charge-charge, charge-dipole, dipole-charge, dipole-dipole interaction

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In the bulk and at the interface of polar solvents and/or ionic liquids, molecules feel the strong electric field and this strong field distort the electron cloud of molecule and induces dipole around atoms. To consider this polarization effect we should consider charge-charge, charge-dipole, dipole-charge, dipole-dipole interaction.

I. CHARGE-CHARGE (C-C) INTERACTION

The coulomb potential ϕ from the point charge $z_i e$ at $\mathbf{r}_i$ is given by

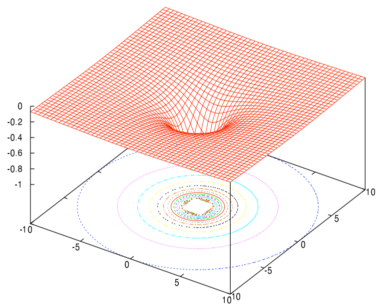


FIG. 1: Coulomb potential of negative charge

$$\phi_{\rm C}(|\mathbf{r}-\mathbf{r}_i|) = \frac{z_i e}{4\pi\epsilon_0}\frac{1}{|\mathbf{r}-\mathbf{r}_i|} \tag{1}$$

The electric field is given by the gradient of the potential

$$\mathbf{E}^i_{\rm C}(\mathbf{r}) \;=\; -\nabla\phi_{\rm C}(|\mathbf{r}-\mathbf{r}_i|) = \frac{z_i e}{4\pi\epsilon_0}\frac{\mathbf{r}-\mathbf{r}_i}{|\mathbf{r}-\mathbf{r}_i|^3} \tag{2}$$

If we put the other point charge $z_j e$ at at $\mathbf{r}_j$ the electrostatic energy $V_{\rm cc}$ is given by

$$V_{\rm cc} \;=\; z_j e\phi_{\rm C}(|\mathbf{r}_j-\mathbf{r}_i|) = \frac{z_i z_j e^2}{4\pi\epsilon_0}\frac{1}{|\mathbf{r}_i-\mathbf{r}_j|} \tag{3}$$

II. CHARGE-DIPOLE (C-D) INTERACTION

In this interaction we consider two cases, i.e. (I) the coulomb potential interact with dipole $\vec{\mu}_j = ez_j\mathbf{p}_j$ and (II) dipole field interact with point charge.

In the case of (I), the C-D interaction becomes

$$V_{\rm cd} \;=\; \frac{z_i(-z_j)e^2}{4\pi\epsilon_0}\frac{1}{|\mathbf{r}_j-\mathbf{r}_i|} + \frac{z_i z_j e^2}{4\pi\epsilon_0}\frac{1}{|\mathbf{r}_j+\mathbf{p}_j-\mathbf{r}_i|} \tag{4}$$

$$\mathbf{r}_j-\mathbf{r}_i \;\equiv\; \mathbf{r}_{ji}, \quad |\mathbf{r}_{ji}| = r_{ji}, \quad (1+x)^{-1/2} \simeq 1 - x/2 + 3x^2/8... \tag{5}$$

$$V_{\rm cd} \;=\; -\frac{z_i z_j e^2}{4\pi\epsilon_0}\left(\frac{1}{r_{ji}} - \frac{1}{\sqrt{r_{ji}^2+2\mathbf{r}_{ji}\cdot\mathbf{p}_j+p_j^2}}\right) = -\frac{z_i z_j e^2}{4\pi\epsilon_0 r_{ji}}\left[1-\frac{1}{(1+2\mathbf{r}_{ji}\cdot\mathbf{p}_j/r_{ji}^2+\mathbf{p}_j^2/r_{ji}^2)^{1/2}}\right]$$

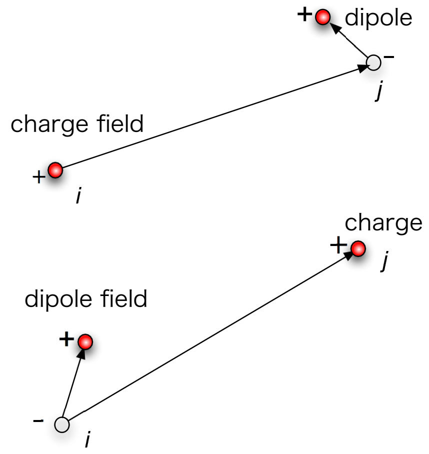


FIG. 2: charge-dipole(C-D) and dipole-charge(D-C) interaction

$$\simeq -\frac{z_i z_j e^2}{4\pi\epsilon_0 r_{ji}}\left[1-1+\frac{1}{2}\frac{2\mathbf{r}_{ji}\cdot\mathbf{p}_j}{r_{ji}^2}+\frac{1}{2}\frac{\mathbf{p}_j^2}{r_{ji}^2}-\frac{3}{8}(2\mathbf{r}_{ji}\cdot\mathbf{p}_j/r_{ji}^2+\mathbf{p}_j^2/r_{ji}^2)^2\right] \quad (6)$$

if we assume $r_{ji} >> p_j$

$$V_{\rm cd} = -\frac{z_i z_j e^2}{4\pi\epsilon_0}\frac{\mathbf{r}_{ji}\cdot\mathbf{p}_j}{r_{ji}^3} = \frac{z_i z_j e^2}{4\pi\epsilon_0}\frac{\mathbf{r}_{ij}\cdot\mathbf{p}_j}{r_{ij}^3} = \frac{z_i e}{4\pi\epsilon_0}\frac{\mathbf{r}_{ij}\cdot\vec{\mu}_j}{r_{ij}^3}, \quad \vec{\mu}_j \equiv z_j e\mathbf{p}_j \quad (7)$$

In the ordinary method the potential is given by $-\vec{\mu}\cdot\mathbf{E}_{\rm C}$

$$\mathbf{E}_{\rm C}^i(\mathbf{r}) = -\nabla\phi_{\rm C}(|\mathbf{r}-\mathbf{r}_i|) = \frac{z_i e}{4\pi\epsilon_0}\frac{\mathbf{r}-\mathbf{r}_i}{|\mathbf{r}-\mathbf{r}_i|^3} \quad (8)$$

$$V_{\rm cd} = -\vec{\mu}_j\cdot\mathbf{E}_{\rm C}^i(\mathbf{r}_j) = -\frac{z_i e}{4\pi\epsilon_0}\frac{\mathbf{r}_{ji}\cdot\vec{\mu}_j}{r_{ji}^3} = \frac{z_i e}{4\pi\epsilon_0}\frac{\mathbf{r}_{ij}\cdot\vec{\mu}_j}{r_{ij}^3} \quad (9)$$

which gives the same results.

In the case of (II), the D-C interaction becomes

$$V_{\rm dc} = \frac{(-z_i)z_j e^2}{4\pi\epsilon_0}\frac{1}{|\mathbf{r}_j-\mathbf{r}_i|}+\frac{z_i z_j e^2}{4\pi\epsilon_0}\frac{1}{|\mathbf{r}_j-\mathbf{r}_i-\mathbf{p}_i|} \quad (10)$$

$$= -\frac{z_i z_j e^2}{4\pi\epsilon_0}\left(\frac{1}{r_{ji}}-\frac{1}{\sqrt{r_{ji}^2-2\mathbf{r}_{ji}\cdot\mathbf{p}_i+\mathbf{p}_i^2}}\right) = -\frac{z_i z_j e^2}{4\pi\epsilon_0 r_{ji}}\left[1-\frac{1}{(1-2\mathbf{r}_{ji}\cdot\mathbf{p}_i/r_{ji}^2+\mathbf{p}_i^2/r_{ji}^2)^{1/2}}\right]$$

$$\simeq -\frac{z_i z_j e^2}{4\pi\epsilon_0 r_{ji}}\left[1-1+\frac{1}{2}\frac{-2\mathbf{r}_{ji}\cdot\mathbf{p}_i}{r_{ji}^2}+\frac{1}{2}\frac{\mathbf{p}_i^2}{r_{ji}^2}-\frac{3}{8}(-2\mathbf{r}_{ji}\cdot\mathbf{p}_i/r_{ji}^2+\mathbf{p}_i^2/r_{ji}^2)^2\right]. \quad \text{if we assume} \quad r_{ji} >> p_j$$

$$= \frac{z_i z_j e^2}{4\pi\epsilon_0}\frac{\mathbf{r}_{ji}\cdot\mathbf{p}_i}{r_{ji}^3} = -\frac{z_i z_j e^2}{4\pi\epsilon_0}\frac{\mathbf{p}_i\cdot\mathbf{r}_{ij}}{r_{ij}^3} = -\frac{1}{4\pi\epsilon_0}\frac{\vec{\mu}_i\cdot\mathbf{r}_{ij}z_j e}{r_{ij}^3}, \quad \vec{\mu}_i \equiv z_i e\mathbf{p}_i \quad (11)$$

Please note that C-D and D-C interaction the sign is different. Since the interaction energy is given by $z_j e\phi(|\mathbf{r}_j-\mathbf{r}_i|)$, the dipoler field is given by

$$\phi_{\rm D}(\mathbf{r}-\mathbf{r}_i) = \frac{1}{4\pi\epsilon_0}\frac{\vec{\mu}_i\cdot(\mathbf{r}-\mathbf{r}_i)}{|\mathbf{r}-\mathbf{r}_i|^3} \quad (12)$$

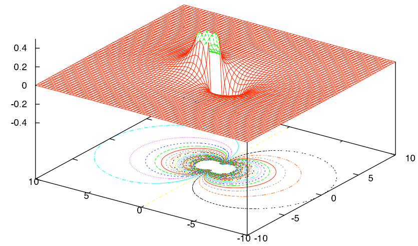


FIG. 3: dipole field

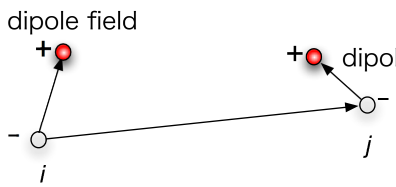


FIG. 4: dipole-dipole interaction

III. DIPOLE-DIPOLE(D-D) INTERACTION

The dipole-dipole(D-D) interaction can be obtained in the same way. Again we assume $r_{ij} >> p_i, p_j$.

$$
\begin{aligned}
V_{\rm dd} &= \frac{(-z_i)(-z_j)e^2}{4\pi\epsilon_0}\frac{1}{|\mathbf{r}_j-\mathbf{r}_i|} + \frac{(-z_i)z_je^2}{4\pi\epsilon_0}\frac{1}{|\mathbf{r}_j+\mathbf{p}_j-\mathbf{r}_i|} + \frac{z_i(-z_j)e^2}{4\pi\epsilon_0}\frac{1}{|\mathbf{r}_j-\mathbf{r}_i-\mathbf{p}_i|} + \frac{z_iz_je^2}{4\pi\epsilon_0}\frac{1}{|\mathbf{r}_j+\mathbf{p}_j-\mathbf{r}_i-\mathbf{p}_i|} \qquad (13)\\
&= \frac{z_iz_je^2}{4\pi\epsilon_0}\left(\frac{1}{r_{ji}} - \frac{1}{\sqrt{r_{ji}^2+2\mathbf{r}_{ji}\cdot\mathbf{p}_j+\mathbf{p}_j^2}} - \frac{1}{\sqrt{r_{ji}^2-2\mathbf{r}_{ji}\cdot\mathbf{p}_i+\mathbf{p}_i^2}} + \frac{1}{\sqrt{r_{ji}^2-2\mathbf{r}_{ji}\cdot\mathbf{p}_i+2\mathbf{r}_{ji}\cdot\mathbf{p}_j+\mathbf{p}_i^2+\mathbf{p}_j^2-2\mathbf{p}_i\cdot\mathbf{p}_j}}\right)\\
&= \frac{z_iz_je^2}{4\pi\epsilon_0 r_{ji}}\left[1 - \frac{1}{(1+2\mathbf{r}_{ji}\cdot\mathbf{p}_j/r_{ji}^2+\mathbf{p}_j^2/r_{ji}^2)^{1/2}} - \frac{1}{(1-2\mathbf{r}_{ji}\cdot\mathbf{p}_i/r_{ji}^2+\mathbf{p}_i^2/r_{ji}^2)^{1/2}}\right.\\
&\left. + \frac{1}{(1-2\mathbf{r}_{ji}\cdot\mathbf{p}_i/r_{ji}^2+2\mathbf{r}_{ji}\cdot\mathbf{p}_j/r_{ji}^2+\mathbf{p}_i^2/r_{ij}^2+\mathbf{p}_j^2/r_{ji}^2-2\mathbf{p}_i\cdot\mathbf{p}_j/r_{ji}^2)^{1/2}}\right]\\
&= \frac{z_iz_je^2}{4\pi\epsilon_0 r_{ji}}\left[1 - 1 + \frac{1}{2}\frac{2\mathbf{r}_{ji}\cdot\mathbf{p}_j}{r_{ji}^2} + \frac{1}{2}\frac{\mathbf{p}_j^2}{r_{ji}^2} - \frac{3}{8}(2\mathbf{r}_{ji}\cdot\mathbf{p}_j/r_{ji}^2+\mathbf{p}_j^2/r_{ji}^2)^2\right.\\
&\quad -1 + \frac{1}{2}\frac{-2\mathbf{r}_{ji}\cdot\mathbf{p}_i}{r_{ji}^2} + \frac{1}{2}\frac{\mathbf{p}_i^2}{r_{ji}^2} - \frac{3}{8}(-2\mathbf{r}_{ji}\cdot\mathbf{p}_i/r_{ji}^2+\mathbf{p}_i^2/r_{ji}^2)^2\\
&\left. +1 - \frac{1}{2}\frac{-2\mathbf{r}_{ji}\cdot\mathbf{p}_i}{r_{ji}^2} - \frac{1}{2}\frac{2\mathbf{r}_{ji}\cdot\mathbf{p}_j}{r_{ji}^2} - \frac{1}{2}\frac{\mathbf{p}_i^2}{r_{ji}^2} - \frac{1}{2}\frac{\mathbf{p}_j^2}{r_{ji}^2} + \underbrace{\frac{1}{2}\frac{2\mathbf{p}_i\cdot\mathbf{p}_j}{r_{ji}^2}}_{\text{survive}} + \frac{3}{8}(\underbrace{\frac{-2\mathbf{r}_{ji}\cdot\mathbf{p}_i}{r_{ji}^2} + \frac{2\mathbf{r}_{ji}\cdot\mathbf{p}_j}{r_{ji}^2}}_{\text{cross term survive}} + \frac{\mathbf{p}_i^2}{r_{ji}^2} + \frac{\mathbf{p}_j^2}{r_{ji}^2} - \frac{2\mathbf{p}_i\cdot\mathbf{p}_j}{r_{ji}^2})^2\right]\\
&= \frac{z_iz_je^2}{4\pi\epsilon_0 r_{ji}}\left[\frac{\mathbf{p}_i\cdot\mathbf{p}_j}{r_{ji}^2} - 3\frac{(\mathbf{r}_{ji}\cdot\mathbf{p}_i)(\mathbf{r}_{ji}\cdot\mathbf{p}_j)}{r_{ji}^4}\right]\\
V_{\rm dd} &= \frac{1}{4\pi\epsilon_0 r_{ij}^3}\left[\vec{\mu}_i\cdot\vec{\mu}_j - 3\frac{(\vec{\mu}_i\cdot\mathbf{r}_{ij})(\mathbf{r}_{ij}\cdot\vec{\mu}_j)}{r_{ij}^2}\right] \qquad (14)
\end{aligned}
$$

If electric field $\mathbf{E}_{\rm D}^i$ from i-th dipole can be calculated from $\phi_{\rm D}$ given above, and the interaction energy can be obtained by $-\vec{\mu}_j \cdot \mathbf{E}_{\rm D}^i(\mathbf{r}_j)$.

$$\begin{aligned}
\mathbf{E}_{\rm D}^i &= -\nabla\phi_{\rm D}(\mathbf{r}-\mathbf{r}_i) = -\left(\mathbf{i}\frac{\partial}{\partial x}+\mathbf{j}\frac{\partial}{\partial y}+\mathbf{k}\frac{\partial}{\partial z}\right)\phi_{\rm D}(\mathbf{r}-\mathbf{r}_i) \\
\phi_{\rm D}(\mathbf{r}-\mathbf{r}_i) &= \frac{1}{4\pi\epsilon_0}\frac{\mu_{ix}(x-x_i)+\mu_{iy}(y-y_i)+\mu_{iz}(z-z_i)}{[(x-x_i)^2+(y-y_i)^2+(z-z_i)^2]^{3/2}} \\
-\nabla\phi_{\rm D}(\mathbf{r}-\mathbf{r}_i)|_x &= -\frac{1}{4\pi\epsilon_0}\frac{1}{|\mathbf{r}-\mathbf{r}_i|^3}\frac{\mu_{ix}\mathbf{i}}{[(x-x_i)^2+(y-y_i)^2+(z-z_i)^2]^{3/2}} \\
&\quad -\frac{1}{4\pi\epsilon_0}\frac{\vec{\mu}_i\cdot(\mathbf{r}-\mathbf{r}_i)}{[(x-x_i)^2+(y-y_i)^2+(z-z_i)^2]^{5/2}}\frac{-3}{2}2(x-x_i)\mathbf{i} \\
\mathbf{E}_{\rm D}^i(\mathbf{r}) &= -\frac{1}{4\pi\epsilon_0|\mathbf{r}-\mathbf{r}_i|^3}\left[\vec{\mu}_i - 3\frac{\vec{\mu}_i\cdot(\mathbf{r}-\mathbf{r}_i)(\mathbf{r}-\mathbf{r}_i)}{|\mathbf{r}-\mathbf{r}_i|^2}\right] \qquad (15) \\
V_{dd} &= -\vec{\mu}_j\cdot\mathbf{E}_d^i(\mathbf{r}_j) = \frac{1}{4\pi\epsilon_0 r_{ij}^3}\left[\vec{\mu}_i\cdot\vec{\mu}_j - 3\frac{\vec{\mu}_i\cdot(\mathbf{r}_i-\mathbf{r}_j)(\mathbf{r}_i-\mathbf{r}_j)\cdot\vec{\mu}_j}{r_{ij}^2}\right] \qquad (16)
\end{aligned}$$

This equation is the same as the equation given above.

IV. UNIFIED DEFINITION OF C-C, C-D, D-C, AND D-D INTERACTIONS

The total electrostatic potential is given by [check sign→OK]

$$\begin{aligned}
4\pi\epsilon_0 V_{\rm tot} &= \sum_{i>j}\left(\underbrace{q_i T_{ij} q_j}_{\rm C-C}\underbrace{-q_i\sum_\alpha T_{ij}^\alpha \mu_{j,\alpha}}_{\rm C-D}+\underbrace{\sum_\alpha \mu_{i,\alpha}T_{ij}^\alpha q_j}_{D-C}\underbrace{-\sum_{\alpha,\beta}\mu_{i,\alpha}T_{ij}^{\alpha\beta}\mu_{j,\beta}}_{\rm D-D}\right) \qquad (17) \\
q_i &= ez_i, \quad \vec{\mu}_i = (\mu_{ix},\mu_{iy},\mu_{iz}) = ez_i\mathbf{p}_i = ez_i(p_{ix},p_{iy},p_{iz}) \qquad (18)
\end{aligned}$$

Here the interaction tensors are given by [check this→OK]

$$\begin{aligned}
T_{ij} &= \frac{1}{r_{ij}} \qquad (19) \\
T_{ij}^\alpha &= \nabla_\alpha T_{ij} = -r_{ij,\alpha}r_{ij}^{-3} \qquad (20) \\
T_{ij}^{\alpha\beta} &= \nabla_\alpha\nabla_\beta T_{ij} = (3r_{ij,\alpha}r_{ij,\beta}-r_{ij}^2\delta_{\alpha\beta})r_{ij}^{-5} \qquad (21) \\
T_{ij}^{\alpha\beta\gamma} &= \nabla_\alpha\nabla_\beta\nabla_\gamma T_{ij} = -[15r_{ij,\alpha}r_{ij,\beta}r_{ij,\gamma}-3r_{ij}^2(r_{ij,\alpha}\delta_{\beta\gamma}+r_{ij,\beta}\delta_{\gamma\alpha}+r_{ij,\gamma}\delta_{\alpha\beta})]r_{ij}^{-7} \qquad (22)
\end{aligned}$$

Here ∇_α means $\frac{\partial}{\partial r_{ij,\alpha}}$ for $\alpha = x, y, z$. $T_{ij}^{\alpha\beta\gamma}$ will be used in the force formulation.

V. POLARIZATION

When a strong electric field is applied to an atom i, the electrons around atom i starts to deform and a dipole moment may be induced.

The dipole moment of atom i in the α direction may be written as the superposition of the electric field $\mathbf{E}_{\rm C}^j$ generated by the charge of atom j and that $\mathbf{E}_{\rm D}^j$ by the dipole of atom j

$$\mu_{i,\alpha} = \mu_{i,\alpha}^{\rm stat} + \mu_{i,\alpha}^{\rm ind} \simeq \mu_{i,\alpha}^{\rm ind} \qquad (23)$$

Usually we take $\mu_{i,\alpha}^{\rm static} = 0$. The electric field at atom i can be written as

$$\mathbf{E}(\mathbf{r}_i) = \sum_{j(\neq i)}[\mathbf{E}_{\rm C}^j(\mathbf{r}_i)+\mathbf{E}_{\rm D}^j(\mathbf{r}_i)] \qquad (24)$$

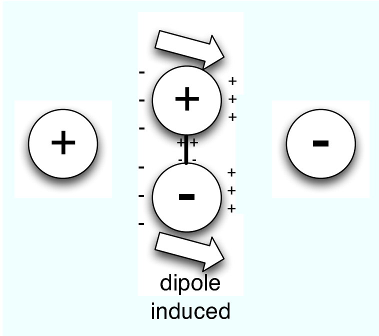


FIG. 5: What's polarization?

$$= \frac{1}{4\pi\epsilon_0}\sum_{j(\neq i)}\left\{z_j e\frac{\mathbf{r}_i-\mathbf{r}_j}{|\mathbf{r}_i-\mathbf{r}_j|^3} - \frac{1}{|\mathbf{r}_i-\mathbf{r}_j|^3}\left[\vec{\mu}_j^{\rm ind} - 3\frac{\vec{\mu}_j^{\rm ind}\cdot(\mathbf{r}_i-\mathbf{r}_j)(\mathbf{r}_i-\mathbf{r}_j)}{|\mathbf{r}_i-\mathbf{r}_j|^2}\right]\right\} \tag{25}$$

$$E_\alpha(\mathbf{r}_i) = \frac{1}{4\pi\epsilon_0}\sum_{j(\neq i)}\left(-T_{ij}^{\alpha}q_j + \sum_\beta T_{ij}^{\alpha\beta}\mu_{j,\beta}^{\rm ind}\right) \tag{26}$$

The induced dipole moment $\mu_{i,\alpha}^{\rm ind}$ is given by

$$\mu_{i,\alpha}^{\rm ind} = \alpha_{\alpha,\beta}^{i}E_\beta(\mathbf{r}_i) \tag{27}$$

Here $\alpha_{\alpha,\beta}^{i}$ polarizability tensor of atom i. If we assume

$$[\alpha^i] = \begin{pmatrix} \alpha^i & 0 & 0 \\ 0 & \alpha^i & 0 \\ 0 & 0 & \alpha^i \end{pmatrix} \tag{28}$$

then, we have

$$\vec{\mu}_i^{\rm ind} = \alpha^i\mathbf{E}(\mathbf{r}_i), \qquad \mu_{i,\alpha}^{\rm ind} = \alpha^i E_\alpha(\mathbf{r}_i) \tag{29}$$

$$\mu_{i,\alpha}^{\rm ind}(\text{out}) = \frac{\alpha^i}{4\pi\epsilon_0}\sum_{j(\neq i)}\left(-T_{ij}^{\alpha}q_j + \sum_\beta T_{ij}^{\alpha\beta}\mu_{j,\beta}^{\rm ind}(\text{input})\right) \tag{30}$$

$$\mu_{i,x}^{\rm ind}(\text{out}) = \frac{\alpha^i}{4\pi\epsilon_0}\sum_{j(\neq i)}\left(-T_{ij}^{x}q_j + \sum_\beta T_{ij}^{x\beta}\mu_{j,\beta}^{\rm ind}(\text{input})\right) \tag{31}$$

$$= \frac{\alpha^i}{4\pi\epsilon_0}\sum_{j(\neq i)}\left(\frac{x_{ij}}{r_{ij}^3}q_j + \sum_\beta[\frac{3x_{ij}r_{ij,\beta}}{r_{ij}^5} - \frac{\delta_{x\beta}}{r_{ij}^3}]\mu_{j,\beta}^{\rm ind}(\text{input})\right) \tag{32}$$

$$= \frac{\alpha^i}{4\pi\epsilon_0}\sum_{j(\neq i)}\left(\frac{x_{ij}}{r_{ij}^3}q_j + \frac{3x_{ij}}{r_{ij}^5}\sum_\beta r_{ij,\beta}\mu_{j,\beta}^{\rm ind}(\text{input}) - \frac{\mu_{j,x}^{\rm ind}(\text{input})}{r_{ij}^3}\right) \tag{33}$$

The last equations should be solved self-consistently.

In the fixed charge model the interaction of C-C is calculated by Ewald method. Then when we consider the induced dipoles at the atom sites we should C-D, D-C, and D-D interaction. The total C-C, C-D, D-C, D-D interaction is given by [check this]

$$4\pi\epsilon_0 V_{\rm tot} = \sum_{i>j}\left(q_iT_{ij}q_j - q_i\sum_\alpha T_{ij}^{\alpha}\mu_{j,\alpha}^{\rm ind} + \sum_\alpha \mu_{i,\alpha}^{\rm ind}T_{ij}^{\alpha}q_j - \sum_{\alpha,\beta}\mu_{i,\alpha}^{\rm ind}T_{ij}^{\alpha\beta}\mu_{j,\beta}^{\rm ind}\right) \tag{34}$$

From Böttcher's book (Theory off Electric Polarization vol 1 Dielectrics in static field 2nd ed. p110), the energy U of the induced dipole system

$$U = -\vec{\mu}_i^{\rm ind} \cdot \mathbf{E}(\mathbf{r}_i) + U_{\rm pol} \tag{35}$$

where $U_{\rm pol}$ is the work of polarization. At equilibrium, the energy will be minimal with an infinitesimal change of induced moment

$$dU \;=\; 0, \quad \text{for all } d\vec{\mu}_i^{\rm ind} \tag{36}$$

Then we have

$$dU_{\rm pol} = -d[-\vec{\mu}_i^{\rm ind} \cdot \mathbf{E}(\mathbf{r}_i)] = \mathbf{E}(\mathbf{r}_i) \cdot d\vec{\mu}_i^{\rm ind} = \frac{\vec{\mu}_i^{\rm ind}}{\alpha^i} \cdot d\vec{\mu}_i^{\rm ind} = \frac{1}{2\alpha^i} d[(\mu_i^{\rm ind})^2] \tag{37}$$

The induced dipole is formed in a reversible process

$$U_{\rm pol} \;=\; \int dU_{\rm pol} = \frac{1}{2\alpha^i} \int_0^{\mu_i{}^{\rm ind}} d[(\mu_i^{\rm ind})^2] = \frac{1}{2\alpha^i} (\mu_i^{\rm ind})^2 \tag{38}$$

If we count all the cotribution

$$U_{\rm pol} \;=\; \sum_i \frac{1}{2\alpha^i} \vec{\mu}_i^{\rm ind} \cdot \vec{\mu}_i^{\rm ind} \tag{39}$$

The MD code with this polarization scheme is available, e.g. Amber or Lucretius.

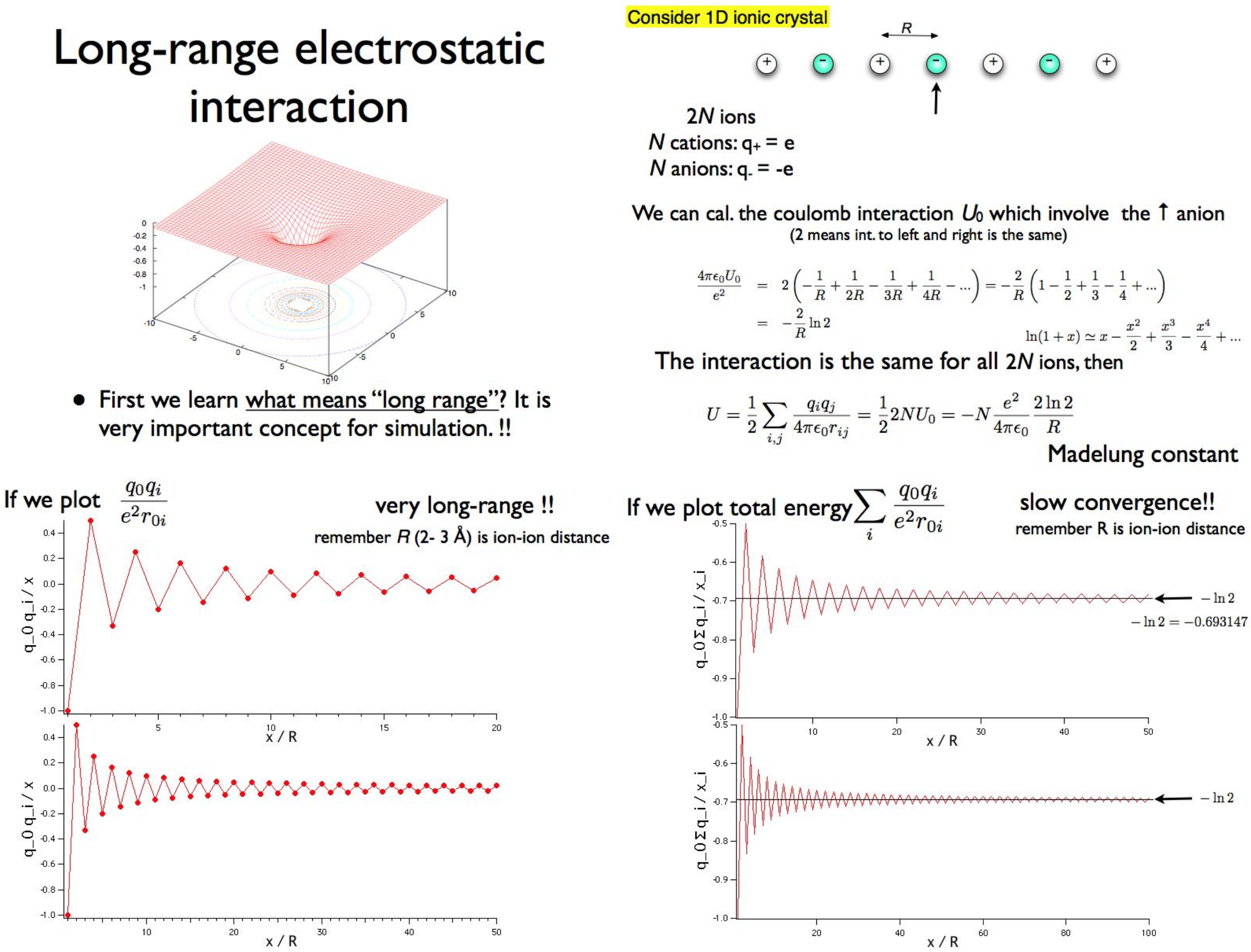
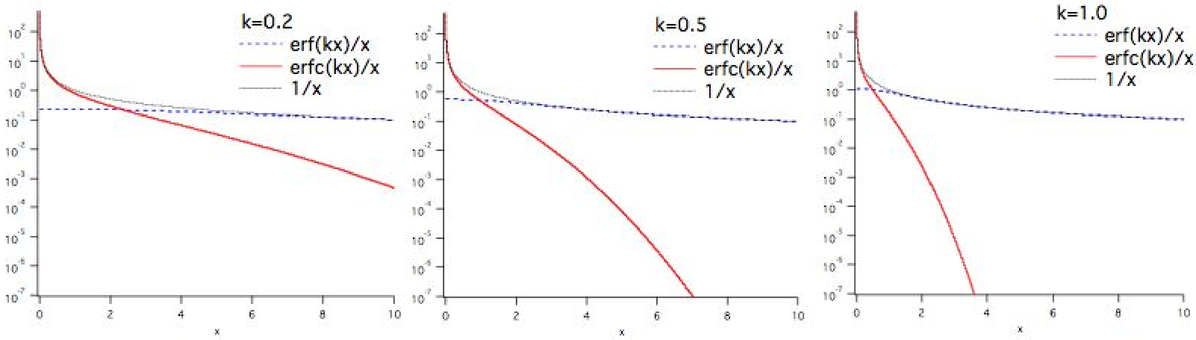


FIG. 6: long-range electrostatic interaction

$x = |\mathbf{R} + \mathbf{r}_j - \mathbf{r}_i|$ $\boldsymbol{R}$ space = erfc(κx)/x, $\boldsymbol{k}$ space sum = erf(κx)/x, total = 1/x



$\kappa \to$ large, $\boldsymbol{R}$ space sum converge at small x and $\boldsymbol{k}$ space sum converge at longer $\boldsymbol{G}$

S. Okazaki　コンピュータシミュレーションの基礎 NaCN + 256 water molecules

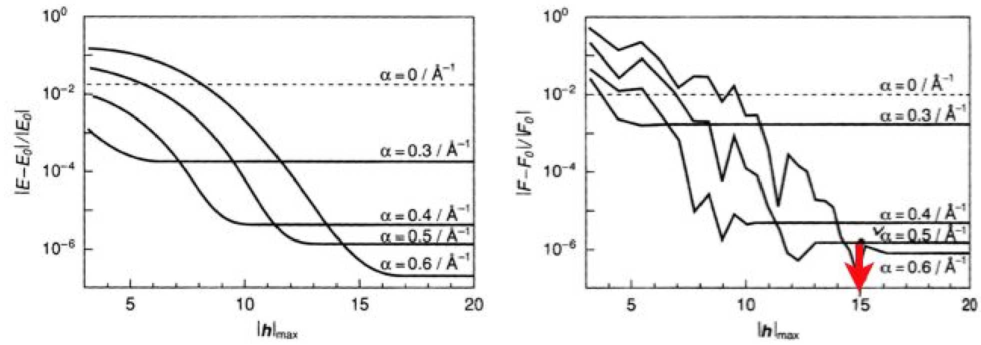


図6.3　全ポテンシャルエネルギーに対して，エワルドの方法を用いた場合の計算誤差の α，$|\boldsymbol{h}|_{\max}$ 依存性
r_c は固定してある．点線はエワルド法を用いず，直接計算したときの誤差．

図6.4　ある水分子にかかる力に対して，エワルドの方法を用いた場合の計算誤差の α，$|\boldsymbol{h}|_{\max}$ 依存性
r_c は固定してある．点線はエワルドの方法を用いず，直接計算したときの誤差．

$$\alpha = \kappa,\ \mathbf{G} = \frac{2\pi}{L},\ r_c = 9.85\text{Å}$$

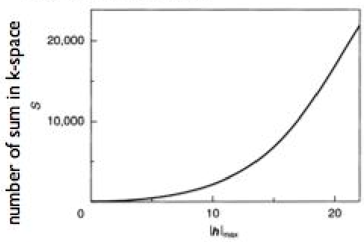


FIG. 7: Ewald sum convergence