Fluctuation formulas for the elastic constants of an arbitrary system

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We derive the general fluctuation expressions for both the isothermal and adiabatic elastic constants of systems with arbitrary interparticle interactions and under arbitrary loading. We find that the expressions for these two kinds of elastic constants have exactly the same form though in general their values would be different. These formulas have the advantage that all elastic constants can be calculated in a single computer simulation run without performing any deformation on the system.

I. INTRODUCTION

Elastic constants yield valuable dynamical and mechanical information about materials. For example, they provide information concerning their strength and stability.[1−5] Furthermore, the comparison between experimentally measured and theoretically calculated elastic constants has been widely used as an important means of probing the interatomic forces.[1,2] In cases where well established potentials are available one should be able to predict the behavior of the material under various conditions of normal or extreme loading.

To compare experimental results with theory, it is necessary not only to have accurate experimental data, but also to have a reliable method of calculation. Recent advances in computer simulation techniques and formalism have made this possible .[1−21]

On the other hand, a fluctuation formulation is very convenient in computer simulation because it avoids numerical differentiation which may require long computational times and have low accuracy. A well-known example of a fluctuation formula is the expression for the specific heat as a fluctuation of the energy instead of a derivative of the energy with respect to temperature.

Squire, Holt, and Hoover were the first to derive the "equilibrium" fluctuation formulas for the isothermal elastic constants[9] in the stress-free state by noticing that the elastic constants are the second derivatives of the Helmholtz free energy. Their method was extended by many people to more complex systems.[12,15−21] The expressions so obtained have the obvious advantage that they converge rapidly for a solid material and all elastic constants can be calculated in a single run without performing any deformation. However, the definition of elastic constants in most papers (see, for instance, Refs. 15–21) uses implicitly the natural (stress-free) reference (initial) configuration, therefore *a priori* the expressions are only valid for systems up to moderate stress. They also do not provide the formulas for the stress-strain stiffnesses which govern stress-strain relations. Moreover, starting from the stress-free configurations makes the expressions complex and not easy to reproduce .[15−21] It consequently discourages attempts to use them. We must emphasize that there are several definitions, differing by some stress-related terms, for the elastic constants for a system under loading, and each physical situation may call for a different relevant quantity.[5,7,11] Consequently, under loading, the traditional elastic constants (we shall refer to them as thermodynamic stiffnesses to distinguish them from the stress-strain stiffnesses) do not describe the elastic properties of a material directly, and in the fluctuation formulas the reference parameters must be the ones of the current (stressed) state.[3−5,7,11] These points must become more and more important with the rapid development of high pressure techniques and for soft condensed matter in which the stress and elastic constants have the same order of magnitude. We should also stress that though different definitions of strains can lead to different "elastic constants," the difference between the stress-strain stiffness and the thermodynamic stiffnesses is not completely due to such a choice. The difference comes from the nonlinear relationship between strains with different reference states.[7,11]

We have recently developed the "equilibrium" fluctuation formulas to calculate the isothermal stress strain stiffness for a central force system under arbitrary stress and at any temperature.[5] It has a relatively simple form and has been applied successfully to several systems, albeit care is required in the choice of algorithms to accurately reproduce the desired ensemble when dealing with highly disordered soft materials.[22−25]

The interatomic force, however, in a real material is in general noncentral. The appropriate expressions for noncentral forces would therefore have a more general applicability. Expressions for the adiabatic stress-strain stiffnesses are also not yet available even for a stress-free state. So we derive both in this work.

We derive the correct fluctuation formulas for both isothermal and adiabatic stress-strain stiffnesses with arbitrary interparticle interactions and under arbitrary loading. Our approach is similar, but much simpler, than the one used in Ref. 21. We show that the expressions for these two sets of constants are exactly the same though in general their values would be different.

The paper is organized as follows. We first present in Sec. II some fundamental expressions on which our discussion is based. Sec. III derives fluctuation formulas for the *isother-*

mal thermodynamic stiffnesses and stress-strain stiffnesses. In Sec. IV we then develop the fluctuation formulas for the *adiabatic* thermodynamic stiffnesses and stress-strain stiffnesses. These sections are followed by a short presentation of their zero temperature static limit and a discussion of boundary conditions. A summary concludes the paper.

II. FUNDAMENTAL EXPRESSIONS

We first present some fundamental expressions on which our discussion is based. Some of them have rarely appeared in the literature.

A. Thermodynamic stiffnesses and stress-strain stiffnesses

To derive the expressions for the thermodynamic stiffnesses, following Ray and Rahman,[15] we introduce the scaled coordinates $\mathbf{q}_i$ and scaled momenta $\tilde{\mathbf{p}}_i$ defined by

$$\mathbf{x}_i = h\mathbf{q}_i \quad \text{or} \quad x_{i\alpha} = h_{\alpha\beta}q_{i\beta}, \quad \text{and so} \quad q_{i\alpha} = h_{\alpha\beta}^{-1}x_{i\beta}, \quad (1)$$

$$\mathbf{p}_i = \tilde{\mathbf{p}}_i h^{-1} \quad \text{or} \quad p_{i\alpha} = h_{\beta\alpha}^{-1}\tilde{p}_{i\beta}, \quad \text{and so} \quad \tilde{p}_{i\alpha} = h_{\beta\alpha}p_{i\beta}, \quad (2)$$

where $\mathbf{x}$ and $\mathbf{p}$ are the real coordinate and momenta of the particle. $h = (\mathbf{a}, \mathbf{b}, \mathbf{c})$, where $\mathbf{a}$, $\mathbf{b}$, and $\mathbf{c}$ are the three vectors forming the simulation cell. Therefore for all atoms i, we have $-0.5 \leq q_{i\alpha} < 0.5$. In these equations, and all subsequent ones, the Einstein summation convention for repeated suffices is followed, except where clarity requires showing explicitly the summations. We also use the convention that Greek indices refer to Cartesian components while Roman indices to particle numbers. The volume of the system is given by $V = \det(h)$.

The strain tensor can then be defined by[15]

$$\eta = \frac{1}{2}[(h_0^{-1})^T \cdot h^T \cdot h \cdot h_0^{-1} - I], \quad (3)$$

where h_0 is the reference value of h and h^T the transpose of h. h_0 can be either stress-free or stressed. η is called the Lagrangian *finite* strain tensor, which can represent any deformation, however large. We should recall here that in the present work we take eventually the limit $h \rightarrow h_0$. We should also point out that Eq. (3) is in fact valid for any simulation cell, not only for rectangular parallelepipeds.

The Hamiltonian of an arbitrary system can be written

$$\mathcal{H} = \sum_{i=1}^{N} \frac{\mathbf{p}_i^2}{2m_i} + U(\{\mathbf{x}_i\})$$

$$= \sum_{i=1}^{N} \frac{1}{2m_i}(\tilde{\mathbf{p}}_i \cdot h^{-1})(\tilde{\mathbf{p}}_i \cdot h^{-1}) + U(\{h \cdot \mathbf{q}_i\}). \quad (4)$$

The thermodynamic stiffnesses are defined by

$$C_{\alpha\beta\nu\tau} \equiv \frac{1}{V_0}\left(\frac{\partial^2 W}{\partial\eta_{\alpha\beta}\partial\eta_{\nu\tau}}\right)_{\eta=0}, \quad (5)$$

where W is the strain energy. W can refer either to the Helmholtz free energy F in the derivation of isothermal thermo-

dynamic stiffnesses (the canonical ensemble) or to the internal energy E in the derivation of adiabatic thermodynamic stiffnesses (the microcanonical ensemble). V_0 is the reference value of the volume. $\eta = 0$ (or $h = h_0$) in Eq. (5) means that the elastic constants are calculated for virtual infinitesimal displacements from the reference configuration which could be a stressed state. Consequently, when using "equilibrium" fluctuation formulas for the calculation of elastic constants, the reference configuration (i.e., before virtual deformations are applied to the system) must be the current one. Note that the subscript $\eta = 0$ or $h = h_0$ is often neglected.[15–21] This could lead to additional and incorrect reference parameters, and make the expressions unnecessarily complex. We also do not distinguish between the isothermal elastic constants and the adiabatic elastic constants in this paper because their expressions have exactly the same form.

We must also emphasize that for a stressed system the $C_{\alpha\beta\nu\tau}$ do not describe elasticity directly. Instead, we need to consider the stress-strain stiffnesses (also called elastic stiffness coefficients) which govern stress-strain relations and are given by[3–5,7,11]

$$c_{\alpha\beta\nu\tau} \equiv C_{\alpha\beta\nu\tau} - \frac{1}{2}(2\sigma_{\alpha\beta}\delta_{\nu\tau} - \sigma_{\alpha\nu}\delta_{\beta\tau}$$
$$- \sigma_{\alpha\tau}\delta_{\beta\nu} - \sigma_{\beta\tau}\delta_{\alpha\nu} - \sigma_{\beta\nu}\delta_{\alpha\tau}). \quad (6)$$

In thermodynamics, a thermodynamic stress tensor $t_{\alpha\beta}$ is introduced:[6]

$$t_{\alpha\beta} = \frac{1}{V_0}\frac{\partial W}{\partial\eta_{\alpha\beta}} = \sigma_{\alpha\beta}(0) + C_{\alpha\beta\nu\tau}\eta_{\nu\tau} + \cdots, \quad (7)$$

where $\sigma_{\alpha\beta}(0)$ is the reference value of the applied stress $\sigma_{\alpha\beta}$ (often the opposite sign for $t_{\alpha\beta}$ is used as in Refs. 15,18). We then have

$$C_{\alpha\beta\nu\tau} = \left(\frac{\partial t_{\alpha\beta}}{\partial\eta_{\nu\tau}}\right)_{\eta=0} = C_{\nu\tau\alpha\beta}. \quad (8)$$

$t_{\alpha\beta}$ should not be confused with the applied stress $\sigma_{\alpha\beta}$ which is formally equal to[7,11]

$$\sigma_{\alpha\beta} = \frac{1}{V(\eta)}\left(\frac{\partial W(\eta_{\alpha\beta}, \eta'_{\alpha\beta})}{\partial h'_{\alpha\beta}}\right)_{\eta'_{\alpha\beta}=0}. \quad (9)$$

The reference configuration is the system deformed by h (or $\eta_{\alpha\beta}$). h' or $\eta'_{\alpha\beta}$ is the small deformation made on that system. So it is a different reference configuration than for $C_{\alpha\beta\nu\tau}$. A nonzero applied (Cauchy) stress of a configuration is given by t when and only when that configuration is chosen as the reference configuration.[7,11] Using Eq. (9), one can show that the difference between the stress-strain stiffnesses and the traditional elastic constants comes from the nonlinear relationship between the strains with different reference states.[7]

B. Strain derivatives

From

$$h_{\alpha\beta}^{-1}h_{\beta\tau}=\delta_{\alpha\tau}, \quad \frac{\partial h_{\alpha\beta}^{-1}}{\partial h_{\kappa\zeta}}=-h_{\alpha\kappa}^{-1}h_{\zeta\beta}^{-1}, \quad (10)$$

we obtain

$$\frac{\partial x_\alpha}{\partial h_{\nu\tau}}=h_{\tau\xi}^{-1}x_\xi\delta_{\alpha\nu}, \text{ and } \frac{\partial p_\alpha}{\partial h_{\nu\tau}}=-h_{\tau\alpha}^{-1}p_\nu. \quad (11)$$

So for an arbitrary scalar $A(\mathbf{x},\mathbf{p})$, we have

$$\frac{\partial A(\mathbf{x},\mathbf{p})}{\partial h_{\alpha\beta}}=\frac{\partial A}{\partial x_\alpha}h_{\beta\nu}^{-1}x_\nu-\frac{\partial A}{\partial p_\nu}h_{\beta\nu}^{-1}p_\alpha, \quad (12)$$

if we use both the scaled coordinates and scaled momenta.

From Eq. (3) follows

$$d\eta=\frac{1}{2}[(h_0^{-1})^T dh^T h h_0^{-1}+(h_0^{-1})^T h^T dh h_0^{-1}]. \quad (13)$$

Note that $dh=h-h_0$ has nine independent components but $d\eta$ has only six. This is because some changes in dh represent an infinitesimal rotation of the whole system. To describe a rigid rotation we have to introduce the antisymmetric rotation tensor[6,7]

$$d\omega=\frac{1}{2}[(h_0^{-1})^T dh^T h h_0^{-1}-(h_0^{-1})^T h^T dh h_0^{-1}]. \quad (14)$$

Note that only in the limit of infinitesimal deformation does the tensor ω represent an infinitesimal rotation. It follows that a finite ω, with a finite $h-h_0$, from Eq. (14) does not give a pure rotation, but includes some strain. Such finite strain effects are often important in the theory of the elasticity of stressed solids. However, since we will always take the limit of $h\to h_0$ in our final results, such effects are irrelevant in the present work.

From Eqs. (13) and (14), we obtain immediately

$$d\omega+d\eta=(h_0^{-1})^T dh^T h h_0^{-1} \quad (15)$$

and

$$dA(h)=\frac{\partial A}{\partial h_{\nu\tau}}dh_{\nu\tau}=\text{Tr}\left(\frac{\partial A}{\partial h}dh^T\right)$$

$$=\text{Tr}\left(h_0 h^{-1}\frac{\partial A}{\partial h}h_0^T(d\eta+dw)\right)$$

$$=h_{0\kappa\zeta}h_{\zeta\nu}^{-1}\frac{\partial A}{\partial h_{\nu\tau}}h_{0\tau\xi}^T(d\eta_{\xi\kappa}+dw_{\xi\kappa}). \quad (16)$$

Finally from Eqs. (12) and (16), one obtains

$$\frac{\partial A(\mathbf{x},\mathbf{p})}{\partial \eta_{\alpha\beta}}=\frac{1}{2}\left(\frac{\partial A}{\partial \eta_{\alpha\beta}}+\frac{\partial A}{\partial \eta_{\beta\alpha}}\right)$$

$$=\frac{1}{2}\left(h_{0\beta\zeta}h_{\zeta\nu}^{-1}\frac{\partial A}{\partial h_{\nu\tau}}h_{0\tau\alpha}^T+h_{0\alpha\zeta}h_{\zeta\nu}^{-1}\frac{\partial A}{\partial h_{\nu\tau}}h_{0\tau\beta}^T\right)$$

$$=\frac{1}{2}\{h_0 h^{-1}[(\mathcal{D}^r+\mathcal{D}^p)A](h^{-1})^T h_0^T\}_{\alpha\beta}, \quad (17)$$

where

$$\mathcal{D}_{\alpha\beta}^r=x_\alpha\frac{\partial}{\partial x_\beta}+x_\beta\frac{\partial}{\partial x_\alpha},$$

$$\mathcal{D}_{\alpha\beta}^p=-p_\alpha\frac{\partial}{\partial p_\beta}-p_\beta\frac{\partial}{\partial p_\alpha}. \quad (18)$$

III. FLUCTUATION FORMULAS FOR THE ISOTHERMAL ELASTIC CONSTANTS

For the canonical ensemble, we followed Lutsko[21] and used both scaled coordinates and scaled momenta to derive the desired expressions. However, it is not necessary to use scaled momenta in this ensemble. It only makes the derivation more complex so we did not follow this procedure in this paper. To exclude the use of the scaled momenta is equivalent to set $\partial\mathbf{p}/\partial h_{\alpha\beta}=0$ and $\mathcal{D}_{\alpha\beta}^p=0$. In this ensemble, the partition function is

$$Z=\int d\mathbf{p}^{3N}d\mathbf{x}^{3N}e^{-\mathcal{H}/k_B T}=\mathcal{C}V^N\int d\mathbf{q}^{3N}e^{-U/k_B T}, \quad (19)$$

where $\mathcal{C}$ is the constant coming from the integral over $3N$ momenta and is irrelevant in our derivation so we will omit it from now on. The Helmholtz free energy F is given by

$$F=-k_B T\ln Z=-k_B T\ln\bar{Z}-Nk_B T\ln V, \quad (20)$$

$$\text{with } \bar{Z}=\int d\mathbf{q}^{3N}e^{-U/k_B T}. \quad (21)$$

For a scalar $\hat{A}(\mathbf{x})$ which is not explicitly dependent on the size of the system, the ensemble average is

$$\langle\hat{A}\rangle=\frac{1}{Z}\int d\mathbf{p}^{3N}d\mathbf{x}^{3N}\hat{A}e^{-\mathcal{H}/k_B T}$$

$$=\frac{1}{\bar{Z}}\int d\mathbf{q}^{3N}\hat{A}e^{-U/k_B T}. \quad (22)$$

It follows from Eqs. (17), (18), and (22) that

$$\frac{\partial \langle \hat{A} \rangle}{\partial \eta_{\alpha\beta}} = \left\langle \frac{\partial \hat{A}}{\partial \eta_{\alpha\beta}} \right\rangle - \frac{1}{k_B T}\left(\left\langle \hat{A}\frac{\partial U}{\partial \eta_{\alpha\beta}}\right\rangle - \langle \hat{A} \rangle \left\langle \frac{\partial U}{\partial \eta_{\alpha\beta}}\right\rangle \right)$$

$$= \frac{1}{2}\left[h_0 h^{-1}\left(\langle \mathcal{D}^r \hat{A} \rangle - \frac{1}{k_B T}(\langle \hat{A}\mathcal{D}^r U \rangle - \langle \hat{A}\rangle \langle \mathcal{D}^r U \rangle) \right) \right.$$

$$\left. \times (h^{-1})^T h_0^T \right]_{\alpha\beta}. \tag{23}$$

From Eqs. (7), (17), (20), and (22), it is easy to find that

$$V_0 t_{\alpha\beta} = \left\langle \frac{\partial U}{\partial \eta_{\alpha\beta}}\right\rangle - nk_B T\frac{\partial V}{\partial \eta_{\alpha\beta}} = V_0\langle t_{\alpha\beta}^B \rangle - nk_B T\frac{\partial V}{\partial \eta_{\alpha\beta}}, \tag{24}$$

where $n=N/V$ is the number density of the system and

$$V_0 t_{\alpha\beta}^B = \frac{\partial U}{\partial \eta_{\alpha\beta}} = \frac{1}{2}[h_0 h^{-1}(\mathcal{D}^r U)(h^{-1})^T h_0^T]_{\alpha\beta}. \tag{25}$$

From Eqs. (23), (24), and (25), we obtain

$$2V_0\frac{\partial t_{\alpha\beta}}{\partial \eta_{\nu\tau}} = V_0\left(\frac{\partial t_{\alpha\beta}}{\partial \eta_{\nu\tau}} + \frac{\partial t_{\nu\tau}}{\partial \eta_{\alpha\beta}} \right)$$

$$= \left[\frac{V_0}{2}\left(h_0 h^{-1}\left(\langle \mathcal{D}^r t_{\alpha\beta}^B \rangle - \frac{1}{k_B T}\cdot(\langle t_{\alpha\beta}^B \mathcal{D}^r U \rangle \right.\right.\right.$$

$$\left.\left. - \langle t_{\alpha\beta}^B \rangle\langle \mathcal{D}^r U \rangle) \right)(h^{-1})^T h_0^T \right)_{\nu\tau}$$

$$+ \frac{1}{2}\left(h_{0\alpha\kappa}\frac{\partial h_{\kappa\zeta}^{-1}}{\partial \eta_{\nu\tau}}\langle \mathcal{D}_{\zeta\xi}^r U \rangle(h^{-1})_{\xi\mu}^T h_{0\mu\beta}^T \right.$$

$$\left.\left. + h_{0\alpha\kappa}h_{\kappa\zeta}^{-1}\langle \mathcal{D}_{\zeta\xi}^r U \rangle\frac{\partial (h^{-1})_{\xi\mu}^T}{\partial \eta_{\nu\tau}}h_{0\mu\beta}^T \right) \right]$$

$$+ \{\text{exchange of } (\alpha\ \beta)\text{ and }(\nu\ \tau)\text{ in the above } [\ ]\}$$

$$- 2nk_B T\left(\frac{\partial^2 V}{\partial \eta_{\alpha\beta}\partial \eta_{\nu\tau}} - \frac{1}{V}\frac{\partial V}{\partial \eta_{\alpha\beta}}\frac{\partial V}{\partial \eta_{\nu\tau}} \right). \tag{26}$$

From Eqs. (10) and (16), we get

$$\left(\frac{\partial h_{\kappa\zeta}^{-1}}{\partial \eta_{\nu\tau}} \right)_{h=h_0} = -\frac{1}{2}(h_{\kappa\tau}^{-1}\delta_{\nu\zeta} + h_{\kappa\nu}^{-1}\delta_{\tau\zeta}). \tag{27}$$

Combining the results from Eqs. (8), (25), (26), and (27), the isothermal thermodynamic stiffnesses $C_{\alpha\beta\nu\tau}$ are then

$$C_{\alpha\beta\nu\tau} = \left(\frac{\partial t_{\alpha\beta}}{\partial \eta_{\nu\tau}} \right)_{\eta=0}$$

$$= \frac{1}{4}\langle \mathcal{D}_{\nu\tau}^r \hat{\sigma}_{\alpha\beta}^B + \mathcal{D}_{\alpha\beta}^r \hat{\sigma}_{\nu\tau}^B \rangle$$

$$- \frac{V_0}{k_B T}(\langle \hat{\sigma}_{\alpha\beta}^B \cdot \hat{\sigma}_{\nu\tau}^B \rangle - \langle \hat{\sigma}_{\alpha\beta}^B \rangle\langle \hat{\sigma}_{\nu\tau}^B \rangle)$$

$$- \frac{1}{2}(\sigma_{\nu\beta}^B\delta_{\alpha\tau} + \sigma_{\alpha\tau}^B\delta_{\nu\beta} + \sigma_{\tau\beta}^B\delta_{\alpha\nu} + \sigma_{\alpha\nu}^B\delta_{\tau\beta})$$

$$+ nk_B T(\delta_{\alpha\tau}\delta_{\beta\nu} + \delta_{\alpha\nu}\delta_{\beta\tau}), \tag{28}$$

where we have used

$$\frac{1}{V_0}\left(\frac{\partial V}{\partial \eta_{\alpha\beta}} \right)_{\eta=0} = \delta_{\alpha\beta}, \frac{1}{V_0}\left(\frac{\partial^2 V}{\partial \eta_{\alpha\beta}\partial \eta_{\nu\tau}} \right)_{\eta=0}$$

$$= \delta_{\alpha\beta}\delta_{\nu\tau} - \delta_{\alpha\tau}\delta_{\beta\nu} - \delta_{\alpha\nu}\delta_{\beta\tau}, \tag{29}$$

$\sigma^B = \langle \hat{\sigma}^B \rangle$ is given by

$$\hat{\sigma}_{\alpha\beta}^B = t_{\alpha\beta}^B|_{h=h_0} = \frac{1}{2V}\mathcal{D}_{\alpha\beta}U = \frac{1}{2V}\left(x_{i\beta}\frac{\partial U}{\partial x_{i\alpha}} + x_{i\alpha}\frac{\partial U}{\partial x_{i\beta}} \right), \tag{30}$$

and the applied stress σ becomes

$$\sigma_{\alpha\beta} = \sigma_{\alpha\beta}^B - nk_B T\delta_{\alpha\beta}. \tag{31}$$

With Eqs. (18) and (30), a direct calculation leads to

$$V_0\mathcal{D}_{\alpha\beta}^r \sigma_{\nu\tau}^B = \frac{1}{2}\langle \mathcal{D}_{\alpha\beta}^r \mathcal{D}_{\nu\tau}^r U \rangle$$

$$= \frac{1}{2}\left\langle x_{i\alpha}\frac{\partial U}{\partial x_{i\tau}}\delta_{\beta\nu} + x_{i\alpha}\frac{\partial U}{\partial x_{i\nu}}\delta_{\beta\tau} + x_{i\beta}\frac{\partial U}{\partial x_{i\nu}}\delta_{\alpha\tau} \right.$$

$$\left. + x_{i\beta}\frac{\partial U}{\partial x_{i\tau}}\delta_{\alpha\nu} + \mathcal{U}_{\alpha\beta\nu\tau} \right\rangle, \tag{32}$$

where

$$\mathcal{U}_{\alpha\beta\nu\tau} = x_{i\alpha}x_{j\nu}\frac{\partial^2 U}{\partial x_{i\beta}\partial x_{j\tau}} + x_{i\alpha}x_{j\tau}\frac{\partial^2 U}{\partial x_{i\beta}\partial x_{j\nu}}$$

$$+ x_{i\beta}x_{j\tau}\frac{\partial^2 U}{\partial x_{i\alpha}\partial x_{j\nu}} + x_{i\beta}x_{j\nu}\frac{\partial^2 U}{\partial x_{i\alpha}\partial x_{j\tau}}. \tag{33}$$

Finally, combining Eqs. (28), (30), and (32), we obtain

$$C_{\alpha\beta\nu\tau} = -\frac{V_0}{k_B T}(\langle \hat{\sigma}_{\alpha\beta}^B \cdot \hat{\sigma}_{\nu\tau}^B \rangle - \langle \hat{\sigma}_{\alpha\beta}^B \rangle\langle \hat{\sigma}_{\nu\tau}^B \rangle)$$

$$- \frac{1}{4}(\sigma_{\beta\nu}^B\delta_{\alpha\tau} + \sigma_{\alpha\tau}^B\delta_{\beta\nu} + \sigma_{\beta\tau}^B\delta_{\alpha\nu} + \sigma_{\alpha\nu}^B\delta_{\beta\tau})$$

$$+ \frac{1}{4}\langle \mathcal{U}_{\alpha\beta\nu\tau} \rangle + nk_B T(\delta_{\alpha\nu}\delta_{\beta\tau} + \delta_{\alpha\tau}\delta_{\beta\nu}). \tag{34}$$

The first term in $C_{\alpha\beta\nu\tau}$ is the "fluctuation term." The second arises from the effect of the stress. The third term is referred to as the "Born term," owing to Born and his collaborator's works on thermodynamic stiffnesses of a "static" system at zero temperature.[1] And the last is sometimes called the "kinetic term."[9] From Eqs. (6) and (34), the stress-strain stiffnesses are then

$$c_{\alpha\beta\nu\tau} = -\frac{V_0}{k_B T}(\langle \hat{\sigma}_{\alpha\beta}^B \cdot \hat{\sigma}_{\nu\tau}^B \rangle - \langle \hat{\sigma}_{\alpha\beta}^B \rangle \langle \hat{\sigma}_{\nu\tau}^B \rangle)$$

$$+ \frac{1}{4}(\sigma_{\beta\nu}^B \delta_{\alpha\tau} + \sigma_{\beta\tau}^B \delta_{\alpha\nu} + \sigma_{\alpha\tau}^B \delta_{\beta\nu} + \sigma_{\alpha\nu}^B \delta_{\beta\tau}$$

$$- 4\sigma_{\alpha\beta}^B \delta_{\nu\tau}) + \frac{1}{4}\langle \mathcal{U}_{\alpha\beta\nu\tau} \rangle + n k_B T \delta_{\alpha\beta} \delta_{\nu\tau}. \quad (35)$$

For a pairwise central-force system, it is not difficult to show that the expressions for the elastic constants reduce to the expressions given in Ref. 5.

IV. ADIABATIC ELASTIC CONSTANTS

To find the adiabatic elastic constants is a little more involved because we have to use the scaled momenta in the first step of the derivation.

A. Formulation of the microcanonical ensemble

The microcanonical ensemble can be defined by using the phase volume via[8,14,2]

$$\phi(E,V,N) = \int_{\mathcal{H} \leqslant E} d\mathbf{p}^{3N} d\mathbf{x}^{3N} = \int \theta(\mathcal{H} - E) d\tau, \quad (36)$$

where E is the energy, $d\tau = d\mathbf{p}^{3N} d\mathbf{x}^{3N}$ and the step function θ is

$$\theta(x) = \begin{cases} 1 & x < 0, \\ 0 & x > 0. \end{cases} \quad (37)$$

The density of states $\omega(E,V,N)$ is defined by

$$\omega = \frac{\partial \phi}{\partial E} = \int \delta(\mathcal{H} - E) d\tau, \quad (38)$$

where δ is the Dirac delta function. The normalized probability density $W(\mathbf{x},\mathbf{p})$ is

$$W(\mathbf{x},\mathbf{p}) = \frac{\delta(\mathcal{H} - E)}{\omega}. \quad (39)$$

The average value of any quantity $f(\mathbf{x},\mathbf{p})$ is determined from $\langle f \rangle = \int W f d\tau$. The entropy is equal to

$$\mathcal{S}(E) = k_B \ln \phi(E) \quad (40)$$

when N is large.[2,8] We have omitted various constant factors which would render ϕ dimensionless since these constant factors would not appear in any of our final results. From Eq. (40), we obtain for the temperature

$$T = \left(\frac{\partial \mathcal{S}}{\partial E}\right)_{V,N}^{-1} = \frac{\phi}{k_B \omega}. \quad (41)$$

Assuming the Hamiltonian is dependent on an additional external parameter, say y, the adiabatic theorem gives[8,14,15]

$$\frac{\partial E}{\partial y}\bigg|_{\mathcal{S},V} = \left\langle \frac{\partial \mathcal{H}}{\partial y} \right\rangle = \frac{1}{\omega} \int \frac{\partial \mathcal{H}}{\partial y} \delta(\mathcal{H} - E) d\tau. \quad (42)$$

From the equipartition theorem,[8,14,15] we obtain

$$\left\langle p_\alpha \frac{\partial \mathcal{H}}{\partial p_\beta} \right\rangle = \frac{\phi}{\omega} \delta_{\alpha\beta} = k_B T \delta_{\alpha\beta}. \quad (43)$$

B. Fluctuation formulas for the adiabatic elastic constants

From Eqs. (7), (17), (42) and (43), with both the scaled coordinates and scaled momenta, we can show that

$$V_0 t_{\alpha\beta} = \frac{\partial E}{\partial \eta_{\alpha\beta}}\bigg|_{\mathcal{S}}$$

$$= \left\langle \frac{\partial \mathcal{H}}{\partial \eta_{\alpha\beta}} \right\rangle$$

$$= \frac{1}{2}[h_0 h^{-1} \langle (\mathcal{D}^r + \mathcal{D}^p)\mathcal{H} \rangle (h^{-1})^T h_0^T]_{\alpha\beta}$$

$$= \frac{1}{2}[h_0 h^{-1} \langle \mathcal{D}^r U \rangle (h^{-1})^T h_0^T]_{\alpha\beta}$$

$$- N k_B T h_{0\alpha\xi} h_{\xi\zeta}^{-1} h_{\mu\zeta}^{-1} h_{0\beta\mu}. \quad (44)$$

To continue the derivation, we do not need to use the scaled momenta, so we set again $\partial \mathbf{p}/\partial \eta_{\alpha\beta} = 0$ and $\mathcal{D}_{\alpha\beta}^p = 0$. There is a small difference between the method we used in this paper and the method using the scaled momenta. We will discuss this difference at the end of this section. What we must stress here is that using the scaled quantities is only a mathematical trick and should have no effect on the final results, as has been confirmed for the isothermal elastic constants.

Now we introduce a new function

$$X(E, \eta, N) = \int t_{\alpha\beta}^B \theta(\mathcal{H} - E) d\tau$$

$$= V^N \int t_{\alpha\beta}^B \theta(\mathcal{H} - E) d\tau', \quad (45)$$

where $d\tau' = d\mathbf{p}^{3N} \cdot \mathbf{q}^{3N}$. We have

$$\left(\frac{\partial X}{\partial \eta_{\nu\tau}}\right)_{\mathcal{S}} = n \frac{\partial V}{\partial \eta_{\nu\tau}} X + \int \frac{\partial t_{\alpha\beta}^B}{\partial \eta_{\nu\tau}} \theta(\mathcal{H} - E) d\tau$$

$$- \int t_{\alpha\beta}^B \delta(\mathcal{H} - E) \left[\frac{\partial U}{\partial \eta_{\nu\tau}} - \left(\frac{\partial E}{\partial \eta_{\nu\tau}}\right)_{\mathcal{S}}\right] d\tau$$

$$= n \frac{\partial V}{\partial \eta_{\nu\tau}} X + \int \frac{\partial t_{\alpha\beta}^B}{\partial \eta_{\nu\tau}} \theta(\mathcal{H} - E) d\tau$$

$$- V_0 \int t_{\alpha\beta}^B t_{\nu\tau}^B \delta(\mathcal{H} - E) d\tau + V_0 \langle t_{\alpha\beta}^B \rangle \langle t_{\nu\tau}^B \rangle \omega$$

$$- N k_B T h_{0\nu\xi} h_{\xi\zeta}^{-1} h_{\mu\zeta}^{-1} h_{0\tau\mu} \langle t_{\alpha\beta}^B \rangle \omega. \quad (46)$$

For a system of many degrees of freedom, the approximation $X = \langle t_{\alpha\beta}^B \rangle \phi$ and

$$\int \frac{\partial t_{\alpha\beta}^B}{\partial \eta_{\nu\tau}} \theta(\mathcal{H}-E) d\tau = \left\langle \frac{\partial t_{\alpha\beta}^B}{\partial \eta_{\nu\tau}} \right\rangle \phi, \qquad (47)$$

must be very accurate, therefore we have

$$\phi\left(\frac{\partial \langle t_{\alpha\beta}^B \rangle}{\partial \eta_{\nu\tau}} \right)_S = n \frac{\partial V}{\partial \eta_{\nu\tau}} \langle t_{\alpha\beta}^B \rangle \phi + \phi\left\langle \frac{\partial t_{\alpha\beta}^B}{\partial \eta_{\nu\tau}} \right\rangle$$
$$- \omega V_0 \langle t_{\alpha\beta}^B t_{\nu\tau}^B \rangle + \omega V_0 \langle t_{\alpha\beta}^B \rangle \langle t_{\nu\tau}^B \rangle$$
$$- N k_B T h_{0\nu\xi} h_{\xi\zeta}^{-1} h_{\mu\zeta}^{-1} h_{0\tau\mu} \langle t_{\alpha\beta}^B \rangle \omega. \quad (48)$$

Using Eq. (27) again, it is easy to show that

$$-n k_B T h_{0\alpha\xi} \frac{\partial(h_{\xi\zeta}^{-1} h_{\mu\zeta}^{-1})}{\partial \eta_{\nu\tau}}\bigg|_{\eta=0} h_{0\beta\mu}$$
$$= n k_B T (\delta_{\alpha\tau}\delta_{\beta\nu} + \delta_{\alpha\nu}\delta_{\beta\tau}). \qquad (49)$$

Using Eqs. (17) and (25), we can find that

$$V_0 \left\langle \frac{\partial t_{\alpha\beta}^B}{\partial \eta_{\nu\tau}} \right\rangle = \frac{V_0}{2} \{ [h_0 h^{-1} \langle \mathcal{D}^r t_{\alpha\beta}^B \rangle (h^{-1})^T h_0^T]_{\nu\tau}$$
$$+ [h_0 h^{-1} \langle \mathcal{D}^r t_{\nu\tau}^B \rangle (h^{-1})^T h_0^T]_{\alpha\beta} \}$$
$$+ \frac{1}{2} \left[h_{0\alpha\kappa} \frac{\partial h_{\kappa\zeta}^{-1}}{\partial \eta_{\nu\tau}} \langle \mathcal{D}_{\zeta\xi}^r U \rangle (h^{-1})_{\xi\mu}^T h_{0\mu\beta}^T \right.$$
$$\left. + h_{0\alpha\kappa} h_{\kappa\zeta}^{-1} \langle \mathcal{D}_{\zeta\xi}^r U \rangle \frac{\partial (h^{-1})_{\xi\mu}^T}{\partial \eta_{\nu\tau}} h_{0\mu\beta}^T \right]. \quad (50)$$

Now we put together Eqs. (44), (48), (49), and (50) (with the exchange of $\{\alpha,\beta\}$ and $\{\nu,\tau\}$ in Eq. (50) to keep the symmetry of $C_{\alpha\beta\nu\tau}$). And then letting $\eta=0$ or $h=h_0$, and using Eqs. (17), we recover Eq. (28) exactly, as well as Eqs. (34) and (35). Therefore, the fluctuation formulas for the adiabatic elastic constants have exactly the same form as those for the isothermal elastic constants.

It is interesting to note, that if we insist on using the scaled momenta to derive the final expressions, after a lengthy calculation, we will find that there is an extra term

$$\left(-\frac{3N k_B T}{V} + \frac{1}{k_B T V m^2} \left\langle \sum_i p_{i\alpha}^4 \right\rangle \right) \delta_{\alpha\beta}\delta_{\beta\nu}\delta_{\nu\tau}, \quad (51)$$

different from Eqs. (34) and (35) for the adiabatic elastic constants. This is the main reason why we do not use the scaled momenta in this paper, except for the derivation of Eq. (44). The equivalence of the two approaches therefore requires that the identity

$$\left\langle \sum_i \frac{1}{m^2} p_{i\alpha}^4 \right\rangle = 3N(k_B T)^2 \qquad (52)$$

should also be valid for the microcanonical ensemble. In the canonical ensemble it is rather simple to get Eq. (52). This result provides one more evidence of the ensemble equivalence for a large system,[2] i.e., the velocities obey the Maxwell distribution in both the canonical and microcanonical

ensembles, a criterion often used to determine whether a system is large enough in computer simulations.[26,27]

V. ZERO TEMPERATURE AND STRESS-FREE LIMIT

At $T=0$, we have to pay some special attention to the limit of the "fluctuation term." We will not present a detailed derivation for this case since it is done in Ref. 21. The stress-strain stiffnesses in this case are

$$c_{\alpha\beta\nu\tau} = -\frac{1}{4V_0} \left(x_{i\alpha}\delta_{\beta\xi} \frac{\partial^2 U}{\partial x_{i\beta}\partial x_{i\xi}} + x_{i\beta}\delta_{\alpha\xi} \frac{\partial^2 U}{\partial x_{i\alpha}\partial x_{i\xi}} \right)$$
$$\times \left(\frac{\partial^2 U}{\partial x_{i\xi}^2} \right)^{-1} \left(x_{i\nu}\delta_{\xi\tau} \frac{\partial^2 U}{\partial x_{i\xi}\partial x_{i\tau}} + x_{i\tau}\delta_{\xi\nu} \frac{\partial^2 U}{\partial x_{i\xi}\partial x_{i\nu}} \right)$$
$$+ \frac{1}{4} \left(x_{i\alpha}x_{i\nu} \frac{\partial^2 U}{\partial x_{i\beta}^2} + x_{i\alpha}x_{i\tau} \frac{\partial^2 U}{\partial x_{i\beta}^2} \right.$$
$$\left. + x_{i\beta}x_{i\tau} \frac{\partial^2 U}{\partial x_{i\alpha}^2} + x_{i\beta}x_{i\nu} \frac{\partial^2 U}{\partial x_{i\alpha}^2} \right). \qquad (53)$$

Note that in the above equation, the sums do not include the first particle since we do not consider the motion of the center of mass.[21]

VI. BOUNDARY CONDITIONS

In the above derivation, all particles are confined in the simulation cell, i.e., the cell formed by the three vectors **a**, **b**, and **c**, with $h=(\mathbf{a},\mathbf{b},\mathbf{c})$. As usual, our expressions should work well for a large system or in the thermodynamic limit, i.e., with $N\to\infty$, $V_0\to\infty$, but with $n\equiv N/V_0$ finite. In this case, the boundary effects are irrelevant. However, in practice one has to deal with boundary conditions since the size of a simulated system is in general quite limited. Periodic boundary conditions (PBC)[27] are the most commonly used in simulations, and it is not difficult to show that they are automatically satisfied in our formulation. With PBC we have a continuous infinite system with no boundaries. The particles in the primary cell given by $\mathbf{x}_i=h\mathbf{q}_i$, where $i=1,N$, and $-0.5 \le q_{i\alpha} < 0.5$ ($\alpha=1,2,3$) are repeated into image cells by translations $\mathbf{R}_n = n_1\mathbf{a}+n_2\mathbf{b}+n_3\mathbf{c}$, where $n_\alpha(\alpha=1,2,3)$ are arbitrary positive and negative integers. Scalar functions such as the potential energy can be viewed as functions $U(\{\mathbf{x}_{i,n}\})$ where

$$\mathbf{x}_{i,n} = h\mathbf{q}_{i,n} = h(\mathbf{q}_{i,0}+\mathbf{R}_n), \qquad (54)$$

and the components of $\mathbf{q}_{i,n}$ are no longer constrained by the limits $[-1/2,1/2)$ but extend over all real numbers. With this extended zone scheme the basic relation given by Eq. (12) still holds and there is no explicit dependence of physical quantities on h. The integrals over $d\mathbf{x}^{3N}$ or $d\mathbf{q}^{3N}$ extend now over $(-\infty,\infty)$. By symmetry the average value of any quantity in an image cell is exactly the same as in the primary cell.

In contrast, for a finite system without PBC, it is indeed necessary to introduce explicitly the dependence of U on h,

such as $U(\{\mathbf{x}_i\},h)$, since the boundary conditions have to be realized by some extra terms, in addition to the interparticle interactions and the external fields. These terms would have a complicated dependence on the size and shape of the system. The partials $\partial U(\{\mathbf{x}\},h)/\partial \eta_{\alpha\beta}$ become much more complex. We do not present expressions for these partials in this work since there is no general way to calculate them. We should also note that in this case, the shape of the system may not even be a parallelepiped, so our derivation would no longer be valid. Finally, it is interesting to note that although the derivation seems to require that the deformations be homogeneous, by taking the limit to infinitesimal strain, what is calculated is the linear response of the system valid also for inhomogeneous deformations.

VII. CONCLUSION

In summary, we have derived the most general fluctuation formulas for both isothermal and adiabatic stress-strain stiffnesses with arbitrary interparticle interactions and under arbitrary loading. We find that the expressions for these two kinds of coefficients are exactly the same, although, in general, their values will be different. We should point out that these expressions are also valid for a two-dimensional system though our derivation in this paper is based on the three-dimensional system. Moreover, they are valid for both Monte Carlo and molecular dynamics computer simulations. These formulas have the advantage that all elastic constants are calculated in a single run without performing any deformation. They may be especially useful in molecular dynamics simulations because they require little additional computer time. They may also permit the derivation of exact formulas for stress-strain stiffnesses at zero temperature for some simple inter-particle interactions in a perfect lattice.

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