\mathbf{r}\, r_\alpha\, f_{I\tau}(\mathbf{r})$$

$$Q^{(2)}_{I,\alpha\tau\beta} = \int d\mathbf{r}\, r_\alpha\, f_{I\tau}(\mathbf{r})\, r_\beta$$

$$Q^{(3)}_{I,\alpha\tau\beta\gamma} = \int d\mathbf{r}\, r_\alpha\, f_{I\tau}(\mathbf{r})\, r_\beta\, r_\gamma$$

where

$$f_{I\tau}(\mathbf{r} - \mathbf{R} - \mathbf{r}_I) = \frac{\partial \rho(\mathbf{r})}{\partial u_{\mathbf{R}I\tau}}$$

(3 x 10 = 30 components)

Induced *current* response tensors:

$$J^{(0)}_{I,\alpha\tau} = \int d\mathbf{r}\, j_{I\tau,\alpha}(\mathbf{r})$$

$$J^{(1)}_{I,\alpha\tau\beta} = \int d\mathbf{r}\, j_{I\tau,\alpha}(\mathbf{r})\, r_\beta$$

$$J^{(2)}_{I,\alpha\tau\beta\gamma} = \int d\mathbf{r}\, j_{I\tau,\alpha}(\mathbf{r})\, r_\beta\, r_\gamma$$

where

$$\mathbf{j}_{I\tau}(\mathbf{r} - \mathbf{R} - \mathbf{r}_I) = \frac{\partial \mathbf{J}(\mathbf{r})}{\partial \dot{u}_{\mathbf{R}I\tau}}$$

$\dot{u}_{\mathbf{R}I\tau}$ motion of atom at some small velocity

(3 x 3 x 6 = 54 components)

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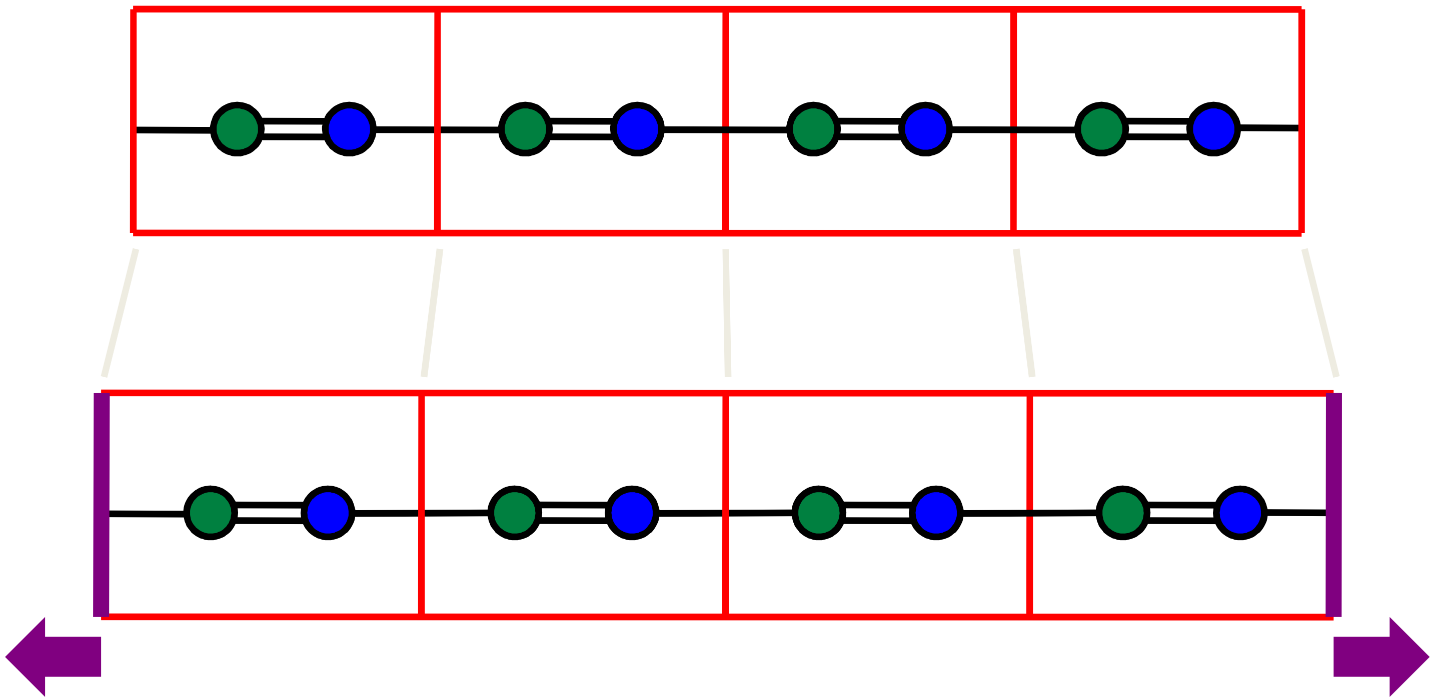
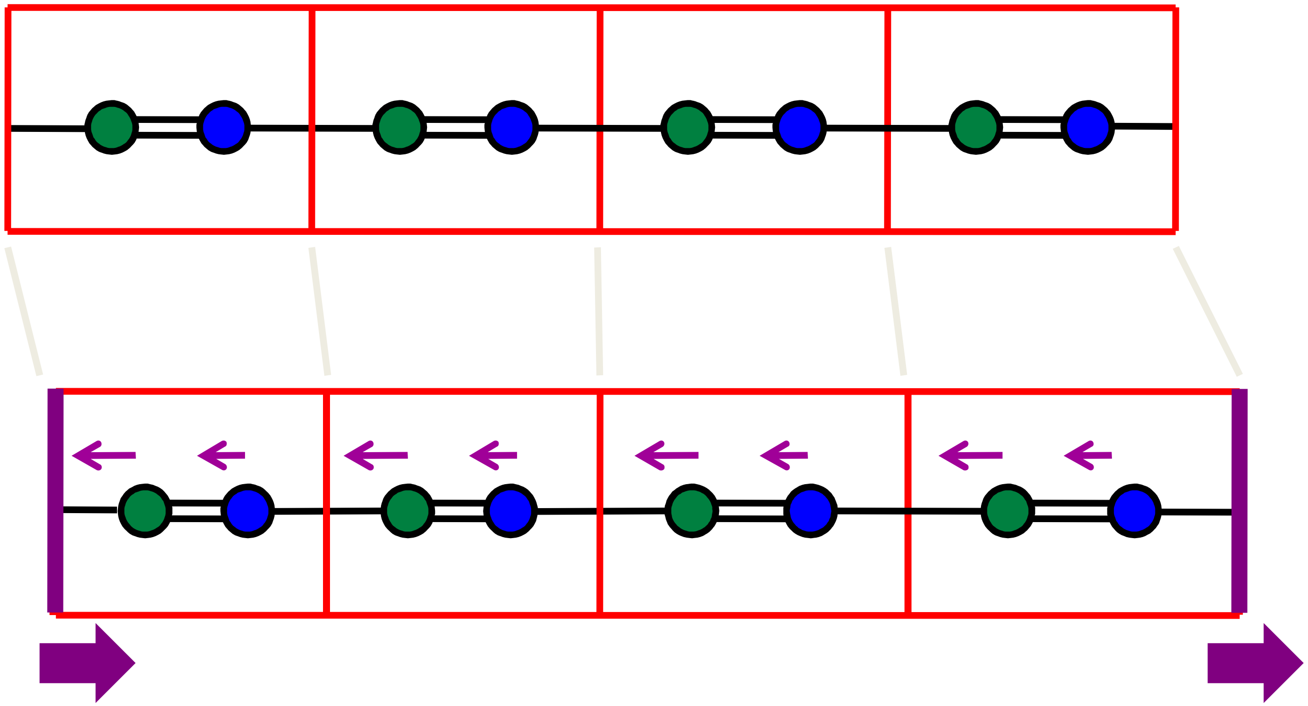
Uniform strain: Piezo



External forces needed to maintain strain

Uniform strain gradient: Flexo

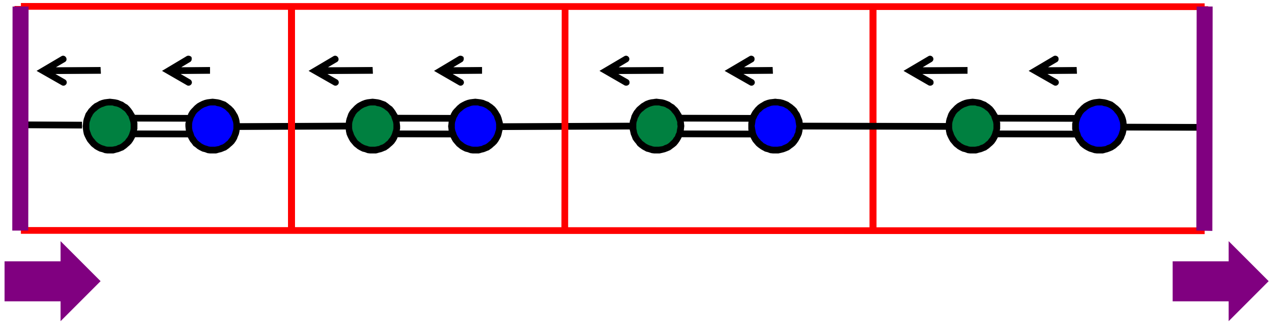


External and internal forces needed
to maintain strain gradient

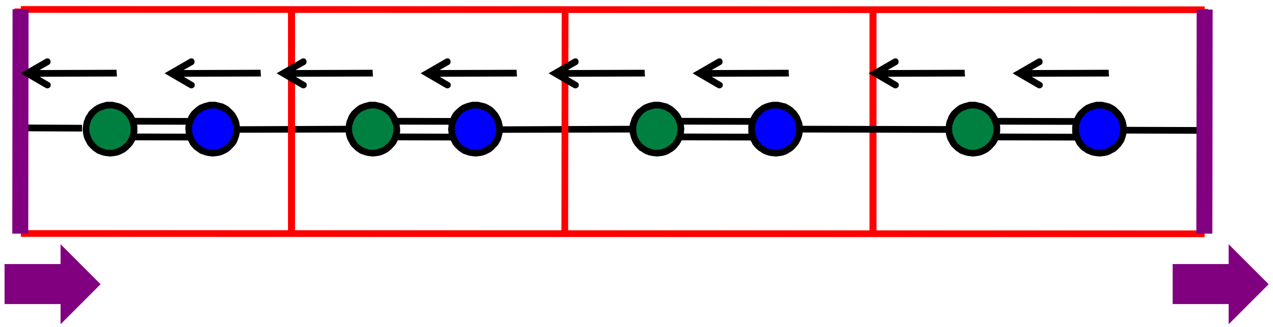
Uniform strain gradient: Flexo

Which force pattern to use?

- Mass-weighted forces

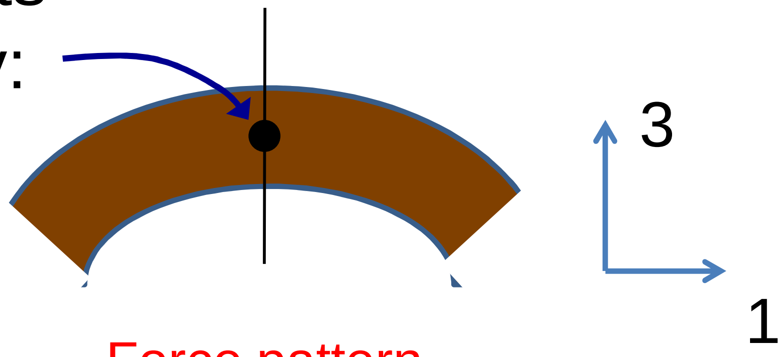


- Evenly weighted forces



Static elasticity: Dependence cancels

Static system has stress gradients that add up to zero force density:



$$P_3 = \mu^{\text{eff}} \frac{\partial \varepsilon_{11}}{\partial x_3}$$

Force pattern dependent

$$\mu^{\text{eff}} = -t\mu_{1111} + (1-t)\mu_{1122}$$

Poisson's ratio

Force pattern independent

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$$f_{I\tau}(\mathbf{r}-\mathbf{R}-\mathbf{r}_I) = \frac{\partial \rho(\mathbf{r})}{\partial u_{\mathbf{R}I\tau}}$$

$$K_{\mathbf{R}I\tau,\mathbf{R}'I'\tau'} = -\frac{dF_{\mathbf{R}I\tau}}{du_{\mathbf{R}'I'\tau'}}$$

1st moment: $Q^{(1)}$

2nd moment: $Q^{(2)}$

3rd moment: $Q^{(3)}$

0th moment: K

1st moment: Λ

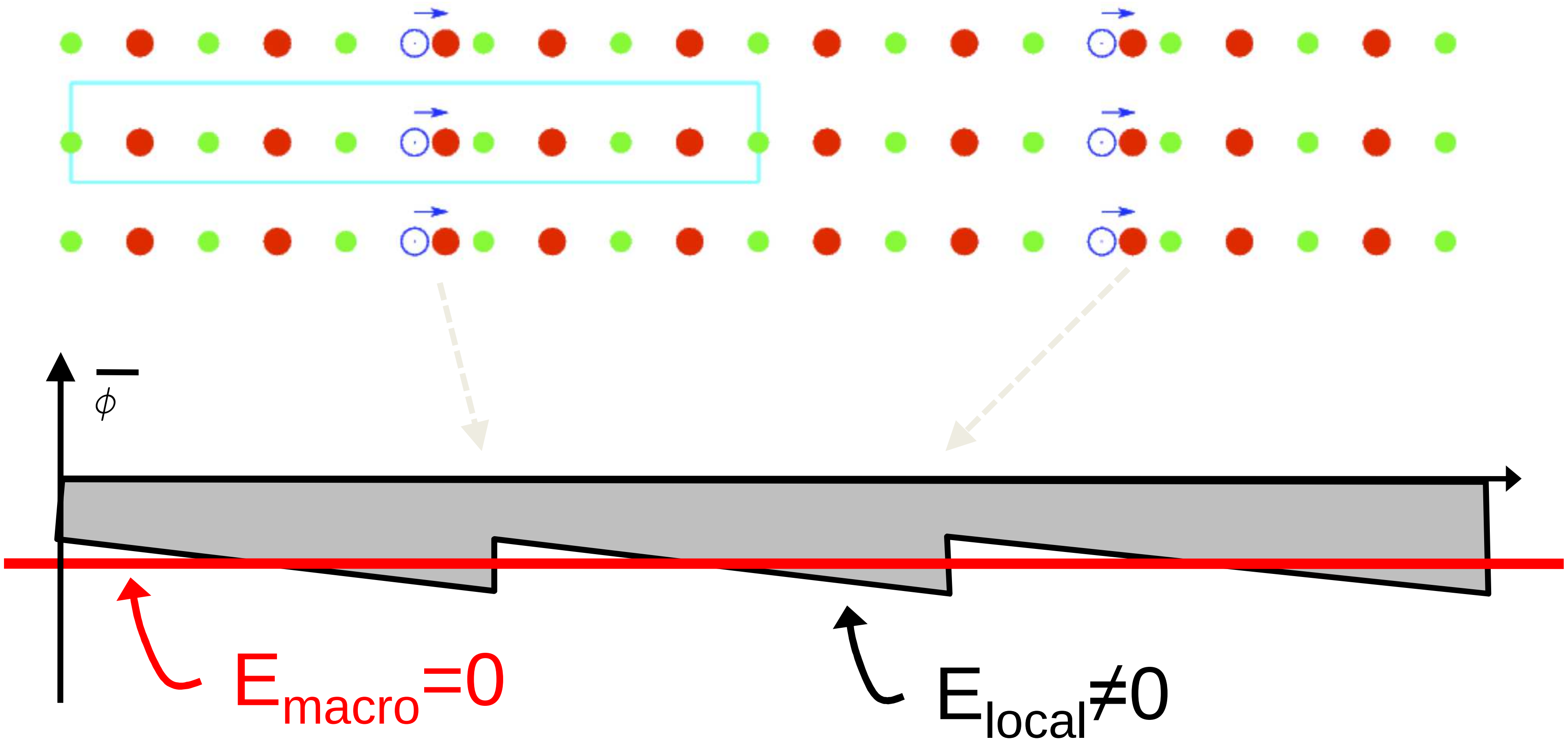
2nd moment: T

$\Gamma = (K)^{-1} \cdot \Lambda$

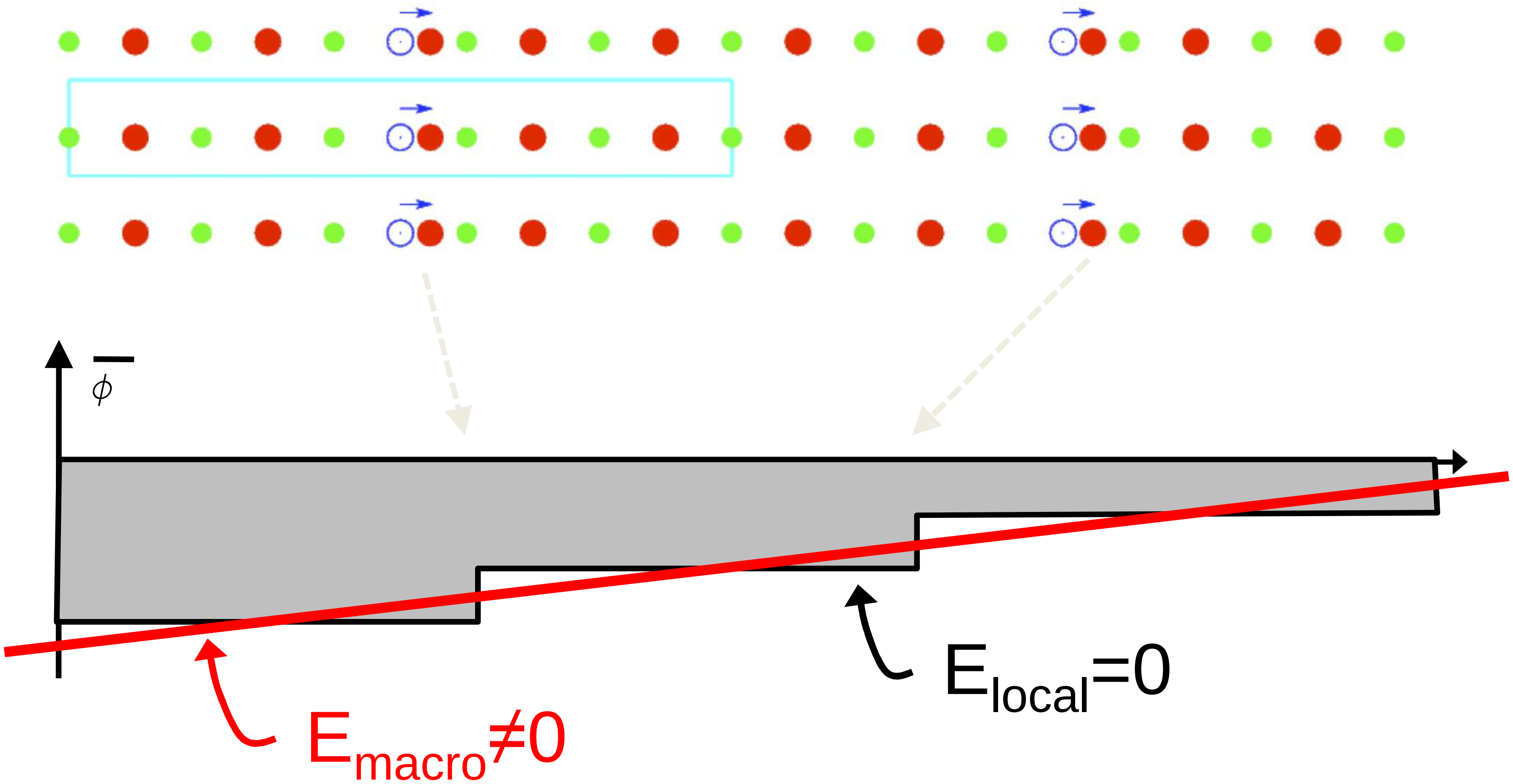
$N = (K)^{-1} \cdot T$

$$\mu_{\alpha\beta\gamma\delta} = \frac{1}{V_c}\sum_I \left[Q^{(1)}_{I\alpha\tau} N_{I\tau\beta\gamma\delta} - \frac{1}{2} Q^{(2)}_{I\alpha\tau\delta} \Gamma_{I\tau\beta\gamma} + \frac{1}{6} Q^{(3)}_{I\alpha\beta\gamma\delta} \right]$$

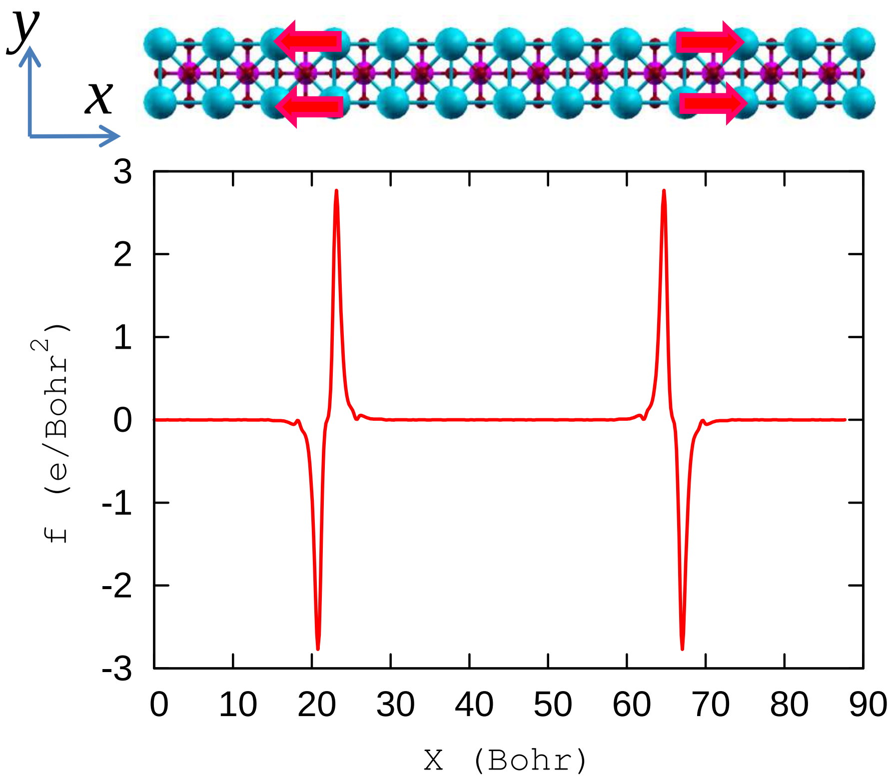
Fixed E_{macro}=0 boundary conditions

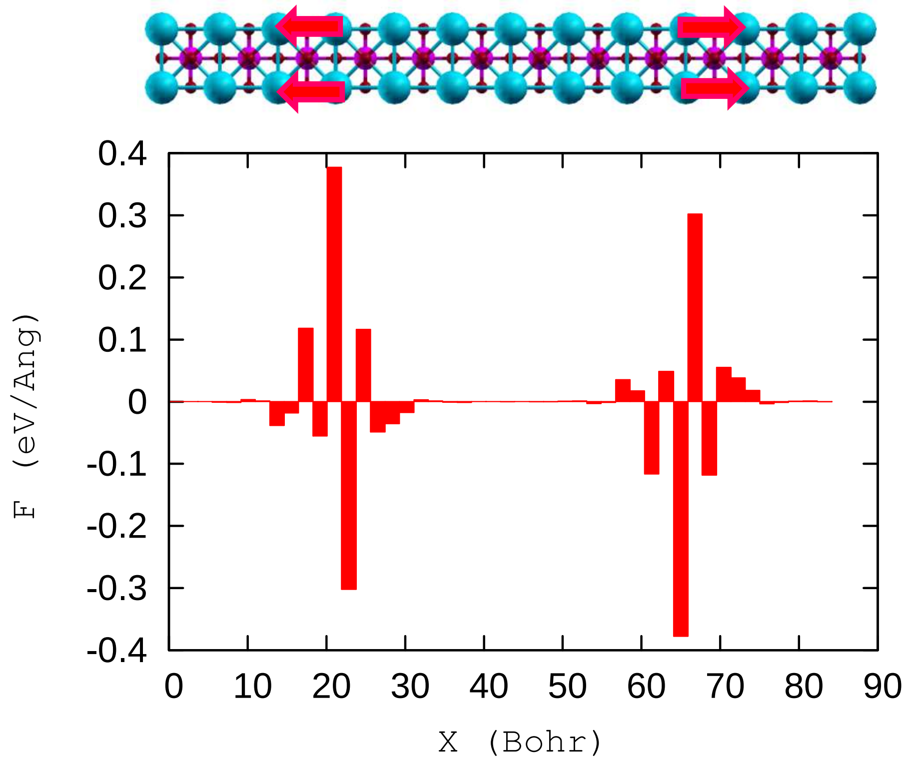


Fixed D=0 boundary conditions



Get *f* and *K* from supercell calculations at fixed D





$$f_{I\tau}(\mathbf{r}-\mathbf{R}-\mathbf{r}_I) = \frac{\partial \rho(\mathbf{r})}{\partial u_{\mathbf{R}I\tau}}$$

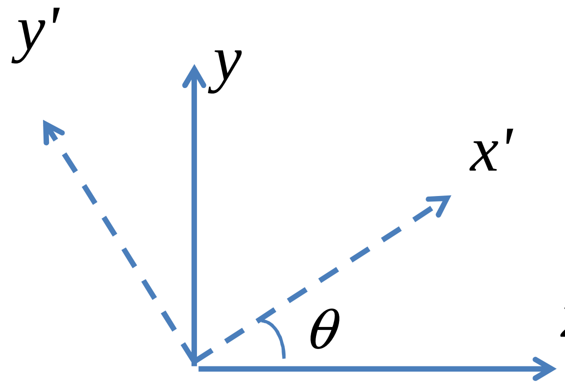
$$K_{\mathbf{R}I\tau,\mathbf{R}'I'\tau'} = -\frac{dF_{\mathbf{R}I\tau}}{du_{\mathbf{R}'I'\tau'}}$$

$\mu_{L1} = \mu_{1111}$ **?** μ_{L2}

How to obtain μ_{L2} ?

μ Original frame

μ' Rotated frame



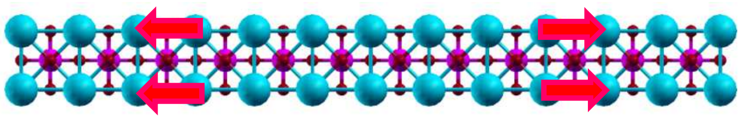
$$\mu'_{\alpha\beta\gamma\delta} = \sum_{ijmn} R_{i\alpha} R_{j\beta} R_{m\gamma} R_{n\delta}\, \mu_{ijmn} \,.$$

$\theta = 45^o$

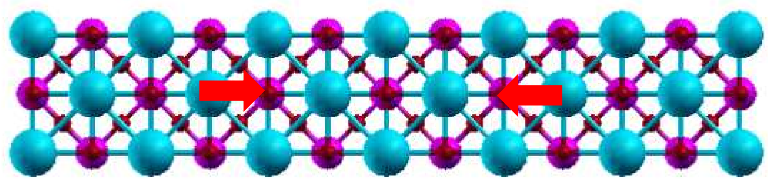
$$R(\theta) = \begin{bmatrix} \cos\theta & -\sin\theta \\ \sin\theta & \cos\theta \end{bmatrix}.$$

$$\begin{aligned} \mu'_{1111} &= \frac{1}{2}(\mu_{1111} + \mu_{1122}) + \mu_{1221} \,, \\ \mu'_{1122} &= \frac{1}{2}(\mu_{1111} + \mu_{1122}) - \mu_{1221} \,, \\ \mu'_{1221} &= \frac{1}{2}(\mu_{1111} - \mu_{1122}) \,. \end{aligned}$$

$$\mu'_{L1} = \frac{1}{2}(\mu_{L1} + \mu_{L2})$$



μ_{L1}



μ_{L2}

Fixed E vs. Fixed D

- Calculations converge best under fixed D
- Fixed E is a more standard usage
- We need conversions:

$$Z^{(\mathcal{E})} = \epsilon^{\infty} \cdot Z^{(D)}$$

$$\bar{\mu}^{(\mathcal{E})} = \epsilon^{\infty} \cdot \bar{\mu}^{(D)}$$

$$K_{IJ}^{(\mathcal{E})} = K_{IJ}^{(D)} - \frac{4\pi}{V_{\mathrm{c}}} Z_I^{(D)} \cdot \epsilon^{\infty} \cdot Z_J^{(D)}$$

$$T_I^{(\mathcal{E})} = T_I^{(D)} - 4\pi Z_I^{(D)} \cdot \epsilon^{\infty} \cdot \bar{\mu}^{(D)}$$

$$\mu^{(\mathcal{E})} = \epsilon^{0} \cdot \mu^{(D)}$$

Fixed E vs. Fixed D

- Calculations converge best under fixed D
- Fixed E is a more standard usage
- We need conversions:
  - Electronic only:

$$\epsilon^{\infty}_{\alpha\lambda}\,\mu^{\mathrm{el},D}_{\lambda\beta\gamma\delta} = \mu^{\mathrm{el},\mathcal{E}}_{\alpha\beta\gamma\delta}$$

(Resta, 2010)

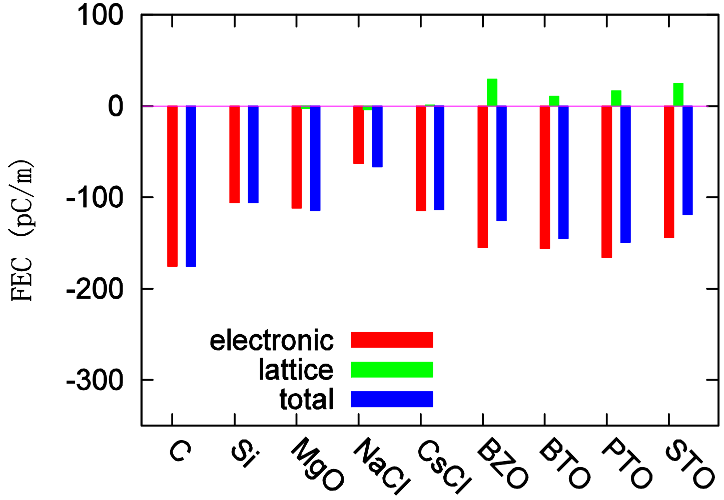
  - Total (electronic + lattice)

$$\epsilon^{0}_{\alpha\lambda}\mu^{(D)}_{\lambda\beta\gamma\delta} = \mu^{(\mathcal{E})}_{\alpha\beta\gamma\delta}$$

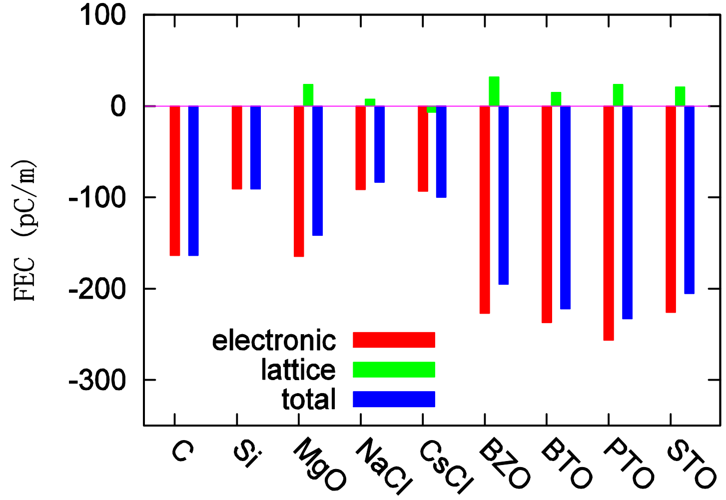
FEC at fixed D

Even force

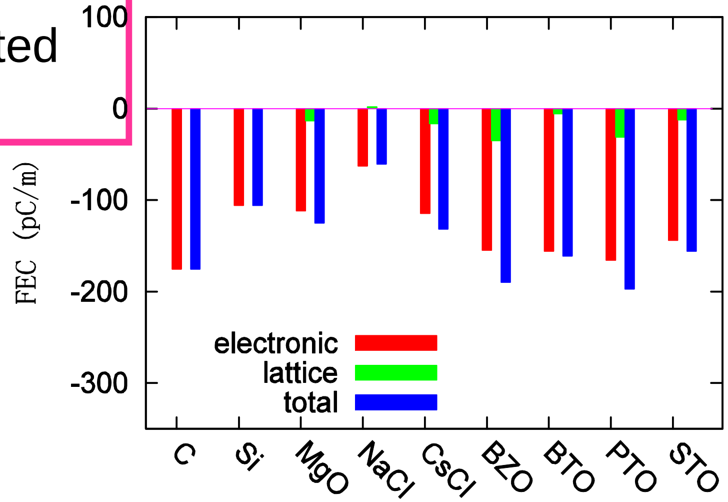
μ_{L1}

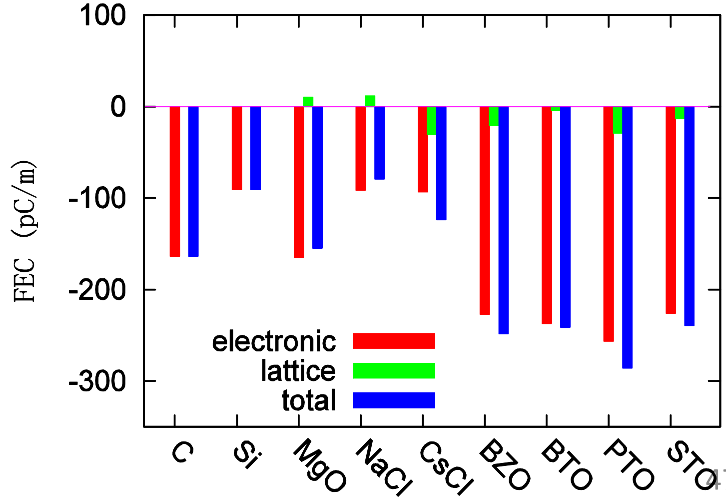


μ_{L2}



Mass-weighted force





FEC at fixed E

$$\epsilon^0_{\alpha\lambda}\mu^{(D)}_{\lambda\beta\gamma\delta} = \mu^{(\mathcal{E})}_{\alpha\beta\gamma\delta}$$

At fixed D
-0.1~-0.2

nC/m

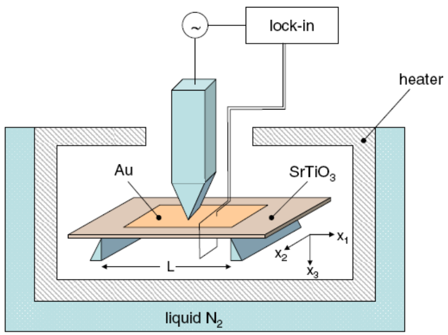
	$\mu^{\mathrm{el}}_{\mathrm{L1}}$	$\mu^{\mathrm{el}}_{\mathrm{L2}}$	$\mu^{\mathrm{latt}}_{\mathrm{L1}}$	$\mu^{\mathrm{latt}}_{\mathrm{L2}}$	μ_{L1}	μ_{L2}	ϵ^0
C	–1.0	–0.9	0.0	0.0	–1.0	–0.9	5.5
Si	–1.3	–1.1	0.0	0.0	–1.3	–1.1	11.9
MgO	–0.3	–0.5	–0.8	–0.9	–1.1	–1.4	9.8
NaCl	–0.1	–0.2	–0.2	–0.3	–0.4	–0.5	5.6
CsCl	–0.2	–0.2	–0.6	–0.5	–0.8	–0.7	7.2
BZO	–0.8	–1.1	–1.1	–1.8	–1.9	–2.9	15
BTO	–1.1	–1.6	–333.1	–509.0	–334.2	–510.6	2300
PTO	–1.5	–2.2	–18.5	–29.0	–20.0	–31.2	134
STO	–0.9	–1.4	–36.0	–62.2	–36.9	–63.7	310

Full FEC at fixed E

Assuming $\mu^{el}_{T} = 0 \qquad \mu^{el}_{1122} = \mu^{el}_{1221}$

nC/m

	Even force				Mass-weighted force			
	μ_{1111}	μ_{1122}	μ_{1221}	μ^{eff}	μ_{1111}	μ_{1122}	μ_{1221}	μ^{eff}
C	−1.0	−0.9	−0.3	−0.3	−1.0	−0.3	−0.3	−0.2
Si	−1.3	−0.4	−0.4	0.0	−1.3	−0.4	−0.4	0.0
MgO	−1.1	−0.4	−0.5	−0.3	−1.2	−0.5	−0.5	−0.3
NaCl	−0.4	0.0	−0.3	−0.4	−0.3	0.1	−0.3	−0.5
CsCl	−0.8	−0.2	−0.3	0.0	−0.9	−0.2	−0.3	0.0
BZO	−1.9	0.0	−1.4	−1.7	−2.9	−0.2	−1.7	−1.8
BTO	−334.3	18.4	−264.5	−309.3	−370.8	2.1	−278.4	−307.9
PTO	−20.0	0.3	−15.7	−15.5	−26.4	−1.9	−18.2	−15.4
STO	−36.9	−1.3	−31.2	−37.5	−48.4	−4.9	−34.6	−37.2



Force pattern dependent

$$\mu^{eff} = -t\mu_{1111} + (1-t)\mu_{1122}$$

Force pattern independent

t: Poisson's ratio

Compared with previous results

μ_{L1} at fixed D (pC/m)

	This work	*ab initio*[(a)]
BTO	-161	-370 $\pm$30
STO	-156	-1380 $\pm$650

μ_{L1} μ_{L2} at fixed E (nC/m)

		This work	Lattice dynamics[(b)]	Exp
BTO	μ_{L1}	-370.8	0.15	10^4 [(c)]
	μ_{L2}	-554.8	-9.27	
STO	μ_{L1}	-48.4	-0.26	0.2 [(d)]
	μ_{L2}	-74.2	-10.9	18.5[(d)]

- Surface effect
- Effective FEC
- Different force pattern

Lattice contribution

$$\mu^{\text{eff}} = -t\mu_{1111} + (1-t)\mu_{1122}$$

[(a)]Hong *et al*, J. Phys. Conds. Matt. 22,112201, (2010)
[(b)]Maranganti *et al.*PRB, 80, 054109 (2009)
[(c)]Ma *et al*, APL, 88, 232902 (2006)
[(d)]Zubko *et al,* PRL, 99, 167601 (2007), PRL, 100, 199906 (2008)

Summary

- Complete first-principles theory of longitudinal part of flexoelectric response
  - Electric boundary conditions
  - Longitudinal vs. transverse
  - Force pattern
- A practical method is proposed for calculating the longitudinal flexoelectric tensors for cubic materials from first principles method.
- The electronic and lattice contribution to FEC are obtained.

Thank you for your attention !