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STRESS-INDUCED PHASE TRANSFORMATIONS IN SOLIDS AND THE ASSOCIATED DOUBLE-WELL POTENTIALS

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Abstract—The one-dimensional continuum modeling of phase transformations in solids presumes the existence of a double-well Helmholtz free energy. The two well-bottoms are separated by a transformation strain e_T and a transformation energy γ_T. Both are in general temperature-dependent material properties. The determination of γ_T, together with certain other thermodynamic properties, is by no means a trivial matter. A heat measurement, in conjunction with an energy identity, is proposed in this paper.

1. INTRODUCTION

When certain polymers are tested in tension the typically observed sequence of events is schematically depicted in Fig. 1 where, for illustration, the half-length L of a symmetric specimen is marked into eight equal intervals of spacing l. When such a specimen is stretched at an appropriate steady rate it first deforms uniformly (stage A) without necking ($S = 0$), and then nonhomogeneous deformation sets in (stage B) with a half-neck length $S = l$. The neck lengthens through an intermediate stage C with $S = 3l$, and eventually develops to the full extent of the specimen (stage D). Additional straining will then lead to homogeneous deformation of the necked material.

The load–elongation curve associated with the sequence of events is depicted in Fig. 1(a) where the normalized load is the nominal stress σ (load/original area) and the normalized elongation is the engineering strain e (elongation/original length). This curve has a number of characteristics: a draw stress σ_d, a maximum stress σ_y, a transformation strain e_T and two moduli E_1 and E_3. The uniform deformations of stage A are characterized by the modulus E_1 and the uniform deformations beyond stage D are completely defined by the modulus E_3, together with the transformation strain e_T which is a stress-free strain for the necked or transformed material. The phenomenon of necking or neck propagation in a tensile specimen is characterized by the fact that, until the time the necks have reached the ends of the specimen, there are always two distinct states of uniform deformation present in the same specimen. It follows that the Helmholtz free energy per unit mass of the material ψ must be double-welled. The relative positions of the two well-bottoms are fixed by the transformation strain e_T and the transformation energy γ_T [Fig. 1(b)]. The transformation strain e_T can be easily determined from the load–elongation curve of Fig. 1(a). The main result of this paper is an energy identity that may be applied to determine γ_T.

The described phenomenon of neck propagation in polymers is often termed cold drawing (Ward, 1971). Emphasizing the mechanical aspects of the problem, Hutchinson and Neale (1983) studied the propagation of an axisymmetric neck via a J_2 flow theory. A finite element formulation was later used by Neale and Tugcu (1985) to examine the same problem. On the basis of the one-dimensional theory of nonlinear elasticity, a nonconvex strain-energy density function was introduced by Ericksen (1975) to model material instabilities. The theory allows deformations with discontinuous displacement gradients and many relevant results may be found in the references of Abeyaratne and Knowles (1988, 1990).

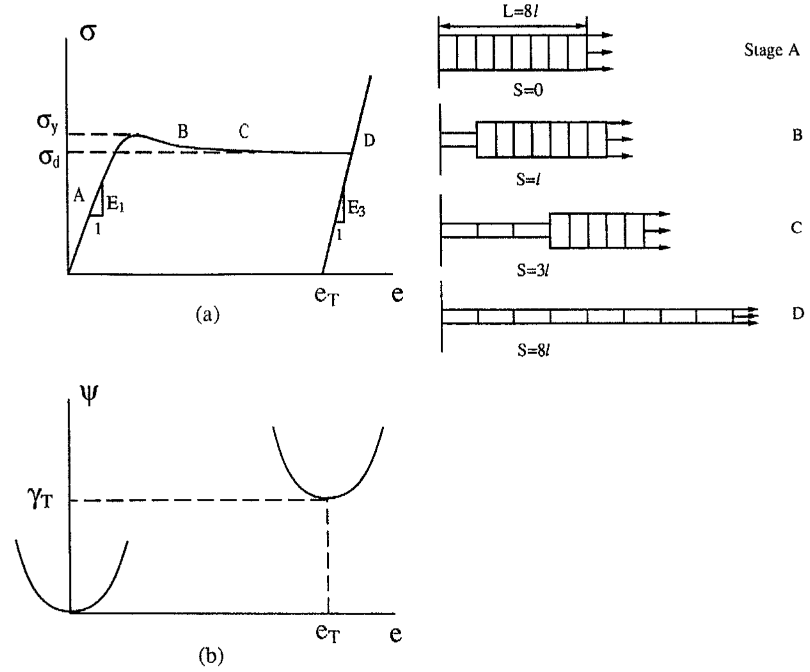

Fig. 1. Overall load–elongation behavior in a tensile test with necking: (a) the four deformation stages and unloading; (b) the Helmholtz free energy and the transformation energy γ_T.

Extending such purely mechanical theories to include thermal effects, the result is a thermoelastic solid capable of producing shape–memory responses (James, 1983; Abeyaratne and Knowles, 1993). The solid–solid phase transformation revealed by such types of theories has many features in common with the first-order phase transitions treated in the classical thermodynamical theory of fluids (Landau and Lifshitz, 1959). In particular, the transition from one homogeneous state to another is abrupt and there is no interfacial property to speak of. This deficiency may be remedied by the inclusion of a "gradient energy" and the most known and accepted result is perhaps the work promulgated by Cahn and Hilliard (1957). This approach was used by Coleman (1983) in dealing with necking and drawing of polymeric fibers where the "gradient energy" was justified as a three-dimensional effect. In the context of phase transformation and spinodal decomposition, the Cahn–Hilliard approach or Cahn–Hilliard equation is now a standard fixture (Khachaturyan, 1983).

In the one-dimensional results of Abeyaratne and Knowles (1988, 1992, 1993) the role of the "driving traction", together with an associated kinetic relation, is emphasized. In particular, the notion of thermally activated phase tarnsitions was explicitly incorporated in the kinetic relation of their 1993 paper. This formula, however, depends on the explicit knowledge of the underlying Helmholtz free energy, which cannot be determined by recording only load–elongation relations. A new measurement, in conjunction with an energy identity, is proposed in this paper.

In connection with the load–elongation behavior of Fig. 1(a), experimental data have been collected and analysed by Kadota and Chudnovsky (1991) for polyethylenes. As a first approximation, they merely take the area under the draw stress σ_d as the transformation energy. The approximation has the net effect of identifying σ_d with the Maxwell stress. Extensive temperature-dependent data have also been collected by Zhou *et al.* (1994) for polycarbonates. In fact, studying their data and discussions with Zhou and Chudnovsky have contributed greatly to the outcome of this paper.

The basic one-dimensional thermomechanical bar theory is summarized in the next section. The theory is then specialized to thermoelasticity in section 3 in which the Helmholtz free energy is constructed for the class of materials with deformation-independent specific heat. Specific examples in the form of polynomials are also presented.

Explicit formulae for Maxwell stress, latent heat, etc. are then obtained for the example material. They serve as a clear guidance for a number of approximations introduced in section 4 where the determination of the Helmholtz energy is finally addressed.

2. THERMODYNAMIC BAR THEORY

A bar is described by a single Lagrangian coordinate X for a point in some reference configuration $V(X)$ where $X\varepsilon[0, L]$ and L is the half-length of the bar (Fig. 1). A motion of the bar is characterized by

$$x = \hat{x}(X, t) = X+u(X, t), \tag{1}$$

which gives the position occupied by the point X at the time t. The position $\hat{x}(X, t)$, or equivalently the displacement u, is assumed to be continuous with piecewise continuous derivatives. The strain and velocity are denoted by

$$e(X, t) = \frac{\partial u}{\partial X} = u_X = u' \tag{2}$$

$$v(X, t) = \frac{\partial u}{\partial t} = u_t = \dot{u}, \tag{3}$$

which also define the notation to be followed in the paper. Thus, $F_\theta(\theta, \ldots) \equiv \partial F/\partial\theta$ where both F and θ are generic.

Let ρ and A denote, respectively, the constant mass density and cross-sectional area of the bar in the reference configuration, $b(X, t)$ the body force per unit mass, and $\sigma(X, t)$ the nominal stress at (X, t). The balance of linear momentum is

$$\frac{\mathrm{d}}{\mathrm{d}t}\int_{X_1}^{X_2} A\rho v \, \mathrm{d}X = A\sigma\Big|_{X_1}^{X_2} + \int_{X_1}^{X_2} A\rho b \, \mathrm{d}X \tag{4}$$

which must hold at every t and for all pairs of X_1 and X_2.

Next, let $q(X, t)$ denote the nominal uniaxial heat flux in the X-direction, $\varepsilon(X, t)$ the internal energy per unit mass, and $h(X, t)$ the source heat per unit mass at (X, t). The balance of energy is

$$\frac{\mathrm{d}}{\mathrm{d}t}\int_{X_1}^{X_2} (A\rho\varepsilon+\tfrac{1}{2}A\rho v^2)\,\mathrm{d}X = (A\sigma v - Aq)\Big|_{X_1}^{X_2} + \int_{X_1}^{X_2} (A\rho bv+A\rho h)\,\mathrm{d}X. \tag{5}$$

Finally, let $\theta(X, t)$ be the absolute temperature and $\eta(X, t)$ the entropy per unit mass. The second law of thermodynamics requires

$$\Gamma(t; X_1, X_2) \geqslant 0 \tag{6}$$

where

$$\Gamma(t; X_1, X_2) \equiv \frac{\mathrm{d}}{\mathrm{d}t}\int_{X_1}^{X_2} A\rho\eta \, \mathrm{d}X - \int_{X_1}^{X_2} A\rho h \frac{1}{\theta}\,\mathrm{d}X + Aq\frac{1}{\theta}\Big|_{X_1}^{X_2} \tag{7}$$

is the rate of entropy production in the portion of the bar between X_1 and X_2.

The local forms of (4)–(6) at every regular point of $[0, L]$ are

$$\sigma' + \rho b = \rho \dot{v} \tag{8}$$

$$\rho \dot{\varepsilon} = \sigma \dot{e} - q' + \rho h \tag{9}$$

$$\rho \theta \dot{\eta} - \rho h + q' - \frac{1}{\theta} q \theta' \geqslant 0. \tag{10}$$

The above results must be modified in the presence of a simple discontinuity. Let $F(X, t)$ be a generic field quantity that has a simple discontinuity at time t for the point $X = S(t)$. It is convenient to introduce the notation

$$[\![F]\!] \equiv F^+ - F^- \equiv F(S(t)+0, t) - F(S(t)-0, t) \tag{11}$$

$$\langle F \rangle \equiv \tfrac{1}{2}(F^+ + F^-) \tag{12}$$

and the identity

$$[\![FG]\!] = \langle F \rangle [\![G]\!] + \langle G \rangle [\![F]\!] \tag{13}$$

where both F and G are generic. The local forms of (4)–(6) at such a singular point are

$$[\![\sigma]\!] + \rho [\![v]\!] \dot{S} = 0 \tag{14}$$

$$[\![\sigma v]\!] - [\![q]\!] + \rho [\![\varepsilon + \tfrac{1}{2} v^2]\!] \dot{S} = 0 \tag{15}$$

$$[\![q]\!] - \rho [\![\theta \eta]\!] \dot{S} \geqslant 0, \tag{16}$$

where continuity in temperature has been assumed in obtaining eqn (16). The requirement that u is continuous across S(t) for all t is

$$[\![e]\!] \dot{S} + [\![v]\!] = 0. \tag{17}$$

Using eqn (13) and the above to simplify $[\![\sigma v]\!]$, we get from eqn (15)

$$[\![q]\!] = [\![\rho \varepsilon - \langle \sigma \rangle e]\!] \dot{S}. \tag{18}$$

Introducing the Helmholtz free energy per unit mass defined by

$$\psi = \varepsilon - \theta \eta \tag{19}$$

we have, upon eliminating q' and ρh between eqns (9) and (10) and then using eqn (19),

$$-\rho(\dot{\psi} + \eta \dot{\theta}) + \sigma \dot{e} - \frac{1}{\theta} q \theta' \geqslant 0 \tag{20}$$

and, upon eliminating $[\![q]\!]$ between eqns (16) and (18),

$$f(t) \dot{S} \geqslant 0 \tag{21}$$

$$f(t) \equiv [\![\rho \psi - \langle \sigma \rangle e]\!]. \tag{22}$$

So far, no specific characterization has been assigned to the underlying material and the last two conditions are the thermodynamic admissibility in its general form. In particular, the left-hand side of eqn (21) is the power dissipated due to the propagation of the discontinuity. Since $\dot{S}$ is a velocity, the function f is termed a driving traction by Abeyaratne and Knowles (1988, 1990, 1992, 1993).

3. THERMOELASTICITY

If the bar material is actually thermoelastic, such that $\psi = \hat{\psi}(e, \theta)$ and

$$\sigma = \hat{\sigma}(e, \theta) \equiv \rho\hat{\psi}_e(e, \theta) \tag{23}$$

$$\eta = \hat{\eta}(e, \theta) \equiv -\hat{\psi}_\theta(e, \theta), \tag{24}$$

then the thermodynamic admissibility condition (20) may be satisfied by the heat conduction law

$$q = \hat{q}(\theta'), \quad \hat{q}(\theta')\theta' \leqslant 0. \tag{25}$$

The energy equation (9) becomes

$$q' + \rho\theta\dot{\eta} = \rho h \tag{26}$$

or, after applying eqns (24) and (25),

$$-\frac{\partial \hat{q}}{\partial \theta'}\theta'' + \rho h = \rho c\dot{\theta} - \theta\hat{\sigma}_\theta\dot{e} \tag{27}$$

where c is the specific heat at constant deformation defined by

$$c = \hat{c}(e, \theta) \equiv \theta\hat{\eta}_\theta(e, \theta) = -\theta\hat{\psi}_{\theta\theta}(e, \theta). \tag{28}$$

The conventional thermoelasticity equations consist of eqns (8) and (23)–(28) for which $\hat{\psi}_{ee}$ is non-negative. Our interest in this section is the construction of Helmholtz free energy expressions for which $\hat{\psi}_{ee}$ is not strictly positive.

In terms of $\hat{\psi}$, the internal energy density $\varepsilon = \hat{\varepsilon}(e, \theta)$ is given by eqn (19) as

$$\hat{\varepsilon}(e, \theta) = \hat{\psi}(e, \theta) + \theta\hat{\eta}(e, \theta). \tag{29}$$

Our starting point is the assumption that the internal energy and the entropy are each divisible into two parts, the first parts being functions of e only and the second parts functions of θ only. Thus

$$\hat{\varepsilon}(e, \theta) = \varepsilon^{(1)}(e) + \varepsilon^{(2)}(\theta), \quad \hat{\eta}(e, \theta) = \eta^{(1)}(e) + \eta^{(2)}(\theta). \tag{30}$$

The associated Helmholtz free energy is

$$\hat{\psi}(e, \theta) = \varepsilon^{(1)}(e) - \theta\eta^{(1)}(e) + \psi^{(2)}(\theta) \tag{31}$$

where

$$\psi^{(2)}(\theta) = \varepsilon^{(2)}(\theta) - \theta\eta^{(2)}(\theta). \tag{32}$$

It follows from eqn (31) that the strain-dependent portion of the Helmholtz free energy is linear in temperature. This fact will be exploited in the construction to follow.

The decomposition (30) was introducd by Chadwick and Creasy (1984) as a way to weaken the concept of strictly entropic elasticity as applied to elastomeric materials which presumes the vanishing of $\varepsilon^{(1)}(e)$ in eqn (30). The inclusion of $\varepsilon^{(1)}(e)$ leads to the notion of modified entropic elasticity, and the associated formulation appears to give a better description of rubberlike thermoelasticity. The intent of this paper is to adopt the decomposition for strain and temperature ranges in which high polymers can undergo phase transition.

The desired form of the Helmholtz free energy [eqn (31)] may also be obtained from another argument. Integrating $-\hat{c}(e,\theta)/\theta$ twice between θ_o, the reference temperature associated with the reference configuration $V(X)$ and θ, and using eqns (24) and (28), there results

$$\hat{\psi}(e,\theta) = \hat{\psi}(e,\theta_o)\frac{\theta}{\theta_o} - \hat{\varepsilon}(e,\theta_o)\left(\frac{\theta}{\theta_o} - 1\right) - \int_{\theta_o}^{\theta}\left(\frac{\theta}{\theta'} - 1\right)\hat{c}(e,\theta')\,\mathrm{d}\theta', \tag{33}$$

where a change of the double integration has been performed. It is seen that if the specific heat is independent of the deformation then the deformation-dependent portion of $\hat{\psi}(e,\theta)$ is again linear in θ.

The last representation may be put into a more convenient form by introducing yet another reference temperature θ_c $(\theta_c > \theta_o)$, and the desired form is

$$\hat{\psi}(e,\theta) = [1-k(\theta)]\hat{\psi}(e,\theta_o) + k(\theta)\hat{\psi}(e,\theta_c) + C(\theta_c)k(\theta) - C(\theta), \tag{34}$$

where

$$k(\theta) = \frac{\theta-\theta_o}{\theta_c-\theta_o} \tag{35}$$

$$C(\theta) = \int_{\theta_o}^{\theta}\left(\frac{\theta}{\theta'} - 1\right)c(\theta')\,\mathrm{d}\theta' \tag{36}$$

and $c(\theta)$ is the presumed strain-independent specific heat. In short, within a temperature range where the specific heat is independent of the strain, eqn (34) effectively expresses $\hat{\psi}(e,\theta)$ in terms of its functional forms at two different temperatures.

Let us now identify θ_o and θ_c with the transformation temperature and critical temperature,† respectively, and use simple polynomials to demonstrate the use of eqn (34). At the critical temperature θ_c, the Helmholtz free energy $\hat{\psi}(e,\theta_c)$ is characterized by a critical strain e_c and a critical stress σ_c. Among the characteristics of $\hat{\psi}(e,\theta_o)$, the Helmholtz free energy at the transformation temperature, there is the maximum stress to be denoted by $\sigma_M(\theta_o)$. The following normalization conditions are adopted:

$$e_c = 1, \quad \theta_c = 1, \quad \sigma_M(\theta_o) = 1. \tag{37}$$

At the transformation temperature θ_o $(0 < \theta_o < \theta_c = 1)$, $\hat{\psi}(e,\theta_o)$ is a typical W-shaped function of e. The simplest of all such possible functions is the fourth-order polynomial‡

$$\hat{\psi}(e,\theta_o) = \frac{3\sqrt{3}}{2\rho}\left[\tfrac{1}{4}(e-1)^4 - \tfrac{1}{2}(e-1)^2 + \tfrac{1}{4}\right] \tag{38}$$

and

$$\hat{\sigma}(e,\theta_o) = \frac{3\sqrt{3}}{2}\left[(e-1)^3 - (e-1)\right] = \frac{3\sqrt{3}}{2}e(e-1)(e-2) \tag{39}$$

$$\hat{\psi}_{ee}(e,\theta_o) = \frac{3\sqrt{3}}{2\rho}\left[3(e-1)^2 - 1\right]. \tag{40}$$

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† The transformation energy associated with the transformation temperature is zero [c.f. Fig. 1(b)] and different phases do not exist at temperatures above the critical temperature.

‡ The function is symmetric with respect to $e = 1$.

At the assumed critical temperature $\theta_c = 1$, the desired $\hat{\psi}(e, \theta_c)$ is again a fourth-order polynomial defined by

$$\hat{\psi}(e, \theta_c) = \frac{1}{\rho}\left\{\frac{3\sqrt{3}\beta^3}{4\sigma_c^2}[(e-1)^4-1]+\sigma_c e\right\} - C(\theta_c) \tag{41}$$

and

$$\hat{\sigma}(e, \theta_c) = \frac{3\sqrt{3}\beta^3}{\sigma_c^2}(e-1)^3+\sigma_c \tag{42}$$

$$\hat{\psi}_{ee}(e, \theta_c) = \frac{9\sqrt{3}\beta^3}{\rho\sigma_c^2}(e-1)^2, \tag{43}$$

where σ_c is the critical stress and β is a coefficient that may be used to adjust the initial modulus associated with eqn (42). The following are first calculated from eqn (39):

$$\hat{\sigma}(0, \theta_o) = 0, \quad \hat{\sigma}_e(0, \theta_o) = 3\sqrt{3}. \tag{44}$$

The equation (42), however, yields

$$\hat{\sigma}(e, \theta_c) = 0, \quad \hat{\sigma}_e(e, \theta_c) = 3\sqrt{3}\beta \tag{45}$$

for $e = 1-\sigma_c/\beta\sqrt{3}$. Thus $\beta < 1$, as the modulus at the higher temperature θ_c, should be lower than that at θ_o. The explicit form of the desired Helmholtz free energy may now be obtained by substituting eqns (38) and (41) into eqn (34). It can be easily checked that the expression is actually normalized by

$$\hat{\psi}(0, \theta_o) = \hat{\psi}_e(0, \theta_o) = \hat{\psi}_\theta(0, \theta_o) = 0. \tag{46}$$

Differentiating eqn (34) and applying eqns (38) and (41), we get

$$\hat{\sigma}(e, \theta) = \sigma_c k(\theta)+\frac{3\sqrt{3}}{2}(e-1)\left\{-[1-k(\theta)]+\left[1-\left(1-\frac{2\beta^3}{\sigma_c^2}\right)k(\theta)\right](e-1)^2\right\} \tag{47}$$

$$\hat{\psi}_{ee}(e, \theta) = \frac{9\sqrt{3}}{2\rho}\left\{\left[1-\left(1-\frac{2\beta^3}{\sigma_c^2}\right)k(\theta)\right](e-1)^2-\tfrac{1}{3}[1-k(\theta)]\right\}. \tag{48}$$

It is now clear that $\hat{\psi}_{ee}(e, \theta)$ is not strictly positive. In fact, it vanishes at

$$e = \begin{Bmatrix} e_m(\theta) \\ e_M(\theta) \end{Bmatrix} = 1 \pm \left\{[1-k(\theta)]/3\left[1-\left(1-\frac{2\beta^3}{\sigma_c^2}\right)k(\theta)\right]\right\}^{1/2}. \tag{49}$$

Thus, for $0 < \theta < \theta_c = 1$,

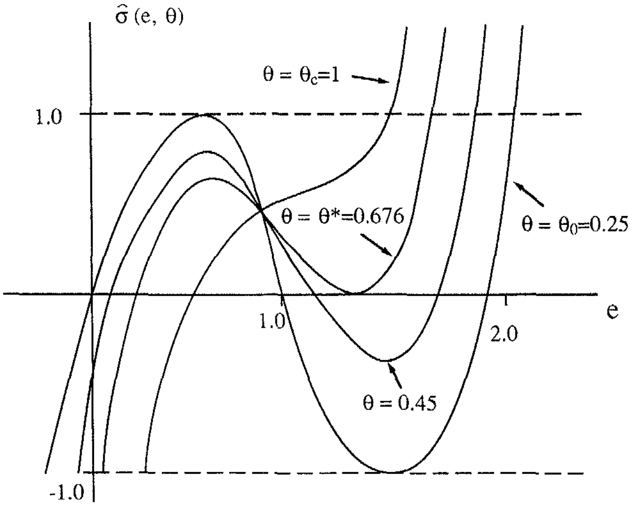

Fig. 2. Isothermal stress–strain curves [eqns (47) and (82)].

$$\hat{\psi}_{ee}(e,\theta) \begin{array}{c} > \\ < 0 \\ > \end{array} \text{ for } \begin{array}{ll} \text{Branch-1} & e < e_{\mathrm{M}} \\ \text{Branch-2} & e_{\mathrm{M}} < e < e_{\mathrm{m}} \\ \text{Branch-3} & e_{\mathrm{m}} < e \end{array} \tag{50}$$

where the branches are referred to as different material phases by Abeyaratne and Knowles (1993). The family of curves $\hat{\sigma}(e, 0)$ is presented in Fig. 2.

The maximum and minimum stresses associated with eqn (47) are defined and computed:

$$\sigma_{\mathrm{M}} \equiv \hat{\sigma}(e_{\mathrm{M}}(\theta),\theta), \quad \sigma_{\mathrm{m}}(\theta) \equiv \hat{\sigma}(e_{\mathrm{m}}(\theta),\theta) \tag{51}$$

$$\left.\begin{array}{c} \sigma_{\mathrm{M}}(\theta) \\ \sigma_{\mathrm{m}}(\theta) \end{array}\right\} = \sigma_c k(\theta) \pm [1-k(\theta)]^{3/2}\left[1-\left(1-\frac{2\beta^3}{\sigma_c^2}\right)k(\theta)\right]^{-1/2}. \tag{52}$$

For a fixed temperature, the equation $\sigma = \hat{\sigma}(e,\theta)$ may be inverted to yield

$$e = \begin{cases} \hat{e}_1(\sigma,\theta), & \sigma < \sigma_{\mathrm{M}}(\theta) \\ \hat{e}_2(\sigma,\theta), & \sigma_{\mathrm{m}}(\theta) < \sigma < \sigma_{\mathrm{M}}(\theta) \\ \hat{e}_3(\sigma,\theta), & \sigma_{\mathrm{m}}(\theta) < \sigma \end{cases} \tag{53}$$

where 1, 2 and 3 refer to the three branches of eqn (50).

The Gibbs free energy per unit reference volume $g(X, t)$ is defined by

$$g = \hat{g}(\sigma,\theta) = \rho\hat{\psi}(\hat{e}(\sigma,\theta),\theta) - \sigma\hat{e}(\sigma,\theta), \tag{54}$$

where $\hat{e}(\sigma,\theta)$ is the inverse of $\sigma = \hat{\sigma}(e,\theta)$. Setting $\hat{e} = \hat{e}_i$ in the above, we get

$$\hat{g}_i(\sigma,\theta) \equiv \rho\hat{\psi}(\hat{e}_i(\sigma,\theta),\theta) - \sigma\hat{e}_i(\sigma,\theta) \tag{55}$$

and hence, for given temperature and stress, the Gibbs free energy densities are different for the three different branches (phases).

Phase equilibrium

The coexistence in equilibrium of branch-1 and branch-3 defined by eqn (52) is now considered. To fix ideas, let us follow the convention of Abeyaratne and Knowles (1993) by assuming that phase (branch)-3 is always on the left, i.e.

$$\begin{aligned}&\text{Phase-3:}\quad 0 < X < S\\&\text{Phase-1:}\quad S < X < L.\end{aligned} \tag{56}$$

Two of the thermodynamic equilibrium conditions are satisfied by

$$\theta(X, t) = \theta(\text{constant}), \quad \sigma(X, t) = \sigma(\text{constant}). \tag{57}$$

It follows from the above and eqn (53) that

$$e(X, t) = \begin{cases}\hat{e}_3(\sigma, \theta), & 0 < X < S\\ \hat{e}_1(\sigma, \theta), & S < X < L\end{cases} \tag{58}$$

provided that σ is the range $\sigma_{\mathrm{m}}(\theta) < \sigma < \sigma_{\mathrm{M}}(\theta)$.

Substituting the above information into the driving traction [eqn (22)], we find

$$f = [\![\rho\psi - \sigma e]\!] = [\![g]\!] = -\hat{g}_1(\sigma, \theta) - \hat{g}_3(\sigma, \theta). \tag{59}$$

The third thermodynamic equilibrium condition is just the vanishing of f, i.e.

$$\hat{g}_1(\sigma, \theta) = \hat{g}_3(\sigma, \theta). \tag{60}$$

Thus, phase-1 and phase-3 cannot be in equilibrium at arbitrary stress and temperature; on the contrary, when one is given, the other is completely determined. The equilibrium condition (60) may be solved to yield the so-called Maxwell stress

$$\sigma = \sigma_{\mathrm{MXW}}(\theta), \tag{61}$$

which defines the phase equilibrium curve in the stress–temperature plane.

The Maxwell stress associated with the example material [eqn (47)] is just

$$\sigma_{\mathrm{MXW}}(\theta) = \sigma_{\mathrm{c}} k(\theta) = \sigma_{\mathrm{c}} \frac{\theta - \theta_{\mathrm{o}}}{\theta_{\mathrm{c}} - \theta_{\mathrm{o}}}. \tag{62}$$

The following strains are defined:

$$e_i(\theta) = \hat{e}_i(\sigma_{\mathrm{MXW}}(\theta), \theta) \quad (i = 1, 2, 3), \tag{63}$$

which, together with $e_{\mathrm{M}}(\theta)$ and $e_{\mathrm{m}}(\theta)$, satisfy the ordering

$$e_1(\theta) < e_{\mathrm{M}}(\theta) < e_2(\theta) < e_{\mathrm{m}}(\theta) < e_3(\theta). \tag{64}$$

The phase equilibrium curve, for the equilibrium between phase-1 and phase-3, in the strain–temperature plane is defined by the curves $e = e_1(\theta)$ and $e = e_3(\theta)$. For the example material, we have $e_2(\theta) = 1$ and

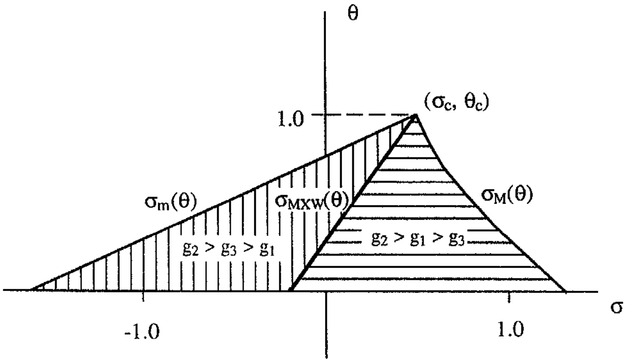

Fig. 3. Phase boundaries [eqns (84) and (85)].

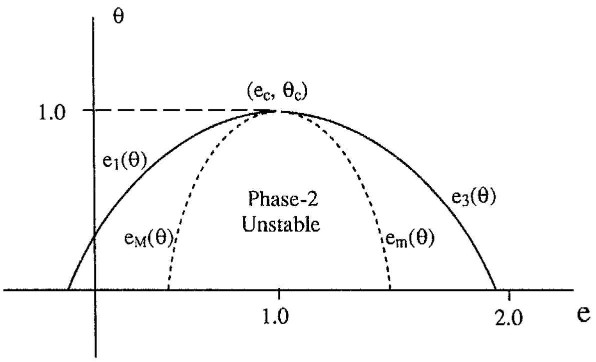

Fig. 4. Phase boundaries [eqns (83) and (86)].

$$\left.\begin{matrix} e_1(\theta) \\ e_3(\theta) \end{matrix}\right\} = 1 \mp \left\{[1-k(\theta)]\Big/\left[1-\left(1-\frac{2\beta^3}{\sigma_c^2}\right)k(\theta)\right]\right\}^{1/2}. \tag{65}$$

The phase equilibrium curves in eqns (62) and (65) are given in Figs 3 and 4 for $\beta = 1/2$, $\sigma_c = 1/2$ and $\theta_o = 1/4$.

In summary, the equilibrium state in eqn (57) may be determined by specifying either θ or σ, but not both. The remaining unknowns are the total elongation Δ and the position of the two-phase boundary S. They are related by

$$e_1(\theta)(L-S)+e_3(\theta)S = \Delta, \tag{66}$$

which is to be accompanied by eqn (61). The above equation is the so-called leverage rule if Δ is replaced by Le with e being the uniform "macroscopic strain".

Equilibrium processes

If the state of the thermoelastic bar is made to evolve along the phase–equilibrium boundary [eqn (59)], the associated evolution may be termed an equilibrium process. All the parameters introduced between eqns (55) and (65) are now conveniently considered as functions of time. Before proceeding and for clarity, we collect the relevant equations as follows:

$$\sigma' = 0, \quad [\![\sigma]\!] = 0 \tag{67}$$

$$q' + p\theta\dot{\eta} = \rho h \quad (X \neq S(t)) \tag{68}$$

$$[\![q]\!] = [\![\rho(\psi+\theta\eta)-\sigma e]\!]\dot{S} \tag{69}$$

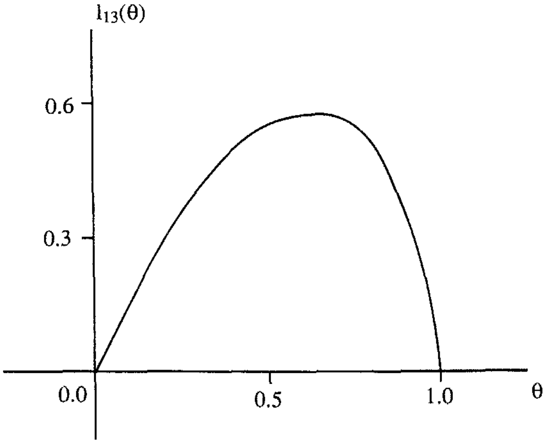

Fig. 5. Latent heat [eqns (76) and (87)].

$$f(t)\dot{S} \geqslant 0, \quad f(t) = [\![\rho\psi - \sigma e]\!]. \tag{70}$$

The static equilibrium conditions (67) are satisfied by $\sigma = \sigma(t)$. For $\theta = \theta(t)$, $q \equiv 0$ and the energy equation (68) may be used to calculate h, which must now be interpreted as the heat that must be supplied to the bar, perhaps via the lateral surface of the bar, to facilitate the equilibrium process. Also, $f(t)$ is identically zero by definition so that eqn (70) is satisfied.

The meaning of the jump [eqn (69)] becomes apparent if the right-hand side is recognized as the enthalpy per unit reference volume ω, i.e.

$$[\![q]\!] = [\![\omega]\!]\dot{S}, \tag{71}$$

where

$$\omega = \rho\varepsilon - \sigma e = \rho(\psi + \theta\eta) - \sigma e = g + \rho\theta\eta. \tag{72}$$

Since the increase in enthalpy during a process at constant stress is equal to the heat gained, eqn (71) gives the meaning of equilibrium latent heat $l_{13}(\theta)$, the heat discharged by a unit reference volume of material in changing from phase-1 to phase-3 at the constant stress $\sigma_{\mathrm{MXW}}(\theta)$, namely

$$l_{13}(\theta) = \omega_1(\theta) - \omega_3(\theta) \quad \text{at} \quad \sigma = \sigma_{\mathrm{MXW}}(\theta), \tag{73}$$

where, in view of eqns (60), (63) and (72),

$$\omega_i(\theta) = \rho\theta\hat{\eta}(e_i(\theta), \theta) \quad (i = 1, 3). \tag{74}$$

The entropy $\hat{\eta}(e, \theta)$ associated with the example material may be calculated from eqns (24), (34), (38) and (41). It is

$$\hat{\eta}(e,\theta) = \left\{\frac{3\sqrt{3}}{8\rho}\left[1 - \frac{2\beta^3}{\sigma_c^2}(e-1)^4 - 2(e-1)^2 + \left(1 + \frac{2\beta^3}{\sigma_c^2}\right)\right] - \frac{\sigma_c}{\rho}e\right\}\frac{1}{\theta_c - \theta_o} + \int_{\theta_o}^{\theta}\frac{c(\theta')}{\theta'}\,\mathrm{d}\theta'. \tag{75}$$

Using eqns (65), (73), (74) and the above we obtain, for the example material,

$$l_{13}(\theta) = \frac{2\sigma_c\theta}{\theta_c - \theta_o}\left\{[1 - k(\theta)] \Big/ \left[1 - \left(1 - \frac{2\beta^3}{\sigma_c^2}\right)k(\theta)\right]\right\}^{1/2}. \tag{76}$$

Thus, for the example material, the heat discharged in changing from phase-1 to phase-3 is positive. It vanishes at $\theta = 0$ and θ_c. The above is plotted in Fig. 5 for $\beta = 1/2$, $\sigma_c = 1/2$ and $\theta_o = 1/4$.

Nonequilibrium processes

For solids, the state of a body may change in such a way that it remains uniform even when two phases should separate for total equilibrium in accordance with eqn (59). Such states, however, are metastable and the appropriate stability boundaries are determined by the convexity of the Helmholtz free energy. These boundaries are defined by the two pairs of functions $\sigma_{\mathrm{m}}(\theta)$, $\sigma_{\mathrm{M}}(\theta)$ and $e_{\mathrm{m}}(\theta)$, $e_{\mathrm{M}}(\theta)$ in the stress–temperature and strain–temperature planes, respectively (see Figs 3 and 4). Thermodynamic evolutions taking place inside the metastable regions are termed nonequilibrium processes. For such processes, the stress and temperature are not related by the equilibrium condition (61).

The underlying conditions for nonequilibrium processes are still eqns (67)–(70). The condition (70), however, is now required to satisfy

$$f(t) = \hat{g}_1(\sigma,\theta)-\hat{g}_3(\sigma,\theta) \gtrless 0 \quad \text{for} \quad \dot{S} \gtrless 0. \tag{77}$$

The forms of possible kinetic relations, as well as a nucleation criterion, have been extensively discussed by Abeyaratne and Knowles (1993). Of particular interest is their explicit result derived from the notion of thermally activated phase transition. Kinetic relations of such a level of sophistication depend on the explicit and full knowledge of the Helmholtz free energy. The determination of such an anticipated double-well potential is by no means a trivial matter. On the other hand, eqn (77) is satisfied by the stress levels

$$\sigma = \begin{cases} \sigma_{\mathrm{M}}^{*}(\theta) \\ \sigma_{\mathrm{m}}^{*}(\theta) \end{cases} \quad \text{for} \quad \dot{S} \gtrless 0, \tag{78}$$

where $\sigma_{\mathrm{m}} < \sigma_{\mathrm{m}}^{*} < \sigma_{\mathrm{MXW}} < \sigma_{\mathrm{M}}^{*} < \sigma_{\mathrm{M}}$. In fact, the most readily available information that can be taken from a tension test is the draw stress [c.f. Fig. 1(a)] σ_{d} which is an admissible σ_{M}^{*}. The draw stress, in general, is neither σ_{MXW} nor σ_{M}. We defer a fuller discussion until the following section.

The increase in enthalpy during a process at constant stress is always equal to the heat gained, regardless of whether or not the process temperature is related to the constant stress by the equilibrium condition (60). Thus, eqn (71) also defines the nonequilibrium latent heat $L_{13}(\sigma,\theta)$ given by

$$L_{13}(\sigma,\theta) = [\hat{g}_1(\sigma,\theta)-\hat{g}_3(\sigma,\theta)]+\rho\theta[\hat{\eta}(\hat{e}_1(\sigma,\theta),\theta)-\hat{\eta}(\hat{e}_3(\sigma,\theta),\theta)]. \tag{79}$$

It is clear that $l_{13}(\theta) = L_{13}(\sigma_{\mathrm{MXW}}(\theta),\theta)$ and, in general, the second term of eqn (79) alone cannot be identified as the latent heat.

We conclude this section with a complete set of formulae and graphs pertaining to the example material. In addition to the normalization conditions of eqn (37), the following are assumed for the remaining parameters:

$$\beta = \tfrac{1}{2}, \quad \sigma_{\mathrm{c}} = \tfrac{1}{2}, \quad \theta_{\mathrm{o}} = \tfrac{1}{4}. \tag{80}$$

We have

$$k(\theta) = \tfrac{1}{3}(4\theta-1) \tag{81}$$

$$\hat{\sigma}(e,\theta) = \tfrac{1}{2}k(\theta)+\frac{3\sqrt{3}}{2}(e-1)[(e-1)^2-(1-k(\theta))] \tag{82}$$

$$\left.\begin{matrix} e_{\mathrm{m}}(\theta) \\ e_{\mathrm{M}}(\theta) \end{matrix}\right\} = 1 \pm \{\tfrac{1}{3}[1-k(\theta)]\}^{1/2} \tag{83}$$

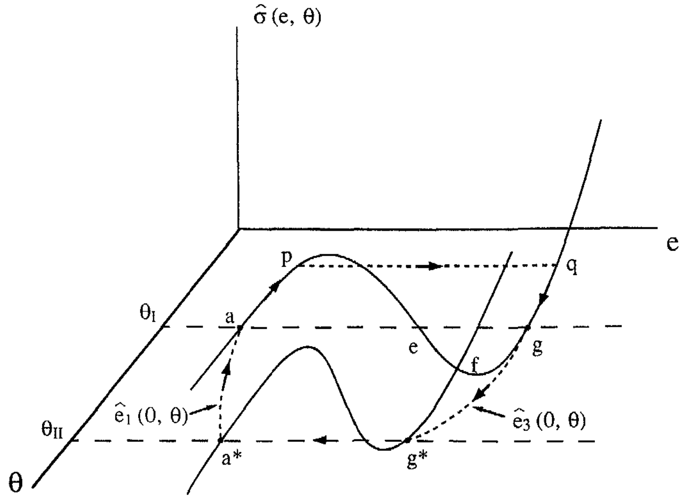

Fig. 6. The shape–memory cycle apqgg*a*a.

$$\left.\begin{array}{l}\sigma_{\mathrm{M}}(\theta)\\ \sigma_{\mathrm{m}}(\theta)\end{array}\right\} = \tfrac{1}{2}k(\theta) \pm [1-k(\theta)]^{3/2} \tag{84}$$

$$\sigma_{\mathrm{MXW}}(\theta) = \tfrac{1}{2}k(\theta), \quad e_2(\theta) = 1 \tag{85}$$

$$\left.\begin{array}{l}e_1(\theta)\\ e_2(\theta)\end{array}\right\} = 1 \mp [1-k(\theta)]^{1/2} \tag{86}$$

$$l_{13}(\theta) = \tfrac{4}{3}\theta[1-k(\theta)]^{1/2} \tag{87}$$

$$\hat{\eta}(e,\theta) = \frac{2}{3\rho}\left[\frac{3\sqrt{3}}{2}(2-e)-1\right] + \int_{\theta_0}^{\theta}\frac{c(\theta')}{\theta'}\,\mathrm{d}\theta'. \tag{88}$$

The family of curves $\sigma = \hat{\sigma}(e,\theta)$ is depicted in Fig. 2, using θ as a parameter. It is seen that $\theta_{\mathrm{m}}(\theta)$ vanishes for $\theta = \theta^*$ which is the root of

$$\sigma_{\mathrm{m}}(\theta) = \tfrac{1}{2}k(\theta) + [1-k(\theta)]^{3/2} = 0. \tag{89}$$

The value of θ^* is found to be 0.676. Thus, for $\theta > \theta^*$, $\hat{\sigma}(e,\theta)$ vanishes only at one value of strain. Using (82), the three branches $\hat{e}_i(\sigma,\theta)$ are implicity defined by the cubic equation $\sigma = \hat{\sigma}(e,\theta)$. The shape–memory cycle depicted in Fig. 6 may be conveniently defined by these functions as follows:

(1) mechanically load phase-1 bar at a temperature $\theta_{\mathrm{I}} < \theta^*$ (a → p)

$$\sigma = \hat{\sigma}(e,\theta_{\mathrm{I}}), \quad \theta = \theta_{\mathrm{I}}, \quad \hat{e}_1(0,\theta_{\mathrm{I}}) < e < e^*_{\mathrm{M}} < e_{\mathrm{M}}(\theta_{\mathrm{I}})\,;$$

(2) snapping to phase-3 (p → q)

$$\sigma = \sigma^*_{\mathrm{M}}(\theta_{\mathrm{I}}) \equiv \hat{\sigma}(e^*_{\mathrm{M}},\theta_{\mathrm{I}}), \quad \theta = \theta_{\mathrm{I}}, \quad e^*_{\mathrm{m}}(\theta_{\mathrm{I}}) < e < \hat{e}_3(\sigma^*_{\mathrm{M}},\theta_{\mathrm{I}})\,;$$

(3) unloading (q → g)

$$\sigma = \hat{\sigma}(e,\theta_{\mathrm{I}}), \quad \theta = \theta_{\mathrm{I}}, \quad \hat{e}_3(0,\theta_{\mathrm{I}}) < e < \hat{e}_3(\sigma^*_{\mathrm{M}},\theta_{\mathrm{I}})\,;$$

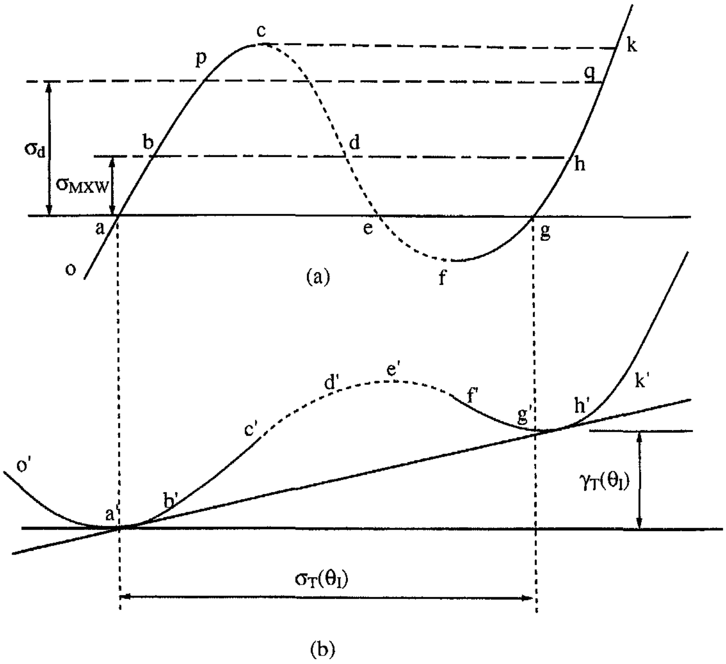

Fig. 7. (a). The stress $\hat{\sigma}(e, \theta_I)$ and (b) the Helmholtz free energy $\hat{\psi}(e, \theta_I)$.

(4) heating to $\theta_{II} < \theta^*$ ($g \rightarrow g^*$)

$$e = \hat{e}_3(0, \theta), \quad \sigma = 0, \quad \theta_I < \theta < \theta_{II},$$

(5) snapping back to phase-1 ($g^* \rightarrow a^*$)

$$\theta = \theta_{II}, \quad \sigma = 0, \quad \hat{e}_1(0, \theta_{II}) < e < \hat{e}_3(0, \theta_{II})\,;$$

(6) cooling ($a^* \rightarrow a$)

$$e = \hat{e}_1(0, \theta), \quad \sigma = 0, \quad \theta_I < \theta < \theta_{II}.$$

It is implied in the above that

$$\sigma_m < \sigma_m^* = 0 < \sigma_{MXW} < \sigma_M^* < \sigma_M,$$

so that condition (78) is met at all times.

4. EXPERIMENTAL DETERMINATION OF THE HELMHOLTZ FREE ENERGY

The continuum approach to the phase transition phenomenon presumes the existence of a double-well Helmholtz energy which, by definition, is merely the integral of a simple load–displacement curve. Unfortunately, the unstable portion of the theoretical load–displacement curve cannot be realized in the laboratory although the two disconnected stable portions can be separately determined. A typical situation is illustrated in Fig. 7(b) where the double-well potential $\hat{\psi}(e, \theta_I)$ associated with the $\hat{\sigma}(e, \theta_I)$ curve of Fig. 6 is given as o′a′b′c′d′e′f′g′h′k′. The curve $\hat{\sigma}(e, \theta_I)$ is also reproduced in Fig. 7(a) as abcdefghk. The dotted portions are associated with the unstable branch. The straight line b′h′ is tangent to $\hat{\psi}(e, \theta_I)$ at b′ and h′, and its slope is proportional to the Maxwell stress $\sigma_{MXW}(\theta_I)$ [c.f. (23)]. The horizontal line bdh is the so-called Maxwell line, which is defined by the fact that the areas bcdb and defghd are equal.

When a phase-1 bar is drawn at a constant strain rate, the experimentally realized stress–strain curve is typically given by oabpqk where the line pq is above the Maxwell line bdh. Theoretically speaking, the level of pq can be as high as that of ck, according to the linear stability criterion. Unloading from k would realize the branch kqhgf. Thus, the two concave portions of the Helmholtz free energy can be separately determined by integrating oabp and fghq. These two portions are tied together by a transformation strain $e_T(\theta_I)$ and a transformation energy $\gamma_T(\theta_I)$ [Fig. 7(b)]. The former can be easily measured and the determination of the transformation energy is crucial to the usefulness of the continuum theory of phase transition.

The transformation strain $e_T(\theta_I)$ is defined by

$$e_T(\theta_I) \equiv \hat{e}_3(0,\theta_I) - \hat{e}_1(0,\theta_I) \quad (\theta_I < \theta^*), \tag{90}$$

where $\hat{e}_i(\sigma,\theta)$ are the three branches defined by (53) and θ^* is the root of $\sigma_m(\theta^*) = 0$. The transformation energy is just

$$\gamma_T(\theta_I) \equiv \hat{\psi}(\hat{e}_3(0,\theta_I),\theta_I) - \hat{\psi}(\hat{e}_1(0,\theta_I),\theta_I). \tag{91}$$

The two concave portions of $\hat{\psi}(e,\theta_I)$ are

$$\begin{gathered} \psi_1(\varepsilon_1,\theta_I) \equiv \hat{\psi}(e,\theta_I) - \hat{\psi}(\hat{e}_1(0,\theta)_I),\theta_I) \\ (\varepsilon_1 = e - \hat{e}_1(0,\theta_I), \quad e < e_M(\theta_I) \end{gathered} \tag{92}$$

$$\begin{gathered} \psi_3(\varepsilon_3,\theta_I) \equiv \hat{\psi}(e,\theta_I) - \hat{\psi}(\hat{e}_3(0,\theta_I),\theta_I) \\ (\varepsilon_3 = e - \hat{e}_3(0,\theta_I), \quad e > e_m(\theta_I)). \end{gathered} \tag{93}$$

which are separately determined.

Let us now perform isothermal tension tests on a sample of unit length and also unit cross-section area. The first test is a mental one in that the sample is assumed to remain uniform and follow the theoretical curve abcdefg. The work done by the external force in going from a to g by following the specified path is

$$\Delta W_M = A[\text{abcdea}] - A[\text{efge}] = \rho\gamma_T(\theta_I) \tag{94}$$

where $A[\ldots]$ indicates the area enclosed by the perimeter [...]. The heat supplied to the sample is

$$\Delta Q_M = \rho\theta_I[\hat{\eta}(\hat{e}_3(0,\theta_I),\theta_I) - \hat{\eta}(\hat{e}_1(0,\theta_I),\theta_I)]. \tag{95}$$

The subscript M attached to ΔW and ΔQ indicates the fact that the work and heat terms are associated with a mental process, which is the presumed theoretical process. The change in internal energy in going from a to g is denoted by $\Delta\mathscr{E}(\text{ag})$ and

$$\Delta\mathscr{E}(\text{ag}) = \rho\gamma_T(\theta_I) + \rho\theta_I[\hat{\eta}(\hat{e}_3(0,\theta_I),\theta_I) - \hat{\eta}(\hat{e}_1(0,\theta_I),\theta_I)], \tag{96}$$

where the right-hand side is merely the sum of eqns (94) and (95).

The second test is a real laboratory experiment and the result is the curve apqg. The work done by the external force in going from a to g by following the experimentally determined path is

$$\Delta W(\text{apqg}) = A[\text{abdhga}] + A[\text{bpqhdb}] \tag{97}$$

where, by the definition of the Maxwell line,

$$A[\text{abdhga}] = \rho\gamma_{\mathrm{T}}(\theta_{\mathrm{I}}). \tag{98}$$

The heat supplied to the sample is

$$\Delta Q(\text{apqg}) = \rho\theta_{\mathrm{I}}[\hat{\eta}(\hat{e}_1(\sigma_{\mathrm{d}},\theta_{\mathrm{I}}),\theta_{\mathrm{I}}) - \hat{\eta}(\hat{e}_1(0,\theta_{\mathrm{I}}),\theta_{\mathrm{I}})] + \rho\theta_{\mathrm{I}}[\hat{\eta}(\hat{e}_3(0,\theta_{\mathrm{I}}),\theta_{\mathrm{I}}) - \hat{\eta}(\hat{e}_3(\sigma_{\mathrm{d}},\theta_{\mathrm{I}}),\theta_{\mathrm{I}})] - L_{13}(\sigma_{\mathrm{d}},\theta_{\mathrm{I}}), \tag{99}$$

where σ_{d} is the so-called draw stress, the stress level associated with pg, and the non-equilibrium latent heat $L_{13}(\sigma_{\mathrm{d}},\theta_{\mathrm{I}})$ links the change from phase-1 to phase-3. Applying eqn (79) to eqn (99), we obtain

$$\Delta Q(\text{apqg}) = \rho\theta_{\mathrm{I}}[\hat{\eta}(\hat{e}_3(0,\theta_{\mathrm{I}}),\theta_{\mathrm{I}}) - \hat{\eta}(\hat{e}_1(0,\theta_{\mathrm{I}}),\theta_{\mathrm{I}})] + \hat{g}_3(\sigma_{\mathrm{d}},\theta_{\mathrm{I}}) - \hat{g}_1(\sigma_{\mathrm{d}},\theta_{\mathrm{I}}), \tag{100}$$

where

$$\hat{g}_3(\sigma_{\mathrm{d}},\theta_{\mathrm{I}}) - \hat{g}_1(\sigma_{\mathrm{d}},\theta_{\mathrm{I}}) = -A[\text{bpqhdb}]. \tag{101}$$

It can now be straightforwardly demonstrated by substitution that

$$\Delta\mathscr{E}(\text{ag}) = \Delta W(\text{apqg}) + \Delta Q(\text{apqg}) \tag{102}$$

which is the experimental counterpart of eqn (96). Thus, by equating the experimentally measured $\Delta\mathscr{E}(\text{ag})$ to that defined by eqn (96), an additional piece of information may be obtained for characterizing the desired Helmholtz energy.

Measuring $\Delta W(\text{apqg})$ is straightforward, but the determination of $\Delta Q(\text{apqg})$ may not be such an easy task. An alternative measurement is proposed as follows:

$$\Delta\mathscr{E}(\text{ga}) = \Delta W(\text{gg}^*\text{a}^*\text{a}) + \Delta Q(\text{gg}^*\text{a}^*\text{a}), \tag{103}$$

which is the change in internal energy in going from g to a. The connecting path gg*a*a is depicted in Fig. 6 where

$$\begin{aligned} \hat{\sigma}(e,\theta_{\mathrm{I}}) &= 0 \quad \text{for} \quad e = e \text{ of points a and g} \\ \hat{\sigma}(e,\theta_{\mathrm{II}}) &= 0 \quad \text{for} \quad e = e \text{ of points a}^* \text{ and g}^*. \end{aligned} \tag{104}$$

It is also implicity assumed that

$$\sigma_{\mathrm{MXW}}(\theta_{\mathrm{II}}) > 0 > \sigma_{\mathrm{m}}(\theta_{\mathrm{II}}), \tag{105}$$

so that the snapping back from phase-3 to phase-1 (g* → a*) is thermodynamically admissible (c.f. the shape–memory cycle described at the end of section 3).

An immediate consequence of eqn (104) is that $\Delta W(\text{gg}^*\text{a}^*\text{a}) = 0$ and hence

$$\Delta\mathscr{E}(\text{ga}) = \Delta Q(\text{gg}^*\text{a}^*\text{a}). \tag{106}$$

Beginning with $\hat{g}_i(\sigma,\theta)$, the Gibbs energy for the ith branch given by eqn (55), we may define the enthalpy for the ith branch by

$$\hat{\omega}_i(\sigma,\theta) \equiv \hat{g}_i(\sigma,\theta) + \rho\theta\hat{\eta}(\hat{e}_i(\sigma,\theta),\theta) \tag{107}$$

where eqn (72) has been used. Since the increase in enthalpy during a process at constant stress is equal to the heat gained, we have

$$\Delta Q(\mathrm{gg^*a^*a}) = [\hat{\omega}_3(0,\theta_{\mathrm{II}}) - \hat{\omega}_3(0,\theta_{\mathrm{I}})] + [\hat{\omega}_1(0,\theta_{\mathrm{II}}) - \hat{\omega}_3(0,\theta_{\mathrm{II}})] + (\hat{\omega}_1(0,\theta_{\mathrm{I}}) - \hat{\omega}_1(0,\theta_{\mathrm{II}})] = \hat{\omega}_1(0,\theta_{\mathrm{I}}) - \hat{\omega}_3(0,\theta_{\mathrm{I}}) = -\Delta\mathscr{E}(\mathrm{ag}), \quad (108)$$

which may be used in place of eqn (102). In summary, the desired energy relation is

$$-\Delta Q(\mathrm{gg^*a^*a}) = \rho\gamma_{\mathrm{T}}(\theta) + \rho\theta[\hat{\eta}(\hat{e}_3(0,\theta),\theta) - \hat{\eta}(\hat{e}_1(0,\theta),\theta)] \quad (109)$$

where θ is a θ_{I}.

We now return to the load–elongation curve of Fig. 1(a). Based on the extensive data reported by Zhou *et al.* (1994) for polycarbonate, the following explicit expressions may be proposed:

$$\rho\hat{\psi}(e,\theta) = \begin{cases} \frac{1}{2}E_1(\theta)[e-\alpha(\theta-\theta_{\mathrm{o}})]^2 - \rho F(\theta) \\ \frac{1}{2}E_3(\theta)[e-\alpha(\theta-\theta_{\mathrm{o}})-e_{\mathrm{T}}]^2 + \rho\gamma_{\mathrm{T}}(\theta) - \rho F(\theta), \end{cases} \quad (110)$$

where the upper expression is for branch-1 and the lower for branch-3. The strain e is defined relative to a reference configuration associated with the unknown transformation temperature θ_{o}. The moduli E_1 and E_3 were reported for the temperature range $280°\mathrm{K} < \theta < 390°\mathrm{K}$, and the glass transition temperature T_{g} for their material is around 420°K. It was reported by them that the tarnsformation strain, e_{T}, is almost independent of the temperature. In eqn (110), the function $F(\theta)$ plays no significant role, and the thermal expansion coefficient α can be easily measured as soon as θ_{o} is determined. The determination of $\gamma_{\mathrm{T}}(\theta)$, which is intertwined with the unknown θ_{o}, is our main objective.

Applying eqn (98) to eqn (110), we find

$$\rho\gamma_{\mathrm{T}}(\theta) = e_{\mathrm{T}}\sigma_{\mathrm{MXW}}(\theta) - \left[\frac{1}{E_1(\theta)} - \frac{1}{E_3(\theta)}\right]\frac{\sigma^2_{\mathrm{MXW}}}{2} \quad (111)$$

which may be approximated by

$$\rho\gamma_{\mathrm{T}}(\theta) = e_{\mathrm{T}}\sigma_{\mathrm{MXW}}(\theta), \quad (112)$$

as the second term of eqn (111) is much smaller than the first for the polycarbonate in question. We further assume that the linear relation (62) holds that

$$\rho\gamma_{\mathrm{T}}(\theta) = e_{\mathrm{T}}\sigma_{\mathrm{c}}\frac{\theta-\theta_{\mathrm{o}}}{\theta_{\mathrm{c}}-\theta_{\mathrm{o}}}. \quad (113)$$

Using eqns (110) and (113), we obtain from eqn (109)

$$\frac{e_{\mathrm{T}}\sigma_{\mathrm{c}}\theta_{\mathrm{o}}}{\theta_{\mathrm{c}}-\theta_{\mathrm{o}}} = \Delta Q = \Delta Q(\mathrm{gg^*a^*a}) \quad (114)$$

where, according to the approximation (113), $\Delta Q(\mathrm{gg^*a^*a})$ must be a constant. The above equation determines θ_{o} if θ_{c} and σ_{c} can be measured.

The draw stress σ_{d} and maximum stress σ_y were both obtained by Zhou *et al.* (1994). Both were shown to be monotonically decreasing functions of temperature. While their tests were not set up with the critical temperature in mind, their data do suggest that σ_y and σ_{d} intersect at a temperature lower than the glass transition temperature. Thus,

$$\sigma_y = \sigma_{\mathrm{d}} = \sigma_{\mathrm{c}} \quad \text{at} \quad \theta = \theta_{\mathrm{c}}. \quad (115)$$

Finally, solving eqn (114) for θ_{o} we obtain

$$\theta_o = \frac{\Delta Q}{\Delta Q + e_T \sigma_c} \theta_c. \tag{116}$$

This completes the determination of γ_T.

5. CONCLUDING REMARKS

The double-well potentials associated with certain stress-induced phase transformations cannot be fully determined from load–displacement curves alone. Following the path of a shape–memory cycle in the stress, strain and temperature space, an energy identity in terms of a heat measurement is established. This new measurement, together with the heretofore known isothermal load–displacement measurements, may be applied to determine the desired transformation energy. The usefulness of the proposed measurement remains to be proven by actual experiments.

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