

Notes on Ewald summation for charges and dipoles

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These notes will summarize recent work on the Ewald methods of Hummer, Pratt, and Garcia extended to systems with point dipoles and induced point dipoles. In the HPG papers from 1996 and 1998, self-energy corrections were discussed which led to remarkably accurate predictions of ion solvation free energies with very few waters [1]. Other references for these notes are our book [2], a paper by Darden *et al.* [3], and the paper by deLeeuw *et al.* [4]. Also the books of Allen/Tildesley [5] and Frenkel/Smit [6], and papers by Adams and McDonald [7] and Nyman and Linse [8].

1 The Ewald Potential

The Ewald potential of HPG is defined as

$$\psi(\mathbf{r}) = \sum_{\mathbf{n}} \frac{\text{erfc}(\eta|\mathbf{r} + \mathbf{n}L|)}{|\mathbf{r} + \mathbf{n}L|} + \frac{4\pi}{L^3} \sum_{\mathbf{k} \neq 0} \left(\frac{e^{-k^2/4\eta^2}}{k^2} \right) e^{i\mathbf{k}\cdot\mathbf{r}} - \frac{\pi}{L^3\eta^2} \quad (1)$$

This potential is periodic in the cubic lattice assumed here, and has several desirable properties as we'll see. (The \mathbf{k} values are chosen to satisfy the periodicity: $\mathbf{k} = 2\pi\mathbf{n}/L$.) This potential is that due to a unit-charge ion and its neutralizing background, in periodic boundaries.

The complementary error function is

$$\text{erfc}(z) = 1 - \frac{2}{\sqrt{\pi}} \int_0^z e^{-u^2} du \quad (2)$$

What properties does this potential have? First, the potential is the solution of the Poisson equation

$$\nabla^2\psi(\mathbf{r}) = -4\pi \left(\delta(\mathbf{r}) - \frac{1}{V} \right) \quad (3)$$

where $V = L^3$. This is just a restatement of the fact that $\psi(\mathbf{r})$ is the periodic potential due to a unit charge plus a neutralizing background in PBC. Second, the integral of the potential over the unit cell is zero:

$$\int_{\text{cell}} \psi(\mathbf{r}) d\mathbf{r} = 0 \quad (4)$$

Making the integral equal to a constant (zero here) yields a unique solution, and we will see later that this choice is related to how we handle a net charge in the simulation box and how we assemble the total electrostatic energy. In addition, the last (constant) term in the potential makes the potential independent of the parameter η . So let's go back and examine these properties of the Ewald potential.

We first show that the integral of the Ewald potential over the cell is zero. The integral of the middle term in $\psi(\mathbf{r})$ is clearly zero due to the plane-wave nature of the integrand. Thus we need to show

$$\int_{\text{cell}} \sum_{\mathbf{n}} \frac{\text{erfc}(\eta|\mathbf{r} + \mathbf{n}L|)}{|\mathbf{r} + \mathbf{n}L|} d\mathbf{r} = \frac{\pi}{\eta^2} \quad (5)$$

We can see that the integral over the real-space sum is equivalent to just extending the integration out to infinity. Let's say $|\mathbf{x}| = \eta|\mathbf{r}|$, so $d\mathbf{x} = \eta^3 d\mathbf{r}$. Then we need

$$\int \int \int_{-\infty}^{\infty} \frac{\text{erfc}(|\mathbf{x}|)}{|\mathbf{x}|} \frac{1}{\eta^2} d\mathbf{x} = \frac{\pi}{\eta^2} \quad (6)$$

The integrand is spherically symmetric, and so we need

$$4\pi \int_0^{\infty} \frac{\text{erfc}(x)}{x} x^2 dx = \pi \quad (7)$$

or

$$\int_0^{\infty} \text{erfc}(x) x dx = 1/4 \quad (8)$$

We can use the IBP trick to show that this is true.

Next we show that the Ewald potential is independent of η . For this derivation, we will use a mathematical identity called the *theta transformation*:

$$\frac{4\eta^3}{\sqrt{\pi}} \sum_{\mathbf{n}} e^{-\eta^2|\mathbf{r}+\mathbf{n}L|^2} = \frac{4\pi}{L^3} \sum_{\mathbf{k}} e^{-k^2/4\eta^2} e^{i\mathbf{k}\cdot\mathbf{r}} \quad (9)$$

Now, take the derivative of the Ewald potential wrt η . For the real-space derivative, we find

$$\frac{\partial \psi_{\text{RS}}(\mathbf{r})}{\partial \eta} = -\frac{2}{\sqrt{\pi}} \sum_{\mathbf{n}} e^{-\eta^2|\mathbf{r}+\mathbf{n}L|^2} \quad (10)$$

and the momentum space part is

$$\frac{\partial \psi_{\text{KS}}(\mathbf{r})}{\partial \eta} = \frac{2\pi}{L^3 \eta^3} \sum_{\mathbf{k} \neq 0} e^{-k^2/4\eta^2} e^{i\mathbf{k}\cdot\mathbf{r}} \quad (11)$$

Finally, the derivative of the third term yields $2\pi/L^3 \eta^3$, but that can be viewed as just the $\mathbf{k} = 0$ term added to Eq. 11. The theta transformation then tells us that the net result is 0, so the Ewald potential is independent of η .

Let's now show that the Ewald potential is the solution of the Poisson equation Eq. 3. Consider the action of the Laplacian on the \mathbf{k} -space part of the Ewald potential:

$$\nabla^2 \left(\frac{4\pi}{L^3} \right) \sum_{\mathbf{k} \neq 0} \frac{e^{-k^2/4\eta^2}}{k^2} e^{i\mathbf{k} \cdot \mathbf{r}} = - \left(\frac{4\pi}{L^3} \right) \sum_{\mathbf{k} \neq 0} e^{-k^2/4\eta^2} e^{i\mathbf{k} \cdot \mathbf{r}} \quad (12)$$

$$= - \left(\frac{4\pi}{L^3} \right) \sum_{\mathbf{k}} e^{-k^2/4\eta^2} e^{i\mathbf{k} \cdot \mathbf{r}} + \frac{4\pi}{L^3} \quad (13)$$

$$= - \left(\frac{4\eta^3}{\sqrt{\pi}} \right) \sum_{\mathbf{n}} e^{-\eta^2|\mathbf{r}+\mathbf{n}L|} + \frac{4\pi}{L^3} \quad (14)$$

The last step uses the theta transformation defined above. Now we need to look at the Laplacian acting on the real-space sum. To do this we notice that all the terms in the sum are spherically symmetric. That is, we can use the radial part of the Laplacian alone. We can try this out for the $\mathbf{n} = 0$ term:

$$\nabla^2 \frac{\text{erfc}(\eta r)}{r} = \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) \frac{\left[1 - \frac{2}{\sqrt{\pi}} \int_0^{\eta r} du e^{-u^2} \right]}{r} \quad (15)$$

We note that $d\mathbf{r} = d(\eta\mathbf{r})/\eta$. Then, after a few steps, we end up with

$$\nabla^2 \frac{\text{erfc}(\eta r)}{r} = \frac{4\eta^3}{\sqrt{\pi}} e^{-\eta^2 r^2} \quad (16)$$

We get the same kind of expression for each term in the real-space sum, so this shows that this term and the \mathbf{k} -space term cancel exactly, leaving the neutralizing background in the charge density. This is true for any point away from the location of the delta function $\delta(\mathbf{r})$. For the $\mathbf{n} = 0$ term, as we approach $r \rightarrow 0$, then we can use Gauss's law (see Jackson's book *Classical Electrodynamics*) to show that the delta function results from the Laplacian acting on the potential at that point. So we've now shown that the Ewald potential satisfies the Poisson equation for a discrete charge plus a neutralizing background in PBC.

2 Assembling the electrostatic energy

Given the Ewald potential discussed above, how do we construct the total electrostatic potential energy for some configuration of charges? We know from electrostatics that the energy is always

$$U = \frac{1}{2} \int \rho(\mathbf{r}) \phi(\mathbf{r}) d\mathbf{r} \quad (17)$$

where $\phi(\mathbf{r})$ is the total electrostatic potential. Then, for the Ewald potential considered above, we get

$$U = \frac{1}{2} \int_{\text{cell}} \left[\sum_i q_i \left(\delta(\mathbf{r} - \mathbf{r}_i) - \frac{1}{L^3} \right) \right] \sum_j q_j \psi(\mathbf{r} - \mathbf{r}_j) d\mathbf{r} = \frac{1}{2} \sum_{i,j} q_i q_j \psi(\mathbf{r}_{ij}) \quad (18)$$

But this energy includes the interaction of each ion with itself, which gives an infinite contribution to the total energy. We want the ions to interact with their periodic images outside the cell, but not with themselves within the cell. Thus we subtract off that contribution:

$$U = \frac{1}{2} \sum_{i \neq j} q_i q_j \psi(\mathbf{r}_{ij}) + \frac{1}{2} \sum_i q_i^2 \lim_{r \rightarrow 0} \left(\psi(r) - \frac{1}{r} \right) \quad (19)$$

Now what is this last (self) term equal to? Let's first worry about the $\mathbf{n} = 0$ term in the RS part. Thus we want

$$\lim_{r \rightarrow 0} \left(\frac{\operatorname{erfc}(\eta r)}{r} - \frac{1}{r} \right) = \lim_{r \rightarrow 0} \left(\frac{1 - \frac{2}{\sqrt{\pi}} \int_0^{\eta r} du e^{-u^2}}{r} - \frac{1}{r} \right) \quad (20)$$

$$= \lim_{r \rightarrow 0} \left(\frac{1 - \frac{2}{\sqrt{\pi}} \int_0^{\eta r} du (1 - u^2)}{r} - \frac{1}{r} \right) \quad (21)$$

$$= \lim_{r \rightarrow 0} \left\{ \frac{1 - \frac{2}{\sqrt{\pi}} [\eta r - (\eta r)^3/3]}{r} - \frac{1}{r} \right\} \quad (22)$$

$$= -\frac{2\eta}{\sqrt{\pi}} \quad (23)$$

Now we can define a new quantity ξ such that

$$\frac{\xi}{L} = \lim_{r \rightarrow 0} \left(\psi(r) - \frac{1}{r} \right) \quad (24)$$

$$= \sum_{\mathbf{n} \neq 0} \frac{\operatorname{erfc}(\eta |\mathbf{n}L|)}{|\mathbf{n}L|} - \frac{2\eta}{\sqrt{\pi}} + \frac{4\pi}{L^3} \sum_{\mathbf{k} \neq 0} \frac{e^{-k^2/4\eta^2}}{k^2} - \frac{\pi}{L^3 \eta^2} \quad (25)$$

If we make $L = 1$, we find that ξ is independent of η and the sum converges to $\xi = -2.837297$ for a cubic lattice. We could derive similar self corrections for arbitrary lattice geometries. Now we can write out the total potential energy as

$$U = \frac{1}{2} \sum_{i \neq j} q_i q_j \psi(\mathbf{r}_{ij}) + \frac{\xi}{2L} \sum_i q_i^2 \quad (26)$$

We note that the total potential energy is also

$$U = \frac{1}{2} \sum_i q_i \phi^{\text{tot}}(\mathbf{r}_i) \quad (27)$$

Now, what is the potential $\phi^{\text{tot}}(\mathbf{r}_i)$? If we insert the formula for ξ and do some re-arranging, we get

$$\begin{aligned} \phi^{\text{tot}}(\mathbf{r}_i) &= \sum_{j=1}^N q_j \left\{ \sum_{\mathbf{n}}' \frac{\operatorname{erfc}(\eta |\mathbf{r}_{ij} + \mathbf{n}L|)}{|\mathbf{r}_{ij} + \mathbf{n}L|} + \left(\frac{4\pi}{L^3} \right) \sum_{\mathbf{k} \neq 0} \frac{e^{-k^2/4\eta^2}}{k^2} e^{i\mathbf{k} \cdot \mathbf{r}_{ij}} \right\} \\ &\quad - \frac{\pi}{L^3 \eta^2} Q - \frac{2\eta}{\sqrt{\pi}} q_i \end{aligned} \quad (28)$$

where the prime on the RS sum indicates the $i = j$ term is omitted when $\mathbf{n} = 0$. The total energy assembled from this total potential is

$$U = \frac{1}{2} \sum_{i,j=1}^N q_i q_j \left\{ \sum_{\mathbf{n}}' \frac{\text{erfc}(\eta|\mathbf{r}_{ij} + \mathbf{n}L|)}{|\mathbf{r}_{ij} + \mathbf{n}L|} + \left(\frac{4\pi}{L^3}\right) \sum_{\mathbf{k} \neq 0} \frac{e^{-k^2/4\eta^2}}{k^2} e^{i\mathbf{k} \cdot \mathbf{r}_{ij}} \right\} - \frac{\pi}{2L^3\eta^2} Q^2 - \frac{\eta}{\sqrt{\pi}} \sum_{i=1}^N q_i^2 \quad (29)$$

We see that when the total charge Q is zero, we get the usual textbook energy.

Consider the case that the net charge on the system is the charge on one ion that we are interested in. Then $Q = q$, and we would like to know the change in total potential energy when we mutate that charge, say from q_0 to q_1 . If $\Delta q = q_1 - q_0$, then we get

$$\Delta U = \Delta q \hat{\phi}(\mathbf{r}_i) + \frac{\xi}{2L} (q_1^2 - q_0^2) \quad (30)$$

where

$$\hat{\phi}(\mathbf{r}_i) = \sum_{j \neq i}^N q_j \left\{ \sum_{\mathbf{n}} \frac{\text{erfc}(\eta|\mathbf{r}_{ij} + \mathbf{n}L|)}{|\mathbf{r}_{ij} + \mathbf{n}L|} + \left(\frac{4\pi}{L^3}\right) \sum_{\mathbf{k} \neq 0} \frac{e^{-k^2/4\eta^2}}{k^2} e^{i\mathbf{k} \cdot \mathbf{r}_{ij}} \right\} \quad (31)$$

We could include the $-\pi/L^3\eta^2$ correction in this potential, but for the case considered we can show that this term cancels out in ΔU .

The PDT expression for the change in free energy upon the mutation $q_0 \rightarrow q_1$ is

$$\beta \Delta \mu^{\text{ex}} = -\ln \langle e^{-\beta \Delta U} \rangle_{q_0} \quad (32)$$

If a second-order cumulant expansion is performed, you should get

$$\beta \Delta \mu^{\text{ex}} \approx \beta \Delta q \left[\langle \hat{\phi} \rangle_{q_0} + \frac{q_0 \xi}{L} \right] - \frac{\beta^2}{2} \Delta q^2 \left[\langle (\hat{\phi} - \langle \hat{\phi} \rangle_{q_0})^2 \rangle_{q_0} - \frac{\xi}{\beta L} \right] \quad (33)$$

after some rearrangements. When these self-energy corrections are made, the electrostatic part of the free energy converges for remarkably small system sizes (only 16 waters around a sodium ion, for example). If the initial charge q_0 is zero, then the formula for the free energy change becomes

$$\beta \Delta \mu^{\text{ex}} = -\ln \langle e^{-\beta q \hat{\phi}} \rangle_{q_0} + \frac{\beta \xi q^2}{2L} \quad (34)$$

This finite-size shift is apparent in plots in Ch. 5 of our book.

Here we mention a couple more points from HPG's 1998 paper concerning dielectric corrections. They say

$$\mu_{\text{therm}} \approx \mu_{\text{elec}} + \frac{1}{2} q^2 \left[-\frac{\xi}{\epsilon} + \frac{4\pi(\epsilon - 1)R_B^2}{3\epsilon L^3} \right] \quad (35)$$

where

$$\mu_{\text{elec}} = \mu_{\text{sim}} + \frac{q^2 \xi}{2L} \quad (36)$$

as we saw above. This continuum dielectric correction tends to be small. The only part of any significance is to replace $q^2\xi/2L$ with $q^2\xi(1 - 1/\epsilon)/2L$. This leads to about a 1% change in the computed value, and we should consider using that formula.

We should also be aware of a surface correction which is related to the work of polarization involving the cell total dipole moment. If we have charges and dipoles, and the surrounding medium has a dielectric constant of ϵ_{sur} , the correction (from the net dipole due to charges and dipoles in the box) to the total energy is

$$U^{\text{sur}} = \frac{2\pi}{(2\epsilon_{\text{sur}} + 1)V} \left[\left(\sum_i q_i \mathbf{r}_i \right)^2 + 2 \left(\sum_i q_i \mathbf{r}_i \right) \cdot \left(\sum_j b f p_j \right) + \left(\sum_i \mathbf{p}_i \right)^2 \right] \quad (37)$$

deLeeuw and coauthors make a big deal about this correction. It is claimed in the Nyman/Linse paper that the best choice for charged and/or dipolar systems is ‘tinfoil’ boundary conditions, that is $\epsilon_{\text{sur}} = \infty$. Then the surface term drops out. We’ll assume that case unless there is some compelling reason to change it.

3 Ewald summation for charges + dipoles (permanent or induced)

We are interested in ions in water, for cases where both the water and ions are polarizable. In the end we will assume that we have point dipoles which are induced, and no permanent dipoles. The formulas are basically the same except for the case of induced dipoles there is an additional term in the energy which is the work to create the polarization. But to start, we’ll take fixed dipoles just to derive the formulas. The general rule is that we replace q_i in the HPG formula for the total energy with $(q_i + \mathbf{p}_i \cdot \nabla_i)$. We also have to worry about any possible new self energies arising from the point dipoles.

First, let’s look at some basic electrostatics for point dipoles. We can think of the potential due to a point dipole as the limit of two charges which approach each other – the charges are scaled up as the distance decreases so as to maintain a constant dipole moment $\mathbf{p} = \sum_i q_i \mathbf{r}_i$. Then the potential some distance from these two charges is

$$\psi_{\text{dip}} = \psi(\mathbf{r} + \mathbf{a}) - \psi(\mathbf{r}) \quad (38)$$

Let’s consider the Coulomb potential itself, and worry about PBC later. If we Taylor expand $\psi(\mathbf{r} + \mathbf{a})$, we get

$$\frac{1}{|\mathbf{r} + \mathbf{a}|} \approx \frac{1}{|\mathbf{r}|} + \mathbf{a} \cdot \nabla \left(\frac{1}{|\mathbf{r}|} \right) \quad (39)$$

Taking the limit such that the dipole is fixed, we get

$$\psi_{\text{dip}}(\mathbf{r}) = -\mathbf{p} \cdot \nabla \left(\frac{1}{|\mathbf{r}|} \right) = \frac{\mathbf{p} \cdot \mathbf{r}}{r^3} \quad (40)$$

for the potential due to the dipole. So that’s where the dipole term comes from in the energy expression. Now what charge density implies this potential? We can proceed as we would

for a point charge. If we let the Laplacian act on this potential, it turns out that away from the point dipole, we get zero. Then we can look at Gauss's law in the form

$$\int \nabla \cdot \mathbf{E} dV = \int \mathbf{E} \cdot \mathbf{n} da = 4\pi Q \quad (41)$$

Is there any net charge? What is the field from the dipole potential? If we take the derivative of the dipole potential, we get

$$\mathbf{E} = \frac{3(\mathbf{p} \cdot \mathbf{n})\mathbf{n} - \mathbf{p}}{r^3} \quad (42)$$

where here \mathbf{n} is a unit vector in the direction of \mathbf{r} . Now from the electrostatics of multipoles (Jackson), we have

$$U = q\phi(0) - \mathbf{p} \cdot \mathbf{E}(0) + \dots \quad (43)$$

so the interaction energy of two dipoles is

$$U = \frac{\mathbf{p}_1 \cdot \mathbf{p}_2 - 3(\mathbf{n} \cdot \mathbf{p}_1)(\mathbf{n} \cdot \mathbf{p}_2)}{r^3} \quad (44)$$

We return to the Gauss's law calculation

$$\mathbf{E} \cdot \mathbf{n} = -\frac{\mathbf{p} \cdot \mathbf{n}}{r^3} + 3\frac{\mathbf{p} \cdot \mathbf{n}}{r^3} = 2\frac{\mathbf{p} \cdot \mathbf{n}}{r^3} \quad (45)$$

Now we integrate this over the surface of a sphere (with the radius fixed) to get

$$\frac{2}{r} \int \int \mathbf{p} \cdot \mathbf{n} \sin \theta d\theta d\phi = 0 \quad (46)$$

Thus there is no delta function charge density like for the case of a point charge. But this is obvious, there's no net charge inside the sphere. What this means is that the hypothetical point dipole should really be considered physically as the limit of two charges coming together, maintaining a constant net dipole, as we discussed above.

We want to assemble the total energy as we did before, but include all the chg-chg, chg-dip, and dip-dip terms. And then we want to worry about possible self-interaction energies that may arise. So our energy formula is

$$U = \frac{1}{2} \sum_{i \neq j} (q_i + \mathbf{p}_i \cdot \nabla_i)(q_j - \mathbf{p}_j \cdot \nabla_j) \psi(\mathbf{r}_{ij}) + (\text{self terms}) \quad (47)$$

Let's first consider the potential due to a point dipole in PBC. We know that the potential due to a single charge is

$$\psi(\mathbf{r}) = \sum_{\mathbf{n}} \frac{\text{erfc}(\eta|\mathbf{r} + \mathbf{n}L|)}{|\mathbf{r} + \mathbf{n}L|} + \frac{4\pi}{L^3} \sum_{\mathbf{k} \neq 0} \left(\frac{e^{-k^2/4\eta^2}}{k^2} \right) e^{i\mathbf{k} \cdot \mathbf{r}} - \frac{\pi}{L^3 \eta^2} \quad (48)$$

Now we add a second charge, close to the first, with opposite sign. The potential at some point is then the sum of the two Ewald potentials due to the additivity of electrostatics:

$$\begin{aligned} \psi_{\text{dip}}(\mathbf{r}) &= \sum_{\mathbf{n}} \frac{\text{erfc}(\eta|\mathbf{r} + \Delta\mathbf{r} + \mathbf{n}L|)}{|\mathbf{r} + \Delta\mathbf{r} + \mathbf{n}L|} - \sum_{\mathbf{n}} \frac{\text{erfc}(\eta|\mathbf{r} + \mathbf{n}L|)}{|\mathbf{r} + \mathbf{n}L|} \\ &+ \frac{4\pi}{L^3} \sum_{\mathbf{k} \neq 0} \left(\frac{e^{-k^2/4\eta^2}}{k^2} \right) e^{i\mathbf{k} \cdot (\mathbf{r} + \Delta\mathbf{r})} - \frac{4\pi}{L^3} \sum_{\mathbf{k} \neq 0} \left(\frac{e^{-k^2/4\eta^2}}{k^2} \right) e^{i\mathbf{k} \cdot \mathbf{r}} \end{aligned} \quad (49)$$

If we expand the two terms involving $\Delta \mathbf{r}$, assuming $\Delta \mathbf{r} \rightarrow 0$, we can easily see that this potential is equivalent to

$$\psi_{\text{dip}}(\mathbf{r}) = -\mathbf{p} \cdot \nabla \psi(\mathbf{r}) \quad (50)$$

which is the same as the expression for a single charge pair in free space, with the Ewald potential substituted.

Now let's go back to our energy expression, and put in the self terms:

$$\begin{aligned} U &= \frac{1}{2} \sum_{i \neq j} (q_i + \mathbf{p}_i \cdot \nabla_i)(q_j - \mathbf{p}_j \cdot \nabla_j) \psi(\mathbf{r}_{ij}) \\ &+ \frac{1}{2} \sum_i \lim_{r \rightarrow 0} \left[\left(q_i^2 + (q_i \mathbf{p}_i - q_i \mathbf{p}_i) \cdot \nabla_i - (\mathbf{p}_i \cdot \nabla_i)(\mathbf{p}_i \cdot \nabla_i) \right) \psi(\mathbf{r}_i) - (\text{sing}) \right] \end{aligned} \quad (51)$$

Note here we are ignoring the removal of intramolecular electrostatic interactions that is in the 1998 paper of HPG. We can add those terms later. We will focus now on the last (self) terms to see what happens with dipoles. The chg-chg part is the same of course. We'll worry about getting the correct signs at the end, and first focus on the differentiation operators ignoring the signs.

We'll proceed in steps, taking the first derivative, then the second. The application of $\mathbf{p} \cdot \nabla$ times the charge should yield any possible self-energy terms for the chg-dip case (where a charge and a dipole exist on the same particle). The application of $\mathbf{p} \cdot \nabla$ to the Ewald potential gives

$$\begin{aligned} \mathbf{p} \cdot \nabla \psi(\mathbf{r}) &= - \sum_{\mathbf{n}} \frac{\mathbf{p} \cdot (\mathbf{r} + \mathbf{n}L)}{|\mathbf{r} + \mathbf{n}L|^2} \left[\frac{2\eta}{\sqrt{\pi}} e^{-\eta^2 |\mathbf{r} + \mathbf{n}L|^2} + \frac{\text{erfc}(\eta |\mathbf{r} + \mathbf{n}L|)}{|\mathbf{r} + \mathbf{n}L|} \right] \\ &+ \frac{4\pi}{L^3} \sum_{\mathbf{k} \neq 0} \frac{e^{-k^2/4\eta^2}}{k^2} e^{i\mathbf{k} \cdot \mathbf{r}} (i\mathbf{p} \cdot \mathbf{k}) \end{aligned} \quad (52)$$

For this chg-dip case we can ignore the charge as it is just a constant out front. Then we have to let the vector $\mathbf{r} \rightarrow 0$. For the $\mathbf{n} \neq 0$ part of the RS sum and the $\mathbf{k} \neq 0$ sum, we can easily see that both of these are zero, since there is always a term to cancel any given term in the sum. Then we need to focus on the $\mathbf{n} = 0$ term, which is

$$\lim_{r \rightarrow 0} \left[-\frac{\mathbf{p} \cdot \mathbf{r}}{r^2} \left(\frac{2\eta}{\sqrt{\pi}} e^{-\eta^2 r^2} + \frac{\text{erfc}(\eta r)}{r} \right) \right] \quad (53)$$

Expand the two terms inside the brackets, and we get

$$\begin{aligned} \lim_{r \rightarrow 0} \left[-\frac{\mathbf{p} \cdot \mathbf{r}}{r^2} \left(\frac{2\eta}{\sqrt{\pi}} (1 - \eta^2 r^2) + \frac{1}{r} - \frac{2\eta}{\sqrt{\pi}} + \frac{2\eta^3 r^2}{3\sqrt{\pi}} \right) \right] \\ = \lim_{r \rightarrow 0} \left[-\mathbf{p} \cdot \mathbf{r} \left(\frac{1}{r^3} - \frac{4\eta^3}{3\sqrt{\pi}} \right) \right] \end{aligned} \quad (54)$$

We have to subtract off the $1/r^2$ singularity, but when that is done, the other term goes to zero with r . Thus there is no self-term correction for the chg-dip part of the interaction. Note also that $(q_i \mathbf{p}_i - q_i \mathbf{p}_i)$ is 0, so maybe the above exercise was a waste.

Next consider the dip-dip term. After we grind through the derivatives and dot products for the $(\mathbf{p} \cdot \nabla)(\mathbf{p} \cdot \nabla)\psi$ operation, we get (we'll leave out the sum over dipoles and the factor of 1/2 for now):

$$\begin{aligned}
(\mathbf{p} \cdot \nabla)(\mathbf{p} \cdot \nabla)\psi &= \sum_{\mathbf{n}} \frac{-|p|^2}{|\mathbf{r} + \mathbf{n}L|^2} \left(\frac{2\eta}{\sqrt{\pi}} e^{-\eta^2|\mathbf{r} + \mathbf{n}L|^2} + \frac{\text{erfc}(\eta|\mathbf{r} + \mathbf{n}L|)}{|\mathbf{r} + \mathbf{n}L|} \right) \\
&+ \sum_{\mathbf{n}} \frac{[\mathbf{p} \cdot (\mathbf{r} + \mathbf{n}L)]^2}{|\mathbf{r} + \mathbf{n}L|^2} \left(\frac{4\eta^3}{\sqrt{\pi}} \right) e^{-\eta^2|\mathbf{r} + \mathbf{n}L|^2} \\
&+ \sum_{\mathbf{n}} \frac{3[\mathbf{p} \cdot (\mathbf{r} + \mathbf{n}L)]^2}{|\mathbf{r} + \mathbf{n}L|^4} \left(\frac{2\eta}{\sqrt{\pi}} \right) e^{-\eta^2|\mathbf{r} + \mathbf{n}L|^2} \\
&+ \sum_{\mathbf{n}} \frac{3[\mathbf{p} \cdot (\mathbf{r} + \mathbf{n}L)]^2}{|\mathbf{r} + \mathbf{n}L|^4} \frac{\text{erfc}(-\eta|\mathbf{r} + \mathbf{n}L|)}{|\mathbf{r} + \mathbf{n}L|} \\
&- \frac{4\pi}{L^3} \sum_{\mathbf{k} \neq 0} \frac{e^{-k^2/4\eta^2}}{k^2} e^{i\mathbf{k} \cdot \mathbf{r}} (\mathbf{p} \cdot \mathbf{k})^2
\end{aligned} \tag{55}$$

We will also use the theta transformation for $\mathbf{r} = 0$:

$$\frac{4\eta^3}{\sqrt{\pi}} \sum_{\mathbf{n}} e^{-\eta^2|\mathbf{n}L|^2} = \frac{4\pi}{L^3} \sum_{\mathbf{k}} e^{-k^2/4\eta^2} \tag{56}$$

which tells us that

$$\frac{4\eta^3}{\sqrt{\pi}} \sum_{\mathbf{n} \neq 0} e^{-\eta^2|\mathbf{n}L|^2} - \frac{4\pi}{L^3} \sum_{\mathbf{k} \neq 0} e^{-k^2/4\eta^2} = - \left(\frac{4\eta^3}{\sqrt{\pi}} - \frac{4\pi}{L^3} \right) \tag{57}$$

We will assume that the dipole vector lies on the x-axis, and that the approach of the distance vector $\mathbf{r} \rightarrow 0$ is perpendicular to that dipole direction. Now examine all the terms in the above sums by first separating out the $\mathbf{n} = 0$ term. Due to the assumption that the approach direction is perpendicular to the dipole direction, all of the terms in the sum drop out except the first (and putting in the correct sign now)

$$- \lim_{r \rightarrow 0} \frac{-|p|^2}{r^2} \left(\frac{2\eta}{\sqrt{\pi}} e^{-\eta^2 r^2} + \frac{\text{erfc}(\eta r)}{r} \right) = \frac{|p|^2}{r^3} - \frac{4\eta^3}{3\sqrt{\pi}} |p|^2 \tag{58}$$

For all of the rest of the terms, we just set $\mathbf{r} = 0$ and analyze the resulting sums. It looks to me like the terms

$$- \left(\frac{2\eta}{\sqrt{\pi}} \right) \sum_{\mathbf{n} \neq 0} \frac{|p|^2 |\mathbf{n}L|^2}{|\mathbf{n}L|^4} e^{-\eta^2 |\mathbf{n}L|^2} \tag{59}$$

and

$$\left(\frac{2\eta}{\sqrt{\pi}} \right) \sum_{\mathbf{n} \neq 0} \frac{3(\mathbf{p} \cdot \mathbf{n}L)^2}{|\mathbf{n}L|^4} e^{-\eta^2 |\mathbf{n}L|^2} \tag{60}$$

and the similar sums involving the erfc terms cancel. That leaves

$$\left(\frac{4\eta^3}{\sqrt{\pi}} \right) \sum_{\mathbf{n} \neq 0} \frac{(\mathbf{p} \cdot \mathbf{n}L)^2}{|\mathbf{n}L|^2} e^{-\eta^2 |\mathbf{n}L|^2} - \frac{4\pi}{L^3} \sum_{\mathbf{k} \neq 0} \frac{e^{-k^2/4\eta^2}}{k^2} (\mathbf{p} \cdot \mathbf{k})^2 \tag{61}$$

We can use the same trick to say that this expression is just

$$|p|^2 \left(\frac{4\eta^3}{3\sqrt{\pi}} \right) \sum_{\mathbf{n} \neq 0} e^{-\eta^2 |\mathbf{n}L|^2} - |p|^2 \left(\frac{4\pi}{3L^3} \right) \sum_{\mathbf{k} \neq 0} e^{-k^2/4\eta^2} \quad (62)$$

which yields

$$-\frac{4\eta^3}{3\sqrt{\pi}} |p|^2 + \frac{4\pi}{3L^3} |p|^2 \quad (63)$$

using our theta transformation trick above.

After we change to the correct (negative) sign again, then the final outcome for the dip-dip self energy is

$$\frac{|p|^2}{r^3} - \frac{4\pi}{3L^3} |p|^2 \quad (64)$$

We have to subtract off the first singular term and we're left with the second term. Thus for a system of charges and fixed dipoles, we get for the total electrostatic energy:

$$U = \frac{1}{2} \sum_{i \neq j} (q_i + \mathbf{p}_i \cdot \nabla_i) (q_j - \mathbf{p}_j \cdot \nabla_i) \psi(\mathbf{r}_{ij}) + \frac{\xi}{2L} \sum_i q_i^2 - \frac{2\pi}{3L^3} \sum_i |p_i|^2 \quad (65)$$

If we consider a system with fixed dipoles \mathbf{p}_i and induced dipoles \mathbf{d}_i , then the total energy includes the work to induce the dipoles also:

$$U = \frac{1}{2} \sum_{i \neq j} (q_i + (\mathbf{p}_i + \mathbf{d}_i) \cdot \nabla_i) (q_j - (\mathbf{p}_j + \mathbf{d}_j) \cdot \nabla_i) \psi(\mathbf{r}_{ij}) + \frac{\xi}{2L} \sum_i q_i^2 - \frac{2\pi}{3L^3} \sum_i |(\mathbf{p}_i + \mathbf{d}_i)|^2 + \frac{1}{2} \sum_i \frac{|\mathbf{d}_i|^2}{\alpha_i} \quad (66)$$

where α_i is the polarizability.

The final step in this is to try to relate this back to the discussion in Darden's paper. Also, we need to put in the 'molecular corrections' as in HPG. Darden and Linse have those corrections included. Finally, we need to get the proper ΔU for this case.

We can see that the final result above is exactly the same as Darden's result. We do this by taking the $i = j$ sums leading to the self energy and putting them back in the sums over i and j . We're left with the self term that came from the $\mathbf{n} = 0$ RS term. The final result is:

$$\begin{aligned} U &= \frac{1}{2} \sum_{i,j=1}^N (q_i + (\mathbf{p}_i + \mathbf{d}_i) \cdot \nabla_i) (q_j - (\mathbf{p}_j + \mathbf{d}_j) \cdot \nabla_i) \\ &\times \left\{ \sum_{\mathbf{n}}' \frac{\text{erfc}(\eta|\mathbf{r}_{ij} + \mathbf{n}L|)}{|\mathbf{r}_{ij} + \mathbf{n}L|} + \left(\frac{4\pi}{L^3} \right) \sum_{\mathbf{k} \neq 0} \frac{e^{-k^2/4\eta^2}}{k^2} e^{i\mathbf{k} \cdot \mathbf{r}_{ij}} \right\} \\ &- \frac{\pi}{2L^3 \eta^2} Q^2 - \frac{\eta}{\sqrt{\pi}} \sum_{i=1}^N q_i^2 \\ &- \frac{2\eta^3}{3\sqrt{\pi}} \sum_i |(\mathbf{p}_i + \mathbf{d}_i)|^2 + \frac{1}{2} \sum_i \frac{|\mathbf{d}_i|^2}{\alpha_i} \end{aligned} \quad (67)$$

This is precisely the same as Darden except for the omission of the intramolecular correction, and the fact that we allow for a net charge Q in the system.

4 One polarizable ion in water

Here we work out the case of one polarizable ion in water. Then there is no self-consistency step for the polarization. We'll just worry about calculating the energy change ΔU for two processes 1) charge change of the ion from $q + 0$ to q_1 and 2) polarizability change from α_0 to α_1 . We'll consider the ion to be the $N + 1$ particle.

The total electrostatic energy for this case is

$$\begin{aligned}
 U &= \frac{1}{2} \sum_{i \neq j}^{N+1} q_i q_j \psi(\mathbf{r}_{ij}) + \sum_{i=1}^N q_i \mathbf{d} \cdot \nabla_{N+1} \psi(\mathbf{r}_{i,N+1}) \\
 &\quad + \frac{\xi}{2L} \sum_{i=1}^{N+1} q_i^2 - \frac{2\pi}{3L^3} |\mathbf{d}|^2 + \frac{1}{2} \frac{|\mathbf{d}|^2}{\alpha}
 \end{aligned} \tag{68}$$

If we just change the charge state of the single ion, keeping the polarizability constant, we get back the same ΔU as we got before:

$$\Delta U = \Delta q \hat{\phi}(\mathbf{r}_i) + \frac{\xi}{2L} (q_1^2 - q_0^2) \tag{69}$$

Note that when we calculate a free energy, the sampling will change depending on the ion polarizability, so the free energy may depend on the chosen α , but not the ΔU for a given configuration.

Now what about if we keep the charge fixed but change the ion polarizability? Then the ion-ion interactions don't change, but the chg-dip, self, and charging terms do change:

$$\begin{aligned}
 \Delta U &= \sum_{i=1}^N q_i (\mathbf{d}_1 - \mathbf{d}_0) \cdot \nabla_{N+1} \psi(\mathbf{r}_{i,N+1}) \\
 &\quad - \frac{2\pi}{3L^3} (|\mathbf{d}_1|^2 - |\mathbf{d}_0|^2) \\
 &\quad + \frac{1}{2} \left(\frac{|\mathbf{d}_1|^2}{\alpha_1} - \frac{|\mathbf{d}_0|^2}{\alpha_0} \right)
 \end{aligned} \tag{70}$$

For this simple case $\mathbf{d} = \alpha \mathbf{E}_{N+1}$. I think the electric field at the $N + 1$ ion should look like

$$\mathbf{E}_{N+1} = - \sum_{i=1}^N q_i \nabla_{N+1} \psi(\mathbf{r}_{i,N+1}) + \frac{4\pi}{3L^3} \mathbf{d} \tag{71}$$

The first term is the field due to all the charges on the waters, and the second term is the field from all the image dipoles. This comes from the energy of interaction of the dipole with the field created by all the periodic images.

Since the induced dipole depends on the field at the ion, we can rearrange to get the net field as

$$\mathbf{E}_{N+1} = \left(\frac{4\pi\alpha}{3L^3} - 1 \right)^{-1} \sum_{i=1}^N q_i \nabla_{N+1} \psi(\mathbf{r}_{i,N+1}) \tag{72}$$

Then we can insert this formula in the above expression for ΔU to get

$$\Delta U = -\frac{1}{2} \left[\frac{\alpha_1}{(1 - 4\pi\alpha_1/3L^3)} - \frac{\alpha_0}{(1 - 4\pi\alpha_0/3L^3)} \right] \left(\sum_{i=1}^N q_i \nabla_{N+1} \psi(\mathbf{r}_{i,N+1}) \right)^2 \quad (73)$$

after some rearrangements. This has the appearance of a Clausius-Mossotti expression. We can see that, if we increase the polarizability, then ΔU becomes more negative. The last term is the square of the field of all the water charges at the location of the polarizable ion. That term should be available from the computation of the forces during the dynamics. Since the polarizability is of atomic size, and we divide by the system volume, the above expression should be very close to

$$\Delta U = -\frac{1}{2} [\alpha_1 - \alpha_0] \left(\sum_{i=1}^N q_i \nabla_{N+1} \psi(\mathbf{r}_{i,N+1}) \right)^2 \quad (74)$$

All of the ion-ion forces should be available from a standard MD code. We'll need to either use a polarizable code to do the dynamics or write our own code for the charge induced dipole forces between the waters and the polarizable ion. In these expressions we have a standard induced point dipole, and haven't included any Thole-type damping functions etc as discussed by Ren/Ponder (JPCB v. 107 p. 5933 2003, Xantheas (JPCA v. 110 p. 4100 2006), and Masia (JCP v. 128 p. 184107 2008). This may create problems with 'over-induced' dipoles (polarization catastrophe), or may not since we don't have a self-consistency step here. We should be careful to examine the induced dipole distributions for the ion as did Masia.

5 Total energy pieces

Let's go back to Eq. (66) for the total energy of a system of charges and permanent and induced dipoles. Here we'll assume there are no induced dipoles, just to simplify the notation. Consider the various parts of the total energy: chg-chg, chg-dip, and dip-dip.

The total energy is

$$U = \frac{1}{2} \sum_{i \neq j} (q_i + \mathbf{p}_i \cdot \nabla_i)(q_j - \mathbf{p}_j \cdot \nabla_j) \psi(\mathbf{r}_{ij}) + \frac{\xi}{2L} \sum_i q_i^2 - \frac{2\pi}{3L^3} \sum_i |\mathbf{p}_i|^2 + \frac{1}{2} \sum_i \frac{|\mathbf{p}_i|^2}{\alpha_i} \quad (75)$$

First let's look at the chg-dip interactions:

$$\frac{1}{2} \sum_{i \neq j} (q_j \mathbf{p}_i \cdot \nabla_i - q_i \mathbf{p}_j \cdot \nabla_j) \psi(\mathbf{r}_{ij}) \quad (76)$$

In the end I get for this contribution

$$\sum_{i \neq j} \left\{ \sum_{\mathbf{n}} \frac{q_i \mathbf{p}_j \cdot (\mathbf{r}_{ij} + \mathbf{nL})}{|\mathbf{r}_{ij} + \mathbf{nL}|^3} \left(\frac{2\eta}{\sqrt{\pi}} |\mathbf{r}_{ij} + \mathbf{nL}| e^{-\eta^2 |\mathbf{r}_{ij} + \mathbf{nL}|^2} + \text{erfc}(\eta |\mathbf{r}_{ij} + \mathbf{nL}|) \right) \right. \quad (77)$$

$$\left. + \left(\frac{4\pi}{L^3} \right) q_i \sum_{\mathbf{k} \neq 0} \frac{e^{-k^2/4\eta^2}}{k^2} [\sin(\mathbf{k} \cdot \mathbf{r}_{ij})] (\mathbf{p}_j \cdot \mathbf{k}) \right\} \quad (78)$$

For the dip-dip interactions, I get

$$\frac{1}{2} \sum_{i \neq j} \left\{ \sum_{\mathbf{n}} \left[\frac{\mathbf{p}_i \cdot \mathbf{p}_j}{|\mathbf{r}_{ij} + \mathbf{n}L|^3} \left(\frac{2\eta}{\sqrt{\pi}} |\mathbf{r}_{ij} + \mathbf{n}L| e^{-\eta^2 |\mathbf{r}_{ij} + \mathbf{n}L|^2} + \operatorname{erfc}(\eta |\mathbf{r}_{ij} + \mathbf{n}L|) \right) \right] \right. \quad (79)$$

$$\left. - \frac{3(\mathbf{p}_i \cdot (\mathbf{r}_{ij} + \mathbf{n}L))(\mathbf{p}_j \cdot (\mathbf{r}_{ij} + \mathbf{n}L))}{|\mathbf{r}_{ij} + \mathbf{n}L|^5} \times \quad (80)$$

$$\left(\frac{4\eta^3}{3\sqrt{\pi}} |\mathbf{r}_{ij} + \mathbf{n}L|^3 e^{-\eta^2 |\mathbf{r}_{ij} + \mathbf{n}L|^2} + \frac{2\eta}{\sqrt{\pi}} |\mathbf{r}_{ij} + \mathbf{n}L| e^{-\eta^2 |\mathbf{r}_{ij} + \mathbf{n}L|^2} + \operatorname{erfc}(\eta |\mathbf{r}_{ij} + \mathbf{n}L|) \right) \Big] \quad (81)$$

$$\left. + \left(\frac{4\pi}{L^3} \right) \sum_{\mathbf{k} \neq 0} \frac{e^{-k^2/4\eta^2}}{k^2} e^{i\mathbf{k} \cdot \mathbf{r}_{ij}} (\mathbf{p}_i \cdot \mathbf{k})(\mathbf{p}_j \cdot \mathbf{k}) \right\} \quad (82)$$

This gives the total energy in a form which can be used to insert the damping factors used by Thole (see below for the induced dipole contributions).

6 Another form for the total energy

Let's look at the total energy again, but now take the case where there are charges and induced dipoles, but no permanent multipole moments. We can extend this easily to include the electrostatic field from the permanent multipole moments also. The total energy is

$$U = \frac{1}{2} \sum_{i \neq j} (q_i + \mathbf{d}_i \cdot \nabla_i)(q_j - \mathbf{d}_j \cdot \nabla_j) \psi(\mathbf{r}_{ij}) + \frac{\xi}{2L} \sum_i q_i^2 - \frac{2\pi}{3L^3} \sum_i |\mathbf{d}_i|^2 + \frac{1}{2} \sum_i \frac{|\mathbf{d}_i|^2}{\alpha_i} \quad (83)$$

We follow Xantheas (JCP 110, 4566, 1999) and rearrange this expression by inserting $\mathbf{d}_i = \alpha_i \mathbf{E}_i^{\text{tot}}$ into the last term (the energy to induce the dipoles). When we make that substitution, we get a very simple form for the total energy

$$U = U^{cc} + \frac{1}{2} \sum_{i \neq j} q_j \mathbf{d}_i \cdot \nabla_i \psi(\mathbf{r}_{ij}) = U^{cc} - \frac{1}{2} \sum_{i \neq j} q_j \mathbf{d}_i \cdot \mathbf{E}_i^c(\mathbf{r}_i) \quad (84)$$

where U^{cc} is the usual chg-chg interaction energy and $\mathbf{E}_i^c(\mathbf{r}_i)$ is the field at the site i due to all the other fixed charges (sum over j).

Here we assumed that the field at the site i is just due to all the other charges, but that field could also include the field due to permanent dipoles, quadrupoles etc. That is what Ren and Ponder have in their AMOEBA paper – it's why they have only terms involving dot products of induced and permanent dipoles etc., and no induced dip-induced dip dot products. (Notice the dipole self energy goes away.) Xantheas calls the term $-\frac{1}{2} \sum_{i \neq j} q_j \mathbf{d}_i \cdot \mathbf{E}_i^c(\mathbf{r}_{ij})$ the polarization energy, which is always negative. Xantheas calls the work to induce the dipoles the induction energy. I think Stone calls the Xantheas's polarization energy the induction energy, so the terminology seems a bit confused in the literature. Notice that the dispersion energy is an entirely different quantum mechanical object involving induced dipoles.

The formula I got above for ΔU for changing the polarizability for the case of a single polarizable ion above falls out easily from the expression above.

7 Thole damping

According to Ren and Ponder, a damping term should be inserted into the real-space part of the interaction. For this chg-dip term they call this damping factor λ_3 :

$$\lambda_3 = 1 - \exp(-au^3) \quad (85)$$

where a is a constant taken as 0.39 by Ren/Ponder, and

$$u = r_{ij}/(\alpha_i\alpha_j)^{1/6} \quad (86)$$

Then we get

$$\sum_{i \neq j} \left\{ \lambda_{3,ij} \sum_{\mathbf{n}} \frac{q_i \mathbf{p}_j \cdot (\mathbf{r}_{ij} + \mathbf{n}L)}{|\mathbf{r}_{ij} + \mathbf{n}L|^3} \left(\frac{2\eta}{\sqrt{\pi}} |\mathbf{r}_{ij} + \mathbf{n}L| e^{-\eta^2 |\mathbf{r}_{ij} + \mathbf{n}L|^2} + \operatorname{erfc}(\eta |\mathbf{r}_{ij} + \mathbf{n}L|) \right) \right. \quad (87)$$

$$\left. + \left(\frac{4\pi}{L^3} \right) q_i \sum_{\mathbf{k} \neq 0} \frac{e^{-k^2/4\eta^2}}{k^2} [\sin(\mathbf{k} \cdot \mathbf{r}_{ij})] (\mathbf{p}_j \cdot \mathbf{k}) \right\} \quad (88)$$

for the chg-dip interactions with the damping.

Putting in the damping for the dip-dip interactions, we get

$$\frac{1}{2} \sum_{i \neq j} \left\{ \sum_{\mathbf{n}} \left[\frac{\lambda_{3,ij} \mathbf{p}_i \cdot \mathbf{p}_j}{|\mathbf{r}_{ij} + \mathbf{n}L|^3} \left(\frac{2\eta}{\sqrt{\pi}} |\mathbf{r}_{ij} + \mathbf{n}L| e^{-\eta^2 |\mathbf{r}_{ij} + \mathbf{n}L|^2} + \operatorname{erfc}(\eta |\mathbf{r}_{ij} + \mathbf{n}L|) \right) \right. \right. \quad (89)$$

$$\left. - \frac{3\lambda_{5,ij} (\mathbf{p}_i \cdot (\mathbf{r}_{ij} + \mathbf{n}L)) (\mathbf{p}_j \cdot (\mathbf{r}_{ij} + \mathbf{n}L))}{|\mathbf{r}_{ij} + \mathbf{n}L|^5} \times \right. \quad (90)$$

$$\left. \left(\frac{4\eta^3}{3\sqrt{\pi}} |\mathbf{r}_{ij} + \mathbf{n}L|^3 e^{-\eta^2 |\mathbf{r}_{ij} + \mathbf{n}L|^2} + \frac{2\eta}{\sqrt{\pi}} |\mathbf{r}_{ij} + \mathbf{n}L| e^{-\eta^2 |\mathbf{r}_{ij} + \mathbf{n}L|^2} + \operatorname{erfc}(\eta |\mathbf{r}_{ij} + \mathbf{n}L|) \right) \right] \quad (91)$$

$$\left. + \left(\frac{4\pi}{L^3} \right) \sum_{\mathbf{k} \neq 0} \frac{e^{-k^2/4\eta^2}}{k^2} e^{i\mathbf{k} \cdot \mathbf{r}_{ij}} (\mathbf{p}_i \cdot \mathbf{k}) (\mathbf{p}_j \cdot \mathbf{k}) \right\} \quad (92)$$

where

$$\lambda_5 = 1 - (1 + au^3) \exp(-au^3) \quad (93)$$

8 Corrections for the molecular ion case

Finally, we add in the corrections to the total energy from removing the solute intramolecular energies from the total electrostatic energy. This follows HPG (1998). This won't be an issue if we have one monatomic polarizable ion, but will be necessary if we have a molecular ion like NO_3^- .

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