

Statistical ensembles and molecular dynamics studies of anisotropic solids

John R. Ray^{a)} and Aneesur Rahman
Argonne National Laboratory, Argonne, Illinois 60439

(Received 4 November 1983; accepted 20 January 1984)

We present a general discussion of the isoenthalpic–isostress molecular dynamics theories of Andersen and Parrinello–Rahman. The Parrinello–Rahman theory is shown to be applicable to the case of nonlinear elasticity if the reference state of zero strain is taken to be the state under zero stress; this brings the theory into accord with the thermodynamics of anisotropic solids for arbitrary values of the strain. For the isoenthalpic–isostress ensemble there is a microcanonical counterpart for which we present fluctuation formulas involving the constant strain specific heat, temperature coefficients of thermodynamic tension, and stiffness coefficients. The use of these various ensembles for the molecular dynamic study of polymorphic transitions in crystals is discussed.

I. INTRODUCTION

Andersen¹ has developed a method of carrying out molecular dynamics calculations allowing the volume of a cubic molecular dynamics cell to vary. His theory generates the isoenthalpic–isobaric or (HPN) ensemble of statistical physics. Here H is the system enthalpy, P the pressure, and N the particle number. Conventional molecular dynamics generates the microcanonical or (EVN) ensemble. As we shall see, for the study of anisotropic systems this last statement needs some elaboration.

In an extension of Andersen's theory, Parrinello and Rahman showed how it could be generalized to allow for changes in both the size and shape of the molecular dynamics cell. In their first work² they dealt with systems subjected to a given external hydrostatic pressure, whereas later they introduced anisotropic stress as well.^{3–5} This latter generalization generates the isoenthalpic–isostress or $(H\sigma N)$ ensemble. It has become customary to say that conventional molecular dynamics generates the microcanonical or (EVN) ensemble. This is not incorrect, but a more precise statement is that it generates an (EhN) ensemble, where h is a tensor constructed from the three vectors forming a parallelepiped, which is the periodically repeating molecular dynamics cell. This, more precise, statement becomes relevant when one is dealing with anisotropic systems such as crystalline solids. If \mathbf{a} , \mathbf{b} , and \mathbf{c} are the three vectors forming the molecular dynamics cell, then the tensor h is constructed from these vectors by $h = (\mathbf{a}, \mathbf{b}, \mathbf{c})$.

An important feature of the Parrinello–Rahman theory is that it may be used to study solid–solid structural transformations as a function of temperature, external stress, and potential energy function of the system.³ A number of recent papers apply the Parrinello–Rahman theory to such studies.^{5–9}

The basic idea behind the Andersen–Parrinello–Rahman theory is to allow the tensor h , which characterizes the molecular dynamics cell, to vary in time as a result of the difference between the varying internal microscopic stress tensor and the constant external stress tensor σ . This is implemented by obtaining equations of motion for the tensor h

whose driving terms are related to the difference between these two stress tensors.

In this paper we first discuss the general structure of the Parrinello–Rahman theory and its relationship to thermodynamics. We show that a more precise definition of the elastic energy allows this theory to agree with the theory of finite elasticity. Secondly, we develop the basic statistical mechanics of the (EhN) ensemble and discuss its relationship to the $(H\sigma N)$ or (HtN) ensembles; as we shall see, t is a tensor related to σ , the usual stress tensor, and is called tensor of thermodynamic tension.

II. PARRINELLO–RAHMAN AND ANALOGOUS THEORIES

A. The Hamiltonian approach

The Hamiltonian version of the Parrinello–Rahman theory has been presented in an earlier paper by Ray.¹⁰ Consider a system described by the Hamiltonian \mathcal{H} :

$$\mathcal{H}(\mathbf{x}, \mathbf{p}) = \sum_a \frac{p_a^2}{2m_a} + \sum_{a < b} U(r_{ab}), \quad (2.1)$$

where we restrict ourselves to spherically symmetric pair potentials for simplicity of notation. We first carry out the canonical transformation

$$s_{ai} = \sum_{j=1}^3 h_{ij}^{-1} x_{aj}, \quad \text{i.e., } s_a = h^{-1} x_a, \quad (2.2)$$

$$\pi_{ai} = \sum_{j=1}^3 h_{ji} p_{aj}, \quad \text{i.e., } \pi_a = h' p_a, \quad (2.3)$$

where h_{ij} are the elements of the h tensor introduced above. We shall employ matrix notation for the coordinate labels i, j, k, \dots as much as possible. The metric tensor G is defined by $G = h' h$, where the prime indicates matrix transpose. After the canonical transformation (2.2) and (2.3) the Hamiltonian has the form

$$\mathcal{H}(\mathbf{s}, \boldsymbol{\pi}, h) = \sum_a \pi_a' G^{-1} \pi_a / (2m_a) + \sum_{a < b} U(r_{ab}). \quad (2.4)$$

The distances r_{ab} are related to the scaled distances by the metric tensor via

$$r_{ab}^2 = s_{ab}' G s_{ab}. \quad (2.5)$$

We now assume that h_{ij} is a time dependent variable $h_{ij}(t)$.

^{a)}Permanent address: Department of Physics and Astronomy, Clemson University, Clemson, South Carolina 29631.

The Newtonian equations of motion for the coordinate s_{ai} can be found from Hamilton's equations applied to \mathcal{H} and have the form

$$m_a \ddot{s}_a = \sum_{b \neq a} \chi_{ab} s_{ab} - m_a G^{-1} \dot{G} \dot{s}_a, \quad (2.6)$$

where $\chi_{ab} = r_{ab}^{-1} \partial U / \partial r_{ab}$ is a scalar quantity depending on the distance r_{ab} .

As discussed by Andersen,¹ in the case when h is time dependent, the equations of motion (2.6) cannot be derived directly from the Hamiltonian (2.1) without neglecting certain terms. In the Hamiltonian version of the theory this shows up clearly if we introduce, as in Goldstein,¹¹ the generating function $F_3(\mathbf{s}, \mathbf{p}, t)$ associated with the canonical transformation (2.2) and (2.3). Following the notation of Goldstein¹¹ this is

$$F_3(\mathbf{s}, \mathbf{p}, t) = - \sum_a p'_a \dot{h} s_a. \quad (2.7)$$

If h is time dependent then the Hamiltonian obtained by applying the canonical transformation to Eq. (2.1) has the form

$$\mathcal{H}'(\mathbf{s}, \pi, h) = \mathcal{H}(\mathbf{s}, \pi, h) + \partial F_3 / \partial t \quad (2.8)$$

or

$$\mathcal{H}'(\mathbf{s}, \pi, h) = \mathcal{H}(\mathbf{s}, \pi, h) - \sum_a p'_a \dot{h} s_a. \quad (2.9)$$

The assumption we make, which is equivalent to the assumption made by Andersen and by Parrinello and Rahman, is to neglect the term $\partial F_3 / \partial t$ and use $\mathcal{H}'(\mathbf{s}, \pi, h)$ as the Hamiltonian, even when h is time dependent. In order to see what this assumption entails we may use Hamilton's equations with \mathcal{H}' to derive

$$p_a = m_a h \dot{s}_a + m_a \dot{h} s_a = m_a \dot{x}_a. \quad (2.10)$$

Neglecting the term $\partial F_3 / \partial t$ in \mathcal{H}' implies neglecting the term $m_a \dot{h} s_a$ in this equation and using

$$p_a = m_a h \dot{s}_a. \quad (2.11)$$

The precise meaning of this approximation needs to be further studied, however, we do not discuss it further in this paper. If we use \mathcal{H}' instead of \mathcal{H} then the equation corresponding to Eq. (2.6) has the form

$$m_a \ddot{s}_a = - \sum \chi_{ab} s_{ab} - m_a h^{-1} \dot{h} \dot{s}_a - 2m_a h^{-1} \dot{h} \dot{s}_a. \quad (2.12)$$

It is possible that one could employ this latter equation of motion instead of Eq. (2.6), but we have not explored this possibility. In this paper we shall use the Hamiltonian \mathcal{H} even when h depends on time.

B. Use of thermodynamic tensors instead of the stress tensor

Thus, in the Andersen–Parrinello–Rahman theory one assumes that h is a dynamical variable. Hence, the new degrees of freedom h will have to be given a kinetic energy K_{cell} and a potential energy U_{cell} , this latter being associated with the elastic energy stored in the system. The new Hamiltonian will then be

$$\mathcal{H}_1(\mathbf{s}, \pi, h, \Pi) = \mathcal{H}(\mathbf{s}, \pi, h) + K_{\text{cell}}(h, \Pi) + U_{\text{cell}}(h), \quad (2.13)$$

where Π is the momentum conjugate to h . For K_{cell} Parrinello and Rahman took

$$K_{\text{cell}} = \frac{1}{2} \text{Tr} \Pi' \Pi / W, \quad (2.14)$$

where W is a constant. For U_{cell} they chose

$$U_{\text{cell}} = \begin{cases} P(V - V_0) & \text{isotropic case} \\ V_0 \text{Tr} \sigma \epsilon & \text{anisotropic case.} \end{cases}$$

With the convention that in the anisotropic case P will be taken to be zero and in the isotropic case $\sigma = P$, they wrote

$$U_{\text{cell}} = P(V - V_0) + V_0 \text{Tr}(\sigma - P)\epsilon, \quad (2.15)$$

where ϵ is the strain tensor, P is the external hydrostatic pressure, σ is the external stress tensor applied to the system, V_0 is the reference volume and V is the system volume which in general depends on time; $V = \det h$ and $V_0 = \det h_0$ where h_0 is the reference value of h . The strain tensor can be written in terms of the metric G and the tensor h_0 , in the form

$$\epsilon = \frac{1}{2}(h_0^{-1} G h_0^{-1} - 1). \quad (2.16)$$

Using this form for ϵ in Eq. (2.15) one obtains U_{cell} as a function of h as indicated in Eq. (2.13):

$$U_{\text{cell}} = P(V - V_0) + \frac{1}{2} \text{Tr} \Sigma G, \quad (2.17)$$

where $\Sigma = V_0 h_0^{-1} (\sigma - P) h_0^{-1}$. The equations of motion for h with these choices for K_{cell} and U_{cell} have the form³

$$W \ddot{h} = (\mathcal{P} - P)A - h\Sigma, \quad (2.18)$$

where \mathcal{P} is the microscopic stress tensor

$$\mathcal{P}_{ij} = V^{-1} \left(\sum_a p_{ai} p_{aj} / m_a - \sum_{a < b} \chi_{ab} r_{abi} r_{abj} / r_{ab} \right), \quad (2.19)$$

and $A = V h^{-1}$ is the "area tensor."

As a consequence of the equations of motion (2.6) and (2.18) the Hamiltonian (2.13) is a constant of the motion. In equilibrium we may neglect the contribution of K_{cell} to the total kinetic energy. Thus, for a system in equilibrium, we obtain the constant of the motion

$$\mathcal{H}_1 = \mathcal{H} + U_{\text{cell}}. \quad (2.20)$$

Using the form of U_{cell} given in Eq. (2.15) we see that \mathcal{H}_1 in Eq. (2.20) is an enthalpy like quantity. In the anisotropic option the constant of the motion is

$$\mathcal{H}_1 = \mathcal{H} + V_0 \text{Tr} \epsilon \sigma. \quad (2.21)$$

To define ϵ , Parrinello and Rahman suggested that h_0 should be taken as the average of h during a molecular dynamics calculation. This prescription implies that the U_{cell} of Eq. (2.15) be interpreted as the elastic energy generated in a deformation around a state of the system which is not a state of zero stress but the state under stress σ . Thus the reference value from which U_{cell} is measured is not zero but the elastic energy in a deformed state.

The above was a summary of the molecular dynamics equations of Parrinello and Rahman. The purpose in presenting it has been firstly to introduce the relevant notation and secondly to put into perspective the following ideas.

The theory of finite elastic deformations has been dealt with by Thurston,¹² Murnaghan,¹³ and Wallace.¹⁴ To bring our formulation into agreement with this theory the quantities σ and ϵ in U_{cell} in Eq. (2.15) must be interpreted different-

ly. For clarity of presentation, however, let us introduce the appropriate terminology and notation. In thermodynamics, in order to construct the enthalpy of finite elasticity one introduces the tensor of thermodynamic tension t_{ij} which is related to the externally applied stress tensor σ by

$$t = V h_0 h^{-1} \sigma h^{-1} h'_0 / V_0 \text{ or } \sigma = V_0 h h_0^{-1} t h_0^{-1} h' / V, \quad (2.22)$$

where h_0 is the value of h when zero stress is applied to the system.

The thermodynamic tension has the important property of being the quantity appearing in the fundamental thermodynamic laws¹²⁻¹⁴

$$TdS = dE + V_0 \text{Tr } t d\epsilon. \quad (2.23)$$

The thermodynamic enthalpy also contains the tension in the form

$$H = E + V_0 \text{Tr } t \epsilon. \quad (2.24)$$

We remind ourselves that in Eqs. (2.22), (2.23), and (2.24) ϵ is defined using the zero stress value of h , namely h_0 .

Based on these thermodynamic considerations we choose for U_{cell} the function $V_0 \text{Tr } t \epsilon$ with t a given constant tensor; this is expected to be more appropriate than $V_0 \text{Tr } \sigma \epsilon$ of Eq. (2.15) for large strains with respect to the state of zero stress. The ensemble generated by this new choice of U_{cell} is the isoenthalpic-isotension or (HtN) ensemble. Using Hamilton's equations with \mathcal{H}_1 given in Eq. (2.13) but with

$$U_{\text{cell}} = V_0 \text{Tr } t \epsilon, \quad (2.25)$$

and the Parrinello-Rahman form for K_{cell} we obtain the h equation of motion

$$W\ddot{h} = \mathcal{P}A - h\Gamma, \quad \Gamma = V_0 h_0^{-1} t h_0^{-1}. \quad (2.26)$$

This equation has the same form as the Parrinello-Rahman equation (2.18) if we set $P = 0$ and identify σ with t . We discuss the difference between Eqs. (2.18) and (2.26) in the following subsection. Equations (2.26) and (2.6) generate an (HtN) ensemble with constant enthalpy

$$H = E + V_0 \text{Tr } t \epsilon. \quad (2.27)$$

C. Choice of h_0 , the reference state

Purely from the point of view of the definition of the strain, $\epsilon = \frac{1}{2}(h_0^{-1} G h_0^{-1} - 1)$ the choice of h_0 is obviously arbitrary. However, in the expression for the elastic energy the choice does make a difference. When this energy is defined as in Eq. (2.25) using the thermodynamic tension t , the value of h_0 should be chosen as the average value of h when the stress is zero, i.e., the stored energy is zero if the system is not acted on by any external agent.

In order to interpret the results of an (HtN) molecular dynamics calculation using Eqs. (2.6) and (2.26) we therefore need the solution for zero stress; the average value of h in this zero stress calculation determines h_0 . With this h_0 and the value of h in the presence of stress one can obtain the thermodynamic tension and the elastic energy.

Thus, in view of the similarity between Eqs. (2.18) and (2.26), the conclusion is that the Parrinello-Rahman equations of motion are appropriate for the study of finite strains

provided the choice of h_0 is made as above, and the stress tensor is interpreted as a thermodynamic tension tensor.

D. The case of hydrostatic pressure

As clearly discussed by Thurston,¹² in the case of an isotropic hydrostatic pressure the enthalpy (2.27) does not equal the enthalpy of ordinary thermodynamics.

If we deal with a system subject to a constant external pressure the form of U_{cell} should be chosen as $U_{\text{cell}} = PV$ which leads to the h equation of motion

$$W\ddot{h} = (\mathcal{P} - P)A, \quad (2.28)$$

which was first presented by Parrinello and Rahman in Ref. 2 and corresponds to their isotropic options in Eq. (2.15). The h equation of motion (2.28) together with Eq. (2.6) generates an (HPN) ensemble with constant enthalpy $H = E + PV$. The form $U_{\text{cell}} = PV$ was also the form used by Andersen in Ref. 1. Andersen's discussion is, however, restricted to cubic molecular dynamics cells $h_{ij} = V^{1/3} \delta_{ij}$.

In summary, for a system subjected to anisotropic stress one should use the elastic energy given by Eq. (2.25) and hence the dynamical equation (2.26), while for a system subjected to hydrostatic pressure the appropriate equation is (2.28), in order to generate a thermodynamically consistent (HtN) or (HPN) ensemble, respectively.

E. The kinetic energy of the cell

The form of the K_{cell} is not unique. As an example we mention that the form chosen by Parrinello and Rahman does not agree with Andersen's form for K_{cell} for the case of a cubic molecular dynamics cell $h_{ij} = V^{1/3} \delta_{ij}$. A form for K_{cell} which agrees with Andersen's choice in the cubic limit has been given by Ray¹⁰

$$K_{\text{cell}} = \frac{1}{2} \text{Tr } (\Pi' G^{-2} \Pi) / c, \quad (2.29)$$

$$\Pi = c G^2 h.$$

where the constant c is related to Andersen's M by $c = 3M$. If we employ this kinetic energy together with Eq. (2.25) we obtain the h equation of motion

$$c\ddot{h} = G^{-2} [\mathcal{P}A - h\Gamma + ch\dot{h}\dot{h}'G + cG\dot{h}\dot{h}' - cG\dot{G}\dot{h} - c\dot{G}\dot{G}h]. \quad (2.30)$$

This equation for h together with Eq. (2.6) will still generate an (HtN) ensemble since the two Hamiltonians differ only by the form of K_{cell} ; in both cases when the system is in equilibrium the average of K_{cell} is the same and is negligible. The motivation for using Eq. (2.29) is that we then directly obtain the virial theorem $1/3 \overline{\text{Tr } \mathcal{P}} = P$ in the case of a cubic molecular dynamics cell and hydrostatic pressure. This point is discussed in detail in Ref. 10.

F. The dynamical equation for h

It is important to note that the equations of motion (2.6) allow for the effects of the variable molecular dynamics cell regardless of the equation of motion chosen for h . In order to explore effects of using alternative h equations of motion for h we could use, for example, the simple h equation

$$c'\dot{h} = \mathcal{P} - \sigma, \quad (2.31)$$

where c' and σ are constants.

In order to avoid confusion it should be pointed out that when we introduce an h equation such as Eq. (2.31) we will not in general generate an (HtN) or any other ensemble. This is because Eq. (2.31) is not derived from a Hamiltonian and, therefore, there is no constant of the motion like the enthalpy. The h equations (2.26), (2.28), and (2.30) are based on Hamiltonians and lead, using Andersen's ideas, to statistical ensembles.

We have used Eqs. (2.26), (2.28), (2.30), and (2.31) in various molecular dynamics calculations on systems of 250, 256, 500 and 1440 particles interacting with both the Lennard-Jones and Morse potentials. In these calculations we have obtained self-consistent results, which we shall report later. Thus, we can study solid→solid structural transformations using any of the above h equations together with Eq. (2.6). Using the h equation (2.31) we can investigate structural transformations, but we would have to use an h equation corresponding to a well defined ensemble in order to calculate equilibrium and transport properties of the system. [Although the use of Eq. (2.31) does not generate an ensemble, for the sake of simplicity of terminology in the rest of this paper we shall still refer to an (HtN) ensemble even when we use the h equation (2.31).]

III. THERMODYNAMICS AND THE (EhN) ENSEMBLE

As already mentioned, when one is investigating anisotropic systems the microcanonical ensemble is (EhN); the constancy of the tensor h obviously contains more constraints than simply the constancy of its determinant, i.e., the volume. In this section we shall investigate the (EhN) ensemble which apparently has not been previously discussed.

We start from the thermodynamic law

$$TdS = dE + V_0 \text{Tr} \, t d\epsilon. \quad (3.1)$$

The strain tensor has the form

$$\epsilon = \frac{1}{2}(h'_0{}^{-1} G h_0^{-1} - 1). \quad (3.2)$$

From Eq. (3.2) we have

$$d\epsilon = \frac{1}{2} h'_0{}^{-1} dG h_0^{-1}, \quad (3.3)$$

which used in Eq. (3.1) yields

$$TdS = dE + \frac{1}{2} V_0 \text{Tr} \, h_0^{-1} t h'_0{}^{-1} dG. \quad (3.4)$$

From this last equation we can write

$$(\partial E / \partial G_{km})_S = -\frac{1}{2} V_0 (h_0^{-1} t h'_0{}^{-1})_{km}. \quad (3.5)$$

The adiabatic theorem in the (EhN) ensemble has the form

$$(\partial E / \partial G_{km})_S = \overline{\partial \mathcal{H} / \partial G_{km}}, \quad (3.6)$$

where \mathcal{H} is given by Eq. (2.4). Combining Eqs. (3.5) and (3.6) relates the Hamiltonian to the thermodynamic tension tensor

$$\overline{\partial \mathcal{H} / \partial G_{km}} = -\frac{1}{2} V_0 (h_0^{-1} t h'_0{}^{-1})_{km}. \quad (3.7)$$

Calculating $\partial \mathcal{H} / \partial G_{km}$ from Eq. (2.4) yields

$$M_{km} = \partial \mathcal{H} / \partial G_{km} = -\frac{1}{2} (h^{-1} V \mathcal{P} h'^{-1})_{km}, \quad (3.8)$$

where \mathcal{P} is the microscopic stress tensor (2.19), and M_{km} is a tensor we shall employ later. Using Eq. (3.8) in Eq. (3.7) gives the relation between the average microscopic stress tensor \mathcal{P}_{ij} and the thermodynamic tension

$$t = V h_0 h^{-1} \overline{\mathcal{P}} h'^{-1} h'_0 / V_0. \quad (3.9)$$

Comparing the thermodynamic relation (2.22) with Eq. (3.9) we obtain the connection between the physical stress tensor σ , necessary to hold h constant, and the average of the microscopic stress tensor \mathcal{P} , namely

$$\sigma = \overline{\mathcal{P}}. \quad (3.10)$$

The relation (3.9) allows us to determine the thermodynamic tension from the average values of \mathcal{P} and the values of h and h_0 , assuming that the latter has been determined. The strain associated with these values of h and h_0 can be found from Eq. (3.2). Thus, using Eqs. (3.2) and (3.9) we can determine the relationship between t and ϵ .

The isentropic stiffness or elastic coefficients can be determined from the tension vs strain relation

$$C_{ij,rs} = -\partial t_{ij} / \partial \epsilon_{rs}. \quad (3.11)$$

Higher order stiffness coefficients could be determined from higher order derivatives of the stiffness-strain relation.

The use of Eq. (3.11) in the method just described is a static method of determining stiffness coefficients. A dynamic method of determining stiffness coefficients, along with other equilibrium properties of the system, is obtained by employing various fluctuation formulas for the (EhN) ensemble which we present in the next section.

Thus in an (EhN) ensemble Eq. (3.10) gives the external stress that is necessary to hold the system at constant h . Its use in Eq. (3.9) and hence in Eq. (3.11) requires determination of h_0 . This is not necessary in the isotropic case where it is not necessary to know the value of V_0 to determine thermodynamic functions. To determine h_0 , i.e., the value of h for zero stress, the most practical way, at present, seems to be the use of an (HtN) ensemble molecular dynamic calculation with $t = 0$. Another possible scheme would be to use a least square approach to the determination of h_0 with data collected from several (EhN) calculations.

The relation (3.10) is a generalization of the (EVN) virial theorem of anisotropic systems in the (EhN) ensemble. The trace of this equation is in fact the usual (EVN) virial theorem.

A different result obtains in the (HPN) or (HtN) ensembles. In Andersen's original (HPN) ensemble, which is restricted to a cubic cell, the h (in this case V) equation has the form

$$M\dot{V} = 1/3 \text{Tr} \, \mathcal{P} - P. \quad (3.12)$$

The average of this equation for a system in equilibrium yields the (EVN) virial theorem $1/3 \overline{\text{Tr} \, \mathcal{P}} = P$. However, for the (HPN) ensemble and a noncubic cell we have the Parrinello-Rahman equation (2.28). The average of this equation yields a modified form of the virial theorem

$$\overline{\mathcal{P}A} = \overline{PA}. \quad (3.13)$$

A similarly modified form of the virial theorem also occurs in the (HtN) ensemble. In using Eq. (2.28) in (HPN) molecu-

lar dynamics calculations we have noticed the approximate equality of $\overline{\mathcal{P}A}$ and \overline{PA} for systems in equilibrium.

IV. FLUCTUATION FORMULAS FOR THE (EhN) ENSEMBLE

In order to derive fluctuation formulas for the (EhN) ensemble we may use the methods of Ray and Graben¹⁵ and Ray.¹⁶ Since these methods are straightforward we shall here just give the final results. Proceeding as in Refs. 15 and 16 we arrive at the kinetic energy fluctuation formula in the (EhN) ensemble.

$$\delta(K^2) = \overline{K^2} - \overline{K}^2 = 3N(k_B T)^2 [1 - 3Nk_B / (2C_\epsilon)] / 2, \tag{4.1}$$

where K is the system kinetic energy C_ϵ the specific heat at constant strain, and T the temperature that enters by way of the relation $\overline{K} = 3/2 Nk_B T$. The relation (4.1) is familiar in

the theory of liquids where C_ϵ is replaced by C_ν , the isometric specific heat.

From the relation (3.9) we can define a microscopic tension tensor

$$\eta = Vh_0 h^{-1} \mathcal{P} h'^{-1} h'_0 / V_0. \tag{4.2}$$

From Eq. (3.9) the average of η gives the tension tensor t ,

$$t = \overline{\eta}. \tag{4.3}$$

The cross correlation between the kinetic energy and the microscopic tension tensor η has the form

$$\delta(\eta K) = k_B T [(h_0 h^{-1} \Sigma \overline{p_a p_a} h'^{-1} h'_0) / V_0 - 3Nk_B T \lambda / (2C_\epsilon)], \tag{4.4}$$

where tensor $\lambda = (\partial t / \partial T)_\epsilon$ is the isentropic temperature coefficients of thermodynamic tension at constant strain. The notation in Eq. (4.4) implies matrix multiplication of the tensor $\Sigma \overline{p_{ai} p_{aj}}$ by the various h matrices.

The final (EhN) fluctuation formula involves the isentropic stiffness coefficients $C_{ij,kl}$, and can be written as a fluctuation formula for the quantity $M_{ij} = (\partial \mathcal{H} / \partial G_{ij})$ introduced in Eq. (3.8). The final result has the form

$$\delta(M_{ij} M_{kn}) = k_B T \{ -V_0 h_{0ip}^{-1} h_{0jk}^{-1} h_{0kr}^{-1} h_{0ns}^{-1} C_{pk,rs} + \Sigma [(G_{rk}^{-1} G_{in}^{-1} + G_{rn}^{-1} G_{ik}^{-1}) G_{js}^{-1} + (G_{jk}^{-1} G_{sn}^{-1} + G_{jn}^{-1} G_{sk}^{-1}) G_{ri}^{-1}] \overline{\pi_{ar} \pi_{as}} / m_a + \Sigma (\overline{\partial^2 U / \partial r_{ab}^2} - \overline{\partial U / \partial r_{ab}} / r_{ab}) s_{abi} s_{abj} s_{abk} s_{abn} / r_{ab}^2 \} / 4. \tag{4.5}$$

Here π_{ar} is the r th component of the momentum of particle a after the canonical transformation and a sum over repeated indices must be carried out in this equation. Equation (4.5) relates the stiffness coefficients to the stress-stress correlations. In the static limit, where the particle positions are fixed, Eq. (4.5) yields

$$-V_0 C_{ij,kn} + \Sigma (\overline{\partial^2 U / \partial r_{ab}^2} - \overline{\partial U / \partial r_{ab}} / r_{ab}) x_{abi} x_{abj} x_{abk} x_{abn} / r_{ab}^2 = 0. \tag{4.6}$$

Equation (4.6) is used to determine stiffness coefficients in this static limit.^{17,18} Equation (4.5) is the dynamical generalization of Eq. (4.6) and, especially at elevated temperatures, should be used to give more realistic values for the stiffness coefficients.

The (EVN) fluctuation formulas corresponding to Eqs. (4.1), (4.4) and (4.5) are derived and discussed in Ref. 15. Besides the equilibrium properties determined by the above fluctuation formulas one could also write expressions for various transport coefficients using time-correlation averages.

It should be mentioned that one can also derive fluctuation formulas in the (HtN) ensemble. These have been presented by Parrinello and Rahman⁴ and Ray.¹⁶

It is not clear to what degree time correlation averages can be used to determine transport coefficients in the (HtN) ensemble. The time correlations would be influenced by the h equation which as we have seen is somewhat arbitrary, and contains an arbitrary constant. However, it is possible that in equilibrium the effects of the h equation would average out and not affect the final results. Only numerical studies could answer this question. Equilibrium properties of fluids in Andersen's (HPN) ensemble have been determined in Ref. 19 using (HPN) fluctuation formulas.

V. MOLECULAR DYNAMICS CALCULATIONS USING BOTH THE (HtN) and (EhN) ENSEMBLES

A combination of the (HtN) and (EhN) ensembles seems to be the best way at present of studying solids using molecular dynamics methods. The (HtN) ensemble is used to deter-

mine if structural transformations take place and the (EhN) ensemble is used to determine equilibrium and transport properties of the system. The structural transformations will not show up in the (EhN) calculations since the molecular dynamics cell is held fixed in size and shape and this inhibits structural transformations in small systems. Using the (EhN) ensemble to determine equilibrium and transport properties of the system removes any question of the h equation having any influence on the results. In a (EhN) molecular dynamics calculation we determine the equilibrium and transport properties of the system for a given value of the matrix h . For example we may determine $\overline{\mathcal{P}}$ and then use Eq. (3.9) to determine the tension tensor t . A different value of h may then be selected and the calculations repeated. At selected times one may use the values of $\overline{\mathcal{P}}$ obtained to run an (HtN) calculation with $\Gamma = h^{-1} \overline{\mathcal{P}} A$. This (HtN) calculation will detect if any structural transformations take place. Systematic studies can be carried out to compare the equilibrium and transport properties of systems as calculated in the (HtN) and (EhN) ensembles. One would expect that the equilibrium properties will be the same when calculated in these two ensembles,¹ but it is not clear whether transport properties will also be the same. We have made a few molecular dynamics calculations using the (HtN) and (EhN) ensembles; (HtN) calculations with a given value of t have been used to deter-

mine the average value of the h tensor. This value of h has then been used in an (EhN) calculation to determine the average value of the microscopic tension tensor η . We have found in these preliminary calculations that this value of $\bar{\eta}$ reproduces the starting value of t in the (HtN) calculation within accuracy of our calculations. One can also proceed in the reverse direction from the (EhN) ensemble to obtain $\bar{\eta} = t$ which can then be used in the (HtN) calculation to determine \bar{h} . Under conditions such that no structural transformation takes place in the (HtN) calculation, we have been able to, within the accuracy of our calculations, obtain the values of \bar{h} which are equal to values of h used in the beginning (EhN) calculation.

VI. CONCLUSIONS

In the molecular dynamics method of Parrinello and Rahman one allows the molecular dynamics cell to vary in size and shape. We have shown how this theory may be brought into accord with the theory of finite elasticity and the thermodynamics of anisotropic solids. The main changes from the original view are to: use the tensor of thermodynamic tension instead of the stress tensor, define the reference state of the system to be the state under zero stress. With these changes the basic structure of the Parrinello–Rahman theory remains intact and is brought into accord with the theory of finite elasticity and the thermodynamics of anisotropic solids.

The statistical ensemble generated by the Parrinello–Rahman theory is the isoenthalpic–isotension or (HtN) ensemble. The microcanonical counterpart to this ensemble is

the constant energy, constant size–shape ensemble. If we describe the size and shape of the molecular dynamics cell by the fixed tensor h then this is the (EhN) ensemble. We have presented various fluctuation formulas for the (EhN) ensemble involving the thermodynamic properties of solids. A combination of the (HtN) and (EhN) ensembles seems to be the best way to study solids at the present time.

- ¹H. C. Andersen, *J. Chem. Phys.* **72**, 2384 (1980).
- ²M. Parrinello and A. Rahman, *Phys. Rev. Lett.* **45**, 1196 (1980).
- ³M. Parrinello and A. Rahman, *J. Appl. Phys.* **52**, 7182 (1981).
- ⁴M. Parrinello and A. Rahman, *J. Chem. Phys.* **76**, 2662 (1982).
- ⁵M. Parrinello and A. Rahman, in *Melting Localization and Chaos*, edited by R. K. Kalia and P. Vashishta (Elsevier, New York, 1982).
- ⁶M. Parrinello, A. Rahman, and P. Vashishta, *Phys. Rev. Lett.* **50**, 1073 (1983).
- ⁷R. G. Munro and R. D. Mountain, *Phys. Rev.* **28**, 2261 (1983).
- ⁸S. Nose and M. L. Klein, *Phys. Rev. Lett.* **50**, 1207 (1983).
- ⁹D. Levesque, J. J. Weis and M. L. Klein, *Phys. Rev. Lett.* **51**, 670 (1983).
- ¹⁰J. R. Ray, *J. Chem. Phys.* **79**, 5128 (1983).
- ¹¹H. Goldstein, *Classical Mechanics* (Addison–Wesley, Reading, Mass., 1951).
- ¹²R. N. Thurston, in *Physical Acoustics*, edited by W. P. Mason (Academic, New York, 1964), Vol. 1, Part A.
- ¹³F. D. Murnaghan, *Finite Deformations of an Elastic Solid* (Wiley, New York, 1951).
- ¹⁴D. C. Wallace, in *Solid State Physics*, edited by H. Ehrenreich, F. Seitz, and D. Turnbull (Academic, New York, 1970), Vol. 25.
- ¹⁵J. R. Ray and H. W. Graben, *Mol. Phys.* **43**, 1293 (1981).
- ¹⁶J. R. Ray, *J. Appl. Phys.* **53**, 6441 (1982).
- ¹⁷M. Born and K. Huang, *Dynamical Theory of Crystal Lattices* (Oxford, London, 1954).
- ¹⁸N. H. Macmillan and A. Kelly, *Proc. Soc. London Ser. A* **330**, 291 (1972).
- ¹⁹J. M. Haile and H. W. Graben, *J. Chem. Phys.* **73**, 2412 (1980).