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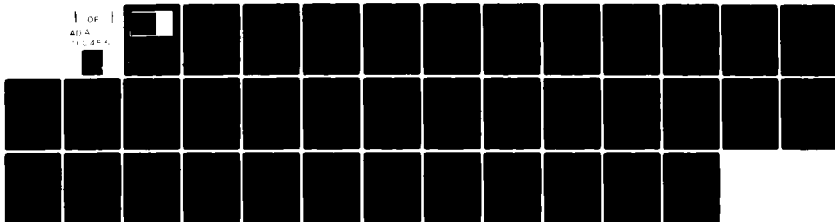
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DYNAMIC PHASE TRANSITIONS
IN A VAN DER WAALS FLUID

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MATHEMATICS RESEARCH CENTER

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ABSTRACT

This paper proves the existence of traveling wave solutions connecting liquid and vapor phases in a van der Waals fluid. The main constitutive assumptions are that the fluid be an elastic fluid (with pressure given by the van der Waals equation of state) possessing a higher order correction given by Korteweg's theory of capillarity and the fluid is a conductor of heat with large specific heat at constant volume. The main mathematical tool in the analysis is the Conley-Easton theory of isolating blocks.

AMS (MOS) Subject Classifications: 80A10, 76T05, 76N99, 35B99, 35M05, 35L65,
35L67

Key Words: phase transitions, van der Waals fluid, traveling waves, isolating
blocks

Work Unit Number 2 - Physical Mathematics

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SIGNIFICANCE AND EXPLANATION

In the study of phase transitions in fluids a typical model given in classical thermodynamics is provided by the equilibrium configurations of a van der Waals fluid. Such equilibria show a fluid may exist in two phases, liquid and vapor. Relatively untouched in classical thermodynamics is the non-equilibrium case. This paper attempts to study this problem from the viewpoint of examining the dynamics of liquid - vapor phase transitions. The main mathematical idea is to look for traveling wave solutions of the relevant balance laws and show the desired connections from one phase to another can be made. Since the equations are analogous to those modeling phase transitions of the "martensitic" or "shape memory" type in solids the results given here may prove of value in that case as well.

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DYNAMIC PHASE TRANSITIONS IN A VAN DER WAALS FLUID

M. Slemrod*

0. Introduction

The purpose of this paper is to prove the existence of traveling wave solutions connecting liquid and vapor phases in a van der Waals fluid. In an earlier paper [1] I considered this problem when the fluid is emersed in a heat bath thus forcing temperature to be constant. Here no such assumption is made; the motions are not isothermal. The constitutive hypotheses made are that the fluid be (i) an elastic fluid with pressure given by the van der Waals equations of state (see (1.7)) possessing (ii) a higher order correction term given by Korteweg's theory of capillarity (see (1.5)) and that the fluid be (iii) a heat conductor with a large specific heat at constant volume. Under these hypotheses I show that given an equilibrium state in the stable part of the liquid (respectively, vapor) phase there is a second equilibrium in the vapor (liquid) phase to which it may be connected with a traveling wave of positive (negative) speed. Thus all the vapor (liquid) is converted into liquid (vapor). I also prove that in both cases the liquid equilibrium phase is at a higher temperature then the vapor equilibrium phase to which it is connected.

The main tool of the analysis is the Conley-Easton theory of isolating blocks [2]. This theory has been applied by Carpenter [3] to prove the existence of traveling wave solutions to a generalization of the Fitzhugh-

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Nagumo equations modeling nerve impulse transmission. Surprisingly the equations governing traveling wave solutions in the phase transition problem given here and the generalized Fitzhugh-Nagumo equations are similar. In fact I show a modification of Carpenter's approach to the wave impulse equations yields the desired traveling wave solution to the phase transition problem.

While this paper is devoted to fluid mechanics, it is closely related to a recent paper of James [4]. In that paper he used a similar constitutive model to discuss phase transitions in a solid exhibiting shape memory. He showed that a knowledge of the non-isothermal dynamical phase transitions can be used to determine certain constitutive parameters, e.g. the well known Maxwell line. Since the theory given here gives conditions for such dynamical phase transitions, it may prove useful in the study of shape memory solids as well as fluids.

1. One dimensional Lagrangian description of compressible fluid flow.

We follow the presentation of Courant and Friedrichs [5] of a Lagrangian description of compressible fluid flow based on the law of conservation of mass. The fluid flow is thought of as taking place in a tube of unit cross section along the x -axis. We attach the value $X = 0$ to any definite "zero" section moving with the fluid. For any other section we let X be equal in magnitude to the mass of the fluid in the tube of unit cross sectional area between that section and the zero section. Analytically the quantity X satisfies the relation

$$X = \int_{x(0,t)}^{x(X,t)} \rho(x,t) dx \quad (1.1)$$

Here $\rho(x,t)$ denotes the density at position x and time t and $x(X,t)$ denotes the position of a particle which encloses a mass X of fluid in the tube bounded by $x(X,t)$ and $x(0,t)$. Differentiation of (1.1) implies $1 = x_x(X,t)\rho(x(X,t),t)$. Set $\rho(x(X,t),t) = \tilde{\rho}(X,t)$, $w(X,t) = \tilde{\rho}(X,t)^{-1}$ (the specific volume), $u(X,t) = x_t(X,t)$ (the velocity).

Also we let

p	the pressure,
τ	the stress,
ϵ	specific internal energy,
$E \equiv \frac{u^2}{2} + \epsilon$	specific total energy,
q	specific heat absorption,
h	heat flux,
b	specific body force,
θ	absolute temperature,
η	specific entropy,
$\psi \equiv \epsilon - \theta\eta$	specific Helmholtz free energy,
c_v	specific heat at constant volume,
α	coefficient of thermal conductivity.

The equations of balance of linear momentum, energy, and mass become

$$\begin{aligned}\rho \ddot{x} &= \tau_x + \rho b \quad , \\ \rho \dot{\epsilon} &= \rho q + \tau \dot{x}_x + h_x \quad , \\ \dot{\rho} + \rho \dot{x}_x &= 0 \quad ,\end{aligned}\tag{1.2}$$

where $\dot{} = \frac{d}{dt}$. We now apply the chain rule and rewrite (1.2) in terms of the independent variables X, t to obtain

$$\begin{aligned}x_{tt} &= \tau_x + b \quad , \\ \epsilon_t &= \tau x_{tX} + h_x + q \quad , \\ (\tilde{\rho} x_x)_t &= 0 \quad ,\end{aligned}\tag{1.3}$$

where we have used the fact that $\dot{\rho}(x, t) = \tilde{\rho}_t(X, t)$. (1.3;c) is automatically satisfied since $\tilde{\rho} x_x = 1$. Hence (1.3) reduces to the first order system

$$\begin{aligned}u_t &= \tau_x + b \quad , \\ w_t &= u_x \quad , \\ E_t &= (\tau u)_x + h_x + q \quad .\end{aligned}\tag{1.4}$$

The above set of balance laws must be supplemented by constitutive relations for τ , ϵ , h , ψ . We assume the fluid is a heat conductor, slightly viscous, with stress given by Korteweg's theory of capillarity [6].

Specifically this means

$$\begin{aligned}
\tau &= -p(w, \theta) + \hat{\mu}(w, \theta)u_x + D(w, \theta)w_x^2 - C(w, \theta)w_{xx} \quad , \\
\epsilon &= \hat{\epsilon}(w, \theta) \quad , \\
h &= \hat{h}(w, u_x, \theta, \theta_x) \quad , \\
\psi &= \hat{\psi}(w, \theta) \quad , \\
\eta &= \hat{\eta}(w, \theta) \quad ,
\end{aligned}
\tag{1.5}$$

where $\hat{\eta}, p$ satisfy the thermodynamic relations

$$\hat{\eta} = -\frac{\partial \hat{\psi}}{\partial \theta}, \quad p = -\frac{\partial \hat{\psi}}{\partial w} \quad , \tag{1.6}$$

and $\hat{\mu}, D, C$ are small.

The reason for introducing Korteweg's theory is the following: Our main interest is in the case where p is a non-monotone function of w for fixed θ so that p_w can be both positive and negative for different values of (w, θ) . For the case of an elastic fluid $\tau = -p(w, \theta)$, (1.4) is a mixed hyperbolic-elliptic initial value problem on fixed isotherms $\theta \equiv \text{constant}$. But such a problem is ill-posed for initial data in lying the in the elliptic domain. One way to circumvent this difficulty is to consider higher order effects which become important precisely in the elliptic domain, namely viscosity and interfacial capillarity. One theory of capillarity is Korteweg's and a discussion of his work may be found in the monograph of Truesdell and Noll [7]. We note that Korteweg's theory has most recently been reconsidered by Serrin [8] who has applied it to the study of finding conditions for equilibrium of fluid and vapor phases in a van der Waals fluid. (A related theory of capillarity based on statistical mechanics has been presented in [9].)

We shall assume p in the constitutive relation (1.5;a) is given by the van der Waals equation of state

$$p(w, \theta) = \frac{R\theta}{w-b} - \frac{a}{w^2} \quad , \quad 0 < b < w < \infty \quad , \tag{1.7}$$

where a, b, R are all positive constants [10], [11], [12]. Pictorially the isotherms of p are represented in Figure 1.

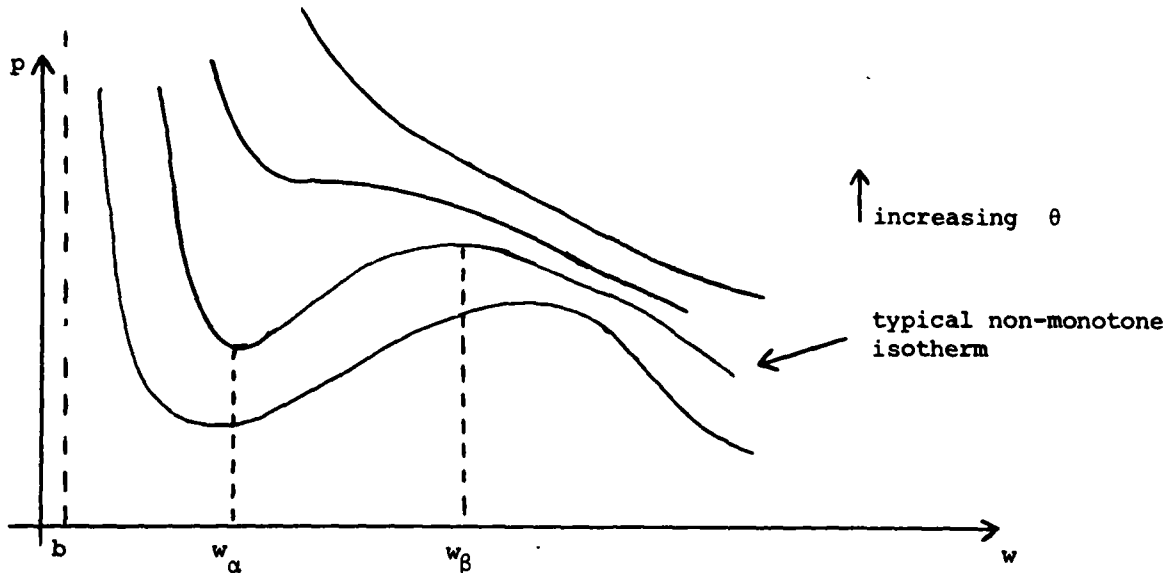


Figure 1

Also we note from (1.6) that $\hat{\psi}$ is given by

$$\hat{\psi} = -R\theta \ln(w-b) - \frac{a}{w^2} + F(\theta)$$

where $F(\theta)$ is an arbitrary function θ . Since $\hat{\epsilon} = \hat{\psi} + \theta\hat{\eta}$ it follows that

$$\hat{\epsilon}(w, \theta) = -\frac{a}{w} + F(\theta) - \theta F'(\theta) .$$

As a simplifying assumption we set (see [12], p. 74) $F(\theta) = -c_v \theta \ln \theta +$

constant where c_v is a positive constant, to obtain

$$\hat{\epsilon}(w, \theta) = -\frac{a}{w} + c_v \theta + \text{constant} . \quad (1.8)$$

2. Dynamic phase transitions

We fix our attention on a typical non-monotone isotherm as shown in Figure 1. The domains (b, w_α) and (w_β, ∞) will be called the α -phase and β -phase respectively;

- (i) $p_w(w, \theta) < 0$, $0 < b < w < w_\alpha$, $w_\beta < w$,
- (ii) $p_w(w_\alpha, \theta) = p_w(w_\beta, \theta) = 0$,
- (iii) $p_w(w, \theta) > 0$ if $w_\alpha < w < w_\beta$.

(Of course w_α , w_β depend on the choice of non-monotone isotherm.) The α -phase corresponds to the fluid being liquid, the β -phase corresponds to the fluid being vapor.

Assume w_- is a constant value of the specific volume lying in α -phase of the θ_- isotherm as shown in Figure 2. Our goal will be to see how a homogeneous equilibrium state of (1.4) (with $b \equiv q \equiv 0$) $w = w_-$, $u = u_-$, $\theta = \theta_-$ associated with the fluid being liquid can be dynamically transferred to (or from) a second equilibrium state $w = w_+$, $u = u_+$, $\theta = \theta_+$ associated with the fluid being vapor. Mathematically this means we shall try to find a traveling wave solution of (1.4) connecting equilibrium states (w_-, u_-, θ_-) and (w_+, u_+, θ_+) , where w_- is in the α -phase of θ_- isotherm and w_+ is in the β -phase of the θ_+ isotherm.

In order to simplify our calculations we take

$$\begin{aligned}
 \hat{\mu}(w, \theta) &= \mu > 0, \mu \text{ a small constant (the viscosity)} ; \\
 C(w, \theta) &= \mu^2 A, A \text{ a positive constant} ; \\
 \hat{h} &= \alpha \theta_x, \alpha \text{ positive constant} ; \\
 D &\equiv 0 ; \\
 b &\equiv q \equiv 0 .
 \end{aligned}
 \tag{2.1}$$

The choice of the scaling for $\hat{\mu}$ and C reflects the idea that viscosity and capillarity become important only when there are large gradients in the flow variables, for example in shock and interfacial layers. While on physical grounds α should also be small ([13], Vol. 1, p. 69) we choose here $\alpha^{-1} = O(1)$ compared with μ , i.e. a small Prandtl number. In this problem this means that the interfacial layer of interest to us will be the one of width $\sim \mu$ and not a wider, secondary, layer $\sim \alpha$. The choice $D \equiv 0$ while simplifying calculations is not crucial; see Theorem 5.8.

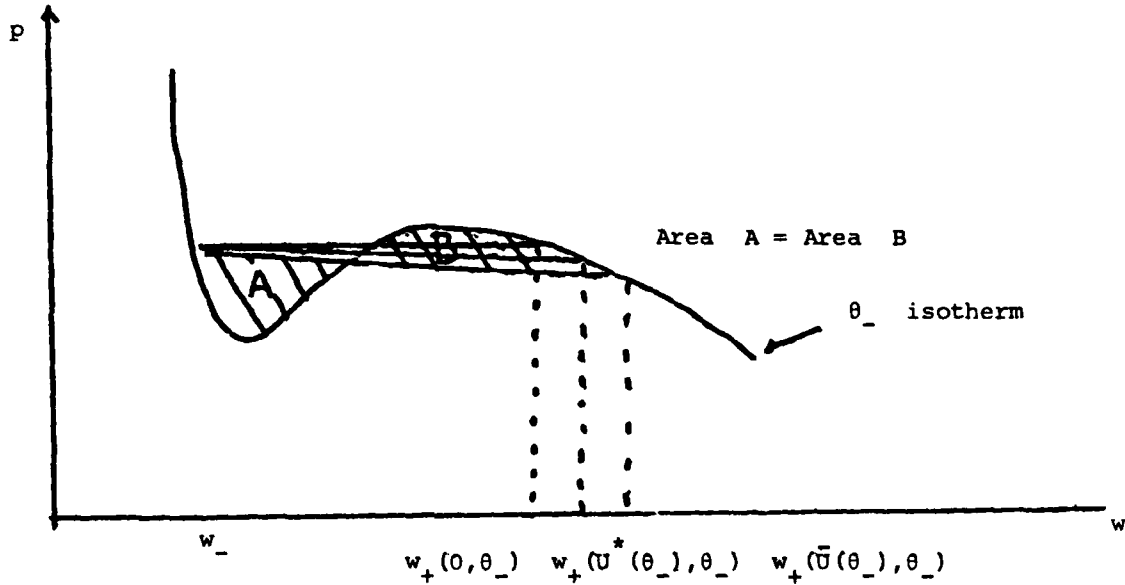


Figure 2

If we insert (2.1) into (1.4) we obtain the system

$$\begin{aligned}
 u_t &= (-p + \mu u_x - \mu^2 A w_{xx})_x, \\
 w_t &= u_x, \\
 E_t &= [u(-p + \mu u_x - \mu^2 A w_{xx})]_x + \alpha \theta_{xx}.
 \end{aligned}
 \tag{2.2}$$

As mentioned above, we seek a traveling wave solution for (2.2) of the form $u = u(\zeta)$, $w = w(\zeta)$, $\theta = \theta(\zeta)$, where $\zeta = \frac{x-Ut}{\mu}$ (U the speed of the traveling wave), subject to

$$w(-\infty) = w_-, u(-\infty) = u_-, \theta(-\infty) = \theta_- . \quad (2.3)$$

Substitution into (2.2) yields the system

$$\begin{aligned} -Uu' &= (-p + u' - Aw'')' \\ -Uw' &= u' \\ -UE' &= [u(-p + u' - Aw'')]' + \frac{\alpha}{\mu} \theta'' \end{aligned} \quad (2.4)$$

where $' = \frac{d}{d\zeta}$.

Set $\epsilon_- = \hat{\epsilon}(w_-, \theta_-)$, $p_- = p(w_-, \theta_-)$, $E_- = \frac{u_-^2}{2} + \epsilon_-$ and integrate (2.4) from $-\infty$ to ζ . We then find u, w, θ satisfy the system

$$\begin{aligned} -U(u-u_-) &= -(p-p_-) + u' - Aw'' \\ -U(w-w_-) &= u-u_- \\ -U(E-E_-) &= u(-p+u' - Aw'') + u_- p_- + \frac{\alpha}{\mu} \theta' . \end{aligned} \quad (2.5)$$

Finally we use (2.4;b) and (2.5;b) to eliminate u and u' from (2.5; a,c).

A straightforward computation shows w, θ satisfy the equations

$$\begin{aligned} w' &= v \\ Av' &= -Uv - U^2(w-w_-) - p(w, \theta) + p_- \\ \theta' &= \frac{\mu}{\alpha} U \{ -(\hat{\epsilon}(w, \theta) - \epsilon_-) - p_-(w-w_-) + \frac{U^2}{2} (w-w_-)^2 \} . \end{aligned} \quad (2.6; U, \mu)$$

In terms of (2.6;U, μ) our goal outlined at the beginning of this section becomes the following: Find a solution of (2.6;U, μ) connecting the equilibrium points $w = w_-, v = 0, \theta = \theta_-, w = w_+, v = 0, \theta = \theta_+$, of

(2.6;U, μ) where w_- is in the α -phase of the θ_- isotherm and w_+ is in the β -phase of the θ_+ isotherm.

We note (2.6;U, μ) is remarkably similar to the system

$$w' = v$$

$$Av' = -Uv + G(w,\theta) \quad (\text{FN} - \text{TW})$$

$$\theta' = \mu U^{-1}H(w,\theta)$$

governing traveling wave solutions of a generalization of the Fitzhugh-Nagumo equations modeling nerve impulse transmission. One obvious difference, however, between (2.6;U, μ) and (FN - TW) is that the equilibrium points of (2.6;U, μ) depend on U, in (FN - TW) they don't. Nevertheless the two sets of equations are sufficiently alike so that a modification of Carpenter's argument [3] proving the existence of a heteroclinic solution of (FN - TW) will yield existence of a solution to (2.6;U, μ) connecting α - and β -phases. It is this topic which will be pursued in the next sections.

3. The singular solution

Since μ is assumed to be small, a useful first step in the analysis of (2.6;U, μ) is the study of (2.6;U,0). This has been done in [1] and we recall those results here. First, however, we introduce some notation.

For w_-,U (respectively w_+,U) given in the α -phase (β -phase) of a non-monotone θ_-, θ_+ isotherm let $w_+(U, \theta_-)$ ($w_-(U, \theta_+)$) denote the solution, if it exists, of

$$U^2 = \frac{-p(w, \theta_-) + p(w_-, \theta_-)}{w - w_-}$$

$$(U^2 = \frac{-p(w_+, \theta_+) + p(w, \theta_+)}{w_+ - w})$$

lying in β -phase (α -phase). Also set

$$f_-(\zeta; U) = U^2(\zeta - w_-) + p(\zeta, \theta_-) - p(w_-, \theta_-) ,$$

$$f_+(\zeta; U) = U^2(\zeta - w_+) + p(\zeta, \theta_+) - p(w_+, \theta_+) .$$

We then recall from [1] the following lemma.

Lemma 3.1 (i) Let w_- be given in the α -phase of the θ_- non-monotone isotherm. If

$$(I) \quad \int_{w_-}^{w_+(0, \theta_-)} f_-(\zeta; 0) d\zeta < 0$$

then there exists a unique $U^*(\theta_-)$, $0 < U^*(\theta_-) < \bar{U}(\theta_-)$ so that (2.6; $U^*(\theta_-), 0$) possesses a solution (w, θ) , $w(-\infty) = w_-$, $w(+\infty) = w_+(U^*(\theta_-), \theta_-)$, $\theta(\zeta) \equiv \theta_-$. Here $\bar{U}(\theta_-)$ is such that

$$\int_{w_-}^{w_+(\bar{U}(\theta_-), \theta_-)} f_-(\zeta; \bar{U}(\theta_-)) d\zeta = 0 .$$

$w_+(U^*(\theta_-), \theta_-)$ lies in the β -phase of the θ_- isotherm.

(ii) Let w_+ be given in the β -phase of the θ_+ non-monotone isotherm. If

$$(II) \quad \int_{w_-(0, \theta_+)}^{w_+} f_+(\zeta; 0) d\zeta > 0$$

then there exists a unique $U^*(\theta_+)$, $\bar{U}(\theta_+) < U^*(\theta_+) < 0$, so that (2.6; $U^*(\theta_+), 0$) possesses a solution (w, θ) , $w(-\infty) = w_-(U^*(\theta_+), \theta_+)$, $w(+\infty) = w_+$, $\theta(\zeta) \equiv \theta_+$. Here $\bar{U}(\theta_+)$ is such that

$$\int_{w_-(U^*(\theta_+), \theta_+)}^{w_+} f_+(\zeta; \bar{U}(\theta_+)) d\zeta = 0.$$

$w_-(U^*(\theta_+), \theta_+)$ lies in α -phase of the θ_+ -isotherm.

Remark. The hypotheses of Lemma 3.1 have a simple interpretation. For example in (i), (I) says the signed area between the chord joining $(w_-, p(w_-, \theta_-))$ and $(w_+(0, \theta_-), p(w_+(0, \theta_-), \theta_-))$ and the graph of $p(w_-, \theta_-)$ between w_- and $w_+(0, \theta_-)$ is negative. $\bar{U}(\theta_-)$ is that positive value of U so that the signed area between the chord joining $(w_-, p(w_-, \theta_-))$ and the graph of $p(w, \theta_-)$ between w_- and $w_+(\bar{U}(\theta_-), \theta_-)$ is zero (see Figure 2). An analogous interpretation holds for (ii).

Since the arguments used in describing the two cases w_- satisfies (I) and w_+ satisfies (II) are analogous we shall assume in what follows that w_- is given in the α -phase of the θ_- isotherm and (I) is satisfied.

Lemma 3.1 assures the existence of an isothermal solution of (2.6; $U^*(\theta_-), 0$) connecting $(w_-, 0, \theta_-)$ to $(w_+(U^*(\theta_-), 0, \theta_-))$. Unfortunately this solution does not satisfy the full system (2.6; $U^*(\theta_-), \mu$) when $\mu \neq 0$. The reason is, of course, that the quantity in braces in (2.6; $U^*(\theta_-), \mu; c$) would have to be identically zero along this isothermal solution and it is not.

We also know however that if μ is small and U is near $U^*(\theta_-)$ solutions of $(2.6; U, \mu)$ stay close to solutions of $(2.6; U^*(\theta_-), 0)$ provided w' or v' is not small. If w' and v' are small and $\mu > 0$, then the "slow" system $(2.6; U, \mu; c)$ becomes "fast" relative to the "fast" system $(2.6; U, \mu; a, b)$. A singular solution of $(2.6; U, \mu)$ will consist of alternating solutions or solution segments of the two systems $(2.6; U^*(\theta_-), 0)$ and $(2.6; U^*(\theta_-), \mu; c)$, the latter being defined where $w' = v' = 0$, i.e. on $w = g(\theta)$, a solution of

$$- U^*(\theta_-)^2 (w - w_-) - p(w, \theta) + p(w_-, \theta_-) = 0 . \quad (3.1)$$

Our hope is that if we can construct a singular solution of $(2.6; U, \mu)$ connecting the state $w = w_-, v = 0, \theta = \theta_-$ in the (liquid) α -phase to a state $w = w_+, v = 0, \theta = \theta_+$ in the (vapor) β -phase we can find a true solution of $(2.6; U, \mu)$ that does the same thing, provided μ is sufficiently small.

From Lemma 3.1 we know the first piece of our singular solution will be a curve in the $\theta = \theta_-, v > 0$ half plane connecting $(w_-, 0, \theta_-)$ to $(w_+, U^*(\theta_-), \theta_-, 0, \theta_-)$. According to our program the next piece of our singular solution will be to follow the flow given by $(2.6; U^*(\theta_-), \mu; c)$ when $w = g(\theta)$. Examination of the van der Waals isotherms (Figure 1) for differing values of θ leads to the graph of g shown in Figure 3.

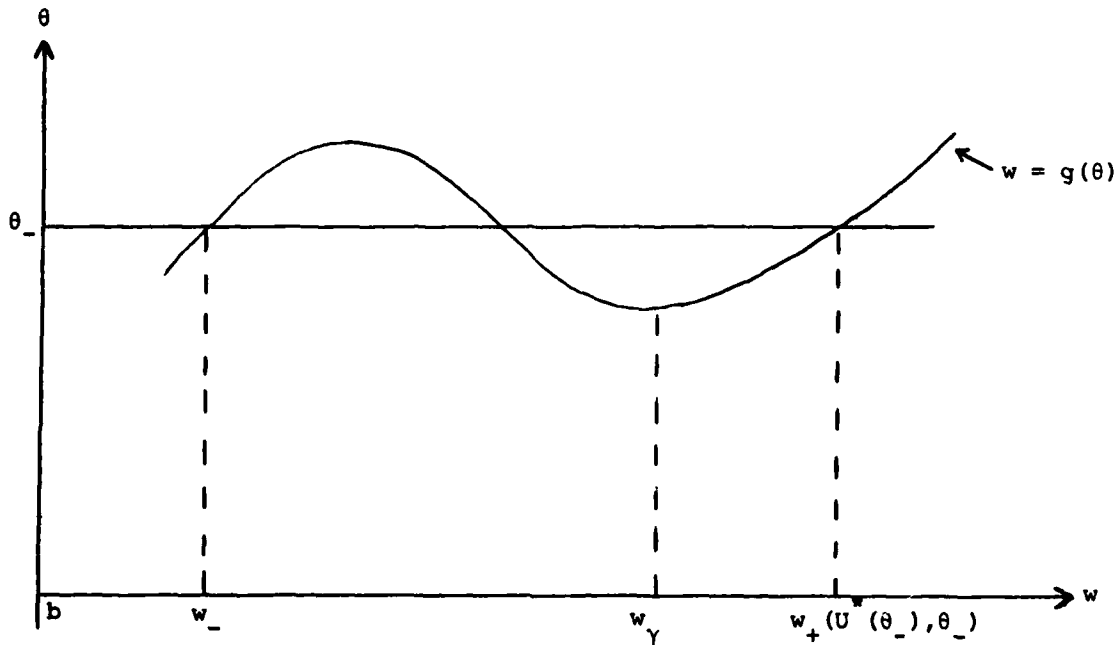


Figure 3

To follow the solution of (2.6; $U^*(\theta_-), \mu; c$) along $w = g(\theta)$ means we are studying the scalar equation

$$\theta' = \mu \frac{U^*}{\alpha} (\theta_-) \left\{ -(\hat{\epsilon}(g(\theta), \theta) - \epsilon_-) - (g(\theta) - w_-)p_- + \frac{U^*(\theta_-)^2}{2} (g(\theta) - w_-)^2 \right\} . \quad (3.2)$$

As the first part of the singular solution took us from $(w_-, 0, \theta_-)$ to $(w_+(U^*(\theta_-), \theta_-), 0, \theta_-)$, it is necessary to study behavior of (3.2) only on the $w > w_\gamma$ branch of $g(\theta)$ where $g'(\theta) > 0$ (Figure 3).

Crucial to the study of (3.2) is knowledge of equilibrium point positions. The equilibrium points of (3.2) are found at the intersections of the graph $w = g(\theta)$ and $w = l(\theta)$ where $w = l(\theta)$ is the solution of

$$-(\hat{\epsilon}(w, \theta) - \epsilon_-) - p_-(w - w_-) + \frac{U^*(u_-)^2}{2} (w - w_-)^2 = 0 \quad (3.3)$$

If we substitute our constitutive relation (1.8) into (3.3) and use the fact that

$$U^*(\theta_-)^2 = \frac{-p(w_+(U^*(\theta_-), \theta_-)) + p_-}{w_+(U^*(\theta_-), \theta_-) - w_-} \quad (3.4)$$

we find $w = \ell(\theta)$ must satisfy

$$c_v(\theta - \theta_-) = a \left(\frac{1}{w^2} - \frac{1}{w_-^2} \right) - \left(\frac{w - w_-}{w_+(U^*(\theta_-), \theta_-) - w_-} \right) \left\{ p_-(w_+(U^*(\theta_-), \theta_-) - \frac{w}{2} - \frac{w_-}{2}) + p(w_+(U^*(\theta_-), \theta_-), \theta_-) \left(\frac{w - w_-}{2} \right) \right\} \quad (3.5)$$

Differentiation of (3.5) with respect to w yields

$$c_v \frac{d\theta}{dw} = \frac{-2a}{w^3} - \left(\frac{1}{w_+(U^*(\theta_-), \theta_-) - w_-} \right) [p_-(w_+(U^*(\theta_-), \theta_-) - w) + p(w_+(U^*(\theta_-), \theta_-), \theta_-) (w - w_-)] \quad (3.6)$$

So if the θ_- isotherm is as shown in Figure 2 with $p(w_+(U^*(\theta_-), \theta_-)) > 0$ we have $\frac{d\theta}{dw} < 0$ for $w_- < w < w_+(U^*(\theta_-), \theta_-)$ and $w = \ell(\theta)$ is a decreasing function of θ on the range $w_- < w < w_+(U^*(\theta_-), \theta_-)$. From (3.6) we then see if c_v is sufficiently large the curves $w = g(\theta)$ and $w = \ell(\theta)$ will intersect at three points in $w - \theta$ plane as shown in Figure 4 giving the equilibrium points of (3.2). Thus (3.2) has an equilibrium point $\theta = \tilde{\theta}_+$ so that $\tilde{w}_+ \equiv g(\tilde{\theta}_+) > w_\gamma$ and $g'(\tilde{\theta}_+) > 0$.

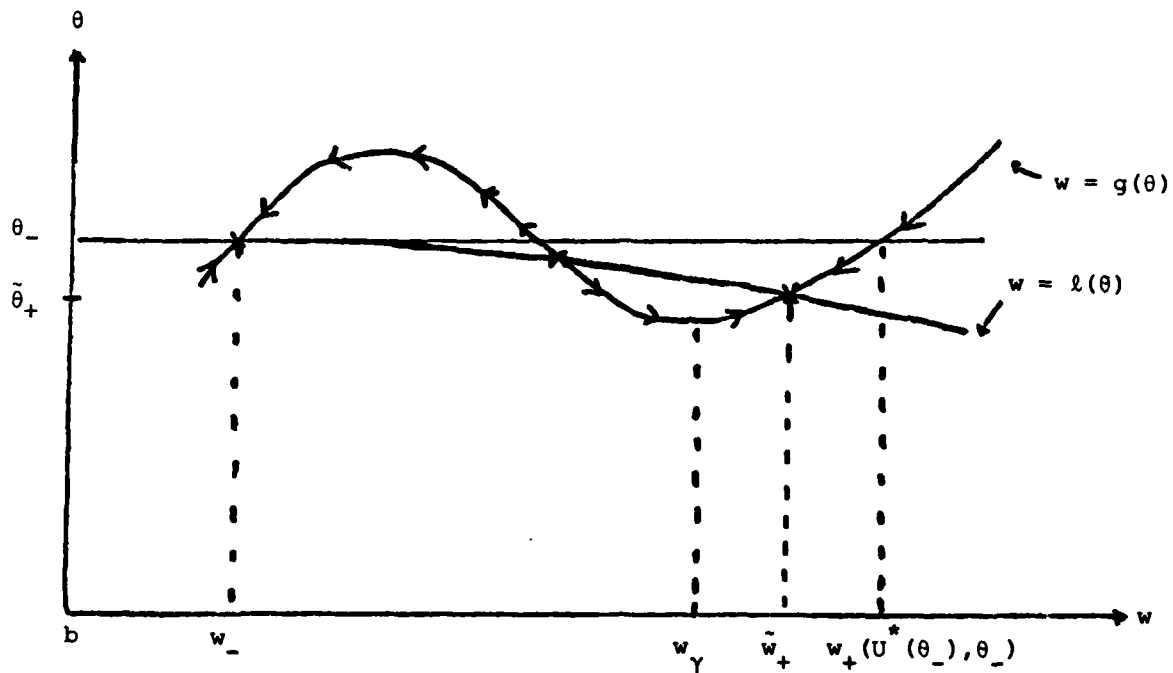


Figure 4

As noted in the preceding paragraph we need $p(w_+(U^*(\theta_-), \theta_-)) > 0$.

Examination of Lemma 3.1 shows that this will be implied by

Assumption $\bar{U}(\theta_-)$:

For $\bar{U}(\theta_-)$ as given in Lemma 3.1 we have $p(w_+(\bar{U}(\theta_-), \theta_-)) > 0$.

We also note the above result depends on c_v being sufficiently large. Otherwise the curve $l(\theta)$ might fail to intersect $g(\theta)$ except at the point (w_-, θ_-) . For this reason we make the basic constitutive assumption

Assumption c_v :

c_v is large enough to (i) force l, g to intersect in three points as shown in Figure 4 and (ii) yield $p(\tilde{w}_+, \theta_+) > 0$.

Actually (ii) follows by continuity from $p(w_+(U^*(\theta_-), \theta_-)) > 0$ when c_v is large.

Lemma 3.2. The equilibrium point $\tilde{\theta}_+$ (where $\tilde{w}_+ = g(\tilde{\theta}_+) > w_\gamma$) of (3.2) is asymptotically stable.

Proof. From Taylor's theorem we know

$$\begin{aligned} \theta' &= \mu \frac{U^*}{\alpha} (\theta_-) \{-\hat{e}_w(\tilde{w}_+, \tilde{\theta}_+) - p(\tilde{w}_+, \theta_+) \} g'(\tilde{\theta}_+) (\theta - \tilde{\theta}_+) \\ &\quad - \mu \frac{U^*}{\alpha} (\theta_-) \hat{e}_\theta(\tilde{w}_+, \tilde{\theta}_+) (\theta - \tilde{\theta}_+) \\ &\quad + o(|\theta - \tilde{\theta}_+|^2) . \end{aligned} \tag{3.8}$$

We note first that $\hat{e}_\theta = c_v > 0$, $\hat{e}_w = \frac{2a}{w^3} > 0$. Secondly Assumption c_v implies $p(\tilde{w}_+, \theta_+) > 0$. So $\tilde{\theta}_+$ is asymptotically stable. In fact the full phase flow of (3.2) is shown in Figure 4 by the arrows on the graph of g .

If we combine Lemmas 3.1 and 3.2 we see we have constructed a singular solution of (2.6; U, μ). The singular solution consists of

- (i) an isothermal solution of (2.6; $U^*(\theta_-), 0$) running from $(w_-, 0, \theta_-)$ to $(w_+(U^*(\theta_-), \theta_-), 0, \theta_-)$ in the $v > 0$, $\theta = \theta_-$ half plane;
- (ii) a solution of (3.2) traveling on the graph of g in the $v = 0$ plane from the point $(w_+(U^*(\theta_-), \theta_-), 0, \theta_-)$ to the equilibrium of (3.2) $\tilde{\theta}_+$.

Pictorially the singular solution is represented in Figure 5.

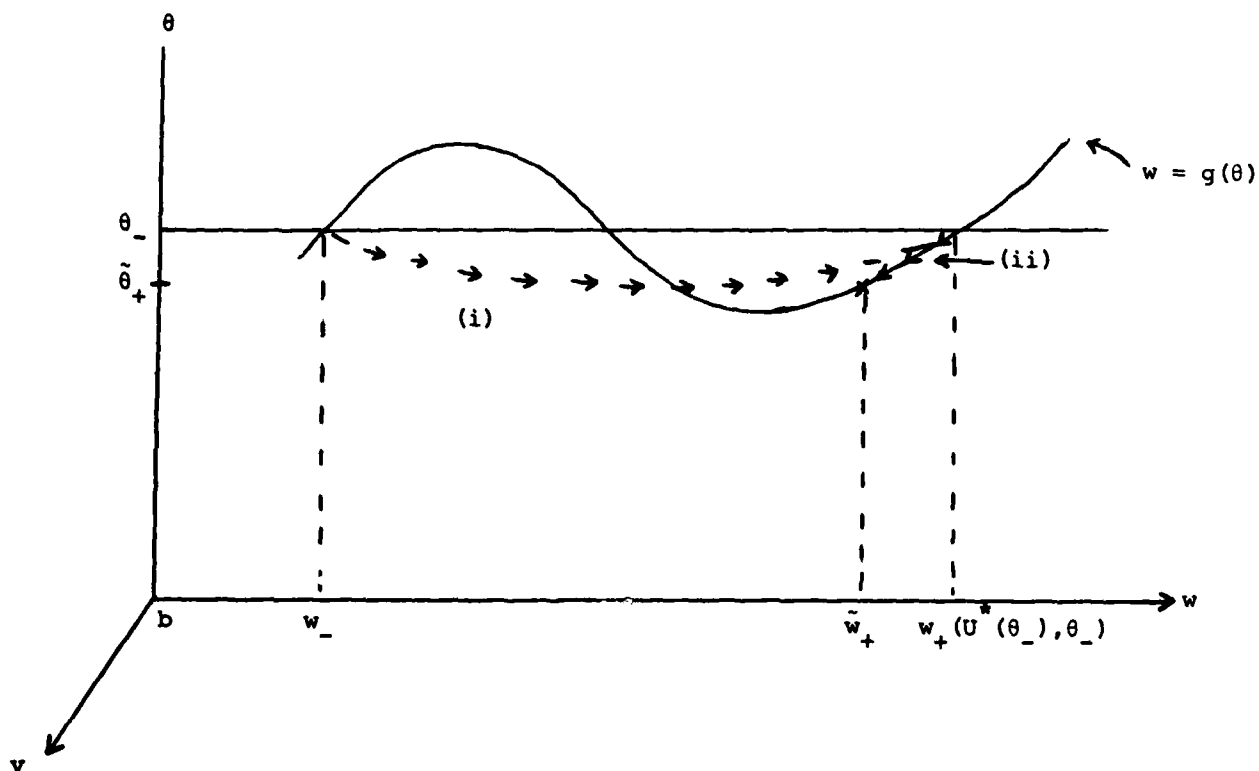


Figure 5. The singular solution

As w_- is in the α -phase of the θ_- isotherm and \tilde{w}_+ is in the β -phase of the $\tilde{\theta}_+$ isotherm we see this singular solution does indeed connect α and β phases.

Our goal now is to show there is a true solution of (2.6; U, μ) for U near $U^*(\theta_-)$ and μ small with the same connecting properties as the singular solution. Before doing this we recall some results from the Conley-Easton theory of isolating blocks.

4. Conley-Easton theory of isolating blocks

In this section the Conley-Easton isolating block theory [2] is outlined. The presentation given here is the same as that given by Carpenter [3] modulo a small generalization (Corollary 4.6).

Consider a system of ordinary differential equations

$$\dot{y} = F(y) \quad (4.1)$$

where $F \in C^1(\Omega; \mathbb{R}^N)$ for Ω an open connected set contained in \mathbb{R}^N . For all initial data $y_0 \in \Omega$ we shall assume (4.1) has globally defined unique solutions $y(t, y_0)$, $y(0, y_0) = y_0$ lying in Ω .

Definition 4.1. B is a block for (4.1) if there exists C^1 functions $f_1, f_2, \dots, f_N : \mathbb{R}^N \rightarrow \mathbb{R}$ so that

$$B \equiv \bigcap_{i=1}^N f_i^{-1}([0, \infty))$$

is homeomorphic to $[0, 1]^N$ and $\dot{f}_i \equiv \nabla f_i \cdot F \neq 0$ on ∂B . b^+ (the entrance set) $\equiv \{y \in \partial B : f_i(y) = 0 \text{ and } \dot{f}_i(y) > 0 \text{ for some } i\}$. b^- (the exit set) $\equiv \{y \in \partial B : f_i(y) = 0 \text{ and } \dot{f}_i(y) < 0 \text{ for some } i\}$.

Example. A block about the saddle point $y_1 = y_2 = 0$ for the system

$$\begin{aligned} \dot{y}_1 &= y_2 \\ \dot{y}_2 &= -y_1 \end{aligned} \quad (4.2)$$

Let $B = \{|y_1| + |y_2| < 1\}$. B is a block with $f_1(y_1, y_2) = 1 - y_1 - y_2$, $f_2(y_1, y_2) = 1 + y_1 + y_2$, etc. $\dot{f}_1(y_1, y_2) = -y_1 - y_2 = -1$ on $f_1(y_1, y_2) = 0$, so $b^- \supseteq f_1^{-1}(0) \cap B$. $\dot{f}_2(y_1, y_2) = y_1 - y_2 = 1$ if $f_2(y_1, y_2) = 0$, so $b^+ \supseteq f_2^{-1}(0) \cap B$. An illustration is given in Figure 6.

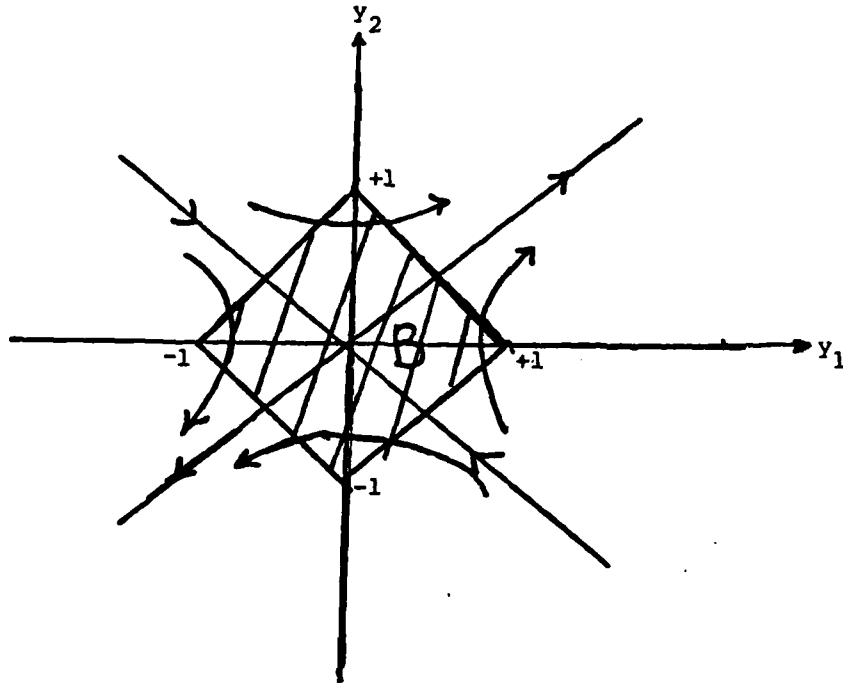


Figure 6

Definition 4.2. If f is a C^1 function from Ω to \mathbb{R} and $y_0 \in \Omega$, $y(t, y_0)$ crosses $\{y ; f(y) = c\}$ transversely if $T \equiv \inf\{t > 0 ; f(y(t, y_0)) = c\} < \infty$ and $\dot{f}(y(t, y_0)) \neq 0$.

$T^\pm(y_0)$ (the time needed for y_0 to reach b^\pm) \equiv

$$\left\{ \begin{array}{ll} 0 & \text{if } y_0 \in b^\pm \\ \sup\{t > 0 : y(t, y_0) \cap b^\pm \text{ is empty}\} & \text{if } y_0 \notin b^\pm \end{array} \right\} .$$

$\phi^\pm(y_0) \equiv y(T^\pm, y_0)$ if $0 < T^\pm(y_0) < \infty$.

$\phi^\pm(y_0)$ is the first point of $y(t, y_0)$ in b^\pm .

$D^\pm = \{y ; 0 < T^\pm(y_0) < \infty \text{ and } \phi^\pm(y_0) \in b\}$.

D^\pm contains the set on which ϕ^\pm is defined and continuous. If $y \in D^\pm$, $y(t, y_0)$ crosses $\{y; f_i(y) = c\}$ transversely at $\phi^\pm(y_0)$ for some i .

In the example given above

$$D^+ = \{y_1, y_2; y_1^2 - y_2^2 < 1\} \cap \\ \{y_1, y_2; y_1 < 0 \text{ and } y_2 > 0, \text{ or } y_1 > 0 \text{ and } \\ y_2 < 0\} - B, \\ D^- = (D^+ \cup B) - b^- \cup S(\langle 0, 0 \rangle).$$

Here $S(\langle 0, 0 \rangle)$ is the stable manifold of (4.2) running into $(0, 0)$.

We now state the following results. Proofs may be found in [3], [14].

Lemma 4.3. (Continuity of maps defined by a block). If B is a block,

T^\pm and ϕ^\pm are continuous on D^\pm .

Consider the parametrized system

$$\dot{y} = F(y, \sigma) \quad (4.3; \sigma)$$

where $F \in C^1(\Omega \times \Sigma; \mathbb{R}^N)$ for Σ, Ω open connected sets contained in $\mathbb{R}^N, \mathbb{R}^k$ respectively.

Lemma 4.4. If B is a block for $(4.3; \sigma^*)$, $\sigma^* \in \Sigma$, there exists a neighborhood Σ^* of σ^* , $\Sigma^* \subset \Sigma$, so that B is a block for $(4.3; \sigma)$ when $\sigma \in \Sigma^*$.

Theorem 4.5. Assume there exists a block B for $(4.3; \sigma)$ for all $\sigma \in \Sigma$ with the following properties.

- (i) There is a equilibrium point y_1 of $(4.3; \sigma)$, $y_1 \notin B$.
- (ii) There is a path $\{z_s, \sigma_s; 0 < s < 1\} \subset D^+ \times \Sigma$ so that $z_s \in U\langle y_1 \rangle$ (the unstable manifold leaving y_1 ; $z_0, z_1 \in D^-$; $\phi^- \circ \phi^+(z_0; \sigma_0)$, $\phi^- \circ \phi^+(z_1; \sigma_1)$ are contained in distinct components of b^-).

Then for some σ_s one positive semiorbit beginning at $\phi^+(z_s; \sigma_s)$ is contained in B .

Since Theorem 4.5 is slightly different from the result given in [3] (Theorem 1.5 of [3]), we present a proof for completeness.

Proof of Theorem 4.5. Since ϕ^+ is continuous it maps a path Π in D^+ to a path in b^+ . If $\phi^+(\Pi)$ is contained in D^- , $\phi^- \circ \phi^+(\Pi)$ is a path in b^- . Thus $\phi^+(\Pi)$ is not contained in D^- if the end points of $\phi^+(\Pi)$ are mapped by ϕ^- to distinct components of b^- . In this case, one positive semiorbit beginning at $\phi^+(\Pi)$ is contained in B .

Corollary 4.6. Assume the hypotheses of Theorem 4.5 hold. Assume in addition there exists a C^1 function $V : \mathbb{R}^N \rightarrow \mathbb{R}$ with the property that

$$\dot{V}(y) \equiv \text{grad } V(y) \cdot F(y, \sigma) < 0 \text{ for } y \in B, \sigma \in \Sigma .$$

Let

$$S = \{y \text{ in } B; \dot{V}(y) = 0\}$$

and M be the largest invariant set in S . If M consists only of equilibrium points of (4.3; σ), then for some σ_g (4.3; σ_g) possesses a heteroclinic solution connecting y_1 to y_2 ($y_1^{(-\infty)} = y_1, y_1^{(+\infty)} = y_2$) where y_2 is an equilibrium point of (4.3; σ_g) lying in B .

Proof. From Theorem 4.5 we know the existence of an orbit which leaves y_1 and eventually enters, never to leave, B . The function V is a Liapunov function in the sense of LaSalle. So LaSalle's invariance principle (Theorem 1.3, Chap. X of [15]) implies this orbit approaches equilibrium point in B as $t \rightarrow \infty$.

5. Construction of the connecting orbit.

In this section we use theory of Section 4 to prove the existence of an orbit connecting the equilibrium point $(w_-, 0, \theta_-)$ of (2.6; U, μ) to another equilibrium point $(w_+, 0, \theta_+)$ where w_- is in the α -phase of the θ_- isotherm and w_+ is in the β -phase of θ_+ isotherm. We shall need the following lemmas.

Lemma 5.1. For $\theta = \theta_-$ the equilibrium point $(w_+(U^*(\theta_-), \theta_-), 0)$ of

$$\begin{aligned} w' &= v \\ Av' &= -U^*(\theta_-)v + U^*(\theta_-)^2(w - w_-) + p(w, \theta) + p(w_-, \theta_-) \end{aligned} \quad (5.1)$$

is a saddle. Furthermore for θ near θ_- the equilibrium points $(g(\theta), 0)$ of (5.1) near $(w_+(U^*(\theta_-), \theta_-), 0)$ are also saddles and possess phase portraits as shown in Figure 7.

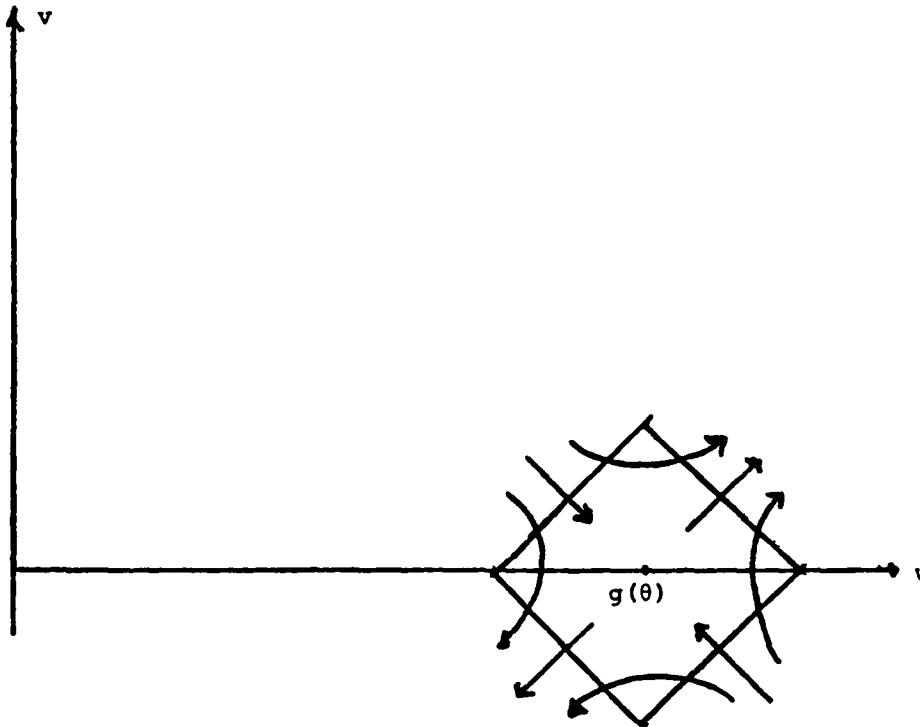


Figure 7. Isolating block B_θ .

Proof. Linearization of (5.1) when $\theta = \theta_-$ about $(w_+(U^*(\theta_-), \theta_-), 0)$ shows the eigenvalues of the linearized system satisfy

$$\lambda^2 + U^*(\theta_-)\lambda + (U^*(\theta_-))^2 + p_w(w_+(U^*(\theta_-), \theta_-), \theta_-) = 0 .$$

Since $U^*(\theta_-)^2 + p_w(w_+(U^*(\theta_-), \theta_-), \theta_-) < 0$ (see Figure 2) the equilibrium point is a saddle. The rest of the lemma follows from continuity with respect to the parameter θ .

Lemma 5.2. For θ near θ_- (5.1) possesses a block B_θ as shown in Figure 7 where the lengths of the sides of B_θ are independent of B_θ .

Proof. Lemma 1.2 of [3].

Lemma 5.3. Define $B = \bigcup_{\tilde{\theta}_+ - v < \theta < \theta_-} B_\theta$

where $\tilde{\theta}_+ - v$ is shown in Figure 5. Then B is a block for (2.6; $U^*(\theta_-), \mu$).

Proof. By Lemma 3.2 solutions of (2.6; $U^*(\theta_-), \mu$) are such that the top and bottom of B are entrance points. We know the sides are points of exit or entrance from Lemma 5.1.

Lemma 5.4. For U near $U^*(\theta_-)$, B is a block for (2.6; U, μ).

Proof. Lemma 4.4 applies.

Lemma 5.5. For μ sufficiently small there exist $U_\mu > 0$ and a solution of (2.6; U_μ, μ) with $w(-\infty) = w_-$, $v(-\infty) = 0$, $\theta(-\infty) = \theta_-$ so that (w, v, θ) is in B for all ζ sufficiently large. Furthermore $U_\mu \rightarrow U^*(\theta_-)$ as $\mu \rightarrow 0+$.

Proof. When $\mu = 0$ linearization of (2.6; $U^*(\theta_-), 0$) about $(w_-, 0, \theta_-)$ shows (2.6; $U^*(\theta_-), 0$) has a one dimensional unstable manifold exiting from $(w_-, 0, \theta_-)$ (see Figure 8). By continuity with respect to parameters, if U is near $U^*(\theta_-)$ and μ is sufficiently small, there is a one-dimensional unstable manifold $U(U, \mu)$ for (2.6; U, μ) exiting from $(w_-, 0, \theta_-)$. Consider

an arc A^* lying in $U(U, \mu)$ (A^* will lie near the arc A shown in Figure 9). As U runs from values slightly greater than $U^*(\theta_-)$ to values slightly less than $U^*(\theta_-)$ we see by continuity with respect to the parameters U, μ that the characteristic features of Figure 9 are preserved for the full system (2.6; U, μ) if μ is small. Namely the end points of A^* will be carried into distinct components of $b_- \in B$. Since Lemma 5.4 tells us B is a block for (2.6; U, μ) for all U near $U^*(\theta_-)$, we know by Theorem 4.5 that for each μ sufficiently small there exists U_μ so that (2.6; U_μ, μ) possesses a solution exiting from $(w_-, 0, \theta_-)$ which enters and remains in B . The proof implies U_μ may be chosen such that $U_\mu \rightarrow U^*(\theta_-)$ as $\mu \rightarrow 0+$.

Lemma 5.6. (i) Along smooth solutions of (2.2) the following equality is satisfied

$$\theta \eta_t = u_x (\mu u_x - \lambda \mu^2 w_{xx}) + \alpha \theta_{xx} \quad (5.2)$$

(ii) Along solutions of (2.6; U, μ) the following equality is satisfied

$$-\theta \eta' = U w'^2 + A w' w'' + \frac{\alpha}{\mu} \theta'' \quad (5.3)$$

Proof. (i) Consider the specific free energy $\hat{\psi}$ with $p = -\frac{\partial \hat{\psi}}{\partial w}$, $\eta = -\frac{\partial \hat{\psi}}{\partial \theta}$.

Then since $\psi = \epsilon - \theta \eta$ we have $\psi_t = \epsilon_t - \theta_t \eta - \theta \eta_t$ and hence

$\hat{\psi}_w w_t + \hat{\psi}_\theta \theta_t = \epsilon_t - \theta_t \eta - \theta \eta_t$. This implies $\epsilon_t + p w_t = \theta \eta_t$. From (2.2;b) we find $\epsilon_t + p u_x = \theta \eta_t$. Now use (2.2;c) to complete the proof.

(ii) Substitute $u = u(\zeta)$, $w = w(\zeta)$, $\theta = \theta(\zeta)$, $\eta(\zeta) = \hat{\eta}(w(\zeta), \theta(\zeta))$ into (5.2).

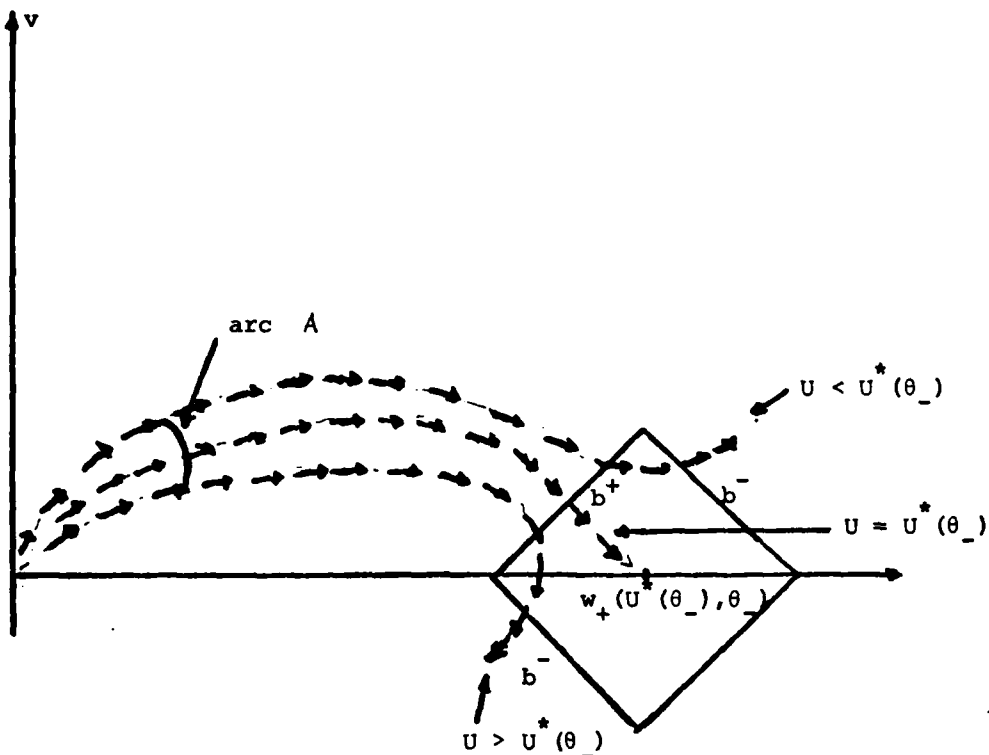


Figure 8

Theorem 5.7. (i) (Compression Wave) Assume w_-, θ_-, u_- are given, w_- satisfies (I) of Lemma 3.1, and the constitutive Assumptions c_v and $\bar{U}(\theta_-)$ are satisfied. Then for μ sufficiently small there exists $U_\mu > 0$ and a solution of (2.6; U_μ, μ) with $w(-\infty) = w_-, v(-\infty) = 0, \theta(-\infty) = \theta_-, w(+\infty) = w_+^*(U_\mu), v(+\infty) = 0, \theta(+\infty) = \theta_+^*(U_\mu) < \theta_-; w_+^*(U_\mu)$ is in the β -phase of $\theta_+^*(U_\mu)$ isotherm. Furthermore $U_\mu \rightarrow U^*(\theta_-) > 0, w_+^*(U_\mu) \rightarrow \tilde{w}_+, \theta_+^*(U_\mu) \rightarrow \tilde{\theta}_+ < \theta_-$ as $\mu \rightarrow 0+$.

(ii) (Expansion wave) Assume w_+, θ_+, u_+ are given, w_+ satisfies (II) of Lemma 3.1, the constitutive Assumption c_v is satisfied and $p(w_+, \theta_+) > 0$. Then for μ sufficiently small there exists $U_\mu < 0$ and a solution of (2.6; U_μ, μ) with $w(-\infty) = w_-^*(U_\mu), v(-\infty) = 0,$

$\theta(-\infty) = \theta_{-}^{*}(U_{\mu}) > \theta_{+}$, $w(+\infty) = w_{+}$, $v(+\infty) = 0$, $\theta(+\infty) = \theta_{+}$, $w_{-}^{*}(U_{\mu})$ is in the α -phase of the $\theta_{-}^{*}(U_{\mu})$ isotherm. Furthermore $U_{\mu} + U^{*}(\theta_{+}) < 0$, $w^{*}(U_{\mu}) + \tilde{w}_{-}$, $\theta_{-}^{*}(U_{\mu}) + \tilde{\theta}_{-} > \theta_{+}$ as $\mu \rightarrow 0+$ where \tilde{w}_{-} , $\tilde{\theta}_{-}$ are obtained in a manner analogous to that given for the construction of \tilde{w}_{+} , $\tilde{\theta}_{+}$.

Proof. (i) Define

$$\begin{aligned}
 V(w, v, \theta) = & \hat{\eta}(w, \theta) + \frac{U}{\theta} \left\{ -(\hat{\epsilon}(w, \theta) - \epsilon_{-}) - p_{-}(w - w_{-}) + \frac{U^2}{2} (w - w_{-})^2 \right\} \\
 & + \frac{A}{\theta} \left(\frac{v^2}{2} \right) .
 \end{aligned}$$

From (5.3) it follows that along solutions of (2.6; U, μ) we have

$$\begin{aligned}
 v' = & -\frac{U}{\theta} w'^2 \left(1 + \frac{A\mu}{2\theta\alpha} \left\{ -(\hat{\epsilon}(w, \theta) - \epsilon_{-}) - p_{-}(w - w_{-}) + \frac{U^2}{2} (w - w_{-})^2 \right\} \right) \\
 & - \frac{\mu U^2}{\alpha \theta^2} \left\{ -(\hat{\epsilon}(w, \theta) - \epsilon_{-}) - p_{-}(w - w_{-}) + \frac{U^2}{2} (w - w_{-})^2 \right\}^2 .
 \end{aligned}$$

Now if (v, w, θ) is in B

$$\left\{ -(\hat{\epsilon}(w, \theta) - \epsilon_{-}) - p_{-}(w - w_{-}) + \frac{U^2}{2} (w - w_{-})^2 \right\}$$

can be bounded independently of μ . Hence for μ sufficiently small we have $v' < -\text{const.}(w'^2 + \theta'^2)$, for some positive constant, when (v, w, θ) is in B. Hence the hypotheses of Corollary 4.6 is satisfied and the result follows.

(ii) This follows by proving a sequence of lemmas analogous to Lemmas 5.1 - 5.5 for the case where (w_{-}, θ_{-}) is replaced (w_{+}, θ_{+}) in (2.6; U, μ). The same Liapunov function given in (i) will work as long as we replace (ϵ_{-}, w_{-}) by (ϵ_{+}, w_{+}) . A pictorial representation of the singular solution for this case is given in Figure 9.

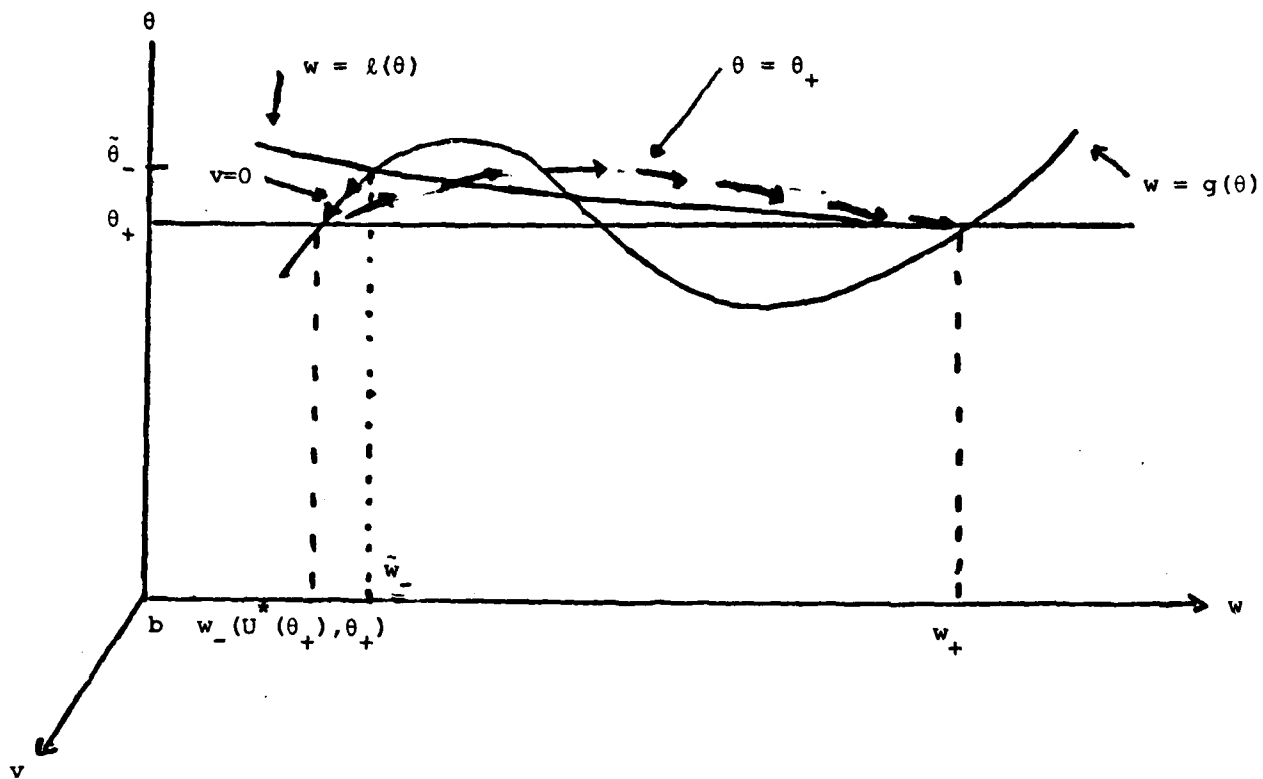


Figure 9

Remark. While the special case of parameters (2.1) greatly simplifies calculations results similar to those given here are valid for the general Korteweg relation (1.5;a). Specifically consider

$$\begin{aligned}
 \hat{\mu}(w, \theta) &= \delta \mu_0(w, \theta) \quad , \\
 C(w, \theta) &= \delta^2 C_0(w, \theta) \quad , \\
 D(w, \theta) &= \delta^2 D_0(w, \theta) \quad , \\
 \hat{h} &= \alpha \theta_x \quad , \\
 b &\equiv q \equiv 0 \quad .
 \end{aligned}
 \tag{5.4}$$

where δ is a small positive constant, $\alpha^{-1} = O(1)$ in δ , $\mu_0(w, \theta) > \bar{\mu} > 0$, $C_0(w, \theta) > \bar{C} > 0$, $\bar{\mu}$, \bar{C} positive constants, and μ_0, C_0, D_0 are smooth functions. In this case (2.6; U, μ) is replaced by

$$w' = v ,$$

$$C_0(w, \theta)v' = -U\mu_0(w, \theta)v \quad (5.5; U, \delta)$$

$$- U^2(w - w_-) - p(w, \theta) + p_- + D_0(w, \theta)v^2 ,$$

$$\theta' = \frac{\delta}{\alpha} U \left\{ - (\varepsilon(w, \theta) - \varepsilon_-) - p_-(w - w_-) + \frac{U^2}{2} (w - w_-)^2 \right\} ,$$

where

$$\xi = \frac{x - Ut}{\delta} .$$

Instead of Theorem 5.7 we can obtain the following more general result.

Theorem 5.8. (i) Assume w_- is given in the α -phase of the θ_- non-monotone isotherm and

$$(I') \int_{w_-}^{w_+(0, \theta_-)} \exp(2 \int_{\lambda}^{w_+(0, \theta_-)} D_0(\xi, \theta_-) C_0(\xi, \theta_-)^{-1} d\xi) C_0(\lambda, \theta_-)^{-1} f_-(\lambda; 0) d\lambda < 0 ,$$

and there exists $\bar{U}(\theta_-)$ so that

$$\int_{w_-}^{w_+(\bar{U}(\theta_-), \theta_-)} \exp(2 \int_{\lambda}^{w_+(0, \theta_-)} D_0(\xi, \theta_-) C_0(\xi, \theta_-)^{-1} d\xi) C_0(\lambda, \theta_-)^{-1} f_-(\lambda; \bar{U}) d\lambda = 0 .$$

Also assume constitutive Assumptions c_v and $\bar{U}(\theta_-)$ are satisfied. Then for δ sufficiently small the conclusion of Theorem 5.7 (i) holds for

(5.5; U, δ).

(ii) Assume w_+ is given in the β -phase of the θ_+ non-monotone isotherm and

$$(II') \int_{w_-(0, \theta_+)}^{w_+} \exp(2 \int_{\lambda}^{w_-(0, \theta_+)} D_0(\xi, \theta_+) C_0(\xi, \theta_+)^{-1} d\xi) C_0(\lambda, \theta_+)^{-1} f_+(\lambda; 0) d\lambda > 0$$

and there exists $\bar{U}(\theta_+)$ so that

$$\int_{w_-(\bar{U}(\theta_+), \theta_+)}^{w_+} \exp \left(2 \int_{\lambda}^{w_-(0, \theta_+)} D_0(\xi, \theta_+) C_0(\xi, \theta_+)^{-1} d\xi \right) C_0(\lambda, \theta_+)^{-1} f_+(\lambda; \bar{U}) d\lambda = 0 .$$

Also assume constitutive Assumption c_v is satisfied and $p(w_+, \theta_+) > 0$. Then for δ sufficiently small the conclusion of Theorem 5.7 (ii) holds for $(5.5; U, \delta)$.

Sketch of proof. The main idea is to use the generalization of Lemma 3.1 given by Lemma 3.8 of [1] to do the isothermal connections. After that everything can be done as before except that we now use the Liapunov function

$$V(w, v, \theta) = \hat{\eta}(w, \theta) + \frac{U}{\theta} \left\{ -(\hat{\epsilon}(w, \theta) - \epsilon_-) - p_-(w - w_-)^2 + \frac{U^2}{2} (w - w_-)^2 \right\} + \frac{C_0(w, \theta)}{\theta} \left(\frac{v}{2} \right)^2 .$$

In this case we find along solutions of $(5.5; U, \delta)$

$$V' = -w'^2 \left(-U\mu_0(w, \theta) - \frac{C_0(w, \theta)}{\theta^2} \frac{\theta'}{2} - \frac{\partial C_0(w, \theta)}{\partial \theta} \frac{\theta'}{2\theta} \right) - \frac{a}{\delta} \frac{\theta'^2}{\theta^2} + \frac{\partial C_0(w, \theta)}{\partial w} \frac{w'^3}{2\theta} + \frac{D_0(w, \theta)}{\theta} w'^3 .$$

As before the θ' terms in the expression in parentheses can be made small for δ sufficiently small. The w'^3 terms also cause no difficulty as they are dominated by w'^2 for B with sufficiently small sides. Hence we again find $V' < -\text{const.}(w'^2 + \theta'^2)$ when (v, w, θ) is in B .

Remark 5.9. We note that as $\mu \rightarrow 0+$ the traveling wave solution given by Theorem 5.7 (i) approaches the functions

$$w(X, t) = \begin{cases} \tilde{w}_+ \\ w_- \end{cases}, \quad u(X, t) = \begin{cases} u_- - U^*(\theta_-)(\tilde{w}_+ - w_-) \\ u_- \end{cases}, \quad \theta(X, t) = \begin{cases} \tilde{\theta}_+ \\ \theta_- \end{cases}$$

for

$$\begin{cases} x > U^*(\theta_-)t \\ x < U^*(\theta_-)t \end{cases} \quad (5.6)$$

(Here $u(x,t)$ is determined by (2.5;b).)

A similar statement, of course holds for Theorem 5.7 (ii). The point, though is that (5.6) is not a distributional solution of the inviscid system

$$\begin{aligned} u_t &= -p(w, \theta)_x, \\ w_t &= u_x, \\ E_t &= -(up)_x + \alpha \theta_{xx}. \end{aligned} \quad (5.7)$$

Mathematically the reason is that (5.7) cannot possess distributional solutions with a jump in θ ; u, w piecewise constant and (5.7;c) implies θ_{xx} is a locally finite Borel measure and hence θ is continuous. This has been noted by Dafermos [16]; a physical explanation is given in ([13], Vol. II, p. 481).

Hence for the problem considered here the internal structure is crucial. Solutions of the viscous problem do not converge to solutions of the inviscid problem as $\mu \rightarrow 0+$. This is a reflection of the $\hat{h} = \alpha \theta_{xx}$ and $\alpha^{-1} = O(1)$ in μ assumptions and not the unusual non-hyperbolic nature of (5.7).

Remark 5.10. We note that Theorem 5.7 (i) says that the states in α -phase determines both an upstream state in the β -phase and a speed of propagation $U_\mu > 0$ so that α -phase (liquid) travels into the β -phase (vapor). This stands in contrast to classical fluid dynamics ($p_w < 0$) where both the state on one side of a shock and the speed of propagation determine the state on the other side of the shock. A similar interpretation can be given for Theorem 5.7 (ii).

Remark 5.11. It may be valuable to note that for μ small Theorem 5.7 predicts that the wave speeds $U^*(\theta_-)$ in (i) or $U^*(\theta_+)$ in (ii) will provide a good approximation to the true wave speeds. Thus while the isothermal equation (2.6; $U, 0$) yields the wrong equilibrium states to which a transition is made it does yield a good approximation to the correct speed of transition (Lemma 3.1).

Remark 5.12. While it is not the purpose of this paper to predict any particular set of experimental data it seems worthwhile to note the observations of Dettleff, Thompson, Meier and Spectman [17]. In that paper they noted the ability to produce a wave which yields complete liquefaction of a superheated vapor, i.e. a complete transition from gas to liquid. The liquids used in their study were of "retrograde type" (their terminology) in that they possessed high specific heat at constant volume (e.g. fluorocarbons). They also noted an increase in temperature from vapor to liquid phases. Remarkably all these observations are consistent with the theory presented in this paper.

The results of [17] are for a compression wave only. I know of no experimental results showing the liquid to vapor expansion wave predicted by Theorem 5.7 (ii). However within the range of solids (e.g. iron) exhibiting phase transitions both expansion and compression waves have been observed [13; Vol. II, p. 751]. The compression waves produced an increase in temperature, the expansion waves a decrease. Again this is consistent with the conclusions of Theorem 5.7.

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