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ENSEMBLES AND COMPUTER SIMULATION CALCULATION OF RESPONSE FUNCTIONS

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1. Statistical Ensembles and Computer Simulation

Calculation of thermodynamic quantities in molecular dynamics (MD) and Monte Carlo (MC) computer simulations is a useful, often employed tool [1–3]. In this procedure one chooses a particular statistical ensemble for the computer simulation. Historically, this was the microcanonical, or (EhN) ensemble for MD and the canonical, or (ThN) ensemble for MC, but there are several choices available for MD or MC. The notations, (EhN), (ThN) denote ensembles by the thermodynamic state variables that are constant in an equilibrium simulation; energy E , shape-size matrix h , particle number N and temperature T . (There could be other thermodynamic state variables, g_i , $i = 1, 2, \dots$, such as electric or magnetic field applied to the system, and these additional variables would be in the defining brackets.) The shape-size matrix is made up of the three vectors defining the computational MD or MC cell. If the vectors defining the parallelepiped, containing the particles in the computational cell, are denoted (\underline{a} , \underline{b} , \underline{c}) then the 3×3 shape-size matrix is defined by having its columns constructed from the three cell vectors, $h = (\underline{a}, \underline{b}, \underline{c})$. The volume V of the computational cell is related to the h matrix by $V = \det(h)$. For simplicity, we assume that the atoms in the simulation are described by classical physics using an effective potential energy function to describe the inter-particle interactions. Unless explicitly stated otherwise we suppose that periodic boundary conditions are applied to the particles in the computational cell. The periodic boundary conditions have the effect of removing surface effects and, conveniently, making the calculated system properties approximately equal to those of bulk matter. We assume the system obeys

the Born–Oppenheimer approximation and can be described by a potential energy U using classical mechanics and classical statistical mechanics.

2. Ensembles

For a single component system there are eight basic ensembles that are convenient to introduce. These ensembles and their connection to their reservoirs are shown in Fig. 1 [4]. Each ensemble represents a system in contact with different types of reservoirs. These eight systems are physically realizable and each can be employed in MD or MC simulations. The combined reservoir is a thermal reservoir, a tension (or stress) and pressure reservoir (the pressure reservoir in Fig. 1 represents a tension and pressure reservoir) and a chemical potential reservoir. The reservoirs are used to impose, respectively,

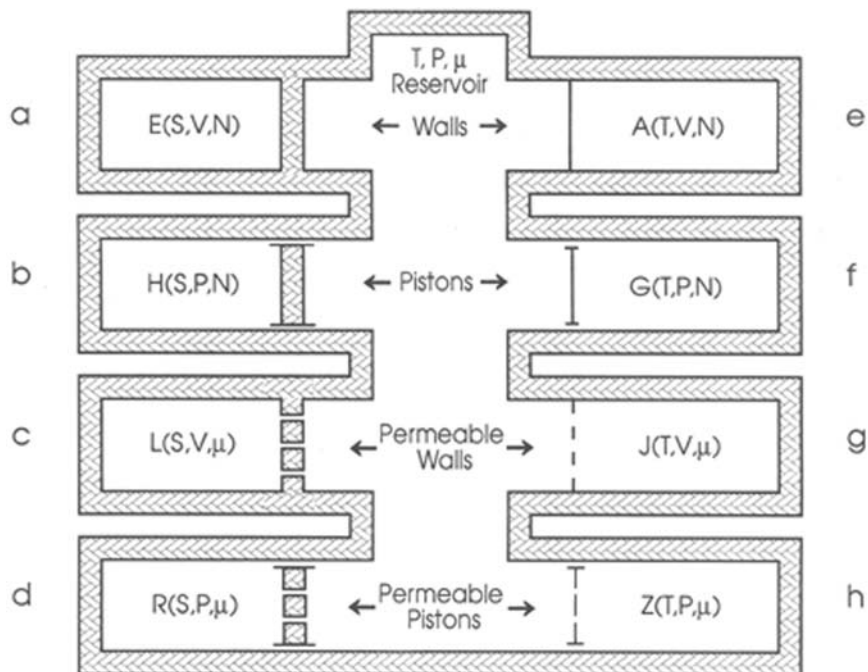


Figure 1. Shown are the eight ensembles for a single component system. The systems interact through a combined temperature, pressure and chemical potential reservoir. The ensembles on the left are adiabatically insulated from the reservoir while those on the right are in thermal contact with the reservoir. Pistons and porous walls allow for volume and particle exchange. Adiabatic walls are shown cross-hatched while diathermal walls are shown as solid lines. Ensembles on the same line like a and e are related by Laplace and inverse Laplace transformations. The pressure stands for the pressure and the tension.

constant temperature, tension and pressure, and chemical potential. The eight ensembles naturally divide into pairs of ensembles. The left-hand column in Fig. 1, a–d are constant energy ensembles while ensembles in the right hand column, e–h have constant temperature. These pairs of ensembles are connected to each other by direct and inverse Laplace transformations, $a \leftrightarrow e$, et cetera. The energies that are associated with each ensemble are related to the internal energy E by Legendre transformations [4].

The eight ensembles may be defined using the state variables that are held constant in the ensemble ([5] pp. 293–304). The eight ensembles include the (EhN) and (ThN) ensembles introduced earlier. Another pair of ensembles is the $(Ht \text{ and } PN)$ and $(Tt \text{ and } PN)$ ensembles where $H = E + V_o \text{Tr}(t\varepsilon) + PV$ is the enthalpy, t_{ij} is the thermodynamic tension tensor, ε_{ij} the strain tensor, P the pressure and Tr represents the trace operation. The thermodynamic tension is a modified stress tensor applied to the system that is introduced in the thermodynamics of anisotropic media. Due to definitions in the thermodynamic of non-linear elasticity we denote the tension and pressure separately. A third pair of ensembles is the $(Lh\mu)$ and $(Th\mu)$, where L is the Hill energy $L = E - \mu N$ and μ the chemical potential for the one component system. The isothermal member of this latter pair of ensembles is Gibb's grand canonical ensemble, $(Th\mu)$ ensemble. The final pair of ensembles is the $(Rt \text{ and } P\mu)$ and $(Tt \text{ and } P\mu)$ ensembles where $R = E + V_o \text{Tr}(t\varepsilon) + PV - \mu N$ is the R -energy. The latter member of this ensemble pair was introduced by Guggenheim [6] and is interesting since it has all intensive variables, T, P, μ , and these are all held fixed, but we know only two of these can be independent. Nevertheless, this ensemble can be used in simulations although its size will increase or decrease in the simulation. The $(Rt \text{ and } P\mu)$ ensemble allows variable particle number along with variable shape/size. These last four ensembles all have constant chemical potential and variable particle number. For multi-component systems there are a series of hybrid ensembles that are useful. As an example, for two component systems we can use the $(Tt \text{ and } P\mu_1 N_2)$ ensemble that is useful for studying the absorption of species 1 in species 2 as for example the absorption of hydrogen gas in a solid [7, 8].

Each of the eight ensembles, for a single component system, may be simulated using either MD or MC simulations. The probability distributions are exponentials for the isothermal ensembles and power laws for the adiabatic ensembles. For example, for the (TVN) ensemble the probability density has the Boltzmann form $P(q; TVN) = C e^{-U(q)/(k_B T)}$ with $U(q)$ the potential energy and C a constant. For the $(Ht \text{ and } PN)$ ensemble $P(q; H, t, P, N) = C V^N (H - V_o \text{Tr}(t\varepsilon) - PV - U(q))^{(3N/2 - 1)}$. The trial MC moves involve particle moves and shape/size matrix moves [9]. For the $(Rt \text{ and } P\mu)$ ensemble MC moves involve particle moves, shape/size matrix moves and attempted creation and destruction events [10]. For MC simulation of these ensembles one uses the probability density directly in the simulation, whereas for MD simulations

ordinary differential equations of motion are solved for equations arising from Hamilton's equations.

An important advancement in using MD to simulate different ensembles was the extended variable approach introduced by Andersen [11]. In this approach, which some variation is used in all but the (*EhN*) ensemble, extra variables are introduced into the system to introduce the variation of the variable in the ensemble. Although these variations are fictitious it can be proven that the correct ensemble is generated using these extended variable schemes. In the original approach for the (*HPN*) ensemble Andersen introduced an equation of motion for the volume that responds to a force that is the difference between the internal microscopic pressure and an external constant pressure imposed by the reservoir. This leads to volume fluctuations that are appropriate to the (*HPN*) ensemble, see Fig. 1. Nose, thereafter, generalized MD to the isothermal ensembles by introducing a mass scaling variable that allows for energy fluctuations in the (*ThN*) and the other isothermal ensembles [12]. These energy fluctuations mimic the interaction of the system with the heat reservoir and allow MD to generate the probability densities of the isothermal ensembles. Which ensemble/ensembles to use, and whether to use MD or MC depends on user preference and the particular problem under consideration. For the variable particle number ensembles (those involving the chemical potential in their designation) one usually employs MC methods since simulations using these ensembles involve attempted creation and destruction of particles and this fits naturally with the stochastic nature of the MC method. However, MD simulations of these ensembles have been investigated and performed [13].

3. Response Function Calculation

Response functions are thermodynamic properties of the system that are often measured, such as specific heats, heat capacities, expansion coefficients, and elastic constants to name a few. Response functions are associated with derivatives of the basic thermodynamic state variables like energy, pressure, entropy and include the basic thermodynamic state variables themselves. We do not include (non-equilibrium) transport properties, such as thermal conductivity, electrical conductivity, and viscosity, in our discussions since they fall under a different calculation schema that uses time correlation functions [14].

Formulas, that may be used to calculate response functions in simulations, may be derived by differentiation of quantities connecting thermodynamic state variables with integrals over functions of microscopic particle variables. These formulas are specific to each ensemble, and are standard statistical mechanics relations. Such a quantity, in the canonical ensemble, is the partition

function $Z(T, h, N)$, which for a N particle system in three-dimensions has the form

$$Z(T, h, N) = \frac{1}{N!(2\pi\hbar)^{3N}} \int e^{-H(q,p,h)/k_B T} d^{3N}q d^{3N}p, \quad (1)$$

where q and p denote the $6N$ -dimensional phase space canonical coordinates of the system, H the system Hamiltonian, k_B Boltzmann's constant, \hbar Plank's constant, and $d\tau = d^{3N}q d^{3N}p$ the phase space volume element. The integral in Eq. (1) is carried out over the entire phase space. Although we have indicated the Hamiltonian depends on the cell vectors, h , it would also depend on additional thermodynamic state variables g_i . For liquids and gases the dependence on h is replaced by simple dependence on the volume V ; for discussions of elastic properties of solids it is important to include the dependence on the shape and size of the system through the shape size matrix h or some function of h .

The Helmholtz free energy $A(T, h, N)$ is obtained from the canonical ensemble partition function

$$A(T, h, N) = -k_B T \ln Z(T, h, N). \quad (2)$$

Average values of phase space functions may be calculated using the phase space probability, which for the canonical ensemble is the integrand in the partition function in Eq. (1). For example, the canonical ensemble average for the phase space function $f(q,p,h)$ is

$$\langle f \rangle = \int f e^{-H/k_B T} d\tau / \int e^{-H/k_B T} d\tau. \quad (3)$$

In an MD or MC simulation the thermodynamic quantity $\langle f \rangle$ is calculated by using a simple average over the simulation configurations, for MD this is an average over time, whereas for MC it is an average over the Markov chain of configurations generated. If the value of f at each configuration (each value of q, p, h) is $f_n, n = 1, 2, 3, \dots, M$. for M time-steps in MD or trials in MC, then the average of f for the simulation is

$$\langle f \rangle = \frac{\sum_{n=1}^M f_n}{M}. \quad (4)$$

In the simulation Eq. (4) is the approximation to the phase space average in Eq. (3). If, for example, $H = f$, then this average gives the thermodynamic energy $E = \langle H \rangle$ and the caloric equation of state $E = E(T, h, N)$. The assumption that Eq. (4) approximates the integral in Eq. (3) is often referred to in the literature by saying that MD or MC "generates the ensemble". The approximate equality of these two results in MD is the quasi-ergodic hypothesis of statistical mechanics which states that ensemble averages, Eq. (3) and time averages, Eq. (4) are equal. This hypothesis has never been proven

for realistic Hamiltonians but it is the pillar on which statistical mechanics rests. In what follows we shall assume that averages over simulation-generated configurations are equal to statistical mechanics ensemble averages. Thus, we use formulas from statistical mechanics but calculate the average values in simulations using Eq. (4) employing MD or MC.

An important point to note is that for calculation of meaningful averages in a simulation we must “equilibrate” the system before collecting the values f_n in Eq. (4). This is done by carrying out the simulation for a “long enough time” and then discarding these configurations and starting the simulation from that point. This removes transient behavior, associated with the particular initial conditions used to start the simulation, from overly influencing the average in Eq. (4). How long one must “equilibrate” the system depends on relaxation rates in the system, that are initially unknown. Tasks like the equilibration of the system, the estimate of the accuracy of calculated values, and so forth are part and parcel of the art of carrying out valid and, therefore, useful simulations and must be learned by actually carrying out simulations. In this aspect computer simulations have a similarity to experimental science, like gaining experience with the measuring apparatus, but, of course, they are theoretical calculations made possible by computers.

From our discussion, so far, it might seem, to those who know thermodynamics, that the problem of calculating all response functions is finished, since if the Helmholtz free energy is known from Eq. (2) then all response functions may be calculated by differentiation of the Helmholtz free energy with respect to various variables. For example, the energy $\langle H \rangle$ may be found from

$$\langle H \rangle = kT^2 \frac{\partial(A/kT)}{\partial T} . \quad (5)$$

Unfortunately, in MC or MD only average values like Eq. (3), that are ratios of phase space integrals, can be easily evaluated in simulations and not the $6N$ -dimensional phase space integral itself, like Eq. (1). The reason for this is that in high-dimensions (dimensions greater than say, 10) the numerical methods used to accurately calculate integrals (e.g., Simpson’s rule) require computer resources beyond those presently available. For example, in 10 dimensions, for a grid of 100 intervals in each dimension, 10^{20} variables are required for the grid. Even with the most advanced computer, this number of variables is not easy to handle. In a typical simulation the dimension is typically hundreds or thousands, not ten. One might think that the high dimensional integrals could be calculated directly by MD or MC methods but this also does not work since the integrand in the high dimensional phase space is rapidly varying and one cannot sample for long enough to smooth out this rapid variation. The integral is determined by the value of the integrand in a few pockets (“equilibrium pockets”) in phase space that will only be sampled infrequently. For the ratio of high dimensional integrals, MD or MC methods have the

effect of focusing the sampling on just those important regions. The difficulty, in high dimensions, of calculating quantities that require the evaluation of an integral as compared to the ratio of integrals leads to a classification of quantities to be calculated by computer simulation as thermal or mechanical properties. Thermal properties require the value of the partition function, or some other high-dimensional integral, for their evaluation whereas mechanical properties do not require the value of the partition function for their evaluation, but are a ratio of two high dimensional integrals. As examples, for the canonical ensemble the Helmholtz free energy is a thermal variable and the energy is a mechanical variable. Other thermal variables are the entropy, chemical potential, and Gibbs free energy. Other mechanical variables are temperature, pressure, enthalpy, thermal expansion coefficient, elastic constants, heat capacity, and so forth. Special methods must be developed for calculating thermal properties and the calculation of thermal properties is, in general, more difficult. We have developed novel methods to calculate thermal variables using different ensembles [15, 16] but shall not discuss them in detail in this contribution.

As an example of the calculation of a mechanical response function, consider the fluctuation formula for the heat capacity in the canonical ensemble. Differentiation of the average energy $\langle H \rangle$ in Eq. (3) with respect to T while holding the cell vectors rigid leads to the heat capacity at constant shape-size C_V

$$C_V = \frac{\partial \langle H \rangle}{\partial T} = \frac{1}{k_B T^2} (\langle H^2 \rangle - \langle H \rangle^2). \quad (6)$$

Recall that in the simulation the average values in Eq. (2) are approximated by simple averages of the quantity. Thus, in a single canonical ensemble simulation, MC or MD we may calculate the heat capacity of the system at the given thermodynamic state point by calculating the average value of the square of the energy, subtracting the average value of the energy squared and dividing by $k_B T^2$. The quantity,

$$\delta H^2 = \langle H^2 \rangle - \langle H \rangle^2, \quad (7)$$

the variance in probability theory, is called the fluctuation in the energy H . The fluctuation of quantities enters into the formulas for response functions for mechanical variables.

It should be noted that a direct way of calculating the heat capacity C_V is to calculate the thermal equation of state at a number of temperatures and then numerically differentiate $\langle H \rangle$ with respect to T . This requires a series of simulations and is not as convenient or as easy to determine an estimate of accuracy but is simple and is a useful check on the value obtained from the fluctuation formula, Eq. (6). We refer to this method of calculating response functions as the direct method. Any mechanical response function can, in principle, be calculated by the direct method.

4. Thermodynamics of Anisotropic Media

For the present we choose the reference state to be the equilibrium state of the system with zero tension applied to the system. The h matrix for this reference state is h_o while for an arbitrary state of tension we have h . The following formulation of the thermodynamics of anisotropic media is consistent with nonlinear or finite elasticity theory. In the following repeated indices are summed over. The elastic energy U_{el} is defined by

$$U_{el} = V_o \text{Tr}(t\varepsilon), \quad (8)$$

where V_o is the reference volume, t is the thermodynamic tension tensor, ε is the strain tensor and Tr implies trace. The h matrix maps the particle coordinates into fractional coordinates, s_{ai} , in the unit cube through the relation $x_{ai} = h_{ij}s_{aj}$. The strain of the system relative to the unstressed state is

$$\varepsilon_{ij} = \frac{1}{2}(h_o^T{}^{-1}Gh_o^{-1} - I)_{ij}, \quad (9)$$

where $G = h^T h$ is the metric tensor. Here h_o is the reference value for measuring strain, that is, the value of h when the system is unstrained. This value can be obtained by carrying out a (*Ht and PN*) simulation, MD or MC with the tension set to zero. Equation (9) can be derived by noting that the deformation gradient can be written in terms of the h matrices as $\partial x_i / \partial x_{oj} = h_{ik}h_{ok}^{-1}$, and using this in the defining relation for the Lagrangian strain of the system. The thermodynamic tension tensor is defined so that the work done in an infinitesimal distortion of the system is given by $dW = V_o \text{Tr}(t d\varepsilon)$. The stress tensor, σ , is related to the thermodynamic tension by

$$\sigma = V_o h h_o^{-1} t h_o^T{}^{-1} h^T / V. \quad (10)$$

The thermodynamic law is

$$T dS = dE + V_o \text{Tr}(t d\varepsilon), \quad (11)$$

where T is the temperature, S the entropy and E the energy of the particles. Using the definition of the strain, Eq. (9), the thermodynamic law can be recast as

$$T dS = dE + V_o \text{Tr}(h_o^{-1} t h_o^T{}^{-1} dG) / 2. \quad (12)$$

From this latter we obtain

$$(\partial E / \partial G_{kn})_S = -(V_o h_o^{-1} t h_o^T{}^{-1})_{kn} / 2. \quad (13)$$

In the (*EhN*) ensemble we have the general relation

$$(\partial E / \partial G_{kn})_S = \langle \partial H / \partial G_{kn} \rangle, \quad (14)$$

where H is the particle Hamiltonian and the average is the (EhN) ensemble average. Combining the last two equations leads to

$$\langle \partial H / G_{kn} \rangle = -(V_o h_o^{-1} t h_o^{T-1})_{kn} / 2. \quad (15)$$

The particle Hamiltonian is transformed by the canonical transformation $x_{ai} = h_{ij} s_{aj}$, $p_{ai} = h_{ij}^{T-1} \pi_{aj}$, into

$$H(s_a, \pi_a, h) = \frac{1}{2} \sum_{a=1}^N \pi_{ai} G_{ij}^{-1} \pi_{aj} / m_a + U(r_{12}, r_{13}, \dots), \quad (16)$$

where the distance between particles a and b is to be replaced by the relationship $r_{ab}^2 = s_{abi} G_{ij} s_{abj}$ and s_{abi} is the fractional coordinate difference between a and b . The microscopic stress tensor Ω_{ij} may be obtained by differentiation of the particle Hamiltonian with respect to the h matrix while holding constant (s_a, π_a) : $\partial H / \partial h_{ij} = \Omega_{ik} A_{kj}$, where A is the area tensor $A = V h^{T-1}$. For the Hamiltonian, Eq. (16), the microscopic stress tensor is

$$\Omega_{ij} = \frac{1}{V} \left(\sum_a p_{ai} p_{aj} / m_a - \sum_{a<b} \frac{\partial U}{\partial r_{ab}} x_{abi} x_{abj} / r_{ab} \right). \quad (17)$$

Differentiating the Hamiltonian with respect to the parameters G_{kn} we obtain

$$M_{kn} \equiv (\partial H / \partial G_{kn}) = -(V h^{-1} \Omega h^{T-1})_{kn} / 2, \quad (18)$$

where Ω is the microscopic stress tensor, Eq. (17). If the average value of Eq. (18) is combined with Eq. (15) we obtain

$$t = V h_o h^{-1} \langle \Omega \rangle h^{T-1} h_o^T / V_o. \quad (19)$$

Comparing Eq. (19) and Eq. (10) we find

$$\sigma = \langle \Omega \rangle \quad (20)$$

the stress tensor is the average of the microscopic stress tensor. Equation (20) holds in all ensembles but the proofs would be different. For the (ThN) ensemble we would use the Helmholtz free energy $A = E - TS$ instead of the energy E . The counterpart to Eq. (14) would be $(\partial A / \partial G_{kn})_T = \langle \partial H / \partial G_{kn} \rangle$.

5. Calculation of Elastic Constants in the (EhN) Ensemble

In order to discuss the calculation of the elastic constants we describe the system by the microcanonical, (EhN) ensemble. The adiabatic elastic constants are defined as the derivative of the tension by the strain

$$C_{ijkl}^{(S)} = -(\partial t_{ij} / \partial \epsilon_{kl})_S. \quad (21)$$

Note the minus sign in Eq. (21) implies that the tension and stress are positive for compressive loading. Often the opposite convention is employed and no minus sign occurs in Eq. (21) in that convention. In the literature of finite elasticity the elastic constants defined in Eq. (21) are often called stiffness coefficients or elastic moduli. Assume the system Hamiltonian describing the system has the form

$$H(x_a, p_a) = \frac{1}{2} \sum_{a=1}^N p_a^2 / m_a + U(r_{12}, r_{13}, \dots), \quad (22)$$

where p_a is the momentum of particle a , r_{ab} is the distance between particle a and b and the system contains N particles. Let the reference value, h_o , denote the shape-size matrix for the unstressed system and h represent an arbitrary state of stress. The (EhN) fluctuation formula involving the adiabatic elastic constants, for a potential that depends only on interparticle distances has the form

$$\begin{aligned} V_o h_{oip}^{-1} h_{0jq}^{-1} h_{okr}^{-1} h_{ons}^{-1} C_{pqrs}^{(S)} &= -4\delta(M_{ij} M_{kn}) / k_B T \\ &+ 2Nk_B (G_{in}^{-1} G_{jk}^{-1} + G_{ik}^{-1} G_{jn}^{-1}) \\ &+ \sum_{\substack{a < b \\ c < d}}^N \langle k(a, b, c, d) s_{abi} s_{abj} s_{abk} s_{abn} \rangle, \end{aligned} \quad (23)$$

where

$$k(a, b, c, d) = (\partial^2 U / \partial r_{ab} \partial r_{cd} - (\partial U / \partial r_{ab}) \delta_{ac} \delta_{bd} / r_{ab}) / (r_{ab} r_{cd}). \quad (24)$$

The averages in Eq. (23) are calculated using (EhN) simulations, MD or MC. In (EhN) MD we would solve Newton's laws for the motion of the particles: $m_a \ddot{x}_{ai} = -\partial U / \partial x_{ai}$ to generate configurations to be used to calculate averages, Eq. (4). In MC we would use the probability density [17]: $W(q) = C(E - U(q))^{3N/2 - 1}$ to generate configurations by attempting a trial move of an atom $q \rightarrow q(\text{trial})$, and accepting the move if $W(q(\text{trial})) / W(q) > \text{random}$, where is a random number between 0 and 1. Equations (23) and (24) also holds for the isothermal elastic constants if one replaces $C_{pqrs}^{(S)}$ by the isothermal elastic constants, $C_{pqrs}^{(T)}$ and calculates the average values in Eq. (23) using (ThN) simulations. The three distinct terms in Eq. (23) are called the fluctuation term (term involving the fluctuation of M), the kinetic term (term with multiplier $2Nk_B$) and Born term (term containing $k(a, b, c, d)$). Equations (23) and (24) are valid for any potential that depends only on the distance between particles; it is valid for many-body forces as long as they can be written in terms of only the distance between particles. In particular, this would include potentials that depend on tetrahedral and dihedral angles and, therefore, have many body forces. For pair wise additive potentials the last term in Eq. (23) reduces to

the simpler form $\sum_{a<b}^N \langle g(a, b) s_{abi} s_{abi} s_{abk} s_{abn} \rangle$, with $g(a, b) = (U'' - 2U')/r_{ab}^4$ where $U' = r(\partial U/\partial r)$.

For many body potentials Eq. (24) will lead to terms that are two-body Born, three-body Born and so forth. This gives an interesting way of analyzing the contribution of the many body pieces of the potential to the elastic constants. It should be emphasized that the calculations based on Eqs. (23) and (24) are exact statistical mechanics formulas that take into account all anharmonic, temperature dependent and fluctuation effects.

The derivation of Eq. (23) can be obtained by the adiabatic differentiation of potential method. Define the potential

$$X_{ij} = \int M_{ij} \Theta(E - H(q, p)) d\tau, \quad (25)$$

where M is defined in Eq. (18) and Θ the unit step function. For Eq. (25) applied to large system one can keep, to good approximation, only the largest term or

$$\langle M_{ij} \rangle \Phi = \int M_{ij} \Theta(E - H(q, p)) d\tau, \quad (26)$$

where Φ the phase volume inside the energy shell, $H(q, p) = E$. The entropy is related to the phase volume by the Boltzmann relation $S = k_B \ln \Phi$. Differentiation of Eq. (26) with respect to G_{kn} leads to

$$V_o h_{oip}^{-1} h_{0jq}^{-1} h_{okr}^{-1} h_{ons}^{-1} C_{pqrs}^{(S)} = -4\delta(M_{ij} M_{kn})/k_B T + 4\langle \partial^2 H / \partial G_{ij} \partial G_{kn} \rangle. \quad (27)$$

Calculating the last term in Eq. (27) leads to Eqs. (23) and (24). More rigorous derivations of Eq. (23) are discussed by Ray [18].

Equations (23) and (24) have been used to calculate elastic constants in a nearest neighbor Lennard–Jones (6–12) system in both the microcanonical and canonical ensemble using MD and compared to calculations of these same quantities in earlier canonical ensemble MC calculations [19, 20]. These calculations have been reproduced by several workers and now can be used to check programs that are written to calculate elastic constants. Since there are thermodynamic relations connecting the adiabatic and isothermal elastic constants (like the thermodynamic formulas connecting C_V and C_P) this makes it possible to calculate the adiabatic elastic constants in either the (EnN) ensemble or the (ThN) ensemble, and the same for the isothermal elastic constants. A comparison of the values in the two ensembles can be looked upon as a stringent test of the validity of the Nose [12] theory for isothermal MD simulations, [20]. Equations (23) and (24) have also been used to calculate the elastic constants of crystalline and amorphous silicon modeled by the Stillinger–Weber potential [21, 22]. Equations (23) and (24) allow one to break down the Born

term into a two-body Born term and a three-body Born term for the Stillinger–Weber potential. These values have also been checked by a number of workers and can now be used as program checks.

Equations (23) and (24) were generalized to apply to potentials with an explicit volume dependent term, such as in metallic potentials, or when using the Ewald method to evaluate the Coulomb potential. The resulting theory was then applied to a model of sodium [23]. Another generalization was to study the calculation of the third-order elastic constants using a generalization of Eqs. (23) and (24) [24]. For systems where the reference state for measuring strain is a stressed state of the system, generalizations of Eqs. (23) and (24) are required. This extension with calculations for a model of solid helium has been developed [25]. A detailed application of Eqs. (23) and (24) was applied to embedded atom method potentials for palladium by Wolf *et al.* [26]. Extension of (Ht and PN) calculations to higher order elastic constants was given by Ray [27].

6. Calculation of Elastic Constants in the (*Ht and PN*) and (*Tt and PN*) Ensembles

In these ensembles the shape-size or strain of the system fluctuates. The Parrinello–Rahman fluctuation formula for the elastic constants involves just this fluctuation [28]

$$\delta(\varepsilon_{ij}\varepsilon_{kl}) = k_B T (C_{ijkl}^S)^{-1} / V_o, \quad (28)$$

where the adiabatic compliance tensor $(C^S)^{-1}$ is the inverse of the elastic constant tensor,

$$(C_{ijkl}^S)^{-1} = -(\partial\varepsilon_{ij}/\partial t_{kl})_S, \quad (29)$$

and S is the entropy. The averages in Eq. (28) are calculated using (*Ht and PN*) MD or MC. The same formula, Eq. (28), holds in the (*Tt and PN*) ensemble if we change to the isothermal elastic constants and calculate averages using isothermal MD or MC. For MD the extended Hamiltonian for variable shape-size ensembles has the form [29]

$$\begin{aligned} H_1(s, \pi, h, \Pi, f, \rho) = & \sum_a (\pi_a^T G^{-1} \pi_a / (2m_a f^2)) + U \\ & + \text{Tr}(\Pi^T \Pi) / (2W) + V_o \text{Tr}(t\varepsilon) + PV \\ & + \rho^2 / (2M) + (3N + 1)k_B T_o \ln(f), \end{aligned} \quad (30)$$

where (s, π) are scaled coordinates and conjugate momenta, U is the potential energy, (h, Π) are the coordinates and momenta of the computational cell, and

(f, ρ) are the Nose mass scaling variable and its conjugate momenta. The constants W and M are introduced so that h and f satisfy dynamical equations; note that in classical statistical mechanics equilibrium properties of the system are independent of the masses and, therefore, are independent of W , M and the particle masses m_a . T_o is the reservoir temperature in the constant temperature ensembles. The physical particle variables (x_a, p_a) are related to the scaled particle variables by $x_a = h s_a$, $p_a = h^{T-1} \pi_a / f$. The relationship between the physical variables and the scaled variables may be described by a canonical transformation defined by h along with a mass scaling transformation with f . The equations of motion following from this Hamiltonian may be written in the form

$$m_a f^2 \ddot{s}_{si} = - \sum (\partial U / \partial r_{ab}) s_{abi} / r_{ab} - m_a (f^2 G^{-1} \dot{G} + 2 f \dot{f}) \dot{s}_{ai}, \quad (31)$$

$$W \ddot{h} = (\Omega - P I) A - h \Gamma, \quad (32)$$

$$M \ddot{f} = 2K / f - (3N + 1) k_B T_o / f, \quad (33)$$

where $\Gamma = V_o h_o^{-1} t h_o^{T-1}$ is related to the tension applied to the system and K is the particle kinetic energy. Equation (31) is just Newton's law applied to the particles with the additional modification of the variable cell and the mass scaling variables. Equation (32) is the Parrinello–Rahman equation [28] as generalized [29, 30] to be valid for finite deformations which involves introducing the tension instead of the stress; this lead to the form of the enthalpy for finite elasticity in agreement with Thurston [31]. Equation (33), [12] is the equation of motion for the mass scaling variable which is introduced to drive the average temperature of the system to the reservoir temperature T_o in an equilibrium simulation. If the Nose mass scaling variable satisfies $f = 1$, $df/dt = 0$ then Eqs. (31) and (32) are the MD equations of motion for the (*Ht and PN*) ensemble and the trajectories yield averages in this ensemble. If the cell matrix satisfies $h = \text{const.}$, $dh/dt = 0$, then Eqs. (30) and (32) are the equations of motion for the (*ThN*) ensemble and the trajectories yield averages in this ensemble. If the previous conditions on h and f are both satisfied then the (*EhN*) ensemble is generated. If Eqs. (30)–(33) are solved in the general case with f and h varying then the (*Tt and PN*) ensemble is generated.

The variable cell equations of motion have great utility in studying solid–solid phase transformations by computer simulation. These same transformations can be studied using MC methods. In the (*Ht and PN*) ensemble the calculation of elastic constants in MD is not as good as in MC. That is, Eq. (28) converges faster using MC than MD. This is illustrated in detail by Fay and Ray, 1992 [9] and Karimi *et al.* 1998 [32]. However, (*Ht and PN*) MC elastic constant calculations do not converge as fast as (*EhN*) MD or MC. The convergence is governed by the fluctuation terms in either Eq. (23) or Eq. (28). The fluctuation of the microscopic stress tensor in Eq. (23) converges

faster than the fluctuation of the shape/size matrix in Eq. (28) in the cases we have investigated. This is unfortunate since the (*EhN*) formulas require values of the second derivatives of the potential whereas the (*Ht and PN*) fluctuation formulas require only first derivatives in MD or no derivatives in MC. The derivatives of the potential may not be easy to calculate for a many body potential although one could employ algebraic computer programs to calculate the derivatives.

One can calculate elastic constants in the variable particle number ensembles but we have not discovered a case where that offers any advantage over the four fixed particle number ensembles discussed. If the second derivatives of the potential can be evaluated or accurately approximated, then the (*EhN*) formulas, Eqs. (23) and (24), using either MD or MC are the best choice for calculating the elastic constants. If the second derivative of the potential is not available then MC using the probability density $P(q; H, t, P, N) = CV^N (H - V_o \text{Tr}(t\varepsilon) - PV - U(q))^{(3N/2-1)}$ with Eq. (28) is the best choice. MC calculations in the (*Ht and PN*) ensemble also offer the advantage of not having to worry about the choice of the different fictitious kinetic energy and mass terms introduced in extended MD; these are not unique. Either Eqs. (23) or (28) offers a convenient way of calculating elastic properties of condensed matter systems as a function of temperature or other parameters in a way that includes all anharmonic effects in an exact manner.

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