Thermodynamic Theory for Binary Fluid Mixtures in the Gravitational Field

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Dedicated to Karl Heinzinger on the occasion of his 60th birthday

The thermodynamic theory for a fluid mixture in a gravitational field under a given pressure is developed. The local density and the local molfraction are varied to minimize the Gibbs free energy of the system. With the approximation of local thermodynamics, a set of coupled linear differential equations of first order is obtained. The non-local van der Waals-Landau contributions, leading to a set of linear differential equations of second order, are discussed for the two component lattice gas. Experimental methods allowing to determine concentration and density gradients are discussed also.

1. Introduction

The gravitational field acting on a pure fluid or a fluid mixture causes an inhomogeneous distribution of the density [1] and of the composition [2]. In this respect, fluids in a gravitational field behave similar to fluids at interfaces [3], fluids interacting with a wall [4] or ionic fluids interacting with electrodes [5]. The inhomogeneity of the density causes a substantial complication of the statistical-mechanical problem [6], which is not present in the theory of non-ionic fluids interacting with uniform electric or magnetic fields [7].

In general, the molecular theory of fluids in external fields may be approached by simulation [8, 9] or analytical methods involving iterative solutions of approximations to the Ornstein-Zernicke equation [10–12] or the Born-Green-Yvon equation [13]. An exact solution for a fluid in a gravitational field is only known for a one-dimensional system of rods interacting by a short-range potential [14].

Beside the molecular statistical approach, the free energy variation method has been proved to be very useful. This method was first applied by van der Waals [15] in his theory of surface tension, which was rederived by Cahn and Hilliard [16] and has been applied in many applications since [17, 18]. An analysis of the density gradient of pure fluids in the gravitational field was given by Sengers and Leeuwen [19]. Earlier work was based on the local equilibrium approximation and did not take into account the contribution of the density gradient to the local free energy [1]. We mention that for a pure fluid in a one-dimensional system interacting with a gravitational field, the local equilibrium approximation turns out to be exact [14].

For fluid mixtures in a gravitational field, a general investigation of the local thermodynamics has not yet been given. In none of the former work the van der Waals-Landau contribution of the inhomogeneity to the local free energy was taken into account. The published work was based on conditions for the local thermodynamic equilibrium [20–23] and did not start from first principles. The variation of density and composition with the height of the sample under a given pressure was not treated in a general manner.

In thermodynamics and statistical mechanics of fluids and fluid mixtures [24, 25] gravitation is commonly not taken into account. This is an accurate approximation in most cases. However, in the vicinity of critical points [1, 2] and in two-phase equilibria, gravitation becomes important. For pure liquids it is known for a long time [26] that in the vicinity of the critical point gravitation causes huge density gradients. Critical opalescence is therefore restricted to a small region in the sample where the density has the critical value.

For liquid mixtures the influence of gravity has not been demonstrated as clearly as for pure fluids near the critical point. For the system nitroethane 3-methylpentane, gravity induced density gradients have been observed above the upper critical solution point [27], while the similar system nitroethane-isooctane did not develope a gravity induced distribution of concentration but a long living non equilibrium concentration gradient [28]. In the system anilin-

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cyclohexane some authors observed developing concentration gradients [29–31] while other did not [32]. In the mixture CH_4/CF_4, concentration gradients have been observed only near the liquid-vapour interface but not in the middle of the li.quid phase [33] as one would expect. A detailed review of the experimental findings was given in [2].

In our investigation we will focus on the molecular and thermodynamic properties which determine the size of the inhomogeneous distribution of density and composition.

2. Theory

A binary fluid mixture under a presure p_0 in a vertical column is considered. The functional of the Gibbs free energy is

$$G = A \int \varrho \left[f(\varrho, \varrho_1) + p \frac{1}{\varrho} + \frac{1}{2} a_{\varrho\varrho} (\nabla \varrho)^2 + a_{\varrho\varrho_1} \nabla \varrho \, \nabla \varrho_1 + \frac{1}{2} a_{\varrho_1\varrho_1} (\nabla \varrho_1)^2 \right] \mathrm{d}z \,. \qquad (1)$$

A is the area of the column.

ϱ is the number density of the mixture and ϱ_1 is the number density of the component labelled one. f is the free energy of a particle in a uniform system with the density ϱ and the concentration ϱ_1. $a_{\varrho\varrho}$, $a_{\varrho\varrho_1}$ and $a_{\varrho_1\varrho_1}$ are coefficients determining the contribution of the inhomogeneity to the local free energy. In general the coefficients a are given by integrals involving the direct correlation-function [34] and therefore depend on density and composition. The molecular expressions in the Bragg-Williams two component lattice gas model are derived in the last section of the paper. p, ϱ, and ϱ_1 are functions of the vertical position z. The Gibbs free energy of the system is given by the minimum of the functional equation (1) satisfying the conditions of conserving the number of particles

$$N = A \int \varrho(z) \, \mathrm{d}z \quad \text{and} \quad N_1 = A \int \varrho_1(z) \, \mathrm{d}z \,, \qquad (2)$$

where $N_1 + N_2 = N$.

It is convenient to replace the density ϱ by the average volume v of a molecule and the concentration ϱ_1 by the mole fraction x of species 1:

$$v = \frac{1}{\varrho} \quad \text{and} \quad \varrho_1 = x \cdot \varrho \,. \qquad (3)$$

The pressure $p(z)$ is given by the external pressure p_0 and the hydrostatic pressure

$$p(z) = p_0 + \int_z^\infty [m_1 x + (1-x) m_2] \, \varrho \, g \, \mathrm{d}z \,. \qquad (4)$$

g is the acceleration in a gravitational or centrifugal field provided the column is short enough for the approximation $g = \text{const}$. The pv contribution to G at a height z includes the potential energy of the particles in the gravitational field.

2.1. The Thermodynamic Approximation

In the thermodynamic approximation, the van der Waals-terms depending on the gradient of the density and of the composition are ignored. Taking into account the conditions (2), the variation of (1) with respect to $v(z)$ gives

$$\frac{\partial G}{\partial v(z)} = -\varrho^2 \left[f(v, x) + \mu + x \mu_1 - v \frac{\partial f}{\partial v} + [m_1 x + m_2 (1-x)] \, g z \right] A \, \mathrm{d}z = 0 \,. \qquad (5)$$

The Lagrange parameters μ and μ_1 ensure that the total number of particles as well as the numbers of the particular molecules are conserved. The term which represents the potential energy in the gravitational field is obtained by taking the derivative of (4) and summing all terms with $z' \leqq z$ as the hydrostatic pressure for all $z' \leqq z$ depends on $\varrho(z)$.

In the same manner the variation with respect to the composition is carried out.

$$\frac{\partial G}{\partial x(z)} = \varrho \left[\frac{\partial f}{\partial x} + \mu_1 + (m_1 - m_2) \, g z \right] A \, \mathrm{d}z = 0 \,. \qquad (6)$$

With (6) μ_1 is eliminated from (5):

$$f(v, x) - v \frac{\partial f}{\partial v} - x \frac{\partial f}{\partial z} + m_2 g z + \mu = 0 \,. \qquad (7)$$

The Lagrange parameters μ and μ_1 are independent of z so that

$$\frac{\partial \mu}{\partial z} = \frac{\partial \mu_1}{\partial z} = 0 \,. \qquad (8)$$

This leads to a system of differential equations determining $v(z)$ and $x(z)$. Using the obvious short hand notations for the partial derivatives we get from (6) and (7)

$$f_{xv}\frac{\partial v}{\partial z}+f_{xx}\frac{\partial x}{\partial z}=-(m_1-m_2)\,g\,, \tag{9}$$

$$[x\,f_{xv}+v\,f_{vv}]\frac{\partial v}{\partial z}+[x\,f_{xx}+v\,f_{vx}]\frac{\partial x}{\partial z}=m_2\,g\,. \tag{10}$$

Equation (10) can be simplified by subtracting (9) multiplied by x:

$$f_{vv}\frac{\partial v}{\partial z}+f_{xv}\frac{\partial x}{\partial z}=(m_1\,x+m_2(1-x))\,\varrho\,g\,. \tag{11}$$

Equations (9) and (10) represent the final set of linear differential equations which has to be solved. Using Cramer's rule we get

$$\frac{\partial v}{\partial z}=\frac{D_1}{D}\quad\text{and}\quad\frac{\partial x}{\partial z}=\frac{D_2}{D}\,, \tag{12}$$

where

$$\begin{aligned}D\;&=f_{vv}\cdot f_{xx}-f_{vx}\cdot f_{xv}\,,\\ D_1&=f_{xx}\,\bar{m}\,\varrho\,g+f_{vx}\,\Delta m\,g\,,\\ D_2&=-f_{vv}\,\Delta m\,g-f_{vx}\,\bar{m}\,\varrho\,g\,,\\ \Delta m&=m_1-m_2\quad\text{and}\quad\bar{m}=x\,m_1+(1-x)\,m_2\,.\end{aligned} \tag{13}$$

To our knowledge this general solution has not been given before.

The second derivatives of f are expressed by the coefficients of the thermal equation of state

$$f_{xx}=\frac{1}{\chi},\quad f_{vv}=\frac{1}{v\varkappa}, \tag{14}$$

$$f_{xv}=-\left(\frac{\partial p}{\partial x}\right)_v=\frac{\left(\frac{\partial v}{\partial x}\right)_p}{\left(\frac{\partial v}{\partial p}\right)_x}=-\frac{\Delta v}{v\varkappa}\,, \tag{15}$$

where $\Delta v=v_1-v_2$.

χ is the osmotic susceptibility and $\varkappa$ the compressibility. Δv is the difference between v_1 and v_2, which agrees with the corresponding difference of the averaged volumes per molecule Δv^0 of the pure compounds if the excess volume v^e can be neglected:

$$\Delta v=\Delta v^0+\frac{\partial v^e}{\partial x}\,. \tag{16}$$

Equations (12) now read explicitly

$$\frac{\partial v}{\partial z}=\frac{\bar{m}\,\varrho^2\varkappa-\Delta v\,\Delta m\,\chi}{1-\Delta v^2\,\frac{\chi}{\varkappa}\,\varrho}\,g\,, \tag{17}$$

$$\frac{\partial x}{\partial z}=\frac{\Delta v\,\bar{m}\,\varrho-\Delta m}{1-\Delta v^2\,\frac{\chi}{\varkappa}\,\varrho}\,\chi\,g\,. \tag{18}$$

Thermodynamic stability [35] requires that the denominator in (18) and (17) is positive. This is always satisfied if the pure components have the same molecular density and if the excess volume gives no contribution to Δv. In this case (17) and (18) simplify to the well known expressions

$$\frac{\partial v}{\partial z}=\bar{m}\,\varrho^2\varkappa\,g,\quad\text{and}\quad\frac{\partial x}{\partial z}=-\Delta m\,\chi\,g\,. \tag{19}$$

The local composition is determined by the difference of the molecular masses and the osmotic pressure coefficient.

If the masses of the molecules are equal, the local composition is determined by

$$\frac{\partial v}{\partial z}=\frac{\bar{m}\,\varrho^2\varkappa}{1-\Delta v^2\,\frac{\chi}{\varkappa}\,\varrho}\,g\quad\text{and}\quad\frac{\partial x}{\partial z}=\frac{\Delta v^2\,\bar{m}\,\varrho}{1-\Delta v^2\,\frac{\chi}{\varkappa}\,\varrho}\,\chi\,g\,. \tag{20}$$

The gradient of the mole fraction is now determined by Δv, which is essentially the difference of the molecular volumes of the pure compounds. The divergence of the gradients, determined by a divergence of $\varkappa$ and/or χ, is modified by the denominator. In fact, the denominator may vanish before $\varkappa$ or χ diverges.

Another special case is expected for mixtures where the mass density of the two components is matched,

$$m_1\,\varrho_1=m_2\,\varrho_2\,. \tag{21}$$

This type of mixtures is used in order to simulate no-gravity conditions in the laboratory [36].

The nominator in (18) vanishes if the condtion (21) is satisfied and if the contribution of the excess volume to Δv can be neglected. The composition does not vary with the height. This does not mean that gravity is of no influence on the system. Gravity may induce density gradients even if the compressibility is not diverging:

$$\frac{\partial v}{\partial z}=\frac{\varrho\,\varkappa-\Delta v^2\,\chi}{1-\Delta v^2\,\frac{\chi}{\varkappa}\,\varrho}\,\bar{m}\,\varrho\,g\,. \tag{22}$$

From (17) and (18) we learn that the biggest influence of gravity on the equilibrium distribution of the composition in a sample is expected if the pure phase of the heavier molecule is more dense than the pure phase of the leighter molecule. If this is not the case, cancellation effects are expected. The analysis is particularly simple for systems where $\Delta v = 0$. All other cases including $\Delta m = 0$ involve the determinant of the stability matrix.

We note that our analysis is very general. It is independent of any particular model for the local free energy, which may be given either by a mean field model or by a non-classical equation of state.

At this stage it is appropriate to discuss the experimental methods probing the gradient of the composition and of the density. Optical methods probe the bending of the beam by the gradient of the refractive index.

Assuming the validity of the Lorentz-Lorenz relation

$$\frac{n^2-1}{n^2+2} = \frac{4\pi}{3}\varrho\,[x\,\alpha_1 + (1-x)\,\alpha_2] = A\,, \tag{23}$$

the refractive index n is

$$n = \left(1 + \frac{3A}{1-A}\right)^{1/2}, \tag{24}$$

so that

$$\frac{\partial n}{\partial z} = \frac{4\pi}{9}\,\frac{(n^2+2)^2}{2n}\left[\bar{\alpha}\,\frac{\partial \varrho}{\partial z} + \varrho\,\Delta\alpha\,\frac{\partial x}{\partial z}\right]. \tag{25}$$

In an optical experiment we may be able to distinguish between the gradients of density and composition if the experiment is carried out at different frequencies provided the polarizabilities α_1 and α_2 of the two components differ in their frequency dependence.

Another possibility is to probe the local composition by dynamic light scattering. In light scattering the fluctuations of the dielectric permittivity are investigated, which with the Lorentz-Lorenz relation are given by

$$\langle \delta\varepsilon^2 \rangle = \frac{(n^2+2)^4}{9}\left(\frac{4\pi}{3}\right)^2 [\bar{\alpha}^2 \langle \delta\varrho^2 \rangle + \Delta\alpha^2 \varrho^2 \langle \delta x^2 \rangle + 2\,\Delta\alpha\,\varrho\,\bar{\alpha}\,\langle \delta \times \delta\varrho \rangle]\,. \tag{26}$$

The fluctutions are determined by a Gaussian distribution involving the second derivatives of the free energy. From the theory of Gaussian distributions [37] it is known that

$$\langle \delta v^2 \rangle = \frac{f_{xx}}{D} = \frac{v\varkappa}{1 - \Delta v^2 \left(\frac{\chi}{\varkappa}\right)\varrho}\,,$$

$$\langle \delta x^2 \rangle = \frac{f_{vv}}{D} = \frac{\chi}{1 - \Delta v^2 \left(\frac{\chi}{\varkappa}\right)\varrho}\,,$$

$$\langle \delta v\, \delta x \rangle = \frac{f_{xv}}{D} = \frac{\Delta v\,\chi}{1 - \Delta v^2 \left(\frac{\chi}{\varkappa}\right)\varrho}\,, \tag{27}$$

using

$$\delta\varrho = -\varrho^2\,\delta v\,. \tag{28}$$

Equation (26) gives

$$\langle \delta\varepsilon^2 \rangle = \frac{(n^2+2)^2(n^2-1)^2}{9}\;\frac{1}{1 - \Delta v^2 \left(\frac{\chi}{\varkappa}\right)\varrho} \cdot \left[\varrho\varkappa + \left(\left(\frac{\Delta\alpha}{\varkappa}\right)^2 + 2\left(\frac{\Delta\alpha\,\Delta v}{\bar{\alpha}\,v}\right)\right)\chi\right]. \tag{29}$$

Comparing (29), (17) and (18) it is obvious that the light scattering intensity and the gradients of density and composition induced by the gravity field are determined by the same thermodynamic coefficients. If $\Delta v = 0$, the spectrum of the scattered light involves the determinant of the stability matrix. In the analysis of the light scattering spectra of liquid mixtures this is conventionally [38, 39] not taken into account.

2.2. Nonlocal Free Energy Contributions

The general functional for the Gibbs free energy in an inhomogeneous system was given in (1). In order to gain insight into the physical meaning of the coefficients, we discuss a two-component lattice gas in the Bragg-Williams approximation. This is equivalent to a three component mixture where all interaction parameters of one of the components are assumed to be zero. A simple cubic lattice is considered. The distribution is assumed to be inhomogeneous in the direction of one of the main axes.

The local concentration $\varrho(i)$ of the particles A in a slice i is

$$\varrho_A(i) = \frac{N_A(i)}{N_F} = x(i)\,\varrho(i)\,. \tag{30}$$

N_F is the number of lattice points in a slice. The coordination number in a simple cubic lattice of dimension d is $2d$. The total energy of the system is then

$$E = N_F \sum_i \varrho(i)^2 \frac{2d-2}{2} [\varepsilon_{AA}\, x(i) + \varepsilon_{BB}(1-x(i)) + 2\Delta\varepsilon\, x(i)\cdot(1-x(i))] + \varepsilon_{AA}\, \varrho_A(i)\, \varrho_A(i+1) + \varepsilon_{BB}\, \varrho_B(i)\, \varrho_B(i+1) + \varepsilon_{AB}\, \varrho_A(i)\, \varrho_B(i+1) + \varepsilon_{AB}\, \varrho_B(i)\, \varrho_A(i+1), \tag{31}$$

where $\Delta\varepsilon = \varepsilon_{AB} - \frac{1}{2}(\varepsilon_{AA} + \varepsilon_{BB})$.

Equation (31) can be rearranged into the bulk energy and a term correcting for the inhomogeneity:

$$E = N_F \sum \varrho_i^2\, d(\varepsilon_{AA}\, x_i + \varepsilon_{BB}(1-x_i) + 2x_i(1+x_i)\, \Delta\varepsilon) - \tfrac{1}{2}\varepsilon_{AA}\, \Delta_i \varrho_A^2 - \tfrac{1}{2}\varepsilon_{BB}\, \Delta_i \varrho_B^2 - \varepsilon_{AB}\, \Delta_i \varrho_A\, \Delta_i \varrho_B, \tag{32}$$

where

$$\Delta_i \varrho_A = \varrho_A(i+1) - \varrho_A(i).$$

Expressing the concentrations by the mole fraction and volume/molecule and neglecting terms of higher order in $\Delta_i v$, we get

$$\Delta_i \varrho_A = \varrho_i \Delta_i x - \varrho_i^2\, x\, \Delta_i v \tag{33}$$

where

$$\Delta_i x = x(i+1) - x(i).$$

This enables us to rewrite (3) as

$$E = N_F \sum \varrho_i^2\, d\langle\varepsilon\rangle_i + \varrho_i^2\, \Delta\varepsilon\, \Delta_i x^2 - \tfrac{1}{2}\varrho_i^4 \langle\varepsilon\rangle_i\, \Delta_i v^2 - \varrho_i^3(2x_i\, \Delta\varepsilon - \varepsilon_{AB} - \varepsilon_{BB})\, \Delta_i x\, \Delta_i v. \tag{34}$$

In order to get the continuous form given in (1) we identify

$$\Delta_i x = \sigma \frac{\partial x}{\partial z}, \tag{35}$$

where σ is the molecular diameter. For the further proceedings it is more convenient to stick to the discontinuous form. Equation (1) reads now

$$G = N_F \sigma^3 \sum \varrho_i \left[f(v_i, x_i) + p_i v_i + \tfrac{1}{2} a_{xx} \left(\frac{\Delta_i x}{\sigma}\right)^2 + a_{xv} \frac{\Delta_i x}{\sigma} \frac{\Delta_i v}{\sigma} + a_{vv} \left(\frac{\Delta_i v}{\sigma}\right)^2 \right], \tag{36}$$

where

$$\tfrac{1}{2} a_{xx} = \frac{1}{\sigma} \varrho_i\, \Delta\varepsilon, \quad a_{xv} = -\frac{1}{\sigma} \varrho_i^2 (2x_i\, \Delta\varepsilon + \varepsilon_{AB} - \varepsilon_{BB}),$$

$$\tfrac{1}{2} a_{vv} = -\frac{1}{\sigma} \varrho_i^3 \langle\varepsilon\rangle.$$

Obviously. the coefficients a_{ii} depend on density and composition. In the following variation of G we neglect all terms of the order $O(\Delta_i^2)$, so that the variation of the coefficients $a_{\mu\nu}$ with the thermodynamic variables is not taken into account.

Noting that

$$\frac{\partial}{\partial x_i} (x_{i+1} - x_i)^2 + (x_i - x_{i-1})^2 = 2(2x_i - x_{i+1} + x_{i-1}) \approx -2 \frac{\partial^2 x}{\partial z^2} \sigma^2, \tag{37}$$

the square bracket in (5) gets the additional terms

$$a_{vv} v \frac{\partial^2 v}{\partial z^2} + a_{vx}\, v \frac{\partial^2 x}{\partial z^2} \tag{38}$$

while the square bracket in (6) is supplemented by

$$-a_{xx} \frac{\partial^2 x}{\partial z^2} - a_{vx} \frac{\partial^2 v}{\partial z^2}. \tag{39}$$

The final set of differential equations is

$$f_{vv} \frac{\partial v}{\partial z} + f_{vx} \frac{\partial x}{\partial z} = \bar{m} \varrho g + a_{vv} v \frac{\partial^3 v}{\partial z^3} + a_{xv} v \frac{\partial^3 x}{\partial z^3},$$

$$f_{xv} \frac{\partial v}{\partial z} + f_{xx} \frac{\partial x}{\partial z} = -\Delta m g + a_{xv} \frac{\partial^3 v}{\partial z^2} + a_{xx} \frac{\partial^3 x}{\partial z^3}. \tag{40}$$

This set of linear third order differential equations is obtained by ignoring all terms leading to non-linear differential equations. Whether this is a realistic approximation or not must be checked by comparing the solutions of (40) to simulations. According to (36) the sign of a_{xx} and a_{vv} is positive while the sign of a_{xv} can be positive or negative. It is therefore difficult to assess the influence of the inhomogeneity contributions without solving the equations. Numerical solutions for particular cases will be given elsewhere. We merely mention that the inhomogeneity corrections are essential in calculations of the variations of density and composition in interfaces. Gravity, which reduces the thickness of the interface may be taken into account by a perturbation method. On the other hand, in one-phase systems gravitation is causing the macroscopic inhomogeneity and the inhomogeneity corrections are expected to be small. Our results (20) and (40) will be of particular importance for mixtures in the supercritical state where the compressibility $\varkappa$ as well as the susceptibility χ may diverge.

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