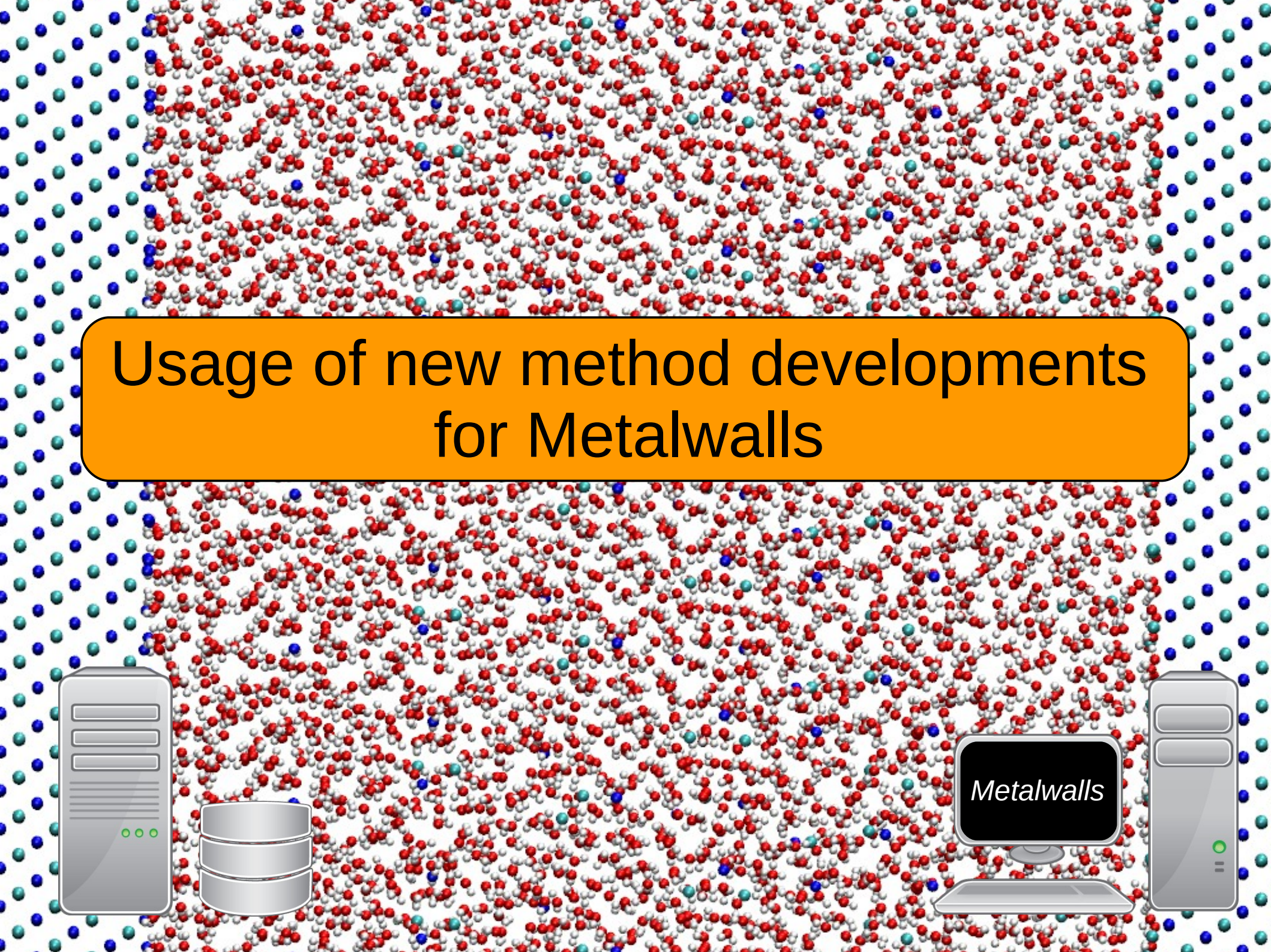
Usage of new method developments for Metalwalls



Finite electric field and electric displacement

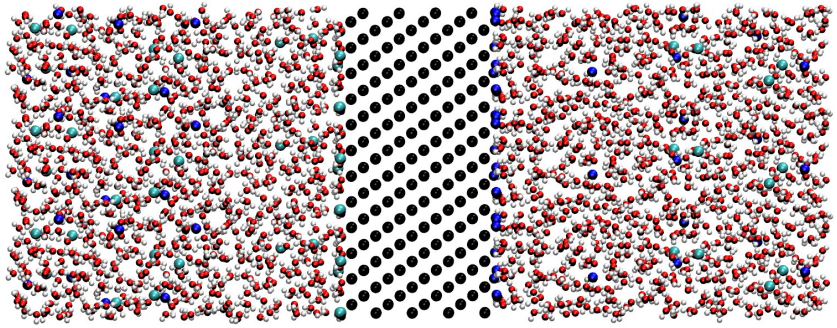
Modification of the dynamics and the electrostatic energy of the system by applying an external field (Vanderbilt and al. 2009)

$$\begin{cases} H = H_0 + H_{field} \\ \mathbf{F}_i = \mathbf{F}_{i,0} + \mathbf{F}_{i,field} \\ \Psi_i = \Psi_{i,0} + \Psi_{i,field} \end{cases}$$

Constant **E**

= constant **electric field**

ΔV



fixes the **potential drop** across the cell

$$H_{field} = - V \, \mathbf{E} \cdot \mathbf{P}$$
$$\mathbf{F}_{i,field} = q \, \mathbf{E}$$
$$\Delta V = - E_z \, L_z$$

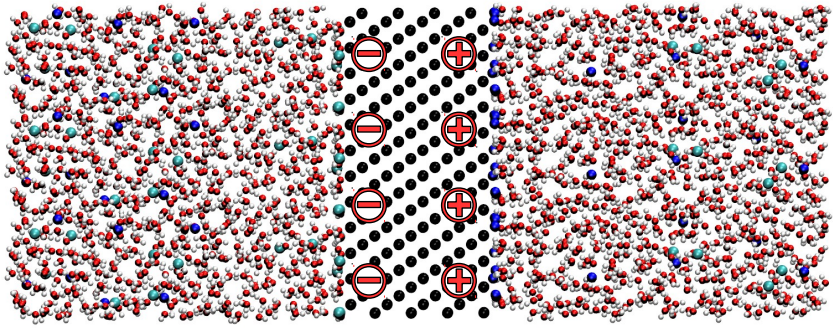
VS

$$\mathbf{D} = \mathbf{E} + 4\pi \, \mathbf{P}$$

Constant **D**

= constant **electric displacement**

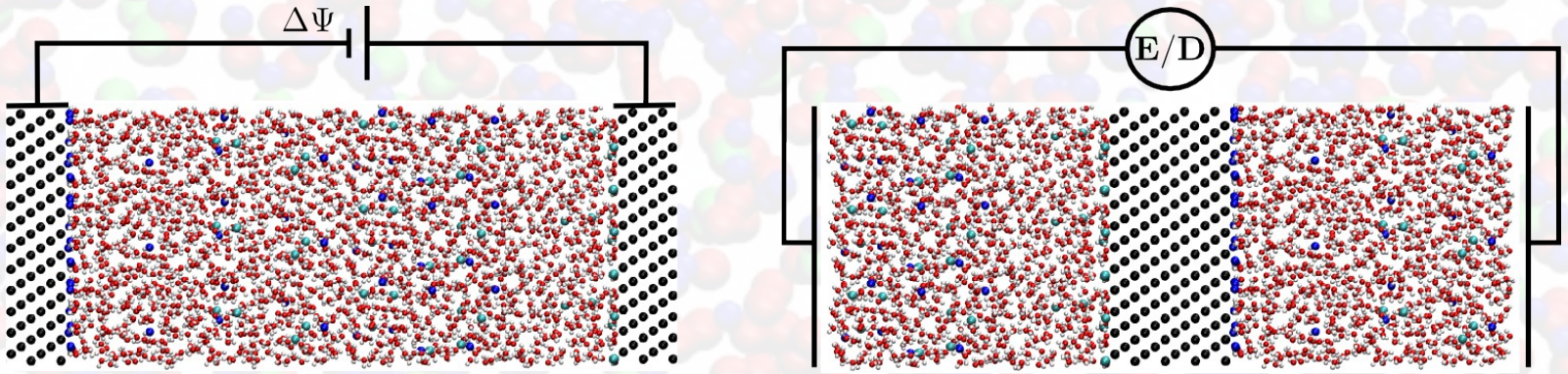
$-\sigma$ σ



fixes the **electrode surface charge**

$$H_{field} = V/8\pi \, [\, \mathbf{D} - 4\pi \, \mathbf{P} \,]^2$$
$$\mathbf{F}_{i,field} = q \, [\, \mathbf{D} - 4\pi \, \mathbf{P} \,]$$
$$\sigma = 4\pi \, D_z$$

Alternative way to impose a potential difference



Modifications in the input file runtime.inpt

- **num_pbc** block

```
num_pbc   3
```

- **electrodes** block

```
force_neutral   true
```

electrode_type subblock

```
potential   0.0
```

- New **external_field** block

```
external_field
   type          *string*                  # possible values: E or D
   direction     *real*  *real*  *real*    # default  0.0  0.0  0.0
   amplitude     *real*                    # default  0.0
```

Example

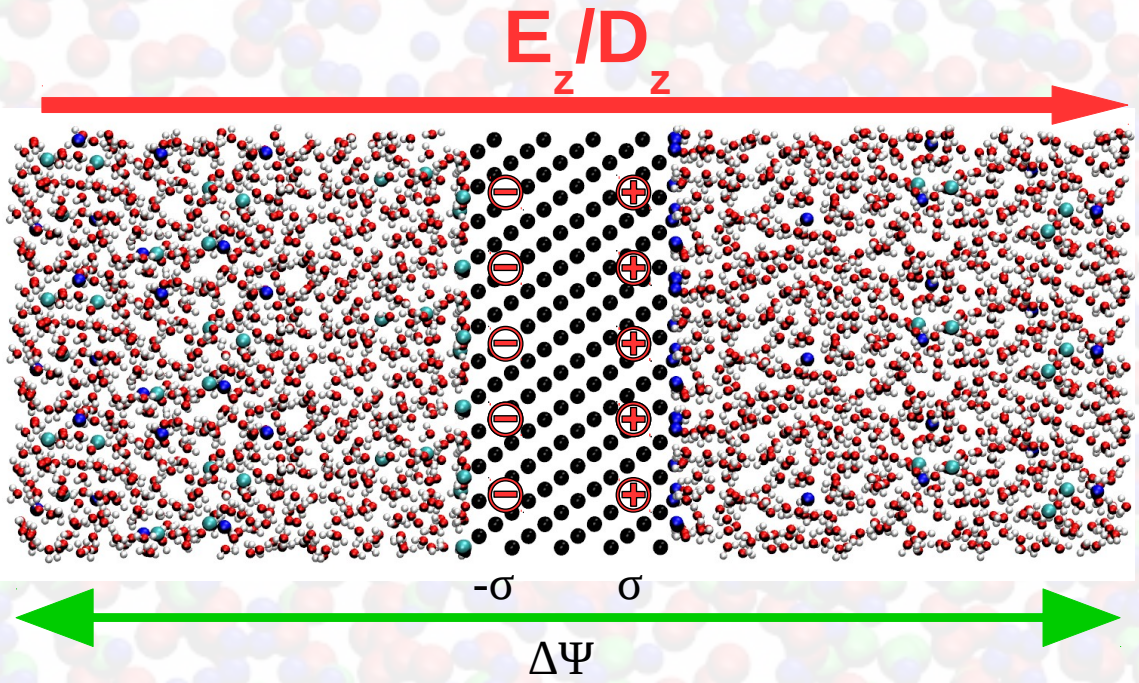
For an electric displacement (D), if
direction = (1;0,5;0) and
amplitude = D

Then we have
D_x = D
D_y = 0,5 D
no field applied along z

⚠ for D, no applied field is not the same as a 0 applied field!

MLshake, polarizability (for now)

Finite fields and capacitance



Integral capacitance:

$C_{int} = \sigma / \Delta\Psi$

Differential capacitance:

$C_{diff} = d\sigma / d\Delta\Psi$

Constant **E**

- Integral capacitance

$$C^{\mathbf{E}}_{int} = \sigma_{\mathbf{E}/\Delta\Psi}$$

$$C^{\mathbf{E}}_{int} = \frac{1}{4\pi L_z}\left[1 + 4\pi P_z/E_z\right]$$

- Differential capacitance

$$C^{\mathbf{E}}_{diff} = C_{void} + \beta S\ (\langle P_z^2\rangle_{\mathbf{E}} - \langle P_z\rangle^2_{\mathbf{E}})$$

$$C^{\mathbf{E}}_{diff} = C_{void} + \beta S\ (\langle \sigma^2\rangle_{\mathbf{E}} - \langle \sigma\rangle^2_{\mathbf{E}})$$

Constant **D**

- Integral capacitance

$$C^{\mathbf{D}}_{int} = \sigma/\Delta\Psi_{\mathbf{D}}$$

$$C^{\mathbf{D}}_{int} = \frac{1}{4\pi L_z}\frac{1}{1 - 4\pi P_z/D_z}$$

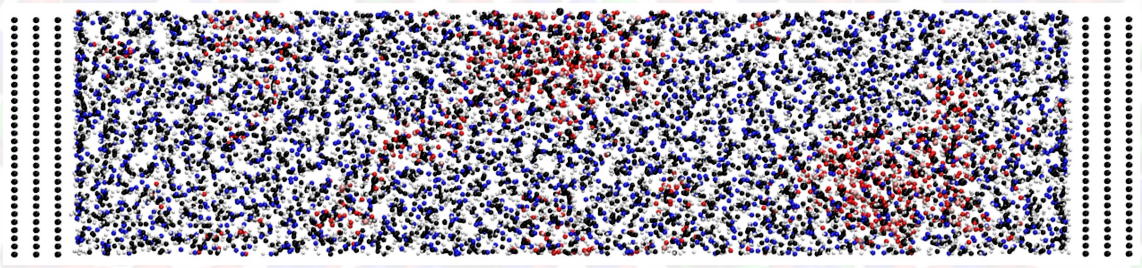
- Differential capacitance

$$C^{\mathbf{D}}_{diff} = \frac{1}{1/C_{void} - (4\pi)^2\beta\Omega L_z\ (\langle P_z^2\rangle_{\mathbf{D}} - \langle P_z\rangle^2_{\mathbf{D}})}$$

$$C^{\mathbf{D}}_{diff} = \frac{1}{1/C_{void} - \beta S\ (\langle \Delta\Psi^2\rangle_{\mathbf{D}} - \langle \Delta\Psi\rangle^2_{\mathbf{D}})}$$

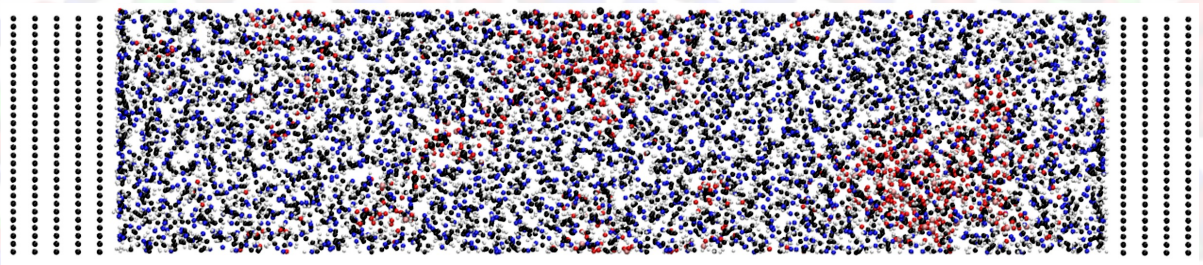
Perform simulations with finite fields

System at constant potential



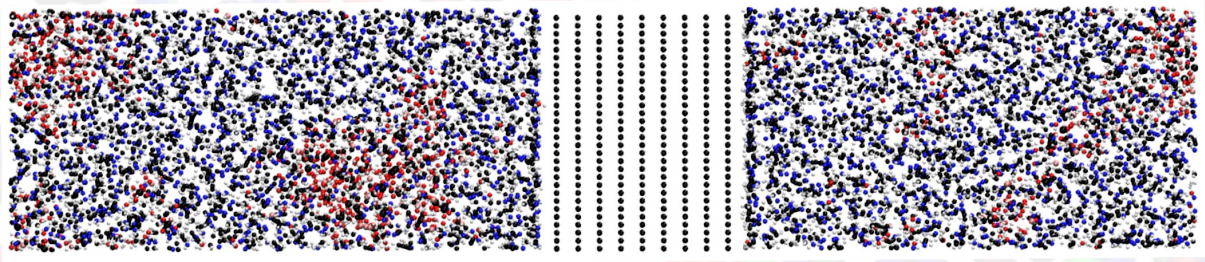
Extend the electrode

- Conserve the geometry of the material



Compute **P**

- Remove the block polarization in data.inpt
- Update the value of L_z (add 1 interlayer)
- Run 1 step to generate a restart.dat with **P**



Translate the electrode

Apply the field

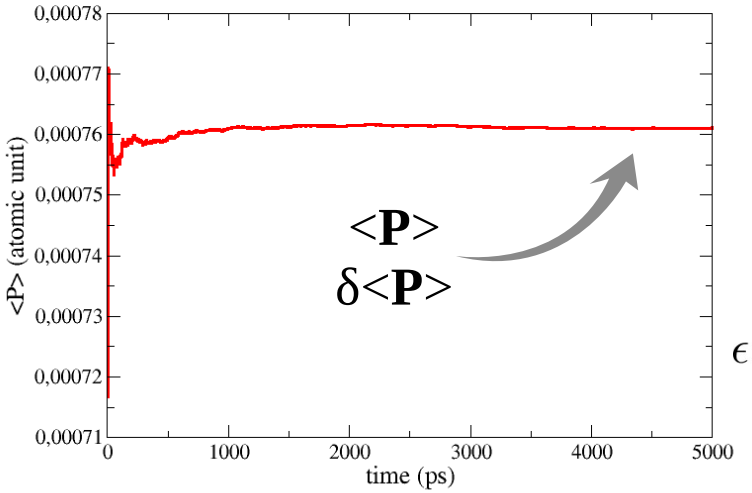
Finite fields and dielectric constant

By definition, the dielectric constant is equal to $\varepsilon = D/E$

This is valid if **P** includes only the contribution of the bound charges

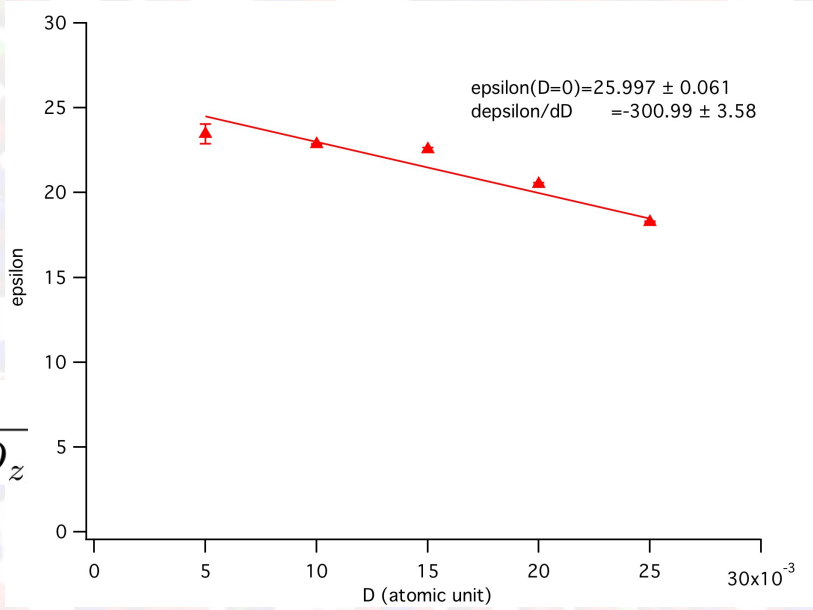
↳ works only for systems composed of **neutral molecules**

- Compute P by reconstructing the molecules
- Write the value of P in the polarization block of the associated data.inpt file
- Apply several values of **D**
- Compute the associated average polarization using the running average
- Extrapolate to obtain the value at zero field

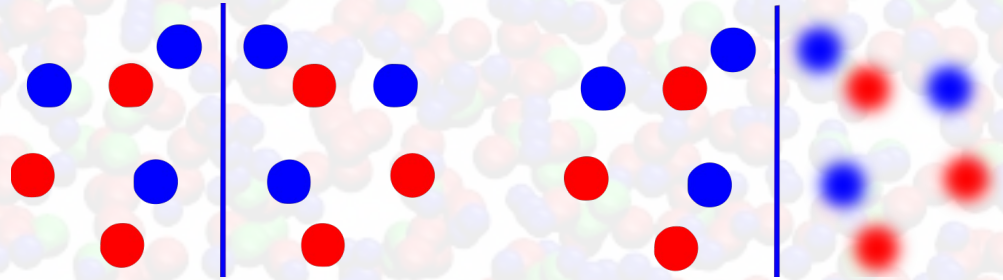


$$\epsilon = \frac{1}{1 - 4\pi\langle P_z\rangle / D_z}$$

$$\delta\epsilon = \epsilon^2 4\pi \frac{\delta P_z}{D_z}$$



Thomas-Fermi model

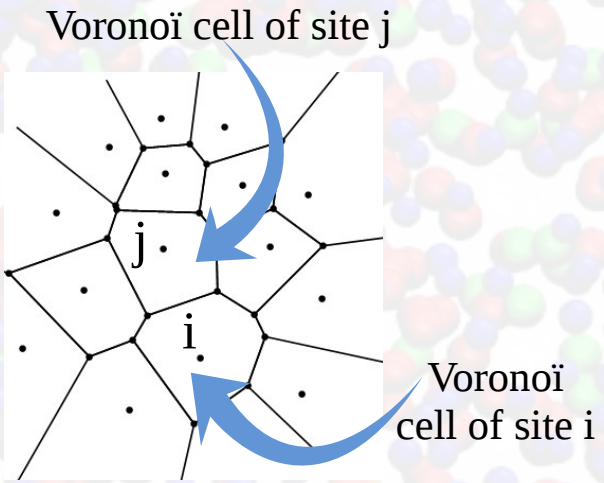


Screening of the electric field over a characteristic length l_{TF}
(Thomas-Fermi length)

Take into account the kinetic energy of the electrons

$$\begin{cases} H = H_0 + H_{TF} \\ H_{TF} = 4\pi\, l_{TF}^{\,2}\, 1/2 \sum_i (1/V_i)\, q_i^{\,2} \end{cases}$$

Voronoï volume
(~1/atomic density)



Modifications in the input file runtime.inpt

electrode_type subblock

```
thomas_fermi_length   *real*      # default  0.0
voronoi_volume        *real*      # default
```