Surface tension in a reactive binary mixture of incompressible fluids

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Abstract

Based on the Cahn-Hilliard free energy, a thermodynamic model for a reactive binary mixture of incompressible and miscible fluids is derived with a distributed form of surface tension. The model describes chemistry, diffusion, viscosity and heat transfer as well as stresses produced by (and at right angles to) concentration gradients. It allows for a rich spectrum of processes and some of these are discussed briefly.

Scaling arguments based on experimental data of Abid et al. [1], lead to considerable simplifications. Saffmann-Taylor stability analysis (here extended to interfaces of finite thickness) agrees with the experimental findings of Abid et al. who argued that the buoyant instability of a reaction diffusion front is controlled by a form of surface tension at the front.

Keywords: Binary mixtures, Surface tension, Irreversible thermodynamics, Hele-Shaw cells

1 Introduction

Recent experiments [1] on miscible, buoyantly unstable reaction diffusion fronts in Hele-Shaw cells give an indication that the observed instabilities are governed by a form of surface tension, a property that is normally associated with interfaces between immiscible fluids. Since an interface between miscible fluids is not vanishingly thin the stress that corresponds to surface tension within the medium must be distributed over the region where the concentrations of different components change. The goal of this article to provide a sound theoretical foundation for this observation by means of a thermodynamic derivation and analysis of the governing equations for the process.

In order to emphasize the basic physics, we shall consider a binary reacting mixture, instead of a more realistic reaction with several species. The fluids used in the experiment are almost incompressible and we shall restrict the model to incompressible fluids.

The constant mass densities of the two constituents differ and therefore a change in the concentration, by diffusion and/or reaction, leads to a change in the total density. The mixture therefore appears to be compressible—it is *quasi-incompressible* in the sense that density changes can arise through changes in composition but not through changes in pressure alone [9, 12]. As

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is usually the case for incompressible fluids [13], the pressure does not appear in the density's equation of state, but must be considered as an additional variable [9, 12].

Our thermodynamic considerations are based on the free energy of the mixture which contains terms for the energy as well as for the entropy of mixing. For these contributions we adopt the celebrated Cahn-Hilliard model [5] according to which the energy of mixing depends on the concentration and its gradient. The latter is known to lead to an effective "surface tension" which decreases as the gradient decreases [5, 2]. As a consequence, the surface tension of a typical chemical reaction wave is very small due to its comparatively large thickness. Surface tension could be measured in [1] only because the difference between the densities of reactants and products was small enough to ensure that a competing buoyancy-driven instability was also very small.

The balance laws for masses of the constituents, momentum, and energy do not form a closed set of field equations a priori, but require constitutive equations for the so-called thermodynamic fluxes. In this paper, the constitutive equations are derived by means of the classical thermodynamics of irreversible processes (TIP) [7]. The basic assumption is the "local equilibrium hypothesis" which in our case gives rise to the Cahn-Hilliard expressions for energy and entropy in non-equilibrium.

In particular, the evaluation of the second law of thermodynamics with the Cahn-Hilliard free energy, according to TIP, leads to expressions for the stress tensor and the chemical potential of the mixture, which govern both diffusion and chemistry in the mixture. Moreover, as a direct consequence of the quasi-incompressibility, the pressure enters the theory as an arbitrary parameter which must be chosen as additional variable.

As well as the pressure, the stress tensor contains the usual viscous contributions plus a term which relates to capillary forces. Since the pressure is somewhat arbitrary, it can be redefined (or normalised) so that the capillary term precisely corresponds to surface tension, i.e. it represents forces perpendicular to the concentration gradient.

TIP also relates the thermodynamic fluxes to the corresponding "thermodynamic forces" through linear relations (phenomenological equations). Linear constitutive laws are in accordance with experimental observations concerning diffusion, heat transfer and viscous stresses, but not chemical reactions. Therefore, the latter are modelled by the Arrhenius law, which is set up properly so that the positivity of the entropy production due to chemical reaction is guaranteed. In particular, it will be seen that an increase in the pressure shifts the chemical equilibrium towards the denser component (Le Chatelier's principle), although it does not directly increase the density by itself.

In general, our approach is a contribution to what is known as *Diffusive-Interface Methods in Fluid Mechanics*—see the extensive review by Anderson et al. [2] for a list of references. Most work in this area is related to immiscible fluids, phase boundaries, etc., which are typical of systems where surface tension can be expected to play a significant role.

Our results and methods are closest to the work by Lowengrub and Truskinovsky [12], but differ in the treatment of the pressure as well as in the emphasis on miscible fluids in our considerations. The paper by Antanovskii [3] served us for inspiration, but our treatment differs considerably from it, since we exploit the second law more thoroughly and thus avoid heuristic arguments. To our knowledge the present work is also the first to combine diffusive-interface methods with flame-like reactions.

Joseph [9] investigated surface tension in miscible fluids experimentally and theoretically. He added surface tension to the momentum balance but considered the classical diffusion equation (Fick's law). As will be seen in the course of our paper, the diffusion may be affected by pressure

gradients and intermolecular forces. In miscible fluids, however, the influence of the latter will hardly be seen explicitly, but merely affect the measurement of the diffusion coefficient. Pressure gradients may cause partial demixing of the constituents, if the density difference is large; with Joseph's very small density differences, Fick's law is indeed appropriate.

Altogether, our model, describing surface tension, chemistry and diffusion as well as viscosity and heat transfer, allows for a rich spectrum of processes and some of these are briefly considered, for example the aforementioned influence of the pressure on diffusion flux and chemical equilibrium. Most of this however, must be referred to later investigations.

The importance of the various processes depends on physical parameters, such as diffusion coefficient, reaction rate, density difference, intermolecular forces, etc. A proper scaling, based on the experimental data of [1] allows for a considerable simplification of the equations. The stability results that were used in [1] are based on the well-known Saffmann-Taylor stability analysis [16] which is originally applicable at interfaces of vanishing thickness. We shall show that the same analysis can be used as well in the case of a finite, but small thickness of the interface.

2 Binary mixture of two ideal fluids

2.1 Ideal fluids

In an incompressible *ideal fluid* the state variables are independent of pressure. Accordingly mass density ϱ and specific internal energy u are functions of temperature T alone. However, because of the well known thermodynamic relation $\left(\frac{\partial u}{\partial p}\right)_T = \frac{T}{\varrho^2}\left(\frac{\partial \varrho}{\partial T}\right)_p + \frac{p}{\varrho^2}\left(\frac{\partial \varrho}{\partial p}\right)_T$, the density must be independent of temperature as well [13] and is therefore a constant.

In an ideal fluid the specific heat c_v is assumed to be constant and its specific internal energy $u(T)$ is given by

$$u(T) = c_\mathrm{v}(T - T_0) + u_0 \tag{1}$$

where u_0 is the specific energy at temperature T_0. Due to the incompressibility, the Gibbs equation reduces to $T\,\mathrm{d}s = \mathrm{d}u$ so that the specific entropy s of the ideal fluid is given by

$$s(T) = c_\mathrm{v} \ln \frac{T}{T_0} + s_0 \tag{2}$$

where s_0 is the entropy at temperature T_0.

2.2 Binary mixture

We consider the mixture of two incompressible ideal fluids with the constant mass densities ϱ_1, ϱ_2, particle masses m_1, m_2, and specific heats c_v^1, c_v^2. Under the assumption that there are no volume changes due to mixing (excess volume) we can write for the density of the mixture

$$\varrho = c\varrho_1 + (1 - c)\varrho_2 \tag{3}$$

where c is a concentration parameter varying between 1 in fluid *1* and 0 in fluid *2*. Obviously, the partial mass densities of the constituents are given by $c\varrho_1$, $(1 - c)\varrho_2$. The energy density of

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the mixture is given by the sum of the partial energies plus an extra term which accounts for the interaction between the constituents,

$$\varrho u = c\varrho_1 u_1 + (1-c)\varrho_2 u_2 + U_{\text{mix}} \tag{4}$$
$$= c\varrho_1 \left(c_v^1(T-T_0) + u_0^1\right) + (1-c)\varrho_2 \left(c_v^2(T-T_0) + u_0^2\right) + U_{\text{mix}}.$$

Similarly the entropy of the mixture is not simply the sum of the two partial entropy densities, but contains an additional term, the entropy of mixing,

$$\varrho s = c\varrho_1 s_1 + (1-c)\varrho_2 s_2 + S_{\text{mix}} \tag{5}$$
$$= c\varrho_1 \left(c_v^1 \ln \frac{T}{T_0} + s_0^2\right) + (1-c)\varrho_2 \left(c_v^2 \ln \frac{T}{T_0} + s_0^2\right) + S_{\text{mix}}.$$

The entropy of mixing is considered later in section 2.4.

2.3 Energy of mixing

The energy of mixing U_{mix} results from the different intermolecular forces between particles of different species [15]. We denote the potential between two particles of types α, β by $V_{\alpha\beta}\left(|r_i^\alpha - r_i^\beta|\right)$; $V_{\alpha\beta}$ is a function of the distance $\xi = |r_i^\alpha - r_i^\beta|$ between the particles. The total potential energy of the $n_\alpha\, \mathrm{d}\mathbf{r}^\alpha$ particles of type α in the volume element $\mathrm{d}\mathbf{r}^\alpha$ and the $n_\beta\, \mathrm{d}\mathbf{r}^\beta$ particles of type β in $\mathrm{d}\mathbf{r}^\beta$ is given by

$$V_{\alpha\beta}\left(|r_i^\alpha - r_i^\beta|\right) n_\alpha\left(r_i^\alpha\right) n_\beta\left(r_i^\beta\right) \mathrm{d}\mathbf{r}^\alpha \mathrm{d}\mathbf{r}^\beta.$$

We now introduce the vectors x_i, ξ_i by

$$x_i = \tfrac{1}{2}\left(r_i^\alpha + r_i^\beta\right), \qquad \xi_i = r_i^\alpha - r_i^\beta$$

so that

$$r_i^\alpha = x_i + \tfrac{1}{2}\xi_i, \quad r_i^\beta = x_i - \tfrac{1}{2}\xi_i \quad \text{and} \quad \mathrm{d}\mathbf{r}^\alpha \mathrm{d}\mathbf{r}^\beta = \mathrm{d}\mathbf{x}\, \mathrm{d}\boldsymbol{\xi}.$$

Thus, the potential energy of particle pairs α, β with middle point x_i in the volume element $\mathrm{d}\mathbf{x}$ and distance vector ξ_i in the volume element $\mathrm{d}\boldsymbol{\xi}$ is given by

$$V_{\alpha\beta}(\xi)\, n_\alpha\left(x_i + \tfrac{1}{2}\xi_i\right) n_\beta\left(x_i - \tfrac{1}{2}\xi_i\right) \mathrm{d}\mathbf{x}\, \mathrm{d}\boldsymbol{\xi}.$$

Integration over all values of the distance vector and division by $\mathrm{d}\mathbf{x}$ gives the potential energy density at x_i stemming from all pairs with middle point in $\mathrm{d}\mathbf{x}$, namely

$$U_{\text{mix}} = \gamma_{\alpha\beta} \int V_{\alpha\beta}(\xi)\, n_\alpha\left(x_i + \tfrac{1}{2}\xi_i\right) n_\beta\left(x_i - \tfrac{1}{2}\xi_i\right) \mathrm{d}\boldsymbol{\xi} \quad \text{with} \quad \gamma_{\alpha\beta} = \begin{cases} \tfrac{1}{2} & \text{if } \alpha = \beta \\ 1 & \text{if } \alpha \neq \beta. \end{cases}$$

The coefficient $\gamma_{\alpha\beta}$ guarantees that pairs of the same species do not contribute twice to the energy.

The potential $V_{\alpha\beta}$ decays rapidly with increasing ξ so that it is reasonable to approximate n_α using the expansion $n_\alpha\left(x_i \pm \tfrac{1}{2}\xi_i\right) \approx n_\alpha(x_i) \pm \tfrac{1}{2}\xi_i \frac{\partial n_\alpha}{\partial x_i}$. Moreover, making use of the concentration c by means of the relations $n_1 = \frac{\varrho_1}{m_1} c$, $n_2 = \frac{\varrho_2}{m_2}(1-c)$ and summing over all possible pairs of species, we find

$$U_{\text{mix}} = ac(1-c) + \tfrac{1}{2}b\frac{\partial c}{\partial x_i}\frac{\partial c}{\partial x_i} + a_{11}c + a_{22}(1-c) \tag{6}$$

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with coefficients a, b given by relevant moments of the interaction potentials,

$$a = \int \left(\frac{\varrho_1}{m_1} \frac{\varrho_2}{m_2} V_{12}(\xi) - \tfrac{1}{2} \left(\frac{\varrho_1}{m_1} \right)^2 V_{11}(\xi) - \tfrac{1}{2} \left(\frac{\varrho_2}{m_2} \right)^2 V_{22}(\xi) \right) \mathrm{d}\boldsymbol{\xi},$$

$$b = \tfrac{1}{6} \int \left(\frac{\varrho_1}{m_1} \frac{\varrho_2}{m_2} V_{12}(\xi) - \tfrac{1}{2} \left(\frac{\varrho_1}{m_1} \right)^2 V_{11}(\xi) - \tfrac{1}{2} \left(\frac{\varrho_2}{m_2} \right)^2 V_{22}(\xi) \right) \xi^2 \, \mathrm{d}\boldsymbol{\xi}.$$

$$(7)$$

The final two terms in (6), involving the coefficients $a_{\alpha\alpha} = \tfrac{1}{2} \left(\frac{\varrho_\alpha}{m_\alpha} \right)^2 \int V_{\alpha\alpha}(\xi) \, \mathrm{d}\boldsymbol{\xi}$, can be absorbed into the energies u_0^α of the single constituents and need not be considered any further.

The coefficient a has the dimension of an energy and the ratio $\sqrt{b/a} = l_{\mathrm{cap}}$ defines a fundamental length scale l_{cap} for capillary forces in the mixture. It should only be of the order of a few molecular diameters. In particular, between immiscible fluids one would expect to find only a slightly diffuse interface of approximate mean thickness l_{cap}. The Taylor expansion used above for $n_\alpha(\cdot)$ is likely to prove most accurate, however, when the interface thickness is large compared with l_{cap}, as it would be at an interface between miscible fluids.

It is worth noting that, according to our simple model, the energy of mixing is independent of temperature. A similar derivation can be found in Cahn & Hilliard's celebrated paper [5]. These authors, however, compute the potential energy associated with a *single* particle, and not, as we have done, the energy of a *pair* of particles. In order to arrive at the above result (6), Cahn and Hilliard had to perform an integration by parts, which appears to be somewhat artificial and is not needed in our approach. More refined models for the energy of mixing can be found in [15].

2.4 Entropy of mixing

In order to calculate the entropy of mixing from a simple argument we consider a volume element $\mathrm{d}\mathbf{x}$ where we have n_1 molecules of fluid *1* and n_2 molecules of fluid *2*. Under the assumption that there are as many places in $\mathrm{d}\mathbf{x}$ as particles, namely $(n_1 + n_2)$, we calculate the entropy of mixing from the well known Boltzmann formula as

$$S_{\mathrm{mix}} = k \ln \frac{(n_1 + n_2)!}{n_1! \, n_2!} = -k \left(n_1 \ln \frac{n_1}{n_1 + n_2} + n_2 \ln \frac{n_2}{n_1 + n_2} \right)$$

where k denotes Boltzmann's constant and we have used the Stirling formula. Again, the number densities can be related to the concentration by $n_1 = \frac{\varrho_1}{m_1} c$, $n_2 = \frac{\varrho_2}{m_2}(1 - c)$ to obtain

$$S_{\mathrm{mix}} = k \left[\frac{\varrho_1}{m_1} c \ln \left(1 + \frac{\varrho_2}{\varrho_1} \frac{m_1}{m_2} \frac{1-c}{c} \right) + \frac{\varrho_2}{m_2} (1-c) \ln \left(1 + \frac{\varrho_1}{\varrho_2} \frac{m_2}{m_1} \frac{c}{1-c} \right) \right]. \qquad (8)$$

2.5 Free energy

The specific free energy of the mixture is given by

$$f = u - Ts = \tfrac{1}{\varrho} \left(c \varrho_1 f_1 + (1 - c) \varrho_2 f_2 + U_{\mathrm{mix}} - T S_{\mathrm{mix}} \right) \qquad (9)$$

with the free energies of the single constituents f_1, f_2 given by

$$f_\alpha(T) = u_\alpha - T s_\alpha = c_{\mathrm{v}}^\alpha \left((T - T_0) - T \ln \frac{T}{T_0} \right) + u_0^\alpha - T s_0^\alpha$$

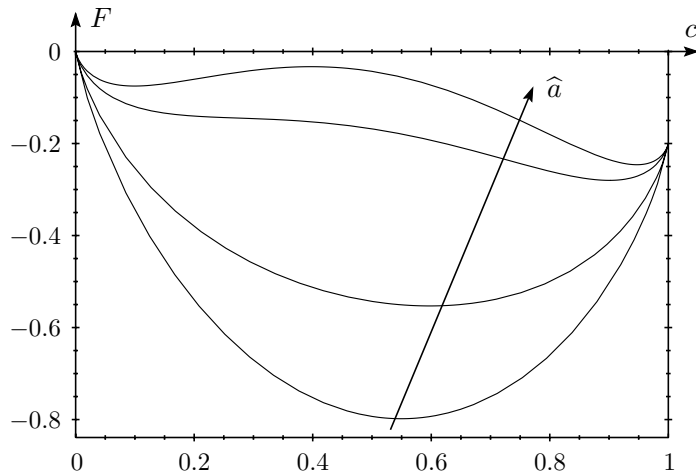and with U_{mix}, S_{mix} given by (6, 8).

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Figure 1: The free energy (10) with $(f_2 - f_1)/(kT/m) = 0.2$ for $\widehat{a} = 0$, 1, 2.5, 3.

Depending on the strength of the intermolecular forces, the free energy (9) is either convex or has the form of a double well potential. To illustrate this, we can consider a case having equal molecular masses and mass densities of the constituents, $m_1 = m_2 = m$, $\varrho_1 = \varrho_2 = \varrho$, and ignore the concentration gradients in U_{mix}. We can then write

$$F = \frac{f - f_2}{kT/m} = \frac{c(f_1 - f_2)}{kT/m} + \widehat{a}c(1-c) + c\ln c + (1-c)\ln(1-c) \tag{10}$$

with the abbreviation $\widehat{a} = \frac{a}{\varrho kT/m}$. In this simplified case, F ceases to be convex ($\frac{\partial^2 F}{\partial c^2} \geq 0$), if $\widehat{a} \geq 2$. Figure 1 shows the free energy (10) for some values of $\widehat{a}$. A non-convex free energy allows for the separation of two phases with different concentrations, i.e. a gap of miscibility [11]. For very large values of $\widehat{a}$, when the interaction energy exceeds the thermal energy, the equilibrium concentrations are given by $c \approx 0, c \approx 1$ and the mixture appears to be immiscible. In the context of this paper we are interested mainly in fully miscible binary mixtures and shall consider cases where the interaction energy is dominated by the thermal energy, for which $\widehat{a} < 2$.

3   Field equations

The thermodynamics of incompressible binary mixtures provides a means of determining the concentration c, velocity v_i and temperature T fields as function of space and time. For this purpose we have the conservation laws of mass, momentum and energy which must be furnished with constitutive relations for diffusion flux, mass production rate, heat flux and stress tensor.

3.1   Balance laws

The balances of mass for the constituents 1, 2 read

$$\frac{\partial}{\partial t}\big(\varrho_1 c\big) + \frac{\partial}{\partial x_k}\big(\varrho_1 c v_k^1\big) = \tau, \quad \frac{\partial}{\partial t}\big(\varrho_2 (1-c)\big) + \frac{\partial}{\partial x_k}\big(\varrho_2 (1-c) v_k^2\big) = -\tau \tag{11}$$

where τ is the mass production rate and v_k^α denotes the centre-of-mass velocity of constituent α. The mass balance of the mixture is the sum of the partial mass balances and assumes the usual form

$$\frac{\partial}{\partial t}\varrho + \frac{\partial}{\partial x_k}\big(\varrho v_k\big) = 0$$

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with the centre-of-mass velocity v_k of the mixture given by

$$\varrho v_k = \varrho_1 c\, v_k^1 + \varrho_2 (1 - c)\, v_k^2.$$

If the diffusion flux J_k is defined as

$$J_k = \varrho_1 c(v_k^1 - v_k) = -\varrho_2 (1 - c) (v_k^2 - v_k)$$

then the equations (11) can be combined to give

$$\dot{c} = -\frac{\varrho}{\varrho_1 \varrho_2}\left(\frac{\partial J_k}{\partial x_k} - \tau\right), \quad \frac{\partial v_k}{\partial x_k} = -\frac{\varrho_1 - \varrho_2}{\varrho}\dot{c} \tag{12}$$

in which $(\cdot)^{\boldsymbol{\cdot}} = \frac{\partial}{\partial t} + v_k \frac{\partial}{\partial x_k}$ denotes the material time derivative. The first equation is the evolution equation for the concentration while the second relates the change of volume to the change in concentration. Thus, as long as the constant densities of the constituents are different, $\varrho_1 \neq \varrho_2$, the mixture appears to be compressible—it is *quasi-incompressible* as described earlier [9, 12].

The balances for momentum and energy of the mixture are assumed to have the same form as for a single fluid, see [13],

$$\varrho \dot{v}_i - \frac{\partial t_{ik}}{\partial x_k} = \varrho g_i, \quad \varrho \dot{u} + \frac{\partial q_k}{\partial x_k} = t_{ij}\frac{\partial v_i}{\partial x_j}. \tag{13}$$

Here, t_{ij} denotes the stress tensor, q_k is the heat flux vector and g_i is an external body force, usually gravity.

With (12, 13) we have six equations for the unknowns $\{T, c, v_k\}$, so that the system appears to be overdetermined. However, it will be seen that the pressure p enters as an additional variable. This is normally the case in the theory of incompressible fluids, see [12, 13].

3.2 The second law of thermodynamics

The equations (12, 13) contain quantities which are not a priori related to the fields $\{T, c, v_k\}$, namely the diffusion flux J_k, the mass production rate τ, the stress tensor t_{ij} and the heat flux q_k. In this section we shall exploit the second law of thermodynamics in order to find constitutive equations for these additional quantities. We shall follow the guidelines of classical thermodynamics of irreversible processes (TIP), see [7] for a classical survey.

Roughly speaking, we construct a balance equation for the entropy and ensure the positiveness of the entropy production by an appropriate choice of the constitutive equations. The starting point is the specific entropy (5,8) which is a function of $\{T, c\}$ or, by eliminating the temperature T with the energy (4 ,6), a function of $\{u, c, \chi\}$, where χ is defined as $\chi = \frac{1}{2}\frac{\partial c}{\partial x_i}\frac{\partial c}{\partial x_i}$. Note, that the dependence on χ leads beyond standard classical TIP, where the entropy depends on equilibrium variables only, and not on gradients. The total differential of the specific entropy reads (Gibbs equation)

$$\mathrm{d}s = \frac{1}{T}\,\mathrm{d}u + \left(\frac{\partial s}{\partial c}\right)_{u,\chi}\mathrm{d}c + \left(\frac{\partial s}{\partial \chi}\right)_{u,c}\mathrm{d}\chi \tag{14}$$

according to which the temperature T can be defined in the usual way, such that

$$\frac{1}{T} = \left(\frac{\partial s}{\partial u}\right)_{c,\chi}.$$

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Considering entropy s and energy u to be functions of $\{T, c, \chi\}$ we find from (14)

$$\left(\frac{\partial s}{\partial c}\right)_{u,\chi} = \left(\frac{\partial s}{\partial c}\right)_{T,\chi} - \frac{1}{T}\left(\frac{\partial u}{\partial c}\right)_{T,\chi} = -\frac{1}{T}\frac{\partial f}{\partial c}$$

$$\left(\frac{\partial s}{\partial \chi}\right)_{u,c} = \left(\frac{\partial s}{\partial \chi}\right)_{T,c} - \frac{1}{T}\left(\frac{\partial u}{\partial \chi}\right)_{T,c} = -\frac{1}{T}\frac{\partial f}{\partial \chi}.$$

Note that by (9) the free energy f is a function of $\{T, c, \chi\}$. With these relations the Gibbs equation leads to

$$\varrho\dot{s} = \frac{1}{T}\varrho\dot{u} - \frac{\varrho}{T}\frac{\partial f}{\partial c}\dot{c} - \frac{\varrho}{T}\frac{\partial f}{\partial \chi}\dot{\chi}.$$

Noting that

$$\dot{\chi} = \tfrac{1}{2}\left(\frac{\partial c}{\partial x_i}\frac{\partial c}{\partial x_i}\right)^{\cdot} = \frac{\partial c}{\partial x_i}\left(\frac{\partial \dot{c}}{\partial x_i} - \frac{\partial v_k}{\partial x_i}\frac{\partial c}{\partial x_k}\right)$$

we can eliminate the time derivatives of u and c by means of the balance laws (12, 13) to get

$$\varrho\dot{s} = -\frac{1}{T}\frac{\partial}{\partial x_k}\left(q_k + \varrho\frac{\partial f}{\partial \chi}\dot{c}\frac{\partial c}{\partial x_k}\right) + \frac{1}{T}\left(\Pi\delta_{ij} + t_{ij} + \varrho\frac{\partial f}{\partial \chi}\frac{\partial c}{\partial x_i}\frac{\partial c}{\partial x_j}\right)\frac{\partial v_i}{\partial x_j} + \tag{15}$$

$$+ \frac{1}{T}\left(\frac{\varrho^2}{\varrho_1\varrho_2}\frac{\partial f}{\partial c} - \frac{\varrho}{\varrho_1\varrho_2}\frac{\partial}{\partial x_i}\left(\varrho\frac{\partial f}{\partial \chi}\frac{\partial c}{\partial x_i}\right) - \frac{\varrho_1 - \varrho_2}{\varrho_1\varrho_2}\Pi\right)\left(\frac{\partial J_k}{\partial x_k} - \tau\right)$$

where Π denotes the generalized pressure, which is an *arbitrary* scalar function since the two terms containing Π cancel each other by means of (12). The generalized pressure will be discussed below after we have finished discussing the constitutive theory.

It is convenient to introduce the irreversible heat flux Q_k, the irreversible stress tensor P_{ij} and the chemical potential μ as

$$q_k = Q_k - \varrho\frac{\partial f}{\partial \chi}\dot{c}\frac{\partial c}{\partial x_k},$$

$$t_{ij} = -\Pi\delta_{ij} - \varrho\frac{\partial f}{\partial \chi}\frac{\partial c}{\partial x_i}\frac{\partial c}{\partial x_j} + P_{ij}, \tag{16}$$

$$\mu = \frac{\varrho^2}{\varrho_1\varrho_2}\frac{\partial f}{\partial c} - \frac{\varrho}{\varrho_1\varrho_2}\frac{\partial}{\partial x_i}\left(\varrho\frac{\partial f}{\partial \chi}\frac{\partial c}{\partial x_i}\right) - \frac{\varrho_1 - \varrho_2}{\varrho_1\varrho_2}\Pi.$$

By referring to Q_k and P_{ij} as *irreversible* we mean that only these parts of heat flux and stress tensor contribute to the production of entropy.

After some rearrangement equation (15) assumes the form of a balance law,

$$\varrho\dot{s} + \frac{\partial \phi_k}{\partial x_k} = \Sigma$$

involving the entropy flux vector

$$\phi_k = \frac{Q_k}{T} - \frac{\mu}{T}J_k$$

and the entropy production rate

$$\Sigma = \tau\left(-\frac{\mu}{T}\right) + \frac{P_{jj}}{3T}\frac{\partial v_k}{\partial x_k} + Q_k\frac{\partial 1/T}{\partial x_k} + J_k\frac{\partial}{\partial x_k}\left(-\frac{\mu}{T}\right) + \frac{P_{\langle ij\rangle}}{T}\frac{\partial v_{\langle i}}{\partial x_{j\rangle}}. \tag{17}$$

The angle brackets $\langle\cdot\rangle$ on the indices i, j denote the symmetric trace-free part of a tensor, such as $P_{\langle ij\rangle} = P_{ij} - \frac{1}{3}P_{kk}\delta_{ij}$. According to the second law of thermodynamics, the entropy production rate Σ must be positive or zero.

3.3 Phenomenological equations

It is convenient to write the entropy production rate Σ as a sum of thermodynamic fluxes F_A and thermodynamic forces X_A,

$$\Sigma = \sum_A F_A X_A \geq 0,$$

in which the fluxes and forces are, from (17)

$$F_A = \left\{ \quad \tau \;, \; \frac{1}{3T} P_{jj} \;, \quad Q_k \quad, \qquad J_k \qquad, \; \frac{1}{T} P_{\langle ij \rangle} \right\},$$

$$X_A = \left\{ -\frac{\mu}{T} \;, \; \frac{\partial v_k}{\partial x_k} \;, \; \frac{\partial 1/T}{\partial x_k} \;, \; \frac{\partial}{\partial x_k}\left(-\frac{\mu}{T}\right) \;, \; \frac{\partial v_{\langle i}}{\partial x_{j \rangle}} \right\}.$$

In linear irreversible thermodynamics the positiveness of the entropy production is ensured by the so-called phenomenological equations [7], by which

$$F_A = \sum_B L_{AB} X_B \quad \text{with} \quad L_{AB} \text{ positive definite}$$

for each value of A. The phenomenological coefficients L_{AB} must be taken to be functions of the same variables as entropy and energy, namely temperature T, concentration c, and concentration gradient $\frac{\partial c}{\partial x_i}$.

In classical irreversible thermodynamics the phenomenological equations are somewhat simplified by the so-called Curie principle, which states, in its simplest form, that thermodynamic fluxes of tensorial rank n (scalars, vectors, tensors, ...) are coupled only to forces of the same tensorial rank [7]. This statement follows from arguments on isotropy of the body under consideration, and is not strictly true in our case, where the phenomenological coefficients L_{AB} can depend on the concentration gradient which is inherently not isotropic [14, 12].

However, being interested in the simplest model obtainable from the second law, we do not consider any cross effects but assume that the fluxes are coupled solely to their corresponding forces. Alternatively, we can argue that the model applies to relatively weak gradients in concentration, with changes occurring over very many molecular diameters. In this case the off-diagonal elements of the matrix L_{AB} should, effectively, be zero and the phenomenological equations then read

$$J_k = -D\frac{\partial}{\partial x_k}\left(\frac{\mu}{T}\right), \quad Q_k = -\kappa\frac{\partial T}{\partial x_k}, \quad P_{jj} = 3\nu\frac{\partial v_k}{\partial x_k}, \quad P_{\langle ij \rangle} = 2\eta\frac{\partial v_{\langle i}}{\partial x_{j \rangle}}. \tag{18}$$

Here, D is the diffusion coefficient, κ the thermal conductivity, and η and ν are the shear and bulk viscosity, respectively; all coefficients must be positive.

We did not set up a similar equation for the chemical reaction rate τ since a linear law, $\tau = -\gamma\frac{\mu}{T}$, is physically correct only close to chemical equilibrium and cannot be used for the description of flame-like reactions. We shall consider the chemistry in Section 3.5.

To close this section, we examine the chemical potential for our binary mixture of incompressible fluids with the free energy (9). We can write $(16)_3$ as

$$\mu = \mu_1 - \mu_2 \tag{19}$$

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in which we define the separate chemical potentials for the constituents *1, 2* as

$$\mu_1 = f_1(T) - \frac{kT}{m_1} \ln\left(1 + \frac{\varrho_2}{\varrho_1}\frac{m_1}{m_2}\frac{1-c}{c}\right)$$
$$+ \frac{1}{\varrho_1}\left(\Pi + \frac{b}{2}\frac{\partial c}{\partial x_k}\frac{\partial c}{\partial x_k} + (1-c)\left[a(1-c) - b\frac{\partial^2 c}{\partial x_k \partial x_k}\right]\right)$$
$$\mu_2 = f_2(T) - \frac{kT}{m_2} \ln\left(1 + \frac{\varrho_1}{\varrho_2}\frac{m_2}{m_1}\frac{c}{1-c}\right) + \frac{1}{\varrho_2}\left(\Pi + \frac{b}{2}\frac{\partial c}{\partial x_k}\frac{\partial c}{\partial x_k} + c\left[ac + b\frac{\partial^2 c}{\partial x_k \partial x_k}\right]\right). \quad (20)$$

Note that it is not imperative to assign the individual terms to the chemical potentials of the constituents in precisely this way, which, all the same, seems to be the most natural choice. In particular, μ_α will reduce to the free enthalpy $f_\alpha + \frac{\Pi}{\varrho_\alpha}$ for a single constituent.

3.4   Pressure and capillary forces

Due to (16,18) the stress tensor reads

$$t_{ij} = -\Pi\delta_{ij} - \varrho\frac{\partial f}{\partial\chi}\frac{\partial c}{\partial x_i}\frac{\partial c}{\partial x_j} + \nu\frac{\partial v_k}{\partial x_k}\delta_{ij} + 2\eta\frac{\partial v_{\langle i}}{\partial x_{j\rangle}}.$$

It is evident that Π, introduced in (15) as an arbitrary scalar function, indeed plays the role of the pressure. Moreover Π can be added as the sixth variable in the set $\{T, c, v_i, \Pi\}$ and will be determined by the field equations and boundary conditions for the stress tensor. However, because of the way that Π was introduced in the theory, we have some freedom over its precise definition and can decompose Π into the usual interpretation of the pressure p and any arbitrary scalar function of the other variables, $\Pi = p + \widehat{\Pi}(T, c, \chi)$. One particular choice for $\widehat{\Pi}(T, c, \chi)$ leads to a transparent and sensible representation of the stress tensor. We set

$$\Pi = p - \varrho\frac{\partial f}{\partial\chi}\frac{\partial c}{\partial x_k}\frac{\partial c}{\partial x_k}$$

and introduce the tensor of capillary stresses as

$$S_{ij} = \varrho\frac{\partial f}{\partial\chi}\left(\frac{\partial c}{\partial x_k}\frac{\partial c}{\partial x_k}\delta_{ij} - \frac{\partial c}{\partial x_i}\frac{\partial c}{\partial x_j}\right). \quad (21)$$

Since this defintion results in the identity, $S_{ij}\frac{\partial c}{\partial x_j} = 0$, this part of the stress tensor contributes only forces perpendicular to the gradient of concentration. Thus, S_{ij} describes a distributed form of the surface tension of any diffusive layer between regions with different concentration.

The complete stress tensor is a sum of three terms, the pressure p, the viscous stresses P_{ij} and the tensor of capillary stresses S_{ij}

$$t_{ij} = -p\delta_{ij} + S_{ij} + P_{ij}.$$

Other redefinitions of Π are possible, see [2] for example, but will not be discussed here. Our choice for the definition of pressure was taken from [3]. However, although that article starts off with the exploitation of the second law, it does not make full use of its possibilities. Instead it derives its expression for the tensor S_{ij} based on heuristic arguments from the energy balance and results in the factor $\varrho\frac{\partial u}{\partial\chi}$ in place of $\varrho\frac{\partial f}{\partial\chi}$. In fact, there is no essential difference between the two results for our simple model where we have $\varrho\frac{\partial f}{\partial\chi} = \varrho\frac{\partial u}{\partial\chi} = b$, see equations (4,9).

3.5 Chemistry

In this section we study the chemistry of our model for a binary mixture with the sole reaction

$$\gamma_1' A + \gamma_2' B \rightleftarrows \gamma_1'' A + \gamma_2'' B.$$
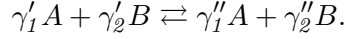
γ_α' and γ_α'' denote the stoichiometric coefficients for the reactant and the products, respectively; A and B stand for the components 1, 2. Due to conservation of mass we have

$$m_1(\gamma_1'' - \gamma_1') = -m_2(\gamma_2'' - \gamma_2'). \tag{22}$$

The mass production rate τ of constituent 1 can be written in terms of the reaction rate density Λ as

$$\tau = m_1(\gamma_1'' - \gamma_1')\Lambda.$$

In order to have a positive production of entropy due to chemical reactions, $\tau(-\mu/T) \geq 0$ must hold or, with the reaction rate Λ and (19,22),

$$\Lambda(A' - A'') \geq 0 \tag{23}$$

where A' and A'' are the chemical affinities, defined as

$$A' = m_1\gamma_1'\mu_1 + m_2\gamma_2'\mu_2, \quad A'' = m_1\gamma_1''\mu_1 + m_2\gamma_2''\mu_2.$$

As we have said before, a linear law for the reaction rate is appropriate only close to chemical equilibrium. For flame-like reactions there are good reasons to believe that the reaction rate density should be of the form

$$\Lambda = K\left(\exp\frac{A'}{kT} - \exp\frac{A''}{kT}\right)$$

with a positive constant K so that the positivity of (23) is ensured. We make the entropic terms of the chemical potentials (20) explicit by setting
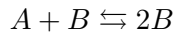
$$\mu_1 = \widehat{\mu}_1 - \frac{kT}{m_1}\ln\left(1 + \frac{\varrho_2}{\varrho_1}\frac{m_1}{m_2}\frac{1-c}{c}\right), \quad \mu_2 = \widehat{\mu}_2 - \frac{kT}{m_2}\ln\left(1 + \frac{\varrho_1}{\varrho_2}\frac{m_2}{m_1}\frac{c}{1-c}\right) \tag{24}$$

and obtain the well-known Arrhenius law [17]

$$\Lambda = K\left(\frac{n_1^{\gamma_1'}n_2^{\gamma_2'}}{n^{\gamma_1'+\gamma_2'}}\exp\frac{m_1\gamma_1'\widehat{\mu}_1 + m_2\gamma_2'\widehat{\mu}_2}{kT} - \frac{n_1^{\gamma_1''}n_2^{\gamma_2''}}{n^{\gamma_1''+\gamma_2''}}\exp\frac{m_1\gamma_1''\widehat{\mu}_1 + m_2\gamma_2''\widehat{\mu}_2}{kT}\right)$$

written with the number densities $n_1 = \frac{\varrho_1}{m_1}c$, $n_2 = \frac{\varrho_2}{m_2}(1-c)$, $n = n_1 + n_2$.

From now on, we shall restrict our attention to the autocatalytic reaction

$$A + B \leftrightarrows 2B$$

with the stoichiometric coefficients $\gamma_1' = \gamma_2' = 1$, $\gamma_1'' = 0$, $\gamma_2'' = 2$. This implies that the molecular masses of the particles are the same, $m_1 = m_2 = m$, so that $mn = \varrho$. The Arrhenius law for this particular reaction reads

$$\Lambda = K\frac{\varrho_1\varrho_2}{\varrho^2}\left(c(1-c)\exp\frac{\widehat{\mu}_1 + \widehat{\mu}_2}{kT/m} - \frac{\varrho_2}{\varrho_1}(1-c)^2\exp\frac{2\widehat{\mu}_2}{kT/m}\right). \tag{25}$$
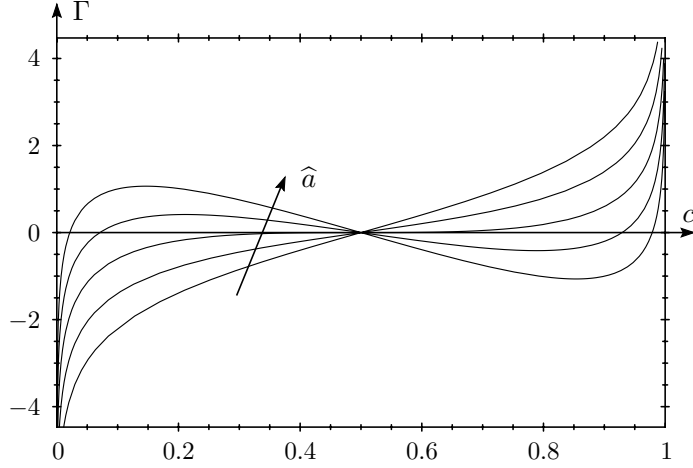
Figure 2: The function $\Gamma = \ln \frac{c}{1-c} + \widehat{a}(1 - 2c)$ for $\widehat{a} = 0$, 1, 2, 3, 5.

Let us consider the chemical equilibrium for the mixture so that $\Lambda = 0$, or

$$\frac{c}{1-c} \exp\{-G\} = \frac{\varrho_2}{\varrho_1} \exp\{F + P\}. \tag{26}$$

The latter equation is the law of mass action for the reaction in question where we have introduced the abbreviations

$$
\begin{aligned}
F &= \frac{f_2(T) - f_1(T)}{k/mT} = \frac{c_{\mathrm{v}}^2 - c_{\mathrm{v}}^1}{k/m}\left(1 - \frac{T_0}{T} - \ln\frac{T}{T_0}\right) + \frac{u_0^2 - u_0^1}{kT/m} - \frac{(s_0^2 - s_0^1)}{k/m} \\
P &= \frac{p}{kT/m}\left(\frac{1}{\varrho_2} - \frac{1}{\varrho_1}\right) \\
G &= \frac{1}{\varrho_2 kT/m}\left(c\left[ac - b\frac{\partial^2 c}{\partial x_k \partial x_k}\right] + \frac{b}{2}\frac{\partial c}{\partial x_k}\frac{\partial c}{\partial x_k}\right) \\
&\quad - \frac{1}{\varrho_1 kT/m}\left((1-c)\left[a(1-c) - b\frac{\partial^2 c}{\partial x_k \partial x_k}\right] - \frac{b}{2}\frac{\partial c}{\partial x_k}\frac{\partial c}{\partial x_k}\right).
\end{aligned}
\tag{27}
$$

The occurrence of the concentration gradients in G complicates the interpretation of the law of mass action (26) but we can state some principal properties nevertheless:

- A higher value of F shifts the equilibrium towards larger values of the concentration, which stabilizes constituent *1*. The value of F is mainly determined by the energy and entropy constants u_0^α, s_0^α.

- An increase of the pressure p shifts the chemical equilibrium towards the denser component —this is a reflection of Le Chatelier's principle.

- The influence of the intermolecular forces on the chemical potential is contained in the function G. Neglecting the concentration gradient and the difference in the densities we have $G = -\widehat{a}(1 - 2c)$. Figure 2 shows the function $\Gamma = \ln\frac{c}{1-c} + \widehat{a}(1 - 2c)$ for several values of the parameter $\widehat{a} = \frac{a}{\varrho kT/m}$. In equilibrium $\Gamma = F + P$, and we can read off from the figure that a larger value of $\widehat{a}$ stabilizes the single constituents. For $\widehat{a} \geq 2$, where the free energy is non-convex, there are three possible equilibrium concentrations for a certain range of $F + P$. Only the outer concentrations, however, correspond to stable equilibria, while the intermediate value for the concentration belongs to an unstable case.

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3.6 Summary of results

With the results of the last section we have a closed system of field equations for the variables T, c, p, v_i. The equations read

$$\dot{c} = -\frac{\varrho}{\varrho_1 \varrho_2}\left(\frac{\partial J_k}{\partial x_k} - \tau\right), \quad \frac{\partial v_k}{\partial x_k} = -\frac{\varrho_1 - \varrho_2}{\varrho}\dot{c}$$

$$\varrho \dot{v}_i + \frac{\partial p}{\partial x_i} - \frac{\partial S_{ik}}{\partial x_k} - \frac{\partial P_{ik}}{\partial x_k} = \varrho g_i \tag{28}$$

$$\varrho c_\mathrm{V} \dot{T} + \frac{\partial Q_k}{\partial x_k} = P_{ij}\frac{\partial v_i}{\partial x_j} + \frac{\varrho_1 \varrho_2}{\varrho}(h_2 - h_1)\dot{c}.$$

Here, we have written the energy balance $(28)_4$ in terms of the variables; c_V is the heat capacity of the mixture, given by

$$\varrho c_\mathrm{V} = c\varrho_1 c_\mathrm{V}^1 + (1-c)\varrho_2 c_\mathrm{V}^2.$$

The heat release due to changes of the concentration is proportional to the difference of generalized enthalpies h_1, h_2 of the constituents, which are given below in equation (30). It is interesting that only the irreversible parts of heat flux and pressure tensor appear in this equation.

The constitutive equations for mass production rate τ, diffusion flux J_k, irreversible heat flux Q_k, tensor of capillary stresses S_{ij} and tensor of viscous stresses P_{ij} read

$$\tau = -\widehat{K}\left(c(1-c)\exp\frac{\widehat{\mu}_1 + \widehat{\mu}_2}{kT/m} - \frac{\varrho_2}{\varrho_1}(1-c)^2 \exp\frac{2\widehat{\mu}_2}{kT/m}\right)$$

$$J_k = -D\frac{\partial}{\partial x_k}\left(\frac{\mu_1 - \mu_2}{T}\right), \qquad Q_k = -\kappa\frac{\partial T}{\partial x_k}, \tag{29}$$

$$S_{ij} = b\left(\frac{\partial c}{\partial x_k}\frac{\partial c}{\partial x_k}\delta_{ij} - \frac{\partial c}{\partial x_i}\frac{\partial c}{\partial x_j}\right), \quad P_{ij} = \nu\frac{\partial v_k}{\partial x_k}\delta_{ij} + 2\eta\frac{\partial v_{\langle i}}{\partial x_{j\rangle}}.$$

The positive coefficients $\widehat{K}$, D, κ, ν, and η must be determined from experiments, the theory is not able to say anything about their values or their dependence on the variables $\{T, c, \alpha\}$. The same is true for the coefficients of capillary forces a and b which follow from intermolecular potentials by (7).

Finally we give the generalized enthalpies of the two constituents which read

$$h_1 = u_1 + \frac{1}{\varrho_1}\left(p - \frac{b}{2}\frac{\partial c}{\partial x_k}\frac{\partial c}{\partial x_k} + (1-c)\left[a(1-c) - b\frac{\partial^2 c}{\partial x_k \partial x_k}\right]\right), \tag{30}$$

$$h_2 = u_2 + \frac{1}{\varrho_2}\left(p - \frac{b}{2}\frac{\partial c}{\partial x_k}\frac{\partial c}{\partial x_k} + c\left[ac + b\frac{\partial^2 c}{\partial x_k \partial x_k}\right]\right).$$

The chemical potentials μ_α, $\widehat{\mu}_\alpha$ are given by (20,24).

4 A simplified model for the Hele-Shaw cell

In this section we reduce our model for the description of processes in Hele-Shaw cells. In particular we shall use the experimental data of [1] in order to weigh the relative importance of the several contributions to the equations.

4.1 Isothermal processes and simplified chemistry

Our main interest in this paper lies in the interplay between chemical reaction and surface tension. In order to focus attention on this behaviour, we introduce some assumptions which will lead to considerable simplifications.

Isothermal processes:
When the heat release of the reaction is small, or the specific heat c_V is large, or the heat conductivity is large, one can expect very small variations in temperature. The temperature can then be assumed to be constant, $T = T_0$, and the energy balance (28)$_4$ can be discarded. Indeed, this condition is met very well in the experimental Hele-Shaw cells of [1], where the heat of reaction is almost immediately absorbed by the walls.

Full reaction:
We assume that the energy and entropy constants u_α^0, s_α^0 are large compared to the contributions of pressure and capillary forces in $\widehat{\mu}_\alpha$ (24), so that $\widehat{\mu}_1(T_0) \simeq u_0^1 - T_0 s_0^1$, $\widehat{\mu}_2(T_0) \simeq u_0^2 - T_0 s_0^2$. Furthermore we presume that $\widehat{\mu}_2(T_0) \ll \widehat{\mu}_1(T_0)$ so that the first term in the mass production rate (29)$_1$ dominates and τ reduces to

$$\tau = -\overline{K} c(1-c) \qquad \text{where} \qquad \overline{K} = \widehat{K} \exp \frac{u_0^1 + u_0^2 - T_0 \left(s_0^1 - s_0^2\right)}{kT_0/m} \tag{31}$$

Now, the reaction rate $\overline{K}$ and the chemical equilibrium are independent of pressure and capillary forces. Equation (31) describes an autocatalytic reaction from constituent 1 ($c = 1$) to constituent 2 ($c = 0$). Constituent 1 alone is stable, but as soon as a bit of constituent 2 is added, a reaction will start and proceed until constituent 1 is fully consumed.

4.2 Diffusion flux and miscibility

In this section we discuss the diffusion flux. In particular we shall define a miscible system and introduce an assumption on the dependence of the diffusion coefficient D on the concentration. To simplify notation we set

$$\widehat{p} = \frac{p}{\varrho_1 kT_0/m}, \quad \widehat{a} = \frac{a}{\varrho_1 kT_0/m}, \quad \widehat{b} = \frac{b}{\varrho_1 kT_0/m} \tag{32}$$

and obtain the diffusion flux from the derivative of the chemical potentials as

$$J_k = -D\frac{k}{m}\left[\frac{1}{c(1-c)}\frac{\partial c}{\partial x_k} - 2\widehat{a}\frac{\partial c}{\partial x_k} - \widehat{b}\frac{\partial^3 c}{\partial x_i \partial x_i \partial x_k} + \right. \tag{33}$$
$$\left. + \left(1 - \frac{\varrho_1}{\varrho_2}\right)\left(\frac{\partial \widehat{p}}{\partial x_k} + 2\widehat{a}c\frac{\partial c}{\partial x_k} + \widehat{b}\left[\frac{\partial c}{\partial x_k}\frac{\partial^2 c}{\partial x_i \partial x_i} + c\frac{\partial^3 c}{\partial x_i \partial x_i \partial x_k} - \frac{\partial^2 c}{\partial x_k \partial x_i}\frac{\partial c}{\partial x_i}\right]\right)\right].$$

Insertion of this flux into the balance of the concentration (28)$_2$ gives the specific form of the Cahn-Hilliard equation for our model. The first term, $\frac{1}{c(1-c)}\frac{\partial c}{\partial x_k}$, stems from the entropy of mixing, and therefore refers to the entropic part of the diffusion flux. This term forbids a total demixing of the constituents ($c = 1$ or $c = 0$) and, if it dominates, leads to a perfectly mixed fluid—as long as there are no chemical reactions to be sure.

According to the first term in the second line a pressure gradient may produce a diffusive flux if the densities of the two constituents differ. This gives rise to some demixing along the pressure gradient. Total demixing, of course, is prohibited by the entropic diffusion.
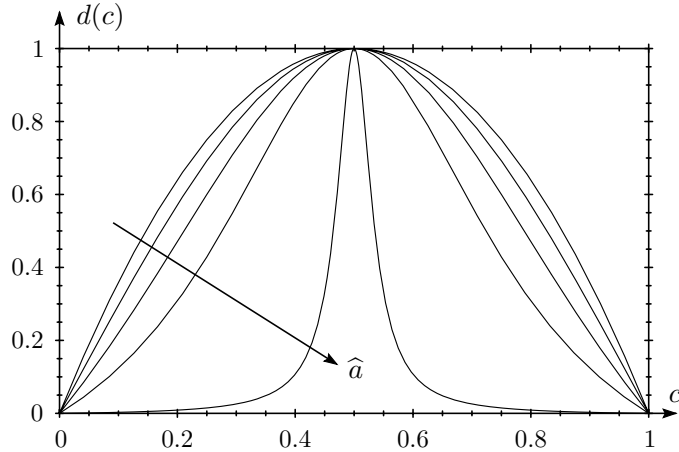
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Figure 3: The function $d(c)$ for $\widehat{a} = 0$, 0.5, 1, 1.5, 1.99.

All other terms are related to the capillary forces and also lead to demixing to some degree.

Summarizing we can say that there are entropic forces (the first term) and energetic forces (pressure gradient and capillary forces) acting against each other. Total demixing is forbidden by the specific form of the entropic contribution to the diffusive flux. Furthermore it becomes clear from (32) that the relative weight of the energetic forces decreases with increasing temperature.

A miscible system can be defined as a mixture where the entropic forces dominate.

The diffusion coefficient D is allowed to be a function of the concentration. Since we want to consider a reactive process where the concentration goes from $c = 1$ to $c = 0$, it is unpractical to choose $D = $ constant. since we then had to face divisions by Zero in the entropic contribution. To overcome this problem we set from now on

$$D\frac{k}{m} = \overline{D}\frac{c(1-c)}{1 - 2\widehat{a}c(1-c)} \quad \text{with} \quad \overline{D} = const. \tag{34}$$

This choice produces the usual form of Fick's law, $J_k = -\overline{D}\frac{\partial c}{\partial x_k}$, in the absence of capillary forces and density differences. Moreover, with (34), we have only one single coefficient, $\overline{D}$, which relates diffusion flux J_k and concentration gradient $\frac{\partial c}{\partial x_k}$, and it is this coefficient which is measured in experiments—just because an experimentalist will assume Fick's law in this form. To illustrate the influence of the interaction energy $\widehat{a}$ on D figure 3 shows the normalized diffusion coefficient

$$d(c) = \frac{c(1-c)}{1 - 2\widehat{a}c(1-c)}\frac{1 - 0.5\widehat{a}}{0.25}$$

for several values of $\widehat{a}$. It is only for values of $\widehat{a} > 1$ that this function differs considerably from the case without interaction energy $\widehat{a} = 0$. In a miscible system, where diffusion is dominated by the entropic effects, we have $\widehat{a} \le 1$ and the influence of the interaction energy manifests itself in a smaller diffusion coefficient $\overline{D}$ but not in its dependence on concentration.

4.3   The flame

We now introduce scales and dimensionless variables which will enable us to weight the different terms in the equations against each other. We assume the flame process to be the most

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dominating and this gives rise to the following scales:

$$t = \widehat{t}\, t_0, \quad t_0 = \frac{\varrho_1}{K}, \quad x_i = \widehat{x}_i L, \quad L = \sqrt{D/K}, \quad v_k = \widehat{v}_k \frac{L}{t_0}$$

The time scale t_0 is the inverse of the reaction frequency, and the length scale L is in the order of magnitude of the thickness of a flame. The concentration is dimensionless of order 1 and must not be scaled; accordingly the concentration gradient is of order $1/L$.

We shall be interested in cases where the densities of the constituents differ only slightly. Therefore we introduce a small parameter ε_ϱ by

$$\varepsilon_\varrho = \frac{\varrho_1}{\varrho_2} - 1.$$

We adopt the values for our scales and coefficients from [1] where we find

$$\frac{L}{t_0} = 2 \times 10^{-4} \ \tfrac{\mathrm{m}}{\mathrm{s}}, \quad \frac{L^2}{t_0} = \frac{\overline{D}}{\varrho_1} = 1.4 \times 10^{-9} \ \tfrac{\mathrm{m}^2}{\mathrm{s}}, \quad \varepsilon_\varrho = 6 \times 10^{-4}$$

hence

$$L = 7 \times 10^{-6} \mathrm{m}, \quad t_0 = 0.035 \mathrm{s}.$$

Moreover, we find in [1] an approximate value for the surface tension,

$$\sigma = \int b \frac{\partial c}{\partial x}\frac{\partial c}{\partial x} dx \approx \frac{b}{L} = 5 \times 10^{-6} \frac{\mathrm{N}}{\mathrm{m}}. \tag{35}$$

As we have said in Section 2.3, the length scale of the capillary forces is given by $l_{\mathrm{cap}} = \sqrt{b/a}$. This length must be expected to be of the order of some molecular diameters, $l_{\mathrm{cap}} \simeq 5 \times 10^{-10} \mathrm{m}$. Using the density and molecular weight of water we have $\varrho_1 \frac{k}{m} T_0 \simeq 1.4 \times 10^8 \ \tfrac{\mathrm{J}}{\mathrm{m}^3}$ ($T_0 = 300$ K) and therefore

$$\frac{\widehat{b}}{L^2} = \frac{b}{\varrho_1 L^2 k T_0/m} \approx 5 \times 10^{-9}, \quad \widehat{a} = \frac{\widehat{b}}{l_{\mathrm{cap}}^2} \approx 1. \tag{36}$$

With $\widehat{a} \approx 1$, interaction energy and thermal energy are of the same order of magnitude. And indeed, a value $\widehat{a} = \mathcal{O}(1)$ is what we expect for miscible fluids in which the molecular forces play a significant role.

With the above dimensionless parameters, the equations for volume change and concentration read

$$\frac{\partial \widehat{v}_k}{\partial \widehat{x}_k} = -\frac{\varepsilon_\varrho}{1 + \varepsilon_\varrho c}\left(\frac{\partial c}{\partial \widehat{t}} + \widehat{v}_k \frac{\partial c}{\partial \widehat{x}_k}\right),$$

$$\frac{\partial c}{\partial \widehat{t}} + \widehat{v}_k \frac{\partial c}{\partial \widehat{x}_k} = -(1 + \varepsilon_\varrho c)\left(\frac{\partial \widehat{J}_k}{\partial \widehat{x}_k} + c(1 - c)\right)$$

the dimensionless diffusion flux reads

$$\widehat{J}_k = -\frac{\partial c}{\partial \widehat{x}_k} + \frac{\widehat{b}}{L^2}\frac{c(1-c)}{(1 - 2\widehat{a}c(1-c))}\frac{\partial^3 c}{\partial \widehat{x}_i \partial \widehat{x}_i \partial \widehat{x}_k} +$$

$$+ \varepsilon_\varrho \frac{c(1-c)}{(1 - 2\widehat{a}c(1-c))}\left[\frac{\partial \widehat{p}}{\partial \widehat{x}_k} + 2\widehat{a}c\frac{\partial c}{\partial \widehat{x}_k} + \frac{\widehat{b}}{L^2}\left(\frac{\partial c}{\partial \widehat{x}_k}\frac{\partial^2 c}{\partial \widehat{x}_i \partial \widehat{x}_i} + c\frac{\partial^3 c}{\partial \widehat{x}_i \partial \widehat{x}_i \partial \widehat{x}_k} - \frac{\partial^2 c}{\partial \widehat{x}_k \partial \widehat{x}_i}\frac{\partial c}{\partial \widehat{x}_i}\right)\right].$$

Our above approximations show that both, $\frac{\widehat{b}}{L^2}$ and ε_ϱ, are so small that the influence of the corresponding terms in the diffusion flux on the concentration profile can be ignored. Keeping only the leading order terms we obtain drastically simplified equations,

$$\frac{\partial \widehat{v}_k}{\partial \widehat{x}_k} = 0, \quad \frac{\partial c}{\partial \widehat{t}} + \widehat{v}_k \frac{\partial c}{\partial \widehat{x}_k} = \frac{\partial^2 c}{\partial \widehat{x}_k \partial \widehat{x}_k} - c\,(1 - c)\,. \tag{37}$$

With no parameters in (37) referring explicitly to the intermolecular forces, it seems that the latter affect neither flame structure nor speed. This is not true, however, since, as we have pointed out in Section 4.2, the intermolecular forces affect the measurement of the diffusion coefficient and are thus implicit in the scaling.

The density difference is assumed to be so small that the quasi-incompressibility can be ignored, and the mixture appears to be incompressible. Accordingly, if the reactant is at rest initially, and no external forces act on it, the mixture will remain resting while the flame travels through.

If one accounted for the difference in the densities, one finds that the flame will push or drag the unburned reactant with the velocity $\varepsilon_\varrho v_F$ where v_F is the flame speed. This would lead to an $\mathcal{O}(\varepsilon_\varrho)$ correction, and these are ignored in the concentration equation. It follows that the flame is described by Fisher's equation [6, 10, 4]

$$\frac{\partial c}{\partial \widehat{t}} = \frac{\partial^2 c}{\partial \widehat{x}_k \partial \widehat{x}_k} - c(1 - c). \tag{38}$$

It is well known, that this equation, also known as KPP equation [10], allows traveling wave solutions with dimensionless speed $v_F = 2$ which connect the constant states $c = 0, c = 1$.

4.4   The Hele-Shaw cell

Next, we consider the momentum equation for the geometry of the Hele-Shaw cell. In a Hele-Shaw cell the flow is confined between two parallel plates. The distance l between the plates is rather small, and one can assume that the flow is purely two-dimensional. With the coordinates chosen such that the plane of the Hele-Shaw cell is spanned by $x_\alpha = \{x_1, x_2\} = \{x, y\}$ we have for the velocity

$$v_i = \{v_\alpha(x_\alpha, z), 0\}$$

and the momentum equation reads

$$\varrho \dot{v}_\alpha + \frac{\partial p}{\partial x_\alpha} - \frac{\partial S_{\alpha i}}{\partial x_i} - \eta \frac{\partial^2 v_\alpha}{\partial x_\beta \partial x_\beta} - \eta \frac{\partial^2 v_\alpha}{\partial z \partial z} = \varrho g_\alpha.$$

Under the assumption that the typical length scale λ in the plane is much larger than the distance of the plates l, we have

$$\eta \frac{\partial^2 v_\alpha}{\partial x_\beta \partial x_\beta} + \eta \frac{\partial^2 v_\alpha}{\partial z \partial z} = \frac{\eta}{\lambda^2} \frac{\partial^2 v_\alpha}{\partial \overline{x}_\beta \partial \overline{x}_\beta} + \frac{\eta}{l^2} \frac{\partial^2 v_\alpha}{\partial \overline{z} \partial \overline{z}} \simeq \frac{\eta}{l^2} \frac{\partial^2 v_\alpha}{\partial \overline{z} \partial \overline{z}} = \eta \frac{\partial^2 v_\alpha}{\partial z \partial z}$$

where $\overline{x}_\alpha$ and $\overline{z}$ are suitable dimensionless coordinates. Thus, the friction with the walls is dominating while the friction inside the fluid plays no role. It is well known that a flow between
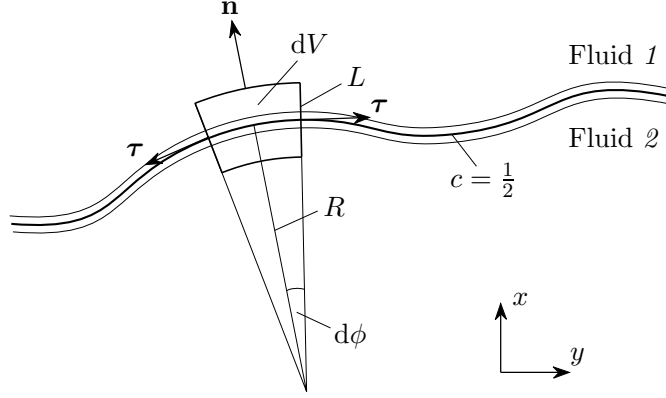
Figure 4: Volume element $\mathrm{d}V$ for determining the jump condition.

parallel plates will develop a parabolic profile (Poisseuille flow) which can be written with the mean velocity $\bar{v}_\alpha = \frac{1}{l}\int_0^l v_\alpha dz$ as

$$v_\alpha = -6\bar{v}_\alpha\left[\left(\frac{z}{l}\right)^2 - \frac{z}{l}\right].$$

Introducing this expression into the momentum equation and averaging along the plate separation l yields [16, 8]

$$\varrho\left(\frac{\partial\bar{v}_\alpha}{\partial t} + \frac{6}{5}\bar{v}_\beta\frac{\partial\bar{v}_\alpha}{\partial x_\beta}\right) + \frac{\partial\bar{p}}{\partial x_\alpha} - \frac{\partial\overline{S}_{\alpha\beta}}{\partial x_\beta} + 12\frac{\eta}{l^2}\bar{v}_\alpha = \varrho g_\alpha \; ; \tag{39}$$

in which the bars indicate mean values. Here, we have assumed that the concentration is independent of the coordinate z, so that $\frac{\partial}{\partial z}S_{\alpha z} = 0$.

As we have said before, the flame travels through the fluid without inducing any significant flow velocity. Moreover, the fluid is not pushed by a pressure gradient and the only external force on the fluid is related to buoyancy. Since the density difference is very small, we can expect only small velocities and henceforth ignore the non-linear term in (39).

Surface tension will only play a role in the reaction zone of thickness L. Thus we can consider two regions of single fluids, connected by jump conditions which we shall determine now. To this end we consider a small volume element around the reaction zone of size $\mathrm{d}V = 2lLR\,\mathrm{d}\phi$ where $2R\,\mathrm{d}\phi$ is the arc length of the curve $c = 0.5$ with the radius of curvature R, and L is the thickness of the reaction wave. L must be chosen so that the concentration gradient at $R \pm L/2$ is negligible. In fact L should strictly be reinterpreted as an intermediate asymptotic parameter that is large compared to the thickness of the reaction wave but small compared with the radius of curvature R and the plate separation l. Although the results below can be written more formally in these terms, we shall simply take concentration gradients to be zero at $R \pm L/2$ and continue to think of L as measuring the thickness of the reaction wave, albeit as a slight overestimate, with $L \ll R$. The value of L does not appear in the final result.

Figure 4 shows the projection into the $\{x, y\}$ plane; $\mathbf{n}$ denotes the normal to the curves of constant concentration which is also the direction of propagation, and τ denotes the tangent vectors. In a frame where $n_\alpha = \{0, 1\}$ one finds $\tau_\alpha = \{\pm\cos\mathrm{d}\phi, \sin\mathrm{d}\phi\} \simeq \{\pm 1, -\mathrm{d}\phi\}$. We write for the surface tension

$$S_{\alpha\beta} = b\left(\frac{\partial c}{\partial x_\gamma}\frac{\partial c}{\partial x_\gamma}\delta_{\alpha\beta} - \frac{\partial c}{\partial x_\alpha}\frac{\partial c}{\partial x_\beta}\right) = b\left(\frac{\partial c}{\partial n}\right)^2(\delta_{\alpha\beta} - n_\alpha n_\beta) = \Sigma(\delta_{\alpha\beta} - n_\alpha n_\beta)$$

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The jump condition follows by integration of the momentum balance over the volume element and subsequent scalar product with n_α. Under the assumption that all quantities do not change considerably along the arc length we find after division by $2lR\,\mathrm{d}\phi$

$$p_2 - p_1 - \frac{\sigma}{R} = n_\alpha \int_2^1 \left[\varrho \frac{\partial \bar{v}_\alpha}{\partial t} + 12\frac{\eta}{l^2}\bar{v}_\alpha - \varrho g_\alpha \right] dL + \left(\frac{p_1 + p_2}{2} - \frac{1}{L}\int_2^1 \bar{p}dL \right) \frac{L}{R} \qquad (40)$$

where σ denotes the total surface tension (35),

$$\sigma = \int_2^1 \Sigma dL.$$

The Hele-Shaw approximation is only valid for curvatures $l/R \ll 1$ and the flame thickness L is much smaller than the distance l, so that $L/R \ll 1$ and the last term on the right hand side of (40) can be ignored.

In immiscible fluids the thickness of the interface is so small (a few molecular diameters) that also the first term on the right is negligible. In our case of a reaction zone, however, this term may become important and must be considered. It is worth comparing the gravitational contribution $\varrho g L$ with the surface tension term $\frac{\sigma}{R}$. Indeed, the gravitational force can only strictly be neglected for radii of curvature $R \ll \frac{\sigma}{\varrho g L} = 7.3 \times 10^{-5}$m. This is still much larger than the the thickness of the reaction wave.

For further simplification we assume the same viscosity for the two fluids [1] and no variation of velocity inside the reaction zone. Being interested in a stationary flame process, we can ignore the time derivative and find finally the jump condition across the reaction zone of thickness L as

$$p_2 - p_1 - \frac{\sigma}{R} = 12\frac{\eta L}{l^2}n_\alpha \bar{v}_\alpha - n_\alpha \int_2^1 \varrho g_\alpha dL.$$

4.5 Saffmann-Taylor stability analysis

With the potential of gravity $U = -g_\alpha x_\alpha = gx_1$ the momentum equation for the single fluid in the stationary case can be written as

$$\frac{\partial \bar{p}}{\partial x_\alpha} + 12\frac{\eta}{l^2}\bar{v}_\alpha = -\varrho \frac{\partial U}{\partial x_\alpha} \quad \text{with} \quad \frac{\partial \bar{v}_\alpha}{\partial x_\alpha} = 0.$$

Following the classical work of Saffmann & Taylor [16], we introduce the velocity potential ϕ by

$$\bar{v}_\alpha = \frac{\partial \phi}{\partial x_\alpha} \quad \text{with} \quad \frac{\partial^2 \phi}{\partial x_\alpha \partial x_\alpha} = 0. \qquad (41)$$

Since $\varrho, \eta = $ constant in the single fluid the momentum equation is easily integrated,

$$\bar{p} = -\varrho U - 12\frac{\eta}{l^2}\phi.$$

We are interested in small disturbances of a plane flame travelling through a fluid at rest in direction $n_\alpha = \pm\{1, 0\}$, with the disturbance of the interface given by

$$\xi = a \exp\left[iky + \omega t\right],$$

ξ refers again to the line $c = 0.5$. Therefore, the location of the boundaries of the reaction zone is given by $x_{1,2} = \xi \pm \frac{L}{2}$ and the interface condition reads

$$12\frac{\eta}{l^2}\left[\phi_1 - \phi_2\right] + (\varrho_1 - \varrho_2)g\xi + \sigma\frac{d^2\xi}{dy^2} - 12\frac{\eta L}{l^2}\frac{d\xi}{dt} = -\frac{\varrho_1 + \varrho_2}{2}gL + \int_2^1 \varrho g\, dL. \qquad (42)$$

Note, that curvature is given by $\frac{1}{R} = -\xi''/(1 + \xi'^2)^{3/2} \simeq -\xi''$, where the choice of sign follows from figure 4, and that the velocity of the fluid at the disturbed interface is given by $\frac{d\xi}{dt}$. The integral on the r.h.s. gives the weight per unit area of the reaction zone and does not change when the reaction zone is displaced.

For the potentials one finds

$$\phi_1 = \phi_1^0 - \frac{a\omega}{k}\exp\left[iky - kx + \omega t\right], \quad \phi_2 = \phi_2^0 + \frac{a\omega}{k}\exp\left[iky + kx + \omega t\right]$$

as the solutions of $(41)_2$ which give the velocity $\frac{d\phi}{dx} = \dot{\xi} = \omega a\exp\left[iky + \omega t\right]$ at $x = 0$ and for which the disturbances vanish at infinity [16]. The constants of integration ϕ_α^0 are set equal to zero in the work of Saffmann & Taylor without discussion, but are important here in order to ensure the validity of the jump condition for the *undisturbed* interface ($\xi = 0$). One finds

$$12\frac{\eta}{l^2}\left[\phi_1^0 - \phi_2^0\right] = -\frac{\varrho_1 + \varrho_2}{2}gL + \int_2^1 \varrho g\, dL,$$

so that the weight of the reaction zone is absorbed in the constants ϕ_α^0. The jump condition (42) gives for the disturbance

$$12\frac{\eta}{l^2}\frac{\omega}{k}(-2 - Lk) - \sigma k^2 + g(\varrho_1 - \varrho_2) = 0.$$

Being interested in waves with wavelengths $\lambda = 2\pi/k$ large compared to the distance l, we can ignore the friction term Lk and arrive at the final result for the dispersion relation

$$\omega = (\varrho_1 - \varrho_2)\frac{gl^2}{24\eta}k - \frac{\sigma l^2}{24\eta}k^3. \qquad (43)$$

This, indeed, is the celebrated Saffmann-Taylor result, which therefore holds also in case of a finite but thin interface between two fluids. Instabilities will develop when ω is positive, i.e. if $\varrho_1 > \varrho_2$, corresponding to lower density of the product, as is the case in the experiments of Abid et al. [1]. The experiments showed a wavelength of approximately $1cm$ and assuming that the instability is governed by the fastest mode,

$$\omega^* = \frac{\sigma l^2}{12\eta}k^{*3}, \quad k^* = \sqrt{(\varrho_1 - \varrho_2)\frac{g}{3\sigma}}, \qquad (44)$$

it was possible to measure the surface tension (35). By changing the angle α of the Hele-Shaw cell against the vertical, so that the effective gravitational acceleration is $g\cos\alpha$, Abid et al. found experimentally that the wavelength $\lambda = 2\pi/k$ is proportional to $1/\sqrt{g\cos\alpha}$. And it is this proportionality which allows the conclusion that the instability is governed by surface tension. If for instance a curvature dependent flame speed were to be of controlling importance [18], one would have expected a proportionality to $1/(g\cos\alpha)$.

5 Conclusion

In this paper we have developed a consistent thermodynamic model for a reactive binary mixture of incompressible fluids with distributed surface tension effects. The model allows for the description of a wide range of processes, and this article has only provided a glimpse of this variety. In particular, we have used our model for the description of experiments in Hele-Shaw cells [1] with buoyancy driven instabilities. Our theoretical findings reinforce the interpretation by Abid et al of these experimental results and provide them with a sound theoretical framework.

The measured values of the parameters a and b, which together account for the intermolecular forces, match expectations very well. In fact, a noticeable aspect of the intermolecular forces requires that thermal energy $c_{\mathrm{V}}T$ and the intermolecular potential energy U_{mix} (4) should be of comparable importance. That is, the dimensionless parameter $\widehat{a} = a/\varrho kT/m$ is of the order $\mathcal{O}(1)$. We have shown that the value $\widehat{a} \approx 1$ arises naturally from the measurement of b and the presumed range of the interaction forces, see equation (36).

As long as $\widehat{a} < 2$, the two fluids are miscible for all concentrations (i.e. without a gap of miscibility, see section 2.5), and Fick's law of diffusion prevails in most cases. The influence of the intermolecular forces on the diffusion is hidden in the measurement of the diffusion coefficient, and could only be more fully qualified by detailed measurements of concentration profiles. However, if the density difference is larger, chemical equilibrium and diffusion will be strongly influenced by changes in the pressure and its gradient.

Investigations of other problems based on the model provided in this article are planned for the future.

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