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About the "normal growth" approximation in the dynamical theory of phase transitions

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Nonequilibrium phase transitions can often be modeled by a surface of discontinuity propagating into a metastable region. The physical hypothesis of "normal growth" presumes a linear relation between the velocity of the phase boundary and the degree of metastability. The phenomenological coefficient, which measures the "mobility" of the phase boundary, can either be taken from experiment or obtained from an appropriate physical model. This linear approximation is equivalent to assuming the surface entropy production (caused by the kinetic dissipation in a transition layer) to be quadratic in a mass flux.

In this paper we investigate the possibility of deducing the "normal growth" approximation from the viscosity-capillarity model which incorporates both strain rates and strain gradients into constitutive functions. Since this model is capable of describing fine structure of a "thick" advancing phase boundary, one can derive, rather than postulate, a kinetic relation governing the mobility of the phase boundary and check the validity of the "normal growth" approximation.

We show that this approximation is always justified for sufficiently slow phase boundaries and calculate explicitly the mobility coefficient. By using two exact solutions of the structure problem we obtained unrestricted kinetic equations for the cases of piecewise linear and cubic stress-strain relations. As we show, the domain of applicability of the "normal growth" approximation can be infinitely small when the effective viscosity is close to zero or the internal capillary length scale tends to infinity. This singular behavior is related to the existence of two regimes for the propagation of the phase boundary – dissipation dominated and inertia dominated.

1 Introduction

Phase transitions in continuum bodies have recently become the subject of intense studies in mechanics and mathematics. Within this mainstream of research activity, considerable interest has focused on the understanding of the principles of the evolution of phase boundaries. It was realized, that the highly localized phase boundaries may be represented by jump discontinuities and that the essential physics of the transformation process can be modeled by the appropriate *jump conditions.* These conditions must comply with the integral form of the basic conservation laws, as well as with additional equation governing the pace of the transformation process. The necessity for an additional jump condition was tacitly assumed by the physicists who used to calculate the phase boundary velocity without any reference to the conservation laws [1, 2].

Two major regimes of subsonic phase boundary migration have been long recognized in the physical theory of phase transformations: diffusion controlled and interface-controlled. In the first case, the rate of the growth of a stable phase is limited by supply of heat (or a constituent) which is governed by diffusion type equation in the bulk phase. Since the /transport is assumed by this approach to be a rate-limiting process, the interface kinetic is taken to be instantaneous in a corresponding time scale. The classical mathematical framework for analyzing this type of process is a Stefan problem and its generalizations. The alternative approximation of the /interface controlled growth (the subject of this paper) is based on an assumption that the heat transport (diffusion) is fast so that the growth of a stable phase is limited by the dissipative processes inside the narrow transition zone. In the limiting case of an infinitely fast heat conductivity, one has an isothermal formulation where the physics of the transformation process is confined in a /kinetic relation, governing the evolution of the phase boundary. Usually in the physical literature it is assumed that the phase boundary velocity depends on a thermodynamic driving force that is the free energy decrease due to the transformation. The hypothesis of "normal growth" assumes the dependence of the velocity on the driving force to be linear.

In a continuum mechanical framework it was first realized that the mixed-type initial value problems, arising for the materials supporting several phases, are ill posed (e.g., [3]). As a condition of uniqueness an extra jump (admissibility) relation was suggested for subsonic phase discontinuities [4, 5, 6, 7]. This additional condition, can either be advanced on phenomenological grounds, an example being the "normal growth" hypothesis, or be derived from the micro-mechanical model of the process inside the narrow transition zone.

In the case of /nondissipative phase boundaries, the kinetic relation, which is an immediate generalization of the phase equilibrium (Maxwell) condition, states that the surface entropy production is equal to zero. If the transformation is /dissipative, one has to account for the irreversible processes inside the phase boundary by specifying the /surface entropy production. Often processes which are only weakly nonequilibrium are of most interest. In the case of a weak metastability of a state ahead of the phase front, one would anticipate small deviation from the Maxwell prescription for the state behind. This is a basis of the "normal growth" hypothesis which, following the pattern of the linear thermodynamics of nonequilibrium processes, presumes the surface entropy production to be a quadratic function of the material velocity of the phase boundary [5]. This assumption guarantees a linear relation between the mass flux and the "driving force," which measures the energetical preference of the state behind the advancing boundary.

Numerous examples of the successful application of the hypothesis of "normal growth" can be found in such diverse areas as the Hertz-Knudsen theory of nonequilibrium condensation [8] or the theory of motion by mean curvature [9]. To answer the question about the validity of the assumption of "normal growth" for the fast phenomena, e.g., the explosive "burst like" martensitic transformations in solids [2], one has to go beyond the quasistatic approximation and consider inertial effects as well [10]. In this paper, by studying the "slow limit " originating from the general /viscosity-capillarity theory, we contribute to the understanding of the domain of application of the hypothesis of "normal growth."

In the viscosity-capillarity theory the basic equations of elastodynamics are regularized by the introduction of /viscosity and gradient type /nonlocality [4, 11]. The effective viscosity is meant to simulate the interface kinetics, while the purpose of the introduction of higher deformation gradients is to bring an internal length – scale of /nondissipative origin into the theory. This approach may not represent the transformation process in its full complexity, however we believe that it provides a reasonable tool for the analysis of the interplay between the /inertia and the /dissipation.

Based on analysis of the one dimensional isothermal model, we show in this paper that the viscosity capillarity theory always leads to a "normal growth" type kinetic relation in a limit of a /weak metastability of the state ahead. We obtain an explicit relation for the "mobility" coefficient as a function of the nondimensional ratio of the viscous and capillary length scales. This dependence is singular at zero viscosity which results in narrowing of the domain of application of the "normal growth" approximation for the materials with progressively weak dissipation. The study of the exact solutions for the structure problem in cases of /piecewise quadratic and /quartic elastic energies provide explicit examples of the unrestricted kinetic relations. The most remarkable feature of the kinetic relations obtained from the viscosity-capillarity theory is that in addition to the slow, dissipation dominated branch of the kinetic curve, meant to be described by the "normal growth" approximation, there exists a fast, inertia dominated branch. This peculiar behavior of kinetic curves was first observed for certain cases [12, 5] and then demonstrated to be generic [10]. Our analysis of the examples shows that not only does the kinetic curve deviate from the straight line upon proceding deeper into the metastable area, but that both steady regimes cease to exist when the critical level of metastability is achieved. This puts a principal limit on a straightforward application of the "normal growth" approximation as well as its polynomial extensions.

In Section 2 we briefly introduce the model of the internal structure of the phase boundary and reformulate the problem of finding the kinetic relation as a /nonlinear eigenvalue problem. We demonstrate in Section 3, that regardless of the particular form of the elastic energy, the "normal growth" approximation can be obtained for a sufficiently slow phase boundary motion. We then show that the corresponding "mobility" coefficient can be presented in an explicit form. Two exactly solvable cases illustrating the general properties of these kinetic relations, are considered in Section 4. Alternative forms of the "normal growth" hypothesis, originating from the different choices of the measure of metastability, are discussed in Section 5. In the last Section we summarize our results.

2 Viscosity-capillarity model

Consider the system of conservation laws

$$\begin{cases} u_t = v_x \\ v_t = \sigma_x \end{cases}, \tag{2.1}$$

where $u = y_x(x,t)$ denotes deformation, $v =_t (x,t)$ – velocity and $\sigma(u)$ – stress; $y(x,t)$ is a displacement of a reference point x; subindices indicate partial derivatives. The system (2.1) or an equivalent nonlinear wave equation

$$y_{tt} = \sigma'(y_x)y_{xx}, \tag{2.2}$$

where the prime stands for the ordinary derivative, constitute the simplest model for /one dimensional isothermal elastodynamics with no body forces and constant reference density ($\rho = 1$); one can conceive either longitudinal or simple shearing motions. It is also well known, that substitution of $V = u^{-1}$ (specific volume) and $p = -\sigma$ (pressure), with the simultaneous transformation to eulerian variables (y,t), allows the use of (2.1) for the description of one dimensional isothermal flows of a compressible fluid as well [5].

For materials, exhibiting phase transitions (shape memory alloys, van der Waals fluid, etc.) the constitutive function $\sigma(u)$ (or $p(V)$ in case of fluids) can be nonmonotone. The simplest nontrivial function $\sigma(u)$ has two disjoint intervals of monotone growth ($u < \alpha$ and $u > \beta$), to which we shall attribute the names of α – and β – phases, accordingly, and the interval of a monotone descent, where the system (2.1) looses hyperbolicity (see Fig. 1). For the sake of definiteness, we assume that

$$\begin{cases} \sigma'(u) > 0, \sigma''(u) \leq 0, & \text{if } u < \alpha, \\ \sigma'(u) > 0, \sigma''(u) \geq 0, & \text{if } u > \beta \end{cases}$$

and will refer to points α and β, where the related stored elastic energy

$$f(u) = \int_0^u \sigma(\mu)d\mu \tag{2.3}$$

looses its convexity, as spinodal points.

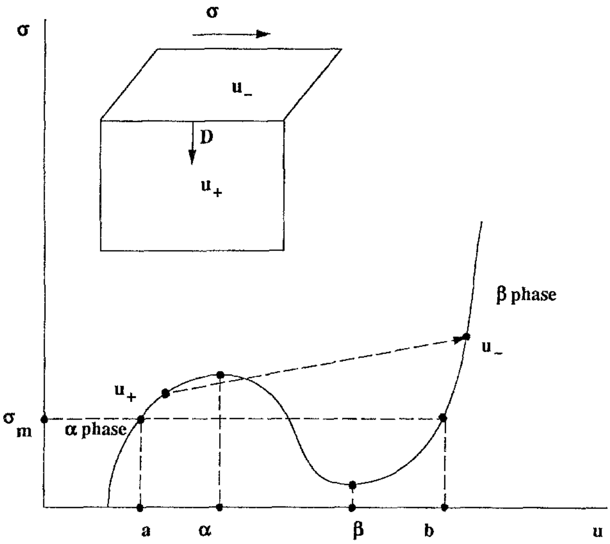

Fig. 1. The typical stress-strain relation for the material undergoing phase transformation. The interval (α, β) corresponds to spinodal (elliptic) region, σ_m- Maxwell stress, a, b- equilibrium strains. The steadily propagating phase boundary with the material velocity D performs switching from state u_+ ahead to the state u_- behind the discontinuity

The horizontal chord on Fig. 1 at $\sigma = \sigma_m$ constitutes the equal area (Maxwell) construction

$$\begin{aligned} &\int_a^b \sigma(\nu)d\nu = \sigma_m(b-a), \\ &\sigma_m = \sigma(a) = \sigma(b), \end{aligned} \tag{2.4}$$

where a and b are the equilibrium strains in the coexisting phases.

Although the system (2.1) with the nonmonotone $\sigma(u)$ allows discontinuities simulating steadily propagating phase boundaries (see transition $u_+ \rightarrow u_-$ on Fig. 1), a generic initial value problem was found to have a nonunique solution [3]. The /viscosity-capillarity model presents a natural regularization of the system (2.1) which substitutes discontinuities with "thick" transition layers and provides an additional selection (admissibility) principle, narrowing the above nonuniqueness.

Two mechanisms have been found to be essential for the proper resolution of the fine structure of the phase interface-dissipation and nonlocality, and none of them alone is capable of describing the whole spectrum of related phenomena. In a formal way, the viscosity-capillarity model can be obtained from (2.1) by augmenting the purely elastic constitutive model for stress σ with viscous stresses and capillary (hyper) stresses [4, 11]

$$\sigma = \sigma(u) + \eta v_x - 2\epsilon u_{xx}, \tag{2.5}$$

where η is an effective viscosity coefficient and ϵ is a positive parameter providing the scale of (weak) nonlocality of a continuum. The last term in (2.5) arises from an explicit (quadratic) dependence of the specific stored energy on the strain gradients. The important feature of the regularization (2.5) is that in a limit $\eta \to 0$, $\epsilon \to 0$, not only do we get a description of phase boundaries as jump discontinuities, but we also obtain a desired selection principle in the form of kinetic relation, which depends on a limit of the nondimensional ratio [5]

$$\mathrm{W} = \eta/\sqrt{\epsilon}. \tag{2.6}$$

To fix the ideas, consider the traveling wave solution of the system (2.1) with σ taken from (2.5). Substitute the ansatz $\xi = x - Dt$ and eliminate $v(\xi)$ to get

$$(\sigma(u) - D^2 u - \eta D\dot{u} - 2\epsilon\ddot{u})^{\bullet} = 0, \tag{2.7}$$

where D is the phase boundary velocity, which we take to be positive, and the superimposed dot indicates the ξ-derivative. Since the parameter ϵ is small, one can invoke the standard reasoning of the theory of matched asymptotic expansions and supplement (2.7) by the boundary conditions at infinity

$$\dot{u}(\pm\infty) = 0 \tag{2.8}$$

$$u(\pm\infty) = u_{\pm}. \tag{2.9}$$

Let us for the sake of definiteness assume that u_+ belongs to phase α, while u_- belongs to phase b (see Fig. 1). Parameters u_+ and u_- correspond to the limiting values of the deformation to the right and to the left of the discontinuity. The solution of (2.7) which describes the internal structure of the phase discontinuity is supposed to deviate considerably from u_+ and u_- only in a narrow region scaled with $\sqrt{\varepsilon}$.

The integration of (2.7) yields

$$\sigma(u) - D^2 u - \eta D\dot{u} - 2\epsilon\ddot{u} = C. \tag{2.10}$$

Boundary conditions (2.8, 2.9) are then used to find the constant C and specify D as a function of u_+ and u_-. We get

$$C = \sigma(u_+) - D^2 u_+ = \sigma(u_-) - D^2 u_- \tag{2.11}$$

and therefore

$$D = \sqrt{\frac{\sigma(u_+) - \sigma(u_-)}{u_+ - u_-}}. \tag{2.12}$$

The necessary condition (2.12) is a classical /Rankine-Hugoniot jump condition, governing the integral balance of momentum. With (2.11) and (2.12) one can rewrite the equation (2.10) in a form

$$2\epsilon\ddot{u} + \eta\dot{u}\sqrt{\frac{\sigma(u_+) - \sigma(u_-)}{u_+ - u_-}} = \sigma(u) - \sigma(u_+) - \frac{\sigma(u_+) - \sigma(u_-)}{u_+ - u_-}(u - u_+). \tag{2.13}$$

The general solution of the second order ODE (2.13) depends on two constants. However, since both (2.13) and the boundary conditions (2.9) are invariant under translations, only one of these constants is nontrivial. Therefore, for the given u_+, the boundary value problem (2.13) is overdetermined and can be considered as a /nonlinear eigenvalue problem with respect to u_-. The specification of the points of /discrete spectrum for this eigenvalue problem constitutes the desired kinetic relation which will be the subject of our main interest in what follows, and it will be convenient to regard this kinetic relation as a locus in a (u_+, u_-) plane.

3 Kinetic relation

It is easy to recognize in (2.13) the equation of motion of a damped mathematical oscillator in a potential field with the energy

$$g(u; u_+, u_-) = \int_{u_+}^{u} \left[\sigma(v) - \sigma(u_+) - \frac{\sigma(u_+) - \sigma(u_-)}{u_+ - u_-}(v - u_+) \right] dv. \tag{3.1}$$

The mass of the oscillator equals 2ε and the linear dissipation is scaled with

$$N(u_+, u_-) = \eta \sqrt{\frac{\sigma(u_+) - \sigma(u_-)}{u_+ - u_-}}. \tag{3.2}$$

The energy integral reads

$$\epsilon \dot{u}^2 + g(u; u_+, u_-) = N(u_+, u_-) \int_{\xi}^{\infty} \dot{u}^2(v) dv, \tag{3.3}$$

where the choice of the integration constant follows from (2.8) and (2.9). The desired (infinite domain) solution, describing the internal structure of the phase boundary, corresponds to the "motion" from one extremum to another. On the phase plane $(u, \dot{u})$ this solution is represented by the heteroclinic separatrix $u_- \to u_+$, connecting two equilibrium points (see Fig. 2).

The fact that both u_+ and u_- are critical points of the energy function $g(u; u+, u-)$ follows directly from the definition (3.1). If these equilibria are saddles, the heteroclinic trajectory is not generic and to guarantee the connection, an extra constraint on u_+ and u_- is required.

Introduce

$$c(u) = \sqrt{\sigma'} \tag{3.4}$$

the local characteristic (sound) velocity. One can show that u_+ (belonging to phase α), and u_- (belonging to phase β), are both energy maxima and the corresponding equilibria on the phase plane ($(0, u_+)$ and $(0, u_-)$) are saddles if and only if

$$D < c(u_+) \quad \text{and} \quad D < c(u_-), \tag{3.5}$$

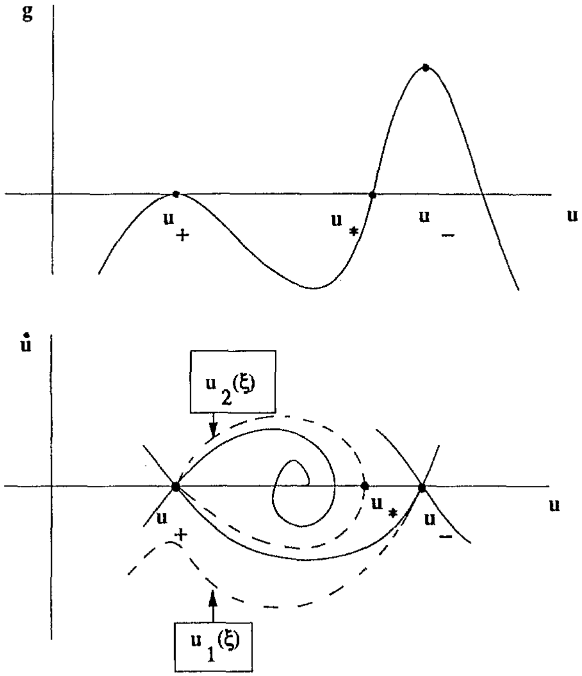

Fig. 2. Sketch of a potential energy $g(u, u_+, u_-)$ together with the corresponding phase portrait, which shows the separatrix connecting the two saddles u_+ and u_-. Phase trajectories for the nondissipative ($\eta = 0$) system $u_1(\xi)$ and $u_2(\xi)$ are shown by dashed lines

which means that the phase boundary is subsonic with respect to the states on both sides of the discontinuity. As is well known, contrary to our case, classical shocks are supersonic with respect to the state ahead. One can show [10] that they are represented on the phase plane by heteroclinic trajectories connecting a saddle with a node (or focus). In terms of our nonlinear eigenvalue problem, conventional shocks correspond to points of continuous spectrum and no extra relation between u_+ and u_- is obtained.

In what follows we focus our attention on subsonic phase boundaries, which satisfy (3.5). To obtain a desired necessary condition relating u_+ and u_-, evaluate (3.3) at $\xi = -\infty$ to get

$$g(u_-; u_+, u_-) = N(u_+, u_-)h(u_+, u_-), \tag{3.6}$$

where

$$h(u_+, u_-) = \int_{-\infty}^{\infty} \dot{u}^2 d\xi. \tag{3.7}$$

Since $u(\xi)$ in (3.7) is an unknown solution of (3.3), the relation between u_+ and u_-, given by (3.6) is implicit, until the boundary value problem (2.13) is solved. Note, however that $u_+ = a$, $u_- = b$ with (2.4) implies $g(b; a, b) = 0$

and $N(a, b) = 0$ so $(u_+, u_-) = (a, b)$ is a solution to (3.6). Since $D = 0$ in this case, it is an equilibrium solution.

In one of its formulations the "normal growth" assumption states, that if u_+ is in the metastable area ($u_+ \in (a, \alpha)$), then $u_- > b$ and, for u_+ close to a, the kinetic relation can be approximated by

$$u_- - b \approx \kappa(u_+ - a), \tag{3.8}$$

where the coefficient κ depends on the parameters of the constitutive model of the transition zone but is independent of u_+ and u_-.

The existence of the corresponding solution of the boundary value problem (3.3) (2.9) for $u_+ \to a$ can be shown by the analysis of the phase plane [11, 13, 14]. Here, in order to check the validity of the approximation (3.8) and, in so doing, arrive at an expression for the coefficient κ, we assume that $u_- = u_-(u_+)$ near $(u_+, u_-) = (a, b)$ and then calculate the derivative du_-/du_+ at $u_+ = a$.

A straightforward calculation provides

$$\begin{aligned}&\frac{d}{du_+} g(u_-(u_+); u_+, u_-(u_+)) = \\ &\frac{u_- - u_+}{2}\left[\frac{du_-}{du_+}(c^2(u_-) - D^2) + c^2(u_+) - D^2\right]\Big|_{u_- = u_-(u_+)},\end{aligned} \tag{3.9}$$

$$\begin{aligned}&\frac{d}{du_+} N(u_+, u_-(u_+)) = \\ &\frac{\eta}{2D(u_- - u_+)}\left[\frac{du_-}{du_+}(c^2(u_-) - D^2) + (D^2 - c^2(u_+))\right]\Big|_{u_- = u_-(u_+)},\end{aligned} \tag{3.10}$$

where D is given by (2.12). Now, by differentiating (3.6) and using (3.9), (3.10) we obtain

$$\begin{aligned}\frac{du_-}{du_+} &= \frac{c^2(u_+) - D^2}{c^2(u_-) - D^2}\left[\frac{D(u_- - u_+)^2 + \eta h(u_+, u_-(u_+))}{D(u_- - u_+)^2 - \eta h(u_+, u_-(u_+))}\right] \\ &+ \left[\frac{\eta(u_- u_+)}{(c^2(u_-) - D^2)(D(u_- - u_+)^2 \eta h(u_+, u_-(u_+)))}\right] D^2(dh/du_+).\end{aligned} \tag{3.11}$$

In the **Appendix** we show that

$$\lim_{\substack{u_+ \to a \\ (D \to 0)}} h(u_+, u_-(u_+)) = \frac{1}{\sqrt{\epsilon}} \int_a^b \sqrt{-g(u; a, b)du}, \tag{3.12}$$

while the limit of $D^2 dh/du_+$ as $u_+ \to a$ and $D \to 0$ is equal to zero. Then, since $\mathbf{W} = 0$ if and only if $\eta = 0$, one obtains from (3.11) that

$$\lim_{\substack{u_+ \to a \\ D \to 0)}} \frac{du_-}{du_+} \equiv \kappa = \begin{cases} c^2(a)/c^2(b), & \text{if } \mathbf{W} \neq 0 \\ -c^2(a)/c^2(b), & \text{if } \mathbf{W} = 0 \end{cases}. \tag{3.13}$$

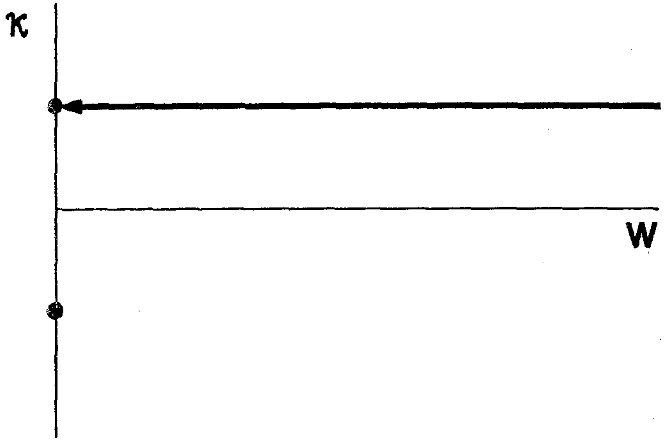

Fig. 3. Singular parametric dependence of the coefficient κ in the "normal growth" law (3.8)

This singular dependence of κ on the parameter $\mathbf{W} = \eta/\sqrt{\epsilon}$ is illustrated in Fig. 3.

We mention that for $\mathbf{W} \neq 0$ the coefficient κ depends only on elastic properties of the equilibrium phases, which explains the universal character of κ. The finite discontinuity in the function $\kappa(\mathbf{W})$ at $\mathbf{W} = 0$ raises a question as to the validity of the "normal growth" approximation for $\mathbf{W}$ close to zero. As we show in [10] for sufficiently small $\mathbf{W}$, the kinetic curve which starts at $u_+ = a$ with the positive slope $\kappa = c^2(a)/c^2(b)$ necessarily terminates at some $u_+ > a$ where it meets another (fast) branch of kinetic relation which does not go through $u_- = b$ at $u_+ = a$ and which has a negative slope du_+/du_-. This provides a nonuniqueness of u_- for the given $u_+ > a$ which we shall illustrate in the next section by two examples.

4 Exact solutions

In order to exhibit closed form solutions to the boundary value problem (2.13) (2.9) we present two specific examples for the constitutive function $\sigma(u)$. The obvious first choice is a /piecewise linear stress strain relation (see Fig. 5), corresponding to the double-well quadratic elastic stored energy. The advantage of this choice is that the equations become linear in both phases and explicit solutions can be matched with the appropriate jump relations. Here we consider the simplest, bilinear material with the discontinuous stress-strain relation; the trilinear material with continuous $\sigma(u)$ was analyzed in [15].

By using the same notations of Maxwell stress (σ_m) and equilibrium strains (a and b) we assume the following expression for the energy f

$$f = \frac{c^2}{2}\left(\left|u - \frac{a+b}{2}\right| - \frac{b-a}{2}\right)^2 + \sigma_\mu, \tag{4.1}$$

where c^2 is a constant speed of elastic waves, which for the sake of simplicity we take to be equal in both phases (see Fig 4).

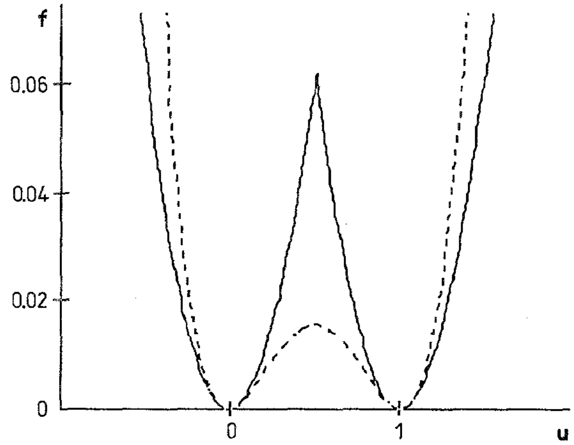

Fig. 4. Sketch of elastic energy $\mathbf{f} = f/(2c^2(b-a)^2)$ vs. $\mathbf{u} = u/(b-a)$ for the two materials considered; solid line - piecewise quadratic energy (4.1), dashed line - quartic polynomial energy (4.12 a). Parameters are taken to be: $a = 0$, $b = 1$, $\sigma_m = 0$, $c^2 = .5$

The related stress strain relation takes the form (see Fig.5)

$$\sigma = c^2\left(\left|u - \frac{a+b}{2}\right| - \frac{b-a}{2}\right)\operatorname{sign}\left(u - \frac{a+b}{2}\right) + \sigma_m. \tag{4.2}$$

With $\sigma(u)$ taken from (4.2), equation (2.10) reduces to

$$(c^2 - D^2)(u - u_+) - D\eta\dot{u} - 2\varepsilon\ddot{u} = 0 \tag{4.3}$$

in the α-phase, where $u < (a+b)/2$ and to

$$(c^2 - D^2)(u - u_-) - D\eta\dot{u} - 2\varepsilon\ddot{u} = 0 \tag{4.4}$$

in the β-phase, where $u > (a+b)/2$.

The solutions of the linear equations (4.3) and (4.4) must be matched at the point $\xi = \xi_*$, where $u = \frac{a+b}{2}$. Because of the translational invariance of the problem, one can put $\xi_* = 0$ without loss of generality. In this case one will have α-phase in $\xi > 0$ and β-phase in $\xi < 0$. At $\xi = 0$, the maximum smoothness one can require is C^1, so that the following jump conditions hold

$$[u] = 0, \ [\dot{u}] = 0, \tag{4.5}$$

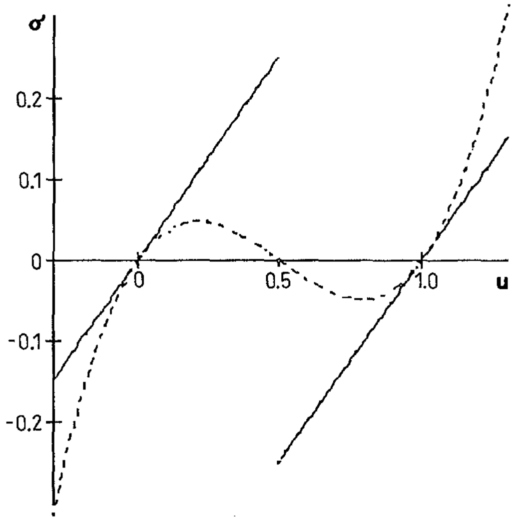

Fig. 5. Sketch of the stress-strain curves $\boldsymbol{\sigma} = \sigma/(2c^2(b-a))$ vs. $\mathbf{u} = u/(b-a)$ for the two materials considered; solid line - piecewise linear material (4.2), dashed line - cubic material (4.12). Parameters are taken to be the same as in Fig. 4

where $[A] = A(\xi \to 0^-) - A(\xi \to 0^+)$ is the discontinuity of the function. The condition of continuity of tractions at $\xi = 0$ reads

$$-2\varepsilon[\ddot{u}] + [\sigma] = 0, \tag{4.6}$$

where, obviously,

$$[\sigma] = c^2(b-a) \tag{4.7}$$

is the discontinuity of the elastic stress while the first term in (4.6) is a contribution due to hyperstress.

Equations (4.3) (4.4) with the boundary conditions (2.8) (2.9) (4.5) (4.6) can be solved explicitly. Introduce $u_\alpha(\xi)$, solution of (4.3) which is defined for $\xi > 0$ only and $u_\beta(\xi)$, solution of (4.4), defined at $\xi < 0$. Then a straightforward calculation provides

$$u_\alpha(\xi) = u_+ + p_1 \frac{u_- - u_+}{p_1 - p_2 e^{p_2 \xi}}, \tag{4.8}$$

$$u\beta(\xi) = u_- + p_2 \frac{u_- - u_+}{p_1 - p_2} e^{p_1 \xi}, \tag{4.9}$$

where

$$p_{1,2} = \frac{D\eta}{4\epsilon}\left[-1 \pm \sqrt{1 + \frac{8}{\mathbf{W}^2}\left(\frac{c^2}{D^2} - 1\right)}\right]. \tag{4.10}$$

Our interest in subsonic phase boundaries requires that $c^2 < D^2$ and therefore $p_1 \geq 0$ while $p_2 \leq 0$, which justifies (4.8) and (4.9). One can see that, in agreement with the general analysis [10], the sufficently slow phase boundaries, represented by (4.8) (4.9) are monotone and the structure gains oscillations only if

$$\frac{D^2}{c^2} > \frac{4\mathbf{W}}{8 - \mathbf{W}^2}.$$

These oscillatory regimes are only available for low viscosity materials with $\mathbf{W}^2 < 8$.

Using (4.8) and (4.9) and the boundary conditions (4.5) (4.6) one obtains a kinetic relation between u_+ and u_- in explicit form

$$\left[1 + \frac{8}{\mathbf{W}^2} \frac{1}{\left(\frac{u_- - u_+}{b-a} - 1\right)}\right] \left[\frac{\frac{u_+ + u_-}{b-a} - \frac{a+b}{b-a}}{\frac{u_- - u_+}{b-a}}\right]^2 = 1. \tag{4.11}$$

As we already mentioned, the parameters ϵ and η enter the kinetic relation (4.11) only through the nondimensional combination $\mathbf{W} = \eta/\sqrt{\epsilon}$. In addition it does not depend on c. Several kinetic curves (for different $\mathbf{W}$), originating from (4.11), are presented at Fig. 6.

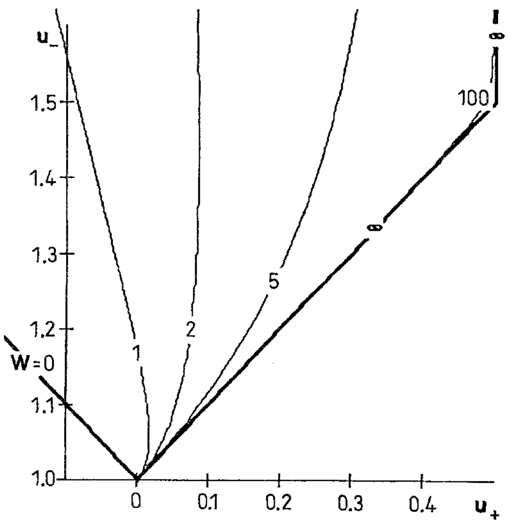

Fig. 6. Kinetic curves $\mathbf{u}_- = u_-/(b-a)$ vs. $\mathbf{u}_+ = u_+/(b-a)$ for the material with piecewise linear stress-strain relation (4.2). Numbers correspond to different $\mathbf{W}$

As we see from Fig. 6, all kinetic curves $u_- = u_-(u_+, \mathbf{W})$ except the one for $\mathbf{W} = 0$, are tangent to the line

$$u_- = u_+ + b - a$$

in accordance with (3.13) and $c(a) = c(b)$. At $\mathbf{W} = 0$, the kinetic curve is tangent to

$$u_- = -u_+ + a + b,$$

which again follows from (3.13). For small positive $\mathbf{W}$, the associated kinetic curve has a vertical tangent turning point at some $\tilde{u}_+ > a$ so that for $0 \leq u_+ < \tilde{u}_+$ two values of u_- correspond to the same value of u_+. This turning point separates the dissipation dominated (slow) branch from the inertia dominated (fast) branch. This is an illustration of the generic behavior of kinetic curves, studied in [10].

The disadvantage of the piecewise linear stress-strain relation, depicted at Fig. 4, is the absence of the spinodal (elliptic) region where $\sigma' < 0$. Therefore it is instructive to consider the next simplest nontrivial example: a function $\sigma(u)$ given by a /cubic polynomial. The two-well elastic stored energy is presented in this case by a quartic polynomial. Using again the same notations as in Section 2, we obtain for $f(u)$

$$f = \frac{k}{4}(u-a)^2(u-b)^2 + \sigma_m u \tag{4.12a}$$

and for $\sigma(u)$

$$\sigma(u) = k(u-a)(u-b)(u - \frac{a+b}{2}) + \sigma_m. \tag{4.12}$$

One can show that the choice $k = 2c^2/(b-a)^2$ matches the elastic properties at the Maxwell stress to those of the piecewise linear material (4.2). For the equation (2.13) with $\sigma(u)$ taken from (4.12) the desired heteroclinic separatrix connecting u_+ and u_- can be presented in a finite form [5]

$$u(\xi) = \frac{u_+ + u_-}{2} - \frac{u_+ - u_-}{2} \tanh\left[\sqrt{\frac{k}{\epsilon}}\frac{u_+ - u_-}{4}(\xi - \xi_*)\right], \tag{4.13}$$

where the reference point ξ_* can again be chosen arbitrarily. Substitution of (4.13) into (2.13) gives an explicit expression for phase boundary velocity D

$$\frac{D}{c} = \frac{3\sqrt{2}}{\mathbf{W}}\left(\frac{u_+ + u_-}{b-a} - \frac{a+b}{b-a}\right). \tag{4.14}$$

Together with the Rankine-Hugoniot condition (2.12), this provides a kinetic relation

$$3(1 - \frac{12}{\mathbf{W}^2})(\frac{u_+ + u_-}{b-a} - \frac{a+b}{b-a})^2 + (\frac{u_- - u_+}{b-a})^2 = 1 \tag{4.15}$$

to be compared with (4.11). It again depends on ϵ and η through $\mathbf{W}$ only and it does not depend on c. Several kinetic curves for different $\mathbf{W}$ are shown in Fig. 7. They terminate at the straight line which describes marginal "sonic" regimes

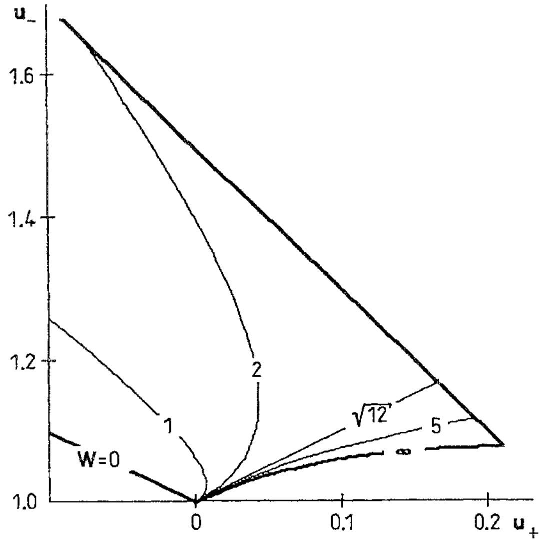

Fig. 7. Kinetic curves $\mathbf{u}_- = u_-/(b-a)$ vs. $\mathbf{u}_+ = u_+/(b-a)$ for the material with cubic stress-strain relation (4.12). Numbers correspond to different **W**.

of phase boundary propagation (Chapman - Jouget regimes), given by

$$u_- + 2u_+ = 1.5(a+b). \tag{4.16}$$

One can see once again that if $\mathbf{W} \neq 0$, the kinetic curves can be approximated by

$$u_- = u_+ + b - a$$

("normal growth" approximation). For small enough u_+ we have two values of u_-, representing slow (dissipation dominated) and fast (inertia dominated) regimes. For small positive **W** no steady phase boundaries are available if the metastability of the state in front, measured by $u_+ - a$, is sufficently large (beyond the turning point associated with the specific **W** under consideration). This puts a limit on the range of application of the "normal growth" hypothesis. As **W** tends to zero, the domain of validity for the approximation (4.16) shrinks to a point.

5 Mobility of phase boundaries

The "normal growth" hypothesis is often formulated in terms of dependence of the phase boundary velocity on the degree of metastability of the state ahead of the moving phase oundary. If the degree of metastability is again measured by $u_+ - a$, the "normal growth" approximation states that D is a linear function of

$u_+ - a$ for $u_+ - a$ sufficently small. In nondimensional form it reads

$$\frac{D}{c(a)} = \mu \frac{u_+ - a}{b - a}. \tag{5.1}$$

The coefficient μ is a measure of "mobility" of the phase boundary. Of cause the global features of the curve $D(u_+)$ can be obtained directly from (2.12). The mobility μ is the normalized slope of this curve as $u_+ - > a$.

The viscosity-capillarity theory developed in Section 2 enables us to calculate the coefficient μ as a function of the nondimensional parameter **W**. Thus from the Rankine-Hugoniot condition (2.12) we get

$$\frac{dD}{du_+} = \frac{c^2(u_-) - D^2}{2D(u_- - u_+)} \left[\frac{du_-}{du_+} - \frac{c^2(u_+) - D^2}{c^2(u_-) - D^2} \right]. \tag{5.2}$$

If we substitute the limiting value for du_-/du_+ as $u_+ - > a$ from (3.13) into (5.2), we obtain the desired expression for μ

$$\mu = \frac{c(a)(b-a)^2}{\mathbf{W} \left[\int_a^b \sqrt{-g(u; a, b)} du \right]^{-1}}. \tag{5.3}$$

As we see from (5.3), contrary to the phenomenological coefficient κ from (3.8), μ is inversely proportional to **W**. The integral in the denominator of (5.3) is readily calculated for the two examples considered in Section 4. Thus for the piecewise linear constitutive law (4.2) one obtains

$$\int_a^b \sqrt{-g(u; a, b)} du = \frac{c}{4\sqrt{2}} (b-a)^2, \tag{5.4}$$

which gives for the mobility coefficient

$$\mu = \frac{4\sqrt{2}}{\mathbf{W}} \approx \frac{5.657}{\mathbf{W}}. \tag{5.5}$$

On the other hand the cubic stress strain relation (4.12) gives

$$\int_a^b \sqrt{-g(u; a, b)} du = \frac{c}{b\sqrt{2}} (b-a)^2, \tag{5.6}$$

corresponding to mobility coefficient

$$\mu = \frac{6\sqrt{2}}{\mathbf{W}} \approx \frac{8.485}{\mathbf{W}}. \tag{5.7}$$

Several "mobility" curves D vs. u_+ for these materials, illustrating the asymptotics (5.5) are shown in Fig. 8. Similar curves for the material with cubic stress - strain relation, illustrating (5.7) are shown in Fig. 9.

It follows from these pictures that for the given state ahead of the phase boundary, one can have two different values of D. However, the two regimes

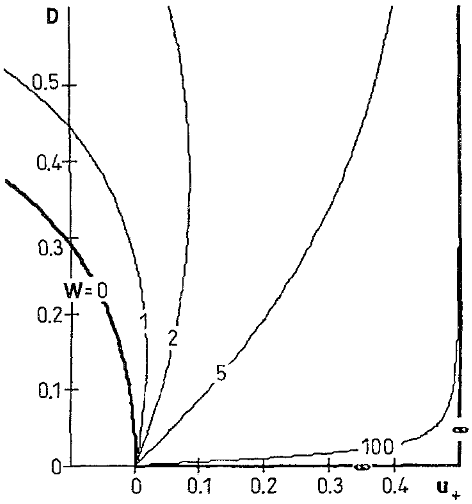

Fig. 8. Kinetic curves $\mathbf{D} = D/c$ vs. $u_+/(b-a)$ for different values of $\mathbf{W}$ and piecewise linear $\sigma(u)$

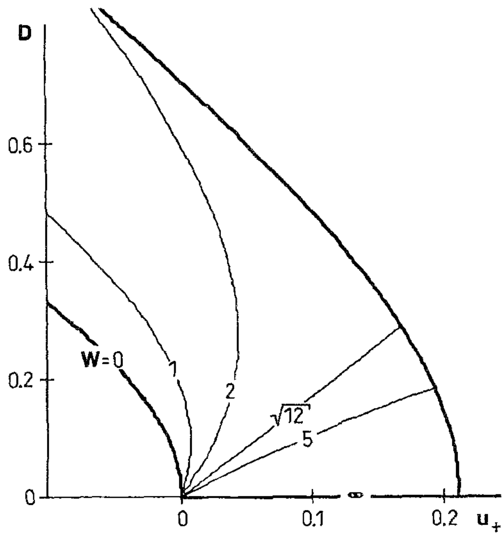

Fig. 9. Kinetic curves $\mathbf{D} = D/c$ vs. $u_+/(b-a)$ for different values of $\mathbf{W}$ and cubic $\sigma(u)$

require different boundary conditions (different "piston") to support the steady state propagation of the phase boundary. That is why this nonuniqueness does not necessarily mean instability of one of the regimes. This is most clearly seen if we choose a different measure of metastability. To justify our choice we will need to adopt more a general point of view [16, 4, 5, 6].

Consider the full system of Rankine-Hugoniot jump conditions on a moving surface of discontinuity in a heat conducting thermoelastic body. Let n be the reference normal to the surface and D its material velocity. Then the balances of momentum and energy on the jump take the form.

$$D[\mathbf{v}] - [\mathbf{Pn} = 0,$$

$$D[e + \frac{\mathbf{v}^2}{2}] - [\mathbf{Pn} \cdot \mathbf{v} - \mathbf{q} \cdot \mathbf{n}] = 0, \tag{5.8}$$

Here $e(F, s)$ is the specific energy which depends on deformation gradient $\mathbf{F}$ and specific entropy s;$\mathbf{v}$ is the velocity, $\mathbf{P} = \rho(\frac{\partial e}{\partial \mathbf{F}})\mathbf{F}^T$ - the stress tensor and $\mathbf{q}$ is a heat flux. The entropy balance takes the form

$$D[s] + \left[\frac{\mathbf{q} \cdot \mathbf{n}}{T}\right] = R \geq= 0, \tag{5.9}$$

where $T = \frac{\partial e}{\partial s}$ is the absolute temperature, while R is the surface entropy production, which is assumed to be nonnegative. If, as in our case, both temperature and displacements are continuous on the jump, (5.8) (5.9) yields

$$RT = GD, \tag{5.10}$$

where [5, 6]

$$G = [f] - \left\{\frac{\partial f}{\partial \mathbf{F}}\right\}[\mathbf{F}]. \tag{5.11}$$

Here we recall that $[A] = A_+ - A_-$ denotes the value of the discontinuity, while $\{A\} = \frac{1}{2}(A_+ + A_-)$ denotes the average of the limiting values on both sides of the discontinuity.

From the expression (5.10) of the surface dissipation, we conclude that G, which is sometimes called the driving traction, is conjugate to D. Then the kinetic model can be formulated as a relation between the "flux" D and the "force" G, using the language of the linear thermodynamics of nonequilibrium processes [5]. Assuming R to be quadratic in D, some theories of "normal growth" provide a linear relation between G and D which reduces to (5.1) as G tends to zero.

Let us use our exact solutions to calculate D vs. G dependence in a nonlinear case. In the isothermal setting the rate of entropy production R is equivalent to the energy release rate, which in our case reads

$$RT = \left[f(u_+) - f(u_-) - \frac{\sigma(u_+) + \sigma(u_-)}{2}(u_+ - u_-)\right] D = \eta D^2 \int_{-\infty}^{\infty} \dot{u}^2 d\xi. \tag{5.12}$$

Now, it is easy to see that

$$G = g(u_-; u_+, u_-), \tag{5.13}$$

and G can be considered as an alternative measure of metastability (replacing $u_+ - a$). For the material with a piecewise linear stress-strain relation, a straightforward calculation gives

$$G = \frac{c^2}{2}(u_+ + u_- - a - b)(b - a), \tag{5.14}$$

which after the substitution of u_+ and u_- from (2.12) and (4.11) yields

$$\frac{G}{c^2(b-a)^2} = \frac{\mathbf{W}}{4\sqrt{2}}\left(\frac{D}{c}\right)\left[\left(1 - \frac{D^2}{c^2}\right)^{-1}\left(1 + \frac{\mathbf{W}^2 - 8}{8}\frac{D^2}{c^2}\right)^{-1/2}\right]. \tag{5.15}$$

This is a desired kinetic relation between G and D illustrated in Fig. 10.

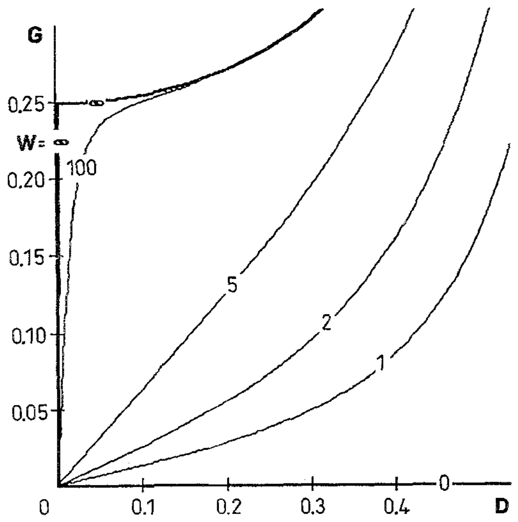

Fig. 10. Kinetic curves $\mathbf{G} = G/(c^2(b-a)^2)$ vs. $\mathbf{D} = D/c$ for different values of $\mathbf{W}$ and $\sigma(u)$ piecewise linear

For the material with a cubic stress strain relation, a similar calculation provides

$$G = \frac{c^2}{2(b-a)^2}(u_- - u_+)^3(u_+ + u_- - a - b). \tag{5.16}$$

Now, we substitute u_+ and u_- from (4.14) (4.15) to get

$$\frac{G}{c^2(b-a)^2} = \frac{\mathbf{W}}{6\sqrt{2}}\left(\frac{D}{c}\right)\left[1 + \frac{12 - \mathbf{W}^2}{6}\frac{D^2}{c^2}\right]^{3/2}. \tag{5.17}$$

The kinetic curves on the G-D plane, originating from (5.15) and (5.17) are shown at Fig. 11.

One can see from Fig. 10, 11 that if we introduce a "natural" measure of metastability G, the nonuniqueness in the kinetic model disappears.

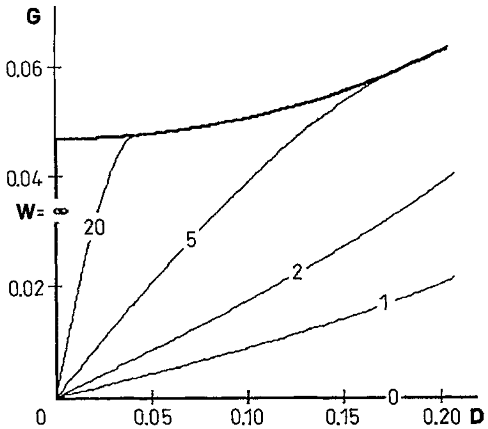

Fig. 11. Kinetic curves $\mathbf{G} = G/(c^2(b-a)^2)$ vs. $\mathbf{D} = D/c$ for different values of $\mathbf{W}$ and $\sigma(u)$ piecewise linear (a) and cubic (b)

6 Discussion

The kinetic relation balances the energy release due to the growth of one phase in expense of the other and the dissipation due to the nonequilibrium nature of the transformation. In a quasistatic approximation it is natural to assume that the surface dissipation is quadratic in phase boundary velocity. The fact that the energy release rate is a product of a "driving force" and the velocity provides a basis for the "normal growth" hypothesis. This reasoning however completely neglects /inertial effects, moreover when the dissipation is weak it is feasible to have purely inertial regimes of phase transformation, when the free energy loss is compensated by the gain in kinetic energy. As we show, these effects are responsible for the formation of the fast branch of the kinetic relation in addition to the slow, dissipation-dominated (normal growth) branch.

Based on the analysis of the kinetic relations, originating from the viscosity capillarity model, we conclude that the limitations of the "normal growth" are threefold. First, even for slow enough phase boundaries, the relation between the phase boundary velocity and the "driving force" may become nonlinear. We mention that assuming the linear dissipative mechanism in the transition region (the Newtonian viscosity) does not guarantee the linearity of the overall kinetic relation. The second limitation stems from the fact that the steady regime of phase boundary migration may not exist when the driving force is high enough. As we show for the low viscosity materials, this critical /metastability limit may be quite low. The last problem with the "normal growth" theories in their classical formulation, arises from their inability to describe fast, inertia dominated branch of kinetic curve. We show, however, that if the "natural" work conjugate variable describing the driving force is chosen, then the kinetic relation becomes single-valued in the whole range of parameters. Contrary to the usual quasistatic "free-energy release" which is a popular choice of a driving force in the physical literature, the "natural" driving force includes the important kinetic energy contribution.

The present model has an obvious shortcoming related to the limitations of the macroscopic approach of continuum mechanics. The real process is taking place in a discrete system of atoms and lattice effects may become important. For example, propagation of the front causes excitation of short waves not described by the continuum model and this radiation, which appears in a form of the dissipation at the macrolevel, can not be adequately described by the isothermal model. On the other hand, the lattice trapping can change the picture for sufficiently slow motions causing the hysteretic phase transformation.

7 Appendix

Since the dependence of the function $h(u_+, u_-)$ on its arguments is implicit, one cannot calculate the limiting value for h and dh/du_+ as $u_+ -> a$ directly, without reference to the equation (3.3). This equation, however, is amenable to qualitative analysis on the phase plane $(u, \dot{u})$.

Consider the case $u_+ = a$. Then (3.3) has a solution with $u_- = b$ and $D = 0$ which represents stationary equilibrium phase boundary. In this case (3.3) integrates to give

$$-\int_{u_-}^{u} \frac{\sqrt{\epsilon}d\mu}{\sqrt{-g(\mu, a, b)}} = \xi - \xi_0$$

and from (3.7), we obtain

$$h(a, b) = \frac{1}{\sqrt{\epsilon}} \int_a^b \sqrt{-g(u, a, b)}du$$

which gives (3.12).

Now consider the branch of kinetic relation starting at the point $(u_+, u_-) = (a, b)$ on the $u_+ - u_-$ plane, which up to the second order terms (in $u_+ - a$) can be approximated near the point (a, b) by

$$u_+ = a + (u_+ - a)$$

$$u_- = b + \left.\frac{du_-}{du_+}\right|_{u=a} (u_+ - a)$$

To calculate the derivative of

$$h(u_+, u_-) = \int_{-\infty}^{\infty} \dot{u}^2 d\xi = -\int_{u_+}^{u-} \dot{u}du$$

along this branch, observe that this function provides the area on the phase plane $(u, \dot{u})$ between the separatrix connecting points u_+ and u_- and the u-axis (see Fig. 2). Suppose for the moment that $\eta = 0$ and introduce two functions $u_1(\xi)$ and $u_2(\xi)$, representing the disconnected separatrixes of the dissipation free analog of (3.3) (see Fig. 2). For the separatrix $u_1(\xi)$ which originates at $u = u_-(\xi = -\infty)$, we can write

$$\dot{u}_1 = \frac{1}{\sqrt{\epsilon}}\sqrt{-g(u_1(\xi); u_+, u_-) + g(u_-; u_+, u_-)}$$

while the separatrix $u_2(\xi)$ which terminates at $u = u_+(\xi = +\infty)$ yields

$$\dot{u}_2 = -\frac{1}{\sqrt{\epsilon}}\sqrt{-g(u_2(\xi); u_+, u_-)}.$$

Since the energy

$$\epsilon\dot{u}^2 + g(u; u_+, u_-),$$

serves as a Lyapunov function for our dynamical system (2.13), it followes that $u(\xi) \in [u_+, u_-]$ gives

$$\dot{u}_1(\xi) \leq \dot{u}(\xi) \leq \dot{u}_2(\xi).$$

Hence

$$h_2(u_+, u_-) \leq h(u_+, u_-) \leq h_1(u_+, u_-) \tag{A.1}$$

where

$$h1(u_+, u_-) = \frac{1}{\sqrt{\epsilon}}\int_{u_+}^{u_-} \sqrt{g(u_-; u_+, u_-) - g(u; u_+, u_-)}du$$

$$h_2(u_+, u_-) = \frac{1}{\sqrt{\epsilon}}\int_{u_+}^{u_*} \sqrt{-g(u; u_+, u_-)}du$$

and $u_*(u_+, u_-)$ denotes a root of the equation

$$g(u; u_+, u_-) = 0$$

located between u_+ and u_- (see Fig. 2). Calculation of the derivatives of $h_1(u_+, u_-(u_+))$ and $h_2(u_+, u_-(u_+))$ yields

$$\frac{dh_1}{du_+} = -\frac{1}{\sqrt{\epsilon}}\sqrt{g(u_-; u_+, u_-)}$$

$$+\frac{D^2 - c^2(u_+)}{4\sqrt{\epsilon}(u_+ - u_-)}\int_{u_+}^{u_-} \frac{(u - u_-)^2}{\sqrt{g(u_-; u_+, u_-) - g(u; u_+, u_-)}}du \tag{A.2}$$

$$+\frac{D^2 - c^2(u_-)}{4\sqrt{\epsilon}(u_+ - u_-)}\left(\frac{du_-}{du_+}\right)\int_{u_+}^{u_-} \frac{(2u_+ - u_- - u)(u - u_-)}{\sqrt{g(u_-; u_+, u_-) - g(u; u_+, u_-)}}du$$

and

$$\frac{dh_2}{du_+} = \frac{1}{\sqrt{\epsilon}}\left(\frac{du_*}{du_+}\right)\sqrt{-g(u_*;u_+,u_-)}$$

$$+\frac{c^2(u_-)-D^2}{4\sqrt{\epsilon}(u_+-u_-)}\left(\frac{du_-}{du_+}\right)\int_{u_+}^{u_*}\frac{(u-u_+)^2}{\sqrt{-g(u;u_+,u_-)}}du \tag{A.3}$$

$$+\frac{c^2(u_+)-D^2}{4\sqrt{\epsilon}(u_+-u_-)}\int_{u_+}^{u_*}\frac{(2u_- - u_+ - u)(u-u_+)}{\sqrt{-g(u;u_+,u_-)}}du.$$

In these formulas, the derivative du_-/du_+ is the same as in (3.11) (along kinetic curve branch $u_-(u_+)$ initially at $(u_+, u_-) = (a, b)$), while du_*/du_- is readily calculated to be

$$\frac{du_*}{du_+} = \frac{(u_*-u_+)}{2(u_+-u_-)}\left\{\frac{(c^2(u_+)-D^2)(u_*+u_+-2u_-)+(D^2-c^2(u_-))(u_*-u_+)\left(\frac{du_-}{du_+}\right)}{\sigma(u_*)-\sigma(u_+)-D^2(u_*-u_+)}\right\}.$$

It is easy to check that all integrals in (A.2) and (A.3) converge and the only singular term in a limit $u_+ \to a$ and $D \to 0$ is the one with du_*/du_- . One can see however, that

$$\lim_{\substack{u_+\to a\\ D\to 0}} D^2\left(\frac{du_*}{du_+}\right) = 0.$$

Therefore

$$\lim_{\substack{u_+\to a\\ D\to 0}} D^2\frac{dh_1}{du_+} = \lim_{\substack{u_+\to a\\ D\to 0}} D^2\frac{dh_2}{du_+} = 0$$

which, together with the inequality (A.1), provides

$$\lim_{\substack{u_+\to 0\\ D\to 0}} D^2\frac{dh}{du_+} = 0.$$

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