Dynamic Phase Transitions in Korteweg Fluids

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Abstract: We describe the qualitative behavior of traveling wave solutions for thermodynamic phase transitions under Landau equation of state and Korteweg's theory of capillarity.

Key Words: Traveling waves, phase transitions

1 Introduction

In this paper, we consider thermodynamic phase transformations modeled by conservation laws of mass, momentum and energy. We write these laws in Lagrangian coordinates to derive the following hyperbolic-elliptic system of equations

$$v_t = u_x \quad (1)$$
$$u_t = T_x \quad (2)$$
$$E_t = (uT)_x + W_x + F_x \quad (3)$$

Here v denotes the specific volume, u the velocity, and T the stress tensor which is defined according to Korteweg's theory of surface tension by the formula $T = -p(v, \theta) + \epsilon u_x - \delta v_{xx}$, where ϵ is the viscosity, δ is the capillarity coefficient measuring the interfacial surface tension according to Korteweg [7], θ is the temperature, and p is the equation of state defined by $p(v, \theta) = -\Psi(v, \theta)_v$ for a nonconvex Landau free energy $\Psi(v, \theta)$ of the following form

$$\begin{aligned} \Psi(v, \theta) = & - c_1\theta \ln \theta + c_1\theta + c_2 \\ & + \frac{a}{2}\theta v^2 + \frac{b}{4}v^4 + \frac{c}{6}v^6 \end{aligned} \quad (4)$$

where the coefficients a and c are positive, and b is negative. These constants are chosen to simulate two phase equilibrium. The choice of this energy provides a good model to both van der Waals fluids and multiphase elastic materials, in addition to its simple theoretical description of conservation laws of mixed type. The interstitial work flux W is added to take into account the working of long range interactions [7], and is given by the formula $W = \delta u_x v_x$ and the total energy E is defined as follows $E = e + \frac{u^2}{2} + \frac{\delta}{2}v_x^2$ where the internal energy e is given by $e = \Psi - \theta\Psi_\theta$. The term $\frac{u^2}{2}$ represents the kinetic energy, and $\frac{\delta}{2}v_x^2$ represents the interfacial energy. The heat flux F is given by Fourier's law $F = \mu\theta_x$ where μ is the heat conductivity coefficient. We choose the temperature θ to be an independent variable instead of the energy and set $c_1 = 1$ to obtain

$$\begin{aligned} v_t &= u_x \\ u_t &= -p(v,\theta)_x + \epsilon u_{xx} - \delta v_{xxx} \\ \theta_t &= \mu\theta_{xx} + (q(v,\theta) + \epsilon u_x)u_x \end{aligned} \tag{5}$$

where the function $q(v,\theta) = \theta\Psi_{\theta v} = a\theta v$. The system of equations (5) differs from the equations modeling the standard adiabatic flow in the presence of higher order derivatives v_{xxx} and in having a nonconvex equation of state of the form

$$p(v,\theta) = -(av\theta + bv^3 + cv^5) \tag{6}$$

The coefficients a, b, c are selected so that the pressure p has a critical temperature at $\theta_{cr} = \frac{9b^2}{20ab}$.

The goal of this study is to describe the characteristics of visco-capillary traveling wave solutions and type of singularity at different phases. Slemrod [15] proved the existence of phase jumps for thermodynamic flows, and Hagan and Serrin [6] showed the existence of phase transformations in a van der Waals fluids.

2 Traveling Waves in Phase Transitions

We seek smooth shock wave profiles of system (5) in the form

$$(v,u,\theta)(x,t) = (v,u,\theta)(x - st) \tag{7}$$

or in scaled form

$$(v,u,\theta)(x,t) = (v,u,\theta)(\frac{x - st}{\sqrt{\delta}}) \tag{8}$$

for small ϵ, μ and δ, here s is the speed of the traveling wave and these profiles satisfy the following boundary conditions

$$\begin{aligned} U(x,0) &= (v(x,0), u(x,0), \theta(x,0)) \\ &= \begin{cases} U_l = (v_l, u_l, \theta_l) & x \to -\infty \\ U_r = (v_r, u_r, \theta_r) & x \to +\infty \end{cases} \end{aligned} \tag{9}$$

where U_l and U_r are constant end states.
The speed s must satisfy the Rankine-Hugoniot (R-H) jump conditions

$$\begin{aligned} s[v] &= -[u] \\ s[u] &= [p] \\ s[E] &= [pu] \end{aligned} \tag{10}$$

here the jump notations defined as follows $[v] = v_r - v_l$. For a fixed end state (v_l, p_l), these conditions define the Hugoniot curve given by

$$\begin{aligned} H(v,p) &\equiv e - e_l + \frac{p + p_l}{2}(v - v_l) \\ &= 0 \end{aligned} \tag{11}$$

This curve describes the necessary conditions for a point to be connected to (v_l, p_l) by a shock wave. We substitute (7) in the system (5), and integrate over $(-\infty, \xi)$ to obtain the following autonomous differential equations

$$\begin{aligned} \delta v'' &= -\epsilon s v' - (p - p_l) - s^2(v - v_l) \\ \mu\theta' &= \frac{\delta}{2} s v'^2 - s[(e - e_l) \\ &+ p_l(v - v_l) - \frac{s^2}{2}(v - v)^2] \end{aligned} \tag{12}$$

Introducing the notation $w = v'$ and

$$\begin{aligned} L(v,\theta) &= p(v,\theta) - p_l + s^2(v - v_l) \\ M(v,\theta) &= e(v,\theta) - e_l + p_l(v - v_l) \\ &- \frac{s^2}{2}(v - v_l)^2 \end{aligned} \tag{13}$$

we rewrite (12) as a first order system of equations

$$\begin{aligned} v' &= w \\ w' &= -\frac{\epsilon s}{\delta} w - \frac{1}{\delta} L(v,\theta) \\ \theta' &= \frac{\delta s}{2\mu} w^2 - \frac{s}{\mu} M(v,\theta) \end{aligned} \tag{14}$$

We seek solutions of (14) with limiting end states U_l, U_r as $x \to \pm\infty$, which correspond to inviscid waves. We also note that the system (12) with zero capillarity ($\delta = 0$) is equivalent to

$$\begin{aligned} v' &= -\frac{1}{\epsilon s} L(v,\theta) \\ \theta' &= -\frac{s}{\mu} M(v,\theta) \end{aligned} \tag{15}$$

The solvability of the autonomous system (14) with van der Waals pressure type and with boundary conditions (9) has been investigated by Slemrod [15] where he showed the existence of travelling wave solutions, Grinfeld [5], and Hagan and Serrin [6]. Here, we present the main propositions and properties related to the curves $H(v,\theta)$, $L(v,\theta)$, and $M(v,\theta)$ for a concrete polynomial equation of state. The systems (14) and (15) admit travelling wave solution (phase transformations) provided there are trajectories (orbits) connecting two singular points which satisfy the necessary Hugoniot relation $H = 0$, and simultaneously they are equilibrium points of M and L. We group the main properties of curves H, M, L in the following lemmas:

Lemma 2.1 *The Hugoniot curve $H(v,\theta)$ uniquely defines θ as a function of v and tends to ∞ as v approaches the value* $(av_l - \sqrt{a^2 v_l^2 + 8a})/2a$

Lemma 2.2 *The function $L(v,\theta)$ uniquely defines θ as a function of $v < 0$, i.e., $\theta = \theta_L(v)$ and $L(v,\theta)$ has the following properties:*

1. $\frac{\partial L}{\partial \theta} = -av > 0$
2. $\theta_L \to \infty$ *as* $v \to 0^-$
3. $\theta_L \to -\infty$ *as* $v \to -\infty$
4. θ_L *has two critical values, whenever* $\theta < \theta_{cr}$

Lemma 2.3 *The function $M(v,\theta)$ uniquely defines θ as a function of $v < 0$, i.e., $\theta = \theta_M(v)$, such that*

1. $\frac{\partial M}{\partial \theta} = 1$, *and* $\frac{d\theta_M}{dv} = -\frac{\partial M}{\partial v}$
2. *the curve θ_M has a unique maximal value $\overline{v}$ which is smaller than the critical values of the curve θ_L*

The proofs of these lemmas are simply derived from the explicit form of these curves. The restriction of v to negative values is physically meaningful in this particular model. We also have

$$H = M + \frac{1}{2}(v - v_l)L \tag{16}$$

It was shown by Slemrod that the capillarity can be used as a selection criterion in the isothermal model (15). Also, there is a possibility of oscillatory phase jump connections. In order to answer these questions in the thermodynamic model we identifiy the classification of critical points of (14) or (15). The singular points are the intersections of $L(v,\theta) = 0$ and $M(v,\theta) = 0$. There are three possibilities for these intersections:

A. θ_L intersects θ_M at a single point

B. θ_L intersects θ_M at two points, where one of them is a tangential intersection i.e.; $\frac{d\theta_L}{dv} = \frac{d\theta_M}{dv}$,

C. θ_L intersects θ_M at three points

We linearize the system (14) and (15) around an arbitrary singular point denoted by $(v_0, 0, \theta_0)$ for (14), and (v_0, θ_0) for (15) to get

$$\begin{pmatrix} v \\ w \\ \theta \end{pmatrix}' = \begin{pmatrix} 0 & 1 & 0 \\ -\frac{1}{\delta}\frac{\partial L}{\partial v} & -\frac{\epsilon s}{\delta} & -\frac{1}{\delta}\frac{\partial L}{\partial \theta} \\ -\frac{s}{\mu}\frac{\partial M}{\partial v} & 0 & -\frac{s}{\mu}\frac{\partial M}{\partial \theta} \end{pmatrix} \begin{pmatrix} v - v_0 \\ w \\ \theta - \theta_0 \end{pmatrix} \tag{17}$$

The characteristic equation of the capillary system (17) is

$$\lambda(\lambda + \frac{\epsilon s}{\delta})(\lambda + \frac{s}{\mu}) - \Delta = 0 \tag{18}$$

where Δ denotes the determinant of the system(18)

$$\Delta = -\frac{s}{\mu\delta}(\frac{\partial L}{\partial v}\frac{\partial M}{\partial \theta} - \frac{\partial L}{\partial \theta}\frac{\partial M}{\partial v}) \tag{19}$$

the corresponding characteristic equation for the viscous system (15) is

$$\begin{vmatrix} \frac{\partial L}{\partial v} - \lambda & \frac{\partial L}{\partial \theta} \\ \frac{\partial M}{\partial v} & \frac{\partial M}{\partial \theta} - \lambda \end{vmatrix} = 0 \tag{20}$$

with the characteristic roots

$$\lambda_{1,2} = \frac{1}{2}(\frac{\partial L}{\partial v} + \frac{\partial M}{\partial \theta}) \pm \sqrt{\frac{1}{4}(\frac{\partial L}{\partial v} + \frac{\partial M}{\partial \theta})^2 + \frac{\partial M}{\partial v}\frac{\partial L}{\partial \theta} - \frac{\partial L}{\partial v}\frac{\partial M}{\partial \theta}} \tag{21}$$

We observe that if the end states U_l and U_r are in the same phase and satisfy the Hugoniot conditions, then there is a connecting orbit for the systems (14) and (15). In addition, the eigenvalues of the viscous system (21) are always real and the profiles of the orbits are monotone. However, the eigenvalues of the capillary system (14) can be complex numbers at U_r, provided U_r is in the same phase as U_l, and δ is large enough. In this case, the corresponding connecting orbits are oscillatory. However, if the end states U_l and U_r are in different phases, then the connecting orbit (phase transformation) is tangential at the right end state U_r, which corresponds to a zero determinant, that is $\Delta = 0$. This leads to real eigenvalues and one of them is zero at the right end state in the capillary system (18) as well in the viscous system (21). Thus, the phase transformations can not be oscillatory.

3 Conclusion

The autonomous differential equations (14) and (15) admit unique travelling wave solution (dynamic phase transition) such that its end states satisfy the Rankine-Hugoniot conditions and the right end state is tangential point to the curves L and M. This type of phase jumps are monotone. We also observe that diffusion and capillarity terms lead to the same selection criterion.

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