CE 530 Molecular Simulation

Lecture 16

Dielectrics and Reaction Field Method

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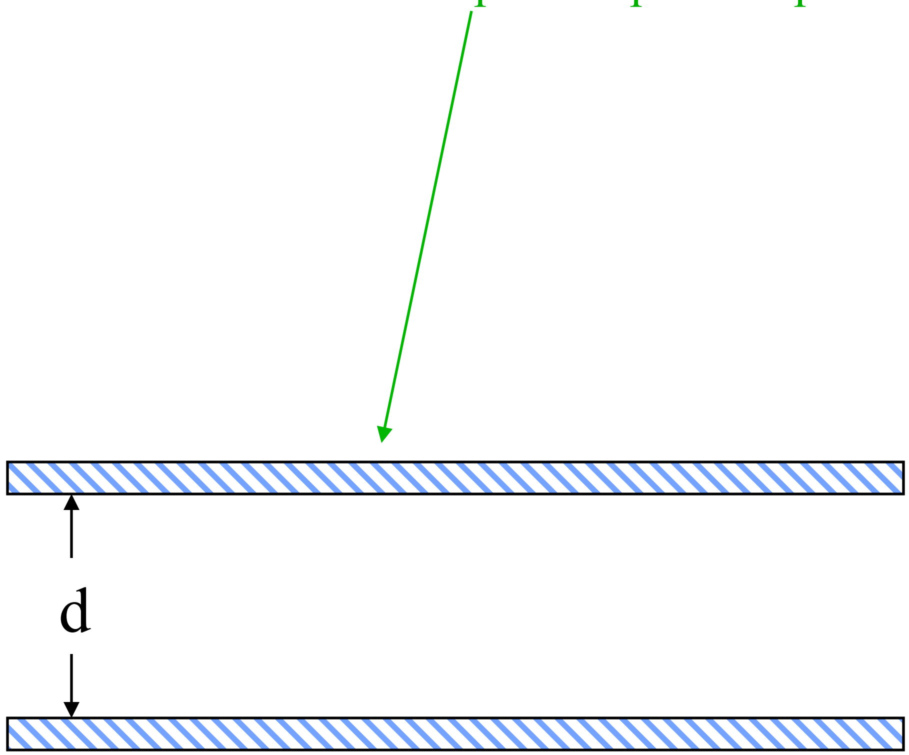
Review

- Molecular models
  - *intramolecular terms: stretch, bend, torsion*
  - *intermolecular terms: van der Waals, electrostatics, polarization*
- Electrostatic contributions may be very long-ranged
  - *monopole-monopole decays as r^{-1}, dipole-dipole as r^{-3}* (in 3D)
- Need to consider more than nearest-image interactions
  - *direct lattice sum not feasible*
- Ewald sum
  - *approximate field due to charges by smearing them*
  - *smeared-charge field amenable to Fourier treatment*
  - *correction to smearing needs only nearest-neighbor sum*

Capacitors

(Infinite) electrically conducting
parallel plates separated by vacuum



A = area of each plate

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Apply an electric potential difference $V = \phi_1 - \phi_2$ across them

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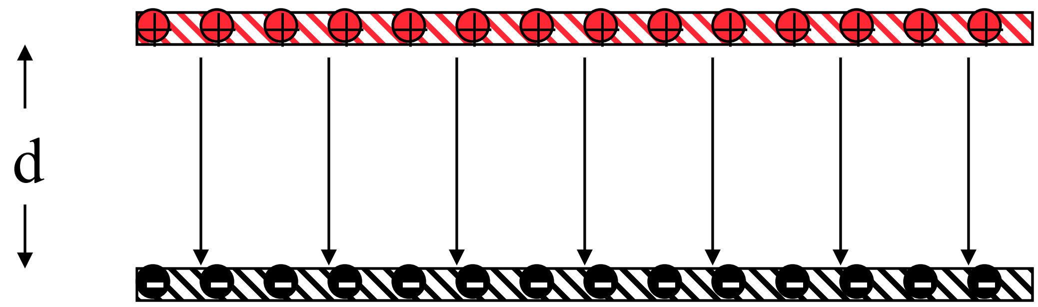

ϕ_1

$$\mathbf{E}_0 = \frac{V}{d}\hat{\mathbf{e}}_z$$

ϕ_2

A = area of each plate

Capacitors

The total charge is proportional to the potential difference

$$Q = \frac{A\varepsilon_0}{d}(\phi_2 - \phi_1)$$

$$Q = CV$$

Capacitance $C = \frac{\varepsilon_0 A}{d}$

(Infinite) electrically conducting parallel plates separated by vacuum

Apply an electric potential difference $V = \phi_1 - \phi_2$ across them

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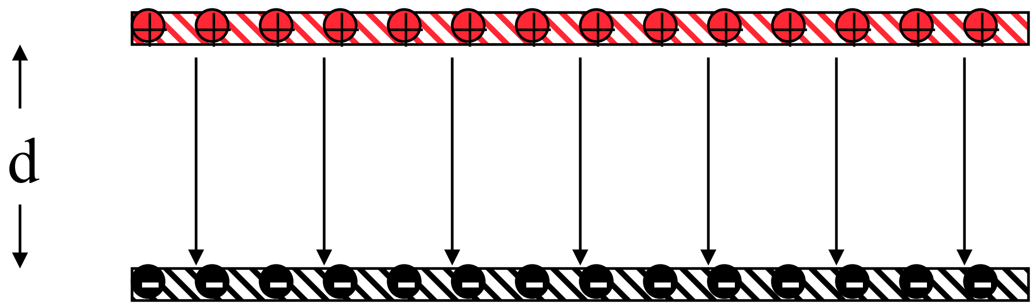

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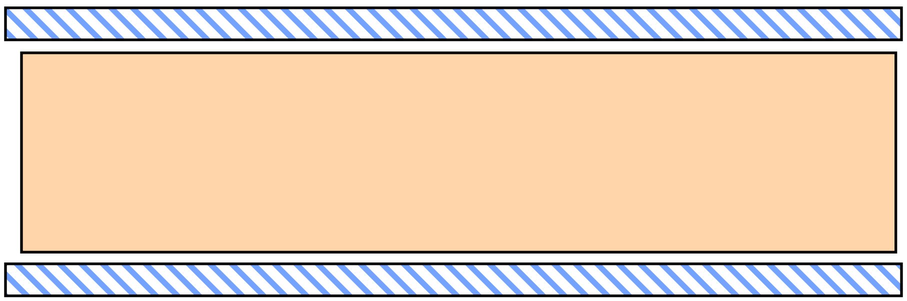
Dielectrics

- A dielectric is another name for an insulator (non-conductor)
- Dielectrics can polarize in the presence of an electric field
  - *distribute charges nonuniformly*
- Capacitor with a dielectric inside



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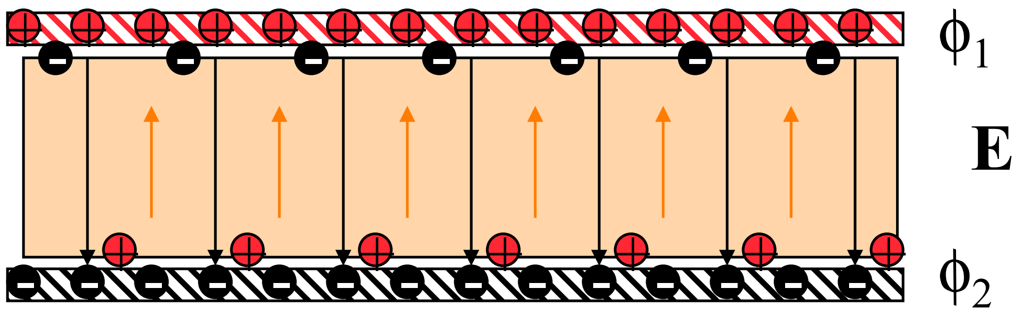

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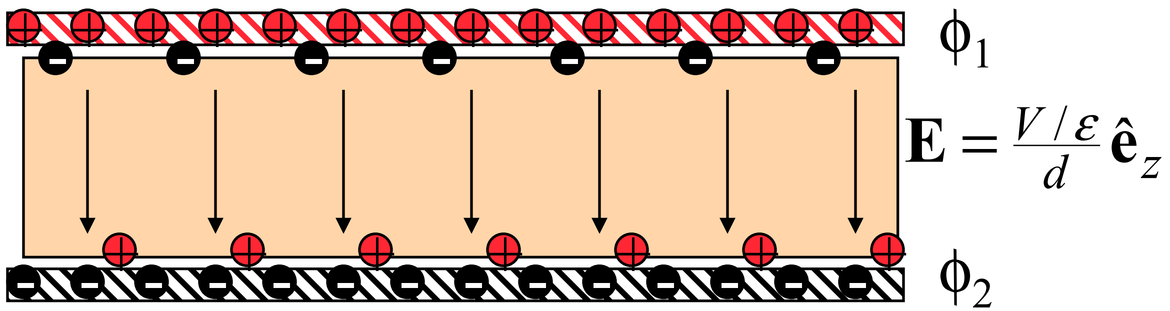
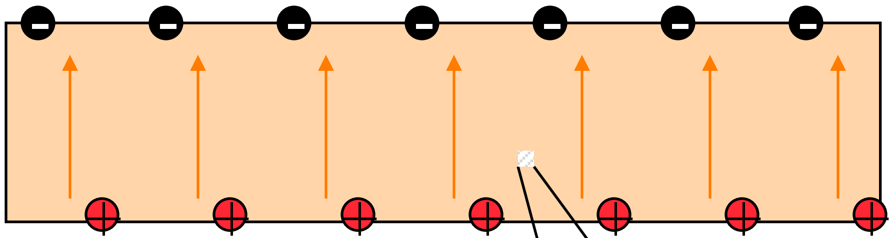


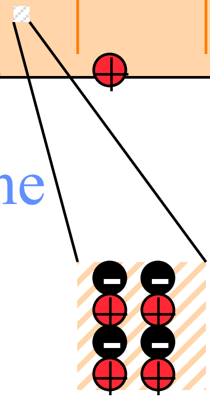
- Capacitance is increased
  - $C = Q/(V/\varepsilon) = \varepsilon C_0$
  - *same charge on each plate, but potential difference is smaller*
  - ε *is the dielectric constant* ($\varepsilon > 1$) (relative permittivity)

Polarization

- The dielectric in the electric field exhibits a net dipole moment **M**



- Every microscopic point in the dielectric also will have a dipole moment



- The polarization vector **P** is the dipole moment per unit volume
  - *in general,* $\mathbf{P} = \mathbf{P}(\mathbf{r})$
  - *for sufficiently small fields*, **P** *is proportional to the local* **E**

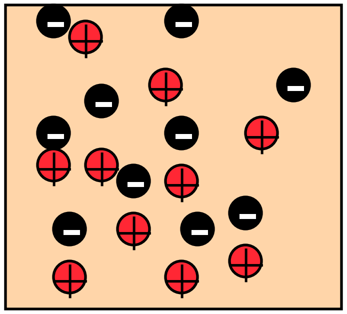
$$\mathbf{P} = \chi \mathbf{E} \qquad \chi = \text{electric susceptibility}$$

  - *this is a key element of linear response theory*

Origins of Polarization

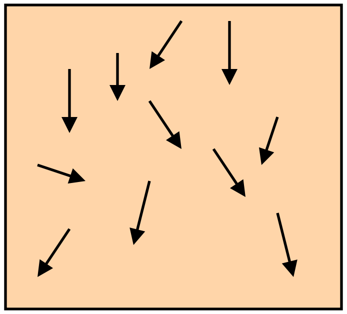
- Polarization originates in the electrostatic response of the constituent molecules
- In ionic systems, charges migrate

$$\mathbf{M} = \sum_{i=1}^{N} q_i \mathbf{r}_i$$

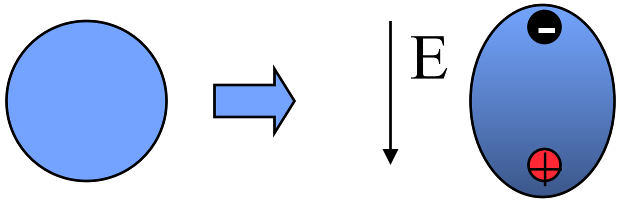


- In dipolar systems, molecular dipoles rotate

$$\mathbf{M} = \sum_{i=1}^{N} \vec{\mu}_i$$

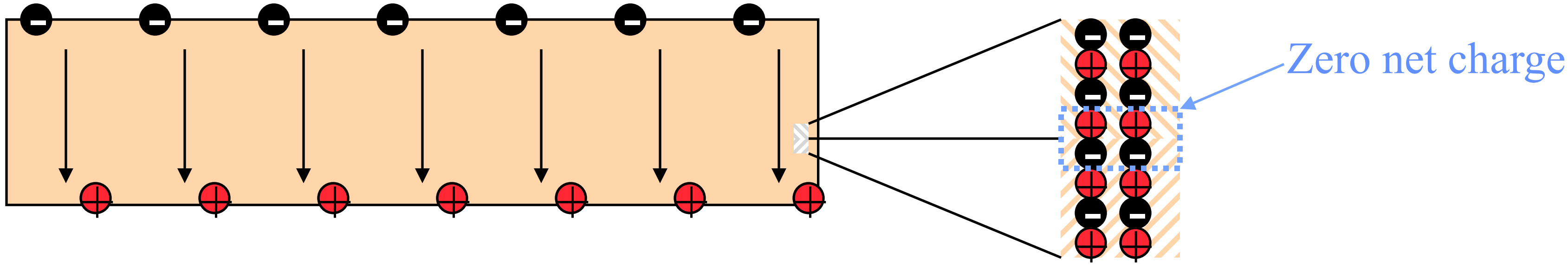


- In apolar systems, dipoles are induced
  - *"bound charges"*



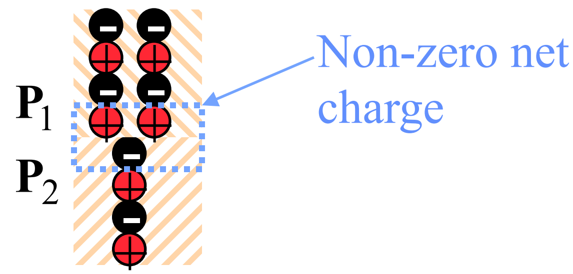
Polarization Charges

- Does polarization imply a nonzero charge density in the dielectric?
  - *No. For uniform* **P**, *the charge inhomogeneities cancel*



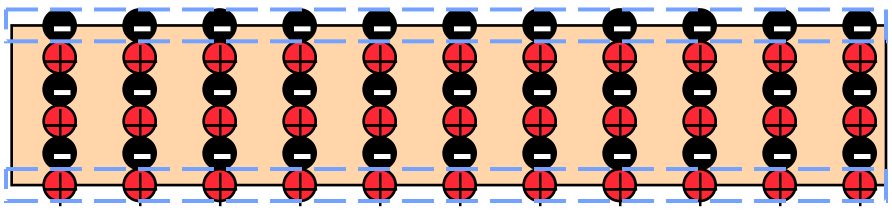
  - *But for nonuniform* **P**, *there* will *be a net charge due to polarization*
  - *In general*

$$\rho_{pol} = -\nabla \cdot \mathbf{P}$$



Surface Charge

- At the dielectric surface, the polarization is discontinuous
  - *i.e., it is non uniform*
  - *non-zero net charge at surfaces*



  - *charge per unit area is the component of* **P** *normal to surface*

$$\sigma_{pol} = \mathbf{P} \cdot \hat{\mathbf{n}}$$

- Relation between physical constants
  - *dielectric constant ε describes increased capacitance due to surface charges*
  - *electric susceptibility χ describes polarization due to electric field, and which leads to the surface charges*

Electrostatic Equations for Dielectrics 1.

- Basic electrostatic formula

$$\nabla \cdot \mathbf{E} = \rho$$

- Separate "free" charges from polarization charges

$$\nabla \cdot \mathbf{E} = (\rho_{\text{free}} + \rho_{\text{pol}})$$
$$= (\rho_{\text{free}} - \nabla \cdot \mathbf{P})$$

- Apply linear response formula

$$\nabla \cdot \mathbf{E} = \left(\rho_{\text{free}} - \nabla \cdot (\chi \mathbf{E})\right)$$
$$\nabla \cdot \left((1+\chi)\mathbf{E}\right) = \rho_{\text{free}}$$

- ρ_{free} relates to the electric field with no dielectric (vacuum)

$$\nabla \cdot \mathbf{E}_0 = \rho_{\text{free}}$$

- The relation follows

$$\left.\begin{array}{r}(1+\chi)\mathbf{E} = \mathbf{E}_0 \\ \varepsilon \mathbf{E} = \mathbf{E}_0\end{array}\right\} \quad \varepsilon = 1 + \chi$$

Note on notation

ε [=] ε_0 ➔ "permittivity"

ε dim'less ➔ "dielectric constant" or "relative permittivity"

Electrostatic Equations for Dielectrics

- Equations are same as in vacuum, but with scaled field

$$\nabla \cdot (\varepsilon \mathbf{E}) = \rho_{\text{free}} \qquad \nabla \times (\varepsilon \mathbf{E}) = 0$$

constant ε

- All interactions between "free" charges can be scaled accordingly
  - *Coulomb's law in a (linear) dielectric*

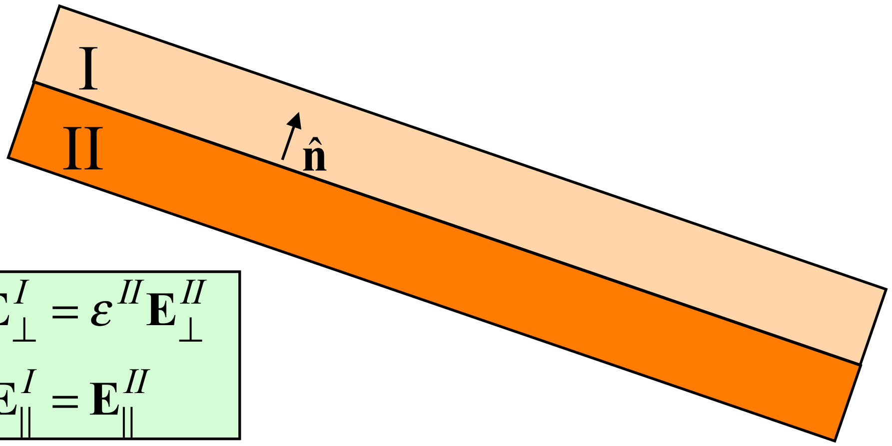
$$\mathbf{F} = \frac{q_1 q_2}{\varepsilon r^2} \hat{\mathbf{r}}$$

q_1 and q_2 are free charges

- Dielectric boundaries
  - ρ_{free} *independent of dielectric*
  - *implies continuity of* $\varepsilon\mathbf{E}$

but only normal component

$$\varepsilon^I \mathbf{E}_\perp^I = \varepsilon^{II} \mathbf{E}_\perp^{II}$$
$$\mathbf{E}_\parallel^I = \mathbf{E}_\parallel^{II}$$



Thermodynamics and Dielectric Phenomena

- Fundamental equation in presence of an electric field

$$d(\beta A) = U d\beta - \beta P dV + \beta\mu dN - \beta \mathbf{E}\cdot d\mathbf{M}$$

M = total dipole moment $\sum \vec{\mu}_i$

  - *Analogous to mechanical work $P\Delta V$, creation of dipole moment **M** in constant field **E** requires work $\boldsymbol{E}\cdot\Delta\boldsymbol{M} = \boldsymbol{E}\cdot\boldsymbol{M}$*

- More convenient to set formalism at constant field **E**

$$\begin{aligned} d\beta A' &\equiv d\beta(A + \mathbf{E}\cdot\mathbf{M}) \\ &= U d\beta - \beta P dV + \beta\mu dN + \mathbf{M}\cdot d\beta\mathbf{E} \\ &= U d\beta - \beta P dV + \beta\mu dN + V\mathbf{P}\cdot d\beta\mathbf{E} \end{aligned}$$

Legendre transform

P = **M**/V

- Electric susceptibility is a 2nd-derivative property

$$\chi = \left(\frac{\partial P_z}{\partial E_z}\right)_{T,V,N} = \frac{1}{V}\left(\frac{\partial^2 A'}{\partial E_z^2}\right)$$

take z as direction of field

Simple Averages 4. Heat Capacity

(from Lecture 6)

- Example of a "2nd derivative" property

$$C_v = \left(\frac{\partial E}{\partial T}\right)_{V,N} = -k\beta^2 \left(\frac{\partial^2 (\beta A)}{\partial \beta^2}\right)_{V,N}$$

$$= -k\beta^2 \frac{\partial}{\partial \beta} \frac{1}{Q(\beta)} \int dr^N dp^N E e^{-\beta E}$$

- Expressible in terms of fluctuations of the energy

$$C_v = k\beta^2 \left[\langle E^2 \rangle - \langle E \rangle^2 \right]$$

Note: difference between two $O(N^2)$ quantities to give a quantity of $O(N)$

- Other 2nd-derivative or "fluctuation" properties
  - *isothermal compressibility* $\kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_{T,N}$

Statistical Mechanics and Dielectric Phenomena

- Formula for electric susceptibility

$$\chi = \left(\frac{\partial P_z}{\partial E_z}\right)_{T,V,N} = \frac{1}{V}\left(\frac{\partial^2 A'}{\partial E_z^2}\right)$$

$$= \frac{1}{V}\frac{\partial}{\partial E_z}\left[\frac{1}{Q(E_z)}\int dr^N d\omega^N dp^N M_z e^{-\beta E} e^{\beta E_z M_z}\right]$$

$$= \frac{\beta}{V}\left[\left\langle M_z^2\right\rangle - \left\langle M_z\right\rangle^2\right]$$

$$= \frac{\beta}{DV}\left[\left\langle \mathbf{M}^2\right\rangle - \left\langle \mathbf{M}\right\rangle^2\right]$$

- Susceptibility is related to fluctuations in the total dipole moment
  - *this is sensible, since χ describes how "loose" the charges are, how easily they can appear/orient in response to an external field*

Dielectric Constant from Molecular Simulation

- Method 1. Ensemble average of dipole fluctuations

$$\varepsilon = 1 + \chi = 1 + \frac{\beta}{DV}\left[\langle \mathbf{M}^2 \rangle - \langle \mathbf{M} \rangle^2\right]$$

$$\mathbf{M} = \sum_{\text{charges, } i} \mathbf{r}_i q_i \qquad \text{or} \qquad \mathbf{M} = \sum_{\text{dipoles, } i} \boldsymbol{\mu}_i$$

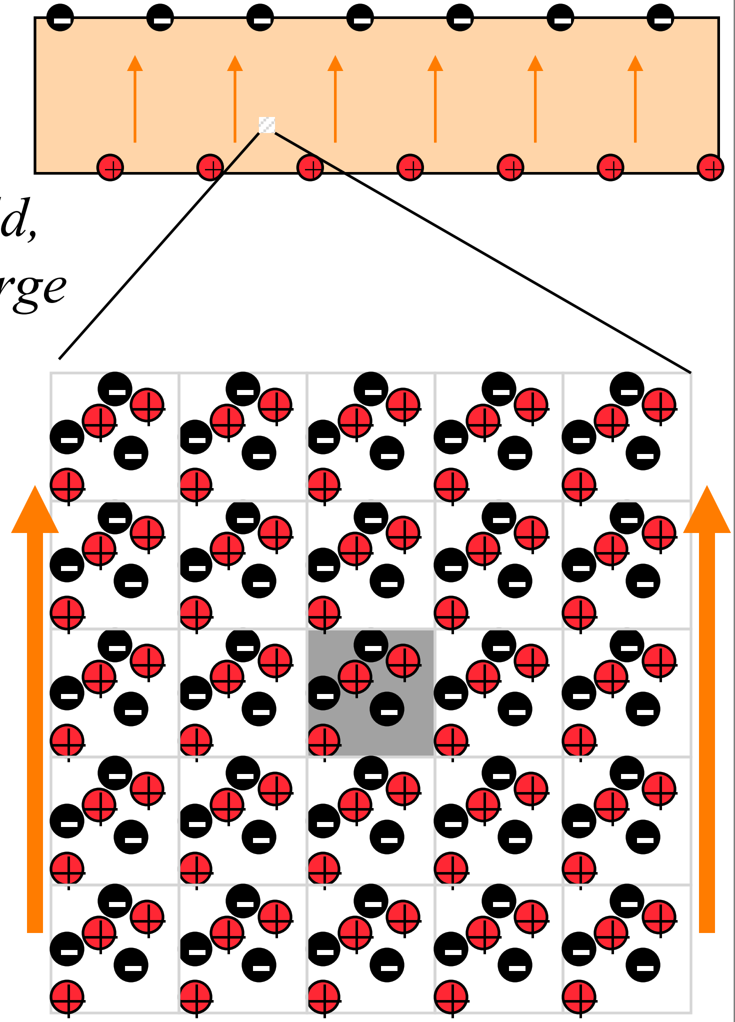
- Method 2. Response to an electric field

$$\mathbf{P} = \chi \mathbf{E}$$

  - *Apply field* $\boldsymbol{E}$, measure response $\mathbf{P}$

Connection to Ewald Sum

- Surface charges on dielectric produce a non-negligible electric field throughout
  - *Local regions inside dielectric feel this field, even though they have no polarization charge*
  - *Surface charges arise when the system has uniform polarization*
    - dipole moment per unit volume
- In simulation of polar systems, at any instant the system will exhibit an instantaneous dipole
  - *This dipole is replicated to infinity*
  - *But in principle it stops at some surface*
  - *Should the resulting field influence the simulated system?*
  - *The boundary conditions at infinity are relevant!*

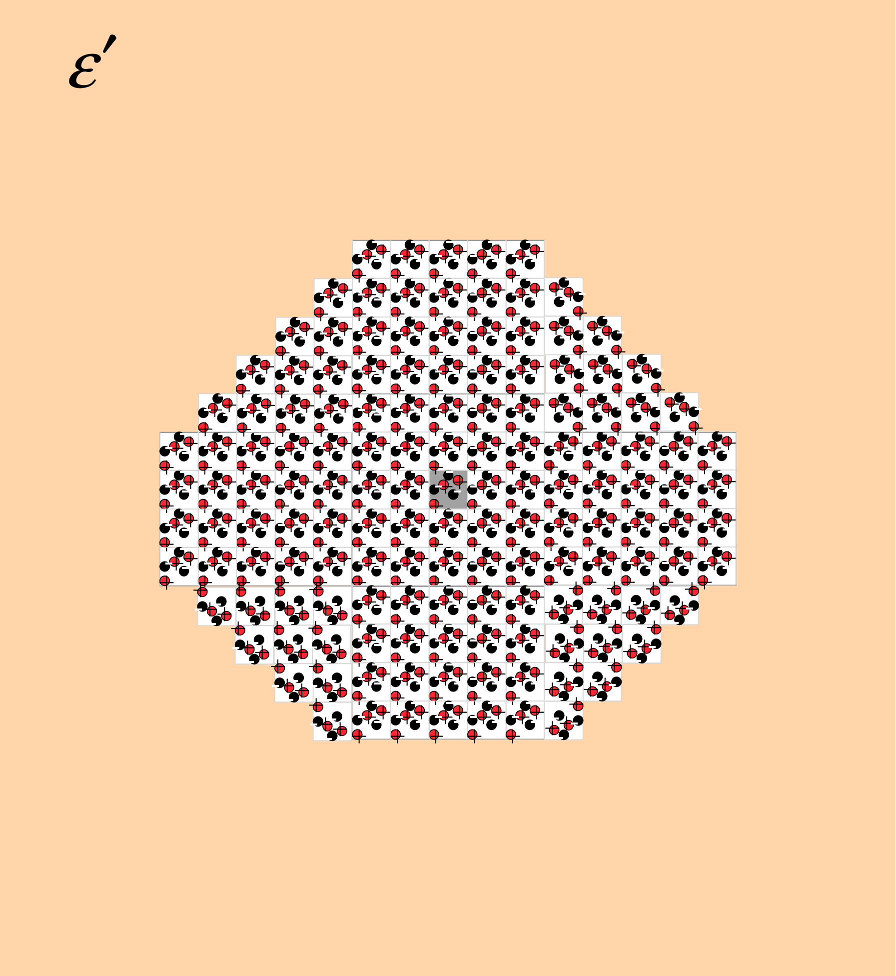


$$U_q = \frac{1}{2}\sum_{\mathbf{k}\neq 0} \frac{4\pi V}{k^2} e^{-k^2/4\alpha} \left|\rho(\mathbf{k})\right|^2$$

k = 0 term corresponds to this effect

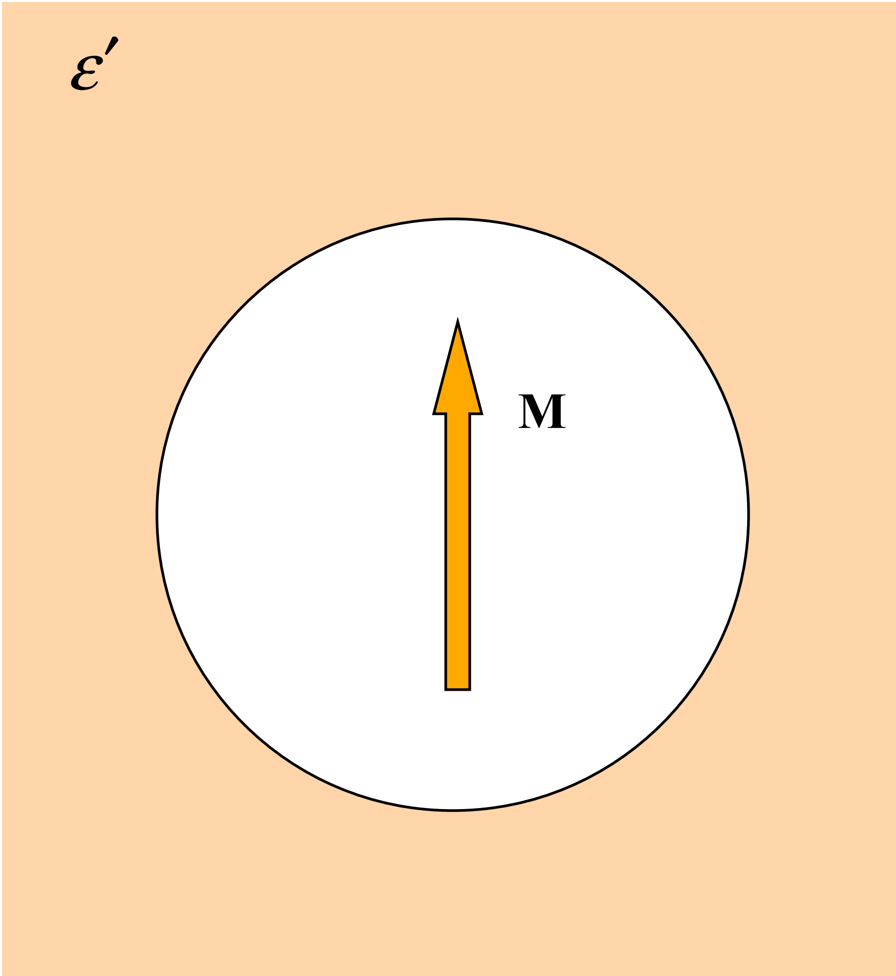
Boundary Conditions for Ewald Sum

- Consider the simulated system embedded in a continuum dielectric



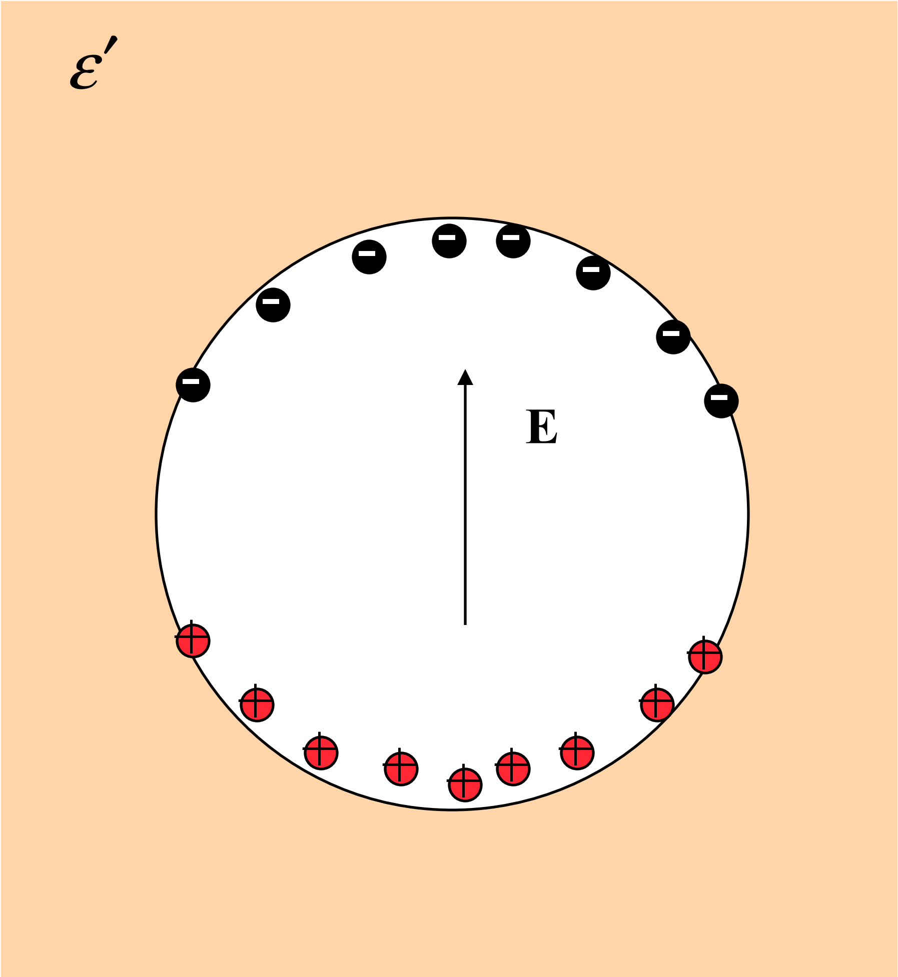
Boundary Conditions for Ewald Sum

- Consider the simulated system embedded in a continuum dielectric
- An instantaneous dipole fluctuation occurs often during the simulation



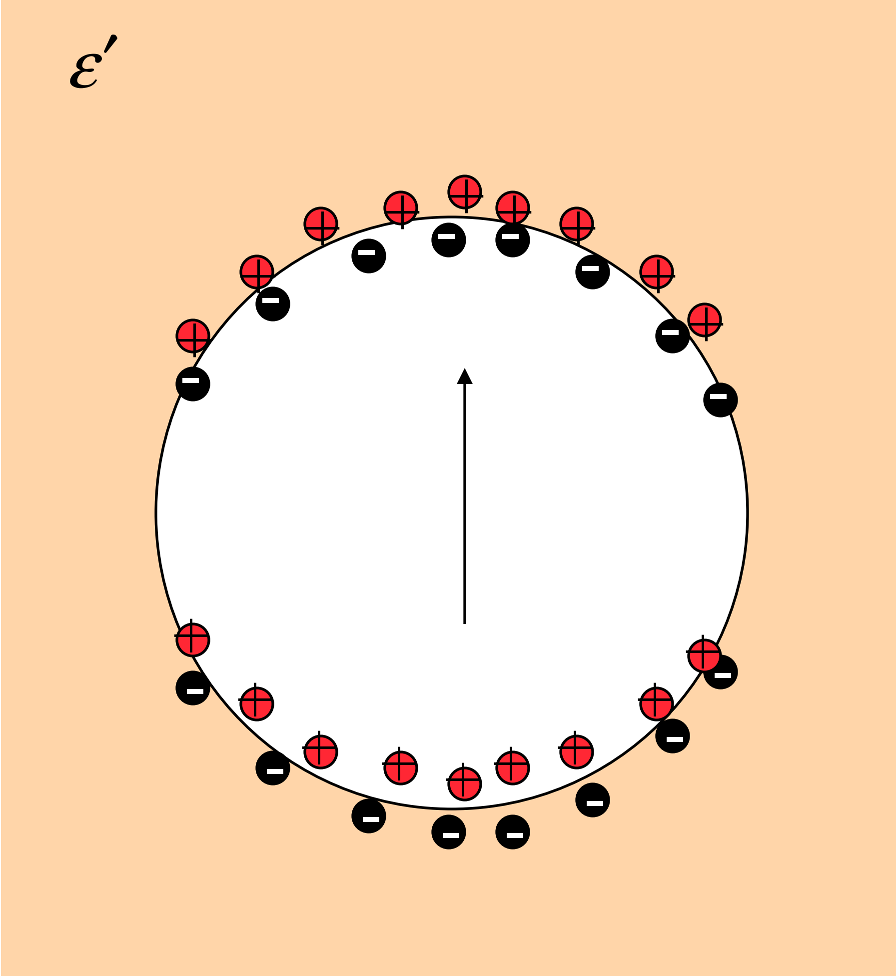
Boundary Conditions for Ewald Sum

- Consider the simulated system embedded in a continuum dielectric
- An instantaneous dipole fluctuation occurs often during the simulation
- The polarization creates a surface charge, and field **E**



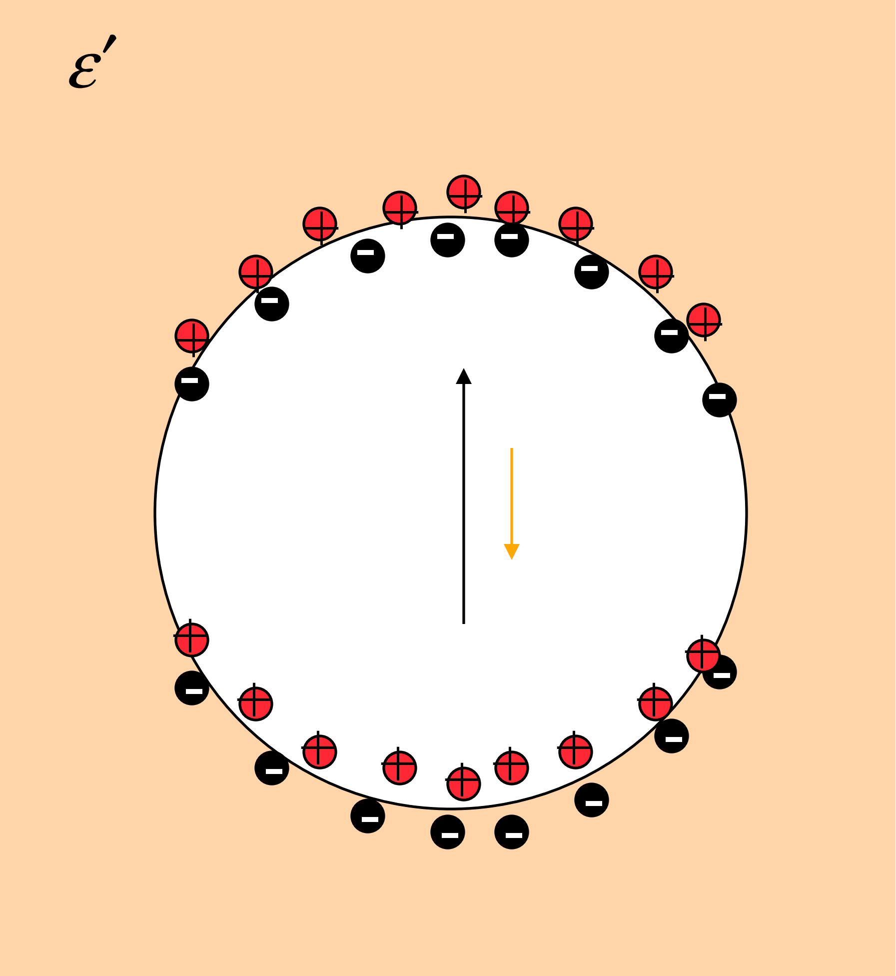
Boundary Conditions for Ewald Sum

- Consider the simulated system embedded in a continuum dielectric
- An instantaneous dipole fluctuation occurs often during the simulation
- The polarization makes a surface charge, and field **E**
- The dielectric responds with a counter charge distribution



Boundary Conditions for Ewald Sum

- Consider the simulated system embedded in a continuum dielectric
- An instantaneous dipole fluctuation occurs often during the simulation
- The polarization makes a surface charge , and field **E**
- The dielectric responds with a surface charge distribution
- This produces a depolarizing field that attenuates the surface-charge field



Boundary Contribution to Hamiltonian

- The field due to the surface charge is

$$\mathbf{E}_p = \frac{2\pi}{3}\mathbf{P}$$

complicated by spherical geometry

- The depolarizing field from the dielectric is

$$\mathbf{E}_d = -\frac{4\pi}{3}\frac{\varepsilon' - 1}{2\varepsilon' + 1}\mathbf{P}$$

- The contribution to the system energy (Hamiltonian) from its interaction with these fields is

$$\begin{aligned} U_{pol} &= -(\mathbf{E}_p + \mathbf{E}_d)\cdot\mathbf{P} \\ &= \frac{2\pi}{3}\left(1 - \frac{2(\varepsilon' - 1)}{2\varepsilon' + 1}\right)|\mathbf{P}|^2 \end{aligned}$$

- Common practice is to use conducting boundary, $\varepsilon' = \infty$

$$U_{pol} = 0$$

Both effects cancel, and we can use the Ewald formula as derived

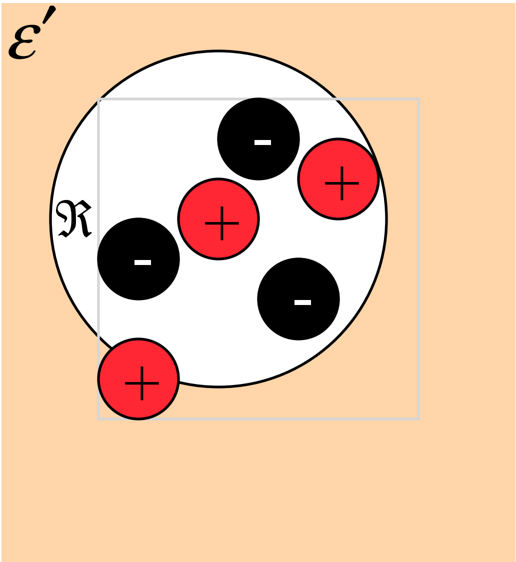
"Tin foil" boundary condition

Reaction Field Method

- Alternative to Ewald sum for treatment of long-range electrostatic interactions
- Define interaction sphere $\Re$ for each particle
- Direct interactions with other particles in $\Re$
- Treat material outside sphere as continuum dielectric
  - *Dielectric responds to instantaneous dipole inside sphere*
  - *Contributes to energy as described before*

$$U_{rf} = \frac{1}{2}\sum_{i=1}^{N}\mu_i \cdot \left[\frac{2(\varepsilon'-1)}{2\varepsilon'+1}\frac{1}{r_c^3}\sum_{j\in\Re_i}\mu_j \right]$$

  - *Aim to make $\varepsilon' = \varepsilon$ (results not sensitive to choice)*



Summary

- Dielectric constant describes increased capacitance associated with insulator placed between parallel plates
- Insulator responds to an external field by polarizing
- Polarization leads to surface charge that offsets imposed field
- Charges at infinitely distant boundary have local effect due to this offsetting field
- If the system is embedded in a conducting medium, it will respond in a way the eliminates the surface-charge effect
- Susceptibility describes linear relation between polarization and external field
    - *2nd-derivative property related to fluctuations in polarization*
- Reaction field method is a simpler and more efficient alternative to the Ewald sum