A fast-Fourier transform method to solve continuum-electrostatics problems with truncated electrostatic interactions: Algorithm and application to ionic solvation and ion-ion interaction

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An iterative algorithm based on fast-Fourier transforms is presented that solves the equations of continuum electrostatics for systems of heterogeneous dielectric permittivity (e.g., solute cavity in a solvent) under periodic boundary conditions. The method makes explicit use of the charge-dipole and dipole-dipole interaction tensors, and is thus applicable both to Coulombic interactions (Ewald scheme) and cutoff-based electrostatic interactions described by any polynomial function (including a Coulombic r^{-1} term), as commonly used in molecular dynamics simulations. The latter case includes, in particular, straight truncation of Coulombic interactions and truncation including a reaction-field correction. After testing and validation by comparison with existing methods, the algorithm is used to investigate the effect of cutoff truncation and artificial periodicity in explicit-solvent simulations of ionic solvation and ion-ion interactions. Both cutoff truncation and artificial periodicity are found to significantly affect the polarization around a spherical ion and its solvation free energy. The nature and magnitude of the two perturbations are analyzed in detail, and approximate analytical correction terms are derived to be applied to the results of explicit-solvent simulations. Cutoff truncation induces strong alterations in the potential of mean force for the interaction between two spherical ions. The present observations based on continuum electrostatics help to rationalize artifacts previously reported from explicit-solvent simulations involving cutoff truncation and, in particular, the unphysical attraction of like charges and repulsion of opposite charges, and the corresponding alterations in the relative stabilities of contact, solvent-separated, and free ion pairs. © 2003 American Institute of Physics. [DOI: 10.1063/1.1624054]

I. INTRODUCTION

Due to their sizeable computational costs, explicit-solvent molecular dynamics (MD) simulations of (bio)molecular systems are currently restricted to truly microscopic systems. As electrostatic interactions are long ranged, this limitation in the system sizes is incompatible with an exact treatment of these interactions through the direct application of Coulomb's law. In practice, explicit-solvent simulations are commonly performed under periodic boundary conditions (PBC), i.e., a microscopic computational box is periodically replicated to form an infinite periodic system, which serves as a model for the macroscopic system. This offers the advantage to remove any possible surface artifact related to the existence of a solvent-vacuum boundary. However, the realism of this approach for the representation of a solution at infinite dilution remains questionable. For all interactions with a range of action shorter than the size of the computational box (e.g., covalent and van der Waals interactions), artificial periodicity is not likely to be a problem. However, electrostatic interactions are effective at distances which typically go beyond the size of the computational box.

There are two alternative practical approaches to handle electrostatic interactions in (bio)molecular simulations,

which represent approximations of a different kind for the description of dilute solutions. The first approximation is to enforce the exact periodicity of the system in the context of Coulombic interactions, i.e., include all Coulombic interactions between any atom in the reference computational box and all atoms in the infinite periodic system. Methods relying on this approximation are called lattice-sum methods, and include Ewald summation¹ and computationally more efficient grid-based methods, such as particle-particle particle-mesh (P₃M),² or particle-mesh Ewald (PME).³ The second approximation is to partially break the periodicity by truncating electrostatic interactions beyond a convenient cutoff distance, i.e., include only interactions between any atom in the reference computational box and the closest (i.e., within the cutoff sphere) atoms in the infinite periodic system. Methods relying on this approximation are called cutoff-based methods and include (i) straight truncation of Coulombic interactions,^{4,5} (ii) smooth truncation of Coulombic interactions by using a switching or shifting function,⁶⁻⁸ and (iii) straight truncation of an effective interaction function including a Coulombic term and a reaction-field correction.⁹⁻¹³ One scheme of the latter type, the Barker-Watts reaction-field method,⁹ deserves particular mention because it is justified by physical arguments. In this approach, the medium beyond the cutoff sphere of each atom is treated as a dielectric continuum with a permittivity equal to that of the solvent. The forces arising from the polarization of this dielec-

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tric medium can be recast into an effective quadratic correction term to Coulomb's law.

As the two classes of methods are approximate, they may lead to artifacts in the simulated physical properties of solutions. The most severe problems are encountered in simulations employing straight truncation of the Coulombic potential. This treatment results in heating in MD simulations, as well as artifacts in the structural and dynamical properties of liquids,^{6,13–16} solvated ions,^{17–22} ion pairs,^{23–32} phase interfaces,^{33–35} and biomolecular systems.^{36–40} However, smooth-truncation and reaction-field methods also exhibit artifacts such as cutoff- or system-size dependence of simulated observables.^{6,18,19,31,32,36,41–44} Periodicity-induced artifacts caused by the exact periodicity of electrostatic interactions in lattice-sum methods have also been reported.^{45–49} The factors that appear to enhance such artifacts include (i) a charged solute, (ii) a strong anisotropy in the solute charge distribution, (iii) a large solute cavity compared to the size of the computational box, and (iv) a low dielectric permittivity of the solvent.

Artifacts linked with the application of approximate electrostatics in molecular simulations are probably best characterized in the context of the solvation of charged species. For lattice-sum methods, ionic solvation free energies are affected by a systematic free-energy offset^{48,50–53} (quadratic in the ionic charge and strongly size dependent) related to the Wigner self-energy of a charge under periodic boundary conditions.^{54,55} The exact value of this offset can be calculated analytically based on continuum electrostatics.⁴⁸ For cutoff-based methods, ionic solvation free energies are also affected by a free-energy offset (quadratic in the ionic charge, strongly cutoff dependent, and moderately size dependent) related to alterations of the solvent polarization around the ion. The value of this offset can also be computed numerically based on continuum electrostatics.^{42–44,56–58} Another case that has been well studied is ion–ion interaction, which was found to be strongly dependent on the electrostatic interaction scheme used in the simulation. For instance, straight truncation of the Coulombic interactions in a system of ferrous–ferric ions in aqueous solution leads to an unphysical attraction between ions of like charges, whereas the same system does not exhibit such behavior with Ewald summation.³¹ Other studies of chloride–chloride ion pairs in water show conflicting results concerning the first minimum in the potential of mean force (PMF), again strongly depending on the treatment of electrostatic interactions: Some studies report a stable contact ion pair,²⁶ some a stable solvent-separated ion pair,²⁵ and some do not observe any minimum at all.^{29,30} Comparable observations have been made for ion pairs with opposite charges.^{28,32} The PMF for the association of the guanidinium cation and acetate anion is also characterized by an unphysical repulsion at long distances when using truncated Coulombic interactions, while the PMF is almost flat when applying a reaction-field correction, and completely flat when using Ewald summation.³² The effect of using approximate electrostatics when simulating more complex systems is also beginning to be investigated. One approach toward this goal is to use continuum electrostatics,^{42–44,46,48,56–62} which per-

mits a systematic analysis of finite-size effects related to both cutoff truncation and artificial periodicity. For simple systems, such as one or two ions in solution, this method has led to analytical or numerical corrections to eliminate finite-size artifacts in the solvation free energies and interaction PMFs.^{22,42–44,48,50–53,56,58,59,63} For more complex systems, such as solvated biomolecules, this method permitted an estimation of the magnitude of finite-size artifacts in the context of lattice-sum methods by comparing continuum-electrostatics calculations under periodic and nonperiodic boundary conditions.^{46,47,49,57}

In this context, a method was recently developed⁵³ to solve the Poisson equation for periodic systems with a heterogeneous dielectric permittivity (solute–solvent systems), which makes use of fast-Fourier transforms (FFTs). As this algorithm relies explicitly on the Fourier coefficients of the charge–dipole and dipole–dipole interaction tensors, it can in principle be generalized to any electrostatic interaction scheme, provided that an analytical expression is available for these Fourier-coefficient tensors. Only the case of the Coulombic tensor (i.e., the Ewald case) was considered in this previous study. The goal of the present article is to present the generalization of the method to any effective interaction function defined by a polynomial (including a Coulombic r^{-1} term) truncated at a specific cutoff distance. This includes, in particular, the case of truncated Coulombic interactions with or without reaction-field correction.

The method is tested for simple model systems consisting of one or two spherical ions, and validated (whenever possible) by comparison with results obtained through algorithms that can solve the problem for specific forms of the electrostatic interactions and boundary conditions,^{42,43,53,58} or with analytical results.^{48,63,64} This is followed by a systematic investigation of the effect of cutoff truncation (possibly including a reaction-field correction), and artificial periodicity on the polarization around a spherical ion, its solvation free energy, and the PMF for the interaction between two spherical ions. In the latter case, the results are found to be in good qualitative agreement with observations made in previous explicit-solvent simulations^{28,31,32} which indicate that artifacts due to the approximate treatment of electrostatic interactions have a major influence on the interaction between charged species in molecular simulations.

II. THEORY

In this section, the FFT-based algorithm introduced previously⁵³ for solving the continuum-electrostatics equation for solute–solvent systems under PBC is generalized to different electrostatic interaction schemes and surface boundary conditions (SBC).

A. Continuum electrostatics in periodic systems

This section gives a summary of the formalism introduced previously,⁵³ concentrating on the generalization of the algorithm to different electrostatic interaction schemes. The discussion focuses on an infinite periodic system constructed by replication of a reference rectangular box containing one (reference) solute molecule (assumed nonpolarizable) surrounded by solvent (see Fig. 2 of Ref.

53). The system is characterized by four electrostatic quantities:^{14,15,65–67} the relative dielectric permittivity $\epsilon(\mathbf{r})$, the vacuum electric field $\mathbf{V}(\mathbf{r})$, the polarization field $\mathbf{P}(\mathbf{r})$, and the electric field $\mathbf{E}(\mathbf{r})$. The corresponding Fourier coefficients are $\hat{\epsilon}(\mathbf{k})$, $\hat{\mathbf{V}}(\mathbf{k})$, $\hat{\mathbf{P}}(\mathbf{k})$, and $\hat{\mathbf{E}}(\mathbf{k})$, where $\mathbf{k} = 2\pi\mathbf{L}^{-1}\mathbf{l}$ with $\mathbf{l} \in \mathbb{Z}^3$, $\mathbf{L}$ being the diagonal matrix defined by the edges of the box.^{48,68}

The dielectric permittivity $\epsilon(\mathbf{r})$ can be written

$$\epsilon(\mathbf{r}) = 1 + (\epsilon_s - 1)H(\mathbf{r}), \quad (1)$$

where ϵ_s is the relative permittivity of the solvent, and $H(\mathbf{r})$ is a function that evaluates to zero inside the reference solute molecule or any of its periodic copies, and to one otherwise.

The two unknowns $\mathbf{E}(\mathbf{r})$ and $\mathbf{P}(\mathbf{r})$ are linked by two equations which have to be solved simultaneously. First, the field equation^{14,15,67,66}

$$\mathbf{E}(\mathbf{r}) = \mathbf{V}(\mathbf{r}) + \int \int \int_{\mathbb{R}^3} d^3r' \mathbf{T}(\mathbf{r} - \mathbf{r}') \mathbf{P}(\mathbf{r}'), \quad (2)$$

where $\mathbf{T}(\mathbf{r})$ is the dipole–dipole (rank two) interaction tensor, i.e., the field generated at $\mathbf{r}$ by a point dipole $\boldsymbol{\mu}$ at the origin is equal to $\mathbf{T}(\mathbf{r})\boldsymbol{\mu}$. The functional form of $\mathbf{T}(\mathbf{r})$ depends on the treatment of the electrostatic interactions within the system and on the boundary conditions imposed at the surface of the infinite periodic system (vacuum, adjusted, or tin-foil SBC). Second, the constitutive equation^{14,15,66,67}

$$\mathbf{P}(\mathbf{r}) = \epsilon_o[\epsilon(\mathbf{r}) - 1]\mathbf{E}(\mathbf{r}) = \epsilon_o(\epsilon_s - 1)H(\mathbf{r})\mathbf{E}(\mathbf{r}). \quad (3)$$

These coupled equations can be solved in reciprocal space using an iterative algorithm.⁵³ The basic idea is to modify the vacuum field inside the solute in such a way that the overall electric field inside the solute becomes zero. Provided that this modified vacuum field $\mathbf{V}'(\mathbf{r})$ can be constructed, Eqs. (2) and (3) can be rewritten in reciprocal space as

$$\hat{\mathbf{E}}'(\mathbf{k}) = \hat{\mathbf{V}}'(\mathbf{k}) + \epsilon_o(\epsilon_s - 1)\hat{\mathbf{T}}(\mathbf{k})\hat{\mathbf{E}}'(\mathbf{k}) = \hat{\boldsymbol{\theta}}(\mathbf{k})\hat{\mathbf{V}}'(\mathbf{k}) \quad (4)$$

with

$$\hat{\boldsymbol{\theta}}(\mathbf{k}) = [\mathbf{1} - \epsilon_o(\epsilon_s - 1)\hat{\mathbf{T}}(\mathbf{k})]^{-1}, \quad (5)$$

and

$$\hat{\mathbf{P}}(\mathbf{k}) = \epsilon_o(\epsilon_s - 1)\hat{\mathbf{E}}'(\mathbf{k}), \quad (6)$$

where $\mathbf{E}'(\mathbf{r})$ is the modified electric field [differing from $\mathbf{E}(\mathbf{r})$ only within the solute] and $\mathbf{P}(\mathbf{r})$ the (unaffected) solvent polarization. The modified vacuum field $\mathbf{V}'(\mathbf{r})$ is constructed by means of an iterative algorithm (see Sec. II C). The polarization is then computed through Eq. (6).

The solvent-generated reaction potential $\Phi_{\text{RF}}(\mathbf{r})$ is related to the polarization through⁶⁵

$$\Phi_{\text{RF}}(\mathbf{r}) = \int \int \int_{\mathbb{R}^3} d^3r' \mathbf{t}(\mathbf{r} - \mathbf{r}') \mathbf{P}(\mathbf{r}'), \quad (7)$$

where $\mathbf{t}(\mathbf{r})$ is the charge–dipole (rank one) interaction tensor, i.e., the potential generated at $\mathbf{r}$ by a point dipole $\boldsymbol{\mu}$ at the origin is equal to $\mathbf{t}(\mathbf{r})\boldsymbol{\mu}$. The functional form of $\mathbf{t}(\mathbf{r})$ depends on the treatment of the electrostatic interactions within the

system and on the boundary conditions imposed at the surface of the infinite periodic system. These boundary conditions will be assumed to impose a vanishing average $\bar{\Phi}_{\text{RF}}$ of $\Phi_{\text{RF}}(\mathbf{r})$ within the reference box, in which case Eq. (7) is easily transformed into

$$\hat{\Phi}_{\text{RF}}(\mathbf{k}) = \hat{\mathbf{t}}(\mathbf{k})\hat{\mathbf{P}}(\mathbf{k})(1 - \delta_k). \quad (8)$$

The electrostatic solvation free energy (including interactions with a homogeneous neutralizing background charge density for non-neutral systems)⁴⁸ can be computed as^{65,69}

$$\Delta G_{\text{solv}} = \frac{1}{2} \sum_i^{N_{\text{at}}} q_i [\Phi_{\text{RF}}(\mathbf{r}_i) - \bar{\Phi}_{\text{RF}}] = \frac{1}{2} \sum_i^{N_{\text{at}}} q_i \Phi_{\text{RF}}(\mathbf{r}_i), \quad (9)$$

where $\mathbf{r}_i$ and q_i represent the coordinate vector and partial charge of an atom i in the reference solute molecule.

The form of the electrostatic interactions within the system must be taken into account at four stages of the algorithm: (i) the vacuum field $\mathbf{V}(\mathbf{r})$ depends on the form of the solute–solvent electrostatic interactions, (ii) the charge–dipole interaction tensor $\mathbf{t}(\mathbf{r})$ also depends on the form of these interactions, and (iii) the reciprocal-space tensor $\hat{\boldsymbol{\theta}}(\mathbf{k})$ in Eq. (5) depends on the form of the solvent–solvent electrostatic interactions through the dipole–dipole interaction tensor $\mathbf{T}(\mathbf{r})$. In addition, it should be noted that the dipole–dipole interaction tensor also depends on the surface boundary conditions (vacuum, adjusted, or tin-foil) imposed on the infinite periodic system.

For Coulombic (CB) interactions, the dipole–dipole interaction tensor reads¹⁴

$$\begin{aligned} \mathbf{T}_{\text{CB}}(\mathbf{r}) &= (4\pi\epsilon_o)^{-1} \nabla \otimes \nabla r^{-1} \\ &= (4\pi\epsilon_o)^{-1} r^{-5} (3\mathbf{r} \otimes \mathbf{r} - r^2 \mathbf{1}), \end{aligned} \quad (10)$$

where the notation $\mathbf{a} \otimes \mathbf{b}$ stands for the tensor with the elements $a_i b_j$. The Fourier coefficients of the interaction tensor describing the field generated by a periodic array of point dipoles in Ewald (EW) electrostatics, namely

$$\mathbf{T}_{\text{EW,vac}}(\mathbf{r}) = \sum_{\mathbf{n} \in \mathbb{Z}^3} \mathbf{T}_{\text{CB}}(\mathbf{r} + \mathbf{L}\mathbf{n}), \quad (11)$$

are given by⁵³

$$\hat{\mathbf{T}}_{\text{EW,vac}}(\mathbf{k}) = -(3\epsilon_o)^{-1} [3k^{-2} \mathbf{k} \otimes \mathbf{k} (1 - \delta_k) + \mathbf{1} \delta_k]. \quad (12)$$

These two expressions are correct under vacuum SBC, i.e., for an infinite periodic system surrounded by a medium of relative dielectric permittivity $\epsilon' = 1$.^{68,70,71} In practice, molecular simulations more commonly rely on conducting (tin-foil) SBC (conducting medium with permittivity $\epsilon' \rightarrow \infty$), or adjusted SBC (permittivity equal to that of the solvent, i.e., $\epsilon' = \epsilon_s$). In these cases, a correction term is required to account for the additional homogeneous field within the system that is generated by the polarization of this surrounding medium. A general expression for this correction term can be derived in the spirit of de Leeuw^{70,72} based on the Onsager

model of a dipole in a spherical cavity.⁷³ Considering a spherical assembly of N cubic boxes with a box dipole moment $\mathbf{M}$, and surrounded by a dielectric continuum of permittivity ϵ' , the Onsager reaction field $\mathbf{R}$ is given by (in the limit $N \rightarrow \infty$)

$$\begin{aligned}\mathbf{R} &= (4\pi\epsilon_o)^{-1} \frac{2\epsilon' - 2}{2\epsilon' + 1} \frac{N\mathbf{M}}{\frac{3}{4\pi}NL^3} \\ &= (3\epsilon_o)^{-1} L^{-3} \frac{2\epsilon' - 2}{2\epsilon' + 1} \mathbf{M}.\end{aligned}\quad (13)$$

As a consequence, an extra term must be included into the dipole–dipole interaction tensor to account for nonvacuum SBC, and Eq. (11) becomes, in the general case,

$$\mathbf{T}_{\text{EW}}(\mathbf{r}) = \sum_{\mathbf{n} \in \mathbb{Z}^3} \mathbf{T}_{\text{CB}}(\mathbf{r} + \mathbf{L}\mathbf{n}) + (3\epsilon_o)^{-1} L^{-3} \frac{2\epsilon' - 2}{2\epsilon' + 1} \mathbf{1}.\quad (14)$$

Similarly, Eq. (12) must be corrected in its $k=0$ term as

$$\hat{\mathbf{T}}_{\text{EW}}(\mathbf{k}) = -\epsilon_o^{-1} \left[k^{-2} \mathbf{k} \otimes \mathbf{k} (1 - \delta_k) + \frac{1}{2\epsilon' + 1} \mathbf{1} \delta_k \right].\quad (15)$$

Equation (12) is recovered for vacuum SBC ($\epsilon' = 1$), while for conducting SBC ($\epsilon' \rightarrow \infty$), Eq. (15) simplifies to

$$\hat{\mathbf{T}}_{\text{EW,cnd}}(\mathbf{k}) = -\epsilon_o^{-1} k^{-2} \mathbf{k} \otimes \mathbf{k} (1 - \delta_k),\quad (16)$$

which implies, in particular, $\hat{\mathbf{T}}_{\text{EW,cnd}}(\mathbf{0}) = \mathbf{0}$.

For all types of SBC, the charge–dipole interaction tensor for Coulombic interactions reads

$$\mathbf{t}_{\text{CB}}(\mathbf{r}) = -(4\pi\epsilon_o)^{-1} \nabla r^{-1} = (4\pi\epsilon_o)^{-1} \frac{\mathbf{r}}{r^3}.\quad (17)$$

The Fourier coefficients of the interaction tensor describing the potential generated by a periodic array of point dipoles, namely

$$\mathbf{t}_{\text{EW}}(\mathbf{r}) = \sum_{\mathbf{n} \in \mathbb{Z}^3} \mathbf{t}_{\text{CB}}(\mathbf{r} + \mathbf{L}\mathbf{n}),\quad (18)$$

are given by⁵³

$$\hat{\mathbf{t}}_{\text{EW}}(\mathbf{k}) = -\epsilon_o^{-1} i k^{-2} \mathbf{k} (1 - \delta_k).\quad (19)$$

B. Generalization to truncated non-Coulombic interactions

This section presents the modifications of the FFT-based algorithm⁵³ required to handle truncated non-Coulombic electrostatic interaction schemes. The discussion focuses on modified interactions defined by a continuous truncated polynomial interaction function $v(r)$

$$v(r) = (4\pi\epsilon_o)^{-1} h(R_c - r) \sum_{m=-1}^M a_m R_c^{-m-1} r^m,\quad (20)$$

where R_c is the cutoff distance ($R_c > 0$), h is the Heaviside function [i.e., $h(x) = 1$ if $x > 0$, $h(x) = 0$ otherwise], and the a_m are arbitrary dimensionless coefficients satisfying the relations

$$a_{-1} = 1\quad (21)$$

and

$$a_0 = -\left(1 + \sum_{m=1}^M a_m\right).\quad (22)$$

These two conditions impose a physically correct short-range behavior and the continuity of the interaction energy at the cutoff distance. The interaction scheme that will be more closely investigated in this article is the truncated Coulombic interaction with a Barker–Watts (BW) reaction-field correction,⁹ characterized by

$$\begin{aligned}v_{\text{BW}}(r) &= (4\pi\epsilon_o)^{-1} h(R_c - r) \\ &\times \left(r^{-1} + \frac{\epsilon' - 1}{2\epsilon' + 1} R_c^{-3} r^2 - \frac{3\epsilon'}{2\epsilon' + 1} R_c^{-1} \right).\end{aligned}\quad (23)$$

This form includes the two limiting cases of straight truncation (ST) of the Coulombic interactions ($\epsilon' = 1$; i.e., $a_{-1} = 1$, $a_0 = -1$, and $a_m = 0$ for $m \geq 1$) and reaction-field (RF) correction in the limit of a conducting medium surrounding the cutoff sphere ($\epsilon' \rightarrow \infty$; i.e., $a_{-1} = 1$, $a_0 = -3/2$, $a_1 = 0$, $a_2 = 1/2$, and $a_m = 0$ for $m \geq 3$). Although there is *a priori* no reason to use the same symbol ϵ' for the permittivity of the medium outside the infinite periodic system in the EW scheme [Eq. (14)] and outside the cutoff sphere in the BW scheme, the two quantities turn out to be equivalent in the limit $R_c \rightarrow \infty$ (see Appendix A).

The dipole–dipole interaction tensor corresponding to the interaction function defined by Eq. (20) can be written

$$\mathbf{T}(\mathbf{r}) = \nabla \otimes \nabla v(r).\quad (24)$$

The corresponding Fourier coefficients are derived for the general case in Appendix A. For the specific case of truncated Coulombic interactions with a Barker–Watts reaction-field correction, $\hat{\mathbf{T}}_{\text{BW}}(\mathbf{k})$ is given by

$$\begin{aligned}\hat{\mathbf{T}}_{\text{BW}}(\mathbf{k}) &= -\epsilon_o^{-1} \left\{ \left[[1 - f(kR_c)] k^{-2} \mathbf{k} \otimes \mathbf{k} \right. \right. \\ &\quad \left. \left. + \frac{1}{2\epsilon' + 1} f(kR_c) \mathbf{1} \right] (1 - \delta_k) + \frac{1}{2\epsilon' + 1} \mathbf{1} \delta_k \right\},\end{aligned}\quad (25)$$

with

$$f(kr) = -\frac{3}{(kr)^2} \cos(kr) + \frac{3}{(kr)^3} \sin(kr).\quad (26)$$

The dipole–dipole interaction tensor in reciprocal space is not directly used in the algorithm, but rather the reciprocal-space tensor $\hat{\boldsymbol{\theta}}(\mathbf{k})$ in Eq. (5). In Appendix B, a general expression for this tensor is derived. The final expression of $\hat{\boldsymbol{\theta}}(\mathbf{k})$ for the BW scheme is

$$\hat{\theta}_{\text{BW}}(\mathbf{k}) = \left\{ \frac{2\epsilon' + 1}{2\epsilon' + 1 + (\epsilon_s - 1)f(kR_c)} \mathbf{1} - \frac{(\epsilon_s - 1)(2\epsilon' + 1)^2[f(kR_c) - 1]}{[2\epsilon' + 1 + (\epsilon_s - 1)f(kR_c)][2(\epsilon_s - 1)\epsilon' f(kR_c) - \epsilon_s(2\epsilon' + 1)]} k^{-2} \mathbf{k} \otimes \mathbf{k} \right\} (1 - \delta_k) + \frac{2\epsilon' + 1}{2\epsilon' + \epsilon_s} \mathbf{1} \delta_k. \quad (27)$$

For comparison, the corresponding expression for the EW scheme is⁵³ [with the inclusion of the $k=0$ term from Eq. (15)]

$$\hat{\theta}_{\text{EW}}(\mathbf{k}) = \left[\mathbf{1} - \frac{\epsilon_s - 1}{\epsilon_s} k^{-2} \mathbf{k} \otimes \mathbf{k} \right] (1 - \delta_k) + \frac{2\epsilon' + 1}{2\epsilon' + \epsilon_s} \mathbf{1} \delta_k. \quad (28)$$

The charge–dipole interaction tensor corresponding to the interaction function defined by Eq. (20) can be written

$$\mathbf{t}(\mathbf{r}) = -\nabla v(r). \quad (29)$$

The corresponding Fourier coefficients are derived for the general case in Appendix C. For the specific case of the BW scheme, $\hat{\mathbf{t}}_{\text{BW}}(\mathbf{k})$ is given by

$$\hat{\mathbf{t}}_{\text{BW}}(\mathbf{k}) = -\epsilon_o^{-1} i k^{-2} \mathbf{k} \left[1 - \frac{2(\epsilon' - 1)}{2\epsilon' + 1} f(kR_c) - \frac{3}{2\epsilon' + 1} \frac{\sin(kR_c)}{kR_c} \right] (1 - \delta_k). \quad (30)$$

A discussion of the behavior of the dipole–dipole and charge–dipole Fourier coefficient tensors corresponding to the EW and BW schemes, in the limiting cases of large cutoff distances or distances very close to the central dipole, can also be found in Appendices A and C. The most interesting result in this context is the observation that for any interaction scheme defined by Eq. (20) and satisfying the constraints of Eqs. (21) and (A28), where the quantity A is defined by Eq. (A19), the interaction tensors become identical to the corresponding EW tensors [Eqs. (15) and (19)] in the limit of an infinite cutoff distance, irrespective of the $M-2$ free parameters of the interaction function. This result is in particular, valid in the case of the BW interaction function.

To complete the description of the algorithm, one has to specify how the vacuum field $\mathbf{V}(\mathbf{r})$ is computed. For Coulombic interactions, the vacuum field generated by the infinite periodic system of charges, $\mathbf{V}_{\text{EW}}(\mathbf{r})$, is conveniently computed using the reciprocal-space component of an Ewald summation.⁵³ On the other hand, for truncated electrostatic interactions, a direct summation of the vacuum fields generated by all solute charges and their periodic copies is the obvious method to use, i.e.,

$$\mathbf{V}(\mathbf{r}) = -\sum_i^{N_{\text{at}}} q_i \sum_{\mathbf{n} \in \mathbb{Z}^3} \nabla v(\|\mathbf{r} - \mathbf{r}_i + \mathbf{L}\mathbf{n}\|). \quad (31)$$

Since $v(r)$ is zero beyond the cutoff distance, the sum over $\mathbf{n}$ only involves a limited number of terms. In the special case where $R_c \leq L_{\text{min}}/2$, L_{min} being the shortest wall-to-wall dis-

tance within the computational box, this sum actually involves a single term. In this case, the vacuum field corresponding to the BW scheme is computed as

$$\mathbf{V}_{\text{BW}}(\mathbf{r}) = (4\pi\epsilon_o)^{-1} \sum_i^{N_{\text{at}}} q_i h(R_c - \|\mathbf{r} - \bar{\mathbf{r}}_i\|) \left[\frac{1}{\|\mathbf{r} - \bar{\mathbf{r}}_i\|^3} - \frac{2(\epsilon' - 1)}{2\epsilon' + 1} \frac{1}{R_c^3} \right] (\mathbf{r} - \bar{\mathbf{r}}_i), \quad (32)$$

where $\bar{\mathbf{r}}_i = \mathbf{r}_i + \mathbf{L}\mathbf{n}$ refers to the periodic copy of atom i that is closest to $\mathbf{r}$.

C. Discretization and iteration procedure

The iterative procedure to solve Eqs. (4) and (6) using FFTs⁵³ is summarized below, concentrating on the generalization of the method to different interaction schemes and surface boundary conditions. The rectangular reference unit cell is discretized by means of a grid G of $N_x \cdot N_y \cdot N_z$ points, $\mathbf{r}_{\mathbf{n}}$ and $\mathbf{k}_{\mathbf{l}}$ denoting the coordinate vectors of points $\mathbf{n}$ or $\mathbf{l}$ on the real or reciprocal-space grids, respectively. The algorithm consists of the following steps:

- (1) Compute the vacuum field $\mathbf{V}(\mathbf{r}_{\mathbf{n}})$ on G according to the chosen solute–solvent electrostatic interaction scheme [Ref. 53 for EW; Eq. (32) for BW]. Define the modified vacuum field at iteration $p=0$ as

$$\mathbf{V}'_{(0)}(\mathbf{r}_{\mathbf{n}}) = H(\mathbf{r}_{\mathbf{n}}) \mathbf{V}(\mathbf{r}_{\mathbf{n}}). \quad (33)$$

- (2) Apply three forward three-dimensional (3D) FFTs to obtain the Fourier coefficients $\hat{\mathbf{V}}'_{(p)}(\mathbf{k}_{\mathbf{l}})$ of $\mathbf{V}'_{(p)}(\mathbf{r}_{\mathbf{n}})$.
- (3) Calculate $\hat{\mathbf{E}}'_{(p)}(\mathbf{k}_{\mathbf{l}})$ from $\hat{\mathbf{V}}'_{(p)}(\mathbf{k}_{\mathbf{l}})$ using Eq. (4) with the reciprocal-space tensor $\hat{\theta}(\mathbf{k}_{\mathbf{l}})$ appropriate for the chosen solvent–solvent electrostatic interaction scheme and SBC [Eq. (28) for EW; Eq. (27) for BW].
- (4) Apply three backward 3D FFTs to obtain $\mathbf{E}'_{(p)}(\mathbf{r}_{\mathbf{n}})$ from its Fourier coefficients $\hat{\mathbf{E}}'_{(p)}(\mathbf{k}_{\mathbf{l}})$.
- (5) Compute the residual electric field $\sigma_{(p)}$ inside the solute as

$$\sigma_{(p)} = \left\{ \frac{\sum_{\mathbf{n} \in G} |\mathbf{E}'_{(p)}(\mathbf{r}_{\mathbf{n}})|^2 [1 - H(\mathbf{r}_{\mathbf{n}})]}{\sum_{\mathbf{n} \in G} [1 - H(\mathbf{r}_{\mathbf{n}})]} \right\}^{1/2}. \quad (34)$$

- (6a) If $\sigma_{(p)}$ is above a predefined threshold τ , choose the modified vacuum field for the next iteration according to

$$\mathbf{V}'_{(p+1)}(\mathbf{r}_{\mathbf{n}}) = \mathbf{V}'_{(p)}(\mathbf{r}_{\mathbf{n}}) - \lambda [1 - H(\mathbf{r}_{\mathbf{n}})] \mathbf{E}'_{(p)}(\mathbf{r}_{\mathbf{n}}), \quad (35)$$

where λ is a relaxation parameter^{53,74} and return to step 2.

- (6b) If $\sigma_{(p)}$ is below the threshold τ , terminate the iteration cycle.

- (7) Compute $\hat{\Phi}_{\text{RF}}(\mathbf{k}_i)$ from $\hat{\mathbf{E}}'_{(p)}(\mathbf{k}_i)$ using Eqs. (6) and (8) with the charge–dipole interaction tensor appropriate for the chosen solute–solvent electrostatic interaction scheme [Eq. (19) for EW; Eq. (30) for BW]. Apply a backward 3D FFT to obtain $\Phi_{\text{RF}}(\mathbf{r}_n)$ and compute the electrostatic solvation free energy ΔG_{solv} using Eq. (9).

The modified vacuum field $\mathbf{V}'_{(0)}(\mathbf{r}_n)$ is characterized by discontinuities: (i) At the solute–solvent boundary, because this field is set to zero inside the solute, (ii) at the cutoff distance for the BW scheme when ϵ' is finite, because the field is zero beyond this distance. In both cases, boundary smoothing is applied, i.e., the value of $\mathbf{V}'_{(0)}(\mathbf{r}_n)$ at a gridpoint $\mathbf{n}$ close to one of these boundaries is determined by scaling the field at this point by the fraction of the grid cell containing this point which lies within the solvent domain and inside the cutoff sphere of the charge. The exact procedure to estimate this fraction relies on discretizing the grid cell into $(2n_{\text{cube}} + 1)^3$ cubelets (see Ref. 53).

For some combinations of ionic radii, cutoff distances and box lengths, the algorithm applied with straight truncation of the electrostatic interactions may fail to converge within an arbitrarily small threshold τ . In these cases, the residual electric field $\sigma_{(p)}$ rapidly decreases during the first few iterations, and slowly increases again. This failure to converge is probably connected with the presence of a sharp discontinuity in the vacuum field at the cutoff distance. In the few cases where this situation occurred (specifically indicated in Table II), the algorithm was terminated at the minimum value of the residual $\sigma_{(p)}$.

III. COMPUTATIONAL DETAILS

Two types of periodic systems were considered, based on the following reference boxes: (i) a single spherical ion in a cubic box and (ii) two spherical ions in a cubic box, aligned along one of the box edges. All computations were performed using a program written in C and relying on the FFT algorithms of the FFTW library.⁷⁵

The single-ion system is characterized by four physical parameters (ionic charge q_i , ionic radius R_i , box edge L , and solvent permittivity ϵ_s), and by the electrostatic interaction scheme considered. The two-ion system is characterized by five physical parameters (ionic charges q_1 and q_2 , restricted here to $q_1 = \pm q_2 = q_i$; ionic radii R_1 and R_2 , restricted here to $R_1 = R_2 = R_i$; interionic distance d ; box edge L ; and solvent permittivity ϵ_s), and by the specific electrostatic interaction scheme considered. For both system types, the interaction schemes considered are exact Coulombic (Ewald) interactions with tinfoil SBC (EW with $\epsilon' \rightarrow \infty$), truncated Coulombic interactions (ST, i.e., BW with $\epsilon' = 1$), or truncated Coulombic interactions with a Barker–Watts reaction-field correction corresponding to a conducting medium surrounding the cutoff sphere (RF, i.e., BW with $\epsilon' \rightarrow \infty$). For the case of truncated interactions, the cutoff radius R_c is an additional physical parameter.

As discussed previously,⁵³ a number of model parameters characterize the method to solve the equations of continuum electrostatics on a grid using FFTs:

- (1) The grid spacing δg , determined by the number of grid points $N_x = N_y = N_z = N$ discretizing the reference (cubic) unit cell along the three Cartesian axes.
- (2) The method used to compute the vacuum field (see Ref. 53 and Sec. IIB of the present article). For the EW scheme, this includes the choice of a charge-shaping function γ and charge width a , and the upper bound m_{max} to the components of the alias vectors included. For the ST and RF schemes, this includes the boundary-smoothing procedure at the cutoff distance, which relies on the choice of a discretization parameter $n_{\text{cube},1}$.
- (3) The smoothing procedure at the solute–solvent boundary, which relies on the choice of a discretization parameter $n_{\text{cube},2}$.
- (4) The relaxation parameter λ to be used in Eq. (35).
- (5) The threshold value τ for the residual electric field inside the solute, see Eq. (34).

The influence of these model parameters was discussed in detail in the previous article.⁵³ In the present work, all calculations were performed using $n_{\text{cube},2} = 4$, $\lambda = 1.5$, and $\tau = 0.3 \text{ kJ mol}^{-1} e^{-1} \text{ nm}^{-1}$. The EW calculations used a spherical parabola charge-shaping function⁷⁶ of width $a = R_i - 0.05 \text{ nm}$ and $m_{\text{max}} = 2$. All BW calculations used $n_{\text{cube},1} = 4$. Different grid-spacing values δg in the range 0.02–0.03 nm were used.

IV. RESULTS

A. Single spherical ion

The radial polarization [radial component of $\mathbf{P}(\mathbf{r})$] around a monovalent spherical ion of radius $R_i = 0.2 \text{ nm}$ in a dielectric continuum of permittivity $\epsilon_s = 78$ is shown in Fig. 1 for the three interaction schemes (EW, ST, and RF; the latter two with a cutoff radius $R_c = 0.8 \text{ nm}$). In addition to

FIG. 1. Radial polarization $p(r)$ around a monovalent spherical ion in a dielectric continuum ($R_i = 0.2 \text{ nm}$; $\epsilon_s = 78$; $L = 3.6 \text{ nm}$ for PBC; $R_c = 0.8 \text{ nm}$ for ST and RF), displayed as a function of the distance r from the ion. Individual points represent estimates for a periodic (P) system from the present FFT-based algorithm (grid spacing $\delta g = 0.02 \text{ nm}$) for the EW, ST, and RF schemes. Lines represent the corresponding values under nonperiodic (NP) boundary conditions, estimated from the Born model (CB) or the one-dimensional integral-equation method (see Refs. 42, 43, and 56) (ST, RF; integration range 5 nm; bin size 0.005 nm).

the case of a periodic (P) system based on a cubic box of edge length $L=3.6$ nm, the corresponding polarizations computed through the one-dimensional integral-equation method^{42,43,56} (ST, RF) for a nonperiodic (NP) system are displayed for comparison.

For the ST scheme, the agreement between the nonperiodic and the periodic estimates is very good (apart from some spurious oscillations in the neighborhood of the cutoff distance), which indicates that for a box of 3.6 nm and a cutoff on 0.8 nm, the application of PBC leads to a negligible distortion of the solvent polarization. This is not the case for the EW and RF schemes, where the introduction of periodicity leads to a systematic decrease of the radial polarization. This depolarization is due to the perturbation of the solvent molecules within the reference box by the periodic copies of the ion and the polarized solvent molecules in their neighborhood. The effect is more pronounced for the EW scheme compared to the RF scheme, while it is very small for the ST scheme. Periodicity effects have a more limited influence on the polarization for cutoff-based schemes, because the field caused by the periodic copies of the ion only acts indirectly in the reference box, i.e., through a propagation via the solvent polarization. This indirect influence is limited in the ST scheme because the solvent polarization outside the cutoff sphere of the ion is reduced compared to the RF scheme.

When comparing the polarizations resulting from the application of the different schemes (under PBC) to the Born polarization, the ST scheme leads to the largest deviation, characterized by a strong overpolarization of the solvent within the cutoff sphere of the ion and a strong underpolarization of the solvent outside of this sphere. The latter arises because the solvent molecules outside the cutoff sphere of the ion only react to the field caused by polarized solvent molecules in the neighborhood of the ion, but not the ionic field itself. As a consequence, the solvent outside the cutoff sphere of the ion has a limited depolarizing effect on the solvent within this sphere, leading to the overpolarization inside the sphere. For both the EW and RF schemes, the solvent is underpolarized at all distances. For the EW scheme, the solvent polarization close to the ion is very similar to the Born polarization, while underpolarization builds up with increasing distance from the ion as a consequence of periodicity (see above). For the RF scheme, the solvent underpolarization is a consequence of both the truncation of electrostatic interactions (as is obvious from the curve in Fig. 1 corresponding to the nonperiodic case) and of periodicity. At long distances from the ion, the radial polarizations for the RF and EW schemes become very similar. In contrast, the polarization at long distances is significantly lower for the ST scheme.

The influence of the ionic radius and cutoff distance on the radial polarization is illustrated in Fig. 2 for the ST and RF schemes. Increasing the cutoff distance reduces the over- and underpolarization effects described above, thereby improving the agreement with the Born polarization. Indeed, it can be proven for both the ST and RF schemes that the polarization under nonperiodic boundary conditions (NPBC) converges toward the Born result in the limit of an infinite cutoff distance.^{42,43,58} Increasing the ionic radius decreases

FIG. 2. Radial polarization $p(r)$ around a monovalent spherical ion in a dielectric continuum ($\epsilon_s=78$; $L=3.6$ nm for PBC), displayed as a function of the distance r from the ion. Results correspond to the ST scheme (a) or the RF scheme (b) for different ionic radii R_i and cutoff distances R_c . Individual points represent estimates for a periodic (P) system from the present FFT-based algorithm (grid spacing $\delta g=0.02$ nm). Lines represent the corresponding values under nonperiodic (NP) boundary conditions, estimated from the Born model (CB) or the one-dimensional integral-equation method (see Refs. 42, 43, and 56) (integration range 5 nm; bin size 0.005 nm).

the polarization of the solvent over the whole range of distances. This is because the range of action of the vacuum field is limited in space to the region between R_i and R_c . As R_i becomes closer to R_c , the effect of the ion on the solvent is reduced. Indeed, in the limit $R_i \rightarrow R_c$, one would find $p(r)=0$.

The influence of the box size on the radial polarization is illustrated in Fig. 3 for the three interaction schemes. In all cases, a reduction of the box size causes a decrease of the radial polarization within the reference box. This larger depolarization is due to enhanced interactions of the solvent molecules in the reference box with the periodic copies of the ion and their neighboring highly-polarized solvent molecules. The magnitude of the polarization change upon decreasing the box size is largest for the EW scheme, less important for the RF scheme, and least important for the ST scheme. As expected, for the three types of interactions, the polarization of the periodic system converges toward the polarization of the nonperiodic system upon increasing L .

Within the continuum-electrostatics approximation, the electrostatic solvation free energy of a nonpolarizable spheri-

FIG. 3. Radial polarization $p(r)$ around a monovalent spherical ion in a dielectric continuum ($R_i=0.2$ nm; $\epsilon_s=78$; $R_c=0.8$ nm for ST and RF), displayed as a function of the distance r from the ion. Results correspond to the EW scheme (a), ST scheme (b), or RF scheme (c) for different box edge lengths L . Individual points represent estimates for a periodic (P) system from the present FFT-based algorithm (grid spacing $\delta g=0.02$ nm). Lines represent the corresponding values under nonperiodic (NP) boundary conditions, estimated from the Born model (CB) or the one-dimensional integral-equation method (see Refs. 42, 43, and 56) (integration range 5 nm; bin size 0.005 nm).

cal ion within a nonperiodic Coulombic dielectric continuum is given by the Born equation⁶⁴

$$\Delta G_{\text{solv}}^{\text{NP, CB}} = -\frac{q_i^2}{8\pi\epsilon_0} \frac{(\epsilon_s - 1)}{\epsilon_s} \frac{1}{R_i}. \quad (36)$$

In the case of the periodic Coulombic case provided by the Ewald scheme, the solvation free energy is known analytically for a cubic box⁴⁸

$$\Delta G_{\text{solv}}^{\text{PEW}} = -\frac{q_i^2}{8\pi\epsilon_0} \frac{(\epsilon_s - 1)}{\epsilon_s} \frac{1}{L} \times \left\{ \xi_{\text{EW}} + \frac{L}{R_i} + \frac{4\pi}{3} \left(\frac{R_i}{L} \right)^2 - \frac{16\pi^2}{45} \left(\frac{R_i}{L} \right)^5 \right\}, \quad (37)$$

where $\xi_{\text{EW}} \approx -2.837\,297$.⁵⁵ Note that, due to the isotropy of the problem, this value is independent of the SBC (i.e., of ϵ'). It is easily seen that Eq. (37) converges toward the Born solvation free energy for large values of L . In the case of

FIG. 4. Solvation free energy of a monovalent spherical ion in a dielectric continuum as a function of the size parameter P (edge length L of the cubic box for EW; cutoff radius R_c for BW). Results are shown for $\epsilon_s=5$ and $R_i=0.4$ nm (a), $\epsilon_s=78$ and $R_i=0.4$ nm (b), or $\epsilon_s=78$ and $R_i=0.2$ nm (c). Individual points correspond to the analytical estimate $\Delta G_{\text{solv}}^{\text{PEW}}$ from Eq. (37) for EW or to numerical estimates $\Delta G_{\text{solv,1D}}^{\text{NP, BW}}$ using the one-dimensional integral-equation method (see Refs. 42, 43, and 56) (integration range = 5 nm; bin size = 0.005 nm) for the BW scheme with $\epsilon'=1$ (ST) or $\epsilon' \rightarrow \infty$ (RF). Solid lines represent a least-squares fit [by Eq. (38)] over the interval $2 \text{ nm} \leq P \leq 15 \text{ nm}$. The fitting parameters are presented in Table I. The horizontal dashed line indicates the Born result $\Delta G_{\text{solv}}^{\text{NP, CB}}$ from Eq. (36).

cutoff-based electrostatic interactions with nonperiodic boundary conditions, the solvation free energy can be determined by numerically solving a one-dimensional integral equation.^{42,43,56} The corresponding estimate for the BW scheme will be referred to as $\Delta G_{\text{solv}}^{\text{NP, BW}}$. It can also be proven that this solvation free energy converges toward the Born result in the limit of an infinite cutoff radius.⁵⁸

To investigate in more detail the convergence toward the Born result, the solvation free energy of a monovalent spherical ion ($R_i=0.2$ or 0.4 nm) in a given solvent ($\epsilon_s=78$ or 5 ; the latter value only for $R_i=0.4$ nm) is displayed in Fig. 4 as a function of a system-size parameter P ($P=L$ for EW, $P=R_c$ for BW), for the EW (arbitrary ϵ') or BW ($\epsilon'=1$ or $\epsilon' \rightarrow \infty$) interaction schemes. To quantify the convergence toward the Born value, the function

$$\Delta G_{\text{solv}}(P) = \Delta G_{\text{solv}}^{\infty} + \alpha P^{-1}, \quad (38)$$

was fitted to the numerical solvation free energies in the

TABLE I. Parameters of the least-squares fit by Eq. (38) of the data points displayed in Fig. 4 over the range $2 \text{ nm} \leq P \leq 15 \text{ nm}$, including the intercept $\Delta G_{\text{solv}}^{\infty}$ and slope α . Electrostatic interactions correspond to either the Ewald scheme (EW), truncated-Coulombic interactions (ST), or truncated-Coulombic interactions with a reaction-field correction corresponding to a conducting medium outside the cutoff sphere (RF). R_i is the ionic radius, and ϵ_s is the dielectric permittivity of the medium outside the ion. The correlation coefficient is, in all cases, 0.96. The corresponding Born solvation free energies $\Delta G_{\text{solv}}^{\text{NP,CB}}$ [Eq. (36)] and theoretical α estimates α^{th} [Eq. (39)] are reported for comparison.

Scheme	R_i (nm)	ϵ_s	$\Delta G_{\text{solv}}^{\infty}$ (kJ mol ⁻¹)	α (kJ nm mol ⁻¹)	$\Delta G_{\text{solv}}^{\text{NP,CB}}$ (kJ mol ⁻¹)	α^{th} (kJ nm mol ⁻¹)
EW	0.4	5	-138.1	149.5	-138.9	157.7
ST	0.4	5	-139.0	43.1	-138.9	55.6
RF	0.4	5	-138.8	89.6	-138.9	83.4
EW	0.4	78	-170.4	184.5	-171.4	194.6
ST	0.4	78	-171.5	47.3	-171.4	68.6
RF	0.4	78	-171.0	103.1	-171.4	102.9
EW	0.2	78	-342.6	192.0	-342.9	194.6
ST	0.2	78	-342.8	46.1	-342.9	68.6
RF	0.2	78	-342.5	103.3	-342.9	102.9

interval $2 \text{ nm} \leq P \leq 15 \text{ nm}$. The fitted curves are also shown in Fig. 4, while the fitting parameters are reported in Table I. Comparing $\Delta G_{\text{solv}}^{\infty}$ with the Born estimate $\Delta G_{\text{solv}}^{\text{NP,CB}}$, one sees that the ionic solvation free energies corresponding to all schemes indeed converge toward the Born result upon increasing the size parameter P . However, for the box sizes and cutoff radii that are typically used in explicit-solvent simulations ($L < 8 \text{ nm}$ and $R_c \approx 1-2 \text{ nm}$), both the deviations from the Born result and the differences between the various interaction schemes are very large. In the limit of very small ions ($R_i \leq P$), and under the approximation that the polarization around the ion for a given electrostatic scheme is close to the Born polarization (i.e., for P sufficiently large), it can be shown⁵⁸ that the error committed in the solvation free energy is related to a self-energy term of the specific interaction scheme. In this case, the approximate value of the coefficient α should be

$$\alpha^{\text{th}} = \frac{q_i^2}{8\pi\epsilon_0} \frac{\epsilon_s - 1}{\epsilon_s} \begin{cases} (-\xi_{\text{EW}}) & \text{for EW} \\ \frac{3\epsilon'}{2\epsilon' + 1} & \text{for BW.} \end{cases} \quad (39)$$

The corresponding values are also reported in Table I. These estimates α^{th} are found to agree reasonably well with the α values obtained from the fitting through Eq. (38). The agreement is particularly good for the EW and RF (BW with $\epsilon' \rightarrow \infty$) schemes, while for the ST scheme (BW with $\epsilon' = 1$), the two estimates differ more significantly. This is because when using the ST scheme, the polarization around an ion differs significantly from the Born polarization, even for reasonably large cutoff distances.^{42,43,58} The good agreement in the EW and RF cases suggests that Eqs. (38) and (39) provide a convenient means of obtaining a first-order correction to ionic solvation free energies computed from explicit-solvent simulations employing these types of interactions.

In order to assess the reliability of the present FFT-based algorithm for the three interaction schemes considered, the ionic solvation free energies $\Delta G_{\text{solv,FFT}}^{\text{P,XX}}$ (for XX=EW, RF, or ST) computed using this algorithm are compared in Table II with the corresponding values $\Delta G_{\text{solv,FI}}^{\text{NP,XX}}$ or $\Delta G_{\text{solv,FI}}^{\text{P,XX}}$ (for

XX=RF or ST) computed using a recently developed finite-integration (FI) algorithm,⁵⁸ $\Delta G_{\text{solv,ID}}^{\text{NP,XX}}$ (for XX=RF or ST) computed using the one-dimensional integral-equation method,^{42,43,56} $\Delta G_{\text{solv,ID}}^{\text{P,XX}}$ (for XX=RF or ST) computed using the same method and an empirical correction for periodicity,⁵⁸ and the analytical result $\Delta G_{\text{solv}}^{\text{PEW}}$ given by Eq. (37).

The agreement between the results of the FFT-based algorithm and those of the finite-integration method is quite good for the two cutoff-based methods, the maximal and root-mean-square deviations being 3.6 kJ mol^{-1} (4.8%) and 1.6 kJ mol^{-1} (1.9%), respectively. The agreement with the one-dimensional integral-equation method (corrected for periodicity) is also good, with maximal and root-mean-square deviations of 2.9 kJ mol^{-1} (5.5%) and 1.6 kJ mol^{-1} (1.9%), respectively. The results for the EW scheme also compare very well to the analytical value [Eq. (37)], with maximal and root-mean-square deviations of 1.3 kJ mol^{-1} (0.5%) and 0.9 kJ mol^{-1} (0.4%), respectively. Considering Table II, the following observations can be made: (i) the solvation free energies are larger in magnitude for the smaller ion, in qualitative agreement with the Born model, although the scaling factor is systematically larger than the ratio of the ionic radii; (ii) the solvation free energies are larger in magnitude for the larger cutoff value, a consequence of including a larger amount of polarized solvent within the cutoff sphere of the ion, (iii) the solvation free energies are larger in magnitude for the ST scheme compared to the RF scheme, a consequence of the solvent overpolarization within the cutoff sphere of the ion for the ST scheme (Fig. 1) and of the inclusion of an additional positive term in the solvation free energy for the RF scheme [see Eqs. (7), (9), and (23)], (iv) the solvation free energies are larger in magnitude under nonperiodic compared to periodic boundary conditions, a consequence of the periodicity-induced solvent depolarization within the reference box (Fig. 1), and (v) the periodicity-induced perturbation of the solvation free energy (NPBC $\rightarrow$ PBC) is larger for the smaller ion, the larger cutoff distance, and the RF compared to the ST scheme. The latter effect is a consequence of the larger periodicity-induced sol-

TABLE II. Solvation free energy of a monovalent spherical ion of radius R_i immersed in a dielectric continuum of permittivity $\epsilon_s = 78$ (water) filling a cubic periodic box of edge L . Electrostatic interactions correspond to either the Ewald scheme (EW), truncated-Coulombic interactions (ST), or truncated-Coulombic interactions with a reaction-field correction corresponding to a conducting medium outside the cutoff sphere (RF). In the two latter cases, R_c is the cutoff radius. The solvation free energy is evaluated either using the present FFT-based method ($\Delta G_{\text{solv,FFT}}^{\text{P,XX}}$; grid spacing $\delta g = 0.03$ nm), a recently developed finite-integration method (see Ref. 58) ($\Delta G_{\text{solv,FI}}^{\text{P,XX}}$; grid spacings of 0.06 and 0.01 nm for the coarse and fine grids), a one-dimensional integral-equation method (see Refs. 42, 43, and 56) ($\Delta G_{\text{solv,1D}}^{\text{NP,XX}}$; bin size 0.005 nm, integration range 5.0 nm), the same method including an empirical correction for periodicity (see Ref. 58) ($\Delta G_{\text{solv,1D}}^{\text{P,XX}}$), and the analytical result $\Delta G_{\text{solv}}^{\text{PEW}}$ [Eq. (37)]. The star indicates calculations that failed to converge within the specified threshold τ (in this case, the algorithm was terminated when the residual $\sigma_{(p)}$ reached a minimum).

Scheme	R_i (nm)	R_c (nm)	L (nm)	$\Delta G_{\text{solv,FFT}}^{\text{P,XX}}$ (kJ mol ⁻¹)	$\Delta G_{\text{solv,FI}}^{\text{P,XX}}$ (kJ mol ⁻¹)	$\Delta G_{\text{solv,1D}}^{\text{NP,XX}}$ (kJ mol ⁻¹)	$\Delta G_{\text{solv,1D}}^{\text{P,XX}}$ (kJ mol ⁻¹)	$\Delta G_{\text{solv}}^{\text{PEW}}$ (kJ mol ⁻¹)
EW	0.2	...	1.8	-238.1	...	...	...	-236.8
EW	0.2	...	3.6	-290.4	...	...	...	-289.1
EW	0.2	...	5.4	-308.2	...	...	...	-306.9
ST	0.2	0.8	1.8	-277.9	-277.0		-277.1	...
ST	0.2	0.8	3.6	-282.7	-281.9	-281.7	-281.6	...
ST	0.2	0.8	5.4	-282.8	-282.0		-281.7	...
RF	0.2	0.8	1.8	-208.6	-208.1		-207.5	...
RF	0.2	0.8	3.6	-215.0	-214.3	-213.7	-213.6	...
RF	0.2	0.8	5.4	-215.6	-214.7		-213.7	...
ST	0.2	1.2	2.6	-301.7	-299.6		-299.3	...
ST	0.2	1.2	3.6	-304.1	-303.3	-303.4	-302.9	...
ST	0.2	1.2	5.4	-304.5	-303.8		-303.4	...
RF	0.2	1.2	2.6	-253.4	-251.7		-250.7	...
RF	0.2	1.2	3.6	-255.9	-255.5	-256.4	-255.0	...
RF	0.2	1.2	5.4	-257.5	-256.9		-256.3	...
EW	0.4	...	1.8	-70.9	...	...	...	-71.2
EW	0.4	...	3.6	-118.1	...	...	...	-118.4
EW	0.4	...	5.4	-135.4	...	...	...	-135.7
ST	0.4	0.8	1.8	-98.2*	-96.3		-96.9	...
ST	0.4	0.8	3.6	-102.6*	-99.7	-100.1	-100.1	...
ST	0.4	0.8	5.4	-103.0*	-99.7		-100.1	...
RF	0.4	0.8	1.8	-45.7	-44.1		-44.1	...
RF	0.4	0.8	3.6	-49.2	-46.9	-46.8	-46.8	...
RF	0.4	0.8	5.4	-49.5	-47.1		-46.8	...
ST	0.4	1.2	2.6	-125.2	-128.8		-125.3	...
ST	0.4	1.2	3.6	-128.8	-128.1	-128.8	-128.4	...
ST	0.4	1.2	5.4	-129.3	-128.5		-128.8	...
RF	0.4	1.2	2.6	-81.9	-81.9		-82.1	...
RF	0.4	1.2	3.6	-85.2	-84.7	-85.9	-84.9	...
RF	0.4	1.2	5.4	-86.5	-86.2		-85.8	...

vent depolarization within the reference box for the RF scheme (Fig. 1).

The influence of periodicity on ionic solvation free energies corresponding to cutoff-based electrostatic interactions is illustrated in Fig. 5, where the relative periodicity-induced perturbation $\gamma(L)$ of the solvation free energy of a monovalent spherical ion ($R_i = 0.2$ nm or 0.4 nm; $\epsilon_s = 78$) is displayed as a function of the edge length L of the (cubic) computational box. The quantity $\gamma(L)$ is defined as

$$\gamma(L) = \frac{\Delta G_{\text{solv,FFT}}^{\text{P,XX}}(L)}{\Delta G_{\text{solv}}^{\text{P,XX}}(L \rightarrow \infty)} - 1, \quad (40)$$

where $\Delta G_{\text{solv}}^{\text{P,XX}}(L \rightarrow \infty)$ is calculated through Eq. (37) for the EW scheme, or approximated by the value of $\Delta G_{\text{solv,FFT}}^{\text{P,XX}}$ at the largest value of L considered for the ST and RF schemes. The following functions were fitted to the resulting data points:

$$\tilde{\gamma}_{\text{EW}}(L) = \frac{R_i}{L} \left\{ \xi_{\text{EW}} + \frac{4\pi}{3} \left(\frac{R_i}{L} \right)^2 - \frac{16\pi^2}{45} \left(\frac{R_i}{L} \right)^5 \right\}, \quad (41)$$

based on Eq. (37) for the EW scheme, or

$$\tilde{\gamma}_{\text{BW}}(L) = -\frac{R_i}{R_c} 10^{\mu L/(2R_c) + \nu}, \quad (42)$$

where μ and ν are (unitless) coefficients, for the ST and RF schemes. The latter functional form was previously found to capture the size dependence of ionic solvation free energies using cutoff-based electrostatics, as estimated via the finite-integration method,⁵⁸ with the parameters $\mu = -2.20$ and $\nu = 1.30$ for ST and $\mu = -1.47$ and $\nu = 0.72$ for RF, both for $\epsilon_s = 78$. The corresponding fitting parameters and correlation coefficients are reported in Table III, while the fitted curves are displayed in Fig. 5. The fitting parameters μ and ν are found to be in reasonable agreement with those obtained previously with the finite-integration method. For both trun-

FIG. 5. Relative periodicity-induced perturbation of the solvation free energy $\gamma(L)$ [see Eq. (40)] for a monovalent spherical ion (radius $R_i=0.2$ or 0.4 nm) in a periodic dielectric continuum ($\epsilon_s=78$), displayed as a function of the edge length L of the cubic box. Results correspond to the EW scheme (a), the ST scheme (b), or the RF scheme (c), the latter two with a cutoff radius R_c . Individual points represent estimates based on the present FFT-based algorithm (grid spacing $\delta g=0.03$ nm). The lines represent fits to $\tilde{\gamma}_{EW}(L)$ [see Eq. (41)] or $\tilde{\gamma}_{BW}(L)$ [see Eq. (42)] to the data points. The fitting parameters are reported in Table III.

cated Coulombic interactions with and without reaction-field correction, $\gamma(L)$ is negative and rapidly approaches zero upon increasing the box size. Solvation free energies obtained using the ST scheme converge faster toward the non-periodic result compared to those obtained using the RF scheme, while the values corresponding to the EW scheme converge significantly slower. This convergence behavior is in line with the previously discussed differences in the magnitude of the solvent depolarization caused by periodicity for the three different schemes.

B. Two spherical ions

This section is concerned with the influence of the electrostatic interaction scheme and boundary conditions on the PMF for the interaction between two spherical ions in solution. The electrostatic free-energy contribution $\Delta G_{el}(d)$ to this PMF can be evaluated as a function of the interionic distance d by summing the vacuum interaction energy of the two ions [calculated using the specific electrostatic interaction scheme, i.e. based on Eq. (20) for truncated interactions

TABLE III. Parameters of the least-squares fit by Eq. (41) for the EW scheme or Eq. (42) for the BW scheme of the data points displayed in Fig. 5, including the unitless parameters μ and ν and the correlation coefficient c . Two limiting cases of the BW scheme are considered, namely truncated Coulombic interactions (ST; $\epsilon'=0$), and truncated Coulombic interactions with a reaction-field correction corresponding to a conducting medium outside the cutoff sphere (RF; $\epsilon'\rightarrow\infty$). R_i is the ionic radius, and R_c the cutoff radius.

	R_i (nm)	R_c (nm)	μ	ν	c
EW	0.2	...	...	...	0.93
	0.4	...	...	...	0.93
ST	0.2	0.8	-2.35	1.48	0.92
	0.4	0.8	-2.41	1.56	0.83
	0.2	1.2	-2.34	1.46	0.89
	0.4	1.2	-2.26	1.38	0.86
RF	0.2	0.8	-1.11	0.37	0.93
	0.4	0.8	-1.14	0.49	0.93
	0.2	1.2	-1.35	0.57	0.91
	0.4	1.2	-1.35	0.66	0.91

or on Ewald summation] and the electrostatic solvation free energy (obtained through the FFT-based algorithm), namely

$$\Delta G_{el}(d) = \Delta E_{vac}(d) + \Delta G_{solv}(d). \quad (43)$$

Note that, although $\Delta G_{el}(d)$ probably represents the leading term in the overall PMF, nonpolar and entropic contributions may also play a role. In addition, the continuum-electrostatics result should be taken with some caution in the short-distance range, because for d comprised between $2R_i$ and $2(R_i + R_s)$, where R_s is the radius of the solvent molecule (~ 1.4 nm for water), the present model uses the dielectric permittivity of the solvent to describe the medium between the ions, although they are so close that no solvent molecule can be accommodated in this region.

The present discussion is restricted to the case of two monovalent spherical ions of identical radii $R_i=0.4$ nm (about the size of a chloride ion) aligned along one edge of a cubic periodic box. The effect of the electrostatic scheme, cutoff radius, and edge length of the computational box on the electrostatic contribution to the PMF is illustrated for charges of identical or opposite signs in Figs. 6 and 7, respectively. Since any constant offset in $\Delta G_{el}(d)$ is irrelevant, the curves are arbitrarily anchored by resetting $\Delta G_{el}(2R_i)$ to zero (contact distance) for ease of comparison. The actual values of $\Delta G_{el}(2R_i)$ are reported in Table IV. The results of the present continuum-electrostatics calculations are in line with previous observations from explicit-solvent simulations. Straight truncation (ST) leads to unphysical behavior (attraction between like charges and repulsion between opposite charges) in the approximate range of interionic distance from $2R_i$ to about $R_c - 0.2$ nm,^{28,31,32,77} causing an artificial stability (like charges) or instability (opposite charges) of the contact ion pair^{23,25-27,29,30} as well as an enhanced (like charges) or decreased (opposite charges) tendency for ions to stay at distances close to the cutoff distance.^{6,20,78} The magnitude of the effect and the range of occurrence of the inverted attraction-repulsion behavior strongly depend on the relationship between the cutoff distance and the box length.

FIG. 6. Electrostatic contribution to the PMF between two monovalent spherical ions (radius $R_i=0.4$ nm; $\epsilon_s=78$) with charges of identical signs. Results correspond to the EW scheme (a), the ST scheme (b), or the RF scheme (c), the latter two with a cutoff radius R_c . L is the edge length of the cubic box, and δg the grid spacing. The value of $\Delta G_{el}(2R_i)$ is arbitrarily reset to zero for all curves (ion–ion contact). The corresponding values are reported in Table IV.

If R_c is approximately equal to half the box length, the repulsion of opposite charges and the attraction of like charges extends over almost the entire range of distances. This is exactly the observation made in previous explicit-solvent simulation studies^{31,32} using $R_c \approx L/2$. When the cutoff radius is smaller than half of the box length, the electrostatic PMF becomes more complex. For ions of like charges [Fig. 6(b)], the PMF can be divided into four regions: (i) close to ion–ion contact, the PMF is attractive, with a minimum at ion–ion contact, (ii) in the approximate range of interionic distances from about $R_c - 0.2$ nm to R_c , the PMF becomes repulsive, with a second minimum at the cutoff distance, (iii) beyond cutoff distance, the PMF is again attractive until it reaches a maximum, and (iv) beyond this maximum, the PMF becomes repulsive again, with a third minimum at $L/2$ [due to periodicity, $\Delta G_{el}(d)$ is symmetric with respect to $d = L/2$]. For two ions of opposite charges [Fig. 7(b)], the behavior is qualitatively the opposite.

For truncated Coulombic interactions with a reaction-

FIG. 7. Electrostatic contribution to the PMF between two monovalent spherical ions (radius $R_i=0.4$ nm; $\epsilon_s=78$) with charges of opposite signs. Results correspond to the EW scheme (a), the ST scheme (b), or the RF scheme (c), the latter two with a cutoff radius R_c . L is the edge length of the cubic box, and δg the grid spacing. The value of $\Delta G_{el}(2R_i)$ is arbitrarily reset to zero for all curves (ion–ion contact). The corresponding values are reported in Table IV.

TABLE IV. Total electrostatic free energies $\Delta G_{el}(2R_i)$ at contact distance for the two-ion systems considered in Figs. 6 and 7. L is the edge length of the cubic box, R_c is the cutoff radius, and δg is the grid spacing.

	L (nm)	R_c (nm)	δg (nm)	$\Delta G_{el}(2R_i)$ (kJ mol ⁻¹)	
				(+/+)	(+/-)
EW	4.2	...	0.023	-343.6	-343.8
	4.2	...	0.035	-342.4	-343.4
	6.3	...	0.035	-339.8	-343.3
ST	4.2	1.2	0.023	-253.4	-255.5
	4.2	1.4	0.023	-273.0	-261.7
	4.2	2.0	0.023	-290.1	-284.2
	4.2	1.2	0.035	-251.5	-254.0
	6.3	1.2	0.035	-249.8	-253.9
RF	4.2	1.2	0.023	-170.0	-170.6
	4.2	1.4	0.023	-189.2	-195.4
	4.2	2.0	0.023	-221.3	-239.7
	4.2	1.2	0.035	-169.1	-170.2
	6.3	1.2	0.035	-172.0	-170.2

field correction (RF), the electrostatic PMFs look completely different. The amplitude of the oscillations is much smaller compared to the ST scheme. The PMFs for two ions with like charges [Fig. 6(c)] show a minimum between ion-ion contact and the cutoff distance, at about $R_c - 0.2$ nm. Beyond about $R_c + 0.2$ nm, they are essentially flat. The PMFs for two ions with opposite charges [Fig. 7(c)] are flat at short distances, exhibit a rapid drop in the range of interionic distances from about $R_c - 0.2$ nm to about $R_c + 0.2$ nm, and are flat again beyond this distance. Finally, the Ewald (EW) scheme is characterized by a monotonic repulsion for ions of like charges [Fig. 6(a)], and an essentially flat PMF for ions of opposite charges [Fig. 7(a)]. This is also in good qualitative agreement with previous observations from explicit-solvent simulations.^{31,32} The SBC (vacuum, adjusted, or tin-foil) chosen for the EW scheme only have an effect on systems where the reference box has a net dipole moment (i.e., for ions with opposite charges). However, even in this case, the effect appears to be very small. For example, for two oppositely charged monovalent spherical ions ($R_i = 0.4$ nm, $\epsilon_s = 78$, and $L = 4.2$ nm), the difference between the solvation free energies computed under vacuum and tin-foil SBC is maximal at ion-ion contact, and amounts to only $0.008 \text{ kJ mol}^{-1}$. Note also the remarkable agreement between the PMFs corresponding to the RF scheme with $R_c \approx L/2$ and those corresponding to the EW scheme. This agreement suggests that with an appropriately large cutoff, the Barker-Watts reaction-field correction is an efficient method for eliminating artifacts in charge-charge interactions related to cutoff truncation of the electrostatic interactions.

V. CONCLUSIONS

In a previous study,⁵³ an iterative algorithm based on FFTs was presented that solves the Poisson equation for solute-solvent systems under PBC. In the present study, this scheme was generalized to interaction functions defined by a polynomial (including a Coulombic r^{-1} term) truncated at a specific cutoff distance, with a special focus on truncated Coulombic interactions with or without reaction-field correction. The derivation of the functional form of the reciprocal-space charge-dipole and dipole-dipole interaction tensors led to some interesting relationships between the different electrostatic interaction schemes and SBC used in explicit-solvent simulations under PBC. The most interesting result is the observation that, in terms of charge-dipole and dipole-dipole interactions, the Ewald scheme is the limiting case of the Barker-Watts reaction-field scheme for an infinite cutoff radius, the permittivity of the medium surrounding the cutoff sphere becoming equal to the permittivity of the medium surrounding the infinite periodic system in this limit.

The algorithm was tested for the case of a single spherical ion, considering different electrostatic interaction schemes [Ewald (EW), straight cutoff truncation (ST), and cutoff truncation with a reaction-field correction corresponding to concluding boundary conditions (RF)], and validated by comparison with other methods: A recently developed finite-integration method⁵⁸ (for ST and RF), a one-dimensional integral-equation method^{42,43,56} possibly corrected for

periodicity using an empirical correction term⁵⁸ (for ST and RF), and an analytical expression (EW). The agreement between the electrostatic solvation free energies computed using the different methods was found to be excellent. Considering the three above electrostatic interaction schemes, the present continuum-electrostatics method was then used to investigate the nature and magnitude of the perturbations induced by the approximate treatment of electrostatic interactions and by artificial periodicity in explicit-solvent simulations of ions and ion pairs.

Investigating the solvent polarization around a monovalent spherical ion in a periodic system with modified electrostatic interactions led to the following observations. The application of cutoff truncation significantly perturbs the polarization around the ion compared to the ideal case of exact Coulombic interactions, i.e., to the Born result under nonperiodic boundary conditions (NPBC) or to the Ewald result under periodic boundary conditions (PBC). In the ST case, the solvent is overpolarized within the cutoff sphere of the ion and underpolarized outside this sphere. Changing to the RF scheme, the agreement with the Born (NPBC) or the EW (PBC) polarization is significantly improved, resulting in a moderate underpolarization that is most significant in the neighborhood of the cutoff distance. In both cases, the perturbation of the solvent polarization decreases in magnitude upon increasing the cutoff distance. It can be shown that the polarization indeed converges toward the Born polarization (NPBC) or EW polarization (PBC) in the limit of an infinite cutoff distance. For these cutoff-based interaction schemes, the solvent polarization itself decreases over the whole range of distances upon increasing the ionic radius. The reason is that the direct interaction between the ion and the solvent is limited to the spherical shell of solvent located between the ionic radius and the cutoff distance. For both Coulombic and truncated-electrostatic interactions, artificial periodicity leads to a systematic depolarization of the solvent (compared to the corresponding result under NPBC) which is caused by the direct or indirect (solvent-mediated) perturbation of the solvent molecules in the reference box by the periodic copies of the ion. This depolarization is very small close to the ion and increases in magnitude with increasing distance from the ion. This periodicity-induced depolarization is more significant for the EW and RF schemes compared to the ST scheme. As expected, the solvent polarization corresponding to the three schemes under PBC converges toward the corresponding curve under NPBC upon increasing the box size.

The effect of modified electrostatic interactions and periodic boundary conditions on the solvent polarization could be used to explain the corresponding errors induced in the ionic solvation free energies. This analysis led to the derivation of correction terms to be applied to ionic solvation free energies resulting from explicit-solvent simulations.

Investigating the PMF for the interaction between two monovalent spherical ions in a periodic system with modified electrostatic interactions led to the following observations. The application of cutoff truncation induces a serious perturbation in the overall electrostatic contribution to the PMF. As previously observed in explicit-solvent simulations, this may lead to unphysical attraction between ions of like

charges and repulsion between ions of opposite charges, and to artifacts in the relative stabilities of the contact, solvent-separated, and free ion pairs. These effects are reduced (although not completely eliminated) by the application of the RF scheme. In contrast, the EW scheme is characterized by a monotonic repulsion of equally charged ions, and an essentially flat PMF for oppositely charged ions. This behavior is in good qualitative agreement with previous observations from explicit-solvent simulations.

Future work will involve further assessment of the validity of the present observations based on continuum electrostatics by means of explicit-solvent simulations. Further applications of the present method will also involve the comparison of approximate electrostatic interaction schemes and the assessment of periodicity-induced artifacts in more complex (bio)molecular systems, such as macromolecules in solution, phase interfaces, or membranes, with the goal of better understanding the consequences of the approximate treatment of electrostatic interactions in explicit-solvent simulations.

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APPENDIX A: DIPOLE–DIPOLE INTERACTION TENSOR

Here, a general expression is derived for the Fourier coefficients of the dipole–dipole interaction tensor [Eq. (24)] corresponding to a continuous truncated polynomial interaction function [Eq. (20)].

The Fourier coefficients of the interaction tensor describing the field generated by a periodic array of point dipoles can be written (under vacuum SBC)

$$\begin{aligned}\hat{\mathbf{T}}(\mathbf{k}) &= \int \int \int_V d^3r e^{-i\mathbf{k}\cdot\mathbf{r}} \sum_{\mathbf{n} \in \mathbb{Z}^3} \mathbf{T}(\mathbf{r} + \mathbf{L}\mathbf{n}) \\ &= \int \int \int_{\mathbb{R}^3} d^3r e^{-i\mathbf{k}\cdot\mathbf{r}} \mathbf{T}(\mathbf{r}),\end{aligned}\quad (\text{A1})$$

where the first integral over the volume of the reference box could be replaced by an integral over the whole space owing to periodicity.⁶⁸ Considering Eqs. (20), (24), and (A1), it is immediately seen that the Fourier-coefficient tensor can be written as a sum of contributions from the different terms of the interaction function, i.e.,

$$\hat{\mathbf{T}}(\mathbf{k}) = \sum_{m=-1}^M a_m R_c^{-m-1} \hat{\mathbf{T}}_m(\mathbf{k}), \quad (\text{A2})$$

with

$$\hat{\mathbf{T}}_m(\mathbf{k}) = (4\pi\epsilon_0)^{-1} \int \int \int_{\Omega(R_c)} d^3r e^{-i\mathbf{k}\cdot\mathbf{r}} \nabla \otimes \nabla r^m, \quad (\text{A3})$$

where $\Omega(R_c)$ is a spherical volume of radius R_c and surface $\Sigma(R_c)$ centered at the origin. An expression for the quantities $\hat{\mathbf{T}}_m(\mathbf{k})$ with $m \geq -1$ is derived below. The cases $k=0$ and $k \neq 0$ must be treated separately.

For $k=0$, Eq. (A3) takes the form

$$\begin{aligned}\hat{\mathbf{T}}_m(\mathbf{0}) &= (4\pi\epsilon_0)^{-1} \int \int \int_{\Omega(R_c)} d^3r \nabla \otimes \nabla r^m \\ &= (4\pi\epsilon_0)^{-1} m R_c^{m-1} \int \int_{\Sigma(R_c)} d^2\sigma \frac{\mathbf{r}}{r} \otimes \frac{\mathbf{r}}{r} \\ &= (4\epsilon_0)^{-1} m R_c^{m+1} \int_0^\pi d\theta \sin(\theta) \mathbf{X}(\theta) \\ &= (3\epsilon_0)^{-1} m R_c^{m+1} \mathbf{1},\end{aligned}\quad (\text{A4})$$

where

$$\begin{aligned}\mathbf{X}(\theta) &= \pi^{-1} \int_0^{2\pi} d\phi \frac{\mathbf{r}}{r} \otimes \frac{\mathbf{r}}{r} \\ &= \begin{pmatrix} \sin^2(\theta) & 0 & 0 \\ 0 & \sin^2(\theta) & 0 \\ 0 & 0 & 2\cos^2(\theta) \end{pmatrix}.\end{aligned}\quad (\text{A5})$$

The second equality in Eq. (A4) follows from applying the gradient theorem in $\Omega(R_c)$ and inserting $\nabla r^m = m r^{m-2} \mathbf{r}$, and the third equality from expressing the integrand in spherical coordinates and integrating over ϕ . This result was derived previously for $m=-1$ and $m=2$ in the context of the calculation of the permittivity of liquids from molecular simulations.^{14,15,67}

For $k \neq 0$, the integrand in Eq. (A3) may be rewritten as

$$\begin{aligned}e^{-i\mathbf{k}\cdot\mathbf{r}} \nabla \otimes \nabla r^m &= \nabla \otimes (e^{-i\mathbf{k}\cdot\mathbf{r}} \nabla r^m) + i\mathbf{k} \otimes (e^{-i\mathbf{k}\cdot\mathbf{r}} \nabla r^m) \\ &= \nabla \otimes (e^{-i\mathbf{k}\cdot\mathbf{r}} \nabla r^m) + i\mathbf{k} \otimes \nabla (e^{-i\mathbf{k}\cdot\mathbf{r}} r^m) \\ &\quad - \mathbf{k} \otimes \mathbf{k} e^{-i\mathbf{k}\cdot\mathbf{r}} r^m.\end{aligned}\quad (\text{A6})$$

Inserting Eq. (A6) into Eq. (A3), applying the gradient theorem in the spherical volume $\Omega(R_c)$, and using $\nabla r^m = m r^{m-2} \mathbf{r}$ leads to

$$\begin{aligned}\hat{\mathbf{T}}_m(\mathbf{k}) &= (4\pi\epsilon_0)^{-1} \left[m R_c^{m-1} \int \int_{\Sigma(R_c)} d^2\sigma e^{-i\mathbf{k}\cdot\mathbf{r}} \frac{\mathbf{r}}{r} \otimes \frac{\mathbf{r}}{r} \right. \\ &\quad + i\mathbf{k} \otimes R_c^m \int \int_{\Sigma(R_c)} d^2\sigma e^{-i\mathbf{k}\cdot\mathbf{r}} \frac{\mathbf{r}}{r} \\ &\quad \left. - \mathbf{k} \otimes \mathbf{k} \int \int \int_{\Omega(R_c)} d^3r e^{-i\mathbf{k}\cdot\mathbf{r}} r^m \right] \\ &= -(4\pi\epsilon_0)^{-1} R_c^{m+1} [m \mathbf{A}(\mathbf{k}; R_c) - i\mathbf{k} \otimes \mathbf{b}(\mathbf{k}; R_c) \\ &\quad - \mathbf{k} \otimes \mathbf{k} c(\mathbf{k}; R_c)].\end{aligned}\quad (\text{A7})$$

The three quantities $\mathbf{A}$, $\mathbf{b}$, and c are calculated separately below. For the tensor $\mathbf{A}$, one has

$$\begin{aligned}
\mathbf{A}(\mathbf{k}; R_c) &= -R_c^{-2} \int \int_{\Sigma(R_c)} d^2\sigma e^{-i\mathbf{k}\cdot\mathbf{r}} \frac{\mathbf{r}}{r} \\
&= -\pi \int_0^\pi d\theta \sin(\theta) \cos[kR_c \cos(\theta)] \mathbf{X}(\theta) \\
&= -\pi \int_{-1}^1 d\tau \cos(kR_c \tau) \begin{pmatrix} 1-\tau^2 & 0 & 0 \\ 0 & 1-\tau^2 & 0 \\ 0 & 0 & 2\tau^2 \end{pmatrix}.
\end{aligned} \tag{A8}$$

The second equality results from expressing the integrand in spherical coordinates with the z axis along $\mathbf{k}$, observing that the imaginary component vanishes due to the symmetry of $\mathbf{r} \otimes \mathbf{r}$, and integrating over ϕ . The last equality follows from the change of variable $\tau = \cos(\theta)$. Substituting

$$\int_{-1}^1 d\tau \cos(kR_c \tau) = \frac{2}{kR_c} \sin(kR_c), \tag{A9}$$

and

$$\begin{aligned}
\int_{-1}^1 d\tau \tau^2 \cos(kR_c \tau) &= \frac{2}{kR_c} \sin(kR_c) + \frac{4}{(kR_c)^2} \cos(kR_c) \\
&\quad - \frac{4}{(kR_c)^3} \sin(kR_c),
\end{aligned} \tag{A10}$$

and noting that, with the z axis along $\mathbf{k}$, the tensor $\mathbf{k} \otimes \mathbf{k}$ has only one nonvanishing element (the zz element) evaluating to k^2 , one obtains

$$\begin{aligned}
\mathbf{A}(\mathbf{k}; R_c) &= 4\pi \left[\frac{1}{(kR_c)^2} \cos(kR_c) - \frac{1}{(kR_c)^3} \sin(kR_c) \right] \mathbf{1} \\
&\quad + 4\pi \left[-\frac{1}{kR_c} \sin(kR_c) - \frac{3}{(kR_c)^2} \cos(kR_c) \right. \\
&\quad \left. + \frac{3}{(kR_c)^3} \sin(kR_c) \right] k^{-2} \mathbf{k} \otimes \mathbf{k}.
\end{aligned} \tag{A11}$$

For the vector $\mathbf{b}$, one has

$$\begin{aligned}
\mathbf{b}(\mathbf{k}; R_c) &= R_c^{-1} \int \int_{\Sigma(R_c)} d^2\sigma e^{-i\mathbf{k}\cdot\mathbf{r}} \frac{\mathbf{r}}{r} \\
&= -2\pi i k^{-1} \mathbf{k} R_c \int_0^\pi d\theta \sin(\theta) \cos(\theta) \\
&\quad \times \sin[kR_c \cos(\theta)] \\
&= -2\pi i k^{-1} \mathbf{k} R_c \int_{-1}^1 d\tau \tau \sin(kR_c \tau) \\
&= 4\pi i k^{-2} \mathbf{k} \left[\cos(kR_c) - \frac{1}{kR_c} \sin(kR_c) \right].
\end{aligned} \tag{A12}$$

The second equality results from using a spherical coordinate system with the z axis along $\mathbf{k}$, observing that the real component vanishes due to the antisymmetry of $\mathbf{r}$, and integrating over ϕ . Since the x and y components vanish after this integration, the resulting vector is parallel to $\mathbf{k}$.

For the scalar c , one has

$$\begin{aligned}
c(\mathbf{k}; R_c) &= -R_c^{-m-1} \int \int \int_{\Omega(R_c)} d^3r e^{-i\mathbf{k}\cdot\mathbf{r}} r^m \\
&= -2\pi R_c^{-m-1} \int_0^{R_c} dr r^{m+2} \\
&\quad \times \int_0^\pi d\theta \sin(\theta) \cos[kr \cos(\theta)] \\
&= -2\pi R_c^{-m-1} \int_0^{R_c} dr r^{m+2} \int_{-1}^1 d\tau \cos(kr \tau) \\
&= -4\pi k^{-1} R_c^{-m-1} \int_0^{R_c} dr r^{m+1} \sin(kr) \\
&= -4\pi k^{-m-3} R_c^{-m-1} [I_m(kR_c) - I_m(0)],
\end{aligned} \tag{A13}$$

with the definition

$$I_m(x) = \int dx x^{m+1} \sin(x). \tag{A14}$$

Using successive integrations by parts and a proof by recursion, it is easily shown⁷⁹ that for $m \geq -1$

$$\begin{aligned}
I_m(x) &= \sum_{j=0}^{\text{int}[(m+1)/2]} (-1)^{j+1} \frac{(m+1)!}{(m-2j+1)!} x^{m-2j+1} \cos(x) \\
&\quad + \sum_{j=0}^{\text{int}[m/2]} (-1)^j \frac{(m+1)!}{(m-2j)!} x^{m-2j} \sin(x),
\end{aligned} \tag{A15}$$

where $\text{int}[s]$ denotes the largest integer that is smaller or equal to s . Noting that $I_m(0)$ vanishes unless m is odd, and introducing the definition

$$\begin{aligned}
t_m(x) &= \sum_{j=1}^{\text{int}[m/2]} (-1)^j \left[-\frac{(m+1)!}{(m-2j+1)!} x^{-2j} \cos(x) \right. \\
&\quad \left. + \frac{(m+1)!}{(m-2j)!} x^{-2j-1} \sin(x) \right] \\
&\quad + \text{odd}[m] (-1)^{(m+1)/2} (m+1)! x^{-m-1} \\
&\quad \times [1 - (1 - \delta_{m,-1}) \cos(x)],
\end{aligned} \tag{A16}$$

where $\text{odd}[m]$ is one if m is odd and zero otherwise, and $\delta_{m,-1}$ is one if $m = -1$ and zero otherwise, one may write

$$\begin{aligned}
c(\mathbf{k}; R_c) &= -4\pi k^{-2} \left[t_m(kR_c) - \cos(kR_c) \right. \\
&\quad \left. + (m+1) \frac{1}{kR_c} \sin(kR_c) \right].
\end{aligned} \tag{A17}$$

The first few functions of the series $t_m(x)$ are listed in Table V. Combining Eqs. (A7), (A11), (A12), and (A17) and using the definition of Eq. (26), one obtains (for $k \neq 0$ and $m \geq -1$)

$$\begin{aligned}
\hat{\mathbf{T}}_m(\mathbf{k}) &= \epsilon_o^{-1} R_c^{m+1} \left\{ \frac{m}{3} f(kR_c) \mathbf{1} - [t_m(kR_c) \right. \\
&\quad \left. + m f(kR_c)] k^{-2} \mathbf{k} \otimes \mathbf{k} \right\}.
\end{aligned} \tag{A18}$$

TABLE V. First six functions of the series $t_m(x)$ introduced in Eq. (A16). The functions $\sin(x)$ and $\cos(x)$ are abbreviated as s and c for conciseness.

m	$t_m(x)$
-1	1
0	0
1	$2(c-1)x^{-2}$
2	$6cx^{-2}-6sx^{-3}$
3	$12cx^{-2}-24sx^{-3}-24(c-1)x^{-4}$
4	$20cx^{-2}-60sx^{-3}-120cx^{-4}+120sx^{-5}$
5	$30cx^{-2}-120sx^{-3}-360cx^{-4}+720sx^{-5}+720(c-1)x^{-6}$
6	$42cx^{-2}-210sx^{-3}-840cx^{-4}+2520sx^{-5}+5040cx^{-6}-5040sx^{-7}$

Taken together, Eqs. (A2), (A4), (A16), and (A18) provide the required expression for $\hat{\mathbf{T}}(\mathbf{k})$. Introducing the definitions

$$A = \sum_{m=-1}^M m a_m, \quad (\text{A19})$$

and

$$\begin{aligned} T(x) &= \sum_{m=-1}^M a_m t_m(x) \\ &= a_{-1} + \sum_{n=2, n \text{ even}}^{M+1} x^{-n} [q_n + c_n \cos(x)] \\ &\quad + \sum_{n=3, n \text{ odd}}^{M+1} x^{-n} s_n \sin(x), \end{aligned} \quad (\text{A20})$$

with

$$q_n = (-1)^{n/2} n! a_{n-1}, \quad (\text{A21})$$

$$c_n = -(-1)^{n/2} \left[a_{n-1} n! + \sum_{m=n}^M a_m \frac{(m+1)!}{(m-n+1)!} \right], \quad (\text{A22})$$

and

$$s_n = (-1)^{(n-1)/2} \sum_{m=n-1}^M a_m \frac{(m+1)!}{(m-n+1)!}, \quad (\text{A23})$$

one can rewrite the final result (valid for any k)

$$\begin{aligned} \hat{\mathbf{T}}(\mathbf{k}) &= -\epsilon_o^{-1} \left\{ \left[T(kR_c) + A f(kR_c) \right] k^{-2} \mathbf{k} \otimes \mathbf{k} \right. \\ &\quad \left. - \frac{A}{3} f(kR_c) \mathbf{1} \right\} (1 - \delta_k) - \frac{A}{3} \mathbf{1} \delta_k. \end{aligned} \quad (\text{A24})$$

Considering the form of Eqs. (A18) and (A24), a number of observations can be made. First, as expected, $\hat{\mathbf{T}}_0(\mathbf{k}) = \mathbf{0}$ and the inclusion of any offset constant (change of the a_0 coefficient) in the interaction function has no effect on the dipole-dipole interaction tensor. Second, the tensor at zero wave vector is always proportional to the unit tensor. Third, in the limit of very small wave vectors ($k \rightarrow 0$, i.e., characterizing the long-range limit), one can use the result $\lim_{x \rightarrow 0} f(x) = 1$ to obtain

$$\lim_{kR_c \rightarrow 0} \hat{\mathbf{T}}(\mathbf{k}) = -\epsilon_o^{-1} \left\{ \left[\lim_{kR_c \rightarrow 0} T(kR_c) + A \right] k^{-2} \mathbf{k} \otimes \mathbf{k} - \frac{A}{3} \mathbf{1} \right\}. \quad (\text{A25})$$

The comparison with the $k=0$ result in Eq (A24) shows that, for truncated electrostatic interactions, $\hat{\mathbf{T}}(\mathbf{k})$ is continuous at the origin when

$$\lim_{x \rightarrow 0} T(x) = -A. \quad (\text{A26})$$

Note that the Ewald tensor [Eq. (15)], which corresponds to nontruncated Coulombic interactions, does not diverge but is not continuous at the origin (irrespective of ϵ'). Fourth, in the limit of very large cutoff distances ($R_c \rightarrow \infty$) with $k \neq 0$, or very large wave vectors ($k \rightarrow \infty$, i.e., characterizing the close neighborhood of a dipole), the form of Eq. (A18) and of the t_m functions (Table V) implies

$$\lim_{kR_c \rightarrow \infty, k \neq 0} \hat{\mathbf{T}}(\mathbf{k}) = -\epsilon_o^{-1} a_{-1} k^{-2} \mathbf{k} \otimes \mathbf{k} = a_{-1} \hat{\mathbf{T}}_{\text{EW}}(\mathbf{k}), \quad (\text{A27})$$

where $\hat{\mathbf{T}}_{\text{EW}}(\mathbf{k})$ is the Ewald dipole-dipole interaction tensor corresponding to Coulombic interactions without cutoff truncation [Eq. (15)]. Due to Eq. (A27), the only physically reasonable choice for the a_{-1} coefficient is the one specified by Eq. (21). Note also that Eq. (A27) generally cannot be extended to the limit of $R_c \rightarrow \infty$ with $k=0$. Irrespective of the value of R_c , $\hat{\mathbf{T}}(\mathbf{0})$ will only be equal to $\hat{\mathbf{T}}_{\text{EW}}(\mathbf{0})$ provided that [Eqs. (15) and (A24)]

$$A = -\frac{3}{2\epsilon' + 1}. \quad (\text{A28})$$

These observations prove a quite interesting result. In the limit of an infinite cutoff radius, the dipole-dipole interaction tensor characterizing any truncated interaction scheme (with $a_{-1}=1$) will always converge to the Ewald tensor for $k \neq 0$, and will also converge to the Ewald tensor for $k=0$ provided that Eq. (A28) is satisfied. Fifth, for any continuously differentiable (cd) interaction function of the form of Eq. (20), one has

$$\left. \frac{dv(r)}{dr} \right|_{r=R_c} = (4\pi\epsilon_o)^{-1} R_c^{-2} A = 0, \quad (\text{A29})$$

where A is the quantity introduced in Eq. (A19), because the derivatives of $v(r)$ just below (left-hand side) and above (zero) the cutoff distance R_c must be identical. As a consequence, the quantity A vanishes and Eq. (A24) becomes

$$\hat{\mathbf{T}}_{\text{cd}}(\mathbf{k}) = -\epsilon_o^{-1} T(kR_c) k^{-2} \mathbf{k} \otimes \mathbf{k} (1 - \delta_k). \quad (\text{A30})$$

This result shows that, for truncated electrostatic interactions, a nonvanishing $\hat{\mathbf{T}}(\mathbf{0})$ and the presence of a term in $\hat{\mathbf{T}}(\mathbf{k})$ proportional to the unit tensor are both consequences of a discontinuity in the derivative of the interaction function at R_c .

At this point of the discussion, it is interesting to consider the specific case of truncated Coulombic interactions with a Barker-Watts reaction-field correction, as defined by Eq. (23). In this case, one finds

$$A = -\frac{3}{2\epsilon' + 1} \quad (\text{A31})$$

and

$$T(x) = 1 + \frac{6(\epsilon' - 1)}{2\epsilon' + 1} \left[\frac{\cos(x)}{x^2} - \frac{\sin(x)}{x^3} \right]$$

$$= 1 - \frac{2(\epsilon' - 1)}{2\epsilon' + 1} f(x). \quad (\text{A32})$$

Inserting these results into Eq. (A24), the corresponding tensor is given by Eq. (25). Note that this interaction function satisfies Eq. (A26) and is thus continuous at the origin irrespective of ϵ' . The corresponding value at zero wave vector also matches the Ewald value, although the Ewald tensor itself [Eq. (15)] is not continuous at the origin. Furthermore, because Eq. (A28) is satisfied, one may write

$$\lim_{R_c \rightarrow \infty} \hat{\mathbf{T}}_{\text{BW}}(\mathbf{k}) = \hat{\mathbf{T}}_{\text{EW}}(\mathbf{k}), \quad (\text{A33})$$

irrespective of k , i.e., in terms of dipole–dipole interactions, the EW scheme is the limiting case of the BW scheme corresponding to an infinite cutoff radius. These observations are in line with previous work, where correspondences between Ewald summation with vacuum boundary conditions and straight truncation of Coulombic interactions, and between Ewald summation with tinfoil boundary conditions and Barker–Watts reaction field with conducting boundary conditions were stated.⁸⁰

APPENDIX B: THETA TENSOR

Here, a general expression is derived for the reciprocal space tensor $\hat{\boldsymbol{\theta}}(\mathbf{k})$ in Eq. (5) for the case of truncated electrostatic interactions. It is convenient to introduce the tensor $\mathbf{K} = k^{-2} \mathbf{k} \otimes \mathbf{k} (1 - \delta_k)$, which satisfies $\mathbf{K}^2 = \mathbf{K}$. As an *ansatz* for $\hat{\boldsymbol{\theta}}(\mathbf{k})$, this quantity is assumed to be of the general form

$$\hat{\boldsymbol{\theta}}(\mathbf{k}) = \alpha_1 \mathbf{1} + \alpha_2 \mathbf{K}. \quad (\text{B1})$$

$$\alpha_2 = - \frac{9(\epsilon_s - 1)[A f(kR_c) + T(kR_c)]}{[3 - (\epsilon_s - 1)A f(kR_c)][3 + (\epsilon_s - 1)[2A f(kR_c) + 3T(kR_c)]]}. \quad (\text{B5})$$

For $k=0$, $\hat{\boldsymbol{\theta}}(\mathbf{k})$ is found directly through Eq. (A24)

$$\hat{\boldsymbol{\theta}}(\mathbf{0}) = [\mathbf{1} - \epsilon_o(\epsilon_s - 1)\hat{\mathbf{T}}(\mathbf{0})]^{-1}$$

$$= \left[\mathbf{1} - \frac{(\epsilon_s - 1)}{3} A \mathbf{1} \right]^{-1}$$

$$= \frac{3}{3 - (\epsilon_s - 1)A} \mathbf{1}. \quad (\text{B6})$$

Taken together, Eqs. (B1), (B4), (B5), and (B6) provide the required expression for $\hat{\boldsymbol{\theta}}$. Using Eqs. (A31) and (A32), this tensor is easily evaluated for the Barker–Watts reaction-field scheme, leading to Eq. (27). Note that, as expected from the discussion of Appendix A,

$$\lim_{R_c \rightarrow \infty} \hat{\boldsymbol{\theta}}_{\text{BW}}(\mathbf{k}) = \hat{\boldsymbol{\theta}}_{\text{EW}}(\mathbf{k}), \quad (\text{B7})$$

If this expression is correct, it is sufficient to determine the constants α_1 and α_2 that satisfy

$$[\mathbf{1} - \epsilon_o(\epsilon_s - 1)\hat{\mathbf{T}}(\mathbf{k})][\alpha_1 \mathbf{1} + \alpha_2 \mathbf{K}] = \mathbf{1}. \quad (\text{B2})$$

The cases $k=0$ and $k \neq 0$ are treated separately.

For $k \neq 0$, the left-hand side of Eq. (B2) is developed in the following way:

$$[\mathbf{1} - \epsilon_o(\epsilon_s - 1)\hat{\mathbf{T}}(\mathbf{k})][\alpha_1 \mathbf{1} + \alpha_2 \mathbf{K}]$$

$$= \left[\mathbf{1} - \epsilon_o(\epsilon_s - 1) \sum_{m=-1}^M a_m R_c^{-m-1} \hat{\mathbf{T}}_m(\mathbf{k}) \right] [\alpha_1 \mathbf{1} + \alpha_2 \mathbf{K}]$$

$$= \left[\mathbf{1} - (\epsilon_s - 1) \sum_{m=-1}^M a_m \left\{ \frac{m}{3} f(kR_c) \mathbf{1} - [t_m(kR_c) + m f(kR_c)] \mathbf{K} \right\} \right] [\alpha_1 \mathbf{1} + \alpha_2 \mathbf{K}]$$

$$= \alpha_1 \left[1 - \frac{\epsilon_s - 1}{3} A f(kR_c) \right] \mathbf{1} + \left\{ \alpha_2 + (\epsilon_s - 1) \right.$$

$$\times \left[\left(\alpha_1 + \frac{2}{3} \alpha_2 \right) A f(kR_c) + (\alpha_1 + \alpha_2) T(kR_c) \right] \mathbf{K}.$$

$$(\text{B3})$$

The first equality results from Eq. (A2), the second from inserting Eq. (A18), and the third uses the definitions of Eqs. (A19) and (A20). Inserting Eq. (B3) into Eq. (B2) and solving for α_1 and α_2 gives

$$\alpha_1 = \frac{3}{3 - (\epsilon_s - 1)A f(kR_c)}, \quad (\text{B4})$$

and

since $\lim_{x \rightarrow \infty} f(x) = 0$, and

$$\lim_{k \rightarrow 0} \hat{\boldsymbol{\theta}}_{\text{BW}}(\mathbf{k}) = \hat{\boldsymbol{\theta}}_{\text{BW}}(\mathbf{0}) = \hat{\boldsymbol{\theta}}_{\text{EW}}(\mathbf{0}), \quad (\text{B8})$$

since $\lim_{x \rightarrow 0} f(x) = 1$, this although

$$\lim_{k \rightarrow 0} \hat{\boldsymbol{\theta}}_{\text{EW}}(\mathbf{k}) \neq \hat{\boldsymbol{\theta}}_{\text{EW}}(\mathbf{0}). \quad (\text{B9})$$

APPENDIX C: CHARGE–DIPOLE INTERACTION TENSOR

Here, a general expression is derived for the Fourier coefficients of the charge–dipole interaction tensor [Eq. (29)] corresponding to a continuous truncated polynomial interaction function [Eq. (20)].

The Fourier coefficients of the interaction tensor describing the potential generated by a periodic array of point dipoles can be written as

$$\begin{aligned}\hat{\mathbf{t}}(\mathbf{k}) &= \int \int \int_V d^3r e^{-i\mathbf{k}\cdot\mathbf{r}} \sum_{\mathbf{n} \in \mathbb{Z}^3} \mathbf{t}(\mathbf{r} + \mathbf{L}\mathbf{n}) \\ &= \int \int \int_{\mathbb{R}^3} d^3r e^{-i\mathbf{k}\cdot\mathbf{r}} \mathbf{t}(\mathbf{r}).\end{aligned}\quad (\text{C1})$$

The Fourier-coefficient tensor can be written as a sum of contributions from the different terms of the interaction function, i.e.,

$$\hat{\mathbf{t}}(\mathbf{k}) = \sum_{m=-1}^M a_m R_c^{-m-1} \hat{\mathbf{t}}_m(\mathbf{k}), \quad (\text{C2})$$

with

$$\hat{\mathbf{t}}_m(\mathbf{k}) = -(4\pi\epsilon_o)^{-1} \int \int \int_{\Omega(R_c)} d^3r e^{-i\mathbf{k}\cdot\mathbf{r}} \nabla r^m, \quad (\text{C3})$$

where $\Omega(R_c)$ is a spherical volume of radius R_c and surface $\Sigma(R_c)$ centered at the origin. The cases $k=0$ and $k \neq 0$ are treated separately.

For $k=0$, Eq. (C3) takes the form

$$\hat{\mathbf{t}}_m(\mathbf{0}) = -(4\pi\epsilon_o)^{-1} \int \int \int_{\Omega(R_c)} d^3r \nabla r^m = \mathbf{0}, \quad (\text{C4})$$

the last equality following symmetry considerations after inserting $\nabla r^m = m r^{m-2} \mathbf{r}$.

For $k \neq 0$ the integrand can be rewritten as

$$e^{-i\mathbf{k}\cdot\mathbf{r}} \nabla r^m = \nabla (e^{-i\mathbf{k}\cdot\mathbf{r}} r^m) + i\mathbf{k} e^{-i\mathbf{k}\cdot\mathbf{r}} r^m. \quad (\text{C5})$$

Inserting this expression into Eq. (C1), applying the gradient theorem in the spherical volume $\Omega(R_c)$, and using $\nabla r^m = m r^{m-2} \mathbf{r}$ leads to

$$\begin{aligned}\hat{\mathbf{t}}_m(\mathbf{k}) &= -(4\pi\epsilon_o)^{-1} R_c^{m+1} \left[R_c^{-1} \int \int \int_{\Sigma(R_c)} d^2\sigma e^{-i\mathbf{k}\cdot\mathbf{r}} \frac{\mathbf{r}}{r} \right. \\ &\quad \left. + i\mathbf{k} R_c^{-m-1} \int \int \int_{\Omega(R_c)} d^3r e^{-i\mathbf{k}\cdot\mathbf{r}} r^m \right] \\ &= -(4\pi\epsilon_o)^{-1} R_c^{m+1} [\mathbf{b}(\mathbf{k}; R_c) - i\mathbf{k} c(\mathbf{k}; R_c)],\end{aligned}\quad (\text{C6})$$

where $\mathbf{b}(\mathbf{k}; R_c)$ and $c(\mathbf{k}; R_c)$ are quantities introduced in Eq. (A7). Combining Eqs. (C6), (A12), and (A17), one obtains (for $k \neq 0$ and $m \geq -1$)

$$\hat{\mathbf{t}}_m(\mathbf{k}) = -\epsilon_o^{-1} i k^{-2} \mathbf{k} R_c^{m+1} \left[t_m(k R_c) + m \frac{\sin(k R_c)}{k R_c} \right]. \quad (\text{C7})$$

Taken together, Eqs. (C2), (C4), and (C7) provide the required expression for $\hat{\mathbf{t}}(\mathbf{k})$. With the definitions of Eqs. (A19) and (A20), one can rewrite the final result (valid for any k) as

$$\hat{\mathbf{t}}(\mathbf{k}) = -\epsilon_o^{-1} i k^{-2} \mathbf{k} \left[T(k R_c) + A \frac{\sin(k R_c)}{k R_c} \right] (1 - \delta_k). \quad (\text{C8})$$

Considering the forms of Eqs. (C7) and (C8), a number of observations can be made: First, $\hat{\mathbf{t}}_0(\mathbf{k}) = \mathbf{0}$ and the inclusion of an offset constant in the interaction function has no effect on the charge–dipole interaction tensor. Second, the tensor at zero wave vector vanishes. Third, in the limit of very small wave vectors ($k \rightarrow 0$), one can use the result $\lim_{x \rightarrow 0} x^{-1} \sin(x) = 1$ to obtain

$$\lim_{k R_c \rightarrow 0} k \hat{\mathbf{t}}(\mathbf{k}) = -\epsilon_o^{-1} i k^{-1} \mathbf{k} \left[\lim_{k R_c \rightarrow 0} T(k R_c) + A \right]. \quad (\text{C9})$$

Thus, $k \hat{\mathbf{t}}(\mathbf{k})$ is continuous at the origin when Eq. (A26) is satisfied. Note that for the Ewald tensor [Eq. (19)], this quantity does not diverge but is discontinuous at the origin. In any case, $\hat{\mathbf{t}}(\mathbf{k})$ itself diverges. Fourth, in the limit of very large cutoff distances ($R_c \rightarrow \infty$) or very large wave vectors ($k \rightarrow \infty$), the form of Eq. (C7) and of the t_m functions (Table V) implies

$$\lim_{k R_c \rightarrow \infty} \hat{\mathbf{t}}(\mathbf{k}) = -\epsilon_o^{-1} a_{-1} i k^{-2} \mathbf{k} (1 - \delta_k) = a_{-1} \hat{\mathbf{t}}_{\text{EW}}(\mathbf{k}), \quad (\text{C10})$$

where $\hat{\mathbf{t}}_{\text{EW}}(\mathbf{k})$ is the Ewald charge–dipole interaction tensor corresponding to Coulombic interactions without cutoff truncation [Eq. (19)]. Thus, the only physically reasonable choice for a_{-1} is again the one specified by Eq. (21). This observation proves that in the limit of an infinite cutoff radius, the charge–dipole interaction tensor characterizing any truncated interaction scheme (with $a_{-1} = 1$) will always converge to the Ewald tensor, irrespective of the value of k . Fifth, for any continuously-differentiable (cd) interaction function of the form of Eq. (20), Eq. (A29) implies that $A = 0$ and Eq. (C8) becomes

$$\hat{\mathbf{t}}_{\text{cd}}(\mathbf{k}) = -\epsilon_o^{-1} i k^{-2} \mathbf{k} T(k R_c) (1 - \delta_k). \quad (\text{C11})$$

In the specific case of the Barker–Watts reaction-field scheme, inserting Eqs. (A31) and (A32) into Eq. (C8) results in Eq. (30). Note that this interaction function satisfies Eq. (A26) and is thus continuous at the origin, irrespective of ϵ' . Furthermore, due to Eq. (C10),

$$\lim_{R_c \rightarrow \infty} \hat{\mathbf{t}}_{\text{BW}}(\mathbf{k}) = \hat{\mathbf{t}}_{\text{EW}}(\mathbf{k}), \quad (\text{C12})$$

irrespective of k , i.e., in terms of the charge–dipole interaction tensor, the EW scheme is the limiting case of the BW scheme corresponding to an infinite cutoff radius.

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