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INSTABILITIES OF A THERMO-MECHANO-CHEMICAL SYSTEM

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Abstract. A Hadamard instability analysis of the partial differential equations governing a coupled thermo-mechano-chemical system predicts instability of the spinoidal decomposition type as well as instability of the "negative creep" type.

I. Introduction. The well-known instability of a chemical system is the Cahn-Hilliard [1] spinoidal decomposition. However, in a thermo-mechano-chemical system more instabilities may occur. "Negative creep", a term introduced by Li [2], has been observed [3, 4] implying negative elastic moduli of the material. Li attempted to explain the phenomenon ad hoc in analogy to chemical spinoidal decomposition. Here we present a full instability analysis of the system of partial differential equations governing a thermo-mechano-chemical system. Constitutive equations for such systems have been developed by Bowen [5], Larché and Cahn [6], and others. We present a Hadamard instability analysis for a one-dimensional thermo-mechano-chemical system. In addition to the chemical spinoidal decomposition type of instability, a "negative creep" type is also shown to occur. Special cases when the thermal conductivity coefficient or the diffusion coefficient vanish are also examined.

II. Governing field equations for a thermo-mechano-chemical system. The governing field equations for a thermo-mechano-chemical system are:

$$\frac{\partial^2 w}{\partial t^2} - \frac{\partial \sigma}{\partial x} = 0 \qquad \text{(momentum)} \tag{1}$$

$$\frac{\partial c}{\partial t} = k\theta \frac{\partial^2 \mu}{\partial x^2} \qquad \text{(diffusion)} \tag{2}$$

$$\frac{\partial}{\partial t}\left[\frac{1}{2}v^2 + \Phi\right] - \frac{\partial}{\partial x}[v\sigma] = \nu \frac{\partial^2 \theta}{\partial x^2} \qquad \text{(energy)} \tag{3}$$

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with the following notation being introduced:

$$
\begin{array}{ll}
w & \text{displacement} \\
v & \text{velocity} \\
\varepsilon & \text{strain} \\
\sigma & \text{stress} \\
\theta & \text{temperature} \\
\eta & \text{entropy} \\
c & \text{concentration} \\
\mu & \text{chemical potential} \\
\Phi & \text{internal energy} \\
\psi & \text{free energy.}
\end{array}
\tag{4}
$$

For a thermo-mechano-chemical system we will make the constitutive assumption that the internal energy depends on either set of state variables (ε, η, c) or $(\varepsilon, \theta, \mu)$. With state variables (ε, η, c):

$$
\begin{aligned}
\Phi &= \widehat{\Phi}(\varepsilon, \eta, c), \\
\sigma &= \widehat{\Phi}_\varepsilon(\varepsilon, \eta, c) = \hat{\sigma}(\varepsilon, \eta, c), \\
\theta &= \widehat{\Phi}_\eta(\varepsilon, \eta, c) = \hat{\theta}(\varepsilon, \eta, c), \\
\mu &= \widehat{\Phi}_c(\varepsilon, \eta, c) = \hat{\mu}(\varepsilon, \eta, c)
\end{aligned}
\tag{5}
$$

or, with state variables $(\varepsilon, \theta, \mu)$:

$$
\begin{aligned}
\Phi &= \Phi(\varepsilon, \theta, \mu), \\
\psi &= \Phi - \theta\eta - \mu c = \psi(\varepsilon, \theta, \mu), \\
\sigma &= \psi_\varepsilon(\varepsilon, \theta, \mu) = \sigma(\varepsilon, \theta, \mu), \\
\eta &= \psi_\theta(\varepsilon, \theta, \mu) = \eta(\varepsilon, \theta, \mu), \\
c &= \psi_\mu(\varepsilon, \theta, \mu) = c(\varepsilon, \theta, \mu),
\end{aligned}
\tag{6}
$$

where subscripts denote differentiation with respect to that variable.

The following relations are obtained by differentiation:

$$
\begin{aligned}
\Phi_\theta &= \psi_\theta + \eta + \theta\eta_\theta + \mu c_\theta = \theta\eta_\theta + \mu c_\theta, \\
\Phi_\mu &= \psi_\mu + \theta\eta_\mu + c + \mu c_\mu = \theta\eta_\mu + \mu c_\mu, \\
\Phi_\varepsilon &= \psi_\varepsilon + \theta\eta_\varepsilon + \mu c_\varepsilon = \sigma + \theta\eta_\varepsilon + \mu c_\varepsilon.
\end{aligned}
\tag{7}
$$

From (5), (6), and (7) and subsequent differentiation it follows that

$$
\begin{aligned}
\sigma_\varepsilon &= \hat{\sigma}_\varepsilon + \hat{\sigma}_\eta\eta_\varepsilon + \hat{\sigma}_c c_\varepsilon, \\
\sigma_\theta &= \hat{\sigma}_\eta\eta_\theta + \hat{\sigma}_c c_\theta, \\
\sigma_\mu &= \hat{\sigma}_\eta\eta_\mu + \hat{\sigma}_c c_\mu,
\end{aligned}
\tag{8}
$$

which combine to give the following relationship between the "moduli":

$$\hat{\sigma}_\varepsilon = \sigma_\varepsilon - \frac{c_\mu \eta_\varepsilon - c_\varepsilon \eta_\mu}{c_\varepsilon \eta_\theta - c_\theta \eta_\mu}\sigma_\theta - \frac{c_\varepsilon \eta_\theta - c_\theta \eta_\varepsilon}{c_\varepsilon \eta_\mu - c_\theta \eta_\mu}\sigma_\mu. \tag{9}$$

From equations (2), (3), and (4) we obtain the reduced field equations

$$\begin{aligned} \frac{\partial^2 w}{\partial t^2} &= \frac{\partial \sigma}{\partial x}, \\ \frac{\partial c}{\partial t} &= k\theta \frac{\partial^2 \mu}{\partial x^2}, \\ \theta \frac{\partial \eta}{\partial t} + \mu \frac{\partial c}{\partial t} &= \nu \frac{\partial^2 \theta}{\partial x^2}, \end{aligned} \tag{10}$$

or, equivalently, reduce to

$$\begin{aligned} \frac{\partial^2 w}{\partial t^2} &= \frac{\partial \sigma}{\partial x}, \\ \frac{\partial c}{\partial t} &= k\theta \frac{\partial^2 \mu}{\partial x^2}, \\ \frac{\partial \eta}{\partial t} &= \frac{\nu}{\theta}\frac{\partial^2 \theta}{\partial x^2} - k\mu \frac{\partial^2 \mu}{\partial x^2}. \end{aligned} \tag{11}$$

It should be noted that in view of the above equations the Clausius-Duhem inequality [7] is automatically satisfied, i.e.,

$$\frac{\partial \eta}{\partial t} + \frac{\partial}{\partial x}\left[-\frac{\nu}{\theta}\frac{\partial \theta}{\partial x} + k\mu \frac{\partial \mu}{\partial x}\right] = \frac{\nu}{\theta^2}\left(\frac{\partial \theta}{\partial x}\right)^2 + k\left(\frac{\partial \mu}{\partial x}\right)^2 > 0. \tag{12}$$

By integration of (12) it follows that

$$\int \eta\, dx \Big|_\infty - \int \eta\, dx \Big|_0 = \int_0^\infty \int \left[\frac{\nu}{\theta^2}\left(\frac{\partial \theta}{\partial x}\right)^2 + k\left(\frac{\partial \mu}{\partial x}\right)^2\right] dx\, dt < \infty. \tag{13}$$

For the right-hand side of (13) to be bounded, one should expect $\frac{\partial \theta}{\partial x} \to 0$ and $\frac{\partial \mu}{\partial x} \to 0$ as $t = \infty$, which implies that the system tends to the state $\theta =$ constant and $\mu =$ constant as $t \to \infty$.

III. Hadamard instability of the linearized system. We next study sufficient conditions for instability of the thermo-mechano-chemical system (2), (3), and (4). By linearization of equation (11) about a constant state $(\varepsilon, \theta, \mu)$ we obtain the system

$$\begin{aligned} \frac{\partial^2 w}{\partial t^2} &= \sigma_\varepsilon \frac{\partial^2 w}{\partial x^2} + \sigma_\theta \frac{\partial \theta}{\partial x} + \sigma_\mu \frac{\partial \mu}{\partial x}, \\ c_\varepsilon \frac{\partial^2 w}{\partial x \partial t} + c_\theta \frac{\partial \theta}{\partial t} + c_\mu \frac{\partial \mu}{\partial t} &= k\theta \frac{\partial^2 \mu}{\partial x^2}, \\ \eta_\varepsilon \frac{\partial^2 w}{\partial x \partial t} + \eta_\theta \frac{\partial \theta}{\partial t} + \eta_\mu \frac{\partial \mu}{\partial t} &= \frac{\nu}{\theta}\frac{\partial^2 \theta}{\partial x^2} - k\mu \frac{\partial^2 \varpi}{\partial x^2}. \end{aligned} \tag{14}$$

In order to investigate Hadamard-type instability of the system, we try solutions of the form

$$
\begin{aligned}
w(x,t) &= ae^{px}e^{\lambda^2 t},\\
\mu(x,t) &= bpe^{px}e^{\lambda^2 t},\\
\theta(x,t) &= gpe^{px}e^{\lambda^2 t}.
\end{aligned} \tag{15}
$$

Setting $\xi \equiv p^2/\lambda^2$, instability will follow if $\lambda \gg 1$ implies $\xi < 0$, in which case bounded initial data will yield solutions exponentially increasing at any time t. Substituting (15) into (14) yields the homogeneous system for a, b, g:

$$
\begin{aligned}
&\lambda^2 a = \xi\sigma_\varepsilon a + \xi\sigma_\mu b + \xi\sigma_\theta g \Rightarrow a = \frac{\xi}{\lambda^2 - \sigma_\varepsilon \xi}[\sigma_\mu b + \sigma_\theta g],\\
&c_\varepsilon a + c_\mu b + c_\theta g = k\theta\xi b,\\
&\eta_\varepsilon a + \eta_\mu b + \eta_\theta g = \frac{\nu}{\theta}\xi g - k\mu\xi b.
\end{aligned} \tag{16}
$$

Setting the determinant of (16) to zero provides the relationship between λ^2 and ξ. In order to investigate the sign of ξ we distinguish the following cases:

Case 1. $k = 0, \nu = 0$. In this case equations $(16)_2$ and $(16)_3$ reduce to

$$
\begin{aligned}
(c_\mu\eta_\theta - c_\theta\eta_\mu)b &= -(c_\varepsilon\eta_\theta - c_\varepsilon\eta_\varepsilon)a,\\
(c_\mu\eta_\theta - c_\theta\eta_\mu)g &= -(c_\mu\eta_\varepsilon - c_\varepsilon\eta_\mu)a,
\end{aligned} \tag{17}
$$

which combined with $(16)_1$ yield the following condition between λ^2 and ξ:

$$
\xi\left\{\sigma_\varepsilon - \frac{\sigma_\varepsilon\eta_\theta - c_\theta\eta_\varepsilon}{c_\mu\eta_\theta - c_\theta\eta_\mu}\sigma_\mu - \frac{c_\mu\eta_\varepsilon - c_\varepsilon\eta_\mu}{c_\mu\eta_\theta - c_\theta\eta_\mu}\sigma_\theta\right\} = \lambda^2. \tag{18}
$$

In view of (9), (18) is written as

$$
\xi\hat{\sigma}_\varepsilon = \lambda^2 \tag{19}
$$

and hence,

$$
\begin{aligned}
&\hat{\sigma}_\varepsilon > 0 \text{ implies stability},\\
&\hat{\sigma}_\varepsilon < 0 \text{ implies instability}.
\end{aligned} \tag{20}
$$

Thus, for vanishing coefficient of diffusion and heat conductivity, the elastic modulus at constant entropy and concentration controls stability. This is the extension of the condition for stability of a thermo-mechano-chemical system at $k = 0$, obtained recently by Markenscoff [8], where it was shown that the addition of diffusion may render the system unstable.

Case 2. $k > 0$ and/or $\nu > 0$. In this case, under the assumption $\lambda \gg 1$, in order to balance terms of the same order of magnitude in equation (16), there are two possibilities: either $\xi = O(1)$ or $\xi = O(\lambda^2)$, which are examined below.

(a) *Roots* $\xi = O(1)$. In this case, from (16), it follows that $a = O(\lambda^{-2})$ and the system of $(16)_2$ and $(16)_3$ reduces to

$$\begin{aligned}(c_\mu - k\theta\xi)b + c_\theta g &= 0,\\ (\eta_\mu + k\mu\xi)b + \left(\eta_\theta - \frac{\nu}{\theta}\xi\right) g &= 0,\end{aligned} \tag{21}$$

with determinant

$$k\nu\xi^2 - \left[\underbrace{k(\theta\eta_\theta + \mu c_\theta)}_{\Phi_\theta} + \frac{\nu}{\theta}c_\mu\right] + (c_\mu\eta_\theta - c_\theta\eta_\mu) = 0. \tag{22}$$

By virtue of (7) and the last two equations (6), (22) is written in the form:

$$k\nu\xi^2 - \left[k\Phi_\theta + \frac{\nu}{\theta}c_\mu\right] + \psi_{\mu\mu}\psi_{\theta\theta} - \psi_{\mu\theta}^2 > 0. \tag{23}$$

For stability it is sufficient that both roots ξ be positive; for instability at least one root ξ should be negative, that is,

$$\left.\begin{aligned}&\Phi_\theta > 0\\ &c_\mu > 0\\ &c_\mu\eta_\theta - c_\theta\eta_\mu = \psi_{\mu\mu}\psi_{\theta\theta} - \psi_{\mu\theta}^2 > 0\end{aligned}\right\} \Rightarrow \textit{stability} \tag{24}$$

while an opposite sign in any one of the above equations implies instability.

Note here that Φ_θ, being the specific heat, is expected to be positive, and so is $c_\mu \equiv -\psi_{\mu\mu}$. The conditions (24) express the convexity of the function $\psi(\varepsilon, -\theta, -\mu)$.

The instability when any one of (24) fails is of the Cahn-Hilliard spinoidal decomposition type. The "negative creep" instability will be obtained below in the treatment of the case where the roots ξ are $O(\lambda^2)$.

(b) *Roots* $\xi = O(\lambda^2)$. Equations $(16)_2$ and $(16)_3$ reduce to

$$(c_\mu\eta_\varepsilon - c_\varepsilon\eta_\mu)b + (c_\theta\eta_\varepsilon - c_\theta\eta_\theta)g = \xi\left\{k(\theta\eta_\varepsilon + \mu c_\varepsilon)b - \frac{\nu}{\theta}c_\varepsilon g\right\} \tag{25}$$

and, for $\xi = O(\lambda^2)$, from (25) we must have

$$\underbrace{k(\theta\eta_\varepsilon + \mu c_\varepsilon)b}_{\Phi_\varepsilon - \sigma} - \frac{\nu}{\theta}c_\varepsilon g \approx 0. \tag{26}$$

Depending on whether the coefficients k and ν are zero or nonzero, we distinguish the following subcases:

(1): $\nu = 0, k > 0$.

$$\begin{aligned}b &\cong 0,\\ a &\cong \frac{\xi}{\lambda^2 - \sigma_\varepsilon\xi}\sigma_\theta g,\\ c_\varepsilon\sigma_\theta\frac{\xi}{\lambda^2 - \sigma_\varepsilon\xi} &= \frac{\theta(c_\theta\eta_\varepsilon - c_\varepsilon\eta_\varepsilon) - c_\theta(\theta\eta_\varepsilon + \mu c_\varepsilon)}{\theta\eta_\varepsilon + \mu c_\varepsilon} = \frac{c_\varepsilon(\theta\eta_\theta + \mu c_\theta)}{\theta\eta_\varepsilon + \mu c_\varepsilon},\end{aligned} \tag{27}$$

which yields

$$-\left\{\sigma_\varepsilon - \frac{\overbrace{\theta\eta_\varepsilon + \mu c_\varepsilon}^{\Phi_\varepsilon - \sigma}}{\underbrace{\theta\eta_\theta + \mu c_\theta}_{\Phi_\theta}} \frac{\sigma_\theta}{c_\varepsilon}\right\}\xi + \lambda^2 = 0 \tag{28}$$

and, in view of (6) and (7),

$$-\left\{\sigma_\varepsilon - \frac{\Phi_\varepsilon - \sigma}{\Phi_\theta}\frac{\sigma_\theta}{c_\varepsilon}\right\}\xi + \lambda^2 = 0. \tag{29}$$

Hence, instability follows if

$$\sigma_\varepsilon - \frac{\Phi_\varepsilon - \sigma}{\Phi_\theta}\frac{\sigma_\theta}{c_\varepsilon} < 0. \tag{30}$$

(2): $\nu > 0, k = 0$.
The system (16) yields

$$\begin{gathered} g \approx 0, \\ a \cong \frac{\xi}{\lambda^2 - \sigma_\varepsilon \xi}\sigma_\mu b - \left\{\sigma_\varepsilon - \frac{c_\varepsilon}{c_\mu}\sigma_\mu\right\}\xi + \lambda^2 = 0, \end{gathered} \tag{31}$$

from which instability occurs if

$$\sigma_\varepsilon - \frac{c_\varepsilon}{c_\mu}\sigma_\mu < 0. \tag{32}$$

(3): $\nu > 0, k > 0$.
The system (16) yields

$$g \cong \frac{k}{\nu}\frac{\theta}{c_\varepsilon}(\theta\eta_\varepsilon + \mu c_\varepsilon)b, \tag{33}$$

$$a \cong \frac{\xi}{\lambda^2 - \sigma\xi_\varepsilon}\left\{\sigma_\mu + \frac{k}{\nu}\frac{\theta}{c_\varepsilon}\sigma_\theta[\theta\eta_\varepsilon + \mu c_\varepsilon]\right\}b, \tag{34}$$

$$\frac{\xi}{\lambda^2 - \sigma\xi_\varepsilon}\left\{c_\varepsilon\sigma_\mu + \frac{k}{\nu}\theta\sigma_\theta[\theta\eta_\varepsilon + \mu c_\varepsilon]\right\} + c_\mu + \frac{k}{\nu}\frac{\theta}{c_\varepsilon}c_\theta[\theta\eta_\varepsilon + \mu c_\varepsilon] = k\theta\xi. \tag{35}$$

Balancing the leading terms in equation (35) gives

$$-\sigma_\varepsilon\xi + \lambda^2 = 0 \tag{36}$$

so that instability follows if

$$\sigma_\varepsilon < 0,$$

that is, if the modulus at constant temperature and chemical potential is negative. This is the instability condition called "negative creep" by Li [2].

In conclusion the instability analysis of the coupled system of partial differential equations and the ensuing analysis of the sign of the eigenvalues for a coupled thermo-mechano-chemical system has provided in a unified way not only the conditions for instability due to spinoidal decomposition, but also the conditions for instability due to "negative creep" type.

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References

[1] J. W. Cahn and John E. Hilliard, *Free energy of a nonuniform system. I. Interfacial free energy*, J. Chemical Phys. **28**, 258–267 (1958)

[2] J. C. M. Li, *Negative creep and mechanochemical spinoidal in amorphous metals*, Materials Science and Engineering **98**, 465–468 (1988)

[3] E. Girt, P. Tomic, I. Gazdic, and T. Mihac, *The relaxation of $Cu_{60}Zr_{40}$ metallic glass under tensile stress*, J. Phys. F. **13**, 747–751 (1983)

[4] P. T. Vianco, *Creep and structural relaxation of amorphous metals*, Ph.D. Thesis, University of Rochester, Rochester, NY, 1986

[5] R. M. Bowen, *Toward a thermodynamics and mechanics of mixtures*, Arch. Rat. Mech. Anal. **24**, 370–403 (1967)

[6] F. C. Larché and J. W. Cahn, *The interactions of composition and stress in crystalline solids*, Acta Metall. **33**, 331–357 (1985)

[7] I. Mueller, *Thermodynamics*, Pitman, London, 1985

[8] X. Markenscoff, *Diffusion induced instability*, Quart. Appl. Math. **59**, 147–151 (2001)