

## Boussinesq approximation of the Cahn-Hilliard-Navier-Stokes equations

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We use the Cahn-Hilliard approach to model the slow dissolution dynamics of binary mixtures. An important peculiarity of the Cahn-Hilliard-Navier-Stokes equations is the necessity to use the full continuity equation even for a binary mixture of two incompressible liquids due to dependence of mixture density on concentration. The quasicompressibility of the governing equations brings a short time-scale (quasiacoustic) process that may not affect the slow dynamics but may significantly complicate the numerical treatment. Using the multiple-scale method we separate the physical processes occurring on different time scales and, ultimately, derive the equations with the filtered-out quasiacoustics. The derived equations represent the Boussinesq approximation of the Cahn-Hilliard-Navier-Stokes equations. This approximation can be further employed as a universal theoretical model for an analysis of slow thermodynamic and hydrodynamic evolution of the multi-phase systems with strongly evolving and diffusing interfacial boundaries, i.e., for the processes involving dissolution/nucleation, evaporation/condensation, solidification/melting, polymerization, etc.

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### I. INTRODUCTION

Fluid mixtures can be classified as being immiscible (e.g., oil-water mixture) or miscible (e.g., honey-water mixture or mixture of two gases). An immiscible system is characterized by a strict interfacial boundary. This boundary cannot be crossed by the molecules of adjoining liquids, which, on molecular scale, can be explained by a high potential barrier due to different intermolecular interactions within the mixture components. At macroscale, the coefficient of surface tension is introduced to define the macroscopic effects of the interfacial potential barrier.

The mixture of two gases is an example of a directly opposite case. As intermolecular forces between gas molecules are negligibly small, no potential barrier at the gases' boundary exists, and gas molecules of initially separated components freely codiffuse. So there is no sense in introduction of an interface, and hence, there is no surface tension on the gases' boundary.

The focus of the current work is on the miscible mixtures of two liquids, for which the intermolecular forces cannot be neglected. As an everyday example, the behavior of a droplet of honey in water may be considered: for such a droplet, a strict interface is visible for a long period after immersion of a droplet into water; however, after a slow dissolution process honey-water mixture becomes homogeneous. Again, the existence of a strict interface between mixture components, on molecular scale, should be associated with a potential barrier. However, in comparison with the immiscible case, for miscible interfaces, some molecules with sufficiently high kinetic energies are able to cross this barrier. It may be further assumed that the molecular flux through an interface gradually diminishes the barrier's height which would result in growing numbers of molecules being diffused from one phase to another and, ultimately, in a complete dissolution of a droplet.

Thus, the concept of interface is required to describe the behavior of a slowly miscible system. The interface, at macroscale, will be characterized by the surface-tension coefficient. In contrast to immiscible systems, surface-tension coefficient varies as the dissolution progresses (see, e.g., Ref. [1]). The cases of completely and partially miscible liquids (e.g., honey-water and butanol-water mixtures) would differ from each other by the fact that the surface-tension coefficient decreases to zero in the first case (as the interface disappears) and is dynamically variable over dissolution process but always remains nonzero in the second case.

The surface energy effects have a twofold influence on the dissolution dynamics; both the morphology of the interface and the rate of mass transfer through the interface are affected. We may argue that the surface tension is sufficiently high to exclude the codiffusion of molecules between immiscible liquids. In the case of miscible systems, the mass transfer through the interface will be not zero but its rate will be restricted by the surface energy effects. Mathematically, this will follow from the fact that classical Fick's law stating the linear proportionality between diffusive flux and concentration gradient is invalid for strong solutions [2]. For instance, there is a strong concentration gradient across the interfacial boundary, but no interfacial diffusion for an equilibrated heterogeneous binary system. An equilibrium state of the binary mixture is defined through the equality of the chemical potentials of the adjoining liquids. A more general law for the interfacial mass transport, generated when the binary system is taken off its equilibrium, should be based on the gradient of chemical potential through the interface. The expression for the chemical potential will already include the surface-tension effects [3] and the effect of barodiffusion [2,3]. The barodiffusion was experimentally observed in the studies of the equilibrium and nonequilibrium concentration profiles in binary mixtures [4–6].

A first review devoted to the physics of slowly miscible systems can be found in Ref. [1]. The phase-field approach was adopted to model the hydrodynamic evolution of a miscible interface. The authors pointed out that there is another

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physical effect that should characterize the evolution of binary mixtures, namely, the quasicompressibility of the hydrodynamic equations: even for a mixture of two incompressible liquids, the fluid velocity is a nonsolenoidal field due to dependence of mixture density on concentration.

The first numerical studies of the evolution of miscible interfaces were based on the governing equations in which the surface energy effects were not taken into account [7]. The Cahn-Hilliard-Navier-Stokes equations, which include all essential physical effects previously discussed by Joseph and Renardy [1], have been derived by Lowengrub and Truskinovsky [3]. These equations fully define the hydrodynamic behavior of miscible binary mixtures, showing that there are two surface energy effects which define the morphology of the interface (the Korteweg stress) and the rate of mass transfer through the interfacial boundary. Nevertheless, the recent numerical studies of the miscible multiphase systems do already take into account the effects of the surface tension in the momentum balance equation but still continue to describe the diffusion process based on the classical impurity-like models [8–10].

The hydrodynamics of immiscible systems has been studied either for density-matched fluids [11–13]—for such fluids, the quasicompressibility effects are eliminated—or by using the Boussinesq-like approximation [14–18]. Since within the phase-field approach it is necessary to assume that the density gradients are large at least in some parts of a computational domain, this makes justification of the Boussinesq approximation difficult. The role of the quasicompressibility effects for a particular system was examined in Refs. [19] (for an analysis of one-dimensional diffusion within a pipe) and [8] (for an analysis of miscible displacements in capillary tubes). Following Ref. [19], the velocity field was divided into incompressible and expansion parts. In both works, the estimations showed that the expansion part of the velocity field is negligibly small. Nevertheless, even such a statement is not sufficient to prove the use of the Boussinesq approximation.

We are unaware of any paper where the Boussinesq approximation of the full Cahn-Hilliard-Navier-Stokes equations has been strictly derived. This is done in the current work on the basis of the multiple-scale method and averaging procedure. First, along with Ref. [3], the quasiacoustic effects will be identified. It will be shown that, similar to the classical acoustics, the quasiacoustics is also characterized by the short time scale, which allows us to filter out these quick process from the governing equations. The resultant equations will define the slow (on the convective and diffusion time scales) dissolution dynamics of a multiphase system. The obtained model will represent the Boussinesq approximation of the full Cahn-Hilliard-Navier-Stokes equations, but it can also be considered as an analog of the low-Mach number approximation used for an analysis of slow nonisothermal flows in compressible media [20–22]. The derived equations are fully incompressible, which significantly simplifies their numerical solution.

To conclude this introductory section, we would like to mention that applications that involve the miscible interfaces are ubiquitous. They include solvent extraction, cleaning, removal of oil spills, waste treatment, enhanced oil recovery,

drug delivery, etc. Frequently, it is assumed that the rate of dissolution and the rate of flow change are not comparable, e.g., dissolution is a slow process and the changes, caused by hydrodynamic flows, happen at much faster rate, or, on the contrary, nucleation is a very fast process and the hydrodynamic flows are much slower. For such cases, different simplified models were proposed which allow these processes to be considered separately. We, however, are interested in slow flows when the typical dissolution and convective time scales are comparable; an example can serve the hydrodynamic flows in capillary tubes or in porous media. Other important examples where the thermodynamic and hydrodynamic processes interact are the flows in near-critical systems.

## II. CAHN-HILLIARD-NAVIER-STOKES-EQUATIONS

In the current work, the phase-field approach is utilized to define the evolution of a multiphase system. The mixture components are called solvent and solute. To characterize a state of the binary mixture the concentration field is used, which we define as the mass fraction of the solute in the solvent phase.

The main idea of the phase-field approach is to artificially smear the interfacial boundary and one system of the Navier-Stokes equations is solved for the entire multiphase system. All variables experience strong but continuous changes through the interface. The position and shape of the interface are tracked by using the concentration field. The fluid behavior in the limit of zero surface thickness is usually analyzed. We, however, should notice that the interface smearing is physically justified for the systems near thermodynamic critical point.

### A. Thermodynamic model

To define a thermodynamic state of a binary mixture we need to introduce the free-energy function. Since, in the phase-field approach, one system of equations is used to define the behavior of an entire multiphase system, it is convenient to introduce the specific free-energy function  $f$ . This function can be either written based on experimental data or derived from a molecular level theory. To take the surface-tension effects into account, Cahn and Hilliard [23] proposed to define  $f$  not only as a function of density and concentration but also as a function of concentration gradient,

$$f(\rho, C, \nabla C) = f_0(\rho, C) + \frac{\epsilon}{2} |\nabla C|^2. \quad (1)$$

Here,  $f_0$  is called the classical part of the free energy,  $C$  is the solute concentration, and  $\epsilon$  is a constant called the capillary coefficient. Coefficient  $\epsilon$  is assumed to be very small, so the second term is not negligible only at the places of strong gradients of concentration, i.e., at interfaces.

The chemical potential  $\mu$ , derived from the free-energy function (1) with the use of assumption of incompressibility of mixture components (i.e.,  $\rho$  is a function of concentration  $C$  and independent of pressure  $p$ ), reads [3]

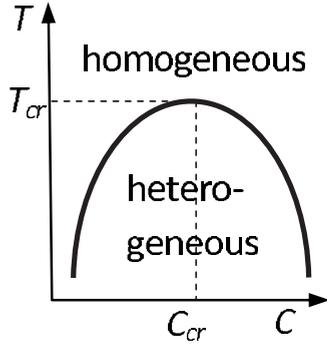


FIG. 1. The phase diagram for a binary system with an upper critical solution temperature.

$$\mu(p, C) = \mu_0(C) - \frac{p}{\rho^2} \frac{d\rho}{dC} - \frac{\epsilon}{\rho} \nabla \cdot (\rho \nabla C), \quad (2)$$

$$\mu_0(C) \equiv \frac{df_0(C)}{dC}. \quad (3)$$

Here,  $\mu_0$  stands for the classical part; the incompressibility assumption brings an explicit dependence of the chemical potential on pressure; and the last term is a nonclassical contribution which stems from the Cahn-Hilliard addition in Eq. (1).

The expression to be adopted for the classical part of the free-energy function,  $f_0$ , is written so as to reproduce the behavior defined by the phase diagram depicted in Fig. 1. In general, there are other different types of phase diagrams characterizing the states of binary systems [2]. The diagram depicted in Fig. 1 is, however, one of the most popular. This diagram defines the mixture with the upper critical solution temperature: a system with the temperature below the critical point may be either homogeneous or heterogeneous depending on concentration (the amount of a second component), while a supercritical system is always homogeneous.

In the current work, we use the expression for the free-energy function originally proposed by Landau and Lifshitz [2] to define a thermodynamic state of a system near its critical point,

$$f_0(C) = a(C - C_{cr})^2 + b(C - C_{cr})^4. \quad (4)$$

In this expression,  $C_{cr}$  is the solute concentration in the critical point, and coefficients  $a$  and  $b$  are the phenomenological parameters which define the choice of a particular binary mixture. It is necessary to note that the coefficient  $a$  absorbs the factor  $(T - T_{cr})$ , i.e., (i)  $a$  tends to zero as the system approaches the critical point and (ii)  $a$  is negative for under-critical conditions and positive for the temperatures above the critical value. Function (4) has two minima for negative values of  $a$  and one minimum for positive  $a$ . An equilibrium of a thermodynamic system corresponds to a minimum of the free-energy function. Two minima characterizing a system below the critical point are associated with two different phases, while in supercritical conditions a binary mixture is homogeneous and is characterized by the only minimum of the free-energy function.

Using function (4) we may derive an expression for the classical part of the chemical potential,

$$\mu_0(C) = 2a(C - C_{cr}) + 4b(C - C_{cr})^3. \quad (5)$$

If, first, the surface tension is not taken into account (the Maxwell theory is adopted) and, second, there is no loss or gain in volume upon liquids' mixing (simple mixtures are considered), then the equilibrium concentrations of the mixture components are defined by  $C_{01,02} = C_{cr} \pm (-\frac{a}{2b})^{1/2}$ .

We will use expression (4) as a simple model for a binary system that, under different conditions, may define both miscible and immiscible solutions. Another popular choice for the free-energy function frequently used to model the behavior of immiscible mixtures reads

$$f_0 = \frac{1}{2}(C - C_{01})^2(C - C_{02})^2. \quad (6)$$

It can be shown that Eq. (6) transforms into Eq. (4) if  $b = 1/2$  and  $C_{01,02} \equiv C_{cr} \pm (-a)^{1/2}$ . That is, formula (4) can be used to define the binary mixtures even under temperatures far from the critical one, where it can be considered as an interpolation of the experimental data; two new phenomenological coefficients  $a$  and  $b$  are determined so as to provide the best fit to the experimental data.

Finally, we notice that a thermodynamic model defines the equilibrium states. A thermodynamic system can reach its equilibrium following a long equilibration process (complete dissolution takes hours for the honey-water mixture). In the present work we aim to define the behavior of a binary system during equilibration to its thermodynamically stable state.

## B. Hydrodynamic model

The evolution of a binary mixture to its thermodynamic equilibrium is defined by the hydrodynamic model. The governing equations for hydrodynamic evolution of the Cahn-Hilliard fluid were derived in Ref. [3]. These equations include the laws of conservation of mass, species, and momentum,

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{v}) = 0, \quad (7)$$

$$\rho \left( \frac{\partial C}{\partial t} + (\mathbf{v} \cdot \nabla) C \right) = \alpha \nabla^2 \mu, \quad (8)$$

$$\rho \left( \frac{\partial \mathbf{v}}{\partial t} + (\mathbf{v} \cdot \nabla) \mathbf{v} \right) = -\nabla p + \nabla \cdot \tau_\eta - \epsilon \nabla \cdot \tau_\epsilon. \quad (9)$$

Here, the constant  $\alpha$  is the coefficient of mobility.

The fluids studied in this paper are assumed to be incompressible, but due to large concentration gradients at the interface the continuity Eq. (7) needs to be taken in its full form. Such fluids are called quasi-incompressible [1,3]. The dependence of the fluid density  $\rho$  on the solute concentration  $C$  has the simplest form for the simple mixtures, for which

$$\frac{1}{\rho} = \frac{1-C}{\rho_{01}} + \frac{C}{\rho_{02}}, \quad (10)$$

where  $\rho_{01}$  and  $\rho_{02}$  are the solvent and solute densities. So for the mixture of water and glycerol, expression (10) is true with 1% accuracy; for the mixture of methanol and water, the accuracy of Eq. (10) is 3.5% [1].

As the velocity field is nonsolenoidal, the divergence term in the expression for the viscous stress tensor  $\tau_\eta$  also needs to be taken into account,

$$\tau_\eta = \eta \left[ \nabla \otimes \mathbf{v} + (\nabla \otimes \mathbf{v})^T - \frac{2}{3} (\nabla \cdot \mathbf{v}) I \right]. \quad (11)$$

In this expression, the symbol  $\otimes$  stands for the tensor product, the index  $T$  denotes the transposed, and  $I$  denotes the unit tensor. The viscosity coefficient  $\eta$ , introduced by expression (11), should, in general, depend on the solute concentration and can be represented by a simple mass-weighted approximation or by an experimental formula.

The tensor  $\tau_\epsilon$ , defined as

$$\tau_\epsilon = \rho \nabla C \otimes \nabla C, \quad (12)$$

introduces the Korteweg interfacial stress.

The right-hand side of Eq. (8) takes into account the species transport due to diffusion. Here, the driving force for the diffusion flux is the gradient of chemical potential. One should also notice that diffusive term of Eq. (8) includes the pressure and surface-tension effects [stemming from expression (2) for the chemical potential].

The full system of equations, defined in this section, is complemented with boundary and initial conditions. As initial conditions, the velocity  $\mathbf{v}$  and concentration  $C$  are assumed to be known. As boundary conditions for the velocity field, the standard no-slip condition is used. For the field of solute concentration, two conditions need to be imposed at each boundary as Eqs. (2) and (8) define the fourth-order system of equations in terms of concentration field  $C$ . The first boundary condition is the zero-flux requirement,

$$\mathbf{n} \cdot \nabla \mu = 0. \quad (13)$$

Here  $\mathbf{n}$  is the vector normal to the boundary. The second boundary condition imposes the local thermodynamic equilibrium of the fluid-wall system. The full form of this condition is discussed in, e.g., Refs. [15,16,24]. For contact angle of  $90^\circ$ , this condition can be written as

$$\mathbf{n} \cdot \nabla C = 0. \quad (14)$$

In such a form, this condition states that the interface is orthogonal to the wall or, in other words, the wall is neutral to components of a binary mixture. It is also easy to write another alternative boundary condition for the field of concentration when the wall firmly attracts the molecules of one of the mixture components, i.e., on the wall,  $C=0$  or  $C=1$ , depending on whether solvent or solute molecules are attached (being the molecules of a perfectly wetting liquid).

At the end of this section, let us enumerate the essential features required for derivation of governing equations [Eqs. (7)–(9)]. The first two requirements have been already mentioned; they are the use of the Cahn-Hilliard free-energy function (1) and the assumption that the mixture components

are incompressible liquids. The third requirement is to define the velocity,  $\mathbf{v}$ , as the mass-averaged quantity over random velocities of different molecules that constitute a fluid particle. The volume-averaged definition for the fluid velocity of a multiphase system is also possible and can even have some advantages as it would automatically produce a divergence-free velocity field for the mixing of two simple incompressible liquids [17,25]. However, a traditional definition for the velocity in fluid mechanics is the mass-averaged quantity. The resultant governing equations based on this definition can be more easily and more naturally compared with the classical equations for a single phase medium.

### III. SEPARATION OF TIME-SCALES

The quasicompressibility of Eqs. (7)–(9) brings short-term (or quasiacoustic) processes, which significantly complicates the numerical solution of the equations. The description of slow diffusion and convective evolution of binary mixtures would frequently be more relevant for practical applications. However, even if the quick (quasiacoustic) processes do not determine the slow evolution, the numerical integration with the time step smaller than the typical quasiacoustic time scale is required in order to obtain a convergent numerical solution. In this section, the time scales that characterize the evolution of a miscible multiphase system are first explicitly identified and then, by using the multiple-scale method, the general governing equations are split into two systems which separately define the fast and slow evolutions.

#### A. Nondimensionalization of governing equations

For further analysis we redefine the density and concentration fields by shifting their reference points by the critical values,  $\rho_{cr}$  and  $C_{cr}$ , namely,

$$(\rho - \rho_{cr}) \rightarrow \rho, \quad (C - C_{cr}) \rightarrow C. \quad (15)$$

We also nondimensionalize the governing equations using the following units of time  $\tau_*$ , velocity  $V_*$ , pressure  $p_*$ , and specific free energy,

$$\tau_* = \frac{L_*}{V_*}, \quad V_* = \mu_*^{1/2}, \quad p_* = \rho_* \mu_*, \quad f_* = \mu_*. \quad (16)$$

Here  $L_*$  is the typical size,  $\rho_*$  is the typical density (e.g.,  $\rho_{cr}$ ), and  $\mu_*$  is the unit of the chemical potential, for which we can use  $\mu_* = b$ . The resultant dimensionless equations then read as

$$\frac{\partial \rho}{\partial t} + (\mathbf{v} \cdot \nabla) \rho = -(1 + \rho) \nabla \cdot \mathbf{v}, \quad (17)$$

$$(1 + \rho) \left( \frac{\partial C}{\partial t} + (\mathbf{v} \cdot \nabla) C \right) = \frac{1}{\text{Pe}} \nabla^2 \mu, \quad (18)$$

$$(1 + \rho) \left( \frac{\partial \mathbf{v}}{\partial t} + (\mathbf{v} \cdot \nabla) \mathbf{v} \right) = -\nabla p + \frac{1}{\text{Re}} \nabla \cdot \tau_\eta - \text{Ca} \nabla \cdot \tau_\epsilon + \text{Ga}(1 + \rho) \gamma, \quad (19)$$

$$p = \frac{1}{\phi} \{-\mu + \mu_0 - \text{Ca}[\nabla^2 C + \phi(1 + \rho)(\nabla C)^2]\}, \quad (20)$$

$$f_0 = AC^2 + C^4, \quad \mu_0 = \frac{df_0}{dC}, \quad (21)$$

$$\rho = \frac{\phi C}{1 - \phi C}, \quad (22)$$

$$\tau_\eta = \eta[\nabla \otimes \mathbf{v} + (\nabla \otimes \mathbf{v})^T - \frac{2}{3}(\nabla \cdot \mathbf{v})\mathbf{I}], \quad (23)$$

$$\tau_\epsilon = (1 + \rho) \nabla C \otimes \nabla C. \quad (24)$$

The last term in Eq. (19) is the gravitational force (with  $\gamma$  being a unit vector directed upward). A nondimensionalized coefficient of viscosity  $\eta$  [in formula (23)] is obtained using the typical value  $\eta_*$  (e.g., the viscosity coefficient of a binary mixture in its critical point).

The nondimensional parameters entering the above equations are the Peclet number,

$$\text{Pe} = \frac{\rho_* L_*}{\alpha \mu_*^{1/2}}, \quad (25)$$

the capillarity parameter,

$$\text{Ca} = \frac{\epsilon}{\mu_* L_*^2}, \quad (26)$$

the Galileo number,

$$\text{Ga} = \frac{gL_*}{\mu_*}, \quad (27)$$

and the Reynolds number,

$$\text{Re} = \frac{\rho_* \mu_*^{1/2} L_*}{\eta_*}. \quad (28)$$

The binary mixture is also characterized by the parameter

$$\phi = \frac{\rho_*}{\rho_{01}} - \frac{\rho_*}{\rho_{02}} \approx \frac{\rho_{02} - \rho_{01}}{\rho_*}, \quad (29)$$

where  $\rho_{01}$  and  $\rho_{02}$  are the densities of the mixture components. The approximate formula is valid for small differences between  $\rho_{01}$  and  $\rho_{02}$ , which is typical for all liquid mixtures. The adopted expression for the free-energy function also contains another nondimensional parameter that defines the distance from the critical point,

$$A = \frac{a}{\mu_*}. \quad (30)$$

This parameter also defines whether the system is heterogeneous (negative  $A$ ) or homogeneous (positive  $A$ ) in equilibrium.

Finally, let us also write the expression for the total energy of the fluid enclosed by volume  $V$ ,

$$E = \int_V (1 + \rho) \left[ \frac{\mathbf{v}^2}{2} + f_0 + \frac{\text{Ca}}{2} (\nabla C)^2 + \text{Ga}(\gamma \cdot \mathbf{r}) \right] dV. \quad (31)$$

Here the first term corresponds to the fluid kinetic energy, the second term is the classical part of free energy, the third term accounts for the energy accumulated by interfaces, and the last term is the potential energy due to gravity. The total energy is measured in the units of  $\rho_* \mu_* L_*^3$ .

## B. Typical time scales

To identify the different time scales characterizing the physical system defined by the full equations written in Sec. III A we consider the evolution of a one-dimensional (along the  $x$ -axis) small-amplitude perturbation on the background of a stationary homogeneous state. For simplicity, we also omit the gravity term for this analysis. A similar stability analysis but for an inviscid binary mixture was first undertaken in Ref. [3].

The evolution of such a perturbation is defined by the following linearized equations:

$$\frac{\partial \rho}{\partial t} = -\frac{\partial v}{\partial x}, \quad (32)$$

$$\frac{\partial C}{\partial t} = \frac{1}{\text{Pe}} \frac{\partial^2 \mu}{\partial x^2}, \quad (33)$$

$$\frac{\partial v}{\partial t} = -\frac{\partial p}{\partial x} + \frac{4}{3\text{Re}} \frac{\partial^2 v}{\partial x^2}, \quad (34)$$

$$p = \frac{1}{\phi} \left( -\mu + 2AC - \text{Ca} \frac{\partial^2 C}{\partial x^2} \right), \quad \rho = \phi C. \quad (35)$$

Seeking a solution in the form of a plane wave,  $C \sim \exp(ikx - i\omega t)$ , where  $i$  is the imaginary unit,  $k$  is the wave-number, and  $\omega$  is the frequency, we obtain the following dispersion relation:

$$\omega^2 = -i\omega \left( \frac{\text{Pe}}{\phi^2} + \frac{4}{3\text{Re}} k^2 \right) + \frac{k^2}{\phi^2} (2A + \text{Ca}k^2). \quad (36)$$

Next, we split  $\omega$  into the real and imaginary parts,  $\omega = \omega_r + i\omega_i$ , and equate the coefficients in front of the like terms to obtain

$$(\omega_r^2 - \omega_i^2) = \omega_i \left( \frac{\text{Pe}}{\phi^2} + \frac{4}{3\text{Re}} k^2 \right) + \frac{k^2}{\phi^2} (2A + \text{Ca}k^2), \quad (37)$$

$$2\omega_r \omega_i = -\omega_r \left( \frac{\text{Pe}}{\phi^2} + \frac{4}{3\text{Re}} k^2 \right). \quad (38)$$

The analysis of the second equation shows that this is satisfied by either

$$\omega_r = 0 \quad (39)$$

or

$$\omega_i = -\frac{1}{2} \left( \frac{\text{Pe}}{\phi^2} + \frac{4}{3\text{Re}} k^2 \right). \quad (40)$$

To simplify further derivations we will use that

$$\frac{k}{\phi} (2A + \text{Ca}k^2)^{1/2} \ll \left( \frac{\text{Pe}}{\phi^2} + \frac{4}{3\text{Re}} k^2 \right) \quad (41)$$

or, equivalently,

$$\phi \ll 1, \quad A \ll 1, \quad \text{Ca} \ll 1, \quad \text{Pe} \sim 1. \quad (42)$$

That is, we assume a small density difference between components of binary mixtures, close to the critical point and the existence of an interface.

Substitution of condition (39) into Eq. (37) produces two formulas for the decrements which define the monotonic decay of the considered one-dimensional perturbation,

$$\omega_{i,1} = - \left( \frac{\text{Pe}}{\phi^2} + \frac{4}{3\text{Re}} k^2 \right), \quad (43)$$

$$\omega_{i,2} = - \frac{\frac{k^2}{\phi^2} (2A + \text{Ca}k^2)}{\frac{\text{Pe}}{\phi^2} + \frac{4}{3\text{Re}} k^2}. \quad (44)$$

Next, we should note that Eq. (37) has no solution if option (40) to satisfy the imaginary part of the dispersion relation is chosen.

Derived dispersion relations (43) and (44) define the linear stability of a homogeneous state and confirm the expected behavior of a binary system, namely, the homogeneous state is unconditionally stable for positive values of  $A$  (supercritical conditions on the phase diagram), while some disturbances would monotonically grow if  $A$  is negative, when the spinodal decomposition should occur as under such conditions the thermodynamically stable state of a binary system is heterogeneous.

In addition, expressions (43) and (44) allow us to conclude that the evolution of the miscible multiphase system defined in Eqs. (17)–(19) is characterized by at least three different time scales,

$$\tau_d = \frac{\text{Pe}}{A}, \quad \tau_c = \text{Re}, \quad \tau_e = \frac{\phi^2}{\text{Pe}}. \quad (45)$$

Here,  $\tau_d$  and  $\tau_c$  are the diffusion and convection time scales and  $\tau_e$  is the fast time scale that we call the expansion time scale (the effect defined by this time scale was called either the expansion [1] or sonic [3] wave). Let us also adduce the expressions for these time scales in the dimensional form,

$$\tau_d^* = \frac{\rho_* L_*^2}{\alpha \mu_*}, \quad \tau_c^* = \frac{\rho_* L_*^2}{\eta_*}, \quad \tau_e^* = \phi^2 \frac{\alpha}{\rho_*}. \quad (46)$$

As it is clear now, inequality (41) reflects the ratio between the quick and slow time scales. For further analysis we will introduce the small parameter  $\chi$  defined as

$$\chi^4 \equiv \frac{\tau_e}{\tau_d} = \frac{\phi^2 A}{\text{Pe}^2}. \quad (47)$$

We are interested in the dissolution dynamics, i.e., in the evolution on the slow diffusive time scale. The main idea of the multiple time-scale method is to explicitly introduce two times, the quick one,  $t_{-2}$ , describing the evolution of a system on the fast expansion time scale and the slow one,  $t_2$ , defining the diffusive and convective evolution. The time derivative can be then written as

$$\frac{\partial}{\partial t} = \frac{1}{\chi^2} \frac{\partial}{\partial t_{-2}} + \chi^2 \frac{\partial}{\partial t_2}. \quad (48)$$

We will also expand all variables in the series of small parameter  $\chi$ ,

$$\mathbf{v} = \chi^2 \mathbf{v}_2 + \chi^4 \mathbf{v}_4 + \dots, \quad (49)$$

$$p = p_0 + \chi^2 p_2 + \chi^4 p_4 + \dots, \quad (50)$$

$$\mu = \chi \mu_1 + \chi^3 \mu_3 + \dots, \quad (51)$$

$$\rho = \chi^2 \rho_2 + \chi^4 \rho_4 + \dots, \quad (52)$$

$$C = \chi C_1 + \chi^3 C_3 + \dots, \quad (53)$$

$$\eta = 1 + \dots, \quad (54)$$

and we relate the nondimensional parameters to different orders of  $\chi$ ,

$$\phi = \phi_1 \chi, \quad A = A_2 \chi^2, \quad \text{Ca} = \text{Ca}_2 \chi^2, \quad (55)$$

$$\text{Re} = \text{Re}_{-2} \frac{1}{\chi^2}, \quad \text{Pe} = \text{Pe}_0, \quad \text{Ga} = \text{Ga}_2 \chi^2. \quad (56)$$

We should note that there are two main conditions implying the choices for the above-written ratios, namely, (i) to save all essential physical effects and (ii) to have a closed system of governing equations. The nondimensional parameters define the ratios between different terms in the governing equations. For derivations, we always assume that all effects in the original equations [Eqs. (17)–(19)] may be important and such values of the nondimensional parameters are chosen which permit us to include all corresponding terms in the final equations. Ratios [Eqs. (55) and (56)] imply that  $\tau_d$  and  $\tau_c$  are of the same order. This only means that the final equations will include both convective and diffusive terms. Following such an approach, we will obtain a comprehensive theoretical model that can be used for the analysis of a wide range of problems. For a particular problem, some terms in the model may be found either small or very large, which would, sometimes, lead to further simplifications. However, our aim is to obtain a general model.

### C. Separation of the processes occurring on different time scales

First, we write down the different orders of Eqs. (17)–(19). The first orders of the mass [Eq. (17)] and species balances [Eq. (18)] are as follows:

$$\frac{\partial \rho_2}{\partial t_{-2}} = 0, \quad \frac{\partial C_1}{\partial t_{-2}} = 0, \quad (57)$$

$$\frac{\partial \rho_4}{\partial t_{-2}} = -\nabla \cdot \mathbf{v}_2, \quad \frac{\partial C_3}{\partial t_{-2}} = \frac{1}{\text{Pe}_0} \nabla^2 \mu_1, \quad (58)$$

$$\frac{\partial C_5}{\partial t_{-2}} + \frac{\partial C_1}{\partial t_2} + (\mathbf{v}_2 \cdot \nabla) C_1 + \rho_2 \frac{\partial C_3}{\partial t_{-2}} = \frac{1}{\text{Pe}_0} \nabla^2 \mu_3. \quad (59)$$

The first orders of the equation of momentum balance [Eq. (19)] read as

$$\frac{\partial \mathbf{v}_2}{\partial t_{-2}} = -\nabla p_0, \quad (60)$$

$$\frac{\partial \mathbf{v}_4}{\partial t_{-2}} = -\nabla p_2 + \text{Ga}_2 \gamma, \quad (61)$$

$$\begin{aligned} \frac{\partial \mathbf{v}_6}{\partial t_{-2}} + \frac{\partial \mathbf{v}_2}{\partial t_2} + (\mathbf{v}_2 \cdot \nabla) \mathbf{v}_2 + \rho_2 \frac{\partial \mathbf{v}_4}{\partial t_{-2}} \\ = -\nabla p_4 + \frac{1}{\text{Re}_{-2}} \nabla \cdot \tau_{\eta,2} - \text{Ca}_2 \nabla \cdot \tau_{\epsilon,2} + \text{Ga}_2 \rho_2 \gamma. \end{aligned} \quad (62)$$

Here, the corresponding orders of the viscous stress tensor and of the Korteweg tensor are

$$\tau_{\eta,2} = \nabla \otimes \mathbf{v}_2 + (\nabla \otimes \mathbf{v}_2)^T - \frac{2}{3} (\nabla \cdot \mathbf{v}_2) I, \quad (63)$$

$$\tau_{\epsilon,2} = \nabla C_1 \otimes \nabla C_1. \quad (64)$$

In these equations, all variables are assumed to be functions of both times,  $t_{-2}$  and  $t_2$ . Next, we will split out the processes on different time scales using the averaging procedure briefly outlined in the next two paragraphs.

First, we assume that all fields can be split into slowly and quickly changing parts,

$$\mathbf{v} = \mathbf{u}(t_2) + \mathbf{w}(t_{-2}, t_2), \quad (65)$$

$$\rho = \bar{\rho}(t_2) + \tilde{\rho}(t_{-2}, t_2). \quad (66)$$

Here,  $\mathbf{u} \equiv 1/T_2 \int_0^{T_2} \mathbf{v} dt$  and  $\mathbf{w} \equiv \mathbf{v} - \mathbf{u}$ . That is,  $\mathbf{u}$  is the fluid velocity averaged over long time scale ( $T_2$  is a time interval much larger than the fast time scale) and  $\mathbf{w}$  defines the quick time-scale fluctuations of the fluid velocity. For scalar quantities, the barred symbol is used to denote the averaged parts and the tilded symbols denote the fluctuating parts. As an example, we show the splitting of density field (66); similar expressions have to be written for concentration, pressure, and chemical potential.

The equations for the long-term evolution will be obtained by averaging the equations. To accomplish averaging, the following general equalities are required to be used:

$$\bar{\bar{V}} = 0, \quad \frac{\partial}{\partial t_{-2}} (\dots) = 0, \quad (67)$$

where  $V$  stands for any quantity.

Averaging gives the following equations for the processes on the diffusive and convective time scales:

$$\bar{p}_0 = 0, \quad \bar{\mu}_1 = 0, \quad (68)$$

$$\nabla \bar{p}_2 + \text{Ga}_2 \gamma = 0, \quad (69)$$

$$\begin{aligned} \frac{\partial \mathbf{u}_2}{\partial t_2} + (\mathbf{u}_2 \cdot \nabla) \mathbf{u}_2 + \overline{(\mathbf{w}_2 \cdot \nabla) \mathbf{w}_2} \\ = -\nabla \bar{p}_4 + \frac{1}{\text{Re}_{-2}} \nabla^2 \mathbf{u}_2 - \text{Ca}_2 \left( \nabla^2 C_1 \nabla C_1 + \nabla \frac{(\nabla C_1)^2}{2} \right) \\ + \text{Ga}_2 \rho_2 \gamma, \end{aligned} \quad (70)$$

$$\nabla \cdot \mathbf{u}_2 = 0, \quad (71)$$

$$\frac{\partial C_1}{\partial t_2} + (\mathbf{u}_2 \cdot \nabla) C_1 = \frac{1}{\text{Pe}_0} \nabla^2 \bar{\mu}_3, \quad (72)$$

$$\bar{p}_2 = \frac{1}{\phi_1} (-\bar{\mu}_3 + 2A_2 C_1 + 4C_1^3 - \text{Ca}_2 \nabla^2 C_1), \quad (73)$$

$$\rho_2 = \phi_1 C_1. \quad (74)$$

Here, we took into account that  $C_1$  and  $\rho_2$  are independent of the quick time [Eq. (57)] so the overbars were omitted for these variables.

Combining Eqs. (69) and (73) together gives the equation of state,

$$\nabla \bar{\mu}_3 = \phi_1 \text{Ga}_2 \gamma + \nabla (2A_2 C_1 + 4C_1^3 - \text{Ca}_2 \nabla^2 C_1). \quad (75)$$

To write down the further equations, it is convenient to introduce the modified pressure,

$$\Pi \equiv \bar{p}_4 + \text{Ca}_2 \frac{(\nabla C_1)^2}{2}, \quad (76)$$

where the gradient-like terms are collected.

Subtracting the averaged parts from the full equations, we obtain the equations for the processes on the quick time scale,

$$\frac{\partial \tilde{\rho}_4}{\partial t_{-2}} = -\nabla \cdot \mathbf{w}_2, \quad \tilde{\rho}_4 = \phi_1 \tilde{C}_3, \quad (77)$$

$$\frac{\partial \tilde{C}_3}{\partial t_{-2}} = \frac{1}{\text{Pe}_0} \nabla^2 \tilde{\mu}_1, \quad (78)$$

$$\frac{\partial \mathbf{w}_2}{\partial t_{-2}} = -\nabla \tilde{p}_0, \quad \tilde{p}_0 = \frac{1}{\phi_1} (-\tilde{\mu}_1). \quad (79)$$

These equations describe a rapidly decaying process. For instance, the field of concentration varies in accordance with the following formula:

$$\tilde{C}_3 = \tilde{C}_{in} \exp\left(-\frac{\text{Pe}_0}{\phi_1^2} t_{-2}\right), \quad (80)$$

where index *in* denotes the initial concentration field. If the averaged equations are characterized by divergence-free fluid velocity (71), for the quick processes, the quasicompressibility effects are essential. However, the divergence of the velocity field also rapidly decreases following a similar exponential decay,

$$(\nabla \cdot \mathbf{w}_2) = (\nabla \cdot \mathbf{w}_{in}) \exp\left(-\frac{\text{Pe}_0}{\phi_1^2} t_{-2}\right). \quad (81)$$

Finally, we note that, first, the quick time-scale processes are damping and, second, there is no energy injection into fast processes as it could, for example, happen in the case of imposed high-frequency vibrations [21,22,26]. These two facts allow us to draw a conclusion that the short-term processes, even if existed at the initial moment, are to be rapidly damped out and are not to affect the long-term evolution on the convective and diffusive time scales.

Omitting indices and bars, the governing equations for the processes on the convective time scale can be finally written as follows:

$$\frac{\partial \mathbf{u}}{\partial t} + (\mathbf{u} \cdot \nabla) \mathbf{u} = -\nabla \Pi + \frac{1}{\text{Re}} \nabla^2 \mathbf{u} - \text{Ca} \nabla^2 C \nabla C + \phi \text{Ga} C \gamma, \quad (82)$$

$$\frac{\partial C}{\partial t} + (\mathbf{u} \cdot \nabla) C = \frac{1}{\text{Pe}} \nabla^2 \mu, \quad (83)$$

$$\nabla \cdot \mathbf{u} = 0, \quad (84)$$

$$\mu \equiv \phi \text{Ga} (\gamma \cdot \mathbf{r}) + 2AC + 4C^3 - \text{Ca} \nabla^2 C. \quad (85)$$

These are strictly incompressible equations; the modified pressure field  $\Pi$  needs to be determined using an incompressibility constraint. The interesting conclusions can be drawn for the diffusion mechanisms of mass transfer, as three different mechanisms can be identified: the classical (Fickian) diffusion with, however, nonconstant diffusion coefficient, barodiffusion arising through the hydrostatic pressure gradient, and the surface energy effects. The product  $\phi \text{Ga}$  forms the solutal analog of the Grashoff number.

The derived equations must be supplemented with the following boundary conditions:

$$\mathbf{v} = 0, \quad \mathbf{n} \cdot \nabla C = 0, \quad \mathbf{n} \cdot \nabla \mu = 0. \quad (86)$$

Here, we would like to remind a reader that the above-written boundary condition for the concentration field is only a simplified formula.

Finally, in order to show that no important effects have been lost during our derivation, let us write down the new expression for the total fluid energy,

$$E = \int_V \left[ \frac{\mathbf{u}^2}{2} + f_0 + \frac{\text{Ca}}{2} (\nabla C)^2 + \text{Ga} \phi C (\gamma \cdot \mathbf{r}) \right] dV, \quad (87)$$

$$f_0 = AC^2 + C^4. \quad (88)$$

Let us also rewrite Eq. (82) so to modify the Korteweg force into the form adopted in Refs. [14,15], i.e.,  $-C \nabla \mu$ . Using equation of state (85) and redefining the incompressible pressure field into

$$\Pi_1 \equiv \Pi + AC^2 + C^4 - \mu C + \phi \text{Ga} C (\gamma \cdot \mathbf{r}), \quad (89)$$

transform Eq. (82) into the following form:

$$\frac{\partial \mathbf{u}}{\partial t} + (\mathbf{u} \cdot \nabla) \mathbf{u} = -\nabla \Pi_1 + \frac{1}{\text{Re}} \nabla^2 \mathbf{u} - C \nabla \mu + 2\phi \text{Ga} C \gamma. \quad (90)$$

Comparison of this equation with the corresponding equation in Refs. [14,15] might suggest that the buoyancy force is doubled in our case, but this occurs only due to an implicit gravity addition in the Korteweg force through the expression for the chemical potential.

The finally derived Eqs. (82)–(84) look quite similar to the model first used in [14,15] as the computational tool for tracking of complex transformations of the interfacial boundary between two immiscible liquids. This computational model, adopted in [14,15], was earlier proposed by several researchers (for derivation and further references, see Refs. [27,28]). In the current work, we have strictly derived the Boussinesq approximation of the Cahn-Hilliard-Navier-Stokes equations, obtaining a general hydrodynamic model for the slow dissolution processes in miscible systems. As one can see, Eqs. (82)–(84) differ from Jacqmin's model in taking into account the barodiffusion effect.

#### IV. CONCLUSIONS

In this paper, we showed that the evolution of a multi-phase system of two incompressible slowly miscible liquids is characterized by three typical time scales, namely, the convective, diffusion, and expansion time [Eq. (46)]. Then, by using the multiple-scale method, we filtered out the short-term expansion (or quasiaoustic) process and, as a result, the equations for the slow evolution of a binary system were derived. Even if the quick processes are not supported and hence should not affect the real physical system, the numerical integration of the full Cahn-Hilliard-Navier-Stokes equations would require time resolution of all processes (the quick processes will be constantly excited due to discretization errors of a numerical scheme) and this would make calculations of long-term dissolution dynamics unfeasible. The general idea of the obtained model is quite similar to the low-Mach number approximation used for description of the convective motion in a compressible media (see, e.g., Refs. [20–22]).

The given derivation is quite similar to the derivation of the classical Boussinesq equations for thermal convection when the nonhomogeneities in density field are caused by temperature variations (see, e.g., [21,22]). These density nonhomogeneities are assumed to be small which is satisfied by assuming that the Boussinesq parameter,  $\beta \Delta T$ , is small ( $\Delta T$  might be not small if  $\beta$  is very small). In our work, the nonhomogeneities of density field are caused by variations in concentration; the role of the Boussinesq parameter plays  $\phi \Delta C$ . For the derivation, the density variations should be assumed small,  $\phi \ll 1$ , which is well satisfied for the binary mixtures of two liquids. We would like also to note that parameter  $\phi$  enters the final equations only in the product with Galileo number, so the requirement on the smallness of  $\phi$  might be relaxed.

The obtained Eqs. (82)–(84) form a closed mathematical model for a general thermodynamic and hydrodynamic evo-

lution of a multiphase system with phase transition. An applicability of the final model is to be considered in a broader extent compared to what is defined by assumptions (55) and not, e.g., only for the binary systems in the vicinity of the critical point. For illustration, we may refer the classical Boussinesq equations for thermal convection: despite the fact that such equations are derived in assumption of finite Rayleigh numbers, most interesting convection problems are considered for large Rayleigh numbers ( $>1000$ ). Nevertheless, such a statement still needs to be verified. We should also note that even the validity of the original Cahn-Hilliard-Navier-Stokes equations to be used for description of the miscible multiphase flows has not been well verified yet. For which, the equations should be applied for reproducing of some experimental data. However, as noted, the numerical solution of the full equations was not feasible due to their quasicompressibility. Currently, we are working on the verification of the general approach by using the derived set of reduced equations.

We should also note that Refs. [3,14,15,19] are all well known within the scientific community interested in hydrodynamics of multiphase flows. However, these papers contain different sets of governing equations, making other researchers provide their additional justifications for the actual models chosen (see, e.g., Refs. [8,17]). Most of the numerical studies, based on the phase-field approach, use Jacqmin's model but, in such papers, the evolution of immiscible systems is targeted. For miscible systems, the most popular approach is the set of impurity-like equations with an addition of the Korteweg stress tensor [8–10]. The main achievement of our work is the derivation of the Boussinesq approximation of the full Cahn-Hilliard-Navier-Stokes equations of Lowengrub and Truskinovsky. The obtained equations are quite similar to the divergence-free equations of Jacqmin but they also include the new term. An important difference of our model from the impurity-like equations lies in the definition of diffusion flux through the gradient of the chemical potential rather than the concentration gradient. Such an amendment takes into account the surface tension and barodiffusion

effects into calculations of the dissolution rate. The surface-tension effects also define the morphology of the interfacial boundary (the Korteweg stress in the Navier-Stokes equation), which is frequently taken into account, but their influence on the diffusion rate is frequently missed out.

We also would like to note that derived Eqs. (82)–(84) are not ready yet for the comprehensive analysis of particular configurations, as the values of the introduced phenomenological parameters  $\epsilon$ ,  $a$ , and  $b$  are unknown. In fact, the value of  $a$  can be relatively easily estimated from the phase diagram for a particular system. Determination of  $\epsilon$  and  $b$  would require a more lengthy investigation. Jacqmin published his equations about ten years ago. Since then, these equations have been applied to different problems [14–18], but they have always been used for immiscible systems, for which a fluid behavior in the limits of  $\epsilon \rightarrow 0$  and  $\mu_* \rightarrow \infty$  is sought. Technically, the equations are successively solved for several values of parameters to reproduce the needed limiting behavior of an immiscible interface (see, e.g., Refs. [14,15,17,18]). For the case of miscible systems, the values of  $\epsilon$  and  $\mu_*$  are finite and should be obtained from a comparison of the numerical solution with the experimental data. In some recent experiments, the estimations and measurements of the surface-tension coefficients for several particular miscible binary systems became available [29–31]. These experiments also contain detailed description of the dissolution dynamics. Such information (time evolution of the surface-tension coefficient and of the dissolution rate) should be sufficient for obtaining the missing values of  $\epsilon$  and  $\mu_*$ . This is the aim of the author's current research work.

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