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Monte Carlo calculations for the restricted primitive model at a point in the molten salt region have been made using a variety of summation methods. The empirical conclusion is that the Ewald summation is an excellent method for this work. It is shown that it does not produce significantly anisotropic pair distributions. It is shown that unlike some of the other methods considered it does not have a systematic bias towards lower energy for some configurations. It is argued that the shape of its effective pair potential does not lead to distortion of the melt structure. However, an *approximate* form of the Ewald summation is shown to produce significant distortions of the melt structure for the case examined.

I. INTRODUCTION

It seems unavoidable in computer simulation by Monte Carlo and molecular dynamics that periodic boundary conditions must be used if surface effects are to be avoided and the bulk phase simulated. It is then un-avoidable that while the particles, periodically repeated around the central cell, extend to infinity, the interactions between pairs of particles must be truncated at some finite separation. If the pair potential is short ranged or falls rapidly to zero this is not a problem, though a tail correction may be needed. However, charged and dipolar systems pose a special problem, not only does the potential fall slowly with separation but it is for some properties essentially infinitely ranged.

An attractive solution to the problem is to make use of the periodicity of the simulation to reorder the summation into two rapidly convergent sums over real space and reciprocal lattice space, both of which may be truncated with minimal error. For the $1/r$ potential, this is the Ewald sum, which has been universally used for the simulation of molten salts.[1] The Ewald method gives a summation that is not only infinite but boundless in that it has no surface, even at infinity, but is electrically closed on itself: the infinite sphere in a perfect conductor.[2]

With computer simulation there is always the possibility that the periodicity, or the finite size, or the cell shape produces a distortion and that the true properties of the bulk fluid are somewhat different. This is a particularly serious possibility for dense ionic systems, because the range of the potential is always substantially larger than the cell size, and because the emphasis which the Ewald method places on the periodicity makes it particularly susceptible to suspicion. Indeed Valleau[3,4] has suggested that the Ewald method leads to gross distortions of the melt structure, and has given three reasons to suppose this. First, he points out that the long-range correlations between dipole moment fluctuations in one region and another are completely different with periodic boundary conditions to what one would expect in ordinary material. Second, the effective pair potential between two ions is flattened, as compared to the bare $1/r$ potential, and this he suggests[4] "... will tend to pull counterions towards the edge of the box, push coions towards the center ..., and no doubt distorts

the short-range structure." Third, the effective pair potential is not radially symmetric, so "... there will be a strong tendency to sweep counterions towards the principal axes, and coions towards the diagonals. This may lead to markedly anisotropic distributions ... ."

The third of these points can be tested quite easily and results are presented in this paper which show that any anisotropy of this form is very small. The first criticism, that the long-range correlations are wrong, is more easily pursued for dipolar systems than for those with free charges. A comparison of results from Ewald and reaction-field calculations for the dipolar Stockmayer potential fluid showed no marked differences,[5] suggesting that the effect on the short-range structure is small.

Even if the Ewald summation were perfect, a positive proof that it is so does not seem possible, one can only accumulate evidence and make reasonable inferences. But though an invaluable device, periodic boundary conditions are not perfect. Even if one could dismiss the accusation that the Ewald sum gives a gross distortion of the melt structure, as has been attempted,[6,7] the question still remains as to how large are the distortions in a small periodic volume with an Ewald sum? Some new calculations are presented, on the basis of which it is concluded that for molten salt simulations the distortions in the radial distribution functions are negligible, at least for a system as large as 512 ions.

II. THE MONTE CARLO CALCULATIONS

Following earlier work[6,7] the restricted primitive model (RPM) has been used. This has the pair potential (in SI units):

$$\phi_{ij}(r) = \begin{cases} \infty , & r < \sigma , \\ e^2 Z_i Z_j/(4\pi\epsilon_0 \epsilon r) , & r \geq \sigma , \end{cases} \quad (1)$$

and is completely specified by two parameters, the packing fraction $\eta \equiv \pi N \sigma^3/6V$ and the Coulombic coupling parameter $\Gamma = 2\eta^{1/3} q$, where $q = (Ze)^2/(4\pi\epsilon_0 \epsilon k T \sigma)$. N/V is the number density, ϵ_0 the permittivity of free space, ϵ the relative permittivity of the continuum between the ions (identically one for a molten salt), and kT Boltzmann's constant times absolute temperature. Once again the parameter values $\Gamma = 50.0$ (or $q = 35.48$) and $\eta = 0.3503$ have been used following the article by

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TABLE I. — U/NkT as calculated by various methods for various configurations.

Source of configuration	Full Ewald	Approx. Ewald	Nearest image	SC0	SC2
NaCl lattice	27.11	23.50	27.17	27.02	27.18
CsCl lattice ($N = 686$)	25.07	22.14	5.82	24.65	24.88
Full Ewald MC	26.40	26.42	26.61	26.72	26.62
Approx. Ewald MC	26.26	27.28	26.49	26.74	26.55
Nearest image MC	24.45	25.77	38.02	24.56	24.42
SC0 MC	26.39	26.47	26.51	27.57	27.19
SC2 MC	26.44	26.56	26.44	27.37	27.05

Valleau and Whittington,[3] which quoted this particular point, taken from the work of Larsen,[8] as an example of a case where they believed that Ewald method might be seriously in error. It is in the molten salt regime. All but one of the Monte Carlo calculations reported here are new. Some are repeats of earlier work[6,7] and in such cases, greater care has been taken over the equilibration. All runs were for half a million steps after equilibration.

The simple method of spherical cutoff (SC), counting only those ions within a given radius (usually half the cell length), is convenient for short-range potentials but totally unsuitable for the $1/r$ potential, as all are agreed.[3,4,6] Its major deficiency can be removed by an electroneutrality correction, a charge distribution equal and opposite to the total net charge in the truncation sphere of each ion is placed at the surface of the truncation sphere. This satisfies the Stillinger–Lovett zero-moment condition and will be referred to as SC0. It has been found to be very size dependent, but at $N = 512$ gave radial distribution functions similar to those from an Ewald calculation.[6] Valleau[4] has pointed out that the effective pair potential of the SC0 method is similar to that of the Ewald sum in that it is flat in the corners of the periodic cell and so the similarity of the radial distribution functions proves nothing.

A more sophisticated correction may be made by assigning charge distributions around the truncation sphere of each ion such that both the zero moment and second moment conditions are satisifed. This will be referred to as the SC2 method, and is described in the Appendix. The radial distribution functions produced by SC2 with 512 ions in the periodic cube have been shown to be very close to those from an Ewald summation, though the method is as number dependent as SC0.[7] Though the effective potential of SC2 is not $1/r$ within the truncation radius, it is also flat outside and therefore the criticism of SC0 given above is equally applicable. This point is discussed in the next section.

Some approximations to the Ewald summation have been reported recently,[9–12] all replace the full Ewald sum with an effective pair potential which is radially symmetric. One calculation is reported here using Soule's original approximation to the Ewald sum[10]:

$$\phi_{ij}(r)/kT = \begin{cases} q z_i z_j \sigma \, \mathrm{erfc}(r/0.35L)/r \, , & r \leqslant 0.5L \, , \\ 0 \, , & r > 0.5L \, , \end{cases} \quad (2)$$

$$\phi_i/kT = -q\sigma/(\sqrt{\pi}\, 0.35L) \, ,$$

where r is the nearest-image distance between ions i and j, $z_i = Z_i/|Z_i|$, erfc is the complementary error function and L is the cell length. ϕ_i is the "self-term" of ion i which is a constant term to be added to the total energy.

The nearest-image summation (NI) sums $Z_i Z_j/r$ over the cube, centered on ion i of the nearest images of every other ion j. It resembles the Evjen method for computing the Madelung constant, and is favored by Valleau because "... the pair potentials are correct throughout the box."[4] It suffers from a severe practical disadvantage at molten salt densities, and this is discussed in the next section.

III. RESULTS AND DISCUSSION

The various summation methods described have been applied to some individual configurations, mostly of $N = 512$ ions in total, and the results are given in Table I. Results from individual configurations are significant because $-U/NkT$ is large and the variations of the energy of individual configurations about the ensemble average are proportionally small.

The spectacular failure of NI to give the correct lattice energy for CsCl deserves special comment. Only configurations of $2n^3$ ions, where n is an integer, can be fitted into a periodic cube using CsCl packing. NI gives $U/NkT \sim -5.9$ when n is odd and ~ -44.4 when n is even. The average of these two is close to the correct value of -27.065. Evidently, it is not sufficient to sum over an electrically neutral region, no matter how large, in order to obtain the correct value for the lattice energy, and one cannot be confident that the NI method will always be even approximately correct.

The large value of $-U/NkT$ given by the NI method for a configuration generated by long equilibration using NI is a well-known effect,[3,4,13–15] sometimes described as a "convergence problem."[4] It has been explained in terms of the shape of the periodic cell.[6] The lowest interaction energy between two coions is found when each is in a corner of the nearest-image cube of the other. This bias in favor of certain special positions, i.e., in the cube corners, rather than the perfect radial symmetry of a real isotropic liquid, operates on every pair of like ions and it is therefore understandable that Brush, Sahlin, and Teller[13] found a marked tendency for simple cubic structures when they used NI summation

TABLE II. Anisotropy of coion and counterion distributions in a cubic periodic cell.

	$\langle D \rangle_{\text{coions}}$	$\langle D \rangle_{\text{counterions}}$
NaCl lattice	0.0174	−0.0374
CsCl lattice ($N = 686$)	0.0063	0.0927
Full Ewald MC	−0.0010	0.0005
Approx. Ewald MC	−0.0001	0.0019
NI MC	0.0075	0.0180

for the one component plasma. The effect is dependent on both the size and shape of the periodic cell and requires the pair potential to be substantial and distance dependent out into the corners of the periodic cell. The flattened shape of the effective potentials of all the other methods considered here has the fortunate effect of suppressing the cube-corner effect. Hoskins and Smith[16] implemented a version of a Ewald sum which was not flattened into the corners and had some difficulties with their small system of 64 ions. However, their implementation of the Ewald summation for an infinite sphere in a vacuum has been criticized on other grounds,[17] and it has been shown that for 216 ions both versions of the Ewald summation produce the same melt structures but different electrical properties.[17] Only the infinite sphere in a perfect conductor version is considered here.

Returning to Table I, we find that in other cases the NI method gives good agreement with the full Ewald method, indeed as close or closer in every case than the SC0 and SC2 values. Any method for calculating the energy of a configuration will, in the course of a Monte Carlo run, tend towards configurations which it estimates to be of low energy, and comparison with other methods will show up this bias. Thus, the approximate Ewald method underestimates both lattice energies, agrees well with the full Ewald method for liquid configurations produced by the full Ewald, SCO and SC2 methods, and is ~ 1/2 to 1 kT per particle lower for the configurations produced by itself, as compared to all other methods. To a lesser extent, the SC0 and SC2 methods also give lower energies for configurations of their own generation, but the Ewald method does not, which we may take as evidence that it has no systematic bias.

Rather than obtaining angle dependent distribution functions as a test for anisotropy,[18] it has been quantified by the Monte Carlo average of $D(\mathbf{r}'_{ij})$ averaged over all pairs of particles i and j, where $\mathbf{r}'_{ij}$ is the vector joining their nearest images, for which $|\mathbf{r}'_{ij}| \le L/2$, half the cell length, and where

$$D(\mathbf{r}) = \frac{9}{26}\left(105\,\frac{x^2 y^2 z^2}{|\mathbf{r}|^6} - 1\right) \qquad (3)$$

and $\mathbf{r} \equiv (x, y, z)$. When the vectors $\mathbf{r}$ are evenly distributed in all directions $\langle D(\mathbf{r})\rangle = 0$. When $\mathbf{r}$ is pointing to a cube corner $D(\mathbf{r}) = 1$, its maximum value, and when $\mathbf{r}$ is parallel to either the X, Y, or Z axis it has its minimum value of $-9/26 \simeq -0.346$. The results obtained are given in Table II. The averages obtained with the

full Ewald summation, which has an anisotropic effective pair potential, are not identically zero but they are very small and of the opposite sign to that expected.[4] While periodic boundary conditions will produce anisotropy even with a spherically truncated short-ranged potential if N is small enough,[18] there is no evidence to suppose that the Ewald summation has a substantial extra effect of the sort suggested by Valleau.[4]

The effective pair potentials for a cube of 512 ions and the parameters given in Sec. II are plotted in Fig. 1. Only the full Ewald potential is angle dependent and Fig. 1 shows the two extremes along a principal axis and along a cube diagonal. There are extra terms of −12.01 and −6.25 per ion to be added to the full and approximate Ewald sums, respectively. Note that in shape the SC2 potential is extremely close to the diagonal Ewald curve for $r < L/2$ and is a closer fit to either of the Ewald curves than is the approximate Ewald potential.

It is hardly surprising, therefore, that the Ewald and SC2 methods give such similar radial distribution functions in this case, and it could be argued that the fact that they do is therefore not real evidence in support of the Ewald method. However, it would be surprising indeed to find that two *different* potentials gave the same structure. The SC2 method is an approximation based on the requirements that the system as a whole is electrically neutral and that the charge distribution around each ion has the same constant second moment at all times. It does not assume that the system is periodic. The Ewald summation, on the other hand, is entirely based on the periodicity of the system and does not necessarily satisfy the second moment condition.[19] That such different arguments lead to such similar po-
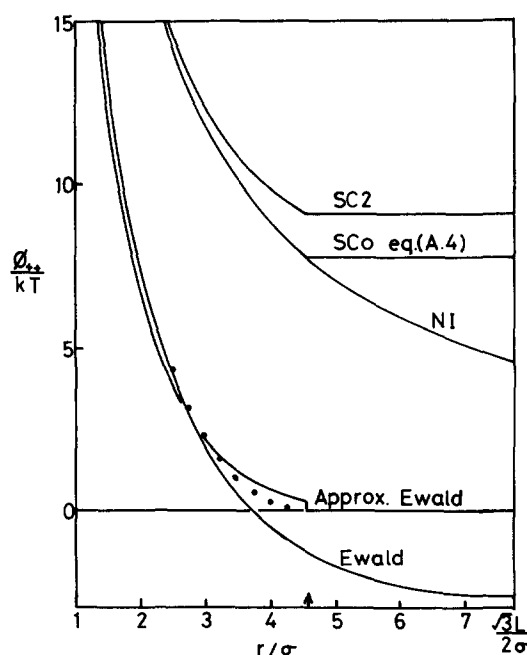

FIG. 1. Pair potentials and effective pair potentials divided by kT. The line marked "Ewald" is the effective pair potential along a cube diagonal, and the dots mark the effective Ewald pair potential along a principal axis. The arrow marks $r = L/2$.
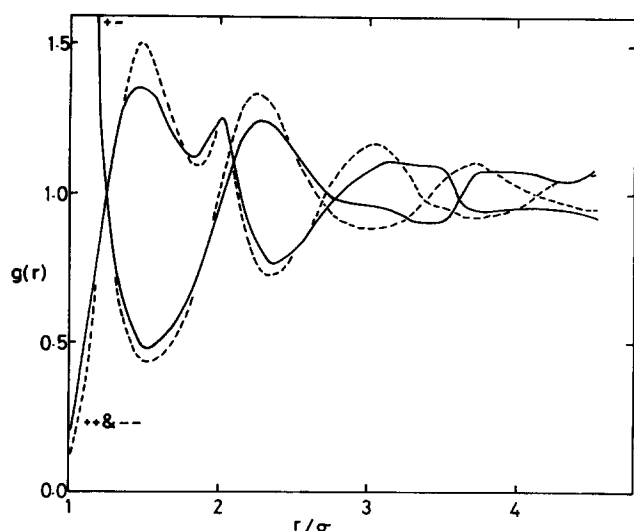
FIG. 2. Radial distribution functions found using the approximate Ewald potential Eq. (2) (full lines), compared with those found using the full summation (dashed lines). A smooth line has been drawn through the Monte Carlo results in each case.

tentials should rather be taken as evidence in their favor.

Figure 2 compares the radial distribution functions using the approximate Ewald potential Eq. (2) with those from the full Ewald summation. The approximation results in a distortion of the melt structure which is large enough to be worrying. It does not follow that time-saving approximations will necessarily lead to incorrect results for glassy systems, but it does show that some care is necessary in their choice. For accurate work, the extra cost of a full Ewald summation, approximately 40% extra computing time in the present case, may be justified.

The SC0 method also leads to substantial deviations in melt structure compared with the Ewald summation. However, it has not been seriously suggested that this method be used in place of the Ewald sum.

The SC2 and Ewald methods lead to very similar but not identical distribution functions. As a final test, both methods have been used with truncated octahedral (TO) boundary conditions[20] with $N = 864$ ions. Table III is a compilation of all the Monte Carlo results. The ensemble average energy using the Ewald sum is the same (within the statistical errors) for the two cell shapes. Because with the SC2 method a larger truncation radius could be used with the larger system, the ensemble average energy shows a significant difference between the two cell shapes, and the larger system gives a result remarkably close to the Ewald one. Note that the contact term $g_{+-}(\sigma)$ and $g_{++}(\sigma)$ vary more with the size and shape of the system than with the summation method. This rather odd result may simply be a reflection of the inherent inaccuracy of the extrapolation to contact, which requires extrapolation of data which is steeply varying and which contains statistical fluctuations. It would be much better, when pressure is required as accurately as possible, to avoid such extrapolation altogether by using constant pressure Monte Carlo.[21]

The radial distribution functions obtained using the

Ewald summation with cube and TO boundary conditions were very close and for the most part the same within the statistical fluctuations, including close to the $L/2$ limit of the smaller system. The largest difference was for $g_{+-}(r)$ close to the second minimum ($r \sim 2.9\sigma$) where for TO boundary conditions it was ~ 0.05 lower.

The two sets of radial distribution functions obtained using SC2 were fairly close. The cube $g_{+-}(r)$ was ~ 0.05 higher at the second maximum ($r \sim 2.3\sigma$) and was ~ 0.05 lower close to $L/2$ ($r \sim 4.6\sigma$). Larger differences were evident in the coion $g(r)$ ($g_{++}(r)$ is the same as $g_{--}(r)$ apart from statistical fluctuations) beyond $\sim 2\sigma$, the peaks and troughs occurring at larger r for the cube. The coion $g(r)$ was also too large by ~ 0.1 close to $L/2$.

Both sets of TO boundary condition radial distribution functions are shown in Fig. 3. Though they are not identical, the two sets are certainly close. The coion $g(r)$ first peaks showed large statistical fluctuations and it is not certain that the difference between the two smoothed curves is statistically significant.

IV. FINAL REMARKS

Small periodic systems, particularly at high density, cannot be identical to truly infinite systems. Pratt and Haan[22] have recently developed theoretical tools for investigating the distortions of periodicity. The present work is a purely empirical study of the special case of long-range forces, which even for relatively large systems ($N = 512$) can give problems, as has been shown, if an unsuitable summation method is used.

There are two complications to the Ewald summation that have not been dealt with here. First, an extra term can be added to the Ewald expression. This arises from the replacement of the medium at infinity, which has infinite dielectric constant (i.e., a perfect conductor), with a medium of some specified finite dielectric constant.[2] For a sufficiently large periodic system this term should have no effect on the thermodynamic properties and the available evidence[17] is that its effects are slight even for $N = 216$. However, the effect of the extra term on other properties, such as dielectric response and electrical conductivity, can be profound. This is perfectly understandable: the thermodynamic

TABLE III. Monte Carlo results. For a cube cell there were a total of 512 ions, while 864 were used in the truncated octahedron (TO).

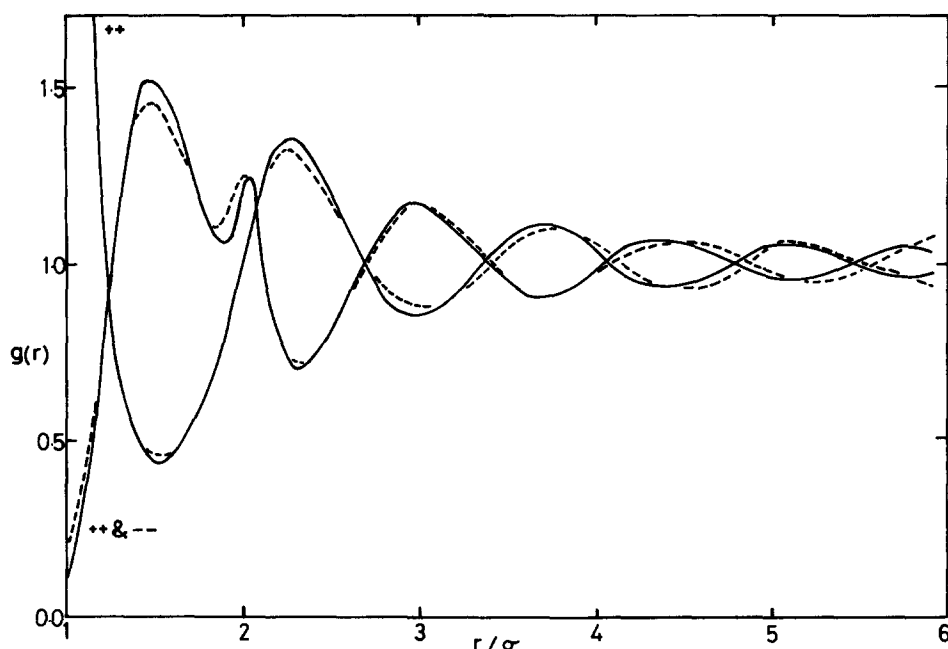| Method	Cell shape	$-\langle U/Nk_BT \rangle$	$g_{+-}(\sigma)$	$g_{++}(\sigma)$
Full Ewald	Cube	26.46	11.4	0.14
Full Ewald	TO	26.52	13.6	0.07
SC2[a]	Cube	26.98	12.2	0.14
SC2	TO	26.68	13.3	0.06
SC0	Cube	27.56	11.4	0.14
Approx. Ewald	Cube	27.17	12.1	0.17
NI	Cube	37.99	7.7	0.5

[a]Reference 7.

FIG. 3. Radial distribution functions found using truncated octahedral boundary conditions with 864 ions in the cell. The full lines are for the Ewald summation and the dashed lines SC2. Smooth lines have been drawn through the Monte Carlo results in each case.

properties of, say, a polar liquid will be the same in a glass or a metal container but its polarization in response to an applied field (as distinct from its dielectric constant) will be different. The experimenter must bear the container in mind, and the computer simulator must be aware of the implications of the presence or absence of the extra term in the Ewald expression.

Second, the accuracy with which the Ewald summation is calculated can have a bearing on the results obtained. Significantly different results have been obtained[23] in the location of the solid/liquid phase transition of the one component plasma when a very accurate Ewald summation has been used, as compared with earlier less precise calculations. An accurate Ewald summation is essential to the investigation of dielectric properties.[24] However, it is broadly true that the thermodynamic and structural results obtained are not sensitive to the truncation of the Ewald summation, provided that the truncation is not as gross as that of Eq. (2).

Together with previously published evidence,[6,7] the present results make a very strong case for believing that the Ewald summation is an excellent method for the simulation of charged systems such as molten salts. Why it should be so is still not quite understood.

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APPENDIX: THE SC0 AND SC2 EFFECTIVE PAIR POTENTIALS

The Stillinger–Lovett moment conditions[25] in the units of Sec. II are

$$\frac{3\eta}{\pi} \int_0^\infty [g_{++}(r) - g_{+-}(r)]\,dr = -1 \tag{A1}$$

and

$$\frac{3\eta}{\pi} \int_0^\infty [g_{++}(r) - g_{+-}(r)]\,r^2\,dr = -\sigma^2/(4\eta q)\ . \tag{A2}$$

The SC0 method satisfies Eq. (A1) by placing a charge at the truncation radius R_T, which exactly cancels the total charge inside. The effective pair potential is then

$$\phi_{ij}^{SC0}(r)/kT = \begin{cases} \infty\ , & r < \sigma\ , \\ q\,z_i z_j\,\sigma(1/r - 1/R_T)\ , & \sigma < r < R_T\ , \\ 0\ , & r \geqslant R_T\ , \end{cases} \tag{A3}$$

with an additional term $-q\sigma/R_T$ for each ion independent of its position. Thus, SC0 is little more than a "shifted potential," commonly used in molecular dynamics with short-ranged potentials. Valleau[4] has pointed out that the $-q\sigma/R_T$ term can be incorporated into the pair potential, giving a potential identical to the bare Coulomb potential for $r < R_T$.

The SC2 method satisfies both Eqs. (A1) and (A2) by placing a second charge at $2R_T$, a position chosen quite arbitrarily, plus an equal and opposite charge at R_T. Then the correction to the energy of ion i, in addition to the SC0 correction of Eq. (A3) is

$$z_i q\,\frac{\sigma}{6}\sum_{j,\,R_j < R_T} z_j\left(\frac{R_j^2}{R_T^3} - \frac{1}{R_T}\right) - \frac{q\sigma}{6R_T} + \frac{z_i\sigma^3}{24\eta R_T^3}\ , \tag{A4}$$

where $R_j = |\,\mathbf{r}_j - \mathbf{r}_i\,|$. Note that the final term, which arises from the right-hand side expression of Eq. (A2) will cancel when summed over all ions i. Incorporating the term $-q\sigma/6R_T$ into the pair potential as before, produces the effective SC2 potential:

$$\phi_{ij}^{SC2}(r)/kT = \begin{cases} \infty\ , & r < \sigma\ , \\ q\,z_i z_j\,\sigma[1/r + r^2/(6R_T^3)]\ , & \sigma \leqslant r < R_T\ , \\ q\,z_i z_j\,\sigma 7/(6R_T)\ , & r > R_T\ . \end{cases} \tag{A5}$$

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