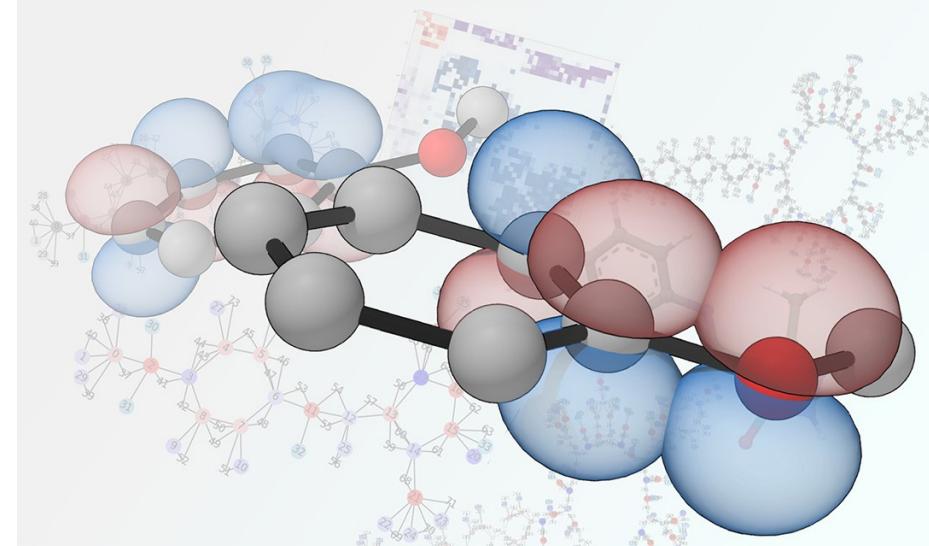


Aula 13 – Modelos de Solventes Contínuos

Ref: Artigos Citados

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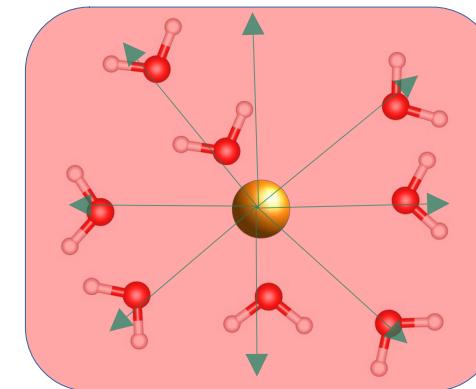
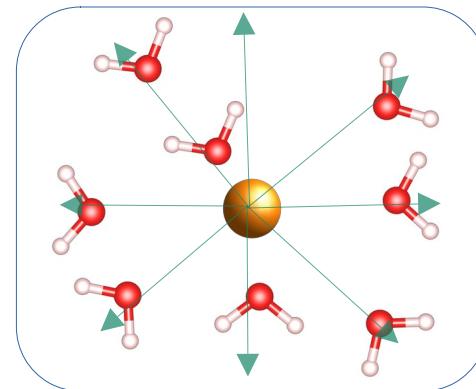
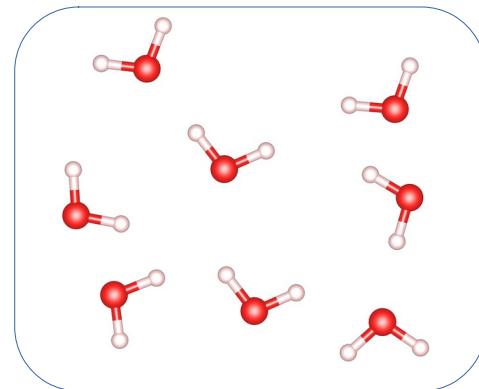


$$i\hbar \frac{\partial}{\partial t} |\Psi\rangle = \hat{H} |\Psi\rangle$$

$$|\Psi\rangle = |\psi\rangle e^{-iEt/\hbar}$$
$$\hat{H} |\psi\rangle = E |\psi\rangle$$

Polarização de um meio

Momento de dipólo por unidade de volume $P = \frac{dp}{dV}$



Polarização

$$\rho_t = \rho + \rho_{\text{pol}}$$

cargas ligadas - induzidas

Equações de Maxwell (meio)

$$\nabla \cdot D = 4\pi\rho$$

$$\nabla \times D = 0$$

Equações de Maxwell (vácuo)

$$\nabla \cdot E = 4\pi\rho_t$$

$$\nabla \times E = 0$$

Unidades gaussianas
 $4\pi\epsilon_0 = 1$

Campo Elétrico no meio

$$P = \epsilon_0 \chi E$$



$$D = E + P$$

$$\epsilon = (1 + \chi_e)$$

Suscetibilidade elétrica

Permissividade elétrica ou constante dielétrica

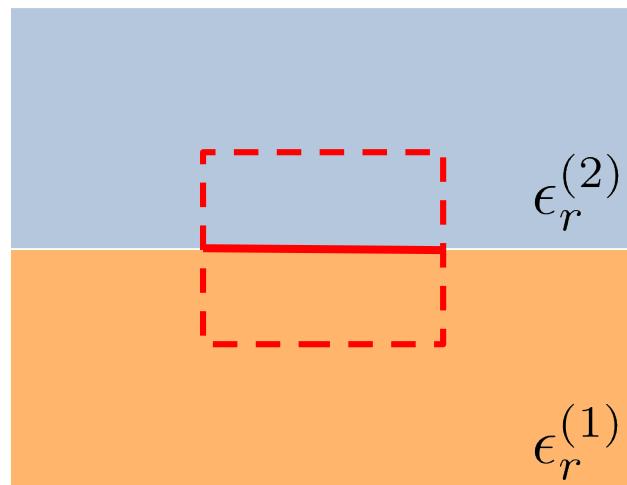
Potencial Eletrostático num meio dielétrico

$$D(\mathbf{r}) = \epsilon(\mathbf{r})E(\mathbf{r}) \rightarrow \nabla \cdot D = 4\pi\rho \rightarrow$$

$$E = -\nabla\phi \rightarrow$$

Potencial Eletrostático

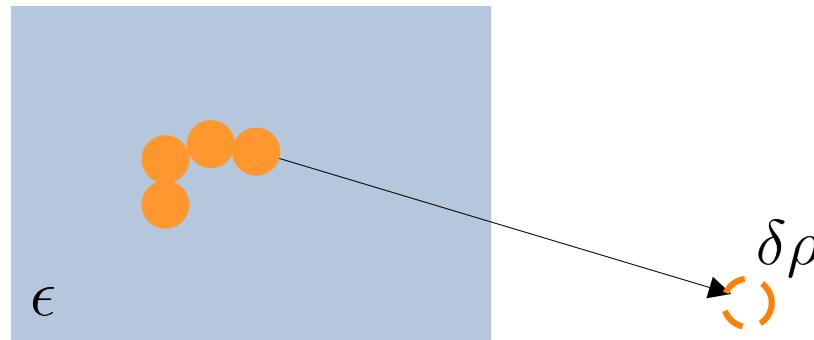
$$\nabla \cdot [\epsilon(\mathbf{r})\nabla\phi(\mathbf{r})] = -4\pi\rho$$



Condições de contorno

$$\left[\epsilon_r^{(1)} \nabla\phi_1 - \epsilon_r^{(2)} \nabla\phi_2 \right] \hat{\mathbf{n}} = 4\pi\sigma$$
$$\phi_2 - \phi_1 = 0$$

Energia de Interação Carga e Dielétrico



$$\delta W = \frac{1}{4\pi} \int_V \delta\rho(\mathbf{r}) \phi(\mathbf{r}) \, d\mathbf{r}$$



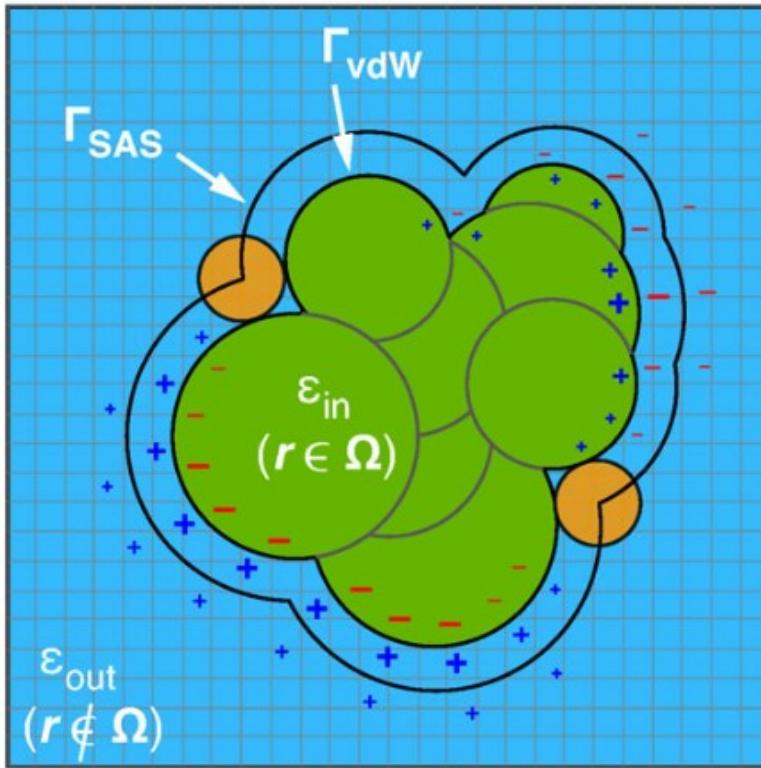
$$\delta W = \delta \left[\frac{1}{2} \frac{1}{4\pi} \int_V \mathbf{D} \cdot \mathbf{E} \, d\mathbf{r} \right]$$



Trabalho total feito para colocar cargas no dielétrico

$$W = \frac{1}{8\pi} \int_V \mathbf{D} \cdot \mathbf{E} \, d\mathbf{r}$$

Molécula em solvente



$$\nabla \cdot [\epsilon(\mathbf{r}) \nabla \phi(\mathbf{r})] = -4\pi\rho$$

reaction field

$$\phi(\mathbf{r}) = \phi^\rho(\mathbf{r}) + \phi_{rxn}(\mathbf{r})$$

$$\phi^\rho(\mathbf{r}) = \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}'$$

$$\mathcal{G}_{elst}[\epsilon(\mathbf{r}), \rho(\mathbf{r})] = \int \rho(\mathbf{r}) \phi_{rxn}(\mathbf{r}) d\mathbf{r}$$

Energia total

$$\begin{aligned}\mathcal{G}_0[\Psi] &= \langle \Psi | \hat{H}_{vac} | \Psi \rangle + \mathcal{G}_{elst} \\ &= \langle \Psi | \hat{H}_{vac} + \frac{1}{2} \mathcal{R}_0 | \Psi \rangle\end{aligned}$$