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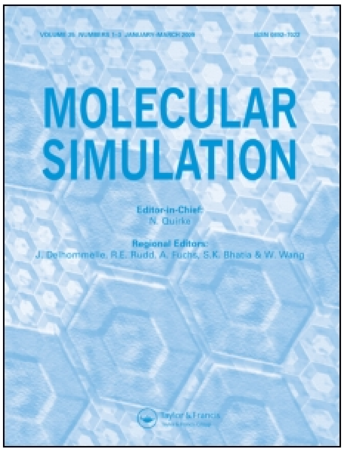

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EWALD SUMMATION IN THE MOLECULAR DYNAMICS SIMULATION OF LARGE IONIC SYSTEMS: THE COHESIVE ENERGY

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The accuracy and efficiency of the direct Ewald summation are discussed in terms of the size of a Molecular Dynamics (MD) ionic system and the ranges of the r-space and q-space summations. The dependence of the convergence parameter α on the size of the system and on the choice of cut-off radius for the short-range potential is given. The possibility of neglecting the q-space term for large ionic systems is discussed in terms of the accuracy and efficiency of the simulation.

KEY WORDS: Ewald summation, Molecular Dynamics, ionic systems

1 INTRODUCTION

In the paper we consider the accuracy and efficiency of the Ewald summation in a Molecular Dynamics (MD) simulation in terms of the size of the system and the cut-off radius R_c. We particularly focus our attention on large ionic systems, the simulation of which will play an important role in the future.

Let us consider a neutral charged system of N ions contained in a cube the side of which is of length L. We call this the origin cell, located at $\mathbf{n} = (0, 0, 0)$. The distance between a pair of ions i-j inside this cell is $r_{ij} = |\mathbf{r}_j - \mathbf{r}_i|$. Because of the slow convergence of the electrostatic potential it is necessary to include in its calculation not only the interactions between the ions from the origin cell but also the interactions of the ions from this cell with those contained in the image cells $\mathbf{n}$. The image cells are located at $L\mathbf{n}$, and the distance between an ion from the origin cell (r_i) and another from the image cell $\mathbf{n}(\mathbf{r}_{jn})$ is equal to $r_{i,jn} = |\mathbf{r}_{jn} - \mathbf{r}_i|$. The total coulombic energy of such a system (including the interactions with image particles) is given by [1]

$$\Phi^c = \frac{1}{2}\sum_{ij}^{N}{}' \sum_{\mathbf{n}} \frac{Z_i Z_j}{r_{i,jn}} \tag{1}$$

where Z_i, Z_j are ionic charges and the prime in the first sum denotes the omission of terms with $i = j$ when $\mathbf{n} = (0, 0, 0)$. Ewald [2] showed that the slowly convergent

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series (1) can be replaced by two rapidly convergent series, one in real space and the other in reciprocal space (q-space), so that

$$\Phi^c = \Phi^r + \Phi^q + \Phi^0 \tag{2}$$

with the r-space term,

$$\Phi^r = \frac{1}{2}\sum_{i,j}^{N}{}' \sum_{\mathbf{n}} Z_i Z_j \frac{\operatorname{erfc}(\alpha r_{i,j\mathbf{n}})}{r_{i,j\mathbf{n}}} \tag{3}$$

the q-space term,

$$\Phi^q = \frac{2\pi}{L^3}\sum_{i,j}^{N} Z_i Z_j \sum_{\mathbf{q}}{}' A(q)\cos(\mathbf{q}\cdot\mathbf{r}_{ij}) \tag{4}$$

and constant term,

$$\Phi^0 = -\frac{\alpha}{\sqrt{\pi}}\sum_{i=1}^{N} Z_i^2 \tag{5}$$

The factor $A(q)$ is

$$A(q) = \frac{1}{q^2}\exp\left(-\frac{q^2}{4\alpha^2}\right) \tag{6}$$

and $\operatorname{erfc}(x)$ denotes the complementary error function,

$$\operatorname{erfc}(x) = 1 - \frac{2}{\sqrt{\pi}}\int_0^x e^{-u^2}\,\mathrm{d}u \tag{7}$$

α is the Ewald convergence parameter, $\mathbf{q}$ is a reciprocal space vector (i.e., for a cubic cell of side L, $\mathbf{q} = (2\pi/L)(k,l,m)$, with k,l,m integers), $q = |\mathbf{q}|$ and the prime in Equation (4) denotes that $\mathbf{q} \neq (0, 0, 0)$. The constant term (5) does not play a practical role in MD simulations since it gives zero contribution to the forces; however its contribution to the energy is significant and it has to be taken into account in order to get the correct value of the energy.

Differentiation of Equations (3) and (4) leads to the expressions for the electrostatic forces. The x component of the r-space force is,

$$F_x^r(i) = Z_i \sum_{j=1}^{N} Z_j \sum_{\mathbf{n}} \frac{x_{i,j\mathbf{n}}}{r^3_{i,j\mathbf{n}}}\left\{\operatorname{erfc}(\alpha r_{i,j\mathbf{n}}) + \frac{2\alpha}{\sqrt{\pi}} r_{i,j\mathbf{n}} \exp(-\alpha^2 r^2_{i,j\mathbf{n}})\right\} \tag{8}$$

and of the q-space force is,

$$F_x^q(i) = \frac{4\pi}{L^3} Z_i \sum_{j=1}^{N} Z_j \sum_{\mathbf{q}} q_x A(q)\sin(\mathbf{q}\cdot\mathbf{r}_{ij}) \tag{9}$$

Doubtless the *direct* Ewald summation or its *tabulated* version [1] is the most suitable and accurate method of evaluating Φ^c in the simulation of ionic systems, although it is a costly method in terms of cpu time. In order to simplify this part of the calculation and make it less expensive some authors have considered approximations of the direct Ewald method (e.g., a *polynomial* method [1] or the methods described in references

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[3–5]). However, these approximations have limited application in the simulation of ionic systems.

In order to simulate large ionic systems ($N > 10^4$) it is necessary to build up an order of N MD program. A classical order of N^2 MD program cannot be used for this purpose since, for $3000\,\Delta t$ and $N = 10^4$ it requires 3 weeks of cpu time on the CDC 962-11 or 2 cpu days on the ETA 10P supercomputer. In recent years several very efficient order of N MD programs (algorithms) for handling short range interactions have been published (e.g., [6–8]). They make it possible to simulate systems of 10^4 particles for $3000\,\Delta t$ in 15–20 minutes on contemporary supercomputers. Conceptually, to obtain an $0(N)$ cpu dependency for short range interactions is rather simple and this is done by selecting – from among all the particles in the MD box – only those particles that are contained within an imposed cut-off sphere (of radius R_c). In the case of coulombic interactions the situation is more complex. As is apparent from Equations (2) to (9) the Ewald summation involves calculations in both, real space and reciprocal space. In a classical MD approach the cpu time for an r-space summation grows with N^2, while in q-space this dependency can be simply changed into an $0(N)$ dependency of cpu on number of particles by the use in Equation (9) of the trigonometrical identity:

$$\sin(\mathbf{q}\cdot\mathbf{r}_{ij}) = \sin(\mathbf{q}\cdot\mathbf{r}_j)\cdot\cos(\mathbf{q}\cdot\mathbf{r}_i) - \sin(\mathbf{q}\cdot\mathbf{r}_i)\cdot\cos(\mathbf{q}\cdot\mathbf{r}_j) \tag{10}$$

where $\mathbf{r}_{ij} = \mathbf{r}_j - \mathbf{r}_i$. More accurately the cpu time needed for the calculation of coulombic forces (Equations (8) and (9)) $t^c = t^r + t^q$ can be expressed as

$$t^r \sim N\cdot R_{\mathrm{CD}}^3 \tag{11}$$

$$t^q \sim N\cdot k_{\max}^3 \tag{12}$$

where R_{CD} is a dimensionless cut-off radius ($R_{\mathrm{CD}} = R_{\mathrm{C}}/H$, $H = L/2$) and $k_{\max}$ denotes the range of the summation in q-space (for a cubic cell $k_{\max} = l_{\max} = m_{\max}$). The values of R_{CD} and $k_{\max}$ depend on the choice of the α parameter. It is convenient to consider α in dimensionless units namely,

$$\alpha_L = \alpha\cdot L \tag{13}$$

Choosing a bigger value for α reduces R_{CD} and so t^r, but causes slower convergence in q-space so that $k_{\max}$ increases and consequently t^q grows rapidly.

2 THE CHOICE OF THE CONVERGENCE PARAMETER α

Because the r-space term in the coulombic forces (Equation (8)) is calculated in the same part of the MD program as that in which the short range forces are calculated it is useful to choose a value for α_L which makes R_{CD} the same as the cut-off radius for the short range interactions. This is especially important for large L. It has been shown [9] that the r-space and q-space terms converge at the same rate if $\alpha_L = \sqrt{\pi}$. From the point of view of accuracy this choice of α_L would be the most satisfactory, but in practical MD it is rather useless, since it requires summation in r-space over r_{ij} beyond the range of the MD Box. In Figure 1 is shown the dependence of the core expression of Equation (8) (contained in { } brackets) on R_{CD}. As follows from this figure, in order to ensure satisfactory convergence of Equation (8) inside an MD box, the value of α_L should be around 5 or bigger. It is worthwhile noticing that the range

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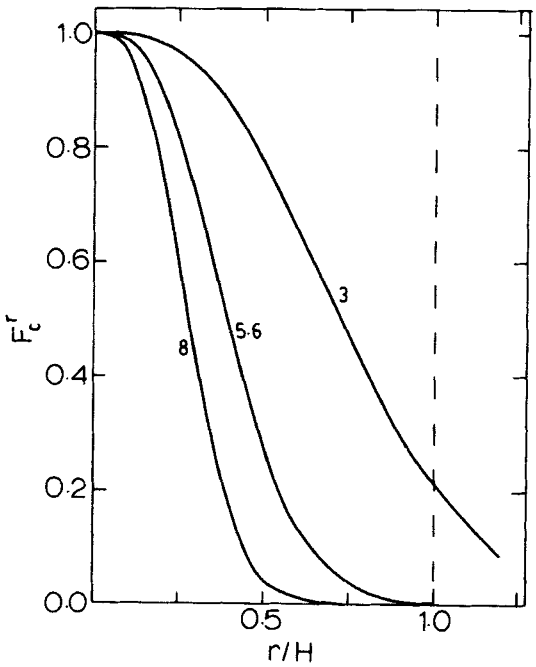

Figure 1 Core expression of r-space force term F_c^r (i.e. the term contained in { } brackets of Equation (8)) vs reduced distance for different values of α_L (3, 5.6, 8). $H = L/2$. The vertical dashed line denotes the edge of the MD box.

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of the function in Figure 1 is mostly determined by its second term (exp), since its first term (erfc) decays more rapidly. Sangster and Dixon [1] showed that for a small system ($N = 216$) the value of $\alpha_L = 5.6$ gives an accuracy in the coulombic force calculation which is of the order of 10^{-3} and this value of α_L has been commonly adopted in the simulation of ionic systems [10]. Smith [11] expressed α in terms of the short-range force cut-off radius and suggested that $\alpha \cdot R_c$ should be ~ 3.5, which corresponds to $\alpha_L \sim 7/R_{CD}$, giving for $R_{CD} = 1$ a value of α_L somewhat bigger than the value of 5.6 given in [1].

In fact the proper value of the α_L parameter depends strongly on the size of the system N and the choice of cut-off radius, and it should be chosen with some regard for accuracy and the cpu time consumed. To establish these relationships we start our considerations from a small N system. As an example we examined δ-Bi_2O_3 superionic crystals of different sizes N. For convenience, in further parts of this paper, we refer to the size of Bi_2O_3 systems as Sn (meaning $n \times n \times n$ crystallographic cells) so that $N = 10 \cdot Sn$. In Figure 2 is shown the coulombic energy of a Bi_2O_3 S3 system ($N = 270$) for different values of R_{CD}. The energy was calculated for a well equilibrated system obtained after 3000 Δt. Similar calculations performed for other configurations obtained after additional 200, 400 and 600 time steps, show negligible differences. For $R_{CD} = 1$ the energy is constant for α_L from about 4 to 8 (solid line in Figure 2). For smaller values of R_{CD} the range of the energy plateau becomes considerably smaller. The first observation is then, that for a given N the value of R_{CD} cannot be smaller than a certain minimum value and this situation cannot be improved by the use of

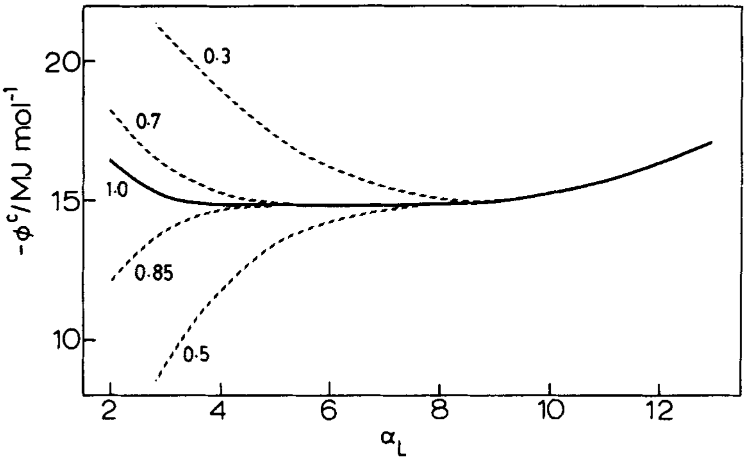

Figure 2 Coulombic energy of Bi_2O_3 ionic systems for different values of cut-off radius R_{CD} (1.0, 0.85, 0.7, 0.5, 0.3) and $k_{max} = 5$. Size of the system: S3 ($3 \times 3 \times 3$ crystallographic cells; $N = 270$). Configuration: thermodynamically equilibrated.

bigger α_L (*cf.* Figure 1). For small N this remark is rather obvious and means that the range of the r-space summation (R_{CD}) which is determined by the value of α_L, has to contain a representative sample of ions, at least one crystallographic cell. In the small α_L region the changes in coulombic energy are almost solely caused by the Φ^r term (Figure 3). For bigger α_L the contribution of the Φ^q term appears to be more

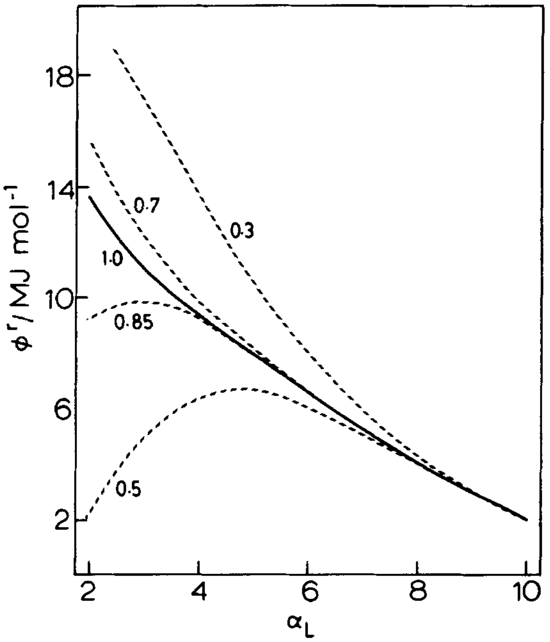

Figure 3 Energy r-space term of S3 ($N = 270$) Bi_2O_3 system. Configuration: thermodynamically equilibrated. Remaining notation as in Figure 2.

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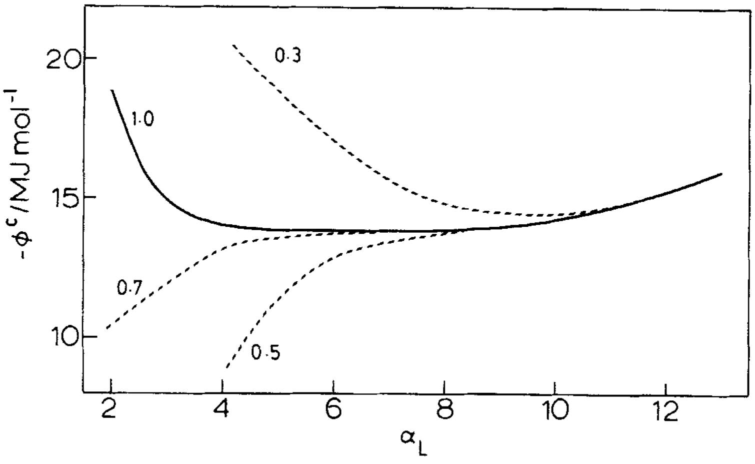

Figure 4 Coulombic energy of S3 Bi_2O_3 systems. Configuration: perfect (fluorite) structure. Remaining notation as in Figure 2.

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significant. Due to the slow convergence of the coulombic energy, its value should depend strongly on the actual configuration of the ions (especially for small systems). Figure 4 is a counterpart of Figure 2, but obtained for a perfect (fluorite) structure of Bi_2O_3. In this case the energy plateau is somewhat smaller (5 to 8) and the results are more sensitive to the value of R_{CD}. In the plateau region the contribution of the Φ^q term to the total Φ^c energy is much smaller than the contribution of Φ^r. In Figure 5 are shown Φ^q curves for equilibrated (Figure 2) and perfect (Figure 3) structures for different values of k_{max}. As one can see, in the range $5 < \alpha_L < 6$ the differences between the calculated values of Φ^q are negligible, regardless of the value of k_{max} used. (Compare Figures 2 and 4 for Φ^c). At the same time, the cpu time needed for the calculation of the q-space term with $k_{max} = 21$ is almost two orders of magnitude bigger than the cpu time for $k_{max} = 5$ (see Table 5). The next two figures show the coulomb energy of a much bigger system S6 ($N = 2160$); Figure 6 – equilibrated structure, Figure 7 – perfect structure Its behaviour is similar to that of the S3 system (Figures 2 and 4). Again the energy plateau for the perfect structure (Figure 7) is somewhat narrower than for an equilibrated structure (Figure 6), and Φ^c perfect is more sensitive to the value of R_{CD}. For α_L up to around 12 the contribution of the Φ^q term to the total energy for an S6 system (Figure 8) is smaller by orders of magnitude than that for the S3 system (Figure 5). In Figs. 9 and 10 are shown curves of Φ^c for S8 ($N = 5120$) and S10 ($N = 10\,000$) systems, both for perfect structures. As in the case of the S6 system in the range of the energy plateau the Φ^q terms for S8 and S10 were smaller than Φ^c by orders of magnitude. We did not perform the calculations for equilibrated S8 and S10 structures, since we used a classical N^2 MD program for which such equilibration runs would require an enormous amount of cpu time (see Table 5).

The results presented in Figures 2, 4, 6, 7, 9 and 10 make it possible to estimate the α_L parameter. Its lower limit α_L^l depends mostly on the choice of R_{CD} and its upper limit α_L^u – on the size of the system. These limits can be roughly expressed as,

$$\alpha_L^l \approx \frac{4.5}{R_{CD}} \qquad \alpha_L^u \approx N^{1/3} \tag{14}$$

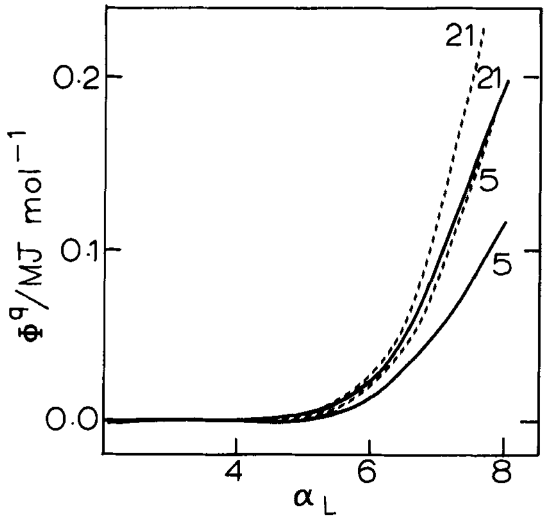

Figure 5 Energy q-space term of S3 Bi_2O_3 systems for k_{max} = 5 and 21. Configuration: equilibrated – solid lines; perfect – dashed lines.

Therefore, the convergence parameter α_L should be set between these limits and its recommended value may be estimated as

$$\alpha_L \approx \tfrac{1}{2}(\alpha_L^u + \alpha_L^l) = \tfrac{1}{2}\left(N^{1/3} + \frac{4.5}{R_{CD}}\right) \tag{15}$$

with the restriction that $R_{CD} > a_0$, where a_0 is the lattice parameter.
Selected values of α_L predicted by Equation (15) are given in Table 1. As one can see these estimates agree fairly well with the data in the corresponding figures.

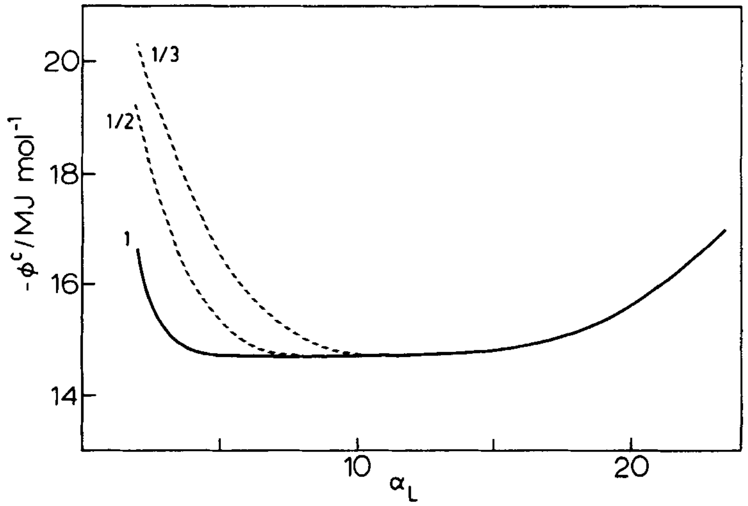

Figure 6 Coulombic energy of S6 (N = 2160) Bi_2O_3 system for different R_{CD} (1, 1/2, 1/3) and k_{max} = 5. Configuration: thermodynamically equilibrated.

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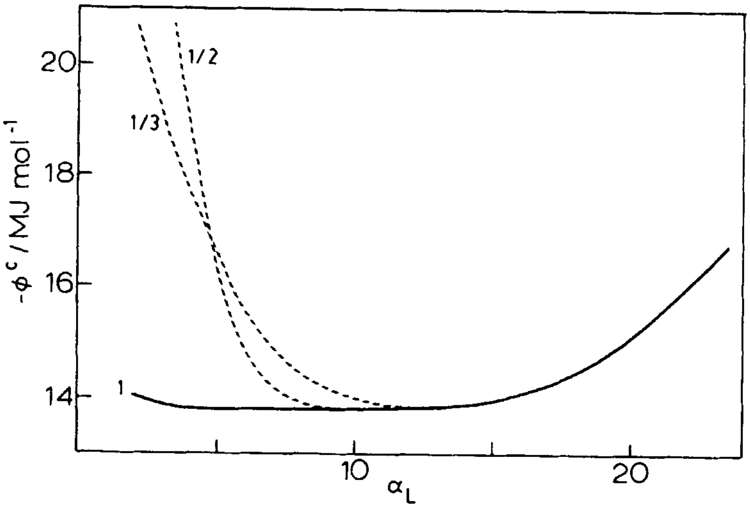

Figure 7 Coulombic energy of S6 (N = 2160) Bi_2O_3 system for different R_{CD} (1, 1/2, 1/3) and k_{max} = 5. Configuration: perfect (fluorite) structure.

3 VALIDITY OF q-SPACE TERM AND NOTES ON THE EFFICIENCY

As is apparent from Figures 5 and 8 the contribution of the q-space energy term is significant (at least for δ-Bi_2O_3) only for α_L greater than the upper limit α_L^u (Equation (14)). This suggests that for smaller α_L the q-space summation can be omitted and this is an even better approximation for larger systems because of the wider range of α_L in which Φ^q is negligible. In fact, one should consider the forces rather than the energy, since for instance, the constant energy term (Equation (5)) is much bigger than

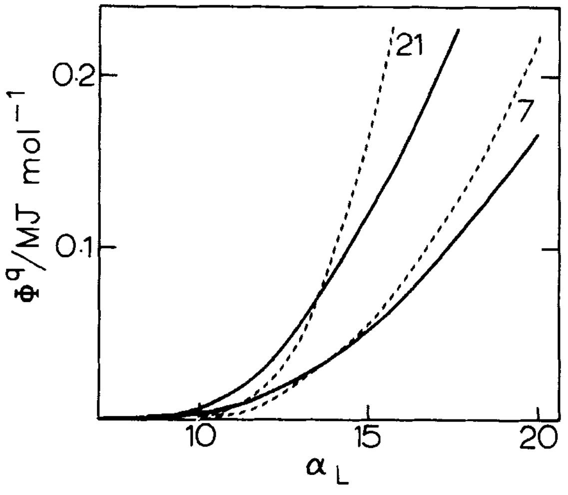

Figure 8 Energy q-space term of S6 (N = 2160) system for k_{max} = 7 and 21. Configuration: equilibrated — solid lines; perfect — dashed lines.

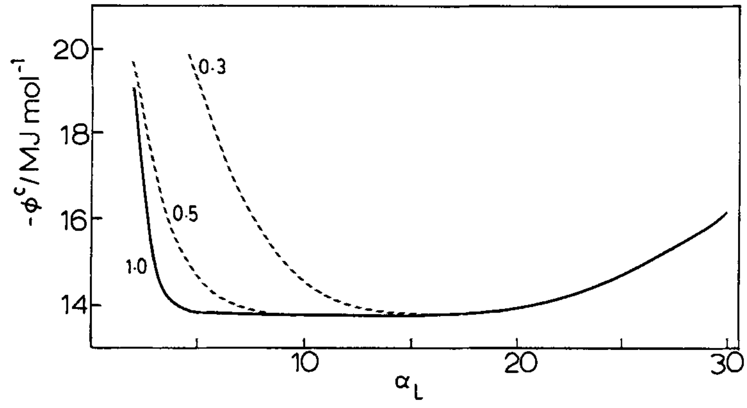

Figure 9 Coulombic energy of S8 ($N = 5120$) system for different R_{CD} (1.0, 0.5, 0.3) and $k_{max} = 5$. Configuration: perfect (fluorite) structure.

Table 1 The values of α_L parameter predicted by Equation (15).

N R_{CD}	270	2160	5120	10000	58320
1	5.5	8.5	11	13	22
2/3	6.5	10	12	14	23
1/2	7.5	11	13	15	24
1/3	–	13	15	17	26
1/4	–	–	17	20	28
1/5	–	–	–	22	31
1/10	–	–	–	–	42

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the q-space term (Equation (4)), although it gives zero contribution to the forces. On the other hand comparing the ratio Φ^q/Φ^r (Equations (3), (4)) with the ratio F^q/F^r (Equations (8), (9)) one can conclude that they should agree within an order of magnitude. Therefore, the contribution of the q-space force term to the total force

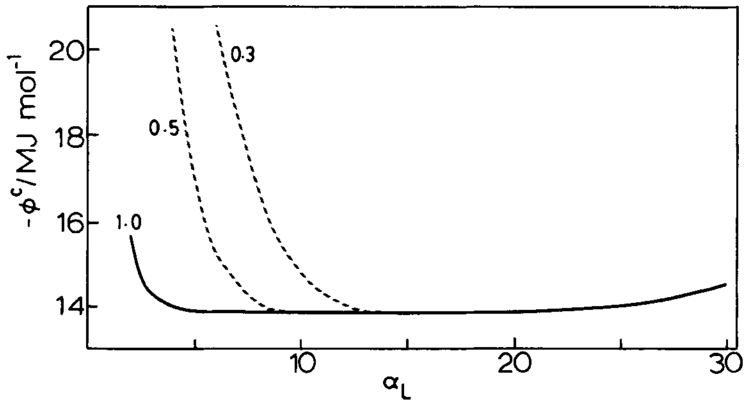

Figure 10 Coulombic energy of S10 ($N = 10\,000$) system for different R_{CD} (1.0, 0.5, 0.3) and $k_{max} = 5$. Configuration: perfect (fluorite) structure.

Table 2 Results of MD simulations for Bi_2O_3 (short run). System size $N = 270$ (S3), $R_{CD} = 1$. Conditions of the simulations: temperature rescaling up to 80 time steps, length of the runs – 200 time steps, initial configuration – equilibrated (*EQ*) or perfect (*P*), requested temperature $T_0 = 1500$ K. Symbols: Φ^c – coulombic energy, Φ_{sr} – short range potential energy, Φ_{tot} – total potential energy, T – temperature. All the quantities given as averages over last 100 time steps. For more details see text.

k_{max}	Φ^c *kJ/mol*	Φ_{sr} *kJ/mol*	Φ_{tot} *kJ/mol*	T *K*	*config.*
0	– 14871	2845	– 12026	1487	*EQ*
5	– 14882	2863	– 12019	1527	*EQ*
(5)	(– 14872)	(2852)	(– 12021)	(1504)	(*EQ*)
11	– 14883	2865	– 12019	1524	*EQ*
21	– 14883	2865	– 12019	1524	*EQ*
0	– 14733	2755	– 11978	1561	*P*
5	– 14740	2764	– 11974	1592	*P*
(5)	(– 14751)	(2778)	(– 11973)	(1582)	(*P*)
11	– 14742	2766	– 11977	1591	*P*
21	– 14742	2766	– 11977	1591	*P*

in the plateau region seems to be rather small. In order to verify this assumption we performed some MD simulations of Bi_2O_3 which are collected in Tables 2, 3, 4. In all these cases the value of R_{CD} was equal to 1 and α_L was 5.6. The value of $k_{max} = 0$ in these tables means that the summation in q-space was switched off. For all simulations, except those in brackets, the temperature was re-scaled at every time step for which the difference between the actual and requested temperatures was bigger than ΔT (= 20 K). The results in brackets were obtained using a different temperature rescaling technique in which the temperature was rescaled when $|T_{av} - T_0| > \Delta T$ where T_{av} is the average temperature over the previous three steps of the simulation.

From the results in Table 2 one can see that even for the small S3 system the results for $k_{max} = 0$ do not differ much from those with finite values of k_{max}. More precisely, the contribution from Φ^q to Φ^c is about 1 part in 1500 even for this minimal value of N. A similar observation holds for the S6 system (Table 3). This tendency is especially well observed for the total energy, while – for example – temperatures show bigger differences. As a reference point for these differences one may compare results obtained for different temperature rescaling (in brackets). For longer MD runs one can expect larger deviations; however, the agreement between the results for different k_{max}, including $k_{max} = 0$, seems to be satisfactory (Table 4).

Table 3 Results of MD simulations for Bi_2O_3 (short run). System size $N = 2160$ (S6), $R_{CD} = 1$. Conditions of the simulations and symbols as in Table 2.

k_{max}	Φ^c *kJ/mol*	Φ_{sr}	Φ_{tot} *kJ/mol*	T *K*	*config.*
0	– 14690	2683	12007	1521	*EQ*
5	– 14689	2685	12004	1517	*EQ*
(5)	(– 14692)	(2687)	(– 12005)	(1504)	(*EQ*)
11	– 14685	2682	– 12003	1509	*EQ*
0	– 14701	2711	– 11991	1541	*P*
5	– 14697	2707	– 11990	1549	*P*
(5)	(– 14710)	2724	(– 11986)	(1576)	(*P*)
11	– 14696	2707	– 11989	1539	*P*

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Table 4 Results of MD simulations for Bi_2O_3 (long run). System size $N = 270$ (S3), $R_{\mathrm{CD}} = 1$. Conditions of the simulations: temperature rescaling up to 1800 time steps, length of the runs – 4000 time steps. All quantities are given as averages over last 2000 time steps. Remaining conditions of the simulations and symbols as in Table 2.

$k_{\max}$	Φ^{c} *kJ/mol*	Φ_{sr}	Φ_{tot} *kJ/mol*	*T* *K*	*config.*
0	−14847	2821	−12026	1511	*EQ*
5	−14839	2837	−12002	1512	*EQ*
(5)	(−14864)	(2845)	(−12019)	(1496)	(*EQ*)
11	−14827	2819	−12008	1539	*EQ*
21	−14825	2818	−12007	1536	*EQ*
0	−14827	2824	−12003	1486	*P*
5	−14874	2851	−12022	1483	*P*
(5)	(−14820)	(2817)	(−12003)	(1465)	(*P*)
11	−14816	2817	11999	1509	*P*
21	−14818	2818	12000	1527	*P*

Although the actual contribution of the Φ^q term to the total energy depends strongly on the ionic configuration, in fact for most ionic systems this contribution is much smaller than those of Φ^r and Φ_{sr} [11]. For small N this contribution might not be negligible (at least for heavily disordered systems) because of the lack of flexibility in the choice of a value for α_L which would minimize the Φ^q term. On the other hand since it is the parameter α_L which controls the distribution of the coulombic energy between the r-space and q-space terms, it seems to be always possible for larger systems, for which the α_L-plateau is bigger, to choose a value from the plateau region that would still minimize the Φ^q term and even make it negligibly small. Although omission of the q-space term is more questionable for small N, this is not so important from the point of view of cpu time, since this time is not too large anyway. In Table 5 we show cpu times for the short-range forces calculation (t_{sr} – which is practically the same as t^r (Equation 11)) and for the calculation of q-space forces (t^q) for a very vectorized order of N^2 MD program.

The calculation of the short-range forces (and therefore of the r-space coulomb term) can be accelerated in an order of N program by two orders of magnitude for $N = 10\,000$ (e.g., t_{sr} in the MDSLAB1 program [6] is equal to ~ 0.3 s per step for such a value of N). However, this requires the use of a relatively small R_{CD} (*ca.* 1/5) and thus a big α_L (see Table 1; $\alpha_L \approx 22$). The big α_L would require – according to current belief – the use of big $k_{\max}$ (see remark following (13)). In consequence the acceleration of t_{sr} by two orders of magnitude would not have any practical significance, since the total cpu time would only be reduced from 80 s per step (35 + 45; Table 5) to 35.3 s (35 + 0.3). Thus the only possibility of significant acceleration of the simulation of

Table 5 Cpu time in seconds (ETA 10P) for the calculation of the q-space forces (t^q at $k_{\max} = 5, 11, 21$) and for the short-range forces) (t_{sr}).

N	t^q			t_{st}
	5	*11*	*21*	
270	0.026	0.25	1.69	0.056
2160	0.12	1.15	8.00	2.1
10000	0.55	5.2	35	45

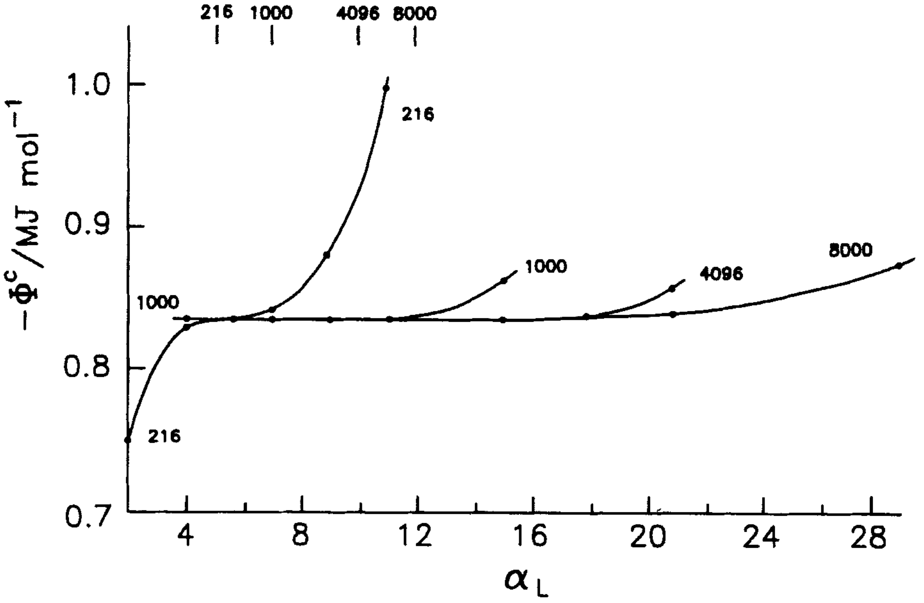

Figure 11 Dependence of the coulombic contribution to the cohesive energy of NaCl on α_L for MD systems of various sizes.

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ionic systems is to perform the q-space summation over a small k_{max} (e.g., $k_{max} = 5$, which gives $t^q = 0.55$ s; Table 5) or to eliminate it entirely as suggested by the results in Tables 2–4 which show that the q-space sum makes a small contribution to the energy and temperature. The last solution, once verified, is much to be preferred and would reduce t_{tot} for $N = 10^4$ from 80 s to *ca.* 0.3 s per step, and so by factor of 250, which means that the completion of an MD run of 3000 Δt would be shortened on the ETA 10P from 3 cpu days to *ca.* 20 minutes.

4 APPLICATION TO SODIUM CHLORIDE, CRYSTALLINE AND MOLTEN

Bismuth oxide is not a typical example of an ionic crystal: the delta phase is stable only over a limited temperature range and its adoption of the fluorite structure means that, on average, one quarter of the anion sites are vacant. It would therefore seem prudent to test the conclusions derived from our study of δ-Bi_2O_3 on some other substance and we have chosen NaCl for this purpose. The interionic potentials used were the same as those employed previously [12] and the starting configuration was the fcc rock-salt structure. Calculations were performed with the requested temperature for the simulated material equal to 1000 K (with the experimental lattice constant); equal to 1250 K with an extrapolated lattice constant; and equal to 1250 K with the lattice expanded by 3%, 6% and 10% to encourage melting of the constant volume system [13]. The number of particles in the MD system varied from 216 to 8000 and all these calculations were performed with $R_{CD} = 1$. The dependence of the coulomb energy Φ^c on the dimensionless Ewald parameter α_L is shown in Figure 11 for crystalline NaCl at 1000 K. This graph shows that a plateau region exists for N in the range 216 <

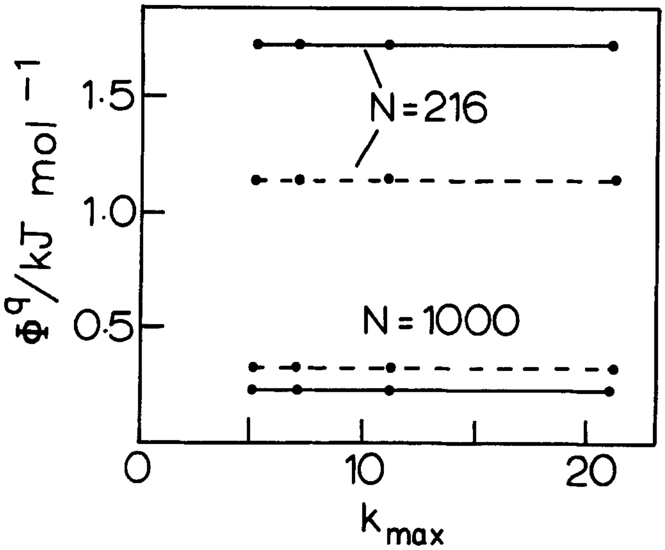

Figure 12 Contributions to the energy from the q-space term for $5 \leqslant k_{max} \leqslant 21$ and $N = 216, 1000$ for crystalline NaCl at 1000 K (solid lines) and for molten NaCl at 1250 K (dashed lines). Results are averaged over 100 steps of the simulation. $R_{CD} = 1$ and $\alpha_L = 5$.

$N < 8000$ and again emphasizes the need for a correct choice for α_L. The vertical bars show that the values of α_L estimated from the formula

$$\alpha_L \approx \tfrac{1}{2}(\alpha_L^u + \alpha_L^l) = \tfrac{1}{2}\left(N^{1/3} + \frac{4.0}{R_{CD}}\right) \tag{16}$$

but it is recommended that an appropriate value of α_L for each substance and each N usually be determined from a preliminary calculation. Only a very small number of time steps should be necessary to establish the plateau region. However, the similarity between Equations (15) and (16) for substances as different as bismuth oxide and sodium chloride suggests that an expression like these could be found which would have general validity. In any case, Equations (15) and (16) should be useful in establishing preliminary choices for α_L.

The data shown in Figure 11 are for $0 < k_{max} < 5$, the results being indistinguishable on the scale of this figure for k_{max} in this range. For bigger k_{max} (not shown in the figure) the results are the same in the flat region which, however, extends to higher values of α_L due to the growing contribution of Φ^q, especially for $k_{max} = 21$. This appears to be a general tendency since it is observed for δ-Bi$_2$O$_3$ as well: larger values of k_{max} increase the upper limit of the energy plateau α_L^u. For this reason one may consider the results in Figure 11 as showing the minimum plateau region, with $k_{max} = 0$. This means that for a properly chosen α_L within the plateau region adding more terms to the q-space sum by increasing k_{max} should not cause an increase in the value of Φ^q. Unlike the results in previous figures, those in Figure 12 were averaged over 100 steps of the simulation. One observes that increasing k_{max} makes practically no difference to the (small) contribution of Φ^q to the total coulomb energy, Φ^c. This contribution is smaller by three orders of magnitude than that of Φ^c and decreases

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Table 6 Cpu time in seconds per time step (on ETA 10P) for the calculation of the q-space forces (t^q) and cpu time in seconds (t) for the whole MD calculation for NaCl systems of various sizes. N is the number of particles and *NRUN* is the number of time steps.

	N	*NRUN*	*time for* $k_{\max}$ =			
			0	*5*	*11*	*21*
t^q/s	216	1000	0	0.0231	0.221	1.492
t/s	–	–	45.5	68.6	266.6	1538
t^q/s	1000	1000	0	0.0626	0.594	4.020
t/s	–	–	515.3	578.0	1110	4534
t^q/s	4096	200	0	0.2336	2.204	14.95
t/s	–	–	1450	1500	1894	4442
t^q/s	8000	100	0	0.4505	4.247	28.77
t/s	–	–	2665	2701	3081	5533

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further in importance as N increases. This justifies its omission altogether for larger systems. It has been found from longer MD runs that NaCl (both crystalline and molten) is less affected by the neglect of the Φ^q term than is δ-Bi_2O_3, in which polarization effects are extremely large. We emphasize that the omission of the Φ^q calculations improves significantly the efficiency of the MD simulation for larger systems. Table 6 shows the time in seconds per MD step for the reciprocal lattice sum and also the total time in seconds, for MD calculations on crystalline NaCl at 1000 K on the ETA 10P. Relative timings on other vector processors would be comparable. These data show clearly that for small N and $k_{\max} = 21$. t^q is the major contributor to the total time expended on the MD calculation. Even for $N = 8000$ particles with $NRUN = 100$, the reciprocal lattice sum with $k_{\max} = 21$ takes about 50% of the total MD time. Here we were using a classical method for the short-range forces, which is of $O(N^2)$. For an $O(N)$ algorithm for ionic systems, such as we have under development, the reciprocal lattice sum would occupy a much larger fraction of the total time expended on the whole calculation. This paper shows that it can be omitted in calculations of the cohesive energy.

One should certainly question whether the neglect of Φ^q is justified only for the perfect, or near-perfect, lattice, or whether it is of more general validity, applying also to highly defective lattices and to ionic melts. The solid lines in Figure 12 refers to a perfect ionic lattice of NaCl, while δ-Bi_2O_3 is an example of a highly defective lattice. In order to ensure melting of the constant -volume system of simulated NaCl at 1250 K the calculations were done four times, using an extrapolated lattice constant, and with the lattice expanded by 3%, 6% and 10%. The calculation with an extrapolated lattice constant showed perfect crystalline behaviour. With the lattice constant a increased by 3% there was some ionic motion and some tendency to form interstitials but the structure was maintained. With a increased by 6% or 10%, the simulated crystal melted. The dashed-line curves in Figure 12 correspond to molten NaCl and show that Φ^q decreases with increasing N for an ionic melt as well as for a perfect crystal. Figures 13(a, b) show the projections of the positions of the Na^+ (at 1250 K, extrapolated lattice constant) at intervals of 0.1 ps over the time interval 7–10 ps. The results in Figure 13(a) were obtained with $k_{\max} = 0$ (*i.e.*, with the reciprocal lattice summation switched off) and those in Figure 13(b) with $k_{\max} = 21$.

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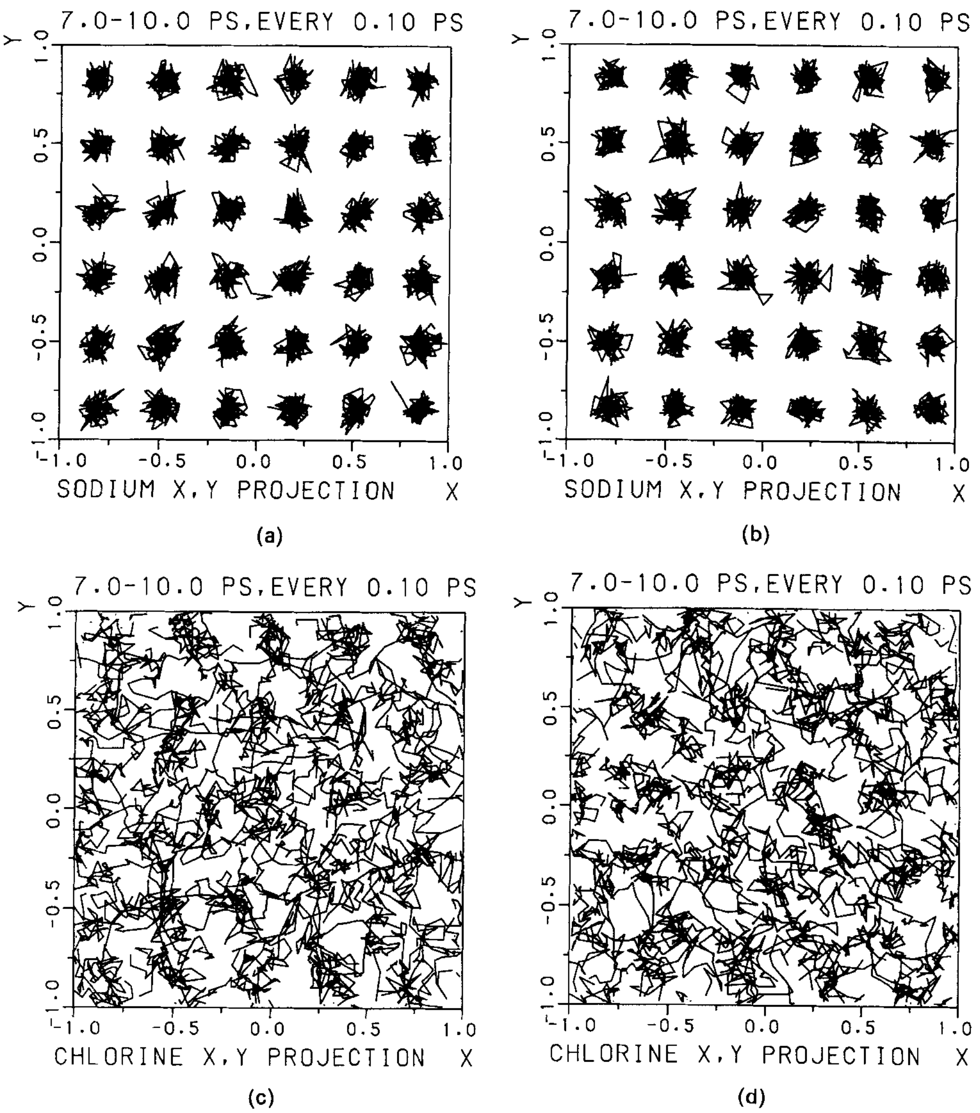

Figure 13 Projections on the XY-plane of the contents of the origin cell. (a), (b) Crystalline NaCl at 1250 K; (c), (d) molten NaCl at 1250 K. For (a), (c) $k_{\max} = 0$; for (b), (d) $k_{\max} = 21$.

Both figures show an essentially perfect lattice though with some rather large excursions from perfect lattice sites. When the lattice constant of the originally perfect fcc (c, d). Qualitatively, there is no discernable difference between the calculation with $k_{\max} = 0$ (Figure 13(c)) and that with $k_{\max} = 21$ (Figure 13(d)). Projections for Na^+ were similar to those shown for Cl^-.

4 SUMMARY

In this paper we have discussed the choice of the convergence parameter α_L in the Ewald sum in terms of a system's size and the cut-off radius. It turns out that α_L depends strongly on both N and R_{CD} and the values of α_L suggested by other authors for small systems should therefore not be used in the case of large N or small R_{CD}. Rules for choosing optimum values of α_L have been given (Equations (15, 16)) for δ-Bi_2O_3 and for NaCl. The second major point discussed is the possibility of neglecting the q-space term altogether in the simulation of large ionic systems. This results in a great speed-up of the simulation. For properly-chosen α_L the q-space contribution to the cohesive energy decreases with the size of the system for NaCl (crystalline or molten) and for δ-Bi_2O_3. Whether this statement is true for other ionic systems remains an open question: however, it is clearly not limited to perfect ionic crystal lattices. It should also be borne in mind that many of the results presented here were obtained from a limited number of time-steps and often for just one perfect or equilibrated configuration. Results calculated as averages for a variety of configurations would be more reliable. However, calculations for systems containing 10^4 ions by an $O(N^3)$ program would require many hours of supercomputer time (see, for e.g. Table 6 for $N = 8000$). Nevertheless, all the NaCl results (Table 6 and Figures 11–13) were obtained as averages over 40–400 time steps (depending on N). Another question, yet to be examined, is whether omission of the q-space summation will be justified (for appropriate N and α_L) in the calculation of other properties. To test this it will be necessary to perform long MD runs for large N and calculate various time-correlation functions. This can only be done with an $O(N)$ MD ionic program with direct Ewald summation. The development of such a program is an objective of our present work. In general, in an MD simulation of an ionic system there are two, to a certain degree independent, cut-off radii. One is determined by the range of short-distance interactions and the second one by the range of the r-space summation of electrostatic interactions. From the point of view of MD efficiency both should be as small as possible, however the cut-off radius actually applied has to fulfil both requirements, which means that it has to be equal to or greater than the larger of these two radii.

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