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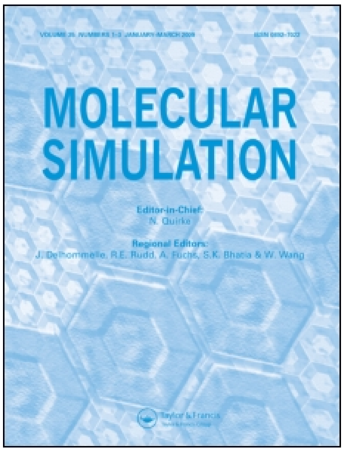

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MOLECULAR DYNAMICS AS A MATHEMATICAL MAPPING. I. DIFFERENTIABLE FORCE FUNCTIONS

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The molecular dynamics technique can be viewed as a deterministic mathematical mapping between, on one side, the force field parameters that describe the potential energy interactions and the input macroscopic conditions, and, on the other, the calculated macroscopic properties of the bulk molecular system.

The differentiability of such a mapping in the conventional molecular dynamics calculations is affected by the discontinuities in particle positions introduced by the periodic boundary conditions and the discontinuities introduced by the minimum image convention and other methods commonly employed to approximate the calculation of interparticle potential and force.

This paper proposes an alternative molecular dynamics framework based on modified force functions which are almost everywhere continuous and differentiable, and exhibit a natural periodicity. These characteristics obviate the need for both the periodic boundary conditions and the minimum image convention, as well as for any corrections for long-range interactions. They also make it possible to apply standard methods of variational calculus for the computation of partial derivatives of the molecular dynamics mapping.

The modified framework is first introduced for the case of simple monoatomic fluids where the nature of the forces exerted between any pair of two particles is identical. A more general model describing the interactions of flexible molecules is then developed. We describe the application of this approach to mixtures of alkane molecules interacting via the NERD force field.

Keywords: Molecular dynamics; Force functions; Minimum image convention

1. INTRODUCTION

Much of the current use of molecular simulation techniques in practical applications [1–3] is in the form of "computational experiments" used to

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generate data points. Typically, one specifies some input conditions and parameters, and performs a simulation to obtain the output properties of interest. In this sense, the computations emulate traditional laboratory experiments performed under specified conditions.

An alternative view of molecular simulation techniques is as a set of formal mathematical mappings ("functions") relating certain (computed) *macroscopic* quantities of direct relevance to practical applications to other (specified) macroscopic quantities and also to a set of parameters describing molecular, atomic, or sub-atomic behavior. In principle, such a formalized view could lead to an improved understanding of the effects both of algorithmic decisions and of physical approximations on the accuracy of the results computed by these techniques. It may also allow a wider range of mathematical manipulations such as the computation of the gradients of the computed ("output") quantities with respect to the specified ("input") ones, as well as various forms of inversion of the mathematical mapping (*e.g.*, for the estimation of molecular parameters from experimental data). Ultimately, representing computational chemistry techniques as formal mathematical functions is an essential prerequisite for embedding them within higher-level computations (*e.g.*, for engineering design purposes).

This three-part paper focuses on molecular dynamics aiming to establish it as a formal mathematical mapping. Part I removes all discontinuities involved in the molecular dynamics computation by eliminating such well established devices as the periodic boundary conditions and the minimum image convention. The key to achieving this is the introduction of a modified interparticle force function that is almost everywhere continuous and differentiable. This force can be derived from any continuous and differentiable interparticle potential function describing non-bonded pairwise interactions. The existence of chemical bonds is shown to result in only a minor modification to the overall approach.

Molecular dynamics computations making use of the above modified force function establish a continuous and differentiable mapping between their input and output quantities. Part II [4] of this paper develops formal procedures for the computation of all partial derivatives of this mapping.

A disadvantage of the modified force function is that it is much more complex than its conventional counterpart. Part III of this paper [5] demonstrates that the mathematical properties of this function are such that efficient interpolation schemes can be used for its computation. An algorithm for constructing interpolation grids of guaranteed accuracy is presented. Moreover, for many commonly used potential functions, including the Lennard–Jones and Coulomb ones, it is possible to construct *a priori* interpolation grids that guarantee the accuracy of the computed force for *any* value of the potential parameters and system density over a specified range.

Section 2 of this first part of the paper introduces the view of molecular dynamics as a formal mathematical mapping. Section 3 discusses the discontinuities introduced through the conventional molecular dynamics framework. Section 4 derives the modified molecular dynamics framework in terms of a general interparticle potential function operating in 3-dimensional space. Section 5 compares the modified framework with a conventional one employing periodic boundary conditions and the minimum image convention, and presents some numerical results.

Throughout Sections 4 and 5, we assume that the nature of the force exerted between any pair of two particles is the same, irrespective of the identity of these two particles, as would be the case for a monoatomic fluid of a single species. We consider the more general case in which different groups of particles interact through forces of different types (*e.g.*, due to chemical bonding) in Section 6.

2. MOLECULAR DYNAMICS AS A MATHEMATICAL MAPPING

A typical algorithm for molecular dynamics in the microcanonical (N, V, E) ensemble can be outlined as follows [6]:

1. Specify the macroscopic condition of a set of N particles in terms of their density ρ and specific internal energy E.
2. Determine the simulation box size L consistent with the density ρ for the given number of particles N.
3. Initialize the system by determining a vector of initial particle positions $\mathbf{r}^0$ consistent with L, and a vector of velocities $\mathbf{v}^0$ consistent with $\mathbf{r}^0$ and the specified energy E.
4. Integrate Newton's equations of motion:

$$\begin{aligned} \dot{\mathbf{r}}_i &= \mathbf{v}_i \\ \dot{\mathbf{v}}_i &= \frac{\mathbf{F}_i(\mathbf{r})}{m_i} \quad i = 1,\ldots,N \end{aligned} \tag{1}$$

subject to the initial conditions $\mathbf{r}(0) = \mathbf{r}^0$, $\mathbf{v}(0) = \mathbf{v}^0$, from the initial time $t = 0$ to a final time $t = t_f$. Here, the forces $\mathbf{F}_i$ are functions of the positions

r and are given by:

$$\mathbf{F}_i(\mathbf{r}) = -\nabla \mathbf{r}_i U, \quad i = 1, \ldots, N \tag{2}$$

where U is the overall potential energy of the system, usually approximated as a sum of effective pairwise potentials:

$$U = \sum_{i<j} U^{\mathrm{eff}}(r_{ij}, \vartheta) \tag{3}$$

where r_{ij} represents the distance between particles i and j, and ϑ is a set of potential parameters.

5. The instantaneous system properties of interest *(e.g.,* temperature, pressure) are functions $\varphi(\mathbf{r}, \mathbf{v})$ of the particle positions **r** and velocities **v**. For any such instantaneous property, the corresponding observable property p can be determined as follows:

$$p = \frac{1}{\tau} \int_{t_f - \tau}^{t_f} \varphi(\mathbf{r}(t), \mathbf{v}(t)) dt \tag{4}$$

The integral in Eq. (4) is evaluated over a final period of length τ of the entire time horizon t_f. The choice of τ is such as to allow the system to reach equilibrium over the initial period of length $t_f - \tau$ (the equilibration period).

The molecular dynamics algorithm as described above can be viewed as the computation of a function of the form:

$$p = \mathcal{P}(q, \vartheta) \tag{5}$$

Here q denotes the vector of macroscopic input quantities, the values of which are specified (*e.g.*, ρ, E), ϑ is a vector of microscopic parameters (*e.g.*, the Lennard-Jones potential constants ε, σ) and p denotes one or more macroscopic properties (*e.g.*, temperature, pressure, diffusion coefficients *etc.*) that are obtained by the molecular dynamics computation.

Since the molecular dynamics computation involves the solution of an initial value problem, the above function is, in principle, well-defined provided the same deterministic procedure for generating the initial condition of the system, and the same time horizon t_f and the equilibration period τ are always used.

It is interesting to ask whether the mapping (5) possesses other mathematical properties, such as continuity and differentiability. From a practical point of view, such properties would be highly desirable if, for instance, the function (5) is to be embedded within higher level computations (*e.g.*, for designing chemical processes or new materials exhibiting certain desirable properties), or if it is somehow to be inverted (*e.g.*, in order to estimate values of the parameters ϑ from a set of experimental values $q^{[k]}$, $p^{[k]}$, $k=1,2,\dots,NE$). In many of these applications, it is important to be able to compute not only the values of p for given values of q and ϑ, but also the values of the partial derivatives $\partial p/\partial q$ and $\partial p/\partial\vartheta$ – assuming, of course, that these derivatives exist.

Consider the solution of $x(t)$ of a set of ordinary differential equations $dx/dt=f(x,\alpha)$ subject to initial conditions $x(0)=x^0(\alpha)$, where t denotes the independent variable ("time") and α is a set of parameters. Then, the values of variables x at some final time t_f are a function $\mathcal{X}$ of the parameters α, *i.e.*,

$$x(t_f)=\mathcal{X}(\alpha) \tag{6}$$

Moreover, if $f(\cdot,\cdot)$ and $x^0(\cdot)$ are continuous and differentiable functions of their arguments, $\mathcal{X}(\alpha)$ is a continuous and differentiable function of α. In fact, the values of the partial derivatives $\partial\mathcal{X}/\partial\alpha$ can be evaluated using standard techniques from variational calculus [7].

However, in the case of molecular dynamics, the differentiability of mapping (5) is affected by the occurrence of a large number of discontinuities. These are caused by two different aspects of the conventional implementation of the molecular dynamics technique. We consider these below.

3. DISCONTINUITIES IN MOLECULAR DYNAMICS CALCULATIONS

The concept of periodic partitioning of the spatial domain under consideration is central to most molecular dynamics computations used to study physical systems by considering only a relatively small number, N, of particles placed in a (usually cubic) reference box of size L. In such cases, the reference box is replicated infinitely in all three spatial directions of interest (as shown in Fig. 1), so that every particle in this box has its exact image in the surrounding boxes, moving at the same velocity and experiencing the same forces as the original particle. One great advantage of the periodicity assumption is that surface effects, which would otherwise be very large for small number of particles, are avoided [8].

The periodic partitioning of the domain is reflected in most conventional molecular dynamics simulations through the implementations of periodic

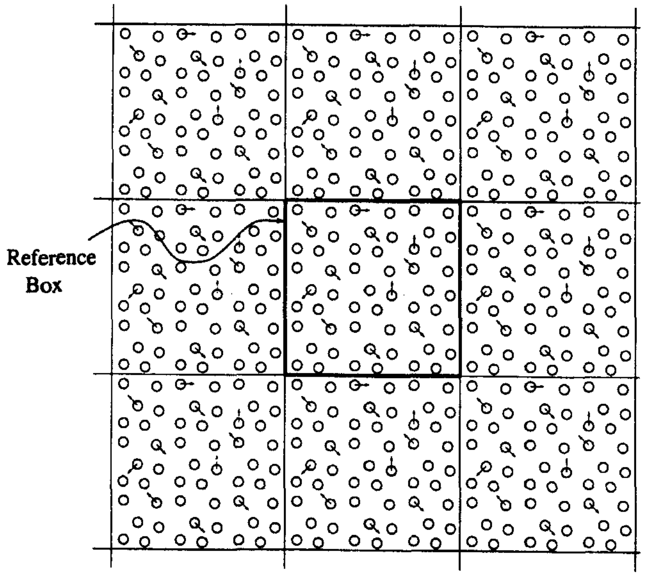

FIGURE 1 Periodic domain partitioning.

boundary conditions and the minimum image convention. As discussed below, these introduce a large number of discontinuities in molecular dynamics computations.

3.1. Discontinuities in Particle Positions

The system of differential equations (1) is subject to periodic boundary conditions [9]. Thus, whenever a particle reaches a face of the reference box and is moving outwards, it is instantaneously transposed to the corresponding position on the *opposite* face, moving inwards with the same velocity vector. In practical terms, the aim of these conditions is to maintain a constant number N of particles within the reference box. However, they also introduce discontinuities in the positions of the N particles under consideration.

3.2. Discontinuities in Interparticle Potential and its Derivatives

The calculation of interparticle forces $-\nabla_{\mathbf{r}}U$ in Eq. (2) in a system that is subject to periodic boundary conditions should, in principle, take account of interactions of each particle in the reference box with the images of all the particles in all boxes in the system. However, in order to limit the amount of required computation, a *minimum image convention* [10] is often introduced, according to which a particle i interacts with the single image of each other particle j that is nearest to it.

The minimum image convention reduces the computational cost of molecular dynamics by limiting the total number of interparticle interactions that needs to be considered to $N(N-1)/2$. It also preserves the continuity of the interparticle potential energy. However, it gives rise to a discontinuity in the force exerted on a particle i by a particle j. The discontinuity occurs at the point at which the identity of the image of j that is nearest to i changes. This happens when the particles are at a distance $L/2$ apart (as measured along any one of the coordinate axes) and moving away from each other (*cf.* Fig. 2).

As a result of this discontinuity, the force instantaneously changes sign and, in most cases (unless particle i happens to be on the straight line between the two images of j involved in this discontinuity), direction. Of course, this change is completely fictitious: in reality, the force exerted on particle i is a continuous function of time. In order to mitigate this effect, the size L of the box must be chosen to be large enough for the force between two particles at a distance $L/2$ apart to be practically zero.

For short-range potentials, the number of interactions that needs to be considered is often further reduced by employing a spherical potential cutoff, *i.e.*, by setting the pair potential to zero at some cutoff distance r_c, where $r_c \leq L/2$ (for consistency with the minimum image convention):

$$U'(r) = \begin{cases} U(r), & r \leq r_c \\ 0, & r > r_c \end{cases} \tag{7}$$

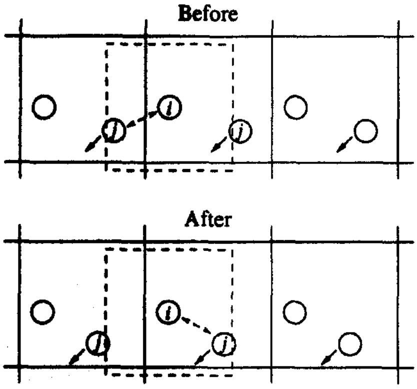

FIGURE 2 Minimum image convention.

In molecular dynamics calculations, the discontinuity in the truncated potential leads to a Dirac delta function in the interparticle force, which introduces instability in the equations of motion and difficulties with energy conservation [11, 2]. It is, therefore, common to introduce a truncated and shifted potential which vanishes at the cutoff radius:

$$U'(r) = \begin{cases} U(r) - U(r_c), & r \leq r_c \\ 0, & r > r_c \end{cases} \tag{8}$$

The above form of potential still exhibits a discontinuity in $\partial U/\partial r$ (and hence in the interparticle force) at r_c. The discontinuity in the force can be removed by using a shifted force potential [12], obtained by *shifting* the force (rather than the potential) between the particle pairs:

$$\frac{\partial U'}{\partial r}(r) = \begin{cases} (\partial U/\partial r)(r) - (\partial U/\partial r)(r_c), & r \leq r_c \\ 0, & r > r_c \end{cases} \tag{9}$$

The modified force defined by Eq. (9) is continuous at $r = r_c$; the step discontinuity has then been shifted to the next higher derivative of the potential (*i.e.*, $\partial^2 U/\partial r^2$ at $r = r_c$). If required, the corresponding pair potential U' can be obtained by integrating the above expression for $\partial U'/\partial r$ over r.

We note that neither the shifted potential (8) nor the shifted force potential (9) correspond to the original potential model $U(r)$; the thermodynamic properties for the original potential are normally obtained through simple perturbation schemes [12, 13].

The properties obtained by simulation based on the truncated, perturbation-corrected shifted and shifted force potential need to be further corrected for the long-range tail of the potential for $r > r_c$. This is normally done by assuming that the pair correlation function of homogeneous fluids is equal to unity for $r > r_c$, which, however, may lead to an overestimation of properties such as pressure and can lead to large errors in calculations of phase equilibria [13, 14]. On the other hand, the minimum image convention is not radially truncated and this form of correction cannot be applied to it.

In summary, all of the above computational devices introduce artificial discontinuities (see Tab. I). A key characteristic of the modified molecular dynamics framework described in the following section is that it removes all these discontinuities.

TABLE I Continuity implications of common modifications of interparticle potentials

	Continuity in potential	*Continuity in force*	*Continuity in force derivative*
Minimum image convention	√	×	×
Potential truncation	×	×	×
Shifted potential	√	×	×
Shifted force potential	√	√	×

4. MODIFIED MOLECULAR DYNAMICS FRAMEWORK

In this section, we develop an alternative framework for molecular dynamics which eliminates the discontinuities inherent in the conventional simulation techniques. In particular, we shall demonstrate that the definition of appropriate force functions that exhibit certain spatial continuity and periodicity properties obviates the need for both the periodic boundary conditions and the force approximation schemes in molecular dynamics.

Consider a system of N identical particles whose pairwise interactions are described by a continuous and differentiable potential function $U(r)$. In general, the force exerted on particle i by particle j $(j \neq i)$ is given by the gradient of the potential, $-\nabla_{\mathbf{r}_i} U(\mathbf{r})$. If we define the interparticle distance r_{ij} as:

$$r_{ij} \equiv \sqrt{(x_i - x_j)^2 + (y_i - y_j)^2 + (z_i - z_j)^2} \tag{10}$$

then the force exerted on particle i by a particle j in the x-direction is given by:

$$-\frac{\partial U}{\partial x_i} = -\left.\frac{\partial U}{\partial r}\right|_{r_{ij}} \times \frac{\partial r_{ij}}{\partial x_i} = -\left.\frac{x_i - x_j}{r_{ij}} \frac{\partial U}{\partial r}\right|_{r_{ij}} \tag{11}$$

Now, let us consider the combined force exerted on particle i by *all* images of particle i, as well as by particles j $(j \neq i)$ and all their images in an infinitely replicated system:

$$\begin{aligned} F_i^x = & -\sum_{\substack{j=1 \\ \neq i}} \sum_{k=-\infty}^{+\infty} \sum_{k'=-\infty}^{+\infty} \sum_{k''=-\infty}^{+\infty} \left.\frac{x_i - x_j - kL}{r_{ijkk'k''}} \frac{\partial U}{\partial r}\right|_{r_{ijkk'k''}} \\ & - \sum_{k=-\infty}^{+\infty} \sum_{k'=-\infty}^{+\infty} \sum_{k''=-\infty}^{+\infty} \left.\frac{kL}{\sqrt{(kL)^2 + (k'L)^2 + (k''L)^2}} \frac{\partial U}{\partial r}\right|_{r_{iikk'k''}} \end{aligned} \tag{12}$$

where we have defined the new interparticle distance $r_{ijkk'k''}$ as:

$$r_{ijkk'k''} \equiv \sqrt{(x_i - x_j - kL)^2 + (y_i - y_j - k'L)^2 + (z_i - z_j - k''L)^2} \tag{13}$$

The second half of the right hand side of Eq. (12) represents the forces exerted on particle i by its images in the surrounding boxes. This term can be shown to be zero:

$$\begin{aligned}
&\sum_{k=-\infty}^{+\infty}\sum_{k'=-\infty}^{+\infty}\sum_{k''=-\infty}^{+\infty}\left(\frac{kL}{\sqrt{(kL)^2+(k'L)^2+(k''L)^2}}\frac{\partial U}{\partial r}\bigg|_{r_{iikk'k''}}\right)\\
&= \sum_{k'=-\infty}^{+\infty}\sum_{k''=-\infty}^{+\infty}\left[\sum_{k=1}^{+\infty}\left(\frac{kL}{\sqrt{(kL)^2+(k'L)^2+(k''L)^2}}\frac{\partial U}{\partial r}\bigg|_{r_{iikk'k''}}\right)\right.\\
&\qquad\left.+\sum_{k=-\infty}^{-1}\left(\frac{kL}{\sqrt{(kL)^2+(k'L)^2+(k''L)^2}}\frac{\partial U}{\partial r}\bigg|_{r_{iikk'k''}}\right)\right]\\
&= \sum_{k'=-\infty}^{+\infty}\sum_{k''=-\infty}^{+\infty}\left[\sum_{k=1}^{+\infty}\left(\frac{kL}{\sqrt{(kL)^2+(k'L)^2+(k''L)^2}}\frac{\partial U}{\partial r}\bigg|_{r_{iikk'k''}}\right)\right.\\
&\qquad\left.+\sum_{k=1}^{+\infty}\left(\frac{-kL}{\sqrt{(-kL)^2+(k'L)^2+(k''L)^2}}\frac{\partial U}{\partial r}\bigg|_{r_{ii,-k,k'k''}}\right)\right]
\end{aligned} \tag{14}$$

By virtue of (13),

$$\begin{aligned}
r_{iikk'k''} &= \sqrt{(kL)^2 + (k'L)^2 + (k''L)^2}\\
&= \sqrt{(-kL)^2 + (k'L)^2 + (k''L)^2} = r_{ii,-k,k',k''}
\end{aligned}$$

Therefore, the two summations within the square brackets in Eq. (14) cancel each other, and Eq. (12) simplifies to:

$$F_i^x = -\sum_{\substack{j=1\\ \neq i}}^{N}\sum_{k=-\infty}^{+\infty}\sum_{k'=-\infty}^{+\infty}\sum_{k''=-\infty}^{+\infty}\frac{x_i - x_j - kL}{r_{ijkk'k''}}\frac{\partial U}{\partial r}\bigg|_{r_{ijkk'k''}} \tag{15}$$

If we define the normalized coordinate distance components as:

$$X_{ij} \equiv \frac{x_i - x_j}{L}, \quad Y_{ij} \equiv \frac{y_i - y_j}{L}, \quad Z_{ij} \equiv \frac{z_i - z_j}{L} \tag{16}$$

and the normalized distance $R_{ijkk'k''}$ as:

$$R_{ijkk'k''} \equiv \frac{r_{ijkk'k''}}{L} = \sqrt{(X_{ij} - k)^2 + (Y_{ij} - k')^2 + (Z_{ij} - k'')^2} \tag{17}$$

then Eq. (15) becomes:

$$F_i^x = -\frac{1}{L} \sum_{\substack{j=1 \\ \neq i}}^{N} \sum_{k=-\infty}^{+\infty} \sum_{k'=-\infty}^{+\infty} \sum_{k''=-\infty}^{+\infty} \frac{X_{ij} - k}{R_{ijkk'k''}} \frac{\partial U}{\partial R} \bigg|_{R_{ijkk'k''}} \tag{18}$$

This can be written as:

$$F_i^x = \sum_{\substack{j=1 \\ \neq i}}^{N} \mathcal{F}^x(X_{ij}, Y_{ij}, Z_{ij}), \quad i = 1, \dots, N \tag{19}$$

where the *modified force function* $\mathcal{F}^x(\cdot)$ is defined as:

$$\mathcal{F}^x(X, Y, Z) \equiv -\frac{1}{L} \sum_{k=-\infty}^{+\infty} \sum_{k'=-\infty}^{+\infty} \sum_{k''=-\infty}^{+\infty} \frac{X - k}{R_{kk'k''}} \frac{\partial U}{\partial R} \bigg|_{R_{kk'k''}} \tag{20}$$

and $R_{kk'k''}$ is defined as:

$$R_{kk'k''} \equiv \sqrt{(X - k)^2 + (Y - k')^2 + (Z - k'')^2} \tag{21}$$

Similarly, we can show that the total forces exerted on particle i in the y and z directions can be written as:

$$F_i^y = \sum_{\substack{j=1 \\ \neq i}}^{N} \mathcal{F}^y(X_{ij}, Y_{ij}, Z_{ij}), \quad i = 1, \dots, N \tag{22}$$

$$F_i^z = \sum_{\substack{j=1 \\ \neq i}}^{N} \mathcal{F}^z(X_{ij}, Y_{ij}, Z_{ij}), \quad i = 1, \dots, N \tag{23}$$

where the modified force functions $\mathcal{F}^y(\cdot)$ and $\mathcal{F}^z(\cdot)$ are defined as:

$$\mathcal{F}^y(X, Y, Z) \equiv -\frac{1}{L} \sum_{k=-\infty}^{+\infty} \sum_{k'=-\infty}^{+\infty} \sum_{k''=-\infty}^{+\infty} \frac{Y - k'}{R_{kk'k''}} \frac{\partial U}{\partial R} \bigg|_{R_{ijkk'k''}} \tag{24}$$

$$\mathcal{F}^z(X, Y, Z) \equiv -\frac{1}{L} \sum_{k=-\infty}^{+\infty} \sum_{k'=-\infty}^{+\infty} \sum_{k''=-\infty}^{+\infty} \frac{Z - k''}{R_{kk'k''}} \frac{\partial U}{\partial R} \bigg|_{R_{ijkk'k''}} \tag{25}$$

The main implication of Eqs. (19), (22) and (23) is that the infinite set of particles and the consequently infinite set of pairwise interactions can be represented exactly by a *finite* set of $N(N-1)/2$ interactions provided one adopts the *modified* force functions given by Eqs. (20), (24) and (25) to describe the forces between two particles at a normalized distance (X, Y, Z) apart, instead of their conventional counterparts:

$$F^x(X,Y,Z) = -\frac{1}{L}\frac{X}{R_{000}}\left.\frac{\partial U}{\partial R}\right|_{R_{000}} \tag{26}$$

$$F^y(X,Y,Z) = -\frac{1}{L}\frac{Y}{R_{000}}\left.\frac{\partial U}{\partial R}\right|_{R_{000}} \tag{27}$$

$$F^z(X,Y,Z) = -\frac{1}{L}\frac{Z}{R_{000}}\left.\frac{\partial U}{\partial R}\right|_{R_{000}} \tag{28}$$

Moreover, just like their conventional counterpart, the modified force functions are well-defined functions of X, Y and Z provided the triple infinite summations appearing on the right hand sides of Eqs. (20), (24) and (25) converge to a finite result. This is clearly not the case if X, Y, Z all take integer values: if $X = k_x$, $Y = k_y$ and $Z = k_z$ where k_x, k_y and k_z are given integers, then $R_{k_x,k_y,k_z} = 0$ (*cf.* Eq. (21)). Now, for all physically realistic potential functions $U(\cdot)$, both the potential energy $U(R)$ and the force $\partial U/\partial R$ tend to infinity as $R \to 0$; consequently, the term for $k = k_x$, $k' = k_y$ and $k'' = k_z$ in each of the summations in Eqs. (20), (24) and (25) also goes to infinity. Since all other terms of these summations continue to be finite, the overall result is a singularity in the force components F^x, F^y and F^z. In physical terms, this singularity is simply caused by one of the particles spatially overlapping with the image of a second particle situated k_x, k_y and k_z boxes away in the x, y and z directions respectively. This corresponds to the case of two particles overlapping in space, which is physically impossible.

On the other hand, the triple sums on the right hand sides of (20), (24), (25) converge[1] for all values of X, Y, Z that are not all integer, provided $\partial U/\partial R$ is of order R^{-s} for some $s \geq 2$, *i.e.*, the conventional force decays

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[1] This is a consequence of Properties II and III (*cf.* Sections 4.2 and 4.3) and the fact that the sum $\sum_{k=1}^{+\infty}\sum_{k'=1}^{+\infty}\sum_{k''=1}^{+\infty}(1/(k^2+k'^2+k''^2))$ is bounded.

faster than $1/R^2$ with distance R. Thus, the domain of definition of the modified force function is:

$$\mathbb{D} = \left\{(X,Y,Z)|(X,Y,Z)\in \mathbb{R}^3 \setminus \mathcal{N}^{[3]}\right\} \tag{29}$$

where $\mathcal{N}^{[3]}$ is the set of all integer triplets. Moreover, these functions are continuous and infinitely differentiable over this domain.

As functions varying over 3-dimensional spaces are rather difficult to visualize, we illustrate the above ideas for the case of a 1-dimensional Lennard–Jones potential. In this case, the force acting on particle i is given by the following expression:

$$F_i = \sum_{\substack{j=1\\ \neq i}}^{N} \sum_{k=-\infty}^{+\infty} \left[\frac{48}{(x_i - x_j - kL)^{13}} - \frac{24}{(x_i - x_j - kL)^7}\right] \tag{30}$$

The above can be expressed more conveniently by normalizing the interparticle distances *via* division by L, and using sums involving only non-negative k terms:

$$F_i = \sum_{\substack{j=1\\ \neq i}}^{N} \left\{ \frac{48}{L^{13}} \sum_{k=0}^{+\infty} \left[\frac{1}{(((x_i - x_j)/L) - k)^{13}}\right] + \frac{48(-1)^{13}}{L^{13}} \sum_{k=0}^{+\infty} \left[\frac{1}{(1 - ((x_i - x_j)/L) - k)^{13}}\right] \right.$$
$$\left. - \frac{24}{L^7} \sum_{k=0}^{+\infty} \left[\frac{1}{(((x_i - x_j)/L) - k)^7}\right] - \frac{24(-1)^7}{L^7} \sum_{k=0}^{+\infty} \left[\frac{1}{(1 - ((x_i - x_j)/L) - k)^7}\right] \right\} \tag{31}$$

which can then be written as:

$$F_i = \sum_{\substack{j=1\\ \neq i}}^{N} \left\{ \frac{48}{L^{13}} \left[\zeta^{[13]}(X_{ij}) - \zeta^{[13]}(1 - X_{ij})\right] - \frac{24}{L^7} \left[\zeta^{[7]}(X_{ij}) - \zeta^{[7]}(1 - X_{ij})\right] \right\} \tag{32}$$

Here $\zeta^{[n]}(s)$ represents the generalized Riemann (or Hurwitz) zeta function [15] of order n defined as:

$$\zeta^{[n]}(s) \equiv \sum_{k=0}^{+\infty} \frac{1}{(k+s)^n} \tag{33}$$

which is a well-defined function for all $n > 1$. The modified force function between two particles at a relative distance X apart is then given by:

$$\mathcal{F}(X) \equiv \frac{48}{L^{13}}\left[\zeta^{[13]}(X) - \zeta^{[13]}(1-X)\right] - \frac{24}{L^{7}}\left[\zeta^{[7]}(X) - \zeta^{[7]}(1-X)\right] \qquad (34)$$

which is illustrated graphically in Figure 3. The singularities in this function at all integer values of X are clearly visible. On the other hand, the function is continuous and differentiable everywhere else – including the point $X = 0.5$ (*i.e.*, an interparticle distance of $0.5L$) unlike the force computed by the minimum image convention which exhibits a discontinuity at this point. Finally, we note that unlike conventional force functions, this function does not tend to zero as the interparticle distance tends to ± ∞; instead, it exhibits a natural periodicity. The *physical* reason for this behavior is simple: if particles i and j are at a distance of, say, $25.1L$ apart, then there is an *image* of j at a distance $0.1L$ from i;[2] consequently, the *combined* force

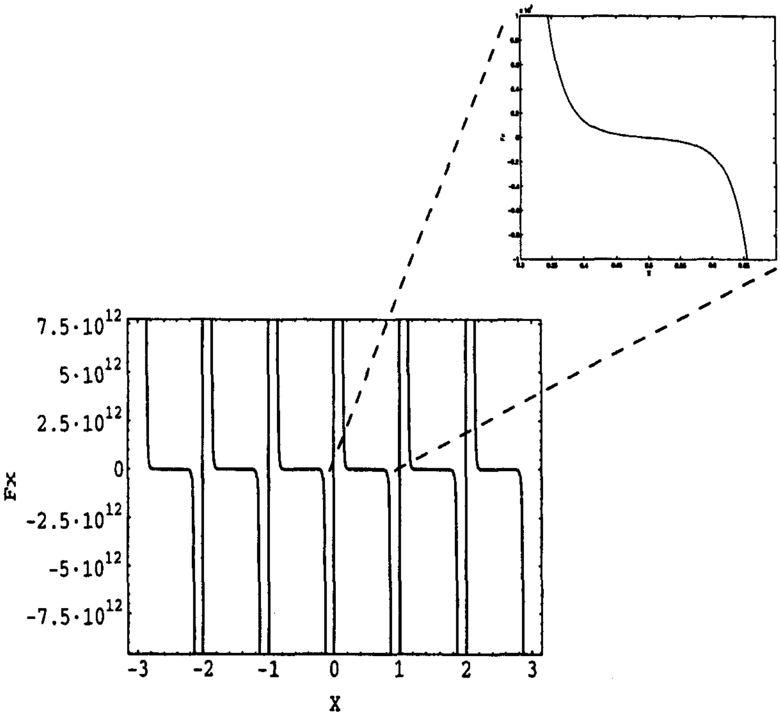

FIGURE 3 1-dimensional interparticle force function ($L = 1$).

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[2] As well as several other images at distances shorter than $25.1L$ on either side of i.

exerted on i by j and all its images is still substantial. Moreover, it is immaterial which of the particles is considered to be the "real" j and which the "images" of this j.

We now proceed to prove formally a number of properties of the modified force functions defined by Eqs. (20), (24), and (25).

4.1. Property I: Invariance Under Integral Shifts

$$\mathcal{F}^x(X-k_x, Y-k_y, Z-k_z) = \mathcal{F}^x(X,Y,Z), \quad \forall\, k_x, k_y, k_z \in \mathbb{Z} \tag{35}$$

Proof From the definition (20):

$$\begin{aligned}&\mathcal{F}^x(X-k_x, Y-k_y, Z-k_z)\\ &\quad\equiv -\frac{1}{L}\sum_{k=-\infty}^{+\infty}\sum_{k'=-\infty}^{+\infty}\sum_{k''=-\infty}^{+\infty}\frac{X-k-k_x}{R_{k+k_x,k'+k_y,k''+k_z}}\frac{\partial U}{\partial R}\bigg|_{R_{ij,k+k_x,k'+k_y,k''+k_z}}\end{aligned} \tag{36}$$

where $R_{k+k_x,k'+k_y,k''+k_z}$ is given by (*cf.* Eq. (21)):

$$R_{k+k_x,k'+k_y,k''+k_z} = \sqrt{(X-k-k_x)^2+(Y-k'-k_y)^2+(Z-k''-k_z)^2} \tag{37}$$

By defining the shifted summation indices:

$$\hat{k} \equiv k + k_x \tag{38}$$

$$\hat{k}' \equiv k' + k_y \tag{39}$$

$$\hat{k}'' \equiv k'' + k_z \tag{40}$$

we can rewrite (36) as:

$$\begin{aligned}&\mathcal{F}^x(X-k_x, Y-k_y, Z-k_z)\\ &\quad= -\frac{1}{L}\sum_{\hat{k}=-\infty+k_x}^{+\infty+k_x}\sum_{\hat{k}'=-\infty+k_y}^{+\infty+k_y}\sum_{\hat{k}''=-\infty+k_z}^{+\infty+k_z}\frac{X-\hat{k}}{R_{\hat{k},\hat{k}',\hat{k}''}}\frac{\partial U}{\partial R}\bigg|_{R_{ij,\hat{k},\hat{k}',\hat{k}''}}\\ &\quad= \mathcal{F}^x(X,Y,Z)\end{aligned} \tag{41}$$

■

The main implication of Property I is that the force function $\mathcal{F}^x(X,Y,Z)$ is naturally periodic in the X, Y and Z directions with a period of 1. There is, therefore, no need for explicitly enforced periodicity conditions designed to keep particles i and j within the reference box. In other words, the particles may be allowed to move freely in space, leaving the reference box within which they were originally positioned. Moreover, the effective force exerted between two particles is *not* a monotonically decreasing function of their distance as the latter goes to infinity. The physical reason for this is that, even if particle j is arbitrarily far away from i, there is still an image of j within distance not exceeding $L/2$ from i.

4.2. Property II: Computation Over a Limited Domain

$$\mathcal{F}^x(X,Y,Z) = \mathcal{F}^x(\Phi(X),\Phi(Y),\Phi(Z)) \tag{42}$$

where the operator $\Phi(X)$ is defined as:

$$\Phi(X) = X - \lfloor X \rfloor \tag{43}$$

where $\lfloor X \rfloor$ is the largest integer number that does not exceed X.

Proof This property is a direct consequence of Property I since $\lfloor X \rfloor$, $\lfloor Y \rfloor$ and $\lfloor Z \rfloor$ are all integers. ■

The main implication of Property II is that, to compute $\mathcal{F}^x(X,Y,Z)$ for *any* X, Y and Z, it is sufficient to be able to compute the function $\mathcal{F}^x(X,Y,Z)$ efficiently over the limited domain $X \in [0,1]$, $Y \in [0,1]$, $Z \in [0,1]$.[3]

4.3. Property III: Further Reduction of the Computational Domain

$$\mathcal{F}^x(1-X,Y,Z) = -\mathcal{F}^x(X,Y,Z) \tag{44}$$

$$\mathcal{F}^x(X,1-Y,Z) = \mathcal{F}^x(X,Y,Z) \tag{45}$$

$$\mathcal{F}^x(X,Y,1-Z) = \mathcal{F}^x(X,Y,Z) \tag{46}$$

Proof Using the definition of the modified force function (20) and the following shifted summation indices:

$$\hat{k} \equiv 1-k; \quad \hat{k}' \equiv k'; \quad \hat{k}'' \equiv k'' \tag{47}$$

---

[3] Excluding the eight points where X, Y and Z are all integer, at which the function $\mathcal{F}^x$ is singular.

we can show that $\mathcal{F}^x(1 - X, Y, Z)$ is given by:

$$\mathcal{F}^x(1 - X, Y, Z) \\ = \frac{1}{L} \sum_{\hat{k}=+\infty+1}^{-\infty+1} \sum_{\hat{k}'=-\infty}^{+\infty} \sum_{\hat{k}''=-\infty}^{+\infty} \frac{X - \hat{k}}{R_{\hat{k},\hat{k}',\hat{k}''}} \frac{\partial U}{\partial R}\bigg|_{R_{ij,\hat{k},\hat{k}',\hat{k}''}} = -\mathcal{F}^x(X, Y, Z) \tag{48}$$

Similarly, by defining the following shifted summation indices:

$$\hat{k} \equiv k; \quad \hat{k}' \equiv 1 - k'; \quad \hat{k}'' \equiv k'' \tag{49}$$

we can show that $\mathcal{F}^x(X, 1 - Y, Z)$ is given by:

$$\mathcal{F}^x(X, 1 - Y, Z) \\ = -\frac{1}{L} \sum_{\hat{k}=-\infty}^{+\infty} \sum_{\hat{k}'=+\infty+1}^{-\infty+1} \sum_{\hat{k}''=-\infty}^{+\infty} \frac{X - k}{R_{\hat{k},\hat{k}',\hat{k}''}} \frac{\partial U}{\partial R}\bigg|_{R_{ij,\hat{k},\hat{k}',\hat{k}''}} = \mathcal{F}^x(X, Y, Z) \tag{50}$$

and the same can be shown for $\mathcal{F}^x(X, Y, 1 - Z)$. ■

Property III, in conjunction with Properties I and II, implies that the domain over which the function $\mathcal{F}^x(X, Y, Z)$ needs to be evaluated can now be further reduced to $X \in [0, 0.5]$, $Y \in [0, 0.5]$, $Z \in [0, 0.5]$.[4] For instance, $\mathcal{F}^x(2.9, -3.4, 0.2) = \mathcal{F}^x(0.9, 0.6, 0.2) = -\mathcal{F}^x(0.1, 0.6, 0.2) = -\mathcal{F}^x(0.1, 0.4, 0.2)$, where we have invoked successively Properties II (Eq. (42)) and III (Eqs. (44) and (45)). In part III of this series of papers, we will exploit this property to develop an efficient scheme for computation of the modified force functions using Hermitian cubic interpolation on an adaptive grid over a finite spatial domain [5].

Properties I–III can also be shown to hold for $\mathcal{F}^y(\cdot)$ and $\mathcal{F}^z(\cdot)$. In addition to the properties that $\mathcal{F}^x(\cdot)$, $\mathcal{F}^y(\cdot)$ and $\mathcal{F}^z(\cdot)$ have on their own, we can also prove some symmetry relations between them, as shown below.

4.4. Property IV: Symmetry Relations Between $\mathcal{F}^x(\cdot)$, $\mathcal{F}^y(\cdot)$ and $\mathcal{F}^z(\cdot)$

$$\mathcal{F}^x(X, Y, Z) = \mathcal{F}^x(X, Z, Y) \tag{51}$$

$$= \mathcal{F}^y(Y, X, Z) \tag{52}$$

$$= \mathcal{F}^y(Y, Z, X) \tag{53}$$

---

[4] Excluding the point $X = Y = Z = 0$ at which the function $\mathcal{F}^x$ is singular.

$$= \mathcal{F}^z(Z, Y, X) \tag{54}$$

$$= \mathcal{F}^z(Z, X, Y) \tag{55}$$

Proof By the definition (20),

$$\mathcal{F}^x(X, Z, Y) = -\frac{1}{L} \sum_{k=-\infty}^{+\infty} \sum_{k'=-\infty}^{+\infty} \sum_{k''=-\infty}^{+\infty} \frac{X-k}{R_{kk'k''}} \frac{\partial U}{\partial R}\bigg|_{R_{ijkk'k''}} = \mathcal{F}^x(X, Y, Z) \tag{56}$$

Equations (53) and (55) can be proven in an analogous manner, showing that similar properties hold for F^y and F^z. Overall, the value of the force in any one of the three coordinates remains unchanged if the interparticle distances in the *other two* coordinates are transposed.

Also, from the definition of $\mathcal{F}^y(\cdot)$ (Eq. (24)), we can write:

$$\mathcal{F}^y(Y, X, Z) = -\frac{1}{L} \sum_{k=-\infty}^{+\infty} \sum_{k'=-\infty}^{+\infty} \sum_{k''=-\infty}^{+\infty} \frac{X-k}{R_{kk'k''}} \frac{\partial U}{\partial R}\bigg|_{R_{ijkk'k''}} = \mathcal{F}^x(X, Y, Z) \tag{57}$$

which proves Eq. (52) above. Equation (54) can be proved in a manner analogous to Eq. (52). ■

The main practical implication of these relations is that, if an efficient procedure is available for the computation of $\mathcal{F}^x(\cdot)$, it can also be used for the computation of $\mathcal{F}^y(\cdot)$ and $\mathcal{F}^z(\cdot)$.

5. COMPARISON OF CONVENTIONAL AND MODIFIED MOLECULAR DYNAMICS FRAMEWORKS

The previous section has introduced modified functions for the computation of pairwise interparticle forces for any continuous and differentiable function $U(r)$ used in the context of molecular dynamics under periodic domain partitioning. These forces have the desirable characteristic that, while considering explicitly only $N(N-1)/2$ interparticle interactions, they take account of an infinite number of such interactions, as is fundamentally consistent with the concept of periodic domain partitioning. Of course, it would appear from Eqs. (20), (24) and (25), that each of these functions would entail an infinite amount of computation. However, it should be remembered that Eqs. (20), (24) and (25) are merely the *definitions* of the force functions and do not necessarily represent the most efficient way of computing them. We shall return to this point in part III of this paper [5].

The previous section has also proved certain mathematical properties of the modified force functions. It is interesting to note that these properties have strong similarities with some aspects of the conventional molecular dynamics technique.

Conventional framework		Modified framework
Periodic boundary conditions	→	Naturally periodic force function (Property I)
Minimum image convention	→	Force evaluation over a limited domain $[0, 0.5L]^3$ (Properties II and III)

In this section, we seek to elucidate the precise relation between the two frameworks through a more formal discussion and also some numerical results.

5.1. The *K*-restricted Modified Molecular Dynamics Framework MOD-K

We start by defining a *K-restricted* modified force function as follows:

$$\mathcal{F}^{x,K}(X,Y,Z) \equiv -\frac{1}{L}\sum_{k=-K}^{K}\sum_{k'=-K}^{K}\sum_{k''=-K}^{K}\frac{X-k}{R_{kk'k''}}\frac{\partial U}{\partial R}\bigg|_{R_{ijkk'k''}} \tag{58}$$

We note that, in the limit $K \to \infty$, Eq. (58) is equivalent to the modified force function (20):

$$\lim_{K\to\infty}\mathcal{F}^{x,K}(X,Y,Z) = \mathcal{F}^{x}(X,Y,Z) \tag{59}$$

We now consider a modified molecular dynamics framework with the following characteristics:

1. We use the *K*-restricted modified force function to compute interparticle forces.
2. We allow the particles to move freely in 3-dimensional space without enforcing any periodic boundary conditions.
3. We employ the following properties of the modified force function to express the force between the two particles at *any* distance (X, Y, Z) in terms of a force computed in the domain $[0, 0.5]^3$:

$$\mathcal{F}^{x}(X-\lfloor X\rfloor, Y-\lfloor Y\rfloor, Z-\lfloor Z\rfloor) = \mathcal{F}^{x}(X,Y,Z) \tag{60}$$

$$\mathcal{F}^x(1-X,Y,Z) = -\mathcal{F}^x(X,Y,Z) \tag{61}$$

$$\mathcal{F}^x(X,1-Y,Z) = \mathcal{F}^x(X,Y,Z) \tag{62}$$

$$\mathcal{F}^x(X,Y,1-Z) = \mathcal{F}^x(X,Y,Z) \tag{63}$$

and similarly for $\mathcal{F}^y$ and $\mathcal{F}^z$.

We call this type of molecular dynamics computation the MOD-K framework.

5.2. Equivalence Between the Conventional and MOD-0 Molecular Dynamics Frameworks

Consider now a system of two particles i and j as illustrated in Figure 4. Figure 4(a) represents the conventional molecular dynamics framework (CON framework) according to which, if either of the particles reaches a face of the central box moving outwards, then it is immediately transposed to the corresponding position on the opposite face (periodic boundary conditions). Moreover, if the distance between i and j in any coordinate $\gamma \in \{x, y, z\}$ exceeds $L/2$ (*i.e.*, $|\gamma_i - \gamma_j| > L/2$), then the force exerted on i by j in this coordinate is that which would be exerted on i by an image of j at a distance $L - |\gamma_i - \gamma_j|$ in the *opposite* direction (minimum image convention).

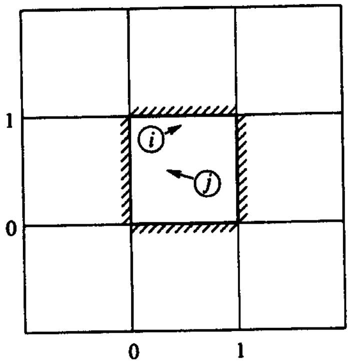
Consider now the special case of the MOD-K framework with $K=0$. In this case, the particles are still allowed to move freely in space (as shown in Fig. 4(b)), and the force between them is computed *via* Eq. (58), which now simply becomes:

$$\mathcal{F}^{x,0}(\hat{X},\hat{Y},\hat{Z}) = -\frac{1}{L}\frac{\hat{X}}{\hat{R}_{000}}\frac{\partial U}{\partial R}\bigg|_{\hat{R}_{000}} \tag{64}$$

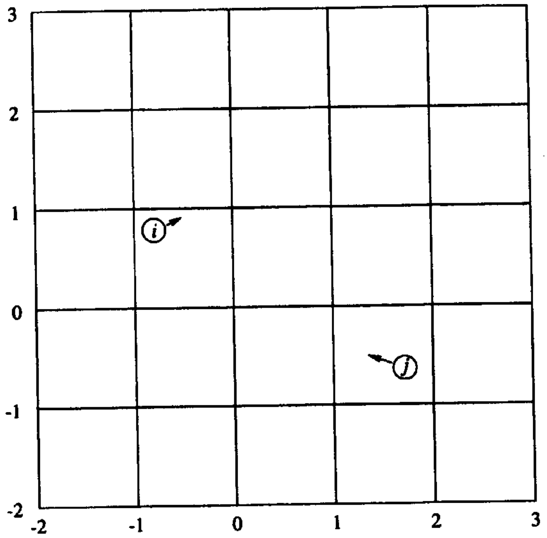
after we have applied properties (60)–(63) to ensure that $(\hat{X},\hat{Y},\hat{Z}) \in [0, 0.5]^3$. We call this type of molecular dynamics computation the MOD-0 framework.

We now introduce certain definitions that will facilitate the comparison between the CON and MOD-0 frameworks.

DEFINITION 1 Projection onto the central box.



(a) Conventional



(b) Modified

FIGURE 4 Conventional *vs.* modified molecular dynamics frameworks.

Given the position $(x, y, z) \in \mathbb{R}^3$ of a particle, the projected positions of the particle onto the central box is given by $(\Pi(x), \Pi(y), \Pi(z))$ where the projection operator $\Pi(\cdot)$ is defined as:

$$\Pi(x) \equiv x - \left\lfloor \frac{x}{L} \right\rfloor L \quad \in [0, L) \qquad (65)$$

DEFINITION 2 Conformance of particle configurations in the CON and MOD-0 frameworks.

Let the positions of particles i and j in the CON framework be defined by (x_k, y_k, z_k), $k = i,j$ and their velocities by (v_k^x, v_k^y, v_k^z), $k = i,j$. Let the corresponding positions and velocities in the MOD-0 framework be denoted by, respectively, $(\tilde{x}_k, \tilde{y}_k, \tilde{z}_k)$ and $(\tilde{v}_k^x, \tilde{v}_k^y, \tilde{v}_k^z)$, $k = i,j$. Then the two configurations are said to be *conformant* if the following conditions hold:

$$\Pi(\tilde{\gamma}_k) = \gamma_k, \quad \gamma \in \{x, y, z\}, \quad k = i,j \tag{66}$$

$$\tilde{v}_k^\gamma = v_k^\gamma, \quad \gamma \in \{x, y, z\}, \quad k = i,j \tag{67}$$

For example, it can be verified that the configurations in Figures 4(a) and (b) are conformant: if we project the particles i and j in Figure 4(b) onto the central box (*i.e.*, the one whose bottom left corner is at the origin $(0, 0)$), we will find that the projections are at identical positions to those shown in Figure 4(a). Moreover, the velocities of i and j are the same in both Figures 4(a) and (b).

With the above definitions in place, it is possible to prove [16] the following theorems:

THEOREM 1 *If the particle configurations in the CON and MOD-*0 *frameworks are conformant, then the interparticle forces in the two frameworks are equal.*

THEOREM 2 *Suppose that the particle configurations in the CON and MOD-*0 *frameworks are conformant at time $t = 0$. Then, they will be conformant at all subsequent times $t > 0$.*

Theorem 2 is interesting in that it shows that conventional molecular dynamics simulations with periodic boundary conditions and the minimum image convention can, in fact, be derived from our modified molecular dynamics framework using the K-restricted force with $K = 0$. However, it is worth noting that the manipulations defined by Eqs. (60)–(63) for the computation of forces are not actually mathematically valid properties of the K-restricted modified force function defined by Eq. (58) for any finite K: their derivation in Sections 4.1 – 4.4 made use of the *infinite* nature of the summations in the force definition (20). Hence, leaving aside any computational issues, the theoretical basis of the conventional framework is not as sound as that of the modified framework.

5.3. Numerical Experiments

Here we consider the molecular dynamics of a system of 256 argon atoms at a density of 39,960 mol/m^3 and energy of -3397 J/mol. The standard Lennard–Jones potential, with $\varepsilon = 119.8$ K and $\sigma = 3.405$ Å, was used for these computations. The simulation was performed over a period of 22 ps, and the averaging of system properties was carried out during the second half of the run. A Verlet leap-frog integration method [17] with a fixed time step of 2 fs was used for the solution of the equations of motion. The energy of the system was conserved within $\pm 2 \times 10^{-3}$%. A typical set of results obtained is shown in Table II.

As expected from the theoretical analysis of Section 5.2, the MOD-0 framework yields results that are identical to those of CON.

It is also interesting to assess the effect of the system size on the calculation of the system properties. Table III indicates that the MOD-10 framework with 256 particles can achieve the same quality of results as the conventional framework with 10976 particles. In fact, results of the correct order of magnitude are also obtained by the MOD-10 framework even with 108 particles; this is certainly not the case with the conventional approach. Of course, these observations are of rather theoretical interest: the computations of the K-restricted modified force function using the expression given by Eq. (58) for $K = 10$ involves the evaluation and summation of $9261 (= (2 \times 10 + 1)^3)$ terms as opposed to the single term in the conventional force function (*cf.* Eq. (26)). Therefore, assuming that the complexity of molecular dynamics computations increases proportionally to the square of the number of particles in the system, it would then be fairer to compare the MOD-10 framework with a conventional one involving about 100 ($\simeq \sqrt{9261}$) times more particles. We will return to address these concerns in part III of this paper [5].

Table III also lists the difference between the CON and MOD-K predictions for various properties of interest. We note that this difference

TABLE II Simulation results in the modified framework

System properties:	*U (J/mol)*	*T (K)*	*P (MPa)*
CON framework	−5553.0	172.8	351.8
MOD-0 framework	−5553.0	172.8	351.8
MOD-1 framework	−5616.1	177.9	356.7
MOD-2 framework	−5600.3	176.7	362.1
MOD-3 framework	−5611.7	177.6	360.0
MOD-4 framework	−5611.4	177.6	360.1
MOD-5 framework	−5617.9	178.1	358.5
MOD-10 framework	−5606.3	177.2	359.8

TABLE III Comparison of effects of system size in the conventional and modified frameworks

		U (J/mol)			*T(K)*			*P(MPa)*		
N	*L*(Å)	*CON*	*MOD*-10	*Difference*	*CON*	*MOD*-10	*Difference*	*CON*	*MOD*-10	*Difference*
256	22	−5553.0	−5606.3	−53.3	172.8	177.2	4.4	351.8	359.8	8.0
108	16	−5499.5	−5634.7	−135.2	168.5	179.4	10.9	333.7	353.4	19.7
32	11	−5259.8	−5922.3	−662.5	149.2	202.5	53.3	255.7	291.9	36.2
10976	77	−5613.0			177.6			359.0		

decreases with increasing number of particles and, consequently, increasing box size L. This is to be expected: as L becomes larger, the contributions to the force function (58) of interactions between particles that are in *different* boxes becomes less significant. Hence, the central term (*i.e.*, the one corresponding to $k = k' = k'' = 0$) becomes the dominant one, and Eq. (58) effectively reduces to the conventional force function.

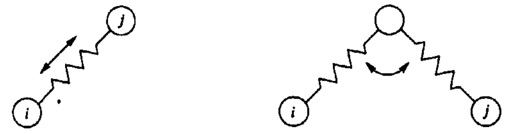
The above observations suggest an alternative view of the force modifications introduced in this paper as a theoretically rigorous and consistent "long-range correction" [6] applied to the conventional molecular dynamics framework.

6. FLEXIBLE MOLECULES

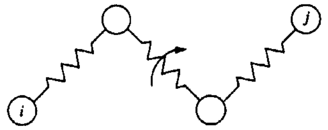
So far in this paper, we have assumed that a single functional form can be used to describe the forces exerted on a particle i by a particle j and all the images of j, this force function being derived from a single interparticle potential function U which solely depends on an interparticle distance r. These assumptions can be justified for systems involving monoatomic molecules of a single species. However, for molecules involving multiple atoms, the existence of chemical bonds may imply that the force exerted on a particle i by a particle j within the same molecule may be of a different nature to that exerted on i by an image of j. Moreover, if the system under consideration involves a mixture of different molecules and/or if the atoms in a molecule are not all identical, then the interactions between different atom pairs may be different. Here we extend the methodology developed in previous sections to consider mixtures of general flexible molecules, and illustrate the ideas presented on the example of the NERD force field [18].

Consider a set of N interacting particles. The nature of the interaction between two particles in the same molecule may be different to that between particles in different molecules. For example, as illustrated in Figure 5, such interactions may be ascribed to bond stretching, bending or torsion. We call these *bonded interactions*.

Let the subset of particles in the system that are involved in bonded interactions with particle i be denoted by $\mathcal{B}_i$. We note that $\mathcal{B}_i$ does not necessarily include all particles in the same molecule as particle i: some of these particles may be too far removed from i for bonding to exert any influence.



(a)Bond stretching (b) Bond bending



(c) Bond torsion

FIGURE 5 Different types of bonded interactions.

The force exerted on particle i comprises three distinct contributions:

1. The force exerted on i due to its bonded interactions with particles $j \in \mathcal{B}_i$ within the same molecule.
2. The force exerted on i due to non-bonded interactions with all the images of particles $j \in \mathcal{B}_i$.
3. The force exerted on particle i due to non-bonded interactions with particles $j \notin \mathcal{B}_i$ and all their images.[5]

This is expressed mathematically as:

$$\begin{aligned} F_i^{\gamma} &= F_i^{\mathrm{B},\gamma}(\mathbf{r}_i; \mathbf{r}_j, j \in \mathcal{B}_i; \vartheta^{\mathrm{B}}_{\mathcal{T}_i}) \\ &+ \sum_{j \in \mathcal{B}_i} \sum_{\substack{k,k',k'' \\ \neq (0,0,0)}} F_{ij}^{\mathrm{NB},\gamma}(x_i - x_j - kL, y_i - y_j - k'L, z_i - z_j - k''L) \\ &+ \sum_{\substack{j \notin \mathcal{B}_i \\ j \neq i}} \sum_{k,k',k''} F_{ij}^{\mathrm{NB},\gamma}(x_i - x_j - kL, y_i - y_j - k'L, z_i - z_j - k''L) \\ & \qquad \forall \gamma \in \{x, y, z\} \end{aligned} \tag{68}$$

where the three terms on the right hand side correspond to the three contributions listed above. In particular, $F_i^{\mathrm{B},\gamma}$ is the force exerted on particle i in coordinate direction $\gamma \in \{x, y, z\}$ due to bonded interactions. The above

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[5] Although strictly speaking $i \notin \mathcal{B}_i$, it is not necessary to account for the influence on i by its own images since these always cancel out (*cf.* Section 4).

equations makes use of the summation operator definition:

$$\sum_{\substack{k,k',k'' \\ \neq(0,0,0)}} w(k,k',k'') \equiv \sum_{k=-\infty}^{+\infty} \sum_{k'=-\infty}^{+\infty} \sum_{k''=-\infty}^{+\infty} w(k,k',k'') - w(0,0,0)$$

where $w(k,k',k'')$ denotes any function of the indices k,k',k''.

6.1. Bonded Interaction Forces

The force $F_i^{\mathrm{B},\gamma}$ is a function of the position of i and the positions of *all* particles $j \in \mathcal{B}_i$. In general, it cannot be expressed as a sum of independent interactions between i and each of the particles j. Moreover, the exact form of this force function may depend on the identity of i (*e.g.*, its position within the molecule).

The bonded interaction force also depends on the set of potential parameters ϑ^{B}. In principle, one could assume that there is a different set of such parameters for each particle i. However, more realistically, the bonded interactions experienced by all particles at identical positions in identical molecules will be the same. In fact, even wider generalizations are often made: for instance, the NERD force field (see Section 6.4) assumes that the bonded interactions experienced by all methylene and methyl groups in all linear alkane molecules can be described by a single set of potential parameters. In order to take the above consideration into account, we introduce the notion of a *category* τ of bonded interactions.

In general, a category τ of bonded interactions is a collection of various *forms* of such interactions (*e.g.*, stretching, bending, torsion) described by a set of parameters $\vartheta_\tau^{\mathrm{B}}$. Each particle i in the system belongs to one such category, denoted by τ_i. The number of *distinct* categories τ of bonded interactions in any particular system under consideration will usually be much smaller than the number of particles, N. For instance, in the case of the NERD framework, there is just one category of interactions that adequately describes *all* linear alkane molecules.

6.2. Non-bonded Interaction Forces

The second type of force function appearing in Eq. (68) is the non-bonded force F^{NB}. More specifically, $F_{ij}^{\mathrm{NB},\gamma}(x_i - x_j, y_i - y_j, z_i - z_j)$ is the force exerted on particle i in coordinate direction γ by another particle j due to non-bonded interactions. The subscripts ij on F^{NB} indicate the fact that the form of the force function may depend on the type of particles i and j under consideration. In particular, F_{ij}^{NB} may be obtained from a potential energy function U_{ij}^{NB} describing non-bonded interactions between particles i and j:

$$F_{ij}^{\mathrm{NB},\gamma} = -\frac{\partial U_{ij}^{\mathrm{NB}}}{\partial \gamma_i} \tag{69}$$

6.3. The Bond Correction Function

If we compare the form of Eq. (68) for polyatomic molecules with that for monoatomic ones (*cf.* Eq. (15)), we can see that the two can be made more consistent if we rewrite Eq. (68) in the form:

$$F_i^{\gamma} = \sum_{\substack{j=1 \\ \neq i}}^{N} \mathcal{F}_{ij}^{\gamma}(X_{ij}, Y_{ij}, Z_{ij}) + \Delta F_i^{\mathrm{B},\gamma}(\mathbf{r}_i; \mathbf{r}_j, j \in \mathcal{B}_i, \vartheta_{\tau_i}^{\mathrm{B}}) \quad \forall \gamma \in \{x, y, z\} \tag{70}$$

Here we have introduced the quantity $\Delta F_i^{\mathrm{B},\gamma}$ defined as:

$$\begin{aligned} &\Delta F_i^{\mathrm{B},\gamma}(\mathbf{r}_i; \mathbf{r}_j, j \in \mathcal{B}_i) \\ &\quad \equiv F_i^{\mathrm{B},\gamma}(\mathbf{r}_i; \mathbf{r}_j; j \in \mathcal{B}_i) \\ &\quad - \sum_{j \in \mathcal{B}_i} F_{ij}^{\mathrm{NB},\gamma}(x_i - x_j, y_i - y_j, z_i - z_j) \quad \forall \gamma \in \{x, y, z\} \end{aligned} \tag{71}$$

Thus, $\Delta F_i^{\mathrm{B},\gamma}$ is the force exerted on particle i due to its bonded interactions with particles $j \in \mathcal{B}_i$ reduced by the forces that particles j would have exerted on i, had they interacted in a non-bonded fashion with it. In other words, $\Delta F_i^{\mathrm{B},\gamma}$ can be viewed as a correction applied to the effective force exerted on particle i to take account of the effects of chemical bonding.

The function $\mathcal{F}_{ij}^{\gamma}(\cdot)$ appearing in (70) is essentially the modified force function (*cf.* Eqs. (20), (24), (25)) given by:

$$\mathcal{F}_{ij}^{\gamma}(X, Y, Z) = -\frac{1}{L} \sum_{k=-\infty}^{+\infty} \sum_{k'=-\infty}^{+\infty} \sum_{k''=-\infty}^{+\infty} \frac{(\gamma_i - \gamma_j)/L - k}{R_{kk'k''}} \frac{\partial U_{ij}^{\mathrm{NB}}}{\partial R}\bigg|_{R_{ijkk'k''}} \tag{72}$$

Thus, the advantage of (70) over (68) is that the former is expressed in terms of force functions that possess all the theoretical properties proven in Section 4, which has important implications regarding the efficiency of their computation [5].

6.4. The NERD Potential Framework

To illustrate the ideas presented in this section, we consider the dynamics of systems of flexible molecules involving bond stretching, bending and torsion in addition to other non-bonded interactions. In particular, we examine the case of flexible alkane molecules interacting *via* the NERD force field [18]. The potential energy functions are given by the following expressions:

Bond stretching potential

$$U^{\mathrm{S}}(d) = k_b \frac{k_d}{2}(d - d_0)^2 \tag{73}$$

where k_b is Boltzmann's constant, k_d is the bond stretching parameter, d is the distance between the two bonded particles, and d_0 is the corresponding equilibrium bond length.

Bond bending potential

$$U^{\mathrm{B}}(\theta) = k_b \frac{k_\theta}{2}(\theta - \theta_0)^2 \tag{74}$$

where k_θ is the bond bending parameter, θ is the angle formed by three successive atom sites, and θ_0 is the equilibrium covalent angle.

Torsional potential

$$U^{\mathrm{T}}(\phi) = k_b(V_0 + V_1(1 + \cos\phi) + V_2(1 - \cos 2\phi) + V_3(1 + \cos 3\phi)) \tag{75}$$

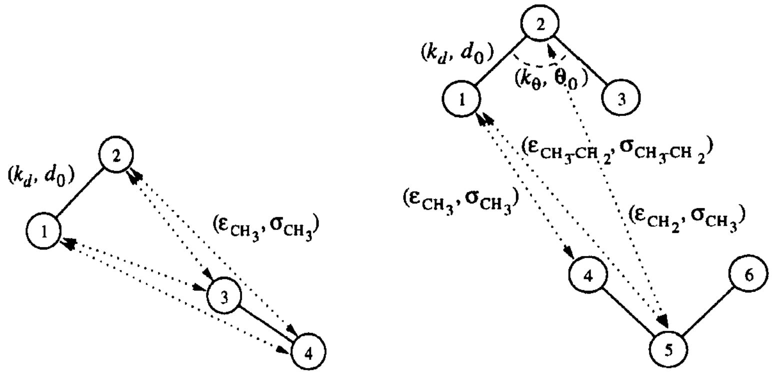
where V_0, V_1, V_2, V_3 are the torsional interaction parameters and ϕ is the torsional angle formed by four successive atoms.

Non-bonded potential
This is given by a standard Lennard–Jones potential of the form:

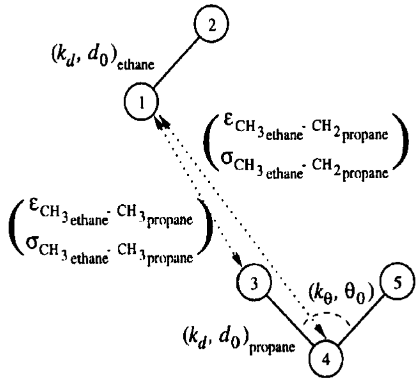
$$U^{\mathrm{NB}}(r) = 4k_b\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right] \tag{76}$$

where ε and σ are the energy and distance parameters respectively. The parameters describing the interactions between unlike sites in different molecules are obtained using the Lorentz–Berthelot mixing rules.

We start with the example of ethane (see Fig. 6(a)) where the only bonded interaction is that due to the bond stretching potential, U^{S}. The non-bonded interactions U^{NB} are described by the Lennard–Jones potential.



(a) Ethane (b) Propane



(c) Ethane and propane

FIGURE 6 Interacting alkane molecules.

Considering particle 1 in Figure 6(a), we identify that the set of particles with which it has bonded interactions is simply:

$$\mathcal{B}_1 = \{2\} \tag{77}$$

The force on particle 1 due to bond stretching is given by:

$$F_1^{\mathrm{B},\gamma} = -\frac{\partial U^{\mathrm{S}}}{\partial \gamma_1} = -k_b k_d \frac{d_{12} - d_0}{d_{12}} (\gamma_1 - \gamma_2) \quad \forall \gamma \in \{x, y, z\} \tag{78}$$

where d_{12} is the distance between particles 1 and 2. The bonding correction function (*cf.* Eq. (71)) is given by the difference of Eq. (78) and the corresponding non-bonded force:

$$\Delta F_1^{\mathrm{B},\gamma} = -k_b k_d \frac{d_{12}-d_0}{d_{12}}(\gamma_1-\gamma_2) \\ -\frac{24k_b\varepsilon}{d_{12}^2}\left[2\left(\frac{\sigma}{d_{12}}\right)^{12}-\left(\frac{\sigma}{d_{12}}\right)^{6}\right](\gamma_1-\gamma_2) \quad \forall\gamma\in\{x,y,z\} \tag{79}$$

In the case of propane (see Fig. 6(b)), the bonded interactions are due both to the bond stretching potential, U^{S}, and to the bond bending potential, U^{B}. Considering particle 1 (one of the methyl groups) in Figure 6(b), we identify the set of particles with which it has bonded interactions to be:

$$\mathcal{B}_1 = \{2,3\} \tag{80}$$

The force exerted on particle 1 due to bonding interactions is given by:

$$\begin{aligned} F_1^{\mathrm{B},\gamma} &= -\frac{\partial U^{\mathrm{S}}}{\partial\gamma_1}-\frac{\partial U^{\mathrm{B}}}{\partial\gamma_1} \\ &= -k_b k_d \frac{d_{12}-d_0}{d_{12}}(\gamma_1-\gamma_2) \\ &\quad + k_b k_\theta \frac{\theta-\theta_0}{\sin\theta}(C_{12,12}C_{23,23})^{-0.5}((C_{12,23}/C_{12,12})(\gamma_1-\gamma_2)-(\gamma_2-\gamma_3)) \\ &\qquad \forall\gamma\in\{x,y,z\} \end{aligned} \tag{81}$$

where we have defined:

$$C_{ij,kl} = C_{kl,ij} = (\mathbf{r}_i-\mathbf{r}_j)^T(\mathbf{r}_k-\mathbf{r}_l) \tag{82}$$

and the angle θ is given by:

$$\cos\theta = C_{12,23}(C_{12,12}C_{23,23})^{-1/2} \tag{83}$$

Hence, the bonding correction function for particle 1 is given by:

$$\Delta F_1^{\mathrm{B},\gamma} = -k_b k_d \frac{d_{12}-d_0}{d_{12}}(\gamma_1-\gamma_2) \\ + k_b k_\theta \frac{\theta-\theta_0}{\sin\theta}(C_{12,12}C_{23,23})^{-0.5}((C_{12,23}/C_{12,12})(\gamma_1-\gamma_2)-(\gamma_2-\gamma_3))$$

$$
\begin{aligned}
&-\frac{24k_b\varepsilon_{\mathrm{CH_2,CH_3}}}{d_{12}^2}\left[2\left(\frac{\sigma_{\mathrm{CH_2,CH_3}}}{d_{12}}\right)^{12}-\left(\frac{\sigma_{\mathrm{CH_2,CH_3}}}{d_{12}}\right)^{6}\right](\gamma_1-\gamma_2)\\
&-\frac{24k_b\varepsilon_{\mathrm{CH_2,CH_3}}}{d_{13}^2}\left[2\left(\frac{\sigma_{\mathrm{CH_2,CH_3}}}{d_{13}}\right)^{12}-\left(\frac{\sigma_{\mathrm{CH_2,CH_3}}}{d_{13}}\right)^{6}\right](\gamma_1-\gamma_3)\\
&\qquad\qquad\forall\gamma\in\{x,y,z\}
\end{aligned}
\tag{84}
$$

Expressions for particle 3 are exactly symmetrical to those of particle 1, where the set of bonded particles is $\mathcal{B}_3=\{1,2\}$. On the other hand, considering particle 2 (one of the methylene groups) in Figure 6(b), we identify the following:

$$\mathcal{B}_2=\{1,3\} \tag{85}$$

and, consequently:

$$
\begin{aligned}
F_2^{\mathrm{B},\gamma}&=-\frac{\partial U^{\mathrm{S}}}{\partial\gamma_2}-\frac{\partial U^{\mathrm{B}}}{\partial\gamma_2}\\
&=k_bk_d\left[\frac{d_{12}-d_0}{d_{12}}(\gamma_1-\gamma_2)-\frac{d_{23}-d_0}{d_{23}}(\gamma_2-\gamma_3)\right]\\
&\quad+k_bk_\theta\frac{\theta-\theta_0}{\sin\theta}(C_{12,12}C_{23,23})^{-0.5}\\
&\quad\times[(C_{12,23}/C_{23,23})(\gamma_2-\gamma_3)-(C_{12,23}/C_{12,12})(\gamma_1-\gamma_2)\\
&\qquad+(\gamma_2-\gamma_3)-(\gamma_1-\gamma_2)]\quad\forall\gamma\in\{x,y,z\}
\end{aligned}
\tag{86}
$$

$$
\begin{aligned}
\Delta F_2^{\mathrm{B},\gamma}&=k_bk_d\left[\frac{d_{12}-d_0}{d_{12}}(\gamma_1-\gamma_2)-\frac{d_{23}-d_0}{d_{23}}(\gamma_2-\gamma_3)\right]\\
&\quad+k_bk_\theta\frac{\theta-\theta_0}{\sin\theta}(C_{12,12}C_{23,23})^{-0.5}\\
&\quad\times[(C_{12,23}/C_{23,23})(\gamma_2-\gamma_3)-(C_{12,23}/C_{12,12})(\gamma_1-\gamma_2)\\
&\qquad+(\gamma_2-\gamma_3)-(\gamma_1-\gamma_2)]\\
&\quad+\frac{24k_b\varepsilon_{\mathrm{CH_2,CH_3}}}{d_{12}^2}\left[2\left(\frac{\sigma_{\mathrm{CH_2,CH_3}}}{d_{12}}\right)^{12}-\left(\frac{\sigma_{\mathrm{CH_2,CH_3}}}{d_{12}}\right)^{6}\right](\gamma_1-\gamma_2)\\
&\quad-\frac{24k_b\varepsilon_{\mathrm{CH_2,CH_3}}}{d_{23}^2}\left[2\left(\frac{\sigma_{\mathrm{CH_2,CH_3}}}{d_{23}}\right)^{12}-\left(\frac{\sigma_{\mathrm{CH_2,CH_3}}}{d_{23}}\right)^{6}\right](\gamma_2-\gamma_3)\\
&\qquad\qquad\forall\gamma\in\{x,y,z\}
\end{aligned}
\tag{87}
$$

Figures 6(a) and (b) show the types of interactions involved in the simulation of pure component ethane and propane fluids respectively. The mixtures of these fluids also need to account for interactions between molecules of ethane and propane, as illustrated in Figure 6(c).

We note that, as far as bonded interactions are concerned, the forces exerted on the individual particles in the mixture are exactly the same as those exerted on them in the pure component cases. Thus, the bonding correction function for methyl groups in ethane and propane molecules is given by Eqs. (79) and (84) respectively. For methylene groups in propane molecules, the bonding correction function is still given by Eq. (87). As far as non-bonded interactions are concerned, the interactions between two groups in different molecules depend both on the nature of the two groups (*i.e.*, methyl or methylene) and on that of the molecules (*i.e.*, ethane and propane), which can be accounted for by applying suitable mixing rules (*e.g.*, Lorentz–Berthelot).

Similar expressions can be derived [16] for butane and higher order alkanes that additionally exhibit torsional effects.

7. CONCLUDING REMARKS

The molecular dynamics framework presented in this paper takes account of interactions of each particle in a reference box with *all* the particles in *all* the boxes surrounding it. In this sense, it is similar to the Ewald summation technique [19] which has been used to deal with long-range (Coulomb) electrostatic interactions. In this case, the infinite summation of the force interactions is expressed as the sum of two rapidly converging series in real (direct) and reciprocal (Fourier) space form [20]. Here, we have considered *general* potential functions for non-bonded interactions, showing that it is possible to describe an infinitely replicated system in terms of a finite number of pairwise interactions, each involving modified interparticle force functions.

The key point is that, given any two particles, the forces between them are well-defined, finite mathematical functions that, just like the forces in conventional molecular dynamics, depend only on the relative particle positions. However, unlike the case of conventional molecular dynamics, these force functions are continuous and differentiable for all interparticle distances except for a set of values corresponding to physically impossible situations (*i.e.*, the two particles essentially occupying the same position in space). Finally, the force functions are naturally periodic. Therefore, the force between two particles is identical to that between any two images of these particles; thus, there is no need to confine the N particles under consideration to remain within any given spatial boundary *via* the imposition of artificial periodic boundary conditions.

The modified force functions (20), (24) and (25) are more complex than their conventional counterparts which effectively correspond to just the central term (*i.e.*, for $k = k' = k'' = 0$) of the triple summations in these expressions. However, the properties of the modified force functions imply that efficient and accurate evaluation procedures are necessary *only* over a cube with side length 0.5, irrespective of the actual values that their arguments X, Y, Z may take during a simulation. We can exploit this to develop an efficient scheme for computation of the modified force functions using Hermitian cubic interpolation on an adaptive grid over a finite spatial domain, as described in part III of this paper [5].

By introducing the notion of a category of bonded interactions and suitable non-bonded parameter mixing rules, we can describe flexible molecules and their interactions in a rigorous and compact manner. It has been shown that only a minor modification to the modified molecular dynamics framework introduced in Section 4 is required to account for the existence of chemical bonds; this is achieved by applying a bond correction function to the modified force function $\mathcal{F}$.

The Newtonian equations of motion (Eq. (1)) making use of these modified force functions define a continuous system of ordinary differential equations. It is now feasible to consider rigorous ways for the computation of the gradients of the mapping $\mathcal{P}(q, \vartheta)$ (*cf.* Eq. (5)) with respect to the variables q and the parameters ϑ. We present these formulations in part II of this paper [4].

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