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Travelling waves near a critical point of a binary fluid mixture

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ABSTRACT

Travelling waves of densities of binary fluid mixtures are investigated near a critical point. The free energy is considered in a non-local form taking account of the density gradients. The equations of motions are applied to a universal form of the free energy near critical conditions and can be integrated by a rescaling process where the binary mixture is similar to a single fluid. Nevertheless, density solution profiles obtained are not necessarily monotonic. As indicated in Appendix, the results might be extended to other topics like in finance or biology.

1. Introduction

In physical chemistry, thermodynamics and condensed matter physics, a critical point specifies the conditions (temperature, pressure and concentration) at which distinct phases do not exist [6,9,29]. There are multiple types of critical points such as vapour–liquid or liquid–liquid critical points. A single fluid has a unique critical point associated with given temperature, pressure and density. For binary mixtures of fluids, in the space of temperature, pressure, concentration, critical points are represented by a curve in a convenient domain [26]; to each temperature we can associate a critical pressure and two critical densities corresponding to the mixture components [13,36].

An important thermodynamical potential is related to the mixture volume free energy [32–34]. At a given temperature, the volume free energy is associated with the *spinodal* curve connecting the two different phases of the binary mixture. Due to conditions of equilibrium of phases, it is possible to form a general expansion of the free energy near a critical point. This form is known in the literature by means of physical chemistry considerations [37] and is the form we use in our calculations.

By calculations in molecular theories, the densities of the components fluctuate near a critical point [24]. In the following, we use a continuous model to investigate how the average variations of densities are related to molecular interactions. Two assumptions are explicit [4,18,38]:

(i) The component densities are assumed to be the smooth functions of the distance from an interface layer which is assumed to be flat on the scale of molecular sizes. The correlation lengths are assumed to be greater than intermolecular distances [21,23]; this is the case when at a given temperature T the parameters are close to the ones of a critical state [35].

(ii) The binary mixture is considered in the framework of a mean-field theory. This means, in particular that the free energy of the mixture is a classical so-called “gradient square functional”. This kind of Landau–Ginzburg model consisting of a quadratic form of the density gradients comes from Maxwell and van der Walls original ideas [27,31,42,44]. At given critical conditions, the coefficients of the quadratic form are constant.

This point of view that, in non-homogeneous regions, the mixture may be treated as bulk phase with a local free-energy density and an additional contribution arising from the non-uniformity which may be approximated by a gradient expansion truncated at the second order is most likely to be successful and perhaps even quantitatively accurate near a critical point [37]. The approximation of mean field theory does provide a good understanding and allows one to explicitly calculate the magnitude of the coefficients of the model. These non-linear equations are able to represent interface layer and bulks and consequently allow to build a complete theory of the mixtures in non-homogeneous domains in dynamics.

In Section 2 we recall the equations of motion in a pure mechanical process obtained through the Hamilton variational principle.

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Section 3 is devoted to travelling waves without dissipation. Due to the fact that the equations are Galilean invariant, the case of equilibrium and the case of motion are analyzed together.

In Section 4, by means of a rescaling process taking the vicinity of a critical point into account, we integrate the equation for equilibrium as well as for motions with dissipation.

Two appendices present the motion equations and the mathematical reason of the choice of the free energy form near a critical point of a binary mixture of fluids obtained by a new method issued from differential geometry.

2. Isothermal motion of a binary fluid mixture near a critical point

We study a mixture of two fluids by a mechanical process. No assumption has to be done about composition or miscibility. The motion of a two-fluid continuum can be represented with two surjective differentiable mappings (see Fig. 1) [1,15,16,22]:

$$\mathbf{z} \to \mathbf{X}_1 = \Phi_1(\mathbf{z}) \quad \text{and} \quad \mathbf{z} \to \mathbf{X}_2 = \Phi_2(\mathbf{z}),$$

where subscripts 1 and 2 are associated with each constituent of the mixture. Term $\mathbf{z}=(t,\mathbf{x})$ denotes Euler variables in space-time $\mathcal{W}$ and terms $\mathbf{X}_1$ and $\mathbf{X}_2$ denote the Lagrange variables of constituents in *reference spaces* $\mathcal{D}_{o1}$ and $\mathcal{D}_{o2}$ respectively.

In the pure mechanical case, the Lagrangian density of the mixture is

$$L = \tfrac{1}{2}\rho_1 \mathbf{v}_1^2 + \tfrac{1}{2}\rho_2 \mathbf{v}_2^2 - e - \rho_1 \Omega_1 - \rho_2 \Omega_2,$$

where $\mathbf{v}_1$ and $\mathbf{v}_2$ denote the velocity vectors of each constituent, ρ_1 and ρ_2 are the densities, Ω_1 and Ω_2 are the external force potentials depending only on $\mathbf{z}=(t,\mathbf{x})$ and e is the volume energy [2,14]. The expression of the Lagrangian is in a general form. In fact dissipative phenomena imply that $\mathbf{v}_1$ is almost equal to $\mathbf{v}_2$; it is the reason why we do not take account of some kinetic energy associated with the relative velocity of the components which is of a smaller order (at least of order 2) and will be negligible in travelling wave behaviour [5,25,28]. Because of the interaction between the constituents, the volume energy e is not the sum of the energies of each constituent of the mixture, like for *Euler mixtures of fluids*. The mixture is assumed not to be chemically reacting. Conservations of masses require

$$\rho_i \det \mathbf{F}_i = \rho_{oi}(\mathbf{X}_i), \tag{1}$$

where subscript i belongs to $\{1,2\}$. At t fixed, the deformation gradient $\partial \mathbf{x}_i/\partial \mathbf{X}_i$ associated with Φ_i is denoted by $\mathbf{F}_i$ and ρ_{oi} is the reference specific mass in $\mathcal{D}_{oi}$.

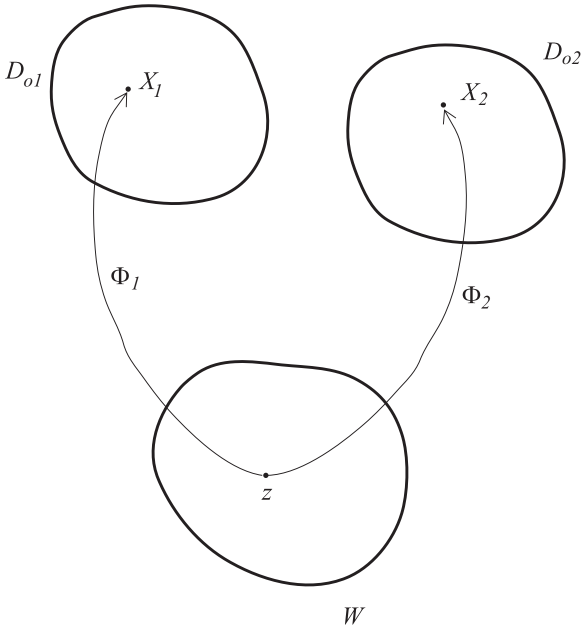

Fig. 1. General representation of a two-fluid continuum motion.

Eq. (1) is equivalent to the Eulerian form:

$$\frac{\partial \rho_i}{\partial t} + \operatorname{div} \rho_i \mathbf{v}_i = 0. \tag{2}$$

The volume energy e is given by the behaviour of the mixture [7,11,12]. In our mechanical case, for an energy depending on gradients of densities, the volume energy is

$$e = e(\rho_1, \rho_2, \operatorname{grad} \rho_1, \operatorname{grad} \rho_2).$$

The potential

$$\mu_i = \frac{\partial e}{\partial \rho_i} - \frac{\partial}{\partial x_\gamma}\left(\frac{\partial e}{\partial \rho_{i,\gamma}}\right)$$

defines the *specific free enthalpy or chemical potential* of the constituent i of the mixture [16]. Subscript γ corresponds to the spatial derivatives associated with gradient terms. Usually, summation is made on repeated subscript γ. In practice, we consider a quadratic form with constant coefficients C_1, C_2, D

$$Q = C_1(\operatorname{grad} \rho_1)^2 + 2D \operatorname{grad} \rho_1 \operatorname{grad} \rho_2 + C_2(\operatorname{grad} \rho_2)^2,$$

such that

$$e = g_o(\rho_1, \rho_2) + \tfrac{1}{2}Q, \tag{3}$$

where $g_o(\rho_1, \rho_2)$ is the value of the volume energy of the homogeneous bulks.

To obtain the equations of motions, we use a variational principle whose original feature is to choice variations in reference spaces (Fig. 1). They are associated with a two-parameter family of virtual motions of the mixture (see Appendix A).

The equation of the motion of each constituent of the mixture writes [19] and the references therein:

$$\mathbf{a}_i + \operatorname{grad}(\mu_i + \Omega_i) = 0, \quad i = \{1,2\}, \tag{4}$$

where $\mathbf{a}_i$, denotes the acceleration of the component i $(i=1,2)$. In applications, the motions are supposed to be isothermal (T denotes the common temperature value of the two components) and correspond to strong heat exchange between components. In thermodynamics, this case corresponds to a function $g_o(\rho_1, \rho_2)$ as the volume free energy of the homogeneous mixture at temperature T.

In our model, the equations of motion (4) yield

$$\begin{cases} \mathbf{a}_1 = \operatorname{grad}\{C_1 \Delta \rho_1 + D \Delta \rho_2 - g_{o,\rho_1}\}, \\ \mathbf{a}_2 = \operatorname{grad}\{D \Delta \rho_1 + C_2 \Delta \rho_2 - g_{o,\rho_2}\}. \end{cases} \tag{5}$$

Taking Eq. (2) into account, we can note that the two equations of system (4) are equivalent to the system:

$$\frac{\partial \rho_i \mathbf{v}_i}{\partial t} + \operatorname{div}(\rho_i \mathbf{v}_i \otimes \mathbf{v}_i) + \operatorname{grad}(\rho_i \mu_i) = \mu_i \operatorname{grad} \rho_i, \quad i = \{1,2\}$$

for which equations of components are not in divergence form, but the summation of the two equations and the fact that $\sum_{i=1}^{2} \mu_i \operatorname{grad} \rho_i = \operatorname{grad} e$ allow to obtain the total motion of the mixture in divergence form [16,19]. Therefore, while the global momentum equation represents a balance law, individually, the equations of system (2) do not.