Isothermal stress and elasticity tensors for ions and point dipoles using Ewald summations

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The isothermal stress tensor and isothermal elasticity tensor for systems of point charges and of nonpolarizable point dipoles are derived from the strain derivatives of the free energy. For the case of point dipoles, it is shown that the angular dependence of the interaction potential gives rise to additional contributions to the stress and elasticity tensors not recognized previously.

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I. INTRODUCTION

Ionic and dipolar interactions play a key role in many biological materials (e.g., tublin, and collagen) and processes (e.g., protein folding). The self-organization of polar molecules into the functional structures of living organisms is often guided by these strong, anisotropic interactions [1,2]. Increasingly, knowledge of the mechanical properties of such biological systems is of prime interest.

In molecular simulations, large polar molecules are normally modeled using a coarse-grained united-atom approach in which groups of atoms are represented by interaction sites that can carry a net Coulombic charge, dipole moment and/or higher order multipoles. Because of the long-range nature of these polar interactions, the Ewald summation technique is commonly used to evaluate the Coulombic and dipolar energies. Given the importance of the elastic constants and the common use of molecular simulations, it is striking that the full expression for the elasticity tensor for multipolar systems using the Ewald formulation does not, to the best of our knowledge, appear in the literature. This paper helps to address this gap by providing a derivation of the fluctuation formula for the isothermal elasticity tensor for systems of ions and non-polarizable dipoles. As a matter of consistency and completeness, the isothermal stress tensor is also derived. A comparison between the derived expressions and related expressions in the literature is also made.

In the theory of elasticity, one is interested in studying the deformation of a material under an applied load. The term *strain* is used to describe the deformation of a body from some reference state. The Lagrangian strain tensor is defined as

$$\epsilon_{ij} = \frac{1}{2}\left(\frac{\partial u_i}{\partial \tilde{r}_j} + \frac{\partial u_j}{\partial \tilde{r}_i} + \frac{\partial u_k}{\partial \tilde{r}_i}\frac{\partial u_k}{\partial \tilde{r}_j} \right), \tag{1}$$

where $u_i = r_i - \tilde{r}_i$, is the displacement of a point, r_i, within the body from its reference state, $\tilde{r}_i$. We see from its definition that the strain tensor is symmetric, i.e., $\epsilon_{ij} = \epsilon_{ji}$. Throughout this paper, subscripts represent the Cartesian coordinates and the standard Einstein summation notation is used. In computer simulations, the linear transformation $r_i = M_{ij}\tilde{r}_j$ relates the position of a particle within the body after a homogeneous deformation is applied to its original position in the reference state of the body. The metric tensor M_{ij} can be defined in terms of the size and shape of the simulation cell by $M_{ij} = h_{ik}\tilde{h}^{-1}_{kj}$ where $\tilde{h}_{ij}$ refers to h_{ij} in the reference state. The matrix h_{ij} is composed of the vectors that represent the length and orientation of the three primary edges of the simulation cell, i.e., in 3D $h_{ij} = \{\vec{a}, \vec{b}, \vec{c}\}$. Consequently, the volume of the system can be written as $V = \det \mathbf{h}$. At the reference state, $h_{ij} = \tilde{h}_{ij}$ and the metric tensor is equal to the identity tensor, $M_{ij} = \delta_{ij}$. Using these definitions the strain tensor can be expressed in terms of the metric tensor as

$$\epsilon_{ij} = \frac{1}{2}(M^{\dagger}_{ik}M_{kj} - \delta_{ij}), \tag{2}$$

where $M^{\dagger}_{ij}$ refers to the transpose of M_{ij}.

We next proceed to derive expressions for the first and second derivatives with respect to ϵ_{ij} of any general thermodynamic quantity. However, in typical computer simulations basic thermodynamic variables (e.g., the volume, internal energy, or stress tensor) are not explicit functions of ϵ_{ij}, but instead depend explicitly on M_{ij}. We thus first require expressions relating the derivatives with respect to ϵ_{ij} to derivatives with respect to M_{ij}. To this end we follow the procedure as outlined by Lutsko [3].

An arbitrary differential change of M_{ij} can be expressed in terms of a differential strain $d\epsilon_{ij}$ and a differential rotation $d\omega_{ij}$ of the simulation cell. Rotations occur because there is no requirement that dM_{ij} remain symmetric. The differential strain is given by the symmetric tensor

$$d\epsilon_{ij} = \frac{1}{2}(dM^{\dagger}_{ik}M_{kj} + M^{\dagger}_{ik}dM_{kj}), \tag{3}$$

and the differential rotation is given by the antisymmetric tensor

$$d\omega_{ij} = \frac{1}{2}(dM^{\dagger}_{ik}M_{kj} - M^{\dagger}_{ik}dM_{kj}). \tag{4}$$

For any general thermodynamic variable, A, that is an explicit function of M_{ij} we have

$$dA = \frac{\partial A}{\partial M_{mn}}dM^{\dagger}_{nm} = \frac{\partial A}{\partial M^{\dagger}_{mn}}dM_{nm}. \tag{5}$$

The differential dA may also be expressed in terms of $d\epsilon_{ij}$ and $d\omega_{ij}$ as

$$dA = \frac{\partial A}{\partial \epsilon_{mn}} d\epsilon^{\dagger}_{nm} + \frac{\partial A}{\partial \omega_{mn}} d\omega^{\dagger}_{nm}. \tag{6}$$

Combining Eqs. (3)–(6) and solving for $\partial A/\partial \epsilon_{ij}$ and $\partial A/\partial \omega_{ij}$ yields

$$\frac{\partial A}{\partial \epsilon_{ij}} = \frac{1}{2}\left(\frac{\partial A}{\partial M^{\dagger}_{im}} M^{\dagger -1}_{mj} + M^{-1}_{im} \frac{\partial A}{\partial M_{mj}} \right) \tag{7}$$

and

$$\frac{\partial A}{\partial \omega_{ij}} = \frac{1}{2}\left(\frac{\partial A}{\partial M^{\dagger}_{im}} M^{\dagger -1}_{mj} - M^{-1}_{im} \frac{\partial A}{\partial M_{mj}} \right). \tag{8}$$

Applying Eq. (7) twice gives for the second strain derivative,

$$\frac{\partial^2 A}{\partial \epsilon_{ij} \partial \epsilon_{kl}} = \frac{1}{4}[D_{ijkl} + D_{jikl} + D_{jilk} + D_{ijlk}]A, \tag{9}$$

where

$$D_{ijkl}A = M^{-1}_{im} \frac{\partial^2 A}{\partial M_{mj} \partial M^{\dagger}_{kn}} M^{\dagger -1}_{nl} - M^{-1}_{im} M^{\dagger -1}_{ml} M^{-1}_{jn} \frac{\partial A}{\partial M_{nk}}. \tag{10}$$

Equations (7) and (9) relate the first and second derivatives with respect to ϵ_{ij} of any general thermodynamic variable to the first and second derivatives with respect to M_{ij}, in terms of which the thermodynamics variables of interest are explicitly expressed. We note that Eqs. (7) and (9) have the expected symmetry properties, i.e., $\partial/\partial \epsilon_{ij} = \partial/\partial \epsilon_{ji}$ and $\partial^2/\partial \epsilon_{ij} \partial \epsilon_{kl} = \partial^2/\partial \epsilon_{kl} \partial \epsilon_{ij}$.

Next, we turn to the derivations of the general expressions for the stress and elasticity tensors. At constant temperature T the stress tensor, σ_{ij}, is given in terms of the free energy by

$$V\sigma_{ij} = \frac{\partial F}{\partial \epsilon_{ij}}. \tag{11}$$

The Helmholtz free energy is given by $F = -k_B T \ln Q$ and the canonical ensemble partition function, Q, is given by

$$Q = \int \exp[-H/k_B T] d\Gamma, \tag{12}$$

where $H = U + K$, and U is the total potential energy, K is the total kinetic energy, k_B is Boltzmann's constant, and Γ represents phase space.

Using Eqs. (7) and (11), the stress tensor is

$$\sigma_{ij} = \langle \sigma^B_{ij} \rangle - \rho k_B T M^{-1}_{im} M^{\dagger -1}_{mj}, \tag{13}$$

where

$$\sigma^B_{ij} = \frac{1}{V} \frac{\partial U}{\partial \epsilon_{ij}}, \tag{14}$$

the density is given by $\rho = N/V$ and the brackets denote an ensemble average.

The isothermal elasticity tensor C_{ijkl} is given in terms of the free energy by

$$VC_{ijkl} = \frac{\partial^2 F}{\partial \epsilon_{ij} \partial \epsilon_{kl}}. \tag{15}$$

Differentiating the free energy using Eq. (9) gives

$$C_{ijkl} = C^B_{ijkl} - \frac{V}{k_B T}[\langle \sigma^B_{ij} \sigma^B_{kl} \rangle - \langle \sigma^B_{ij} \rangle \langle \sigma^B_{kl} \rangle] + C^K_{ijkl}, \tag{16}$$

where

$$C^B_{ijkl} = \frac{1}{V} \left\langle \frac{\partial^2 U}{\partial \epsilon_{ij} \partial \epsilon_{kl}} \right\rangle \tag{17}$$

and

$$C^K_{ijkl} = \rho k_B T (M^{-1}_{im} M^{\dagger -1}_{mk} M^{-1}_{jn} M^{\dagger -1}_{nl} + M^{-1}_{im} M^{\dagger -1}_{ml} M^{-1}_{jn} M^{\dagger -1}_{nk}). \tag{18}$$

The first term in Eq. (16) is the so-called Born term and is related to the zero temperature elastic constants. The second term is the stress fluctuation term and accounts for the finite temperature effects. The last term in Eq. (16) is the ideal gas contribution and is related to the derivatives of the volume with respect to the strain tensor.

From Eqs. (13) and (16), we can compute the stress and elasticity tensor for any given potential energy function, U. In Sec. II we derive the desired expressions for a system of pairwise interacting point charges and in Sec. III for nonpolarizable point dipoles. The contribution to the stress and elasticity tensor arising from charge-dipole interactions are also given in Sec. III for completeness.

II. POINT CHARGES

We first summarize the results for the stress and elasticity tensors for systems of point charges. The potential energy of a system of point charges using Ewald summations is given by [4]

$$U = U^r + U^k + U^s + U^f. \tag{19}$$

The real space contribution to the energy is

$$U^r = \sum_{a=1}^{N-1} \sum_{b=a+1}^{N} q^a q^b B_0, \tag{20}$$

where q^a is the charge on particle a. The scalar coefficient B_0 is given by

$$B_0 = \frac{1}{r} \operatorname{erfc}(\alpha r), \tag{21}$$

where α is the Ewald convergence parameter, $r = \sqrt{r_i r_i}$ is the distance between particles a and b, and $r_i = r^b_i - r^a_i$ is their separation vector. The reciprocal space contribution to the energy is given by

$$U^k = \sum_{\vec{k} \neq 0}^{\vec{k}_{max}} A(k) S S^*, \tag{22}$$

where

$$A(k) = \frac{2\pi}{V} \frac{\exp[-k^2/(4\alpha^2)]}{k^2}, \tag{23}$$

and

$$S = \sum_{a=1}^{N} q^a \exp(-ik_m r_m). \tag{24}$$

The reciprocal space wave vector has the form $k_i = M^{\dagger -1}_{ij} \tilde{k}_j$ and $\tilde{k}_i = 2\pi \tilde{h}^{-1}_{ij} n_j$ is the wave vector in the reference state, while S^* denotes the complex conjugate of S and the vector n_i is a set of three integers. The self-interaction energy is given by

$$U^s = -\sum_{a=1}^{N} \frac{\alpha}{\sqrt{\pi}} (q^a)^2 \tag{25}$$

and the energy due to the boundary condition is

$$U^f = \frac{2\pi}{2\eta + 1} \frac{\mathbb{M}^2}{V}, \tag{26}$$

where η is the dielectric constant of the reaction field and $\mathbb{M}_i$ is the total dipole moment of the system.

Differentiating Eq. (19) with respect to ϵ_{ij}, gives the configurational part of the stress tensor,

$$\sigma^B_{ij} = -\frac{1}{V} \sum_{a=1}^{N-1} \sum_{b=a+1}^{N} q^a q^b B_1 r_i r_j - \frac{1}{V} \sum_{k \neq 0}^{k_{max}} A(k) SS^* \Theta_{ij} + \frac{2\pi}{2\eta + 1} \frac{1}{V^2} [2\mathbb{M}_i \mathbb{M}_j - \mathbb{M}^2 \delta_{ij}], \tag{27}$$

where

$$\Theta_{ij} = \delta_{ij} - 2\frac{k_i k_j}{\lambda^2} \tag{28}$$

and

$$\frac{1}{\lambda^2} = \frac{1}{4\alpha^2} + \frac{1}{k^2}. \tag{29}$$

It is noted here that the recursion formula

$$B_{n+1} = -\frac{1}{r} \frac{\partial B_n}{\partial r} \tag{30}$$

describes the higher order derivatives of the scalar B_0. Differentiating Eq. (19) twice with respect to the strain tensor gives for the Born term

$$C^B_{ijkl} = \frac{1}{V} \left\langle \sum_{a=1}^{N-1} \sum_{b=a+1}^{N} q^a q^b B_2 r_i r_j r_k r_l \right\rangle + \frac{1}{V} \left\langle \sum_{k \neq 0}^{k_{max}} A(k) SS^* \Omega_{ijkl} \right\rangle + \frac{2\pi}{2\eta + 1} \frac{1}{V^2} [\langle \mathbb{M}^2 \rangle (\delta_{ij}\delta_{kl} + \delta_{ik}\delta_{jl} + \delta_{il}\delta_{jk}) - 2(\delta_{ij} \langle \mathbb{M}_k \mathbb{M}_l \rangle + \langle \mathbb{M}_i \mathbb{M}_j \rangle \delta_{kl})], \tag{31}$$

where

$$\Omega_{ijkl} = \Theta_{ij}\Theta_{kl} + (\delta_{ik}\delta_{jl} + \delta_{il}\delta_{jk}) + 4\frac{k_i k_j k_k k_l}{k^4} - 2\frac{k_i \delta_{jk} k_l + k_j \delta_{ik} k_l + k_j \delta_{il} k_k + k_i \delta_{jl} k_k}{\lambda^2}. \tag{32}$$

The last terms in Eqs. (27) and (31) arise from U^f because the total dipole moment $\mathbb{M}_i$ depends on ϵ_{ij}. Similar but not equivalent expressions for C^B_{1111} and C^B_{1122} are given in Ref. [5].

III. POINT DIPOLES

We now extend the results of Sec. II to the case of point dipole particles. The total potential energy for a system of dipoles is given by [6]

$$U = U^r + U^k + U^s + U^f. \tag{33}$$

The real space term has the form

$$U^r = \sum_{a=1}^{N-1} \sum_{b=a+1}^{N} (\mu^a_n \mu^b_n) B_1 - (\mu^a_n r_n)(\mu^b_m r_m) B_2, \tag{34}$$

while the reciprocal space term is

$$U^k = \sum_{k \neq 0}^{k_{max}} A(k) \mathbb{S}\mathbb{S}^*, \tag{35}$$

where

$$\mathbb{S} = -\sum_{a=1}^{N} i(\mu^a_m k_m) \exp[-ik_n r_n]. \tag{36}$$

The self-interaction term is

$$U^s = -\sum_{a=1}^{N} \frac{2\alpha^3}{3\sqrt{\pi}} (\mu^a_m \mu^a_m) \tag{37}$$

and the boundary term again has the form

$$U^f = \frac{2\pi}{2\eta + 1} \frac{\mathbb{M}^2}{V}. \tag{38}$$

Upon application of a finite strain, the position and orientation of a point dipole change, i.e., they are functions of the strain tensor. Because the potential energy depends explicitly on the orientations of the dipoles, which are considered independent of their positions, the stress and elasticity tensors will therefore contain terms which involve strain derivatives of the dipoles. However, because we are restricting ourselves to the case of nonpolarizable dipoles, the magnitude of the dipole moment must remain constant. Under this constraint, the dipole moment can be expressed in terms of the dipole moment in the reference state, $\tilde{\mu}_i$, and the metric tensor, M_{ij}, according to

$$\mu_i = \left(\frac{\tilde{\mu}_q \tilde{\mu}_q}{\tilde{\mu}_m M_{mn}{}^{\dagger} M_{np} \tilde{\mu}_p} \right)^{1/2} M_{i\alpha} \tilde{\mu}_\alpha. \tag{39}$$

The fact that the dipole depends on the metric tensor, and hence the strain tensor, was not included in previous deriva-

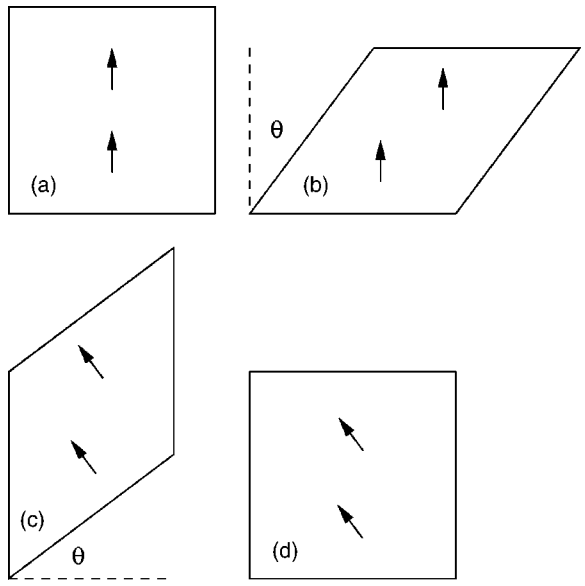

FIG. 1. Deformation sequence assuming point dipoles do not rotate when the system is strained: (a) reference state, (b) after shear strain by angle θ, (c) after counter-clockwise rotation by angle θ, and (d) after final shear strain by angle θ.

tions for the stress tensor, i.e., the assumption that $\mu_i = \tilde{\mu}_i$ was incorrectly made. For this reason, terms in the strain derivative of the potential energy that involve the dipole are given below.

Figures 1 and 2 illustrate the key point that a point dipole may rotate upon elastic deformation. Consider a deformation pathway whereby the system is elastically deformed by first shear straining it clockwise through an angle θ [(b) in Figs. 1 and 2]. Next, the system is rotated counter-clockwise by θ [(c) in Figs. 1 and 2]. Finally a shear strain is applied in the direction orthogonal to the first shear deformation such that the system is brought back to its original shape and orientation [(d) in Figs. 1 and 2]. Clearly, the point dipoles must rotate when the system rotates during the second step in this pathway. If one assumes that a point dipole does not rotate during the two shear strain steps, the net result of this deformation pathway is that the dipoles have rotated by θ (Fig. 1), which is inconsistent because the net strain and rotation of the overall system is zero. However, if the dipoles rotate according to Eq. (39) when the system is strained, the orientations of the point dipoles will return to their original state after the final step (Fig. 2). The conclusion here is the same for point dipoles as well as physical dipoles which occupy an extended region of space.

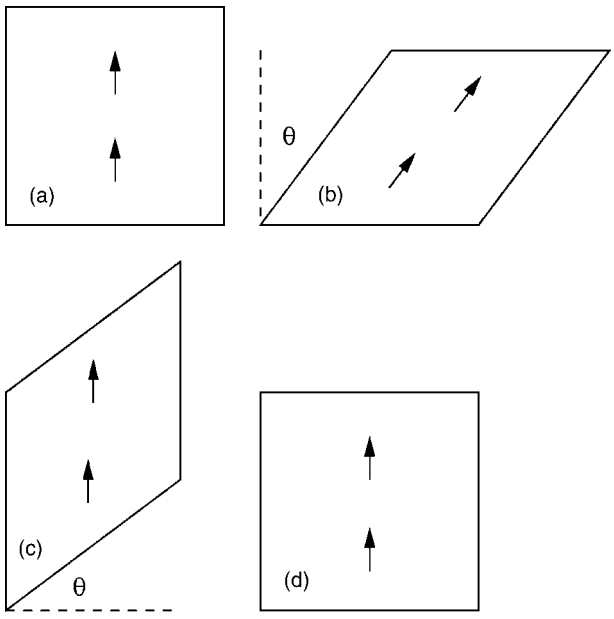

FIG. 2. Deformation sequence assuming point dipoles rotate according to Eq. (39): (a) reference state, (b) after shear strain by angle θ, (c) after counter-clockwise rotation by angle θ, and (d) after final shear strain by angle θ.

In our discussion below, a normalized dipole dyadic product is defined as

$$\hat{\mu}_\alpha \hat{\mu}_\beta = \frac{\mu_\alpha \mu_\beta}{\mu_m \mu_m}. \tag{40}$$

For terms that involve the product of two dipoles we have

$$\frac{\partial(\mu_m^a \mu_m^b)}{\partial \epsilon_{ij}} = M_{i\alpha}^{-1}[\mu_\alpha^a \mu_\beta^b + \mu_\alpha^b \mu_\beta^a - (\mu_m^a \mu_m^b)(\hat{\mu}_\alpha^a \hat{\mu}_\beta^a + \hat{\mu}_\alpha^b \hat{\mu}_\beta^b)] M_{\beta j}^{\dagger -1}. \tag{41}$$

For terms that involve the product of a dipole and a separation vector, the first strain derivative is given by

$$\frac{\partial(\mu_m r_m)}{\partial \epsilon_{ij}} = M_{i\alpha}^{-1}[\mu_\alpha r_\beta + r_\alpha \mu_\beta - (\mu_m r_m)\hat{\mu}_\alpha \hat{\mu}_\beta] M_{\beta j}^{\dagger -1}, \tag{42}$$

and for terms that involve the product of a dipole and the reciprocal space vector, we have

$$\frac{\partial(\mu_m k_m)}{\partial \epsilon_{ij}} = -(\mu_m k_m) M_{i\alpha}^{-1} \hat{\mu}_\alpha \hat{\mu}_\beta M_{\beta j}^{\dagger -1}. \tag{43}$$

Then using Eqs. (41)–(43) evaluated at zero strain, the configurational part of the stress tensor is given by

$$\sigma_{ij}^B = -\frac{1}{V}\sum_{a=1}^{N-1}\sum_{b=a+1}^{N}\{(\mu_m^a \mu_m^b) B_2 r_i r_j - (\mu_m^a r_m)(\mu_n^b r_n) B_3 r_i r_j + (\mu_m^a r_m) B_2 Z_{ij}^b + (\mu_m^b r_m) B_2 Z_{ij}^a - B_1 W_{ij}^{ab}\} - \frac{1}{V}\sum_{k\neq 0}^{k_{max}} A(k) \times [\mathbb{S}\mathbb{S}^* \Theta_{ij} - \mathbb{S}^* \Psi_{ij} - \mathbb{S}\Psi_{ij}^*] + \frac{1}{V^2}\frac{4\pi}{2\eta+1}\left\{\sum_{a=1}^{N-1}\sum_{b=a+1}^{N} W_{ij}^{ab} - \mathbb{M}^2 \delta_{ij}\right\}, \tag{44}$$

where

$$W_{ij}^{ab} = \mu_i^a \mu_j^b + \mu_i^b \mu_j^a - (\mu_m^a \mu_m^b)(\hat{\mu}_i^a \hat{\mu}_j^a + \hat{\mu}_i^b \hat{\mu}_j^b), \tag{45}$$

$$Z_{ij}^a = \mu_i^a r_j + r_i \mu_j^a - (\mu_m^a r_m)\hat{\mu}_i^a \hat{\mu}_j^a, \tag{46}$$

and

$$\Psi_{ij} = i\sum_{a=1}^{N} (\mu_n^a k_n)\hat{\mu}_i^a \hat{\mu}_j^a e^{-ik_m r_m}. \tag{47}$$

Note that Eq. (44) is different from previously derived expressions [7–9]. Heyes and Aguado *et al.* assumed that

$$\frac{\partial(\mu_m^a \mu_m^b)}{\partial \epsilon_{ij}} = 0, \tag{48}$$

implying that

$$\frac{\partial(\mu_m^a \mu_m^b)}{\partial M_{ij}} = 0. \tag{49}$$

However, the following argument demonstrates that this assumption is not in general justified. Let $dU = (\partial U/\partial \omega_{mn}) d\omega_{nm}^{\dagger}$ be the change in energy due to a small rigid rotation $d\omega_{ij}$ of the entire system. It is clear that $dU = 0$ for any isolated system [10]. Let us consider a system of point dipoles in which $\alpha = 0$ and $\eta = 0$. For this choice of parameters, $U^k = 0$, $U^s = 0$, and $U^f = 0$ so that $U = U^r$. This choice is only made for reasons of simplicity and clarity in this illustration; the following discussion applies regardless of the choice of α and η. This choice also servers to illustrate that Eq. (39) is appropriate even when the Ewald summation method is not used. Now if we evaluate $\partial U/\partial \omega_{ij}$ for this system, assuming that dipole orientation does not depend on M_{ij}, we get for $\omega_{ij} = 0$

$$\frac{\partial U}{\partial \omega_{ij}} = \sum_{a=1}^{N-1}\sum_{b=a+1}^{N} \frac{1}{2} B_2(r)[(\mu_i^a r_j - r_i \mu_j^a)(\mu_m^b r_m) + (\mu_i^b r_j - r_i \mu_j^b) \times (\mu_n^a r_n)]. \tag{50}$$

This expression is not equal to 0 unless $\mu_i^a r_j = r_i \mu_j^a$. If instead, we let μ_i depend on M_{ij} according to Eq. (39), it can be shown that

$$\frac{\partial U}{\partial \omega_{ij}} = 0, \tag{51}$$

which is the required relation. In other words the energy is constant with respect to rigid rotations of the system when the orientation of the dipoles depend on M_{ij} according to Eq. (39). Therefore, they also depend on ϵ_{ij} and this must be taken into account when evaluating the stress and elasticity tensors. Although in some cases the contribution of the additional terms in the expression for the stress tensor may be negligible when ensemble averages are considered, it is not clear that this is generally the case. The difference may also be important when evaluating the elasticity tensor because of contributions from the fluctuations of the stress tensor.

We next move to the more complex problem of calculating second derivative quantities and the elasticity tensor. Only the results for the derivatives of terms which involve μ_i, which were neglected in early work, are summarized here. The second derivatives of the products involving μ_i are

$$\begin{aligned}\frac{\partial^2(\mu_m^a \mu_m^b)}{\partial \epsilon_{ij}\partial \epsilon_{kl}} = {} & 3(\mu_m^a \mu_m^b) M_{i\alpha}^{-1}(\hat{\mu}_\alpha^a \hat{\mu}_\beta^a M^{\dagger -1}_{\beta j} M_{kp}^{-1} \hat{\mu}_p^a \hat{\mu}_q^a \\ & + \hat{\mu}_\alpha^b \hat{\mu}_\beta^b M^{\dagger -1}_{\beta j} M_{kp}^{-1} \hat{\mu}_p^b \hat{\mu}_q^b) M^{\dagger -1}_{ql} \\ & + (\mu_m^a \mu_m^b) M_{i\alpha}^{-1}(\hat{\mu}_\alpha^a \hat{\mu}_\beta^a M^{\dagger -1}_{\beta j} M_{kp}^{-1} \hat{\mu}_p^b \hat{\mu}_q^b \\ & + \hat{\mu}_\alpha^b \hat{\mu}_\beta^b M^{\dagger -1}_{\beta j} M_{kp}^{-1} \hat{\mu}_p^a \hat{\mu}_q^a) M^{\dagger -1}_{ql} - M_{i\alpha}^{-1}(\hat{\mu}_\alpha^a \hat{\mu}_\beta^a \\ & + \hat{\mu}_\alpha^b \hat{\mu}_\beta^b) M^{\dagger -1}_{\beta j} M_{kp}^{-1}(\mu_p^a \mu_q^b + \mu_p^b \mu_q^a) M^{\dagger -1}_{ql} \\ & - M_{i\alpha}^{-1}(\mu_\alpha^a \mu_\beta^b + \mu_\alpha^b \mu_\beta^a) M^{\dagger -1}_{\beta j} M_{kp}^{-1}(\hat{\mu}_p^a \hat{\mu}_q^a \\ & + \hat{\mu}_p^b \hat{\mu}_q^b) M^{\dagger -1}_{ql}, \end{aligned} \tag{52}$$

$$\begin{aligned}\frac{\partial^2(\mu_m r_m)}{\partial \epsilon_{ij}\partial \epsilon_{kl}} = {} & 3(\mu_m r_m) M_{i\alpha}^{-1} \hat{\mu}_\alpha \hat{\mu}_\beta M^{\dagger -1}_{\beta j} M_{kp}^{-1} \hat{\mu}_p \hat{\mu}_q M^{\dagger -1}_{ql} \\ & - M_{i\alpha}^{-1} \hat{\mu}_\alpha \hat{\mu}_\beta M^{\dagger -1}_{\beta j} M_{kp}^{-1}(\mu_p r_q + r_p \mu_q) M^{\dagger -1}_{ql} \\ & - M_{i\alpha}^{-1}(\mu_\alpha r_\beta + r_\alpha \mu_\beta) M^{\dagger -1}_{\beta j} M_{kp}^{-1} \hat{\mu}_p \hat{\mu}_q M^{\dagger -1}_{ql}, \end{aligned} \tag{53}$$

and

$$\frac{\partial^2(\mu_m k_m)}{\partial \epsilon_{ij}\partial \epsilon_{kl}} = 3(\mu_m k_m) M_{i\alpha}^{-1} \hat{\mu}_\alpha \hat{\mu}_\beta M^{\dagger -1}_{\beta j} M_{kp}^{-1} \hat{\mu}_p \hat{\mu}_q M^{\dagger -1}_{ql}. \tag{54}$$

Using Eqs. (52)–(54) evaluated at $\epsilon_{ij} = 0$, we have for the Born term in the elasticity tensor

$$\begin{aligned} C_{ijkl}^B = {} & \frac{1}{V}\left\langle \sum_{a=1}^{N-1}\sum_{b=a+1}^{N} \{B_1 X_{ijkl}^{ab} + [(\mu_m^a \mu_m^b) B_3 - (\mu_m^a r_m) \right. \\ & \times (\mu_n^b r_n) B_4] r_i r_j r_k r_l + [(\mu_m^a r_m) B_3 Z_{ij}^b + (\mu_n^b r_n) B_3 Z_{ij}^a \\ & - B_2 W_{ij}^{ab}] r_k r_l + r_i r_j [(\mu_m^a r_m) B_3 Z_{kl}^b + (\mu_m^b r_m) B_3 Z_{kl}^a \\ & - B_2 W_{kl}^{ab}] - B_2[(\mu_m^b r_m) Y_{ijkl}^a + (\mu_m^a r_m) Y_{ijkl}^b + Z_{ij}^a Z_{kl}^b \\ & \left. + Z_{ij}^b Z_{kl}^a]\} \right\rangle + \frac{1}{V}\left\langle \sum_{k\neq 0}^{k_{max}} A(k)[\mathbb{S}^* \Phi_{ijkl} + \mathbb{S}\Phi_{ijkl}^* + \mathbb{S}\mathbb{S}^* \Omega_{ijkl} \right. \\ & + \Psi_{ij}\Psi_{kl}^* + \Psi_{ij}^* \Psi_{kl} - \Theta_{ij}(\Psi_{kl}\mathbb{S}^* + \Psi_{kl}^* \mathbb{S}) - (\mathbb{S}^* \Psi_{ij} \\ & \left. + \mathbb{S}\Psi_{ij}^*)\Theta_{kl}] \right\rangle + \frac{1}{V^2}\frac{2\pi}{2\eta+1}\langle \mathbb{M}^2 \rangle(\delta_{ij}\delta_{kl} + \delta_{ik}\delta_{jl} + \delta_{il}\delta_{jk}) \\ & + \frac{1}{V^2}\frac{4\pi}{2\eta+1}\left\langle \sum_{a=1}^{N-1}\sum_{b=a+1}^{N} [X_{ijkl}^{ab} - W_{ij}^{ab}\delta_{kl} - \delta_{ij} W_{kl}^{ab}] \right\rangle, \end{aligned} \tag{55}$$

where

$$\begin{aligned} X_{ijkl}^{ab} = {} & (\mu_m^a \mu_m^b)[3(\hat{\mu}_i^a \hat{\mu}_j^a \hat{\mu}_k^a \hat{\mu}_l^a + \hat{\mu}_i^b \hat{\mu}_j^b \hat{\mu}_k^b \hat{\mu}_l^b) + (\hat{\mu}_i^a \hat{\mu}_j^a \hat{\mu}_k^b \hat{\mu}_l^b \\ & + \hat{\mu}_i^b \hat{\mu}_j^b \hat{\mu}_k^a \hat{\mu}_l^a)] - (\hat{\mu}_i^a \hat{\mu}_j^a + \hat{\mu}_i^b \hat{\mu}_j^b)(\mu_k^a \mu_l^b + \mu_k^b \mu_l^a) \\ & - (\mu_i^a \mu_j^b + \mu_i^b \mu_j^a)(\hat{\mu}_k^a \hat{\mu}_l^a + \hat{\mu}_k^b \hat{\mu}_l^b), \end{aligned} \tag{56}$$

$$\begin{aligned} Y_{ijkl}^a = {} & 3(\mu_m^a r_m) \hat{\mu}_i^a \hat{\mu}_j^a \hat{\mu}_k^a \hat{\mu}_l^a - \hat{\mu}_i^a \hat{\mu}_j^a (\mu_k^a r_l + r_k \mu_l^a) \\ & - (\mu_i^a r_j + r_i \mu_j^a) \hat{\mu}_k^a \hat{\mu}_l^a, \end{aligned} \tag{57}$$

and

$$\Phi_{ijkl} = -3i\sum_{a=1}^{N}(\mu_m^a k_m)\hat{\mu}_i^a\hat{\mu}_j^a\hat{\mu}_k^a\hat{\mu}_l^a e^{-ik_n r_n}. \tag{58}$$

In systems which contain point charges and point dipoles, cross interaction terms must also be included. The real-space energy due to ion-dipole interactions is given by

$$U^r = \sum_{a=1}^{N-1}\sum_{b=a+1}^{N} B_1[q^a(\mu_m^b r_m) - q^b(\mu_n^a r_n)]. \tag{59}$$

The reciprocal-space contribution to the energy from the ion-dipole interactions is given by

$$U^k = \sum_{k=0}^{k_{max}} A(k)[\mathbb{S}^* S + S^*\mathbb{S}]. \tag{60}$$

Consequently the ion-dipole interaction also contributes to the stress and elasticity tensors. These additional terms are given by

$$\sigma_{ij}^B = -\frac{1}{V}\sum_{a=1}^{N-1}\sum_{b=a+1}^{N}\{B_1(q^b Z_{ij}^a - q^a Z_{ij}^b) + [q^a(\mu_m^b r_m) - q^b(\mu_n^a r_n)]B_2 r_i r_j\} - \frac{1}{V}\sum_{k\neq 0}^{k_{max}} A(k)[(\mathbb{S}^* S + S^*\mathbb{S})\Theta_{ij} - S^*\Psi_{ij} - S\Psi_{ij}^*] \tag{61}$$

and

$$C_{ijkl}^B = \frac{1}{V}\left\langle \sum_{a=1}^{N-1}\sum_{b=a+1}^{N}\{B_1(q^a Y_{ijkl}^b - q^b Y_{ijkl}^a) - B_2(q^a Z_{ij}^b - q^b Z_{ij}^a)r_k r_l - B_2 r_i r_j(q^a Z_{kl}^b - q^b Z_{kl}^a) + B_3(q^a\mu_m^b r_m - q^b\mu_n^a r_n)r_i r_j r_k r_l\}\right\rangle + \frac{1}{V}\left\langle \sum_{k\neq 0}^{k_{max}} A(k)[S^*\Phi_{ijkl} + S\Phi_{ijkl}^* + (\mathbb{S}^* S + S^*\mathbb{S})\Omega_{ijkl} - \Theta_{ij}(S\Phi_{kl}^* + S^*\Phi_{kl}) - (S\Phi_{ij}^* + S^*\Phi_{ij})\Theta_{kl}]\right\rangle. \tag{62}$$

Therefore the full stress tensor is given by Eq. (13) where σ_{ij}^B is given by the sum of Eqs. (27), (44), and (61). The full elasticity tensor is given by Eq. (16) where C_{ijkl}^B is given by the sum of Eqs. (31), (55), and (62). Note that the expressions derived here are valid when no other internal or external constraints exist.

IV. CONCLUSION

Many synthetic and biological materials are composed of ionic and dipolar particles. A computational understanding of the elastic properties of these materials requires a sound theoretical description of the stress and elasticity tensors for ionic and dipolar systems. Previous theoretical descriptions of these tensors in ionic and dipolar systems assumed that the orientation of the dipoles are independent of the strain tensor, thereby neglecting contributions to the stress and elasticity tensors that could be important. Our new expressions for the elasticity and stress tensors of ionic and dipolar systems should provide a sound foundation for computational studies aimed at understanding the elastic properties of biological structures where the constituent elements exhibit very large monopole and/or dipole moments that may dominate their mechanical properties.

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