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# Strain fluctuations and elastic constants<sup>a)</sup>

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It is shown that the elastic strain fluctuations are a direct measure of elastic compliances in a general anisotropic medium; depending on the ensemble in which the fluctuation is measured either the isothermal or the adiabatic compliances are obtained. These fluctuations can now be calculated in a constant enthalpy and pressure, and hence, constant entropy, ensemble due to recent developments in the molecular dynamics techniques. A calculation for a Ni single crystal under uniform uniaxial 100 tensile or compressive load is presented as an illustration of the relationships derived between various strain fluctuations and the elastic moduli. The Born stability criteria and the behavior of strain fluctuations are shown to be related.

## I. INTRODUCTION

It was in a paper by Lebowitz, Percus, and Verlet<sup>1</sup> that a study was made of the ensemble dependence of fluctuations; in the same paper it was shown that fluctuations of the kinetic energy in a molecular dynamics calculation (which generates members of a micro-canonical ensemble of states) is related to the constant volume heat capacity. It has now become standard practice in molecular dynamics and Monte Carlo calculations to use fluctuations of various phase space functions to determine the thermodynamic properties of the system.

Recently, we have<sup>2</sup> presented a Lagrangian formulation for molecular dynamics calculations in which the ensemble of states corresponds to constant stress  $\mathbf{S}$ , enthalpy  $H$  (heat function), and number of particles  $N$ . A special case of this is where the constant stress is a hydrostatic pressure, thus giving a  $(p, H, N)$  ensemble. This was presented in another paper.<sup>3</sup>

In the following paper we show how the fluctuations of strain in an  $(\mathbf{S}, H, N)$  ensemble are related to adiabatic (constant entropy  $S$ ) compliances and hence to the elastic moduli of the system. In the case of the  $(p, H, N)$  ensemble the relevant compliance is the adiabatic compressibility.

## II. THE $(p, H, N)$ ENSEMBLE

There is no difference in principle between the treatment of the  $(p, H, N)$  and the  $(\mathbf{S}, H, N)$  ensemble for the purpose in hand. Hence, first because one is more familiar with the former and second, because of the simplicity in writing equations involving variables without indices, we shall first deal briefly with the  $(p, H, N)$  ensemble.

The thermodynamic relations are stated in the Appendix for completeness. As shown in Landau and Lifshitz,<sup>4</sup> in a  $(p, \beta, N)$  ensemble the volume fluctuations are

$$\langle (\Delta V)^2 \rangle_{p, \beta, N} = (V/\beta) \chi_S, \quad (1)$$

where  $\chi_S$ , the isothermal compressibility  $= -(1/V)(\partial V/\partial p)_T$ ; using Eqs. (A1) and (A3) and combining with Eq. (1)

$$\langle (\Delta V)^2 \rangle_{p, \beta, N} + (\partial \beta / \partial H)_p (\partial V / \partial \beta)_p^2 = (V/\beta) \chi_S. \quad (2)$$

From Lebowitz *et al.*<sup>1</sup> [their Eq. (2.12)], we see that the left-hand side of the above equation is precisely  $\langle (\Delta V)^2 \rangle_{p, H, N}$ . Hence (as has already been shown by Haile and Graben<sup>5</sup>)

$$\langle (\Delta V)^2 \rangle_{p, H, N} = (V/\beta) \chi_S. \quad (3)$$

Thus, volume fluctuations in a system with constant pressure, constant enthalpy, and constant number of particles are just a measure of the adiabatic compressibility. (See the last remark in the Appendix.)

## III. THE $(\mathbf{S}, H, N)$ ENSEMBLE

In dealing with anisotropic media under the influence of a general stress tensor the elastic energy,  $V_{e1}$ , is usually written as

$$V_{e1} = \Omega_0 \text{Tr}(\mathbf{S}\epsilon), \quad (4)$$

where  $\Omega_0$  is the unstrained volume and  $\epsilon$  the strain tensor, assumed small enough for the above expression to be a valid approximation. (The sign convention is usually taken to be  $\mathbf{S} = -p$  when  $\mathbf{S}$  is isotropic.)

With the above  $V_{e1}$ , the expression for the probability of a fluctuation takes the form<sup>4</sup>

$$\omega \propto \exp[-\beta/2 \{ \Delta T \Delta S + \Omega_0 \text{Tr}(\Delta \mathbf{S} \Delta \epsilon) \}]. \quad (5)$$

But

$$\Delta S = C_\epsilon \Delta T/T - \Omega_0 \text{Tr}[(\partial \mathbf{S} / \partial T) \Delta \epsilon],$$

where  $C_\epsilon$  is the heat capacity at constant strain. Hence

$$\omega \propto \exp[-\beta/2 \{ (C_\epsilon/T)(\Delta T)^2 + \Omega_0 (\partial S_{ij} / \partial \epsilon_{kl})_T \Delta \epsilon_{ij} \Delta \epsilon_{kl} \}], \quad (6)$$

where summation over repeated indices is understood. From this it follows that in a  $(\mathbf{S}, \beta, N)$  ensemble

$$\langle \Delta \epsilon_{ij} \Delta \epsilon_{kl} \rangle_{\mathbf{S}, \beta, N} = (kT/\Omega_0) (\partial \epsilon_{ij} / \partial S_{kl})_T. \quad (7)$$

The equation corresponding to Eq. (2.12) of Ref. (1) is now

<sup>a)</sup>Work supported by the U. S. Department of Energy.

$$\langle \Delta \epsilon_{ij} \Delta \epsilon_{kl} \rangle_{S, H, N} = \langle \Delta \epsilon_{ij} \Delta \epsilon_{kl} \rangle_{S, \beta, N} + (\partial \beta / \partial H)_S (\partial \epsilon_{ij} / \partial \beta)_S (\partial \epsilon_{kl} / \partial \beta)_S. \quad (8)$$

Analogous to Eq. (A3) we have  $(\partial \beta / \partial H)_S = -k\beta^2 / C_S$ , where  $C_S$  is the constant stress heat capacity; the equation analogous to Eq. (A1) is

$$(\partial \epsilon_{ij} / \partial S_{kl})_S = (\partial \epsilon_{ij} / \partial S_{kl})_S + \Omega_0 (k\beta^3 / C_S) (\partial \epsilon_{ij} / \partial \beta)_S (\partial \epsilon_{kl} / \partial \beta)_S. \quad (9)$$

Using Eq. (7) and Eq. (9) we get from Eq. (8)

$$\langle \Delta \epsilon_{ij} \Delta \epsilon_{kl} \rangle_{S, H, N} = (kT / \Omega_0) (\partial \epsilon_{ij} / \partial S_{kl})_S. \quad (10)$$

It is customary to use elastic moduli  $C_{ij,kl}^S \equiv (\partial S_{kl} / \partial \epsilon_{ij})_S$  rather than the compliances. Let us denote by  $C^S$  the  $9 \times 9$  matrix of the adiabatic elastic moduli so that the modulus  $C_{ij,kl}^S$  is the  $(ij, kl)$  element of  $C^S$ . Then we can go from the moduli to the compliances by a matrix inversion, to get

$$\langle \Delta \epsilon_{ij} \Delta \epsilon_{kl} \rangle_{S, H, N} = (kT / \Omega_0) (C^S)^{-1}_{ij,kl}. \quad (11)$$

#### IV. BORN STABILITY CRITERIA

We have shown in Sec. III that at constant stress, constant enthalpy, and constant number, (in other words at constant entropy) the strain-strain correlation function is given by the adiabatic elastic compliance. The matrix of the adiabatic elastic moduli  $C_{ij,kl}^S = (\partial S_{kl} / \partial \epsilon_{ij})_S$ , was denoted by  $C^S$ . In other words,  $S = C^S \epsilon$  and hence  $\epsilon = (C^S)^{-1} S$ ; the compliance  $(\partial \epsilon_{ij} / \partial S_{kl})_S = (C^S)^{-1}_{ij,kl}$  [Eq. (11)]. This element of  $(C^S)^{-1}$  is the algebraic complement of the element  $C_{kl,ij}^S$  of  $C^S$  divided by the determinant of  $C^S$ . [Similar statements of course can be made for the  $(S, \beta, N)$  ensemble as well except that instead of the superscript  $S$  for constant entropy one will show  $T$  to indicate isothermal elastic moduli.]

The stability criteria of Born state that a *necessary* condition for crystal stability is that the quadratic form  $\epsilon C \epsilon \equiv C_{ij,kl} \epsilon_{ij} \epsilon_{kl}$  be positive definite.<sup>8</sup> Instability can occur with the vanishing of a principal minor of the determinant of  $C$ . This implies that a divergence in some of the correlations  $\langle \Delta \epsilon_{ij} \Delta \epsilon_{kl} \rangle$  will occur when the Born stability criteria are violated.

#### V. MOLECULAR DYNAMICS AT CONSTANT APPLIED STRESS

The three stages prior to the formulation of new molecular dynamics equations of relevance here were the following.

(i) The traditional case of generating a microcanonical ensemble of states using the Lagrangian

$$\mathcal{L}_1 = \frac{1}{2} \sum m_i \dot{\mathbf{r}}_i^2 - V(\mathbf{r}_1, \dots, \mathbf{r}_N). \quad (12)$$

Periodic boundary conditions are applied, most often, in the form of a repeating cubic cell of volume  $L^3$ . The point to note is that  $L$  is a constant and can be used as the unit of length.

(ii) The introduction of a time dependent volume  $\Omega(t)$  by Andersen<sup>7</sup> who used

$$\mathcal{L}_2 = \Omega^{2/3} \frac{1}{2} \sum m_i \dot{\mathbf{s}}_i^2 - V + \frac{1}{2} C \dot{\Omega}^2 - p \Omega, \quad (13)$$

where  $\mathbf{s}_i = \mathbf{r}_i / \Omega^{1/3}$ . Periodic boundary conditions of the usual kind give a pulsating cubic box which changes in time according to a Lagrangian equation of motion.<sup>7</sup> The role of the constant  $C$  in Eq. (13) is discussed by Andersen.<sup>7</sup>

(iii) The introduction of a time dependent shape by Parrinello and Rahman<sup>3</sup> who used vectors  $\mathbf{a}(t)$ ,  $\mathbf{b}(t)$ , and  $\mathbf{c}(t)$  to define the molecular dynamics cell and used (a prime indicating the transpose)

$$\mathcal{L}_3 = \frac{1}{2} \sum m_i \dot{\mathbf{s}}_i' \mathbf{G} \dot{\mathbf{s}}_i - V + \frac{1}{2} W \text{Tr} \dot{\mathbf{h}} \dot{\mathbf{h}} - p \Omega, \quad (14)$$

where  $\mathbf{r}_i = \mathbf{h} \mathbf{s}_i$ ,  $\mathbf{h}(t) = \{\mathbf{a}, \mathbf{b}, \mathbf{c}\}$ ,  $\mathbf{G} = \mathbf{h}' \mathbf{h}$ , and  $\Omega = \|\mathbf{h}\|$  and  $W$  is a mass associated with the coordinates  $h_{\lambda\mu}$ . Periodic boundary conditions of the usual kind give a pulsating molecular dynamics cell of arbitrary shape which changes according to Lagrangian equations of motion.<sup>3</sup>

The final step in this development is the introduction of an anisotropic stress tensor  $\mathbf{S}$  in place of  $p$  in  $\mathcal{L}_3$ .

This was done by the authors<sup>2</sup> in the following manner. The elements that are used in constructing  $\mathcal{L}_3$  naturally lend themselves to the introduction of the notion of strain. The concept of strain and that of the metric tensor are intimately connected and, as surely has been noticed,  $\mathbf{G}$  the metric tensor is an integral part of the Lagrangian  $\mathcal{L}_3$ .

In describing a strained state of a system one needs a so-called reference state; for this we shall use the matrix  $\mathbf{h}_0$  and the corresponding volume  $\Omega_0 = \|\mathbf{h}_0\|$ . The matrix  $\mathbf{h}_0$  can be used to set up a mapping between space points  $\mathbf{r}$  and a dimensionless vector  $\xi$ , i.e.,  $\mathbf{r} = \mathbf{h}_0 \xi$ . A homogeneous distortion changes  $\mathbf{h}_0$  to  $\mathbf{h}$ , moving  $\mathbf{r}$  to  $\mathbf{d}$ , where  $\mathbf{d} = \mathbf{h} \xi = \mathbf{h} \mathbf{h}_0^{-1} \mathbf{r}$ . Hence the displacement  $\mathbf{u}$  (at  $\mathbf{r}$ ) due to the distortion is  $\mathbf{d} - \mathbf{r}$  or

$$\mathbf{u} = (\mathbf{h} \mathbf{h}_0^{-1} - 1) \mathbf{r}. \quad (15)$$

The strain tensor  $\epsilon$  is defined as<sup>8</sup>

$$\epsilon_{\lambda\mu} = \frac{1}{2} \left( \frac{\partial u_\lambda}{\partial r_\mu} + \frac{\partial u_\mu}{\partial r_\lambda} + \sum_\nu \frac{\partial u_\nu}{\partial r_\mu} \frac{\partial u_\nu}{\partial r_\lambda} \right). \quad (16)$$

Hence, we find

$$\epsilon = \frac{1}{2} (\mathbf{h}_0'^{-1} \mathbf{G} \mathbf{h}_0^{-1} - 1). \quad (17)$$

If  $\mathbf{S}$  denotes the external stress the elastic contribution to the energy will be, from Eq. (4),

$$V_{\mathbf{S}} = \frac{1}{2} \Omega_0 \text{Tr} \mathbf{S} (\mathbf{h}_0'^{-1} \mathbf{G} \mathbf{h}_0^{-1} - 1). \quad (18)$$

The new Lagrangian  $\mathcal{L}_s$ , which takes account of the anisotropic strain will then be, on leaving out inconsequential constant energy terms,

$$\mathcal{L}_s = \frac{1}{2} \sum m_i \dot{\mathbf{s}}_i' \mathbf{G} \dot{\mathbf{s}}_i - V + \frac{1}{2} W \text{Tr} \dot{\mathbf{h}} \dot{\mathbf{h}} + \frac{1}{2} \text{Tr} \sum \mathbf{G}, \quad (19)$$

where

$$\Omega_0^{-1} \sum = \mathbf{h}_0^{-1} \mathbf{S} \mathbf{h}_0'^{-1}. \quad (20)$$

The equations of motion arising out of  $\mathcal{L}_s$  are simple

to write down and have been given elsewhere. The point of interest here is that the above Lagrangian gives a constant of motion  $\mathcal{H}$  which is

$$\mathcal{H} = \sum_i \frac{1}{2} m_i \mathbf{v}_i^2 + V + \frac{1}{2} W \text{Tr} \dot{\mathbf{h}} \dot{\mathbf{h}} - \Omega_0 \text{Tr} \mathbf{S} \boldsymbol{\epsilon}, \quad (21)$$

with  $\mathbf{v}_i$  indicating  $\mathbf{h} \dot{\mathbf{s}}_i$ .

In equilibrium, at temperature  $T$ , the term in  $W$  contributes  $(9/2)k_B T$  while the term with  $m_i$ 's contributes  $(3N/2)k_B T$ . Hence to an accuracy of  $3:N$ , the enthalpy

$$H = E - V_{\text{el}}, \quad (22)$$

$$E = \sum_i \frac{1}{2} m_i \mathbf{v}_i^2 + V, \quad (23)$$

is a constant of the motion.

The formal development of Sec. III and the fact that under  $\mathcal{L}_s$  one generates an  $(\mathbf{S}, H, N)$  ensemble allows us to conclude that in a molecular dynamics calculation using  $\mathcal{L}_s$  the elastic constants of the system can be determined from Eq. (10) of Sec. III.

## VI. SPECIAL CASE OF TETRAGONAL SYMMETRY

As an application of the above general development we shall consider a system having tetragonal symmetry with  $[100]$  as the direction of tetragonal symmetry. We can write the following set of nonredundant equations [using for notation  $D = C_{11,11}(C_{22,22} + C_{22,33}) - 2C_{11,22}^2$  and  $\epsilon^{\pm} = (\epsilon_{22} \pm \epsilon_{33})/\sqrt{2}$ ],

$$\langle \Delta \epsilon_{11} \Delta \epsilon_{11} \rangle = (kT/\Omega_0)(C_{22,22} + C_{22,33})/D, \quad (24.1)$$

$$\langle \Delta \epsilon_{11} \Delta \epsilon^+ \rangle = (kt/\Omega_0)\sqrt{2}(-C_{11,22})/D, \quad (24.2)$$

$$\langle \Delta \epsilon^+ \Delta \epsilon^+ \rangle = (kT/\Omega_0)C_{11,11}/D, \quad (24.3)$$

$$\langle \Delta \epsilon^- \Delta \epsilon^- \rangle = (kt/\Omega_0)/(C_{22,22} - C_{22,33}), \quad (24.4)$$

$$\langle \Delta \epsilon_{23} \Delta \epsilon_{23} \rangle = (kT/\Omega_0)/C_{23,23}, \quad (24.5)$$

$$\langle \Delta \epsilon_{12} \Delta \epsilon_{12} \rangle = (kT/\Omega_0)/C_{12,12}. \quad (24.6)$$

The Born conditions for this case are

$$C_{11,11} > 0; \quad C_{11,11}C_{22,22} - C_{11,22}^2 > 0;$$

$$(C_{22,22} - C_{22,33})D > 0; \quad C_{23,23} > 0; \quad C_{12,12} > 0.$$

These are equivalent to

$$C_{11,11} > 0; \quad C_{22,22} - C_{22,33} > 0; \quad D > 0; \quad C_{23,23} > 0; \quad C_{12,12} > 0.$$

Thus the four denominators in Eqs. (24.1)–(24.6) are the quantities whose vanishing defines the boundary of the elastic stability region

$$C_{11,11}(C_{22,22} + C_{22,33}) - 2C_{11,22}^2 = 0, \quad (25.1)$$

$$C_{22,22} - C_{22,33} = 0, \quad (25.2)$$

$$C_{23,23} = 0, \quad (25.3)$$

$$C_{12,12} = 0. \quad (25.4)$$

The condition  $C_{11,11} = 0$  need not be included in the list of conditions that define the boundary of the region of stability since for a sufficiently small and positive  $C_{11,11}$  the condition in Eq. (25.1) is already satisfied.

## VII. CONCLUDING REMARKS AND AN ILLUSTRATION

The general result given in Eq. (11) and hence also the special case of tetragonal symmetry shown in Eq. (24), implies that certain strain fluctuations will be enhanced as a result of a reduction in the value of one or more of the principal minors of the matrix of elastic moduli. In this context of enhanced strain fluctuations we recall the Lindemann criterion for mechanical instability in crystals and assert that mechanical failure will occur when these fluctuations are so large that the underlying atomic displacements become a sizable fraction of the atomic spacing.

However, one should not overlook the possible presence of short wavelength phonons which due to the vanishing of the vibration frequency can also lead to instability even when none of the minors of the matrix of elastic moduli is small enough to produce large strain fluctuations that are being discussed here.

The possible divergent behavior of strain fluctuations is similar to what occurs at the liquid–gas phase transition where the bulk modulus goes to zero and volume fluctuations diverge. Hence if there is an elastically driven second order transition between different polymorphic crystalline phases then there will occur divergences in the strain fluctuations for the appropriate values of temperature and stress.

From Eq. (11) we expect that one or more of the strain fluctuations will be enhanced if, under suitable conditions of temperature and external stress, the elastic constants are brought close to the Born condition  $\det \mathbf{C} = 0$ . Light scattering experiments using a crystal at a suitable temperature and/or suitable conditions of external stress might indeed confirm this phenomenon.

As regards the special case treated in Sec. VI, there are certain aspects of Eqs. (24) and Eqs. (25) which are worth dwelling upon. The four conditions, Eq. (25.1) to Eq. (25.4), are independent, and hence when one holds the other three need not be satisfied.

When Eq. (25.1) is satisfied, i.e., when  $D$  defined in Sec. VI is zero, then Eqs. (24.1), (24.2), and (24.3) show a divergence whereas Eq. (24.4), (24.5), and (24.6) remain finite. Thus, when the condition  $D = 0$  is approached,  $\epsilon_{22}$  and  $\epsilon_{33}$  must fluctuate in phase so as to prevent  $\epsilon^- = (\epsilon_{22} - \epsilon_{33})/\sqrt{2}$  from having large fluctuations. On the other hand, when the condition  $C_{22,22} - C_{22,33} = 0$  is approached we must have  $\epsilon_{22}$  and  $\epsilon_{33}$  fluctuating out of phase.

Thus, even if the theoretical stability limits [Eqs. (25.1) to (25.4)] are not reached, and this will be so in most practical situations, we expect that the trends described above may be observable under suitable temperature and stress conditions. We have recently reported on a molecular dynamics study<sup>2</sup> of the effect of uniaxial stress on a single crystal of Ni. This data is being analyzed from the point of view of the behavior of strain fluctuations dealt with in the present paper. To illustrate the observation made above about the phase relation between the fluctuations of  $\epsilon_{22}$  and  $\epsilon_{33}$  we will

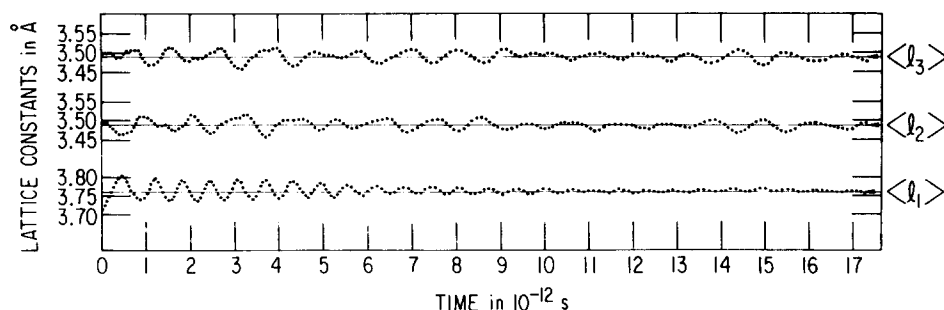


FIG. 1. Fluctuation of the three lattice constants of a tetragonal structure generated by applying a tensile load to an fcc crystal of Ni. Strain components can be calculated from the  $l_i$  shown above;  $(l_i - \langle l_i \rangle) / \langle l_i \rangle$  is a good approximation (Ref. 2) for  $\epsilon_{ii}$ . The condition  $C_{22,22} = C_{22,33}$  is close to being satisfied at this load; see Eqs. (24.3) and (24.4) for consequences.

briefly mention one of the several calculations on Ni already reported.<sup>2</sup>

On applying a [100] tensile load to a single crystal of fcc Ni one obtains a face-centered tetragonal structure. Under conditions of zero load and a temperature of 356 K the model<sup>9</sup> of Ni we have used<sup>2</sup> gave a stable perfect fcc lattice in thermal motion, the lattice constant being  $3.55 \pm 0.09$  Å. As the load was increased the lattice became tetragonal and at a tensile load of  $8.6 \times 10^{10}$  dyn cm<sup>-2</sup> and 330 K, the two lattice constants became  $3.76 \pm 0.01$  and  $3.49 \pm 0.01$  Å. This state of the system was perfectly stable over a long MD calculation of  $1.7 \times 10^{11}$  s. Further details about many such calculations are in Ref. 2. One more detail from Ref. 2 is relevant. According to static calculations of Milstein<sup>10</sup> at about  $16 \times 10^{10}$  dyn cm<sup>-2</sup>, the Born condition [Eq. (25.2)]  $C_{22,22} = C_{22,33}$  is satisfied. (Our dynamical calculation<sup>2</sup> showed system failure to occur already at  $\sim 11 \times 10^{10}$  dyn/cm<sup>2</sup>.)

The time behavior of the three lattice constants for the system described above, i.e., for a stable tetragonal structure at 330 K and tensile [100] load of  $8.6 \times 10^{10}$  dyn cm<sup>-2</sup> is shown in Fig. 1. In spite of the noisy features we see from this figure that  $\epsilon_{22}$  and  $\epsilon_{33}$  are out of phase, in complete accord with the prediction of Eqs. (24.3) and (24.4).

On applying a compressive [100] load the static calculations of Milstein<sup>10</sup> show that at a load of about  $7 \times 10^{10}$  dyn cm<sup>-2</sup> the instability criterion  $D=0$  [Eq. (25.1)] is satisfied. (Our dynamical calculations<sup>2</sup> showed a polymorphic transition to occur at a value slightly lower than  $7 \times 10^{10}$  dyn cm<sup>-1</sup>.)

The time behavior of the three lattice constants for a stable tetragonal structure at 356 K and compressive [100] load of  $5.25 \times 10^{10}$  dyn cm<sup>-2</sup> is shown in Fig. 2. In spite of the noise we can see (i) that  $\epsilon_{22}$  and  $\epsilon_{33}$  are in phase, (ii) that  $\epsilon_{11}$  is out of phase with those two, and (iii) that the fluctuation  $\epsilon_{11}$  is larger than that of the other two. Statement (i) is in accord with Eqs. (24.3) and (24.4), (ii) is a consequence of Eq. (24.2) since<sup>11</sup>  $C_{11,22} > 0$ , and (iii) is in accord with Eq. (24.1).

The time scale of the fluctuations shown in Figs. 1 and 2 is dependent on the choice of  $W$ , see Eq. (19). The statistical averages we have dealt with here do not depend on this choice. This has been discussed by Andersen,<sup>7</sup> Haile and Graben,<sup>5</sup> and Parrinello and Rahman.<sup>2,3</sup>

We finally note that a different method for the numerical calculation of the isothermal elastic constants of crystalline systems has been proposed by Squire *et al.*<sup>12</sup> An extension of their method to noncrystalline systems

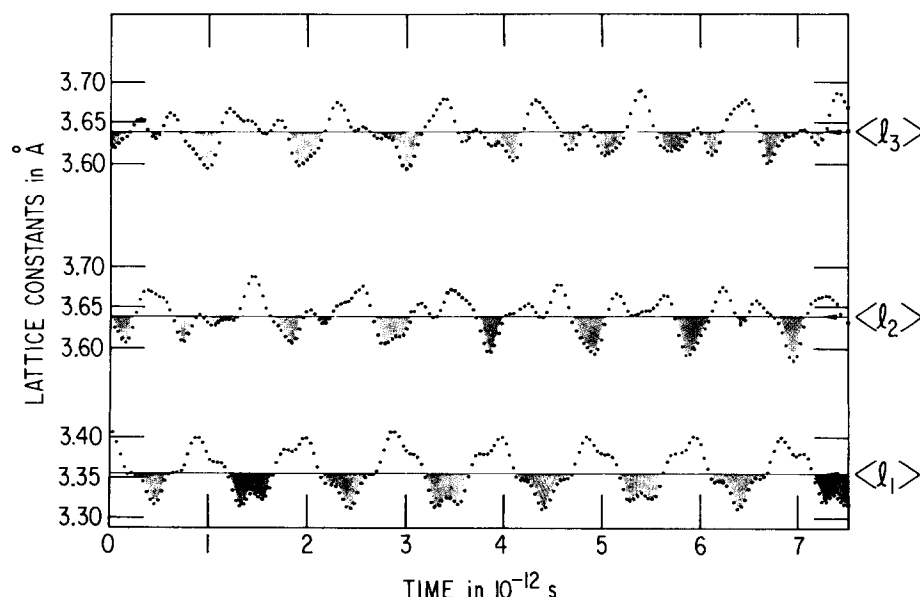


FIG. 2. System under a compressive load. The condition  $D = C_{11,11}(C_{22,22} + C_{22,33}) - 2C_{11,22}^2 = 0$  is close to being satisfied; see Eqs. (24.1), (24.2), (24.3), and (24.4) for consequences. The shading is to show the phase relation between  $\Delta\epsilon_{11}$ ,  $\Delta\epsilon_{22}$ , and  $\Delta\epsilon_{33}$ .

does not seem to be straightforward. In contrast, the computational scheme described above seems to be suitable for all systems, crystalline or otherwise. This remark is of particular significance in the study of superionic conductors. These have normal solid-like elastic behavior but one or more of the constituents have large liquid-like constants of self-diffusion. However, extensive calculations are necessary before one can assess the practical merits and limitations of the method. We plan to undertake such calculations in the near future.

## APPENDIX

Using  $p, T$  as variables,

$$\begin{aligned} \left(\frac{\partial V}{\partial p}\right)_S &= \left(\frac{\partial V(p, T)}{\partial p}\right)_{S(p, T)} = \left(\frac{\partial V}{\partial p}\right)_T + \left(\frac{\partial V}{\partial T}\right)_p \left(\frac{\partial T}{\partial p}\right)_S \\ &= \left(\frac{\partial V}{\partial p}\right)_T - \left(\frac{\partial V}{\partial T}\right)_p \left(\frac{\partial T}{\partial S}\right)_p \left(\frac{\partial S}{\partial p}\right)_T \\ &= \left(\frac{\partial V}{\partial p}\right)_T - (T/C_p) \left(\frac{\partial V}{\partial T}\right)_p \left[-\left(\frac{\partial V}{\partial T}\right)_p\right] \end{aligned} \quad (\text{A1})$$

or

$$\left(\frac{\partial V}{\partial p}\right)_S = \left(\frac{\partial V}{\partial p}\right)_T - k\beta^3/C_p \left(\frac{\partial V}{\partial \beta}\right)_p^2. \quad (\text{A1})$$

We also have the enthalpy  $H = U + pV$ , and

$$dH = dS/k\beta + Vdp, \quad (\text{A2})$$

$$\left(\frac{\partial \beta}{\partial H}\right)_p = -k\beta^2/C_p. \quad (\text{A3})$$

We note finally from Eq. (A2) that for  $p$  and  $H$  constant  $dS = 0$ .

- <sup>1</sup>J. L. Lebowitz, J. K. Percus, and L. Verlet, *Phys. Rev.* **153**, 250 (1967).
- <sup>2</sup>M. Parrinello and A. Rahman, *J. Appl. Phys.* **52**, 7182 (1981).
- <sup>3</sup>M. Parrinello and A. Rahman, *Phys. Rev. Lett.* **45**, 1196 (1980).
- <sup>4</sup>L. D. Landau and E. M. Lifshitz, *Statistical Physics* (Addison-Wesley, Reading, Mass., 1958).
- <sup>5</sup>J. M. Haile and H. W. Graben, *Mol. Phys.* **40**, 1433 (1980).
- <sup>6</sup>M. Born and K. Huang *Dynamical Theory of Crystal Lattices* (Clarendon, Oxford, 1954).
- <sup>7</sup>H. C. Andersen, *J. Chem. Phys.* **72**, 2384 (1980).
- <sup>8</sup>L. S. Landau and E. M. Lifshitz, *Theory of Elasticity* (Addison-Wesley, Reading, Mass., 1959).
- <sup>9</sup>F. Milstein, *J. Appl. Phys.* **44**, 3825 (1973).
- <sup>10</sup>F. Milstein, *J. Appl. Phys.* **44**, 3833 (1973).
- <sup>11</sup>As is shown by Milstein (Ref. 10), for central pairwise interactions, the conditions  $C_{23,23}$  and  $C_{22,22} > 0$  are equivalent to  $C_{11,22} > 0$ . In the same paper Milstein has given a plot of  $C_{11,22}$  against stress.
- <sup>12</sup>D. R. Squire, A. C. Holt, and W. G. Hoover, *Phys.* **42**, 388 (1969).