

# Fluctuations and thermodynamics properties of the constant shear strain ensemble

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We develop the statistical mechanics of a pair of new ensembles called the constant shear strain ensembles that include the uniform dilation ensemble used frequently in computer simulations. We present a direct calculation of fluctuation formulas for the elastic constants, the specific heat, and the thermal expansion tensor in these new ensembles. © 2001 American Institute of Physics.  
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## I. INTRODUCTION

The fluctuation formula is very useful in computer simulation since it can avoid the differentiating calculation that may need long computational time. A well-known example of the fluctuation formula is that the specific heat in canonical ensemble can be found by calculating the fluctuation of energy instead of differentiating energy with respect to temperature.

There are many ensembles of statistical mechanics used in molecular dynamics (MD) simulation. The microcanonical (*EVN*) ensemble,<sup>1</sup> canonical (*TVN*) ensemble,<sup>2-4</sup> isoenthalpic–isobaric (*HPN*) ensemble,<sup>5,6</sup> and isothermal–isobaric (*TPN*) ensemble<sup>1,5,6</sup> are often used to simulate the system of well-known symmetry. Where  $E$  is the energy,  $V$  is the volume,  $N$  is the particle number,  $T$  is the temperature,  $H$  is the enthalpy, and  $P$  is the hydrostatic pressure of the system. To deal with anisotropic solids subjected to arbitrary stress, Parrinello and Rahman modified Andersen's method for (*HPN*) ensemble<sup>5</sup> to develop a new ensemble called the ( $H\sigma N$ ) ensemble,<sup>7-9</sup> where  $\sigma$  is the applied stress tensor and is kept as a constant in simulation. Furthermore, the ( $EhN$ ), ( $ThN$ ), ( $T\sigma N$ ), ( $HtN$ ), and ( $TtN$ ) ensembles<sup>8,10-15</sup> were also proposed to simulate the anisotropic systems, with  $t$  being the thermodynamic stress tensor and  $h$  being the tensor constructed from the three vectors forming a parallelepiped, which is the periodically repeating MD cell.

The difference among these ensembles, in the terminology of thermodynamics, is the choice of the different set of independent variables for specifying the thermodynamic state of the system. In general, the different constraint on the system leads to a different choice of the independent variables and so the different thermodynamic function and fluctuation formula. For instance, in the ( $H\sigma N$ ) ensemble  $h$  can fluctuate but in the ( $EhN$ ) ensemble  $h$  is a constant so that the fluctuation formulas between the ( $H\sigma N$ ) ensemble and the ( $EhN$ ) ensemble are quite different, as we can see in the next section.

It could be thought that when  $\sigma$  was isotropic, the ( $H\sigma N$ ) or ( $T\sigma N$ ) ensembles would be reduced into the

(*HPN*) or (*TPN*) ensembles. But this is only true if there is not any other constraint on the system except for  $\sigma$  being isotropic. However, in the (*HPN*) or (*TPN*) ensembles, the shape of the MD cell cannot change so it may prevent the structural transformation which may happen in the ( $H\sigma N$ ) or ( $T\sigma N$ ) ensembles even with isotropic  $\sigma$ .<sup>8</sup> This is because the variation of the shear strain is allowed in the ( $H\sigma N$ ) or ( $T\sigma N$ ) ensembles but is inhibited in the (*HPN*) or (*TPN*) runs, as we shall show in Sec. III. Therefore, the existing fluctuation formula obtained from the ( $H\sigma N$ ) or ( $T\sigma N$ ) ensembles may be no longer valid in the (*HPN*) or (*TPN*) ensembles. Since the (*TPN*) and (*HPN*) ensembles are among the most commonly used ensembles in computer simulations, to find the correct fluctuation properties in these ensembles is a significant topic.

In this paper we introduce a pair of new ensembles, which includes both the (*HPN*) and (*TPN*) ensembles, in classical statistical mechanics. The new ensembles are characterized by choosing the diagonal components of  $\sigma$  and the off-diagonal components of strain (shear strain) as independent variables so we call them as constant shear strain ensembles. We derive the fluctuation formulas for the elastic constants, the specific heat and the thermal expansion tensor in these ensembles. We indicate that in computer simulations these new formulas work practically only for four kinds of the shape of the MD unit cell which correspond to the system with orthogonal or hexagonal or tetragonal or cubic symmetry.

This paper is organized as follows. We make a short review about some well-known fluctuation formulas in the next section for the convenience of comparison. In Sec. III we first give the reason why it needs to introduce the constant shear strain ensemble and then present the formulation of the ( $H, \sigma_{ii}, \eta_{ij}, N, i \neq j$ ) ensemble, where  $\eta$  is the Lagrangian strain tensor. In Sec. IV we derive the fluctuation formulas for ( $H, \sigma_{ii}, \eta_{ij}, N, i \neq j$ ) ensemble. In Sec. V, we discuss shortly about the results in the ( $T, \sigma_{ii}, \eta_{ij}, N, i \neq j$ ) ensemble, a pair ensemble of the ( $H, \sigma_{ii}, \eta_{ij}, N, i \neq j$ ) ensemble. And we conclude with a discussion.

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## II. FLUCTUATION IN THE (*EhN*), (*ThN*), (*HtN*), AND (*TtN*) ENSEMBLES

Assuming the system is described by the Hamiltonian

$$\mathcal{H} = \mathcal{H}(q, p, \eta, N), \quad (2.1)$$

where  $q$  and  $p$  represent the coordinates and momenta of the  $N$  particles, the existing fluctuation formulas in MD can be divided into the following two categories.

(1) The ensembles with constant  $h$ . It includes both (*EhN*) and (*ThN*) ensembles. (*EVN*) and (*TVN*) ensembles also belong to this category. In these ensembles  $\sigma$  and  $t$  are allowed to fluctuate but  $h$  and so  $\eta$  are kept fixed. The formulas for either adiabatic elastic constants ( $C^S$ ) or isothermal elastic constants ( $C^T$ ) are<sup>12,13,15,16</sup>

$$C_{ijkl} = \frac{1}{V_0} \left\langle \frac{\partial^2 \mathcal{H}}{\partial \eta_{ij} \partial \eta_{kl}} \right\rangle_{\eta=0} - \frac{V_0}{k_B T} \Delta(t_{ij} t_{kl})_{\eta=0}, \quad (2.2)$$

where  $V_0$  is the volume of the system at reference state which can be either stressed or stress-free,  $k_B$  the Boltzmann constant,  $\Delta(AB) = \langle AB \rangle - \langle A \rangle \langle B \rangle$ , and the  $\langle \dots \rangle$  designates ensemble averages.

In (*ThN*) ensemble, Eq. (2.2) can be derived straightforward from

$$F = -k_B T \ln Z, \quad (2.3)$$

$$Z = \frac{1}{\mathcal{C}} \int e^{-\mathcal{H}/k_B T} d\tau, \quad (2.4)$$

and the definition of elastic constants

$$C_{ijkl}^T = \frac{1}{V_0} \left( \frac{\partial^2 F}{\partial \eta_{ij} \partial \eta_{kl}} \right)_{T, \eta=0} = - \left( \frac{\partial t_{ij}}{\partial \eta_{kl}} \right)_{\eta=0}, \quad (2.5)$$

where  $\mathcal{C}$  is a constant and  $d\tau$  the differential volume element in  $6N$ -dimensional phase space.

The specific heat  $C_\eta$  can be found from

$$\Delta(K^2) = \frac{3}{2} N (k_B T)^2 \left( 1 - \frac{3Nk_B}{2C_\eta} \right) \quad (2.6)$$

in (*EhN*) ensemble, where  $K$  is the kinetic energy of the system.

In (*ThN*) ensemble, the specific heat is

$$\Delta(\mathcal{H}^2) = k_B T^2 C_\eta. \quad (2.7)$$

The thermal expansion tensor  $\alpha = (\partial \eta / \partial T)_\sigma$  in (*EhN*) can be obtained from

$$\frac{V_0}{k_B T} \Delta(t_{ij} K) + \left\langle \frac{\partial K}{\partial \eta_{ij}} \right\rangle = - \frac{3Nk_B T V_0 \sum_{kl} C_{ijkl}^S \alpha_{kl}}{2C_\eta}. \quad (2.8)$$

In the (*ThN*) ensemble, the formula is

$$\Delta(t_{ij} \mathcal{H}) = k_B T^2 \sum_{kl} C_{ijkl}^T \alpha_{kl}. \quad (2.9)$$

(2) The ensembles with constant  $\sigma$  or  $t$  that include the (*HσN*), (*TσN*), (*HtN*), and the (*TtN*) ensembles. In these ensembles  $h$  and so  $\eta$  are allowed to fluctuate but  $\sigma$  or  $t$  are kept fixed. The corresponding formula for the elastic constants is<sup>10,17</sup>

$$\frac{k_B T}{V_0} (C)_{ijkl}^{-1} = \Delta(\eta_{ij} \eta_{kl}). \quad (2.10)$$

Similar to Eq. (2.2), in the (*TtN*) ensemble Eq. (2.10) can be derived from

$$\mathbf{A} = -k_B T \ln \Theta,$$

$$\Theta = \frac{1}{\mathcal{C}} \int e^{-(\mathcal{H} + V_0 \text{Tr}(t\eta))/k_B T} d\tau, \quad (2.11)$$

and the definition of  $C^T$ . Where the integral is over all  $3N$  coordinates,  $3N$  momenta, and six independent microscopic strain components  $\epsilon_{ij}$ .

The specific heat  $C_\sigma$  in the (*HσN*) ensemble can be found from

$$\Delta(K^2) = \frac{3}{2} N (k_B T)^2 \left( 1 - \frac{3Nk_B}{2C_\sigma} \right). \quad (2.12)$$

It is in the same form as that of the (*EhN*) ensemble.

In the (*TσN*) ensemble, the specific heat is

$$\Delta(\mathcal{H}'^2) = k_B T^2 C_\sigma, \quad (2.13)$$

where

$$\mathcal{H}' = \mathcal{H} + V_0 \text{Tr}(\sigma \eta). \quad (2.14)$$

The thermal expansion tensor for the (*HσN*) ensemble becomes

$$\Delta(\eta_{ij} K) = - \frac{3}{2} N (k_B T)^2 \frac{\alpha_{ij}}{C_\sigma}, \quad (2.15)$$

and for the (*TσN*) ensemble

$$\Delta(\eta_{ij} \mathcal{H}') = k_B T^2 \alpha_{ij}. \quad (2.16)$$

Before ending this section, we point out that Eqs. (2.8), (2.9), (2.13), and (2.16) do not seem to be available in literatures. An isotropic form [i.e., in the (*EVN*) ensemble] of Eq. (2.8) can be found in Ref. 18.

## III. FORMULATION OF THE (*H, σ<sub>ii</sub>, η<sub>ij</sub>, N, i ≠ j*) ENSEMBLE

It is easy to show that the uniform dilation corresponds to keep a vanishing shear strain.

Let  $h = (\mathbf{a}, \mathbf{b}, \mathbf{c})$ , where  $\mathbf{a}, \mathbf{b}$ , and  $\mathbf{c}$  are the three vectors forming the MD cell, then the definition of strain in MD is (see, for instance, Refs. 12 and 13),

$$\eta = \frac{1}{2} (h_0'^{-1} G h_0^{-1} - 1), \quad (3.1)$$

where  $h_0$  is the reference value of  $h$ ,  $G$  is the metric tensor given by  $G = h' h$ , and the prime indicates matrix transpose. If we consider a system with the constraint of the constant angle<sup>19</sup> so  $h$  can be written

$$h = gL, \quad \text{with } h_0 = gL_0, \quad (3.2)$$

where  $g$  is a constant matrix and  $L_0, L$  are the diagonal matrix,  $L_{0,ij} = l_{0,i} \delta_{ij}$  and  $L_{ij} = l_i \delta_{ij}$ , it is not difficult to show that  $\eta$  is diagonal if and only if one of the following three conditions is satisfied.

- (1)  $l_1/l_{0_1}=l_2/l_{0_2}$  and  $\mathbf{c}$  is perpendicular to both  $\mathbf{a}$  and  $\mathbf{b}$  so that one can write  $g_{3i}=g_{i3}=\delta_{i3}$ . It includes the system with hexagonal or tetragonal or cubic symmetry.
- (2)  $g$  is a unit matrix, i.e., a system of tetragonal or orthogonal or cubic symmetry.
- (3)  $l_1/l_{0_1}=l_2/l_{0_2}=l_3/l_{0_3}$ , i.e., a system of uniform dilation.

Note that in general the condition of the constant angle does not lead to a vanishing shear strain, nor even a constant shear strain. Therefore to derive the general formulas with constant angle ensemble will be more practical. However, it does not seem to be a simple issue, since for the constant angle ensemble in general the six components of strain are not independent. On the other hand, to express explicitly the general conditions of the constant shear strain in term of components of  $h$  is also not a simple task. Fortunately, the above three cases with vanishing shear strain contain almost all the situations of interest in the computer simulation for the isobaric ensemble so that to find the general conditions for the constant shear strain may not be a necessity. We can then investigate the simpler constant shear strain ensemble as in this work instead of the constant angle ensemble.

From the above arguments, in computer simulation we may work on a constant shear strain ensemble. In such an ensemble the independent variables must be  $\sigma_{ii}$  and  $\eta_{ij}$  with  $i \neq j$ . It is obvious that Eq. (2.10) fails to provide correct elastic constant for those components related to the fluctuation of shear strain and so we may need some new fluctuation formulas. An interesting thing is that this is an ensemble ‘‘between’’ constant  $\sigma$  and constant  $h$  so that we can expect to find formulas partly the same as that of the constant  $\sigma$  ensemble and partly the same as that of the constant  $h$  ensemble. Moreover, we can develop two ensembles by choosing two sets of independent variables, one is the  $(H, \sigma_{ii}, \eta_{ij}, N, i \neq j)$  ensemble and the other the  $(T, \sigma_{ii}, \eta_{ij}, N, i \neq j)$  ensemble. Since  $N$  will always be fixed and  $i \neq j$  or (and)  $k \neq l$  always required in the following of this paper, we shall suppress them.

Following the derivation for the  $H\sigma N$  ensemble,<sup>10</sup> we can define the  $(H, \sigma_{ii}, \eta_{ij})$  ensemble by using the phase volume via

$$\phi(H, \sigma_{ii}, \eta_{ij}) = \int_{\mathcal{H} \leq H - V_0 \sum_i \sigma_{ii} \epsilon_{ii}} dq dp d\epsilon_{11} d\epsilon_{22} d\epsilon_{33}, \tag{3.3}$$

where  $H$  is the enthalpy, the integral in Eq. (3.3) is over all  $3N$  coordinates,  $3N$  momenta, and three independent diagonal microscopic strain components  $\epsilon_{ii}$ .

The enthalpy  $H$  is defined by

$$H = E + V_0 \sum_i \sigma_{ii} \eta_{ii}, \tag{3.4}$$

where  $E$  is the energy of the system and  $\eta_{ii} = \langle \epsilon_{ii} \rangle$ . The phase volume can be written

$$\phi(H, \sigma_{ii}, \eta_{ij}) = \int \theta \left( \mathcal{H} - \left( H - V_0 \sum_i \sigma_{ii} \epsilon_{ii} \right) \right) d\tau, \tag{3.5}$$

where the step function

$$\theta(x) = \begin{cases} 1 & x < 0, \\ 0 & x > 0, \end{cases} \tag{3.6}$$

and  $d\tau = dq dp d\epsilon_{11} d\epsilon_{22} d\epsilon_{33}$ . The density of states  $\omega(H, \sigma_{ii}, \eta_{ij})$  is defined by

$$\omega = \left( \frac{\partial \phi}{\partial H} \right)_{\sigma_{ii}, \eta_{ij}} = \int \delta \left( \mathcal{H} - \left( H - \sum_i V_0 \sigma_{ii} \epsilon_{ii} \right) \right) d\tau, \tag{3.7}$$

where  $\delta$  is the Dirac delta function. The normalized probability density  $W(q, p, \epsilon_{ii})$  is

$$W(q, p, \epsilon_{ii}) = \frac{\delta(\mathcal{H} - (H - \sum_i V_0 \sigma_{ii} \epsilon_{ii}))}{\omega}. \tag{3.8}$$

The average value of any quantity  $f(q, p, \eta_{ij}, \sigma_{ii})$  is determined from  $\langle f \rangle = \int W f d\tau$ . The entropy is defined by

$$S(H, \sigma_{ii}, \eta_{ij}) = k_B \ln \phi(H, \sigma_{ii}, \eta_{ij}). \tag{3.9}$$

We have omitted various constant factors which would render  $\phi$  dimensionless since these constant factors would not appear in any of our final results. From Eq. (3.9), we obtain for the temperature

$$T = \left( \frac{\partial S}{\partial H} \right)_{\sigma_{ii}, \eta_{ij}} = \frac{\phi}{k_B \omega}. \tag{3.10}$$

The similar arguments as those used in the microcanonical ensemble<sup>18,20</sup> leads to the equipartition theorem

$$\left\langle x_j \frac{\partial \mathcal{H}}{\partial x_k} \right\rangle = \frac{\phi}{\omega} \delta_{jk}, \tag{3.11}$$

where  $x_i$  stands for one of  $q$  or  $p$  variables.

Next we consider the adiabatic theorem for this ensemble. The Hamiltonian is now assumed to be dependent on an additional external parameter, say  $y$ . The generalized force associated with this parameter is  $\partial \mathcal{H} / \partial y$ . Calculating the average value of this generalized force, just as in the microcanonical ensemble,<sup>18,20</sup> leads to the adiabatic theorem

$$\begin{aligned} \left\langle \frac{\partial \mathcal{H}}{\partial y} \right\rangle &= \frac{1}{\omega} \int \frac{\partial \mathcal{H}}{\partial y} \delta \left( \mathcal{H} - \left( H - \sum_i V_0 \sigma_{ii} \epsilon_{ii} \right) \right) d\tau \\ &= - \frac{1}{\omega} \left( \frac{\partial \phi}{\partial y} \right)_{H, \sigma_{ii}, \eta_{ij}} = \left( \frac{\partial H}{\partial y} \right)_{S, \sigma_{ii}, \eta_{ij}}. \end{aligned} \tag{3.12}$$

#### IV. FLUCTUATION IN THE $(H, \sigma_{ii}, \eta_{ij})$ ENSEMBLE

The thermodynamic law in the  $(H, \sigma_{ii}, \eta_{ij})$  ensemble is

$$dH = T dS + V_0 \sum_i \eta_{ii} d\sigma_{ii} - V_0 \sum_{i \neq j} \sigma_{ij} d\eta_{ij}. \tag{4.1}$$

It follows

$$\begin{aligned} V_0 \eta_{ii} &= \left( \frac{\partial H}{\partial \sigma_{ii}} \right)_S, \\ V_0 \sigma_{ij} &= - \left( \frac{\partial H}{\partial \eta_{ij}} \right)_S. \end{aligned} \tag{4.2}$$

We can derive the fluctuation formulas of the adiabatic elastic constants in a similar way as Ray *et al.* did.<sup>10,18,21</sup> Defining a potential

$$X_{ii} = \int \epsilon_{ii} \theta \left( \mathcal{H} - \left( H - V_0 \sum_i \sigma_{ii} \epsilon_{ii} \right) \right) d\tau, \quad (4.3)$$

using Eq. (4.2) we obtain

$$\begin{aligned} \left( \frac{\partial X_{ii}}{\partial \sigma_{jj}} \right)_S &= \int \epsilon_{ii} \delta \left( \mathcal{H} - \left( H - \sum_i V_0 \sigma_{ii} \epsilon_{ii} \right) \right) \\ &\quad \times (V_0 \langle \epsilon_{jj} \rangle - V_0 \epsilon_{jj}) d\tau \\ &= -\omega V_0 (\langle \epsilon_{ii} \epsilon_{jj} \rangle - \langle \epsilon_{ii} \rangle \langle \epsilon_{jj} \rangle) \\ &= -\omega V_0 \Delta(\epsilon_{ii} \epsilon_{jj}). \end{aligned} \quad (4.4)$$

For a system of many degrees of freedom, the approximation  $X_{ii} = \langle \epsilon_{ii} \rangle \phi = \eta_{ii} \phi$  is very accurate, hence Eq. (4.4) becomes

$$\Delta(\epsilon_{ii} \epsilon_{jj}) = -\frac{\phi}{\omega V_0} \left( \frac{\partial \eta_{ii}}{\partial \sigma_{jj}} \right)_S. \quad (4.5)$$

Using Eq. (3.10) we can further reduce the above equation into

$$\Delta(\epsilon_{ii} \epsilon_{jj}) = \frac{k_B T}{V_0} (C_{ijij}^S)^{-1}. \quad (4.6)$$

To derive the formula for the elastic constants with  $i \neq j$  and  $k \neq l$ , we introduce a new function,

$$Z(H, \sigma_{ii}, \eta_{ij}) = \int \mathcal{S}_{ij} \theta \left( \mathcal{H} - \left( H - V_0 \sum_i \sigma_{ii} \epsilon_{ii} \right) \right) d\tau, \quad (4.7)$$

where  $\mathcal{S}_{ij}$  is the microscopic stress tensor defined by

$$V_0 \mathcal{S}_{ij} = -\frac{\partial \mathcal{H}}{\partial \eta_{ij}}. \quad (4.8)$$

We have

$$\begin{aligned} \left( \frac{\partial Z}{\partial \eta_{kl}} \right)_S &= \int \frac{\partial \mathcal{S}_{ij}}{\partial \eta_{kl}} \theta \left( \mathcal{H} - \left( H - V_0 \sum_i \sigma_{ii} \epsilon_{ii} \right) \right) d\tau \\ &\quad - \int \mathcal{S}_{ij} \delta \left( \mathcal{H} - \left( H - V_0 \sum_i \sigma_{ii} \epsilon_{ii} \right) \right) \\ &\quad \times \left( \frac{\partial \mathcal{H}}{\partial \eta_{kl}} - \left( \frac{\partial H}{\partial \eta_{kl}} \right)_S \right) d\tau \\ &= -\frac{1}{V_0} \int \frac{\partial^2 \mathcal{H}}{\partial \eta_{ij} \partial \eta_{kl}} \\ &\quad \times \theta \left( \mathcal{H} - \left( H - V_0 \sum_i \sigma_{ii} \epsilon_{ii} \right) \right) d\tau \\ &\quad + V_0 \int \mathcal{S}_{ij} \mathcal{S}_{kl} \delta \left( \mathcal{H} - \left( H - V_0 \sum_i \sigma_{ii} \epsilon_{ii} \right) \right) d\tau \\ &\quad - V_0 \langle \mathcal{S}_{ij} \rangle \langle \mathcal{S}_{kl} \rangle \omega. \end{aligned} \quad (4.9)$$

Again, by using  $Z = \langle \mathcal{S}_{ij} \rangle \phi$  and

$$\int \frac{\partial^2 \mathcal{H}}{\partial \eta_{ij} \partial \eta_{kl}} \theta \left( \mathcal{H} - \left( H - V_0 \sum_i \sigma_{ii} \epsilon_{ii} \right) \right) d\tau = \left\langle \frac{\partial^2 \mathcal{H}}{\partial \eta_{ij} \partial \eta_{kl}} \right\rangle \phi, \quad (4.10)$$

we get

$$\begin{aligned} -\phi \left( \frac{\partial \langle \mathcal{S}_{ij} \rangle}{\partial \eta_{kl}} \right)_S &= \frac{\phi}{V_0} \left\langle \frac{\partial^2 \mathcal{H}}{\partial \eta_{ij} \partial \eta_{kl}} \right\rangle - \omega V_0 \langle \mathcal{S}_{ij} \mathcal{S}_{kl} \rangle \\ &\quad + \omega V_0 \langle \mathcal{S}_{ij} \rangle \langle \mathcal{S}_{kl} \rangle \end{aligned} \quad (4.11)$$

or

$$(C^S)_{ij,kl} = \frac{1}{V_0} \left\langle \frac{\partial^2 \mathcal{H}}{\partial \eta_{ij} \partial \eta_{kl}} \right\rangle - \frac{V_0}{k_B T} \Delta(\mathcal{S}_{ij} \mathcal{S}_{kl}). \quad (4.12)$$

Note that Eq. (4.6) has exactly the same form as Eq. (2.10) and Eq. (4.12) is the same as Eq. (2.2).

Next we consider the specific heat. Define a new potential  $Y$  by

$$Y(H, \sigma_{ii}, \eta_{ij}, \lambda) = \int K \theta \left( \mathcal{H} - \left( H - V_0 \sum_i \sigma_{ii} \epsilon_{ii} \right) \right) d\tau, \quad (4.13)$$

where  $K = \Sigma(p^2/2m) = \lambda \Sigma(p^2/2)$  is the kinetic energy and  $\lambda = m^{-1}$  is the reciprocal mass of the particles. Differentiation of  $Y/\lambda$  with respect to  $\lambda$  yields

$$\begin{aligned} -\frac{\lambda^2}{\omega} \left( \frac{\partial(Y/\lambda)}{\partial \lambda} \right)_{S, \sigma_{ii}, \eta_{ij}} &= \int K \delta \left( \mathcal{H} - \left( H - \sum_i V_0 \sigma_{ii} \epsilon_{ii} \right) \right) \\ &\quad \times \left( \frac{\partial \mathcal{H}}{\partial \lambda} - \left( \frac{\partial H}{\partial \lambda} \right)_{S, \sigma_{ii}, \eta_{ij}} \right) d\tau \\ &= \Delta(K^2) = \langle K^2 \rangle - \langle K \rangle^2. \end{aligned}$$

Using  $Y = \langle K \rangle \phi$ , we obtain

$$\begin{aligned} \Delta(K^2) &= -\frac{\lambda^2 \phi}{\omega} \left( \frac{\partial(\langle K \rangle / \lambda)}{\partial \lambda} \right)_{S, \sigma_{ii}, \eta_{ij}} \\ &= k_B T \left( \langle K \rangle - \lambda \left( \frac{\partial \langle K \rangle}{\partial \lambda} \right)_{S, \sigma_{ii}, \eta_{ij}} \right). \end{aligned}$$

Furthermore, by using

$$\begin{aligned} \left( \frac{\partial \langle K \rangle}{\partial \lambda} \right)_{S, \sigma_{ii}, \eta_{ij}} &= \left( \frac{\partial \langle K \rangle}{\partial \lambda} \right)_{H, \sigma_{ii}, \eta_{ij}} \\ &\quad + \left( \frac{\partial \langle K \rangle}{\partial H} \right)_{\lambda, \sigma_{ii}, \eta_{ij}} \left( \frac{\partial H}{\partial \lambda} \right)_{S, \sigma_{ii}, \eta_{ij}} \end{aligned}$$

and the adiabatic theorem

$$\begin{aligned} \left( \frac{\partial H}{\partial \lambda} \right)_{S, \sigma_{ii}, \eta_{ij}} &= \frac{\langle \partial \mathcal{H} \rangle}{\partial \lambda} = \frac{\langle K \rangle}{\lambda} = \frac{3Nk_B T}{2\lambda}, \\ \left( \frac{\partial \langle K \rangle}{\partial H} \right)_{\lambda, \sigma_{ii}, \eta_{ij}} &= \frac{3Nk_B}{2C_{\sigma_{ii}, \eta_{ij}}}, \end{aligned} \quad (4.14)$$

we find

$$\Delta(K^2) = \frac{3}{2} N (k_B T)^2 \left( 1 - \frac{3Nk_B}{2C_{\sigma_{ii}, \eta_{ij}}} \right), \quad (4.15)$$

where  $C_{\sigma_{ii}} = (\partial H / \partial T)_{\sigma_{ii}, \eta_{ij}}$  is the specific heat. Again, it is interesting to note that Eq. (4.15) has the same form as Eq. (2.6). The equation  $(\partial \langle K \rangle / \partial \lambda)_{H, \sigma_{ii}, \eta_{ij}} = 0$  was used in the above derivation and it can be shown as follows. Using the definition of  $\phi$ , we obtain

$$\left( \frac{\partial \phi}{\partial \lambda} \right)_{H, \sigma_{ii}, \eta_{ij}} = - \frac{\omega}{\lambda} \langle K \rangle. \quad (4.16)$$

It follows, together with Eqs. (3.9)–(3.11),

$$\left( \frac{\partial S}{\partial \lambda} \right)_{H, \sigma_{ii}, \eta_{ij}} = - \frac{3Nk_B}{2\lambda}, \quad (4.17)$$

so

$$S = - \frac{3Nk_B}{2} \ln \lambda + f(H, \sigma_{ii}, \eta_{ij}), \quad (4.18)$$

where  $f(H, \sigma_{ii}, \eta_{ij})$  is an arbitrary function of  $H, \sigma_{ii}$ , and  $\eta_{ij}$ . Since the temperature is defined by

$$T^{-1} = \left( \frac{\partial S}{\partial H} \right)_{\sigma_{ii}, \eta_{ij}, \lambda} = \left( \frac{\partial f(H, \sigma_{ii}, \eta_{ij})}{\partial H} \right)_{\sigma_{ii}, \eta_{ij}}, \quad (4.19)$$

it is independent on  $\lambda$  and so is for  $\langle K \rangle$ .

Now we consider the diagonal components of the thermal expansion tensor. Differentiating  $X_{ii}$  with respect to  $\lambda$  yields

$$\begin{aligned} \left( \frac{\partial X_{ii}}{\partial \lambda} \right)_{S, \sigma_{ii}, \eta_{ij}} &= - \int \epsilon_{ii} \delta \left( \mathcal{H} - \left( H - V_0 \sum_i \sigma_{ii} \epsilon_{ii} \right) \right) \cdot \left( \frac{\partial \mathcal{H}}{\partial \lambda} \right. \\ &\quad \left. - \left( \frac{\partial H}{\partial \lambda} \right)_{S, \sigma_{ii}, \eta_{ij}} \right) d\tau = - \frac{\omega}{\lambda} \Delta(\epsilon_{ii} K) \end{aligned} \quad (4.20)$$

or

$$\Delta(\epsilon_{ii} K) = - \lambda k_B T \left( \frac{\partial \langle \epsilon_{ii} \rangle}{\partial \lambda} \right)_{S, \sigma_{ii}, \eta_{ij}}. \quad (4.21)$$

This can be further reduced into, following Refs. 10, 18 and 21,

$$\Delta(\epsilon_{ii} K) = - \frac{3}{2} N (k_B T)^2 \frac{\alpha_{ii}}{C_{\sigma_{ii}, \eta_{ij}}}. \quad (4.22)$$

It is exactly in the same form as Eq. (2.15).

We find no way to calculate the remaining components of  $C^S$  (i.e., the crossover components with  $i=j$  but  $k \neq l$  or  $i \neq j$  but  $k=l$ ) and  $\alpha$  (the off-diagonal components) in the new ensembles. This is because they relate to the differential of the independent variables  $\sigma_{ii}$  or (and)  $\eta_{ij}$ , which do not fluctuate in this ensemble. However, to find the elastic constants in a system of isotropic or cubic or hexagonal or orthogonal symmetry, it is enough to find the components with  $i=j, k=l$  and  $i \neq j, k \neq l$ .

## V. RESULTS FOR THE $(T, \sigma_{ii}, \eta_{ij})$ ENSEMBLE

To derive the expressions in the  $(T, \sigma_{ii}, \eta_{ij})$  ensemble is a little simpler. The thermodynamic potential  $\mathbf{A}$  in the ensemble is

$$\mathbf{A} = E - TS + V_0 \sum_i \sigma_{ii} \eta_{ii}. \quad (5.1)$$

Note that  $\mathbf{A}$  is neither the usual Helmholtz free energy nor the Gibbs free energy. The thermodynamic law is

$$d\mathbf{A} = -S dT + V_0 \sum_i \eta_{ii} d\sigma_{ii} - V_0 \sum_{i \neq j} \sigma_{ij} d\eta_{ij}, \quad (5.2)$$

follows

$$\sigma_{ij} = - \frac{1}{V_0} \left( \frac{\partial \mathbf{A}}{\partial \eta_{ij}} \right)_{T, \sigma_{ii}}, \quad \eta_{ii} = \frac{1}{V_0} \left( \frac{\partial \mathbf{A}}{\partial \sigma_{ii}} \right)_{T, \eta_{ij}}. \quad (5.3)$$

The fundamental connection between thermodynamics and statistical mechanics gives

$$\mathbf{A} = -k_B T \ln \Theta, \quad (5.4)$$

$$\Theta = \frac{1}{\mathcal{C}} \int e^{-(\mathcal{H} + V_0 \sum_i \sigma_{ii} \epsilon_{ii}) / k_B T} d\tau. \quad (5.5)$$

It is straightforward to derive

$$\frac{k_B T}{V_0} (C^T)_{ii jj}^{-1} = \Delta(\epsilon_{ii} \epsilon_{jj}), \quad (5.6)$$

$$(C^T)_{ijkl} = V_0 \left\langle \frac{\partial^2 \mathcal{H}}{\partial \eta_{ij} \partial \eta_{kl}} \right\rangle_{\eta=0} - \frac{V_0}{k_B T} \Delta(S_{ij} S_{kl})_{\eta=0}. \quad (5.7)$$

We find again that Eq. (5.6) is the same as Eq. (2.10) and Eq. (5.7) is the same as Eq. (2.2). For a uniform dilation system, this result has been reported in Ref. 22.

Similar to Eq. (2.13), the specific heat is

$$\Delta(\mathcal{H}'^2) = k_B T^2 C_{\sigma_{ii}, \eta_{ij}}, \quad (5.8)$$

where

$$\mathcal{H}' = \mathcal{H} + V_0 \sum_i \sigma_{ii} \epsilon_{ii}. \quad (5.9)$$

The diagonal part of the thermal expansion tensor becomes

$$\Delta(\epsilon_{ii} \mathcal{H}') = k_B T^2 \alpha_{ii}. \quad (5.10)$$

Finally, in the same reason as for the  $(H, \sigma_{ii}, \eta_{ij})$  ensemble, no fluctuation formula is available for the remaining components of  $C^T$  and  $\alpha$ .

## VI. CONCLUSIONS

We derived the correct fluctuation formulas for the constant shear strain ensemble which include the  $(HPN)$  and  $(TPN)$  ensembles. Since the  $(HPN)$  and  $(TPN)$  ensembles are used so frequent in computer simulations, these formulas may be very useful. We found that for a scalar or for those



quantities that are independent on the shear strain, the fluctuation formulas in the constant shear strain ensemble are the same as that of constant  $\sigma$  ensemble. This is not surprising since the new ensemble is more like the constant  $\sigma$  one and whether the shear strain can or cannot fluctuate has no effect on these quantities. We showed that the fluctuation formulas for the elastic constants are a mixture of that of the constant  $h$  ensemble and the constant  $\sigma$  ensemble. This is also a natural result since the new ensemble is just “between” constant  $h$  and constant  $\sigma$  ensembles. We also found that unlike constant  $h$  or constant  $\sigma$  ensembles, the fluctuation formula for a tensor in the constant shear strain ensemble is incomplete. Such an incompleteness could limit the usage of these formulas. However, if the system has special symmetries especially for an isotropic system, the fluctuation formulas we obtained are enough. Furthermore, our above results are dependent on neither the detail of the Hamiltonian nor the equation of motion, so it is valid in both Monte Carlo and MD simulations. We should also point out that these new formulas work appropriately only for the system with orthogonal or hexagonal or tetragonal or cubic symmetry.

For the system with a spherically symmetric pair potential  $\phi(r)$ , i.e.,

$$\mathcal{H} = \sum_a \frac{p_a^2}{2m} + \sum_{a>b} \Phi(r_{ab}), \quad (6.1)$$

and in the canonical ensemble, Eq.(2.2) can be reduced further into<sup>23</sup>

$$\begin{aligned} C_{\alpha\beta\gamma\tau}^T = & \frac{1}{V} \left\langle \sum_{i<j} r_\alpha(ij)r_\beta(ij)r_\gamma(ij)r_\tau(ij) \frac{1}{r^2} \left( \Phi'' - \frac{\Phi'}{r} \right) \right\rangle \\ & - \frac{1}{k_B T V} \left\langle \Delta \left( \sum_{i<j} r_\alpha(ij)r_\beta(ij) \frac{\Phi'}{r} \right. \right. \\ & \left. \left. \cdot \sum_{i<j} r_\gamma(ij)r_\tau(ij) \frac{\Phi'}{r} \right) \right\rangle \\ & + \frac{Nk_B T}{V} (\delta_{\alpha\gamma}\delta_{\beta\tau} + \delta_{\alpha\tau}\delta_{\beta\gamma}), \quad (6.2) \end{aligned}$$

where  $r_\alpha(ij) = r_{i\alpha} - r_{j\alpha}$  and  $r_{ij}^2 = (\mathbf{r}_i - \mathbf{r}_j)^2$ . Equation (6.2) has been applied successfully into many systems.<sup>12,13,22-28</sup> Bearing in mind the similarity between Eqs. (2.2) and (5.7), it is obvious that for those components with  $\alpha \neq \beta$  and  $\gamma \neq \tau$ , Eq. (6.2) still work in the constant shear strain ensembles and results from MD simulation<sup>22</sup> support this conclusion.

As pointed out by Sprik *et al.*<sup>17</sup> and others,<sup>12,13</sup> the rate of convergence of Eq. (2.10) is unsatisfactory. This can be understood if one observes that Eq. (2.10) follows the fluctuations in a macroscopic quantity which evolves slowly. We

can expect that Eqs. (4.6) or (5.6) should have the same problem. In contrast, Eq. (6.2) which comes from Eqs. (2.2) or (5.7) calculates the elastic constants by probing microscopic features of the system where fluctuations occur on a shorter time scale and consequently should converge faster. Therefore, to find all the elastic constants it is in general much more efficient to first determine the equilibrium lattice constant for the stress of interest using a constant  $\sigma$  or constant  $P$  simulation, and then do a simulation in the corresponding constant  $h$  ensemble<sup>13</sup> using formulas obtained from Eq. (2.2) or (6.2). However, if we focus on the behaviors of shear modulus or specific heat, the constant shear strain ensemble and so the (*HPN*) and (*TPN*) ensembles can be as efficient as that of the constant  $h$  ensembles.

So far we do not yet exhaust the possibility of constructing the ensembles of statistical mechanics. At least, to derive the general formulas with constant angle ensemble is an intriguing topic. Moreover, for instance, we can define an “uniaxial stress” ensemble by choosing  $\sigma_{11}$  and all of  $\eta_{ij}$  except  $\eta_{11}$  as independent variables. But such an ensemble does not seem to be useful that it is out of any interest.

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