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Ewald methods in molecular dynamics for systems of finite extent in one of three dimensions

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We describe a new method for the treatment of molecular-dynamics computer simulation for systems with long-range interactions when the system to be simulated is only infinite in two of the dimensions of the three-dimensional space. Such problems arise, for example, in the study of surfaces. We report a method to deal with these problems based on Ewald techniques but involving several new features. Numerical tests show that our methods are fast and accurate enough to be feasible for study of the systems of interest, though not quite as fast as the corresponding techniques for bulk systems. We report results of a simulation of water between two dielectric walls using the new methods.

I. INTRODUCTION

Molecular-dynamics simulations have become an important tool for the study of the classical statistical mechanics of many-body systems. In many models of practical interest, it is necessary to consider Coulomb interactions between the particles. As a practical matter, even with the most modern computers one cannot make computations on systems having these long-range interactions which are large enough to adequately describe bulk systems without special techniques. The techniques used include estimation, by the reaction field approximation or by other mean-field methods, of the field due to the particles not in the finite-size sample. The most accurate method, however, is the use of an extension of the Ewald method[1] for calculation of electric fields in ionic crystals.[2] In this method, the entire molecular-dynamics sample is reproduced an unlimited number of times in all three Cartesian directions [see Fig. 1(a)] and the resulting electric fields and electrostatic potentials are calculated by Ewald methods. Thus the simulated system at any moment in time has the symmetry of a crystal with a large unit cell containing all the particles.

In many problems of interest in condensed-matter and statistical physics and chemistry, one encounters systems which are effectively finite in some directions and infinite in others. Examples include a polar fluid or an electrolyte trapped between two plates (as in some electrochemical configurations) and a beam of charged particles in an accelerator. In the first example, just two dimensions are effectively infinite while in the second, there is only one macroscopic dimension. This paper presents modifications of the Ewald method for the treatment of Coulomb interactions in molecular-dynamics simulations of such systems. In the past, there have been some attempts[3] to deal with these systems by using the same three-dimensional codes which were developed for bulk fluids, merely reproducing the system many times in the finite directions [as sketched in Fig. 1(b)]. This method can lead to errors, however, unless the reproduced finite systems are made so far apart that the calculations become quite impractical as one can see by the following argument: If the molecular-dynamics sample is charge neutral, then the unphysical periodic replicas of the system

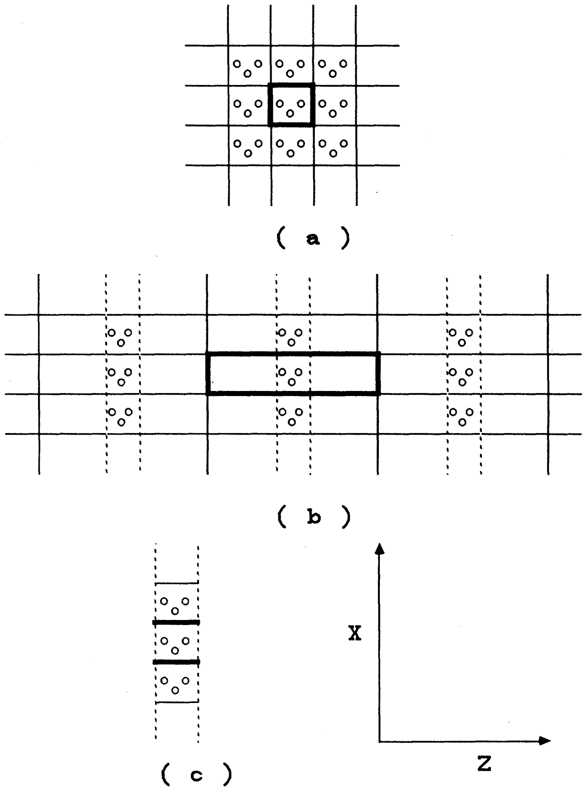

FIG. 1. (a) Schematic illustration of the Ewald technique for a bulk system. (b) Illustration of the treatment of a system with two boundless dimensions and one finite dimension by means of "slabs" reproduced periodically both in the direction of finite extent and in the directions of infinite extent. (c) Illustration of the method used here in which the system is replicated only in the directions of infinite extent.

in the finite directions [the z direction in Fig. 1(b)] will not lead to any unphysical fields in the mean-field approximation. But a particle in the sample will observe fields arising from inhomogeneities in the charge distribution of the periodically replicated cells. Such inhomogeneities occur up to a scale L which is the size of the molecular-dynamics sample in the infinite directions. This means that to avoid a significant effect from these unphysical fields, one must make the system much larger in the finite directions than in the infinite directions with consequent loss of computational efficiency. To avoid this problem, several workers have used mean-field estimates of various kinds[4,5] to account for the electric fields arising from charges outside the molecular-dynamics or Monte Carlo sample. Such methods do not take into account the short-wavelength structure in the fluid near the molecular-dynamics cell.

Finally one may attempt to use Ewald methods in these quasi-two-dimensional systems. Various versions of such methods have been considered, for example, by Heyes and co-workers.[6] The same group has also used multipole expansions of the fields arising from the reproduced cells as well as Evjen summation techniques. Here we report a method for the treatment of this problem which combines Ewald techniques with multipole expansions in a way which we have found numerically satisfactory and which appears to be new. We have redeveloped the Ewald methods from the beginning for a two-dimensional Ewald sum on a three-dimensional sample reproduced an infinite number of times in two of the three directions [Fig. 1(c)]. We have tested the resulting formulation numerically using several different functions in order to separate the coordinate and reciprocal space sums. Although this method still does not take into consideration the fact that there are artificial spatial correlations between the charge fluctuations in different cells, we believe, nevertheless, that it represents an advance on previous work. In Sec. II we describe the formal development and in Sec. III we present the results of the numerical tests. Section IV contains conclusions and discussion.

II. FORMAL DEVELOPMENT

To do the Ewald method for the case of interest, we reproduce the cell an infinite number of times in two of the three Cartesian directions. We regard the system as finite in both directions along the third coordinate (as if, for example, water were sandwiched between two parallel planes). We can later introduce boundary conditions and fields at the two ends of the sample in the direction normal to the wall which correspond to such physical effects as the charging of an electrode, the Debye-Huckel-Gouy-Chapman screening of fields, the diffusion of ions up to a metal surface, and possibly the tunneling of electrons from one metal plate to another across a small gap filled with water.

It is not sufficient to simply use the three-dimensional Ewald codes for a narrow sheet in the middle of the three-dimensional cell because long-wavelength charge fluctuations in the sample would result in fields which cause unphysical interactions between the sheets. Instead, we reformulate the problem. The charge density is

$$n(\mathbf{r})=\sum_{j,\boldsymbol{\nu}} q_j \delta(\mathbf{r}-\mathbf{r}_j+\boldsymbol{\nu}) \tag{1}$$

in which the charges q_j are both in the sample (positions $\mathbf{r}_j$) and at the periodically continued positions $(\mathbf{r}_j+\boldsymbol{\nu})$. This can be written

$$n(\mathbf{r})=(1/\Omega)\sum_{\mathbf{k}} n(\mathbf{k})e^{i\mathbf{k}\cdot\mathbf{r}} \tag{2}$$

in which

$$n(\mathbf{k})=\sum_j q_j e^{-i\mathbf{k}\cdot\mathbf{r}_j}\sum_{\mathbf{G}}\left[\frac{2\pi}{L}\right]^2 \delta^{(2)}(\mathbf{k}_s-\mathbf{G}) \ . \tag{3}$$

L is the length of a side of the unit cell, $\delta^{(2)}$ is a two-dimensional δ function, and $\mathbf{k}_s$ is the projection of the three-dimensional vector $\mathbf{k}$ onto the xy plane. Inserting this in the Poisson equation $\nabla^2\phi(\mathbf{r})=-4\pi n(\mathbf{r})$ and solving by Fourier transform gives

$$\phi(\mathbf{r})=4\pi/A\sum_j q_j\sum_{\mathbf{G}}\int\frac{dk_z}{2\pi}\frac{e^{-ik_z(z_j-z)}}{k_z^2+\mathbf{G}^2}e^{-i\mathbf{G}\cdot(\mathbf{s}_j-\mathbf{s})} \ , \tag{4}$$

where the $\mathbf{G}$ are reciprocal lattice vectors corresponding to the two-dimensional lattice of repeated cells. A is L^2. The total electrostatic potential energy V_N of the system is then

$$V_N=\tfrac{1}{2}\int n(\mathbf{r})\phi(\mathbf{r})d\mathbf{r}-\tfrac{1}{2}\sum_j q_j^2\int\frac{\delta(\mathbf{r}-\mathbf{r}_j)}{|\mathbf{r}-\mathbf{r}_j|}d\mathbf{r} \ , \tag{5}$$

where the second term corrects for a self-energy occurring in the first. We insert the previous expressions for $\phi(\mathbf{r})$ and $n(\mathbf{r})$ in this. The term involving $\mathbf{G}=0$ in the sum on reciprocal lattice vectors must be treated separately. We find

$$V_N=\tfrac{1}{2}\sum_{j,l} q_j q_l \psi(|z_{lj}|,\mathbf{s}_{lj})-\frac{\pi}{A}\sum_{j,l} q_j q_l |z_{lj}| -\tfrac{1}{2}\sum_i q_i^2\int dr\,\delta(r)/r \ . \tag{6}$$

The second term can be understood physically as the energy of the interaction which the charges would have if they were spread smoothly over the x and y directions while the first term takes account of the inhomogeneity of the charge distribution in the x and y directions. $\psi(|z|,\mathbf{s})$ is defined by

$$\psi(|z|,\mathbf{s})=\frac{2\pi}{A}\sum_{\mathbf{G}}{}'\,\frac{e^{-G|z|}}{G}e^{-i\mathbf{G}\cdot\mathbf{s}} \ . \tag{7}$$

The prime on the sum on reciprocal lattice vectors means that the term with $\mathbf{G}=0$ is to be omitted. $\mathbf{s}$ is a position vector in the plane parallel to the boundary walls so that $\mathbf{r}=(\mathbf{s},z)$. To use the Ewald method we must introduce a function $f(\alpha,G,z)$ which plays the role of separating the expression for V_N into a sum on lattice vectors and a sum on reciprocal lattice vectors. By a suitable choice of f we wish to cause both sums to converge at a sufficiently rapid rate to make the method practicable. f is introduced into the previous expression for ψ as follows:

$$\psi(|z|,\mathbf{s})=\frac{2\pi}{A}\sum_{\mathbf{G}}{}'\frac{e^{-G|z|}}{G}[1-f(\alpha,G,z)]e^{-i\mathbf{G}\cdot\mathbf{s}}+\frac{2\pi}{A}\sum_{\mathbf{G}}{}'\frac{e^{-G|z|}}{G}f(\alpha,G,z)e^{-i\mathbf{G}\cdot\mathbf{s}}\ . \tag{8}$$

We require that $f(\alpha,0,z)=1$. The parameter α will control how fast f approaches zero for large $|G|$. The first term will be calculated as a sum on lattice vectors. To express it in that way we define

$$F(\alpha;z;\mathbf{s})=\int\frac{d^2G}{(2\pi)}\frac{e^{-G|z|}}{G}[1-f(\alpha,G,z)]e^{i\mathbf{G}\cdot\mathbf{s}}\ . \tag{9}$$

$F(\alpha;z;\mathbf{s})$ depends only on the magnitude of its third argument. We find that the first term of Eq. (8) can be expressed in terms of the "effective interaction" F as

$$\sum_{\nu}F(\alpha;z;\mathbf{s}-\nu)+\frac{2\pi}{A}\left.\frac{\partial f(\alpha,G,z)}{\partial G}\right|_{G=0}\ . \tag{10}$$

[For a choice of f which we use below, $F(\alpha;0;s)$ is compared with $1/s$ in Fig. 2.] In the first term of Eq. (10) one can separate out the term with $i=j$ and show that it contains an infinity which cancels the infinite last term of Eq. (6) up to an additive finite constant. The final form for the potential energy is

$$V_N=\frac{\pi}{A}\sum_{i,j}{}'\sum_{[G]}{}'q_iq_je^{-i\mathbf{G}\cdot\mathbf{s}_{ij}}\frac{e^{-G|z_{ij}|}}{G}f(\alpha,G,z_{ij})+\tfrac{1}{2}\sum_{i,j}{}'\sum_{[\nu]}q_iq_jF(\alpha;z_{ij};\mathbf{s}_{ij}-\nu)-\frac{\pi}{A}\sum_{i,j}q_iq_j|z_{ij}|+c_1(\alpha,\{z_{ij}\})+c_2(\alpha)\ . \tag{11}$$

Expressions for $c_1(\alpha,\{z_{ij}\})$ and $c_2(\alpha)$ are derived in Appendix A. In practice, $c_2(\alpha)$ plays no role in the molecular-dynamics simulation except that it depends on the function f and thus can be useful in confirming that a code is behaving correctly by checking that the potential energy is independent of the choice of the function f, as it must be.

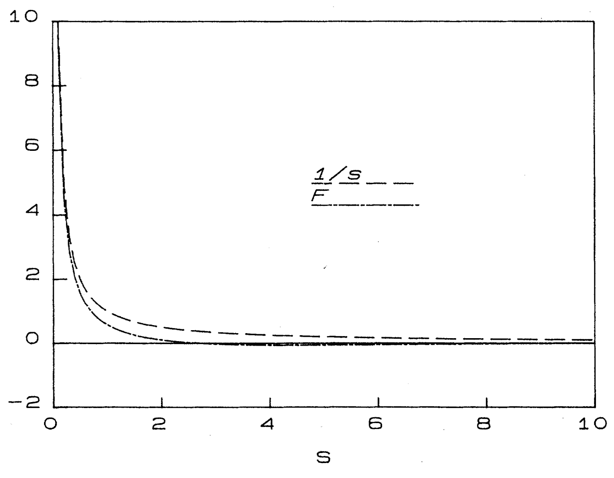

FIG. 2. Function $F(\alpha;0;s)$ compared with the function $1/s$ using the form in Eq. (13) for $f(\alpha,G,z)$ and $N=3$.

The electrostatic part of the forces on the particles in a molecular-dynamics simulation are determined by differentiation of V_N in the usual way. Full expressions for the forces are given in Appendix B.

We have considered several possible forms for the function $f(\alpha,G,z)$. First we tried forms which were independent of z,

$$f(\alpha,G)=e^{-(\alpha G)^n}\ , \tag{12}$$

with $n=1,2,3$. The choice $n=2$ corresponds to the choice made in the usual Ewald method. The resulting function $F(\alpha;z;\mathbf{s})$ must then be calculated on a two-dimensional array associated with the variables z and s. The resulting algorithm gave reasonable results but required a very large amount of storage for this array. We could avoid the necessity for this two-dimensional array by using an explicit z dependence in f,

$$f(\alpha,G,z)=e^{|\mathbf{G}|z}e^{-(\alpha G)^n}\ . \tag{13}$$

The z dependence is chosen to exactly compensate the factor $e^{-|\mathbf{G}|z}$ in the second term in the integrand of the definition of $F(\alpha;z;\mathbf{s})$ [see Eq. (9) and Appendix A] so that the large array is not necessary. This choice also simplifies the calculation of the sums in reciprocal space by permitting use of the identity

$$\sum_{i,j}q_jq_ie^{i\mathbf{G}\cdot(\mathbf{r}_i-\mathbf{r}_j)}=\left|\sum_i q_ie^{i\mathbf{G}\cdot\mathbf{r}_i}\right|^2\ .$$

As a consequence of the second advantage, the computation time for the sums in reciprocal space increases linearly with particle number instead of as the square of the particle number. The price which is paid for the advantages is that the short range part of the forces have a part which decays algebraically at long distances s instead of exponentially. Physically, this corresponds to the multipole fields of the sample charge arising from the finite width of the sample in the z direction. We have made such a multipole expansion of the relevant terms in order to deal with these effects. The details are described in Appendix B. Using this last choice for $f(\alpha,G,z)$, one finds without great difficulty that

$$F(\alpha;z;\mathbf{s})=\frac{1}{(s^2+z^2)^{1/2}}-\int_0^\infty dG\,J_0(Gs)e^{-(\alpha G)^n}\ ,$$

where $J_0(GS)$ is the zero-order Bessel function.

III. NUMERICAL TESTS

To implement the method set out formally in Sec. II one must choose values of α and n. The function $F(\alpha;z;s)$ is then computed and tabulated. In the molecular-dynamics simulation, this function is used to evaluate the coordinate space sums in Eqs. (11) and (B3). In tests of the algorithms with separation function (12) we evaluated the electrostatic potential and force for each of 250 particles placed for convenience in a bcc array in a cubic box which was continued periodically in the x and y directions in order to test the various functions $f(\alpha,G)$. We found, unlike the implementation of the Ewald method in three dimensions, that we could not efficiently confine the coordinate space sums to one cell. Twenty-five cells (up to the third-neighbor "square shell") were required in both coordinate and reciprocal space. The best results were obtained with $n=3$ and $\alpha/L=0.116$. The resulting code is not as fast as corresponding Ewald codes for a bulk system written by ourselves and others[7,8] but it would be fast enough to make the method practical if it were not for the large memory requirements. Various checks on the accuracy of the calculated forces were carried out.

To test the alternative separation function (13) we used the Toukan-Rahman[9] molecular-dynamics model of water. That model describes the water molecules in terms of central forces between three points (one oxygen and two hydrogen atoms) in each molecule. In addition to short-range forces described in Ref. 9, the oxygens have charge $-0.82|e|$ and the hydrogens have charge $0.41|e|$. Using this method we tested the method on a sample of 216 molecules of water between two rigid "walls" in normal to the z direction. The water-wall potential was taken to be

$$V_w(z)=A/z^9-B/z^3 ,$$

where $A=43.1$ a.u. Å^9 and $B=0.10$ a.u. Å^3 for the oxygen-wall component of the water-wall interaction and A takes the same value while $B=0$ for the hydrogen-wall interaction. This water-wall potential is the same as one used in simulations of two ideal classical metal walls[10] and is discussed somewhat further in Ref. 10. We tested the algorithm for $n=2$ and $n=3$ and for a range of α values. With $n=3$ we found better convergence than with $n=2$. The convergence was not sensitive to the value of α in the range $0.07\leq\alpha/L\leq0.15$. When we used $\alpha/L=0.11$ the calculation time was 0.574 seconds per step in the molecular-dynamics calculation. In this calculation, 9 cells (up to the second square shell) were included in coordinate space and 709 reciprocal lattice vectors in reciprocal space were included. To estimate whether this number of coordinate space shells was sufficient, we calculated the forces for the next square shell in a few instances and found that the next shell contribute a correction of only about one part in 10^4. We find pair correlation functions which indicate that the water model is behaving reasonably in this two-dimensional configuration. In Fig. 3, we show the density of the oxygens (Gwo) and hydrogens (Gwh) as a function of distance from the walls after simulation for 10 ps of real time. A comparison of these resutls with the results of Ref. 10 shows that the peaks are slightly broader but almost exactly the same distance from the wall as those found in the simulation of water between ideal classical metal walls. [The full width at half maximum (FWHM) of the first peak is 1.38 Å here and 1.30 Å in Ref. 10.]

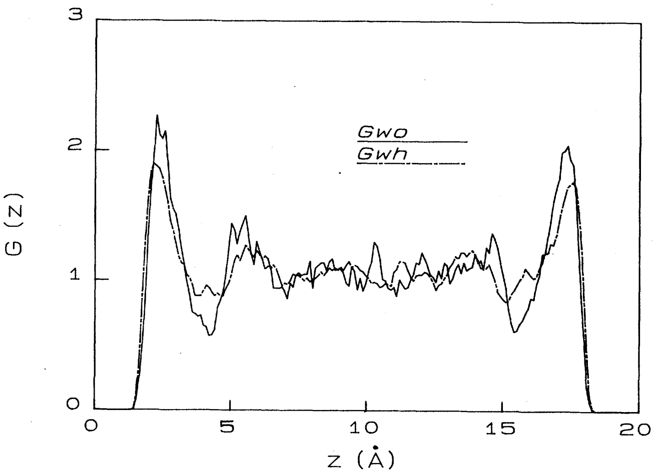

FIG. 3. Density of oxygen (Gwo) and hydrogen (Gwh) as a function of distance across space between two rigid walls in the Toukan-Rahman model of water calculated using the methods described here.

IV. DISCUSSION AND CONCLUSIONS

These studies show that an Ewald method which is practical exists for the kinds of constrained geometries in which we are interested. The most detailed studies with which we may compare this work are those of Heyes and co-workers.[6,11–13] Our Ewald method is related to that of Ref. 13 as follows. We rewrite the charge distribution

$$n(\mathbf{r})=\sum_{j,\nu} q_j\delta(\mathbf{r}-\mathbf{r}_j+\boldsymbol{\nu}) , \tag{14}$$

as

$$n(\mathbf{r})=\bar{n}(\mathbf{r})+[n(\mathbf{r})-\bar{n}(\mathbf{r})] , \tag{15}$$

where

$$\bar{n}(\mathbf{r})=\sum_{j,\nu}\delta(z-z_j)e^{-(\mathbf{s}_j-\mathbf{s}+\boldsymbol{\nu})^2/4\alpha^2}/4\pi\alpha^2 . \tag{16}$$

Following the steps of Appendix A of Ref. 13 we find that the first term of Eq. (15) gives precisely the reciprocal space part of our result in Eq. (11) while the second term of (15) gives the real-space sum, as long as we choose $n=2$ in Eq. (11). Thus the differences between our methods and those of Ref. 13 are that (1) in the Heyes method, the Gaussian spreading is applied to the charges in the z direction normal to the repeat directions as well as in the transverse directions, even though there is no periodicity in that direction, whereas, with a Gaussian separation function f, we apply the spreading only in the directions in which the sample is periodically repeated, and (2) the method of Ref. 13 is confined to Gaussian separation functions [$n=2$ in Eq. (11) of the present paper]. We have found, as explained above that $n=3$ in Eq. (11) gives a faster algorithm. With regard to comparing the computational speed of the methods, we note that in Ref. 11 the Ewald method of Ref. 13 is reported to be slower than the depolarized Evjen method. But the reported computational time for the latter method is 0.14 sec/step for 216 particles on the Cray 1-S. Our calculations are for 648 particles on the Cray-2. Because the clock time of the Cray-2 is about three times shorter than that of the Cray 1-S we estimate that our algorithm would require about $0.574\times 3/9\approx 0.2$ sec/step for 216 particles on the Cray 1-S. This time is comparable to that reported for the depolarized Evjen method so that on the basis of the report of Ref. 11, our algorithm is probably faster than that of Ref. 13. Of course, we have not completely explored the space of functions $f(\alpha,G,z)$ and it is possible that further improvements can be made in this direction. The extension of these results to systems with two finite dimensions and one infinite one is straightforward. We have worked out the formal methods for doing this but have not yet tested the resulting algorithms numerically. The development of this method opens the way to study of a variety of problems involving charged fluids at surfaces by molecular-dynamics techniques.

ACKNOWLEDGMENTS

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APPENDIX A: DERIVATION OF THE EXPRESSIONS FOR $c_1(\alpha,\{z_{ij}\})$ AND $c_2(\alpha)$

By Fourier transforming the definition of the effective interaction $F(\alpha;z;\mathbf{s})$ we find

$$\frac{e^{-G|z|}}{G}[1-f(\alpha,G,z)]=\frac{1}{2\pi}\int d^2s\,F(\alpha;z;\mathbf{s})e^{i\mathbf{G}\cdot\mathbf{s}} \,. \tag{A1}$$

Substituting this into Eq. (6) using (8), the first term becomes

$$\begin{aligned}\tfrac{1}{2}\sum_{i,j}q_iq_j\frac{1}{A}\int d^2s'F(\alpha;z_{ij};\mathbf{s}')\left[\sum_{\{\mathbf{G}\}}e^{i\mathbf{G}\cdot(\mathbf{s}_{ij}-\mathbf{s}')}-1\right]&=\tfrac{1}{2}\sum_{i,j}q_iq_j\frac{1}{A}\int d^2s'F(\alpha;z_{ij};\mathbf{s}')\left[A\sum_{[\boldsymbol{\nu}]}\delta(\mathbf{s}-\mathbf{s}_{ij}+\boldsymbol{\nu})-1\right]\\&=\tfrac{1}{2}\sum_{i,j}q_iq_j\sum_{[\boldsymbol{\nu}]}F(\alpha;z_{ij};\mathbf{s}_{ij}-\boldsymbol{\nu})-\tfrac{1}{2}\sum_{i,j}q_iq_j\frac{1}{A}\int d^2s'F(\alpha;z_{ij};\mathbf{s}') \,.\end{aligned} \tag{A2}$$

This gives Eq. (11) in which

$$c_1(\alpha,\{z_{ij}\})=-\frac{1}{2A}\sum_{i,j}q_iq_j\int d^2s'F(\alpha;z_{ij};\mathbf{s}') \,.$$

From (A1)

$$c_1(\alpha,\{z_{ij}\})=-\frac{\pi}{A}\sum_{i,j}q_iq_j\lim_{G\to 0}\left[\frac{e^{-G|z_{ij}|}}{G}[1-f(\alpha,G,z_{ij})]\right]=\frac{\pi}{A}\sum_{i,j}q_iq_j\left.\frac{\partial f(\alpha,G,z_{ij})}{\partial G}\right|_{G=0} \,. \tag{A3}$$

The constant $c_2(\alpha)$ in Eq. (11) comes from the contribution of the $i=j$ term in Eq. (A2) together with the self-energy correction in Eq. (6),

$$c_2(\alpha)=\tfrac{1}{2}\sum_i\sum_{[\bar{\nu}]}q_i^2F(\alpha;0;\boldsymbol{\nu})-\tfrac{1}{2}\sum_i q_i^2\int\frac{1}{r}\delta(r)dr=\tfrac{1}{2}\sum_i q_i^2\sum_{[\boldsymbol{\nu}]}{}'F(\alpha;0;\boldsymbol{\nu})+\tfrac{1}{2}\sum_i q_i^2\lim_{r\to 0}[F(\alpha;z;\mathbf{s})-1/r] \,.$$

But $F(\alpha;z;\mathbf{s})$ can be written as

$$F(\alpha;z;\mathbf{s})=\frac{1}{r}-\frac{1}{2\pi}\int d\mathbf{G}\,e^{i\mathbf{G}\cdot\mathbf{s}}f(\alpha,G,z)\frac{e^{-G|z|}}{G} \,.$$

Thus $c_2(\alpha)$ is given by

$$c_2(\alpha)=\tfrac{1}{2}\sum_i q_i^2\sum_{[\boldsymbol{\nu}]}{}'F(\alpha;0;\boldsymbol{\nu})-\tfrac{1}{2}\sum_i q_i^2\int_0^\infty dG\,f(\alpha,G,0) \,.$$

APPENDIX B: TREATMENT OF ALGEBRAICALLY DECAYING TERMS IN THE SHORT-RANGE INTERACTION

Using $f(\alpha,G,z)$ from Eq. (13) in Eqs. (11) and (A3) one has, defining $g(\alpha,G)=e^{(\alpha G)^n}$, that

$$c_1(\alpha,\{z_{ij}\})=\frac{\pi}{A}\sum_{i,j}q_iq_j|z_{ij}|+\frac{\pi}{A}\sum_{i,j}q_iq_j\left.\frac{\partial g(\alpha,G)}{\partial G}\right|_{G=0} \,, \tag{B1}$$

$$V_N=\frac{\pi}{A}\sum_{\{\mathbf{G}\}}{}'\frac{g(\alpha,G)}{G}\left|\sum_j q_j e^{i\mathbf{G}\cdot\mathbf{s}_j}\right|^2+\tfrac{1}{2}\sum_{i,j}{}'\sum_{\{\boldsymbol{\nu}\}}q_iq_jF(\alpha;z_{ij};\mathbf{s}_{ij}-\boldsymbol{\nu})+\frac{\pi}{A}\sum_{i,j}q_iq_j\left.\frac{\partial g(\alpha,G)}{\partial G}\right|_{\mathbf{G}=0}+c_2(\alpha)\ . \tag{B2}$$

The last two terms in V_N are independent of the positions of the particles and do not contribute to the force. The force $\mathbf{F}_k$ on the kth particle is then given by differentiation of the other terms as

$$\mathbf{F}_k=\frac{2\pi}{A}\sum_{\{\mathbf{G}\}}{}'\frac{\mathbf{G}}{G}g(\alpha,G)\sum_j q_kq_j\sin(\mathbf{G}\cdot\mathbf{s}_{kj})+\sum_{j\neq k}\sum_{\{\boldsymbol{\nu}\}}q_kq_j(\mathbf{s}_{kj}+\boldsymbol{\nu})\left[\frac{1}{(|\mathbf{s}_{kj}+\boldsymbol{\nu}|^2+z_{kj}^2)^{3/2}}+\frac{df\,s(\alpha;|\mathbf{s}_{kj}+\boldsymbol{\nu}|)}{|\mathbf{s}_{kj}+\boldsymbol{\nu}|}\right]$$
$$+\sum_{j\neq k}\sum_{\{\boldsymbol{\nu}\}}q_kq_j\hat{z}\frac{z_{kj}}{(|\mathbf{s}_{kj}+\boldsymbol{\nu}|^2+z_{kj}^2)^{3/2}}\ , \tag{B3}$$

where

$$df\,s(\alpha;s)=\frac{\partial}{\partial s}\left[\int_0^\infty dG\,J_0(Gs)g(\alpha,G)\right]\ .$$

In the second term of the last equation for the force, we add and subtract the term $1/|\mathbf{s}_{kj}+\boldsymbol{\nu}|^3$ in order to separate the sum into a short-range part and a part which can be treated by a multipole expansion in the charge moments of the layer

$$\sum_{\boldsymbol{\nu}}\left[\frac{1}{|\mathbf{s}_{kj}+\boldsymbol{\nu}|^2+z_{kj}^2)^{3/2}}+\frac{df\,s(\alpha;|\mathbf{s}_{kj}+\boldsymbol{\nu}|)}{|\mathbf{s}_{kj}+\boldsymbol{\nu}|}\right](\mathbf{s}_{kj}+\boldsymbol{\nu})=\sum_{\boldsymbol{\nu}}\left[\frac{1}{|\mathbf{s}_{kj}+\boldsymbol{\nu}|^3}+\frac{df\,s(\alpha;|\mathbf{s}_{kj}+\boldsymbol{\nu}|)}{|\mathbf{s}_{kj}+\boldsymbol{\nu}|}\right](\mathbf{s}_{kj}+\boldsymbol{\nu})$$
$$+\sum_{\{\boldsymbol{\nu}\}}\left[\frac{1}{(|\mathbf{s}_{kj}+\boldsymbol{\nu}|^2+z_{kj}^2)^{3/2}}-\frac{1}{|\mathbf{s}_{kj}+\boldsymbol{\nu}|^3}\right](\mathbf{s}_{kj}+\boldsymbol{\nu})\ .$$

Because $df\,s(\alpha,s)\rightarrow -1/s^2$ as $s\rightarrow\infty$, the first term of the last expression contains summands which fall off rapidly with $|\boldsymbol{\nu}|$ while the second term can be expanded to give the aforementioned multipole expansion. Suppose that the summands in the first term become negligible after $|\boldsymbol{\nu}|>\nu_{c_1}$ whereas a multipole expansion to order n is valid for values of $\boldsymbol{\nu}$ in the second term for which $|\boldsymbol{\nu}|>\nu_{c_2}$. Then we can rewrite the last expression as

$$\sum_{\boldsymbol{\nu}}^{\max(\nu_{c_1},\nu_{c_2})}\left[\frac{1}{(|\mathbf{s}_{kj}+\boldsymbol{\nu}|^2+z_{kj}^2)^{3/2}}+\frac{df\,s(\alpha;|\mathbf{s}_{kj}+\boldsymbol{\nu}|)}{|\mathbf{s}_{kj}+\boldsymbol{\nu}|}\right](\mathbf{s}_{kj}+\boldsymbol{\nu})+\sum_{|\boldsymbol{\nu}|>\max(\nu_{c_1},\nu_{c_2})}\left[\frac{1}{(|\mathbf{s}_{kj}+\boldsymbol{\nu}|^2+z_{kf}^2)^{3/2}}-\frac{1}{|\mathbf{s}_{kj}+\boldsymbol{\nu}|^3}\right]$$
$$\times(\mathbf{s}_{kj}+\boldsymbol{\nu})\ .$$

The multipole expansion can now be made in the last term. It is convenient to subtract and add the terms in the multipole expansion for $0<|\boldsymbol{\nu}|\leq\max(\nu_{c_1},\nu_{c_2})$ to the first and second terms of this expression, respectively. Then the last term becomes the multipole expansion summed over all values of $|\boldsymbol{\nu}|>0$. We have found numerically that a Taylor (multipole) expansion of the last term up to second (quadrupole) order gives very good accuracy as explained in the text when $\max(\nu_{c_1},\nu_{c_2})$ is set so that the sum in the first term is restricted to the first nine cells in the square lattice in the water problem. The force on the kth particle then becomes

$$\mathbf{F}_k=\frac{2\pi}{A}\sum_{\mathbf{G}}{}'\frac{\mathbf{G}}{G}g(\alpha,G)\sum_j q_kq_j\sin(\mathbf{G}\cdot\mathbf{s}_{kj})$$
$$+\sum_{j\neq k}\sum_{\{\boldsymbol{\nu}\}}q_kq_j(\mathbf{s}_{kj}+\boldsymbol{\nu})\left[\frac{1}{(|\mathbf{s}_{kj}+\boldsymbol{\nu}|^2+z_{kj}^2)^{3/2}}+\frac{df\,s(\alpha;|\mathbf{s}_{kj}+\boldsymbol{\nu}|)}{|\mathbf{s}_{kj}+\boldsymbol{\nu}|}+\frac{3z_{kj}^2}{2\nu^5}-\frac{15(z_{kj}^4+2z_{kj}^2|\mathbf{s}_{kj}+\nu|^2-2z_{kj}^2\nu^2)}{8\nu^7}\right]$$
$$+\sum_{j\neq k}\sum_{\{\boldsymbol{\nu}\}}q_kq_j\hat{z}z_{kj}\left[\frac{1}{(|s_{kj}+\boldsymbol{\nu}|^2+z_{kj}^2)^{3/2}}-\frac{1}{\nu^3}\right]+\mathbf{F}_k^{(q)}$$

n which

$$\mathbf{F}_k^{(q)}=\sum_{j\neq k}q_jq_k\left[-3z_{kj}^2\mathbf{s}_{kj}\sum_{\{\boldsymbol{\nu}\}}\frac{1}{2\nu^5}+\frac{15}{8}\mathbf{s}_{kj}(z_{kj}^4+2z_{kj}^2s_{kj}^2)\sum_{\{\boldsymbol{\nu}\}}\frac{1}{\nu^7}+\frac{15}{2}z_{kj}^2\mathbf{s}_{kj}\cdot\sum_{\{\boldsymbol{\nu}\}}\frac{\boldsymbol{\nu}\boldsymbol{\nu}}{\nu^7}+\hat{z}z_{kj}\sum_{\{\boldsymbol{\nu}\}}\frac{1}{\nu^3}\right]\ .$$

The sums over $\{\boldsymbol{\nu}\}$ can be done explicitly in the expression for $\mathbf{F}_k^{(q)}$ giving

$$\sum_{\{\mathbf{v}\}} 1/v^3 = 9.031\,783/L^3\ ,$$

$$\sum_{\{\mathbf{v}\}} 1/v^5 = 5.090\,258/L^5\ ,$$

$$\sum_{\{\mathbf{v}\}} 1/v^7 = 4.423\,117/L^7\ ,$$

$$\sum_{\{\mathbf{v}\}} \mathbf{v}\mathbf{v}/v^7 = 2.545\,129(\hat{x}\hat{x}+\hat{y}\hat{y})/L^5\ .$$

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[*] Deceased.

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