Notes for Lecture #4

Electrostatic energy

Section 1.11 in Jackson's text

The total electrostatic potential energy of interaction between point charges $\{q_i\}$ at the positions $\{\mathbf{r_i}\}$ is given by

$$W = \frac{1}{4\pi\varepsilon_0} \sum_{i<j} \frac{q_i q_j}{|\mathbf{r_i} - \mathbf{r_j}|} = \frac{1}{8\pi\varepsilon_0} \sum_{i \neq j} \frac{q_i q_j}{|\mathbf{r_i} - \mathbf{r_j}|}. \tag{1}$$

In this expression, the first form explicitly counts all pairs, while the second form counts all interactions and divides by 2 to compensate for double counting.

For a finite system of charges, this expression can be evaluated directly, however, for a large or infinite system, the expression 1 does not converge and numerical tricks must be used to evaluate the energy. In fact, for the infinite system, one has an infinite amount of charge and the energy of interaction is undefined. If the system is neutral, it is possible to define a meaningful interaction energy by use of an Ewald transformation.

The basic idea of the Ewald approach is as follows. The error function $\mathrm{erf}(x)$ and its complement $\mathrm{erfc}(x)$ are defined as:

$$\mathrm{erf}(x) = \frac{2}{\sqrt{\pi}} \int_0^x e^{-t^2} dt \quad \text{and} \quad \mathrm{erfc}(x) = 1 - \mathrm{erf}(x) = \frac{2}{\sqrt{\pi}} \int_x^\infty e^{-t^2} dt. \tag{2}$$

Ewald noted that

$$\frac{1}{r} = \frac{\mathrm{erf}(\frac{1}{2}\sqrt{\eta}r)}{r} + \frac{\mathrm{erfc}(\frac{1}{2}\sqrt{\eta}r)}{r}. \tag{3}$$

In this expression, the first term goes to a constant $(\sqrt{\eta/\pi})$ as $r \to 0$, but has a long range tail as $r \to \infty$. The second term has a singular behavior as $r \to 0$, but vanishes exponentially as $r \to \infty$. Thus, Ewald's idea is to replace a single divergent summation with two convergent summations. The first summation has a convergent summation in the form of its Fourier transform and the second has a convergent direct summation. Thus the calculation of the electrostatic energy would be evaluated using:

$$W = \frac{1}{8\pi\varepsilon_0} \sum_{i \neq j} \frac{q_i q_j}{|\mathbf{r_i} - \mathbf{r_j}|} = \frac{1}{8\pi\varepsilon_0} \left(\sum_{i \neq j} \frac{q_i q_j \mathrm{erf}(\frac{1}{2}\sqrt{\eta}|\mathbf{r_i} - \mathbf{r_j}|)}{|\mathbf{r_i} - \mathbf{r_j}|} + \sum_{i \neq j} \frac{q_i q_j \mathrm{erfc}(\frac{1}{2}\sqrt{\eta}|\mathbf{r_i} - \mathbf{r_j}|)}{|\mathbf{r_i} - \mathbf{r_j}|} \right). \tag{4}$$

For an appropriate choice of the parameter η, the second summation in Eq. 4 converges quickly and can be evaluated directly. The first term in the summation of Eq. 4 must be transformed into Fourier space.

In order to described these summations explicitly, we assume that we have a periodic lattice so that every ion can be located by $\mathbf{r_i} = \tau_\alpha + \mathbf{T}$ a location τ_α within a unit cell and a periodic translation vector $\mathbf{T}$, In this way, the summation becomes:[1]

$$\sum_{ij} = N \sum_{\alpha\beta\mathbf{T}}, \tag{5}$$

where N denotes the number of unit cells in the system. Since we have a periodic system, N is infinite, but the energy per unit cell W/N is well defined. The other identity that we must use is that a sum over lattice translations $\mathbf{T}$ may be transformed into an equivalent sum over "reciprocal lattice translations" $\mathbf{G}$ according to the identity:

$$\sum_{\mathbf{T}} \delta^3(\mathbf{r} - \mathbf{T}) = \frac{1}{\Omega} \sum_{\mathbf{G}} e^{i\mathbf{G}\cdot\mathbf{r}}, \tag{6}$$

where Ω denotes the unit cell volume. The proof of this relation is given in the appendix.

The first term of Eq. 4 thus becomes

$$\sum_{i\neq j} \frac{q_i q_j \mathrm{erf}(\frac{1}{2}\sqrt{\eta}|\mathbf{r_i} - \mathbf{r_j}|))}{|\mathbf{r_i} - \mathbf{r_j}|} = N \left(\sum_{\alpha\beta} q_\alpha q_\beta \sum_{\mathbf{T}} \frac{\mathrm{erf}(\frac{1}{2}\sqrt{\eta}|\tau_\alpha - \tau_\beta + \mathbf{T}|)}{|\tau_\alpha - \tau_\beta + \mathbf{T}|} - \sum_\alpha q_\alpha^2 \sqrt{\frac{\eta}{\pi}} \right), \tag{7}$$

where the last term in Eq. 7 comes from subtracting out the self-interaction $(i = j)$ term from the complete lattice sum. Using the short hand notation, $\tau_{\alpha\beta} \equiv \tau_\alpha - \tau_\beta$, the lattice sum can be evaluated:

$$\sum_{\mathbf{T}} \frac{\mathrm{erf}(\frac{1}{2}\sqrt{\eta}|\tau_{\alpha\beta} + \mathbf{T}|)}{|\tau_{\alpha\beta} + \mathbf{T}|} = \int d^3r \sum_{\mathbf{T}} \delta^3(\mathbf{r} - \mathbf{T}) \frac{\mathrm{erf}(\frac{1}{2}\sqrt{\eta}|\tau_{\alpha\beta} + \mathbf{r}|)}{|\tau_{\alpha\beta} + \mathbf{r}|}. \tag{8}$$

This becomes,

$$\frac{1}{\Omega} \sum_{\mathbf{G}} \int d^3r e^{i\mathbf{G}\cdot\mathbf{r}} \frac{\mathrm{erf}(\frac{1}{2}\sqrt{\eta}|\tau_{\alpha\beta} + \mathbf{r}|)}{|\tau_{\alpha\beta} + \mathbf{r}|} = \frac{4\pi}{\Omega} \left(\sum_{\mathbf{G}\neq\mathbf{0}} \frac{e^{-i\mathbf{G}\cdot\tau_{\alpha\beta}} e^{-G^2/\eta^2}}{G^2} + \frac{1}{2} \int_0^{\frac{1}{2}\sqrt{\eta}} \frac{du}{u^3} \right), \tag{9}$$

where the last term, which is infinite, comes from the $\mathbf{G} = \mathbf{0}$ contribution.

If the last term of Eq. 9 cannot be eliminated, it is clear that the electrostatic energy is infinite. The term can be eliminated if and only if the system is neutral. Thus, it is only meaningful to calculate the electrostatic energy of a neutral periodic system. If the actual system has a net charge of $Q \equiv \sum_\alpha q_\alpha$, we could calculate a meanful energy if we add to the actual charge density, a compensating uniform density charge density of $-Q/\Omega$. Taking all of the terms into account, we find the final Ewald expression to be:

$$\frac{W}{N} = \sum_{\alpha\beta} \frac{q_\alpha q_\beta}{8\pi\varepsilon_0} \left(\frac{4\pi}{\Omega} \sum_{\mathbf{G}\neq\mathbf{0}} \frac{e^{-i\mathbf{G}\cdot\tau_{\alpha\beta}} e^{-G^2/\eta}}{G^2} - \sqrt{\frac{\eta}{\pi}}\delta_{\alpha\beta} + {\sum_{\mathbf{T}}}' \frac{\mathrm{erfc}(\frac{1}{2}\sqrt{\eta}|\tau_{\alpha\beta} + \mathbf{T}|)}{|\tau_{\alpha\beta} + \mathbf{T}|} \right) - \frac{4\pi Q^2}{8\pi\varepsilon_0\Omega\eta}, \tag{10}$$

where the $\prime$ in the summation over lattice translations $\mathbf{T}$ indicates that all self-interaction terms should be omitted.

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[1]Note that for any two lattice translations $\mathbf{T_i}$ and $\mathbf{T_j}$, $\mathbf{T_i} - \mathbf{T_j} = \mathbf{T_k}$, where $\mathbf{T_k}$ is also a lattice translation.

Appendix I – comments on lattice vectors and reciprocal lattice vectors

In this discussion, will assume we have a 3-dimensional periodic system. It can be easily generalized to 1- or 2- dimensional systems. In general, a translation vector can be described a linear combination of the three primitive translation vectors $\mathbf{T_1}$, $\mathbf{T_2}$, and $\mathbf{T_3}$:

$$\mathbf{T} = n_1\mathbf{T_1} + n_2\mathbf{T_2} + n_3\mathbf{T_3}, \tag{11}$$

where $\{n_1, n_2, n_3\}$ are integers. Note that the unit cell volume Ω can be expressed in terms of the primitive translation vectors according to:

$$\Omega = |\mathbf{T_1} \cdot (\mathbf{T_2} \times \mathbf{T_3})|. \tag{12}$$

The reciprocal lattice vectors $\mathbf{G}$ can generally be written as a linear combination of the three primitive reciprocal lattice vectors $\mathbf{G_1}$, $\mathbf{G_2}$, and $\mathbf{G_3}$:

$$\mathbf{G} = m_1\mathbf{G_1} + m_2\mathbf{G_2} + m_3\mathbf{G_3}, \tag{13}$$

where $\{m_1, m_2, m_3\}$ are integers. The primitive reciprocal lattice vectors are determined from the primitive translation vectors according to the identities:

$$\mathbf{G_i} \cdot \mathbf{T_j} = 2\pi\delta_{ij}. \tag{14}$$

Note that the "volume" of the primitive reciprocal lattice is given by

$$|\mathbf{G_1} \cdot (\mathbf{G_2} \times \mathbf{G_3})| = \frac{(2\pi)^3}{\Omega}. \tag{15}$$

Some examples of this are given below.

"Proof" of Eq. 6

Consider the geometric series

$$\sum_{k=-M}^{+M} e^{ik(\mathbf{G_1}\cdot\mathbf{r})} = \frac{\sin\left((M+\frac{1}{2})\mathbf{G_1} \cdot \mathbf{r}\right)}{\sin(\mathbf{G_1} \cdot \mathbf{r}/2)}. \tag{16}$$

The behavior of the right hand side of Eq. (16) is that it is small in magnitude very except when the denominator vanishes. This occurs whenever $\mathbf{G_1} \cdot \mathbf{r}/2 = \mathbf{n_1}\pi$, where n_1 represents any integer. If we take the limit $M \to \infty$, we find that the function represents the behavior of a sum of delta functions:

$$\lim_{M\to\infty} \frac{\sin\left((M+\frac{1}{2})\mathbf{G_1} \cdot \mathbf{r}\right)}{\sin(\mathbf{G_1} \cdot \mathbf{r}/2)} = 2\pi \sum_{n_1} \delta(\mathbf{G_1} \cdot (\mathbf{r} - \mathbf{n_1}\mathbf{T_1})). \tag{17}$$

The summation over all lattice translations $n_1\mathbf{T_1}$ is due to the fact that $\sin(\mathbf{G_1} \cdot \mathbf{r}/2) = 0$ whenever $\mathbf{r} = \mathbf{n_1}\mathbf{T_1}$. Carrying out the geometric summations in the right hand side of Eq. 6 for all three reciprocal lattice vectors and taking the limit as in Eq. 17,

$$\sum_{\mathbf{G}} e^{i\mathbf{G}\cdot\mathbf{r}} = (2\pi)^3 \sum_{n_1,n_2,n_3} \delta(\mathbf{G_1} \cdot (\mathbf{r} - \mathbf{n_1}\mathbf{T_1}))\delta(\mathbf{G_2} \cdot (\mathbf{r} - \mathbf{n_2}\mathbf{T_2}))\delta(\mathbf{G_3} \cdot (\mathbf{r} - \mathbf{n_3}\mathbf{T_3})). \tag{18}$$

Finally, the right hand side of Eq. 18 can be simplified by eliminating the reciprocal lattice vectors from the δ functions:

$$\sum_{\mathbf{G}} e^{i\mathbf{G}\cdot\mathbf{r}} = \frac{(2\pi)^3}{|\mathbf{G_1}\cdot(\mathbf{G_2}\times\mathbf{G_3})|}\sum_{\mathbf{T}}\delta^3(\mathbf{r}-\mathbf{T}) = \Omega\delta^3(\mathbf{r}-\mathbf{T}), \qquad (19)$$

which is consistent with Eq. 6.

Appendix II – examples

In these examples, denote the length of the unit cell by a.

CsCl structure

There are two kinds of sites – $\tau_{\mathrm{Cs}} = 0$ and $\tau_{\mathrm{Cl}} = \frac{a}{2}(\hat{\mathbf{x}} + \hat{\mathbf{y}} + \hat{\mathbf{z}})$.

$$\mathbf{T_1} = a\hat{\mathbf{x}} \quad \mathbf{T_2} = a\hat{\mathbf{y}} \quad \mathbf{T_3} = a\hat{\mathbf{z}}. \qquad (20)$$

$$\mathbf{G_1} = \frac{2\pi}{a}\hat{\mathbf{x}} \quad \mathbf{G_2} = \frac{2\pi}{a}\hat{\mathbf{y}} \quad \mathbf{G_3} = \frac{2\pi}{a}\hat{\mathbf{z}}. \qquad (21)$$

It is convenient to define $\eta \equiv \mu^2/a^2$. Also we will denote by q the unit charge. In these terms, Eq. 10 becomes for this case:

$$\frac{W}{N} = \frac{q^2}{8\pi\varepsilon_0 a}(\mathcal{T}_1 + \mathcal{T}_2), \qquad (22)$$

where

$$\mathcal{T}_1 \equiv \frac{1}{\pi}\sum_{m_1,m_2,m_3\neq\mathbf{0}} 2\frac{\left(1 - e^{i\pi(m_1+m_2+m_3)}\right)e^{-\frac{4\pi^2}{\mu^2}(m_1^2+m_2^2+m_3^2)}}{m_1^2 + m_2^2 + m_3^2} - \frac{2\mu}{\sqrt{\pi}} \qquad (23)$$

and

$$\mathcal{T}_2 \equiv \sum_{n_1,n_2,n_3\neq\mathbf{0}} \frac{2\,\mathrm{erfc}(\frac{\mu}{2}\sqrt{n_1^2+n_2^2+n_3^2})}{\sqrt{n_1^2+n_2^2+n_3^2}} - \sum_{n_1,n_2,n_3}\frac{2\,\mathrm{erfc}(\frac{\mu}{2}\sqrt{(\frac{1}{2}+n_1)^2+(\frac{1}{2}+n_2)^2+(\frac{1}{2}+n_3)^2})}{\sqrt{(\frac{1}{2}+n_1)^2+(\frac{1}{2}+n_2)^2+(\frac{1}{2}+n_3)^2}}. \qquad (24)$$

In this expression, the sum over α and β has a total of 4 contributions – 2 pairs of identical contributions. For Cs-Cs or Cl-Cl interactions, $\tau_{\alpha\beta} = 0$ and $q_\alpha = q_\beta$ resulting in repulsive contributions. For Cs-Cl or Cl-Cs interations, $\tau_{\alpha\beta} = \pm\frac{a}{2}(\hat{\mathbf{x}} + \hat{\mathbf{y}} + \hat{\mathbf{z}})$ and $q_\alpha = q_\beta$ resulting in attractive contributions. This expression can be evaluated using Maple, which gives the result

$$\frac{W}{N} = \frac{q^2}{8\pi\varepsilon_0 a}(-4.071). \qquad (25)$$

NaCl structure

There are two kinds of sites – $\tau_{\text{Na}} = 0$ and $\tau_{\text{Cl}} = \frac{a}{2}\hat{\mathbf{x}}$.

$$\mathbf{T_1} = \frac{a}{2}(\hat{\mathbf{x}} + \hat{\mathbf{y}}) \quad \mathbf{T_2} = \frac{a}{2}(\hat{\mathbf{y}} + \hat{\mathbf{z}}) \quad \mathbf{T_3} = \frac{a}{2}(\hat{\mathbf{x}} + \hat{\mathbf{z}}). \tag{26}$$

$$\mathbf{G_1} = \frac{2\pi}{a}(\hat{\mathbf{x}} + \hat{\mathbf{y}} - \hat{\mathbf{z}}) \quad \mathbf{G_2} = \frac{2\pi}{a}(-\hat{\mathbf{x}} + \hat{\mathbf{y}} + \hat{\mathbf{z}}) \quad \mathbf{G_3} = \frac{2\pi}{a}(\hat{\mathbf{x}} - \hat{\mathbf{y}} + \hat{\mathbf{z}}). \tag{27}$$