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Molecular dynamics scheme for precise estimation of electrostatic interaction via zero-dipole summation principle

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We propose a novel idea, zero-dipole summation, for evaluating the electrostatic energy of a classical particle system, and have composed an algorithm for effectively utilizing the idea for molecular dynamics. It conceptually prevents the nonzero-charge and nonzero-dipole states artificially generated by a simple cutoff truncation. The resulting energy formula is nevertheless represented by a simple pairwise function sum, which enables facile application to high-performance computation. By following a heuristic approach to derive the current electrostatic energy formula, we developed an axiomatic approach to construct the method consistently. Explorations of the theoretical details of our method revealed the structure of the generated error, and we analyzed it by comparisons with other methods. A numerical simulation using liquid sodium chloride confirmed that the current method with a small damping factor yielded sufficient accuracy with a practical cutoff distance region. The current energy function also conducts stable numerical integration in a liquid MD simulation. Our method is an extension of the charge neutralized summation developed by Wolf *et al.* [J. Chem. Phys. **110**, 8254 (1999)]. Furthermore, we found that the current method becomes a generalization of the preaveraged potential method proposed by Yakub and Ronchi [J. Chem. Phys. **119**, 11556 (2003)], which is based on a viewpoint different from the neutrality. The current study presents these relationships and suggests possibilities for their further applications. © *2011 American Institute of Physics*. [doi:10.1063/1.3582791]

I. INTRODUCTION

The Coulombic interaction plays an essential role in the behaviors of materials in equilibrium or nonequilibrium phases. For computational studies of materials in a realistic manner, even in a classical point charge system, the appropriate treatment of this interaction is thus important.[1] However, it is difficult to handle the Coulombic interaction, due to its long-ranged nature and the existence of both positive and negative signatures for the potential function. Thus, various methods have been developed,[2–4] including truncation methods,[5,6] lattice-sum methods, such as the Ewald summation,[7,8] the reaction field method,[9,10] and the fast multipole method.[11] Although each of these methods has advantageous features, it is difficult to fulfill all of the following requirements: (i) High accuracy and low computational cost; (ii) Freedom from artifacts, such as those caused by the simple application of a cutoff truncation[12,13] or the unnatural deformation of a potential function often employed in truncation methods,[14,15] and by a periodicity assumption in the application of lattice sum methods to inherently nonperiodic systems;[16,17] and (iii) Ease of implementation, which enhances the availability for use in high-performance computational architectures.

Recently, new approaches to calculate the Coulombic energy have been developed, including local molecular field theory,[18] the single sum technique,[19] and Wolf's charge-neutralizing idea.[20] Wolf proposed an effective method that is compatible with the cutoff method, and full investigations[21] with extensions[22,23] have been made. Mainly, ensuring the charge neutrality in the cutoff sphere and incorporating a certain damping factor are very effective to approach the true total energy, e.g., the Madelung energy for ion systems. Since this method is based on a simple pairwise sum formulation, it only requires a simple implementation and entails no massive computational cost. In addition, this approach is formally free from the periodicity assumption, and thus we can avoid the relevant artifacts. Its effective features have been numerically confirmed in various systems.[21–32]

The direct application of this scheme to a molecular dynamics (MD) study, however, contains a difficulty in that the pair potential cannot be differentiated at the cutoff length, which causes problems, such as energy nonconservation in NEV (microcanonical) simulations. Such problems become emphasized as the damping parameter α is reduced, whereas the choice of a small α value is in accordance with one of the strategies of Wolf *et al.*,[21] in which the contribution from the error-function term is neglected, except for the self-term. To overcome the problems, following the efforts including those by Wolf *et al.*,[21] Zahn, Schilling, and Kast,[22] and Fennell and Gezelter,[23] we previously proposed[33] a scheme applying the force switching technique.[34] This method, which we call the force-switching Wolf (FSw-Wolf) method, presents a consistently derived force function and establishes the compatibility between the force and potential functions, which are sufficiently smooth to conduct a stable MD simulation. It yields a consistent MD method endowed with a nontrivial suitable total-energy correction. However, there is still room

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for the improvement of the degree of approximation in estimating the interaction. Higher accuracy with a shorter cutoff length is not simply attained, e.g., by only a parameter adjustment. Besides, there is no explicit appearance of the neutralizing effect (or the mirror image charge effect on the cutoff sphere) with respect to the force function.

Yakub and Ronchi[35] have reached another type of pairwise potential, by taking account of the spatially uniformity in order to avoid the artifact caused by the cubic symmetry in the periodicity assumption. Their energy formula is based on the Ewald summation expansion, and is obtained by averaging the functions in the expansion over the spherical angular variables. This averaging corresponds to the situation of treating an isotropic system. By applying it to a number of physical systems, they have shown the numerical evidence of the effectiveness in disordered systems, including a one-component plasma and a two-component fluid.[36,37] Furthermore, their protocol (see also the recent work of Jha *et al.*[38]) yields good results, even for nonspherical systems, such as NaCl (fcc) (Ref. 35) and CsCl (bcc) (Ref. 36) crystal systems. The method was also used to investigate phase transitions and to evaluate the melting point of uranium dioxide through MD simulations.[39,40]

Such a pairwise potential function approach has recently been reexamined, and various approaches, including the force matching method,[41,42] isotropic periodic summation,[43,44] and the screening scheme using the Yukawa potential,[45] have been intensively developed. In general, the simple pairwise summation approach is expected to show both good computational scalability with respect to the system size and simple application to high-performance computation and special purpose architectures.[46]

In this paper, we present an alternative method for estimating the Coulombic interaction, by introducing a zero-charge zero-dipole summation, which is an extension of the zero-charge summation idea.[21,33] The current method, the zero-dipole Wolf method, claims that the summation for which the involved dipole moments yield zero should be considered, in order to attain the total energy in an effective manner. We assume that a sufficiently equilibrated system prefers a zero dipole moment, which is realized inside any sufficiently large sphere, and thus the excess moments must be near the surface of the sphere. The method we propose here provides consistency in the force, the potential function, and the total energy, as in our previous method.[33] However, as compared with the previous method, the current method provides a more accurate pairwise sum expression of the excess part. In addition, the atomic force expression includes the neutralizing effect. Another remarkable feature is that the current scheme also results in a generalization of the scheme of Yakub and Ronchi stated above, which is based on a different view from the zero-dipole principle.

In Sec. II, we first discuss the physical motivation for considering the current zero-dipole Wolf method and provide a heuristic derivation of the energy formula. In Sec. III, we introduce a theoretical framework to justify the formula, by providing the notions of zero-dipole state and zero-dipole summation, and construct a scheme for approximating the true energy. The characteristic features of the current energy formula are investigated, and the approximation is analyzed by decomposing it. We describe the numerical results of the current scheme in Sec. IV, in comparison with the previously proposed scheme. In Sec. V, we discuss the relationships to other methods, and conclude with remarks in Sec. VI.

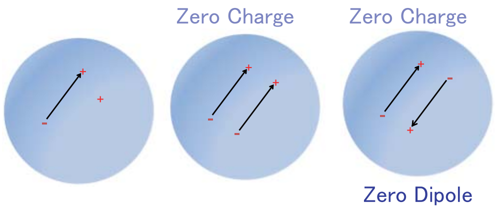


FIG. 1. Schematic representations of states. (Left) Nonzero-charge with nonzero-dipole state; (middle) zero-charge with nonzero-dipole state, (right) zero-charge with zero-dipole state.

II. INTRODUCTION OF THE ZERO-DIPOLE WOLF METHOD

A. Motivation

The motivation for introducing the zero-dipole (ZD) and zero-charge (ZC) state is based on the simple observation that a ZC and ZD state (Fig. 1, right) is physically preferable as compared with a ZC and non-ZD state (Fig. 1, middle), and further, as compared with a non-ZC and non-ZD state (Fig. 1, left). If we create a summation method reflecting the ZC and ZD state to evaluate the electrostatic energy, then the sum captures the characteristic of such a realistic state x and incorporates more information about x. To understand that such a summation must reach a good approximation to the true energy, we consider what kind of state is taken into account in a conventional summation employed in a cutofflike method, and how we should modify the method. Suppose that the total system has no dipole and no charge. Consider first the worst situation, i.e., we take account of a simple cutoff truncation. Then the no-dipole, no-charge feature cannot always be captured, as long as the cutoff length is finite and small. Rather, it expressly generates an artificial non-ZC, non-ZD state in the cutoff sphere, especially at the surface. The physically undesirable states thus generated will yield energy values that are either too large or too small, leading to considerable deviations to the true total energy (e.g., large oscillation occurs in the energy estimation while varying the cutoff length). In other words, the pure atomic-distance-judged truncation, which takes into account all of the contributions from other particles inside the cutoff sphere, is not suitable for considering a system possessing an electrostatic structure (in contrast to a system, e.g., possessing only masses). To avoid the undesirable states, while retaining the simplicity of the cutoff truncation, we need an efficient method for either suitably clipping certain interactions from all contributions in the cutoff sphere or appropriately attaching certain interactions to all contributions in the sphere. A method that is based on the cutoff method, but it takes account of the charge neutrality, is better and avoids many undesirable states. However, it would still create the (ZC but) non-ZD state in the sphere, which may lead to an error in the energy estimation. A ZD method provides a manner for clipping or attaching suitable interactions against all interactions in the cutoff sphere, in order to properly count the interactions on a ZC and ZD state.

B. Heuristic derivation by mirror image charges (MICs)

In a heuristic derivation of the zero-dipole method provided here, MICs are attached on the cutoff sphere to cancel out the artificially generated charges and dipoles in the sphere. The introduction of a MIC itself was originally proposed by Wolf *et al.* In fact, they introduced a charge-neutralized sum by introducing a MIC against each particle in the cutoff sphere around every fixed particle; the MIC is positioned on the cutoff surface and has the opposite charge from that of the target particle. Note that the "derivation" here is heuristic and not complete, but its essence, via a simple example, would provide useful inspiration for further studies.

Consider a cutoff sphere with radius r_c centered about atom i. For any atom j with charge q_j in the cutoff sphere, we introduce two MICs with values a_1 and a_2, in order to cancel out the dipole generated from atom j. To do so, e.g., the two MICs are set to be $a_1 = -a_2 = q_j r_{ij}/2r_c$ and are arranged in the direction of x_{ij} on the cutoff surface, where x_{ij} is a vector directed from atom j to atom i with a length of r_{ij}; see Fig. 2(a). In fact, the target dipole vanishes: $q_j x_{ij} + a_1(-p) + a_2 p = 0$, where $p = r_c x_{ij}/r_{ij}$. The force acting on atom i from atom j and from the MICs is thus

$$q_i q_j F(r_{ij})\frac{x_{ij}}{r_{ij}} + q_i a_1 F(r_c)\frac{-p}{r_c} + q_i a_2 F(r_c)\frac{p}{r_c} \tag{1a}$$

$$= q_i q_j f(r_{ij})\frac{x_{ij}}{r_{ij}}, \tag{1b}$$

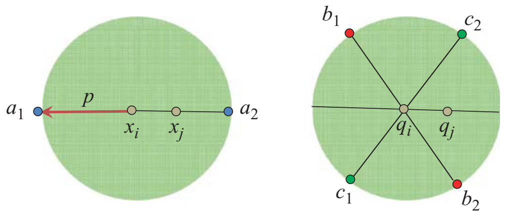
where

$$f(r) \equiv F(r) - \frac{F(r_c)}{r_c} r \tag{2}$$

with $F(r)$ being $1/r^2$ in the bare Coulomb case or a certain function value, e.g., taking into account a damping factor. By gathering all of the similar contributions from every atom j inside the sphere, the force acting on atom i is $\sum_{j(\neq i), r_{ij}<r_c} q_i q_j f(r_{ij}) x_{ij}/r_{ij}$. Thus, the energy corresponding to this force is given by $E_0(x) \equiv \frac{1}{2}\sum_i \sum_{j(\neq i), r_{ij}<r_c} q_i q_j u(r_{ij})$, where

$$u(r) \equiv V(r) + \frac{1}{2}\frac{F(r_c)}{r_c} r^2 + u_c \tag{3}$$

with $F(r) = -DV(r)$ (the negative of the derivative of V at r). u_c is an arbitrary constant that is independent of r.



(a) (b)

FIG. 2. MICs are set at the cutoff surface of radius r_c centered about particle i. (a) Two MICs with $a_1 = -a_2 = q_j r_{ij}/2r_c$ are placed in order to cancel out the dipole generated by particle j with charge q_j. (b) Two MICs with $b_1 = b_2 = -q_j/2$ are placed in order to cancel out the charge generated by particle j, and two MICs with $c_1 = c_2 = -q_i/2$ are placed in order to cancel out the charge generated by particle i itself.

Next, in order to cancel out the charge $q_i + q_j$, we also introduce two MICs with values b_1 and b_2 regarding atom j, and further add two MICs for atom i with values c_1 and c_2. We place the MICs, e.g., as depicted in Fig. 2(b), and set $b_1 = b_2 = -q_j/2$ and $c_1 = c_2 = -q_i/2$. Then, the total charges with dipoles vanish, and the energy E_0 is changed as follows:

$$\begin{aligned} E_H(x) \equiv\ & \frac{1}{2}\sum_i \sum_{\substack{j(\neq i)\\ r_{ij}<r_c}} [q_i q_j u(r_{ij}) + q_i b_1 u(r_c) + q_i b_2 u(r_c)] \\ & + \frac{1}{2}\sum_i [q_i c_1 u(r_c) + q_i c_2 u(r_c)] \\ =\ & \frac{1}{2}\sum_i \sum_{\substack{j(\neq i)\\ r_{ij}<r_c}} [q_i q_j u(r_{ij}) - q_i q_j u(r_c)] \\ & - \frac{1}{2}\sum_i q_i^2 u(r_c). \end{aligned} \tag{4}$$

The above intuitive approach is simple enough, and it would provide a new method in the ZC and ZD condition, as an extension of that in the ZC condition. However, there are several essential problems in establishing the potential and the force in a consistent manner. First, the above arbitrary constant value cannot be given systematically, and the results depend on it. For example, for u_c such that $u(r_c) = 0$, the self-MIC term, viz., the second term in Eq. (4), vanishes, whereas the MIC term should be essential for the ZD condition [the arbitrary constant u_c may correspond to an arbitrary constant added to $E_H(x)$ in Eq. (4), but its determination for each system in a simple and an accurate way would not be trivial]. Second, the results also depend on the combination and the ordering of the treatment about the target condition (ZC or ZD) and quantity (force or potential), and the difference between individual results is not necessarily constant. For example, if we consider the potential energy, instead of the force, in the first stage considering the ZD condition, and then if we consider the force, instead of the potential energy, in the second stage considering the ZC condition, we do not obtain Eq. (4), but rather have the original energy $\frac{1}{2}\sum_i \sum_{j(\neq i)} q_i q_j V(r_{ij})$ [moreover, it depends on supplementary conditions; cf. Ref. 47]. In fact, we have already encountered such a situation in a conventional derivation of the ZC energy:[21,23,33] if we consider an *energy* via a MIC of value b_1 with position S_1 such that $b_1 + q_j = 0$ and $\|x_i - S_1\| = r_c$, then we have an energy $\frac{1}{2}\sum_i \sum_{j(\neq i), r_{ij}<r_c} q_i q_j [V(r_{ij}) - V(r_c)] - \frac{1}{2}V(r_c)\sum_i q_i^2$; while, if we consider a *force* with the same conditions along with a more specific condition $S_1 = x_i - r_c x_{ij}/r_{ij}$, then we have a force, $\sum_{j(\neq i), r_{ij}<r_c} q_i q_j [F(r_{ij}) - F(r_c)] x_{ij}/r_{ij}$; however, the former energy and the latter force are not compatible.

Although more general aspects are discussed in detail in Ref. 47, these problems with indefiniteness and confusions will not be solved, as long as we obey only these considerations. The problems may originate from the fact that the MICs considered for each q_i are not real particles, but image or ghost particles in that they interact with only q_i. For these reasons, we note that the above derivation is just one of the possible interpretations for understanding the current scheme, and that the scheme should be constructed on the basis of certain consistent considerations.

III. THEORY OF ZERO-DIPOLE SUMMATION

We provide a theoretical framework for the ZD energy formula heuristically introduced in Sec. II. The framework systematically characterizes a ZD state and provides a notion of a ZD summation, which is a summation capturing the ZD state and corresponding to a method for clipping out the interactions in the cutoff sphere. The energy E_{H}, aside from the arbitrary constant, is justified as an approximate ZD sum in a consistent manner, without introducing an artificial object, MIC. The meaning of the approximation for the ZD sum will become clear, and we will see that the degree of approximation is better than that for the ZC sum about a ZD state.

A. Formalism

Our method is based on the following two strategies: (*1*: *Conceptual*) For each particle i, the summation with respect to all other atoms is replaced by the one with respect to the following neutralized subset $\mathcal{M}_i$, whose existence is assumed; (*2*: *Specific*) A pair potential function is redefined so that we can simply handle the summation defined in (*1*) above using a usual pairwise-sum form.

1. Conceptual strategy

Let $x \equiv (x_1, \ldots, x_N)$ be N particle configurations in a coordinate phase space Γ and q_j be the charge of particle j that moves in space $\mathbb{R}^d$ (the main concern is in $d = 3$) for $j \in \mathcal{N} \equiv \{1, \ldots, N\}$. We assume the following conditions, i.e., for state $x \in \Gamma$ and for any particle $i \in \mathcal{N}$, there exists a subset $\mathcal{M}_i \subset \mathcal{N}_i \equiv \mathcal{N} - \{i\}$ such that

$$\forall j \in \mathcal{M}_i, \quad r_{ij} < r_{\mathrm{c}}, \tag{5a}$$

$$\sum_{j \in \mathcal{M}_i \cup \{i\}} q_j = 0, \tag{5b}$$

$$\sum_{j \in \mathcal{M}_i \cup \{i\}} q_j x_{ij} = 0 \in \mathbb{R}^d, \tag{5c}$$

$$\forall j \in \mathcal{N}_i - \mathcal{M}_i, \quad (r_{ij} < r_{\mathrm{c}} \Rightarrow r_{ij} \simeq r_{\mathrm{c}}), \tag{5d}$$

where $r_{ij} \equiv \|x_{ij}\|$ with $x_{ij} \equiv x_i - x_j \in \mathbb{R}^d$ and $r_{\mathrm{c}} > 0$ is the cutoff length of the interactions. The conditions (5a), (5b), and (5d) are the same as the zero-charge conditions;[21,33] viz., (a) all particles in $\mathcal{M}_i$ are inside the cutoff sphere, (b) the sum of the charges, including q_i, in $\mathcal{M}_i$ is zero, and (d) a particle (except i) that does not belong to $\mathcal{M}_i$ but is inside the sphere is located near the cutoff surface. The third condition (5c) is currently introduced, requiring that the total dipole, measured by the coordinate with the origin x_i, in $\mathcal{M}_i$ is zero. Namely, $\mathcal{M}_i$ is now a *zero-charge zero-dipole subset*, which we refer to as a *ZD subset*; see Fig. 3. Physically, we can imagine a ZD subset as a member of particles inside a sufficiently large sphere around each particle and suppose that the condition is realized for equilibrated configurations observed in, e.g., a sufficiently equilibrated or disordered system, as discussed in Ref. 21. For simplicity, we often call $x \in \Gamma$ as a ZD state.[48] For a ZD state, a summation method that reflects this new condition (5) promises to provide a good approximation to estimate the energy.

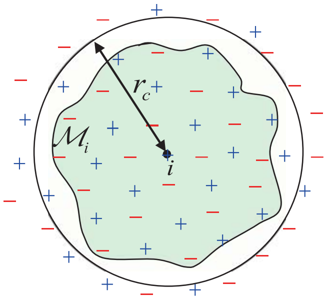


FIG. 3. The conventional simple cutoff method takes into account all charges in a cutoff sphere with radius r_{c}. The current zero-dipole sum method conceptually deals with the particles only in the shaded region, which schematically represent the zero-dipole subset $\mathcal{M}_i$.

Below, we set specifically

$$V(r) = \frac{\mathrm{erfc}(\alpha r)}{r}, \tag{6}$$

which is a Coulomb potential function accompanying a damping factor $\mathrm{erfc}(\alpha r)$, a complementary error function of αr, with $\alpha \geq 0$ [$V(r) = 1/r$, if $\alpha = 0$], and has the corresponding force function,

$$F(r) \equiv -DV(r) = \frac{\mathrm{erfc}(\alpha r)}{r^2} + \frac{2\alpha}{\sqrt{\pi}} \frac{\exp(-\alpha^2 r^2)}{r}. \tag{7}$$

We calculate the total Coulombic energy $E(x)$ for $x \in \Gamma$ via V, following the scheme suggested by Wolf *et al.*:

$$\begin{aligned} E(x) & \\ &= \frac{1}{2} \sum_{i \in \mathcal{N}} \sum_{j \in \mathcal{N}_i} \frac{q_i q_j}{r_{ij}} && (8) \\ &= \frac{1}{2} \sum_{i \in \mathcal{N}} \sum_{j \in \mathcal{N}_i} q_i q_j V(r_{ij}) + \frac{1}{2} \sum_{i \in \mathcal{N}} \sum_{j \in \mathcal{N}_i} q_i q_j \left[\frac{1}{r_{ij}} - V(r_{ij}) \right] && (9) \\ &\approx \frac{1}{2} \sum_{i \in \mathcal{N}} \sum_{j \in \mathcal{M}_i} q_i q_j V(r_{ij}) - \frac{\alpha}{\sqrt{\pi}} \sum_{i \in \mathcal{N}} q_i^2. && (10) \end{aligned}$$

Here, in the first term of Eq. (10) we have used the currently introduced strategy, i.e., the replacement

$$\sum_{j \in \mathcal{N}_i} q_j V(r_{ij}) \rightarrow \sum_{j \in \mathcal{M}_i} q_j V(r_{ij}); \tag{11}$$

namely, the only contributions that should be counted are those from the ZD subset for every i (viz., which corresponds to the clipping idea discussed in Sec. II A). In other words, we assume the approximation

$$\sum_{i\in\mathcal{N}}\sum_{j\in\mathcal{N}_i} q_i q_j V(r_{ij}) \approx \sum_{i\in\mathcal{N}}\sum_{j\in\mathcal{M}_i} q_i q_j V(r_{ij}). \tag{12}$$

The sum with respect to $\mathcal{M}_i$ is called a *zero-charge zero-dipole summation*, or, in short, a *ZD summation*. The second term of Eq. (9) can be read as

$$\frac{1}{2}\sum_{i\in\mathcal{N}}\sum_{j\in\mathcal{N}} \frac{q_i q_j}{r_{ij}}\operatorname{erf}(\alpha r_{ij}) - \frac{1}{2}\lim_{r\to 0}\frac{\operatorname{erf}(\alpha r)}{r}\sum_{i\in\mathcal{N}} q_i^2, \tag{13}$$

and we have adopted the observations by Wolf *et al.*,[21] in which the first term in Eq. (13) can be negligible if one chooses a small α, thus obtaining for Eq. (10)

$$\frac{1}{2}\sum_{i\in\mathcal{N}}\sum_{j\in\mathcal{N}_i} q_i q_j \left[\frac{1}{r_{ij}} - V(r_{ij})\right] \sim -\frac{\alpha}{\sqrt{\pi}}\sum_{i\in\mathcal{N}} q_i^2, \quad \text{for small } \alpha. \tag{14}$$

Hence, we get

$$E(x) \simeq \frac{1}{2}\sum_{i\in\mathcal{N}}\sum_{\substack{j\in\mathcal{N}_i\\ r_{ij}<r_c}} q_i q_j V(r_{ij}) - \hat{E}(x) - \frac{\alpha}{\sqrt{\pi}}\sum_{i\in\mathcal{N}} q_i^2. \tag{15}$$

Here, we have used the relation

$$\sum_{j\in\mathcal{M}_i} = \sum_{\substack{j\in\mathcal{N}_i\\ r_{ij}<r_c}} - \sum_{j\in\mathcal{J}_i}, \tag{16}$$

where $\mathcal{J}_i \equiv \{j \in \mathcal{N}_i - \mathcal{M}_i \mid r_{ij} < r_c\}$, and defined

$$\hat{E}(x) \equiv \frac{1}{2}\sum_{i\in\mathcal{N}}\sum_{j\in\mathcal{J}_i} q_i q_j V(r_{ij}). \tag{17}$$

Namely, $\hat{E}(x)$ corresponds to the energy *excess* from the ordinary cutoff truncation sum $\sum_{j\in\mathcal{N}_i,\, r_{ij}<r_c}$ for every i, in the sense that we should remove the quantity defined on the *excess subset* $\mathcal{J}_i$, which corresponds to, namely, the *nonzero dipole subset* in the cutoff sphere. It should be noted that we assume, for excess subsets $\mathcal{J}_1, \ldots, \mathcal{J}_N$, the following consistency condition:

$$j \in \mathcal{J}_i \Leftrightarrow i \in \mathcal{J}_j, \quad \text{for all } i, j \in \mathcal{N}. \tag{18}$$

This is required in order to subtract each excess interaction consistently: if we decide to remove the interaction with j for i, viz., $j \in \mathcal{J}_i$, then we should also remove the interaction with i for j, viz., $i \in \mathcal{J}_j$.

2. Specific strategy

For Eq. (15) to be effectual in applications, we should find an easily computable expression for estimating $\hat{E}(x)$, which is conceptually given for the excess subset $\mathcal{J}_i$. To accomplish this, we approximate $\hat{E}(x)$ by a pairwise summation formula. The approximation is based on the fact, from condition (5d), that $\mathcal{J}_i$ is *small* in the sense that particles belonging in $\mathcal{J}_i$ are contained in a small area. Its smallness can be measured by the displacement from the position of the target particle to the cutoff surface. We first introduce a displacement vector for any $x \in \Gamma$,

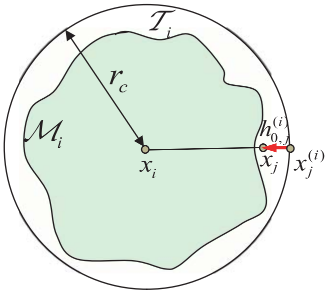


FIG. 4. The particle in the nonshaded region represents a member of the excess subset $\mathcal{J}_i$. Particle j at position x_j is one of the members, and $x_j^{(i)}$ is the shifted position of x_j toward the cutoff surface along the vector $x_j - x_i$. For a particle belonging to the zero-dipole subset $\mathcal{M}_i$ (shaded region), $x_j^{(i)} = x_j$.

$$h_0^{(i)} \equiv x - x^{(i)} \in \mathbb{R}^{dN}, \tag{19}$$

where

$$x^{(i)} \equiv (x_1^{(i)}, \ldots, x_N^{(i)}), \tag{20}$$

$$x_j^{(i)} \equiv \left\{\begin{matrix} x_i + r_c\frac{x_{ji}}{r_{ji}}, & \text{if } j \in \mathcal{J}_i \\ x_j, & \text{otherwise} \end{matrix}\right\} \tag{21}$$

for each $i \in \mathcal{N}$. Namely, for $j \in \mathcal{J}_i$, $x_j^{(i)}$ is the shifted position of x_j obtained by expanding it along vector x_{ji} to the cutoff surface; and for $j \notin \mathcal{J}_i$, we set $x_j^{(i)}$ to be the original position, to maintain a consistent description (see Fig. 4). The displacement vector is small,

$$h_0^{(i)} \equiv \left(h_{0,1}^{(i)}, \ldots, h_{0,N}^{(i)}\right) \sim 0 \in \mathbb{R}^{dN}, \tag{22}$$

by virtue of

$$\left\| h_{0,j}^{(i)} \right\| = \left\{\begin{matrix} r_c - r_{ij}, & \text{if } j \in \mathcal{J}_i \\ 0, & \text{otherwise} \end{matrix}\right\} \simeq 0. \tag{23}$$

Second, we suppose a motion (or perturbation) of the displacement vector, in order to specifically investigate the influence of the smallness of $\mathcal{J}_i$ upon the degree of approximation for $\hat{E}$. Such a motion is basically done along the vector $h_0^{(i)}$, and we denote its domain by $I \equiv I_i^x$; for details see Appendix A. According to the motion of $h^{(i)} \in I_i^x$, the positions $x^{(i)} + h^{(i)}$ are varied.

Based on these formulations, for each $i \in \mathcal{N}$, we see that the quantity (the contribution via atom i to the excess energy)

$$\hat{E}_i(y) \equiv \sum_{j\in\mathcal{J}_i} q_i q_j V(\|y_{ij}\|) \tag{24}$$

for any $y \in \Gamma$ can be approximated by

$$\check{E}_i(y) \equiv \sum_{j\in\mathcal{J}_i} q_i q_j \check{V}(\|y_{ij}\|) \tag{25}$$

with

$$\check{V}(r) \equiv V(r_c) - \frac{F(r_c)}{2r_c}(r^2 - r_c^2), \tag{26}$$

in the following sense: for any fixed $x \in \Gamma$ and $i \in \mathcal{N}$,

$$(\hat{E}_i - \check{E}_i)(x^{(i)} + h^{(i)}) = o(h^{(i)}) \ \ (I_i^x \ni h^{(i)} \to 0). \tag{27}$$

This can be proved from the smoothness of V and the definition of I_i^x, as detailed in Appendix B.

Hence, for the excess energy equation (17), we find

$$\hat{E} = \check{E} + \Delta, \tag{28}$$

where

$$\check{E} = \frac{1}{2}\sum_{i\in\mathcal{N}} \check{E}_i, \tag{29}$$

and

$$\Delta \equiv \sum_{i\in\mathcal{N}} u_i \tag{30}$$

with

$$u_i(x^{(i)} + h^{(i)}) = o(h^{(i)}) \ \ (I_i^x \ni h^{(i)} \to 0) \tag{31}$$

for any $x \in \Gamma$ and $i \in \mathcal{N}$. Here, Δ is negligible, so that

$$\hat{E} \simeq \check{E}. \tag{32}$$

In fact, for every $x \in \Gamma$ and $i \in \mathcal{N}$, we have $x = x^{(i)} + h_0^{(i)}$, implying $u_i(x) = u_i(x^{(i)} + h_0^{(i)})$, which is $\simeq 0$ by virtue of the behavior, Eq. (31), and the smallness of the displacement vector, Eq. (22) [note $h_0^{(i)} \in I_i^x$].

On the other hand, the approximate excess energy becomes

$$\check{E}(x) = \frac{1}{2}\sum_{i\in\mathcal{N}}\sum_{j\in\mathcal{J}_i} q_i q_j \check{V}(r_{ij}) \ \ (x \in \Gamma) \tag{33}$$

$$= -\frac{1}{2}\sum_{i\in\mathcal{N}}\sum_{j\in\mathcal{J}_i} q_i q_j \frac{F(r_\mathrm{c})}{2r_\mathrm{c}} r_{ij}^2 + \frac{1}{2}\left[V(r_\mathrm{c}) + \frac{1}{2}F(r_\mathrm{c})r_\mathrm{c}\right]\sum_{i\in\mathcal{N}}\sum_{j\in\mathcal{J}_i} q_i q_j. \tag{34}$$

For this reason, we should estimate the summations $\sum_{i\in\mathcal{N}}\sum_{j\in\mathcal{J}_i}$ in Eq. (34). The summation in the second term is easily calculated, since the excess charge equals the total charge in the cutoff sphere:

$$\sum_{j\in\mathcal{J}_i} q_j = \sum_{\substack{j\in\mathcal{N}_i\\ r_{ij}<r_\mathrm{c}}} q_j - \sum_{j\in\mathcal{M}_i} q_j \tag{35a}$$

$$= \sum_{\substack{j\in\mathcal{N}_i\\ r_{ij}<r_\mathrm{c}}} q_j + q_i, \tag{35b}$$

deduced from Eqs. (16) and (5b). Meanwhile, the summation in the first term in Eq. (34) can be evaluated with the aid of the consistency condition (18) and the fact that

$$\sum_{j\in\mathcal{M}_i\cup\{i\}} q_j x_j = 0 \in \mathbb{R}^d \tag{36}$$

holds for every $x \in \Gamma$ and $i \in \mathcal{N}$ [Note that Eqs. (36) and (5c) are interchangeable in condition (5)]. The results are

$$\sum_{i\in\mathcal{N}}\sum_{j\in\mathcal{J}_i} q_i q_j r_{ij}^2 = \sum_{i\in\mathcal{N}}\sum_{\substack{j\in\mathcal{N}_i\\ r_{ij}<r_\mathrm{c}}} q_i q_j r_{ij}^2, \tag{37}$$

viz., the summation can be replaced by an ordinary pairwise summation. As shown in Appendix C, Eq. (37) can be obtained purely algebraically from conditions (5a), (5b), (36), and (18).

Therefore, from Eqs. (28), (34), (35), and (37), we obtain

$$\hat{E} = \check{E} + \kappa + \Delta. \tag{38}$$

Here,

$$\check{E}(x) \equiv \frac{1}{2}\sum_{i\in\mathcal{N}}\sum_{\substack{j\in\mathcal{N}_i\\ r_{ij}<r_\mathrm{c}}} q_i q_j \left[V(r_\mathrm{c}) - \frac{F(r_\mathrm{c})}{2r_\mathrm{c}}(r_{ij}^2 - r_\mathrm{c}^2)\right] \tag{39}$$

is a pairwise expression,

$$\kappa \equiv \frac{1}{2}\left[V(r_\mathrm{c}) + \frac{1}{2}F(r_\mathrm{c})r_\mathrm{c}\right]\sum_{i\in\mathcal{N}} q_i^2 \tag{40}$$

is a constant, and Δ is the negligible part, as demonstrated.

Combining Eqs. (38)–(40) with Eq. (15), we conclude that an approximation to the total energy, for $x \in \Gamma$, is given by the ZD energy, viz.,

$$E(x) \simeq E_\mathrm{ZD}(x) \tag{41}$$

with

$$E_\mathrm{ZD}(x) \equiv \frac{1}{2}\sum_{i\in\mathcal{N}}\sum_{\substack{j\in\mathcal{N}_i\\ r_{ij}<r_\mathrm{c}}} q_i q_j \left[V(r_{ij}) - V(r_\mathrm{c}) + \frac{F(r_\mathrm{c})}{2r_\mathrm{c}}(r_{ij}^2 - r_\mathrm{c}^2)\right] - \left[\frac{V(r_\mathrm{c})}{2} + \frac{1}{4}F(r_\mathrm{c})r_\mathrm{c} + \frac{\alpha}{\sqrt{\pi}}\right]\sum_{i\in\mathcal{N}} q_i^2. \tag{42}$$

This is simply the expression, $E_\mathrm{H}(x)$, heuristically obtained in Eq. (4), except for the self-energy term $(-\alpha/\sqrt{\pi})\sum_{i\in\mathcal{N}} q_i^2$. Since the self-energy term comes from the decomposition of $1/r$ using $V(r)$, represented by Eq. (9), and from the approximation given by Eq. (14), the result, Eq. (42), can be a justification of E_H. Besides, in the current scheme the constant term is uniquely fixed by κ [Eq. (40); in other words, we should have chosen $u_\mathrm{c} = 0$ in Eq. (3)]. Thus, we have consistently determined the energy formula for the ZD state. Furthermore, the current considerations clarify the structure of the approximation for the energy function. Namely, in addition to the approximation in Eq. (14), two other kinds of approximations have currently been used: one is Eq. (12), regarding the replacement strategy; and the other is Eq. (32), regarding the neglect of the $o(h^{(i)})$ term, Δ. These approximations are analyzed in Subsection III B.

B. Features

1. On the approximations

First, we discuss the second approximation, viz., the neglect of Δ, and demonstrate that it is still more accurate than that in the scheme using the ZC energy. The following first two terms in the ZC energy,

$$\frac{1}{2}\sum_{i\in\mathcal{N}}\sum_{\substack{j\in\mathcal{N}_i\\ r_{ij}<r_{\mathrm{c}}}} q_iq_j[V(r_{ij})-V(r_{\mathrm{c}})]-\frac{1}{2}\sum_{i\in\mathcal{N}} q_i^2V(r_{\mathrm{c}}) -\frac{\alpha}{\sqrt{\pi}}\sum_{i\in\mathcal{N}} q_i^2, \tag{43}$$

can be obtained by an approximation of the ZD summation for a ZD state. Specifically, using the three conditions (5a) and (5b), and (5d), as in Ref. 33, we can derive these terms for atom i with an approximation of the ZD sum:

$$\sum_{j\in\mathcal{M}_i} q_iq_jV(r_{ij})\simeq\sum_{\substack{j\in\mathcal{N}_i\\ r_{ij}<r_{\mathrm{c}}}} q_iq_j[V(r_{ij})-V(r_{\mathrm{c}})]-q_i^2V(r_{\mathrm{c}}). \tag{44}$$

We can now view this approximation through an approximation of the ith excess energy $\hat{E}_i(x)\equiv\sum_{j\in\mathcal{J}_i}q_iq_jV(r_{ij})$ [recall Eq. (24)]. That is, the excess energy, the second term on the right side in the following exact relation,

$$\sum_{j\in\mathcal{M}_i} q_iq_jV(r_{ij})=\sum_{\substack{j\in\mathcal{N}_i\\ r_{ij}<r_{\mathrm{c}}}} q_iq_jV(r_{ij})-\sum_{j\in\mathcal{J}_i} q_iq_jV(r_{ij}), \tag{45}$$

can be approximated by

$$\tilde{E}_i(x)\equiv\sum_{\substack{j\in\mathcal{N}_i\\ r_{ij}<r_{\mathrm{c}}}} q_iq_jV(r_{\mathrm{c}})+q_i^2V(r_{\mathrm{c}}) \tag{46}$$

as follows: for any $x\in\Gamma$ and $i\in\mathcal{N}$,

$$(\hat{E}_i-\tilde{E}_i)(x^{(i)}+h^{(i)})=o(1)\ \ (I_i^x\ni h^{(i)}\to 0), \tag{47}$$

which is described in Appendix B. Thus, as seen in Eq. (28), we have

$$\hat{E}=\tilde{E}+\tilde{\Delta}, \tag{48}$$

where $\tilde{E}\equiv\frac{1}{2}\sum_{i\in\mathcal{N}}\tilde{E}_i$ and $\tilde{\Delta}\equiv\sum_{i\in\mathcal{N}}\tilde{u}_i$, with $\tilde{u}_i(x^{(i)}+h^{(i)})=o(1)$ $(h^{(i)}\to 0)$. Although $\tilde{\Delta}\simeq 0$, as stated to derive Eq. (32), the accuracy of the approximation of $\hat{E}$ by $\tilde{E}$ is of the $o(1)$ level in the above ZC scheme, which is lower than that of $\hat{E}$ by $\check{E}$ with the $o(h^{(i)})$ level in the current ZD scheme.

On the other hand, the above approximating feature in the ZC scheme is also helpful to explain the first approximation in the ZD scheme, viz., Eq. (12) concerning the replacement strategy. That is, on the ZD state we obtain the following relations:

$$\frac{1}{2}\sum_{i\in\mathcal{N}}\sum_{j\in\mathcal{N}_i} q_iq_jV(r_{ij}) \tag{49}$$

$$\simeq\frac{1}{2}\sum_{i\in\mathcal{N}}\sum_{\substack{j\in\mathcal{N}_i,\\ r_{ij}<r_{\mathrm{c}}}} q_iq_j[V(r_{ij})-V(r_{\mathrm{c}})]-\frac{V(r_{\mathrm{c}})}{2}\sum_{i\in\mathcal{N}} q_i^2 \tag{50}$$

$$\simeq\frac{1}{2}\sum_{i\in\mathcal{N}}\sum_{j\in\mathcal{M}_i} q_iq_jV(r_{ij}). \tag{51}$$

The first near equality [in Eq. (50)] is indicated by the fact that the ZC energy works well, as investigated by Wolf *et al.*[21] and intensively examined in many reports, as discussed in Sec. I. The second near equality is due to the preceding discussion. The above relation is one of the quantitative justifications of Eq. (12). Of course, as stated in Sec. II A, the qualitative issues supporting the direct justification of Eq. (12) are that the ZD sum captures the features of the whole system with zero dipole and zero charge, and that the ZD sum prevents the energy error, which is due to the non-ZD or non-ZC state artificially generated by a simple scheme, such as a pure cutoff truncation.

2. Force

The force acting on each atom i is derived from Eq. (42), by

$$\mathcal{F}_i(x)\equiv-\nabla_iE_{\mathrm{ZD}}(x) \tag{52a}$$

$$=\sum_{\substack{j\in\mathcal{N}_i\\ r_{ij}<r_{\mathrm{c}}}} q_iq_j\left[F(r_{ij})-\frac{F(r_{\mathrm{c}})}{r_{\mathrm{c}}}r_{ij}\right]\frac{x_{ij}}{r_{ij}}\in\mathbb{R}^d \tag{52b}$$

for any $x\in\Gamma$. We see that the first term $\sum_{j\in\mathcal{N}_i,\,r_{ij}<r_{\mathrm{c}}}q_iq_jF(r_{ij})x_{ij}/r_{ij}$ is the usual cutoff pairwise expression originating from $\frac{1}{2}\sum_{i\in\mathcal{N}}\sum_{j\in\mathcal{N}_i}q_iq_jV(r_{ij})$, but we may wonder what the second term

$$\check{F}_i(x)\equiv\sum_{\substack{j\in\mathcal{N}_i\\ r_{ij}<r_{\mathrm{c}}}} q_iq_j\frac{F(r_{\mathrm{c}})}{r_{\mathrm{c}}}x_{ij}, \tag{53}$$

currently added, actually represents. This is, in fact, an approximation of the *excess force*

$$\hat{F}_i(x)\equiv\sum_{j\in\mathcal{J}_i} q_iq_jF(r_{ij})\frac{x_{ij}}{r_{ij}}. \tag{54}$$

Namely, we have

$$\mathcal{F}_i(x)\simeq\sum_{\substack{j\in\mathcal{N}_i\\ r_{ij}<r_{\mathrm{c}}}} q_iq_jF(r_{ij})\frac{x_{ij}}{r_{ij}}-\hat{F}_i(x) \tag{55a}$$

$$=\sum_{j\in\mathcal{M}_i} q_iq_jF(r_{ij})\frac{x_{ij}}{r_{ij}}. \tag{55b}$$

The situation is analogous to that of the energy: a computationally efficient expression E_{ZD}, which may not be physically understandable (but see Sec. V), is an approximation of a physically understandable expression, which may not be computationally efficient. The latter expression is the right side of Eq. (15), which is the usual cutoff pairwise quantity minus the excess quantity (aside from a constant). The subtraction of the excess quantity represents the neutralizing effect, which appears in both the energy and force formulas in the current scheme. The approximation at issue can be represented by

$$\hat{F}_i-\check{F}_i=v_i, \tag{56a}$$

$$v_i(x^{(i)}+h^{(i)})=o(1)\ \ (I_i^x\ni h^{(i)}\to 0) \tag{56b}$$

for any $x \in \Gamma$ and $i \in \mathcal{N}$, as proved in a similar manner to that for the preceding excess-energy approximation (see Appendix B).

3. Properties of pair functions

The behaviors of the pairwise functions should be clarified only on the interval $(0, r_c]$, in terms of the cutoff scheme. The pair force function f given by

$$f(r) \equiv F(r) - \frac{F(r_c)}{r_c} r, \tag{57}$$

which defines an atomic force $\mathcal{F}_i$, is positive and (strictly) monotone decreasing on $(0, r_c]$ if F is so [the target function, Eq. (7), applies for any $\alpha \geq 0$], and f reaches 0 at $r = r_c$. Then, the corresponding pair potential function given by

$$u(r) \equiv V(r) + \frac{1}{2} \frac{F(r_c)}{r_c} r^2 \tag{58}$$

is strictly monotonic decreasing on the interval. Using such a *normal* pair function, we find that the total energy, Eq. (42), can be expressed as

$$E_{\mathrm{ZD}}(x) = \frac{1}{2} \sum_{i \in \mathcal{N}} \sum_{\substack{j \in \mathcal{N}_i \\ r_{ij} < r_c}} q_i q_j [u(r_{ij}) - u(r_c)] - \frac{1}{2} \left[u(r_c) + \frac{2\alpha}{\sqrt{\pi}} \right] \sum_{i \in \mathcal{N}} q_i^2. \tag{59}$$

The current shifted pair potential function $u - u(r_c)$ is positive on $(0, r_c]$ and reaches zero at $r = r_c$ in a C^1 manner [which ensures Eq. (52)].

The right side of Eq. (59) is a form equivalent to the Wolf energy expression (43) using the current induced function u, rather than the original function V. As the parameter α is large, this pair potential $u - u(r_c)$, indicated in Figs. 5(a) and 5(b), approaches the original Wolf pair potential $V - V(r_c)$ in Eq. (43): the difference $\delta(r) \equiv |u(r) - u(r_c) - (V(r) - V(r_c))| = F(r_c)(r_c^2 - r^2)/(2r_c)$ is strictly monotone decreasing with respect to α for each $r_c > r > 0$, and δ converges uniformly on $(0, r_c]$ to 0 as $\alpha \to \infty$. Thus, and also from the decrease in $u(r_c) - V(r_c)$ [the difference between the constant-term factors; cf. Figs. 5(c) and 5(d)] monotonically to 0 with respect to α, we see that $E_{\mathrm{ZD}}(x)$ approaches Eq. (43) as α increases. Similarly, the energy of the FSw-Wolf method[33] and E_{ZD} are closer as $\alpha \to \infty$ under ordinary conditions. Note that, in this context, the resemblance among the damping-function approaches with large damping factors has been pointed out in Ref. 23, regarding shifted-force and shifted-potential functions.

IV. NUMERICAL SIMULATION

The specific performance of the current method as a MD scheme is discussed via numerical investigations. To measure the validity of the current theory, we used a simple system and performed fundamental tests. A comparison between the current method and the Ewald method was made. We also confirmed the efficiency enhancement of the current zero-dipole MD scheme, the ZD-Wolf method, against the zero-charge MD scheme, the FSw-Wolf method, which we previously reported.[33]

We examined a NaCl system composed of 2304 ions, using the three-dimensional periodic boundary conditions. To investigate the accuracy of the method, we sampled various particle configurations of the system and calculated the error of the electrostatic energy. Using a simulation protocol, as described in Ref. 33, $n_x = 1000$ liquid configurations obeying the Born–Mayer–Huggins potential[49] were selected through the NTV (canonical) MD simulations at a temperature of 1100 K. The energy error in the current method at configuration x was estimated through the difference between the current Coulombic energy $E_{\mathrm{ZD}}(x)$ and the reference energy $E(x)$, which was evaluated by the Ewald method,[7] and we averaged the error ratio over each configuration as

$$\Delta_{\mathrm{ZD}} \equiv \frac{1}{n_x} \sum_x |E_{\mathrm{ZD}}(x) - E(x)|/|E(x)|. \tag{60}$$

In the Ewald method, the damping parameter was 0.35 Å^{-1} and the cutoff length of the real part evaluation was 12 Å.

Figure 6 shows the results for several values of the cutoff length r_c and the damping parameter α in the current method. We see that a larger r_c yields more accurate results, as expected. A large α shows a small error even in a small r_c, along with rapid convergence. In contrast, a small α exhibits an error decrease from a considerably large value at small r_c toward a very small value at large r_c, accompanying a relatively large oscillation, which is considered to be relevant to a certain structure in a liquid phase. The oscillating behaviors of the errors stated above are not unusual, and, in fact, were observed in the FSw-Wolf ZC scheme.[33]

However, the accuracy itself is significantly improved in the current method, as shown in Table I. Here, the energy error ratio of the FSw-Wolf method, Δ_{FSw}, was calculated in a similar manner as above [viz., using the energy of the FSw-Wolf method, $E_{\mathrm{FSw}}(x)$, instead of $E_{\mathrm{ZD}}(x)$ in Eq. (60), along with the same ion configurations]. Note that the discussions in Sec. III regarding the accuracy enhancement of the ZD scheme against the ZC scheme are applicable when both schemes employ the same pair potential function V and the same cutoff length, viz., the same α and the same r_c in the current case. To confirm this, the two values $\Delta_{\mathrm{ZD}} \equiv \Delta_{\mathrm{ZD}}(\alpha, r_c)$ and $\Delta_{\mathrm{FSw}} \equiv \Delta_{\mathrm{FSw}}(\alpha, r_c)$ in Table I can be used. In a practical cutoff range, as used in typical MD simulations, the error in the current method is smaller than 10^{-1}–10^{-3} of the error in the FSw-Wolf method. A smaller α improves the accuracy, and a larger α provides less improvement. In fact, the two energy formulas for the two methods approach for large α, as stated in Sec. III B 3. On the other hand, as is relatively apparent in a higher α case, such as $\alpha = 0.2$ Å^{-1}, the improvement will be less with a significant large cutoff length. However, this is not surprising, but is rather natural in that any correct cutoff method with $r_c \to \infty$ should give the same results (although the approach may not be monotonic). Although it suffers from these limitations, the current method is valuable, since it

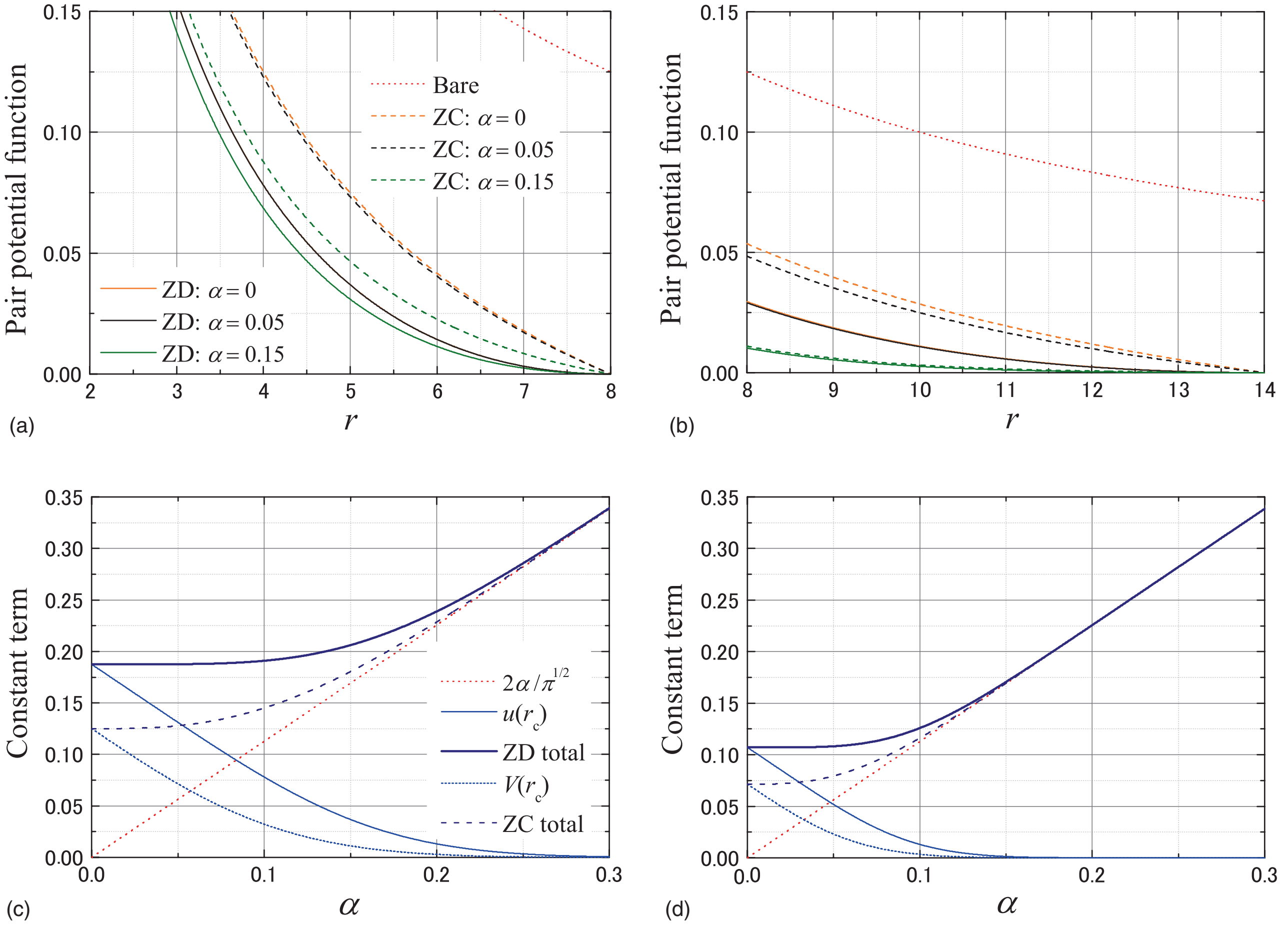


FIG. 5. (a) Potential functions with cutoff length $r_c = 8$ Å: solid lines show the pair potential $u(r) - u(r_c)$ in the current ZD energy with (right) damping factor $\alpha = 0$ (Å^{-1}), (middle) $\alpha = 0.05$, and (left) $\alpha = 0.15$ (the difference between $\alpha = 0$ and 0.05 is invisible). Dashed lines show the original Wolf pair potential $V(r) - V(r_c)$ with (right) $\alpha = 0$, (middle) $\alpha = 0.05$, and (left) $\alpha = 0.15$. For comparison, the bare Coulomb potential $1/r$ without the cutoff is indicated by a dotted line. (b) The same potential functions in (a), but with a larger cutoff length, $r_c = 14$ Å. (c) The dependence of the constant terms in the ZD energy, (dotted line) $2\alpha/\sqrt{\pi}$, (thin bold line) $u(r_c)$, and (thick bold line) $u(r_c) + 2\alpha/\sqrt{\pi}$, on the parameter α; and those in the ZC energy, (thin dashed line) $V(r_c)$, (thick dashed line) $V(r_c) + 2\alpha/\sqrt{\pi}$. The cutoff length r_c is 8 Å. (d) The same quantities in (c), but with a larger cutoff length, $r_c = 14$ Å.

provides a higher accuracy in a practical cutoff length in a MD study, as shown by the difference between the two methods.

When we have an accurate electrostatic phase-space energy function, fundamentally, we can attain physically reliable results, provided that the total potential energy function, including the electrostatic one, is reliable. However, in addition to the accuracy of the energy function, in order to use the function safely in the MD scheme, we need stability in integrating the MD equations of motion. This kind of stability comes from the smoothness of the energy function. To investigate the stability, we performed NEV MD simulations of the NaCl system. The initial configurations were those obtained in the NTV MD simulation stated above, and the velocity Verlet integrator with a time step of 2 fs was used, via the myPresto program.[50] Figure 7 shows the trajectory of the total energy (the kinetic energy plus the total potential

TABLE I. The error ratio (%) of the electrostatic energy in the FSw-Wolf method Δ_{FSw} (upper line) and that in the current method Δ_{ZD} (lower line), using the same values of the parameters, cutoff length r_c (Å), and damping factor α (Å^{-1}).

r_c	9	10	11	12	13	14	15	16
$\alpha = 0.05$	8.749	49.039	5.124	29.109	9.446	15.593	8.984	7.339
	0.629	0.016	0.296	0.062	0.150	0.057	0.064	0.049
$\alpha = 0.1$	4.554	17.846	1.161	7.513	1.781	2.707	1.152	0.831
	0.569	0.029	0.232	0.042	0.106	0.022	0.028	0.025
$\alpha = 0.15$	1.862	4.400	0.127	1.117	0.129	0.185	0.080	0.058
	0.387	0.059	0.082	0.030	0.054	0.022	0.021	0.027
$\alpha = 0.2$	0.603	0.646	0.061	0.154	0.064	0.063	0.071	0.070
	0.212	0.090	0.047	0.069	0.073	0.070	0.070	0.070

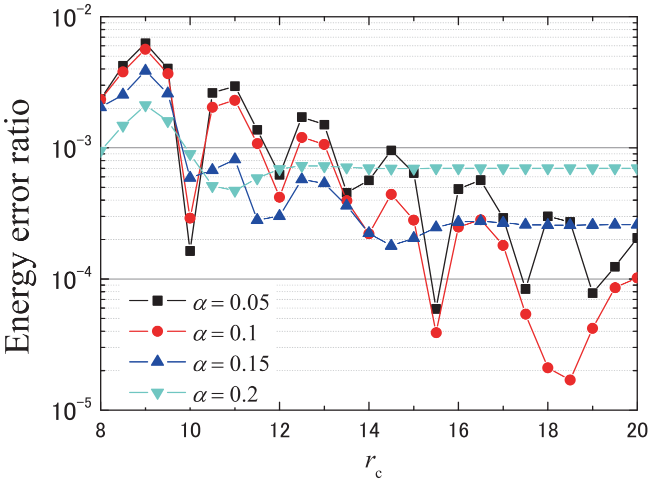


FIG. 6. The electrostatic energy of the current ZD-Wolf method against the Ewald method is shown via $\Delta_{\rm ZD}$, the energy error ratio (no dimension), which was averaged over 1000 configurations for a liquid NaCl system of 2304 ions. The parameters r_c (Å) and α (Å^{-1}) indicate the cutoff length and the damping factor, respectively, involved in the energy formula in the ZD method.

energies) obtained in the simulation. A typical cutoff length of $r_c = 12$ Å was used and the potential damping parameter was $\alpha = 0.15$ Å^{-1}. Several values for α, which affects the smoothness of the function (flatness near the cutoff length), nevertheless gave very similar results (not shown). The total energy deviations for the current method are sufficiently small. This situation is comparable to that observed in the FSw-Wolf method (ZC MD scheme), which is fairly good and better than that in the pure cutoff method (non-ZD and non-ZC MD scheme).[33] These results indicate that the current ZD-Wolf method (ZD and ZC MD scheme) can afford a reliable MD protocol.

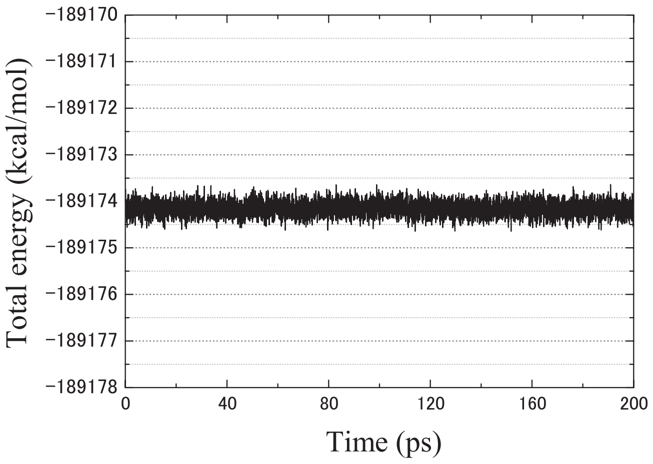


FIG. 7. Total-energy trajectory of the *NEV* MD simulation for the NaCl liquid system, obtained by the velocity Verlet integrator with a 2 fs timestep. The cutoff length is 12 Å and $\alpha = 0.15$ Å^{-1}.

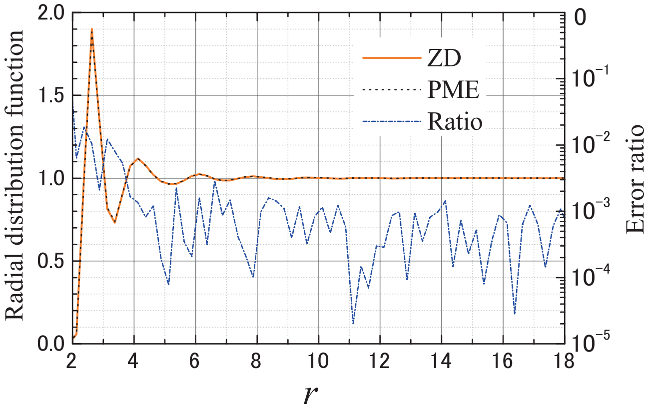


FIG. 8. Radial distribution functions (no dimension) with respect to the atomic distance r (Å) for the liquid NaCl system of 2304 ions, obtained by the current ZD-Wolf method (solid line) and the particle mesh Ewald method (dotted line). The error ratio defined by the two functions is shown by the dashed line.

The degree of accuracy of the energy surface in the phase space may not necessarily correspond to that of another property of the system in general. Structural property is one of the important properties of the system, and we have calculated the radial distribution functions (RDFs) for the liquid NaCl system as an example, using the coordinate data produced in NTV MD simulations at 1100 K. Figure 8 shows the normalized RDF obtained by the ZD-Wolf method, $g_{\rm ZD}$, and that by the particle mesh Ewald method,[51] g. These two functions agree well in a whole range of the atomic distance, r. In fact, the error ratio, $|g_{\rm ZD}(r) - g(r)|/|g(r)|$, is less than 10^{-2}, which is comparable to the error ratio of the energy indicated in Fig. 6.

V. DISCUSSION: RELATION TO THE PREAVERAGING (PA) METHOD

The current method based on the ZD condition is, in fact, intimately related to other methods based on other conditions. We discuss the relationships between them to observe them from different viewpoints.

One of the characteristic points of the current scheme is that the current energy, Eq. (42), becomes a generalization of the results obtained from the PA procedure introduced by Yakub and Ronchi.[35] Their energy formula was obtained by using the Ewald summation expansion and by averaging the quantities in the expansion over the spherical angular coordinates (φ, θ). This corresponds to a situation treating a uniformly distributed system. The energy formula is

$$E_{\rm PA}(x) \equiv \frac{1}{2}\sum_{i\in\mathcal{N}}\sum_{\substack{j\in\mathcal{N}_i\\ r_{ij}<r_{\rm m}}} q_i q_j \frac{1}{r_{ij}}\left\{1+\frac{1}{2}\frac{r_{ij}}{r_{\rm m}}\left[\left(\frac{r_{ij}}{r_{\rm m}}\right)^2-3\right]\right\} - \frac{3}{4r_{\rm m}}\sum_{i\in\mathcal{N}} q_i^2, \tag{61}$$

where $r_{\rm m}$ is the radius of the volume-equivalent sphere of the MD cubic cell with edge L:

$$\frac{4}{3}\pi r_{\rm m}^3 = L^3. \tag{62}$$

Namely, the energy is based on the PA potential $V_{\rm PA}(r) \equiv (1/r)\{1 + (\frac{1}{2})(r/r_{\rm m})^3\}$, and the pairwise sum is defined by a pair potential $V_{\rm PA}(r) - V_{\rm PA}(r_{\rm m})$. Now, we can straightforwardly see that the energy of the current scheme, Eqs. (42) or

(59), perfectly gives Eq. (61) when we set $\alpha = 0$ and $r_c = r_m$, noting that the current potential u then corresponds to V_{PA}.

The PA method is very successful; it gives an accurate energy in, e.g., crystal systems and one-component plasma. However, the fact that the cutoff length intrinsic to the PA formalism is r_m seems inconvenient, in terms of a MD study, for the following reasons: first, $r_m > L/2$ does not permit the ordinary minimum image convention technique in calculating the interactions, although some algorithms to suitably perform this cutoff may exist; second, the cutoff length r_m should be set proportional to the MD cell size L, which could be a severe practical limitation if one treats a large system, e.g., with a size of several nanometers, as in biological studies.

On the contrary, our scheme indicates that we are not required to take $r_c = r_m$, if we obey the zero-dipole principle. Namely, we can use the usual minimum image convention by taking $r_c < L/2$, without any special care even for high-performance computational architectures, and can apply the method to arbitrarily large systems, without the constraint on the cutoff length. For example, in the simulation of the current ZD method discussed in Sec. IV, a cutoff length larger than 20 Å may lead to a very small error, especially in the condition of $\alpha = 0$ and $r_c = r_m$ [$\simeq 26.4$ (Å) $> L/2 \simeq 21.3$ (Å), half of the length of the MD cubic cell used], yielding the PA method. Here, note that the $\alpha = 0$ case (not shown in Fig. 6) gave almost identical results to those of the $\alpha = 0.05$ case, which is due to the fact that the pair potential function shapes and the constant term values in the former case are almost identical, respectively, to those in the latter case, as seen in Fig. 5. Thus, the $\alpha = 0.05$ results suggest those in the ideal conditions of $\alpha = 0$ and $r_c = r_m$. However, in the actual simulation shown in Fig. 6, we see that a smaller r_c with a positive α value provides a sufficiently high accuracy, viz., it is a practical solution with respect to the efficiency. These observations will be useful in considering more realistic applications, especially to large systems.

The reason why the current scheme includes Yakub–Ronchi's PA potential method, which is derived by the spherical average rationale, would be that the isotropic property, which indicates the absence of a special direction in a system in an electromagnetic sense, leading to angular symmetry and allowing the spherical average, implies a zero-dipole validity in the system, especially at the local level. In contrast, the converse is not always true, i.e., a ZD state does not necessary imply an isotropic state, considering a certain perfect ionic crystal. These views might also explain why the PA method yields, as stated in Ref. 35, "surprisingly positive" results in perfect crystal systems, which are not isotropic: the PA method becomes a ZD method with $\alpha = 0$ and $r_c = r_m$, and then it will be applicable to a ZD state, which is not necessarily isotropic. It should be noted that although we have stated the existence of the ZD state that is not isotropic, we do not affirm that any anisotropic state becomes a ZD state; e.g., totally dipolar systems, such as ferroelectric solid materials, exhibit non-ZD states.

To confirm that the ZD method is actually applicable to the perfect-crystal anisotropic state, we calculated the Coulombic energy of the NaCl fcc crystal. We estimated the energy of the crystal state x_C, using 7^3 unit cells (2744 ions) with the periodic boundary conditions, and the error of the energy obtained by the ZD method was estimated by

$$(E_{ZD}(x_C) - E(x_C))/E(x_C), \tag{63}$$

where the reference energy value $E(x_C)$ was calculated by the Ewald method, as in the liquid study. The results are shown in Fig. 9. As in the liquid-states results, oscillating behavior toward the convergence is observed (in the linear scale for the error, the amplitude of the oscillation is smaller as the parameter α is large). However, in contrast to the liquid case, a larger α shows a smaller error, and it can take a very small value with increasing r_c; e.g., as shown in the inset, the absolute value of the error for $\alpha = 0.2$ is 1.4×10^{-6} at $r_c = 16$ Å.

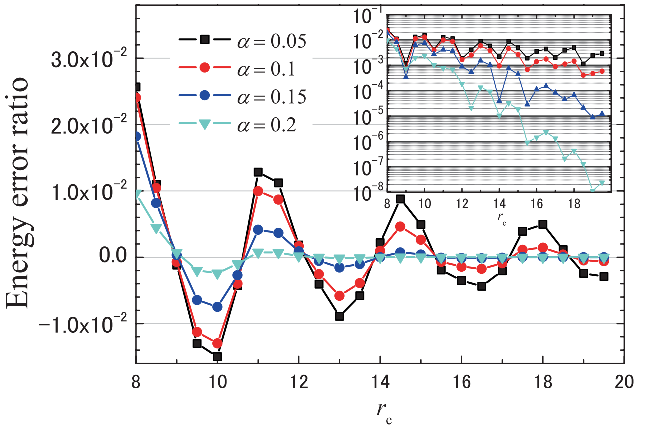


FIG. 9. The electrostatic energy of the current ZD-Wolf method against the Ewald method is shown via Eq. (63), the energy error ratio (no dimension), which was obtained for NaCl crystal configuration. The parameters r_c (Å) and α (Å^{-1}) are the same as those in Fig. 6. The inset shows the absolute values (logarithmic scale) of the error ratio Eq. (63).

Finally, we point out that the pair potentials represented by $V_{RF}(r) \equiv (1/r)\{1 + [(\epsilon - 1)/(2\epsilon + 1)](r/r_c)^3\}$ and $V_{RF}(r) - V_{RF}(r_c)$ used in the reaction field method[52,53] tend to $V_{PA}(r)$ and $V_{PA}(r) - V_{PA}(r_m)$, respectively, as the dielectric constant parameter ϵ goes to ∞ and the cutoff r_c tends to r_m. In addition, note that $V_{RF}(r)$ [or $V_{RF}(r) - V_{RF}(r_c)$] with $\epsilon \to \infty$ corresponds to $u(r)$ [or $u(r) - u(r_c)$, respectively] with $\alpha = 0$, which is the pair potential represented by Eq. (58) used in the current ZD method.

VI. CONCLUDING REMARKS

We have proposed a novel idea, zero-charge zero-dipole summation, for evaluating the electrostatic energy, and we composed an algorithm for effectively executing the idea. Namely, our method employs two strategies: (i) for each particle i, the summation $\sum_{j \in \mathcal{N}_i} q_j V(r_{ij})$ is replaced by the one with respect to the neutralized subset, $\sum_{j \in \mathcal{M}_i} q_j V(r_{ij})$; and (ii) the pair potential function V is redefined, in order that the above neutralized summation can be managed through a simple pairwise-sum form. While our method is conceptually based on the charge neutralizing summation idea developed by Wolf *et al.*, we emphasize the importance of an axiomatic approach, which leads to a unique, consistent result. In fact, the heuristic derivation of the current scheme, with the mirror image charge arrangements, still seems to be incomplete, although it is interesting in that it provides a specifically geometric view.

In this work, the quantitative features of our method illustrated by a numerical simulation using a simple liquid sodium chloride system, along with the mathematical details of our method, were discussed in a fundamental manner. The current method, with a small damping factor α, provides a sufficient accuracy in a practical cutoff distance region. Specifically, the electrostatic energy error is smaller, by several orders of the magnitude, than that of our previous force-switching Wolf MD method. These results conform to the general fact that the difference in the methods is clearer for a small damping factor and a small cutoff length. Although we have emphasized the theoretical aspects of the current method, numerical investigations for the physical properties, including structural characteristics, dynamical behaviors, and thermodynamic free energies, must still be addressed.

We revealed that the errors originate from several factors: the validity of the replacement of the all pair summation with the neutral-subset summation, the accuracy of an analytical expression of the energy in the excess region, and the neglect of the term corresponding to the Fourier part in the Ewald summation. Numerical simulations comparing the zero-charge scheme and the zero-dipole scheme have suggested that increasing the energy accuracy in the excess region is important. The addition of the zero-dipole condition into a zero-charge condition must lead to an enhancement of the charge distribution expression for a physically reasonable state.

Numerical examinations of the electrostatic energy-surface traceability result in a major investigation of how many states actually apply to the zero-dipole condition currently introduced. With the exceptions of a state such as that with very high energy accompanying a large dipole or a system containing a significant quantity of explicit nonvanishing dipoles, the current method could provide a good approximation in many realistic applications. For the latter case, for example, it may be satisfactory if we apply a special treatment to such a target dipole. In any case, more numerical examinations in the current method will be necessary to clarify its applicability, as well as limitations, to various systems. We shall apply the current method to biomolecular systems and investigate these issues.

If we possess an accurate energy surface, then fundamentally, we can attain physically reliable results. In this sense, our method can be used for, e.g., a Monte Carlo calculation. In addition to the reliability of the phase-space energy function, in order to use the function safely in a MD scheme, numerical integration for a MD equation must be stable. We have confirmed that the current function performs well stably in a liquid MD simulation, using a standard Verlet integration scheme. Noting that our energy function has just C^1 smoothness, more detailed investigations in various simulation conditions and with higher order integrators[54] will facilitate further studies. Combining the force-switching scheme[33,34] and the current method will provide a smoother function.

We have found that the current summation eventually becomes a generalization of the preaveraged potential method proposed by Yakub and Ronchi, which is based on the Ewald summation and conducted by an isotropic averaging procedure to solve the problem regarding the cubic symmetry in the periodic boundary conditions. It may be surprising to reach similar results from two distinct bases, the symmetry in the preaveraged method, and the electric neutrality in the current method. However, this correspondence may be the reason why the preaveraged method is significantly positive in a nonisotropic system as well as an isotropic system. Furthermore, the current idea opens the door to use the damping factor and an arbitrary cutoff length in the preaveraged method. In particular, the free choice of the cutoff length significantly enhances the utility of the method in a large system, which is used in, e.g., a crucial topic in biological studies.

In this paper, we have introduced the zero-charge zero-dipole summation method in estimating the Coulomb energy and force. Along this line, the method that takes into account higher-order moments can be constructed and will be discussed elsewhere. It could provide a more accurate expression of the excess energy. In addition, a method for assigning suitable parameter values is worthwhile. The current scheme may be coupled with the function optimization approach, thus providing an improved expression for estimating the energy.

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APPENDIX A: DESCRIPTION OF THE DISPLACEMENT VECTOR

For arbitrarily fixed $x \in \Gamma$ and $i \in \mathcal{N}$, the domain of the displacement vector, $I \equiv I_i^x \subset \mathbb{R}^{Nd}$, should satisfy the following conditions:

$$\text{(i)}\quad I \subset \Gamma - x^{(i)} \equiv \left\{ x - x^{(i)} \in \mathbb{R}^{Nd} \mid x \in \Gamma \right\},$$

$$\text{(ii)}\quad 0 \notin I,$$

$$\text{(iii)}\quad I + x^{(i)} \subset J_1 \times \cdots \times J_N,$$

$$\text{where } J_j \equiv \begin{Bmatrix} \text{a line connecting } x_j \text{ and } x_j^{(i)}, & \text{if } j \in \mathcal{J}_i \\ \{x_j\}, & \text{otherwise} \end{Bmatrix},$$

$$\text{(iv)}\quad x - x^{(i)} \in I.$$

Here, condition (i) ensures that $x^{(i)} + h^{(i)}$ is in the phase space, in order to avoid the collisions between the particles during the motion of $h^{(i)} \in I$. Condition (ii) is required to establish a function sum in any case with respect to the excess subset, such as

$$\sum_{j \in \mathcal{J}_i(x^{(i)}+h^{(i)})} f_j(x^{(i)} + h^{(i)}).$$

It should be noticed that the zero-dipole subset $\mathcal{M}_i$ depends on $x \in \Gamma$, although this notion may not be emphasized in the text. Hence, $\mathcal{J}_i$ also depends on x, viz., we are considering $\mathcal{J}_i \equiv \mathcal{J}_i(x)$, and in this case, $\mathcal{J}_i(x^{(i)}+h^{(i)})$. If $h^{(i)}=0$, however, then $\mathcal{J}_i(x^{(i)}+0)$ becomes an empty set, and thus the above sum is not well defined. Condition (iii) may be the simplest setting and enables us to prevent particle $j \in \mathcal{J}_i$ from falling out of the cutoff sphere. Condition (iv) is a trivial requirement to include the *initial* value $h_0^{(i)} \equiv x - x^{(i)}$ in I. In addition, we require that

$$\text{(v)}\ \ \forall h^{(i)} \in I,\ \ \mathcal{M}_i(x^{(i)}+h^{(i)}) = \mathcal{M}_i(x),$$

viz., we can keep the set $\mathcal{M}_i$ constant during the motion of $h^{(i)}$.

Now, we specifically define I_i^x by

$$I_i^x \equiv \prod_{j\in\mathcal{N}} I^{(j)} \cap (\Gamma_{\rm b} - x^{(i)}), \tag{A1}$$

where $I^{(j)} \equiv \{\lambda_j(x_j - x_j^{(i)}) \in \mathbb{R}^d \mid \lambda_j \in (0,1]\}$. By this definition, the above five conditions can be satisfied, as is straightforwardly confirmed. The constancy of the subsets also holds: for $\forall h^{(i)} \in I_i^x$, $x^{(i)}+h^{(i)} \in \Gamma$ and $\mathcal{R}_i(x^{(i)}+h^{(i)}) = \mathcal{R}_i(x)$ as well as $\mathcal{J}_i(x^{(i)}+h^{(i)}) = \mathcal{J}_i(x)$, where

$$\mathcal{R}_i \equiv \mathcal{R}_i(x) \equiv \{j \in \mathcal{N}_i \mid r_{ij} < r_{\rm c}\}. \tag{A2}$$

Besides, to establish the asymptotic behavior of $I_i^x \ni h^{(i)} \to 0$, we require that $0 \in \mathbb{R}^{Nd}$ is an accumulation point of I_i^x. Namely, it must be verified that for any $\varepsilon > 0$, there exists $h^{(i)} \in I_i^x$ such that $0 < \|h^{(i)}\| < \varepsilon$. We can show that this requirement can be met by taking $h^{(i)} \equiv \lambda(x - x^{(i)})$ with

$$0 < \lambda < \min\{\gamma_1, \gamma_2, 1\},$$

$$\gamma_1 \equiv \frac{\varepsilon/\sqrt{N}}{\max\limits_{j\in\mathcal{J}_i}\left\|x_j - x_j^{(i)}\right\|} > 0,$$

$$\gamma_2 \equiv \min_{j,k\in\mathcal{R}_i} \frac{r_{\rm c} - r_{ik}}{r_{\rm c} - r_{ij}} > 0.$$

APPENDIX B: PROOFS OF APPROXIMATIONS

We prove some formulas regarding the approximations used in the text. Fix any given $x\in\Gamma$ and $i \in \mathcal{N}$, and denote the motion of the displacement vector by a map:

$$\begin{aligned}\varphi = (\varphi_1,\dots,\varphi_N) : I_i^x &\to \Gamma \subset \mathbb{R}^{dN},\\ h^{(i)} \mapsto x^{[i]} &\equiv \left(x_1^{[i]},\dots,x_N^{[i]}\right)\\ &\overset{\rm d}{=} x^{(i)}+h^{(i)}\\ &\equiv \left(x_1^{(i)}+h_1^{(i)},\dots,x_N^{(i)}+h_N^{(i)}\right).\end{aligned}$$

1. Proof of Eq. (27)

Equation (27) can be shown as follows. We see that

$$(\hat{E}_i - \check{E}_i)(x^{[i]}) \tag{B1a}$$

$$= \sum_{j\in\mathcal{J}_i} q_i q_j (V - \check{V})\left(r_{ij}^{[i]}\right), \tag{B1b}$$

where

$$r_{ij}^{[i]} \equiv \left\|x_j^{[i]} - x_i^{[i]}\right\| = \left\|y' + h_j^{(i)}\right\|\ (j\in\mathcal{J}_i)$$

with

$$y' \equiv r_{\rm c} x_{ji}/\|x_{ji}\| \in \mathbb{R}^d\backslash\{0\}.$$

From the differentiability of a map, $\mathbb{R}^d\backslash\{0\} \ni y \mapsto v(y) \equiv V(\|y\|)$, at y', we have

$$u(h) \equiv v(y'+h) - v(y') - Dv(y')(h) = o(h)\ \ (I_{y'} \ni h \to 0),$$

where $I_{y'} \equiv \mathbb{R}^d\backslash\{-y'\}$. Thus, for $j\in\mathcal{J}_i$, by noticing the fact that $u(0)=0$ and $\pi_j(I_i^x) \subset I_{y'}$, with

$$\pi_j : \mathbb{R}^{Nd} \to \mathbb{R}^d,\ \ (a_1,\dots,a_N) \mapsto a_j$$

being a projection, we obtain $u(h_j^{(i)}) = o(h^{(i)})$ $(I_i^x \ni h^{(i)} \to 0)$. Hence, we have

$$V\left(\left\|y' + h_j^{(i)}\right\|\right) = V(\|y'\|) + DV(\|y'\|)\left(y'|h_j^{(i)}\right)/\|y'\| + o(h^{(i)})$$

for $j \in \mathcal{J}_i$, so that

$$\begin{aligned} V\left(r_{ij}^{[i]}\right) &= V(r_{\rm c}) + DV(r_{\rm c})\left(r_{ij}^{[i]} - r_{\rm c}\right) + o(h^{(i)})\ \ \left(I_i^x \ni h^{(i)} \to 0\right)\\ &= \check{V}\left(r_{ij}^{[i]}\right) + \Bigg[V(r_{\rm c}) + DV(r_{\rm c})\left(r_{ij}^{[i]} - r_{\rm c}\right) - V(r_{\rm c})\\ &\quad - \frac{DV(r_{\rm c})}{2r_{\rm c}}\left(\left(r_{ij}^{[i]}\right)^2 - r_{\rm c}^2\right)\Bigg] + o(h^{(i)})\\ &= \check{V}\left(r_{ij}^{[i]}\right) - \frac{DV(r_{\rm c})}{2r_{\rm c}}\left(r_{\rm c} - r_{ij}^{[i]}\right)^2 + o(h^{(i)})\\ &= \check{V}\left(r_{ij}^{[i]}\right) + o(h^{(i)}),\end{aligned}$$

where $r_{\rm c} - r_{ij}^{[i]} = \|h_j^{(i)}\|$ has been used to obtain the last line. Thus, Eq. (B1) leads to Eq. (27).

2. Proof of Eq. (47)

Equation (47) can be shown as follows. Notice that the quantity $\overset{\approx}{E}_i$ defined in the following is equal to $\tilde{E}_i$ (which depends on x):

$$\begin{aligned}\overset{\approx}{E}_i\ (x) &\equiv \sum_{j\in\mathcal{J}_i} q_i q_j V(r_{\rm c})\\ &= q_i V(r_{\rm c})\left(\sum_{j\in\mathcal{R}_i} q_j - \sum_{j\in\mathcal{M}_i} q_j\right)\\ &= q_i V(r_{\rm c})\left(\sum_{j\in\mathcal{R}_i} q_j + q_i\right) = \tilde{E}_i(x),\end{aligned}$$

where we have used Eq. (16) and condition (5b). Thus, for $\forall h^{(i)} \in I_i^x$,

$$(\hat{E}_i - \tilde{E}_i)(x^{(i)}+h^{(i)}) = (\hat{E}_i - \overset{\approx}{E}_i)(\varphi(h^{(i)})) \tag{B2a}$$

$$= \sum_{j\in\mathcal{J}_i} q_i q_j [V(\|\varphi_{ij}(h^{(i)})\|) - V(r_{\rm c})], \tag{B2b}$$

where $\varphi_{ij} \equiv \varphi_i - \varphi_j$. Since $\lim_{h^{(i)} \to 0, h^{(i)} \in I_i^x \setminus \{0\}} \varphi_j(h^{(i)}) = \lim_{h^{(i)} \to 0, h^{(i)} \in I_i^x \setminus \{0\}} \pi_j(h^{(i)}) + x_j^{(i)} = x_j^{(i)}$, we have

$$\lim_{\substack{h^{(i)} \to 0 \\ h^{(i)} \in I_i^x \setminus \{0\}}} \varphi_{ij}(h^{(i)}) = x_i^{(i)} - x_j^{(i)} = r_{\mathrm{c}} x_{ij} / r_{ij} \tag{B3}$$

for $j \in \mathcal{J}_i$. It follows from Eqs. (B2) and (B3) [and the continuity of V] that

$$\lim_{\substack{h^{(i)} \to 0 \\ h^{(i)} \in I_i^x \setminus \{0\}}} (\hat{E}_i - \tilde{E}_i)(x^{(i)} + h^{(i)}) = 0.$$

This implies Eq. (47).

3. Proof of Eq. (56)

Equation (56) can be proved similarly to Eq. (47). Notice

$$\begin{aligned} \check{F}_i(x) &\equiv \sum_{j \in \mathcal{J}_i} q_i q_j \frac{F(r_{\mathrm{c}})}{r_{\mathrm{c}}} x_{ij} \\ &= q_i \frac{F(r_{\mathrm{c}})}{r_{\mathrm{c}}} \left(\sum_{j \in \mathcal{R}_i} q_j x_{ij} - \sum_{j \in \mathcal{M}_i} q_j x_{ij} \right) \\ &= q_i \frac{F(r_{\mathrm{c}})}{r_{\mathrm{c}}} \sum_{j \in \mathcal{R}_i} q_j x_{ij} = \check{F}_i(x), \end{aligned}$$

using $\sum_{j \in \mathcal{M}_i} q_j x_{ij} = \sum_{j \in \mathcal{M}_i \cup \{i\}} q_j x_{ij} = 0$ due to condition (5c). Thus, for $\forall h^{(i)} \in I_i^x$,

$$v_i(x^{(i)} + h^{(i)}) = (\hat{F}_i - \check{F}_i)(\varphi(h^{(i)})) \tag{B4a}$$

$$= \sum_{j \in \mathcal{J}_i} q_i q_j \left[F(\|\varphi_{ij}(h^{(i)})\|) \frac{\varphi_{ij}(h^{(i)})}{\|\varphi_{ij}(h^{(i)})\|} - \frac{F(r_{\mathrm{c}})}{r_{\mathrm{c}}} \varphi_{ij}(h^{(i)}) \right] \tag{B4b}$$

with $\varphi_{ij} \equiv \varphi_i - \varphi_j$. From Eqs. (B4) and (B3) and the continuity of F, we get

$$\lim_{\substack{h^{(i)} \to 0 \\ h^{(i)} \in I_i^x \setminus \{0\}}} v_i(x^{(i)} + h^{(i)}) = 0,$$

implying $v_i(x^{(i)} + h^{(i)}) = o(1)$ $(I_i^x \ni h^{(i)} \to 0)$.

APPENDIX C: PROOF OF EQ. (37)

For any $x \in \Gamma$, using condition (18), we have

$$\sum_{i \in \mathcal{N}} \sum_{j \in \mathcal{J}_i} q_i q_j \|x_j\|^2 \tag{C1a}$$

$$= \sum_{j \in \mathcal{N}} \sum_{i \in \mathcal{J}_j} q_i q_j \|x_j\|^2 \tag{C1b}$$

$$= \sum_{i \in \mathcal{N}} \sum_{j \in \mathcal{J}_i} q_i q_j \|x_i\|^2. \tag{C1c}$$

Thus,

$$\begin{aligned} &\sum_{i \in \mathcal{N}} \sum_{j \in \mathcal{J}_i} q_i q_j r_{ij}^2 \\ &= \sum_{i \in \mathcal{N}} \sum_{j \in \mathcal{J}_i} q_i q_j [\|x_i\|^2 + \|x_j\|^2 - 2(x_i | x_j)] \\ &= 2 \left[\sum_{i \in \mathcal{N}} \sum_{j \in \mathcal{J}_i} q_i q_j \, \|x_i\|^2 - \sum_{i \in \mathcal{N}} \left(q_i x_i \,\middle|\, \sum_{j \in \mathcal{J}_i} q_j x_j \right) \right], \end{aligned} \tag{C2}$$

where $(\cdot|\cdot)$ is the standard inner product on $\mathbb{R}^d$. With the aid of Eq. (35), we can express the first term in Eq. (C2) as $\sum_{i \in \mathcal{N}} \sum_{j \in \mathcal{J}_i} q_i q_j \|x_i\|^2 = \sum_{i \in \mathcal{N}} q_i \|x_i\|^2 \sum_{j \in \mathcal{R}^i} q_j$, where $\mathcal{R}^i \equiv \{j \in \mathcal{N} \mid r_{ij} < r_{\mathrm{c}}\}$. On the other hand, because it follows from Eq. (36) that $\sum_{j \in \mathcal{J}_i} q_j x_j = \sum_{j \in \mathcal{R}_i} q_j x_j - \sum_{j \in \mathcal{M}_i} q_j x_j = \sum_{j \in \mathcal{R}_i} q_j x_j + q_i x_i = \sum_{j \in \mathcal{R}^i} q_j x_j$, the second term in Eq. (C2) is $\sum_{i \in \mathcal{N}} (q_i x_i | \sum_{j \in \mathcal{J}_i} q_j x_j) = \sum_{i \in \mathcal{N}} \sum_{j \in \mathcal{R}^i} q_i q_j (x_i | x_j)$. Hence, we have

$$\begin{aligned} &\sum_{i \in \mathcal{N}} \sum_{j \in \mathcal{J}_i} q_i q_j r_{ij}^2 \\ &= \sum_{i \in \mathcal{N}} \sum_{j \in \mathcal{R}^i} q_i q_j \, \|x_i\|^2 + \sum_{i \in \mathcal{N}} \sum_{j \in \mathcal{R}^i} q_i q_j \, \|x_i\|^2 \\ &-2 \sum_{i \in \mathcal{N}} \sum_{j \in \mathcal{R}^i} q_i q_j \, (x_i | \, x_j). \end{aligned}$$

Notice that the second term is equal to $\sum_{i \in \mathcal{N}} \sum_{j \in \mathcal{R}^i} q_i q_j \|x_j\|^2$ [as can be seen using the algebra similar to Eq. (C1); obviously, $j \in \mathcal{R}^i \Leftrightarrow i \in \mathcal{R}^j$ for all $i, j \in \mathcal{N}$], so that

$$\begin{aligned} &\sum_{i \in \mathcal{N}} \sum_{j \in \mathcal{J}_i} q_i q_j r_{ij}^2 \\ &= \sum_{i \in \mathcal{N}} \sum_{j \in \mathcal{R}^i} q_i q_j [\|x_i\|^2 + \|x_j\|^2 - 2(x_i | x_j)] \\ &= \sum_{i \in \mathcal{N}} \sum_{j \in \mathcal{R}^i} q_i q_j r_{ij}^2 = \sum_{i \in \mathcal{N}} \sum_{j \in \mathcal{R}_i} q_i q_j r_{ij}^2. \end{aligned}$$

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[47] See supplementary material at http://dx.doi.org/10.1063/1.3582791 for further analysis of the heuristic derivation.
[48] Exactly speaking, we should consider that the phase space Γ is not just the bare phase space $\Gamma_\mathrm{b} \equiv \{x \in \mathbb{R}^{dN} | x_i \neq x_j \text{ for } i \neq j (\forall i, j \in \mathcal{N})\}$, but a subset of all $x \in \Gamma_\mathrm{b}$ having $\mathcal{M}_i \subset \mathcal{N}_i$ such that condition (5) holds for any $i \in \mathcal{N}$, instead of assuming that every $x \in \Gamma_\mathrm{b}$ has such $\mathcal{M}_i$ for all i. Although $\mathcal{M}_i$ is not necessarily fixed uniquely, the choice does not affect the results. Note that to simply conduct an extensive application, it would be better to weaken the conditions by replacing the equalities with near equalities in conditions (5b) and (5c).
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