Stability criteria for homogeneously stressed materials and the calculation of elastic constants

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Second-order elastic constants cannot be applied directly to the study of the mechanical stability of a stressed material. We derive general expressions for stability criteria by constructing appropriate thermodynamic potentials. For a system under isotropic initial stress, elastic stiffness coefficients which govern stress-strain relations can be used as stability criteria. However, for a system under anisotropic initial stress, stability criteria are different from either elastic constants or elastic stiffness coefficients. We show that stability conditions in the constant pressure ensemble are stronger than in the constant volume ensemble, i.e., a state can be stable in the constant volume ensemble but unstable in the constant pressure ensemble. From the general formalism simple fluctuation formulas for the stability criteria are deduced for systems in the canonical ensemble, for arbitrary stress.[S0163-1829(96)01130-7]

I. INTRODUCTION

Elastic constants provide important information concerning the strength of materials, and often act as stability criteria or order parameters to study the problem of structural transformations. For comparison of experimental results with theory, it is necessary not only to have accurate experimental data, but also to have a reliable method of calculation. Recent advances in computer-simulation techniques and formalism have made this possible.[1–8]

In spite of significant progress, there are still some outstanding issues, in particular on how to deal with systems under stress, especially when far from their equilibrium configuration. For systems under arbitrary stress, we derive a general stability criterion and clarify some points concerning the calculation of the relevant elastic constants when using ''equilibrium'' fluctuation formulas.

Elastic constants are often used as stability criteria without giving much justification. Barron and Klein[9] were the first to clarify this situation. They pointed out that the traditional definition of the elastic constants derived from the internal energy or Helmholtz free energy cannot be directly applied to the study of the stress-strain relationship of a stressed state. They derived the correct form of the stress-strain relations for a stressed system in the microcanonical or canonical ensembles. Wang and co-workers[10,11] demonstrated, however, that elastic constants cannot be used as stability criteria for a stressed system. They suggested the use of elastic stiffness coefficients as stability criteria for isotropic stress. For anisotropic stress, they obtained a more general form from path-dependent finite displacements.[11] We establish the thermodynamic foundation of their argument and elaborate on their significance.

We also show that stability conditions are dependent on the ensemble used. In particular, stability conditions are stronger in the constant pressure ensemble than in the constant volume ensemble, i.e., a state can be stable in the constant volume ensemble but unstable in the constant pressure ensemble. In systems with anisotropic stress, several ensembles can also be envisaged.

We emphasize in this paper that, when using ''equilibrium'' fluctuation formulas for the calculation of elastic constants, the reference configuration (i.e., before virtual deformations are applied to the system) must be the stressed one. With a single shape tensor, simple fluctuation formulas, convenient for computer simulations, are obtained for a system under arbitrary stress in the canonical ensemble.

The paper is organized as follows. After a brief review of some fundamental concepts in Sec. II, Sec. III establishes the connection between stability criteria and elastic constants. Section IV derives stability criteria for a stressed system for both isotropic and anisotropic stresses, with and without volume fluctuations. In Sec. V we present, within the canonical ensemble, general fluctuation formulas for elastic constants, elastic stiffness coefficients, and stability criteria, and specific ones for systems with central force interactions. A simple illustrative example is given at the end of the section. A summary concludes the paper.

II. FUNDAMENTAL CONCEPTS

We first recall some fundamental concepts to introduce the formulas on which our discussion is based. The variety of terminology and symbols used in this field make this presentation necessary.

A. Strain

In the theory of elastic continuum, we can assign to every point in the material a coordinate $\mathbf{x}$.[9,12–14] After deformation, the displacement of a point initially at $\mathring{\mathbf{x}}$ is

$$\mathbf{u}(\mathring{\mathbf{x}}) = \mathbf{x}(\mathring{\mathbf{x}}) - \mathring{\mathbf{x}}$$

or

$$u_\alpha(\mathring{\mathbf{x}}) = x_\alpha(\mathring{\mathbf{x}}) - \mathring{x}_\alpha, \quad \alpha = 1,2,3. \tag{1}$$

$\mathring{\mathbf{x}}$ is also referred to as the reference position of $\mathbf{x}$. The reference state can be either stressed or stress free.

For a small deformation, we can write

$$u_\alpha(\mathring{\mathbf{x}}) = \frac{\partial u_\alpha(\mathring{\mathbf{x}})}{\partial \mathring{x}_\beta}\mathring{x}_\beta \equiv u_{\alpha\beta}(\mathring{\mathbf{x}})\mathring{x}_\beta . \tag{2}$$

In this equation, and all subsequent, the Einstein summation convention for repeated suffices is followed. Note that in general $u_{\alpha\beta} \neq u_{\beta\alpha}$. Sometimes the deformation parameters $u_{\alpha\beta}$ are also called the strain tensor (for instance, see Refs. 13 and 15).

For simplicity, we shall consider only systems under homogeneous deformation,[9,12–14,16] so the $u_{\alpha\beta}(\mathring{\mathbf{x}})$ are independent of $\mathring{\mathbf{x}}$.

$u_{\alpha\beta}$ can be written as

$$u_{\alpha\beta} = e_{\alpha\beta} + \omega_{\alpha\beta}, \tag{3}$$

with

$$e_{\alpha\beta} = \tfrac{1}{2}(u_{\alpha\beta} + u_{\beta\alpha}) = e_{\beta\alpha} \tag{4}$$

and

$$\omega_{\alpha\beta} = \tfrac{1}{2}(u_{\alpha\beta} - u_{\beta\alpha}) = -\omega_{\beta\alpha}, \tag{5}$$

where $e_{\alpha\beta}$ are the components of the elongation or pure strain tensor, and $\omega_{\alpha\beta}$ those of the rotation tensor.[9,14] In general, $\omega_{\alpha\beta}$ are disregarded for a small deformation since they represent an infinitesimal rotation of the whole system, and in the absence of internal torques cannot give rise to stresses.

The elongation $e_{\alpha\beta}$ is preferably used in experiments, since it is what is measured. In constrast, another strain, the Lagrangian strain tensor,[9,14] defined by

$$\eta_{\alpha\beta} \equiv \tfrac{1}{2}(u_{\alpha\beta} + u_{\beta\alpha} + u_{\gamma\alpha}u_{\gamma\beta}) = \eta_{\beta\alpha}, \tag{6}$$

is more often used in theoretical models, as it can completely determine the deformation of the system.[9,13,14] An advantage of the Lagrangian strain tensor is that, if we expand a function in a power series of η, the expansion coefficients will automatically satisfy the requirement of rotational invariance.[13]

In the following, when we refer to strain, we shall refer to the Lagrangian strain tensor. Another often used symbol for the Lagrangian strain tensor is $\epsilon_{\alpha\beta}$.[4–7]

B. Elastic constants

Elastic constants, or more exactly, second-order elastic constants, are in general defined by

$$\mathring{C}_{\alpha\beta\sigma\tau} \equiv \frac{1}{V_o}\left(\frac{\partial^2 W}{\partial \eta_{\alpha\beta}\partial \eta_{\sigma\tau}}\right)_{\eta=0}, \tag{7}$$

where W is the strain energy. It can refer either to the Helmholtz free energy F in the derivation of isothermal elastic constants (the canonical ensemble) or to the internal energy E in the derivation of adiabatic elastic constants (the microcanonical ensemble). V_o is the reference value of the volume V, i.e., before deformation. By definition the elastic constants have the following symmetries:

$$\mathring{C}_{\alpha\beta\sigma\tau} = \mathring{C}_{\sigma\tau\alpha\beta} = \mathring{C}_{\alpha\beta\tau\sigma}. \tag{8}$$

Equation (8) reduces the number of independent elastic constants from 81 to 21, which are often expressed in the condensed Voigt notation (for instance $\mathring{C}_{1111} = \mathring{C}_{11}$, $\mathring{C}_{1122} = \mathring{C}_{12}$, $\mathring{C}_{1212} = \mathring{C}_{44}$, etc.).

For a central force system, we can derive $\mathring{C}_{\alpha\beta\sigma\tau}$ straightforwardly from its definition, since the strain energy W can be written explicitly as a function of η by using[9,12,14]

$$\mathbf{x}^2 - \mathring{\mathbf{x}}^2 = 2\,\eta_{\alpha\beta}\mathring{x}_\alpha\mathring{x}_\beta . \tag{9}$$

But for a noncentral force system, we have to use a different approach since in general it is impossible to express the strain energy explicitly as a function of η. Instead, we can expand $(W - W_o)/V_o$ as a Taylor series,[12]

$$\frac{W - W_o}{V_o} = \mathring{S}_{\alpha\beta}u_{\alpha\beta} + \tfrac{1}{2}\mathring{S}_{\alpha\beta\sigma\tau}u_{\alpha\beta}u_{\sigma\tau} + \cdots \tag{10}$$

$$= \mathring{c}_{\alpha\beta}\eta_{\alpha\beta} + \tfrac{1}{2}\mathring{C}_{\alpha\beta\sigma\tau}\eta_{\alpha\beta}\eta_{\sigma\tau} + \cdots, \tag{11}$$

where W_o is the reference value of W. $\mathring{S}_{\alpha\beta}$ is the component of the applied stress tensor[9,13,14] for the reference state. The tensors $\mathring{S}_{\alpha\beta\sigma\tau}$ related to the elastic constants are sometimes called displacement gradient moduli.

We do not discuss the higher-order terms of Eqs. (10) and (11) in this paper. They are only necessary when the stability criteria are zero.

Substituting Eq. (6) into Eq. (11) and using Eq. (10), we find,[9] with the assumption of rotational invariance,

$$\mathring{c}_{\alpha\beta} = \mathring{S}_{\alpha\beta} \quad \text{and} \quad \mathring{C}_{\alpha\beta\sigma\tau} = \mathring{S}_{\alpha\beta\sigma\tau} - \mathring{S}_{\beta\tau}\delta_{\alpha\sigma}. \tag{12}$$

These relations in Eq. (12) assume rotational invariance, in particular $\mathring{S}_{\alpha\beta} = \mathring{S}_{\beta\alpha}$.

C. Stress-strain relations

In thermodynamics, a thermodynamic stress tensor $t_{\alpha\beta}$, defined by

$$t_{\alpha\beta} = \frac{1}{V_o}\frac{\partial W}{\partial \eta_{\alpha\beta}} = \mathring{S}_{\alpha\beta} + \mathring{C}_{\alpha\beta\sigma\tau}\eta_{\sigma\tau}, \tag{13}$$

is introduced.[14] (Often an opposite sign for $t_{\alpha\beta}$ is used than that in Refs. 4 and 7.) $t_{\alpha\beta}$ should not be confused with the applied stress $T_{\alpha\beta}$.

The actual measurable stress $T_{\alpha\beta}$ corresponds to the strained system,[9] and its reference configuration is different from that of $\mathring{C}_{\alpha\beta\sigma\tau}$. $T_{\alpha\beta}$ is formally equal to

$$T_{\alpha\beta} = \frac{1}{V(u)}\left(\frac{\partial W(u_{\alpha\beta}, v_{\alpha\beta})}{\partial v_{\alpha\beta}}\right)_{v_{\alpha\beta}=0}. \tag{14}$$

The reference configuration is the system deformed by $u_{\alpha\beta}$, and $v_{\alpha\beta}$ is the small deformation made on that system.

Using

$$x_\alpha(\mathring{\mathbf{x}}) = (\delta_{\alpha\beta} + u_{\alpha\beta})(\delta_{\beta\gamma} + v_{\beta\gamma})\mathring{x}_\gamma \tag{15}$$

an expansion of $W(u_{\alpha\beta}, v_{\alpha\beta})$ leads, as shown by Barron and Klein,[9] to

$$T_{\alpha\beta}=\mathring{S}_{\alpha\beta}+(\mathring{S}_{\alpha\beta\sigma\tau}-\mathring{S}_{\alpha\beta}\delta_{\sigma\tau}+\mathring{S}_{\alpha\tau}\delta_{\beta\sigma})u_{\sigma\tau} \tag{16}$$

$$=\mathring{S}_{\alpha\beta}+\mathring{c}_{\alpha\beta\sigma\tau}\eta_{\sigma\tau}+\mathring{S}_{\beta\tau}\omega_{\alpha\tau}+\mathring{S}_{\alpha\tau}\omega_{\beta\tau} \tag{17}$$

where they introduce another symbol, the elastic stiffness coefficient[10]

$$\mathring{c}_{\alpha\beta\sigma\tau}\equiv\mathring{C}_{\alpha\beta\sigma\tau}-\tfrac{1}{2}(2\mathring{S}_{\alpha\beta}\delta_{\sigma\tau}-\mathring{S}_{\alpha\sigma}\delta_{\beta\tau}-\mathring{S}_{\alpha\tau}\delta_{\beta\sigma}-\mathring{S}_{\beta\tau}\delta_{\alpha\sigma}-\mathring{S}_{\beta\sigma}\delta_{\alpha\tau}). \tag{18}$$

$\mathring{c}_{\alpha\beta\sigma\tau}$ is symmetric with respect to the interchanges (α,β) or (σ,τ). However, it does not have the full symmetry of Eq. (8). Instead, it satisfies the equalities

$$\mathring{c}_{\alpha\beta\sigma\tau}-\mathring{c}_{\sigma\tau\alpha\beta}=\mathring{S}_{\sigma\tau}\delta_{\alpha\beta}-\mathring{S}_{\alpha\beta}\delta_{\sigma\tau}. \tag{19}$$

The thermodynamic stress $t_{\alpha\beta}$ and the applied stress $T_{\alpha\beta}$ are related by the relation

$$t_{\alpha\beta}=\det(J)J^{-1}_{\alpha\sigma}J^{-1}_{\beta\tau}T_{\sigma\tau}, \tag{20}$$

where $J_{\alpha\beta}=\delta_{\alpha\beta}+u_{\alpha\beta}$ [$\det(J)$ is the ratio V/V_0]. This follows in a straightforward way from Eqs. (12), (13), and (16), and the assumption of rotational invariance. The two quantities $t_{\alpha\beta}$ and $T_{\alpha\beta}$ are equal when u, or η, is zero.

In a direct experiment $T_{\alpha\beta}$ and $e_{\alpha\beta}$ (or $u_{\alpha\beta}$) are measured, and hence $\mathring{c}_{\alpha\beta\sigma\tau}$.

D. Unstressed system

For an unstressed system, $\mathring{S}_{\alpha\beta}=0$, therefore, we have

$$\mathring{C}_{\alpha\beta\sigma\tau}=\mathring{S}_{\alpha\beta\sigma\tau}=\mathring{c}_{\alpha\beta\sigma\tau} \tag{21}$$

$$T_{\alpha\beta}=\mathring{C}_{\alpha\beta\sigma\tau}u_{\sigma\tau}=\mathring{C}_{\alpha\beta\sigma\tau}\eta_{\sigma\tau}=t_{\alpha\beta}, \tag{22}$$

$$\frac{W-W_o}{V_o}=\frac{1}{2}\mathring{C}_{\alpha\beta\sigma\tau}\eta_{\alpha\beta}\eta_{\sigma\tau}. \tag{23}$$

In this situation, the different definitions of the elastic constants are identical.

The symmetry of the crystal reduces the number of independent elastic constants to less than 21. For example, for an isotropic system, there are only two independent elastic constants. Traditionally $\lambda\equiv\mathring{C}_{1122}\equiv\mathring{C}_{12}$ and $\mu\equiv\mathring{C}_{1212}\equiv\mathring{C}_{44}$ are chosen to characterize the system.

III. STABILITY CRITERIA AND ELASTIC CONSTANTS

One of the most important applications of elastic moduli, such as elastic constants in theoretical models, is to use them as stability criteria. The stability of any system is essentially determined by the second law of thermodynamics. For a system with a fixed number of particles undergoing an arbitrary but small transformation from state A to state B, the second law says[18–20]

$$\Delta\mathcal{W}\geqslant\Delta E-T\Delta S=\Delta F \tag{24}$$

where $-\Delta\mathcal{W}$ is the work done by the system during the transformation. The equality sign applies for reversible transformations. If state A is an equilibrium configuration, stability requires that in moving to a nearby state $\Delta F-\Delta\mathcal{W}>0$.

For a mechanically isolated, i.e., constant volume system, or unstressed system, $\Delta\mathcal{W}=0$, and Eq. (24) leads to the requirement that W (E or F) be minimum in microcanonical or canonical ensembles for stability.

A. Unstressed system

For W in Eq. (23) to be a minimum in the absence of strain, $\mathring{C}_{\alpha\beta\sigma\tau}$ must be a positive definite tensor, i.e., all its eigenvalues must be positive.

Explicitly, for a three-dimensional (3D) cubic solid the stability conditions are[10]

$$\mathring{C}_{11}+2\mathring{C}_{12}>0,\qquad \mathring{C}_{44}>0,\qquad \mathring{C}_{11}-\mathring{C}_{12}>0. \tag{25}$$

For an isotropic solid $\mathring{C}_{11}-\mathring{C}_{12}=2\mathring{C}_{44}$ and conditions (25) reduce to

$$3B=2\mathring{C}_{44}+3\mathring{C}_{12}>0,\qquad \mathring{C}_{44}>0, \tag{26}$$

where B is the bulk modulus and C_{44} the shear modulus. Similar conditions are obtained for two-dimensional (2D) isotropic solids, to which belongs the triangular lattice

$$B=\mathring{C}_{44}+\mathring{C}_{12}>0,\qquad \mathring{C}_{44}>0. \tag{27}$$

B. Stressed sytem

In the same way, for a stressed system, Eq. (24) leads to the requirement that $H=W-\mathcal{W}$ be minimum in constant stress ensembles for stability. For a system under constant hydrostatic pressure, $-\mathcal{W}=pV$, so that the stability criteria can be derived by requiring that the the traditional Gibbs' free energy or the enthalpy be minimum. It is equivalent to finding the minimum of the Legendre transform[21] of W, i.e., $H=W+pV$, and use p instead of V as an *independent state variable*. However, for a system under anisotropic loading, the traditional Gibbs' free energy or enthalpy requires a more careful definition. We will discuss this point in detail later.

IV. STABILITY CRITERIA FOR A STRESSED SYSTEM

A. System with isotropic initial stress and constant volume

For a system with isotropic reference stress[14]

$$\mathring{S}_{\alpha\beta}=-p\,\delta_{\alpha\beta}, \tag{28}$$

where p is the isotropic stress, *positive for compression*.

To study the problem of stability in both microcanonical and canonical ensembles, we need to check if W is minimum. In those ensembles the minimum of W must be achieved at constant volume, so shape changes are allowed

without volume fluctuations. The instantaneous volume V can be written as $V=V_o \det(\delta_{\alpha\beta}+u_{\alpha\beta})$,[14] where V_0 is the volume of the stressed system before deformation. This leads to

$$\frac{V-V_o}{V_o}=\eta_{\alpha\alpha}+\frac{1}{2}(\delta_{\alpha\beta}\delta_{\sigma\tau}-\delta_{\alpha\sigma}\delta_{\beta\tau}-\delta_{\alpha\tau}\delta_{\beta\sigma})\eta_{\alpha\beta}\eta_{\sigma\tau} \tag{29}$$

to second order in the strain. To fix the volume requires $V-V_o=0$ or

$$\eta_{\alpha\alpha}=\mathrm{Tr}\eta=-\tfrac{1}{2}(\delta_{\alpha\beta}\delta_{\sigma\tau}-\delta_{\alpha\sigma}\delta_{\beta\tau}-\delta_{\alpha\tau}\delta_{\beta\sigma})\eta_{\alpha\beta}\eta_{\sigma\tau}. \tag{30}$$

Substituting Eq. (30) into Eq. (11) leads to

$$\frac{W-W_o}{V_o}=\frac{1}{2}C_{\alpha\beta\sigma\tau}\eta_{\alpha\beta}\eta_{\sigma\tau}, \tag{31}$$

where

$$C_{\alpha\beta\sigma\tau}\equiv\mathring{C}_{\alpha\beta\sigma\tau}+p(\delta_{\alpha\beta}\delta_{\sigma\tau}-\delta_{\alpha\sigma}\delta_{\beta\tau}-\delta_{\alpha\tau}\delta_{\beta\sigma}). \tag{32}$$

Equation (31) has to be a positive definite quadratic form, with the constraints given by Eq. (30).

Note that the $C_{\alpha\beta\sigma\tau}$ have the same symmetry as the elastic constants, so they can be condensed using the Voigt notation. With the constraints of Eqs. (30) this leads to

$$\frac{W-W_o}{V_o}=\frac{1}{2}f_{\alpha\beta}S_\alpha S_\beta,\quad \alpha,\beta=2,\ldots,6, \tag{33}$$

where

$$\begin{gathered}
f_{22}=C_{11}+C_{22}-2C_{12},\\
f_{23}=f_{32}=C_{11}+C_{23}-C_{12}-C_{13},\\
f_{24}=f_{42}=C_{24}-C_{14},\quad f_{25}=f_{52}=C_{25}-C_{15},\\
f_{26}=f_{62}=C_{26}-C_{16},\quad f_{33}=C_{11}+C_{33}-2C_{13},\\
f_{34}=f_{43}=C_{34}-C_{14},\quad f_{35}=f_{53}=C_{35}-C_{15},\\
f_{36}=f_{63}=C_{36}-C_{16},\quad f_{44}=C_{44},\\
f_{45}=f_{54}=C_{45},\quad f_{46}=f_{64}=C_{46},\\
f_{55}=C_{55},\quad f_{56}=f_{65}=C_{56},\quad f_{66}=C_{66},
\end{gathered} \tag{34}$$

and

$$\begin{gathered}
S_2=\eta_{22},\quad S_3=\eta_{33},\quad S_4=2\eta_{23},\\
S_5=2\eta_{31},\quad S_6=2\eta_{12}.
\end{gathered} \tag{35}$$

The S_α are a set of independent strains. Stability requires that Eq. (33) be a positive definite quadratic form, so the stability conditions reduce to an eigenvalue problem for $f_{\alpha\beta}$.

Explicitly the stability conditions for a three-dimensional cubic solid are

$$C_{44}>0\quad\text{and}\quad C_{11}-C_{12}>0. \tag{36}$$

For an isotropic solid, either two or three dimensional, only the first condition remains,

$$C_{44}>0. \tag{37}$$

B. System with isotropic initial stress and allowing volume fluctuations

Keeping the volume constant is, however, too restrictive. In general, instability is always accompanied by volume fluctuations. To allow for volume fluctuations we study the minimum of the Legendre transform[21] of W, i.e., $H=W+pV$, which is the enthalpy or the Gibbs' free energy, and fix the pressure instead of the volume.

This problem is quite similar to the stability problem in the study of membranes using the curvature model,[22–24] in which the Legendre transform requires two parameters, one is the surface tensile stress and the other the pressure. Peterson[24] clarified the distinction between the conditions of fixed volume and fixed pressure.

By using Eqs. (11), (12), and (29), we obtain

$$\frac{H-H_o}{V_o}=\tfrac{1}{2}C_{\alpha\beta\sigma\tau}\eta_{\alpha\beta}\eta_{\sigma\tau}, \tag{38}$$

and hence the same quadratic form as in Eq. (31) but now without the volume constraints. The stability conditions reduce to an eigenvalue problem for the $C_{\alpha\beta\sigma\tau}$ tensor as opposed to $\mathring{C}_{\alpha\beta\sigma\tau}$ for the stress-free case.

From Eqs. (18), (12), and (32), it is easy to show that in this case, $C_{\alpha\beta\sigma\tau}$ is identical to $\mathring{c}_{\alpha\beta\sigma\tau}$, the elastic stiffness coefficient. Since the stress-strain relations are still linear in the strains, with Eq. (17) simplifying to

$$T_{\alpha\beta}=-p\delta_{\alpha\beta}+\mathring{c}_{\alpha\beta\sigma\tau}u_{\sigma\tau}=-p\delta_{\alpha\beta}+\mathring{c}_{\alpha\beta\sigma\tau}\eta_{\sigma\tau}, \tag{39}$$

$\mathring{c}_{\alpha\beta\sigma\tau}$ and hence also $C_{\alpha\beta\sigma\tau}$ and $\mathring{C}_{\alpha\beta\sigma\tau}$ have the same symmetry relations as in the unstressed state. Moreover, we can expect that $C_{\alpha\beta\sigma\tau}$ will yield the same stability conditions as those obtained from the long acoustic lattice wave theory as the latter contains the effects of stress. This point will be illustrated in Sec. II C, with an example of a central force system. We can also confirm this by noticing that the equations of motion in the isotropic state can be reduced to[9]

$$\mathring{\rho}\frac{\partial^2 u_\alpha(\mathring{\mathbf{x}})}{\partial t^2}=\mathring{c}_{\alpha\beta\sigma\tau}\frac{\partial^2 u_\sigma(\mathring{\mathbf{x}})}{\partial\mathring{x}_\beta\partial\mathring{x}_\tau} \tag{40}$$

where $\mathring{\rho}$ is the reference density, and $\mathring{c}_{\alpha\beta\sigma\tau}$ plays the same role as the elastic constants in the stress-free state.

The stability conditions are obtained by substituting in Eqs. (25), (26), and (27), the $\mathring{C}$'s with the C's. Explicitly, for a cubic system, the relevant elastic constants are

$$\begin{gathered}
C_{11}=\mathring{C}_{11}-p,\\
C_{12}=\mathring{C}_{12}+p=\lambda,\\
C_{44}=\mathring{C}_{44}-p=\mu.
\end{gathered} \tag{41}$$

This is what has been suggested by Wang *et al.*[10] Earlier, using a different approach, the same result was obtained by Basinski *et al.*[15] in a system at zero temperature, where the pressure results from the electronic cloud.

It is interesting to note that Eq. (31) or (33) will be a positive definite quadratic form provided Eq. (38) is, but the converse is not necessarily true. Therefore, we can conclude that the condition of stability for the constant pressure ensemble is stronger than in the constant volume ensemble. For instance, for an isotropic solid, in the constant pressure ensemble, $B>0$ is necessary for stability, but this is not required with constant volume. As a consequence, a state stable in the constant volume ensemble may be unstable in the constant pressure ensemble. This may account for the fact that two-phase coexistence is allowed in the constant volume ensemble but prohibited in the constant pressure ensemble.

C. System with anisotropic initial stress

For a system under anisotropic stress, it is even more crucial to consider volume fluctuations; since a system without volume and shape fluctuations is always in mechanical equilibrium, no stability criteria is required. In general, shape fluctuations require mechanical works, so stability is not achieved by requiring W to be minimum.

1. System with constant $t_{\alpha\beta}$

At first thought, one could try using the traditional Gibbs' free energy $G=F-V_o t_{\alpha\beta}\eta_{\alpha\beta}$ or enthalpy, $=E-V_o t_{\alpha\beta}\eta_{\alpha\beta}$,[13,14,17] to determine the stability of an anisotropic stressed system as we did in the last two sections. But since the quantity conjugate to the strain $\eta_{\alpha\beta}$ is the thermodynamic stress tensor $t_{\alpha\beta}$, the minimum must be achieved under the condition of *constant* $t_{\alpha\beta}$. In this case it follows from Eqs. (11) and (12) that stability requires that the elastic constant tensor $\mathring{C}_{\alpha\beta\sigma\tau}$ be a positive definite tensor. The constant $t_{\alpha\beta}$ ensemble can be realized in computer simulations.[4,5] However, as seen from Eq. (20), the applied stress $T_{\alpha\beta}$ fluctuates in this ensemble. Also, a diagonal $t_{\alpha\beta}$ does not lead to a diagonal, or isotropic, $T_{\alpha\beta}$, and this is why the corresponding stability criteria are different from those obtained in Secs. IV A and IV B. Therefore, this constant $t_{\alpha\beta}$ ensemble is not equivalent to the ensemble of constant applied stress, and so one has to be careful in comparing the results obtained from this ensemble with experiments or theory. We can also see this point by noting that under constant loading, $\Delta\mathcal{W}\neq V_o t_{\alpha\beta}\eta_{\alpha\beta}$. Instead, for a quasistatic process,[11,13,14,17]

$$\Delta\mathcal{W}=V_o\int \det(J)J^{-1}_{\alpha\sigma}J^{-1}_{\beta\tau}T_{\sigma\tau}d\epsilon_{\alpha\beta}=V_o T_{\alpha\beta}\xi_{\alpha\beta}, \quad (42)$$

where

$$\xi_{\alpha\beta}=\int \det(J)J^{-1}_{\sigma\alpha}J^{-1}_{\tau\beta}d\epsilon_{\sigma\tau} \quad (43)$$

are variables conjugated to $T_{\alpha\beta}$ and $\epsilon_{\alpha\beta}$ vary along some path from $\epsilon_{\alpha\beta}=0$ to $\epsilon_{\alpha\beta}=\eta_{\alpha\beta}$. Thus the minimum of the traditional Gibbs' free energy or enthalpy is in general different from that of $H=W-\mathcal{W}$.

2. System with constant applied stress

From the above discussion, for the constant loading ensemble we need a thermodynamic potential using $T_{\alpha\beta}$ instead $t_{\alpha\beta}$ as independent-state variables, and stability criteria can then be derived by requiring this thermodynamic potential to be minimum. Such a thermodynamic potential can be obtained by a Legendre transform[21]

$$H=W-V_o T_{\alpha\beta}\xi_{\alpha\beta}. \quad (44)$$

To find the stability criteria, we need to consider a small deformation from some reference configuration. To first order in $u_{\alpha\beta}$, we have

$$\begin{aligned}\det(J)J^{-1}_{\sigma\alpha}J^{-1}_{\tau\beta}&=(1+u_{ii})(\delta_{\sigma\alpha}-u_{\sigma\alpha})(\delta_{\tau\beta}-u_{\tau\beta})\\&=(1+u_{ii})(\delta_{\sigma\alpha}\delta_{\tau\beta}-u_{\sigma\alpha}\delta_{\tau\beta}-u_{\tau\beta}\delta_{\sigma\alpha})\\&=\delta_{\sigma\alpha}\delta_{\tau\beta}+\delta_{\sigma\alpha}\delta_{\tau\beta}u_{ii}-u_{\sigma\alpha}\delta_{\tau\beta}-u_{\tau\beta}\delta_{\sigma\alpha}.\end{aligned} \quad (45)$$

Neglecting the rotational terms $\omega_{\alpha\beta}$,

$$\det(J)J^{-1}_{\sigma\alpha}J^{-1}_{\tau\beta}=\delta_{\sigma\alpha}\delta_{\tau\beta}+\eta_{ii}\delta_{\sigma\alpha}\delta_{\tau\beta}-\eta_{\sigma\alpha}\delta_{\tau\beta}-\eta_{\tau\beta}\delta_{\sigma\alpha}. \quad (46)$$

Therefore, to second order in $\eta_{\alpha\beta}$,

$$\begin{aligned}\xi_{\alpha\beta}&=\int(\delta_{\sigma\alpha}\delta_{\tau\beta}+\epsilon_{ii}\delta_{\sigma\alpha}\delta_{\tau\beta}-\epsilon_{\sigma\alpha}\delta_{\tau\beta}-\epsilon_{\tau\beta}\delta_{\sigma\alpha})d\epsilon_{\sigma\tau}\\&=\eta_{\alpha\beta}+\int(\epsilon_{\sigma\sigma}d\epsilon_{\alpha\beta}-\epsilon_{\sigma\alpha}d\epsilon_{\sigma\beta}-\epsilon_{\sigma\beta}d\eta_{\sigma\alpha})\\&=\eta_{\alpha\beta}+\tfrac{1}{2}\int[\epsilon_{\sigma\sigma}d\epsilon_{\alpha\beta}+\epsilon_{\alpha\beta}d\epsilon_{\sigma\sigma}+\epsilon_{\sigma\sigma}d\epsilon_{\alpha\beta}-\epsilon_{\alpha\beta}d\epsilon_{\sigma\sigma}\\&\quad-2d(\epsilon_{\alpha\sigma}\epsilon_{\beta\sigma})]\\&=\eta_{\alpha\beta}+\tfrac{1}{2}\eta_{\sigma\sigma}\eta_{\alpha\beta}-\eta_{\alpha\sigma}\eta_{\beta\sigma}\\&\quad+\tfrac{1}{2}\int(\epsilon_{\sigma\sigma}d\epsilon_{\alpha\beta}-\epsilon_{\alpha\beta}d\epsilon_{\sigma\sigma})\end{aligned} \quad (47)$$

and

$$\begin{aligned}T_{\alpha\beta}\xi_{\alpha\beta}&=T_{\alpha\beta}(\eta_{\alpha\beta}+\tfrac{1}{2}\eta_{\sigma\sigma}\eta_{\alpha\beta}-\eta_{\alpha\sigma}\eta_{\beta\sigma})\\&\quad+\frac{1}{2}T_{\alpha\beta}\int(\epsilon_{\sigma\sigma}d\epsilon_{\alpha\beta}-\epsilon_{\alpha\beta}d\epsilon_{\sigma\sigma})\\&=T_{\alpha\beta}(\eta_{\alpha\beta}+\tfrac{1}{2}\eta_{\sigma\sigma}\eta_{\alpha\beta}-\eta_{\alpha\sigma}\eta_{\beta\sigma})\\&\quad+\frac{1}{2}\mathcal{B}_{\alpha\beta\sigma\tau}\int\epsilon_{\sigma\tau}d\epsilon_{\alpha\beta},\end{aligned} \quad (48)$$

where

$$\mathcal{B}_{\alpha\beta\sigma\tau}=T_{\alpha\beta}\delta_{\sigma\tau}-T_{\sigma\tau}\delta_{\alpha\beta}=-\mathcal{B}_{\sigma\tau\alpha\beta}. \quad (49)$$

The last term in Eqs. (47) and (48), $T_{\alpha\beta}\xi'_{\alpha\beta}$, where

$$\xi'_{\alpha\beta} \equiv \int \epsilon_{\sigma\sigma} d\epsilon_{\alpha\beta} - \epsilon_{\alpha\beta} d\epsilon_{\sigma\sigma}, \tag{50}$$

is path dependent, and of the same order of magnitude as $\eta_{\alpha\beta}\eta_{\sigma\tau}$. The deformation-path-dependent nature of $\xi'_{\alpha\beta}$ was first pointed out by Wang *et al.*[11] For instance, along a path defined by

$$\epsilon_{\alpha\beta} = \begin{cases} \eta_{\alpha\beta}\left(1 - \cos\frac{\pi}{2}x\right), & \alpha \neq \beta \\ \eta_{\alpha\beta}\sin\frac{\pi}{2}x, & \alpha = \beta, \end{cases} \tag{51}$$

$\xi'_{\alpha\beta} = [(\pi/2) - 1](1 - \delta_{\alpha\beta})\eta_{\alpha\beta}\eta_{\sigma\sigma}$ (no summation for α and β). Equation (50) can be rewritten as

$$\xi'_{\alpha\beta} = \int (\epsilon_{\sigma\sigma})^2 d\left(\frac{\epsilon_{\alpha\beta}}{\epsilon_{\sigma\sigma}}\right). \tag{52}$$

Along a straight line it is trivial to see that $\xi'_{\alpha\beta} = 0$. The same applies to volume-preserving paths ($\epsilon_{\sigma\sigma} = 0$). And if one considers $T_{\alpha\beta}\xi'_{\alpha\beta}$, it will be zero if $T_{\alpha\beta}\epsilon_{\alpha\beta}$ is proportional to the volume change $\epsilon_{\sigma\sigma}$. This is similar to the isotropic case, where the work is always proportional to the volume change.

The important thing for our purpose is that paths can be paired. To every path l,

$$\epsilon_{\alpha\beta} = f_{\alpha\beta}(x), \quad f_{\alpha\beta}(0) = 0, \quad f_{\alpha\beta}(1) = \eta_{\alpha\beta},$$

$$\xi'_{\alpha\beta}(l) = \int_0^1 [f_{\sigma\sigma}(x) f'_{\alpha\beta}(x) - f_{\alpha\beta}(x) f'_{\sigma\sigma}(x)]dx, \tag{53}$$

$$f'_{\alpha\beta}(x) = \frac{df_{\alpha\beta}(x)}{dx},$$

there exists another path l',

$$\epsilon_{\alpha\beta} = \eta_{\alpha\beta} - f_{\alpha\beta}(1 - x), \tag{54}$$

such that $\xi'_{\alpha\beta}(l) + \xi'_{\alpha\beta}(l') = 0$. From which it follows that

$$\langle \xi'_{\alpha\beta} \rangle = 0. \tag{55}$$

This allows us to define a thermodynamic potential for each point in spite of the path-dependence of the work. We define the change in H, in going from one point to another, as an average over all possible paths. The path-dependent term is eliminated because $\langle \xi'_{\alpha\beta} \rangle = 0$. This is also what is obtained by following a straight line between two points. Choosing the average is more convenient than looking for the minimum. As discussed in the Appendix, extrema of $\xi'_{\alpha\beta}$ do not usually exist for general deformations in the anisotropic case.

In discussing stability, the $T_{\alpha\beta}\xi'_{\alpha\beta}$ term is not required. Stability criteria are always with respect to infinitesimal displacements from some equilibrium configuration; displacements, in such limits, are linear, hence the $T_{\alpha\beta}\xi'_{\alpha\beta}$ term is zero anyway.

Therefore, up to second order in $\eta_{\alpha\beta}$, $H = W - V_o T_{\alpha\beta}\xi_{\alpha\beta}$ can be written as

$$H = W - V_o T_{\alpha\beta}\eta_{\alpha\beta} - \tfrac{1}{2} V_o \mathcal{A}_{\alpha\beta\sigma\tau}\eta_{\alpha\beta}\eta_{\sigma\tau}, \tag{56}$$

with

$$\xi_{\alpha\beta} = \eta_{\alpha\beta} - \eta_{\alpha\sigma}\eta_{\beta\sigma} + \tfrac{1}{2}\eta_{\alpha\beta}\eta_{\sigma\sigma} \tag{57}$$

and

$$2\mathcal{A}_{\alpha\beta\sigma\tau} = T_{\alpha\beta}\delta_{\sigma\tau} + T_{\sigma\tau}\delta_{\alpha\beta} - T_{\tau\beta}\delta_{\alpha\sigma} - T_{\tau\alpha}\delta_{\beta\sigma} - T_{\alpha\sigma}\delta_{\beta\tau} - T_{\beta\sigma}\delta_{\alpha\tau}. \tag{58}$$

$\mathcal{A}_{\alpha\beta\sigma\tau}$ has the same symmetry as elastic constants.

Between any two points in configuration space, the difference in this thermodynamic potential H is the change in the free energy W minus the average work between the two points, which is the same as the work along a direct straight-line segment joining the two points. One has to be careful not to infer from this that, when connecting two points by a trajectory made of small straight line segments, that the work done by the system, is the same as if the points had been connected by a single direct straight-line segment. The path dependence of the work requires us always to consider the work as being an average over all trajectories connecting the two points.

Requiring that H_o be a minimum leads, from Eqs. (11) and (12), to

$$T_{\alpha\beta} = \mathring{S}_{\alpha\beta}, \tag{59}$$

and the corresponding energy variation close to the minimum is of the form

$$\frac{H - H_o}{V_o} = \frac{1}{2} C_{\alpha\beta\sigma\tau}\eta_{\alpha\beta}\eta_{\sigma\tau}, \tag{60}$$

where $\mathring{S}_{\alpha\beta}$ is fixed and not diagonal, and

$$\begin{aligned} C_{\alpha\beta\sigma\tau} &\equiv \mathring{C}_{\alpha\beta\sigma\tau} - \mathcal{A}_{\alpha\beta\sigma\tau} \equiv \tfrac{1}{2}(\mathring{c}_{\alpha\beta\sigma\tau} + \mathring{c}_{\sigma\tau\alpha\beta}) \\ &= \mathring{C}_{\alpha\beta\sigma\tau} - \tfrac{1}{2}(\mathring{S}_{\alpha\beta}\delta_{\sigma\tau} + \mathring{S}_{\sigma\tau}\delta_{\alpha\beta} - \mathring{S}_{\alpha\sigma}\delta_{\beta\tau} - \mathring{S}_{\alpha\tau}\delta_{\beta\sigma} \\ &\quad - \mathring{S}_{\beta\tau}\delta_{\alpha\sigma} - \mathring{S}_{\beta\sigma}\delta_{\alpha\tau}) \end{aligned} \tag{61}$$

is the positive definite quantity for stability. Note that the only difference between $\mathring{c}_{\alpha\beta\sigma\tau}$ and $C_{\alpha\beta\sigma\tau}$ is that the term $2\mathring{S}_{\alpha\beta}\delta_{\sigma\tau}$ in $\mathring{c}_{\alpha\beta\sigma\tau}$ is replaced by $\mathring{S}_{\alpha\beta}\delta_{\sigma\tau} + \mathring{S}_{\sigma\tau}\delta_{\alpha\beta}$.

It is easy to check that $C_{\alpha\beta\sigma\tau}$ has the proper isotropic limit. Condensed expressions in terms of the Voigt notation are still possible, but the number of independent elements determined, not only by the symmetry of the crystal but also by the symmetry of the applied stress $T_{\alpha\beta}$, will likely be increased, this, in particular, since the reference state itself will usually have a lower symmetry, and hence more elastic constants $\mathring{C}_{\alpha\beta\sigma\tau}$ will be required.

It should be noted that for a stressed system $C_{\alpha\beta\sigma\tau}$, $\mathring{c}_{\alpha\beta\sigma\tau}$, and $\mathring{C}_{\alpha\beta\sigma\tau}$ are dependent on the stress. They are no longer intrinsic properties of the system, and hence cannot be used as probes of the interatomic forces.

This result is the same as the one recently obtained by Wang *et al.*[11] for isothermal systems. They considered $\Delta\mathcal{G} = \Delta F - \Delta\mathcal{W}$ and required $\Delta\mathcal{G} > 0$ for stability, a condition identical to minimizing $\mathcal{G} = F - \mathcal{W}$. We strengthen their argu-

ment by considering in detail the effect of the deformation path-dependent term $\xi'_{\alpha\beta}$. As pointed out above, without considering it, the positive definiteness of $C_{\alpha\beta\sigma\tau}$ does not automatically lead to $\Delta\mathcal{G}>0$ or $\mathcal{G}$ minimum.

V. CALCULATION OF THE ELASTIC CONSTANTS

There are various approaches to calculating elastic constants: direct computation of the stress-strain relations by deformation of the simulation cell, strain-strain fluctuation methods where the elastic constants are extracted from the fluctuations in the shape of the simulation cell, and the ''equilibrium'' fluctuation method. It is this last technique that we shall discuss. In this method, a formal expression is derived for the elastic constants, from the second derivative of the free energy [see Eq. (7)]. The elastic constants are directly obtained from the microscopic fluctuations within the system. The method has the advantage that no actual deformations are made, so no symmetry breaking occurs, and all elastic constants can be obtained from a single run. It must be emphasized that the derivatives are taken with respect to a reference configuration, the one on which virtual deformations $\eta_{\alpha\beta}$ are applied for the purpose of calculating the elastic constants. Hence, at every step of a computer run, *the reference configuration and volume must be the instantaneous one*.

A. Equilibrium fluctuation formulas in the canonical ensemble

Since the reference configuration is the instantaneous configuration, a straightforward derivation of the elastic constants can be accomplished as in Ref. 3, resulting in easy to program formulas. The canonical ensemble is used because it is the most commonly used ensemble, and the most appropriate for the calculation of elastic constants.[6] There are difficulties in calculating elastic constants on other ensembles, such as the constant pressure ensemble.[25,26] W is in this ensemble the Helmholtz free energy F. With the Hamiltonian $\mathcal{H}$,

$$\mathcal{H}=\mathcal{H}(\mathbf{x},\mathbf{p},\eta,N), \tag{62}$$

$\mathbf{x}$ and $\mathbf{p}$ representing the coordinates and momenta of the N particles,

$$F=-k_BT\ln Z \text{ with } Z=\frac{1}{\mathcal{C}}\int e^{-\mathcal{H}/k_BT}d\tau. \tag{63}$$

$\mathcal{C}$ is a constant, $d\tau$ the differential volume element in the 6 N-dimensional phase space, and k_B the Boltzmann constant. It follows from Eqs. (7) and (12) that[3]

$$\mathring{S}_{\alpha\beta}=\mathring{C}_{\alpha\beta}=\frac{1}{V_0}\left\langle\frac{\partial\mathcal{H}}{\partial\eta_{\alpha\beta}}\right\rangle_{\eta=0}-\frac{Nk_BT}{V_o}\left(\frac{\partial\ln V}{\partial\eta_{\alpha\beta}}\right)_{\eta=o}$$
$$=\frac{1}{V_0}\left\langle\frac{\partial\mathcal{H}}{\partial\eta_{\alpha\beta}}\right\rangle_{\eta=0}-\frac{Nk_BT}{V_o}\delta_{\alpha\beta} \tag{64}$$

and

$$\mathring{C}_{\alpha\beta\sigma\tau}=\frac{1}{V_o}\left\langle\frac{\partial^2\mathcal{H}}{\partial\eta_{\alpha\beta}\partial\eta_{\sigma\tau}}\right\rangle_{\eta=0}$$
$$-\frac{1}{k_BTV_o}\left\langle\delta\left(\frac{\partial\mathcal{H}}{\partial\eta_{\alpha\beta}}\right)\delta\left(\frac{\partial\mathcal{H}}{\partial\eta_{\sigma\tau}}\right)\right\rangle_{\eta=0}$$
$$+\frac{Nk_BT}{V_o}(\delta_{\alpha\sigma}\delta_{\beta\tau}+\delta_{\alpha\tau}\delta_{\beta\sigma}), \tag{65}$$

where the $\langle\ldots\rangle$ designates configurational averages and $\delta(A)=A-\langle A\rangle$. The last term comes from the identity

$$\left(\frac{\partial^2\ln V}{\partial\eta_{\alpha\beta}\partial\eta_{\sigma\tau}}\right)_{\eta=o}=-(\delta_{\alpha\sigma}\delta_{\beta\tau}+\delta_{\alpha\tau}\delta_{\beta\sigma}). \tag{66}$$

The Nk_BT/V_o terms can be simply understood as resulting from the finite size of the sample. One way to look at it is that, if the spatial coordinates are scaled to the simulation box coordinates to maintain them constant under deformations, V^N appears in front of the partition function leading to an $N\ln V$ term in the free energy. In this way we can avoid the use of the scaled momenta used in Refs. 4–8, and the kinetic energy in the Hamiltonian does not depend on the strain.

From Eq. (18) we get the elastic stiffness coefficients which are the quantities determined from direct experiment,

$$\mathring{c}_{\alpha\beta\sigma\tau}=\frac{1}{V_o}\left\langle\frac{\partial^2\mathcal{H}}{\partial\eta_{\alpha\beta}\partial\eta_{\sigma\tau}}\right\rangle_{\eta=0}$$
$$-\frac{1}{k_BTV_o}\left\langle\delta\left(\frac{\partial\mathcal{H}}{\partial\eta_{\alpha\beta}}\right)\delta\left(\frac{\partial\mathcal{H}}{\partial\eta_{\sigma\tau}}\right)\right\rangle_{\eta=0}$$
$$-\frac{1}{2}\left(2\left\langle\frac{\partial\mathcal{H}}{\partial\eta_{\alpha\beta}}\right\rangle_{\eta=0}\delta_{\sigma\tau}-\left\langle\frac{\partial\mathcal{H}}{\partial\eta_{\alpha\sigma}}\right\rangle_{\eta=0}\delta_{\beta\tau}\right.$$
$$-\left\langle\frac{\partial\mathcal{H}}{\partial\eta_{\alpha\tau}}\right\rangle_{\eta=0}\delta_{\beta\sigma}-\left\langle\frac{\partial\mathcal{H}}{\partial\eta_{\beta\tau}}\right\rangle_{\eta=0}\delta_{\alpha\sigma}$$
$$\left.-\left\langle\frac{\partial\mathcal{H}}{\partial\eta_{\beta\sigma}}\right\rangle_{\eta=0}\delta_{\alpha\tau}\right)+\frac{Nk_BT}{V_o}\delta_{\alpha\beta}\delta_{\sigma\tau}. \tag{67}$$

Replacing $2\langle\partial\mathcal{H}/\partial\eta_{\alpha\beta}\rangle_{\eta=0}\delta_{\sigma\tau}$ in the above expression by $\langle\partial\mathcal{H}/\partial\eta_{\alpha\beta}\rangle_{\eta=0}\delta_{\sigma\tau}+\langle\partial\mathcal{H}/\partial\eta_{\sigma\tau}\rangle_{\eta=0}\delta_{\alpha\beta}$, we get the elements of the positive definite tensor $C_{\alpha\beta\sigma\tau}$ which determines stability:

$$C_{\alpha\beta\sigma\tau}=\frac{1}{V_o}\left\langle\frac{\partial^2\mathcal{H}}{\partial\eta_{\alpha\beta}\partial\eta_{\sigma\tau}}\right\rangle_{\eta=0}$$
$$-\frac{1}{k_BTV_o}\left\langle\delta\left(\frac{\partial\mathcal{H}}{\partial\eta_{\alpha\beta}}\right)\delta\left(\frac{\partial\mathcal{H}}{\partial\eta_{\sigma\tau}}\right)\right\rangle_{\eta=0}$$
$$-\frac{1}{2}\left(\left\langle\frac{\partial\mathcal{H}}{\partial\eta_{\alpha\beta}}\right\rangle_{\eta=0}\delta_{\sigma\tau}+\left\langle\frac{\partial\mathcal{H}}{\partial\eta_{\sigma\tau}}\right\rangle_{\eta=0}\delta_{\alpha\beta}\right.$$
$$-\left\langle\frac{\partial\mathcal{H}}{\partial\eta_{\alpha\sigma}}\right\rangle_{\eta=0}\delta_{\beta\tau}-\left\langle\frac{\partial\mathcal{H}}{\partial\eta_{\alpha\tau}}\right\rangle_{\eta=0}\delta_{\beta\sigma}$$
$$\left.-\left\langle\frac{\partial\mathcal{H}}{\partial\eta_{\beta\tau}}\right\rangle_{\eta=0}\delta_{\alpha\sigma}-\left\langle\frac{\partial\mathcal{H}}{\partial\eta_{\beta\sigma}}\right\rangle_{\eta=0}\delta_{\alpha\tau}\right)$$
$$+\frac{Nk_BT}{V_o}\delta_{\alpha\beta}\delta_{\sigma\tau}. \tag{68}$$

The first term in $C_{\alpha\beta\sigma\tau}$ is referred to as the ''Born term,'' since it corresponds to elastic constants at zero temperature. The second term is the ''fluctuation term.'' The third arises from the effect of the stress. The last, discussed above, is sometimes called ''the kinetic term.''[1]

We mentioned earlier that the reference state should be the instantaneous state. The effects of the choice of the reference state will be negligible for small deformations (relative to the stress-free state) but not for large deformations. The definition of elastic constants in most papers (for instance, see Refs. 4–8 and 14) requires implicitly the natural (stress-free) reference (initial) configurations, therefore *a priori* their expressions are only valid for systems under moderate stress. Their expressions involve a tensor h constructed from the three vectors forming a parallelipiped, which is the periodic simulation cell. By definition, from Eq. (7), its reference value h_0 should have the value of the instantaneous stressed system. In other words $h_0=h$. However, if $h_0\neq h$, Eq. (4.3) in Ref. 7 will differ from the formulas given below; for the simplest case of isotropic stress by an additional unrequired factor $(V/V_0)^{4/3}$.

B. Special case of the central force system

For a central force system,

$$\mathcal{H}=\sum_i \frac{p_i^2}{2m}+\sum_{i<j}\Phi(|\mathbf{x}_i-\mathbf{x}_j|). \tag{69}$$

By using Eqs. (9) and (64)–(69), it is straightforward to derive

$$\mathring{S}_{\alpha\beta}=\mathring{C}_{\alpha\beta}=\frac{1}{V}\left\langle\sum_{i<j}\Delta x_\alpha(ij)\Delta x_\beta(ij)\frac{\Phi'}{r}\right\rangle-\frac{Nk_BT}{V}\delta_{\alpha\beta}, \tag{70}$$

$$\mathring{C}_{\alpha\beta\sigma\tau}=\frac{1}{V}\left\langle\sum_{i<j}\Delta x_\alpha(ij)\Delta x_\beta(ij)\Delta x_\sigma(ij)\Delta x_\tau(ij)\frac{1}{r^2}\left(\Phi''-\frac{\Phi'}{r}\right)\right\rangle$$
$$-\frac{1}{k_BTV}\left\langle\delta\left(\sum_{i<j}\Delta x_\alpha(ij)\Delta x_\beta(ij)\frac{\Phi'}{r}\right)\delta\left(\sum_{i<j}\Delta x_\sigma(ij)\Delta x_\tau(ij)\frac{\Phi'}{r}\right)\right\rangle+\frac{Nk_BT}{V}(\delta_{\alpha\sigma}\delta_{\beta\tau}+\delta_{\alpha\tau}\delta_{\beta\sigma}), \tag{71}$$

$$\mathring{c}_{\alpha\beta\sigma\tau}=\frac{1}{V}\left\langle\sum_{i<j}\Delta x_\alpha(ij)\Delta x_\beta(ij)\Delta x_\sigma(ij)\Delta x_\tau(ij)\frac{1}{r^2}\left(\Phi''-\frac{\Phi'}{r}\right)\right\rangle$$
$$-\frac{1}{k_BTV}\left\langle\delta\left(\sum_{i<j}\Delta x_\alpha(ij)\Delta x_\beta(ij)\frac{\Phi'}{r}\right)\delta\left(\sum_{i<j}\Delta x_\sigma(ij)\Delta x_\tau(ij)\frac{\Phi'}{r}\right)\right\rangle-\frac{1}{2V}\left(2\left\langle\sum_{i<j}\Delta x_\alpha(ij)\Delta x_\beta(ij)\frac{\Phi'}{r}\right\rangle\delta_{\sigma\tau}\right.$$
$$-\left\langle\sum_{i<j}\Delta x_\alpha(ij)\Delta x_\sigma(ij)\frac{\Phi'}{r}\right\rangle\delta_{\beta\tau}-\left\langle\sum_{i<j}\Delta x_\alpha(ij)\Delta x_\tau(ij)\frac{\Phi'}{r}\right\rangle\delta_{\beta\sigma}-\left\langle\sum_{i<j}\Delta x_\beta(ij)\Delta x_\tau(ij)\frac{\Phi'}{r}\right\rangle\delta_{\alpha\sigma}$$
$$\left.-\left\langle\sum_{i<j}\Delta x_\beta(ij)\Delta x_\sigma(ij)\frac{\Phi'}{r}\right\rangle\delta_{\alpha\tau}\right)+\frac{Nk_BT}{V}\delta_{\alpha\beta}\delta_{\sigma\tau}, \tag{72}$$

where we have dropped the symbol ''^{0}'' for the reference state, and $\eta=0$ on the averages for simplicity. In addition, $\Delta x_\alpha(ij)$ and r were defined as

$$\Delta x_\alpha(ij)=x_\alpha(i)-x_\alpha(j), \tag{73}$$

$$r^2=|\Delta x_\alpha(ij)|^2. \tag{74}$$

$C_{\alpha\beta\sigma\tau}$ is obtained by replacing the terms

$$2\Delta x_\alpha(ij)\Delta x_\beta(ij)\frac{\Phi'}{r}\delta_{\sigma\tau}$$

in $\mathring{c}_{\alpha\beta\sigma\tau}$ with

$$\Delta x_\alpha(ij)\Delta x_\beta(ij)\frac{\Phi'}{r}\delta_{\sigma\tau}+\Delta x_\sigma(ij)\Delta x_\tau(ij)\frac{\Phi'}{r}\delta_{\alpha\beta}.$$

It is interesting to note that for the central force system, the Cauchy relations[12] (in Voigt's notation)

$$\mathring{C}_{23}=\mathring{C}_{44},\ \mathring{C}_{31}=\mathring{C}_{55},\ \mathring{C}_{12}=\mathring{C}_{66},\ \mathring{C}_{14}=\mathring{C}_{56},\mathring{C}_{25}=\mathring{C}_{64}$$
$$\mathring{C}_{36}=\mathring{C}_{45},$$

hold at zero temperature for arbitrary stress, but for $\mathring{c}_{\alpha\beta\sigma\tau}$ and $C_{\alpha\beta\sigma\tau}$ the Cauchy relations require both conditions of zero temperature and zero stress.

For a cubic crystal under hydrostatic pressure, $\mathring{C}_{\alpha\beta\sigma\tau}$ in Eq. (71) reduces to the form obtained by Squire, Holt and Hoover,[1] and is valid even for high pressures. The relevant quantities for stability are the related $C_{\alpha\beta\sigma\tau}$. The three independent ones in the condensed notation are given in Eq. (41). The pressure p is obtained from Eqs. (28) and (70).

C. An example

In two dimensions at zero temperature, Eq. (72) with Eq. (41) yields

$$\lambda=\frac{1}{V}\sum\frac{\phi''}{r^2}(\Delta x)^2(\Delta y)^2-\frac{1}{V}\sum\frac{\phi'}{r^3}(\Delta x)^2(\Delta y)^2-\frac{1}{2V}\sum r\phi', \tag{75}$$

$$\mu=\frac{1}{V}\sum\frac{\phi''}{r^2}(\Delta x)^2(\Delta y)^2-\frac{1}{V}\sum\frac{\phi'}{r^3}(\Delta x)^2(\Delta y)^2+\frac{1}{2V}\sum r\phi'. \tag{76}$$

It follows from Eqs. (75) and (76) that, for a two-dimensional isotropic crystal under hydrostatic pressure and at zero temperature, if $p>0$, then $\lambda+\mu>2\mu$, and the shear instability will always occur prior to the spinodal instability (in the sense of vanishing bulk modulus, i.e., $B=\lambda+\mu=0$). In contrast, if $p<0$, then $\lambda+\mu<2\mu$, and the spinodal instability will always occur prior to the shear instability. We can expect these conclusions also to be valid at low temperature. But they cannot be applied to bulk systems since in three dimensions $B=(3\lambda+2\mu)/3$.

As an example, we consider a two-dimensional system with a piecewise linear interparticle interaction,

$$\Phi(r)=\begin{cases}\frac{1}{2}\kappa(r-d_0)^2-\kappa w^2, & r\leqslant d_0+w\\ -\frac{1}{2}\kappa(r-d_0-2w)^2, & d_0+w<r\leqslant d_0+2w\\ 0, & r>d_0+2w.\end{cases} \tag{77}$$

with $w=0.15d_0$. This choice of w corresponds to one broken bond in the core of a dislocation.[27] When the density $\rho=(d_0/d)^2<1.78$, the system forms a triangular lattice, and only nearest-neighbor interactions need to be considered. From the above equation, it follows that

$$\mu\equiv C_{44}=\frac{\sqrt{3}}{4}(4-3\rho^{1/2})\kappa, \tag{78}$$

$$\lambda\equiv C_{12}=\frac{\sqrt{3}}{4}(5\rho^{1/2}-4)\kappa, \tag{79}$$

where ρ is the density relative to equilibrium. This agrees with the results obtained from a long-wave expansion,[28] and gives the correct shear instability at $\rho=\frac{16}{9}$. In contrast,

$$\mathring{C}_{44}=\mathring{C}_{12}=\frac{\sqrt{3}}{4}\rho^{1/2}\kappa \tag{80}$$

does not show any instability.

VI. CONCLUSION

The stability of homogeneously stressed systems has been discussed in a thermodynamic framework by requiring that the appropriate thermodynamic potential be a minimum with respect to infinitesimal displacements about an equilibrium configuration. The general stability criterion under constant loading conditions is the same as the one derived by Wang *et al.*[11] through finite deformations: it is the positive definiteness of

$$C_{\alpha\beta\sigma\tau}\equiv\mathring{C}_{\alpha\beta\sigma\tau}-\tfrac{1}{2}(\mathring{S}_{\alpha\beta}\delta_{\sigma\tau}+\mathring{S}_{\sigma\tau}\delta_{\alpha\beta}-\mathring{S}_{\alpha\sigma}\delta_{\beta\tau}-\mathring{S}_{\alpha\tau}\delta_{\beta\sigma}-\mathring{S}_{\beta\tau}\delta_{\alpha\sigma}-\mathring{S}_{\beta\sigma}\delta_{\alpha\tau}). \tag{81}$$

Only for unstressed systems ($S_{\alpha_\beta}=0$) do we have the usual condition of a positive definite elastic constant tensor $\mathring{C}_{\alpha\beta\sigma\tau}$. With isotropic stress $C_{\alpha\beta\sigma\tau}=\mathring{c}_{\alpha\beta\sigma\tau}$, the elastic stiffness tensor. But for arbitrary anisotropic stress $C_{\alpha\beta\sigma\tau}$ will be distinct from both. We have also shown that, in the isotropic case, the stability conditions are stronger in the constant pressure ensemble than in the constant volume ensemble.

It should be noted that each physical situation may call for a different relevant quantity. Acoustic experiments, related to the stability question, would measure $C_{\alpha\beta\sigma\tau}$ in the absence of stress and for isotropic stress. In direct experiments, such as elongation, the elastic stiffness coefficients $\mathring{c}_{\alpha\beta\sigma\tau}$ are measured. When constructing interatomic potentials, it may be preferable to work with an unstressed system, the only situation where the elastic constants $\mathring{C}_{\alpha\beta\sigma\tau}$ probe intrinsic properties of the system. The formalism has been developed assuming a rotational invariance, i.e., rotations produce no stress. There is, however, no obstacle in generalizing to systems where rotations produce internal stresses. But this would mean, from Eq. (7), a significant increase in the total number of elastic constants to be considered.[29]

A thermodynamic potential H under constant loading condition $T_{\alpha\beta}$ can be defined even in the anisotropic case, where the work has a path-dependent component, by considering the average over all paths. In principle, therefore, we have, for a specific $T_{\alpha\beta}$, an H for all values of strain $\eta_{\alpha\beta}$. In small deformations of a reference configuration, the work for straight line paths are simply obtained, but for more complex deformations a path-dependent term should also be considered.

Finally, we have clarified the problem of the choice of the reference configuration in the calculation of elastic quantities (it has to be the instantaneous one). The same applies to other ensembles such as (HtN),[6] (TtN),[5] and $(H,T_{\alpha\beta},N)$.[26] Simple fluctuation formulas are given for the stability criteria of a system under arbitrary stress in the canonical ensemble.

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APPENDIX: EXTREME DEFORMATION PATHS FOR $T_{\alpha\beta}\xi'_{\alpha\beta}$

Using Eq. (50) with $\epsilon_{\alpha\beta}=\epsilon_{\alpha\beta}(x)$, where x is a path parameter, we have, for an arbitrary path

$$T_{\alpha\beta}\xi'_{\alpha\beta}=\int (T_{\alpha\beta}\dot{\epsilon}_{\alpha\beta}\epsilon_{\sigma\sigma}-T_{\alpha\beta}\epsilon_{\alpha\beta}\dot{\epsilon}_{\sigma\sigma})dx. \quad \text{(A1)}$$

The Euler equations for the deformation paths maximizing $T_{\alpha\beta}\xi'_{\alpha\beta}$ are

$$T_{\alpha\beta}\delta_{\sigma\tau}\dot{\epsilon}_{\alpha\beta}-T_{\sigma\tau}\dot{\epsilon}_{\alpha\alpha}=0. \quad \text{(A2)}$$

For isotropic stress ($T_{\alpha\beta}=-p\delta_{\alpha\beta}$), the above equation is satisfied automatically. But for anisotropic stress, Eq. (A2) with $\sigma\neq\tau$, yields $\dot{\epsilon}_{\alpha\alpha}=0$, or $\epsilon_{\alpha\alpha}=0$, using the initial boundary condition, and $\eta_{\alpha\alpha}=0$. These are volume-preserving deformations, reached by volume-preserving paths. The $\sigma=\tau$ terms then give $T_{\alpha\beta}\dot{\epsilon}_{\alpha\beta}=0$, or $T_{\alpha\beta}\epsilon_{\alpha\beta}=0$ along the path, and the final value $T_{\alpha\beta}\eta_{\alpha\beta}=0$. For these special paths, it follows immediately that $T_{\alpha\beta}\xi'_{\alpha\beta}=0$. The linear deformation paths to $\eta_{\alpha\alpha}$, satisfying the above two conditions, are obviously part of this set. Therefore there may exist, in anisotropic cases, a set of volume-preserving deformation directions with extreme paths attaining them, which have path-independent work with the above constraints. For arbitrary $\eta_{\alpha\beta}$, however, there usually will be no extremum path. If $\epsilon_{\alpha\beta}$ are bounded, the extremum path will be determined by the boundary.

For the case of uniaxial tension $T_{\alpha\beta}=-p\delta_{1\alpha}\delta_{1\beta}$, and $T_{\alpha\beta}\epsilon_{\alpha\beta}=-p\epsilon_{11}=0$; or $\epsilon_{11}=0$ with constant volume. Deformations obeying these constraints have a path-independent work with $T_{\alpha\beta}\xi'_{\alpha\beta}=0$.

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