The homogeneity condition: A simple way to derive isotropic periodic sum potentials for efficient calculation of long-range interactions in molecular simulation

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ABSTRACT

Isotropic periodic sum (IPS) is a method to calculate long-range interactions based on the homogeneity of simulation systems. By using the isotropic periodic images of a local region to represent remote structures, long-range interactions become a function of the local conformation. This function is called the IPS potential, which folds long-ranged interactions into a short-ranged potential and can be calculated as efficiently as a cutoff method. Analytic solutions of IPS potentials have been solved for many interaction types. To further simplify the application of the IPS method, this work presents the homogeneity condition, which requires the sum of interaction energies for any particle to be independent of cutoff distances for a truly homogeneous system. Using the homogeneity condition, one can avoid the complicated mathematic work to solve analytic solutions and can instead use simple functions as IPS potentials. Example simulations are performed for model systems of a series of interaction types. Energies, volumes, and their fluctuations from these simulations demonstrate that simple IPS potentials obtained through the homogeneity condition can satisfactorily describe long-range interactions. The homogeneity condition makes the IPS method a convenient way to handle long-range interactions of any type.

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I. INTRODUCTION

Accurate molecular energies are essential for molecular simulation studies. Long-range interactions often account for a significant part of molecular energies and are required to be calculated accurately. However, it is impractical to include all long-range particles in a molecular simulation. Particles in the long range are either neglected, such as in the cutoff methods,^{1,2} or treated as a uniform background by adding a density dependent correction term, or treated as a field, such as the reaction field³ and molecular field,⁴ or replaced by images created with periodic boundary conditions (PBCs), such as lattice sum methods.⁵ Although employing PBC images introduces PBC symmetry into a simulation system, this is a widely accepted approach to account for long-range interactions. The isotropic periodic sum (IPS) method^{6,7} represents remote particles with isotropic periodic images to calculate long-range

interactions. The difference between lattice sum and IPS is in the images. The PBC images discretely distribute throughout the space at lattice points defined by the PBC. The interaction with PBC images is orientation dependent. A summation over the discretized images is difficult, and special methods, such as Ewald sum,⁵ Particle-meshed-Ewald (PME),^{8–14} and fast multipole algorithm (FMA),^{15,16} were developed to tackle this numerically difficult problem. The IPS method uses isotropic periodic images that continuously distribute in space and are orientation independent. The isotropic periodic images are imaginary, and their interactions result in the IPS potential. They do not exist explicitly in a simulation system and do not interfere with any PBC. IPS potentials for many interaction types have been analytically solved.⁶ The IPS potential is short ranged and can be calculated as efficiently as a cutoff method, whereas it is comparable with PME in capturing long-range interactions. The IPS method has been extended

to many interaction types^{7,17–24} and has been applied in many studies.^{25–28}

Even though IPS potentials can be solved analytically for many potential types, complicated mathematic work remains a burden for new interaction types. In addition, analytic solutions are often complicated in functional forms and are inconvenient to be implemented directly into simulation software. Therefore, it is desired to have a simple way to derive IPS potentials that can accurately describe long-range interactions.

In this work, we propose the homogeneity condition that allows simple functions to be used as IPS potentials. Using the homogeneity condition, simple polynomial IPS potentials for interactions, $\frac{1}{r^n}$, $n = 1-14$, are presented. Model systems are designed to examine the behavior of these IPS potentials, and NVT and NPT simulations are performed to demonstrate their application.

II. METHOD AND ALGORITHM

A. IPS potentials

The isotropic periodic sum (IPS) method,^{6,7} like the lattice sum methods, is also an image based method. Instead of using the lattice images created by PBC, IPS uses isotropic periodic images to represent remote structures. The sum of interactions with IPS images is a function of distance for each pair of atoms within the local region

$$E_i = \frac{1}{2} \sum_j \epsilon(r_{ij}) \approx \phi^{\text{IPS}}(0, r_c) + \frac{1}{2} \sum_j r_{ij} < r_c (\epsilon(r_{ij}) + \phi^{\text{IPS}}(r_{ij}, r_c)). \quad (1)$$

We call $\phi^{\text{IPS}}(r_{ij}, r_c)$ the IPS potential, which depends on the distance, r_{ij} , and the local region radius, or the cutoff distance, r_c . $\phi^{\text{IPS}}(0, r_c)$ is the interaction with self-images. The distribution of the IPS images determines the functional form of the IPS potential. For example, with a random shell distribution plus an axial placement, the IPS potential between a pair of point charges has the following analytical form:⁶

$$\phi_{\text{ele}}^{\text{IPS}}(r, r_c) = -\frac{1}{2r_c} \left(2\gamma + \psi\left(1 - \frac{r}{2r_c}\right) + \psi\left(1 + \frac{r}{2r_c}\right) \right), \quad (2)$$

where $\gamma = \lim_{n \rightarrow \infty} \left(\sum_{k=1}^n \frac{1}{k} - \log n \right) \approx 0.577216$ is Euler's constant and $\psi(z)$ is the digamma function: $\psi(z) = \frac{\Gamma'(z)}{\Gamma(z)}$ and $\Gamma(z) = \int_0^\infty t^{z-1} e^{-t} dt$. Here in Eq. (2) and in the following discussions, we drop the charges for convenience.

The digamma functions in Eq. (2) are complicated to calculate directly during molecular simulations. Because any analytical IPS potential can be expanded to a polynomial series of distance, r , e.g.,

$$\begin{aligned} \phi_{\text{ele}}^{\text{IPS}}(r, r_c) = & 0.300514 \frac{r^2}{r_c^3} + 0.064808 \frac{r^4}{r_c^5} + 0.015756 \frac{r^6}{r_c^7} \\ & + 0.003914 \frac{r^8}{r_c^9} + 0.000977 \frac{r^{10}}{r_c^{11}} + O(r^{12}), \end{aligned} \quad (3)$$

it is more convenient to fit it with a polynomial function

$$\phi_{\text{ele}}^{\text{IPS}}(r, r_c) \approx \frac{1}{26r_c} \left(8 \left(\frac{r}{r_c} \right)^2 + \left(\frac{r}{r_c} \right)^4 + \left(\frac{r}{r_c} \right)^6 \right). \quad (4)$$

One characteristic of IPS potentials is their zero derivatives at the cutoff boundary

$$\left. \frac{d}{dr} \epsilon^{\text{IPS}}(r, r_c) \right|_{r=r_c} = \left. \frac{d}{dr} (\epsilon(r) + \phi^{\text{IPS}}(r, r_c)) \right|_{r=r_c} = 0. \quad (5)$$

Equation (5) is called the IPS boundary condition. Therefore, any function that satisfies the IPS boundary condition could be used as an IPS potential. Different IPS potentials may represent different distributions of IPS images.

It is more convenient to separate the IPS potential into two parts,

$$\begin{aligned} \epsilon^{\text{IPS}}(r, r_c) &= \epsilon^{\text{IPS}}(r, r_c) - \epsilon^{\text{IPS}}(r_c, r_c) + \epsilon^{\text{IPS}}(r_c, r_c) \\ &= \epsilon_{\text{pair}}^{\text{IPS}}(r, r_c) + b^{\text{IPS}} \epsilon(r_c), \end{aligned} \quad (6)$$

where

$$\epsilon_{\text{pair}}^{\text{IPS}}(r, r_c) = \epsilon^{\text{IPS}}(r, r_c) - \epsilon^{\text{IPS}}(r_c, r_c) \quad (7a)$$

is called the IPS pair potential and

$$b^{\text{IPS}} = \epsilon^{\text{IPS}}(r_c, r_c) / \epsilon(r_c) \quad (7b)$$

is called the IPS boundary constant. $\epsilon_{\text{pair}}^{\text{IPS}}(r, r_c)$ satisfies the boundary condition, Eq. (5), and approaches zero at the cutoff boundary

$$\epsilon_{\text{pair}}^{\text{IPS}}(r_c, r_c) = 0. \quad (8)$$

In other words, $\epsilon_{\text{pair}}^{\text{IPS}}(r, r_c)$ is continuous and smooth at the boundary. Equation (8) is called the continuity condition. A Monte Carlo (MC) simulation requires a continuous potential function, and a molecular dynamics (MD) simulation requires a smooth potential function.

The boundary constant b^{IPS} is important for energy and virial calculation⁶

$$E^{\text{IPS}} = E_{\text{pair}}^{\text{IPS}} + E_{\text{bound}}^{\text{IPS}}, \quad (9a)$$

$$E_{\text{pair}}^{\text{IPS}} = \frac{1}{2} \sum_i^N \sum_j^{r_{ij} < r_c} \epsilon_{\text{pair}}^{\text{IPS}}(r_{ij}, r_c), \quad (9b)$$

$$E_{\text{bound}}^{\text{IPS}} = \frac{1}{2} \sum_i^N \sum_j^{r_{ij} < r_c} b_{ij}^{\text{IPS}} \epsilon(r_c) \approx \frac{2\pi r_c^3}{3V} \sum_i^N \sum_j^N b_{ij}^{\text{IPS}} \epsilon(r_c), \quad (9c)$$

$$W^{\text{IPS}} = W_{\text{pair}}^{\text{IPS}} + W_{\text{bound}}^{\text{IPS}}, \quad (9d)$$

$$W_{\text{pair}}^{\text{IPS}} = \frac{1}{3} \sum_i^N \mathbf{r}_i \mathbf{f}_i, \quad (9e)$$

$$W_{\text{bound}}^{\text{IPS}} = E_{\text{bound}}^{\text{IPS}}. \quad (9f)$$

Previously, the IPS potential for interactions, $\frac{1}{r^n}$, $n = 1, 2$, and 3, is defined with a reference potential at $r = 0$ so that $\phi^{\text{IPS}}(0, r_c) = 0$. This reference potential is arbitrarily defined, which corresponds to an arbitrary boundary constant. This arbitrarily defined boundary constant does not contribute to the total energy or total virial as long as the total moments are zero, such as in a charge neutral system. In cases the total moments are not zero, such as in a plasma that has net charges, the boundary constant needs to be properly determined. This task can be accomplished through the homogeneity condition to be introduced.

B. The homogeneity condition

The IPS method is designed for homogeneous systems. For truly homogeneous systems, the interaction energy is independent of the size of the local region or the cutoff distance. We define the homogeneity condition as that for a truly homogeneous system, any particle's energy should be independent of the cutoff distance. Because a truly homogeneous system has a constant radial distribution, $g(r) = 1$, the homogeneity condition can be described by the following expression:

$$\begin{aligned} E_i|_{g(r)=1} &= \frac{1}{2} \int_0^{r_c} 4\pi r^2 \epsilon^{\text{IPS}}(r, r_c) g(r) dr \Big|_{g(r)=1} \\ &= \int_0^{r_c} 2\pi r^2 \epsilon^{\text{IPS}}(r, r_c) dr = C. \end{aligned} \quad (10)$$

Here, C is a constant independent of r_c . Insert Eq. (6) into Eq. (10), we have

$$E_i|_{g(r)=1} = \int_0^{r_c} 2\pi r^2 \epsilon_{\text{pair}}^{\text{IPS}}(r, r_c) dr + \frac{2}{3} \pi r_c^3 b^{\text{IPS}} \epsilon(r_c) = C. \quad (11)$$

Therefore, the boundary constant can be determined by the following equation:

$$b^{\text{IPS}} = \left(\frac{3C}{2\pi} - 3 \int_0^{r_c} r^2 \epsilon_{\text{pair}}^{\text{IPS}}(r, r_c) dr \right) / (r_c^3 \epsilon(r_c)). \quad (12)$$

To illustrate the application of the homogeneity condition, we consider the potential

$$\epsilon(r) = \frac{1}{r^n}. \quad (13)$$

Below is a 1-term polynomial IPS pair potential with a power of m , which satisfies the boundary condition, Eq. (5), and the continuity condition, Eq. (8),

$$\epsilon_{\text{pair}}^{\text{IPS}}(r, r_c) = \frac{1}{r^n} - \frac{1}{r_c^n} + \frac{n}{m r_c^{n+m}} (r^m - r_c^m). \quad (14)$$

From Eq. (12), we can solve

$$b^{\text{IPS}} = \begin{cases} \frac{(m+n)n}{(m+3)(n-3)} + \frac{3C}{2\pi} r_c^{n-3} & n \neq 3, m > -3 \\ \frac{6+m}{3+m} - 3 \ln r_c + \frac{3C}{2\pi} & n = 3, \end{cases} \quad (15)$$

C is a constant of any value. In this work, we choose $C = 0$ so that b^{IPS} is independent of r_c . When $n = 3$, b^{IPS} always depends on $\ln r_c$ no matter what C value is.

C. Algorithm of the IPS method

To illustrate the application of the IPS potential, we describe the implementation in molecular simulations.

With IPS potentials, the pairwise interaction can be written in the following form:

$$\epsilon^{\text{pair}} = \begin{cases} (\chi - 1)\epsilon(r) + \epsilon_{\text{pair}}^{\text{IPS}}(r, r_c) & r \leq r_c \\ 0 & r > r_c. \end{cases} \quad (16)$$

Here, χ is a scaling factor that many force fields employ to adjust contribution from covalent bonded atom pairs, which typically takes the following form:

$$\chi = \begin{cases} 0 & 1-1, 1-2, \text{ and } 1-3 \text{ covalent bonded atom pairs} \\ \chi^{(1-4)} & 1-4 \text{ covalent bonded atom pairs} \\ 1 & \text{otherwise.} \end{cases} \quad (17)$$

Note that the covalent bonding adjusting only applies to the direct interaction part, $\epsilon(r)$, not the long-range IPS potential part, because IPS image atoms are at least r_c distance away and are not directly covalent-bonded with the calculating atom. Therefore, the total energy is the sum over all atom pairs within r_c , including the excluded atoms (such as self-pairs and covalent-bonded pairs, which are normally excluded in nonbonded interactions).

In addition to the pairwise interactions, the boundary energy and virial are calculated either with the pairwise interactions, or for smoothness, by averaging over the whole system as shown in Eqs. (9c) and (9f).

FIG. 1. Model potentials examined in this work. Bottom: Interaction potentials defined by Eq. (18) with $n_a = 12$ and $n_c = 1-9$. Middle: IPS potentials defined by Eq. (19). Top: IPS pair potentials defined by Eq. (7a).

III. SIMULATION DETAILS

To demonstrate the performance of the IPS potentials for $\frac{1}{r^n}$ type interactions, we use a $n_a - n_c$ potential of the following form:

$$\varepsilon(r) = \varepsilon_0 \left(\frac{n_c}{n_a - n_c} \left(\frac{\sigma}{r} \right)^{n_a} - \frac{n_a}{n_a - n_c} \left(\frac{\sigma}{r} \right)^{n_c} \right). \quad (18)$$

This potential function has a repulsive part in the form of $\frac{1}{r^{n_a}}$ and an attractive part in the form of $\frac{1}{r^{n_c}}$. The potential is constructed to have a minimum of $-\varepsilon_0$ at $r = \sigma$. When applying the IPS method, the IPS potentials are added to the $\frac{1}{r^{n_a}}$ and $\frac{1}{r^{n_c}}$ terms, respectively,

$$\varepsilon^{\text{IPS}}(r) = \varepsilon_0 \left(\frac{n_c \sigma^{n_a}}{n_a - n_c} \left(\frac{1}{r^{n_a}} + \phi_{n_a}(r, r_c) \right) - \frac{n_a \sigma^{n_c}}{n_a - n_c} \left(\frac{1}{r^{n_c}} + \phi_{n_c}(r, r_c) \right) \right). \quad (19)$$

We set the repulsive power, $n_a = 12$, and the attractive power, $n_c = 1-9$. Figure 1 shows the potentials with or without the IPS potentials. The bottom panel shows the $n_a - n_c$ potential, $\varepsilon(r)$, which is long-ranged and has a minimum of $-\varepsilon_0$ at $r = \sigma$. The smaller the attractive power is, the slower the tail decays. The middle panel shows $\varepsilon^{\text{IPS}}(r, r_c)$ with $r_c = 3\sigma$, which is short ranged until the boundary at $r = 3\sigma$ and is not continuous at the boundary. The values at the boundary are $b^{\text{IPS}}\varepsilon(3\sigma)$. The top panel shows $\varepsilon_{\text{pair}}^{\text{IPS}}(r, r_c)$, which is continuous and smooth at the boundary.

A cubic box of 500 particles is simulated with $\varepsilon_0 = 119.8$ K = 0.238 kcal/mol and $\sigma = 3.405$ Å, which are the Lennard-Jones

parameters for argon. The PBC cubic box side for the *NVT* simulations is 28.53 Å. To keep the system a fluid, the temperatures are set to 1000 K, 500 K, 500 K, 500 K, 140 K, 100 K, 100 K, 100 K, and 100 K for systems with $n_c = 1-9$, respectively, in both *NVT* and *NPT* simulations. For the *NPT* simulations, to keep the volumes around the initial values, pressures are set to 8750 atm, 8220 atm, 10 700 atm, 2760 atm, 400 atm, 400 atm, 800 atm, 1080 atm, and 1280 atm for systems with $n_c = 1-9$, respectively. These pressures are chosen from the results of the *NVT* simulations. At each cutoff distance of 6, 8, 10, 12, 15, and 20 Å, 10 ns molecular dynamics simulations are performed to calculate the average properties. As a comparison, a straight cutoff method, which truncates energy at $r = r_c$, is also used for simulations.

IV. RESULTS AND DISCUSSION

This work proposes the homogeneity condition to allow simple functions to be used as IPS potentials so that the complicated mathematical work to solve analytic solutions of IPS potentials can be avoided. The central concept of the IPS method is that for homogeneous systems the IPS potential can represent remote interactions beyond the cutoff distance. All fluids are typically ordered in the near range and disordered in the long range. The interactions with the disordered long-range region can be represented by the IPS potential and total interaction energies should be independent of the cutoff distance when the region beyond the cutoff distance is fully homogeneous. A good IPS potential should produce ensemble averages

TABLE I. Polynomial functions fitting into the IPS analytic solutions. The standard deviations of the fitting are shown in the brackets. The potential is expressed in the following form: $\varepsilon^{\text{IPS}}(r, r_c) = \varepsilon(r) + \varepsilon(r_c) \left(\phi_{\text{pair}}^{\text{IPS}}(r, r_c) + b^{\text{IPS}} \right)$.

$\varepsilon(r)$	1-term $\phi_{\text{pair}}^{\text{IPS}}(r, r_c) [\delta_1]$	1-term b^{IPS}	2-term $\phi_{\text{pair}}^{\text{IPS}}(r, r_c) [\delta_2]$	2-term b^{IPS}	3-term $\phi_{\text{pair}}^{\text{IPS}}(r, r_c) [\delta_3]$	3-term b^{IPS}
$\frac{1}{r}$	$\frac{r^2}{2r_c^2} - \frac{3}{2} [6.5 \times 10^{-2}]$	$-\frac{3}{10}$	$\frac{7r^2}{25r_c^2} + \frac{11r^4}{100r_c^4} - \frac{139}{100} [1.9 \times 10^{-3}]$	$-\frac{569}{1750}$	$\frac{16r^2}{53r_c^2} + \frac{3r^4}{53r_c^4} + \frac{3r^6}{106r_c^6} - \frac{147}{106} [1.5 \times 10^{-4}]$	$-\frac{1217}{3710}$
$\frac{1}{r^2}$	$\frac{r^2}{r_c^2} - 2 [5.3 \times 10^{-2}]$	$-\frac{8}{5}$	$\frac{73r^2}{89r_c^2} + \frac{8r^4}{89r_c^4} - \frac{170}{89} [6.7 \times 10^{-4}]$	$-\frac{5048}{3115}$	$\frac{82r^2}{99r_c^2} + \frac{7r^4}{99r_c^4} + \frac{r^6}{99r_c^6} - \frac{21}{11r_c^2} [5.2 \times 10^{-5}]$	$-\frac{2408}{1485}$
$\frac{1}{r^3}$	$\frac{3r^2}{2r_c^2} - \frac{5}{2} [1.7 \times 10^{-1}]$	$\frac{8}{5} - 3 \ln r_c$	$\frac{8r^2}{9r_c^2} + \frac{11r^4}{36r_c^4} - \frac{79}{36} [4.5 \times 10^{-3}]$	$\frac{482}{315} - 3 \ln r_c$	$\frac{16r^2}{17r_c^2} + \frac{3r^4}{17r_c^4} + \frac{7r^6}{102r_c^6} - \frac{223}{102} [3.0 \times 10^{-4}]$	$\frac{8156}{5355} - 3 \ln r_c$
$\frac{1}{r^4}$	$\frac{r^2}{r_c^2} - 2 [2.2 \times 10^{-1}]$	$\frac{32}{7}$	$\frac{57r^2}{58r_c^2} + \frac{59r^4}{174r_c^4} - \frac{202}{87} [7.6 \times 10^{-3}]$	$\frac{6028}{1305}$	$\frac{45r^2}{52r_c^2} + \frac{19r^4}{52r_c^4} + \frac{21r^6}{208r_c^6} - \frac{485}{208} [3.2 \times 10^{-4}]$	$\frac{4633}{1001}$
$\frac{1}{r^5}$	$\frac{5r^4}{4r_c^4} - \frac{9}{4} [1.2 \times 10^{-1}]$	$\frac{45}{14}$	$\frac{23r^2}{28r_c^2} + \frac{47r^4}{84r_c^4} - \frac{50}{21} [5.0 \times 10^{-3}]$	$\frac{2017}{630}$	$\frac{49r^2}{69r_c^2} + \frac{31r^4}{69r_c^4} + \frac{41r^6}{184r_c^6} - \frac{1315}{552} [2.5 \times 10^{-4}]$	$\frac{170167}{53130}$
$\frac{1}{r^6}$	$\frac{3r^4}{2r_c^4} - \frac{5}{2} [5.8 \times 10^{-2}]$	$\frac{20}{7}$	$\frac{13r^2}{22r_c^2} + \frac{53r^4}{66r_c^4} - \frac{79}{33} [7.9 \times 10^{-3}]$	$\frac{1372}{495}$	$\frac{85r^2}{156r_c^2} + \frac{17r^4}{39r_c^4} + \frac{19r^6}{48r_c^6} - \frac{1483}{624} [1.2 \times 10^{-3}]$	$\frac{8273}{3003}$
$\frac{1}{r^7}$	$\frac{7r^6}{6r_c^6} - \frac{13}{6} [1.3 \times 10^{-1}]$	$\frac{91}{36}$	$\frac{10r^2}{17r_c^2} + \frac{99r^4}{136r_c^4} - \frac{315}{136} [1.8 \times 10^{-2}]$	$\frac{171}{68}$	$\frac{33r^2}{100r_c^2} + \frac{31r^4}{50r_c^4} + \frac{193r^6}{500r_c^6} - \frac{292}{125} [2.0 \times 10^{-3}]$	$\frac{115261}{45500}$
$\frac{1}{r^8}$	$\frac{3r^6}{3r_c^6} - \frac{7}{3} [5.7 \times 10^{-2}]$	$\frac{112}{45}$	$\frac{2r^2}{5r_c^2} + \frac{9r^4}{10r_c^4} - \frac{23}{10} [9.5 \times 10^{-3}]$	$\frac{664}{275}$	$\frac{15r^2}{68r_c^2} + \frac{9r^4}{17r_c^4} + \frac{37r^6}{68r_c^6} - \frac{39}{17} [1.4 \times 10^{-3}]$	$\frac{18636}{7735}$
$\frac{1}{r^9}$	$\frac{3r^6}{2r_c^6} - \frac{5}{2} [8.5 \times 10^{-2}]$	$\frac{5}{2}$	$\frac{3r^4}{4r_c^4} + \frac{r^{12}}{2r_c^{12}} - \frac{9}{4} [9.1 \times 10^{-3}]$	$\frac{163}{70}$	$\frac{59r^2}{292r_c^2} + \frac{221r^4}{292r_c^4} + \frac{148r^6}{511r_c^6} - \frac{1149}{511} [9.1 \times 10^{-4}]$	$\frac{86519}{37230}$
$\frac{1}{r^{10}}$	$\frac{5r^8}{4r_c^8} - \frac{9}{4} [4.2 \times 10^{-2}]$	$\frac{180}{77}$	$\frac{21r^4}{37r_c^4} + \frac{143r^6}{222r_c^6} - \frac{491}{222} [4.5 \times 10^{-3}]$	$\frac{8812}{3883}$	$\frac{9r^2}{71r_c^2} + \frac{48r^4}{71r_c^4} + \frac{202r^6}{497r_c^6} - \frac{1098}{497} [5.9 \times 10^{-4}]$	$\frac{95672}{42245}$
$\frac{1}{r^{11}}$	$\frac{11r^8}{8r_c^8} - \frac{19}{8} [6.0 \times 10^{-2}]$	$\frac{19}{8}$	$\frac{19r^4}{47r_c^4} + \frac{147r^6}{188r_c^6} - \frac{411}{188} [3.3 \times 10^{-3}]$	$\frac{29367}{13160}$	$\frac{4r^2}{51r_c^2} + \frac{29r^4}{51r_c^4} + \frac{164r^6}{357r_c^6} - \frac{752}{357} [4.5 \times 10^{-4}]$	$\frac{225119}{104040}$
$\frac{1}{r^{12}}$	$\frac{6r^{10}}{5r_c^{10}} - \frac{11}{5} [3.0 \times 10^{-2}]$	$\frac{88}{39}$	$\frac{7r^6}{11r_c^6} + \frac{45r^8}{88r_c^8} - \frac{189}{88} [5.4 \times 10^{-3}]$	$\frac{1372}{627}$	$\frac{5r^2}{99r_c^2} + \frac{4r^4}{9r_c^4} + \frac{358r^6}{693r_c^6} - \frac{1394}{693} [1.3 \times 10^{-3}]$	$\frac{10478}{5049}$
$\frac{1}{r^{13}}$	$\frac{13r^{12}}{12r_c^{12}} - \frac{25}{12} [4.2 \times 10^{-2}]$	$\frac{13}{6}$	$\frac{r^6}{2r_c^6} + \frac{5r^{16}}{8r_c^{16}} - \frac{17}{8} [3.0 \times 10^{-3}]$	$\frac{1231}{570}$	$\frac{9r^4}{49r_c^4} + \frac{29r^{10}}{49r_c^{10}} + \frac{311r^{18}}{882r_c^{18}} - \frac{1877}{882} [8.0 \times 10^{-4}]$	$\frac{289271}{133770}$
$\frac{1}{r^{14}}$	$\frac{7r^{12}}{6r_c^{12}} - \frac{13}{6} [2.4 \times 10^{-2}]$	$\frac{364}{165}$	$\frac{3r^6}{8r_c^6} + \frac{47r^{16}}{64r_c^{16}} - \frac{135}{64} [1.7 \times 10^{-3}]$	$\frac{895}{418}$	$\frac{r^4}{9r_c^4} + \frac{23r^{10}}{36r_c^{10}} + \frac{43r^{20}}{120r_c^{20}} - \frac{253}{120} [8.2 \times 10^{-4}]$	$\frac{147757}{69069}$

independent of cutoff distances when the cutoff distance reaches the fully homogeneous region. Here, we perform *NVT* and *NPT* simulations of the model systems to examine the cutoff distance dependence of ensemble averages.

A. Rationalized polynomial IPS potentials

Based on series expansions as shown by Eq. (3), we know that polynomials of even powers are reasonable choices to fit IPS analytic solutions. We use short polynomials that satisfy the boundary condition, Eq. (5), and the continuity condition, Eq. (8), to fit analytic IPS pair potentials⁶ to achieve an accurate and efficient calculation. Using the homogeneity condition, Eq. (10) or Eq. (12), we calculate the boundary constants for the polynomials. To minimize implementation mistakes, we pick rationalized coefficients for the polynomials. As a result, the boundary constants are also rational numbers, except for interaction type, $\frac{1}{r^3}$.

Table I lists the best fit 1-term, 2-term, and 3-term polynomials and their boundary constants. For 1-term polynomials, the boundary condition requires it to take the form of Eq. (14) and the only adjustable parameter is the power, m . The 1-term polynomials listed in Table I are those with the minimum deviations from the analytic solutions. Because only one parameter can be adjusted, the 1-term functions have large root-mean-square deviations (rmsd), e.g., 22% for $\frac{1}{r^4}$. For 2-term and 3-term polynomials, there are adjustable coefficients in addition to powers to improve the fit and their rmsds are well under 1%. More than 3 terms will have a neglectable effect in fitting accuracy.

B. *NVT* simulations

In *NVT* simulations, the average potential energies and energy fluctuations are good measures of ensemble distributions. Figure 2 shows the average potential energies as functions of the cutoff

FIG. 2. Average potential energies at different cutoff distances from the *NVT* simulations using the cutoff method and the 1-term, 2-term, and 3-term IPS potentials. The 9 panels show the results of the $12 - n_c$ model systems with $n_c = 1-9$. The attractive potential types of the model systems are labeled in each panel.

distance for the 9 model systems. The simulation results using the strict cutoff method are shown as a comparison. Clearly, we can see that the IPS potentials show little dependence on the cutoff distance when $r_c \geq 8 \text{ \AA}$. For small cutoff distances, e.g., $r_c < 8 \text{ \AA}$, the near-range ordered structure of fluids dominates the local region that makes it far from homogeneous and causes large deviations from the averages with long cutoffs.

For the model systems with $n_c = 1-3$, the improvement of the IPS method over the cutoff method is dramatic. It is well known that their potential energies do not converge when the cutoff distance grows, as shown by the cutoff results in Fig. 2. The IPS results are all flat, almost independent of the cutoff distance for all IPS potentials. Therefore, the IPS results represent converged values. Because the long-range summation of these potentials does not converge, the cutoff results do not approach the converged values of the IPS results. As n_c goes to 4 and higher, the sum of

pairwise interactions from the cutoff method converges, and the higher the n_c is, the faster the energy converges. For $n_c = 4$ or 5, the total energies from the cutoff method are far away from the converged values, i.e., the IPS results, and for $n_c \geq 6$, the total energies reach the IPS results when r_c is large. For all IPS potentials, their results converge to the same values after $r_c \geq 8 \text{ \AA}$. One important information from these results is that the 1-term IPS function is almost as good as the 2-term or 3-term IPS potentials. Therefore, the functional forms are not very critical, as long as they obey the IPS boundary condition and the homogeneity condition.

Further comparisons are shown in Fig. 3 where the potential energy fluctuations, which are related to heat capacities, from the cutoff method and the IPS method are plotted against the cutoff distance. The cutoff method produces large deviations in the energy fluctuations when the cutoff distance is smaller than $10 \text{ \AA}$.

FIG. 3. Potential energy fluctuations at different cutoff distances from the NVT simulations using the cutoff method and the 1-term, 2-term, and 3-term IPS potentials. The 9 panels show the results of the $12 - n_c$ model systems with $n_c = 1-9$. The attractive potential types of the model systems are labeled in each panel.

Clearly, the IPS potentials produce better results than the cutoff method.

C. *NPT* simulations

A *NPT* simulation provides a way to examine the accuracy of viral calculation which has a significant portion coming from long-range interactions. Volume is directly related to virial and is a sensitive property to examine the calculation of long-range interaction.

Figure 4 shows the average volumes in the 9 model systems obtained with the cutoff method and the IPS potentials. For the cutoff method, a larger cutoff distance results in a smaller volume. This is because a larger cutoff distance will include more atom pairs to be calculated. For pair distance beyond the radius, $\sigma = 3.405$ Å, pairwise interactions are attractive by nature, and more attractions will lead to smaller volume. Because for $n_c = 1-3$, the long-range sum of pair interactions does not converge, the volumes decrease with

no convergent value to approach and move away from the IPS volumes. For $n_c = 4-9$, the IPS volumes are almost flat and the values at 20 Å can be approximated as the converging values. Again, for $n_c = 4$ or 5, at a cutoff of 20 Å, the cutoff method produces volumes still far away from the IPS volumes, while for $n_c = 6-9$, the cutoff method reaches the IPS volumes when the cutoff distance is large.

Similar convergence is observed in the volume fluctuations (Fig. 5). Compared with the energy fluctuations shown in Fig. 3, the volume fluctuations of the cutoff method converge much slower. The IPS results again are independent of the cutoff distance after $r_c \geq 8$ Å.

D. IPS potential functional forms

IPS potentials represent interactions with the so-called isotropic periodic images. Obviously, the distribution of the isotropic

FIG. 4. Average volumes at different cutoff distances from *NPT* simulations using the cutoff method and the 1-term, 2-term, and 3-term IPS potentials. The 9 panels show the results of the 12 – n_c model systems with $n_c = 1-9$. The attractive potential types of the model systems are labeled in each panel.

FIG. 5. Volume fluctuations at different cutoff distances from *NPT* simulations using the cutoff method and the 1-term, 2-term, and 3-term IPS potentials. The 9 panels show the results of the $12 - n_c$ model systems with $n_c = 1-9$. The attractive potential types of the model systems are labeled in each panel.

periodic images affects the function form of IPS potentials. Originally, the IPS potential was solved with the isotropic period images that distribute on spherical shells and along the axis passing through the two interacting particles. The analytical solutions are complicated in functional forms and are not necessarily the best functional form to describe image interactions. The polynomial functions listed in Table I are simpler functions than the analytical solutions. *NVT* and *NPT* simulations shown above demonstrate that simple functions, here, 1-term, 2-term, and 3-term polynomials can equally well describe long-range interactions.

For the $\frac{1}{r}$ Coulomb interaction, the analytical IPS potential solved from the isotropic periodic images is shown in Eq. (2). Because the summation of $\frac{1}{r}$ interactions does not converge, the IPS potential is solved as a relative value in reference to the potential at $r = 0$. This reference is arbitrary that would cause

problem in systems with net charges. Now, the homogeneity condition solves this problem and allows the IPS method to calculate absolute energies.

The *NVT* and *NPT* simulations results show that the 1-term, 2-term, and 3-term IPS potentials listed in Table I produce very similar results and are insensitive to the cutoff distances when $r_c \geq 8 \text{ \AA}$ or 2.4σ . To further examine the effect of function forms, we examine 1-term IPS potentials of different powers, r^1 , r^2 , r^3 , r^4 , r^5 , and r^6 , for the $\frac{1}{r^4}$ type interaction, i.e., the IPS potentials shown by Eqs. (14) and (15) with $n = 4$ and $m = 1-6$. Figure 6 shows the 3-term IPS potential listed in Table I and the 1-term IPS potentials (lower panel) and their pairwise parts (upper panel).

Figure 7 shows the average potential energies from the *NVT* simulations and the average volumes from the *NPT* simulations for the $12-4$ model system with the 1-term IPS potentials, as well as the

FIG. 6. The 3-term IPS potential and the 1-term IPS potentials with powers from 1 to 6 for the $\frac{1}{r^{12}}$ interaction. Lower panel: The IPS potentials and upper panel: the IPS potentials subtracted from boundary values.

3-term IPS and the cutoff method. Except for r^1 , all other functions show reasonable cutoff distance independency for $r_c \geq 8 \text{ \AA}$. All energies and volumes converge to the same values. The insets of Fig. 7 compare the IPS results with the cutoff results. Clearly, the cutoff results have huge deviations from the IPS results and have strong cutoff distance dependence.

Therefore, any reasonable polynomial function that satisfies the IPS boundary condition, Eq. (5), and the homogeneity condition, Eq. (10), can be used as an IPS potential to calculate long-range interactions. The physics behind different function forms of the IPS potential is that they are due to different distributions of the isotropic periodic images. Through the homogeneity condition, we get rid of the explicit summation process over the isotropic periodic images to obtain IPS potentials. The homogeneity condition makes the IPS method simple to use. The simpler IPS potentials obtained through the homogeneity condition make the calculation of nonbonded interactions more efficient. It is expected that the homogeneity condition can be extended to other types of homogeneous systems, such as two-dimensional (2D) and one-dimensional (1D) homogeneous systems,⁶ so that simple IPS potentials for those systems can be derived.

FIG. 7. Average potential energies from the *NVT* simulations (lower panel) and average volumes from the *NPT* simulations (upper panel) for the 12-4 model system. 3-term IPS potential results are compared with 1-term IPS potential results. In the insets, the cutoff results are compared with the 1-term IPS potential results.

V. CONCLUSIONS

We propose the homogeneity condition for the derivation of simple IPS potentials. This simplification makes the IPS method straightforward for any type of long-range interaction. Applying the homogeneity condition to the 1-term, 2-term, and 3-term polynomials that fit the analytic solutions of the IPS pair potentials, we obtain the corresponding 1-term, 2-term, and 3-term IPS potentials for interaction types, $\frac{1}{r^n}$, $n = 1-14$. We examine the behavior of the IPS potentials, through model systems interacting with a n_a-n_c potential. Model systems with $n_a = 12$ and $n_c = 1-9$ are simulated in both *NVT* and *NPT* ensembles using the IPS potentials as well as the cutoff method. The simulation results with all IPS potentials are almost independent of the cutoff distance when $r_c \geq 8 \text{ \AA}$ or 2.4σ . Simulations with the cutoff method show strong cutoff distance dependence, especially for model systems with small n_c values. Simple functions such as 1-term polynomials of any power can be used as IPS potentials as long as they satisfy the IPS boundary condition and the homogeneity condition. Using the IPS boundary condition and the homogeneous condition, one can easily derive IPS potentials for long-range interactions of any type.

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