Electrostatics interaction energies under the presence of dipoles and charges with a reaction field

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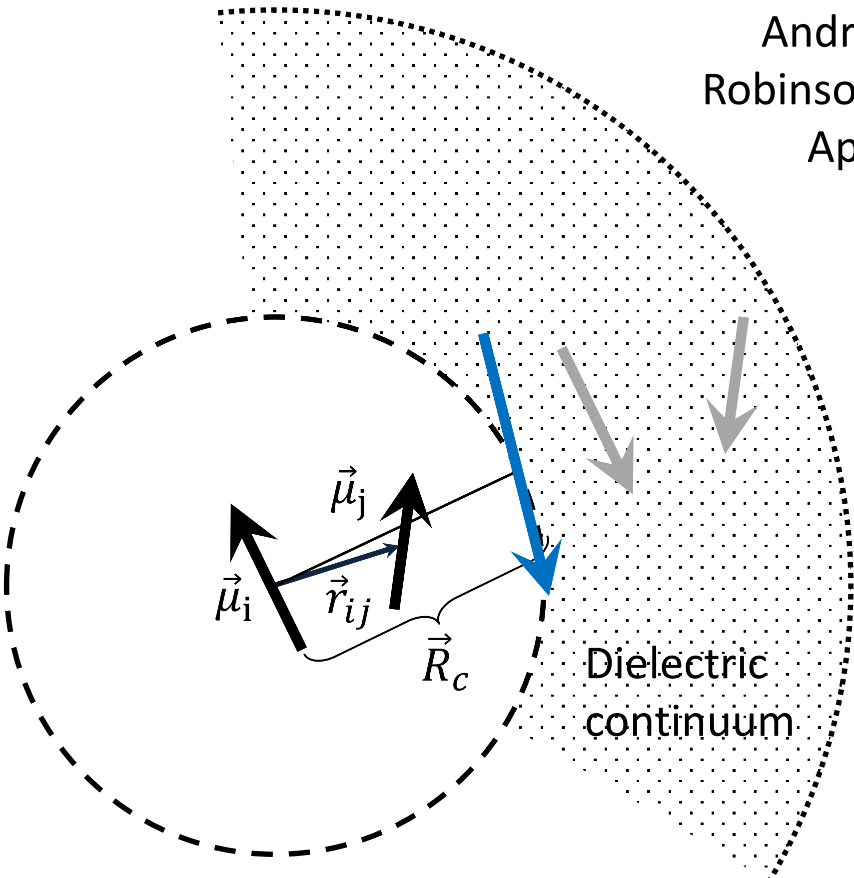
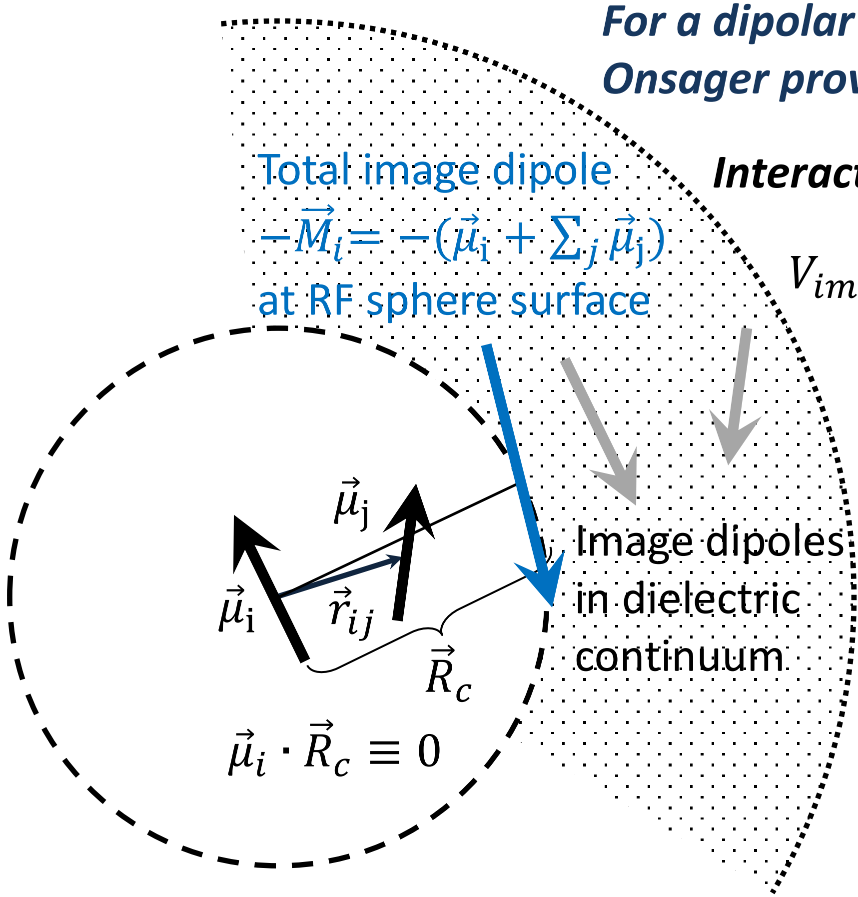


Dipole-dipole interaction with reaction field

$$k = \frac{1}{4\pi\varepsilon_0 n^2}$$
$$\kappa = \frac{2(\varepsilon_{RF} - n^2)}{2\varepsilon_{RF} + n^2}$$

For a dipolar field leaving the reaction sphere
Onsager provides the reaction field ...



Interaction with total image dipole:

$$V_{image} = -k\kappa \frac{\vec{\mu}_\mathrm{i} \cdot \left(\vec{M}_i - 3\left(\vec{M}_\mathrm{i} \cdot \hat{R}_c\right) \cdot \hat{R}_c\right)}{R_c^3} = -k\kappa \frac{\vec{\mu}_\mathrm{i} \cdot \vec{M}_i}{R_c^3}$$

Reaction field potential energy:

$$\Rightarrow V_{RF} = V_{image} = -k \frac{2(\varepsilon_{RF} - n^2)}{2\varepsilon_{RF} + n^2} \frac{\vec{\mu}_\mathrm{i} \cdot \vec{M}_i}{R_c^3}$$

Pair-wise interaction potential energy:

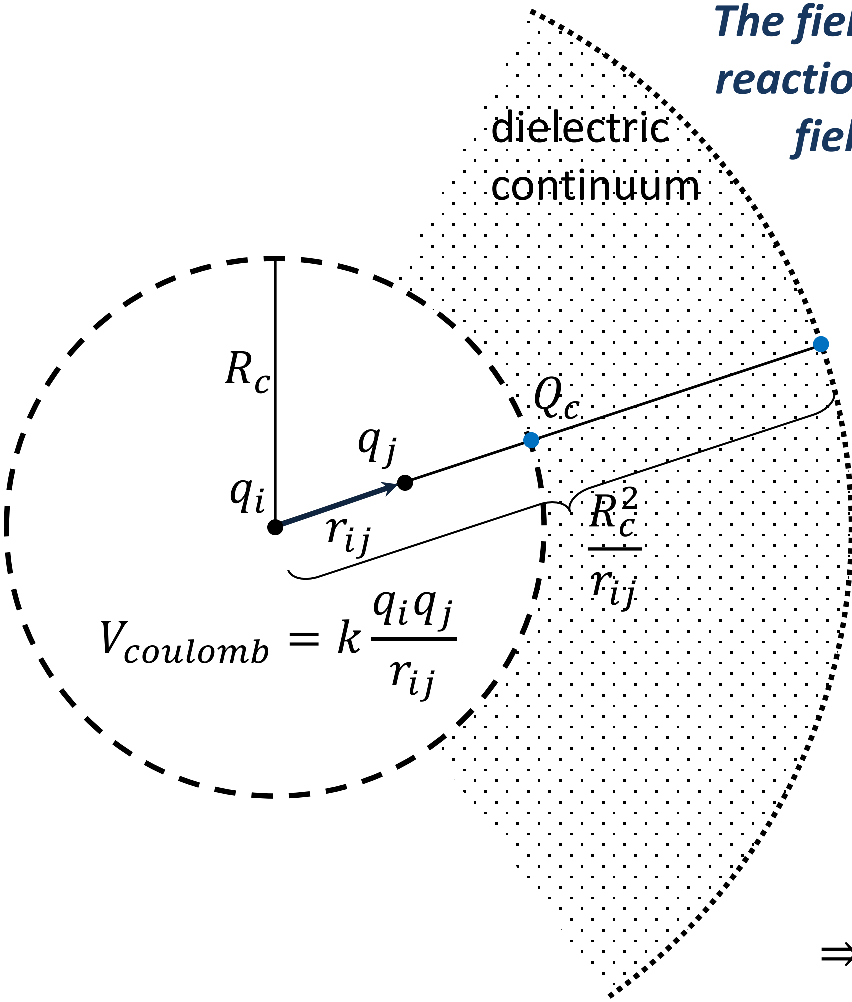
$$V_{ij}^{\mu\mu} = k \frac{\vec{\mu}_\mathrm{i} \cdot (\vec{\mu}_\mathrm{j} - 3(\vec{\mu}_\mathrm{j} \cdot \hat{r}_{ij}) \cdot \hat{r}_{ij})}{r_{ij}^3}$$

Note: *The self-term μ_i^2 can be omitted in MC type calculations b/c it will always stay constant for each point dipole (if it would change don't omit it)*

Overall potential energy with RF contribution:

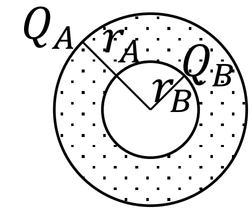
$$\mathrm{V_i} = \sum_j V_{ij}^{\mu\mu} - \frac{1}{4\pi\varepsilon_0 n^2} \frac{2(\varepsilon_{RF} - n^2)}{2\varepsilon_{RF} + n^2} \frac{\mu_i^2 + \vec{\mu}_\mathrm{i} \cdot \sum_j \vec{\mu}_\mathrm{j}}{R_c^3}$$

Charge-charge interaction with reaction field



The field leaving a neutral reaction sphere in the far-field will be dipolar …

Gauss's law:



$$\frac{Q_A}{Q_B} = \frac{r_A^3}{r_B^3} \Longrightarrow Q_B = Q_A\frac{r_B^3}{r_A^3}$$

Image charge:

$$-\frac{R_c}{r_{ij}}q_j$$

Gauss's law applied to image charge:

$$Q_C = -\frac{R_c}{r_{ij}}q_j\frac{R_c^3}{\left(\frac{R_c^2}{r_{ij}}\right)^3} = -q_j\frac{r_{ij}^2}{R_c^2}$$

$$\Rightarrow V_{image} = k\kappa\frac{q_i Q_c}{R_c} = -k\kappa q_i q_j\frac{r_{ij}^2}{R_c^3}$$

Reaction field potential energy:

$$\Rightarrow V_{RF} = -\frac{1}{2}V_{image} = k\frac{\varepsilon_{RF} - n^2}{2\varepsilon_{RF} + n^2}q_i q_j\frac{r_{ij}^2}{R_c^3}$$

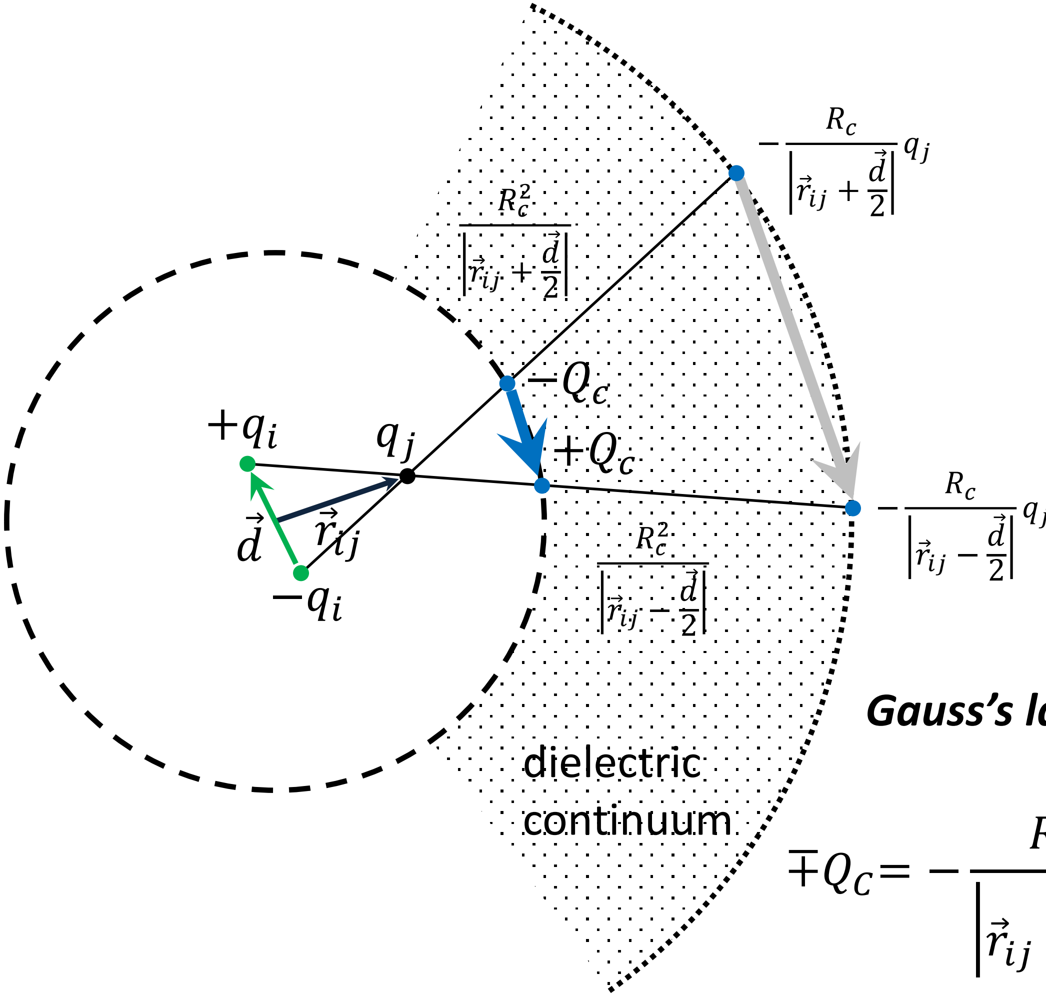
Pair-wise potential energy with RF contribution:

$$\Longrightarrow \mathrm{V_{ij}} = \frac{q_i q_j}{4\pi\varepsilon_0 n^2}\left(\frac{1}{r_{ij}} + \frac{\varepsilon_{RF} - n^2}{2\varepsilon_{RF} + n^2}\frac{r_{ij}^2}{R_c^3}\right)$$

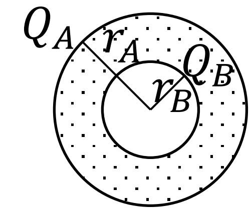
$$k = \frac{1}{4\pi\varepsilon_0 n^2}$$

$$\kappa = \frac{2(\varepsilon_{RF} - n^2)}{2\varepsilon_{RF} + n^2}$$

Dipole-charge image charge energy derivation



Gauss's law:



$$\frac{Q_A}{Q_B}=\frac{r_A^3}{r_B^3}\Longrightarrow Q_B=Q_A\frac{r_B^3}{r_A^3}$$

$$k=\frac{1}{4\pi\varepsilon_0 n^2}$$

$$\kappa=\frac{2(\varepsilon_{RF}-n^2)}{2\varepsilon_{RF}+n^2}$$

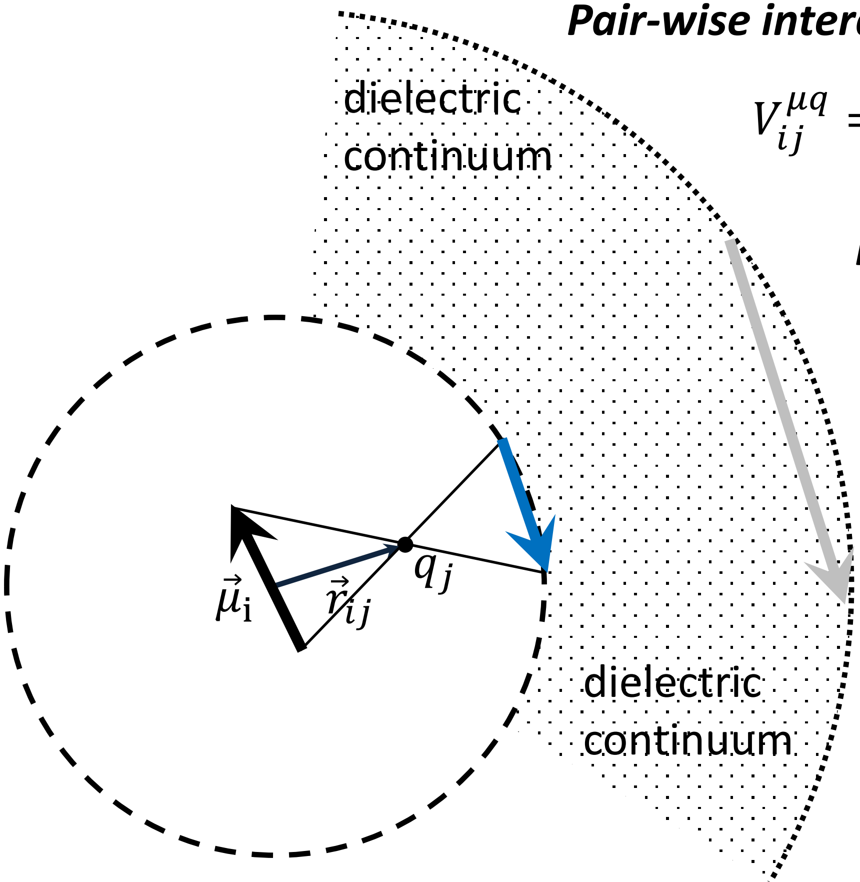
Gauss's law applied to image charges:

$$\mp Q_C=-\frac{R_c}{\left|\vec{r}_{ij}\pm\frac{\vec{d}}{2}\right|}q_j\frac{R_c^3}{\left(\frac{R_c^2}{\left|\vec{r}_{ij}\pm\frac{\vec{d}}{2}\right|}\right)^3}=-q_j\frac{\left|\vec{r}_{ij}\pm\frac{\vec{d}}{2}\right|^2}{R_c^2}$$

Image charge energy:

$$\Rightarrow V_{Image}=k\kappa\frac{q_iq_j}{R_c^3}\left(\left|\vec{r}_{ij}+\frac{\vec{d}}{2}\right|^2-\left|\vec{r}_{ij}-\frac{\vec{d}}{2}\right|^2\right)=k\kappa\frac{2q_iq_j\vec{r}_{ij}\cdot\vec{d}}{R_c^3}=k\kappa\frac{2q_j\vec{r}_{ij}\cdot\vec{\mu}_i}{R_c^3}$$

Dipole-charge interaction with reaction field



Pair-wise interaction energy:

$$V_{ij}^{\mu q} = k\frac{q_j\vec{r}_{ij}\cdot\vec{\mu}_\mathrm{i}}{r_{ij}^3}$$

Image charge interaction energy:

$$V_{image} = k\kappa\frac{2q_j\vec{r}_{ij}\cdot\vec{\mu}_\mathrm{i}}{R_c^3}$$

Reaction field potential energy:

$$\Rightarrow V_{RF} = -\frac{1}{2}V_{image} = -k\kappa\frac{q_j\vec{r}_{ij}\cdot\vec{\mu}_\mathrm{i}}{R_c^3}$$

Note:
For simplicity the self-term $\vec{\mu}_\mathrm{i}\cdot\vec{\mu}_\mathrm{i}$ is omitted, but but one needs to include it somewhere (here, it is included in V_i of the dipole-dipole interaction)

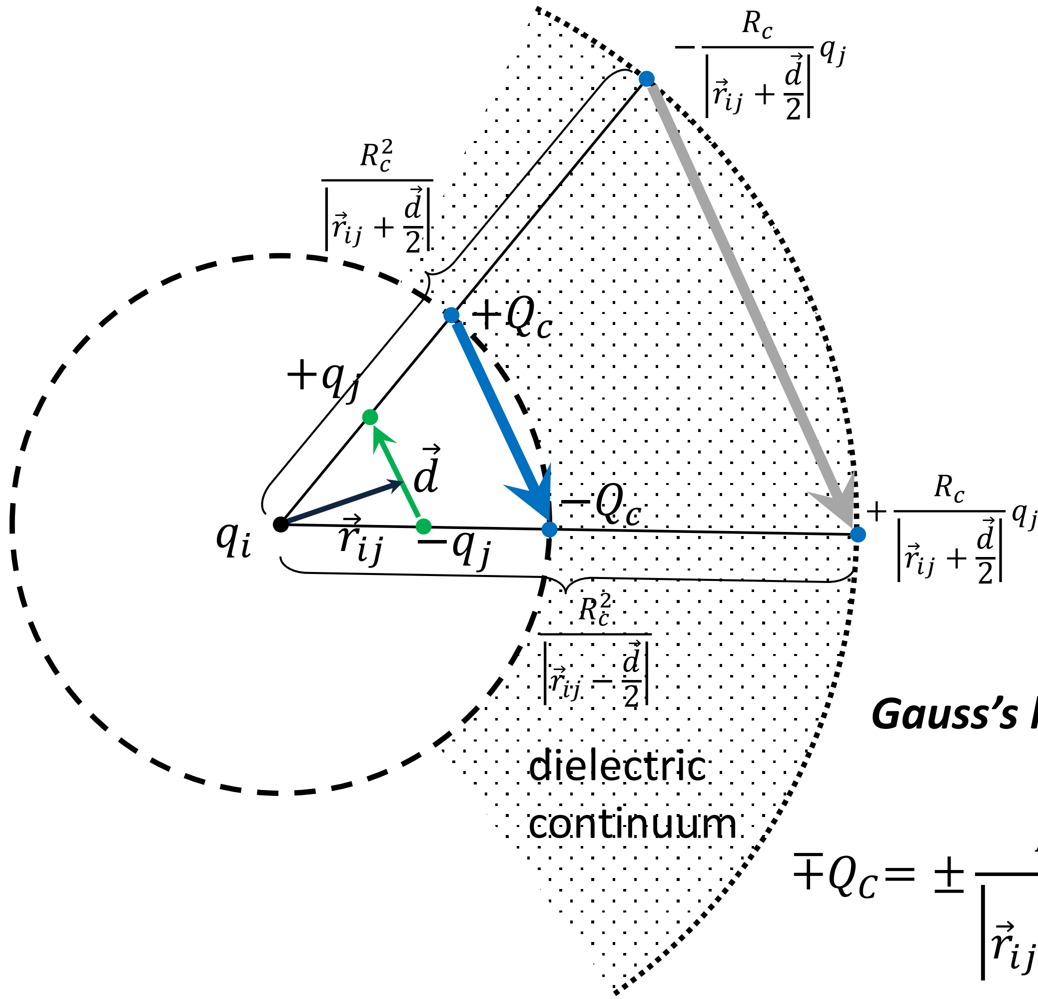
Pair-wise potential energy with RF contribution:

$$\Longrightarrow \mathrm{V_{ij}} = \frac{q_j\vec{r}_{ij}\cdot\vec{\mu}_\mathrm{i}}{4\pi\varepsilon_0 n^2}\left(\frac{1}{r_{ij}^3} - \frac{2(\varepsilon_{RF}-n^2)}{2\varepsilon_{RF}+n^2}\frac{1}{R_c^3}\right)$$

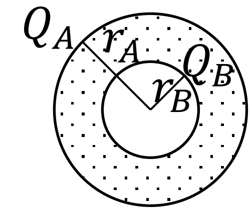
$$k = \frac{1}{4\pi\varepsilon_0 n^2}$$

$$\kappa = \frac{2(\varepsilon_{RF}-n^2)}{2\varepsilon_{RF}+n^2}$$

Charge-dipole image charge energy derivation



Gauss's law:



$$\frac{Q_A}{Q_B}=\frac{r_A^3}{r_B^3}\Longrightarrow Q_B=Q_A\frac{r_B^3}{r_A^3}$$

$$k=\frac{1}{4\pi\varepsilon_0 n^2}$$

$$\kappa=\frac{2(\varepsilon_{RF}-n^2)}{2\varepsilon_{RF}+n^2}$$

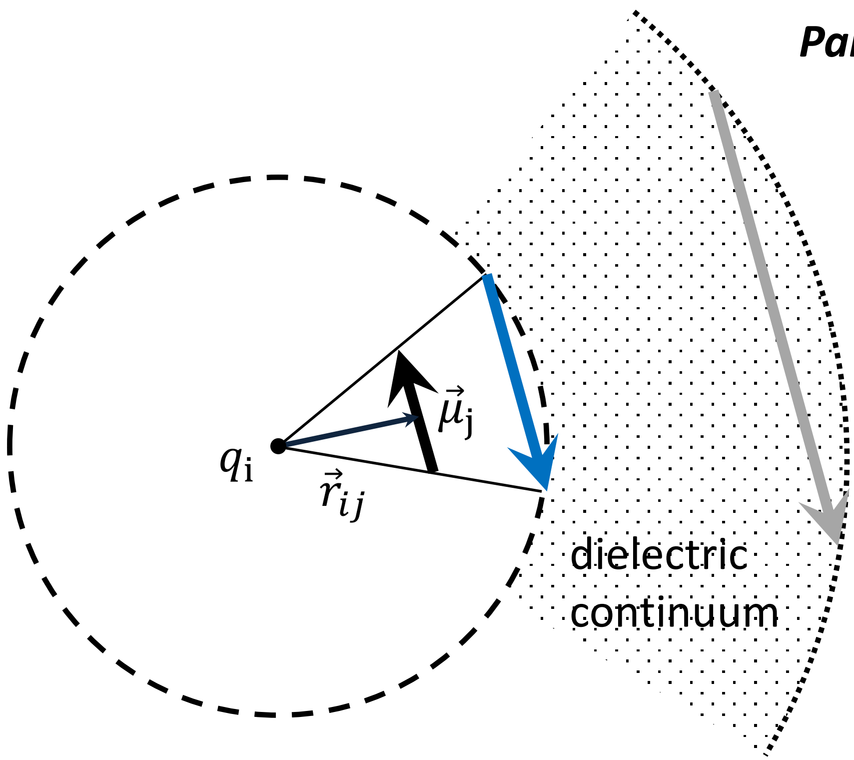
Gauss's law applied to image charges:

$$\mp Q_C=\pm\frac{R_c}{\left|\vec{r}_{ij}\pm\frac{\vec{d}}{2}\right|}q_j\frac{R_c^3}{\left(\frac{R_c^2}{\left|\vec{r}_{ij}\pm\frac{\vec{d}}{2}\right|}\right)^3}=\pm q_j\frac{\left|\vec{r}_{ij}\pm\frac{\vec{d}}{2}\right|^2}{R_c^2}$$

Image charge energy:

$$\Rightarrow V_{Image}=-k\kappa\frac{q_i q_j}{R_c^3}\left(\left|\vec{r}_{ij}+\frac{\vec{d}}{2}\right|^2-\left|\vec{r}_{ij}-\frac{\vec{d}}{2}\right|^2\right)=-k\kappa\frac{2q_i q_j\vec{r}_{ij}\cdot\vec{d}}{R_c^3}=-k\kappa\frac{2q_i\vec{r}_{ij}\cdot\vec{\mu}_j}{R_c^3}$$

Charge-dipole interaction with reaction field



Pair-wise interaction energy:

$$V_{ij}^{q\mu} = -k\,\frac{q_i \vec{r}_{ij} \cdot \vec{\mu}_{\mathrm{j}}}{r_{ij}^3}$$

Interaction with image dipole:

$$V_{image} = -k\kappa\,\frac{2 q_i \vec{r}_{ij} \cdot \vec{\mu}_{\mathrm{j}}}{R_c^3}$$

Reaction field potential energy:

$$V_{RF} = -\frac{1}{2} V_{image} = k\kappa\,\frac{q_i \vec{r}_{ij} \cdot \vec{\mu}_{\mathrm{j}}}{R_c^3}$$

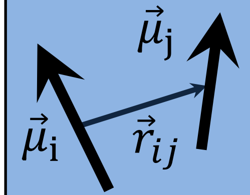
Pair-wise potential energy with RF contribution:

$$\Longrightarrow \mathrm{V_{ij}} = -\frac{q_i \vec{r}_{ij} \cdot \vec{\mu}_{\mathrm{j}}}{4\pi\varepsilon_0 n^2}\left(\frac{1}{r_{ij}^3} - \frac{2(\varepsilon_{RF} - n^2)}{2\varepsilon_{RF} + n^2}\frac{1}{R_c^3}\right)$$

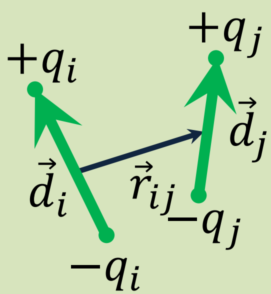
$$k = \frac{1}{4\pi\varepsilon_0 n^2}$$

$$\kappa = \frac{2(\varepsilon_{RF} - n^2)}{2\varepsilon_{RF} + n^2}$$

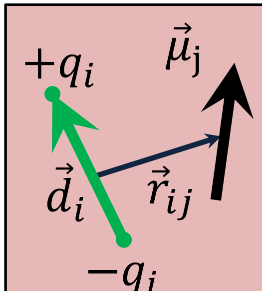
Overall reaction field energies in the dipole limit



$$V_{RF} \propto -2\vec{\mu}_i(\vec{\mu}_i + \vec{\mu}_j) - 2\vec{\mu}_j(\vec{\mu}_i + \vec{\mu}_j) = \boldsymbol{-2\{\mu_i^2 + \mu_j^2 + 2\vec{\mu}_i\vec{\mu}_j\}}$$



$$V_{RF} \propto 2q_iq_j(-\vec{\imath} + \vec{r}_{ij} + \vec{\jmath})^2 - 2q_iq_j(-\vec{\imath} + \vec{r}_{ij} - \vec{\jmath})^2 - 2q_iq_j(\vec{\imath} + \vec{r}_{ij} + \vec{\jmath})^2$$
$$+2q_iq_j(\vec{\imath} + \vec{r}_{ij} - \vec{\jmath})^2 - 2q_i^2d_i^2 - 2q_j^2d_j^2$$
$$= 2q_iq_j\{\cancel{r_{ij}^2} + (-\vec{\imath} + \vec{\jmath})^2 + \cancel{2\vec{r}_{ij}(-\vec{\imath} + \vec{\jmath})} - \cancel{r_{ij}^2} - (-\vec{\imath} - \vec{\jmath})^2 - \cancel{2\vec{r}_{ij}(-\vec{\imath} - \vec{\jmath})}$$
$$- \cancel{r_{ij}^2} - (\vec{\imath} + \vec{\jmath})^2 - \cancel{2\vec{r}_{ij}(\vec{\imath} + \vec{\jmath})} + \cancel{r_{ij}^2} + (\vec{\imath} - \vec{\jmath})^2 + \cancel{2\vec{r}_{ij}(\vec{\imath} - \vec{\jmath})}\}$$
$$- 2\mu_i^2 - 2\mu_j^2$$
$$= -2q_iq_j\{2(\vec{\imath} + \vec{\jmath})^2 - 2(\vec{\imath} - \vec{\jmath})^2\} - 2\mu_i^2 - 2\mu_j^2$$
$$= -2\{\mu_i^2 + \mu_j^2 + q_iq_j(4\vec{\imath}\cdot\vec{\jmath} - 2(-2\vec{\imath}\cdot\vec{\jmath}))\} = -2\{\mu_i^2 + \mu_j^2 + 2q_iq_j\vec{d}_i\vec{d}_j\}$$
$$= \boldsymbol{-2\{\mu_i^2 + \mu_j^2 + 2\vec{\mu}_i\vec{\mu}_j\}}$$



$$V_{RF} \propto 2q_i(-\vec{\imath} + \cancel{\vec{r}_{ij}})\vec{\mu}_j - 2q_i(\vec{\imath} + \cancel{\vec{r}_{ij}})\vec{\mu}_j - 2\mu_j^2 - 2q_i^2d_i^2 - 2q_i(\cancel{-\vec{r}_{ij}} + \vec{\imath})\vec{\mu}_j$$
$$+ 2q_i(\cancel{-\vec{r}_{ij}} - \vec{\imath})\vec{\mu}_j$$
$$= -2\mu_i^2 - 2\mu_j^2 + 2q_i\vec{\mu}_j(-4\vec{\imath}) = -2\{\mu_i^2 + \mu_j^2 + 2q_i\vec{\mu}_j\vec{d}_i\}$$
$$= \boldsymbol{-2\{\mu_i^2 + \mu_j^2 + 2\vec{\mu}_i\vec{\mu}_j\}}$$

Proportionality constant in all cases is: $\frac{k\kappa}{2R_c^3}$

Self-consistency with Onsager in the dipole limit …

$\vec{\imath} = \frac{\vec{d}_i}{2}$; $\vec{\jmath} = \frac{\vec{d}_j}{2}$

Non-neutral reaction sphere with charge $\sigma = q_i + \sum_j q_j \neq 0$

- *for neutral molecules (neutral charge group) easiest solution is to include whole molecule (which is implemented in this case)*
- *for ions (charge groups with residual charge) one could either find the counterion and include it **explicitly** (expensive to find and may not always be close by) or,*
- *because the whole simulation volume is neutral and hence counter charges to residual charge σ of reaction sphere **do exist** outside the sphere, one can include them **implicitly** by placing the counter charge -σ at the reaction sphere boundary (from within b/c in the explicit solution these charges would also simply be included)*

Correction term for reaction sphere with q_i ***at center:***

$$V_{i\sigma} = -\frac{q_i \sigma}{4\pi\varepsilon_0 n^2}\left(\frac{1}{R_c} + \frac{\varepsilon_{RF} - n^2}{2\varepsilon_{RF} + n^2}\frac{R_c^2}{R_c^3}\right) = -\frac{q_i}{4\pi\varepsilon_0 n^2}\frac{1}{R_c}\left(1 + \frac{\varepsilon_{RF} - n^2}{2\varepsilon_{RF} + n^2}\right)\left(q_i + \sum_j q_j\right)$$

Note: *Since the counter charge is spread over the entire reaction sphere surface it will not have an effect on dipoles at the center and only needs to be applied to a charge at the center of the reaction field.*

Correction term for whole reaction sphere with q_i ***at center:***

$$\boxed{\Longrightarrow V_{i\sigma} = -\frac{q_i\left(q_i + \sum_j q_j\right)}{4\pi\varepsilon_0 n^2}\frac{1}{R_c}\left(1 + \frac{\varepsilon_{RF} - n^2}{2\varepsilon_{RF} + n^2}\right)}$$