Unified thermodynamic stability analysis in fluids and elastic materials

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A B S T R A C T

Thermodynamic stability provides the range of admissible properties of fluids and deformable solids. It also allows determination if a substance can exist in given conditions. When a fluid reaches its limit of thermodynamic stability, it should change phase. In deformable solids, instability may lead to failure, and cracks are formed, the bulk solid stays the same, but work from tension is converted to surface energy. In single-component fluids, thermodynamic stability leads to the dual conditions that the isothermal compressibility and the heat capacity be positive at constant volume. In solids, both in 2D and 3D, the bulk modulus K and the Lamé constant μ should be positive; these two conditions arise from the mechanical stability. The thermal stability requires that the heat capacity to be positive.

The criteria of thermodynamic stability in fluids and deformable solids are often derived on different approaches. In fluids, the derivations are based on a minimum of thermodynamic functions such as internal energy or Helmholtz free energy. In solids, various expressions are based on volumetric behavior, geometrical, dynamic, and energy expressions. We are not aware of generalized derivations for both fluids and solids.

In this work, we derive the criteria of thermodynamics stability of fluids, and deformable solids in 1D, 2D, and 3D. The derivations are based on the minimum of the Helmholtz free energy. The motivation from this work is to set a basis for expansion to thermodynamic stability of fluid-solid systems in relation to effect of different fluids on failure of solids.

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1. Introduction

Thermodynamic stability provides the criteria for the stability of phase existence at specified conditions. There may exist basic differences between the thermodynamic stability of solids and fluids. In order to see the difference, the derivations should use the same approach. Apparently, a generalized derivation for thermodynamic stability of fluids and deformable solids has not been attempted in the past.

Thermodynamic stability in fluids provides the limit at which a fluid will undergo change between two fluid states, say from gas to liquid or from liquid to gas state. The conditions for stability can be derived from the global minimum of thermodynamic functions U, F, and G, which are internal energy, Helmholtz free energy, and Gibbs free energy, respectively. The minimum is subject to constraints and variables of the thermodynamic functions. Alternatively, the maximum of entropy may be used. In single-component fluids, a fluid may stay in the current phase state as long as its

isothermal compressibility and its heat capacity at constant volume are simultaneously positive. The condition of mechanical stability applies at constant temperature path which requires only the compressibility to be positive. The thermodynamic stability allows a fluid exists in a negative pressure. The thermodynamic stability conditions for two-component and multi-component fluids are well established [1].

In elastic deformable solids, the thermodynamic stability and mechanical stability have not been derived with the same rigor as in fluids. In general, due to the tensorial nature of stress and strain in solids, the derivations are not as simple as in fluids where pressure and volume are scalars and serve as the variables. In solids, different expressions based on geometry have been used to derive the conditions of mechanical stability. As an example, the expression for the shear deformation (also known-as the first Lamé constant), $\mu = E/(2(1+\nu))$, is often used to find one of the two limits of Poisson's ratio. Often $\nu > -1$ is derived as the lowest limit for the Poisson's ratio. Therefore, materials with a negative Poisson's ratio are theoretically possible and have been presented [2,3]. The physical meaning is that upon extension in one direc-

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tion, there may be swelling in the other directions. The other parameter in the above expression is E, the Young modulus. The expression for volumetric strain $e_v = [(1 - 2\nu)(\sigma_x + \sigma_y + \sigma_z)]/E$ is often used to obtain the upper limit for the Poisson's ratio $\nu \leq 0.5$. The limit $\nu = 0.5$ is for in-compressible materials. The above limits, $-1 < \nu \leq 0.5$ is for 3D elastic solids. There is growing interest in 2D deformable solids [4]. In such materials the limits on the Poisson's ratio are given by $-1 < \nu < 1$ [5]. Both in 2D and 3D, it is known that the Young modulus E should be positive.

In 1D elastic materials [6], the Spring constant k which has the same numerical value as the Young modulus E is positive ($k > 0$), and the line thermal expasion coefficient h is positive ($h > 0$). Comprehensive derivations for stability of deformable media have been presented by Kochmann and Drugan [5]. These authors classify the methods as energy and dynamic in both 2D and 3D. The conditions are derived such that $\mu > 0$ and $K > 0$, μ is the first Lamé constant, and K is the bulk modulus. In terms of μ, and λ (second Lamé constant), the 3D criteria becomes $\mu > 0$ and $\lambda + (2/3)\mu > 0$. In 2D the criteria are given by $\mu > 0$ and $\lambda + \mu > 0$. The results by Kochman and Drugan are in agreement with the derivations in this work. Landau and Lifshitz [7] have formulated the expression for the Helmholtz free energy of a deformable isotropic solid and present the condition $K > 0$ and $\mu > 0$ for mechanical stability. The steps in the derivations are not presented. Morris and Krenn [8] have also investigated the stability of elastic materials. The authors use the stability from the variation principle $\delta F[\delta \mathbf{u}(\mathbf{x})] \geq 0$, where F is the Helmholtz energy, and $\delta \mathbf{u}(\mathbf{x})$ is the variational displacement. Morris and Krenn derive the mechanical stability condition in the form of $\xi_{ijkl}\delta\varepsilon_{ij}\delta\varepsilon_{kl} \geq 0$, where ξ_{ijkl} is the symmetric part of the moduli that governs the variation in the Cauchy stress tensor. Final expressions are not provided in terms of the Lamé constants or Poisson's ratio. Dunwoody and Ogden [9] investigate thermodynamic stability of heat conducting 3D elastic materials. The authors investigate a time-dependent problem. They derive the mechanical stability condition for an isotropic body in terms of Lamé constants $3\lambda + 2\mu > 0$, and thermal conductivity $k > 0$. The result in terms of thermal conductivity relates to conduction heat flux which is different from thermal stability that we are seeking in this work. A large number of other authors in different contexts have discussed thermodynamic stability of solids. Mouhat and Coudert [10] present basic derivations of mechanical stability of crystalline lattices. In cubic crystals, the Born stability criteria in three separate relations are presented in terms of the second order elastic constants. In the rhombohedral class, there are four criteria in terms of the elastic constants. The authors state that the criteria have not been presented in the literature. In a classical work by Truesdell and Noll "The Non-linear Field Theories of Mechanics" [11] only the two expression for mechanical stability for elastic material are presented in terms of μ and λ. There are no derivations. Chen et al. [12,13] have examined mechanical stability based on the Born criteria for a tetragonal structure relevant to TaSi (5/3) desilicides and Mo_5Si_3 silicides. The focus is the influence of vacancy defects on elastic and electronic properties from first-principles calculations

The work by Landau and Lifshitz, and Kochmann and Drugan are perhaps, the most comprehensible in the literature on the mechanical stability of isotropic deformable bodies. A direct mathematical derivation of thermodynamic stability analysis applicable to both fluids and deformable bodies along with details of derivations has not appeared in the literature to the best of our knowledge. A unified thermodynamic derivation may set the stage for better understanding. Deformable solids beyond the limit of thermodynamics stability would lead to rupture and creation of new surfaces. This is the whole idea of the concept proposed by Griffith in 1921 [14,15]. He suggested that the work from tensile should be equal to the surface energy of the created fractures. In fluids be-

yond the limit of thermodynamic stability, one may have a phase change. Despite the fact that solid failure and phase change in fluids may seem very different, the thermodynamic analysis show equivalency of the two processes. Generalized derivations of thermodynamic stability analysis in fluids and deformable isotropic solids is the main motivation of our work. There is very interesting observation in relation to failure of solid materials which is very different from instability in fluids. Failure of solids depends on contact with fluids. Let us consider a piece of shale rock and apply stress through different fluids. The breaking of the rock will depend on the type of fluid. When the shale rock is contact with water, the break down pressure may be two times higher than carbon dioxide. The effect of different fluids on failure of rocks in relation to fracturing fluids has not been fully resolved. In a recent work we have analyzed the effect of three different fluids in fracturing of rocks [16]. Through Griffith's idea, the effect of different fluids is introduced and the potential energy of the rock is converted to the fluid-rock interfacial free energy of the created surface. As a first step the thermodynamic stability of bulk rock is the key.

In the following, we will present our derivations of thermodynamic stability of deformable isotropic linear elastic solids. The same approach will be used for fluid stability.

2. Mechanics of elastic bodies

The basic expression in relating the strain to displacement (when the space derivatives of the deformation are small) is given by [17]

$$\boldsymbol{\varepsilon} = \frac{1}{2}\left[\nabla \mathbf{s} + (\nabla \mathbf{s})^T\right]. \tag{1}$$

where $\mathbf{s}$ is the displacement. Using Eq. (1), the expression for the element ε_{ij} is given by

$$\varepsilon_{ij} = \frac{1}{2}\left[\frac{\partial s_i}{\partial x_j} + \frac{\partial s_j}{\partial x_i}\right]. \tag{2}$$

The expression for work per unit volume for solid displacement is given by

$$dw = \boldsymbol{\sigma} : d\boldsymbol{\varepsilon} \tag{3}$$

where : represents the double dot product of two tensors. In Eq. 3, the work done on the solid from the tension adds to the potential energy of the solid and is considered positive. Eq. (3) can be written as,

$$dw = \sum_{i=1}^{n}\sum_{j=i}^{n}\sigma_{ij}d\varepsilon_{ij}, \tag{4}$$

where σ_{ij} and ε_{ij} are the ij-th element of the tensor $\boldsymbol{\sigma}$ and $\boldsymbol{\varepsilon}$, respectively. The dimension of the solid body is denoted by n. Eq. (4) gives the expression for work per unit volume. Next, we write the expression for Hooke's law in general form [18,19]

$$\boldsymbol{\sigma}(T, \boldsymbol{\varepsilon}) = (T - T_0)\mathbf{B} + \mathbb{C}\boldsymbol{\varepsilon}, \tag{5}$$

where T_0 is the temperature of the initial unloaded state, $\mathbf{B}$ is a second order tensor with n^2 elements, and $\mathbb{C}$ is a fourth order tensor with n^4 elements (81 in 3D and only one in 1D). Using Eq. (5), the expression for the element σ_{ij} is given by

$$\sigma_{ij}(T, \boldsymbol{\varepsilon}) = -b_{ij}(T - T_0) + \sum_{k=1}^{n}\sum_{l=1}^{n}C_{ijkl}\varepsilon_{kl}, \tag{6}$$

where b_{ij} and C_{ijkl} are the ij-th and $ijkl$-th element of tensor $\mathbf{B}$ and $\mathbb{C}$, respectively. In 1D,

$$F = h(T - T_0) + k(x - x_0) \tag{7}$$

where F is the force, h is the linear thermal expansion

$$h = -k \left(\frac{\partial x}{\partial T} \right)_F, \tag{8}$$

k is the Spring constant, and x is displacement from the original position x_0. In higher dimensions ($n > 1$), the expression for the element σ_{ij} in terms of Lamé constant λ and μ is given by (in isotropic medium) [20,21]

$$\sigma_{ij}(T, \boldsymbol{\varepsilon}) = -\beta(T - T_0)\delta_{ij} + \lambda\delta_{ij}\sum_{k=1}^{n} \varepsilon_{kk} + 2\mu\varepsilon_{ij}, \tag{9}$$

where δ_{ij} is the Kroneker delta function, $\beta = \alpha[\lambda + (2/n)\mu]$, α is the coefficient of thermal expansion

$$\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_\sigma = -\frac{1}{\rho} \left(\frac{\partial \rho}{\partial T} \right)_\sigma, \tag{10}$$

where $\rho = m/V$, m is the total mass, and V is the volume of the body. In the derivation of Eq. (10) one may use,

$$\frac{dV}{V} = \sum_{i=1}^{n} d\varepsilon_{ii}. \tag{11}$$

The inverse of Hooke's law relating the strain to the stress is given by

$$\varepsilon_{ij}(T, \boldsymbol{\sigma}) = \frac{\beta(T - T_0)}{n\lambda + 2\mu}\delta_{ij} + \frac{1}{2\mu}\sigma_{ij} - \frac{\delta_{ij}\lambda}{2\mu(n\lambda + 2\mu)}\sum_{k=1}^{n} \sigma_{kk}. \tag{12}$$

Based on Eq. (12), the expressions for strain in 2D, and 3D are provided below.

$$\varepsilon_{ij}^{(2D)} = \frac{\beta(T - T_0)}{2(\lambda + \mu)} + \frac{1}{2\mu}\sigma_{ij} - \delta_{ij}\frac{\lambda}{4\mu(\lambda + \mu)}(\sigma_{11} + \sigma_{22}),$$
$$i, j = 1, 2, \tag{13}$$

$$\varepsilon_{ij}^{(3D)} = \frac{\beta(T - T_0)}{3\lambda + 2\mu} + \frac{1}{2\mu}\sigma_{ij} - \delta_{ij}\frac{\lambda}{2\mu(3\lambda + 2\mu)}(\sigma_{11} + \sigma_{22} + \sigma_{33}),$$
$$i, j = 1, 2, 3. \tag{14}$$

2.1. Young modulus and Poisson's ratio

The Young modulus is defined by

$$E = \frac{\sigma_{ii}}{\varepsilon_{ii}}. \tag{15}$$

Note that the above definition is the ratio of stress on the i direction to strain on the same direction while the stress on the other directions (in 2D and 3D) are constant. That is, $\sigma_{jj} = 0$, $j \neq i$. Combining Eqs. (15) and (12), and the condition stated above provides the expression for the Young modulus

$$E = \frac{2\mu(n\lambda + 2\mu)}{(n-1)\lambda + 2\mu}. \tag{16}$$

Poisson's ratio is defined by

$$\nu = -\frac{\varepsilon_{ii}}{\varepsilon_{11}} \tag{17}$$

Poisson's ratio and the Lamé constants are well defined in 2D and 3D. Let the stress on the direction other than i be equal to zero, i.e., $\sigma_{jj} = 0$, $j \neq i$. As a results, combining Eqs. (12) and (17) gives the expression for Poisson's ratio

$$\nu = \frac{\lambda}{(n-1)\lambda + 2\mu}. \tag{18}$$

The expressions for Young modulus and Poisson's ratio in terms of Lamé constants in 2D and in 3D are (from Eqs. (16) and (18)),

$$E^{(2D)} = \frac{4\mu(\lambda + \mu)}{\lambda + 2\mu}, E^{(3D)} = \frac{\mu(3\lambda + 2\mu)}{\lambda + \mu}, \tag{19}$$

$$\nu^{(2D)} = \frac{\lambda}{\lambda + 2\mu}, \nu^{(3D)} = \frac{\lambda}{2\lambda + 2\mu}. \tag{20}$$

Moreover, using Eqs. (16) and (18), the Lamé constants can be expressed in terms of Young modulus and Poisson's ratio:

$$\lambda = \frac{E\nu}{(1 + \nu)[1 - (n-1)\nu]}, \tag{21}$$

$$\mu = \frac{E}{2(1 + \nu)}. \tag{22}$$

In 2D, and 3D, Eq. (21) reads as

$$\lambda^{(2D)} = \frac{E\nu}{(1 + \nu)(1 - \nu)}, \lambda^{(3D)} = \frac{E\nu}{(1 + \nu)(1 - 2\nu)}. \tag{23}$$

Note that the relation $\mu = \mu(E, \nu)$ in Eq. (22) is independent of n.

2.2. Bulk modulus

The bulk modulus K is the volumetric modulus, while E is the line modulus. The bulk modulus is defined by

$$K = -V \left(\frac{\partial p}{\partial V} \right)_T. \tag{24}$$

where $p = -\delta_{ij}\sigma_{ij}$, for all $i, j = 1, \ldots, n$. Using Eq. (11), one can derive

$$K = \frac{1}{n} \left(\frac{\partial \mathrm{Tr}\boldsymbol{\sigma}}{\partial \mathrm{Tr}\boldsymbol{\varepsilon}} \right)_T, \tag{25}$$

where we have used $\mathrm{Tr}\boldsymbol{\sigma} = \sum_{i=1}^{n} \sigma_{ii}$, and $\mathrm{Tr}\boldsymbol{\varepsilon} = \sum_{i=1}^{n} \varepsilon_{ii}$. Using Hooke's law (9),

$$\mathrm{Tr}\boldsymbol{\sigma}(T, \mathrm{Tr}\boldsymbol{\varepsilon}) = -n\beta(T - T_0) + (n\lambda + 2\mu)\mathrm{Tr}\boldsymbol{\varepsilon}. \tag{26}$$

Combining Eqs. (25) and (26) one arrives at the general expression of bulk modulus

$$K = \lambda + \frac{2}{n}\mu. \tag{27}$$

3. Thermodynamics of stability

The first law of thermodynamics is stated as

$$du = Tds + dw, \tag{28}$$

where u is the internal energy per unit volume, T is temperature and s is the entropy per unit volume. Using Eq. (3), the first law of thermodynamics reads as

$$du = Tds + \boldsymbol{\sigma} : d\boldsymbol{\varepsilon}, \tag{29}$$

The Helmholtz free energy per volume $f = f(T, \boldsymbol{\varepsilon})$ can be obtained from the first Legendre transformation of u

$$df = -sdT + \boldsymbol{\sigma} : d\boldsymbol{\varepsilon}, \tag{30}$$

where $s = s(T, \boldsymbol{\varepsilon})$ is the entropy per volume. Since tensors $\boldsymbol{\sigma}$ and $\boldsymbol{\varepsilon}$ are symmetrical, the Helmholtz free energy per volume can be a function of ε_{ij} with $i \leq j$. Therefore,

$$df = -sdT + \sum_{i=1}^{n} \sigma_{ii}d\varepsilon_{ii} + 2\sum_{i<j} \sigma_{ij}d\varepsilon_{ij}, \tag{31}$$

i.e., there are only $1 + n + n(n-1)/2$ independent variables.

3.1. Stability based on f

According to [1,22,23] the state is locally stable, if the Helmholtz free energy is concave in temperature and convex in the extensive variables. Let us denote

$$\mathbf{y} = \left(\varepsilon_{11}, \ldots, \varepsilon_{nn}; \varepsilon_{12}, \ldots, \varepsilon_{1n}; \varepsilon_{23}, \ldots, \varepsilon_{2n}; \ldots, \varepsilon_{(n-1)n}\right)^T$$
$$\in \mathbb{R}^{n+n(n-1)/2}. \tag{32}$$

Then, the state is locally stable if the Hessian matrix $\mathbf{H}_\varepsilon$

$$\mathbf{H}_\varepsilon(\mathbf{y}) = \begin{pmatrix} \frac{\partial f}{\partial y_1 \partial y_2} & \frac{\partial f}{\partial y_1 y_2} & \cdots & \frac{\partial f}{\partial y_1 y_m} \\ \frac{\partial f}{\partial y_2 y_1} & \frac{\partial f}{\partial y_2 y_2} & \cdots & \frac{\partial f}{\partial y_2 y_m} \\ \vdots & \vdots & \ddots & \vdots \\ \frac{\partial f}{\partial y_m y_1} & \frac{\partial f}{\partial y_m y_2} & \cdots & \frac{\partial f}{\partial y_m y_m} \end{pmatrix}, \tag{33}$$

where y_i is the i-th component of vector $\mathbf{y}$, is positive definite, and

$$\frac{\partial^2 f}{\partial T^2} < 0. \tag{34}$$

The positive definiteness can be examined using the Sylvester criterion [24] or other method from linear algebra. In 1D, based on Eq. (7), the expression for the Helmholtz free energy is

$$df = -sdT + Fdx. \tag{35}$$

Then, the second derivative reads as

$$\left(\frac{\partial^2 f}{\partial x^2}\right)_T = k, \tag{36}$$

$$\left(\frac{\partial^2 f}{\partial T^2}\right)_x = -\left(\frac{\partial s}{\partial T}\right)_x. \tag{37}$$

In higher dimensions, combining Eqs. (9) and (31) results in

$$\frac{\partial f}{\partial \varepsilon_{ii}} = \sigma_{ii} = -\beta + \lambda \sum_{k=1}^n \varepsilon_{kk} + 2\mu\varepsilon_{ii}, \quad i = 1, \ldots, n, \tag{38}$$

$$\frac{\partial f}{\partial \varepsilon_{ij}} = 2\sigma_{ij} = 4\mu\varepsilon_{ij}, \quad i < j \text{ and } i, j = 1, \ldots, n, \tag{39}$$

$$\left(\frac{\partial f}{\partial T}\right)_\varepsilon = -s. \tag{40}$$

Using Eqs. (38)–(40), the second derivatives of the Helmholtz free energy f with respect to ε_{ij} and T read as

$$\frac{\partial^2 f}{\partial \varepsilon_{ii}^2} = \lambda + 2\mu, \quad i = 1, \ldots, n, \tag{41}$$

$$\frac{\partial^2 f}{\partial \varepsilon_{ii}\varepsilon_{jj}} = \lambda, \quad i < j, i = 1, \ldots, n, \tag{42}$$

$$\frac{\partial^2 f}{\partial \varepsilon_{ij}^2} = 4\mu, \quad i < j, i, j = 1, \ldots, n, \tag{43}$$

$$\left(\frac{\partial^2 f}{\partial T^2}\right)_\varepsilon = -\left(\frac{\partial s}{\partial T}\right)_\varepsilon. \tag{44}$$

The other second derivatives are zero.

Now, we present stability conditions in one, two, and three dimensions. First, we present the thermal condition. In 1D, the concavity argument in temperature results in condition

$$\left(\frac{\partial^2 f}{\partial T^2}\right)_x = -\left(\frac{\partial s}{\partial T}\right)_x < 0. \tag{45}$$

Using the specific heat capacity at constant displacement c_x defined by

$$c_x = T\left(\frac{\partial s}{\partial T}\right)_x, \tag{46}$$

the thermal stability condition (45) reads as

$$c_x > 0. \tag{47}$$

In 2D and 3D, the concavity argument in temperature results in condition

$$\left(\frac{\partial^2 f}{\partial T^2}\right)_\varepsilon = -\left(\frac{\partial s}{\partial T}\right)_\varepsilon < 0. \tag{48}$$

Since the specific heat capacity at constant strain c_ε

$$c_\varepsilon = T\left(\frac{\partial s}{\partial T}\right)_\varepsilon, \tag{49}$$

the thermal stability condition (48) reads as

$$c_\varepsilon > 0. \tag{50}$$

The mechanical stability arises from the convexity argument of the Helmholtz free energy in ε. In 1D, we readily obtain $k > 0$. In 2D, the strain variables are $\mathbf{y} = (\varepsilon_{11}, \varepsilon_{22}, \varepsilon_{12})^T$, and the Hessian matrix reads as

$$\mathbf{H}_\varepsilon^{(2D)}(\mathbf{y}) = \begin{pmatrix} \lambda + 2\mu & \lambda & 0 \\ \lambda & \lambda + 2\mu & 0 \\ 0 & 0 & 4\mu \end{pmatrix}. \tag{51}$$

Using the Sylvester criteria we get three conditions

$$\lambda + 2\mu > 0, \tag{52}$$

$$(\lambda + 2\mu)^2 - \lambda^2 > 0, \tag{53}$$

$$4\mu\left[(\lambda + 2\mu)^2 - \lambda^2\right] > 0. \tag{54}$$

In order to be positive definite, all three conditions must be satisfied. The solution is $\mu > 0$ and $\lambda + \mu > 0$. In 3D, the strain variables are $\mathbf{y} = (\varepsilon_{11}, \varepsilon_{22}, \varepsilon_{33}, \varepsilon_{12}, \varepsilon_{13}, \varepsilon_{23})^T$, and the Hessian matrix reads as

$$\mathbf{H}_\varepsilon^{(3D)}(\mathbf{y}) = \begin{pmatrix} \lambda + 2\mu & \lambda & \lambda & 0 & 0 & 0 \\ \lambda & \lambda + 2\mu & \lambda & 0 & 0 & 0 \\ \lambda & \lambda & \lambda + 2\mu & 0 & 0 & 0 \\ 0 & 0 & 0 & 4\mu & 0 & 0 \\ 0 & 0 & 0 & 0 & 4\mu & 0 \\ 0 & 0 & 0 & 0 & 0 & 4\mu \end{pmatrix}. \tag{55}$$

Using the Sylvester criteria we get six conditions

$$\lambda + 2\mu > 0, \tag{56}$$

$$(\lambda + 2\mu)^2 - \lambda^2 > 0, \tag{57}$$

$$(\lambda + 2\mu)^3 + 2\lambda^3 - 3\lambda^2(\lambda + 2\mu) > 0, \tag{58}$$

$$4\mu\left[(\lambda + 2\mu)^3 + 2\lambda^3 - 3\lambda^2(\lambda + 2\mu)\right] > 0, \tag{59}$$

$$16\mu^2\left[(\lambda + 2\mu)^3 + 2\lambda^3 - 3\lambda^2(\lambda + 2\mu)\right] > 0, \tag{60}$$

$$64\mu^3\left[(\lambda + 2\mu)^3 + 2\lambda^3 - 3\lambda^2(\lambda + 2\mu)\right] > 0. \tag{61}$$

Table 1
Stability conditions in different dimensions.

dimension	Mechanical			Thermal
	λ, μ	E, ν	K, μ	c_*
1D	-	$k > 0$	-	$c_x > 0$
2D	$\mu > 0, \lambda + \mu > 0$	$E > 0, -1 < \nu < 1$	$\mu > 0, K > 0$	$c_\varepsilon > 0$
3D	$\mu > 0, \lambda + (2/3)\mu > 0$	$E > 0, -1 < \nu \leq 0.5$	$\mu > 0, K > 0$	$c_\varepsilon > 0$

In order to be positive definite, all six conditions must be satisfied. The solution is $\mu > 0$ and $\lambda + 2/3\mu > 0$.

Therefore, in 2D and 3D, the mechanical stability is given by

$$
\begin{aligned}
\mu &> 0, \\
n\lambda + 2\mu &> 0.
\end{aligned}
\tag{62}
$$

3.2. Stability in terms of Young modulus and Poisson's ratio

Using Eqs. (21)–(22), the mechanical stability conditions can be expressed in terms of the Young modulus and Poisson's ratio. The stability condition $\mu > 0$ and Eq. (22) gives

$$
\frac{E}{2(1 + \nu)} > 0.
\tag{63}
$$

Therefore,

$$
(E > 0 \text{ and } \nu > -1) \text{ or } (E < 0 \text{ and } \nu < -1).
\tag{64}
$$

Next, we analyze the second stability condition $n\lambda + 2\mu > 0$. Using Eqs. (21)–(22), the stability condition can be transformed to

$$
\frac{E}{(1 - (n-1)\nu)} > 0.
\tag{65}
$$

Therefore,

$$
\left(E > 0 \text{ and } \nu < \frac{1}{n-1} \right) \text{ or } \left(E < 0 \text{ and } \nu > \frac{1}{n-1} \right),
$$
$$
n = 2 \text{ and } 3.
\tag{66}
$$

Combining Eqs. (64) and (66) leads to the final form of the stability conditions in terms of the Young modulus and Poisson's ratio

$$
E > 0 \text{ and } \nu \in \left(-1; \frac{1}{n-1} \right), \quad n = 2 \text{ and } 3.
\tag{67}
$$

3.3. Stability in terms of Bulk modulus

The mechanical stability conditions can be expressed in terms of Bulk modulus K and one other parameter. Using Eq. (27), $K = \lambda + (2/n)\mu$, and the condition from Eq. (62) results in

$$
K > 0 \text{ and } \mu > 0.
\tag{68}
$$

3.4. Summary of the stability conditions

In Table 1, we summarize the stability conditions in the three basic dimensions.

4. Thermodynamic stability of fluids

We will also use the Helmholtz free energy to derive the stability condition for fluids. For a single-component fluid, the Helmholtz free energy is given by

$$
df = -s dT - p d\nu,
\tag{69}
$$

which is obtained from Eq. (31) by

$$
\boldsymbol{\sigma} = -p\mathbf{I},
\tag{70}
$$

$$
d\nu = \sum_{i=1}^{3} d\varepsilon_{ii},
\tag{71}
$$

where $\mathbf{I}$ is the unit tensor. We will use the same method as in solids to get the well-known stability conditions for fluids [1]. The second derivative of f with respect to ν is,

$$
\left(\frac{\partial^2 f}{\partial \nu^2} \right)_T = -\left(\frac{\partial p}{\partial \nu} \right)_T.
\tag{72}
$$

Using the convexity argument, we get the condition

$$
-\left(\frac{\partial p}{\partial \nu} \right)_T > 0,
\tag{73}
$$

which is the mechanical stability condition. The thermal condition is derived from the concavity argument of the Helmholtz free energy in temperature. Therefore, the thermal condition reads as

$$
\left(\frac{\partial^2 f}{\partial T^2} \right)_\nu = -\left(\frac{\partial s}{\partial T} \right)_\nu < 0.
\tag{74}
$$

Since

$$
\left(\frac{\partial s}{\partial T} \right)_\nu = \frac{c_\nu}{T},
\tag{75}
$$

the condition (74) implies

$$
c_\nu > 0.
\tag{76}
$$

In our review of the literature on thermodynamic stability of elastic solids we observed the focus has been on mechanical stability without consideration of thermal stability. The criterion of thermal stability of isotropic deformable solids is given by Eq. (47) for 1D, and by Eq. (50) for 2D and 3D materials. One application relates to geothermal energy and calculation of energy transfer from hot rock by a working fluid for geothemal energy production as state of stress changes.

5. Concluding remarks

We have derived the criteria of thermodynamic stability of fluids and deformable and isotropic materials using Helmholtz free energy in a unified manner. The main conclusions from our work are:

1. The Helmholtz free energy can be used to derive the criteria of mechanical and thermal stability of both fluids and deformable isotropic solids based on Sylvester's approach to establish matrix definiteness.

2. The concavity of Helmholtz free energy in temperature can provide thermal stability. In fluids and in deformable solids the convexity with respect to strain, and volume, respectively, provides mechanical stability. Well known criteria of thermodynamic stability in 1D, 2D, and 3D in deformable solids, and fluids are then readily established.

3. The derivations in solids are more general and can be used to derive the expressions in fluids. From fluids one may not extend the derivations for deformable solids

Despite simplicity the derivations are rigorous; they will set the stage for investigation of effect of different fluids on failure of deformable materials. Fracturing of rocks by fluids such as CO_2 and water is a clear example of high industrial importance. The idea introduced by Griffith is in support of effect of different fluids on failure of elastic bodies [14–16,25].

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

CRediT authorship contribution statement

Tomáš Smejkal: Investigation, Writing – original draft. **Abbas Firoozabadi:** Conceptualization, Writing – original draft, Supervision. **Jiří Mikyška:** Supervision, Funding acquisition.

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Supplementary material

Supplementary material associated with this article can be found, in the online version, at 10.1016/j.fluid.2021.113219

References

[1] A. Firoozabadi, Thermodynamics and Applications in Hydrocarbon Energy Production, McGraw-Hill Education, New York, 2016.

[2] R. Lakes, Foam structures with a negative Poisson's ratio, Science 235 (4792) (1987) 1038–1040, doi:10.1126/science.235.4792.1038.

[3] R. Lakes, K.W. Wojciechowski, Negative compressibility, negative poisson's ratio, and stability, Physica status solidi (b) 245 (3) (2008) 545–551, doi:10.1002/pssb.200777708.

[4] K.N. Kudin, G.E. Scuseria, B.I. Yakobson, C2f, BN, And c nanoshell elasticity from ab initio computations, Physical Review B 64 (23) (2001), doi:10.1103/physrevb.64.235406.

[5] D.M. Kochmann, W.J. Drugan, Analytical stability conditions for elastic composite materials with a non-positive-definite phase, Proceedings of the Royal Society A: Mathematical, Physical and Engineering Sciences 468 (2144) (2012) 2230–2254, doi:10.1098/rspa.2011.0546.

[6] M. Liu, V.I. Artyukhov, B.I. Yakobson, Mechanochemistry of one-dimensional boron: structural and electronic transitions, J. Am. Chem. Soc. 139 (5) (2017) 2111–2117, doi:10.1021/jacs.6b12750.

[7] L.D. Landau, E.M. Lifshitz, Course of theoretical physics, theory of elasticity, volume 7, 3, Pergamon Press, 1986.

[8] J.W. Morris, C.R. Krenn, The internal stability of an elastic solid, Philos. Mag. A 80 (12) (2000) 2827–2840, doi:10.1080/01418610008223897.

[9] J. Dunwoody, R.W. Ogden, On the thermodynamic stability of elastic heat-conducting solids subject to a deformation−temperature constraint, Mathematics and Mechanics of Solids 7 (3) (2002) 285–306, doi:10.1177/108128602027736.

[10] F. Mouhat, F.-X. Coudert, Necessary and sufficient elastic stability conditions in various crystal systems, Physical Review B 90 (22) (2014), doi:10.1103/physrevb.90.224104.

[11] C. Truesdell, W. Noll, The Non-linear Field Theories of Mechanics, 3, Springer Berlin Heidelberg, Berlin, Heidelberg, 2003.

[12] J. Chen, X. Zhang, C. Ying, H. Ma, J. Li, F. Wang, H. Guo, The influence of vacancy defects on elastic and electronic properties of TaSi (5/3) desilicides from a first-principles calculations, Ceram Int 46 (8) (2020) 10992–10999, doi:10.1016/j.ceramint.2020.01.115.

[13] J. Chen, X. Zhang, L. Yang, F. Wang, The vacancy defects and oxygen atoms occupation effects on mechanical and electronic properties of Mo5Si3 silicides, Commun Theor Phys 73 (4) (2021) 045702, doi:10.1088/1572-9494/abe367.

[14] A.A. Griffith, VI. the phenomena of rupture and flow in solids, Philosophical Transactions of the Royal Society of London. Series A, Containing Papers of a Mathematical or Physical Character 221 (582–593) (1921) 163–198, doi:10.1098/rsta.1921.0006.

[15] A.A. Griffith, The theory of rupture, in: First International Congress for Applied Mechanics, 1924, pp. 55–63.

[16] Y. Feng, K. Haugen, A. Firoozabadi, Phase-field simulation of hydraulic fracturing by CO_2, water and nitrogen in 2D and comparison with laboratory data, submitted to Journal of Geophysical Research: Solid Earth (2021).

[17] W. Slaughter, The Linearized Theory of Elasticity, Birkhäuser, Boston, 2002.

[18] F. Maršík, Termodynamika kontinua, Academia, Praha, 1999.

[19] W. Nowacki, Problems of thermoelasticity, Prog. Aerosp. Sci. 10 (1970) 1–63, doi:10.1016/0376-0421(70)90003-5.

[20] F. Maršík, Consequences of thermodynamical conditions of stability for thermoviscous fluids and thermoviscoelastic solids, Acta Physica Hungarica 66 (1989) 198–2020, doi:10.1007/BF03155792.

[21] R.M. Christensen, Theory of Viscoelasticity, Academic Press, New York, 1982.

[22] H.B. Callen, Thermodynamics and an Introduction to Thermostatistics; 2nd ed, Wiley, New York, NY, 1985. URL https://cds.cern.ch/record/450289

[23] V.A. Lubarda, On the Gibbs conditions of stable equilibrium, convexity and the second-order variations of thermodynamic potentials in nonlinear thermoelasticity, Int J Solids Struct 45 (1) (2008) 48–63, doi:10.1016/j.ijsolstr.2007.07.010.

[24] R. Horn, Matrix analysis, Cambridge University Press, Cambridge New York, 2012.

[25] T. Wu, A. Firoozabadi, Calculation of solid–fluid interfacial free energy with consideration of solid deformation by molecular dynamics simulations, The Journal of Physical Chemistry A 125 (26) (2021) 5841–5848, doi:10.1021/acs.jpca.1c00735.