General formulation of pressure and stress tensor for arbitrary many-body interaction potentials under periodic boundary conditions

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Three distinct forms are derived for the force virial contribution to the pressure and stress tensor of a collection of atoms interacting under periodic boundary conditions. All three forms are written in terms of forces acting on atoms, and so are valid for arbitrary many-body interatomic potentials. All three forms are mathematically equivalent. In the special case of atoms interacting with pair potentials, they reduce to previously published forms. (i) The atom-cell form is similar to the standard expression for the virial for a finite nonperiodic system, but with an explicit correction for interactions with periodic images. (ii) The atom form is particularly suited to implementation in modern molecular dynamics simulation codes using spatial decomposition parallel algorithms. (iii) The group form of the virial allows the contributions to the virial to be assigned to individual atoms. © *2009 American Institute of Physics*. [doi:10.1063/1.3245303]

I. INTRODUCTION

Molecular dynamics (MD) simulation is an extremely popular and widely used method to provide an atomic-level description of the physical and chemical properties and processes of diverse materials. Simulations within the isothermal-isobaric (*NPT*) ensemble are particularly useful when complementing experimental observations at known temperatures and pressures. Thus, it is important that the thermodynamic quantity of pressure be accurately calculated during such simulations. Two expressions for the calculation of pressure have been used for decades.[1,2] However, as recently pointed out by Louwerse and Baerends,[3] one of these expressions applies only to nonperiodic cells, while the other is specific to pair potentials. The purpose of this paper is to provide generalizations of these two expressions that apply to periodic systems with arbitrary interatomic potentials. The expressions are formulated in terms of force contributions to atoms, and so are independent of the details of the interaction potential. This is particularly useful when implementing interatomic potentials involving complex many-body interactions. Each of the forms has its own advantages and disadvantages, but they are mathematically equivalent. It should be noted that several methods have been developed for computing the pressure via finite expansion or contraction of the periodic cell vectors. These methods can be used with arbitrary interatomic potentials. However, like all finite difference methods, they are not exact.[4]

In Sec. II we review the derivations of the standard forms for the virial for nonperiodic systems and for pair potentials under periodic boundary conditions. In Sec. III we derive new general virial forms for arbitrary many-body potentials under periodic boundary conditions. In Sec. IV we demonstrate that all of these forms agree with each other to machine accuracy.

II. STANDARD EXPRESSIONS FOR THE VIRIAL

The macroscopic pressure P of a set of N interacting atoms contained in a volume V can be derived in a number of ways, including continuum mechanics, classical mechanics, and statistical mechanics.[5,6] All of these derivations result in the following well-established relation:

$$P = \frac{Nk_BT}{V} + \frac{\langle W \rangle}{3V}, \tag{1}$$

where T is the temperature, k_B is Boltzmann's constant, and U is the potential energy due to interactions between the atoms. The angle brackets in the second term denote an appropriate ensemble average of the internal virial W, which represents the contribution to the total virial due to forces acting between the atoms. It is defined by the following relation:

$$W(\mathbf{r}^N) = -3V\frac{dU}{dV}. \tag{2}$$

The virial, like the forces and potential energy, depends only on the instantaneous atom positions $\mathbf{r}^N = \mathbf{r}_1, \ldots, \mathbf{r}_N$ and the interactions between them. It is an extensive quantity and represents the contribution of the interaction potential to the pressure. The calculation of pressure requires that the virial be correctly sampled during the course of the simulation.

We consider first the case of a finite nonperiodic system of N atoms interacting with some interaction potential func-

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tion $U(\mathbf{r}^N)$. The atoms are confined to a volume V by a container which exerts external forces on the atoms. In computing the volume derivative, we assume that volume change occurs via a homogeneous affine expansion or contraction of all the atom positions so that

$$\frac{d\mathbf{r}_i}{dV} = \frac{\mathbf{r}_i}{3V}. \tag{3}$$

Applying the chain rule to Eq. (2) and substituting in from Eq. (3) yields a particularly simple expression for the virial,

$$W(\mathbf{r}^N) = \sum_{i=1}^{N} \mathbf{r}_i \cdot \mathbf{F}_i, \tag{4}$$

where $\mathbf{F}_i$ is the total force acting on the ith atom due to interactions with other atoms,

$$\mathbf{F}_i = -\frac{d}{d\mathbf{r}_i} U(\mathbf{r}^N). \tag{5}$$

In the case of a pair potential $u(r)$, the potential energy function has the form

$$U(\mathbf{r}^N) = \sum_{i=1}^{N} \sum_{j>1}^{N} u(r_{ij}), \quad r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|. \tag{6}$$

Substituting this expression in Eq. (4) yields

$$W(\mathbf{r}^N) = \sum_{i=1}^{N} \sum_{j>1}^{N} \mathbf{F}_{ij} \cdot \mathbf{r}_{ij}, \tag{7}$$

where $\mathbf{F}_{ij}$ is the force on atom i due to the pair interaction with atom j,

$$\mathbf{F}_{ij} = -\frac{d}{d\mathbf{r}_i} u(r_{ij}). \tag{8}$$

Derivation of Eq. (7) relies on the identity $\mathbf{F}_{ij} = -\mathbf{F}_{ji}$, which follows from the symmetry of the pair potential function.

In molecular simulation, finite systems are rarely used. Instead, the system is often modeled as a set of N atoms in a parallelepiped volume bounded by three vectors: $\mathbf{a}$, $\mathbf{b}$, and $\mathbf{c}$. This volume, which we will refer to as the local cell, is surrounded by an infinite, three-dimensional array of equivalent replicas of the local cell, shifted by integer multiples of $\mathbf{a}$, $\mathbf{b}$, and $\mathbf{c}$. This configuration constitutes periodic boundary conditions. We will refer to the atoms in the local cell and the replicas as local and image atoms, respectively. In the case of a pair potential, the potential energy for the atoms in the local cell has the form

$$U(\mathbf{r}^N) = \sum_{\mathbf{n} \in Z^3} \sum_{i=1}^{N} \sum_{j>1}^{N} u(r_{ij\mathbf{n}}) + \sum_{\mathbf{n} \in Z^3}{}' \sum_{i=1}^{N} u(r_{ii\mathbf{n}}),$$
$$r_{ij\mathbf{n}} = |\mathbf{r}_i - \mathbf{r}_{j\mathbf{n}}|, \quad \mathbf{r}_{j\mathbf{n}} = \mathbf{r}_j + \mathbf{H}\mathbf{n}. \tag{9}$$

The columns of the matrix $\mathbf{H}$ are the periodic cell vectors $\mathbf{a}$, $\mathbf{b}$, and $\mathbf{c}$ so that $\mathbf{r}_j + \mathbf{H}\mathbf{n}$ is the position of one of the periodic images of the jth atom. $\mathbf{n} \in Z^3$ is a vector of three integers representing the x, y, and z offsets of the periodic images relative to the local cell. The restrictions on the summations are chosen so that *exactly one periodic image* of each pair interaction is included. Except for the case $\mathbf{n} = \mathbf{0}$, the restriction $j > i$ serves to arbitrarily include an interaction between a local atom at $\mathbf{r}_i$ and an image atom at $\mathbf{r}_j + \mathbf{H}\mathbf{n}$, while excluding an equivalent interaction between a local atom at $\mathbf{r}_j$ and an image atom at $\mathbf{r}_i - \mathbf{H}\mathbf{n}$. The second summation handles self-interactions between periodic images of the same atom, which typically do not arise, but are included here for completeness. The prime indicates that the summation over $\mathbf{n}$ excludes $\mathbf{n} = \mathbf{0}$ and includes only one of $\mathbf{n}$ and $-\mathbf{n}$ for every nonzero $\mathbf{n}$.

As for the finite nonperiodic case, volume change is assumed to occur via homogeneous affine expansion of the infinite periodic space. Other choices are possible, and these will change the definition of the instantaneous pressure, but will yield equivalent ensemble averages.[6] The assumption of affine expansion implies the following relation:

$$\frac{d\mathbf{r}_{i\mathbf{n}}}{dV} = \frac{\mathbf{r}_{i\mathbf{n}}}{3V}. \tag{10}$$

Substituting Eq. (9) and this expression into Eq. (2) yields

$$W(\mathbf{r}^N) = \sum_{\mathbf{n} \in Z^3} \sum_{i=1}^{N} \sum_{j>1}^{N} \mathbf{F}_{ij\mathbf{n}} \cdot \mathbf{r}_{ij\mathbf{n}} + \sum_{\mathbf{n} \in Z^3}{}' \sum_{i=1}^{N} \mathbf{F}_{ii\mathbf{n}} \cdot r_{ii\mathbf{n}}, \tag{11}$$

where $\mathbf{F}_{ij\mathbf{n}}$ is the force on atom i due to the pair interaction with the image of atom j located at $\mathbf{r}_j + \mathbf{H}\mathbf{n}$,

$$\mathbf{F}_{ij\mathbf{n}} = -\frac{d}{d\mathbf{r}_i} u(r_{ij\mathbf{n}}). \tag{12}$$

As before, Eq. (11) relies on the fact that $\mathbf{F}_{ij\mathbf{n}} = -\mathbf{F}_{ji\text{-}\mathbf{n}}$. Equation (11) closely resembles the previous nonperiodic expression for pair potentials, Eq. (7). If $\mathbf{r}_{ij\mathbf{n}}$ is defined using the minimum-image convention, where each local atom interacts only with the closest image of every other local atom,[2] then the two forms can be expressed using identical computer code. Perhaps because of this similarity, it is sometimes erroneously assumed that Eq. (4) can also be used without modification for periodic systems. This is particularly tempting for complex many-body potentials, where a general analog of Eq. (11) has not been previously published.

Louwerse and Baerends showed that the correct form of Eq. (4) under periodic boundary conditions is

$$W(\mathbf{r}^N) = \sum_{i=1}^{N} \mathbf{r}_i \cdot \mathbf{F}_i - 3V\left(\frac{\partial U}{\partial V}\right)_{\mathbf{r}^N}, \tag{13}$$

where $\mathbf{F}_i$ is as before the total force acting on the ith atom. The additional correction term accounts for the fact that under periodic boundary conditions, changing the volume changes the positions of image atoms, even when the local atoms positions are fixed. Louwerse and Baerends[3] indicated that correct calculation of the pressure for an arbitrary interatomic potential under periodic boundary conditions would require either numerical evaluation of the derivative in Eq. (2) or deriving analytic derivatives for the correction term on the right-hand side of Eq. (13), both of which are described as requiring "much effort." Indeed, the latter option poses a

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particular challenge when using complex, many-body interaction potentials. The authors' call for an alternative, simple method to correctly calculate the pressure for periodic system given at the end of their paper is quite understandable. It is our hope that the expressions derived below will provide such a method.

III. GENERAL EXPRESSIONS FOR THE VIRIAL

We begin by defining the potential energy for a finite nonperiodic system as the sum of K group energy terms, each of which depends only on the positions of a small group of the atoms,

$$U(\mathbf{r}^N) = \sum_{k=1}^{K} u_k(\mathbf{r}^{N_k}), \quad \mathbf{r}^{N_k} = \mathbf{r}_1^k, \mathbf{r}_2^k, \ldots, \mathbf{r}_{N_k}^k, \tag{14}$$

where $\mathbf{r}_w^k$ is the position of the wth atom in the group. The number of groups, the number of atoms in each group, and the number of groups in which an atom participates are completely arbitrary.

Substituting Eq. (14) into Eq. (2), applying the chain rule and Eq. (3) yields another expression for the virial of a finite nonperiodic system,

$$W(\mathbf{r}^N) = \sum_{k=1}^{K} \sum_{w=1}^{N_k} \mathbf{r}_w^k \cdot \mathbf{F}_w^k, \tag{15}$$

where $\mathbf{F}_w^k$ is the force due to the atoms in the kth group on the wth atom in that group,

$$\mathbf{F}_w^k = -\frac{d}{d\mathbf{r}_w^k} u_k(\mathbf{r}^{N_k}). \tag{16}$$

Equation (15) may appear to introduce an arbitrary dependence on the choice of coordinate system, but this is not the case. It is physically reasonable to require that each group energy function depend only on the relative positions of atoms in the group, and be independent of their absolute position. We can express this group-wise translational invariance in differential form

$$\sum_{w=1}^{N_k} \delta\mathbf{r} \cdot \frac{d}{d\mathbf{r}_w^k} u_k(\mathbf{r}^{N_k}) = \mathbf{0}, \tag{17}$$

where $\delta\mathbf{r}$ is an arbitrary infinitesimal displacement vector. Substituting in from Eq. (16) allows us to express this translational invariance as

$$\sum_{w=1}^{N_k} \mathbf{F}_w^k = \mathbf{0}. \tag{18}$$

Because of this property, adding a constant displacement to all the atoms in one group has no effect on the contribution of that group to the virial. Moreover, by gathering terms in Eq. (15) by atom, we can write the virial in a different way,

$$W(\mathbf{r}^N) = -\sum_{i=1}^{N} \mathbf{r}_i \cdot \sum_{k=1}^{K} \frac{d}{d\mathbf{r}_i} u_k(\mathbf{r}^{N_k}). \tag{19}$$

Comparing to Eqs. (14) and (5), we find

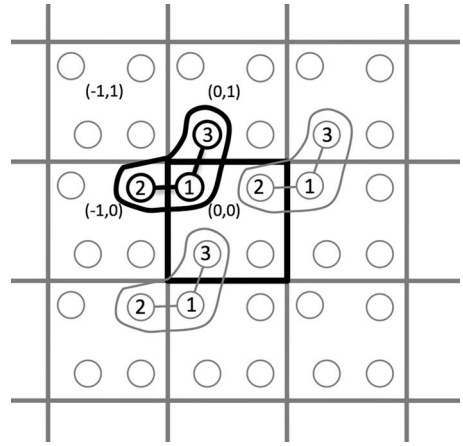

FIG. 1. Two-dimensional schematic illustrating how group images are associated with periodic replicas. The black square indicates the local cell, which is surrounded by an infinite array of periodic replicas. The closed curves indicate periodic images of a potential energy group involving three atoms. The curve in black indicates the group image associated with the local cell; it was chosen because its reference atom (the central atom, labeled 1) is contained in the local cell. Vectors indicating the values of $\mathbf{n}$ for the local cell and three replicas are also shown.

$$W(\mathbf{r}^N) = \sum_{i=1}^{N} \mathbf{r}_i \cdot \mathbf{F}_i, \tag{20}$$

which is the same as Eq. (4). We will refer to Eq. (15) as the group form for the virial, while Eq. (20) will be referred to as the atom form.

The same construction can now be used to derive an expression for an infinite periodic system. We must first ensure that the potential energy is defined correctly. To do this, we associate each of the infinite number of equivalent periodic images of each group with exactly one of the infinite number of periodic cell replicas. This association is arbitrary to some extent, and may be chosen for computational simplicity.

However, it must be done in such a way that every group image is associated with one and only one replica (it is possible to relax this requirement by having groups be shared by multiple replicas, but this results in duplicated computation). If we add the additional restriction that each group image be associated with a replica containing one of its atoms, this still results in up to N_k candidate group images for each replica since each group image can extend over arbitrarily many replicas. One conceptually simple way to proceed would be to associate each group image with the replica containing its center of mass. However, for specific potential functions more convenient choices are usually available. We will assume that every group has an identifiable reference atom and this atom is always first in the group list, i.e., its position is given by $\mathbf{r}_1^k$. The reference atom may be chosen based on the form of the group potential, or it could simply be the atom in the group with the lowest local index i. The restriction $j > i$ used in Eq. (11) is an example of the latter method.[7] We can then associate each group image with a replica $\mathbf{n}$, such that the reference atom of the group image lies in replica $\mathbf{n}$, i.e., for some local atom i, $\mathbf{r}_1^k = \mathbf{r}_{i\mathbf{n}}$. Figure 1 illustrates the approach with an example of a group involving three atoms.

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There are three images of this group that have an atom in the local cell. The reference atom in the group image outlined in bold is in the local cell and so this group image is associated with the local cell. The other group images are associated with neighboring replicas.

With this approach we can now write the potential energy of the local cell in an unambiguous manner,

$$U(\mathbf{r}^N) = \sum_{k\in\mathbf{0}} u_k(\mathbf{r}^{N_k}), \quad \mathbf{r}^{N_k} = \mathbf{r}_1^k, \mathbf{r}_2^k, \ldots, \mathbf{r}_{N_k}^k. \tag{21}$$

The summation is over all group images associated with the local cell. By construction, the first atom is in the local cell, i.e., $\mathbf{r}_1^k = \mathbf{r}_{i\mathbf{0}}$. All the other atoms may be located in the local cell or in nearby replicas. We note that the potential energy is now defined explicitly in terms of the positions of atoms in the local cell and in nearby replicas. Because of this, we can proceed in the same way as for the finite nonperiodic system. Substituting into Eq. (2), applying the chain rule and Eq. (10) yields the group form for the virial of the local cell in an infinite periodic system,

$$W(\mathbf{r}^N) = \sum_{k\in\mathbf{0}} \sum_{w=1}^{N_k} \mathbf{r}_w^k \cdot \mathbf{F}_w^k. \tag{22}$$

The position and group force are properties of the wth atom in the kth group which may or may not be in the local cell. The above expression is valid for any potential energy function that can be broken up into finite-range group terms, each of which depends only on the relative positions of the atoms in the group. It is not valid for potentials with explicit volume dependence such as arise in the treatment of lattice sum electrostatics and tail corrections. These require specialized treatments.[6]

By gathering terms in Eq. (22) by atom, we can write the virial in a different way,

$$W(\mathbf{r}^N) = -\sum_{\mathbf{n}\in Z^3} \sum_{i=1}^{N} \mathbf{r}_{i\mathbf{n}} \cdot \sum_{k\in\mathbf{0}} \frac{d}{d\mathbf{r}_{i\mathbf{n}}} u_k(\mathbf{r}^{N_k}). \tag{23}$$

We can write this expression in a more natural way by defining the following partial force,

$$\mathbf{F}'_{i\mathbf{n}} = -\sum_{k\in\mathbf{0}} \frac{d}{d\mathbf{r}_{i\mathbf{n}}} u_k(\mathbf{r}^{N_k}). \tag{24}$$

Substituting this expression into Eq. (23) allows us to write the virial as

$$W(\mathbf{r}^N) = \sum_{\mathbf{n}\in Z^3} \sum_{i=1}^{N} \mathbf{r}_{i\mathbf{n}} \cdot \mathbf{F}'_{i\mathbf{n}}. \tag{25}$$

We see that this expression is very similar to the atom form for the virial of a nonperiodic system [Eq. (15)], but it differs from the nonperiodic version in two respects. First, the summation is not just over local particles but also over image particles that contribute to the groups associated with the local cell. Second, the prime indicates that $\mathbf{F}'_{i\mathbf{n}}$ is not the total force on an atom but rather the partial force on the atom located at $\mathbf{r}_i + \mathbf{Hn}$ due to all the groups associated with the local cell.

Even in the case of local atoms, this partial force may be different from the full force because the forces due to groups associated with other replicas are not included. These partial forces arise naturally in calculations for periodic systems when the potential energy is defined using Eq. (21). The total force on each local atom is built up from partial forces accumulated on both local and image atoms,

$$\mathbf{F}_i = \sum_{\mathbf{n}\in Z^3} \mathbf{F}'_{i\mathbf{n}}. \tag{26}$$

Finally, we can obtain a third expression for the virial by substituting $\mathbf{r}_{i\mathbf{n}} = \mathbf{r}_i + \mathbf{Hn}$ and gathering terms in $\mathbf{r}_i$ yielding

$$W(\mathbf{r}^N) = \sum_{i=1}^{N} \mathbf{r}_i \cdot \mathbf{F}_i + \sum_{\mathbf{n}\in Z^3} \mathbf{Hn} \cdot \sum_{i=1}^{N} \mathbf{F}'_{i\mathbf{n}}. \tag{27}$$

This result is identical to the expression developed by Bekker *et al.*[8] for pair potentials under periodic boundary conditions. The second term is a sum over partial forces for atoms in each periodic replica. Comparison with Eq. (13) reveals that this sum is the correction term identified by Louwerse and Baerends.[3] The group form [Eq. (22)], atom form [Eq. (25)], and the atom-cell form [Eq. (27)] for the virial constitute the primary results of this paper. All three forms are mathematically equivalent and are valid for any translationally invariant potential consisting of a sum of group terms.

When implementing these forms in computer programs, the atom and atom-cell forms have the advantage that the virial product is not calculated in the innermost loop of the force calculation but rather is computed later in a separate loop over all atoms. The atom form is particularly well suited to implementation in parallel MD simulation codes, as the partial forces of image atoms are equivalent to the partial forces of ghost atoms used in spatial decomposition schemes. The group form has the advantage that individual contributions to the virial associated with each atom are computed explicitly.

IV. VERIFICATION

In order to verify the equivalence of the different forms, we have used the atom and group forms to compute the instantaneous stress tensor in short MD simulations of simple crystals using several different interatomic potentials. We begin with the definition of the global stress tensor $\mathbf{P}$ for a collection of N particles contained in a volume V,

$$\mathbf{P}V = \langle \sum_{i=1}^{N} m_i \mathbf{v}_i \otimes \mathbf{v}_i + \mathbf{W}(\mathbf{r}^N) \rangle, \tag{28}$$

where m_i and v_i are the mass and instantaneous velocity of the ith particle. The symbol $\otimes$ indicates the outer, dyadic, or direct tensor product. $\mathbf{W}$ is the global virial tensor. It is related to the scalar virial discussed in Secs. II and III by $W = \mathrm{Tr}\,\mathbf{W}$. Depending on the situation, it may be appropriate to replace the kinetic contribution to the instantaneous stress by the corresponding thermodynamic average $Nk_BT\mathbf{I}$,[9] but in either case, the definition of the virial tensor is the same. The atom and group forms of the virial tensor can be derived in

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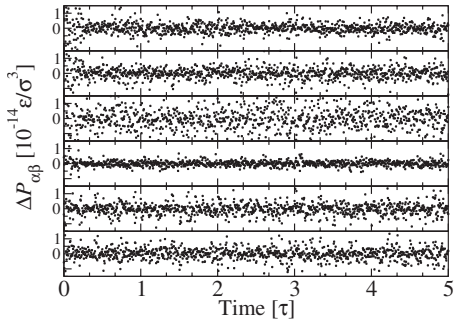

FIG. 2. Difference in pressure tensor components calculated using the standard [Eq. (31)] and atom [Eq. (29)] forms from a *NVE* dynamics simulation of a periodic Lennard-Jones crystal. Reading from top to bottom, the graphs correspond to pressure tensor components P_{xx}, P_{yy}, P_{zz}, P_{xy}, P_{xz}, and P_{yz}.

the same manner as was used for the scalar virial in Sec. III. The result for the atom form is

$$\mathbf{W}(\mathbf{r}^N) = \sum_{\mathbf{n}\in Z^3} \sum_{i=1}^{N} \mathbf{r}_{i\mathbf{n}} \otimes \mathbf{F}'_{i\mathbf{n}}, \tag{29}$$

while the result for the group form is

$$\mathbf{W}(\mathbf{r}^N) = \sum_{k\in\mathbf{0}} \sum_{w=1}^{N_k} \mathbf{r}_w^k \otimes \mathbf{F}_w^k. \tag{30}$$

We first tested the validity of the atom form by comparison with the standard definition of the virial tensor for atoms interacting with a pair potential,

$$\mathbf{W}(\mathbf{r}^N) = \sum_{\mathbf{n}\in Z^3} \sum_{i=1}^{N} \sum_{j>i}^{N} \mathbf{F}_{ij\mathbf{n}} \otimes \mathbf{r}_{ij\mathbf{n}} + \sum_{\mathbf{n}\in Z^3}{}' \sum_{i=1}^{N} \mathbf{F}_{ii\mathbf{n}} \otimes \mathbf{r}_{ii\mathbf{n}}. \tag{31}$$

We initialized a $10\times10\times10$ fcc perfect periodic crystal of particles interacting with the Lennard-Jones pair potential with density $0.99\sigma^{-3}$ and random velocities corresponding to temperature ε, where σ and ε are the Lennard-Jones diameter and energy, respectively. We truncated the potential at 2.5σ, and ran *NVE* dynamics for 1000 steps using velocity-Verlet time integration with a time step of 0.005τ, where $\tau = \sigma(m/\varepsilon)^{1/2}$ is the characteristic timescale of the crystal. At each time step we calculated the global stress tensor using both Eqs. (29) and (31).

The differences in the six independent components of the stress tensor are plotted in Fig. 2 as a function of time. It can be seen that the average difference is of order $10^{-14}\varepsilon/\sigma^3$, which is comparable to the accuracy of the double precision (64 bits) arithmetic used to do the calculation. This indicates that the atom form of the virial tensor is mathematically equivalent to the standard form for pair potentials.

We cannot perform the same test for many-body potentials since there is no general many-body expression analogous to Eq. (31). Instead, we test the mutual consistency of our atom and group forms, Eqs. (29) and (30), respectively. We initialized a $1\times1\times1$ perfect periodic diamond-cubic crystal of eight silicon atoms with lattice constant 5.43 Å and random velocities corresponding to temperature 300 K. Using the Stillinger–Weber potential[10] we ran *NVE* dynamics

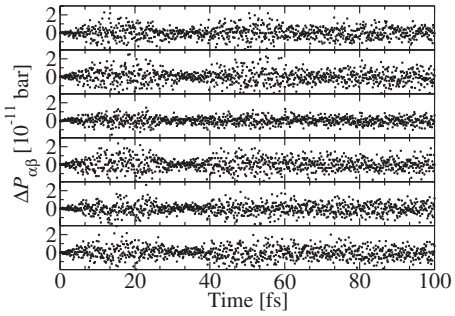

FIG. 3. Difference in pressure tensor components calculated using the group [Eq. (30)] and atom [Eq. (29)] forms from a *NVE* dynamics simulations of a periodic silicon crystal using the Stillinger–Weber potential. Reading from top to bottom, the graphs correspond to pressure tensor components P_{xx}, P_{yy}, P_{zz}, P_{xy}, P_{xz}, and P_{yz}.

for 1000 steps with a time step of 0.1 fs. The difference between the pressure tensor components calculated using the atom and group forms of the virial are shown in Fig. 3. We have also performed a similar calculation using the ReaxFF reactive interatomic potential.[11] The corresponding differences for the ReaxFF potential are shown in Fig. 4. For the Stillinger–Weber potential, the differences are on the order of 10^{-11} bar, while for the ReaxFF potential the differences are on the order of 10^{-9} bar. The increasing magnitude of the differences in going from Lennard-Jones to Stillinger–Weber to ReaxFF is consistent with the increasing computational complexity of these potentials. In all cases the differences are consistent with the accuracy of the double precision machine arithmetic. We conclude that all the different forms of the virial are computationally and mathematically equivalent.

V. SUMMARY AND DISCUSSION

We have derived three distinct forms for the instantaneous force virial contribution to the pressure and stress tensor of a collection of atoms interacting under periodic boundary conditions. All three forms are written in terms of forces acting on atoms, and so are valid for arbitrary interatomic potentials. In the special case of atoms interacting with pair potentials, they reduce to previously published forms. As a result, we have clarified and eliminated the difficulties iden-

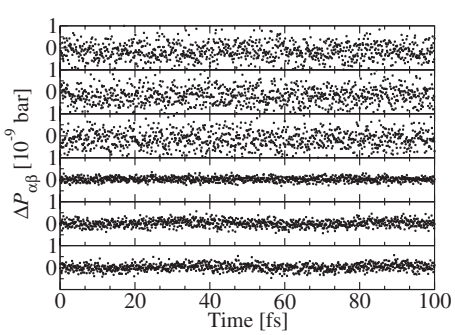

FIG. 4. Difference in pressure tensor components calculated using the group [Eq. (30)] and atom [Eq. (29)] forms from a *NVE* dynamics simulations of a periodic silicon crystal using the ReaxFF potential. Reading from top to bottom, the graphs correspond to pressure tensor components P_{xx}, P_{yy}, P_{zz}, P_{xy}, P_{xz}, and P_{yz}.

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tified by Louwerse and Baerends[3] when extending the expressions for simple pair potentials to more complicated interatomic potential functions.

The atom-cell form of the virial is similar to the standard expression for a finite nonperiodic system, but with an explicit correction for interactions with periodic images. This correction term was formally identified by Louwerse and Baerends,[3] but they indicated that there was no straightforward way to evaluate it for arbitrary potentials. We have been able to write the correction term directly in terms of partial forces acting on periodic image atoms. The correction term is identical to the one derived by Bekker *et al.*[8] for pair potentials.

The atom form of the virial is particularly suited to implementation in MD simulation codes that use spatial decomposition parallel algorithms. In many modern parallel MD simulation codes, the forces are calculated using a generalization of this concept. Every group in the total potential energy function is associated with a particular processor. This association is usually achieved by decomposing the simulation domain into processor subdomains. The groups can be associated with subdomains in exactly the same way that we associated groups with periodic replicas. In this context, the treatment of interactions between periodic replicas can be seen as a special case of the interaction between subdomains.

Finally, the group form of the virial naturally leads to a simple, general scheme for computing the virial tensor for individual atoms. While these per-atom virials do not have a direct physical interpretation, they provide a convenient means for grouping contributions to the virial in space, allowing the spatial variation of the stress tensor to be estimated in strongly inhomogeneous systems, such as in the vicinity of a shockwave.[12]

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[1] J. J. Erpenbeck and W. W. Wood, in *Modern Theoretical Chemistry, Statistical Mechanics, Part B: Time Dependent Processes*, edited by B. J. Berne (Plenum, New York, 1977).
[2] M. P. Allen and D. J. Tildesley, *Computer Simulation of Liquids* (Clarendon, Oxford, 1991).
[3] M. J. Louwerse and E. J. Baerends, Chem. Phys. Lett. **421**, 138 (2006).
[4] G. J. Gloor, G. Jackson, F. J. Blas, and E. de Miguel, J. Chem. Phys. **123**, 134703 (2005).
[5] G. Hummer, N. Grønbech-Jensen, and N. Neumann, J. Chem. Phys. **109**, 2791 (1998).
[6] P. H. Hünenberger, J. Chem. Phys. **116**, 6880 (2002).
[7] In the case of groups containing one or more periodic images of the same local atom, the reference atom of each group image must be a different periodic image of the local atom.
[8] H. Bekker, E. J. Dijkstra, M. K. R. Renardus, and H. J. C. Berendsen, Mol. Simul. **14**, 137 (1995).
[9] A. I. Murdoch, J. Elast. **88**, 113 (2007).
[10] F. H. Stillinger and T. A. Weber, Phys. Rev. B **31**, 5262 (1985).
[11] K. Chenoweth, S. Cheung, A. C. T. van Duin, W. A. Goddard, and E. M. Kober, J. Am. Chem. Soc. **127**, 7192 (2005).
[12] J. Budzien, A. P. Thompson, and S. Zybin, J. Phys. Chem. B **113**, 13142 (2009).

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