Computing dielectric constants of liquid water and electric double layer at electrified interface

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1. Computing the dielectric constant ϵ at constant dielectric displacement $\mathbf{D}$

1.1 Constant E and D hamiltonians

- The method is the finite temperature classical variant of the constant $\mathbf{D}$ method developed by Stengel, Spaldin and Vanderbilt [1].
- The extended Hamiltonian at constant displacement field $\mathbf{D}$ is:

$$U(\mathbf{D}, v) = H_{\mathrm{PBC}}(v) + \frac{\Omega}{8\pi}(\mathbf{D} - 4\pi\mathbf{P}(v))^2 \qquad (1)$$

- The polarization $\mathbf{P}$ is a multi-valued quantity, but molecular structure provides a natural gauge.
- Through Legendre transform, it can be shown that the extended Hamiltonian at constant macroscopic field $\mathbf{E}$ is [1]:

$$F(\mathbf{E}, v) = H_{\mathrm{PBC}}(v) - \Omega\,\mathbf{E}\cdot\mathbf{P}(v) \qquad (2)$$

- They are corresponding to constant charge and constant voltage setups of a "virtual" parallel plate capacitor.

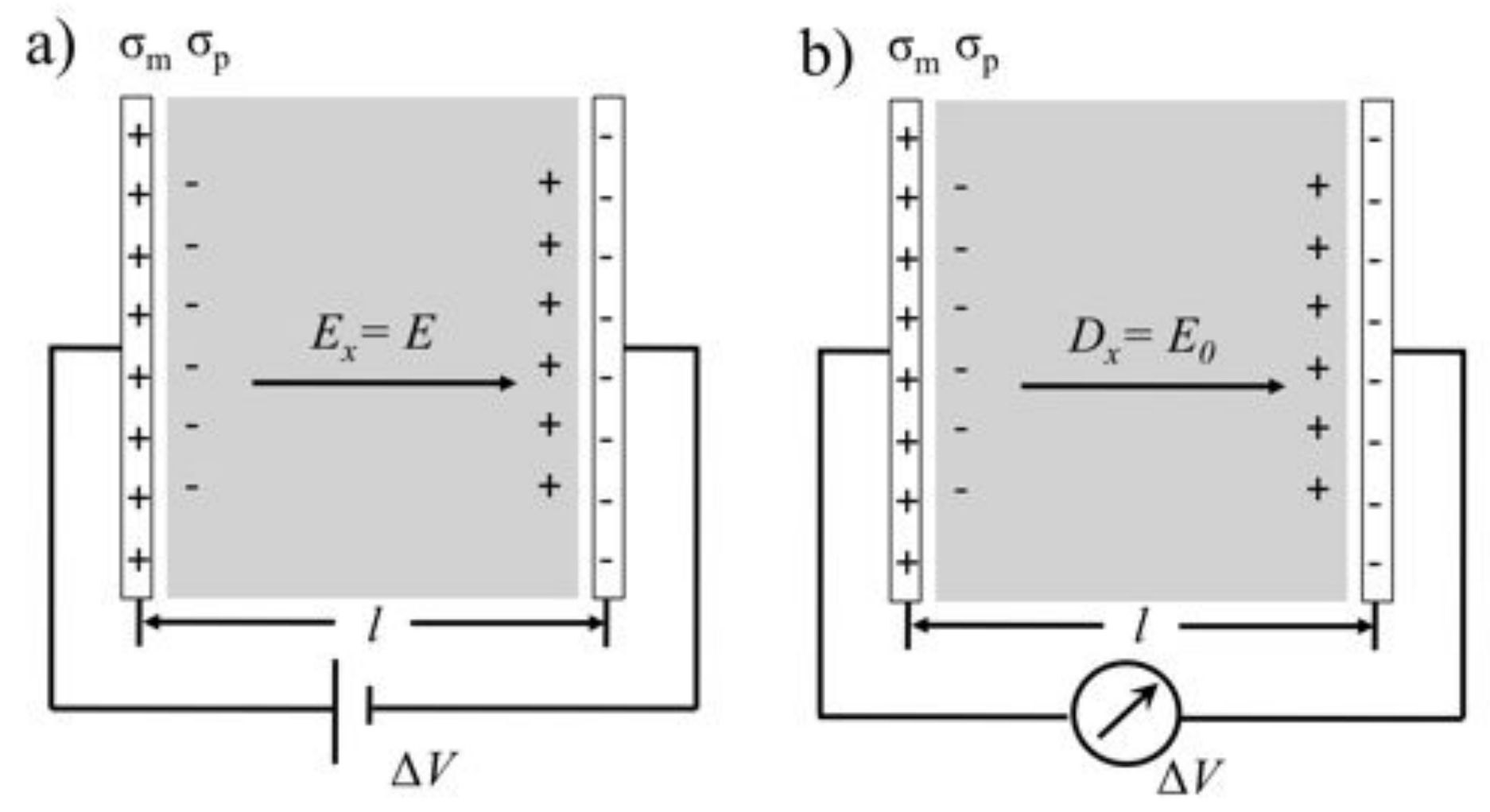

Figure 1: *Parallel plate capacitor at a) constant electric field E_x and b) at constant electric displacement D_x.*

1.2 Polarization fluctuation and relaxation of liquid water at $\mathbf{E} = 0$ and $\mathbf{D} = 0$

- A change of electric boundary not only affects the size of polarization fluctuation but also the time scale of polarization relaxations.
- The ratio according to Debye theory is $\tau_T/\tau_L = \epsilon$. From our molecular dynamics (MD) simulation, τ_T is 10.3 ps and τ_L is 0.3 ps (short time oscillations).

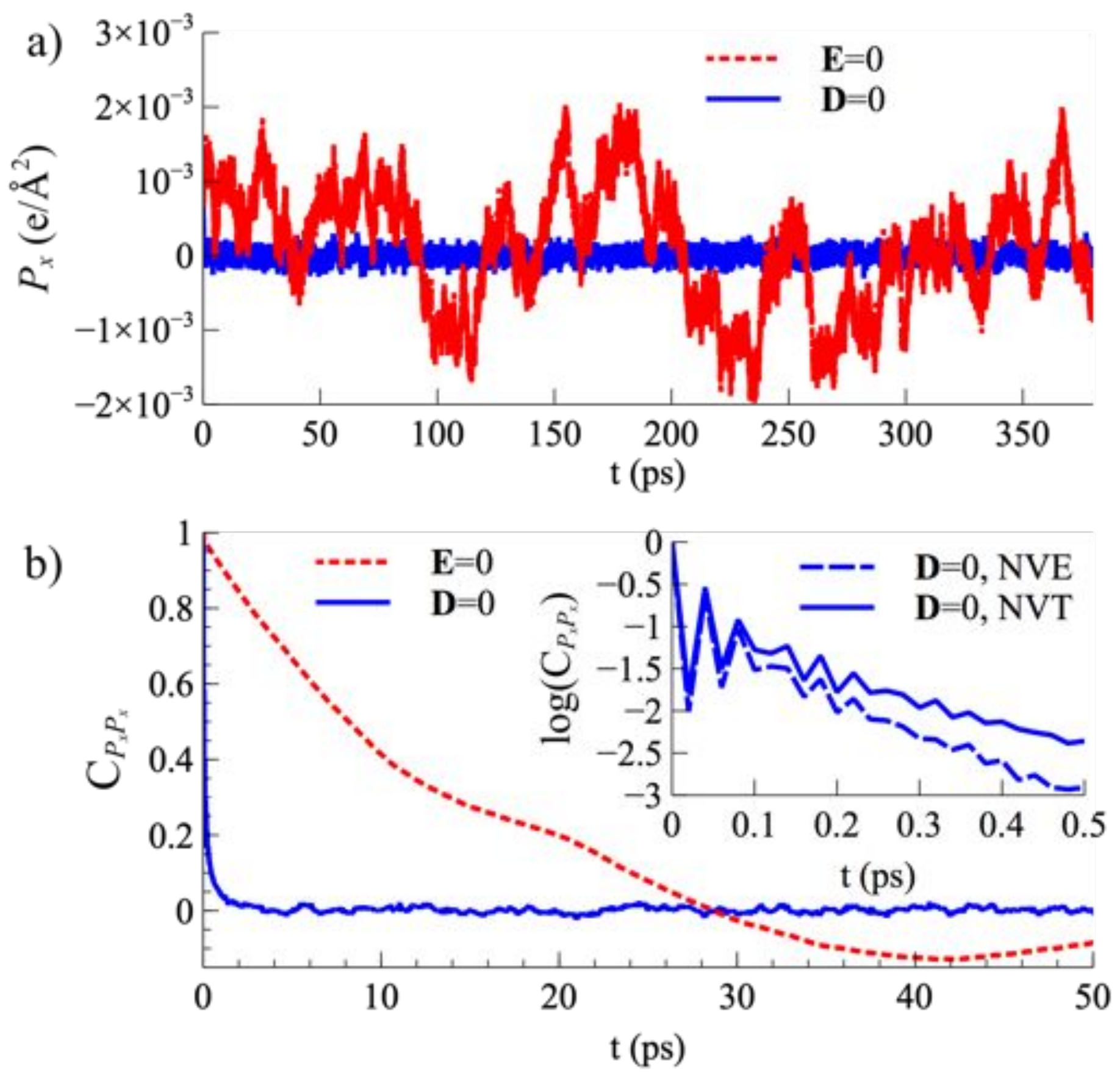

Figure 2: *Simulation of bulk liquid water (SPC/E) at $\mathbf{E} = 0$ using the hamiltonian of Eq. 2 and $\mathbf{D} = 0$ using the hamiltonian of Eq. 1: a) Time evolution of P_x, the x component of the polarization; b) Corresponding autocorrelation function defined as $C_{P_xP_x} = \langle P_x(0)P_x(t)\rangle / \langle P_x(0)P_x(0)\rangle$. The inset shows the short time behaviour of $C_{P_xP_x}$ for $\mathbf{D} = 0$.*

- We can show that the variance of polarization at $E = 0$ and $D = 0$ has the following relation [2]:

$$\epsilon = \frac{\langle \mathbf{P}^2\rangle_{\mathbf{E}=0} - \langle \mathbf{P}\rangle^2_{\mathbf{E}=0}}{\langle \mathbf{P}^2\rangle_{\mathbf{D}=0} - \langle \mathbf{P}\rangle^2_{\mathbf{D}=0}} \qquad (3)$$

From our simulations, we found the ratio is 71 for SPC/E water (ϵ of SPC/E water is about 72).

- This relation is also reflected in the distance dependent Kirkwood G-factor $G_K(r)$.

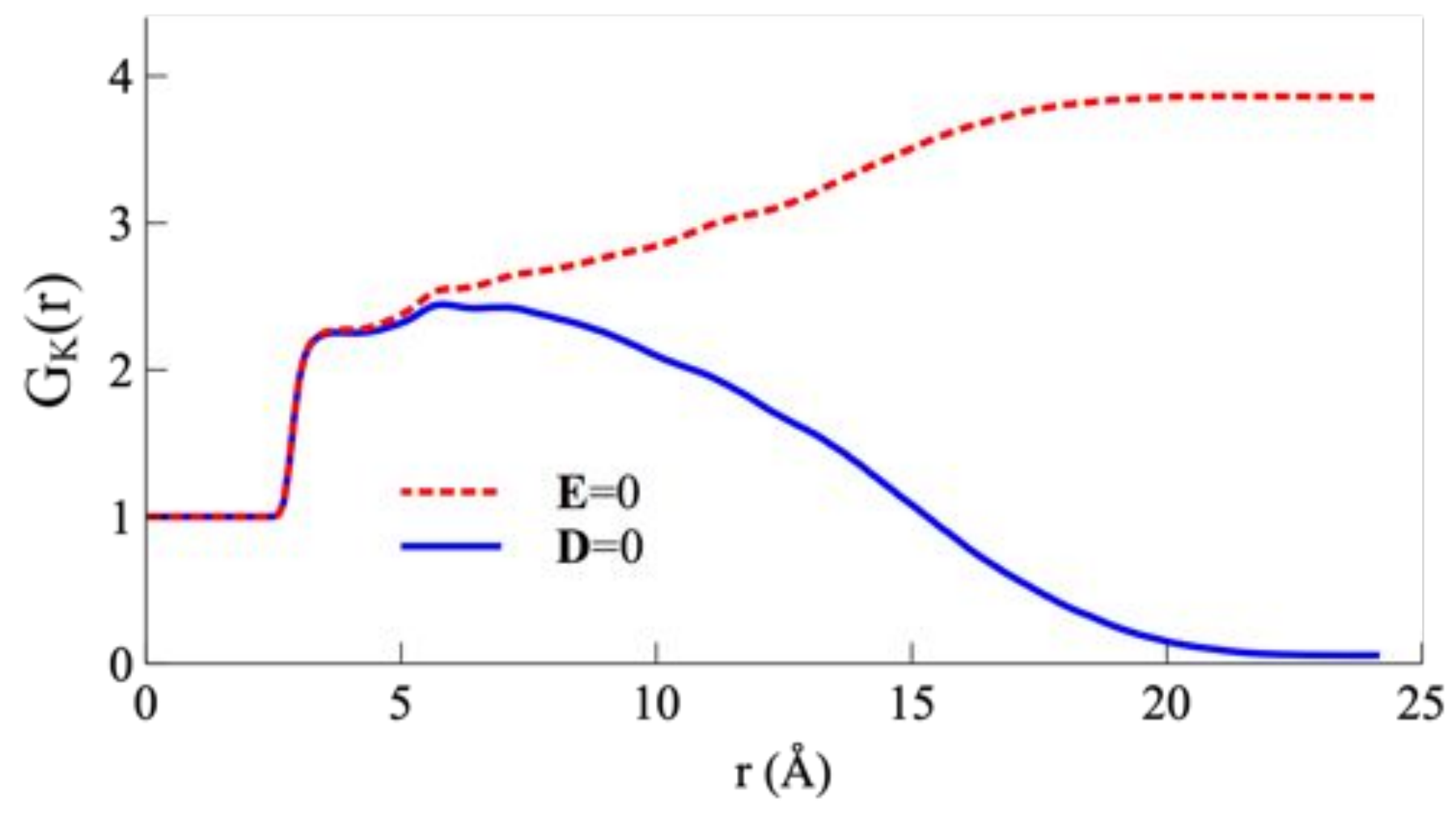

Figure 3: *Comparison of the distance dependence of the Kirkwood G-factor $G_{\mathrm{K}}(r)$ evaluated under $\mathbf{E} = 0$ and $\mathbf{D} = 0$ constraints.*

1.3 Non-linearity of the dielectric constant and the polarization at finite $\mathbf{E}$ and finite $\mathbf{D}$

- We found the non-linear effect in the $P_x(D)$ curve is much less pronounced than that in the $P_x(E)$.

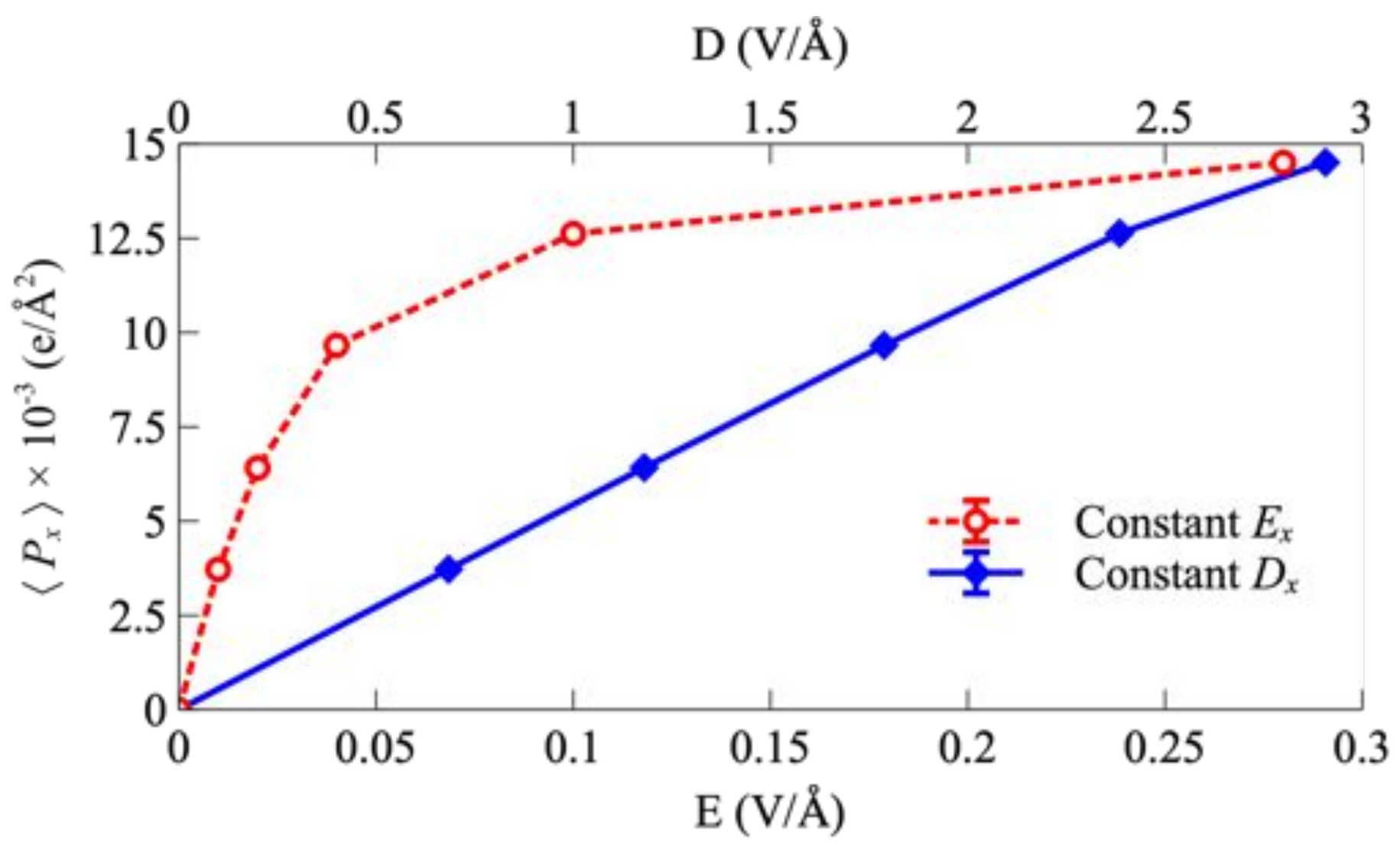

Figure 4: *Polarization as a function of electric field E and displacement D determined from constant E_x and constant D_x molecular dynamics of liquid water respectively.*

- It is found that the curvature of the curvature in $\epsilon(D)$ is opposite to the curvature in $\epsilon(E)$.
- The convergence time of the dielectric constant under constant D_x turns out to be shorter.
- The constant $\mathbf{D}$ method may be therefore the best option for density functional theory (DFT) based MD.

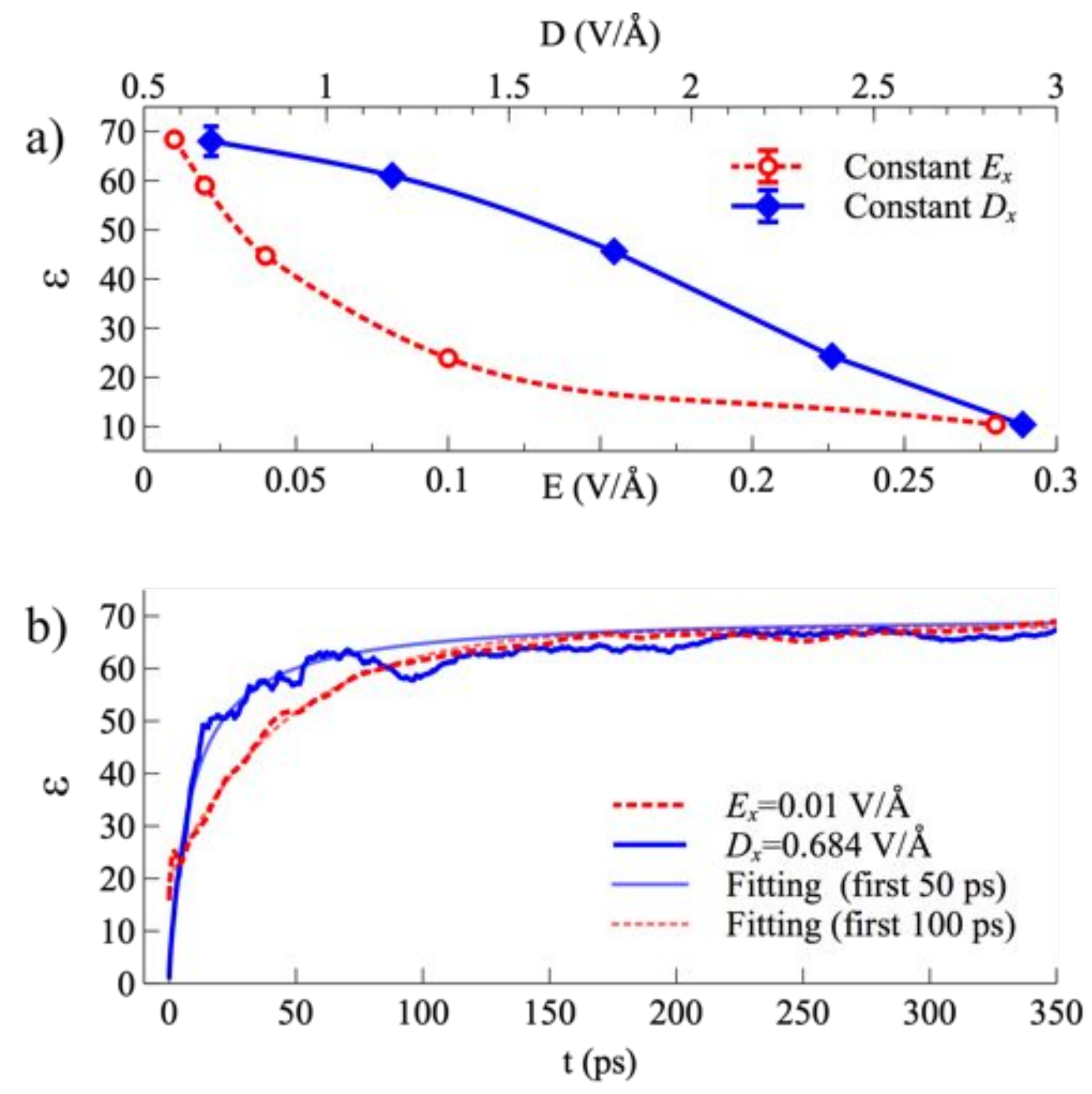

Figure 5: *a) The static dielectric constant ϵ at constant E_x and constant D_x; b) The accumulating average of ϵ at $E_x = 0.01$ V/Å and $D_x = 0.684$ V/Å.*

2. Computing the dielectric constant of the electric double layer (EDL) at electrified interface

2.1 Supercell modeling of electrolyte-electrified interface with a net total dipole

- We are interested in modeling EDL at electrolyte-oxide interface at high pH.
- Unlike our previous approach [3], the current setup contains two chemically inequivalent EDLs (net dipole).
- The charging of the EDL is therefore done at fixed chemical composition.
- The remaining field in the oxide leads to a pair of non-neutral EDLs.
- We tested the above idea with a classical toy model.

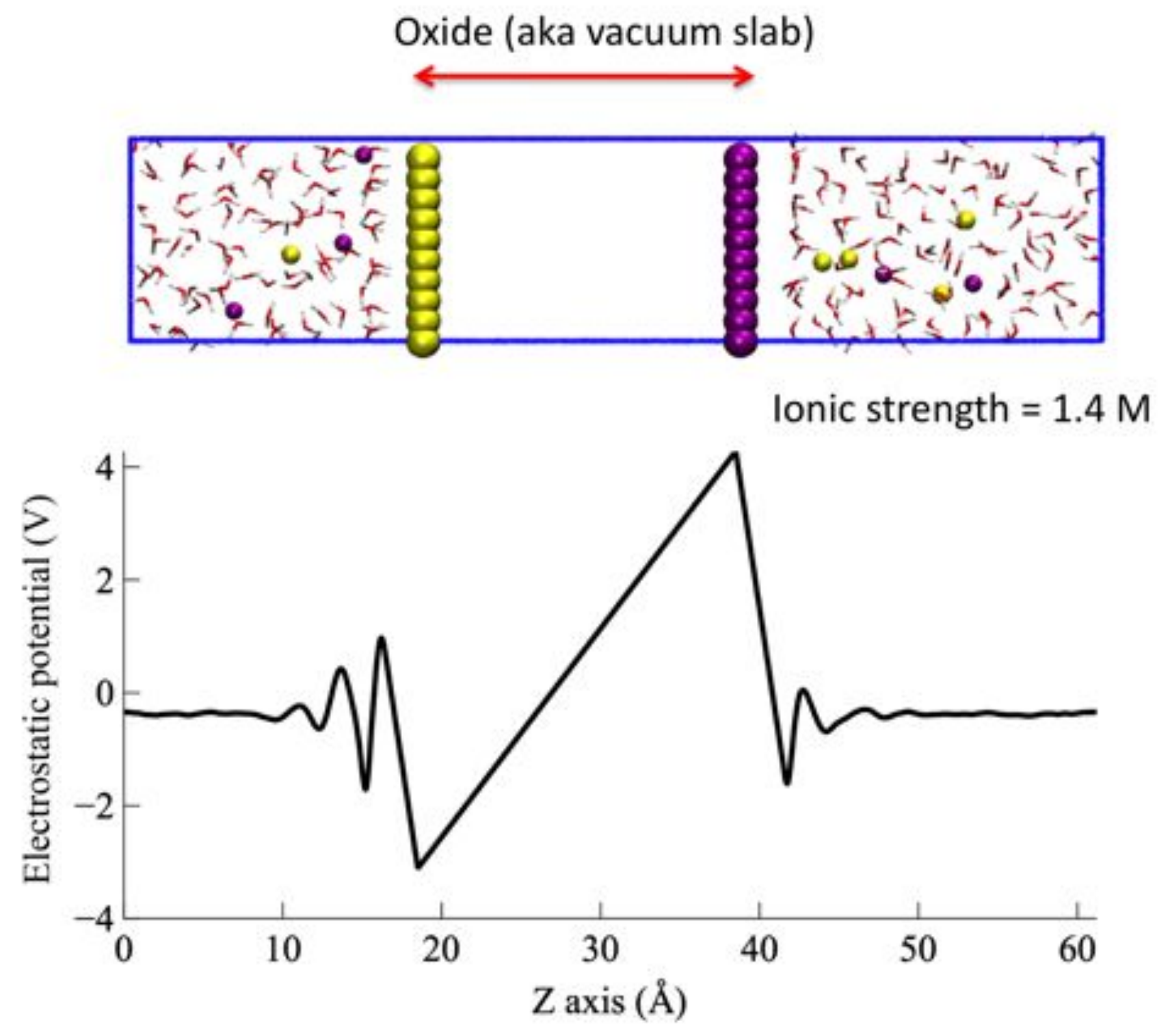

Figure 6: *The electrostatic potential of the classical electrolyte-electrified interface system with a net total dipole.*

2.2 Periodic EDL model

- We solved the Maxwell equations for the corresponding continuum EDL model under periodic boundary condition. The total energy is

$$U_{tot} = 2\pi A\sigma_0^2 l_{vac-slab} 2l_{EDL}/(l_{vac-slab}\epsilon_{EDL} + 2l_{EDL}) \qquad (4)$$

and the net charge of the EDL is

$$Q_{net} = (\sigma_0 - \sigma)A = \sigma_0 A 2l_{EDL}/(l_{vac-slab}\epsilon_{EDL} + 2l_{EDL}) \qquad (5)$$

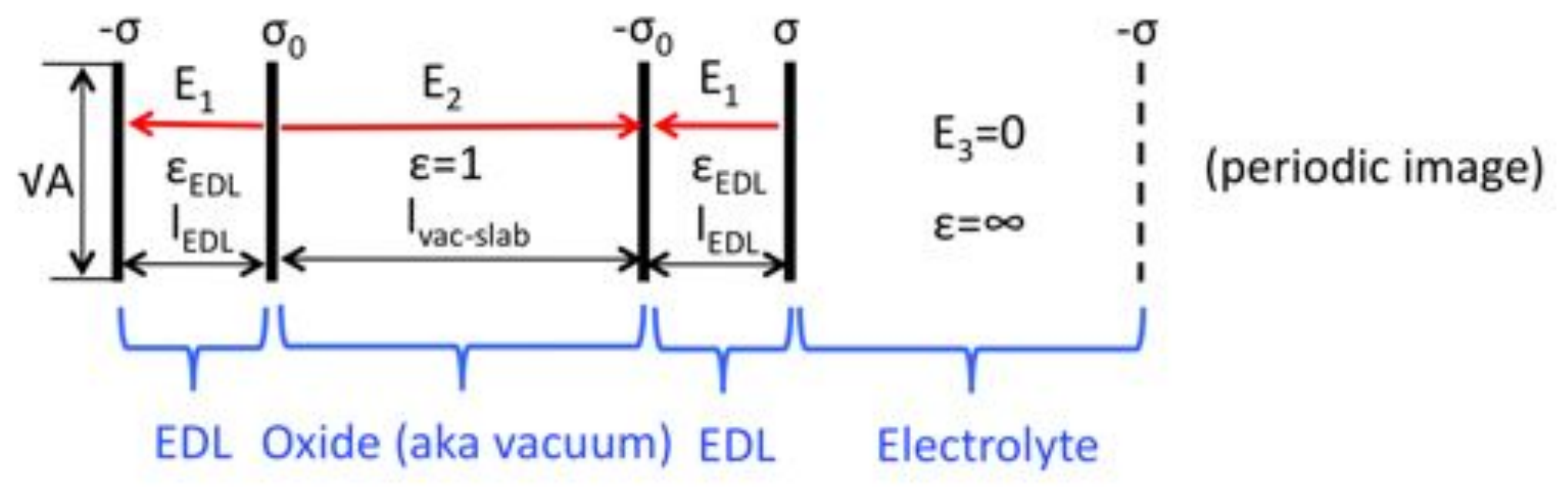

Figure 7: *The corresponding continuum EDL model with periodic boundary condition.*

2.3 Extracting the dielectric constant of EDL

- The dielectric constant of EDL can be extracted by fitting the continuum solution to the MD data.

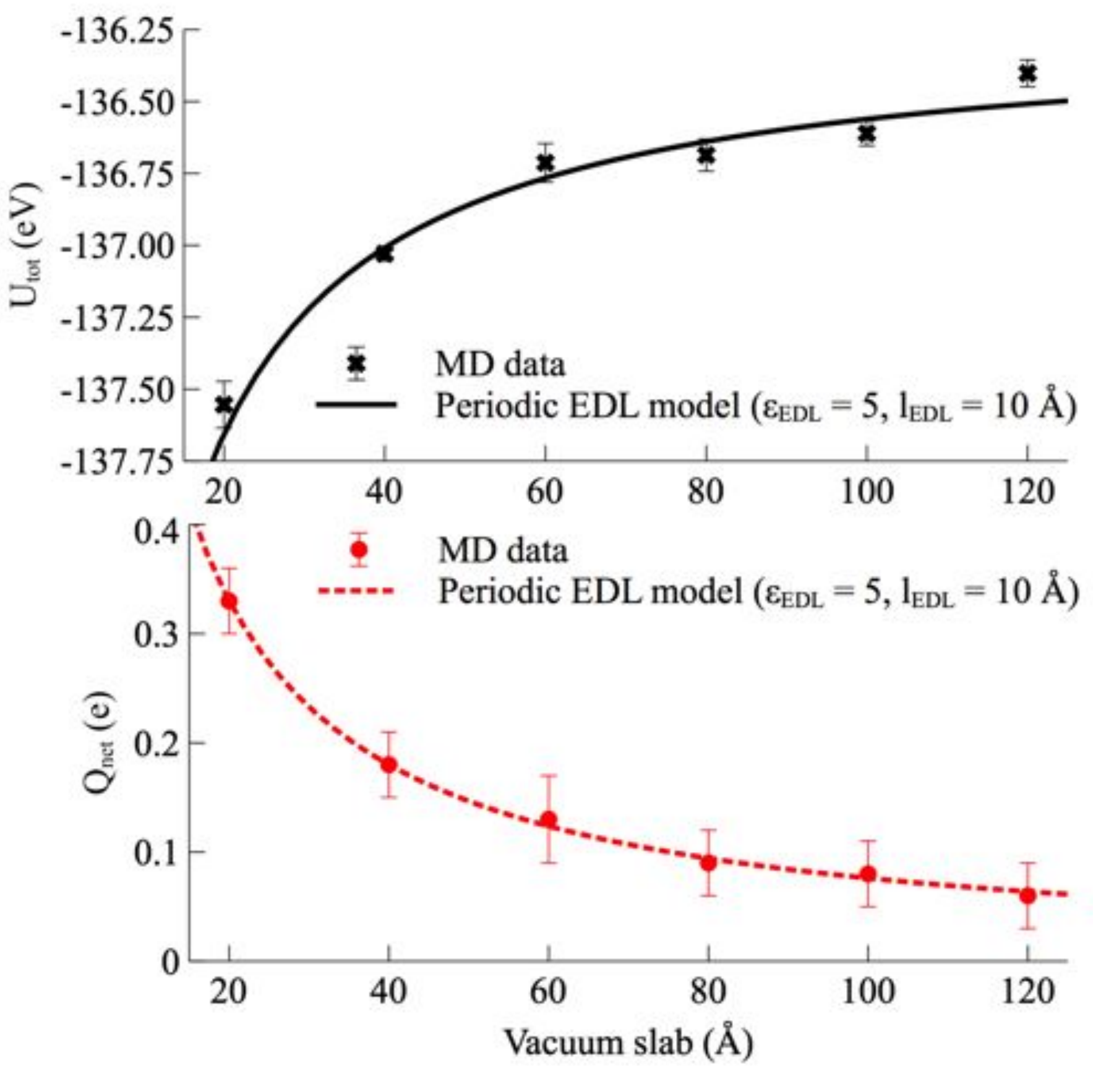

Figure 8: *The total potential energy and the net charge as functions of the the vacuum slab size.*

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References

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