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Expressions for the stress and elasticity tensors for angle-dependent potentials

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The stress and elasticity tensors for interatomic potentials that depend explicitly on bond bending and dihedral angles are derived by taking strain derivatives of the free energy. The resulting expressions can be used in Monte Carlo and molecular dynamics simulations in the canonical and microcanonical ensembles. These expressions are particularly useful at low temperatures where it is difficult to obtain results using the fluctuation formula of Parrinello and Rahman [J. Chem. Phys. **76**, 2662 (1982)]. Local elastic constants within heterogeneous and composite materials can also be calculated as a function of temperature using this method. As an example, the stress and elasticity tensors are derived for the second-generation reactive empirical bond-order potential. This potential energy function was used because it has been used extensively in computer simulations of hydrocarbon materials, including carbon nanotubes, and because it is one of the few potential energy functions that can model chemical reactions. To validate the accuracy of the derived expressions, the elastic constants for diamond and graphite and the Young's Modulus of a (10,10) single-wall carbon nanotube are all calculated at $T=0$ K using this potential and compared with previously published data and results obtained using other potentials.

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I. INTRODUCTION

In computational material science, molecular simulations play a critical role in relating atomic structure to bulk mechanical properties. The understanding of the relationship between stress and strain, i.e., elastic constants, in a particular material is of major importance for the design and engineering of new materials and devices.

Typical molecular simulation methods are implemented in a constant-volume ensemble, i.e., the canonical or microcanonical ensemble. In these ensembles, there are two common techniques for calculating the elastic constants. In the first, the mechanical properties are determined by evaluating the stress response due to the application of a finite strain to the material of interest. Many simulations at different applied strains must be done to determine the elastic constants, or elasticity tensor, of the material. This can be time consuming and has the potential to introduce errors because the elastic constants are defined in the limit of zero strain. The advantages to this approach are that only simple constant-volume simulations are required and only the stress tensor, which can be determined directly from the forces, needs to be evaluated. In the second technique, the elastic constants are calculated directly from the second derivative with respect to the strain tensor of the free energy.^{1,2} Some advantages of this method are that it works well at low temperatures, it converges more quickly than other fluctuation methods, only one simulation needs to be performed, and that the elastic constants are consequently evaluated in the limit of zero strain. However, the second derivative with respect to strain of the

interatomic potential needs to be evaluated, which can be particularly challenging for multibody potential functions that depend explicitly on intramolecular bond and dihedral angles.

An alternative approach to calculating the elasticity tensor is to use the constant-stress ensemble of Parrinello and Rahman³ and the strain-fluctuation formula for the elasticity tensor.⁴ This approach gives the full elasticity tensor in a single simulation, but requires the use of a more complicated simulation technique in which the size and shape of the simulation box become new degrees of freedom. This method is difficult to use near the melting point or glass transition temperature⁵ when the shape of the box is free to “flow” and highly elongated states are likely to occur. The strain fluctuations are also slow to converge in these situations.^{6,7}

In this work, the expressions for the stress and elasticity tensors for potentials that depend explicitly on bond and dihedral angles are derived. As an example, the equations for the second-generation reactive empirical bond-order (REBO) potential^{8,9} are derived. However, the equations are applicable to all the so-called bond-order potentials^{8–19} and useful for other angle-dependent potentials. In addition to the advantages mentioned above, the stress-fluctuation expressions for the elasticity tensor provide information regarding *local* or *atomic* stress and elastic constants^{5,20} and their relative contributions to the bulk elastic constants. However, due to the complexity of angle-dependent potentials, the derivation and implementation of these expressions can be tedious. This is particularly true for bond-order potentials,^{8–19} such as, the second-REBO potential.

Tersoff was the first to introduce a bond-order potential

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for carbon¹⁰ and later he extended it to silicon and germanium.¹¹ Brenner *et al.* adapted Tersoff's formalism and created the REBO potential for C–H interactions.^{12,13} The REBO potential has spawned a number of potentials for C–Si–H interactions,^{15,16,18} a potential for Si–H interactions,¹⁴ and a potential for C–H interactions that includes intermolecular forces.¹⁷ Recently, Brenner *et al.* updated the form of the REBO potential and produced the second-generation REBO potential.⁸ Several potentials based on this slightly changed formalism have appeared in the literature. These include a potential for C–O–H interactions¹⁹ and the adaptive intermolecular reactive bond-order (AIREBO) potential.¹⁷ One unique feature of the bond-order potentials is that chemical reactions can be modeled. This allows the REBO potential to model processes where bonds are broken and formed such as what might occur when two surfaces are in sliding contact.^{21–24} Intermolecular forces were added to the REBO potential, to create the AIREBO potential, in such a way as to preserve the ability to model chemical reactions by Stuart *et al.*⁹ This potential has been used to model compression- and shear-induced polymerization in monolayers composed of diacetylene chains²⁵ and to model thermal conductivity of nanotubes.²⁶

The REBO potential has also been used in many studies of the elastic properties of carbon nanotube systems.^{27–44} The mechanical properties of amorphous carbon films have also been studied.²³ In all these works, the mechanical properties were determined by evaluating the stress response due to the application of a finite strain to the material of interest. Using the results presented here, it is now possible to calculate the elasticity tensor for these systems and to examine their mechanical properties at the local and atomic levels as a function of temperature. For example, we have recently calculated the elastic properties of diamond as a function of temperature using the stress-fluctuation method.⁴⁵

In Sec. II, the general expressions for the stress and elasticity tensors in terms of the strain derivatives of the free energy are given. Special attention is given to the strain derivatives of angle-dependent terms in typical multibody potentials. A brief description of the second-generation REBO potential and an outline of its many terms is given in Sec. III. In Sec. IV, the first and second strain derivatives of the terms that make up the REBO potential, and contribute to the stress and elasticity tensors, are presented. Results for the elasticity tensors for diamond and graphite at zero temperature are given. Finally, the Young's Modulus of a (10,10) single-wall carbon nanotube at 0 K is also calculated. The (10,10) nanotube was selected, in part, due to the fact that these tubes are the most abundant product in the laser ablation apparatus.⁴⁶ In addition, we have used (10,10) nanotubes as model scanning probe microscope tips in molecular dynamics simulations⁴¹ and examined the mechanical properties of these tubes filled with C₆₀, butane, and other molecules.^{27,36}

Throughout this paper, Greek subscripts (α, β, μ, ν) represent Cartesian coordinates and Latin subscripts (i, j, k, l) represent atomic indices.

II. ANGLE-DEPENDENT POTENTIALS

The stress and elasticity tensors are derived by taking the first and second derivatives of the free energy with respect to strain. For a detailed discussion on evaluating strain derivatives, see Refs. 47 and 48. In the canonical ensemble, the stress tensor is

$$\sigma_{\alpha\beta} = \langle \sigma_{\alpha\beta}^B \rangle - \rho k_B T \delta_{\alpha\beta} \quad (1)$$

and the elasticity tensor is

$$C_{\alpha\beta\mu\nu} = \langle C_{\alpha\beta\mu\nu}^B \rangle - \frac{V}{k_B T} [\langle \sigma_{\alpha\beta}^B \sigma_{\mu\nu}^B \rangle - \langle \sigma_{\alpha\beta}^B \rangle \langle \sigma_{\mu\nu}^B \rangle] + \rho k_B T (\delta_{\alpha\mu} \delta_{\beta\nu} + \delta_{\alpha\nu} \delta_{\beta\mu}), \quad (2)$$

where

$$\sigma_{\alpha\beta}^B = \frac{1}{V} \frac{\partial U}{\partial \epsilon_{\alpha\beta}}, \quad (3)$$

and

$$C_{\alpha\beta\mu\nu}^B = \frac{1}{V} \frac{\partial^2 U}{\partial \epsilon_{\alpha\beta} \partial \epsilon_{\mu\nu}}. \quad (4)$$

Here, the total potential energy of the system is U , k_B is Boltzmann's constant, T is the temperature, V is the volume, ρ is the density of the system, and $\delta_{\alpha\beta}$ is the identity tensor. The first term in Eq. (2), the Born term, is the configurational contribution to the elasticity tensor. The second term is the stress-fluctuation term and the last term is the ideal gas contribution, which is related to the strain derivatives of the volume. Typically, only the first two terms contribute significantly to the elastic constants.

Although the stress-fluctuation formula for the elasticity tensor has several advantages, its use has been limited by the difficulty in evaluating the Born term for complex atomic potentials.^{6,49} For many potentials, multibody interactions such as bending and torsion make the use of the stress-fluctuation formula unattractive. Exact expressions for the Born term for potentials that include bending and torsional contributions have not previously appeared in the literature. An approximate method for estimating the Born term for potentials that only depend on interatomic forces was recently proposed by Yoshimoto *et al.*⁵⁰ One advantage of this method is that it only requires knowledge of the interatomic distances.

Bending and torsional potentials commonly contain terms that include the cosines of the bond angles ($\cos \theta_{jik}$) and dihedral angles ($\cos \omega_{kijl}$), i.e., the total potential energy can be written as

$$U = \sum_{ijk} u_{ijk}(\cos \theta_{jik}) + \sum_{ijkl} u_{ijkl}(\cos \omega_{kijl}), \quad (5)$$

where the summations include all atoms that participate in each bond. Note that only the contributions from the bonds are considered here; typical potentials have additional pairwise contributions that will not be discussed here. The first step is to evaluate the first and second strain derivatives of Eq. (5). The first derivative of the potential energy is

$$\frac{\partial U}{\partial \epsilon_{\alpha\beta}} = \sum_{ijk} \frac{\partial u_{ijk}}{\partial \cos \theta_{jik}} \frac{\partial \cos \theta_{jik}}{\partial \epsilon_{\alpha\beta}} + \sum_{ijkl} \frac{\partial u_{ijkl}}{\partial \cos \omega_{kijl}} \frac{\partial \cos \omega_{kijl}}{\partial \epsilon_{\alpha\beta}}, \quad (6)$$

and the second derivative is

$$\begin{aligned} \frac{\partial^2 U}{\partial \epsilon_{\alpha\beta} \partial \epsilon_{\mu\nu}} = & \sum_{ijk} \left[\frac{\partial^2 u_{ijk}}{\partial \cos^2 \theta_{jik}} \frac{\partial \cos \theta_{jik}}{\partial \epsilon_{\alpha\beta}} \frac{\partial \cos \theta_{jik}}{\partial \epsilon_{\mu\nu}} + \frac{\partial u_{ijk}}{\partial \cos \theta_{jik}} \frac{\partial^2 \cos \theta_{jik}}{\partial \epsilon_{\alpha\beta} \partial \epsilon_{\mu\nu}} \right] \\ & + \sum_{ijkl} \left[\frac{\partial^2 u_{ijkl}}{\partial \cos^2 \omega_{kijl}} \frac{\partial \cos \omega_{kijl}}{\partial \epsilon_{\alpha\beta}} \frac{\partial \cos \omega_{kijl}}{\partial \epsilon_{\mu\nu}} + \frac{\partial u_{ijkl}}{\partial \cos \omega_{kijl}} \frac{\partial^2 \cos \omega_{kijl}}{\partial \epsilon_{\alpha\beta} \partial \epsilon_{\mu\nu}} \right]. \end{aligned} \quad (7)$$

Next, the strain derivatives of the cosines of the bond angles that appear in Eqs. (6) and (7) are evaluated (Fig. 1).

The bond angle θ_{jik} formed by the vectors \vec{r}_{ji} and \vec{r}_{ki} can be expressed in terms of the distances r_{ij} , r_{jk} , and r_{ki} by using the law of cosines. Likewise, the dihedral angle ω_{kijl} formed by the plane containing atoms k, i, j and the plane containing atoms i, j, l can be expressed in terms of the distances between atoms i, j, k , and l by using the law of cosines in a tetrahedron.^{51,52} These expressions for θ_{jik} and ω_{kijl} can then be used to obtain the Born term using the general formula provided Ray,⁵³ which depends only on the interatomic distances. However, this procedure is tedious and leads to complicated expressions, especially for the dihedral term.

The approach used here is to express the cosines of the bond and dihedral angles in terms of the bond vectors between atom pairs (Fig. 1). Using this technique, the bond angle is given by

$$\cos \theta_{jik} = \frac{\vec{r}_{ji} \cdot \vec{r}_{ki}}{r_{ji} r_{ki}}, \quad (8)$$

where $\vec{r}_{ji} = \vec{r}_j - \vec{r}_i$ and $r_{ji} = |\vec{r}_{ji}|$. The dihedral angle is given by

$$\cos \omega_{kijl} = \frac{\vec{r}_{ki} \times \vec{r}_{ji}}{|\vec{r}_{ki} \times \vec{r}_{ji}|} \cdot \frac{\vec{r}_{ij} \times \vec{r}_{lj}}{|\vec{r}_{ij} \times \vec{r}_{lj}|}. \quad (9)$$

For clarity, the substitutions $\vec{u} = \vec{r}_{ji}$, $\vec{v} = \vec{r}_{ki}$, and $\vec{w} = \vec{r}_{lj}$ are made. Then the bond angle is

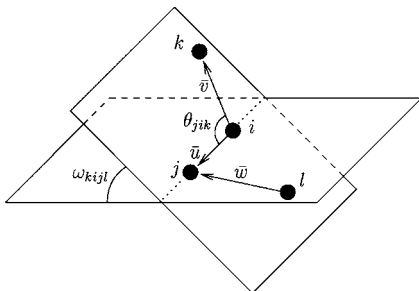


FIG. 1. Vectors defining the angle θ_{jik} and dihedral angle ω_{kijl} .

$$\cos \theta_{jik} = \frac{\vec{u} \cdot \vec{v}}{uv}, \quad (10)$$

and the dihedral angle is

$$\cos \omega_{kijl} = \frac{\vec{v} \times \vec{u}}{|\vec{v} \times \vec{u}|} \cdot \frac{\vec{u} \times \vec{w}}{|\vec{u} \times \vec{w}|}. \quad (11)$$

For the dihedral angle, the further substitutions $\vec{m} = \vec{v} \times \vec{u}$ and $\vec{n} = \vec{u} \times \vec{w}$ are made, so that

$$\cos \omega_{kijl} = \frac{\vec{m} \cdot \vec{n}}{mn}. \quad (12)$$

The strain derivative of the product of two vectors appears repeatedly in the derivation of the following results. For this reason, this tensor is given explicitly here for reference. For two general vectors \vec{v} and \vec{w} that depend explicitly on the strain tensor, the derivative of their product at arbitrary strain is given by

$$\frac{\partial \vec{v} \cdot \vec{w}}{\partial \epsilon_{\alpha\beta}} = \tilde{v}_\alpha \tilde{w}_\beta + \tilde{w}_\alpha \tilde{v}_\beta. \quad (13)$$

Symbols with a tilde, e.g., \tilde{v}_α , indicate that this vector quantity is evaluated in the reference state, i.e., at zero strain, and is therefore considered a constant in subsequent strain derivatives. The fact that the derivative in Eq. (13) is a constant with respect to strain for arbitrary values of the strain tensor is a consequence of the definition of the strain derivative.⁴⁷

For convenience, we give formulae for the strain derivatives of natural log of the cosine of the angles. If required, it is then trivial to obtain the derivatives of the angles themselves. The first derivative of $\cos \theta_{jik}$ comes from

$$\frac{\partial \ln \cos \theta_{jik}}{\partial \epsilon_{\alpha\beta}} = \frac{\tilde{u}_\alpha \tilde{v}_\beta + \tilde{v}_\alpha \tilde{u}_\beta}{\vec{u} \cdot \vec{v}} - \left(\frac{\tilde{u}_\alpha \tilde{u}_\beta}{u^2} + \frac{\tilde{v}_\alpha \tilde{v}_\beta}{v^2} \right), \quad (14)$$

and the second derivative comes from

$$\frac{1}{\cos \theta_{jik}} \frac{\partial^2 \cos \theta_{jik}}{\partial \epsilon_{\alpha\beta} \partial \epsilon_{\mu\nu}} = \frac{\partial^2 \ln \cos \theta_{jik}}{\partial \epsilon_{\alpha\beta} \partial \epsilon_{\mu\nu}} + \frac{\partial \ln \cos \theta_{jik}}{\partial \epsilon_{\alpha\beta}} \frac{\partial \ln \cos \theta_{jik}}{\partial \epsilon_{\mu\nu}}, \quad (15)$$

where

$$\frac{\partial^2 \ln \cos \theta_{jik}}{\partial \epsilon_{\alpha\beta} \partial \epsilon_{\mu\nu}} = - \frac{(\tilde{v}_\alpha \tilde{u}_\beta + \tilde{u}_\alpha \tilde{v}_\beta)(\tilde{v}_\mu \tilde{u}_\nu + \tilde{u}_\mu \tilde{v}_\nu)}{(\tilde{u} \cdot \tilde{v})^2} + 2 \left(\frac{\tilde{u}_\alpha \tilde{u}_\beta \tilde{u}_\mu \tilde{u}_\nu}{u^4} + \frac{\tilde{v}_\alpha \tilde{v}_\beta \tilde{v}_\mu \tilde{v}_\nu}{v^4} \right). \quad (16)$$

For the dihedral angle, it is more convenient to work with $\ln \cos^2 \omega_{kijl}$. The first derivative comes from

$$\frac{\partial \ln \cos^2 \omega_{kijl}}{\partial \epsilon_{\alpha\beta}} = \frac{1}{(\tilde{m} \cdot \tilde{n})^2} \frac{\partial (\tilde{m} \cdot \tilde{n})^2}{\partial \epsilon_{\alpha\beta}} - \frac{1}{m^2} \frac{\partial m^2}{\partial \epsilon_{\alpha\beta}} - \frac{1}{n^2} \frac{\partial n^2}{\partial \epsilon_{\alpha\beta}} \quad (17)$$

and the second derivative is given by

$$\begin{aligned} \frac{\partial^2 \ln \cos^2 \omega_{kijl}}{\partial \epsilon_{\alpha\beta} \partial \epsilon_{\mu\nu}} = & - \frac{1}{(\tilde{m} \cdot \tilde{n})^4} \frac{\partial (\tilde{m} \cdot \tilde{n})^2}{\partial \epsilon_{\alpha\beta}} \frac{\partial (\tilde{m} \cdot \tilde{n})^2}{\partial \epsilon_{\mu\nu}} \\ & + \frac{1}{(\tilde{m} \cdot \tilde{n})^2} \frac{\partial^2 (\tilde{m} \cdot \tilde{n})^2}{\partial \epsilon_{\alpha\beta} \partial \epsilon_{\mu\nu}} + \frac{1}{m^4} \frac{\partial m^2}{\partial \epsilon_{\alpha\beta}} \frac{\partial m^2}{\partial \epsilon_{\mu\nu}} \\ & - \frac{1}{m^2} \frac{\partial^2 m^2}{\partial \epsilon_{\alpha\beta} \partial \epsilon_{\mu\nu}} + \frac{1}{n^4} \frac{\partial n^2}{\partial \epsilon_{\alpha\beta}} \frac{\partial n^2}{\partial \epsilon_{\mu\nu}} \\ & - \frac{1}{n^2} \frac{\partial^2 n^2}{\partial \epsilon_{\alpha\beta} \partial \epsilon_{\mu\nu}}, \end{aligned} \quad (18)$$

where

$$\begin{aligned} \frac{\partial \tilde{m} \cdot \tilde{n}}{\partial \epsilon_{\alpha\beta}} = & (\tilde{v} \cdot \tilde{u})(\tilde{u}_\alpha \tilde{w}_\beta + \tilde{w}_\alpha \tilde{u}_\beta) + (\tilde{u} \cdot \tilde{w})(\tilde{v}_\alpha \tilde{u}_\beta + \tilde{u}_\alpha \tilde{v}_\beta) \\ & - (\tilde{v} \cdot \tilde{w})(\tilde{u}_\alpha \tilde{u}_\beta + \tilde{u}_\alpha \tilde{u}_\beta) - (\tilde{u} \cdot \tilde{u})(\tilde{v}_\alpha \tilde{w}_\beta + \tilde{w}_\alpha \tilde{v}_\beta), \end{aligned} \quad (19)$$

$$\begin{aligned} \frac{\partial^2 \tilde{m} \cdot \tilde{n}}{\partial \epsilon_{\alpha\beta} \partial \epsilon_{\mu\nu}} = & (\tilde{v}_\alpha \tilde{u}_\beta + \tilde{u}_\alpha \tilde{v}_\beta)(\tilde{w}_\mu \tilde{u}_\nu + \tilde{u}_\mu \tilde{w}_\nu) \\ & + (\tilde{w}_\alpha \tilde{u}_\beta + \tilde{u}_\alpha \tilde{w}_\beta)(\tilde{v}_\mu \tilde{u}_\nu + \tilde{u}_\mu \tilde{v}_\nu) \\ & - (\tilde{v}_\alpha \tilde{w}_\beta + \tilde{w}_\alpha \tilde{v}_\beta)(\tilde{u}_\mu \tilde{u}_\nu + \tilde{u}_\mu \tilde{u}_\nu) \\ & - (\tilde{u}_\alpha \tilde{u}_\beta + \tilde{u}_\alpha \tilde{u}_\beta)(\tilde{v}_\mu \tilde{w}_\nu + \tilde{w}_\mu \tilde{v}_\nu), \end{aligned} \quad (20)$$

$$\frac{\partial m^2}{\partial \epsilon_{\alpha\beta}} = 2[u^2 \tilde{v}_\alpha \tilde{v}_\beta + v^2 \tilde{u}_\alpha \tilde{u}_\beta - (\tilde{v} \cdot \tilde{u})(\tilde{v}_\alpha \tilde{u}_\beta + \tilde{u}_\alpha \tilde{v}_\beta)], \quad (21)$$

$$\frac{\partial n^2}{\partial \epsilon_{\alpha\beta}} = 2[u^2 \tilde{w}_\alpha \tilde{w}_\beta + w^2 \tilde{u}_\alpha \tilde{u}_\beta - (\tilde{w} \cdot \tilde{u})(\tilde{w}_\alpha \tilde{u}_\beta + \tilde{u}_\alpha \tilde{w}_\beta)], \quad (22)$$

$$\begin{aligned} \frac{\partial^2 m^2}{\partial \epsilon_{\alpha\beta} \partial \epsilon_{\mu\nu}} = & 4(\tilde{v}_\alpha \tilde{v}_\beta \tilde{u}_\mu \tilde{u}_\nu + \tilde{u}_\alpha \tilde{u}_\beta \tilde{v}_\mu \tilde{v}_\nu) - 2(\tilde{v}_\alpha \tilde{u}_\beta + \tilde{u}_\alpha \tilde{v}_\beta) \\ & \times (\tilde{v}_\mu \tilde{u}_\nu + \tilde{u}_\mu \tilde{v}_\nu), \end{aligned} \quad (23)$$

and

$$\begin{aligned} \frac{\partial^2 n^2}{\partial \epsilon_{\alpha\beta} \partial \epsilon_{\mu\nu}} = & 4(\tilde{w}_\alpha \tilde{w}_\beta \tilde{u}_\mu \tilde{u}_\nu + \tilde{u}_\alpha \tilde{u}_\beta \tilde{w}_\mu \tilde{w}_\nu) - 2(\tilde{w}_\alpha \tilde{u}_\beta + \tilde{u}_\alpha \tilde{w}_\beta) \\ & \times (\tilde{w}_\mu \tilde{u}_\nu + \tilde{u}_\mu \tilde{w}_\nu). \end{aligned} \quad (24)$$

The strain derivatives of the cosine of the bond angle are determined by the combination of Eqs. (14)–(16). The strain derivatives of the cosine of the dihedral angle are determined by combination of Eqs. (17)–(24). The stress and elasticity tensors can then be obtained by combination with Eqs. (1)–(4), (6), and (7).

III. REBO POTENTIAL

In what follows, a brief outline of the second-generation REBO potential is provided. The terms that are given below have been included because they are presented in a slightly different, but equivalent, form than originally published in an effort to make their implementation more clear or because they are discussed later in the manuscript. Full descriptions of the REBO potential, including parameter values and spline coefficients, are given elsewhere.^{8,9}

The total potential energy is given by

$$U = \frac{1}{2} \sum_{i,j \neq i} V_{ij}^r + b_{ij} V_{ij}^a, \quad (25)$$

where V_{ij}^r and V_{ij}^a are the pairwise repulsive and attractive terms, respectively. The bond-order term, b_{ij} , is a many-body term, which modifies the attractive part of the potential based on the local environment of atoms i and j .

Both the pairwise repulsive and attractive terms contain a cutoff function, w_{ij} , which is piecewise continuous and depends on the distance, r_{ij} , between atoms i and j . The function w_{ij} is given by

$$w_{ij} = \begin{cases} 1, & \text{for } (0, r_{ij}^{\min}) \\ \frac{1}{2} [1 + \cos(\pi(r_{ij} - r_{ij}^{\min})/(r_{ij}^{\max} - r_{ij}^{\min}))], & \text{for } (r_{ij}^{\min}, r_{ij}^{\max}) \\ 0, & \text{for } (r_{ij}^{\max}, \infty), \end{cases} \quad (26)$$

where r_{ij}^{\min} and r_{ij}^{\max} are parameters that depend on the atom types of i and j .

The angular dependence enters the REBO through the bond-order term, b_{ij} . The bond order is the sum of the covalent and the π contributions to the bond order and is given by

$$b_{ij} = \frac{1}{2} [p_{ij}^{\sigma\pi} + p_{ji}^{\sigma\pi}] + \pi_{ij}^{rc} + \pi_{ij}^{dh}. \quad (27)$$

The covalent contribution to the bond order, $p_{ij}^{\sigma\pi}$, contains a fifth-order spline, g_{jik} , that is a function of the bond angle θ_{jik} between atoms j , i , and k , where i is at the vertex of the angle. If atom i is a carbon atom, then

$$g_{jik}(\cos \theta_{jik}) = g_C^{(1)} + S_{ij}(N_{ij})(g_C^{(2)} - g_C^{(1)}), \quad (28)$$

and if atom i is a hydrogen atom, then $g_{jik}(\cos \theta_{jik}) = g_H$. Additional details regarding the spline functions $g_C^{(1)}(\cos \theta_{jik})$, $g_C^{(2)}(\cos \theta_{jik})$, and $g_H(\cos \theta_{jik})$ can be found elsewhere.^{8,9}

A number of terms within the REBO potential depend on the local coordination number, N_{ij} . For example, the two- and three-dimensional spline functions $P_{ij}(N_{ij}^C, N_{ij}^H)$ and $\pi_{ij}^{rc}(N_{ij}, N_{ji}, N_{ij}^{\text{conj}})$ and the switching function S_{ij} are all functions of N_{ij} . The form of the S_{ij} function is identical to that of the w_{ij} switching function with the distances, r_{ij} , replaced by the local coordination, N_{ij} . The local coordination number is the sum of the carbon and hydrogen coordination numbers, $N_{ij} = N_{ij}^C + N_{ij}^H$. The functions N_{ij}^C and N_{ij}^H have the same form with N_{ij}^C given by

$$N_{ij}^C = \sum_{k \neq i,j} \delta_{kC} w_{ik}. \quad (29)$$

The three-dimensional cubic spline function π_{ij}^{rc} depends on N_{ij} , N_{ji} , and the local degree of conjugation, N_{ij}^{conj} , which is defined as $N_{ij}^{\text{conj}} = 1 + X_{ij}^2 + Y_{ij}^2$, where

$$X_{ij} = \sum_{k \neq i,j} \delta_{kC} w_{ik} S_{ik}^{\text{conj}}(N_{ki}). \quad (30)$$

The function Y_{ij} has the same form as X_{ij} except in this case the summation is over atom l instead of atom k . The function S_{ij}^{conj} has the same form as S_{ij} , but with slightly different values for the parameters N^{min} and N^{max} .

The remaining contribution to the bond-order term, π_{ij}^{dh} , is related to the dihedral angles formed by the local neighbors of the bond between i and j and is given by $\pi_{ij}^{dh} = T_{ij}(N_{ij}, N_{ji}, N_{ij}^{\text{conj}}) Z_{ij}$, where

$$Z_{ij} = \sum_{k \neq i,j} \sum_{l \neq i,j,k} \sin^2 \omega_{kijl} w'_{ik} w'_{jl} \times \Theta(\sin \theta_{jik} - s^{\text{min}}) \Theta(\sin \theta_{ijl} - s^{\text{min}}), \quad (31)$$

and $T_{ij}(N_{ij}, N_{ji}, N_{ij}^{\text{conj}})$ is another three-dimensional cubic spline function. The dihedral angle ω_{kijl} is defined in Fig. 1. The function w'_{ij} has the same form as w_{ij} , but with slightly different values for r^{min} and r^{max} , and Θ is the Heaviside step function.

IV. THE REBO POTENTIAL DERIVATIVES

The first strain derivative of the REBO potential energy is

$$\frac{\partial U}{\partial \epsilon_{\alpha\beta}} = \frac{1}{2} \sum_{i,j \neq i} \frac{\partial V_{ij}^r}{\partial \epsilon_{\alpha\beta}} + \frac{\partial b_{ij}}{\partial \epsilon_{\alpha\beta}} V_{ij}^a + b_{ij} \frac{\partial V_{ij}^a}{\partial \epsilon_{\alpha\beta}}. \quad (32)$$

The second strain derivative of the REBO potential energy is

$$\begin{aligned} \frac{\partial^2 U}{\partial \epsilon_{\alpha\beta} \partial \epsilon_{\mu\nu}} = & \frac{1}{2} \sum_{i,j \neq i} \frac{\partial^2 V_{ij}^r}{\partial \epsilon_{\alpha\beta} \partial \epsilon_{\mu\nu}} + \frac{\partial^2 b_{ij}}{\partial \epsilon_{\alpha\beta} \partial \epsilon_{\mu\nu}} V_{ij}^a + \frac{\partial V_{ij}^a}{\partial \epsilon_{\alpha\beta}} \frac{\partial b_{ij}}{\partial \epsilon_{\mu\nu}} \\ & + \frac{\partial b_{ij}}{\partial \epsilon_{\alpha\beta}} \frac{\partial V_{ij}^a}{\partial \epsilon_{\mu\nu}} + b_{ij} \frac{\partial^2 V_{ij}^a}{\partial \epsilon_{\alpha\beta} \partial \epsilon_{\mu\nu}}, \end{aligned} \quad (33)$$

where

$$\frac{\partial V_{ij}^r}{\partial \epsilon_{\alpha\beta}} = \frac{1}{r_{ij}} \frac{\partial V_{ij}^r}{\partial r_{ij}} \tilde{r}_{ij\alpha} \tilde{r}_{ij\beta} \quad (34)$$

and

$$\frac{\partial^2 V_{ij}^r}{\partial \epsilon_{\alpha\beta} \partial \epsilon_{\mu\nu}} = \frac{1}{r_{ij}^2} \left(\frac{\partial^2 V_{ij}^r}{\partial r_{ij}^2} - \frac{1}{r_{ij}} \frac{\partial V_{ij}^r}{\partial r_{ij}} \right) \tilde{r}_{ij\alpha} \tilde{r}_{ij\beta} \tilde{r}_{ij\mu} \tilde{r}_{ij\nu}. \quad (35)$$

The derivatives of V_{ij}^a are defined similarly. In what follows, only the strain derivatives of the individual terms in the REBO potential are provided. Due to the large number of terms in the REBO potential, it is impractical to provide single expressions for the stress and elasticity tensors. However, their construction should be clear using the following equations.

It should also be noted that although the REBO potential was carefully constructed such that its first derivative is a continuous function, the same is not true of subsequent derivatives. One example of this is the switching function, w_{ij} . A discontinuity arises for r values of r^{min} and r^{max} , but is well defined at these values. Special care must be taken at the points of discontinuity when evaluating the second derivatives of the terms in the REBO potential. The convention used here is to take the midpoint of the left and right hand side values as the value at the point of discontinuity. For example, if the second derivative of the function $f(x)$ has a discontinuity at $x=x_0$, then $f''(x_0)$ takes the value

$$f''(x_0) = \frac{1}{2} \left[\lim_{x \rightarrow x_0^-} f''(x) + \lim_{x \rightarrow x_0^+} f''(x) \right]. \quad (36)$$

Despite the fact that the second derivative is discontinuous, its evaluation over the entire domain of interest is possible and does not prevent the evaluation of the elasticity tensor.

The resulting expressions for the first and second derivatives for the terms of second-generation REBO potential are given below. Because several terms in the potential have similar forms, only the strain derivatives of one term with each particular form is presented. It is a simple matter, though time consuming, to construct all the required terms. This task is left to the reader for the sake of brevity.

$$\frac{\partial b_{ij}}{\partial \epsilon_{\alpha\beta}} = \frac{1}{2} \left[\frac{\partial p_{ij}^{\sigma\pi}}{\partial \epsilon_{\alpha\beta}} + \frac{\partial p_{ji}^{\sigma\pi}}{\partial \epsilon_{\alpha\beta}} \right] + \frac{\partial \pi_{ij}^{rc}}{\partial \epsilon_{\alpha\beta}} + \frac{\partial \pi_{ij}^{dh}}{\partial \epsilon_{\alpha\beta}}, \quad (37)$$

$$\begin{aligned} \frac{\partial^2 b_{ij}}{\partial \epsilon_{\alpha\beta} \partial \epsilon_{\mu\nu}} = & \frac{1}{2} \left[\frac{\partial^2 p_{ij}^{\sigma\pi}}{\partial \epsilon_{\alpha\beta} \partial \epsilon_{\mu\nu}} + \frac{\partial^2 p_{ji}^{\sigma\pi}}{\partial \epsilon_{\alpha\beta} \partial \epsilon_{\mu\nu}} \right] + \frac{\partial^2 \pi_{ij}^{rc}}{\partial \epsilon_{\alpha\beta} \partial \epsilon_{\mu\nu}} \\ & + \frac{\partial^2 \pi_{ij}^{dh}}{\partial \epsilon_{\alpha\beta} \partial \epsilon_{\mu\nu}}, \end{aligned} \quad (38)$$

$$\frac{\partial p_{ij}^{\sigma\pi}}{\partial \epsilon_{\alpha\beta}} = -\frac{1}{2} p_{ij}^{\sigma\pi 3} \left[\sum_{k \neq i,j} \left\{ \frac{\partial w_{ik}}{\partial \epsilon_{\alpha\beta}} g_{jik} e^{\lambda_{jik}} + w_{ik} \frac{\partial g_{jik}}{\partial \epsilon_{\alpha\beta}} e^{\lambda_{jik}} + w_{ik} g_{jik} e^{\lambda_{jik}} \frac{\partial \lambda_{jik}}{\partial \epsilon_{\alpha\beta}} \right\} + \frac{\partial P_{ij}}{\partial \epsilon_{\alpha\beta}} \right], \quad (39)$$

$$\begin{aligned} \frac{\partial^2 p_{ij}^{\sigma\pi}}{\partial \epsilon_{\alpha\beta} \partial \epsilon_{\mu\nu}} = & \frac{3}{p_{ij}^{\sigma\pi}} \frac{\partial p_{ij}^{\sigma\pi}}{\partial \epsilon_{\alpha\beta}} \frac{\partial p_{ij}^{\sigma\pi}}{\partial \epsilon_{\mu\nu}} - \frac{1}{2} p_{ij}^{\sigma\pi 3} \left[\frac{\partial^2 P_{ij}}{\partial \epsilon_{\alpha\beta} \partial \epsilon_{\mu\nu}} + \sum_{k \neq i,j} \left\{ g_{jik} \frac{\partial^2 w_{ik}}{\partial \epsilon_{\alpha\beta} \partial \epsilon_{\mu\nu}} + \frac{\partial g_{jik}}{\partial \epsilon_{\alpha\beta}} \frac{\partial w_{ik}}{\partial \epsilon_{\mu\nu}} + g_{jik} \frac{\partial \lambda_{jik}}{\partial \epsilon_{\alpha\beta}} \frac{\partial w_{ik}}{\partial \epsilon_{\mu\nu}} + \frac{\partial w_{ik}}{\partial \epsilon_{\alpha\beta}} \frac{\partial g_{jik}}{\partial \epsilon_{\mu\nu}} \right. \right. \\ & \left. \left. + w_{ik} \frac{\partial^2 g_{jik}}{\partial \epsilon_{\alpha\beta} \partial \epsilon_{\mu\nu}} + w_{ik} \frac{\partial \lambda_{jik}}{\partial \epsilon_{\alpha\beta}} \frac{\partial g_{jik}}{\partial \epsilon_{\mu\nu}} + g_{jik} \frac{\partial w_{ki}}{\partial \epsilon_{\alpha\beta}} \frac{\partial \lambda_{jik}}{\partial \epsilon_{\mu\nu}} + w_{ik} \frac{\partial g_{jik}}{\partial \epsilon_{\alpha\beta}} \frac{\partial \lambda_{jik}}{\partial \epsilon_{\mu\nu}} + w_{ik} g_{jik} \left(\frac{\partial \lambda_{jik}}{\partial \epsilon_{\alpha\beta}} \frac{\partial \lambda_{jik}}{\partial \epsilon_{\mu\nu}} + \frac{\partial^2 \lambda_{jik}}{\partial \epsilon_{\alpha\beta} \partial \epsilon_{\mu\nu}} \right) \right\} e^{\lambda_{jik}} \right], \quad (40) \end{aligned}$$

$$\frac{\partial w_{ik}}{\partial \epsilon_{\alpha\beta}} = \frac{1}{r_{ik}} \frac{\partial w_{ik}}{\partial r_{ik}} \tilde{r}_{ik\alpha} \tilde{r}_{ik\beta}, \quad (41)$$

$$\frac{\partial^2 w_{ik}}{\partial \epsilon_{\alpha\beta} \partial \epsilon_{\mu\nu}} = \frac{1}{r_{ik}^2} \left(\frac{\partial^2 w_{ik}}{\partial r_{ik}^2} - \frac{1}{r_{ik}} \frac{\partial w_{ik}}{\partial r_{ik}} \right) \tilde{r}_{ik\alpha} \tilde{r}_{ik\beta} \tilde{r}_{ik\mu} \tilde{r}_{ik\nu}, \quad (42)$$

$$\frac{\partial \lambda_{jik}}{\partial \epsilon_{\alpha\beta}} = 4 \delta_{iH} \left(\frac{\tilde{r}_{ij\alpha} \tilde{r}_{ij\beta}}{r_{ij}} - \frac{\tilde{r}_{ik\alpha} \tilde{r}_{ik\beta}}{r_{ik}} \right), \quad (43)$$

$$\frac{\partial^2 \lambda_{jik}}{\partial \epsilon_{\alpha\beta} \partial \epsilon_{\mu\nu}} = 4 \delta_{iH} \left(\frac{\tilde{r}_{ik\alpha} \tilde{r}_{ik\beta} \tilde{r}_{ik\mu} \tilde{r}_{ik\nu}}{r_{ik}^3} - \frac{\tilde{r}_{ij\alpha} \tilde{r}_{ij\beta} \tilde{r}_{ij\mu} \tilde{r}_{ij\nu}}{r_{ij}^3} \right), \quad (44)$$

$$\frac{\partial g_{jik}}{\partial \epsilon_{\alpha\beta}} = \frac{\partial g_C^{(1)}}{\partial \cos \theta_{jik}} \frac{\partial \cos \theta_{jik}}{\partial \epsilon_{\alpha\beta}} + \frac{\partial S_{ij}}{\partial N_{ij}} \frac{\partial N_{ij}}{\partial \epsilon_{\alpha\beta}} (g_C^{(2)} - g_C^{(1)}) + S_{ij} \left(\frac{\partial g_C^{(2)}}{\partial \cos \theta_{jik}} - \frac{\partial g_C^{(1)}}{\partial \cos \theta_{jik}} \right) \frac{\partial \cos \theta_{jik}}{\partial \epsilon_{\alpha\beta}}, \quad (45)$$

$$\begin{aligned} \frac{\partial^2 g_{jik}}{\partial \epsilon_{\alpha\beta} \partial \epsilon_{\mu\nu}} = & \left[\frac{\partial^2 g_C^{(1)}}{\partial \cos \theta_{jik}^2} + \frac{\partial^2 S_{ij}}{\partial N_{ij}^2} (g_C^{(2)} - g_C^{(1)}) \frac{\partial N_{ij}}{\partial \epsilon_{\alpha\beta}} \frac{\partial N_{ij}}{\partial \epsilon_{\mu\nu}} + \frac{\partial S_{ij}}{\partial N_{ij}} (g_C^{(2)} - g_C^{(1)}) \frac{\partial^2 N_{ij}}{\partial \epsilon_{\alpha\beta} \partial \epsilon_{\mu\nu}} + \frac{\partial S_{ij}}{\partial N_{ij}} \left(\frac{\partial g_C^{(2)}}{\partial \cos \theta_{jik}} - \frac{\partial g_C^{(1)}}{\partial \cos \theta_{jik}} \right) \right. \\ & \times \left(\frac{\partial \cos \theta_{jik}}{\partial \epsilon_{\alpha\beta}} \frac{\partial N_{ij}}{\partial \epsilon_{\mu\nu}} + \frac{\partial N_{ij}}{\partial \epsilon_{\alpha\beta}} \frac{\partial \cos \theta_{jik}}{\partial \epsilon_{\mu\nu}} \right) + S_{ij} \left(\frac{\partial^2 g_C^{(2)}}{\partial \cos \theta_{jik}^2} - \frac{\partial^2 g_C^{(1)}}{\partial \cos \theta_{jik}^2} \right) \left. \frac{\partial \cos \theta_{jik}}{\partial \epsilon_{\alpha\beta}} \frac{\partial \cos \theta_{jik}}{\partial \epsilon_{\mu\nu}} + \left[\frac{\partial g_C^{(1)}}{\partial \cos \theta_{jik}} \right. \right. \\ & \left. \left. + S_{ij} \left(\frac{\partial g_C^{(2)}}{\partial \cos \theta_{jik}} - \frac{\partial g_C^{(1)}}{\partial \cos \theta_{jik}} \right) \right] \frac{\partial^2 \cos \theta_{jik}}{\partial \epsilon_{\alpha\beta} \partial \epsilon_{\mu\nu}} \right], \quad (46) \end{aligned}$$

$$\frac{\partial P_{ij}}{\partial \epsilon_{\alpha\beta}} = \frac{\partial P_{ij}}{\partial N_{ij}^C} \frac{\partial N_{ij}^C}{\partial \epsilon_{\alpha\beta}} + \frac{\partial P_{ij}}{\partial N_{ij}^H} \frac{\partial N_{ij}^H}{\partial \epsilon_{\alpha\beta}}, \quad (47)$$

$$\frac{\partial^2 P_{ij}}{\partial \epsilon_{\alpha\beta} \partial \epsilon_{\mu\nu}} = \frac{\partial^2 P_{ij}}{\partial N_{ij}^{C^2}} \frac{\partial N_{ij}^C}{\partial \epsilon_{\alpha\beta}} \frac{\partial N_{ij}^C}{\partial \epsilon_{\mu\nu}} + \frac{\partial P_{ij}}{\partial N_{ij}^C} \frac{\partial^2 N_{ij}^C}{\partial \epsilon_{\alpha\beta} \partial \epsilon_{\mu\nu}} + \frac{\partial^2 P_{ij}}{\partial N_{ij}^C \partial N_{ij}^H} \left(\frac{\partial N_{ij}^C}{\partial \epsilon_{\alpha\beta}} \frac{\partial N_{ij}^H}{\partial \epsilon_{\mu\nu}} + \frac{\partial N_{ij}^H}{\partial \epsilon_{\alpha\beta}} \frac{\partial N_{ij}^C}{\partial \epsilon_{\mu\nu}} \right) + \frac{\partial^2 P_{ij}}{\partial N_{ij}^{H^2}} \frac{\partial N_{ij}^H}{\partial \epsilon_{\alpha\beta}} \frac{\partial N_{ij}^H}{\partial \epsilon_{\mu\nu}} + \frac{\partial P_{ij}}{\partial N_{ij}^H} \frac{\partial^2 N_{ij}^H}{\partial \epsilon_{\alpha\beta} \partial \epsilon_{\mu\nu}}, \quad (48)$$

$$\frac{\partial N_{ij}^C}{\partial \epsilon_{\alpha\beta}} = \sum_{m \neq i,j} \delta_{mC} \frac{\partial w_{im}}{\partial \epsilon_{\alpha\beta}}, \quad (49)$$

$$\frac{\partial^2 N_{ij}^C}{\partial \epsilon_{\alpha\beta} \partial \epsilon_{\mu\nu}} = \sum_{m \neq i,j} \delta_{mC} \frac{\partial^2 w_{im}}{\partial \epsilon_{\alpha\beta} \partial \epsilon_{\mu\nu}}, \quad (50)$$

$$\frac{\partial \pi_{ij}^{rc}}{\partial \epsilon_{\alpha\beta}} = \frac{\partial \pi_{ij}^{rc}}{\partial N_{ij}} \frac{\partial N_{ij}}{\partial \epsilon_{\alpha\beta}} + \frac{\partial \pi_{ij}^{rc}}{\partial N_{ji}} \frac{\partial N_{ji}}{\partial \epsilon_{\alpha\beta}} + \frac{\partial \pi_{ij}^{rc}}{\partial N_{ij}^{\text{conj}}} \frac{\partial N_{ij}^{\text{conj}}}{\partial \epsilon_{\alpha\beta}}, \quad (51)$$

$$\begin{aligned}
\frac{\partial^2 \pi_{ij}^{rc}}{\partial \epsilon_{\alpha\beta} \partial \epsilon_{\mu\nu}} = & \frac{\partial \pi_{ij}^{rc}}{\partial N_{ij}} \frac{\partial^2 N_{ij}}{\partial \epsilon_{\alpha\beta} \partial \epsilon_{\mu\nu}} + \frac{\partial \pi_{ij}^{rc}}{\partial N_{ji}} \frac{\partial^2 N_{ji}}{\partial \epsilon_{\alpha\beta} \partial \epsilon_{\mu\nu}} + \frac{\partial \pi_{ij}^{rc}}{\partial N_{ij}^{\text{conj}}} \frac{\partial^2 N_{ij}^{\text{conj}}}{\partial \epsilon_{\alpha\beta} \partial \epsilon_{\mu\nu}} + \frac{\partial^2 \pi_{ij}^{rc}}{\partial N_{ij}^2} \frac{\partial N_{ij}}{\partial \epsilon_{\alpha\beta}} \frac{\partial N_{ij}}{\partial \epsilon_{\mu\nu}} + \frac{\partial^2 \pi_{ij}^{rc}}{\partial N_{ji}^2} \frac{\partial N_{ji}}{\partial \epsilon_{\alpha\beta}} \frac{\partial N_{ji}}{\partial \epsilon_{\mu\nu}} \\
& + \frac{\partial^2 \pi_{ij}^{rc}}{\partial N_{ij}^{\text{conj}^2}} \frac{\partial N_{ij}^{\text{conj}}}{\partial \epsilon_{\alpha\beta}} \frac{\partial N_{ij}^{\text{conj}}}{\partial \epsilon_{\mu\nu}} + \frac{\partial^2 \pi_{ij}^{rc}}{\partial N_{ij} \partial N_{ji}} \left(\frac{\partial N_{ij}}{\partial \epsilon_{\alpha\beta}} \frac{\partial N_{ji}}{\partial \epsilon_{\mu\nu}} + \frac{\partial N_{ji}}{\partial \epsilon_{\alpha\beta}} \frac{\partial N_{ij}}{\partial \epsilon_{\mu\nu}} \right) + \frac{\partial^2 \pi_{ij}^{rc}}{\partial N_{ji} \partial N_{ij}^{\text{conj}}} \left(\frac{\partial N_{ji}}{\partial \epsilon_{\alpha\beta}} \frac{\partial N_{ij}^{\text{conj}}}{\partial \epsilon_{\mu\nu}} + \frac{\partial N_{ij}^{\text{conj}}}{\partial \epsilon_{\alpha\beta}} \frac{\partial N_{ji}}{\partial \epsilon_{\mu\nu}} \right) \\
& + \frac{\partial^2 \pi_{ij}^{rc}}{\partial N_{ij}^{\text{conj}} \partial N_{ij}} \left(\frac{\partial N_{ij}^{\text{conj}}}{\partial \epsilon_{\alpha\beta}} \frac{\partial N_{ij}}{\partial \epsilon_{\mu\nu}} + \frac{\partial N_{ij}}{\partial \epsilon_{\alpha\beta}} \frac{\partial N_{ij}^{\text{conj}}}{\partial \epsilon_{\mu\nu}} \right)
\end{aligned} \quad (52)$$

$$\frac{\partial N_{ij}^{\text{conj}}}{\partial \epsilon_{\alpha\beta}} = 2 \left(X_{ij} \frac{\partial X_{ij}}{\partial \epsilon_{\alpha\beta}} + Y_{ij} \frac{\partial Y_{ij}}{\partial \epsilon_{\alpha\beta}} \right), \quad (53)$$

$$\frac{\partial^2 N_{ij}^{\text{conj}}}{\partial \epsilon_{\alpha\beta} \partial \epsilon_{\mu\nu}} = 2 \left(\frac{\partial X_{ij}}{\partial \epsilon_{\alpha\beta}} \frac{\partial X_{ij}}{\partial \epsilon_{\mu\nu}} + X_{ij} \frac{\partial^2 X_{ij}}{\partial \epsilon_{\alpha\beta} \partial \epsilon_{\mu\nu}} + \frac{\partial Y_{ij}}{\partial \epsilon_{\alpha\beta}} \frac{\partial Y_{ij}}{\partial \epsilon_{\mu\nu}} + Y_{ij} \frac{\partial^2 Y_{ij}}{\partial \epsilon_{\alpha\beta} \partial \epsilon_{\mu\nu}} \right), \quad (54)$$

$$\frac{\partial X_{ij}}{\partial \epsilon_{\alpha\beta}} = \sum_{k \neq i,j} \delta_{kc} \left(\frac{\partial w_{ik}}{\partial \epsilon_{\alpha\beta}} S_{ik}^{\text{conj}} + w_{ik} \frac{\partial S_{ik}^{\text{conj}}}{\partial \epsilon_{\alpha\beta}} \right), \quad (55)$$

$$\frac{\partial^2 X_{ij}}{\partial \epsilon_{\alpha\beta} \partial \epsilon_{\mu\nu}} = \sum_{k \neq i,j} \delta_{kc} \left(S_{ik}^{\text{conj}} \frac{\partial^2 w_{ik}}{\partial \epsilon_{\alpha\beta} \partial \epsilon_{\mu\nu}} + \frac{\partial S_{ik}^{\text{conj}}}{\partial \epsilon_{\alpha\beta}} \frac{\partial w_{ik}}{\partial \epsilon_{\mu\nu}} + \frac{\partial w_{ik}}{\partial \epsilon_{\alpha\beta}} \frac{\partial S_{ik}^{\text{conj}}}{\partial \epsilon_{\mu\nu}} + w_{ik} \frac{\partial^2 S_{ik}^{\text{conj}}}{\partial \epsilon_{\alpha\beta} \partial \epsilon_{\mu\nu}} \right), \quad (56)$$

$$\frac{\partial \pi_{ij}^{dh}}{\partial \epsilon_{\alpha\beta}} = \frac{\partial T_{ij}}{\partial \epsilon_{\alpha\beta}} Z_{ij} + T_{ij} \frac{\partial Z_{ij}}{\partial \epsilon_{\alpha\beta}}, \quad (57)$$

$$\frac{\partial^2 \pi_{ij}^{dh}}{\partial \epsilon_{\alpha\beta} \partial \epsilon_{\mu\nu}} = \frac{\partial^2 T_{ij}}{\partial \epsilon_{\alpha\beta} \partial \epsilon_{\mu\nu}} Z_{ij} + \frac{\partial Z_{ij}}{\partial \epsilon_{\alpha\beta}} \frac{\partial T_{ij}}{\partial \epsilon_{\mu\nu}} + \frac{\partial^2 Z_{ij}}{\partial \epsilon_{\alpha\beta} \partial \epsilon_{\mu\nu}} T_{ij} + \frac{\partial T_{ij}}{\partial \epsilon_{\alpha\beta}} \frac{\partial Z_{ij}}{\partial \epsilon_{\mu\nu}}, \quad (58)$$

$$\frac{\partial T_{ij}}{\partial \epsilon_{\alpha\beta}} = \frac{\partial T_{ij}}{\partial N_{ij}} \frac{\partial N_{ij}}{\partial \epsilon_{\alpha\beta}} + \frac{\partial T_{ij}}{\partial N_{ji}} \frac{\partial N_{ji}}{\partial \epsilon_{\alpha\beta}} + \frac{\partial T_{ij}}{\partial N_{ij}^{\text{conj}}} \frac{\partial N_{ij}^{\text{conj}}}{\partial \epsilon_{\alpha\beta}}, \quad (59)$$

$$\begin{aligned}
\frac{\partial^2 T_{ij}}{\partial \epsilon_{\alpha\beta} \partial \epsilon_{\mu\nu}} = & \frac{\partial T_{ij}}{\partial N_{ij}} \frac{\partial^2 N_{ij}}{\partial \epsilon_{\alpha\beta} \partial \epsilon_{\mu\nu}} + \frac{\partial T_{ij}}{\partial N_{ji}} \frac{\partial^2 N_{ji}}{\partial \epsilon_{\alpha\beta} \partial \epsilon_{\mu\nu}} + \frac{\partial T_{ij}}{\partial N_{ij}^{\text{conj}}} \frac{\partial^2 N_{ij}^{\text{conj}}}{\partial \epsilon_{\alpha\beta} \partial \epsilon_{\mu\nu}} + \frac{\partial^2 T_{ij}}{\partial N_{ij}^2} \frac{\partial N_{ij}}{\partial \epsilon_{\alpha\beta}} \frac{\partial N_{ij}}{\partial \epsilon_{\mu\nu}} + \frac{\partial^2 T_{ij}}{\partial N_{ji}^2} \frac{\partial N_{ji}}{\partial \epsilon_{\alpha\beta}} \frac{\partial N_{ji}}{\partial \epsilon_{\mu\nu}} \\
& + \frac{\partial^2 T_{ij}}{\partial N_{ij}^{\text{conj}^2}} \frac{\partial N_{ij}^{\text{conj}}}{\partial \epsilon_{\alpha\beta}} \frac{\partial N_{ij}^{\text{conj}}}{\partial \epsilon_{\mu\nu}} + \frac{\partial^2 T_{ij}}{\partial N_{ij} \partial N_{ji}} \left(\frac{\partial N_{ij}}{\partial \epsilon_{\alpha\beta}} \frac{\partial N_{ji}}{\partial \epsilon_{\mu\nu}} + \frac{\partial N_{ji}}{\partial \epsilon_{\alpha\beta}} \frac{\partial N_{ij}}{\partial \epsilon_{\mu\nu}} \right) + \frac{\partial^2 T_{ij}}{\partial N_{ji} \partial N_{ij}^{\text{conj}}} \left(\frac{\partial N_{ji}}{\partial \epsilon_{\alpha\beta}} \frac{\partial N_{ij}^{\text{conj}}}{\partial \epsilon_{\mu\nu}} + \frac{\partial N_{ij}^{\text{conj}}}{\partial \epsilon_{\alpha\beta}} \frac{\partial N_{ji}}{\partial \epsilon_{\mu\nu}} \right) \\
& + \frac{\partial^2 T_{ij}}{\partial N_{ij}^{\text{conj}} \partial N_{ij}} \left(\frac{\partial N_{ij}^{\text{conj}}}{\partial \epsilon_{\alpha\beta}} \frac{\partial N_{ij}}{\partial \epsilon_{\mu\nu}} + \frac{\partial N_{ij}}{\partial \epsilon_{\alpha\beta}} \frac{\partial N_{ij}^{\text{conj}}}{\partial \epsilon_{\mu\nu}} \right),
\end{aligned} \quad (60)$$

$$\frac{\partial Z_{ij}}{\partial \epsilon_{\alpha\beta}} = \sum_{k \neq i,j} \sum_{l \neq i,j,k} \left(\frac{\partial \sin^2 \omega_{kijl}}{\partial \epsilon_{\alpha\beta}} w'_{ik} w'_{jl} + \sin^2 \omega_{kijl} \frac{\partial w'_{ik}}{\partial \epsilon_{\alpha\beta}} w'_{jl} + \sin^2 \omega_{kijl} w'_{ik} \frac{\partial w'_{jl}}{\partial \epsilon_{\alpha\beta}} \right) \times \Theta(\sin \theta_{jik} - s^{\min}) \Theta(\sin \theta_{ijl} - s^{\min}), \quad (61)$$

$$\begin{aligned}
\frac{\partial^2 Z_{ij}}{\partial \epsilon_{\alpha\beta} \partial \epsilon_{\mu\nu}} = & \sum_{k \neq i,j} \sum_{l \neq i,j,k} \left(\frac{\partial^2 \sin^2 \omega_{kijl}}{\partial \epsilon_{\alpha\beta} \partial \epsilon_{\mu\nu}} w'_{ik} w'_{jl} + w'_{jl} \frac{\partial w'_{ik}}{\partial \epsilon_{\alpha\beta}} \frac{\partial \sin^2 \omega_{kijl}}{\partial \epsilon_{\mu\nu}} + w'_{ik} \frac{\partial w'_{jl}}{\partial \epsilon_{\alpha\beta}} \frac{\partial \sin^2 \omega_{kijl}}{\partial \epsilon_{\mu\nu}} + w'_{jl} \frac{\partial \sin^2 \omega_{kijl}}{\partial \epsilon_{\alpha\beta}} \frac{\partial w'_{ik}}{\partial \epsilon_{\mu\nu}} \right. \\
& + \sin^2 \omega_{kijl} \frac{\partial^2 w'_{ik}}{\partial \epsilon_{\alpha\beta} \partial \epsilon_{\mu\nu}} w'_{jl} + \sin^2 \omega_{kijl} \frac{\partial w'_{jl}}{\partial \epsilon_{\alpha\beta}} \frac{\partial w'_{ik}}{\partial \epsilon_{\mu\nu}} + w'_{ik} \frac{\partial \sin^2 \omega_{kijl}}{\partial \epsilon_{\alpha\beta}} \frac{\partial w'_{jl}}{\partial \epsilon_{\mu\nu}} + \sin^2 \omega_{kijl} \frac{\partial w'_{ki}}{\partial \epsilon_{\alpha\beta}} \frac{\partial w'_{jl}}{\partial \epsilon_{\mu\nu}} \\
& \left. + \sin^2 \omega_{kijl} w'_{ik} \frac{\partial^2 w'_{jl}}{\partial \epsilon_{\alpha\beta} \partial \epsilon_{\mu\nu}} \right) \Theta(\sin \theta_{jik} - s^{\min}) \Theta(\sin \theta_{ijl} - s^{\min}),
\end{aligned} \quad (62)$$

$$\frac{\partial \sin^2 \omega_{kijl}}{\partial \epsilon_{\alpha\beta}} = -2 \cos \omega_{kijl} \frac{\partial \cos \omega_{kijl}}{\partial \epsilon_{\alpha\beta}}, \quad (63)$$

$$\frac{\partial^2 \sin^2 \omega_{kijl}}{\partial \epsilon_{\alpha\beta} \partial \epsilon_{\mu\nu}} = -2 \left(\frac{\partial \cos \omega_{kijl}}{\partial \epsilon_{\alpha\beta}} \frac{\partial \cos \omega_{kijl}}{\partial \epsilon_{\mu\nu}} + \cos \omega_{kijl} \frac{\partial^2 \cos \omega_{kijl}}{\partial \epsilon_{\alpha\beta} \partial \epsilon_{\mu\nu}} \right). \quad (64)$$

V. RESULTS

To verify the accuracy of the expressions provided here, the elastic constants of diamond and graphite, as well as Young's Modulus for a (10,10) carbon nanotube, at absolute zero were calculated and compared to values available in the literature. The elastic constants given in Table I are in good agreement with the literature values. Harrison *et al.* estimated the Young's Modulus of a (10,10) nanotube at 300 K to be 960 GPa by applying a strain along the axial direction of the tube.⁴¹ In a subsequent work, the universal force field was used to calculate the modulus of the (10,10) tube and a value of 1.02 TPa at 0 K was obtained.⁵⁴ In this work, a Young's Modulus of 1.15 TPa at 0 K for the (10,10) nanotube was obtained using the second-generation REBO potential and the expressions derived here. This value is in good agreement with values obtained at nonzero temperature and using other potential energy functions.

The authors have also evaluated the temperature dependence of the elastic constants of diamond using the stress-fluctuation formula given in this work.⁴⁵ In our previous work, we calculate the internal stress tensor for a potential containing three- and four-body terms. In the appendix, we show that the tensor can be calculated using a formula similar to that used for two-body potentials. The results were in good agreement with the elastic constants calculated using the strain-fluctuation formula and with those calculated using the direct method. In that work, the simulation box contained approximately 1000 atoms and the time step was 0.25 fs for all simulations. Because the time steps were the same regardless of the calculation method used, a comparison of efficiency can be obtained by comparing the number of simulation steps required to obtain a set of elastic constants at a given temperature. When the direct method was used to calculate the elastic constants at a given temperature, 12 simulations of 400 000 steps, or 4.6 million steps, were required. The strain-fluctuation method yielded the three independent elastic constants in a single simulation, which took on the

order of 20 million steps. In contrast, the stress-fluctuation formula yielded converged values of the elastic constants at a given temperature in 400 000 steps.

VI. SUMMARY

The stress and elasticity tensors were derived for multi-body potentials that include bending and dihedral angle contributions. While expressions of this type have been derived for two-body potentials⁶ and for ions and point dipoles,⁴⁷ they have not been published for angle-dependent potentials. The expression derived here can be used in Monte Carlo or molecular dynamics simulations in the canonical and micro-canonical ensembles. The stress-fluctuation method has the advantage of converging faster than other methods for calculating elastic constants, being stable at low temperatures, and it allows for all the elastic constants to be determined in a single simulation. In addition, local elastic constants of heterogeneous materials, such as polymer glasses, can also be calculated.²⁰ As an example, the first- and second-strain derivatives of the second-generation REBO potential were presented. This multibody potential was used because of its widespread use. The expressions presented here were used to evaluate the elastic constants of diamond and graphite at absolute zero and to calculate Young's Modulus for a (10,10) single-wall carbon nanotube. The results agree well with previously published work. In a separate work, the expressions presented here were used to calculate the elastic constants of diamond as a function of temperature.⁴⁵ The values obtained were in good agreement with other methods for calculating the elastic constants.

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APPENDIX: INTERNAL STRESS TENSOR FOR THREE-BODY INTERACTIONS

The multi-body term of the REBO potential contains three-body and four-body terms. In this appendix, we show that the equation for the internal stress tensor, given below, can be calculated using a formula similar to that for a two-

TABLE I. Results for the 0 K elastic constants.

Material	Constant (GPa)	References 8 and 9	This work
Diamond	C_{11}	1070	1075.6
	C_{12}	120	125.4
	C_{44}	720	738.0
Graphite	C_{11}	1060	999.4
	C_{12}	150	146.8

body potential. We have used this equation to calculate the stress tensor in diamond as a function of temperature.⁴⁵

The internal stress tensor is given by

$$\sigma_{\alpha\beta} = \frac{1}{V} \left(\sum_i m_i v_{i\alpha} v_{i\beta} + \sum_{(i<j)} r_{ij\alpha} f_{ij\beta} \right), \quad (\text{A1})$$

where $\sigma_{\alpha\beta}$ is the $\alpha\beta$ component of the stress tensor, V is the volume of the system, m_i and v_i are mass and velocity of atom i , respectively, $r_{ij\alpha}$ is the Cartesian component of the vector from atom j to atom i in the α direction, and $f_{ij\beta}$ is the force acting on atom i by atom j in the β direction.

To show that this equation is valid for multi-body terms, we take the three-body term,

$$U_3 = \sum_{ijk} u_{ijk}, \quad (\text{A2})$$

as the example. The four-body term can be dealt with the same way. The stress tensor from this term is⁴⁸

$$\sigma_{\alpha\beta} = -\frac{1}{V} \frac{\partial U_3}{\partial \epsilon_{\alpha\beta}} = -\frac{1}{V} \sum_{ijk} \frac{\partial u_{ijk}}{\partial \epsilon_{\alpha\beta}}. \quad (\text{A3})$$

Split into three terms using the chain rule,

$$\sigma_{\alpha\beta} = -\frac{1}{V} \sum_{ijk} \left[\frac{\partial u_{ijk}}{\partial r_{ij}} \frac{\partial r_{ij}}{\partial \epsilon_{\alpha\beta}} + \frac{\partial u_{ijk}}{\partial r_{ik}} \frac{\partial r_{ik}}{\partial \epsilon_{\alpha\beta}} + \frac{\partial u_{ijk}}{\partial r_{jk}} \frac{\partial r_{jk}}{\partial \epsilon_{\alpha\beta}} \right]. \quad (\text{A4})$$

Here we assume that the potential is only a function of the distance between each pair of particles, which is the case for REBO potential. Next, swap k and j in the second term and switch $i \rightarrow k$, $j \rightarrow i$, and $k \rightarrow j$ in the third term,

$$\begin{aligned} \sigma_{\alpha\beta} = & -\frac{1}{V} \sum_{ijk} \frac{\partial u_{ijk}}{\partial r_{ij}} \frac{\partial r_{ij}}{\partial \epsilon_{\alpha\beta}} - \frac{1}{V} \sum_{ikj} \frac{\partial u_{ikj}}{\partial r_{ij}} \frac{\partial r_{ij}}{\partial \epsilon_{\alpha\beta}} \\ & - \frac{1}{V} \sum_{kij} \frac{\partial u_{kij}}{\partial r_{ij}} \frac{\partial r_{ij}}{\partial \epsilon_{\alpha\beta}}. \end{aligned} \quad (\text{A5})$$

Change order of summations and combine,

$$\begin{aligned} \sigma_{\alpha\beta} = & -\frac{1}{V} \sum_{ijk} \frac{\partial}{\partial r_{ij}} (u_{ijk} + u_{ikj} + u_{kij}) \frac{\partial r_{ij}}{\partial \epsilon_{\alpha\beta}} \\ = & -\frac{1}{V} \sum_{ijk} \frac{\partial u_{ijk}^o}{\partial r_{ij}} \frac{\partial r_{ij}}{\partial \epsilon_{\alpha\beta}}, \end{aligned} \quad (\text{A6})$$

where $u_{ijk}^o = u_{ijk} + u_{ikj} + u_{kij}$. Then split into two terms and switch i and j in the second term,

$$\sigma_{\alpha\beta} = -\frac{1}{2V} \sum_{ijk} \frac{\partial u_{ijk}^o}{\partial r_{ij}} \frac{\partial r_{ij}}{\partial \epsilon_{\alpha\beta}} - \frac{1}{2V} \sum_{jik} \frac{\partial u_{jik}^o}{\partial r_{ji}} \frac{\partial r_{ji}}{\partial \epsilon_{\alpha\beta}}. \quad (\text{A7})$$

Change order of summation, use $r_{ij} = r_{ji}$ in the second term, and combine,

$$\sigma_{\alpha\beta} = -\frac{1}{2V} \sum_{ijk} \frac{\partial}{\partial r_{ij}} (u_{ijk}^o + u_{jik}^o) \frac{\partial r_{ij}}{\partial \epsilon_{\alpha\beta}}. \quad (\text{A8})$$

Plug in $\partial r / \partial \epsilon_{\alpha\beta} = r_{\alpha} r_{\beta} / r$,⁴⁸

$$\sigma_{\alpha\beta} = -\frac{1}{2V} \sum_{ijk} \frac{\partial u_{ijk}^*}{\partial r_{ij}} \frac{r_{ij\alpha} r_{ij\beta}}{r_{ij}}, \quad (\text{A9})$$

where $u_{ijk}^* = u_{ijk}^o + u_{jik}^o$. On the other hand, the force on particle i from the interaction U_3 is

$$f_{i\alpha} = -\frac{\partial U_3}{\partial r_{i\alpha}} = -\sum_{ljk} \frac{\partial u_{ljk}}{\partial r_{i\alpha}} \quad (\text{A10})$$

Therefore,

$$f_{i\alpha} = -\sum_{jk} \frac{\partial}{\partial r_{i\alpha}} (u_{ijk} + u_{jik} + u_{jki}) = -\sum_{jk} \frac{\partial u_{jki}^o}{\partial r_{i\alpha}}. \quad (\text{A11})$$

As u_{ijk} is only a function of the distance between each pair of particles,

$$f_{i\alpha} = -\sum_{jk} \left(\frac{\partial u_{jki}^o}{\partial r_{ij}} \frac{\partial r_{ij}}{\partial r_{i\alpha}} + \frac{\partial u_{jki}^o}{\partial r_{ik}} \frac{\partial r_{ik}}{\partial r_{i\alpha}} \right), \quad (\text{A12})$$

$$f_{i\alpha} = -\sum_{jk} \left(\frac{\partial u_{jki}^o}{\partial r_{ij}} \frac{r_{ij\alpha}}{r_{ij}} + \frac{\partial u_{jki}^o}{\partial r_{ik}} \frac{r_{ik\alpha}}{r_{ik}} \right), \quad (\text{A13})$$

$$f_{i\alpha} = -\sum_{jk} \frac{\partial u_{jki}^o}{\partial r_{ij}} \frac{r_{ij\alpha}}{r_{ij}} - \sum_{jk} \frac{\partial u_{jki}^o}{\partial r_{ik}} \frac{r_{ik\alpha}}{r_{ik}}. \quad (\text{A14})$$

Switching j and k in the second term, we have

$$f_{i\alpha} = -\sum_{jk} \frac{\partial u_{jki}^o}{\partial r_{ij}} \frac{r_{ij\alpha}}{r_{ij}} - \sum_{jk} \frac{\partial u_{kji}^o}{\partial r_{ij}} \frac{r_{ij\alpha}}{r_{ij}}, \quad (\text{A15})$$

$$f_{i\alpha} = -\sum_{jk} \frac{\partial}{\partial r_{ij}} (u_{jki}^o + u_{kji}^o) \frac{r_{ij\alpha}}{r_{ij}} = -\sum_{jk} \frac{\partial u_{ijk}^*}{\partial r_{ij}} \frac{\partial r_{ij\alpha}}{r_{ij}}. \quad (\text{A16})$$

Rewrite Eq. (A16),

$$f_{i\alpha} = \sum_j f_{ij\alpha}, \quad (\text{A17})$$

where

$$f_{ij\alpha} = -\sum_k \frac{\partial u_{ijk}^*}{\partial r_{ij}} \frac{r_{ij\alpha}}{r_{ij}}, \quad (\text{A18})$$

which is the total interaction force between atom i and j . Finally, using Eq. (A18), Eq. (A9) becomes

$$\sigma_{\alpha\beta} = \frac{1}{2V} \sum_{ij} f_{ij\alpha} r_{ij\beta}. \quad (\text{A19})$$

In term of the sum of each pair of atoms,

$$\sigma_{\alpha\beta} = \frac{1}{V} \sum_{(i<j)} f_{ij\alpha} r_{ij\beta}. \quad (\text{A20})$$

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