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# A relation between the jump in temperature across a propagating phase boundary and the stability of solid phases

RICHARD D. JAMES

*Division of Engineering, Brown University, Providence, RI 02912, USA*

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## Abstract

Unlike the phases of ordinary fluids, solid phases are often found to occur in metastable equilibrium. At constant temperature, a stress-extension test on a bar made of a material which allows the co-existence of two phases will often produce a large hysterysis loop. It is then impossible, by static measurements alone, to determine the values of stress $\tau^*$ and temperature $\theta^*$ at which the two phases have the same specific free energy. I show that by a measurement of the jump in temperature across a propagating phase boundary, $(\tau^*, \theta^*)$ can be determined in several cases of interest.

The analysis offers insight into the general behavior of propagating phase boundaries as well as the thermodynamics of solid phases.

The discussion is centered around the so-called shape-memory alloys.

## 1. Introduction

Intuitively, an equilibrium state is metastable if after having been disturbed *slightly,* the dynamic motion which takes place returns to the equilibrium state or at least does not stray very far away from it. This concept has never been made precise with any generality in continuum mechanics. Elementary examples show that the class of metastable states is very sensitive to the precise interpretation given to the word "slightly."

One theory in which we can begin to explore a definite concept of metastability is Gibbs's stability theory [1]. To fix the ideas, consider an isothermal force-stretch relation for a thermoelastic bar like the one pictured in Fig. 1, which permits the co-existence of two phases. The dashed line cuts off equal areas of the curve above and below; it is called the *Maxwell Line* [2]. Suppose a bar at temperature $\theta_e$ with this force-stretch relation is loaded in a dead loading device with an assigned load $\sigma_0$. The appropriate Gibbs potential is

$$G=\int_0^L\{\phi(y'(X),\theta_e)-\sigma_0 y'(X)\}\mathrm{d}X, \tag{1.1}$$

$y(X)$ being the deformation of the bar, $u=y'(X)$ being the stretch, and $\phi(u,\theta)$ being the free energy: $\sigma=\phi_u$. I shall say that a state $\tilde{y}$ is *stable* if it minimizes [1] $G$ relative to

[1] Precise statements of these conditions are contained in [4]. The class of functions $y(X)$ considered is the class of continuous, piecewise differentiable functions.

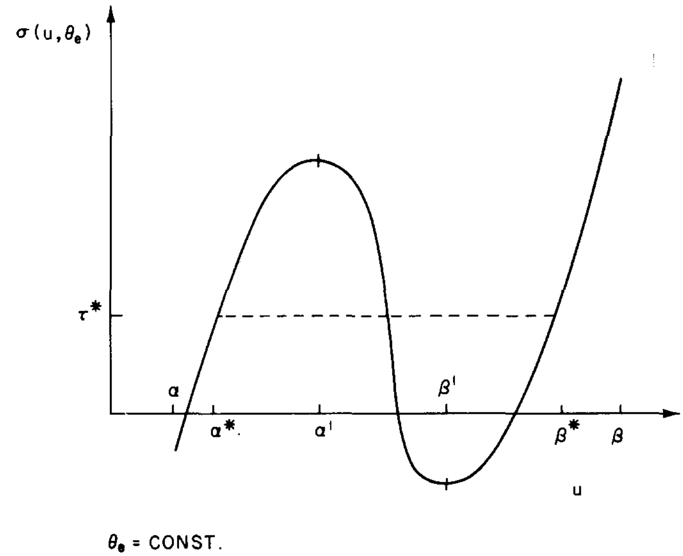


Figure 1. A force-stretch relation at constant temperature. The Maxwell Line is dashed.

all other states in the domain of $G$, *metastable* if it minimizes $G$ relative to all other states $y$ in the domain of $G$ which satisfy

$$|y'(X)-\tilde{y}'(X)|<\varepsilon, \qquad \forall X\in[0,L], \tag{1.2}$$

for some sufficiently small $\varepsilon>0$.

The significance of the Maxwell Line is the following: *if $\tilde{y}$ is stable, then $\tilde{y}'(X)$ must lie in the interval* $[\alpha, \alpha^*]$ *or the interval* $[\beta, \beta^*]$ *for each $X$ in* $[0, L]$. Thus, if we were always to seek stable deformations, and we loaded the bar incrementally with an increasing sequence of dead loads, we would find that the bar would first "yield" at a load $\sigma_0$ equal to $\tau^*$ shown in Fig. 1. In Gibbs's theory "yielding" occurs when one or more discontinuities of $y'(X)$, or *phase boundaries*, appear in the bar, separating regions of large stretch $u=\beta^*$ from regions of small stretch $u=\alpha^*$. For $\sigma_0>\tau^*$ the bar is homogeneously deformed in the phase of large stretch ($\beta$-phase). Upon unloading the bar returns to the phase of small stretch ($\alpha$-phase) exactly at $\sigma_0=\tau^*$, so no hysteresis is seen. Simple proofs of these statements are found in the paper by Ericksen [4].

A few materials behave much like this, those being among the so-called shape-memory alloys. Figure 2a shows an example. [2] For these materials (at the appropriate temperatures) the Maxwell Line can be located instantly. The thermoelastic bar theory used here can be easily generalized to include a body force and a non-uniform cross-section, and for these materials many problems can be solved [3].

Most bars which permit the co-existence of two solid phases, including the shape-memory alloys at most temperatures, do not behave like the stable deformations. They yield at loads presumably greater than $\tau^*$, and having yielded, they may continue to

[2] The experiments pictured in Fig. 2 are representative of those carried out in a hard loading device. Theory predicts the same stress-extension *curves* for *stable* deformations in the hard and dead loading devices.

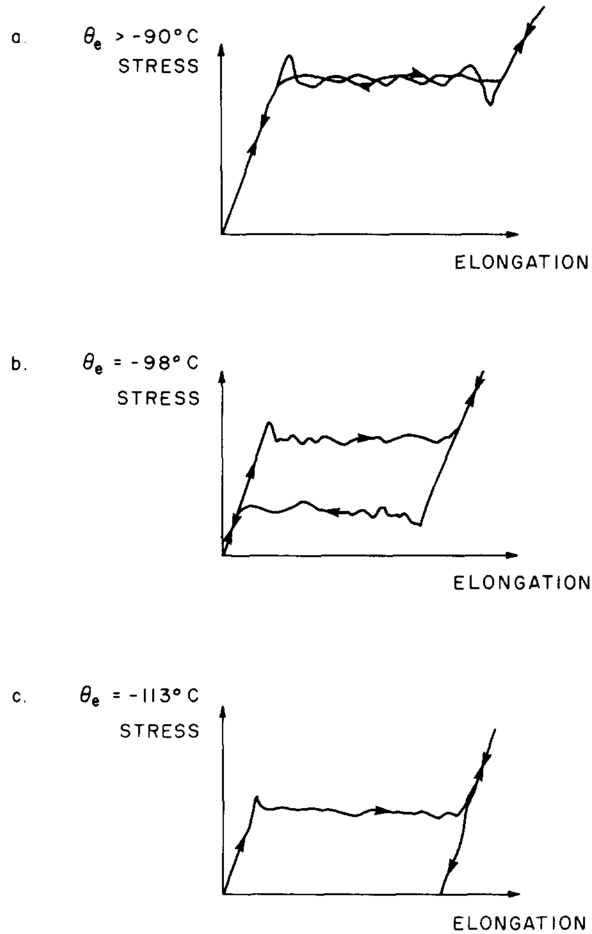


Figure 2. Representative static stress-elongation curves for thin bars of the shape-memory alloy Cu-14.2Al-4.3Ni(w + %) in a hard loading device ([5] p. 68).

support the two phases if the load is then decreased to zero. Two examples are shown in Figs. 2b and 2c. A number of polymers show similar behavior. I have adopted the definition of metastability given just before (1.2) in response to these observations. This definition of metastability implies that if $\tilde{y}$ is metastable, then $\tilde{y}'(X)$ must have values on the intervals $[\alpha, \alpha^1)$ or $(\beta^1, \beta]$ (see Fig. 1). Of course it must also be equilibrated: [3]

$$\sigma(y'(X), \theta_e) = \sigma_0, \qquad X \in [0, L]. \tag{1.3}$$

The definition [4] does not predict a definite yield point. However, experiments on shape-memory alloys also do not seem to give a reproducible value of the yield point (cf. [5], p. 424).

[3] The conditions stated are both necessary and sufficient for metastability [3].

[4] It is easily seen from this definition of metastability that such classical statements as Gibbs's phase rule and the Clausius-Clapeyron equation fail for metastable states. Rodriguez and Brown ([5] p. 34) have also questioned the validity of the Clausius-Clapeyron equation for these transformations.

The theory is sensitive to the precise meaning given to the term metastability. If (1.2) is replaced by either of the following commonly used norms,

$$\max_{[0,L]} |y(X) - \tilde{y}(X)| < \varepsilon, \quad \text{or}$$

$$\int_0^L |y'(X) - \tilde{y}'(X)|^n \mathrm{d}X < \varepsilon, \qquad n \geqslant 1, \tag{1.4}$$

then behavior as is shown in Figs. 2b and 2c cannot be predicted by Gibbs's theory.

If we accept that a bar often equilibrates in metastable states, then there is generally no way to determine the Maxwell Line from static stress-elongation curves. It is the purpose of this paper to show how the Maxwell Line can be determined. The calculations lead to a suggestion for an experimental program (Section 7) designed to determine the Maxwell Line.

If it be admitted that bars often equilibrate in metastable states, then of what use is the Maxwell Line? One answer comes from the discussion above; if $\sigma_0 < \tau^*$ then states of homogeneous deformation in the $\alpha$-phase are *stable*. On this basis one can argue that $\tau^*$ is the ultimate safe load designers should use to prevent failure of this kind. For the shape-memory alloys this "failure" is desired, and the hysteresis which arises from yielding at loads other than $\tau^*$ is responsible for the shape-memory effect. [5] It is not possible to assess the usefulness of the shape-memory effect without a knowledge of $\tau^* = \tilde{\tau}^*(\theta_e)$. In particular, the calculation of efficiency of a shape-memory engine due to Wayman ([5], p. 3]) requires that the temperature at which $\tau^*$ vanishes be known.

To this end I propose to study a fully general thermodynamic theory for a one-dimensional bar. I regard the specific heats of each of the phases alone as known, as well as the stress-elongation curves over an interval of temperatures. Only for free energies with special properties are these sufficient to determine the Maxwell Line. Additional information may come from a variety of sources, but I argue that by a measurement of the jump in temperature across a moderately fast moving phase boundary, the Maxwell Line can be determined for a variety of shape-memory alloys. This measurement also provides a check on the theory as a whole for an alloy whose Maxwell Line has been determined by other means. For smooth solutions of the thermodynamic equations which depend on the single variable $X - Vt$, the jump in temperature is independent, in a precise sense (Section 3), of the dynamic theory used. The properties of these solutions serve to clarify some general features of the thermodynamics of finite deformation of solids. They provide examples of arbitrary slow motions for which the Clausius-Duhem inequality holds with strict inequality, as well as fast motions for which the usual form of the adiabatic approximation is not valid.

The jump in temperature is generally quite large for moderately fast moving phase boundaries; this is shown by the interesting experiments of Rodriguez and Brown ([5] p. 36]) who observe a temperature rise of about 12°C at an overall rate of (relative) extension of 0.2/sec for CuAlNi.

[5] The shape-memory effect is illustrated by Fig. 2. A bar is loaded at constant temperature according to the stress-elongation curve $2c$. When the load is removed some part of the bar remains in the $\beta$-phase. Upon heating at zero load the $\beta$-phase becomes unstable and the bar snaps back to its original shape. If a load is applied to the bar as it snaps back, the bar will lift the load and, for some alloys, the work done exceeds the work done originally to deform the bar. A heat engine can be built based upon this phenomenon.

I determine the Maxwell Line for a variety of materials in Sections 6a–6f. These include alloys like the one pictured in Fig. 2 as well as some alloys for which the Maxwell Line is not known at any temperature. There remains a certain special class of materials (of which I know no examples in nature) for which I am not able to determine the Maxwell Line.

## 2. Thermodynamic bar theory

A bar is described by a single material co-ordinate

$$X \in [0, L]. \tag{2.1}$$

$L$ is the length of the undeformed bar. A solution of the equations of thermodynamic bar theory is a pair of functions

$$y(X, t), \qquad \eta(X, t) \qquad X \in [0, L], \qquad t \geqslant 0. \tag{2.2}$$

The first gives the position occupied by the point $X$ at the time $t$. The second gives the specific entropy at $(X, t)$. The *stretch* and *velocity* are denoted by

$$u = y_X, \qquad v = y_t. \tag{2.3}$$

The functions $y$ and $\eta$ are subject to the equations of balance of mass, momentum, and energy and the Clausius-Duhem inequality [6]:

$$\begin{aligned}
&u\rho = \rho_0,\\
&\int_0^X \rho_0 v \,\mathrm{d}X\big|_0^T = \int_0^T \sigma \,\mathrm{d}t\big|_0^X,\\
&\int_0^X \rho_0\left(\varepsilon + \tfrac{1}{2}v^2\right)\mathrm{d}X\big|_0^T = \int_0^T (\sigma v - q)\,\mathrm{d}t\big|_0^X + \int_0^T\int_0^X r\,\mathrm{d}X\,\mathrm{d}t,\\
&\int_0^X \rho_0 \eta \,\mathrm{d}X\big|_0^T \geqslant -\int_0^T \frac{1}{\theta} q \,\mathrm{d}t\big|_0^X + \int_0^T\int_0^X \frac{r}{\theta}\,\mathrm{d}X\,\mathrm{d}t.
\end{aligned} \tag{2.4}$$

In (2.4) $\rho_0 =$ const. is the *density* (mass per unit length) *of the undeformed bar*, $\rho$ is the *density of the deformed bar*, $\sigma$ is the *axial force*, $\varepsilon$ is the *specific internal energy*, $q$ is the *axial heat flux*, $r$ is the *lateral heat absorption* and $\theta > 0$ is the absolute *temperature*. If a solution $\{y, \eta\}$ of $(2.4)_{2,3,4}$ is known, Eqn. $(2.4)_1$ determines the density of the deformed bar, which is in no other way restricted. The condition of invertibility $u = y_X > 0$ shall be assumed. The lateral heat absorption $r$ represents the heat flux directed into the side of the bar at a point $X$ due to both radiation and conduction to the ambient; it is by no means unimportant in bar theory. Classically, it is given by the assumption $r =$ const.$(\theta - \theta_0)$, $\theta_0$ being an effective ambient temperature. More generally, it depends upon both the constitution of the body and the conditions of the environment.

The unknown functions $y$ and $\eta$ are related to the specific internal energy, axial force, temperature and axial heat flux by constitutive equations. For general motions of solid bars which may change phase, it is not yet clear what form these relations should take. In fluid mechanics the situation is better understood due to the works of van der Waals [7] and Korteweg [8], who assumed that the density varies smoothly across a phase boundary. The theories of these authors do not satisfy the principle of local action; in van der Waals' theory the pressure at a point in the fluid is a functional of the density in a neighborhood of the point. Korteweg assumed that the pressure depends upon the density and its first and second gradients in a particular way. Chemical engineers [9] have measured the profile of a stationary phase boundary so as to determine the material functions in Korteweg's theory. I know of no such measurements in solids. The analogue of the Korteweg assumption for thermoelastic bars would be that the axial force depend upon the stretch and its first and second gradients. According to recent work by Slemrod [10], the one-dimensional dynamic theory which emerges from Korteweg's assumption yields uniqueness when it is desired, unlike the purely elastic theory [11]. Slemrod [10] has also shown that a purely mechanical theory with a small viscosity, e.g., $\sigma = \hat{\sigma}(u, \eta) + \mu v$, $\mu = \text{const.} > 0$, yields *unreasonable* predictions.

Internal variables provide an alternative approach. For the shape-memory materials, an internal variable might represents the density of twins in the margensitic ($\beta$-) phase. The statistical-mechanical theory of Müller [12] gives a nice model of the martensitic phase in terms of snap-springs, from which an interpretation of an internal variable and the appropriate kinetics might arise. The problem of what constitutive relations are appropriate for general motions of solids which may change phase is plainly not trivial.

I shall make an assumption which is consistent with many formulations of the theories described above. Let there exist a twice differentiable equation of state for the specific internal energy,

$$e(u, \eta), \tag{2.5}$$

dependent upon the stretch and entropy. Let $\tau$ and $\mu$ be fixed, finite constitutive parameters. The constitutive relations will be subject to

**Assumption 1.** *Given* $\xi > 0$ *there is a* $\delta > 0$ *such that if*

$$\begin{aligned} &\sup\{|u-u_0| + |u_X| + |u_{XX}| + |u_t| + |\eta - \eta_0| + |\eta_X| + |\eta_t|\} < \delta, \\ &X \in [X_0 - \mu, X_0 + \mu] \\ &t \in [t_0 - \tau, t_0] \end{aligned} \tag{2.6}$$

*then*

$$\begin{aligned} &\left|\theta(X_0, t_0) - \frac{\partial e}{\partial \eta}(u_0, \eta_0)\right| < \xi, \\ &\left|\sigma(X_0, t_0) - \rho_0 \frac{\partial e}{\partial u}(u_0, \eta_0)\right| < \xi, \\ &|\varepsilon(X_0, t_0) - e(u_0, \eta_0)| < \xi, \\ &|q(X_0, t_0)| < \xi, \end{aligned} \tag{2.7}$$

*where* $u_0 = u(X_0, t_0)$ *and* $\eta_0 = \eta(X_0, t_0)$. [6]
The assumption states that if the body has been held close to equilibrium in the sense of (2.6) on an interval of length $2\mu$ centered at $X_0$, for a duration of time $\tau$, then the relations of classical thermostatics are approximately satisfied. The material constants $\mu$ and $\tau$ denote, respectively, the extent of the nonlocal action and the duration of the

[6] All derivatives involved are assumed to exist and be continuous.

memory. The Assumption 1 could be easily generalized to include nonlocal actions of infinite extent, as in the van der Waals theory, and memories of infinite duration, as in the theory of fading memory. Ordinary theories of viscosity and heat conduction are included.

As an example of a set of constitutive assumptions which satisfies Assumption 1, we may choose relations motivated by the Korteweg theory:

$$\begin{aligned}
&\theta = e_\eta(u, \eta),\\
&\sigma = \rho_0 e_u(u, \eta) + c(u, \eta) u_X^2 + d(u, \eta) u_{XX} + f(u, \eta) u_t,\\
&\varepsilon = e(u, \eta),\\
&q = \kappa(u, \eta)\theta_X. \qquad (2.8)
\end{aligned}$$

Alternatively, we might choose constitive relations motivated in part by the theory of van der Waals, and in part by the theory of fading memory:

$$\begin{aligned}
&\theta = e_\eta(u, \eta) + \Theta_{\mu,\tau}[u(\cdot), \eta(\cdot)],\\
&\sigma = \rho_0 e_u(u, \eta) + \Sigma_{\mu,\tau}[u(\cdot), \eta(\cdot)],\\
&\varepsilon = e(u, \eta),\\
&q = \kappa(u, \eta)\theta_X. \qquad (2.9)
\end{aligned}$$

Here, $\Theta_{\mu,\tau}$ and $\Sigma_{\mu,\tau}$ are functionals defined over pairs of smooth functions $[u(\cdot), \eta(\cdot)]$, which are themselves restricted to the domain $[X-\mu, X+\mu]\times[t-\tau, t]$. So as to ensure consistency with Assumption 1, we assume that the functionals

$$\frac{\partial}{\partial X}\Theta_{\mu,\tau}, \Theta_{\mu,\tau}, \Sigma_{\mu,\tau} \qquad (2.10)$$

exist, are continuous in the norm (2.6), and vanish when $u$ and $\eta$ are constant on $[X-\mu, X+\mu]\times[t-\tau, t]$.

Finally, Assumption 1 is consistent with some theories having internal variables, for example

$$\begin{aligned}
&\theta = \tilde{\theta}(u, \eta, \xi),\\
&\sigma = \tilde{\sigma}(u, \eta, \xi),\\
&\varepsilon = \tilde{\varepsilon}(u, \eta, \xi),\\
&q = \kappa(u, \eta, \xi)\theta_X,\\
&\xi_t = \Xi(u, \eta, u_t, \eta_t, u_X, \eta_X, \xi), \qquad \xi \in [\hat{\alpha}, \hat{\beta}]. \qquad (2.11)
\end{aligned}$$

Here, $\Xi$ satisfies conditions which make the internal variable "relax" to one of its extreme values $\hat{\alpha}$ or $\hat{\beta}$, in a time interval of length $\tau$, whenever the hypothesis (2.6) is fulfilled. It is reasonable to lay down assumptions on $\Xi$ which imply that $\xi \to \hat{\alpha}$ when $(u_0, \eta_0) \in \mathfrak{D}_\alpha$ and $\xi \to \hat{\beta}$ when $(u_0, \eta_0) \in \mathfrak{D}_\beta$, the sets $\mathfrak{D}_\alpha$ and $\mathfrak{D}_\beta$ being disjoint subsets of the domain of $e$ associated with the two stable phases.[7] The functions $\tilde{\theta}$, $\tilde{\sigma}$ and $\tilde{\varepsilon}$

[7] It is not clear what we should assume about the behavior of $\xi$ when $(u_0, \eta_0)$ corresponds to values $(u_0, \theta_0)$ at which $\phi_{uu} < 0$. Thus, (2.11) may be consistent with Assumption 1 only on a subset of the domain of $e$. When we come to apply Assumption 1 in §3, we shall do so only at points where $\phi_{uu} > 0$.

must reduce to $e_\eta$, $\rho_0 e_u$ and $e$ if $(u_0, \eta_0) \in \mathfrak{D}_\alpha$ and $\xi = \hat{\alpha}$ or if $(u_0, \eta_0) \in \mathfrak{D}_\beta$ and $\xi = \hat{\beta}$. [8]

Assumptions on $\Xi$ that insure the behavior just described are not difficult to formulate, but I shall omit them. Of the three theories mentioned I lean toward the third (cf. (2.11)) for the shape-memory alloys. In formulating these theories the guiding principle has been simplicity rather than generality of equipresence.

We shall use the notation

$$\sigma_e = \rho_0 \frac{\partial e}{\partial u},$$
$$\theta_e = \frac{\partial e}{\partial \eta}, \tag{2.12}$$

and we shall call these quantities the *equilibrium axial force* and *equilibrium temperature*, respectively. From Assumption 1 we have

$$\left.\begin{aligned} \sigma &= \sigma_e, \\ \theta &= \theta_e, \\ q &= 0, \end{aligned}\right\} \quad \text{at} \quad (X_0, t_0), \tag{2.13}$$

whenever $u$ and $\eta$ are constant on $[X_0 - \mu, X_0 + \mu] \times [t_0 - \mu, t_0]$.

The *specific heat at constant stretch* is defined by

$$C_u \equiv \frac{\dfrac{\partial e}{\partial \eta}}{\dfrac{\partial^2 e}{\partial \eta^2}}. \tag{2.14}$$

I shall assume that $C_u > 0$ so $e_\eta(\cdot, u)$ has an inverse; then we can solve $(2.12)_2$ locally [9] to obtain

$$\eta = \hat{\eta}(u, \theta_e). \tag{2.15}$$

We may then express $e$ in terms of $\theta_e$ and $u$,

$$\hat{e}(u, \theta_e) \equiv e(u, \hat{\eta}(u, \theta_e)), \tag{2.16}$$

and define the free energy by

$$\hat{\phi}(u, \theta_e) = \hat{e}(u, \theta_e) - \theta_e \hat{\eta}(u, \theta_e). \tag{2.17}$$

The equilibrium axial force may now be expressed in two equivalent ways, *viz.*,

$$\sigma_e = \rho_0 \frac{\partial e}{\partial u}(u, \hat{\eta}(u, \theta_e)) = \rho_0 \frac{\partial \hat{\phi}}{\partial u}(u, \theta_e). \tag{2.18}$$

The graph of $\sigma_e$ vs. $u$ at fixed $\theta_e$ is shown in Fig. 1. Of course, for general time dependent or inhomogeneous solutions of the equations of thermodynamics, the

[8] Actually a more general possibility is realized by (2.11). The functions $\tilde{\varepsilon}(u, \eta, \hat{\alpha})$ and $\tilde{\varepsilon}(u, \eta, \hat{\beta})$ could be defined on domains $\mathfrak{D}_\alpha$ and $\mathfrak{D}_\beta$, respectively, which have a non-empty intersection. Then, "the" internal energy would be double-valued (or multivalued if several internal variables were involved). Such behavior is reminiscent of the Dauphiné twin in quartz, the phases of which appear to have different internal energies at the same strain and entropy.

[9] Later I shall lay down assumptions on the domain of $e$ which insure that $e_\eta(\cdot, u)$ has a global inverse.

quantities with subscript $e$ have no physical interpretation, except in the special, and probably inappropriate, case where $\sigma$ and $\theta$ are given exactly by constitutive assumptions of the form (2.12).

From now on I shall assume explicitly that the graph of $\sigma_e = \rho_0(\partial\hat{\phi}/\partial u)(\theta_e, u)$ vs. $u$ has the features shown in Fig. 1. The quantities $\alpha$, $\alpha^*$, $\alpha^1$, $\beta^1$, $\beta^*$, $\beta$ shown there will depend upon the equilibrium temperature. A precise statement of these features is contained in

**Assumption 2.** *There are four continuous functions*

$$\alpha(\theta_e) < \alpha^1(\theta_e) \leqslant \beta^1(\theta_e) < \beta(\theta_e), \qquad \theta_e \in [\theta_{\min}, \theta_{\max}] \tag{2.19}$$

*such that*

$$\begin{aligned} &\hat{\phi}_{uu} > 0 \quad \text{for} \quad \alpha(\theta_e) \leqslant u < \alpha^1(\theta_e) \quad \text{or} \quad \beta^1(\theta_e) < u \leqslant \beta(\theta_e), \\ &\hat{\phi}_{uu} < 0 \quad \text{for} \quad \alpha^1(\theta_e) < u < \beta^1(\theta_e). \end{aligned} \tag{2.20}$$

For a typical shape-memory alloy, such as Nitinol ([5] p. 292]) or the alloy pictured in Fig. 1, the functions $\alpha^1(\theta_e)$ and $\beta^1(\theta_e)$ satisfy

$$\begin{aligned} &\alpha^1(\theta_e) = \beta^1(\theta_e) \quad \text{for} \quad \theta_e \geqslant M, \\ &\alpha^1(\theta_e) < \beta^1(\theta_e) \quad \text{for} \quad \theta_e < M \end{aligned} \tag{2.21}$$

for some temperature $M$ (about 100°C for Nitinol). By analogy to the equilibrium of fluid phases we may call $M$ the critical temperature. The domain of $\hat{\phi}$ for a typical shape-memory alloy is shown in Fig. 3. As explained in the Introduction, the hatched region cannot be determined by static experiments.

Also shown in Fig. 3 are dashed lines which represent the functions $\alpha^*(\theta_e)$ and $\beta^*(\theta_e)$. These functions have the same interpretation as in Fig. 1; they give the values

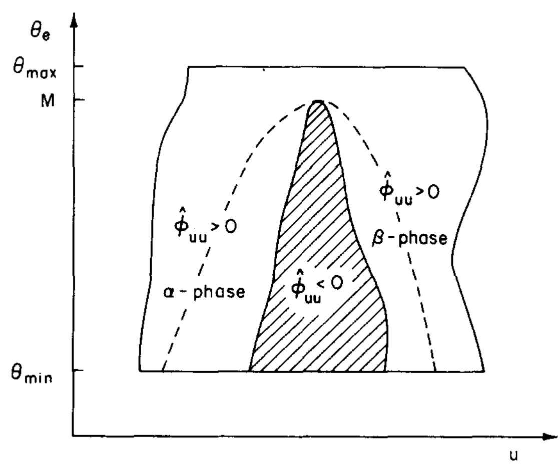


Figure 3. The domain of the equilibrium free energy $\hat{\phi}(u, \theta_e)$. The dashed lines represent the curves $\alpha^*(\theta_e)$ and $\beta^*(\theta_e)$ associated with the Maxwell Line (compare with Fig. 1).

of stretch at the ends of the Maxwell Line at temperature $\theta_e$. Values of $(u, \theta_e)$ to the left of the hatched region in Fig. 3 are in the $\alpha$-phase; those to the right are in the $\beta$-phase. If $\alpha^1(\theta_e) = \beta^1(\theta_e)$, as in Fig. 3 in the case $\theta_e \geqslant M$, the phases will still be distinguished by $(2.20)_1$ for simplicity.

The functions $\alpha(\theta_e)$, $\beta(\theta_e)$ and the constants $\theta_{\min}$, $\theta_{\max}$ are established by the limiting conditions to which the constitutive theory the theorist has chosen is applicable. For example $\beta(\theta_e)$ might represent the force at which the bar breaks, or the force at which ordinary plastic deformation sets in.

## 3. Steady propagation of a phase boundary

If the functions appearing in (2.4) are smooth, then (2.4) is equivalent to the system

$$u_t = v_X,$$
$$\rho_0 v_t = \sigma_X,$$
$$\rho_0 \varepsilon_t = \sigma v_X - q_X + r,$$
$$\rho_0 \eta_t \geqslant -\left(\frac{1}{\theta} q\right)_X + \frac{r}{\theta}. \tag{3.1}$$

I have left off $(2.4)_1$ since it only serves to determine $\rho$. The analysis of (3.1) is made difficult by the presence of $r$, since $r$ is the only term not differentiated. I shall assume that the environment of the bar is so adjusted that

$$r \equiv 0. \tag{3.2}$$

When $r$ is given by the simple assumption $r = c(\theta - \theta_0)$, $c = \text{const.}$, $\theta_0$ being an effective ambient temperature, $r$ will vanish if $\theta_0 = \theta$ or $c = 0$. The former is met if we make the effective temperature of the environment coincide with the temperature of the bar at each $(X, t)$; this is not easy to accomplish in practice when $\theta$ is not constant. Otherwise we can cause $c$ to vanish by placing the bar in an adiabatic environment, e.g., a vacuum.

I seek a solution of (3.1) which corresponds to a single phase boundary propagating at constant velocity. If functions $(u, v, \eta)$ depending upon a single variable $\zeta = X - Vt$, $V = \text{const.}$ are sought, then for a large class of constitutive relations, the equations (3.1) reduce to a system of ordinary differential equations. The equations (2.8) motivated by the Korteweg theory obviously have this property; (2.11) will also have this property if we assume $\xi = \hat{\xi}(X - Vt)$. Even (2.9) in some special cases yields ordinary differential equations. The question of existence remains open. We should like to have a solution for which the stretch and entropy and their first derivatives tend to constant values as $\zeta$ approaches $+\infty$ and $-\infty$, so we can utilize Assumption 1. For the same reason we should also like to have the limiting values as $\zeta \to +\infty$ and $-\infty$ of the stretch $u$ and temperature $\theta$ approach values in the $\alpha$-phase and $\beta$-phase, respectively.

There seems to be very little known about the existence of such solutions. An exception is the work of Slemrod [10] on the Korteweg theory. I shall simply assume existence in the following form:

**Assumption 3.** *There is a solution of* (3.1) *dependent upon* $\zeta = X - Vt$, $V =$ const., *with* $r \equiv 0$:

$$\left.\begin{aligned} v &= \hat{v}(\zeta) \\ u &= \hat{u}(\zeta) \\ \eta &= \hat{\eta}(\zeta) \\ \varepsilon &= \hat{\varepsilon}(\zeta) \\ \sigma &= \hat{\sigma}(\zeta) \\ q &= \hat{q}(\zeta) \end{aligned}\right\} \in C^2_{[-\infty,+\infty]}. \tag{3.3}$$

*The limiting values of u and η satisfy the conditions*

$$\left.\begin{aligned} & u \to u^{\pm} \\ & \eta \to \eta^{\pm} \\ & u_{\zeta\zeta}, u_{\zeta} \to 0 \\ & \eta_{\zeta} \to 0 \end{aligned}\right\} \quad \text{as} \quad \zeta \to \pm\infty, \quad \text{and} \tag{3.4}$$

$$\left(u^+, \frac{\partial e}{\partial \eta}(u^+, \eta^+)\right) \in \alpha\text{-phase},$$

$$\left(u^-, \frac{\partial e}{\partial \eta}(u^-, \eta^-)\right) \in \beta\text{-phase}. \tag{3.5}$$

Assumptions 2 and 3 imply that the equilibrium force, temperature and internal energy (cf. Eqn. (2.12)) satisfy certain jump conditions which I shall now derive. If we let prime denote the derivative with respect to $\zeta$ and we substitute (3.3) into (3.1), we get

$$\begin{aligned} & -Vu' = v', \\ & -\rho_0 V v' = \sigma', \\ & -\rho_0 V \varepsilon' = \sigma v' - q', \\ & -\rho_0 V \eta' \geqslant -\left(\frac{1}{\theta} q\right)'. \end{aligned} \tag{3.6}$$

I shall use the notation $[\![ f ]\!] = f^+ - f^-$. If we integrate (3.6) from $\zeta = -\infty$ to $\zeta = +\infty$, we get (assuming existence of the limits),

$$\begin{aligned} & -V[\![ u ]\!] = [\![ v ]\!], \\ & -\rho_0 V[\![ v ]\!] = [\![ \sigma ]\!], \\ & -\rho_0 V[\![ \varepsilon ]\!] = -V[\![ \sigma u ]\!] + \rho_0 \frac{V^3}{2}[\![ u^2 ]\!] - [\![ q ]\!], \\ & -\rho_0 V[\![ \eta ]\!] \geqslant -[\![ \frac{1}{\theta} q ]\!]. \end{aligned} \tag{3.7}$$

To arrive at the right hand side of $(3.7)_3$, I have used the following argument:

$$\begin{aligned}\int_{-\infty}^{\infty} \sigma v' \mathrm{d}\zeta &= -V\int_{-\infty}^{\infty} \sigma u' \mathrm{d}\zeta \\ &= -V\int_{-\infty}^{\infty} [(\sigma u)' - \sigma' u]\mathrm{d}\zeta \\ &= -V[\![\sigma u]\!] + \rho_0 V^3 \int_{-\infty}^{\infty} u u' \mathrm{d}\zeta \\ &= -V[\![\sigma u]\!] + \rho_0 \frac{V^3}{2}[\![u^2]\!]. \end{aligned} \tag{3.8}$$

The term $(3.8)_4$ simplifies if we introduce the notation

$$\langle f\rangle = \tfrac{1}{2}(f^+ + f^-), \tag{3.9}$$

and notice that for any $f$ and $g$,

$$[\![fg]\!] = \langle f\rangle[\![g]\!] + \langle g\rangle[\![f]\!]. \tag{3.10}$$

By applying (3.10) to (3.8) and making use of $(3.7)_{1,2}$, we derive that

$$\begin{aligned}\int_{-\infty}^{\infty} \sigma v' \mathrm{d}\zeta &= -V\{\langle\sigma\rangle[\![u]\!] + \langle u\rangle[\![\sigma]\!] - \rho_0 V^2\langle u\rangle[\![u]\!]\} \\ &= -V\langle\sigma\rangle[\![u]\!]. \end{aligned} \tag{3.11}$$

Hence, for the right hand side of $(3.7)_3$ we can substitute the simpler expression $-V\langle\sigma\rangle[\![u]\!] - [\![q]\!]$.

So far we have derived conditions which will hold for any set of constitutive relations, as long as that set permits the existence of differentiable solutions as functions of $X - Vt$. Assumption 3 contains additional restrictions summarized by (3.4) and (3.5). Consider two points $(X_0^+, t)$ and $(X_0^-, t)$. If $X_0^+$ is sufficiently large, the values of $u_X$, $u_t$, $u_{XX}$, $\eta_X$ and $\eta_t$ will be uniformly small on a neighborhood $[X_0^+ - \mu, X_0^+ + \mu] \times [t_0 - \tau, t_0]$ according to the assumptions $(3.4)_{3,4}$. Also the differences $|u - u^+|$ and $|\eta - \eta^+|$ will be uniformly small on the same neighborhood according to $(3.4)_{1,2}$. Assumption 1 then implies that the values of $\theta$, $\sigma$, $\varepsilon$ and $q$ at $(X_0^+, t)$ are approximated by their equilibrium values: $e_\eta(u^+, \eta^+)$, $\rho_0 e_u(u^+, \eta^+)$, $e(u^+, \eta^+)$ and 0. As $X_0^+$ tends to $\infty$ (with $t$ held fixed) the approximation becomes exact. An analogous argument holds for $X_0^-$.

We have shown that in (3.7) the limits exist and all quantities can be replaced by their values at equilibrium. If we now make use of the remark following (3.11), we may write (3.7) in the form

$$\begin{aligned}&-V(u^+ - u^-) = v^+ - v^-, \\ &-V(v^+ - v^-) = e_u(u^+, \eta^+) - e_u(u^-, \eta^-), \\ &-V(e(u^+, \eta^+) - e(u^-, \eta^-)) = \tfrac{1}{2}V[e_u(u^+, \eta^+) + e_u(u^-, \eta^-)](u^+ - u^-) \\ &-V(\eta^+ - \eta^-) \geqslant 0. \end{aligned} \tag{3.12}$$

The reader may recognize that these are the same conditions that would arise if we had assumed that the equilibrium constitutive relations (2.12) had held for time-dependent motions and that the phase boundary had propagated as an adiabatic shock. This coincidence is just that; it neither supports the idea that the equilibrium constitutive relations are appropriate for general motions of phases nor the idealization that the slow moving phase boundaries are adiabatic shocks. The coincidence merely reflects the fact that a variety of theories may yield the same results for a special class of motions. It is this fact which makes such motions useful, and motivated the approach I have adopted.

## 4. The jump in temperature across a propagating phase boundary

The jump conditions (3.12) impose restrictions on the limiting values of the stretch, velocity and entropy far from the phase boundary under the Assumptions 1, 2 and 3. It is illuminating to study these conditions in detail. We assume here that the function $e(u, \eta)$ is known.

A reasonable physical problem is set up if we fix the temperature and stretch, or equivalently the entropy and stretch, far ahead of the phase boundary. One can imagine an experiment in which a thin bar in a vacuum is fixed at one end, and a weight is hung at the other end. If the weight is of appropriate magnitude (and a tiny notch is made at the fixed end), the weight will fall and a phase boundary will be initiated at the fixed end and will propagate with nearly constant speed after some time has passed. Far ahead of the phase boundary the bar will be essentially statically deformed in the $\alpha$-phase, the values of the stretch and entropy being determined by the magnitude of the load and the initial temperature of the bar. Far behind the phase boundary the velocity is zero, and the bar is essentially statically deformed in the $\beta$-phase. The problem then is to predict the stretch and entropy far behind the phase boundary, and the velocity far ahead of the phase boundary.

Alternatively, we might fix one end of the bar and cause the other end to move with constant velocity. Then the temperature and velocity would be given far ahead of the phase boundary, and the velocity far behind the phase boundary would be zero. The problem would be to find the stretch and entropy far behind the phase boundary, and the stretch far ahead of the phase boundary.

We shall be interested in the extent to which these unknown quantities are determined by the jump conditions (3.12).

In the former problem let constants $u_0^+$ and $\eta_0^+$ be given and assume

$$\begin{aligned} u^+ &= u_0^+, \\ \eta^+ &= \eta_0^+, \\ v^- &= 0. \end{aligned} \tag{4.1}$$

Let

$$\begin{aligned} \sigma_0^+ &= \rho_0 e_u(u_0^+, \eta_0^+), \\ \theta_0^+ &= e_\eta(u_0^+, \eta_0^+), \end{aligned} \tag{4.2}$$

and assume

$$(u_0^+, \theta_0^+) \in \alpha\text{-phase}. \tag{4.3}$$

It is natural to seek a solution of (3.12) with $V = 0$, and then to perturb away from this solution to find solutions for $V > 0$. To avoid trivial perturbations we shall first cancel $V$ from $(3.12)_{3,4}$. Then, we shall have to solve,

$$\begin{aligned} & v_0^+ = 0, \\ & \sigma_0^+ - \rho_0 e_u(u_0^-, \eta_0^-) = 0, \\ & \mathfrak{S}(u_0^+, u_0^-; \eta_0^+, \eta_0^-) = 0, \\ & \eta_0^+ - \eta_0^- \leqslant 0, \end{aligned} \tag{4.4}$$

in which

$$\mathfrak{S}(u^+, u^-; \eta^+, \eta^-) \equiv e(u^+, \eta^+) - e(u^-, \eta^-) - \frac{\sigma_0^+}{\rho_0}(u^+ - u^-). \tag{4.5}$$

Equation $(4.4)_1$ determines $v_0^+$. I shall assume that $\sigma_0^+$ is in the range of the function $\rho_0 e_u(\cdot, \cdot)$ for some value of stretch and entropy in the $\beta$-phase. Since, by (2.19),

$$e_{uu} = \hat{\phi}_{uu} - e_{u\eta}\hat{\eta}_u \tag{4.6}$$

and

$$e_{u\eta}\hat{\eta}_u = -e_{\eta\eta}(\hat{\eta}_u)^2 = \frac{-\theta_e}{C_u}(\hat{\eta}_u)^2 < 0, \tag{4.7}$$

we have $e_{uu}(u, \eta) > 0$ in the $\beta$-phase (or $\alpha$-phase). Hence we can solve $(4.4)_2$ locally to get

$$u_0^- = f(\eta_0^-); \qquad \rho_0 e_u(f(\eta_0^-), \eta_0^-) = \sigma_0^+. \tag{4.8}$$

It remains to satisfy $(4.4)_{3,4}$. If we put (4.8) into the left hand side of $(4.4)_3$, we get

$$\tilde{\mathfrak{S}}(\eta_0^-) \equiv e(u_0^+, \eta_0^+) - e(f(\eta_0^-), \eta_0^-) - \frac{\sigma_0^+}{\rho_0}(u^+ - f(\eta_0^-)). \tag{4.9}$$

To satisfy $(4.4)_3$ we must choose $\eta_0^-$ to make $\tilde{\mathfrak{S}}(\eta_0^-)$ vanish. Note that

$$\begin{aligned} \frac{d}{d\eta_0^-}\tilde{\mathfrak{S}} &= -e_u f' - e_\eta + \frac{\sigma_0^+}{\rho_0} f', \\ &= -e_\eta(f(\eta_0^-), \eta_0^-) = -\theta_0^- < 0, \end{aligned} \tag{4.10}$$

so $\tilde{\mathfrak{S}}$ is a strictly monotonically decreasing function of $\eta_0^-$. Assuming $f$ to be defined for the value $\eta_0^+$ we may evaluate $\tilde{\mathfrak{S}}$ at $\eta_0^+$. Then $\tilde{\mathfrak{S}}$ may be interpreted according to an "area rule" in the graph of $e(u, \eta)$ vs. $u$ at fixed $\eta$. *If the value of* $\tilde{\mathfrak{S}}(\eta_0^+)$ *is negative, then there is no solution of the jump conditions* (4.4). To see this observe that since $\tilde{\mathfrak{S}}$ is strictly decreasing,

$$\tilde{\mathfrak{S}}(\eta_0^-) = 0 \quad \text{and} \quad \tilde{\mathfrak{S}}(\eta_0^+) < 0 \Rightarrow \eta_0^+ > \eta_0^-, \tag{4.11}$$

which contradicts $(4.4)_4$. Thus, still assuming $f$ to be defined at $\eta_0^+$, we must have

$$\tilde{\mathfrak{S}}(\eta_0^+) \geqslant 0. \tag{4.12}$$

Then, we simply determine the unique value of $\eta_0^-$ which makes $\tilde{\mathfrak{S}}$ vanish, still assuming that $\tilde{\mathfrak{S}}$ is defined on a large enough domain. This value will satisfy the entropy inequality $(4.4)_4$.

It is quite possible that the jump conditions do not have any solution for $V = 0$ or even $V$ near zero for a phase boundary connecting a given state in the $\alpha$-phase to any state in the $\beta$-phase. From the analysis above one can see several roads to non-existence: $f$ not having a sufficiently large domain, $\tilde{\mathfrak{S}}(\eta_0^+)$ being negative. One can invent reasonable constitutive relations, reasonable in the sense that all the restrictions of thermodynamics (cf. Section 2) are satisfied, and still fail to have a solution of the jump conditions at $V = 0$. Without explicit forms of the equilibrium constitutive relations, no more can be said.

In the ordinary theory of the propagation of weak adiabatic shock waves, $(3.11)_3$ is used to show that the jump in entropy is of third order in the jump of the stretch. On these grounds its jump across shocks is neglected altogether in linear thermoelasticity. Here, since $u^+ - u^-$ is large no such result follows: the jump in entropy or temperature can be substantial. For example, when $V = 0$, we have from (4.10)

$$\eta_0^- - \eta_0^+ = \frac{1}{\theta_0^*}\tilde{\mathfrak{S}}(\eta_0^*), \tag{4.13}$$

where $\theta_0^*$ is some temperature between the values

$$e_\eta(f(\eta_0^+), \eta_0^*) \quad \text{and} \quad e_\eta(f(\eta_0^-), \eta_0^-). \tag{4.14}$$

Here one can construct reasonable examples, reasonable in the sense used above but not necessarily corresponding to any particular shape-memory alloy, in which $\tilde{\mathfrak{S}}(\eta_0^*)$ has any positive value. It seems that a purely mechanical theory of rapidly propagating phase boundaries, unlike the purely mechanical theory of weak shocks, would rest upon unsure foundations.

*Suppose a solution* $(u_0^-, \eta_0^-, v_0^+ = 0)$ *of the jump conditions* (4.4) *exists for* $V = 0$, *given the values* $u_0^+, \eta_0^+, v^- = 0$ *consistent with* (4.2) *and* (4.3). Assume that $(u_0^-, \eta_0^-)$ is in the $\beta$-phase and that the entropy inequality is satisfied with strict inequality. I wish to explore the existence of solutions of the jump conditions (3.12) for $V > 0$. To do so, I must solve the equations

$$\begin{aligned}
&V(u_0^+ - u^-) + v^+ = 0,\\
&Vv^+ + e_u(u_0^+, \eta_0^+) - e_u(u^-, \eta^-) = 0,\\
&e(u_0^+, \eta_0^+) - e(u^-, \eta^-) - \tfrac{1}{2}\big(e_u(u_0^+, \eta_0^+) + e_u(u^-, \eta^-)\big)(u^+ - u^-) = 0,\\
&\eta_0^+ - \eta^- \leqslant 0.
\end{aligned} \tag{4.15}$$

This system is satisfied with $V = 0$ at the ground state $u = u_0^-$, $\eta^- = \eta_0^-$, $v^+ = 0$, by assumption. The Jacobian of $(4.15)_{1,2,3}$ with respect to $(u^-, \eta^-, v^+)$ evaluated at $V = 0$ and the ground state is simply

$$\theta_0^- e_{uu}(u_0^-, \eta_0^-) > 0. \tag{4.16}$$

Hence, by the implicit function theorem, there is a one-parameter family of twice differentiable solutions of (4.15):

$$u^-(V), \eta^-(V), v^+(V), \tag{4.17}$$

and if $V$ is sufficiently small the entropy inequality $(4.15)_4$ is satisfied. *Therefore, near* $V = 0$ *the jump conditions do not uniquely determine the state* $(u^-, \eta^-)$ *behind the phase boundary, given the stretch and temperature ahead of the phase boundary.* In fact (4.17) shows that there is a one-parameter family of such solutions. A similar conclusion would be reached if we had given the velocity and temperature ahead of the phase boundary, with one mild additional assumption.

Thus, while the data suggest a well-posed problem, the jump conditions are not sufficient to determine a unique solution to it. This conclusion by itself indicates that the adiabatic thermoelastic theory is not adequate to describe a propagating phase boundary, since in that theory the relations (4.15) are both necessary and sufficient.

We remark that to order $V^2$ the functions in (4.17) are given by the formulae

$$u^- = \frac{1}{\theta_0^- e_{uu}^-}\left(2\theta_0^- + e_{u\eta}^-(u_0^+ - u_0^-)\right)(u_0^+ - u_0^-)V^2 + \dots,$$
$$\eta^- = \frac{-(u_0^+ - u_0^-)^2}{\theta_0^-}V^2 + \dots,$$
$$v^+ = (u_0^+ - u_0^-)V + 0 + \dots. \tag{4.18}$$

To linear approximation the quantities $u^-$ and $\eta^-$ are unaffected by the velocity of the phase boundary. At low temperatures, however, the second order effect upon these quantities is substantial.

## 5. The heat evolved during the passage of a phase boundary

This section comprises a critique of some informal ideas associated with the thermodynamics of large deformation of solids in light of the present analysis. The reader only interested in the determination of the Maxwell Line should skip to the next section.

It is sometimes alleged that the heat evolved during the passage of a phase boundary is related to the area between the line connecting $(u^+, \sigma^+)$ to $(u^-, \sigma^-)$ and the Maxwell Line in the graph of $\hat{\phi}(u, \theta)$ vs. $u$. The solutions I have been studying in the preceding two sections offer no insight into this allegation, since I have assumed that the bar is infinite and that $r = 0$. Thus, no heat is transmitted to the ambient.

It seems that the only way to study this claim is to consider isothermal solutions of the equations and allow heat absorption. Thus I shall assume $\theta = \text{const.}$ and $r \neq 0$. I shall suppose that the equations still admit solutions as functions of $X - Vt$ with the properties outlined in Assumption 2, and I shall assume $q \equiv 0$, consistent with the constitutive relations of Section 2. If we then integrate the analogue of (3.6) with respect to $X$ from $-\infty$ to $+\infty$, we get

$$-V[\![u]\!] = [\![v]\!],$$
$$-\rho_0 V[\![v]\!] = [\![\sigma]\!],$$
$$-\rho_0 V[\![\varepsilon]\!] = -V\langle\sigma\rangle[\![u]\!] + R,$$
$$-\rho_0 V[\![\eta]\!] \geqslant \frac{1}{\theta}R, \tag{5.1}$$

where

$$R = \int_{-\infty}^{\infty} r(X, t)\,\mathrm{d}X. \tag{5.2}$$

Here $R$ is the rate of absorption of heat by the bar. From Assumption 1 and $(5.1)_3$ we derive

$$R=\rho_0 V\{e(u^+,\eta^+)-e(u^-,\eta^-)-\tfrac{1}{2}(e_u(u^+,\eta^+)+e_u(u^-,\eta^-))(u^+-u^-)\}. \quad (5.3)$$

If we substitute (2.17) into (5.3) and recall that $\theta^+=\theta^-=\theta=$ const., by assumption, then (5.3) becomes

$$R=\rho_0 V\{\hat{e}(u^+,\theta)-\hat{e}(u^-,\theta)-\tfrac{1}{2}(\hat{\phi}_u(u^+,\theta)+\hat{\phi}_u(u^-,\theta))(u^+-u^-)\}. \quad (5.4)$$

*Neither* (5.3) *nor* (5.4) *have any simple interpretation in terms of areas as alleged*. Each of these equations is an exact consequence of the assumptions. Note that generally $\hat{e}_u \neq \hat{\phi}_u$.

Suppose now that we eliminate $R$ from $(5.1)_3$ and $(5.1)_4$. Then we get

$$V\{\hat{\phi}(u^+,\theta)-\hat{\phi}(u^-,\theta)-\tfrac{1}{2}(\hat{\phi}_u(u^+,\theta)+\hat{\phi}_u(u^-,\theta))(u^+-u^-)\}\geqslant 0. \quad (5.5)$$

Equation (5.5) says nothing about $R$, but it does restrict the sign of the velocity according to whether the line which connects $(u^+, \hat{\phi}_u(u^+, \theta))$ to $(u^-, \hat{\phi}_u(u^-, \theta))$ in the graph of $\hat{\phi}(u, \theta)$ vs. $u$ lies above more or less area than the function $\hat{\phi}(u, \theta)$.

It is also sometimes alleged that for arbitrarily slow motions the Clausius-Duhem inequality holds with near equality. Granted the assumptions made in this Section, this claim also appears to have no basis. If we put equality in $(5.1)_4$ and eliminate $R$ between $(5.1)_3$ and $(5.1)_4$ then we get (5.5) with equality. Cancell $V$ from (5.5) and let $V \to 0$. We reach the conclusion that $u^+$ and $u^-$ must be the stretches at the ends of the Maxwell Line. But the experiments mentioned in the Introduction, which appear to be conducted under isothermal, slow conditions, do not support this conclusion. *Thus, the hypothesis of quasistatic equilibrium* ($V \neq 0$ *but* = *in* $(5.1)_4$) *is invalid.*

## 6. Determination of the Maxwell Line

From ordinary static experiments the equilibrium force vs. stretch relation,

$$\sigma_e=\rho_0\frac{\partial\hat{\phi}}{\partial u}(u,\theta_e), \quad (6.1)$$

can be determined outside the hatched region of Fig. 3. The experimenter may not be able to determine its value right up to the boundary of the hatched region, but certainly he or she will be able to determine it on some region $\mathcal{D}_e$ which includes the area outside the dotted hump in Fig. 3, since this area contains the stable states.

From calorimetric measurements the experimenter can also determine the specific heat at constant stretch,

$$C_u=\theta_e\frac{\partial\hat{\eta}}{\partial\theta}(u,\theta_e)=-\theta_e\frac{\partial^2\hat{\phi}}{\partial\theta_e^2}(u,\theta_e), \quad (6.2)$$

on $\mathcal{D}_e$. To derive (6.2) from (2.14), we differentiate $(2.12)_2$ with respect to $\theta_e$, having substituted for $\eta$ from (2.15), and then compare the result with (2.14) and the second derivative of (2.17) with respect to $\theta_e$. Sometimes it is easier to measure the specific heat at constant axial force, but this quantity can be related to $C_u$ by a classical argument. That argument uses the fact that $\hat{\phi}_{uu} \neq 0$, which is true on $\mathcal{D}_e$.

$\mathfrak{D}_e$ may be a disconnected domain, though Fig. 3 pictures a connected one. This fact will imply that the Maxwell Line cannot generally be determined from the functions (6.1) and (6.2). To see this, we write $\mathfrak{D}_e = \bar{\mathfrak{D}}_\alpha \cup \bar{\mathfrak{D}}_\beta$, $\mathfrak{D}_\alpha \cap \mathfrak{D}_\beta = \phi$, $\mathfrak{D}_\alpha \subset \alpha$-phase, $\mathfrak{D}_\beta \subset \beta$-phase. I assume that $\{\theta_e = \text{const.}\} \cap \mathfrak{D}_\alpha$ and $\{\theta_e = \text{const.}\} \cap \mathfrak{D}_\beta$ are each connected intervals. Then, we can integrate (6.1) on $\mathfrak{D}_\alpha$ to obtain

$$\hat{\phi}(u, \theta_e) = \int_1^u \rho_0 \frac{\partial \hat{\phi}}{\partial u}(s, \theta_e) \mathrm{d}s + g_\alpha(\theta_e), \tag{6.3}$$

$g_\alpha(\theta_e)$ being, so far, an arbitrary function. We now differentiate (6.3) with respect to $\theta_e$ twice and use (6.2). We get [10]

$$g_\alpha''(\theta_e) = -\frac{\partial^2}{\partial \theta_e^2} \int_1^u \rho_0 \hat{\phi}_u(s, \theta_e) \mathrm{d}s + \frac{C_u}{\theta_e}. \tag{6.4}$$

We obtain the following result. *On $\mathfrak{D}_\alpha$ $\hat{\phi}$ is determined up to an arbitrary linear function of $\theta_e$:*

$$\hat{\phi}(u, \theta_e) = f_\alpha(u, \theta_e) + c_\alpha^1 \theta_e + c_\alpha^2, \tag{6.5}$$

$f_\alpha$ being a known function defined on $\mathfrak{D}_\alpha$ and $c_\alpha^1$ and $c_\alpha^2$ being arbitrary constants. *Similarly, on $\mathfrak{D}_\beta$ we have*

$$\hat{\phi}(u, \theta_e) = f_\beta(u, \theta_e) + c_\beta^1 \theta_e + c_\beta^2, \tag{6.6}$$

$f_\beta$ being a known function defined on $\mathfrak{D}_\beta$ and $c_\beta^1$ and $c_\beta^2$ being arbitrary constants. The results (6.5) and (6.6) are equivalent to (6.1) and (6.2), so (6.1) and (6.2) have been completely exploited.

I claim that the Maxwell Line cannot be determined from (6.5) and (6.6). This can be easily seen by drawing a graph of $\hat{\phi}$ vs. $u$ at fixed $\theta_e$. Analytically, the Maxwell Line is determined by the functions $\alpha^*(\theta_e)$ and $\beta^*(\theta_e)$ (cf. Fig. 1). In turn these functions are uniquely determined by the "equal-area rule", *viz*:

$$\begin{aligned} &\hat{\phi}(\beta^*(\theta_e), \theta_e) - \hat{\phi}(\alpha^*(\theta_e), \theta_e) = \frac{\tau^*(\theta_e)}{\rho_0}(\beta^*(\theta_e) - \alpha^*(\theta_e)), \\ &\tau^*(\theta_e) = \rho_0 \hat{\phi}_u(\beta^*(\theta_e), \theta_e) = \rho_0 \hat{\phi}_u(\alpha^*(\theta_e), \theta_e); \\ &\alpha^*(\theta_e) \in \alpha\text{-phase}, \\ &\beta^*(\theta_e) \in \beta\text{-phase}. \end{aligned} \tag{6.7}$$

By inserting (6.5) and (6.6) into (6.7), we see that at any fixed $\theta_e$ we can adjust the constants $c_\alpha^1$, $c_\alpha^2$, $c_\beta^1$, $c_\beta^2$ so that *any* two equilibrated stretches in the appropriate phases lie at the ends of the Maxwell Line. We see also that only the differences

$$\begin{aligned} &c^1 \equiv c_\beta^1 - c_\alpha^1, \quad \text{and} \\ &c^2 \equiv c_\beta^2 - c_\alpha^2 \end{aligned} \tag{6.8}$$

need be found in order that the Maxwell Line be determined.

[10] This shows that we only need to determine $C_u(u, \theta_e)$ at one fixed stretch. See for example Kestin [13] (p. 550).

Depending upon the domain of $e(u, \eta)$, we consider several alternatives. Here $\overline{\mathcal{D}}$ stands for the closure of a set $\mathcal{D}$.

**a.** $\overline{\mathcal{D}}_\alpha \cap \overline{\mathcal{D}}_\beta$ *contains two points* $(u^1, \theta_e^1)$ *and* $(u^2, \theta_e^2)$ *at distinct temperatures*: $\theta_e^2 \neq \theta_e^1$

This case clearly includes the domain pictured in Fig. 3; any two temperatures between $M$ and $\theta_{\max}$, with appropriate stretches, will do. At the two points $(u^1, \theta_e^1)$ and $(u^2, \theta_e^2)$ the free energy has the same value. Thus, from (6.5) and (6.6)

$$c^1\theta_e^1 + c^2 = \Delta f^1,$$
$$c^1\theta_e^2 + c^2 = \Delta f^2, \tag{6.9}$$

where

$$\Delta f^i = f_\alpha(u^i, \theta_e^i) - f_\beta(u^i, \theta_e^i), \qquad i = 1, 2. \tag{6.10}$$

But if $\theta_e^1 \neq \theta_e^2$ we can solve (6.9) uniquely for $c^1$ and $c^2$. Then (6.7) determines the Maxwell Line at all temperatures between $\theta_{\min}$ and $\theta_{\max}$.

No use was made of the results found for propagating phase boundaries, and those results provide no additional information. However, once $c^2$ has been determined, all functions on the left hand side of (3.12) are known, so the results for propagating phase boundaries can be compared with experiment *at a variety of temperatures.* This would provide a test of the whole theory for a broad class of constitutive relations.

**b.** *The Maxwell Line is known at two distinct temperatures* $\theta_e^2 \neq \theta_e^1$

Figure 2 shows an example of an alloy for whch the Maxwell Line is known at high temperatures but not at low ones. If we know the Maxwell Line at two distinct temperatures, then (6.7) tells us that

$$c^1\theta_e^i + c^2 = \Delta f^i + \frac{\tau^*(\theta_e^i)}{\rho_0}\left(\beta^*(\theta_e^i) - \alpha^*(\theta_e^i)\right), \qquad i = 1, 2, \tag{6.11}$$

from which $c^1$ and $c^2$ can be determined. Then, (6.7) determines the Maxwell Line at all other temperatures. The results of this calculation can be compared with the results for Subsection **a** if $\mathcal{D}_e$ meets those conditions, and the results for propagating phase boundaries.

**c.** $\overline{\mathcal{D}}_\alpha \cap \overline{\mathcal{D}}_\beta$ *contains one point* $(\bar{u}, \bar{\theta}_e)$

This case is like Fig. 3, except with $M = \theta_{\max}$. From the practical point of view, even if $M < \theta_{\max}$ but $M$ is very close to $\theta_{\max}$, this idealization is probably appropriate. Such is the case with the alloy Nitinol. Now we shall have

$$c^1\bar{\theta}_e + c^2 = \Delta f \equiv f_\alpha(\bar{u}, \bar{\theta}_e) - f_\beta(\bar{u}, \bar{\theta}_e). \tag{6.12}$$

Suppose we also measure the jump in stretch and temperature across a single propagating phase boundary, and the Assumptions 1, 2, and 3 are fulfilled. Then we shall also have satisfied the relation $(3.12)_3$. In terms of $\hat{\phi}$ this relation becomes

$$\hat{\phi}(u^+,\theta^+)-\hat{\phi}(u^-,\theta^-)+\theta^+\hat{\eta}(u^+,\theta^+)-\theta^-\hat{\eta}(u^-,\theta^-)$$
$$-\tfrac{1}{2}\big(\hat{\phi}_u(u^+,\theta^+)+\hat{\phi}_u(u^-,\theta^-)\big)(u^+-u^-)=0. \tag{6.13}$$

If we now substitute (6.5) and (6.6) for $\hat{\phi}$ in (6.13), we get in obvious notation

$$f_\alpha^+ - f_\beta^- - c^2 - \theta^+ f_{\alpha_\theta}^+ + \theta^- f_{\beta_\theta}^- - \tfrac{1}{2}\big(f_{\alpha_u}^+ + f_{\beta_u}^-\big)=0. \tag{6.14}$$

From (6.14) we get $c^2$ and then from (6.12) we get $c^1$. Note that $c^1$ does not enter (6.14). Again (6.14) at various temperatures and stretches provides a test of the whole theory.

**d.** *The Maxwell Line is known at a single temperature* $\bar{\theta}_e$

This case bears the same relationship to **c** as **b** does to **a**. Knowledge of the Maxwell Line at one temperature and the results for propagating phase boundaries yield the Maxwell Line at all temperatures in $[\theta_{\min}, \theta_{\max}]$.

**e.** *We adopt the Nernst postulate and* $\theta_{\min}=0$

Rarely if ever are equilibium quantities for shape-memory materials determined down to absolute zero. Some physicists even argue that $\theta_e=0$ is "unattainable", that all equilibium functions can only be determined for $\theta_e >$ const. for some const. $> 0$. What happens between $\theta_e=0$ and $\theta_e=$ const. is then unknown, so any statement which involves the limit of constitutive functions as $\theta_e \to 0$ is meaningless. As the study of phase transitions has shown, large effects can be felt over small temperature ranges. For these reasons I doubt the usefulness of the Nernst posulate.

Nevertheless, if we adopt it we may write

$$\hat{\eta}(u,0)=0, \tag{6.15}$$

and conclude that

$$c^1=\Delta f_\theta|_{\theta=0}. \tag{6.16}$$

Then $c^2$ may be determined from (6.13) and (6.14) as before. Note that $c^2$ cannot be determined from any statement about $\hat{\eta}$ or its derivatives.

**f.** $\overline{\mathfrak{D}}_\alpha \cap \overline{\mathfrak{D}}_\beta = \phi$ and $\theta_{\min} > 0$

If the phases are completely disconnected, the Maxwell Line is not known at any temperature and we disregard the Nernst postulate, I have no way to determine the Maxwell Line. Of course $c^2$ may be determined from (6.13) and (6.14), granted the Assumptions, but $c^1$ is still unknown. Once $c^2$ has been determined from one experiment, however, all functions in the jump conditions (3.12) are known, so a test of the jump conditions over a range of temperatures can be carried out.

## 7. An experimental program suggested

We may summarize the results by suggesting an experimental program. A one dimensional bar theory, like the one used here, can only yield reasonable predictions for *slender* bars of uniform cross section. The word slender means that the maximum diameter of the cross section is small compared to the length of the bar. We assume that the specific heat at constant stretch (or the specific heat at constant axial force) and the stress-elongation curves at various temperatures have been measured by conventional means. Then, according to the discussion of Section 6, the free energy in each of the phases by itself can be determined (cf. (6.5) and (6.6)) up to an arbitrary linear function of temperature. Depending upon the domain of the free energy, we are left with several alternatives for the determination of the Maxwell Line summarized in **6a** through **6f**.

In each case the constant $c^2$ of $(6.8)_2$ can be determined by a single experiment, granted the Assumptions 1, 2 and 3. This experiment consists of a measurement of the temperature and stretch on each side of a travelling phase boundary for a bar isolated from its environment. The values obtained $(u^+, u^-, \theta^+, \theta^-)$ are placed into (6.14), which is simply a restatement of the jump condition $(3.12)_3$; from (6.14) we calculate $c^2$.

Ideally, the experiment is carried out in a vacuum chamber where inside walls are coated with reflective material. The bar should be sufficiently long so that the temperature away from the phase boundary is sensibly constant. One end of the bar should be fixed and the other end should be pulled at a constant rate, or loaded by a weight which moves at constant velocity. It is perhaps easiest if the phase boundary is initiated at one end of the bar. By slightly thinning the cross section at one place, the experimenter can cause the phase boundary to start there. The temperature might conveniently be measured by the method of infared stroboscopy [14], so as not to encumber the specimen.

To provide a good test of the whole theory the measurement should be repeated at a variety of temperatures between the extremes $\theta_{min}$ and $\theta_{max}$, and with the phase boundary propagating at various speeds. Each of these measurements should give rise to the same value of $c^2$ as calculated from (6.14).

If not, then one or more of the Assumptions 1, 2 or 3 is not fulfilled. Assumption 2 is easy to assess; one simply observes the domain of the free energy $\hat{\phi}$. If Assumption 1 is at fault, then most theories proposed for the coexistence of phases of which I am aware are in doubt. Assumption 3 is less sure. Even if we arrange boundary data to be consistent with (3.4) and (3.5), it is not certain that the theory which best describes the phase boundary has a unique solution (as a function of $X - Vt$) corresponding to this data. In principle, one would like to measure the variation of the stretch, velocity, axial force, etc. across the phase boundary to completely assess Assumption 3.

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## References

[1] J. Willard Gibbs, *On the equilibrium of heterogeneous substances.* In: The Scientific Papers of J. Willard Gibbs, Vol. 1, Longmans, Green and Co.: London-New York-Bombay (1906).
[2] James Clerk Maxwell, On the dynamical evidence of the molecular constitution of bodies. *Nature* XI (1875) 357.
[3] R.D. James, Co-existent phases in the one-dimensional static theory of elastic bars. *Arch. Rational Mech. Anal.* 72 (1979) 99.
[4] J.L. Ericksen, Equilibrium of bars. *J. Elasticity* 5 (1975) 191.
[5] J. Perkins (ed.), Shape Memory Effects in Alloys, Plenum Press: New York-London (1975).
[6] C. Truesdell and R. Toupin, The Classical Field Theories. In: The Encyclopedia of Physics, Vol. III/1, Springer-Verlag: Berlin-Heidelberg-New York (1965).
[7] J.D. van der Waals, Théorie thermodynamique de la capillarité, dans l'hypothèse d'une variation continue de densité. *Archives Néerlandaises des Sciences exactes et naturelles* 28 (1895) 121.
[8] D.J. Korteweg, Sur la forme que prennent les équations du mouvement des fluides si l'on tient compte des forces capillaries causée par des variations de densité considérables mais continues et sur la théorie de la capillarité dans l'hypothèse d'une variation continue la densité. *Archives Néerlandaises des Sciences exactes et naturelles,* Ser. II 6 (1901) 1.
[9] V. Bongiorno, L.E. Scriven and H.T. Davis. Molecular theory of fluid interfaces. *J. Colloid and Interface Science* 57 (1967) 462–475.
[10] M. Slemrod, Admissibility criteria for propagating phase boundaries in a van der Waals fluid. *Arch. Rational Mech. Anal.* 81 (1983) 301.
[11] R.D. James, The propagation of phase boundaries in elastic bars. *Arch. Rational Mech. Anal.* 73 (1980) 125.
[12] Ingo Müller, A model for a body with shape-memory. *Arch. Rational Mech. Anal.* 70 (1979) 61.
[13] J. Kestin, *A Course in Thermodynamics,* Vol. 1, Blaisdell: Waltham-Toronto-London (1966).
[14] R.H. Blanc and E. Giacometti, Infared stroboscopy – a method for the study of thermomechanical behavior of materials and structures at high rates of strain. *Int. J. Solids Structures* 17 (1981) 531.