The Statistical Mechanical Foundations of Peridynamics
I. Mass and Momentum Conservation Laws

Mark P. Sears* and R. B. Lehoucq†

Multiscale Dynamic Materials Modeling,

and Applied Math and Applications,

Sandia National Laboratories, Albuquerque, NM 87185‡

(Dated: March 5, 2009)

Sandia National Labs Technical Report 2009-0791J

Abstract

Peridynamics is a continuum theory where the internal force density in the balance of linear momentum is given by an integral operator. This operator sums internal forces separated by a finite distance in contrast to a continuum theory where only contact forces are assumed. The goal of this paper is to derive mass and momentum conservation laws for peridynamics using the principles of statistical mechanics. In particular, we show that the peridynamic force density integral operator is the phase space expected value of internal force density given by a general multibody interatomic potential. Our approach avoids the standard limitation of a pairwise decomposition of the interatomic potential by exploiting the use of the symmetry principles of translation, rotation, and reflection. We analyze the close relationship of the peridynamic integral operator and the divergence of the microscopic Cauchy stress. This work represents a significant generalization of previous definitions of microscopic stress to arbitrary multibody potentials. We also discuss how the integral operator can be replaced by a force density arising from the classical notion of contact forces.

PACS numbers: 02.70.Ns, 02.70.Rr, 05.10.-a, 31.15.Qg, 62.20.Dc, 63.20.-e

*Electronic address: mpsears@sandia.gov

†Electronic address: rblehou@sandia.gov; URL: `http://www.sandia.gov/~rblehou/`

‡Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under contract DE-AC04-94AL85000.

Sandia National Labs Technical Report 2009-0791J

Contents

1. Introduction 2

2. Preliminaries 5

3. Conservation of mass 7

4. Conservation of linear momentum 8

5. Symmetric Cauchy stress tensor 12

6. Conservation of angular momentum 14

7. Peridynamics and classical continuum mechanics 15

8. Conclusions 16

Acknowledgements 17

References 17

Appendix 18

1. INTRODUCTION

Dynamics in continuum mechanics is established from the balance laws describing conservation of mass, momentum, and energy. In Eulerian form, the balance laws for conservation of mass and linear momentum are

$$\partial_t \rho + \partial_\mu (\mathbf{v}^\mu \rho) = 0 \tag{1a}$$

$$\partial_t \boldsymbol{\pi}^\nu + \partial_\mu (\mathbf{v}^\mu \boldsymbol{\pi}^\nu) = \partial_\mu \boldsymbol{\sigma}^{\mu\nu}, \tag{1b}$$

respectively, where $\boldsymbol{\pi}$ is momentum density given by the product $\rho\mathbf{v}$ of mass density and material velocity, and $\boldsymbol{\sigma}$ is the Cauchy stress tensor. The balance law for the conservation of angular momentum follows from the symmetry of the Cauchy stress tensor. We expect to treat energy conservation in a following paper and will not discuss it further here.

The peridynamic linear momentum balance law is instead given by

$$\partial_t \boldsymbol{\pi}^\nu + \partial_\mu(\mathbf{v}^\mu \boldsymbol{\pi}^\nu) = \partial_\mu \boldsymbol{\sigma}_K^{\mu\nu} + \int_{\mathbf{x}'} \left(\mathbf{T}^\nu(\mathbf{x},\mathbf{x}') - \mathbf{T}^\nu(\mathbf{x}',\mathbf{x})\right) d\mathbf{x}' \tag{2}$$

where $\boldsymbol{\sigma}_K^{\mu\nu}$ is the kinetic stress, and $\mathbf{T}(\mathbf{x},\mathbf{x}')$ (resp. $\mathbf{T}(\mathbf{x}',\mathbf{x})$) is a vector quantity representing the *force state* at $\mathbf{x}$ (resp. at $\mathbf{x}'$), and has units of force per volume per volume. The integrated difference of force states represents the internal force density of the source term. Our paper demonstrates that the peridynamic force state corresponds naturally to microscopic notions of molecules and atoms interacting by way of potentials that extend over finite distance. Bond-based peridynamics was proposed in [1] by Silling, and subsequently generalized in [2] to peridynamic states as given by the conservation of linear momentum in (2). Peridynamic stress was the subject of [3], and further generalized in [4]. This latter paper also presents an analysis to explain when the integral operator of (2) can be approximated by the divergence of a stress tensor (1b) arising from the classical notion of contact forces. The recent review [5] provides many citations to the peridynamic research literature including an overview of several applications. We remark that (2) is the spatial or Eulerian description of the conservation of linear momentum, in contrast to the reference or Lagrangian description associated with [1–3, 5].

Our goal in this paper is to derive mass and momentum conservation laws for peridynamics using the principles of statistical mechanics. In particular, we show that the peridynamic force density integral operator is the phase space expected value of internal force density given by a general multibody interatomic potential. The major motivation for this is that a statistical mechanical derivation lends significant insight into the meaning of the force state concept at the heart of (2). Our approach avoids the standard limitation of a pairwise interatomic potential, and the peridynamic integral operator sidesteps the significant issues associated with determining a stress tensor given a multibody interatomic potential. We also derive a microscopic symmetric Cauchy stress tensor such that the divergence of this stress tensor is equal to the peridynamic force density integral operator. We are thus able to generalize previous definitions of microscopic stress to arbitrary multibody potentials. We also discuss how the integral operator in (2) can be replaced by a force density arising from the classical notion of contact forces.

The first derivation of the balance law for linear momentum of classical continuum mechanics using the principles of statistical mechanics was laid out in the seminal paper by

Sandia National Labs Technical Report 2009-0791J

Irving and Kirkwood [6]. We employ the implicit definition of stress given in [6]. That is, stress is defined as the field that produces a source term for the balance of linear momentum. Since no surfaces are needed for this definition there is no need for considering the action of the particles in the system at any kind of wall. Moreover, no time averaging is required so the resulting stress is defined both instantaneously and locally. The major difficulty encountered by Irving–Kirkwood was in the use of Dirac delta functions to represent the particles, which results in a somewhat inelegant set of expressions for microscopic stress involving an infinite expansion of nonlocal terms. Moreover, their derivation is only valid for pair potentials.

Further progress was made by Noll [7] (see the English translation [8] and associated commentary [9]). In this work the use of delta functions [6] is avoided by assuming that expectation occurs in phase space. Noll also significantly anticipated Hardy in the derivation of a stress formula that avoids the infinite expansion of [6] by use of a mathematically rigorous result [7, Lemma I]. However, Noll only applied Lemma I in the case of central force interactions.

Hardy [10] avoided deriving the needed expectations in phase space, and made an elegant derivation of a stress formula using a method similar to Irving and Kirkwood, replacing the delta functions by a smooth localized function such as a Gaussian. This allows a great simplification of the stress formula. Hardy did not use Noll's Lemma, but obtained his result with a direct transformation on the localization function. However, the restriction to central force interactions was retained. See also the related paper by Murdoch and Bedeaux [11] where Hardy's approach avoiding phase space expectation and use of localization functions was independently derived and Noll's Lemma I was employed.

The procedure we follow is simple in principle and parallels the Irving–Kirkwood approach closely, up to a certain point. We take a microscopic model and assume that observables are given by expectation values of physical quantities in an ensemble defined by a phase space probability density that is arbitrary except that it represents an ensemble of states governed by the Hamiltonian mechanics of the system. Therefore we can use Liouville's equation and Green's theorem to convert time derivatives of expectations into expectations of time derivatives.

The microscopic model that we begin with is very general. We assume that we have N classical particles (we do not deal with quantum mechanics in this paper) interacting by a

Sandia National Labs Technical Report 2009-0791J

multibody potential U that depends only on the particle positions. Under the assumption that U is invariant under translation, rotation, and reflection (parity), U can be written as a function of interparticle distances $r_{ij} = |\mathbf{x}_i - \mathbf{x}_j|$. This is certainly true of potentials commonly used in molecular dynamics simulations. Although the distance representation may not be the most numerically convenient, it is easily established, for example, that dependence on bond angles and torsions can be replaced with a distance representation. Thus the potential that we use is certainly not restricted to pair potentials, but is valid for multibody potentials that satisfy the required three symmetry principles. Moreover, we show that these symmetry principles are sufficient to show that the Hardy and Noll stress tensors are equivalent when derived as expected values in phase space.

Sandia National Labs Technical Report 2009-0791J

2. PRELIMINARIES

The Hamiltonian of an atomic system is assumed to be

$$H = \sum_i \frac{\mathbf{p}_i^2}{2m_i} + U \tag{3}$$

where the particle masses are m_i, momenta are $\mathbf{p}_i$, and U is the potential given as a function of all the particle positions $\mathbf{x}_i$. We use lower-case Roman letters i, j, k etc., for particle indices (with no implied summation), and lower-case Greek letters μ, ν etc., with implied summation on repeated indices.

If U is invariant under operations of translation, rotation, and reflection we can construct the positions of the particles from the distances between particles (pair distances) modulo a symmetry group operation: Assume that the first four particles are not in a degenerate configuration and that all the pair distances are given (we actually only need the distances to the first four particles). Begin by translating and rotating such that the first particle is at the origin, the second particle lies on the positive x axis, and the third lies in the upper half of the x, y plane. The fourth particle can be placed in a tetrahedral position either above or below this plane. By reflection we can choose arbitrarily either one side or the other. Now for all the remaining particles we have more distances than are needed to locate them with respect to the first four. For each additional particle we can use the distances to the first three particles to find two possible locations above and below the x, y plane but because of the additional constraint of the distance to the fourth particle there will be only one solution

that is feasible. Therefore there is a unique (modulo a symmetry group operation) mapping from distances to the particle positions.

Practical molecular dynamics simulations often use potentials written in terms of pairwise distances, bond angles, and bond torsions; in the appendix we derive some simple formulas for conversion of these angle terms to functions of pairwise distances.

We are thus free to write U as a function of *distance parameters* ξ_{jk} defined as

$$\xi_{jk} \equiv \frac{1}{2} r_{jk}^2 = \frac{1}{2} \left| \mathbf{x}_j - \mathbf{x}_k \right|^2 , \tag{4}$$

for each pair of atoms j an k. These distance parameters are a little more convenient in the derivation than the distances themselves and are equivalent. For example, the gradient of a distance parameter with respect to particle position i is

$$\nabla_{\mathbf{x}_i} \xi_{jk} = (\mathbf{x}_j - \mathbf{x}_k)(\delta_{ij} - \delta_{ik}) \tag{5}$$

using Kronecker delta notation. Thus using the chain rule, we can write

$$\nabla_{\mathbf{x}_i} U = \frac{1}{2} \sum_{j,k} (\mathbf{x}_j - \mathbf{x}_k)(\delta_{ij} - \delta_{ik}) G_{jk} \tag{6}$$

$$= \sum_j (\mathbf{x}_i - \mathbf{x}_j) G_{ij} \tag{7}$$

for the corresponding gradient of U, where we define the pair functions G_{ij} as

$$G_{ij} = G_{ji} = \frac{\partial U}{\partial \xi_{ij}} \quad j \neq k, \qquad G_{jj} = 0. \tag{8}$$

The factor of 1/2 appears in (6) so as to avoid double counting because $\xi_{jk} = \xi_{kj}$. Although G_{ij} references atoms i and j, G_{ij} does in principle depend on all the distance pairs; however for a central force interaction G_{ij} depends only upon ξ_{ij}. It will be important in what follows to remember that G_{ij} is symmetric in the indices i, j, and that each of the other factors in (7) is antisymmetric. The G_{ij} can be thought of as generalized forces with dimensions of force per unit length. The symmetry of G_{ij} is the representation of Newton's third law in the context of this model and the use of the pair functions G_{ij} results in an extremely simple and well defined expression for the stress tensor.

The force $\mathbf{F}_i$ exerted on atom i by the remainder of the atoms can be decomposed into pairwise forces $\mathbf{f}_{ij}$ by defining

$$\mathbf{f}_{ij} \equiv -(\mathbf{x}_i - \mathbf{x}_j) G_{ij} \tag{9}$$

Sandia National Labs Technical Report 2009-0791J

so that

$$\mathbf{F}_i = -\nabla_{\mathbf{x}_i} U = \sum_j \mathbf{f}_{ij} \tag{10}$$

where $\mathbf{f}_{ij} = -\mathbf{f}_{ji}$ and $\mathbf{f}_{ii} = 0$. This can easily be verified by substitution of (9) into (7). But this decomposition is not unique (even for central force interactions), even with the constraint that $\mathbf{f}_{ij} = -\mathbf{f}_{ji}$. This can be easily seen for three atoms, since we can write a transformed set of $\mathbf{f}_{ij}$: $\mathbf{f}'_{12} = \mathbf{f}_{12} + \mathbf{a}$, $\mathbf{f}'_{13} = \mathbf{f}_{13} - \mathbf{a}$, and $\mathbf{f}'_{23} = \mathbf{f}_{23} + \mathbf{a}$ that leaves $\mathbf{F}_i$ invariant for an arbitrary vector $\mathbf{a}$. The atom forces $\mathbf{F}_i$ are well defined but they do not determine a unique pairwise decomposition, and therefore pairwise forces are not measurable physical quantities.

In the remainder of our paper we will develop continuum equations using the following well known methodology (see [6, eq. (2.4)], and [12, Chapter 3] for a more extended discussion) based on Liouville's equation. Suppose we have an operator α that is given as a function of the state variables $\mathbf{p}_i, \mathbf{x}_i$, and possibly other variables such as $\mathbf{x}$ *but not time*, then we can deduce from standard statistical mechanics that the time derivative of the expectation of α is

$$\partial_t \langle \alpha \rangle = \left\langle \sum_i \frac{\partial \alpha}{\partial \mathbf{x}_i^\mu} \mathbf{v}_i^\mu \right\rangle - \left\langle \sum_i \frac{\partial \alpha}{\partial \mathbf{p}_i^\mu} \frac{\partial U}{\partial \mathbf{x}_i^\mu} \right\rangle \tag{11}$$

where $\mathbf{v}_i = \mathbf{p}_i / m_i$ is the velocity of particle i. The brackets denote an ensemble average (phase space expectation) with respect to phase space density, which otherwise does not appear in any expressions. By selecting α equal to various density operators, the RHS of (11) can be manipulated to result in the desired continuum balance laws. For the remainder of our paper, we often denote the phase space expectation of an operator α by $\hat{\alpha}$, e.g.

$$\hat{\alpha} \equiv \langle \alpha \rangle \,. \tag{12}$$

3. CONSERVATION OF MASS

We define an operator whose phase space expectation is mass density. Each particle has mass m_i and we can associate a function $\phi(\mathbf{x} - \mathbf{x}_i)$ with each atom that represents the fact that exact positions are not observable. Insofar as ϕ is arbitrary, so are the resulting equations. Irving–Kirkwood used a delta function, but this is unnecessary as was demonstrated by Noll [7]. Hardy [10] restricted the choice of ϕ only by some simple properties: ϕ is assumed to be well localized, non-negative, and it must integrate to 1 over real space.

Sandia National Labs Technical Report 2009-0791J

The units of this function must therefore be per unit volume (of real space). We will use the notation $\phi_i = \phi(\mathbf{x} - \mathbf{x}_i)$ to simplify what follows. We see immediately that

$$\nabla_{\mathbf{x}_i}\phi_i = -\nabla_{\mathbf{x}}\phi_i, \tag{13}$$

and if ϕ is not smooth then this statement is to be understood in a distributional sense.

We now define an operator that represents the mass density at a point $\mathbf{x}$ as

$$\rho = \sum_i m_i\phi(\mathbf{x} - \mathbf{x}_i) = \sum_i m_i\phi_i. \tag{14}$$

We can now state the result obtained by previous authors (e.g. section IV of [6]) for conservation of mass, namely

$$\partial_t\hat{\rho} + \partial_\mu\hat{\boldsymbol{\pi}}^\mu = 0, \tag{15}$$

where the momentum density $\hat{\boldsymbol{\pi}}$ is the phase space expectation of the momentum density operator

$$\boldsymbol{\pi} = \sum_i m_i\mathbf{v}_i\phi_i = \sum_i \mathbf{p}_i\phi_i. \tag{16}$$

This result bears a little discussion. In the continuum mechanics literature, the primary variables are mass density and material velocity. But from a microscopic point of view the primary variables are mass and momentum densities. Evidently material velocity must be *defined* in terms of mass and momentum densities. That is

$$\hat{\rho}\mathbf{v} = \hat{\boldsymbol{\pi}} \tag{17}$$

defines the material velocity field $\mathbf{v}$. Note that (15) is a linear equation. This means that we can apply an averaging procedure to (15) and obtain another linear equation in the averaged quantities, so that the averaged mass density is pushed around by an averaged momentum density. No such simple procedure is available when velocity is chosen as a basic variable.

4. CONSERVATION OF LINEAR MOMENTUM

We now compute the time derivative for phase space expectation of the momentum density operator given in (15). The momentum density operator depends on both the momentum and position variables $\mathbf{p}_i$ and $\mathbf{x}_i$, respectively, so both terms in (11) contribute to the desired result. Thus,

$$\partial_t\hat{\boldsymbol{\pi}}^\nu = \left\langle \sum_i \frac{\partial\boldsymbol{\pi}^\nu}{\partial\mathbf{x}_i^\mu}\mathbf{v}_i^\mu \right\rangle - \left\langle \sum_i \frac{\partial\boldsymbol{\pi}^\nu}{\partial\mathbf{p}_i^\mu}\frac{\partial U}{\partial\mathbf{x}_i^\mu} \right\rangle,$$

Sandia National Labs Technical Report 2009-0791J

and a straightforward manipulation (see section V of [6]) results in

$$\partial_t \boldsymbol{\pi}^\nu + \partial_\mu(\mathbf{v}^\mu \boldsymbol{\pi}^\nu) = \partial_\mu \boldsymbol{\sigma}_K^{\mu\nu} - \left\langle \sum_i \frac{\partial \boldsymbol{\pi}^\nu}{\partial \mathbf{p}_i^\mu} \frac{\partial U}{\partial \mathbf{x}_i^\mu} \right\rangle, \tag{18}$$

where $\boldsymbol{\sigma}_K$ is the *kinetic stress* tensor is

$$\boldsymbol{\sigma}_K^{\mu\nu} = -\left\langle \sum_i m_i (\mathbf{v}_i^\mu - \mathbf{v}^\mu)(\mathbf{v}_i^\nu - \mathbf{v}^\nu)\phi_i \right\rangle. \tag{19}$$

The LHS of (18) is now in the desired conservation law form where the material velocity $\mathbf{v}$ is given by (17). As originally noted by Irving–Kirkwood the kinetic stress represents stress due to averaged thermal motion $\mathbf{v}_i - \mathbf{v}$ of the atoms and represents, for example, pressure in an ideal gas.

We have thus far not varied significantly from the results established by previous authors but at this point we will make a departure. The remaining work is to convert the second term on the RHS of (18) to a form convenient for peridynamics. Rather than assuming central force interactions, we use the expression (7) derived for $\nabla_{\mathbf{x}_i} U$ in terms of derivatives with respect to the distance parameters ξ_{ij}. Therefore, (7) implies that

$$\left\langle \sum_i \frac{\partial \boldsymbol{\pi}^\nu}{\partial \mathbf{p}_i^\mu} \frac{\partial U}{\partial \mathbf{x}_i^\mu} \right\rangle = \left\langle \sum_i \phi_i \sum_j (\mathbf{x}_i^\nu - \mathbf{x}_j^\nu) G_{ij} \right\rangle \tag{20}$$

$$= \left\langle \sum_{i,j} (\mathbf{x}_i^\nu - \mathbf{x}_j^\nu) \phi_i G_{ij} \right\rangle, \tag{21}$$

where

$$\frac{\partial \boldsymbol{\pi}^\nu}{\partial \mathbf{p}_i^\mu} = \phi_i \delta_{\mu\nu}.$$

Therefore (18) can be rewritten as

$$\partial_t \boldsymbol{\pi}^\nu + \partial_\mu(\mathbf{v}^\mu \boldsymbol{\pi}^\nu) = \partial_\mu \boldsymbol{\sigma}_K^{\mu\nu} - \left\langle \sum_{i,j} (\mathbf{x}_i^\nu - \mathbf{x}_j^\nu) \phi_i G_{ij} \right\rangle. \tag{22}$$

By assumption

$$\int_{\mathbf{x}'} \phi_j' \, d\mathbf{x}' = 1, \qquad \phi_j' = \phi(\mathbf{x}' - \mathbf{x}_j), \tag{23}$$

so that

$$\partial_t \boldsymbol{\pi}^\nu + \partial_\mu(\mathbf{v}^\mu \boldsymbol{\pi}^\nu) = \partial_\mu \boldsymbol{\sigma}_K^{\mu\nu} - \int_{\mathbf{x}'} \left\langle \sum_{i,j} (\mathbf{x}_i^\nu - \mathbf{x}_j^\nu) \phi_i \phi_j' G_{ij} \right\rangle d\mathbf{x}'. \tag{24}$$

Sandia National Labs Technical Report 2009-0791J

Now note that

$$\left\langle \sum_{i,j} (\mathbf{x}_i^\nu - \mathbf{x}_j^\nu)\phi_i\phi_j' G_{ij} \right\rangle = -\left\langle \sum_{i,j} (\mathbf{x}_j^\nu - \mathbf{x}_i^\nu)\phi_i\phi_j' G_{ij} \right\rangle$$
$$= -\left\langle \sum_{j,i} (\mathbf{x}_i^\nu - \mathbf{x}_j^\nu)\phi_j\phi_i' G_{ji} \right\rangle$$
$$= -\left\langle \sum_{j,i} (\mathbf{x}_i^\nu - \mathbf{x}_j^\nu)\phi_i\phi_j' G_{ij} \right\rangle,$$

where the last step follows because $G_{ji} = G_{ij}$, and the fact that the integrand of (24) is antisymmetric with respect to $\mathbf{x}$ and $\mathbf{x}'$. If we make the identifications

$$\mathbf{T}^\nu(\mathbf{x},\mathbf{x}') = -\left\langle \sum_{i,j} \mathbf{x}_i^\nu \phi_i\phi_j' G_{ij} \right\rangle, \qquad \mathbf{T}^\nu(\mathbf{x}',\mathbf{x}) = -\left\langle \sum_{i,j} \mathbf{x}_j^\nu \phi_i\phi_j' G_{ij} \right\rangle, \tag{25}$$

then the peridynamic balance of linear momentum (2) results. Evidently, the differential force density $(\mathbf{T}(\mathbf{x},\mathbf{x}') - \mathbf{T}(\mathbf{x}',\mathbf{x}))\, d\mathbf{x}'$ is the phase space expectation of the force per unit volume squared for atoms located near $\mathbf{x}$ and $\mathbf{x}'$.

Several remarks are in order. First, rewriting the internal force density (rightmost term of (22)) as the integral of a force density per volume (rightmost term of) (24) is due to Noll [7]. This is a crucial step not taken by Irving-Kirkwood, and leads to a closed form expression for the potential stress given by Lemma I of [7]. Second, in general,

$$(\mathbf{T}(\mathbf{x},\mathbf{x}') - \mathbf{T}(\mathbf{x}',\mathbf{x})) \times (\mathbf{x}' - \mathbf{x}) \neq \mathbf{0}, \tag{26}$$

regardless of whether the atom interaction corresponds to a central force (e.g. G_{ij} is only a function of the distance parameter ξ_{ij}). Bond-based peridynamics [1] does assume that $\mathbf{x}' - \mathbf{x}$ is collinear with $\mathbf{T}(\mathbf{x},\mathbf{x}') - \mathbf{T}(\mathbf{x}',\mathbf{x})$ (an *ordinary* peridynamic material), while the more general peridynamic state theory [2] allows for the weak form of Newton's third law (or a *nonordinary* peridynamic material).

Third, let τ be a region in real space. Because $\mathbf{T}^\nu(\mathbf{x},\mathbf{x}') - \mathbf{T}^\nu(\mathbf{x}',\mathbf{x})$ is antisymmetric, we have that

$$\int_{\mathbf{x}\in\tau}\int_{\mathbf{x}'} (\mathbf{T}^\nu(\mathbf{x},\mathbf{x}') - \mathbf{T}^\nu(\mathbf{x}',\mathbf{x}))\, d\mathbf{x}'\, d\mathbf{x} = \int_{\mathbf{x}\in\tau}\int_{\mathbf{x}'\notin\tau} (\mathbf{T}^\nu(\mathbf{x},\mathbf{x}') - \mathbf{T}^\nu(\mathbf{x}',\mathbf{x}))\, d\mathbf{x}'\, d\mathbf{x}. \tag{27}$$

The mechanical interpretation is that the RHS of (27) represents the internal force on the region τ exerted by the region outside of τ. Now integrate (24) over the region τ in real

Sandia National Labs Technical Report 2009-0791J

space to obtain

$$\int_{\mathbf{x}\in\tau} (\partial_t \boldsymbol{\pi}^\nu + \partial_\mu(\mathbf{v}^\mu \boldsymbol{\pi}^\nu))\, d\mathbf{x} = \int_{\partial\tau} \boldsymbol{\sigma}_K^{\mu\nu} \mathbf{n}^\mu \, dA - \int_{\mathbf{x}\in\tau} \int_{\mathbf{x}'\notin\tau} (\mathbf{T}^\nu(\mathbf{x},\mathbf{x}') - \mathbf{T}^\nu(\mathbf{x}',\mathbf{x}))\, d\mathbf{x}'\, d\mathbf{x}, \quad (28)$$

where $\mathbf{n}$ is the normal to the surface $\partial\tau$ of τ. In words, the rate of change of linear momentum is balanced by the sum of forces external to τ. The balance law (28) obviates the need for periodic boundary conditions when considering subsets of the N atoms because the interaction with the remainder of the atoms is given by the RHS of (28).

The fourth remark is that the rightmost expression (21) bears a superficial resemblance to the rightmost term of eq. (5.8) of [6]. If we assume central force interactions, then that equation is a specialized application of our derivation in which the bond-based peridynamic [1] conservation of linear momentum (2) results. The use of the generalized force G_{ij} allows us to avoid the partitioning of the potential into pairwise terms that only depend on the positions $\mathbf{x}_j$ and $\mathbf{x}_k$ (see the discussion following eq. (3.6) of [6]). Similar restrictions are used by other authors, see eq. (1.1) of [8] and eq. (3.2) of [10]. Several papers [13–15] have tried to generalize beyond central force interactions using a notion of the force of particle i upon particle j. However, the details of these decompositions are unspecified and generally require some arbitrary partitioning of the potential U. Moreover, as Noll [16] explains, the principle of material frame indifference implies that any force interaction that only depends upon particles i and j must be a central force interaction (e.g. G_{ij} is only a function of the distance parameter ξ_{ij}). Apparently this was not appreciated by Irving and Kirkwood [6], who initially assume pairwise interactions, and then further assume (superfluously) central force interactions. We believe that the current derivation is the first applicable to a general multibody potential. We conjecture that the use of generalized forces is the *only* way to derive simple formulas for the peridynamic force state or for microscopic stress for a general multibody potential, since (7) does not induce an obvious pairwise decomposition into forces.

Our fifth remark is that we have *not* established that any peridynamic internal force density is derivable as expectation in phase space. An example of such a peridynamic force density is given by [2, Section 17] associated with a nonordinary material containing a couple. Instead, for an interatomic potential U invariant under translation, rotation, and reflection, expectation in phase space results in a peridynamic internal force density that is the integrated difference of force states (e.g. the rightmost term of the RHS of (2)).

Sandia National Labs Technical Report 2009-0791J

Sandia National Labs Technical Report 2009-0791J

5. SYMMETRIC CAUCHY STRESS TENSOR

We now explain how the RHS of (22) may be recast as the divergence of a microscopic symmetric stress tensor field, or the Cauchy stress tensor. Moreover, we show that the two seemingly distinct expressions for the stress tensor derived first by Noll [7] and then by Hardy [10] are indeed the same.

We first consider Hardy's stress tensor. First, the identity

$$\phi_i = \frac{1}{2}(\phi_i - \phi_j) + \frac{1}{2}(\phi_i + \phi_j) \tag{29}$$

implies that

$$\left\langle \sum_{i,j} (\mathbf{x}_i^\nu - \mathbf{x}_j^\nu)\phi_i G_{ij} \right\rangle = \frac{1}{2}\left\langle \sum_{i,j} (\mathbf{x}_i^\nu - \mathbf{x}_j^\nu)(\phi_i - \phi_j) G_{ij} \right\rangle, \tag{30}$$

because

$$\frac{1}{2}\left\langle \sum_{i,j} (\mathbf{x}_i^\nu - \mathbf{x}_j^\nu)(\phi_i + \phi_j) G_{ij} \right\rangle = 0,$$

which follows by exchanging the labels i and j. Therefore, (30) implies that we may rewrite (22) as

$$\partial_t \boldsymbol{\pi}^\nu + \partial_\mu(\mathbf{v}^\mu \boldsymbol{\pi}^\nu) = \partial_\mu \boldsymbol{\sigma}_K^{\mu\nu} - \left\langle \sum_{i,j} \frac{1}{2}(\mathbf{x}_i^\nu - \mathbf{x}_j^\nu)(\phi_i - \phi_j) G_{ij} \right\rangle. \tag{31}$$

Second, following Hardy [10], we define a function $\beta(\mathbf{x}_i, \mathbf{x}_j, \mathbf{x})$ such that

$$\phi_i - \phi_j = -(\mathbf{x}_i - \mathbf{x}_j) \cdot \nabla_{\mathbf{x}} \beta(\mathbf{x}_i, \mathbf{x}_j, \mathbf{x}) \tag{32}$$

where the bond function β depends only on the function ϕ. The solution given by Hardy is

$$\beta(\mathbf{x}_i, \mathbf{x}_j, \mathbf{x}) = \int_0^1 d\lambda\, \phi(\mathbf{x} - \lambda \mathbf{x}_i - (1-\lambda)\mathbf{x}_j). \tag{33}$$

If we substitute (32) into (31), and pull the operator $\nabla_{\mathbf{x}}$ outside the expectation, we have

$$\partial_t \boldsymbol{\pi}^\nu + \partial_\mu(\mathbf{v}^\mu \boldsymbol{\pi}^\nu) = \partial_\mu \boldsymbol{\sigma}_K^{\mu\nu} + \partial_\mu \boldsymbol{\sigma}_H^{\mu\nu} \tag{34}$$

where we identify a microscopic stress tensor field $\boldsymbol{\sigma}_H$ as

$$\boldsymbol{\sigma}_H^{\mu\nu}(\mathbf{x}) = \frac{1}{2}\left\langle \sum_{i,j} (\mathbf{x}_i^\mu - \mathbf{x}_j^\mu)(\mathbf{x}_i^\nu - \mathbf{x}_j^\nu) G_{ij} \beta(\mathbf{x}_i, \mathbf{x}_j, \mathbf{x}) \right\rangle. \tag{35}$$

We see that

$$\partial_\mu\left(\boldsymbol{\sigma}_H^{\mu\nu}\right) = \int_{\mathbf{x}'} \left\langle \sum_{i,j} (\mathbf{x}_i^\nu - \mathbf{x}_j^\nu)\phi_i \phi_j' G_{ij} \right\rangle d\mathbf{x}',$$

and therefore the peridynamic conservation of linear momentum is equivalent to

$$\partial_t \boldsymbol{\pi}^\nu + \partial_\mu(\mathbf{v}^\mu \boldsymbol{\pi}^\nu) = \partial_\mu \left(\boldsymbol{\sigma}_K^{\mu\nu} + \boldsymbol{\sigma}_H^{\mu\nu}\right), \tag{36}$$

where $\boldsymbol{\sigma} = \boldsymbol{\sigma}_K + \boldsymbol{\sigma}_H$ is a Cauchy stress tensor that is explicitly symmetric. The stress tensor field given by (35) is a compact and general representation of the non-kinetic, or potential part of the stress. Compare, for example, the corresponding expression in [17] that is only carried out for the Tersoff [18, 19] potential.

The continuum stress is now given as the expectation of a microscopic operator that is explicitly symmetric, for a general multibody potential U. The symmetry of the stress tensor is a consequence of the derivation in terms of distance parameters, that in turn is enabled directly by the assumption of the invariance of the potential under translation, rotation, *and* reflection. Moreover, *there is no need to partition the potential energy U between pairs of atoms.* The derivatives G_{ij} are defined in terms of the total potential energy U without regard to any such partitioning and there is no arbitrariness in the definition of the microscopic stress other than the choice of the smoothing function ϕ.

Lemma I of [7] (again, see the English translation [8] and associated commentary [9]) may also be used to derive another expression for a symmetric potential stress $\boldsymbol{\sigma}_N^{\mu\nu}$ so that

$$\partial_\mu \left(\boldsymbol{\sigma}_N^{\mu\nu}\right) = \left\langle \int_{\mathbf{x}'} \sum_{i,j} (\mathbf{x}_i^\nu - \mathbf{x}_j^\nu) \phi_i \phi_j' G_{ij} \, d\mathbf{x}' \right\rangle,$$

where

$$\boldsymbol{\sigma}_N^{\mu\nu}(\mathbf{x}) = \frac{1}{2} \left\langle \sum_{i,j} \int_{\mathbf{z}} \eta(\mathbf{x}_i, \mathbf{x}_j, \mathbf{x}, \mathbf{z}) \, G_{ij} \; \mathbf{z}^\mu \, \mathbf{z}^\nu \, d\mathbf{z} \right\rangle, \tag{37}$$

with

$$\eta(\mathbf{x}_i, \mathbf{x}_j, \mathbf{x}, \mathbf{z}) = \int_0^1 d\lambda \, \phi(\mathbf{x} + \lambda \mathbf{z} - \mathbf{x}_i) \phi(\mathbf{x} - (1-\lambda)\mathbf{z} - \mathbf{x}_j). \tag{38}$$

Note that $\boldsymbol{\sigma}_N^{\mu\nu} = \boldsymbol{\sigma}_N^{\nu\mu}$ easily follows, and so the Noll stress $\boldsymbol{\sigma}_N$ is symmetric.

We now establish that $\boldsymbol{\sigma}_N = \boldsymbol{\sigma}_H$. Subtracting (36) from

$$\partial_t \boldsymbol{\pi}^\nu + \partial_\mu(\mathbf{v}^\mu \boldsymbol{\pi}^\nu) = \partial_\mu \left(\boldsymbol{\sigma}_K^{\mu\nu} + \boldsymbol{\sigma}_N^{\mu\nu}\right),$$

leads to $\partial_\mu \left(\boldsymbol{\sigma}_N^{\mu\nu} - \boldsymbol{\sigma}_N^{\mu\nu}\right) = 0$. Therefore $\boldsymbol{\sigma}_N$ and $\boldsymbol{\sigma}_H$ differ by a solenoidal tensor that must be nonsymmetric. Because each of $\boldsymbol{\sigma}_N$ and $\boldsymbol{\sigma}_H$ are symmetric, this solenoidal tensor must be the zero tensor, and so we conclude that

$$\boldsymbol{\sigma}_N = \boldsymbol{\sigma}_H. \tag{39}$$

Sandia National Labs Technical Report 2009-0791J

This equivalence is crucially dependent upon symmetry of $\boldsymbol{\sigma}_N$ and $\boldsymbol{\sigma}_H$, which in turn depends upon the assumption that the interatomic potential is invariant under reflection. To the best of our knowledge, this equivalence has not appeared in the literature. See [20, 21] for other comparisons between $\boldsymbol{\sigma}_N$ and $\boldsymbol{\sigma}_H$. In the remainder of the paper, we refer to

$$\boldsymbol{\sigma}_U \tag{40}$$

as the potential stress and the context determines whether the representations $\boldsymbol{\sigma}_N$ or $\boldsymbol{\sigma}_H$ are used.

Sandia National Labs Technical Report 2009-0791J

6. CONSERVATION OF ANGULAR MOMENTUM

The second remark at the end of Section 4 explained that in general, the difference of force states at $\mathbf{x}$ and $\mathbf{x}'$, respectively, is not collinear with the line through $\mathbf{x}$ and $\mathbf{x}'$; see (26). This implies that the opposing forces $(\mathbf{T}(\mathbf{x},\mathbf{x}') - \mathbf{T}(\mathbf{x}',\mathbf{x}))\, d\mathbf{x}'\, d\mathbf{x}$ and $(\mathbf{T}(\mathbf{x}',\mathbf{x}) - \mathbf{T}(\mathbf{x},\mathbf{x}'))\, d\mathbf{x}\, d\mathbf{x}'$ only satisfy the weak form of Newton's third law. Therefore, the peridynamic conservation of angular momentum must be considered. From (2), it follows that the peridynamic balance law for the conservation of angular momentum is

$$\int_{\mathbf{x}\in\tau} \mathbf{x} \times (\partial_t \boldsymbol{\pi} + \partial_\mu(\mathbf{v}\boldsymbol{\pi}))\, d\mathbf{x} = \int_{\partial\tau} \mathbf{x} \times \boldsymbol{\sigma}_K \mathbf{n}\, dA + \int_{\mathbf{x}\in\tau}\int_{\mathbf{x}'\in\tau} \mathbf{x} \times (\mathbf{T}(\mathbf{x},\mathbf{x}') - \mathbf{T}(\mathbf{x}',\mathbf{x}))\, d\mathbf{x}'\, d\mathbf{x}, \tag{41}$$

where $\mathbf{n}$ is the normal to the surface $\partial\tau$ of a region τ of real space. In words, (41) states that the rate of change of angular momentum is balanced by the sum of torques exerted on τ.

Section 5 demonstrated that

$$\nabla \cdot \boldsymbol{\sigma}_U = \int_{\mathbf{x}'\in\tau} (\mathbf{T}(\mathbf{x},\mathbf{x}') - \mathbf{T}(\mathbf{x}',\mathbf{x}))\, d\mathbf{x}' \tag{42}$$

and $\boldsymbol{\sigma}_U^T = \boldsymbol{\sigma}_U$. Hence, we have that

$$\begin{aligned}\int_{\mathbf{x}\in\tau}\int_{\mathbf{x}'\in\tau} \mathbf{x} \times (\mathbf{T}(\mathbf{x},\mathbf{x}') - \mathbf{T}(\mathbf{x}',\mathbf{x}))\, d\mathbf{x}'\, d\mathbf{x} &= \int_{\mathbf{x}\in\tau} \mathbf{x} \times \left(\int_{\mathbf{x}'\in\tau} (\mathbf{T}(\mathbf{x},\mathbf{x}') - \mathbf{T}(\mathbf{x}',\mathbf{x}))\, d\mathbf{x}'\right) d\mathbf{x} \\ &= \int_{\partial\tau} \mathbf{x} \times \boldsymbol{\sigma}_U \mathbf{n}\, dA + \int_{\mathbf{x}\in\tau} \mathcal{E} : \boldsymbol{\sigma}_U^T\, d\mathbf{x} \\ &= \int_{\partial\tau} \mathbf{x} \times \boldsymbol{\sigma}_U \mathbf{n}\, dA\end{aligned}$$

where $\mathcal{E}\colon \boldsymbol{\sigma}_U^T$ denotes the contraction of the third-order permutation tensor $\mathcal{E}$ (where $\varepsilon^{\mu\nu\xi} = -\varepsilon^{\xi\nu\mu}$) with the transpose of the potential stress tensor $\boldsymbol{\sigma}_U$. Therefore the balance law for the conservation of angular momentum (41) is equivalent to

$$\int_{\mathbf{x}\in\tau} \mathbf{x} \times (\partial_t \boldsymbol{\pi} + \nabla \cdot (\mathbf{v}\boldsymbol{\pi}))\, d\mathbf{x} = \int_{\partial\tau} \mathbf{x} \times \boldsymbol{\sigma}\mathbf{n}\, dA, \tag{43}$$

where $\boldsymbol{\sigma} = \boldsymbol{\sigma}_K + \boldsymbol{\sigma}_U$, if and only if $\boldsymbol{\sigma}_U^T = \boldsymbol{\sigma}_U$. Again, the latter condition follows from the assumption that the interatomic potential is invariant under reflection, as explained in Section 5.

7. PERIDYNAMICS AND CLASSICAL CONTINUUM MECHANICS

The Cauchy stress $\boldsymbol{\sigma}$ for simple nonpolar materials [22], typically associated with constitutive models used within engineering solid mechanics, is understood to be a local tensor. That is $\boldsymbol{\sigma}(\mathbf{x})$ only depends upon $\mathbf{x}$ and so leads to the *contact* force

$$\int_{\partial\tau} \boldsymbol{\sigma}\mathbf{n}\, dA$$

where $\mathbf{n}$ is the normal to the surface $\partial\tau$ of the region τ of real space. The quantity $\mathbf{t}(\mathbf{x},\mathbf{n}) = \boldsymbol{\sigma}(\mathbf{x})\mathbf{n}$ is the traction vector. A continuum theory where a contact force is assumed is colloquially referred to as a classical continuum theory.

In contrast to a *local* Cauchy stress tensor, $\boldsymbol{\sigma}_K + \boldsymbol{\sigma}_U$ is a *nonlocal* Cauchy stress tensor because the bond function β (33) (or equivalently the bond function η (38)) is given by a weighted average. This nonlocality originates in the integral operator of the source term associated with (24) because $\mathbf{x}' \neq \mathbf{x}$ are involved. Lemma II of [7] gives that the traction force associated with the potential stress $\boldsymbol{\sigma}_N$ is

$$\int_{\partial\tau} \boldsymbol{\sigma}_N \mathbf{n}\, dA = \int_{\mathbf{x}\in\tau} \int_{\mathbf{x}'\notin\tau} (\mathbf{T}(\mathbf{x},\mathbf{x}') - \mathbf{T}(\mathbf{x}',\mathbf{x}))\, d\mathbf{x}'\, d\mathbf{x}, \tag{44}$$

where

$$\boldsymbol{\sigma}_N(\mathbf{x})\mathbf{n} = \frac{1}{2}\left\langle \sum_{i,j} \int_{\mathbf{z}} \eta(\mathbf{x}_i,\mathbf{x}_j,\mathbf{x},\mathbf{z})\, G_{ij}\ \mathbf{z}\ (\mathbf{z}\cdot\mathbf{n})\ d\mathbf{z} \right\rangle, \tag{45}$$

and η is given by (38). The identity (44) is easily established via the divergence theorem and (27). The traction vector $\boldsymbol{\sigma}_N(\mathbf{x})\mathbf{n}$ is nonlocal because of the dependence upon $\mathbf{x}' \neq \mathbf{x}$ and so does *not* lead to a contact force.

Sandia National Labs Technical Report 2009-0791J

A mechanical interpretation of $\boldsymbol{\sigma}_N(\mathbf{x})\mathbf{n}$ is as follows. The differential force $d\mathbf{f}$ between $\mathbf{x}+\lambda\mathbf{z}-\mathbf{x}_i$ and $\mathbf{x}-(1-\lambda)\mathbf{z}-\mathbf{x}_j$ is

$$d\mathbf{f} = \frac{1}{2}\left\langle \sum_{i,j} \eta(\mathbf{x}_i,\mathbf{x}_j,\mathbf{x},\mathbf{z})\, G_{ij} \right\rangle \mathbf{z}\,(d\lambda\, d\mathbf{z})^2,$$

where $d\mathbf{z}$ is differential volume. If $dA = (d\lambda\, d\mathbf{z})\,/\,(\mathbf{z}\cdot\mathbf{n})$ is a differential area, then

$$\frac{d\mathbf{f}}{dA} = \frac{1}{2}\left\langle \sum_{i,j} \eta(\mathbf{x}_i,\mathbf{x}_j,\mathbf{x},\mathbf{z})\, G_{ij} \right\rangle \mathbf{z}\;(\mathbf{z}\cdot\mathbf{n})\, d\lambda\, d\mathbf{z}. \tag{46}$$

Integrating (46) over $\lambda = 0$ to $\lambda = 1$, and over all $\mathbf{z}$ results in (45). In particular, the stress tensor $\boldsymbol{\sigma}_N(\mathbf{x})$ represents a sum of forces per unit area *through* $\mathbf{x}$ in contrast to the (local) Cauchy stress of the classical continuum theory.

Sufficient conditions for when $\boldsymbol{\sigma}_U$ and $\nabla\cdot\boldsymbol{\sigma}_U$ can be approximated by the corresponding local quantities are given by the analysis [4]. These conditions are that if the motion, constitutive model, and any nonhomogeneities are sufficiently smooth, then the peridynamic integral operator may be replaced by a local stress tensor when the volume of force interactions about $\mathbf{x}$ is small relative to the volume τ. The balance of linear momentum for classical continuum mechanics is a direct result of an approximation given sufficient conditions to the peridynamic balance of linear momentum. The latter balance law is derived from an ensemble average in phase space. The path from Newton's second law to the classical balance of linear momentum (for simple nonpolar materials) traverses peridynamics. We are not aware that this two step process has been demonstrated in the existing literature.

8. CONCLUSIONS

The main results established in this paper are the derivation of microscopic expressions for mass and momentum conservations laws, and the nonlocal Cauchy stress. In combination with the standard results for the kinetic stress, we now have microscopic understanding of peridynamic force states. These expressions are derived for a general multibody potential that is given as a function of the square of the particle distances. In particular, the potential does not have to be a sum of pairwise potentials, it can be any multibody potential that depends only on particle positions and that is invariant under translation, rotation, and reflection. It is also not necessary to partition this general potential among the atoms. The

Sandia National Labs Technical Report 2009-0791J

only arbitrariness in the formalism comes from the function ϕ that can be thought of as representing the averaging procedure applied to measurement of atom positions. Finally, we also discussed how the peridynamic balance law for the conservation of linear momentum can approximated by the classical continuum balance of linear momentum that assumes contact forces.

Acknowledgements

The authors gratefully acknowledge discussions with John Aidun, Aidan Thompson, Steve Plimpton, Stewart Silling, and Jon Zimmerman of Sandia National Laboratories. R.B. Lehoucq acknowledges helpful discussions with Nikhil Admal and Ellad Tadmor of the University of Minnesota.

Sandia National Labs Technical Report 2009-0791J

[1] S. A. Silling, J. Mech. Phys. Solids **48**, 175 (2000).

[2] S. A. Silling, M. Epton, O. Weckner, J. Xu, and E. Askari, J. Elasticity **88**, 151 (2007).

[3] R. B. Lehoucq and S. A. Silling, J. Mech. Phys. Solids **56**, 1566 (2008).

[4] S. A. Silling and R. B. Lehoucq, J. Elasticity **93**, 13 (2008).

[5] E. Askari, F. Bobaru, R. B. Lehoucq, M. L. Parks, S. A. Silling, and O. Weckner, in *SciDAC 2008, 13-17 July, Washington* (IOP Publishing, 2008), vol. 125 of *Journal of Physics: Conference Series*, p. (012078).

[6] J. H. Irving and J. G. Kirkwood, J. Chem. Phys. **18**, 817 (1950).

[7] W. Noll, Indiana Univ. Math. J. **4**, 627 (1955), original publishing journal was the J. Rational Mech. Anal., URL `http://www.iumj.indiana.edu/IUMJ/FULLTEXT/1955/4/54022`.

[8] W. Noll, Tech. Rep. SAND 2007-5382, Sandia National Laboratories (2007), translation by R. B. Lehoucq and O. Anatole von Lilienfeld, to be published (with corrections) by the Journal of Elasticity., URL `http://arxiv.org/abs/0810.0337v3`.

[9] R. B. Lehoucq, Tech. Rep. 2009-1110J, Sandia National Laboratories, Albuquerque, NM 87185 (2009), to be published by the J. Elasticity.

[10] R. Hardy, J. Chem. Phys. **76**, 622 (1982).

[11] A. Murdoch and D. Bedeaux, Proc. Roy. Soc. London A **445**, 157 (1994).

[12] D. J. Evans and G. Morriss, *Statistical Mechanics of Nonequilibrium Liquids* (Cambridge University Press, 2008), 2nd ed.

[13] R. Hardy, S. Root, and D. Swanson (AIP, 2001), p. 363.

[14] J. Zimmerman, E. Webb, J. Hoyt, R. Jones, P. Klein, and D. Baumann, Modelling Simul. Mater. **12**, S319 (2004).

[15] H. Heinz, W. Paul, and K. Binder, Phys. Rev. E **72**, 66704 (2005).

[16] W. Noll, Journal of Elasticity (2009), in press.

[17] Y. Chen, J. Chem. Phys. **124**, 054113 (2006).

[18] J. Tersoff, Phys. Rev. Lett. **56**, 632 (1985).

[19] J. Tersoff, Phys. Rev. B **39**, R5566 (1989).

[20] N. C. Admal and E. B. Tadmor, Tech. Rep., University of Minnesota (2009), in preparation.

[21] A. I. Murdoch, J Elasticity **88**, 113 (2007).

[22] W. Noll, Arch. Ration. Mech. Anal. **48**, 1 (1972).

[23] A. M. et. al., *The Encyclopedia of Computational Chemistry* (1998).

[24] D. C. et. al., J. Comp. Chem. **26**, 1668 (2005).

[25] F. H. Stillinger and T. A. Weber, Phys. Rev. B **31**, 5262 (1984).

Sandia National Labs Technical Report 2009-0791J

APPENDIX

Here we include some simple formulas for distance parameter representation of common multibody terms.

Let $\mathbf{x}_1, \mathbf{x}_2, \mathbf{x}_3, \mathbf{x}_4$ be four position vectors. We can write the dot product

$$(\mathbf{x}_1 - \mathbf{x}_2) \cdot (\mathbf{x}_3 - \mathbf{x}_4) = \xi_{14} - \xi_{13} + \xi_{23} - \xi_{24}, \tag{47}$$

which we can easily establish by expanding each of the distance parameters ξ_{ij}. For the cosine of a bond angle θ between $\mathbf{x}_2 - \mathbf{x}_1$ and $\mathbf{x}_3 - \mathbf{x}_1$ we have

$$\cos\theta = \frac{(\mathbf{x}_2 - \mathbf{x}_1) \cdot (\mathbf{x}_3 - \mathbf{x}_1)}{|\mathbf{x}_2 - \mathbf{x}_1|\,|\mathbf{x}_3 - \mathbf{x}_1|}$$

and using the dot product formula above we get cosine of the bond angle in distance parameter form:

$$\cos\theta = \frac{\xi_{12} + \xi_{13} - \xi_{23}}{r_{12} r_{13}} \tag{48}$$

For torsion or dihedral angles we can suppose that we want to compute the torsion angle around the bond $\mathbf{x}_2, \mathbf{x}_3$ which is the angle between the plane containing the points $\mathbf{x}_1, \mathbf{x}_2, \mathbf{x}_3$ and the plane containing $\mathbf{x}_2, \mathbf{x}_3, \mathbf{x}_4$. The cosine of this angle is obviously

$$\cos\phi = \frac{((\mathbf{x}_1 - \mathbf{x}_2) \times (\mathbf{x}_1 - \mathbf{x}_3)) \cdot ((\mathbf{x}_4 - \mathbf{x}_2) \times (\mathbf{x}_4 - \mathbf{x}_3))}{|\mathbf{x}_1 - \mathbf{x}_2|\,|\mathbf{x}_1 - \mathbf{x}_3|\,|\mathbf{x}_4 - \mathbf{x}_2|\,|\mathbf{x}_4 - \mathbf{x}_3|} \tag{49}$$

and after simplification

$$\cos\phi = \frac{\xi_{12}(\xi_{34} - \xi_{24} + \xi_{23}) + \xi_{13}(\xi_{24} - \xi_{34} + \xi_{23}) - \xi_{23}^2}{r_{12}r_{13}r_{24}r_{34}} \tag{50}$$

Note that $\sin\phi$ is *not* invariant under reflection, so it cannot be computed in the distance parameter representation. Therefore potential terms proportional to something like $cos(n\phi + \delta)$ where δ is a phase factor parameter are not generally invariant under reflection. However, many commonly used potential parameterizations only use torsion phases that are 0 or π and so this problem does not occur.

We can imagine potentials which depend on the area of a triangle defined by three atoms or the volume of a tetrahedron defined by four atoms. For the unsigned area of a triangle one can use Herod's classical formula, and implicitly we see that there must be such a formula for the unsigned volume of a tetrahedron. In fact this is given by the formula of Piero della Francesca.

These formulas are sufficient to transform most standard molecular dynamics potentials into the distance parameter representation. With the above caveat about torsion potentials the stress and force state formulas derived in this paper should be applicable to multibody force fields such as CHARMM[23] and Amber[24]. As another example, the well-known Stillinger-Weber[25] potential for silicon is given as a sum of two body terms and three body terms

$$U = \frac{1}{2}\sum_{ij} f(r_{ij}) + \sum_{i,j,k} g(r_{ij})g(r_{ik})\left(\cos\theta_{ijk} - \frac{1}{3}\right)^2 \tag{51}$$

where f, g are specified functions. Therefore in distance-parameter form the Stillinger-Weber potential is given by

$$U = \frac{1}{2}\sum_{ij} f(2\sqrt{\xi_{ij}}) + \sum_{i,j,k} g(2\sqrt{\xi_{ij}})g(2\sqrt{\xi_{ik}})\left(\frac{\xi_{ij} + \xi_{ik} - \xi_{jk}}{2\sqrt{\xi_{ij}\xi_{ik}}} - \frac{1}{3}\right)^2. \tag{52}$$

Given these formulas the generalized forces G_{ij} are computed by simple differentiation using (8).

Sandia National Labs Technical Report 2009-0791J