KINKS VERSUS SHOCKS

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Abstract. Localized phase transitions as well as shock waves can often be modeled by material discontinuities satisfying Rankine-Hugoniot (RH) jump conditions. The use of Maxwell, Gibbs-Thompson, Hertz-Knudsen, and similar (supplementary to RH) relations in the theory of dynamic phase changes suggest that the classical system of jump conditions is at least incomplete in the case of phase transitions. While the propagation of a shock wave is completely determined by the conservations laws, the boundary conditions of the problem and the condition that the entropy increases in the process, the same is not true for the propagation of phase boundaries. Additional condition must be added to the RH conditions in order to provide sufficient data for the unique determination of the transformation process. The necessity was tacitly assumed by those who attacked the calculation of the phase boundary velocity without even trying to determine this parameter from the conservation laws and boundary conditions alone.

In order to be able to point out the contrast between shock waves and phase boundaries we treat both of them on the basis of the same assumption that the process takes place over a zone of finite width and consider a rather general model of the internal structure of the interface with special emphasis on the interplay between dispersion and dissipation effects. Our extended model of the continuum, capable of describing a "thick" interface, incorporates a weak form of nonlocality together with a number of dissipative mechanisms. Analysis of a model-type solution of the structure problem clarifies the distinction between supersonic (*shock*) and subsonic (*kink*) discontinuities and provides explicit examples of additional jump relations in the case of kinks (which simulate subsonic phase boundaries).

It is emphasized, that an extended system of jump relations for kinks may depend on the ratios of internal scales of length introduced by a more detailed description. An original theory, which provides discontinuous solutions, must therefore be complemented by these nondimensional parameters, even though internal scales by themselves are considered to be zero in this theory.

1. Introduction. There is a long history of studies of highly localized "switching" waves in continuum mechanics; shock waves and combustion waves are among the most well known. Dynamic phase changes (condensation and liquefaction shocks, crystallization fronts, moving domain, martensitic, antiphase and twin boundaries, etc.) are similar to both shocks and flames; in all these cases one homogeneous state gains at the expense of the other through the spatial advance of a transitional region. At a scale which is much larger than the width of the transition zone, these processes can be described by the motion of the surface of discontinuity. On this surface material parameters experience abrupt changes, so that modeling is possible in terms of corresponding jump conditions. In spite of the mentioned similarity, the problem of jump relations is not trivial, since even the number of conditions is different for shock waves and flames. Furthermore, phase boundaries can be essentially different from the waves known in both classical gas dynamics and combustion theory.

Localized phase transitions considered as material discontinuities must satisfy Rankine-Hugoniot (RH) jump conditions. Wide use of (supplementary to RH) phase equilibrium or kinetic relations in the physical theory of phase changes suggest that the classical system of jump conditions being satisfactory for shocks is

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at least incomplete in the case of phase transitions [24,41]. It is also known that an application of hyperbolic theory to mixed type systems typical for the materials undergoing phase changes (materials with nonmonotonic stress strain law), causes difficulties with uniqueness of weak solutions that are not resolved by the *RH* conditions and the entropy inequality [2,19,49,65,66,74,79]. To select physically appropriate solutions, a number of additional admissibility conditions have been proposed on phenomenological grounds (normal growth, maximum entropy rate, etc. [3,19,48,58,86]). An alternative approach to admissibility, which we follow in this paper, is based on the availability of a fine structure solution for the discontinuity [4,11,27,75,78,79,83].

According to this criterion the jump is admissible if it "admits structure" [20,32,33]. Usually the original equations do not contain parameters with the scale of length, so the interfaces have no *internal structure*. One has to go beyond the limits of "ideal" theory to obtain a continuous description of the "thick" transition layers. There seem to be two known ways for the system to cope with the (nonlinearity driven) profile steepening–by dispersion and dissipation. Such a regularization can often be accomplished by the introduction of nonlocal and memory effects. Usually that means a singular perturbation of an original system by terms with higher derivatives, which results in a formation of internal boundary layers simulating the discontinuity structure. The goal can sometimes be achieved by incorporating a longer spatial or temporal memory e.g., by introducing internal variables.

The broader theory, used for a detailed description of the processes inside the interface, brings with it a few material constants which characterize dispersive and dissipative properties of the medium and which may be normalized as characteristic lengths. If these lengths have different orders of magnitude, the structure will break into a sequence of embedded boundary layers with the layer thicknesses scaled by the corresponding parameters. In the classical limit, all these length scales are equal to zero but not necessarily their ratios. The limiting values of these ratios may or may not influence jump conditions. If they do, one faces a multiplicity of weak solutions of the original equations and uniqueness can be achieved by specifying appropriate nondimensional criteria. It is in this way that an incomplete (asymptotic) theory can inherit information from the more sophisticated one.

To see how the number of jump conditions can be different for different types of discontinuous solutions, consider an example of a structure problem when higher derivatives are used in an extended theory as singular perturbations. The external solution neglects the front structure and leads to an ideal theory where the front is considered to be a discontinuity surface. In an inner problem which is essentially one-dimensional, substitution of a self-similar (traveling) extended coordinate leads to the boundary-value problem for a system of ordinary differential equations with boundary conditions at infinity. The desired solution is described by a heteroclinic orbit connecting two singular (equilibrium) points. Since these points specify steady solutions of an ideal system, the limiting values of parameters at infinity meet *RH* jump conditions. Now if the sum of dimensions of the stable and unstable manifolds containing the heteroclinic trajectory exceeds the dimension of the ODE's phase

space, the connection is structurally stable (e.g. saddle-to-node orbit in the 2-D case) that gives a family of solutions for the boundary value problem and provides no new jump conditions. If, however, such a connection is not generic (e.g. saddle-to-saddle orbit in the 2-D case), an additional (equality-type) restriction on the limiting values of parameters of the external problem is obtained.

Since the internal problem is overdetermined, the jump velocity must be found as the eigenvalue from the condition of existence of the traveling wave solution. As we saw, the spectrum of the nonlinear internal boundary value problem may contain both *continuous* and *discrete* parts. While points of the continuous spectrum are distinguished by inequalities, those of the discrete spectrum provide new jump relations, supplementary to the *RH* conditions. These additional constraints may depend on the nondimensional coefficients of the ODE's so that the parameters of an extended theory can penetrate an ideal model.

The difference between the two aforementioned types of discontinuous solutions (pertaining to continuous and discrete spectrum) which occur naturally in nonstrictly hyperbolic and mixed type systems of quasilinear PDE's has been long recognized (evolutionary and nonevolutionary discontinuities [53], similarity solutions of first and second-order [8], compressive and undercompressive shocks [77], strong and weak (eigenvalue) detonation waves [31,68], etc.). In plasma physics [90], the theory of necking in polymers [47], multicomponent filtration theory [10], and the theory of ferroelectric transmission lines [55] interesting examples of both types of solutions are found.

In the present survey paper, by considering a rather general continuum mechanical framework for the regularization of the discontinuous solutions originating from the mechanics of nonlinear materials exhibiting phase changes, we contribute to the understanding that shock waves and supersonic phase boundaries belong to one category of jumps, while subsonic phase boundaries naturally fit the other. We revisit the problem of the internal structure of the interface for both shock waves waves and phase boundaries. In terms of the structure analysis, the first kind of discontinuity is associated with a *continuous* spectrum of the corresponding boundary value problem, while a discontinuity of the second kind relate to points of a *discrete* spectrum. This, in turn, provides inequalities in the first case and equalities in the second case as admissibility conditions indicative of higher order discontinuity structure. In the absence of established terminology we refer to the first group of waves as *shocks*, and to the second, as *kinks*. Kinks are known in modern nonlinear physics as localized traveling waves (domain walls) in multistable continuous systems, which switch from *metastable* to *stable* states [14]. Additional jump conditions in the case of kinks can also be regarded as constitutive relations for the discontinuity surface [42,83]. The fact that subsonic kinks can adjust their velocity based on "information" from the state ahead, creates a basis for such a "constitutive behavior".

In Section 2 we introduce *RH* jump conditions, review the phenomenological approach to the modelling of localized phase transitions and demonstrate, within the context of an elementary example, the nonevolutionarity of subsonic phase

boundaries (and the necessity of the imposition of an additional jump condition). The nonlocal gradient-type constitutive model for material inside the transition layer is introduced in Section 3. By coupling *mechanical* and *kinetic* problems, our extended model generalizes the approaches originated by Ginzburg-Landau [13,16,46,67,71,87,89] and van der Waals-Korteweg [17,29,73,75,79,83]. We then set up the differential equations governing the transition across the interface and investigate under which circumstances these equations possess solutions satisfying the boundary conditions imposed on the ends of the transition zone. The differential equations in the interior of the transition zone express the same conservation laws as *RH* conditions, but take into account dissipation and nonlocality.

In Section 4 we analyze the structure of both shock waves and phase boundaries in a compressible fluid with Ginsburg-Landau type relaxation. We show that nonlocality brings oscillations to the structure of shocks in relaxing media and provides additional smoothing of the internal discontinuities. For slow enough phase boundaries, when the mechanical problem can be uncoupled, we obtain a modification of a "phase field" model which provides particular examples of additional jump relations of the "normal growth" type.

In Section 5 we give a detailed consideration of shocks and kinks in a van der Waals type nonlocal viscous fluid (viscosity-capillarity model). This model is rich enough to describe simultaneously classical shock waves, both supersonic (strong) and subsonic (weak) phase boundaries, and the "flame-like" travelling waves (connecting unstable states inside the *elliptic/spinodal* region with the thermodynamically stable states) as different points of the eigenvalue spectrum of the nonlinear boundary value problem. We demonstrate an unusual general property of the solutions of the truly dynamical problem when two kinks – slow and fast – exist for the given state in front of the discontinuity. An important prediction of this model is that the speed of the kink can be negligible until a *critical level of metastability* is achieved. For slow kinks we again obtain the normal growth condition which signify that an adequate model of slow kinetics is provided by an augmentation involving excess viscosity. However, if the effective viscosity is low (reaction rate is high), the normal growth hypothesis is no longer correct.

Two Appendixes contain supplementary material. In the first we discuss alternative dissipation mechanisms inside the interface, including the generalization of the *Cahn-Hilliard model*, while in the second we briefly indicate an interesting similarity between kinks and *crack tips*.

This paper is based in part on our previous publications [83-87, 71-72]. For more information on the subject we refer to the expository papers [5,8,20,28,31,33,34,41,51, 56,59] and the literature cited therein.

2. Jump conditions. The distinction between *shocks* and *kinks* can be demonstrated without any reference to structure. Consider the classical *RH* jump conditions on a moving surface of discontinuity in a heat-conducting thermoelastic body. Assume that eulerian cartesian coordinates are used and the moving interface is characterized by its normal vector $\mathbf{n}$ and its normal velocity D. Introduce: e-specific internal energy, ρ-density, $\mathbf{v}$-velocity vector, $\mathbf{P}$-Cauchy stress tensor and

q-heat flux vector. The balances of mass, momentum and energy on the jump take the form

$$
\begin{aligned}
&[\rho(D-\mathbf{v}\cdot\mathbf{n})] = 0\\
&[\rho(D-\mathbf{v}\cdot\mathbf{n})\mathbf{v}+\mathbf{P}\mathbf{n}] = 0\\
&\left[\rho(D-\mathbf{v}\cdot\mathbf{n})\left(e+\frac{\mathbf{v}^2}{2}\right)+\mathbf{P}\mathbf{n}\cdot\mathbf{v}-\mathbf{q}\cdot\mathbf{n}\right] = 0
\end{aligned}
\tag{2.1}
$$

where the square brackets denote a jump: $[\,] := (\,)_+ - (\,)_-$ and $\mathbf{n}$ faces the side $+$.

Zeroes on the right hand sides of (2.1) indicate that we omit surface supplies of mass, momentum and energy; in particular, we ignore surface tension. These effects are irrelevant to the subject of this paper (see [42]).

We may not, however, ordinarily ignore the surface entropy production $\Re$

$$
\Re = [\rho s(\mathbf{v}\cdot\mathbf{n}-D)] + \left[\frac{\mathbf{q}\cdot\mathbf{n}}{T}\right], \tag{2.2}
$$

where s and T are specific entropy and absolute temperature. According to the second law of thermodynamics,

$$
\Re \geq 0. \tag{2.3}
$$

One can find in the literature different opinions about a constitutive status of $\Re$. Thus, a specialist in shock waves would say that $\Re$ in (2.2) is defined by the right hand side and (2.3) yields an inequality-type restriction on the possible jumps [53,56]. However this does not always uniquely specify a solution [19,49]. Therefore, experts in phase transitions would rather take the view that a fundamental constitutive relation is assumed for the surface entropy production $\Re$, and that (2.3), being a form of Clausius-Duhem inequality, provides restrictions on the constitutive structure [2,3,41,42].

These restrictions may take the form of a functional relation between the surface quantities [83]. For example, a "natural" assumption that the surface entropy production depends on the material velocity of the discontinuity (mass flux through the unit cross section)

$$
m = \rho(\mathbf{v}\cdot\mathbf{n}-D) \tag{2.4}
$$

gives

$$
\Re = \hat{\Re}(m); \tag{2.5}
$$

a quadratic function seems to be a reasonable choice for slow enough motions ($m \to 0$). Relation (2.5) combined with (2.2) then offers an additional jump condition, which does not follow from (2.1) (kinetic relation [3,42,86]).

One can show that (2.5) generalizes the classical Maxwell-Gibbs condition of phase equilibrium, which says

$$
\Re = 0. \tag{2.6}
$$

To present it in more familiar terms, let us specify the model by taking a hyperelastic body with the energy $e = e(\mathbf{F}, s)$, where $\mathbf{F}$ is a deformation gradient. Then $T = \partial e/\partial s$, $\mathbf{P} = \rho(\partial e/\partial \mathbf{F})\mathbf{F}^T$. If both temperature and displacements are continuous on the jump, (2.2), combined with (2.1), can be rewritten as

$$-\Re T = m\left([f] - \left\{\frac{\partial f}{\partial \mathbf{F}}\right\} \cdot [\mathbf{F}]\right) \tag{2.7}$$

Here, $f = e - Ts$ is a specific free energy and $\{\ \} := \frac{1}{2}((\ )_+ + (\ )_-)$. A relation equivalent to (2.7) was first derived for quasistatic processes in [52] and in its full dynamic form appeared in [83], where it was interpreted as the dynamic generalization of Gibbs' phase equilibrium condition. It was independently suggested in [3] and [86] in the form (2.7), with velocities excluded (see [42] for an account of surface effects).

Assuming $\Re$ to be quadratic in m, theories of "normal growth" provide a linear relation between "thermodynamic force" (sometimes called "*driving traction*" or "*energy release rate*")

$$G = [f] - \left\{\frac{\partial f}{\partial \mathbf{F}}\right\} \cdot [\mathbf{F}] \tag{2.8}$$

and the "flux" m. For a nondissipative process ($\Re = 0$), one obtains the dynamic generalization of the Maxwell ("equal area") condition

$$G = 0,$$

which for stationary fluids further reduces to the classical Gibbs' equality of chemical potentials

$$\left[f + \rho\frac{\partial f}{\partial \rho}\right] = 0$$

and for stationary coherent boundaries in solids satisfying

$$[\mathbf{P}\mathbf{n}] = 0$$
$$[\mathbf{F}] = \mathbf{l} \otimes \mathbf{n}$$

may be transformed into the form [1,26,69]

$$[f] - \frac{\partial f}{\partial \mathbf{F}} \cdot [\mathbf{F}] = 0.$$

Substitution of (2.7) into (2.2) gives in the general case

$$m(T[s] + G) = [\mathbf{q} \cdot \mathbf{n}] \tag{2.9}$$

which is a classical Stefan condition (known in the theory of crystallization) extended to a nonequilibrium ($G \neq 0$) case [3,86].

The resolution of an apparent contradiction between the theory of shocks which operates with the entropy inequality (2.3), and the theory of dynamic phase transitions which specifies $\Re$ and uses equality (2.5), lies in an observation that "classical" shocks are supersonic with respect to a state ahead, while "classical" phase boundaries are subsonic. We shall illustrate this with a simple example. Consider an isothermal one dimensional flow (in the form of a plane wave) of a compressible fluid with the zero body forces. The governing equations are

$$\begin{aligned} \dot{\rho} + \rho v_x &= 0 \\ \rho \dot{v} + p_x &= 0 \end{aligned} \tag{2.10}$$

where $p(\rho) = \rho^2(\partial f/\partial \rho)$ is the fluid pressure, and the sub-index denotes a partial derivative with respect to the corresponding variable. The superposed dot denotes the usual Lagrangian derivative along a particle path:

$$\dot{(\ )} = (\ )_t + v(\ )_x.$$

The *RH* conditions (2.1) take the form

$$\begin{aligned} [\rho(v - D)] &= 0 \\ [\rho(v - D)^2 + p] &= 0. \end{aligned} \tag{2.11}$$

A typical subcritical isotherm $p = p(V, T = \text{const})$, where $V = 1/\rho$, which allows for phase transformations is sketched in Figure 1(a)[1].

Two types of jumps are identified readily on Figure 1:

$\mathbf{A} \to \mathbf{B}$ (*shocks*), which satisfy the Lax (entropy) condition [56]:

$$\rho_B^2 c_B^2 \leq m^2 = -[p]/[1/\rho] \leq \rho_A^2 c_A^2$$

$\mathbf{A} \to \mathbf{B}'$ (*kinks*), for which

$$\begin{aligned} m^2 &< \rho_A^2 c_A^2 \\ m^2 &< \rho_{B'}^2 c_{B'}^2 \end{aligned}$$

Here we introduce $c^2 = dp/d\rho$–the local sound (characteristic) speed. One can see that shocks are supersonic with respect to the state ahead of the jump (state $\mathbf{A}$),

[1] To obtain a corresponding 1D theory for a homogeneous solid which supports a martensitic transformation (or twinning), one has to replace the actual (Eulerian) coordinate x in (2.10) by the material (Lagrangian) coordinate $y = \int^x \rho dx$, and substitute for pressure p the stress $\sigma = -p$. Then (2.10) transforms into the equations of motion for a one-dimensional elastic bar with unit reference density and zero body force in Lagrangian coordinates; $\dot{w} = v_y$, $\dot{v} = \sigma_y$, where $v = x(y,t)_t$ is a velocity, $w = x(y,t)_y$ is the only nontrivial component of the deformation gradient $\mathbf{F}$, and $\sigma(w)$ denotes the corresponding component of the Piola stress tensor. The motion described by these governing equations may be either longitudinal or transverse with a suitable redefinition of v, w and σ in the latter case. The *RH* jump conditions, i.e., $D_0[w] + [v] = 0, D_0[v] + [\sigma] = 0$, include the material velocity of the discontinuity $D_0 = -m$. The detailed analysis of this case can be found in [88].

while kinks are subsonic. In other words, the flow ahead of a shock is supersonic and subsonic ahead of a kink (the flow is here always understood relative to the transformation front). Both types of discontinuities are subsonic with respect to a state behind themselves (state **B** or **B′**). Figure 1(b) and (c) show the arrangement of characteristics of (2.10) near the discontinuity for shocks (b) and kinks (c). In the case of shocks three characteristics are bringing data from ahead and from behind, which, together with two *RH* conditions, is enough to find four parameters of the flow and the mass flux m. In the case of kinks, only two characteristics are incoming together, which suggests that an additional jump condition is at least necessary for uniqueness.

In what follows, from the discussion of the internal mechanism of the phase transformation, we shall obtain the desired additional condition which make unique determination of the whole process possible by excluding certain processes which would be compatible with the conservation laws in the form of the *RH* conditions.

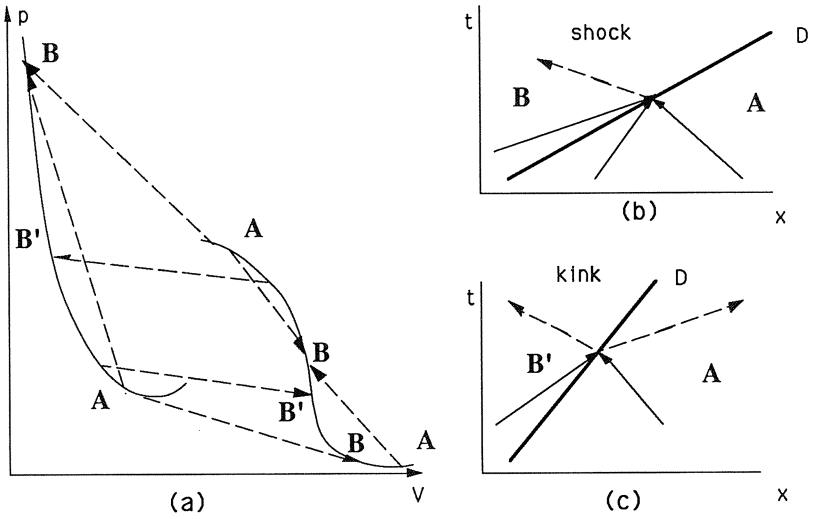

Figure 1. Two types of discontinuous solutions: *shocks* **A** → **B** and *kinks* **A** → **B′**; state **A** is in front of the discontinuity, state **B** is behind; (a)–arrows show admissible jumps of both types; (b) and (c)–arrows show incoming (solid lines) and departing (dashed lines) characteristics; D (heavy line) is a discontinuity.

3. Model of an interface. As we mentioned already, in order to smooth out sharp discontinuities, one is motivated to consider a regularized theory which includes the original model as a limiting case. In the classical theory of shock waves, the introduction of viscous dissipation is known to be sufficient to build a structure [32, 53]. This is not always the case in the theory of phase boundaries, because kinks may be nondissipative. Therefore, pure dispersive contributions to constitutive relations, including higher derivatives or integral terms, appear to be necessary.

Since the original continuum description admits nonunique extensions, the particular extension adopted should be based on a detailed account of relevant molecular processes neglected by the ideal model. Incorporation of nonequilibrium states may require the introduction of extra variables which describe for example the degree of deviation of the system from equilibrium, or the degree of local inhomogeneity at a scale for which the original theory regarded the material as homogeneous. If these internal variables do not adjust simultaneously with the change of controlling parameters, one may need to account for the kinetics of relaxation. Analogous long or short "spatial memory", having its origin in the nonclassical interaction of neighboring representative material particles, is required for a continuum description of highly inhomogeneous regions.

To be specific, consider the model of an elastic fluid with an internal parameter ξ which characterizes the state of the material in an interface layer. This parameter could be an order parameter which describes the current pattern of local microstructural arrangement, the state of a mixture or the extent of a transformation. We deliberately do not specify its nature in order to emphasize the generality of the approach; the technique also can be used in, say, crystal plasticity theory [69] or the mechanics of continuous damage [50]. The space of allowed nonequilibrium states is selected to be one-dimensional in order to avoid nonessential complications.

Since stationary (equilibrium) kinks should possess structure, we shall introduce a scale of length into the conservative part of the constitutive model which we imagine to have been originally described through specific internal energy

$$e = e(\rho, s, \xi). \tag{3.1}$$

The simplest nonlocal generalization of (3.1), having its origin in van der Waals' theory of capillarity, is

$$e = e(\rho, s, \xi, \nabla\rho, \nabla\xi), \tag{3.2}$$

where ∇ is an eulerian gradient. In what follows, we shall use general ideas from the theory of liquid crystals [23,54,57], and develop a consistent thermodynamic theory for a material with the energy (3.2).

First, to justify further definitions, consider the variation of the internal energy of a finite body, i.e.,

$$E = \int_{\Omega} e\rho dv,$$

when one varies independently the actual positions of material particles $\delta\mathbf{x} = \mathbf{x}'(\mathbf{y},t) - \mathbf{x}(\mathbf{y},t)$ as well as the field of the order parameter $\delta\xi = \xi'(\mathbf{y},t) - \xi(\mathbf{y},t)$, at fixed entropy distribution $s(\mathbf{y},t)$. In this case, we have

$$\delta E = \int_\Omega \left(\frac{\partial e}{\partial \rho}\delta\rho + \frac{\partial e}{\partial \nabla\rho}\delta\nabla\rho + \frac{\partial e}{\partial \xi}\delta\xi + \frac{\partial e}{\partial \nabla\xi}\delta\nabla\xi \right) \rho dv,$$

where, for the mass balance,

$$\delta\rho = -\rho \operatorname{div}(\delta\mathbf{x}).$$

Now, taking into account that the variation at fixed $\mathbf{y}$ and the partial derivative at fixed $\mathbf{x}$ do not commute, and using Stokes' theorem, we have

$$\delta E = \int_\Omega (\rho\mathcal{A}\delta\xi - \operatorname{div}\mathbf{P}\cdot\delta\mathbf{x})dv + \int_{\partial\Omega} (\mathbf{P}\mathbf{n}\cdot\delta\mathbf{x} + (\mathbf{t}\cdot\mathbf{n})\operatorname{div}(\delta\mathbf{x}) + (\mathbf{r}\cdot\mathbf{n})\delta\xi)dS. \tag{3.3}$$

Here

$$\mathbf{P} = -\rho^2\frac{\delta' e}{\delta\rho}\mathbf{1} - \rho\frac{\partial e}{\partial\nabla\rho}\otimes\nabla\rho - \rho\frac{\partial e}{\partial\nabla\xi}\otimes\nabla\xi \tag{3.4}$$

is a (conservative) Cauchy stress tensor,

$$\mathbf{t} = -\rho^2\frac{\partial e}{\partial\nabla\rho} \tag{3.5}$$

is a couple stress vector[2],

$$\mathbf{r} = \rho\frac{\partial e}{\partial\nabla\xi} \tag{3.6}$$

is a (generalized) surface force which works on variations of ξ, and

$$\mathcal{A} = \frac{\delta' e}{\delta\xi} \tag{3.7}$$

is an affinity;

$$\frac{\delta'}{\delta\ldots} = \frac{\partial}{\partial\ldots} - \frac{1}{\rho}\operatorname{div}\left(\rho\frac{\partial}{\partial\nabla\ldots}\right)$$

is a generalization of a variational derivative.

The variational identity (3.3) has a form which suggests that in the conservative theory

$$A = \int_{\partial\Omega} (\mathbf{P}\mathbf{n}\cdot\mathbf{v} + (\mathbf{t}\cdot\mathbf{n})\operatorname{div}\mathbf{v} + (\mathbf{r}\cdot\mathbf{n})\dot{\xi})dS$$

[2]Stresses and couple stresses are not uniquely determined since one can move terms between $\mathbf{P}$ and $\mathbf{t}$ without altering the volume integral in (3.3).

be considered as a rate of work contribution in the integral form of the first law of thermodynamics ($\mathbf{v} = \dot{\mathbf{x}}$). The constitutive relations (3.4-3.7), describing the conservative part of the model, then may be obtained from an argument which uses the Clausius-Duhem inequality in a now-standard way (see, for example, [21,22]). Hence we now turn to consider the "dissipative" part of the constitutive model and introduce nonconservative contributions $\mathbf{P}'$, $\mathbf{t}'$ and $\mathbf{r}'$. Then

$$A = \int_{\partial\Omega} \Big((\mathbf{P} + \mathbf{P}')\mathbf{n} \cdot \dot{\mathbf{x}} + ((\mathbf{t} + \mathbf{t}') \cdot \mathbf{n}) \operatorname{div} \dot{\mathbf{x}} + ((\mathbf{r} + \mathbf{r}') \cdot \mathbf{n})\dot{\xi} \Big)\, dS.$$

According to the first law of thermodynamics

$$\dot{E} + \dot{K} = A + Q \tag{3.8}$$

where E and A have been already defined,

$$K = (1/2) \int_{\Omega} \rho |v|^2 dv$$

is the kinetic energy, and

$$Q = - \int_{\partial\Omega} (\mathbf{q} \cdot \mathbf{n}) dS$$

is the rate of heat supplied to the system through the surface. We have tacitly assumed that body forces and external radiation are absent. Combining (3.2) with (3.8), along with the balance of mass

$$\dot{\rho} = -\rho \operatorname{div} \mathbf{v},$$

for smooth fields we get

$$\begin{aligned} &\int_{\Omega} \Big(\rho T \dot{s} + \rho \mathcal{A} \dot{\xi} + (\rho \dot{\mathbf{v}} - \operatorname{div} \mathbf{P}) \cdot \mathbf{v} \Big)\, dv + \\ &\int_{\partial\Omega} (\mathbf{q} \cdot \mathbf{n} - (\mathbf{r}' \cdot \mathbf{n})\dot{\xi} - (\mathbf{t}' \cdot \mathbf{n}) \operatorname{div} \mathbf{v} - \mathbf{P}'\mathbf{n} \cdot \mathbf{n}) dS = 0, \end{aligned} \tag{3.9}$$

where we have used[3]

$$T = \partial e / \partial s.$$

In a local form, (3.9) yields

$$\rho T \dot{s} = -\rho \mathcal{A} \dot{\xi} - (\rho \dot{\mathbf{v}} - \operatorname{div} \mathbf{P}) \cdot \mathbf{v} - \operatorname{div}(\mathbf{q} - \mathbf{r}' \dot{\xi} - \mathbf{t}' \operatorname{div} \mathbf{v} - \mathbf{P}'^{T} \mathbf{v}). \tag{3.10}$$

[3]This is another result of the conservative theory coming from the variation of the entropy field in (3.3) or the equivalent argument based on the Clausius-Duhem inequality.

Now, according to the second law of thermodynamics in the form of the Clausius-Duhem inequality, we note that the internal dissipation

$$\rho\chi \equiv \rho\dot{s} + \operatorname{div} J \tag{3.11}$$

satisfies

$$\rho\chi \geq 0$$

where J is an entropy flux. By taking

$$J = \mathbf{q}/T + \mathbf{h}, \tag{3.12}$$

we finally obtain

$$-\rho\mathcal{A}\dot{\xi} - (\rho\dot{\mathbf{v}} - \operatorname{div}\mathbf{P})\cdot\mathbf{v} - \frac{\mathbf{q}}{T}\cdot\nabla T + \operatorname{div}\omega \geq 0, \tag{3.13}$$

where

$$\boldsymbol{\omega} = \mathbf{h} + \mathbf{r}'\dot{\xi} + \mathbf{t}'\operatorname{div}\mathbf{v} + \mathbf{P}'^{T}\mathbf{v}.$$

It is natural to start with the special case of an isothermal, dissipation free process defined by

$$\begin{aligned} \mathcal{A} &= 0, \\ \rho\dot{\mathbf{v}} - \operatorname{div}\mathbf{P} &= 0 \end{aligned} \tag{3.14}$$

and

$$\mathbf{h} = 0, \quad \mathbf{r}' = 0, \quad \mathbf{t}' = 0, \quad \mathbf{P}' = 0.$$

Both equations (3.14) have *identical* Euler-Lagrange structure (which would have been more transparent if the energy had included $\dot{\xi}$ and $\mathbf{x}$ among its arguments). Using the constitutive equations we get, accordingly,

$$\frac{\partial f}{\partial \xi} - \frac{1}{\rho}\operatorname{div}\left(\rho\frac{\partial f}{\partial \nabla\xi}\right) = 0,$$

and

$$\rho\dot{\mathbf{v}} - \operatorname{div}\left(-\rho^2\left(\frac{\partial f}{\partial \rho} - \frac{1}{\rho}\operatorname{div}\left(\rho\frac{\partial f}{\partial \nabla\rho}\right)\right)\mathbf{1} - \rho\left(\frac{\partial f}{\partial \nabla\rho}\otimes\nabla\rho + \frac{\partial f}{\partial \nabla\xi}\otimes\nabla\xi\right)\right) = 0,$$

where f is the specific free energy. Although the tensor $\mathbf{P}$ in our fluid is nonhydrostatical, it has a special structure, which has long been known in the theory of liquid crystals, namely one can prove the identity

$$\operatorname{div}\mathbf{P} = -\rho\nabla M,$$

where

$$M = f + \rho\frac{\delta f}{\delta \rho},$$

and δ/δ is the standard variational derivative

$$\frac{\delta}{\delta \dots} = \frac{\partial}{\partial \dots} - \operatorname{div}\left(\frac{\partial}{\partial \nabla \dots}\right).$$

This in turn can be used to show that fluid dynamic integrals from the classical theory persist for dissipation free motions of a nonlocal (in ρ and ξ) fluid[4]. Moreover, this result is equally true for the material with

$$e = e(\rho, \nabla\rho, \nabla\nabla\rho, \dots, \xi, \nabla\xi, \nabla\nabla\xi, \dots, s)$$

if the variational derivative in the definition of M is generalized accordingly. Some special cases have been investigated previously in [18,22,71,84].

We are now in a position to model the "dissipation related" part of the extended constitutive model. As we show in the **Appendix 1** a number of dissipation mechanisms are thermodynamically consistent. In what follows we shall focus on one of them.

Let us assume that the process is isothermal and

$$\rho\dot{\mathbf{v}} - \operatorname{div}\mathbf{P} = 0,$$

$$\mathbf{h} = 0, \quad \mathbf{r}' = 0, \quad \mathbf{t}' = 0, \quad \mathbf{P}' = 0,$$

but

$$\mathcal{A} \neq 0.$$

Then we have

$$\dot{s} = -\frac{\mathcal{A}}{T}\dot{\xi} \geq 0.$$

The only dissipative process is now a relaxation of the internal parameter ξ. Consider the simplest *kinetic* (*evolution*) equations for ξ, which closes the system of equations

$$\dot{\xi} = -\Gamma\mathcal{A} \tag{3.15}$$

or

$$\dot{\xi} = -\Gamma\left(\frac{\partial e}{\partial \xi} - \frac{1}{p}\operatorname{div}\left(\rho\frac{\partial e}{\partial \nabla \xi}\right)\right)$$

where Γ is material parameter [87]. This model describes the relaxation of the "nonconserved order parameter", and has a wide range of applications from plasma physics to liquid crystals. The model provides nonnegative internal dissipation since

$$\rho\chi = \rho\Gamma\mathcal{A}^2 \geq 0 \tag{3.16}$$

[4]Thus, for example, in a steady flow one has the Bernoulli integral: $(1/2)\mathbf{v}^2 + \mathbf{M} = \text{const}$ along the stream line.

if the (kinetic) coefficient Γ, characterizing the time of relaxation, is nonnegative. Two nondissipative limiting cases correspond to $\Gamma \to \infty$ (equilibrium process, considered above) and $\Gamma \to 0$ (internal parameter is frozen). If $\rho = \text{const}$ and if we take

$$e = e_0(\xi, T_0) + \varepsilon(T_0)|\nabla\xi|^2 \tag{3.17}$$

then (3.15) yields a well known Ginzburg-Landau equation [13,16,46,67,71,87,89],

$$\dot{\xi} = -\Gamma\left(\frac{\partial e_0}{\partial \xi} - 2\varepsilon\Delta\xi\right) \tag{3.18}$$

The classical model of a relaxing fluid corresponds to the limit $\varepsilon \to 0$.

In the following analysis of the discontinuity structure, we shall consider a special model which includes standard viscosity (see **Appendix 1**), Ginzburg-Landau type relaxation (3.15), and Fourier heat conduction

$$\begin{aligned} &\rho\dot{\mathbf{v}} - \operatorname{div}(\mathbf{P} + \mathbf{P}') = 0 \\ &\dot{\xi} = -\Gamma\mathcal{A} \\ &\mathbf{q} = -æ\nabla T \end{aligned} \tag{3.19}$$

Here

$$\mathbf{P}' = (\lambda tr\mathbf{D})\mathbf{1} + 2\mu\mathbf{D}$$

is a standard viscous stress tensor, $\mathbf{D} = \frac{1}{2}(\nabla\mathbf{v} + (\nabla\mathbf{v})^T)$ is a strain rate tensor. Further, we have assumed that $\mathbf{h} = 0$, $\mathbf{r}' = 0$, $\mathbf{t}' = 0$. More general cases, including viscosity-kinetics coupling, are discussed in [71].

Now the closed system of equations consists of an equation of mass conservation, four evolution equations ((3.19$_{1,2}$), including equations of momentum balance) and the equation of the entropy balance (3.10). Since we assume the process of transformation to be strictly one-dimensional (plane front), the following 1D equations will suffice:

$$\begin{aligned} &\dot{\rho} = -\rho v_x \\ &\rho\dot{v} = \left(-\rho^2\left(\frac{\partial e}{\partial \rho} - \frac{1}{\rho}\left(\rho\frac{\partial e}{\partial \rho_x}\right)_x\right) - \rho\left(\frac{\partial e}{\partial \rho_x}\rho_x + \frac{\partial e}{\partial \xi_x}\xi_x\right) + \eta v_x\right)_x \\ &\dot{\xi} = -\Gamma\left(\frac{\partial e}{\partial \xi} - \frac{1}{\rho}\left(\rho\frac{\partial e}{\partial \xi_x}\right)_x\right) \\ &\rho T\dot{s} = \rho\Gamma\left(\frac{\partial e}{\partial \xi} - \frac{1}{\rho}\left(\rho\frac{\partial e}{\partial \xi_x}\right)_x\right)^2 + \eta v_x^2 + æT_{xx} \end{aligned} \tag{3.20}$$

where $\eta = \lambda + 2\mu$ is an effective viscosity. The last equation can be as well expressed in energy balance form

$$\begin{aligned} \rho\dot{e} = &\left[-\rho^2\left(\frac{\partial e}{\partial \rho} - \frac{1}{\rho}\left(\rho\frac{\partial e}{\partial \rho_x}\right)_x\right) - \rho\left(\frac{\partial e}{\partial \rho_x}\rho_x + \frac{\partial e}{\partial \xi_x}\xi_x\right)\right] v_x \\ &+ \eta v_x^2 + \left(\rho\frac{\partial e}{\partial \rho_x}\dot{\rho} + \rho\frac{\partial e}{\partial \xi_x}\dot{\xi}\right)_x + æT_{xx}. \end{aligned}$$

To specify the model further, one may take a weakly nonlocal contribution to the energy in a van der Waals-Ginzburg-Landau form

$$e = e_0(\rho, \xi, s) + \varepsilon_1|\nabla\rho|^2 + \varepsilon_2|\nabla\xi|^2 + \varepsilon_3(\nabla\rho \cdot \nabla\xi)$$

where $\varepsilon_i (i = 1, 2, 3)$ are "small" parameters (function of ρ, ξ, s) characterizing long wave dispersive corrections to the "local" model.

The deviation of this extended model form an ideal model is now scaled with six dimensional parameters

$$\zeta = \{æ, \eta, \Gamma, \varepsilon_i\}$$

but only five of them are independent after the scale of length is selected, say

$$\mathbf{W} = \left\{ \frac{\eta}{\sqrt{\varepsilon_1}}, \frac{æ}{\Gamma\varepsilon_1}, \Gamma^2\varepsilon_1, \frac{\varepsilon_2}{\varepsilon_1}, \frac{\varepsilon_3}{\varepsilon_1} \right\}. \tag{3.21}$$

This choice is certainly not unique; for example, $\eta/æ$ may be substituted for any of the first three components of $\mathbf{W}$. In the classical limit, all components of ζ tend to zero, however, as we shall see in the next two sections, the limiting discontinuous solution may well depend upon the components of $\lim_{\zeta\to 0} \mathbf{W}$.

4. Ginzburg-Landau type structure. The system of equations (3.20) in its full complexity seems intractable at the moment; however, special cases give an idea of possible effects that can be studied in some detail. Consider, first, the *local fluid* and omit the density gradient from the list of arguments of the specific internal energy. To specify the model further, suppose that the energy is given by

$$e(\rho, s, \xi, \nabla\xi) = e_0(\rho, s, \xi) + \varepsilon_0(\rho, \xi)|\nabla\xi|^2.$$

Then, system (3.20) reduces to

$$\begin{aligned}
\dot\rho &= -\rho v_x, \\
\rho\dot v &= \left(-p - \left[\rho^2 \frac{\partial\varepsilon_0}{\partial\rho} + 2\varepsilon_0\rho \right] \xi_x^2 + \eta v_x \right)_x, \\
\dot\xi &= -\Gamma \left(M - \left(2\frac{\partial\varepsilon_0}{\partial\rho} + \frac{2\varepsilon_0}{\rho} \right) \rho_x\xi_x - 2\varepsilon_0\xi_{xx} - \frac{\partial\varepsilon_0}{\partial\xi}\xi_x^2 \right), \\
\rho T\dot s &= \rho\Gamma \left(M - \left(2\frac{\partial\varepsilon_0}{\partial\rho} + 2\frac{\varepsilon_0}{\rho} \right) \rho_x\xi_x - 2\varepsilon_0\xi_{xx} - \frac{\partial\varepsilon_0}{\partial\xi}\xi_x^2 \right)^2 + \eta v_x^2 + æ T_{xx},
\end{aligned} \tag{4.1}$$

where $p = \rho^2 \frac{\partial\varepsilon_0}{\partial\rho}$, $T = \frac{\partial\varepsilon_0}{\partial s}$ and $M = \frac{\partial\varepsilon_0}{\partial\xi}$. As a further simplification we shall assume that $\varepsilon_0 = \varepsilon/\rho$, where $\varepsilon = \text{const}$.

To analyze the structure of a moving discontinuity, assume that the flow, when observed from a frame moving with the instantaneous velocity of the phase boundary, is steady in the neighborhood of the transformation front. It is equivalent to consider a traveling wave solution to (4.1), which depends on the similarity variable

$z = x - Dt$. Then, letting $\rho = \rho(z)$, $v = v(z)$, $\xi = \xi(z)$, and $T = T(z)$ integrate $(4.1)_{1,2}$ to obtain

$$\begin{aligned} &\rho(v - D) = m, \\ &p + \frac{m^2}{\rho} + \varepsilon\xi_z^2 + \frac{\eta m}{\rho^2}\rho_z = \pi, \end{aligned} \tag{4.2}$$

where m and π are the constants of integration. The two remaining equations of (4.1) may now be written as

$$\begin{aligned} &2\varepsilon\Gamma\xi_{zz} - \rho\Gamma M - m\xi_z = 0, \\ &mTs_z = \rho\Gamma\left(M - \frac{2\varepsilon}{\rho}\xi_{zz}\right)^2 + \eta\frac{m^2}{\rho^4}\rho_z^2 + \text{æ}T_{zz}. \end{aligned} \tag{4.3}$$

We now concentrate on the combined effects of kinetics and nonlocality. To make the problem more tractable, we shall neglect viscosity ($\eta = 0$) and assume the flow to be isothermal[5]. The interplay between the viscosity and "local" kinetics has been considered in [68] where the transformation of an *unstable* state was studied as an analog of weak detonation.

After these simplifications, the system (4.2) and (4.3) of ODE's reduces to an autonomous dynamical system on a plane [72], i.e.,

$$\begin{aligned} &\phi_z = (2\varepsilon V)^{-1}M(\xi, V) + (2\varepsilon\Gamma)^{-1}m\phi, \\ &\xi_z = \phi, \end{aligned} \tag{4.4}$$

where we have replaced ρ with $V = \rho^{-1}$ and introduced a new variable $\phi = \xi_z$. The function $V(\xi, \phi)$ is given implicitly by $(4.2)_2$, i.e.,

$$p(\xi, V) + m^2V + \varepsilon\phi^2 = \pi. \tag{4.5}$$

The system (4.4), which represent an internal problem that is to be matched with a classical external problem, is supposed to be considered on an infinite domain with the following boundary conditions:

$$\begin{aligned} V &\to \begin{cases} V_1, & z \to -\infty \\ V_2, & z \to +\infty \end{cases} \\ \xi &\to \begin{cases} \xi_1, & z \to -\infty \\ \xi_2, & z \to +\infty \end{cases} \end{aligned} \tag{4.6}$$

Thus, using subscripts 1 and 2 to denote fields evaluated at $z = -\infty$ and $z = +\infty$, respectively, we have from (4.4)

$$\begin{aligned} \phi_1 = \phi_2 = 0, \\ M_1 = M_2 = 0, \\ p_1 + m^2V_1 = p_2 + m^2V_2, \end{aligned}$$

[5]Spatially uniform temperature will not be explicitly listed as a variable in constitutive functions.

so that both limiting states are in equilibrium $\left(\frac{\partial f_0}{\partial \xi} = 0, f_0(\xi, V, T) = e_0 - Ts\right)$ and the RH conditions are satisfied.

Consider *shocks* first [72]. Our assumptions concerning the constitutive functions $p = -\frac{\partial f_0}{\partial V}$ and $M = \frac{\partial f_0}{\partial \xi}$ are summarized below (see Figure 2)

$$\frac{\partial^2 f_0}{\partial V^2} > 0, \quad \frac{\partial^2 f_0}{\partial \xi^2} > 0, \quad \frac{\partial^3 f_0}{\partial V^3} < 0, \quad \frac{\partial^2 f_0}{\partial \xi \partial V} < 0$$
$$\frac{\partial f_0}{\partial V} \to -\infty \text{ as } V \to 0.$$

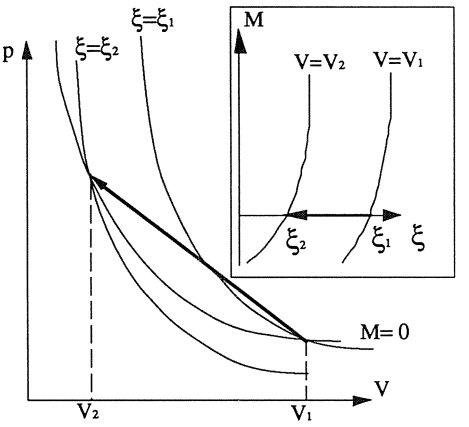

Figure 2. Sketch of a family of typical isotherms for $p = p(V, \xi)$ at $\xi = \xi_1$ and $\xi = \xi_2$, and $M = M(V, \xi)$ (in the box) at $V = V_1$ and $V = V_2$. Also given is an equilibrium curve $p = p(V, \tilde{\xi}(V))$, where $\tilde{\xi}(V)$ is a solution of $M(V, \tilde{\xi}(V)) = 0$.

One can introduce two characteristic (sound) speeds for an equilibrium state ξ_1, V_1:

$$c_0^2 = -V_1^2 \frac{dp}{dV}(V_1, \tilde{\xi}(V_1)) \tag{4.7}$$

and

$$c_\infty^2 = -V_1^2 \frac{\partial p}{\partial V}(V_1, \xi_1) \tag{4.8}$$

where, in (4.7), the function $\tilde{\xi}(V)$ is a solution of $M(V, \tilde{\xi}(V)) = 0$ and in (4.8) the derivative is taken when $\xi = \xi_1$ is fixed. Because the point (ξ_1, V_1) corresponds to a stable equilibrium $\left(\frac{\partial^2 f_0}{\partial \xi^2}(V_1, \xi_1) > 0\right)$, the "equilibrium" acoustic speed c_0 is always less than or equal to the "frozen" acoustic speed $c_\infty (c_\infty \geq c_0)$.

The structure of the shock wave will depend on m^2, and several qualitatively different regimes are presented in Figure 3 for the case when $m > 0$ (see [72] for details).

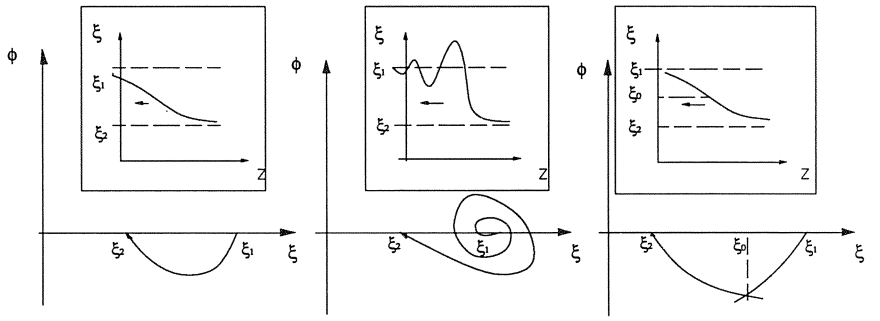

Figure 3. Three qualitatively different patterns of the shock wave structure in a nonlocal relaxing inviscid fluid: phase portraits and internal parameter profiles (in the boxes); (a) $c_*^2 > m^2V_1^2 > c_0^2$, (b) $c_\infty^2 > m^2V_1^2 > c_*^2$, (c) $m^2V_1^2 > c_\infty^2$, where c_0 is the "equilibrium" acoustic speed, c_∞ is the "frozen" acoustic speed, and c_* is a parameter given in the text.

A solution of the eigenvalue problem (4.4–4.6) does not exist if $m^2V_1^2 < c_0^2$ (there is only one equilibrium point), so all shocks are supersonic with respect to the front state and it is the equilibrium sound speed of the front state c_0 that is essential here. For $m^2V_1^2 > c_0^2$ the dynamical system (4.4) has two points of equilibrium:
$(\xi = \xi_1, \phi = 0)$, which is a saddle, and
$(\xi = \xi_2, \phi = 0)$, which is a

unstable node for	$c_*^2 >$	$m^2V_1^2 > c_0^2$	(Figure 3 (a)),
unstable focus for	$c_\infty^2 >$	$m^2V_1^2 > c_*^2$	(Figure 3 (b)),
saddle for		$m^2V_1^2 > c_\infty^2$	(Figure 3 (c)).

the special speed c_* is given by:

$$c_*^2 = c_\infty^2 \left(\frac{1-W}{2}\right)\left\{1+\left\{1+\frac{4W}{(1-W)^2}\frac{c_0^2}{c_\infty^2}\right\}^{1/2}\right\},$$

where

$$W = \Gamma^2\varepsilon\left(\frac{8V}{c_\infty^2}\frac{\partial^2 f_0}{\partial\xi^2}\right)_{V_1} \tag{4.9}$$

is a nondimensional parameter (essential combination $\Gamma^2\varepsilon$ was mentioned in (3.21)). As one can see from Figure 3, a shock with intermediate strength has oscillations

in its frontal part. The effect of spatial dispersion scales with W (or ε) and disappears at $W = 0$. Sufficiently strong (supersonic with respect to c_∞) shocks possess smooth (but not C^2–smooth) $\xi(z)$ structure: as is well known in physico-chemical gas dynamics, this is not the case for the "local" ($\varepsilon = 0$) model in which $\xi(z)$ may not be continuously differentiable [53]. The heteroclinic trajectories indicated on Figure 3 are structurally stable; therefore, no equality-type additional jump conditions for the external problem are provided. The last statement is not so obvious for $m^2 V_1^2 > c_\infty^2$ (Figure 3(c)), where the connection is saddle to saddle. However, the $V(\phi, \xi)$ surface in this case is two-sheeted so phase trajectories in the (ϕ, ξ) plane may intersect. An additional degree of freedom comes from the arbitrariness of the point ξ_0, where V and ξ_{zz} experience a finite discontinuity [72].

The solutions examined above correspond to usual shock waves with structure supported by (nonlocal) kinetics. To emphasize the role of kinetics in the modelling of the subsonic phase boundaries (*kinks*), we now turn to consider the case of *slow motion*, so the inertial effects can be neglected. Furthermore, let us assume that the "reactive" stresses (scaled with ε) are small and

$$p(V, \xi) \approx p_1$$

satisfies (4.5). The mechanical and kinetic problems can be decoupled, if the derivative $\frac{\partial p}{\partial \xi}$ $(= -\frac{\partial M}{\partial V})$ is also small, so that the evolution of the phase field $\xi(z)$ does not involve any mechanical motions. Then

$$V = \widetilde{V}(p_1, \xi) \approx V_1$$

and the system (4.4) reduces to [87]

$$\begin{aligned} \phi_z &= (2\varepsilon V_1)^{-1} M(\xi, V_1) - (2\varepsilon V_1 \Gamma)^{-1} D\phi \\ \xi_z &= \phi \end{aligned} \tag{4.10}$$

where $D = -mV_1$ is the speed of the kink ($v \ll D$). This limit, to which actual situation frequently come very near, has always been assumed in the theory of slow moving laminar flames (deflagration waves). The main difference is that in the present case the unreacted state is *metastable* (equilibrated) rather than *unstable* (nonequilibrated), which eliminates the problem of the "cold boundary" [31,53,91].

The only parameter experiencing an abrupt change on a phase boundary will be the "order parameter" ξ, and the wave will perform "switching" from the one equilibrium state ($M = 0$), say $\xi = \xi_1$ to the other, say $\xi = \xi_2$ (see Figure 4).

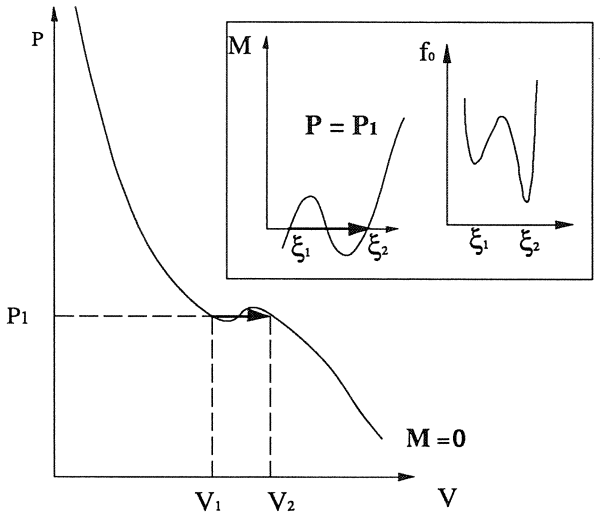

Figure 4. Sketch of an equilibrium ($M(V, \widetilde{\xi}(V)) = 0$) isothermal curve $p(V, \widetilde{\xi}(V))$ for a fluid with a phase transformation ($V_1 \approx V_2$). A corresponding function $M(\xi, \widetilde{V}(p_1, \xi))$ and its primitive at fixed $p \approx p_1$ are shown in the box.

A straightforward analysis shows that both equilibrium states ξ_1 and ξ_2 correspond to saddles on the (ξ, ϕ) phase plane, so a heteroclinic connection exists only for special values of the parameter D. To rewrite (4.10) in dimensionless form, introduce normalized variables

$$\mu' = M/M_0,$$
$$z' = z/\ell,$$

with

$$\ell = \sqrt{\frac{2\varepsilon V}{M_0}}.$$

Then, (4.10) takes the form

$$\xi_{z'z'} + D'\xi_{z'} = \mu'(\xi, p_1), \tag{4.11}$$

where

$$D' = \frac{D}{c_\infty \sqrt{W}}, \tag{4.12}$$

$$W = \Gamma^2 \varepsilon \left(\frac{2V}{c_\infty^2} M_0 \right). \tag{4.13}$$

Comparison of (4.13) with (4.9) shows that W essentially the same nondimensional parameter $\left(\text{take } M_0 = 4\left(\frac{\partial^2 f_0}{\partial \xi^2}\right)(V_1, \xi_1)\right)$.

In order to have an orbit from ξ_1 to ξ_2 when $D > 0$[6] one must interchange ξ_1

[6] This means $m < 0$ so the wave moves to the right.

and ξ_2 by replacing the boundary conditions (4.6) with

$$\xi \to \begin{cases} \xi_1, & z' \to \infty \\ \xi_2, & z' \to -\infty \end{cases} \tag{4.14}$$

Then, (4.11) integrates once to give

$$\xi_{z'}^2 - g(\xi, p_1) + g(\xi_2, p_1) = -D' \int_{-\infty}^{z'} \xi_z^2 dz, \tag{4.15}$$

where we have introduced the nondimensional potential $g(\xi, p_1)$ by

$$\mu' = \frac{\partial g}{\partial \xi}$$

It then follows from (4.15) that

$$[g] = -D' \int_{\infty}^{-\infty} \xi_{z'}^2 dz' \leq 0 \tag{4.16}$$

where $[g] = g(\xi_2, p_1) - g(\xi_1, p_1)$. The necessary condition (4.16) indicates that it is the metastable state ξ_1 (a relative minimum of $g(\xi, p_1)$) that transforms to a state ξ_2 corresponding to an absolute minimum.

Equation (4.16) gives an explicit functional relation between the internal structure of the discontinuity provided by $\xi(z')$ and the (normalized) *driving traction* $G = [g]$ (see (2.8)). Having expressed the right hand side of (4.16) in terms of D' one obtains an additional jump condition for a kink that supplements the classical *RH* system of jump relations.

The problem discussed here is supposed to correspond to slowly moving or even stationary kinks. In fact, if there exists $p_1 = \tilde{p}$ such that $g(\xi_1(\tilde{p}), \tilde{p}) = g(\xi_2(\tilde{p}), \tilde{p})$, then equation (4.16) gives $D' = 0$ and (4.15) can be integrated

$$\int_{\xi}^{\xi_2(\tilde{p})} \frac{dv}{\sqrt{(g(v, \tilde{p}) - g(\xi_2(\tilde{p}), \tilde{p}))}} = z_0' - z'.$$

For p_1 close to $\tilde{p}$, the corresponding $[g]$ is close to zero and the asymptotic relation for the kink speed is found to be

$$D' = \gamma[g], \tag{4.17}$$

where the mobility of the kink is given by

$$\gamma = \left[\int_{\xi_1(\tilde{p})}^{\xi_2(\tilde{p})} \sqrt{(g(\xi, \tilde{p}) - g(\xi_2(\tilde{p}), \tilde{p}))} d\xi \right]^{-1}$$

Equation (4.17) presents an example of a "normal growth" model which is characterized by a linear relation between the driving traction $[g]$ and the flux D'. Let us note that the "kinetic coefficient" γ does not depend on details of an extension of $g(\xi)$ into the spinodal region $\left(\frac{\partial^2 f_0}{\partial \xi^2} \leq 0\right)$.

Linear kinetic relations are valid only for sufficiently slow kinks, meaning weak metastability of the front state (p_1 is close to $\tilde{p}$). Some analytical results are also available for kinks of intermediate speed, those for which the right hand side of (4.15) can no longer be neglected but which are yet slow enough to justify the continued neglect of inertial terms. Thus if μ' can be approximated by a cubic polynomial

$$\mu' = (\xi - \xi_1)(\xi - \xi_0)(\xi - \xi_2),$$

then equation (4.15) has an analytical solution, which is well known for reaction-diffusion systems [92]

$$\xi(z') = \frac{\xi_1 + \xi_2}{2} + \frac{\xi_1 - \xi_2}{2} th \left[\frac{\xi_2 - \xi_1}{2\sqrt{2}}(z' - z'_0)\right] \tag{4.18}$$

In view of (4.18) the integral in the right hand side of (4.16) yields [87]

$$D' = (6\sqrt{2})\frac{[g]}{(\xi_1 - \xi_2)^3}$$

which is a desired nonlinear generalization of (4.17). Substitution of D' into (4.12) shows explicitly how the nondimensional parameter W enters the resulting jump conditions.

Heat transfer, as well as interface kinetics, might be a rate limiting process in dynamic phase transitions. Consider an example of a thermo-kinetical analysis for our simplified "mechanically inert" system.

With both the entropy (4.3_2) and the kinetic (4.3_1) equations coupled, one obtains in 3D a closed system of equations [87,89]:

$$\begin{aligned} \dot{\xi} &= -\Gamma(M(\xi, T) - 2\varepsilon V \Delta\xi) \\ c_p \dot{T} + L\dot{\xi} &= \Gamma(M(\xi, T) - 2\varepsilon V \Delta\xi)^2 + æ\Delta T \end{aligned} \tag{4.19}$$

where we have introduced both the specific heat $c_p(\xi, T) = T\frac{\partial s}{\partial T}$ and the thermal effect of the transformation $L(\xi, T) = T\frac{\partial s}{\partial \xi}$. Equations (4.19) provide a natural regularization of the Stefan model. Modulo the important first term in the right hand side of $(4.19)_2$, which gives a kinetic contribution to the entropy production, this system is known as the "phase field model" [16]. Recently, an alternative approach, aimed at achieving the thermodynamic consistency of the phase field model, has been set forth in [67].

Traveling wave solutions of (4.19), describing the structure of a kink in a heat conducting body, obey the system of ODE's

$$\begin{aligned} D\xi_z &= \Gamma(M - 2\varepsilon V \xi_{zz}) \\ -c_p D T_z - LD\xi_z &= \Gamma(M - 2\varepsilon V \xi_{zz})^2 + æ T_{zz} \end{aligned} \tag{4.20}$$

If c_p and L are each constant in (4.20), then two characteristic length scales can be introduced [87]

$$\ell_1 = \sqrt{\frac{2\varepsilon V}{M_0}}, \quad \ell_2 = \sqrt{\frac{æ V}{\Gamma M_0 c_p}}.$$

The ratio of these scales defines the nondimensional parameter

$$W_1 = \frac{\varepsilon \Gamma}{æ}(2c_p)$$

akin to those mentioned in (3.21). By introducing nondimensional variables

$$\begin{aligned} z' &= z/\ell_2, \\ T' &= T_z/T_0, \\ \mu' &= M/M_0, \\ L' &= L/M_0, \end{aligned}$$

where $T_0 = M_0/c_p$, one obtains from (4.20)

$$\begin{aligned} \widetilde{D}\xi_{z'} &= \mu'(\xi, T') - W_1 \xi_{z'z'}, \\ -\widetilde{D}T'_{z'} - \widetilde{D}L'\xi_{z'} &= (\mu'(\xi, T') - W_1 \xi_{z'z'})^2 + T_{z'z'}. \end{aligned} \tag{4.21}$$

where

$$\widetilde{D} = D' \sqrt{\frac{c_p}{æ \Gamma V M_0}}$$

is a normalized speed of the kink.

Consider the case of vastly differing length scales, with $\ell_1 \ll \ell_2$ or

$$W_1 \ll 1.$$

Then (4.21) is a singularly perturbed system and yields to the method of matched asymptotic expansions. An outer solution (zero approximation in W_1) satisfies

$$\begin{aligned} \widetilde{D}\xi_{z'} &= \mu', \\ -\widetilde{D}T_{z'} - \widetilde{D}L'\xi_{z'} &= T'_{z'z'} + (\mu')^2. \end{aligned}$$

The length scale for the inner problem is given by ℓ_1, therefore we introduce an extended coordinate

$$z'' = z'/\sqrt{W_1}$$

together with the normalized jump velocity

$$\tilde{\widetilde{D}} = \frac{\widetilde{D}}{\sqrt{W_1}}$$

The zero approximation for W_1 in (4.19) then gives

$$\begin{aligned} &T'_{z''z''} = 0 \\ &\xi_{z''z''} + \tilde{\widetilde{D}}\xi_{z''} - \mu'(\xi, T') = 0. \end{aligned} \tag{4.22}$$

One can see that equation $(4.22)_2$ is analogous to (4.11), so the corresponding analysis applies.

The structure of the phase boundary therefore has two embedded layers [87]. The internal parameter ξ changes most over a narrow ($\sim \ell_1$) isothermal transformation zone. A wide ($\sim \ell_2$) thermal boundary layer ahead of the moving "reaction" zone contains much less significant variations in ξ but accumulates most of the temperature change. These asymptotics are well known in the theory of laminar flames [53,91].

The eigenvalue velocity $\tilde{\tilde{D}}$ can be found from (4.22) (a condition for existence of a saddle-to-saddle orbit). The constant temperature T' of the internal layer plays the same role in this problem as the pressure p_1 did in the isothermal case (see the analysis centered around Figure 4); it is obtained after matching external and internal expansions. Thus the external problem supplies a system of jump conditions

$$\begin{aligned} [T'] &= 0, \\ [T'_{z'}] &= -\tilde{D}Q, \end{aligned} \tag{4.23}$$

where

$$Q = T'[s] + [g] \tag{4.24}$$

and T' comes from (cf. (4.16))

$$[g] = -\tilde{\tilde{D}} \int_{-\infty}^{\infty} \xi_{z''}^2 \, dz''. \tag{4.25}$$

The classical Stefan conditions for a planar front are identical with (4.23); however, the analogs of (4.24) and (4.25) are far more special:

$$\begin{aligned} Q &= T'[s], \\ [g] &= 0. \end{aligned} \tag{4.26}$$

One can show that equations (4.26) follow from (4.24) and (4.25) in the case of infinitely fast kinetics ($\Gamma^2 \varepsilon \to \infty$). If relaxation is not instantaneous, the dimensionless parameter W enters the resulting jump conditions through $\tilde{\tilde{D}} = \frac{D}{c_\infty \sqrt{W}}$. The second nondimensional parameter W_1 enters the extended system of jump relations through $\tilde{D} = \frac{D}{c_\infty} \sqrt{\frac{W_1}{W}}$ (see (4.23_2)).

5. Viscosity-capillarity type structure. As demonstrated in the previous section, the generalized Ginzburg-Landau model provides a description of both shocks and kinks. However, we were able to give a comprehensive analysis of kinks only in the case of slow (overdamped) motion when all inertial effects could be neglected. In this section, we shall focus on qualitative effects which emerge from an interplay between inertia and viscosity in cases of both fast and slow moving kinks.

For simplicity, we shall neglect the kinetic part of the model by assuming instantaneous response in ξ-space. This does not ignore kinetics entirely because (bulk) viscosity may have its origin in kinetic hindrance of density adjustments following the change of stress in the course of phase transformations; the model therefore gives a different description of kinetic dissipation inside the interface. By the same argument, our effective viscosity may differ for shocks and kinks.

Suppose we neglect the $\nabla\xi$ contributions to the energy so that

$$e = e(\xi, \rho, \nabla\rho, s). \tag{5.1}$$

The kinetic equation then takes the standard form

$$\dot{\xi} = -\Gamma\frac{\partial e}{\partial \xi}. \tag{5.2}$$

Letting $\Gamma \to \infty$, which is the assumption of instantaneous response, yields an equilibrium equation

$$\frac{\partial e}{\partial \xi}(\xi, \rho, \nabla\rho, s) = 0 \tag{5.3}$$

Suppose now that (5.3) can be solved for ξ and write the solution:

$$\xi = \tilde{\xi}(\rho, \nabla\rho, s). \tag{5.4}$$

whereupon substitution of this $\tilde{\xi}$ into the energy e provides

$$e = e(\tilde{\xi}(\rho, \nabla\rho, s), \rho, \nabla\rho, s) \equiv \tilde{e}(\rho, \nabla\rho, s). \tag{5.5}$$

This yields the model of a weakly nonlocal fluid of van der Waals-Korteweg type. If instead we would have left $\nabla\xi$ in the energy expression, then the equilibrium equation would have taken the form

$$\frac{\partial e}{\partial \xi} - \frac{1}{\rho}\operatorname{div}\left(\rho\frac{\partial e}{\partial \nabla\xi}\right) = 0, \tag{5.6}$$

in which case, inversion of (5.6) would give ξ as a functional of ρ, s and the boundary conditions for ξ. By taking (5.4) and (5.5) we limit outselves to a long wave approximation of an actual dispersion relation, using the language of a linear theory.

The simplest analysis of the discontinuity structure in a fluid with the energy (5.5), occurs in the isothermal (T = const) case. The system of equations (3.20) then has the form [79,85]:

$$\begin{aligned} \dot{\rho} &= -\rho v_x, \\ \rho\dot{v} &= \left(-\rho^2\frac{\partial e}{\partial \rho} + \rho\left(\rho\frac{\partial e}{\partial \rho_x}\right)_x - \rho\left(\frac{\partial e}{\partial \rho_x}\rho_x\right) + \eta v_x\right)_x, \end{aligned} \tag{5.7}$$

where η is an effective viscosity. Consider an energy of the form (ξ is already eliminated)

$$\tilde{e} = e_0(\rho) + \varepsilon_0(\rho)|\nabla\rho|^2, \tag{5.8}$$

where the local part of the energy e_0, taken as a function of $V = 1/\rho$, may be nonconvex. Although homogeneous spinodal states with $\frac{\partial^2 e_0}{\partial V^2} < 0$ are thermodynamically unstable, they would be expected to stabilize through evolution into narrow highly homogeneous zones (with the width $\leq \sqrt{\varepsilon_0}$), within which the second term on the right hand side of (5.8) dominates. Substitution of (5.8) into (5.7) gives

$$\begin{aligned} \dot{V} &= Vv_x, \\ \dot{v} &= V(-p(V) - 2\varepsilon V_{xx} + \frac{\partial \varepsilon}{\partial V} V_x^2 + \eta v_x)_x, \end{aligned} \tag{5.9}$$

where $V = 1/\rho$, $p(V) = -\frac{\partial e_0}{\partial V}$, and $\varepsilon(V) = \varepsilon_0(1/V)/V^4$. For the sake of simplicity we take $\varepsilon(V) = \text{const} > 0$, however all results are equally true for rather general nonnegative functions $\varepsilon(V)$. If $\varepsilon = \text{const}$ introduction of the extended coordinate $z' = z/\sqrt{\varepsilon}$ shows that η and ε will occur in (5.9) only in a nondimensional combination (cf. (3.21))

$$W = \eta/\sqrt{\varepsilon}.$$

For traveling wave solutions dependent on $z = x - Dt$ only, the system (5.9) integrates to give

$$\begin{aligned} (v - D)V^{-1} &= m, \\ p(V) + m^2 V + 2\varepsilon V_{zz} - \eta m V_z &= \pi, \end{aligned} \tag{5.10}$$

Where m and π are again the constants of integration. The second order ordinary differential equation (5.10_2) may be rewritten as a first order dynamical system

$$\begin{aligned} V_z &= \phi, \\ \phi_z &= (2\varepsilon)^{-1}\left[\eta m\phi - (p + m^2 V - \pi)\right]. \end{aligned} \tag{5.11}$$

Suppose that $m > 0$ and that the state ahead of the discontinuity with $V = V_2$ transforms to the state behind the discontinuity with $V = V_1$. Hence the boundary conditions are

$$V(z) \to \begin{cases} V_1, & z \to +\infty \\ V_2, & z \to -\infty \end{cases}. \tag{5.12}$$

Now the *RH* conservation laws follow immediately for any regular solution of (5.11) since at equilibria

$$p_1 + m^2 V_1 = p_2 + m^2 V_2 = \pi.$$

The system (5.11) with the boundary conditions (5.12) is clearly overdetermined (from every solution satisfying the boundary conditions one obtains a set of others by substituting $z + \text{const}$), therefore we obtained an eigenvalue problem: the solutions can be expected to exist only if the coefficients of the differential equations (5.11) m and π or the boundary values V_1 and V_2 satisfy *additional relation*. This relation may be considered a condition for the mass flux m, dissipation $\Re$, etc.

To fix the ideas, consider the subcritical van der Waals isotherm as a model $p(V)$ function (Figure 5).

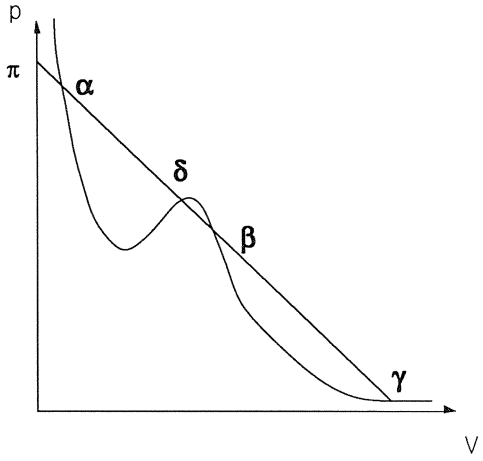

Figure 5. Sketch of an isotherm of the van der Waals' type; the Rayleigh line can intersect it in up to four points. It intersects the p-axis at $p = \pi$.

According to (5.12) the equilibria of the system (5.11) correspond to the intersection of a $p(V)$-isotherm with the Rayleigh line $p + m^2 V = \pi$. There can be up to four such points of intersection (Figure 5).

It is easy to check that the dynamical system (5.11) has only two type of equilibrium points: saddles (points α and β) and unstable nodes-focuses (points δ and γ). The prospective heteroclinic trajectories are as follows [85]:

1. *Shocks*

   (i) classical shock waves:

   $\gamma \to \beta$

   $\delta \to \alpha$ or $\delta \to \beta$, if δ is outside the spinodal $\left(\frac{\partial p}{\partial V} > 0\right)$ region;

   (ii) supersonic phase boundaries:

   $\gamma \to \alpha$

   (node(focus)-to-saddle orbits, the flow is supersonic with respect to states ahead and subsonic with respect to states behind; the Lax entropy criterion is satisfied)

2. "*Flames*"

   $\delta \to \alpha$ or $\delta \to \beta$, with δ in a spinodal (elliptic) region

   (node(focus)-to-saddle orbits, sound speed on one (δ) side is complex)

3. *Kinks*

   subsonic phase boundaries:

   $\beta \leftrightarrow \alpha$

   (saddle-to-saddle connection, the flow is subsonic with respect to both states ahead and behind; the Lax criterion is violated.)

For classical shock waves and supersonic phase boundaries the analysis is rather straightforward. As mentioned earlier, only the "entropy inequality" comes from an extended model. Nonlocality can manifest itself in the formation of an oscillating tail ahead of a sufficiently strong shock [12,85]. Suppose

$$c_2^2 = -V_2^2 \left(\frac{\partial p}{\partial V}(V_2) \right)$$

is the sound speed of the state in front and c_* is a critical speed defined by

$$c_*^2 = \frac{8}{8 - W^2} c_2^2.$$

Oscillations occur for

$$m^2 V_2^2 > c_*^2$$

and such a "dispersive" behavior is possible unless $W^2 \geq 8$. In the latter case viscosity dominates and all unstable equilibria are nodes.

Little can be said about "flames" without complete analyses of the nonsteady case. These solutions describe uniformly translating transformation fronts propagating into an unstable state. Such solutions can occur in a system that is suddenly quenched, if the ensuing dynamics are dominated by well-developed fronts moving in form the boundary. The dynamic stability of "flames" is questionable because it is apparently not the only way in which an unstable state may disintegrate. Although the spectrum of these nonlinear waves is continuous, experience with an analogous reaction-diffusion system (the Fisher-Kolmogorov equation) shows that some type of dynamical velocity selection may take place and a particular traveling wave may become an attractor for at least a portion of initial data [6,91].

Let's turn our attention to *kinks*. The saddle-to-saddle connections are singular and can be destroyed by a variation of the parameters m and π. If a desired solution (solutions) exists for a given π, the special m-values ensuring connection can be found as eigenvalues of a corresponding nonlinear boundary value problem; the resulting function $m^2(\pi; W)$ may not be single-valued. The occurrence of this relation gives rise to an additional constraint on the choice of the limiting values of the parameters beyond those given by the *RH* conditions. Some qualitative information about this dependence can be obtained without solving differential equations [83,85,86] (see also [28,45,75,76,79,80]).

Integrating of (5.11) gives

$$\varepsilon V_z^2 + g(V) = \eta m \int_{-\infty}^{z} V_z^2 dz + \text{const.}, \tag{5.13}$$

where

$$\begin{aligned} g(V) &= g(V; m^2, \pi) \\ &= \int^{V} (p + m^2 V - \pi) dV \end{aligned}$$

is defined up to a constant. Equation (5.13) is similar to (4.15) with the important distinction that g now depends on m^2 as a parameter. Following the line of reasoning which gave (4.16), now yields

$$[g] = -\eta m \int_{-\infty}^{\infty} V_z^2 dz,$$

where

$$\begin{aligned}
[g] &= g(V_2) - g(V_1), \\
&= \frac{p_1 + p_2}{2}(V_1 - V_2) - \int_{V_2}^{V_1} p dV, \\
&= [f] + \{p\}[V], \\
&= G.
\end{aligned}$$

Therefore

$$mG = -m^2 \eta \int_{-\infty}^{\infty} V_z^2 dz \leq 0. \tag{5.14}$$

The right hand side of (5.14) gives an explicit functional relation between the dissipation $\Re$ (see (2.7)) and the density (specific volume) distribution inside the interface:

$$\Re T = m^2 \eta \int_{-\infty}^{\infty} V_z^2 dz \geq 0. \tag{5.15}$$

For stationary ($m = 0$) solutions of (5.13) the RH condition gives $[p] = 0$ while the additional jump relation, $\Re = 0$, takes the form (Maxwell condition)

$$f(V_1^*) - f(V_2^*) + p^*(V_1^* - V_2^*) = 0,$$

where p^* is the common pressure in both phases, and V_1^*, V_2^* are the corresponding equilibrium volumes. Integration of (5.13) then gives:

$$\sqrt{\varepsilon} \int_{V_2^*}^{V} \frac{dv}{\sqrt{\tilde{g}(V_2^*) - \tilde{g}(v)}} = z - z_0,$$

where $\tilde{g}(V) = \int^{V} (p(v) - p^*) dv$. For solutions that are not stationary but with p close to p^* ($[g]$ close to zero), the dissipation $\Re$ is again quadratic in m, so delivering the explicit asymptotic result

$$m = -\gamma[g],$$

where the mobility of the phase boundary

$$\gamma = \left[\frac{\eta}{\sqrt{\varepsilon}} \int_{V_2^*}^{V_1^*} \sqrt{\int_{V_2^*}^{V} (p^* - p(v)) dv dV} \right]^{-1}$$

does not depend on the detailed behavior of the energy in the spinodal region.

The obvious mechanical analogy for (5.13) is that of a nonlinear pendulum with potential energy $g(V; m^2, \pi)$ and viscosity ηm. Without loss of generality one can take $m < 0$. Then, transitions from a maximum of potential energy to a minimum correspond to shocks, while transitions from a maximum to a maximum provide the structure of kinks.

Consider the behavior of the function $g(V; m^2, \pi)$ in a space of parameters m^2 and π. The bifurcation diagram, taken from [85], is presented at Figure 6.

The dividing lines on the bifurcation diagram (Figure 6) represent degenerate regimes (where maxima and minima coalesce); the corresponding marginal discontinuities, singled out from others by the property that the flow of the transforming material is sonic when observed from the transformation front, will be referred to as Chapman-Jouget (CJ) regimes. One can also see that the $\pi(m^2)$ curve depicted in Figure 6 represents *Legendre's transformation* of the function $p(V)$ from Figure 5[7].

Analysis of Figure 6 shows that kinks are possible only for the states inside the curvilinear quadrangle **BDEF**, while there is no apparent distinction between shock waves and supersonic phase boundaries on this diagram. All classical shocks will have nonoscillatory structure if the "pendulum" is overdamped ($W^2 > 8$). The Maxwell (**M**) line, corresponding to equilibrium phase transition, is given by the curve **ACG**. It is conceivable to have transitions from α to β (or to δ) that include intermediate visitations to a neighborhood of γ; we shall not discuss here these interesting regimes (see [35,85]).

It is instructive to look in more detail inside the curvilinear quadrangle **BDEF** and it will be convenient to deal with the plane (m^2, V) rather than (m^2, π). The transformation is given implicitly by

$$m^2 = m^2, \pi = p(V) + m^2 V.$$

Since our main interest is in $\alpha \leftrightarrow \beta$ type kinks, we shall choose two parameters $V = V_\alpha$ and $V = V_\beta$ instead of one π (two of four roots of the equation $\pi = p(V) + m^2 V$, specified in Figure 5). The transformation to the new variables corresponds geometrically to cutting the (m^2, π) plane along the **AG** line, which turns into two lines (there are two Maxwell states). The most interesting fragment of the new bifurcation diagram (inside the heavy box in Figure 6), together with schematically drawn functions $m^2(V, W)$ for different $W > 0$, are presented in Figure 7.

[7] In fact, for CJ regimes $\pi(m^2) = p(V) + m^2 V$, $m^2 = \frac{\partial p}{\partial V}$.

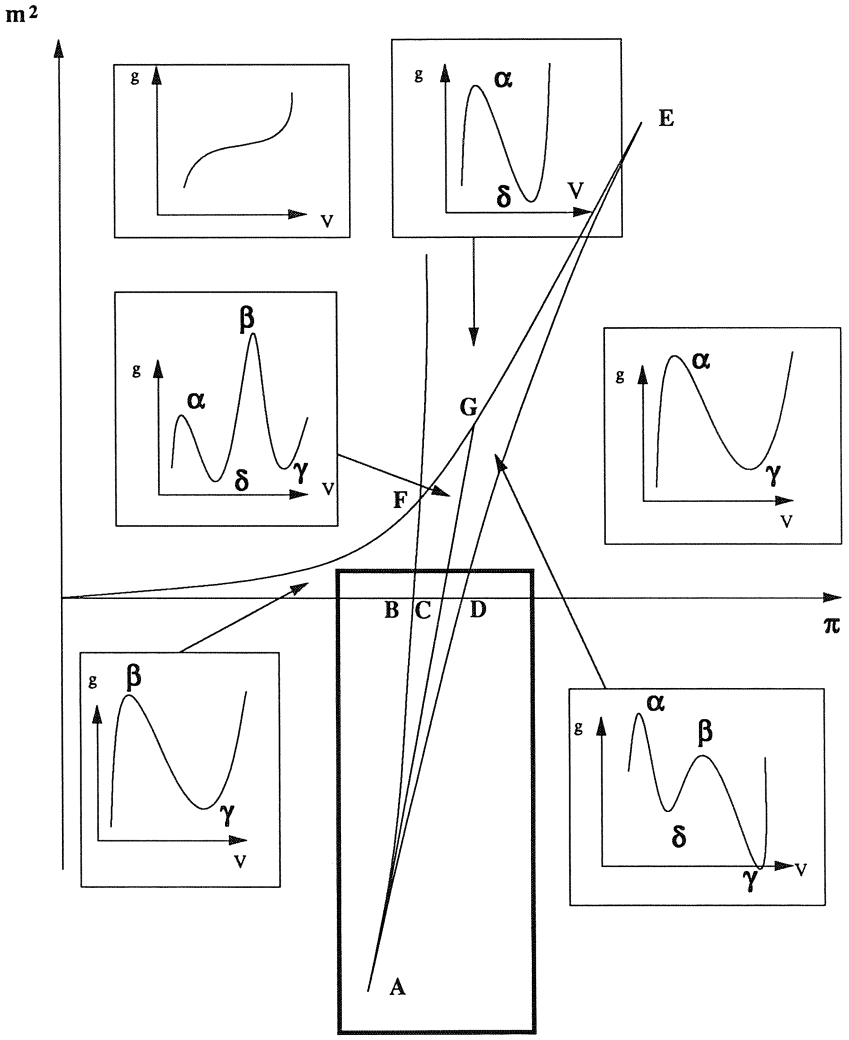

Figure 6. Bifurcation diagram for the potential function $g(V; m^2, \pi)$ from (5.13); $\alpha, \beta, \gamma, \delta$ are the same as in Figure 5. Boundaries, separating areas with the qualitatively different behavior of g (shown in boxes), correspond to Chapman-Jouget (CJ) regimes. The content of the heavy box is shown in more detail (in different coordinates) in Figure 7.

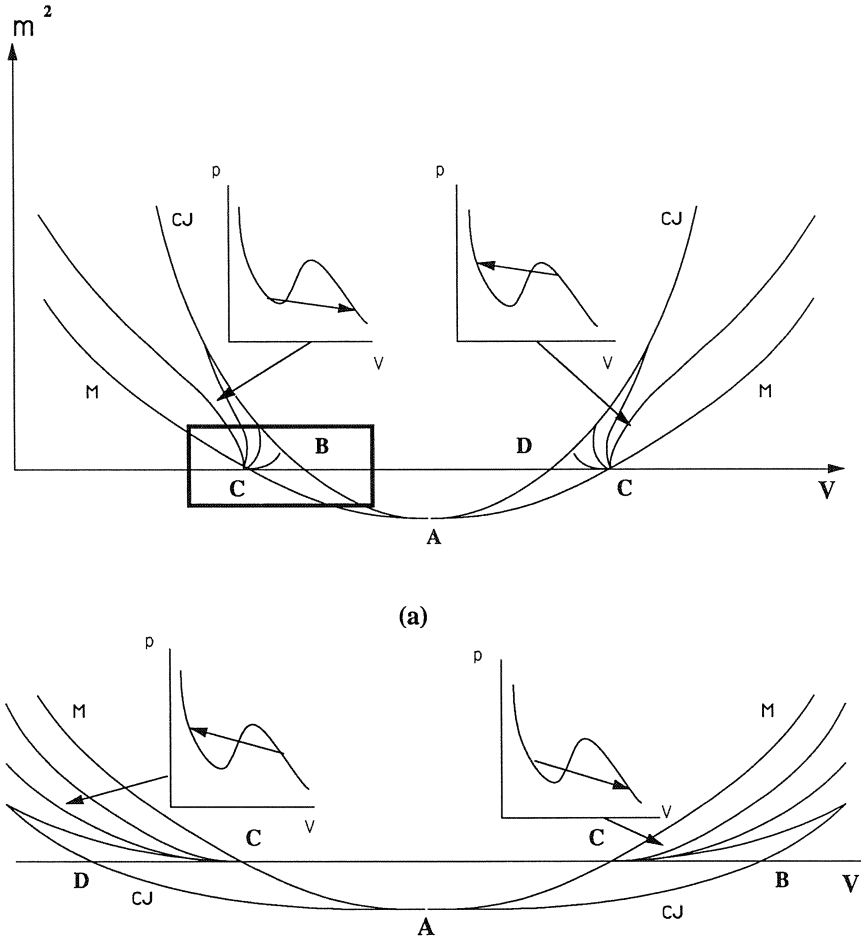

Figure 7. A fragment of the bifurcation diagram from Figure 6 (blow-up of the heavy box) in (m^2, V) coordinates with $m^2(V, W)$ sketched for different W; (a) $m > 0$, i.e. m^2 is given as a function of the state ahead of the kink (of V_2); (b) $m < 0$, i.e. m^2 is given as a function of the state behind the kink (of V_1). Although $m^2(V)$-functions for the same W look different in (a) and (b), these figures contain identical information. Corresponding kinks are shown in the boxes. The content of the heavy box is shown in more detail in Figure 8.

We now consider the qualitative behavior of the function $m^2(V)$ corresponding to saddle-to-saddle orbits. According to (5.13) these functions for different η and ε can be found implicitly from the system of equations

$$g(V_1) - g(V_2) = \eta m \int_{-\infty}^{\infty} V_z^2 dz, \tag{5.16}$$

$$p(V_1) + m^2 V_1 = \pi, \qquad p(V_2) + m^2 V_2 = \pi, \tag{5.17}$$

where $V(z)$ is a saddle-to-saddle connection that satisfies

$$\begin{gathered} \varepsilon(V)V_z^2 + g(V) - g(V_2) = \eta m \int_{-\infty}^{z} V_z^2 dz, \\ V \to \begin{cases} V_1, & z \to +\infty \\ V_2, & z \to -\infty \end{cases}. \end{gathered} \tag{5.18}$$

After the boundary value problem (5.18) is solved and the integral on the right hand side of (5.16) is known as a function of T, m, V_1, V_2, η, and ε, the desired relation between m and π can be obtained form (5.16) with V_1 and V_2 taken form (5.17). In the two limiting cases the function $m^2(V_2)$ is known. The first, when $\eta = 0$, gives rise to a reversible transition in which the dynamical system is Hamiltonian and the Maxwell (equal area) construction gives

$$\begin{gathered} \int_{V_1}^{V_2} (p + m^2 V - \pi) dV = 0 \\ p(V_2) + m^2 V_2 = p(V_1) + m^2 V_1 = \pi \end{gathered} \tag{5.19}$$

These regimes are represented in Figures 6 and 7 by the curve **AC**. In the opposite limiting case of a very viscous material ($\eta \to \infty$) the appropriate (m, π)-pairs are

$$\begin{aligned} m &= 0 \\ \pi &= p(V_1) = p(V_2) \end{aligned} \tag{5.20}$$

Admissibility relations (5.20), predicting mechanically equilibrated *metastable stationary configurations*, have been used in [65,74]. If $\varepsilon = \text{const}.$, (5.20) corresponds to the case $W = \eta/\sqrt{\varepsilon} = \infty$; these regimes are represented in Figures 6 and 7 by the segments **CB** and **CD**.

A general feature of weakly dissipative system (W small), discovered for the special case in [60], is that m^2, taken as a function of the state in front of the discontinuity ($m^2(V_2), m > 0$), must be two-valued [86,88] (see Figures 7 and 8).

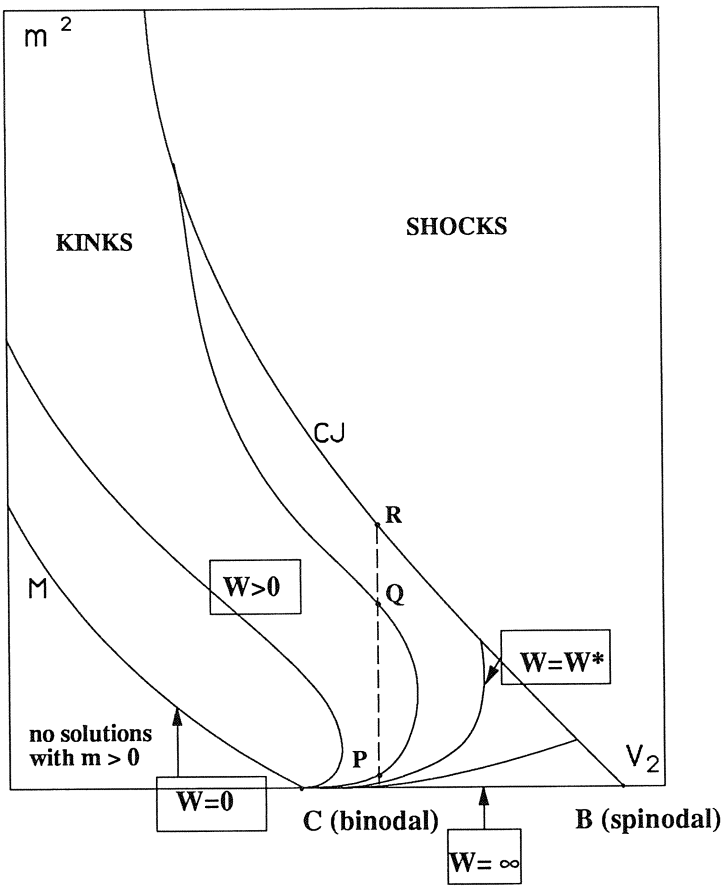

Figure 8. A fragment of the diagram from Figure 7 (blow-up of a heavy box). P and Q are slow and fast kinks, corresponding to the same state ahead of the discontinuity, R is a Chapman-Jouget (CJ) regime.

To show this two-valuedness, a straightforward calculation, based on (5.16, 5.17) gives

$$\frac{\partial \pi}{\partial V_2} = \frac{\partial p}{\partial V_2} + m^2 + \frac{\partial m^2}{\partial V_2} V_2,$$

$$\frac{\partial}{\partial V_2}(g(V_1) - g(V_2)) = \left(\frac{V_1^2 - V_2^2}{2}\right) \frac{\partial m^2}{\partial V_2} - (V_1 - V_2)\frac{\partial \pi}{\partial V_2},$$

$$\frac{\partial}{\partial V_2}\left(\eta m \int_{-\infty}^{\infty} V_z^2 dz\right)\Bigg|_{\substack{V_2=V_2^* \\ m=0}} = \frac{\partial m}{\partial V_2}\Bigg|_{\substack{V_2=V_2^* \\ m=0}} \int_{V_2^*}^{V_1^*} \frac{\eta}{\sqrt{\varepsilon}} \left[\int_{V_2^*}^{V} (p^* - p(v))dv\right]^{1/2} dV,$$

and hence

$$(5.21)\qquad \frac{1}{2}\frac{\partial m^2}{\partial V_2} \to \begin{cases} \dfrac{\left.\frac{\partial p}{\partial V_2}\right|_{V_2^*}}{V_1^* - V_2^*} & < 0, \ (\eta = 0) \\ m\left[\dfrac{\left.\frac{\partial p}{\partial V_2}\right|_{V_2^*}(V_2^* - V_1^*)}{\int_{V_2^*}^{V_1^*} \frac{\eta}{\sqrt{\varepsilon}}\left[\int_{V_2^*}^{V}(p^* - p(v))dv\right]^{1/2} dV}\right] & > 0, \ (\eta > 0) \end{cases}$$

when $V_2 \to V_2^*$, $m \to 0 (m \geq 0)$.

It is clear from (5.21), that $m^2(V_2) > 0$ for $\eta > 0$ and sufficiently small positive V_2 (the graph of $m^2(V_2)$ initially goes to the right of the point C (see Figure 8)). On the other hand, for small η, $m^2(V_2)$ must be close to the equilibrium (Maxwell) line $m^2(V_2, 0, \varepsilon)$. Furthermore direct calculation gives

$$(5.22)\qquad \frac{1}{2}\frac{\partial m^2}{\partial \eta} \to \frac{\int_{V_2}^{V_1}\left(\frac{1}{\sqrt{\varepsilon}}\sqrt{\int_{V_2}^{V}\left(p(V_2) - p(\mu) - \frac{p(V_1)-p(V_2)}{V_2 - V_1}(\mu - V_2)d\mu\right)}\right)dV}{(V_1 - V_2)^2} > 0$$

when $\eta \to 0$ and $V_2 < V_2^*$[8]. This ensures the presence of "almost equilibrium" curves $m^2(V_2)$ lying above the Maxwell line (for $V_2 < V_2^*$) and approaching it as $\eta \to 0$. But, according to (5.21), these curves start with $V_2 > V_2^*$. We thus conclude the existence of a turning point and, at least in the vicinity of this point, two subsonic solutions, m_1 and m_2, are available for a given V_2 (see Figure 8); for $W > W^*$ the turning point will be in the supersonic (shock) domain (see Figure 8).

The discussion in section 4 of an alternative (Ginzburg-Landau) model neglected inertial terms and so was only able to describe initial (slow) segments of the curve $m^2(V_2)$; this segment of a "normal growth" becomes infinitely narrow as $W \to 0$. At the same time, the analysis of viscous structure supports an idea, known from acoustics of relaxing fluids [61], that for sufficiently slow mechanical processes relaxation of internal parameters can be adequately described with the aid of an effective bulk viscosity.

Since equations (5.18) and (4.15) are identical in form, an analytical solution analogous to (4.18) is available for (5.18) whenever g is a fourth order polynomial [60,86]. In this case the function $\Re(m)$ can be written in an explicit form [86].

Suppose for example that the isotherm $T = T_0$ is given by the cubic polynomial:

(5.23)

$$p(V, T_0) = p^*(T_0) - K(T_0)(V - V_1^*(T_0))(V - V_2^*(T_0))\left(V - \frac{V_1^*(T_0) + V_2^*(T_0)}{2}\right),$$

where the parameters have been chosen in such a way that $V_1^*(T_0)$ and $V_2^*(T_0) < V_1^*(T_0)$ are Maxwell (equilibrium) specific volumes of coexisting phases, $p^*(T_0)$ is

[8]The value $V_1 = V_1(V_2)$ in the r.h.s. of (5.22) is calculated from the solution of (5.19) corresponding to the dynamic Maxwell ($\eta = 0$) regime with the prescribed state ahead of the phase boundary (V_2).

a Maxwell pressure and $K(T_0)$ characterizes the width of the pressure range Δp between binodal and spinodal (between points **C** and **D** or **C** and **B** in Figures 6-8):

$$\Delta p = \left(\sqrt{3}/144\right) K(\Delta V)^3.$$

The anticipated solution of (5.18) with $p(V)$ taken from (5.23) is exactly analogous to (4.18):

$$V(z) = \frac{V_2 + V_1}{2} + \frac{V_2 - V_1}{2} th\left[\sqrt{\frac{K}{\varepsilon}}\frac{V_2 - V_1}{4}(z - z_0)\right] \tag{5.24}$$

where $V_2 = V(-\infty) < V_1 = V(+\infty)$ and $m > 0$ so that the wave moves to the left and the state with $V = V_2$ transforms into the state with $V = V_1$; the width of the phase boundary scales with

$$\frac{\sqrt{\varepsilon}}{\sqrt{K}|V_2 - V_1|}.$$

A relation between V_1 and V_2 is obtained by introducing the normalized variables

$$x = \frac{V_2 + V_1}{\Delta V} - \frac{V_1^* + V_2^*}{\Delta V}$$
$$y = \frac{V_1 - V_2}{\Delta V}$$

where $\Delta V = V_1^* - V_2^*$. This relation (a result of the substitution of (5.24) into the (5.23)) takes the form [86]:

$$y^2 + \zeta x^2 = 1 \tag{5.25}$$

where $\zeta = 3\left(1 - \frac{12}{W^2}\right)$. The calculation shows that

$$m = \frac{3\sqrt{K}}{W}\Delta V x$$
$$\Re T_0 = \frac{1}{4} K m (\Delta V)^4 y^3 x$$

and finally

$$\Re(m) = \frac{a}{T_0} m^2 (1 + bm^2)^{3/2} \tag{5.26}$$

where

$$a = \frac{W\sqrt{K}(\Delta V)^3}{12}, \quad b = \frac{12 - W^2}{3(\Delta V)^2 K}.$$

Relation (5.26) gives in *explicit form* of an additional jump condition required for kinks.

For slow kinks

$$\Re(m) = \frac{am^2}{T_0} + \frac{3ab}{2T_0} m^4 + \ldots,$$

and a quadratic (normal growth) approximation for the entropy production is adequate up to the terms of fourth order in m, moreover it is *exact* if $W^2 = 12$. It can be shown that the envelope of the family of kinetic curves $G = -\Re T_0/m$ vs. m, parametrized by W, corresponds to the CJ regimes

$$V_1 + 2V_2 = \frac{3}{2}(V_1^* + V_2^*)$$

or

$$\frac{G}{K(\Delta V)^4} = -\frac{3}{4}\left(\frac{1}{4} + \left(\frac{m}{\sqrt{K}\Delta V}\right)^2\right)^2$$

Different kinetic relations between the thermodynamic "force" G and the "flux" m, stemming from (5.25), are presented in Figure 9[9]. Graphical representation of V_1 and m as functions of V_2 can be found in [88].

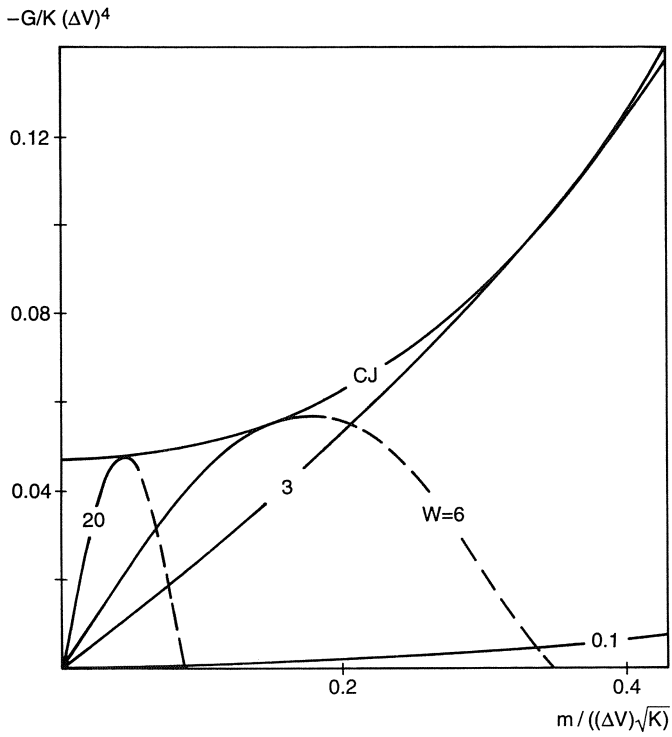

Figure 9. Kinetic laws, following from the exact solution (5.24) for different W; here G is the "driving traction" and m is the conjugate mass flux; solid lines – kinks, dashed lines – flames.

[9] Another exact solution of (5.18), recently obtained in [4] for the piecewise quadratic energy function, gives qualitatively similar kinetic relations.

An interesting property of this solution is that, if the viscosity is sufficiently large ($W^2 \gg 12$), then the phase transformation remains nearly "frozen" until the critical driving traction is achieved whereupon the phase boundary travels at close to the local acoustic velocity. One can expect threshold phenomena to be associated with this case for

$$G^* \approx -(3/64)K(\Delta V)^4 = (9\sqrt{3}/4)\Delta p \Delta V.$$

This also explains "stability" of the metastable states for $0 > G > G^*$; recall that $m(W) \to 0$ as $W \to \infty$, so that mechanically (but not "chemically") equilibrated metastable configurations become admissible in the limit of $\varepsilon \to 0$, $\eta \to 0$, but $\eta^2/\varepsilon \to \infty$.

We felt that for the sake of simplicity we could disregard heat conduction. However, the analogy between slow moving viscous kinks and nonequilibrium Ginzburg-Landau type kinks may be pursued further and the coupled thermomechanical problem can be solved in a case in which the thermal and capillary length scales are separated ($W_1 = \frac{\varepsilon}{\varkappa^2} \to 0$) [81,85]. The analysis of the structure problem in the full thermomechanical setting can be found in [36,44,62].

6. Summary and conclusions. It is the intention of this paper to offer a unified discussion of the question of determinancy for phase transitions, namely to decide which of the transformation processes, still permitted by the conservation laws, are excluded through the combined action of dissipation and nonlocality. We consider two types of discontinuous (weak) solutions which occur naturally in a quasilinear nonstrictly hyperbolic or mixed (elliptic-hyperbolic) type system of conservation laws. A discontinuity of the first type (*shock*), supersonic with respect to particles ahead of it, is a classical object of study in the mechanics of shock waves. The discontinuity of the second type, which we, borrowing terminology from the modern physics, refer to as a *kink*, is subsonic. While dissipative terms play an essential role in the formation of the structure of shocks, dispersion is necessary for smoothing kinks. In contrast to shocks, where constitutive parameters of an extended system can at most influence the interface width, the behavior of kinks strongly depends on the nondimensional combinations of these parameters through an additional jump condition. In a classical limit of an infinitely thin interface, these parameters, characterizing dissipative and dispersive properties of the system, tend to zero. The limits of their nondimensional combinations (necessary for the closure of the original system of equations), should be considered as an *essential supplement* to the classical description.

Two important questions have not been addressed in this paper.

The first relates to a case of nonplanar interfaces. For moderate curvatures, geometrical corrections to the resulting jump relations are known (e.g. Gibbs-Thompson conditions and their generalizations [42]) and in some cases can be obtained from consideration of the interface structure. One would still anticipate novel effects whenever one of the curvature radii is on the order of the interface width.

The second problem, not completely independent of the first problem, deals with the structural and morphological stability of kinks. A particularly important

question is whether or not the observed formation of a macroscopic two phase liquid-vapor mixture in dynamic experiments [82] is a manifestation of a *2D instability* of a subsonic plane front. Such a possibility is strongly suggested by the Landau theory of turbulization of flames, although a number of stabilizing mechanisms are also available. Another possibility is that the formation of mixtures might result from an internal *1D instability* of the monotonous structure of kinks with a transition to a nearby "mixture"-containing nonsteady regime characterized by vigorous oscillations of density in a spinodal region. We realize, however, that our model is inadequate for the simulation of *equilibrium mixtures*. The corresponding theory would require at least two internal scales of length in the conservative part of the model [7].

Appendix 1. Relaxation described by the kinetic equation (3.15) is not the only possible dissipative mechanism in the interphase region. Thus, one may consider other types of kinetic equations, for example,

$$\rho\dot{\xi} = \operatorname{div}(D\nabla\mathcal{A}) \qquad (\textit{diffusion}) \tag{A1.1}$$

or

$$\operatorname{div}(\lambda\nabla\dot{\xi}) = \rho\mathcal{A} \qquad (\textit{viscosity}) \tag{A1.2}$$

If material parameters D and λ are positive, both models (A1.1) and (A1.2) provide a positive definite internal dissipation up to a pure *divergence* term which may be eliminated by the suitable choice of the vector $\boldsymbol{\omega}$ in (3.13).

Consider (A1.1) first. Suppose that we can neglect heat conduction ($\mathbf{q} = 0$, $T = T_0$) and a flow is "dissipation free in the narrow sense" ($\rho\dot{\mathbf{v}} - \operatorname{div}\mathbf{P} = 0$), so that the standard terms do not complicate the entropy production inequality. Following the pattern of diffusion theory (cf. also [39,40]), define

$$\mathbf{h} = \frac{D}{T_0}\mathcal{A}\nabla\mathcal{A},$$
$$\mathbf{r}' = 0,\ \mathbf{t}' = 0,\ \mathbf{P}' = 0$$

so that (A1.1) implies

$$\rho\chi = D|\nabla\mathcal{A}|^2 \geq 0.$$

The kinetic equation (A1.1), i.e.

$$\rho\dot{\xi} = \operatorname{div}\left(D\nabla\left(\frac{\partial e}{\partial\xi} - \frac{1}{\rho}\operatorname{div}\left(\rho\frac{\partial e}{\partial\nabla\xi}\right)\right)\right) \tag{A1.3}$$

generalizes a classical diffusion equation, where ξ plays the role of concentration. If the expression (3.17) is taken for the energy, then (A1.1) gives

$$\rho\dot{\xi} = \operatorname{div}\left(D\nabla\left(\frac{\partial e_0}{\partial\xi} - 2\varepsilon\Delta\xi\right)\right),$$

which is a Cahn-Hilliard equation [15,39,40,63,64]. Unlike the relaxation model (3.15), (A1.3) with suitable (no-flux) boundary conditions yields conservation of the volumetric average of ξ.

Suppose now that the second mechanism of dissipation, (A1.2), applies. We term λ the generalized viscosity. If we assume that

$$\text{(A1.4)} \qquad \begin{aligned} &\mathbf{r}' = \lambda \nabla \dot{\xi}, \\ &\mathbf{h} = 0,\ \mathbf{t}' = 0,\ \mathbf{P}' = 0 \end{aligned}$$

and since the kinetics is governed by (A1.2), the internal dissipation takes the form

$$\rho\chi = \lambda |\nabla \dot{\xi}|^2 \geq 0.$$

The kinetic equation (A1.2)

$$\operatorname{div}(\lambda \nabla \dot{\xi}) = \rho \left(\frac{\partial e}{\partial \xi} - \frac{1}{\rho} \operatorname{div} \left(\rho \frac{\partial e}{\partial \nabla \xi} \right) \right)$$

under the additional assumption (3.17) further reduces to

$$\operatorname{div}(\lambda \nabla \dot{\xi}) = \rho \left(\frac{\partial e_0}{\partial \xi} - 2\varepsilon \Delta \xi \right).$$

To emphasize the name of the generalized viscosity for λ, consider the analogous approach for another dissipative term $(\rho \dot{\mathbf{v}} - \operatorname{div} \mathbf{P}) \cdot \dot{\mathbf{x}}$ in (3.13), bearing in mind that $(\rho \dot{\mathbf{v}} - \operatorname{div} \mathbf{P})$ and $\dot{\mathbf{x}}$ replace $\rho \mathcal{A}$ and $\dot{\xi}$, respectively. For the sake of simplicity, we temporarily consider ξ to be constant and neglect heat conduction so that

$$\rho T \dot{s} = (\rho \dot{\mathbf{v}} - \operatorname{div} \mathbf{P}) \cdot \dot{\mathbf{x}} - \operatorname{div}(\mathbf{h} + \mathbf{t}' \operatorname{div} \mathbf{v} + \mathbf{P}'^{T} \mathbf{v}).$$

Following (A1.4), assume

$$\mathbf{P}' = \mathbf{L}[\nabla \dot{\mathbf{x}}],$$

$$\mathbf{h} = 0,\ \mathbf{t}' = 0,\ \mathbf{r}' = 0,$$

where we have introduced a fourth-order tensor of viscous moduli $\mathbf{L}$ with suitable symmetry properties.

A kinetic equation, analogous to (A1.2), takes the form

$$\operatorname{div} \mathbf{L}[\nabla \dot{\mathbf{x}}] = \rho \dot{\mathbf{v}} - \operatorname{div} \mathbf{P}$$

or

$$\rho \dot{\mathbf{v}} - \operatorname{div}(\mathbf{P} + \mathbf{P}') = 0.$$

The internal dissipation is now

$$\rho\chi = (\nabla \dot{\mathbf{x}}) \cdot \mathbf{L}[\nabla \dot{\mathbf{x}}] \geq 0,$$

and the conditions of its positive definiteness are well known. Hence, we obtain the classical model of a viscous fluid, modified by the inclusion of weak (differential) nonlocality (in ρ). This model is known as the viscosity-capillarity model [29,31,75,79,83]. The new model (A1.2) describes a "Stokes' approximation" in the dynamics of the scale ξ-field.

Let us mention that any *combination* of kinetic mechanisms providing nonnegative dissipation may be considered as well. The choice of the particular model to be used depends on the nature of an internal parameter ξ and is determined by the *microscale analysis* of the physics of the dissipative process. The obvious advantage of the consistent thermodynamic approach outlined above is that it guarantees a universal Lyapunov function.

Appendix 2. In this paper, our main goal was to calculate the entropy production associated with the motion of a *surface defect*. For the moving *line defect*, which models, for example, the tip of a semi-infinite crack, the total energy release rate (the analog of our dissipation) is given by a formula similar to (2.7), where the role of driving traction G in (2.8) is played by the J-integral – a "thermodynamic force" that is a work conjugate to the amount of crack advance [70,43]. The common origin of both quantities in the Eshelby energy-momentum tensor is well known [25,26,69].

When the fracture is *ideally elastic-brittle* and no dissipation is assumed ("equilibrium Griffith crack"), the analog of the Maxwell pressure–a *critical applied stress intensity factor*–can be found from the condition $J = 0$ (no dissipation, no singularity)[10]. The domain of integration for J can be divided into two parts: an exterior domain, where linear elasticity theory is legitimate and an interior (cohesive) domain, where deformations are large and nonlinear elasticity theory must be used. The exterior part of the J-integral can be rewritten in terms of the *applied stress intensity factor*, which completely characterizes a singular "far field" solution of a linear external problem. The "Maxwell condition" therefore specifies a *critical value* of this parameter by linking it to a solution of a nonlinear internal problem. As in the case of kinks, the details of a cohesive zone (CZ) structure have no influence on the "equilibrium" critical stress intensity factor.

The asymptotic approach to a CZ structure in the theory of cracks [8,9] is equivalent to our approach to the problem of the fine structure of the discontinuity. Namely, the external solution is constructed, corresponding to the singular solution of the problem of linear elasticity theory for a cracked body subjected to applied loads. This solution holds everywhere except for a neighborhood of the crack tip region. The internal solution has a characteristic linear scale of the tip region which is said to be autonomous (separation of scale lengths). In the classical limit the "nonlinear" domain shrinks to a point, however its contribution to J remains finite and is sometimes expressed in terms of a surface (or fracture) energy. The related internal boundary value problem is one dimensional and is formulated for an integral equation that assumes *strong nonlocality*. In a Dugdale-Barenblatt CZ model, one can introduce two characteristic lengths; the critical crack opening displacement δ

[10]If inertial effects are neglected, this condition does not involve the speed of the crack.

and the size of a cohesive zone h. In the classical limit, both δ and h tend to zero while $\delta/\sqrt{h}$ remains finite. This ratio, when multiplied by a proper elastic modulus, determines (up to a numerical multiplier) the critical stress intensity factor and therefore controls the singular solution.

Consideration of crack dynamics requires the analysis of irreversible processes in a zone surrounding the crack tip. Thus, if the fracture is not ideally brittle and dissipation is present, then the condition $J = 0$ (the Maxwell condition) is no longer justified; one may then seek the kinetic relation between J and the crack propagation speed [9,30,69,70]. This description of crack mobility is not unlike a kinetic relation of the type shown on Figure 9 (case $W^2 \gg 12$). Any applied supercritical load ($J > 0$) then gives rise to crack motion, although it may be indetectable. The idea that the crack is almost stationary until attaining a critical "driving traction" (critical J in this case) is supported by elastoplastic fracture mechanics, where Irwin's concept of a critical applied stress intensity factor (*fracture toughness*) as a threshold for a catastrophic failure has proven to be useful [30].

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