ADMISSIBILITY CRITERIA FOR PROPAGATING PHASE BOUNDARIES IN A van der WAALS FLUID

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This paper gives admissibility criteria for weak solutions to the partial differential equations governing isothermal motion of a van der Waals fluid. The main issue is that an admissibility criterion based on viscosity alone is too restrictive—it rules out all slowly propagating phase boundaries. Instead a criterion based on viscosity and capillarity is proposed. The viscosity-capillarity condition is studied and shown to imply that the state on one side of a phase boundary specifies both the speed of the phase boundary and the state on the other side of the phase boundary (a result which is different from classical gas dynamics).

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Typically real fluids exhibit the property that under different configurations of pressure, density, temperature they can exist in different phases. For example water may exhibit vapor, liquid, and ice phases. Classical thermodynamics usually studies the co-existence of phases at equilibria so the term "thermodynamics" in this sense is a misnomer. In this paper the problem of true dynamic phase transitions is studied. In particular conditions are given for the existence of a propagating phase boundary separating liquid and vapor phases. The results are also applicable to phase transitions in solids undergoing "martensitic" or "shape-memory" phase transitions.
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0. INTRODUCTION

The purpose of this paper is to present admissibility criteria for weak solutions to the equations governing isothermal motion of a van der Waals fluid. The idea of admissibility criteria is quite well known in the study of hyperbolic conservation laws (see for example Lax [1],[2]). However for the case of a van der Waals fluid the balance laws of linear momentum and conservation of mass lead to a mixed hyperbolic - elliptic initial value problem. Thus new issues appear which are not present in classical hyperbolic equations of inviscid compressible fluid dynamics.

The most obvious difficulty with a mixed hyperbolic - elliptic initial value problem is the classical Hadamard instability of solutions lying in the unstable elliptic regime. To circumvent this difficulty it is natural then to consider only initial value problems where the data is given in the stable hyperbolic domains. Thus we should expect to find "weak" or "generalized solutions" to the equations of motion where such solutions take on values only in the stable hyperbolic domains. These weak solutions will in general possess propagating singular surfaces separating states in one hyperbolic domain from states in another hyperbolic domain. These singular surfaces are called propagating phase boundaries. The question then becomes one of knowing in what sense such phase boundaries are admissible.

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Two admissibility criteria are discussed here. The first is a standard viscosity criterion. This will be discarded as too slowly restrictive: it rules out all propagating phase boundaries. The second is a viscosity-capillarity condition. It allows for propagating phase boundaries to exist but only in very special cases. Namely for a propagating phase boundary to be admissible according to the viscosity-capillarity condition the state on one side of the phase boundary will determine both the propagation speed and the state on the other side of the boundary.

While this paper is devoted to fluid dynamics, the issues involved are quite similar to those discussed in a recent paper of James [3]. In that paper James has studied propagating phase boundaries in one-dimensional non-linear elasticity where the choice of constitutive relation leads to a mixed hyperbolic-elliptic initial value problem similar to the one studied here. Hence it may be that a criterion analogous to the viscosity-capillarity condition may prove useful in elasticity as well as fluid dynamics.
1. One dimensional Lagrangian description of compressible fluid flow

We follow the presentation of Courant & Friedrichs [4] of a Lagrangian description based on the law of conservation of mass. The fluid flow is thought of 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 of the mass of the fluid in the tube of unit cross section area between that section and the zero section. Analytically the quantity $X$ satisfies the relation

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

Here $\rho(x,t)$ denotes the density at position $x$ and time $t$ and $x=X(X,t)$ denotes the position of the 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

$$1 = \dot{X}X_t(X,t)p(X_t(X,t),t).$$

Set $\rho(X,X,t) = \tilde{\rho}(X,t)$, $w(X,t) = \tilde{\rho}(X,t)^{-1}$ (the specific volume), $\dot{X}X_t(X,t) = u(X,t) = X_e(X,t)$ (the velocity).

We denote the stress by $\tau$, the specific internal energy by $\epsilon$, the specific heat absorption by $q$, the heat flux by $h$, and the specific body force by $b$. Then the equations of balance of linear momentum, energy, and mass become

$$\rho \dot{x} = \tau_x + \rho b ,$$

$$\rho \dot{c} = \rho q + \tau \dot{x} + h_x ,$$

$$\dot{\rho} + \rho \dot{x}_x = 0 ,$$

where $\dot{\cdot} = \frac{d}{dt}$. We now apply the chain rule and rewrite this system in terms of the independent variables $X,t$ to obtain
\[ x_{tt} = \tau_x + b , \]
\[ \varepsilon_t = q + \tau_x X + h_x , \]
\[ (\rho X)_{tt} = 0 \] (1.1)

where we have used the fact that \( \dot{\rho}(x,t) = \dot{\rho}_t(X,t) \). The third of these equations is automatically satisfied since \( \dot{\rho} X = 1 \).

The above set of balance laws must be supplemented by constitutive relations. We assume the fluid is compressible and thermo-elastic so that the stress, internal energy, heat flux satisfy
\[
\tau = \hat{\tau}(w, T) ,
\]
\[
\varepsilon = \hat{\varepsilon}(w, T) ,
\]
\[
h = \hat{h}(w, T, T_x) ,
\]
Furthermore we assume for simplicity that the fluid is imbedded in a "heat bath" so that the motion is isothermal (T=positive constant) and there are no body forces. Mathematically this means (i) that \( q \) in (1.1.b) is assumed to be adjusted so (1.1.b) will always be satisfied identically and (ii) \( b=0 \). In this case (1.1) equivalent to the first order system
\[
u_t = \tau_X ,
\]
\[
w_t = u_X .
\] (1.2)

A \( C^1 \) curve \( \Gamma : X = \gamma(t) \) across which \( u,w \) experience jumps is called a singular surface. If \( \Gamma \) is a singular surface let \( (\gamma(\xi), \xi) \) be a fixed point on the graph of \( \Gamma \) and \( U = \dot{\gamma}(\xi) \). Denote by \( u_+, w_+, u_-, w_- \) the respective limits from the right and left as \( (X,t) \rightarrow (\gamma(\xi), \xi) \) for \( u,w \). If we put \([u] = u_+ - u_- , [w] = w_+ - w_- \) , etc.
then classically we know the Rankine-Hugoniot jump conditions must be satisfied, i.e.

\[ U[u] + [\tau] = 0 \]
\[ U[w] + [u] = 0 \]  

(1.3)

Of course (1.3) implies \( U^2 \) satisfies the equation

\[ U^2 = \frac{[\tau]}{[w]} \]  

(1.4)

As we shall always be working on a fixed isotherm let us set \( \tau(w,T) = -p(w) \). In this case (1.2) becomes

\[ u_t = -p(w)X \]
\[ w_t = uX \]  

(1.5)

As is easily seen (1.5) is either hyperbolic or elliptic depending on the sign of \( p'(w) \).

It is well known that conservation laws of the form (1.5) do not in general admit smooth solution. Typically discontinuities (shocks) will form in a finite time even for smooth initial data. Hence we must be satisfied solving (1.5) in the sense of distributions. Such solutions are termed weak solutions. Unfortunately as is also well known weak solutions are not generally uniquely determined by their initial values. To pick out the physically relevant ones some additional principle must be introduced. It is this issue which is pursued in the next sections.
2. Admissibility with respect to the viscosity criterion

Let us imbed the inviscid equations (1.6) in a viscous formulation, i.e. we take

\[ \tau = -p(w) + \mu(w)u_x. \]  \hspace{1cm} (2.1)

Typically (see [11]) we like to know that if \( u(X,t;u), w(x,t;w) \) sequence of solutions to (1.2), (2.1) which tend to a limit \( u(X,t;0), w(X,t;0) \) boundedly, almost everywhere as \( \mu(w) \to 0^+ \), then the limit functions \( u(X,t;0), w(X,t;0) \) satisfy (1.5) in the sense of distributions. In order to be sure that the term \( (u(w)u_x)_x \) entering (1.2a) does indeed converge to zero as \( \mu \to 0^+ \) in the distributional sense we require \( \mu(w) = \mu_0 \), a positive constant.

Now let \( \Gamma : X = \gamma(t) \) be a singular surface for (1.5). We now ask the question: Are solutions of (1.5) in the neighborhood of the singular surface \( \Gamma \) limits of solutions (1.2), (2.1) as \( \mu_0 \to 0^+ \)? While this problem has a history dating back to Rayleigh [5] it is the more recent discussions of Wendroff [6] and Dafermos [7] we shall follow.

Let \( (\gamma(\xi),\xi) \) be a fixed point on the graph \( \Gamma \) and let \( u_+, w_+, u_-, w_- \), \( U \) be as in Section 1. We look for a traveling wave solution of (1.2), (2.1) given by

\[ u(X,t) = \hat{u}(\xi), \quad w(X,t) = \hat{w}(\xi), \quad \xi = \frac{X - Ut}{\mu_0} \]

It follows that \( \hat{u}, \hat{w} \) must satisfy

\[ -\hat{u}' = (-p + \hat{u}') \]
\[ -\hat{w}' = \hat{u}' \]

where ' denotes \( \frac{d}{d\xi} \).
In order for \( \hat{u}, \hat{w} \) to approximate the discontinuous profile of the solution to \((1.6)\) we require
\[
(\hat{u}(-\infty), \hat{w}(-\infty), \hat{u}(+\infty), \hat{w}(+\infty)) = (u_-, w_-, u_+, w_+) . \tag{2.3}
\]
The above considerations motivate the following definition.

**Definition 2.1** If there exists \( u, w \) so that \((2.2),(2.3)\) are satisfied for all points \((\gamma(E), T)\) we will say the singular surface \( \Gamma \) satisfies the **viscosity admissibility criterion**.

**Theorem 2.2** The viscosity admissibility criterion is satisfied if and only if
\[
-u^2 + \left( -\frac{p(w) + p(w_-)}{w-w_-} \right) > 0 (\leq 0) \text{ if } U > 0 (< 0) \tag{2.4}
\]
for every value \( w \) between \( w_- \) and \( w_+ \). In other words for
\[
(w_+ - w_-) U > 0 \text{ (or } (w_+ - w_-) U < 0) \text{ the chord which joins } (w_-, p(w_-)) \text{ to } (w_+, p(w_+)) \text{ lies above (below) the graph of the function } p(w) \text{ for } w \text{ between } w_- \text{ and } w_+.
\]

**Proof** While proofs are presented in [6] and [7] we shall provide one for completeness.

Integrate \((2.2)\) from \(-\infty\) to \( \xi \). It follows that
\[
-u(\hat{u}(\xi)-u_-) = -p(\hat{w}(\xi)) + p(w_-) + \hat{u}'(\xi) ,
\]
\[
-u(\hat{w}(\xi)-w_-) = \hat{u}(\xi)-u_- , \tag{2.5}
\]
which it turn yields the first order equation
\[
u^2(\hat{w}(\xi)-w_-) + p(\hat{w}(\xi)) - p(w_-) = -U \hat{w}'(\xi) . \tag{2.6}
\]
If \( w_- < w_+ \) then we must have \( w'(\xi) > 0 \) and hence, \((2.4)\) follows.
A similar argument is used if \( w_+ < w_- \).
3. The van der Waals equation of state

On a fixed isotherm the van der Waals equation of state reads

\[ p'(w) = \frac{RT}{w-b} - \frac{a}{w^2}, \quad 0 < b < w < \infty, \quad (3.1) \]

where \( a, b, R, T \) are all positive constants ([8],[9]). Pictorially \( p(w) \) is represented in Fig. 1 if \( T \) is sufficiently small.

As we shall not need anything so specific as (3.1) in our analysis let us suppose in what follows that \( p(w) \) has basically the same type of graph as in Fig. 1, namely,

(i) \( p'(w) < 0 \), \( 0 < b < w < w_\alpha, \quad w_\beta < w \);

(ii) \( p'(w_\alpha) = p'(w_\beta) = 0 \), \( (3.2) \)

(iii) \( p'(w) > 0 \) if \( w_\alpha < w < w_\beta \).

The domains \( (b, w_\alpha) \) and \( (w_\beta, \infty) \) will be called the \( \alpha \)-phase and \( \beta \)-phase respectively. The \( \alpha \)-phase corresponds to the fluid being liquid, the \( \beta \)-phase corresponds to the fluid being vapor.

**Definition 3.1** A singular surface \( \Gamma \) will be called a phase boundary (shock) if for every point on \( \Gamma \) \( w_+, w_- \) lie in different (the same) phase.

**Theorem 3.2** For \( p \) satisfying (3.2) no phase boundary is admissible according to the viscosity criterion (Defn. 2.1) if \( |U| \) is sufficiently small.

**Proof** The chord joining \( (w_-, p(w_-)) \) to \( (w_+, p(w_+)) \) must cut the graph of \( p(w) \) and hence the viscosity criterion cannot be satisfied.

Since no slow phase boundaries are admissible according to the viscosity criterion it seems worthwhile to consider a less severe admissibility criterion. Indeed it may be that other
higher order effects other than viscosity should be considered. One such effect that is particularly pronounced in the liquid-vapor interface will be capillarity. A theory of interfacial capillarity was proposed in [10] by Korteweg and a discussion of his theory may be found in the monograph of Truesdell and Noll [11]. Korteweg's theory has most recently been reconsidered by Serrin [12] who has applied it to study condition for equilibrium between liquid and vapor phases in a van der Waals fluid. (A related theory based on statistical mechanics has been presented in [13]).

According to Korteweg's theory the stress \( \tau \) in our one-dimensional Lagrangian formulation will be given by

\[
\tau = -p(w) + D(w)w_x^2 - C(w)w_{xx} + u(w)u_x .
\]  

(3.3)

As in the discussion of constitutive relation (2.1) we would like to know that solutions of (1.2),(3.3) which tend to a limit boundedly, almost everywhere, as \( u(w) \to 0^+ \), \( D(w) \to 0 \), \( C(w) \to 0 \), will converge to solutions of (1.5). So in order to be sure that extra terms in (1.2),(3.3) due to the consideration of viscosity and capillarity tend to zero in the sense of distributions as \( u(w) \to 0^+ \), \( D(w) \to 0 \), \( C(w) \to 0 \), we set

\[
\begin{align*}
C(w) &= \mu_0^2 A , \\
D(w) &= 0 , \\
u(w) &= \mu_0 .
\end{align*}
\]

(3.4)

Thus in this special case (1.2),(3.3) becomes

\[
\begin{align*}
u_t &= (-p(w) - \mu_0^2 A w_{xx} + \mu_0 u_x)u_x , \\
w_t &= u_x .
\end{align*}
\]

(3.5)

Now let \( \Gamma \) be a phase boundary and \( \gamma(t), u_+ , u_- , w_+ , w_- \) be as in Section 1. Again we look for a traveling wave solution

\[
u(X,t) = u(\xi) , \quad w(X,t) = w(\xi) , \quad \xi = \frac{X-Ut}{\mu_0} .
\]

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From (3.5) it then follows that $\hat{u}, \hat{w}$ must satisfy

$$
\begin{align*}
- U\hat{u} &= (-p(\hat{w}) - \hat{w}'' + \hat{u}'), \\
- \hat{w}' &= \hat{u}' .
\end{align*}

(3.6)

So that $\hat{u}, \hat{w}$ will approximate the discontinuous profile of the solution to (1.5) we require

$$
(\hat{u}(-\infty), \hat{w}(-\infty), \hat{u}(+\infty), \hat{w}(+\infty)) = (u_-, w_-, u_+, w_+). 

(3.7)
$$

These considerations motivate the following definition.

**Definition 3.3** If there exists $\hat{u}, \hat{w}$ so that (3.6), (3.7) are satisfied for all points $(y(E), E)$ we will say the singular surface $\Gamma$ satisfies the **viscosity-capillarity admissibility** condition.

For $w_-, U (w_+, U)$ given in the $\alpha$-phase ($\beta$-phase) let $w_+(U)$ ($w_-(U)$) denote the solution (if it exists) of

$$
U^2 = \frac{[p]}{[w]} 
\quad (3.8)
$$

lying in the $\beta$-phase ($\alpha$-phase). Also set

$$
\begin{align*}
 f_-(\zeta; U) &= U^2(\zeta - w_-) + p(\zeta) - p(w_-) , \\
f_+(\zeta; U) &= U^2(\zeta - w_+) + p(\zeta) - p(w_+) .
\end{align*}
$$

Integration of (3.6) for $-\infty$ to $\zeta$ and the obvious substitution shows a solution $\hat{w}$ of (3.6), (3.7) must satisfy the second order equation

$$
\hat{A} \hat{w}'' + U\hat{w}' + f_-(\hat{w}; U) = 0 
\quad (3.9)
$$

with boundary conditions

$$
\hat{w}(-\infty) = w_-, \quad \hat{w}(+\infty) = w_+ 
\quad (3.10)
$$

**Lemma 3.4** Assume $A > 0$ .

(i) Let $w_-$ be given and assume
Then there exists a unique $U^*$, $0 < U^* < \bar{U}$, so that (3.9) possesses a solution with $w(-\infty) = w_-, w(\infty) = w_+(U^*)$. Here $\bar{U}$ is such that
\[ \int_{w_-} f_-(\zeta; U) d\zeta = 0. \]

(ii) Let $w_+$ be given and assume
\[ f_+(\zeta; 0) d\zeta > 0. \]
Then there exists a unique $U^*$, $\bar{U} < U^* < 0$, so that (3.9) possesses a solution with $w(-\infty) = w_-(U^*), w(\infty) = w_+$. Here $\bar{U}$ is such that
\[ \int_{w_-} f_+ (\zeta; \bar{U}) d\zeta = 0. \]

Remark 3.5 The hypotheses of the lemma have a simple interpretation. For example in (i), (I) says that the signed area between the chord joining $(w_-, p(w_-))$ and $(w_+(0), p(w_+(0)))$ and the graph of $p(w)$ between $w_-$ and $w_+(0)$ is negative. $\bar{U}$ is that positive value of $U$ so that the signed area between the chord joining $(w_-, p(w_-))$ and $(w_+(\bar{U}), p(w_+(\bar{U})))$ and the graph of $p(w)$ between $w_-$ and $w_+(\bar{U})$ is zero (see Fig. 1). Analagous interpretations hold for (ii).

Proof of Lemma (i) Let $y(w(\xi)) = \hat{y}'(\xi)$. Then (3.9) may be rewritten as
\[ \frac{A}{2} \frac{d}{dw} y^2(w) + U y(w) + f_-(w; U) = 0. \]
Integration from $w_-$ to $w$ yields
Figure 1 van der Waals isotherm; $w_-$ and $w_+ (\bar{U})$ so that area $A = \text{area } B$. 
Let us now consider the case $U = 0$. Let $w^*(0)$ denote that value of $w$ for which the chord connecting $(w_-, p(w_-))$ and $(w^+(0), p(w^+(0)))$ intersects the graph of $p(w)$, $w_\alpha < w^*(0) < w_\beta$. Since $f_-(\zeta, 0) > 0$ for $w^*(0) < \zeta < w^+_+(0)$ it follows that

$$\frac{A}{2} y^2(w) = - U \int_{w_-}^{w} y(\zeta) \, d\zeta - \int_{w_-}^{w} f_-(\zeta; U) \, d\zeta . \quad (3.11)$$

by (I). Hence if (I) holds and $U = 0$ the solution of (3.9) with $w(-\infty) = w_-$ always stays above the line $y = 0$.

Now let $U$ increase from zero to $\bar{U}$. The solutions of (3.9) form a nested sequence in $w-y$ plane; see Figure 2. By continuity with respect to the parameter $U$ all that is needed to establish the existence of a unique $U^*$ so that $w(\infty) = w_+(U^*)$ is to show that the solution for $U = \bar{U}$ crosses the line $y = 0$. But from (3.11) we see

$$0 < \frac{A}{2} y^2(w_+(\bar{U})) = - \bar{U} \int_{w_-}^{w} y(\zeta) \, d\zeta$$

So $y(\zeta)$ must go from positive to negative values for $\zeta$ between $w_-$ and $w_+(\bar{U})$.

(ii) The proof is similar to (i).

Theorem 3.6 Assume $A > 0$,

$(u_-, w_-) \ ((u_+, w_+))$ is to be a state to the left (right) of a point $(\gamma(\overline{t}), \overline{t})$ on a phase boundary $\Gamma$ and the hypothesis I (II) of Lemma 3.4 holds. Then $\Gamma$ is an admissible phase boundary according to the viscosity-capillarity condition if
Figure 2 Phase plane plot of solutions of (3.9) for $w_-$
fixed and $U$ increasing zero, $0 < U_1 < U_2 < U^* < \bar{U}$. 
and only if
\[ w_+ = w_(U^*), \quad u_+ = u_- - U^*(w_+(U^*) - w_-), \]
\[ \gamma(t) = U^* > 0 \quad (w_- = w_-(U^*), \quad u_- = u_+ + U^*(w_+ - w_-)) \]
\[ \gamma(t) = U^* < 0 \quad \text{where} \ U^* \text{ and } w_+(U^*) \ (U^* \text{ and } w_-(U^*)) \text{ are given by Lemma 3.4 (i) (ii)).} 

**Proof** The result follows immediately from Lemma 3.4 and the Rankine-Hugoniot jump conditions (1.3).

**Corollary 3.7** Let \( \Gamma \) be a singular surface (either shock or phase boundary) which is admissible according to the viscosity-capillarity condition for some \( A > 0 \). Let \( u_+, w_+, u_-, w, U \) be as in Section 2. Then the "entropy" inequality
\[ U \left( \int_{w_-}^{w_+} p(\zeta) d\zeta - (w_+ - w_-)(p(w_+) + p(w_-)) \right) < 0 \quad (3.12) \]
is satisfied. That is to say: \( U \) times the signed area between the graph of \( p(\zeta) \) between \( w_- \) and \( w_+ \) and chord joining \( (w_-, p(w_-)) \) to \( (w_+, p(w_+)) \) is negative.

**Proof** If there is a solution \( \hat{w}(\xi) \) to (3.9), then multiplication of (3.9) by \( \hat{w}'(\xi) \) yields
\[ \frac{d}{d\xi} \left[ \frac{A}{2} \hat{w}'(\xi)^2 + \int_{w_-}^{w_+} f_-(\zeta; U) d\zeta \right] = - U \hat{w}'(\xi)^2 \quad (3.13) \]
Integration of (3.13) from \(-\infty\) to \(\infty\) implies
\[ \int_{w_-}^{w_+} f_-(\zeta; U) d\zeta = - U \int_{-\infty}^{\infty} \hat{w}'(\xi)^2 d\xi. \]
or
\[ U \int_{w_-}^{w_+} f_-(\zeta; U) d\zeta < 0. \quad (3.14) \]
The integral indicated in (3.14) is precisely the bracketed expression in (3.12).
While we have argued that the choice \( \mu(w) = \mu_0, D(w) \equiv 0, \)
\( C(w) = \mu_0^2 \) is a natural assumption from the computational viewpoint one might still question whether the results of Theorem 3.6 carry over to a more general case. The answer is yes and is provided by the following result.

Assume \( \mu(w) = \varepsilon \mu_0(w), C(w) = \varepsilon^2 C_0(w), D(w) = \varepsilon^2 D_0(w) \)
where \( \varepsilon > 0 \) and \( \mu_0(w) > \bar{\mu}_0 > 0, C_0(w) > \bar{C}_0 > 0; \mu_0, C_0 \) constants. In this case (1.2), (3.3) becomes

\[
\frac{\partial u}{\partial t} = (-p(w) + \varepsilon^2 D_0(w) w^2 - \varepsilon^2 C_0(w) w^2 + \varepsilon \mu_0(w)) w_x, \\
\frac{\partial w}{\partial t} = \hat{u}_x.
\] (3.15)

Set \( \xi = \frac{X-Ut}{\varepsilon} \) and \( u = \hat{u}(\xi), w = \hat{w}(\xi) \). It follows that

\[
\hat{u}(\xi), \hat{w}(\xi) \text{ satisfy} \\
- \hat{u}'' = (-p(\hat{w}) + D_0(\hat{w}) \hat{w}^2 - C_0(\hat{w}) \hat{w}^2 + \mu_0(\hat{w}) \hat{u})', \\
- \hat{w}' = \hat{u}.
\] (3.16)

where we again impose boundary conditions (3.7). Integration of (3.16) from \(-\infty\) to \( \xi \) implies

\[
C_0(\hat{w}) \hat{w}'' + U \mu_0(\hat{w}) \hat{w}' - D_0(\hat{w}) \hat{w}'^2 + p(\hat{w}) - p(w_-) - U^2(\hat{w}-w_-) = 0
\] (3.17)

we have boundary conditions (3.10). We now state the following generalization of Lemma 3.4.

Lemma 3.8

(i) Let \( w_- \) be given and assume

\[
\begin{align*}
\int_{w_-}^{w_+} & e^{2 \int_{\xi}^\eta D_0(\xi) C_0(\xi)^{-1} d\xi} C_0(\gamma)^{-1} f_- (\gamma;0) d\gamma < 0 \\
\int_{w_-}^{w_+} & e^{2 \int_{\xi}^\eta D_0(\xi) C_0(\xi)^{-1} d\xi} C_0(\gamma)^{-1} f_- (\gamma;\bar{U}) d\gamma = 0.
\end{align*}
\]
Then there exists a unique $U^*$, $0 < U^* < \overline{U}$, so that (3.17) possesses a solution with $w(-\infty) = w_-$, $w(+\infty) = w_+(U^*)$.

(ii) Let $w_+$ be given and assume

\begin{equation}
(II^*) \int_{w_-(0)}^{w_+(0)} \exp\left(2 \int_{\eta} D_0(\zeta) C_0(\zeta)^{-1} d\zeta\right) C_0(\eta)^{-1} f_+(\eta; 0) d\eta > 0
\end{equation}

and that there exists $\overline{U} < 0$ so that

\begin{equation}
\int_{w_-(\overline{U})}^{w_+(\overline{U})} \exp\left(2 \int_{\eta} D_0(\zeta) C_0(\zeta)^{-1} d\zeta\right) C_0(\eta)^{-1} f_+(\eta; \overline{U}) d\eta = 0.
\end{equation}

Then there exists a unique $U^*$, $\underline{U} < U^* < 0$, so that (3.17) possesses a solution with $w(-\infty) = w_-(U^*)$, $w(+\infty) = w_+$.

The proof is similar to the proof of Lemma 3.4 and is omitted.
4. Relation to the Lax shock criterion

In this section we compare the viscosity-capillarity admissibility condition to the well known Lax shock criterion ([1],[2]) in the case $p' < 0$, i.e. (1.6) is strictly hyperbolic.

**Definition 4.1** For system (1.6) with $p' < 0$ we shall say a shock $\Gamma : X = \gamma(t)$ joining states $(u_+,w_+),(u_-,w_-)$ at $(\bar{t},\gamma(\bar{t}))$ satisfies the **Lax shock condition** if either

\[ (-p'(w_+))^\frac{1}{2} < U < (-p'(w_-))^\frac{1}{2} \]

or

\[ -(p'(w_+))^\frac{1}{2} < U < -(p'(w_-))^\frac{1}{2} \]

where $U = \gamma'(t)$.

**Theorem 4.1** If $p' < 0$ and $p'' \neq 0$, a shock $\Gamma$ which is admissible according to the viscosity-capillarity condition for any $A > 0$ is admissible according to the Lax shock condition.

**Proof** In this case (3.9) possesses two equilibrium points $(w_-,0)$ and $(w_+,0)$. If we know there is a connecting orbit for $U > 0$ then either $(w_-,0)$ and $(w_+,0)$ are both saddles or $(w_-,0)$ is a saddle and $(w_+,0)$ is stable node. The condition $p'' \neq 0$ and linearization about $(w_-,0)$ shows the two saddle case is impossible. Finally it follows easily that saddle-node case implies the Lax shock condition. The case $U < 0$ is proved in the same way.

**Theorem 4.2** If $p' < 0$ and $p'' > 0$ a shock wave $\Gamma$ which is admissible according to the Lax shock criterion is admissible according to the viscosity-capillarity condition for any $A > 0$. 

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Proof Consider the case \((-p'(w_{+}))^{\frac{1}{n}} < U < (-p'(w_{-}))^{\frac{1}{n}}\); the other case is analogous. Let \(A > 0\) be fixed and let

\[ V(\hat{w},\hat{w}') = \frac{A\hat{w}'^2}{2} + \int_{\hat{w}}^{\hat{w}'} f_{-}(\zeta; U) d\zeta. \]

Since \(p'' > 0\) we have \(V \to \infty\) as \(|(\hat{w},\hat{w}')| \to \infty\) and

\[ \frac{dV(\hat{w},\hat{w}')}{} \leq 0 \]

along solutions of (3.9). Then all orbits are bounded in the \((w,w')\) plane and by LaSalle's Invariance Principle [14] they must approach an equilibrium. These facts combined with Lemma 4.1 of [15] yield the theorem.
5. An elementary Riemann problem for a van der Waals fluid.

Consider (1.6) where \( p(w) \) has graph similar to that of Fig. 1, i.e. \( p \) satisfies (3.2). The Riemann initial value problem consists of specifying initial conditions

\[
\begin{align*}
  u &= u_0, & u &= u_1, \\
  w &= w_0, & w &= w_1
\end{align*}
\]

\( X < 0; \quad X > 0, \quad u_0, u_1, w_0, w_1 \) constants. (5.1)

In this section we consider the special choice of data \( u_0, w_0, u_1, w_1 \) so that \( w_0 \) is in the \( \alpha \)-phase, \( w_1 \) is in the \( \beta \)-phase and \( u_0, w_0, u_1, w_1 \) satisfying Rankine-Hugoniot jump conditions for some \( U \). This of course implies \( p(w_0) > p(w_1) \) if \( w_0 < w_1 \), \( p(w_0) < p(w_1) \) if \( w_0 > w_1 \). It is a trivial observation that

\[
\begin{align*}
  u &= u_0, & u &= u_1, \\
  w &= w_0, & w &= w_1
\end{align*}
\]

\( X < Ut; \quad X > Ut \) (5.2)

is a weak solution of (1.6), (5.1). The sign of \( U \) is as of yet undetermined. The line \( X = Ut \) is a phase boundary. From our previous results we can then conclude the following

**Theorem 5.1**  The phase boundary \( X = Ut \) in the solution (5.2) of (1.5), (5.1), (3.2) is inadmissible according to the viscosity criterion (Definition 2.1). If \( w_0 = w_0 \) satisfies (I) of Lemma 3.4 there is a unique \( U^* > 0, w_1 = w_+(U^*), u_1 = u_0 - U^*(w_+(U^*) - w_0) \), so that \( X = U^*t \) is an admissible phase boundary according to the viscosity-capillarity condition. If \( w_+ = w_1 \) satisfies (II) of Lemma 3.4 there is a unique \( U^* < 0, w_0 = w_-(U^*), u_0 = u_1 + U^*(w_0 - w_-(U^*)) \), so that \( X = U^*t \) is an admissible phase boundary according to the viscosity-capillarity condition.
Thus while (5.1) provides infinitely many possible solutions to a Riemann problem for \((u_0, w_0)\) fixed and \((u_1, w_1)\) allowed to vary, the viscosity-capillarity conditions says that solutions of the form (5.2) will be allowed only for one choice of \((u_1, w_1)\) if \(w_0\) satisfies (I) of Lemma 3.4. Of course a similar statement holds if \(w_1\) satisfies (II) of Lemma 3.4.
6. A possible experimental method for computing the coefficient \( A \) in Korteweg's theory.

In the preceding section we have seen that under certain conditions for a given \( A \) in the capillarity formulae (3.3), (3.4) a propagating phase boundary will be admissible with a certain speed \( U^* \). This result then presents an inverse problem. Consider an experiment in which a propagating phase boundary is observed for a van der Waals type fluid. Can one find an \( A \) so that the theory of Section 3 matches the experiment? If one can find such an \( A \) (possibly using numerical integration of (3.9)) then an estimate of the coefficient \( A \) is obtained.

In contrast to the above dynamic experiment an observation of a steady state phase boundary (\( \dot{\gamma}(t) \equiv 0 \)) will not provide an identification of \( A \). For if \( \dot{\gamma}(t) \equiv 0 \) have \( p(w_-) = p(w_+) \) and from (3.9) we have

\[
\int_{w_-}^{w_+} (p(\zeta) - p(w_-)) d\zeta = 0 \quad (6.1)
\]

for all choices of \( A > 0 \). Of course (6.1) is just a statement of Maxwell's equal area rule [8], [9], [12]. The point here is that calculating the non-zero speed of propagation of a phase boundary can provide an estimate of \( A \); such a determination will not follow from studying a steady state phase boundary.

Needless to say the above discussion has the implicit premise that the coefficient \( D \) in Korteweg's theory is zero. This may or may not be the case. If \( D \equiv 0 \) (6.1) shows the Maxwell equal area rule holds. However the converse is not true. Serrin
has shown in [12] that the equal area rule may hold even for non-zero D. Hence experimental knowledge of the equal area rule's applicability for a given fluid would not in itself imply $D = 0$. The converse is true, however, i.e. if the equal area rule does not hold for phase equilibrium then $D \neq 0$. This follows immediately from the remarks preceding (6.1). Of course in such cases as $D \neq 0$, and for more general choices of $u(w)$, $C(w)$, Lemma 3.8 may prove of value in parameter identification.
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ADMISSIBILITY CRITERIA FOR PROPAGATING PHASE BOUNDARIES IN A van der WAALS FLUID

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Phase transitions, viscosity criterion, viscosity-capillarity criterion, propagating phase boundary, van der Waals fluid

This paper gives admissibility criteria for weak solutions to the partial differentials equations governing isothermal motion of a van der Waals fluid. The main issue is that an admissibility criterion based on viscosity alone is too restrictive; it rules out all slowly propagating phase boundaries. Instead a criterion based on viscosity and capillarity is proposed. The viscosity-capillarity condition is studied and shown to imply that the state on one side of a phase boundary specifies both the speed of the phase boundary and the state on the other side of the phase boundary (a result which is different from classical gas dynamics).