

Improved simulation method for the calculation of the elastic constants of crystalline and amorphous systems using strain fluctuations

Kevin Van Workum and Juan J. de Pablo

Department of Chemical Engineering, University of Wisconsin–Madison, Madison, Wisconsin 53706

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In this paper, a method is proposed for calculating the elastic constants of arbitrarily soft or stiff systems using strain fluctuations. For stiff materials, for example, strain fluctuations may be enhanced by appropriate choice of elastic constants for the bath. Example calculations of the isothermal elastic constants of the nearest-neighbor Lennard-Jones fcc crystal demonstrate improved convergence properties over standard techniques. Elastic constants for a model amorphous polymer system are also presented.

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I. INTRODUCTION

The elastic constants are an important property of a material. Significant effort has therefore been devoted to their calculation in anisotropic (crystalline) solids using molecular simulations [1–4]. Less work has been aimed at simulating the elastic properties of amorphous polymer glasses. Direct application of the molecular simulation techniques developed for crystalline solids becomes difficult for these softer materials.

The isothermal elastic constant tensor can be expressed in terms of the thermal strain fluctuations at zero applied stress [5] according to

$$C_{ijkl} = \frac{k_B T}{V_0} [\langle \epsilon_{ij} \epsilon_{kl} \rangle - \langle \epsilon_{ij} \rangle \langle \epsilon_{kl} \rangle]^{-1}, \quad (1)$$

where ϵ_{ij} is the strain tensor, k_B is Boltzmann's constant, T is the temperature, and V_0 is the average volume. The indices represent the Cartesian coordinates in three dimensions and run from 1 to 3. The strain tensor is given by

$$\epsilon_{ij} = \frac{1}{2} [\langle \tilde{h} \rangle_{ik}^{-1} G_{kl} \langle h \rangle_{lj}^{-1} - \delta_{ij}]. \quad (2)$$

If \mathbf{a} , \mathbf{b} , and \mathbf{c} are the principal axes of the simulation box, then $h_{ij} = \{\mathbf{a}, \mathbf{b}, \mathbf{c}\}_{ij}$ (the so-called the scaling matrix) describes its size and shape. The matrix $\langle h \rangle_{ij}$ describes the reference box and $\langle \tilde{h} \rangle_{ij}^{-1}$ is the inverse of the transpose of $\langle h \rangle_{ij}$. The metric tensor is defined as $G_{ij} = \tilde{h}_{ik} h_{kj}$. Summation over repeated indices is implied.

In terms of the fluctuations in stress and strain, the isothermal elastic constant tensor [6] is given by

$$C_{ijkl} = \langle \epsilon_{ij} \sigma_{pq} \rangle \langle \epsilon_{qp} \epsilon_{kl} \rangle^{-1}, \quad (3)$$

where the stress tensor is $\sigma_{ij} = -(P_{ij} - P_0 \delta_{ij})$ and the pressure tensor is given by

$$P_{ij} = \frac{1}{V} \left[\sum_{\alpha} p_{\alpha i} p_{\alpha j} / m_{\alpha} - \sum_{\beta > \alpha} r_{\alpha\beta}^{-1} u'_{\alpha\beta} r_{\alpha\beta i} r_{\alpha\beta j} \right]. \quad (4)$$

The potential energy between interaction sites α and β is denoted by $u_{\alpha\beta}$, $r_{\alpha\beta}$ is the distance between them, p_{α} and

m_{α} are the momentum and mass, respectively, of site α , and the prime indicates a derivative with respect to $r_{\alpha\beta}$. Equation (3) has been shown [6] to have improved convergence properties over Eq. (1).

The derivation of Eqs. (1)–(3), using theory of linear elasticity assumes small strain values and small strain fluctuations. Small thermal strain fluctuations are typically encountered in stiff, low-temperature solids such as crystals. For stiff materials, these small strain fluctuations can hinder adequate sampling of accessible strain values, thus reducing the precision of the averages in the fluctuation formulas. Alternatively, the presence of large thermal strain fluctuations as a material becomes softer limits the use of the above linear theory. In this paper, we present a simulation technique that facilitates fast and accurate calculation of the elastic constants of anisotropic and/or amorphous materials from molecular simulations.

II. SIMULATIONS

Configurations of interest are generated in the isothermal-isostress-isobaric (N - σ - T) ensemble using a simple Metropolis Monte Carlo method. One Monte Carlo move consists of a sequence of random attempts to displace all the particle positions r_{α} , and the scaling matrix h_{ij} . Trial configurations are accepted with the following probability:

$$P_{trans} = \min\{1, \exp(-\Delta H/k_B T)\}, \quad (5)$$

where ΔH is the change in enthalpy associated with the displacement. The enthalpy change is given by

$$\Delta H = \Delta U + P_0 \Delta V - N k_B T \ln(V^{new}/V^{old}) + V_0 \sigma_{ij} \Delta \epsilon_{ji}, \quad (6)$$

where ΔU is the change in energy of the proposed move, P_0 is the external pressure, $\Delta V = V^{new} - V^{old}$ is the change in volume, $V_0 = \det(\langle h \rangle)$ is the volume of the reference state, and N is the number of particles. The change in strain is $\Delta \epsilon_{ij} = \epsilon_{ij}^{new} - \epsilon_{ij}^{old}$. Random displacements of each element in h_{ij} are generated according to

$$h_{ij}^{new} = h_{ij}^{old} + \Delta h_{max} (2 \xi_{ij} - 1), \quad (7)$$

where Δh_{max} is the maximum allowed displacement of an element of h_{ij} , and ξ_{ij} is a random number uniformly distributed between 0 and 1. In order to prevent rotations of the simulation box, we impose the constraint that $h_{ij}=h_{ji}$.

III. ELASTIC BATH METHOD

For small strains, the strain energy per unit volume of a deformed system can be written in general as

$$\hat{E}_s = \frac{1}{2} C_{ijkl} \epsilon_{lk} \epsilon_{ji}. \quad (8)$$

For an isotropic material, the strain energy per unit volume [7] is given by

$$\hat{E}_s = \frac{1}{2} \lambda \epsilon_{ii}^2 + \mu \epsilon_{ij}^2, \quad (9)$$

where λ and μ are the *Lamé coefficients*. If we immerse the system in an elastic bath with appropriately chosen elastic constants, we can amplify (or attenuate) thermal strain fluctuations. By using an appropriate choice of elastic bath, we can control the strains that are subsequently used in Eq. (1). To do this, we include the strain energy of the elastic bath from either Eq. (8) or Eq. (9) in the Monte Carlo acceptance criteria. Equation (6) then becomes

$$\Delta H = \Delta U + P_0 \Delta V - N k_B T \ln(V^{\text{new}}/V^{\text{old}}) + V_0 \sigma_{ij} \Delta \epsilon_{ji} + \Delta E_s^b, \quad (10)$$

where ΔE_s^b is the change in energy of the elastic bath. Using Eq. (8), ΔE_s^b can be written as

$$\Delta E_s^b = \frac{1}{2} V_0 C_{ijkl}^b [\epsilon_{lk}^{\text{new}} \epsilon_{ji}^{\text{new}} - \epsilon_{lk}^{\text{old}} \epsilon_{ji}^{\text{old}}], \quad (11)$$

where C_{ijkl}^b is the chosen elastic constant tensor of the elastic bath. Because the elastic bath is only a mathematical construction, we are free to choose any C_{ijkl}^b , including non-physical values, i.e., less than zero. The simulation is then carried out as outlined above, and the elastic constants of the material including the elastic bath, C_{ijkl}^t , can be calculated using Eq. (1). To recover the elastic constant tensor of the system of interest, we use the continuum theory of linear elasticity of composites with uniform strain fields to arrive at

$$C_{ijkl} = C_{ijkl}^t - C_{ijkl}^b. \quad (12)$$

Note that the volume fraction of both the elastic bath and the system of interest is unity.

At all times the elastic bath and the system of interest have identical strains, and both take as their reference state, $\epsilon_{ij}^0 = 0$. Therefore the equilibrium state for the combined system will also be the reference state, $\epsilon_{ij}^0 = 0$. The addition of the strain energy of the bath, Eq. (8), would apply an additional effective average stress to the system. This additional applied stress is zero on average with this choice of reference state, i.e.,

$$\sigma_{ij}^b = C_{ijkl}^b \epsilon_{lk}^0 = 0. \quad (13)$$

If the elastic constants of the bath are too large, poor sampling of relevant phase space will reduce the accuracy of the fluctuation formula, Eq. (1). The elastic bath method is most useful for very soft or very stiff systems. In these cases, an appropriate choice of C_{ijkl}^b is always available, i.e., of order -10 to 10 .

By adding a term to the energy expression, Eq. (8), this approach follows in the spirit of umbrella sampling [8] or extended Hamiltonian [9] simulation techniques. In this method, the additional term depends on the strain tensor of the system, and not explicitly on the particle positions. Otherwise, our approach should simply be viewed as a standard umbrella method for mechanical constants.

IV. FCC CRYSTAL

To verify the above procedure, we employ the previously studied first-nearest-neighbor Lennard-Jones fcc crystal model [2,4,10–13]. The system consists of 500 particles arranged in an fcc crystal at an isotropic pressure of 0 Pa. All simulations in this study were performed in the N - σ - T ensemble. All components of the applied stress tensor, σ_{ij} , were set to zero for all simulation runs. Reported elastic constants are expressed in dimensionless Lennard-Jones units, and are represented using the Voigt matrix notation [14]. For fcc systems, there are three groups of nonzero, independent elements of the elastic constant matrix

$$\begin{aligned} C_{11} &= C_{22} = C_{33}, \\ C_{12} &= C_{13} = C_{23}, \\ C_{44} &= C_{55} = C_{66}. \end{aligned} \quad (14)$$

The average value of each group is given by $\langle C_{ij} \rangle$.

In Fig. 1, we show $\langle C_{11} \rangle$, $\langle C_{12} \rangle$, and $\langle C_{44} \rangle$ as a function of temperature calculated using Eq. (1). Each simulation was equilibrated for 2.5×10^6 Monte Carlo (MC) steps. The ensemble averages were then computed from an additional 5×10^6 MC steps. Two different strengths of the elastic bath were used by setting the Lamé coefficients of the bath to $\lambda^b = \mu^b = 0$ and $\lambda^b = \mu^b = 10$. C_{ij}^b is expressed in terms of the Lamé coefficients as $C_{11}^b = 2\mu^b + \lambda^b$, $C_{12}^b = \lambda^b$, and $C_{44}^b = \mu^b$. For each temperature below $T=0.225$, an additional set of Lamé coefficients, namely $\lambda^b = \mu^b = -10$, was also used. There is excellent agreement between all sets of data. Table I lists the isothermal elastic constants in units of $Nk_B T/V$ for three temperatures for comparison with literature data [6]. Values of the elastic constants for all three sets of the bath coefficients agree well with available data.

When $\mu^b = \lambda^b = 0.0$, Eq. (10) reduces to Eq. (6) and corresponds to the usual strain fluctuation technique, i.e., without an elastic bath. At $T=0.01$, the thermal strain fluctuations are extremely small, and the convergence of $\langle C_{11} \rangle$ from Eq. (1) is slow [Fig. 2(a)]. The convergence of $\langle C_{11} \rangle$ is also slow at this temperature when using Eq. (3) [Fig. 2(b)].

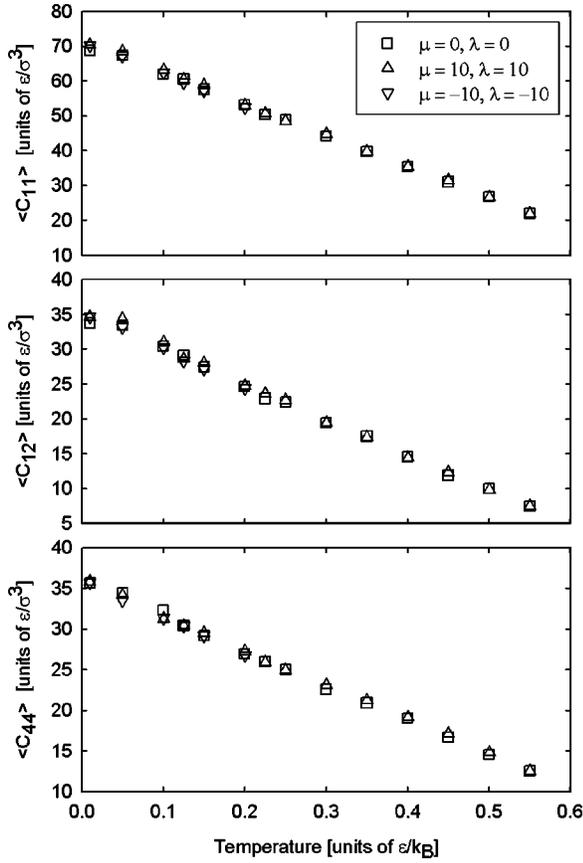


FIG. 1. The elastic constants of the fcc crystal as a function of temperature: (\square) zero elastic bath, (\triangle) positive elastic bath, and (∇) negative elastic bath. All values are shown in dimensionless units of ϵ/σ^3 .

When $\mu^b = \lambda^b = 10$, the system is immersed in a positive-stiffness, isotropic elastic bath. In this case, the composite system is “stiffer” than in the previous case, and the strains due to thermal fluctuations are attenuated. Using Eq. (12), we obtain the correct elastic constants from Eq. (1), as shown in Table I and Fig. (1).

With $\mu^b = \lambda^b = -10$, the system is immersed in a negative-stiffness elastic bath. Now, the overall composite material is softer than in the absence of the bath. Using Eq.

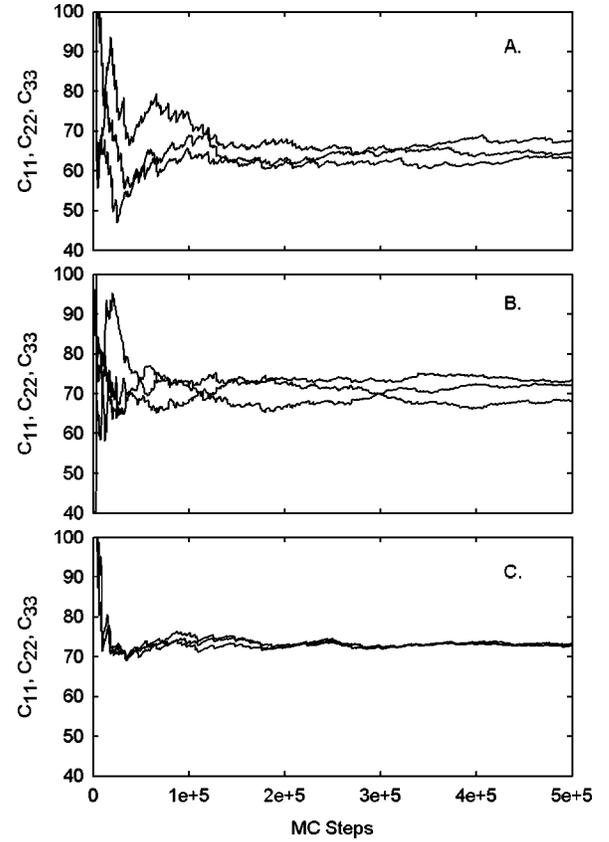


FIG. 2. Convergence of $\langle C_{11} \rangle$ for the fcc crystal at $T=0.01$. (a) Using Eq. (1) with zero elastic bath. (b) Using Eq. (3) with zero elastic bath. (c) Using Eq. (1) with negative elastic bath.

(1) and Eq. (12) with C_{ij}^b as before, we recover the correct elastic constants as shown in Table I and Fig. 1. In this case, the strain fluctuations are amplified and the convergence of Eq. (1) is improved. Figure 2(c) shows that the value of $\langle C_{11} \rangle$ converges to within a few percent of the correct value almost immediately when a negative bath is applied. Table I shows that at $T=0.125$, the accuracy of the calculation is improved when negative Lamé coefficients are used for the elastic bath. Results are not provided for $T=0.225$ and $T=0.3$ because at these higher temperatures, the composite

TABLE I. Values of the elastic constants of the fcc crystal (in units of $Nk_B T/V$) calculated from Eq. (1) for three different sets of Lamé coefficients of the elastic bath. Data from the literature [6] are shown in the last column (NA stands for not available).

T	$\langle C_{ij} \rangle$	$\mu=0, \lambda=0$	$\mu=10, \lambda=10$	$\mu=-10, \lambda=-10$	Ref. [6]
0.125	$\langle C_{11} \rangle$	491.5 ± 1.4	494.2 ± 3.6	489.5 ± 0.8	490.6 ± 0.8
	$\langle C_{12} \rangle$	235.1 ± 1.3	236.7 ± 0.9	233.9 ± 0.4	234.4 ± 0.3
	$\langle C_{44} \rangle$	249.5 ± 1.0	249.6 ± 0.8	249.0 ± 0.4	248.5 ± 0.7
0.225	$\langle C_{11} \rangle$	236.9 ± 0.5	238.8 ± 0.3		235.0 ± 1.0
	$\langle C_{12} \rangle$	108.0 ± 0.3	110.3 ± 1.7	NA	108.4 ± 0.7
	$\langle C_{44} \rangle$	121.7 ± 0.6	121.6 ± 1.2		121.0 ± 0.2
0.300	$\langle C_{11} \rangle$	157.0 ± 0.5	157.6 ± 0.4		155.3 ± 0.6
	$\langle C_{12} \rangle$	69.0 ± 0.2	69.3 ± 0.5	NA	68.1 ± 0.3
	$\langle C_{44} \rangle$	82.0 ± 0.3	82.5 ± 0.2		80.6 ± 0.4

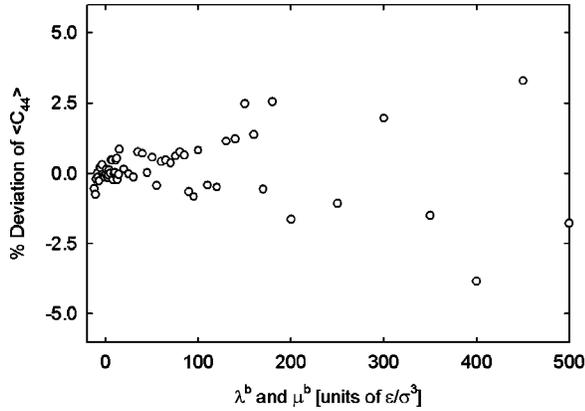


FIG. 3. The percent deviation of $\langle C_{44} \rangle$ for the fcc crystal as a function of the strength of the elastic bath in units of ϵ/σ^3 . Here the choice $\lambda^b = \mu^b$ is taken for convenience.

system becomes mechanically unstable with this choice of Lamé coefficients for the elastic bath.

Care must be taken when choosing appropriate values for the elastic constants of the bath. Figure 3 shows the percent deviation of $\langle C_{44} \rangle$ for the fcc crystal at $T=0.125$ as a function of the strength of the elastic bath. The percent deviation is defined as

$$D = \frac{\langle C_{44} \rangle - \langle C_{44} \rangle_{\lambda^b=0}}{\langle C_{44} \rangle_{\lambda^b=0}} \times 100. \quad (15)$$

For all values of the elastic bath, the correct average is obtained. However, if the composite system becomes too stiff, the strain fluctuations are reduced and the convergence and accuracy of the resulting elastic constants are decreased (the errors are larger). Deviations of less than 2% occur for $\lambda^b, \mu^b > 150$. If the composite system becomes too soft, the strains due to thermal fluctuations may grow so large that the use of Eq. (1) may become inappropriate. The system may also become mechanically unstable with an inappropriate choice for the elastic constants of the immersing bath. For this system at these conditions, this happens with $\lambda^b, \mu^b < -12$. Note that the useful range of appropriate values of the elastic bath will depend on the particular system under study.

V. AMORPHOUS POLYMER

In this section we apply the above methods to a softer glass, namely, a model polymer system as it approaches a glass transition. Our polymer model consists of linear chains of 16 Lennard-Jones interaction sites connected by harmonic springs. The interaction potential is truncated at $r=2.5\sigma$. Each simulation box contains 56 chains and the usual periodic boundary conditions are used. All simulations are carried out at an external pressure of 2.0 in units of ϵ/σ^3 .

In order to use the methods outlined above, the zero-stress reference state must first be calculated. To do this, the polymer system is equilibrated in the N - P - T ensemble at each temperature in order to relax any nonisotropic stresses. The reference box shape, $\langle h_{ij} \rangle$, is subsequently chosen to corre-

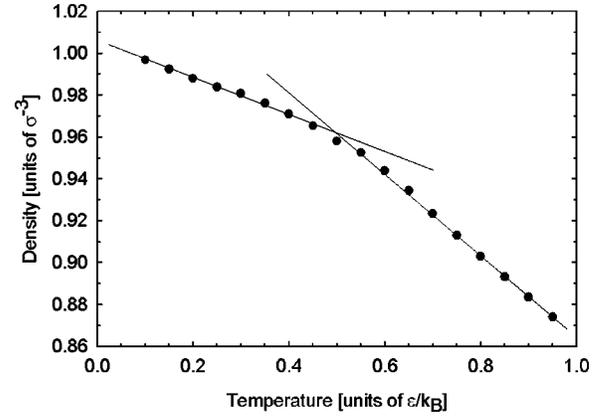


FIG. 4. Density as a function of temperature for the model amorphous polymer.

spond to the average equilibrium density at each temperature. Figure 4 shows the density as a function temperature for the model polymer system. An apparent glass transition temperature T_g is often assumed to correspond to the temperature at which the slope of the density changes, here $T_g \approx 0.5$.

Simulations are then conducted in the N - σ - T ensemble at an external pressure of 2.0 with zero applied stress, $\sigma_{ij}=0$. Figure 5 shows one component of the strain tensor, ϵ_{33} , as a function of MC steps at $T=0.8$ with and without the effect of an elastic bath. For the elastic bath, $\mu^b=50$ and $\lambda^b=50$ are as in Eq. (9).

The magnitude of the strains can be as high as 0.1 when no elastic bath is used. Furthermore, the scaling matrix h_{ij} can drift significantly from the reference state during the course of the simulation. When an adequate, strong elastic bath is used, the magnitude of the strains can be reduced to less than 0.05, well within the limit of small strains implied in Eqs. (1) and (3). The drift of the scaling matrix is also eliminated.

Figure 6 shows the contribution of the polymer to the composite's Young's modulus (ΔE) as a function of temperature using an isotropic elastic bath with $\mu^b=50$ and $\lambda^b=50$. The Young's modulus is given by

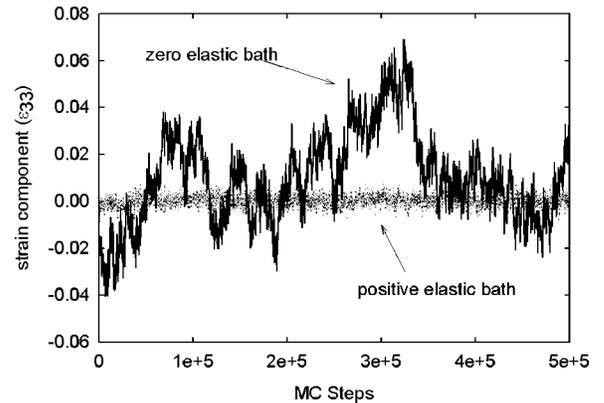


FIG. 5. One component of the strain tensor, ϵ_{33} , vs MC step for the amorphous polymer at $T=0.8$ with and without the elastic bath.

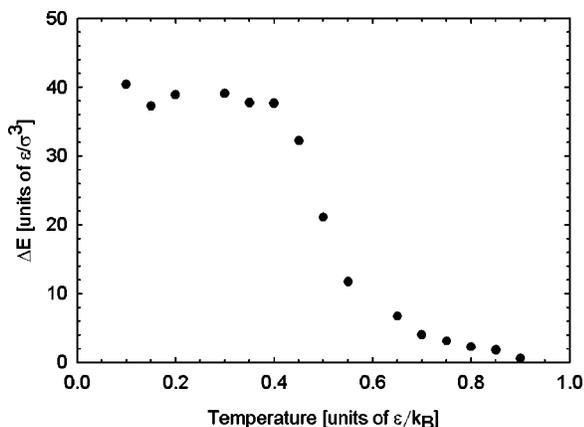


FIG. 6. Contribution of the polymer to the Young's modulus as a function of temperature.

$$E = \frac{(3\lambda + 2\mu)\mu}{\lambda + \mu}, \quad (16)$$

where λ and μ are the isotropic Lamé coefficients. Interestingly, a sharp decay of ΔE is observed precisely in the temperature range where the density changes slope ($T=0.5$). As the material undergoes a glass transition, the contribution of the polymer to the composite's modulus exhibits a sharp decay, thereby providing a useful mechanical diagnosis to identify or characterize glass transition phenomena by simulations.

VI. CONCLUSION

We have presented a simulation method that facilitates calculation of the elastic constants of anisotropic or amorphous materials. This was achieved by immersing the system in a perfectly elastic bath, thereby creating an ideal composite material whose properties can be tuned artificially. We demonstrated the use of the method by simulating the well-known Lennard-Jones fcc crystal and showed that, relative to previous work, the method improves convergence properties at low temperature when a negative elastic bath is used. We also applied our method to a model polymer system and examined the behavior of the Young's modulus of the resulting composite below T_g . This method can provide a useful framework to characterize the mechanical behavior of glass-forming systems upon vitrification. Because the evaluation of forces is not required, this method is also useful for systems in which the calculation of stresses is difficult or time consuming. Studies of the elastic moduli of a binary glass will be presented in a future paper.

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