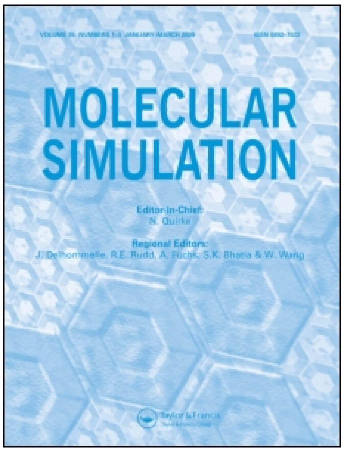

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Cutoff Errors in the Ewald Summation Formulae for Point Charge Systems

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CUTOFF ERRORS IN THE EWALD SUMMATION FORMULAE FOR POINT CHARGE SYSTEMS

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Closed formulae for both real and reciprocal space parts of cutoff errors in the Ewald summation method in cubic periodic boundary conditions are derived. Such estimates are useful in tuning parameters in molecular simulations. Errors in both the electrostatic energy and forces are considered. The estimates apply to a disordered configuration of point charges and, with some limitations, also to point-charge molecular models. The accuracy of our estimates is tested and confirmed using simulated configurations of two systems (molten salt and diethylether) under a variety of conditions.

KEY WORDS: Coulomb forces, Ewald summation, cutoff errors

1 INTRODUCTION

The coming generation of massively parallel supercomputers with multigigaflops performance will permit the simulation of molecular systems of very high complexity. Systems such as ionically conducting polymers or aqueous solutions of polyelectrolytes, colloids and proteins contain many thousands of point charges. There is now general agreement that such systems must be simulated in truly periodic boundary conditions with an appropriate dielectric environment if the results of the simulations are not to be dominated by artifacts of finite system electrostatics [1–3].

There are now a number of competing algorithms for doing the infinite sum over periodic replicas of the simulation box [1, 4, 5]. Of these, the most widely used is the Ewald algorithm, where the complexity has been shown to grow as $N^{3/2}$ with the number N of charges [3]. More recently the fast multipole method has been published with a probable complexity of N [4].

One of the advantages of the latter method is that rigorous errors bounds are available, although the originally published estimates are several orders of magnitude too large.

It seems to be difficult to obtain good error bounds for the Ewald method (and too pessimistic values are of low practical importance), but standard deviations of the errors can be estimated under a variety of assumptions about the spatial correlation of charges. The errors in turn give two relations between three Ewald

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*Permanent address: E. Hála, Laboratory of Thermodynamics, Institute of Chemical Process Fundamentals, 16502 Praha 6-Suchdol, Czechoslovakia parameters, the real space cutoff c, reciprocal space cutoff K and the separation parameter α.

Given the errors, the remaining free parameter is usually chosen experimentally to optimize the performance of the program. This is relatively straightforward for a moderate number of charges on a serial machine, but is a more complex affair if a large number of charges is involved, especially on a multiprocessor grid where there may be a further relation between the number of processors, their topology, splitting a macromolecule between processors and the potential cutoff. *The performance optimization problem is now too complex to be solved in any efficient way by experimentation.*

We are thus led to the conclusion that the efficient simulation of large Coulomb systems on multiprocessor systems requires good a priori estimates of the errors in the energy and forces. These are already available for the fast multipole method and the aim of this paper is to derive and verify reliable asymptotic formulae appropriate for the Ewald method.

A methodology of measuring errors is proposed in section 2. For the purpose of establishing a notation the Ewald summation formulae are briefly reviewed in section 3. Section 4 deals with disordered point charge systems as a molten salt. More realistic interaction site molecular models are discussed in section 5 using the OPLS model of diethylether as an example. An example of optimization on a multiprocessor system is given in section 6.

2 METHODOLOGY

The errors of any method evaluationg Coulomb interactions may be expressed in several ways. The simplest possibility is the error in the total electrostatic energy. If it is guaranteed that this error will not exceed some sufficiently low value, then the Boltzmann probability of each configuration and all measured quantities will also be accurate enough.

This accuracy requirement is too pessimistic, especially for large systems. Information in molecular statistical systems is distributed and accurate sampling of small portions of the system is sufficient. The appropriate quantity which reflects this phenomenon is the energy of one charge (atom, group, molecule). This is the natural quantity for Monte Carlo calculations where the single particle energy is evaluation in each step. In the molecular dynamics method the forces acting on the charges are evaluated rather than their energies and the forces (of accelerations) then replace energy for the purpose of analyzing errors.

In this paper we concentrate on the molecular dynamics method and hence on the errors of forces acting on each charge, $\Delta \mathbf{f}_i = \mathbf{f}_{i,\mathrm{approx}} - \mathbf{f}_{i,\mathrm{exact}}$. The standard deviation of $\Delta \mathbf{f}$,

$$\delta \mathbf{f} = \langle \Delta \mathbf{f}^2 \rangle^{1/2} = \left(N^{-1} \sum_i \Delta \mathbf{f}_i^2 \right)^{1/2}, \tag{1}$$

is a good global measure of the errors provided that the probability distruction of $\Delta \mathbf{f}$ is a 3D Gaussian distribution (this assumption will be verified later). The sum in (1) is over all N charges in the system and the charges are assumed to have the same absolute values.

This definition does not suit molecules with possible constraints and different charges. Since the integrated trajectories are controlled by the accelerations rather than forces, we propose the following measure of the error:

$$\delta\mathbf{a} = \langle \Delta\mathbf{a}^2 \rangle^{1/2} = \left(N^{-1} \sum_i (\Delta\mathbf{f}_i^t/m_i)^2 \right)^{1/2}, \tag{2}$$

where $\delta\mathbf{f}_i^t$ denotes the error of the force on charge (i) with the components tangent to the constraint surface only (the components normal to the constraint surface do not influence the trajectories and are removed) and m_i is the mass if site (i). The sum in (2) is over all sites while N is the number of molecules; $\delta\mathbf{a}$ is thus cumulative over all sites in molecules.

3 THE EWALD SUMMATION

Let us consider N point charges $q_j (1 \leq j \leq N)$ contained in a cube of edge L. The positions of the charges are described by vectors $\mathbf{r}_j$. An array of periodic copies of the basic cell is surrounded at infinity by a uniform dielectric with dielectric constant ϵ'. The total charge of the system must be zero. We write the total electrostatic energy of this sytem in the form [1, 2]

$$E = E_r + E_k + \frac{2\pi}{(2\varepsilon' + 1) L^3} \left(\sum_{j=1}^{N} q_j \mathbf{r}_j \right)^2 \alpha\pi^{-1/2} Q. \tag{3}$$

Here α is a parameter with the dimension of [length^{-1}]

$$Q = \sum_{j=1}^{N} q_j^2. \tag{4}$$

The real-space part of the energy is

$$E_r = \sum_{\mathbf{n}} \sum_{(j,m)} q_j q_m \alpha\, e(\alpha |\mathbf{r}_j - \mathbf{r}_m + L\mathbf{n}|), \tag{5}$$

where

$$e(x) = x^{-1} \operatorname{erfc} x = x^{-1}\, 2\pi^{-1/2} \int_x^{\infty} \exp(-t^2)\, dt \tag{6}$$

and the sums in (5) are over all integer vectors $\mathbf{n}$ and all pairs of charges (j, m) excluding the divergent terms $j = m$ for $\mathbf{n} = \mathbf{0}$. The function e(x) rapidly decreases with increasing x. It is then possible to truncate the sums (5), neglecting all terms for which $|\mathbf{r}_j - \mathbf{r}_m + L\mathbf{n}| > c$, where c is a suitable cutoff distance. If $c \leq L/2$, the nearest image convention may be applied [1].

The k-space (reciprocal-space) part of the energy is

$$E_k = (2\pi L)^{-1} \sum_{\mathbf{k}} k^{-2} \exp[-(\pi k/\alpha L)^2] \sum_{j=1}^{N} \sum_{m=1}^{N} q_j q_m \exp[2\pi i \mathbf{k} \cdot (\mathbf{r}_j - \mathbf{r}_m)/L], \tag{7}$$

where the first sum is over all nonzero integer vectors $\mathbf{k}$ and $k = |\mathbf{k}|$. It is seen that the terms decrease rapidly with increasing k. The **k**-sum is thus well approximated by restricting to $k \leq K$. Note also that the double sum in (7) may be replaced by a square of a single sum [1] which is more suitable for numerical calculations.

The electrostatic force acting on charge (m) is evaluated by taking a minus $\mathbf{r}_m$-gradient of (3). Its real-space part is

$$\mathbf{f}_{r,m} = q_m \sum_{\mathbf{n}} \sum_{j} q_j(\mathbf{r}_j - \mathbf{r}_m + L\mathbf{n})\, \alpha^3\, z(\alpha\,|\,\mathbf{r}_j - \mathbf{r}_m + L\mathbf{n}\,|), \tag{8}$$

where

$$z(x) = -e'(x)/x \tag{9}$$

and the k-space part is

$$\mathbf{f}_{k,m} = 2L^{-2} q_m \sum_{\mathbf{k}} k^{-2} \exp[-(\pi k/\alpha L)^2]\, \mathbf{k} \sum_{j=1}^{N} q_j \sin[2\pi \mathbf{k} \cdot (\mathbf{r}_j - \mathbf{r}_m)/L]. \tag{10}$$

A form more suitable for evaluation is also available [1].

4 DISORDERED POINT-CHARGE SYSTEMS

4.1 Real-Space Errors

In this section we derive estimates of standard deviations of real-space cutoff errors in the energy and forces. To do this, we assume that positions of charges separated by distances greater than the cutoff value c are distributed randomly. This is a sound assumption for fluids of point charges like molten salts or plasmas because the pair correlation functions tend rapidly to unity. With limitations discussed later in section 5, it is also correct for molecular models containing charges. This assumption may not be valid for crystalline solids or fluids of dipolar molecules or molecule models containing large point charges of opposite signs close together.

Let us estimate first the c-cutoff error in the energy of one fixed charge (m). It follows from (5) that this error is given by

$$q_m \sum_{j'} q_j\, \alpha\, e(\alpha\,|\,\mathbf{r}_{j'} - \mathbf{r}_m\,|), \tag{11}$$

where the sum is over such pairs (j′, m) that $|\,\mathbf{r}_{j'} - \mathbf{r}_m\,| > c$ and subscript j′ runs over all periodic images $\mathbf{r}_{j'} = \mathbf{r}_j + L\mathbf{n}$ of particle (j) except j′ = m. Since the arguments of function e(x) in (11) are large, the integral in (6) may be approximated by the asymptotic expansion using the formula

$$\int_A^\infty \exp(-Bx^2)\, f(x)\, dx \approx \exp(-BA^2)\, f(A)/2BA, \tag{12}$$

which is valid if $B > 0$ and

$$d[f(x)/2Bx]/dx \ll f(x) \tag{13}$$

for $x \geqslant A$. Assuming that the charges are distributed randomly for $|\,\mathbf{r}_{j'} - \mathbf{r}_m\,| > c$, formula (A.3) of Appendix A may be used to obtain the fluctuation of the c-cutoff error of the energy of charge (m):

$$\delta E_{r,m}^2 \approx q_m^2\, Q\, L^{-3} \int_c^\infty \alpha^2\, e^2(\alpha r)\, 4\pi r^2\, dr. \tag{14}$$

The integral may be again estimated by the asymptotic formula (12). The standard deviation of the error in the energy of charge (m) is thus approximately

$$\delta E_{r,m} \approx |q_m| (Qc/L^3)^{1/2} (\alpha c)^{-2} \exp(-\alpha^2 c^2). \tag{15}$$

For calculating the fluctuation of the error in the total energy it is reasonable to assume that all pair contributions beyond the cutoff are independent. The sum of $\delta E^2_{r,m}$ over all charges (m) contains each pair contribution twice and thus the fluctuation of the real-space cutoff error of the energy is one half of this sum. The resulting standard deviation of the real-space cutoff error of the total energy is thus

$$\delta E_r \approx Q\ (c/2L^3)^{1/2} (\alpha c)^{-2} \exp(-\alpha^2 c^2). \tag{16}$$

The derivation of the expected real-space cutoff error of the force acting on one particle proceeds in the same way. By using equation (A.3), we have

$$\delta f^2_{r,m} \approx q^2_m\ Q\ L^{-3} \int_r^\infty \alpha^6\, r^2\, z^2(\alpha r)\, 4\pi r^2\, dr. \tag{17}$$

We now insert the asymptotic expansion for z(x) (see (9) and (12)) into equation (17) and use formula (12) to approximate the integral. The resulting standard deviation of the real-space cutoff error of the forces acting on charge (m) is then estimated as

$$\delta f_{r,m} \approx 2 |q_m| (Q/cL^3)^{1/2} \exp(-\alpha^2 c^2). \tag{18}$$

4.2 Reciprocal-Space Errors

In this section we derive estimates of standard deviations for the k-space cutoff errors of the energy and forces. We make the same assumptions as were made in the case of the real-space errors. The most important additional computation is approximating the sum over vectors **k**, $|\mathbf{k}| > K$, by an integral.

As in section 4.1, we first estimate the k-space cutoff errors for one pair of charges (j, m). It follows from (7) and (10) that this error is

$$\delta_{k,jm} = q_m\, q_j \sum_{\substack{\mathbf{k} \\ k>K}} k^{-2} \exp[-(\pi k/\alpha L)^2] \begin{cases} \exp[2\pi i \mathbf{k}\cdot\mathbf{r}/L]/2\pi L \\ 2\mathbf{k}L^{-2} \sin[2\pi \mathbf{k}\cdot\mathbf{r}/L] \end{cases}, \tag{19}$$

where the top expression holds for the energy, the bottom for the force, and **r** stands for $\mathbf{r}_j - \mathbf{r}_m$. For large K we try to approximate the sum in (19) by the integral,

$$\sum_{\substack{\mathbf{k} \\ k>K}} \approx \int_{k>K} d\mathbf{k} = \int_K^\infty k^2\, dk \int_{-1}^{1} dz \int_0^{2\pi} d\phi, \tag{20}$$

where (k, θ, ϕ) are the spherical coordinates chosen so that the z-coordinate of **k** is in the direction of the vector **r**, $\cos\theta = z$, and $\mathbf{k}\cdot\mathbf{r} = krz$. In addition, the angle ϕ does not appear in the integrand. If **r** was a vector in an infinite 3D space then it would follow from the symmetry around the z-axis that the error of the forces was parallel to **r**. In our periodic box this simplification works only approximately because **r** has many representations differing by **Ln**: we must choose the shortest **r**, i.e. the nearest image convention, because then there is at least one **k**-vector sampling each half-wave of $\sin[2\pi\mathbf{k}\cdot\mathbf{r}/L]$ or $\exp[2\pi i\mathbf{k}\cdot\mathbf{r}/L]$ in (19) and the approximation (20) is valid. Under this assumption it is enough to calculate the projection of the error of the force on the z-axis, i.e. to replace the vector **k** in the bottom part of (19) by kz. After performing the integrations over dz and dϕ we get

$$\delta_{k,jm} \approx q_m q_j \int_K^{\infty} dk \exp[-(\pi k/\alpha L)^2] \begin{cases} 2L^{-1} X^{-1} \sin X \\ 8\pi k L^{-2}(X^{-2} \sin X - X^{-1} \cos X) \end{cases} \tag{21}$$

where $X = 2\pi kr/L$. The asymptotic expansion (12) may be used for estimating (21) only if the condition (13) is satisfied. Since the fastest varying part of the integrand in (21) is $\sin X$ or $\cos X$, we may write in the notation of equations (12) and (13)

$$g'(k) \approx 2\pi r L^{-1}\, g(k) = 2\pi r L^{-1}\, f(k)/[2K(\pi/\alpha L)^2]. \tag{22}$$

It is seen from (22) that the condition (13) holds for $r \ll r_K$, where

$$r_K = \pi K/L\alpha^2. \tag{23}$$

Then

$$\delta_{k,jm} \approx q_m q_j \exp[-(\pi K/\alpha L)^2] \begin{cases} \alpha^2 L\pi^{-2} K^{-1} Y^{-1} \sin Y \\ 4\alpha^2 \pi^{-1}(Y^{-2} \sin Y - Y^{-1} \cos Y) \end{cases} \tag{24}$$

for $r \ll r_K$ where Y stands for $2\pi Kr/L$. In addition, we may assume that $\delta_{k,jm} \approx 0$ for $r \gg r_K$ because the integrand is rapidly varying, and both positive and negative half waves of the sin and cos functions cancel.

The essential approximation made here is extending the range of validity of (24) to $r < r_K$ and $\delta_{k,jm} \approx 0$ to $r > r_K$.

The approximation (20) is justified only if $r = |\mathbf{r}_j - \mathbf{r}_m| < L/2$ (and the same holds for (A.3) which we wish to use later). The value of r_K hence should not exceed L/2. If the approximate relations for the optimum values of parameters, (B.2) and (B.3), are inserted into (23) it appears that $r_K \approx c$. As follows from (B.4), for $N \leqslant 64\pi^3 \approx 2000$ it may be efficient to use $c > L/2$ and then also $r_K > L/2$. The inequality $c > L/2$ in pracice means a more complicated (and probably less efficient) program because sums (5) and (8) cannot be computed in the nearest image convention. From the practical point of view, we may thus assume $r_K \leqslant L/2$.

The total K-cutoff error of the energy is now given by the sum over all pairs (with the top parts of formulae applied for $\delta_{k,jm}$)

$$\sum_{j=1}^{N} \sum_{m=1}^{N} \delta_{k,jm}. \tag{25}$$

Note that $\delta_{k,jm}$ depends on $r = |\mathbf{r}_j - \mathbf{r}_m|$ and contains the product $q_m q_j$, The diagonal terms (j = m) are thus positive and do not depend on the positions of the charges and we get a systematic contribution to the cutoff error of the energy which (using (19)) reads as

$$E_{diag} \sim (2\pi L)^{-1}\, Q \sum_{\substack{\mathbf{k} \\ k>K}} k^{-2} \exp[-(\pi k/\alpha L)^2], \tag{26}$$

where we recall that Q is defined by (4). The value of E_{diag} does not depend on the configuration and may be thus computed in advance using a sufficiently large second cutoff, $K_2 > k > K$, in (26). Alternatively, the sum in (26) may be replaced by an integral and (12) gives the approximation

$$E_{\text{diag}} \approx Q\,\alpha^2\,L\,\pi^{-2}\,K^{-1}\exp[-(\pi K/\alpha L)^2]. \tag{27}$$

The off-diagonal terms of the sum (25) have alternating signs and thus the statistical approach (already used to estimate the real-space errors) is valid. From formula (A.3) it follows for the fluctuation of the error of all interactions of one selected particle (m)

$$\delta E_{k,m}^2 \approx q_m^2\,Q\,\alpha^4\,L^{-1}\,\pi^{-4}\,K^{-2}\exp[-2(\pi K/\alpha L)^2]\int_0^{r_K} Y^{-2}\sin^2 Y\,4\pi r^2\,dr, \tag{28}$$

where $r_K \leq L/2$ is assumed (see (23)). Using (B.4) it may be easily shown that in typical cases there are many oscillations of $\sin Y = \sin(2\pi K r/L)$ for $r < r_K$. Then $\sin^2 Y$ may be replaced by its mean value of 1/2 and the integration in (28) gives

$$\delta E_{k,m} \approx |q_m|\,(Q/2K^3)^{1/2}\,\alpha\,\pi^{-2}\exp[-(\pi K/\alpha L)^2]. \tag{29}$$

It follows from (7) that the energy contributions of pairs (j, m) and (m, j) are identical. The sum (25) (without the diagonal terms that have been taken into account by (26)) may be thus written as a sum over pairs, i.e.

$$\sum_{(k,m)} 2\delta_{k,jm}. \tag{30}$$

Exactly the same argument which led to formula (16) then gives the standard deviation of the k-space cutoff error of the total energy

$$\delta E_k \approx Q\,\alpha\,\pi^{-2}\,K^{-3/2}\exp[-(\pi K/\alpha L)^2]. \tag{31}$$

It is worth noting that in typical cases (given by (B.3)) the statistical error of the k-space part of the energy (31) is less than the systematic error approximated by (27). It is then important to include the correction (26) in the calculations.

Since $\delta_{k,jj} = 0$ for the forces, there is no systematic part of the error. The derivation of the statistical part of the error proceeds exactly in the same way as of the statistical part for the energy. The additional approximation involved is neglecting $Y^{-2}\sin Y$ in comparison to $Y^{-1}\cos Y$ in (24). The resulting standard deviation of the k-space cutoff error of the forces acting on charge (m) is

$$\delta F_{k,m} \approx |q_m|\,\alpha L^{-1}\,\pi^{-1}\,(8Q/K)^{1/2}\exp[-(\pi K/\alpha L)^2]. \tag{32}$$

4.3 Numerical Test for a Molten Salt

The test system, a simple model of a molten salt, consists of N atoms (N/2 of charge $+q$ and N/2 of charge $-q$) contained in a cubic box. In addition to the Coulomb forces the repulsive term $\varepsilon(\sigma/r)^{12}$ prevents overlapping of the atoms. The energy parameter ε is set to q^2/σ and reduced units are adopted: σ measures distances and ε/k_B temperature. The sample configurations were obained by the standard Monte Carlo method with the nearest image convention [1]. The reduced density was $N/L^3 = 0.6859$ and the reduced temperature $T = 4$. A sufficient number of Monte Carlo steps was performed to obtain equilibrium configurations.

The calculations of the Ewald sums were done using 64 bit double precision

Table 1 Parameters of four analyzed configurations of molten salt. N is the number of ions, L the box size, E the total electrostatic energy, **f** the electrostatic force acting on one ion, r_{min} the minimum ion–ion distance in the configuration and $\langle\cdot\rangle$ denotes the average over N ions.

N	L	E/N	$\langle \mathbf{f}^2\rangle^{1/2}$	$\mathbf{f}_{max}/\langle \mathbf{f}^2\rangle^{1/2}$	r_{min}
32	3.6	-0.51307	1.67096	1.83	0.81389
108	5.4	-0.48830	1.81500	1.83	0.79638
500	9.0	-0.40563	2.10575	2.08	0.76238
2048	14.4	-0.40037	2.15201	2.46	0.76579

numbers (accuracy better than 10^{-15}). The approximation of functions e(x) and z(x) (equations (6) and (9)) by hyperbolic splines involved errors of the order of 10^{-10} for shorter distances and rather less for longer distances. The dielectric constant ε' at infinity was set to infinity.

One selected configuration was analyzed for each number of particles with many combinations of the value of parameters. the benchmark values of the energy and forces were evaluated first using very pessimistic values of cutoffs (expected errors less than 10^{-15}). This procedure was repeated for a different value of α to check the consistency of the program; the errors did not exceed 10^{-10} which corresponds to the accuracy of functions e(x) and z(x). The results for different values of parameters α, K, and c were then calculated. This represents the error in the total energy and the estimate of the standard deviation of the errors of the forces (1). (The electrostatic energy of each charge was not recorded because this quantity is not used in molecular dynamics). As there are N forces available in the configuration, the statistical uncertainty of these forces is about $N^{-1/2}$. In addition, the maximum error of the forces has been measured and is discussed later in this section. The parameters for the four configurations considered are shown in Table 1.

Table 2 compares both the theoretical and experimental results of the real-space errors for selected sets of Ewald parameters (more extensive data are available upon request). It is seen that the theoretical estimates work surprisingly well. For

Table 2 Molten salt: real-space cutoff errors of energy and forces. L is the box size, α the Ewald parameter with the dimension of [length^{-1}], and c the cutoff distance. ΔE and $\Delta\mathbf{f}$ are the experimental errors while δE_r and δf_r are the estimated standard deviations and $\gamma = |\Delta \mathbf{f}_{max}|/\langle\Delta \mathbf{f}^2\rangle^{1/2}$, where $\langle\cdot\rangle$ denotes the average over N ions.

N	L	α	c	$\delta E_r/N$	$\Delta E/N$	δf_r	$\langle\Delta \mathbf{f}^2\rangle^{1/2}$	γ
32	3.6	1.0	2.5	5.06e-05	7.44e-05	2.02e-03	1.71e-03	1.63
		3.0	1.0	1.42e-06	2.02e-07	2.04e-04	2.27e-04	2.03
108	5.4	1.0	3.5	4.12e-08	1.66e-08	4.24e-06	4.16e-06	1.85
		2.0	1.5	9.46e-07	5.38e-07	1.67e-04	1.75e-04	2.22
		3.0	1.2	1.12e-08	-1.64e-08	3.56e-06	3.75e-06	2.35
500	9.0	0.7	4.5	2.75e-07	3.31e-08	3.83e-05	3.58e-05	2.75
		0.4	2.5	1.62e-08	-4.86e-10	5.01e-06	4.81e-06	2.23
2048	14.4	0.4	7.2	1.05e-06	2.02e-06	1.54e-04	1.33e-04	2.46
		0.8	4.0	9.03e-08	-1.78e-07	2.96e-05	2.81e-05	2.63
			5.0	2.04e-10	8.84e-11	8.34e-08	8.05e-08	3.07
		1.2	3.0	4.07e-09	-3.55e-09	2.25e-06	2.24e-06	2.64
		1.6	2.0	6.38e-08	-9.47e-08	4.18e-05	4.34e-05	3.31

Table 3 Molten salt: reciprocal-space cutoff errors of energy and forces. α is the Ewald parameter, K the k-space cutoff. E_{diag} is the systematic part of the error in the energy, ΔE and $\Delta \mathbf{f}$ are the experimental errors (ΔE is corrected for E_{diag}), δE_k and δf_k are the estimated standard deviations, $\gamma = |\Delta \mathbf{f}_{max}| / \langle \Delta \mathbf{f}^2 \rangle^{1/2}$, and $\langle \cdot \rangle$ denotes the average over N ions.

N	α	K	E_{diag}		δE_k	ΔE	δf_k	$\langle \Delta f^2 \rangle^{1/2}$	γ
			Approx. (27)	Exact (26)					
32	1.0	4	4.66e−07	4.53e−07	6.47e−08	3.21e−08	3.61e−06	3.34e−06	1.47*
	2.0	8	9.32e−07	1.00e−06	4.57e−08	−9.91e−08	5.11e−06	6.20e−06	1.64
	3.0	12	1.40e−06	1.46e−06	3.74e−08	−5.65e−09	6.26e−06	7.03e−06	1.73
108	1.0	6	4.66e−07	3.63e−07	3.52e−08	−6.54e−09	3.61e−06	3.32e−06	2.19*
	2.0	12	9.32e−07	9.75e−07	2.49e−08	3.62e−08	5.11e−06	5.70e−06	1.94
	3.0	18	1.40e−06	1.36e−06	2.03e−08	−9.95e−09	6.26e−06	6.78e−06	2.17
500	0.7	7	3.26e−07	3.37e−07	1.96e−08	1.63e−08	3.02e−06	3.76e−06	2.42*
	1.4	14	6.52e−07	6.19e−07	1.38e−08	7.79e−09	4.28e−06	4.82e−06	2.18
	2.8	25	1.73e−05	1.68e−05	1.37e−07	4.23e−08	7.57e−05	7.71e−05	2.08
2048	0.4	6	8.69e−07	6.93e−07	6.16e−08	6.70e−08	1.03e−05	1.08e−05	2.34*
	0.8	10	5.50e−05	5.34e−05	1.51e−06	2.25e−06	4.22e−04	5.06e−04	2.32
		12	1.74e−06	1.80e−06	4.36e−08	7.13e−08	1.46e−05	1.87e−05	2.49
		14	3.12e−08	2.97e−08	7.23e−10	−6.52e−10	2.83e−07	3.37e−07	2.36
	1.2	20	1.90e−07	1.89e−07	2.46e−09	1.67e−09	1.38e−06	1.62e−06	2.57
	1.6	25	1.34e−06	1.32e−06	1.16e−08	1.56e−08	8.13e−06	9.20e−06	2.45

*$r_K > L/2$ (see equation (23))

the energy, the experimental errors are within the range of the estimated standard deviations (in two thirds of the cases). The agreement for the errors of the forces is even more convincing because both the experimental and estimated values agree in most cases to within 20% which is much better than required in practice.

The k-space errors are shown in Table 3. The results are again very good. A small systematic underestimate of the errors for large N is probably caused by the too crude approximation of the range of validity of (24) to $r < r_K$ and $\delta_{k,jm} \approx 0$ to $r > r_K$. The agreement also slightly deteriorates for very low (unrealistic in practice) values of K where replacing the sum over k-vectors by the integral is indeed very crude.

The probability distribution of the errors was not recorded because it is reasonable to assume that it is Gaussian. An indirect (but from the practical point of view most important) verification of this assumption is the fact that the maximum error Δf_{max} found is only a small multiple of the standard deviation δf, $\Delta f_{max} = \gamma \delta f$. A simple mathematical model of Δf_{max} assumes that errors Δf_i of all $1 \leqslant j \leqslant N$ forces are independent random variables with the 3D Gaussian distribution with the probability density

$$\phi(r) = (2/\pi)^{1/2} \sigma^{-3} r^2 \exp(-r^2/2\sigma^2), \tag{33}$$

where $\sigma^2 = \delta f^2/3$. The probability density of the random variable $\Delta f_{max} = \max\{\Delta f_i\}$ is $d\Phi^N(x)/dx$, where

$$\Phi(x) = \int_0^x \phi(r)\, dr \tag{34}$$

Table 4 Dependence of the expected maximum error in the forces on the number of particles N in the model of independent Gaussian variables. γ.103 $\Delta f_{max}/\delta f$, where δf denotes the standard deviation of the error in the forces and Δf_{max} the maximum error found in the configuration of N particles.

N	$\langle\gamma\rangle$	$(Var\ \gamma)^{1/2}$
32	1.822	0.241
108	2.050	0.214
500	2.302	0.189
2048	2.510	0.173

is the probability that a single error Δf_i is less than x and $\Phi^N(x)$ is the probability that all $\Delta f_{j'}$, $1 \leq j \leq N$, are less than x. The numerical results for the expected value and standard deviation of γ (note that the probability distribution of γ is far from Gaussian) are given in Table 4. It is seen that the data compare well with the experimental results shown in the last column of Tables 2 and 3.

5 INTERACTION SITE MOLECULAR MODELS

A large family of realistic models (TIPS [6], EPEN [7], OPLS [8]) is based on the concept of interaction sites. The sites correspond to atoms or simple groups. The shape of molecules is described either by constraints (fixed bond lengths and angles) or strong spring-like potentials. There are repulsive, dispersion and Coulomb forces defined between pairs of sites.

Since the positions of charges are highly correlated in these models one cannot expect that the results of section 4 will work particularly well. To be more precise, the k-space cutoff errors may be well predicted only if K is so large that the wave length L/K is less than a typical intramolecular distance and, similarly, a validity of the estimates of the real-space cutoff errors in section 4.1 is guaranteed only if $1/\alpha$ is less than this distance. Below we give some alternative estimates of the errors. It is assumed that the molecules are electrically neutral and not too large so that replacing the intramolecular charge distribution by a dipole is valid for some range of parameters.

5.1 Real-Space Errors

If $1/\alpha$ is large then the real-space contributions from a group of point charges of one molecule are strongly correlated and the whole group interacts as a dipole (or a higher multipole). One additional assumption must be satisfied: all the individual charges of the group must be treated together, i.e., not divided by the cutoff to a part for which the real-space contributions are evaluated and a part for which they are not. Such an algorithm (let us call it B) may be advantageous for small molecules.

The derivation of the expected real-space cutoff error in the total energy follows that of section 4.1 and requires analogous assumptions. The result is

$$\delta E_r^{DD} \approx \tfrac{4}{3}\, \alpha^2\, M\, (c/2L^3)^{1/2} \exp(-\alpha^2 c^2), \tag{35}$$

where

$$M = \sum_{i=1}^{N} \mu_i^2 \tag{36}$$

and μ_i is the dipole moment of molecule (i).

Since the point-charge forces and accelerations are the basic quantities in our molecular dynamics study, the charge-dipole interactions should be considered to estimate their errors instead of the dipole-dipole ones. The standard deviation of the real-space error of the force acting on charge (j) caused by dipoles outside the cutoff sphere is approximated by

$$\delta f_{r,j}^{CD} \approx 4\, \alpha^2\, |q_j|\, (Mc/3L^3)^{1/2} \exp(-\alpha^2 C^2). \tag{37}$$

5.2 Reciprocal-Space Errors

The k-space cutoff errors contain, unlike the real-space sums, contributions from those intramolecular pairs of sites which do not interact by Coulomb forces. This leads to systematic errors both in the energy and forces:

$$E_{int} = \sum_{j} \sum_{m \neq j} \delta_{k,jm}, \tag{38}$$

$$f_{int} = \left[\sum_{j} \left(\sum_{m \neq j} \delta_{k,jm} \right)^2 \right]^{1/2}. \tag{39}$$

where $\delta_{k,jm}$ is defined by (19) (note that $\delta_{k,jm}$ is a vector for the forces and a scalar for the energy) and both j and m run over all sites in a molecule. The terms $m = j$ are omitted for the energy because it is assumed that they have been taken into account by (26). Unlike (26), $\delta_{k,jm}$ for $j \neq m$ does depend on the configuration. It does not in approximation (21) provided that the charged skeleton of a molecule is rigid (like in diethylether). The approximated force errors are central and thus they cancel out if projections to the constraint surface are considered.

It follows from the above considerations that the systematic part of the k-space error of the energy cannot be easily corrected. It can also be shown (see the comparison of E_{diag} and ΔE_k in section 4.2) that the systematic part is larger than the statistical part. That is why we did not derive the statistical part in the dipole-dipole approximation.

The above comparison does not hold true for the forces. The expected k-space cutoff error of the force acting on one charge caused by a disordered configuration of dipoles is approximated using the methods of section 4.2 by

$$\delta f_{k,j}^{CD} \approx 4\, \alpha\, L^{-2}\, |q_j|\, (\tfrac{2}{3} KM)^{1/2} \exp[-(\pi K/\alpha L)^2]. \tag{40}$$

5.3 Numerical Test for Diethylether

The particular system under investigation is a realistic OPLS model of diethylether [8]. The model molecule consists of five interaction sites corresponding to two

Table 5 Parameters of two analyzed configurations of diethylether. N is the number of molecules, L the box size, E the total energy of the configuration, **f** the force acting on one site, **a** the acceleration (with components of forces normal to the constraint surface removed), and $\langle\cdot\rangle$ denotes the sum over all sites in a molecule and average over all molecules.

N	L [Å]	E/N [J]	$\langle \mathbf{f}^2\rangle^{1/2}$ [N]	$\langle \mathbf{a}^2\rangle^{1/2}$ [m/s^2]
128	27.906	3.391e−20	5.591e−10	1.743e+16
1024	55.811	3.444e−20	5.308e−10	1.670e+16

methyl groups, two methylene groups, and oxygen. The methyl groups are electrically neutral while the charges of the oxygens and methylenes are −0.5e and 0.25e, respectively. The molecule has fixed bond lengths and fixed bond angles.

The simulations which are part of another project [9] were carried out by molecular dynamics with the Ewald summation included (Table 5). The bond lengths and angles were kept fixed by the constraint dynamics in the Lagrange formulation [10]. The state point of the simulated microanonical ensemble was approximately the one reported in [8] and the computed intermolecular energy and pressure were in accordance with the Monte Carlo results [8]. (The dihedral angle distribution was close to the theorectical ideal gas distribution but was in disagreement with the results of [8], probably because the authors of [8] did not take into account the metric determinant of constraints [11].)

As mentioned above, one may imagine two algorithms to calculate the real-space sums. The more straightforward algorithm (let us call it A) treats each point charge separately and the cutoff test applies to each charge–charge distance. The results for the errors obtained by this method are collected in Table 6. They are compared with the error estimates derived in section 4.1 using the assumption that all charges are independent. In addition, the estimated error in the accelerations contains the factor of $(2/3)^{1/2}$ to correct for components normal to the constraint surface. Although the agreement is not so good as in the case of molten salt, the estimates of the errors in the forces and accelerations are satisfactory. It is not surprising because (with the exception of the smallest α's for N = 1024) the values of $z(\alpha r)$

Table 6 Diethylether: real-space cutoff errors for algorithm A. N is the number of molecules, α the Ewald parameter, and c the cutoff distance. ΔE is the experimental error in the total energy, $\Delta\mathbf{f}$ ($\Delta\mathbf{a}$) is the error of the force (acceleration) acting on one charge, while δE_r, δf_r, and δa_r are the estimates assuming uncorrelated positions of charges, see section 4.1. $\langle\cdot\rangle$ denotes the sum over all charges in a molecule and average over all molecules.

N	α [Å^{-1}]	c [Å]	$\delta E_r/N$ [J]	$\Delta E/N$ [J]	δf_r [N]	$\langle \mathbf{f}^2\rangle^{1/2}$ [N]	δa_r [ms^{-2}]	$\langle \mathbf{a}^2\rangle^{1/2}$ [ms^{-2}]
128	0.20	L/2	8.19e−25	5.43e−25	1.46e−13	9.72e−14	4.72e+12	2.64e+12
	0.30	12	2.61e−27	3.78e−27	9.02e−16	7.41e−16	2.91e+10	1.98e+10
	0.40	9	2.26e−27	2.03e−28	1.04e−15	8.77e−16	3.36e+10	2.37e+10
	0.50	7	4.29e−27	4.21e−27	2.40e−15	2.11e−15	7.74e+10	5.96e+10
1024	0.10	L/2	4.13e−25	−1.51e−25	1.04e−13	5.54e−14	3.36e+12	1.48e+10
	0.15	22	1.18e−26	7.68e−27	5.28e−15	3.50e−15	1.70e+11	9.25e+10
	0.20	18	1.13e−27	−6.78e−29	7.36e−16	5.48e−16	2.37e+10	1.49e+10
	0.30	12	9.23e−28	−1.84e−28	9.02e−16	7.45e−16	2.91e+10	2.03e+10

Table 7 Diethylether: real-space cutoff errors for algorithm B. δE_r^{DD}, δf_r^{CD}, and δa_r^{CD} are the dipole-dipole and charge-dipole error estimates of section 5.1. Other symbols are the same as in Table 6.

N	α [Å^{-1}]	c [Å]	$\delta E_r^{DD}/N$ [J]	$\Delta E/N$ [J]	δf_r^{CD} [N]	$\langle f^2\rangle^{1/2}$ [N]	δa_r [ms^{-2}]	$\langle \mathbf{a}^2\rangle^{1/2}$ [ms^{-2}]
128	0.20	L/2	1.41e−25	−1.63e−24	6.07e−14	1.19e−13	1.96e+12	2.60e+12
	0.30	11	1.28e−26	−5.14e−25	5.49e−15	3.18e−14	1.77e+11	6.39e+11
	0.40	9	2.59e−27	−1.84e−25	1.11e−15	1.94e−14	3.59e+10	4.20e+11
	0.50	7	7.26e−27	−1.45e−24	3.12e−15	1.33e−13	1.01e+11	3.00e+12
1024	0.10	L/2	1.78e−26	−3.37e−25	2.16e−14	3.13e−14	6.98e+11	6.65e+11
	0.15	22	1.60e−27	−7.65e−26	1.94e−15	3.85e−15	6.26e+10	7.46e+10
	0.20	18	3.24e−28	−2.84e−26	3.94e−16	1.32e−15	1.27e+10	2.51e+10
	0.30	12	5.95e−28	−8.62e−26	7.24e−16	5.32e−15	2.33e+10	1.07e+11

change significantly for different charges within a molecule and the charges are thus effectively independent. The remaining correlations cause a moderate decrease of the errors. Similar conclusions can be drawn also for the energy.

The alternative algorithm B calculates the nearest image distance of two reference points in the respective molecules (we used the centre of charges in absolute values) and if this distance is less than the cutoff value then all charge-charge contributions of the pair of molecules are evaluated. The results are shown in Table 7 along with the error estimates based on the assumption that the charge distribution in a molecule may be replaced by a dipole. This assumption is satisfied for N = 1024 and smallest α's only. Then the errors in the forces and accelerations are lower than those obtained by algorithm A and are also predicted by the theory. In other cases the errors for algorithm B are higher than for algorithm A and, of course, the theoretical estimates do not work. The errors of the energy are much higher than predicted by the random dipole approximation (35) and all are negative. This systematic error can be explained by ordering of dipoles outside the cutoff sphere. This phenomenon is for algorithm A hidden in the charge-charge terms caused by splitting molecules at the cutoff sphere.

The k-space results are shown in Table 8. It is seen that the errors in the energy are systematic. For medium values of K they compare well with the estimate (38). The agreement deteriorates for higher values of K which can be explained by observing formula (19); then $2\pi\mathbf{k}\cdot\mathbf{r}/L$ is comparable to π, the values of the terms in (19) may be both high and small or eventually negative and the accuracy of estimates (20)–(24) worsens. The agreement is also worse for very low K.

The errors in the forces are both systematic and statistical. The estimates of the statistical errors are lower, nevertheless, still comparable to the systematic errors. The combined estimate of the errors satisfactorily reproduces the pseudoexperimental values with the exception of the smallest values of K. For the sake of completeness we include also the charge-charge estimate (32), which in most cases seriously overestimates the errors except for a very high K. In this region both the charge-charge and dipole-charge estimates are close to their respective limits of validity.

The systematic part of the errors of the accelerations cancels out in both approximations. The interpretation of the data is then simpler because only the estimate of the statistical part, (40), has to be compared with experiment. The conclusions of the above paragraph are confirmed.

Table 8 Diethylether: reciprocal-space cutoff errors. δf_k and δa_k are the charge-charge estimates of section 4.2, E_{int} and f_{int} are the systematic intramolecular contributions to the errors (section 4.2), while δf_k^{CD}, and δa_k^{CD} are the charge-dipole estimates of the errors (section 5.2). K denotes the k-space cutoff and other symbols are the same as in Table 6.

N	α [Å^{-1}]	K	E_{int} [J]	ΔE [J]	f_{int} [N]	δf_k [N]	δf_k^{CD} [N]	$\langle \Delta f^2 \rangle^{1/2}$ [N]	δa_k [ms^{-2}]	δa_k^{CD} [ms^{-2}]	$\langle \Delta a^2 \rangle^{1/2}$ [ms^{-2}]
128	0.10	3	8.43e−26	4.65e−26	2.08e−16	2.03e−15	5.09e−16	2.36e−16	6.54e+10	1.64e+10	4.83e+0
	0.20	6	1.20e−25	8.70e−26	8.82e−16	2.87e−15	1.44e−15	1.86e−15	9.24e+10	4.64e+10	3.70e+1
	0.30	9	5.47e−26	5.77e−26	9.55e−16	3.51e−15	2.65e−15	3.67e−15	1.13e+11	8.53e+10	8.29e+1
	0.40	12	7.93e−26	−8.77e−26	7.00e−16	4.06e−15	4.07e−15	5.32e−15	1.31e+11	1.31e+11	1.43e+1
1024	0.05	3	4.46e−26	2.40e−26	3.03e−17	1.43e−15	1.80e−16	6.91e−17	4.62e+10	5.80e+09	1.42e+0
	0.10	5	3.38e−24	3.57e−24	6.03e−15	7.25e−14	1.52e−14	1.33e−14	2.34e+12	4.89e+11	2.67e+1
	0.15	8	1.45e−24	1.57e−24	5.84e−15	2.89e−14	9.66e−15	1.15e−14	9.30e+11	3.11e+11	2.35e+1
	0.20	12	1.20e−25	1.18e−25	8.82e−16	2.87e−15	1.44e−15	2.47e−15	9.24e+10	4.64e+10	4.92e+1
	0.30	18	5.47e−26	5.26e−26	9.55e−16	3.51e−15	2.65e−15	4.20e−15	1.13e+11	8.53e+10	9.48e+1

6 OPTIMIZATION OF PARAMETERS

Our task is not to set parameters α, K, and c so that the electrostatic interactions are calculated with sufficient accuracy and the computer time is as short as possible.

The first problem is to choose the accuracy with which the forces (or accelerations or energies) are to be calculated. Let us analyze first the way in which the errors propagate in molecular simulation calculations. The cutoff errors in the forces cause inaccurate sampling which leads to inaccurate values of thermodynamic quantities. Their values are also directly affected by the cutoff errors. The former reason is much more important for global quantities as the energy or virial. The relative errors of the forces should be then of the same order of magnitude as the desired relative errors of measured quantities. On the other hand, the cutoff errors are both positive and negative and one thus can expect some cancellations of the errors when averages are calculated. The relative error of the forces may be thus larger. In addition, the real-space cut off potential is step-wise which may cause problems if a higher order and less stable integrator of the differential equations is used while the k-space cut off potential is still continuous with all derivatives. It then makes sense to use larger k-space errors.

Having three parameters, α, K, and c, and two relations (e.g. equations (18) and (32)) there is one free parameter left which is to be set to minimize the computer time. Since the inequality $c \leq L/2$ is to be satisfied in most cases, it is reasonable to choose the real space cutoff c as this free parameter. Given a value of c, the parameters α and K are obtained by solving equations (18) and (32) (or similar) for given accuracy. By trying several values of c and measuring or estimating the computer time the best c is obtained.

The following example is based on our first experiments with a parallel program for the Meiko T40 transputer array. It implements a highly efficient code for the Ewald summation as well as for the functions e(x) and z(x) and used the link cell method to calculate the pair sums. Although the performance of the program is affected by many factors (number of processors, presence of a vector coprocessor or even cache memory), we believe that the timing results are qualitatively relevant for any calculation with many charges.

The simulated system was a mixture of ions and oligomers of poly (ethylene oxide) in the OPLS and TIPS models. The cumulative computer time of one molecular dynamics step, i.e. the measured time of one step multiplied by the number of processors, was approximately

$$N[1.05e{-}2+4.0e{-}5(K+1)^3+3.9e{-}6\,\text{Å}^{-3}\,c^3]\,s, \tag{41}$$

where N denotes the total number of sites (of these, 0.72N are charged). Note that the absolute term is rather high because it contains the cost of communication, constraint dynamics, initializing the link cell lists, etc. The accuracy requirement was 1e−14 N for the real space part of the force on the maximum charge (i.e. the ion) and 3e−14N for the k-space part which is to be compared with the average force on a site which was 9e−11N (with all interactions included and the constraint forces removed).

Formula (18) was used for estimating the real space errors while a combined formula of (32) (for ion–ion terms) and (40) (for interactions of ion with the CH2–0–CH2 groups) for estimating the k-space errors.

The calculated optimum values of the parameters and the computer time for

Table 9 Optimum values of Ewald parameters, c, α and K for a simulation of polyelectrolytes on a Meiko transputer array. N is the total number of sites (charged and uncharged), L the box size and the time is summed over all processors.

N	*c/L*	αL	*K*	*time/s*
1136	0.500	6.7	6.6	49
1e4	0.340	9.8	9.5	999
1e5	0.227	14.5	13.9	2.7e4
1e6	0.152	21.5	20.4	7.9e5

several sizes of the system are shown in Table 9. It is seen that for $N < 1136$ (800 charges) the predicted cutoff is greater than half the box size and $c = L/2$ must be used. On the other hand, using $c = L/2$ for large systems is very inefficient (by a factor of 5 for $N = 100000$).

7 CONCLUDING REMARKS

The present article proposed closed formulae for both real and reciprocal space cutoff errors in the Ewald summation. The estimates work with precision higher than required by practice for a disordered configuration of point charges (molten salt). Satisfactory estimates were found also for point charge molecular models where, however, different estimates apply to different ranges of parameters and the errors have both statistical and systematic contributions. The estimates were found useful for setting and optimizing the Ewald parameters in simulations. Our experience shows that careful setting of the Ewald parameters avoids both errors in calculations and unnecessary inefficiency.

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APPENDIX A

Let us consider a statistical system consisting of N point charges $\{q_i\}_{i=1}^N$, $\Sigma_{i=1}^N q_i = 0$, contained in volume V. The errors throughout this paper are often expressed in the form

$$F(\{q_i, \mathbf{r}_i\}) = \sum_{i=1}^{N} q_i f(\mathbf{r}_i), \tag{A.1}$$

where f is a certain function of distance. The values of (A.1) may be both positive and negative and (since they are sums of many small contributions) it is reasonable to assume that they have a Gaussian distribution. The estimate of the standard deviation of F is defined by

$$\delta F = \langle F^2 \rangle^{1/2}, \tag{A.2}$$

where the expectation is over all configurations. It is easy to evaluate δF provided that positions of all charges in volume V are uncorrelated (ideal gas assumption). The result is

$$\delta F^2 = V^{-1} \sum_{i=1}^{N} q_i^2 \int_V f^2(\mathbf{r})\, d\mathbf{r}. \tag{A.3}$$

APPENDIX B

In this Appendix we derive approximate optimum values of the parameters α, K, and c. The results are not intended as a guide or recommendation for setting these parameters in the simulations but rather as a rough estimate of the range of the values that eanbles us to make some reasonable assumptions in the derivations of approximate error formulae.

There are $\frac{4}{3}\pi c^3 N L^{-3}$ particles within the cutoff c-sphere. The computer time needed to compute the real-space part of the Ewald summation formulae is then proportional to $\frac{4}{3}\pi c^3 N^2 L^{-3}$ provided that a suitable algorithm is chosen (e.g. a link cell method if $c \ll L$). Similarly, the work necessary to compute the k-space part if $\frac{4}{3}\pi K^3 N$. These overheads should be approximately equal for the optimum choice of parameters and thus we obtain the relation

$$K \approx N^{1/3} c/L. \tag{B.1}$$

The real-space part of the cutoff error contains the exponential $\exp(-\alpha^2 c^2)$. Let us consider $\exp(-\pi^2) \approx 5 \times 10^{-5}$ as the acceptable error. Then

$$\alpha c \approx \pi. \tag{B.2}$$

Similarly, the k-space part contains $\exp[-\pi K/\alpha L)^2]$, and hence

$$K \approx \alpha L. \tag{B.3}$$

On combining (B.1)–(B.3) we obtain finally

$$\begin{aligned} K &\approx \pi L \approx \alpha^{1/2} N^{1/6} \\ c &\approx L\pi^{1/2}/N^{1/6}. \end{aligned} \tag{B.4}$$

Another consequence of (B.4) is that the computational overhead to calculate all forces scales as $N^{3/2}$.