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Thermodynamics of mixtures and phase field theory

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Abstract

The phase field model is considered as a special case of thermodynamics of a binary mixture. The customary $|\nabla c|^2$-term in the free energy is thus recognized as a term that represents the kinetic energy of the diffusive motion of the two phases. This interpretation deviates from the usual one by which the $|\nabla c|^2$-term represents a "smeared-out" interfacial energy. © 2001 Elsevier Science Ltd. All rights reserved.

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1. Introduction

The consideration of phase transitions has a long tradition in mathematics. In the classical Stefan problem (Hoffmann and Sprekels, 1990), the interfaces between the phases were considered to be sharp, so that each point is occupied by *one* phase only. This is undoubtedly the correct view, if we look very closely into wet vapour, – or fog –, a suspension of liquid droplets in vapour. However, more recently there is also a coarse view of the fog [1] in which we perceive a homogeneous mixture of the two phases with a concentration c of vapour (say). The latter view is the one of the *phase field theory* (Caginalp, 1990; Colli, 1997); and c – the ratio of the mass of vapour in a volume element to the total mass – may then be considered as the phase field. This is the interpretation of the phase field embraced in this paper. [2]

As a rule, the mathematical literature makes no explicit use of the mixture character of the fog. Rather it derives the field equation for the phase field by variation from a free energy density of the form

$$f\left(c, \frac{\partial c}{\partial x_i}\right) = f_0(c) + \frac{v}{2}\frac{\partial c}{\partial x_i}\frac{\partial c}{\partial x_i}. \tag{1.1}$$

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[1] Mathematicians often speak of a "mushy region" which is the solid–liquid analogue to the liquid–vapour fog.

[2] It is difficult to pin the mathematicians down as to the physical nature of the phase field. Most prefer not to commit themselves and they speak vaguely of an order parameter "in some sense".

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The gradient term represents a smeared-out interfacial energy of the phase boundaries – again "in some sense" – while $f_0(c)$ is a more conventional free energy with minima at $c = 0$ and $c = 1$, the limiting values of c. Thus, a typical phase field equation reads

$$\tau\dot{c} - \frac{\partial}{\partial x_i}\left(v\frac{\partial c}{\partial x_i}\right) = \frac{\partial f_0}{\partial c}. \tag{1.2}$$

A thermodynamicist who looks at Eq. (1.2) would have an immediate conditioned reflex which would say: *diffusion equation*. He would interpret

$$J_i = -v\frac{\partial c}{\partial x_i} \tag{1.3}$$

as the diffusion flux of the two phases – an interpretation that has nothing at all to do with interfacial energies. For the thermodynamicist, therefore, the gradient term in f, Eq. (1.1), would be a term proportional to J^2, which is the kinetic energy of the diffusive motion.

I have never been able to understand "smeared-out" interfacial energies, and therefore, I am happy to accept the thermodynamicist's interpretation of the gradient term in f as a kinetic energy.

This paper presents a thermodynamic theory of a multicomponent mixture of fluids as is discussed in the field of thermodynamics of irreversible processes. The first objective is to show how the kinetic energy of the diffusive motion enters the free energy. The second objective is to reconcile the kinetic energy term in the free energy with the more common gradient term.

As a historical quirk, I also mention this: A theory with phase field gradients – or order parameter gradients – is sometimes called a Landau and Ginzburg (1950) theory. This harks back to a semi-quantum-mechanical paper of these authors in 1950 on superconductivity. They wanted a $\partial c/\partial x_i$-term in the free energy, and for isotropy, they were sure that the term had to be of the form $|\text{grad } c|^2$. What they were not sure of was the coefficient. So, they argue as follows:

".. (the term) looks like the density of kinetic energy in quantum mechanics. Thus(!!), we shall write the corresponding expression in the form

$$\frac{\hbar^2}{2m}|\text{grad } c|^2 = \frac{1}{2m}|-i\hbar \text{ grad } c|^{2}\text{''}.$$

The idea was, of course, that $(\hbar/i)(\partial/\partial x_i)$ is the operator which in quantum mechanics corresponds to the momentum p_i and the kinetic energy is $p^2/(2m)$. Therefore we conclude that even for Landau and Ginzburg (1950) the gradient term in the free energy was related to the kinetic energy. In that sense, those authors have anticipated the gist of the present paper: albeit by a quantum mechanical ruse.

2. Equations of balance for constituents α

We consider the phase field theory (Caginalp, 1991; Colli, 1997) as a binary mixture theory of two phases. To fix the ideas, we think of "wet vapour" as finely dispersed droplets in their vapour. The equations are based on the following equations of balance:

$$\text{masses}\quad \tfrac{\partial\rho_\alpha}{\partial t}+\tfrac{\partial\rho_\alpha v_i^\alpha}{\partial x_i}=\tau_\alpha,$$
$$\text{momenta}\quad \tfrac{\partial\rho_\alpha v_j^\alpha}{\partial t}+\tfrac{\partial\left(\rho_\alpha v_j^\alpha v_i^\alpha-t_{ij}^\alpha\right)}{\partial x_i}=m_i^\alpha,$$
$$\text{energies}\quad \tfrac{\partial\rho_\alpha\left(\varepsilon_\alpha+\frac{1}{2}v_\alpha^2\right)}{\partial t}+\tfrac{\partial}{\partial x_i}\left(\rho_\alpha\left(\varepsilon_\alpha+\tfrac{1}{2}v_\alpha^2\right)v_i^\alpha+q_i^\alpha-t_{ij}^\alpha v_j^\alpha\right)=e_\alpha,$$
$$\text{entropies}\quad \tfrac{\partial\rho_\alpha s_\alpha}{\partial t}+\tfrac{\partial\left(\rho_\alpha s_\alpha v_i^\alpha+\frac{q_i^\alpha}{T}\right)}{\partial x_i}=\sigma^\alpha.$$

τ_α, m_α, e_α and σ_α are the production densities of mass, momentum, energy and entropy, respectively, of phase α. All other quantities are denoted by the canonical letters, used in the bulk of the relevant literature, e.g., see Eckart (1940) or Müller (1984). Note that the non-convective partial entropy flux is assumed to be given by q_i^α/T.

3. Equations of balance of mixture

Conservation of mass, momentum, energy and growth of entropy requires

$$\sum_{\alpha=1}^{v}\tau_\alpha=0,\quad \sum_{\alpha=1}^{v}m_i^\alpha=0,\quad \sum_{\alpha=1}^{v}e_\alpha=0,\quad \sum_{\alpha=1}^{v}\sigma_\alpha\geqslant 0.$$

(For generality, we assume v-constituents – or phases – rather than 2.)

Define $\rho=\sum_\alpha\rho_\alpha$ and $\rho v_i=\sum_\alpha\rho_\alpha v_i^\alpha$; hence,

$$\text{mass balance}\quad \frac{\partial\rho}{\partial t}+\frac{\partial\rho v_i}{\partial x_i}=0.$$

Define $t_{ij}=\sum_\alpha\left(t_{ij}^\alpha-\rho_\alpha u_i^\alpha u_j^\alpha\right)$ and $u_i^\alpha\equiv v_i^\alpha-v_i$ (diff. velocity); hence,

$$\text{momentum balance}\quad \frac{\partial\rho v_j}{\partial t}+\frac{\partial\left(\rho v_j v_i-t_{ij}\right)}{\partial x_i}=0.$$

Define $\varepsilon=\sum_\alpha\frac{\rho_\alpha}{\rho}\left(\varepsilon_\alpha+\frac{1}{2}u_\alpha^2\right)$ and $q_i=\sum_\alpha\left(q_i^\alpha+\rho_\alpha\left(\varepsilon_\alpha+\frac{1}{2}u_\alpha^2\right)u_i^\alpha-t_{ij}^\alpha u_j^\alpha\right)$; hence,

$$\text{energy balance}\quad \frac{\partial\rho\varepsilon}{\partial t}+\frac{\partial(\rho\varepsilon v_i+q_i)}{\partial x_i}=t_{ij}\frac{\partial v_i}{\partial x_j}.$$

Define $s=\sum_\alpha\frac{\rho_\alpha}{\rho}s_\alpha,\quad \mu_\alpha=\varepsilon_\alpha-Ts_\alpha+\frac{p_\alpha}{\rho_\alpha}$; hence,

$$\text{energy balance}\quad \frac{\partial\rho s}{\partial t}+\frac{\partial\left\{\rho s v_i+\left[q_i-\sum_{\alpha=1}^{v}\mu_\alpha\rho_\alpha u_i^\alpha-\sum_{\alpha=1}^{v}\rho_\alpha\frac{1}{2}u_\alpha^2\right]+\sum_\alpha\left(t_{\langle ij\rangle}^\alpha-\pi_\alpha\delta_{ij}\right)u_i^\alpha\right\}}{\partial x_i}\geqslant 0.$$

$t_{\langle ij\rangle}^\alpha$ has been introduced as the deviatoric part of the partial stress tensor t_{ij}^α. We have

$$t_{ij}^\alpha=t_{\langle ij\rangle}^\alpha-(p_\alpha+\pi_\alpha)\delta_{ij},$$

where p_α is the equilibrium pressure and π_α is the dynamic pressure, the non-equilibrium part of the pressure. μ_α is the chemical potential of constituent α.

4. Fields and field equations

Objective: determine $\rho_\alpha, v_i^\alpha, T$. Thus, there are $4v+1$ fields to be determined for which we need $4v+1$ field equations. For these, we choose the equations of balance of partial masses $\frac{\partial\rho_\alpha}{\partial t} + \frac{\partial\rho_\alpha v_i^\alpha}{\partial x_i} = \tau_\alpha,$

partial momenta $\frac{\partial\rho_\alpha v_j^\alpha}{\partial t} + \frac{\partial\rho_\alpha v_j^\alpha v_i^\alpha - t_{ij}^\alpha}{\partial x_i} = m_j^\alpha,$

(internal) energy $\frac{\partial\rho\varepsilon}{\partial t} + \frac{\partial(\rho\varepsilon v_i + q_i)}{\partial x_i} = t_{ij}\frac{\partial v_i}{\partial x_j}.$

This set of equations is not closed because there are a number of constitutive quantities, viz. τ_α, t_{ij}^α, m_j^α, ε, q_i.

5. Alternative fields and field equations

The alternative set of fields are

$$\rho_\alpha, v_i^\alpha, T \iff \rho, c_\alpha, v_i, J_i^\alpha, T.$$

$c_\alpha = \rho_\alpha/\rho$ is called the concentration of constituent α, – here the phase α – and $J_i^\alpha = \rho_\alpha u_i^\alpha$ is its diffusion flux. We introduce the material derivative $\partial/\partial t + v_i\partial/\partial x_i$, indicated by a superposed dot, and write the equations of balance in the form,

$$\dot\rho + \rho\frac{\partial v_i}{\partial x_i},$$

$$\rho\dot c_\alpha + \frac{\partial J_i^\alpha}{\partial x_i} = \tau_\alpha,$$

$$\rho\dot v_i - \frac{\partial t_{ij}}{\partial x_j} = 0,$$

$$\dot J_i^\alpha + J_j^\alpha\left(\frac{\partial v_i}{\partial x_j} + \frac{\partial v_e}{\partial x_e}\delta_{ij}\right) + \rho_\alpha\dot v_i - \frac{\partial(t_{ij}^\alpha - \rho_\alpha u_i^\alpha u_j^\alpha)}{\partial x_j} = m_i^\alpha - \tau_\alpha v_i,$$

$$\rho\dot\varepsilon + \frac{\partial q_i}{\partial x_i} = t_{ij}\frac{\partial v_i}{\partial x_j}.$$

The constitutive may now be written as

$$\tau_\alpha, \quad t_{ij}^\alpha, \quad M_i^\alpha \equiv m_i^\alpha - \tau_\alpha v_i^\alpha, \quad \varepsilon, \quad q_i.$$

M_i is called the interaction force on constituent α due to the other constituents. The constitutive equations may be derived from the balance of entropy in the manner of thermodynamics of irreversible processes: by relating thermodynamic forces and fluxes.

6. Local equilibrium assumption: Gibbs equations

$s_\alpha(\rho_\alpha, T)$, $\varepsilon_\alpha(s_\alpha, T)$, $p_\alpha(s_\alpha, T)$ are given by the "equations of state" of each constituent so that the Gibbs equations hold:

$$\dot s_\alpha = \frac{1}{T}\left(\dot\varepsilon_\alpha - \frac{p_\alpha}{\rho_\alpha^2}\dot\rho_\alpha\right).$$

The Gibbs equation for the mixture results by multiplication with ρ_α and summation over all α:

$$\underbrace{\left(\sum_{\alpha=1}^{v}\rho_\alpha s_\alpha\right)^{\bullet}}_{\rho s}=\frac{1}{T}\left(\underbrace{\left(\sum_{\alpha=1}^{v}\rho_\alpha\varepsilon_\alpha\right)^{\bullet}}_{\rho\varepsilon-\sum_{\alpha=1}^{v}\frac{1}{2}\rho_\alpha u_\alpha^2}-\sum_{\alpha=1}^{v}\mu_\alpha\dot{\rho}_\alpha\right)\quad\text{(cf. Section 3)},$$

$$\rho\dot{s}=\frac{1}{T}\left(\rho\dot{\varepsilon}-\frac{1}{\rho}\left[\sum_{\alpha=1}^{v}p_\alpha-\sum_{\alpha}\rho_\alpha u_\alpha^2\right]\dot{\rho}-\sum_{\alpha=1}^{v}\left(\mu_\alpha-\tfrac{1}{2}u_\alpha^2\right)\rho\dot{c}_\alpha-\sum_{\alpha=1}^{v}u_i^\alpha\dot{J}_i^\alpha\right).$$

7. Entropy balance

On the right-hand side of the Gibbs equation, we use the equations of balance of Section 5 to replace $\rho\dot{\varepsilon}$, $\dot{\rho}$, $\rho\dot{c}_\alpha$ and $\dot{J}_i^\alpha$. After this is done, we may decompose the right-hand side into a divergence term – the divergence of the entropy flux – and a residue that determines the non-negative entropy production. A lengthy calculation leads to the following entropy balance equation:

$$\begin{aligned}&\rho\dot{s}+\frac{\partial}{\partial x_i}\left\{\frac{1}{T}\left(q_i-\sum_{\alpha=1}^{v}(\mu_\alpha+\tfrac{1}{2}u_\alpha^2)J_i^\alpha+\sum_{\alpha}(t_{\langle ij\rangle}^\alpha-\pi_\alpha\delta_{ij})u_j^\alpha\right)\right\}\\&\quad=-\frac{1}{T}\sum_{\alpha=1}^{v}(\mu_\alpha-\tfrac{1}{2}u_\alpha^2)\tau_\alpha-\frac{1}{T}\sum_{\alpha=1}^{v}\pi_\alpha\frac{\partial v_i^\alpha}{\partial x_i}+q_i^{\mathrm{II}}\frac{\partial\frac{1}{T}}{\partial x_i}\\&\qquad+\sum_{\alpha=1}^{v}\Bigg[\underbrace{-\frac{1}{T}\sum_{\beta=1}^{v}F_{\alpha\beta}M_i^\beta-\frac{\partial\frac{\mu_\alpha-\mu_v}{T}}{\partial x_i}+\frac{1}{T}\left(\frac{1}{\rho_\alpha}\frac{\partial p_\alpha}{\partial x_i}-\frac{1}{\rho_v}\frac{\partial p_v}{\partial x_i}\right)}_{D_i^\alpha}\Bigg]J_i^\alpha+\frac{1}{T}\sum_{\alpha=1}^{v}t_{\langle ij\rangle}^\alpha\frac{\partial v_i^\alpha}{\partial x_j}\\&\quad\geqslant 0.\end{aligned}$$

In writing this, we have defined for abbreviation

$$q_i^{\mathrm{II}}\equiv\sum_{\alpha=1}^{v}\left(q_i^\alpha+\rho_\alpha\left(\varepsilon_\alpha+\frac{p_\alpha}{\rho_\alpha}\right)u_i^\alpha\right)\quad\text{and}\quad F_{\alpha\beta}=\frac{1}{\rho_\alpha}\delta_{\alpha\beta}+\frac{1}{\rho_v}.$$

Also, we have indicated by the brace a new quantity, viz. D_i^α, which serves as a convenient abbreviation for the expression in angular brackets.

Among the densities τ_α of mass production, only n are independent, where n is the number of independent chemical reactions or phase changes. We write

$$\tau_\alpha=\sum_{a=1}^{n}\gamma_i^a M_\alpha\mu_0\lambda^a.$$

$a=1,2,\ldots,n$ is an index for the independent reactions or phase changes. γ_α^a are the corresponding stoichiometric coefficients, M_α, the relative molecular masses and μ_0 is the atomic mass unit. λ^a denotes the rate of reaction a.

8. Phenomenological equations

The right-hand side of the entropy balance is the non-negative entropy production. An inspection shows that it is a sum of products of thermodynamic forces and thermodynamic fluxes.

Thermodynamic forces	Thermodynamic fluxes
λ^a	$\sum_\alpha \gamma_\alpha^a M_\alpha \mu_0 \left(\mu_\alpha - \frac{1}{2}u_\alpha^2\right)$
π_α	$\frac{\partial v_i^\alpha}{\partial x_i}$
q_i^{II}	$\frac{\partial \frac{1}{T}}{\partial x_i}$
D_i^α	J_i^α
$t_{\langle ij \rangle}^\alpha$	$\frac{\partial v_{<i}^\alpha}{\partial x_{j>}}$

We relate these linearly and obtain

$$\boxed{\begin{aligned} \lambda^a &= \sum_{b=1}^{n} L^{ab} \left(\sum_\alpha \gamma_\alpha^b M_\alpha \mu_0 \left(\mu_\alpha - \tfrac{1}{2}u_\alpha^2\right) \right) + \sum_\beta L_\beta^a \frac{\partial v_i^\beta}{\partial x_i}, \\ \pi^\alpha &= \sum_{b=1}^{n} L_\beta^\alpha \left(\sum_\alpha \gamma_\alpha^b M_\alpha \mu_0 \left(\mu_\alpha - \tfrac{1}{2}u_\alpha^2\right) \right) + \sum_\beta L^{\alpha\beta} \frac{\partial v_i^\beta}{\partial x_i}, \end{aligned}}$$

$$\boxed{\begin{aligned} q_i^{\mathrm{II}} &= Q_T \frac{\partial \frac{1}{T}}{\partial x_i} + \sum_{\beta=1}^{\nu-1} Q_T^\beta J_i^\beta, \\ D_i^\alpha &= D_T^\alpha \frac{\partial \frac{1}{T}}{\partial x_i} + \sum_\beta D_J^{\alpha\beta} J_i^\beta, \end{aligned}}$$

$$\boxed{t_{\langle ij \rangle}^\alpha = \sum_\beta \mu^{\alpha\beta} \frac{\partial v_{<i}^\alpha}{\partial x_{j>}}.}$$

The coefficient matrices

$$\begin{vmatrix} L^{ab} & L_\beta^a \\ L_b^\alpha & L^{\alpha\beta} \end{vmatrix}, \quad \begin{vmatrix} Q_T & Q_J^\beta \\ D_T^\alpha & D_J^{\alpha\beta} \end{vmatrix}, \quad \mu^{\alpha\beta}$$

must be positive or negative definite as dictated by the entropy inequality.

The framed equations are called phenomenological equations in thermodynamics of irreversible processes, because the original – much simpler – form of these equations was deduced from observed phenomena by scientists such as Fourier, Fick, Navier and Stokes.

9. Fick's law

Fick's law proper is a mutilated form of the balance of relative momentum – the equation starting with $\dot{J}_i^\alpha$. We have

$$\dot{J}_i^\alpha + J_i^\alpha\left(\frac{\partial v_i}{\partial x_j}+\frac{\partial v_e}{\partial x_e}\delta_{ij}\right)+\rho_\alpha\dot{v}_i-\frac{\partial\left(t_{ij}^\alpha-\rho_\alpha u_i^\alpha u_j^\alpha\right)}{\partial x_j}=M_i^\alpha$$

or with $\dot{v}_i=(1/\rho)\,(\partial t_{ij}/\partial x_j)$

$$\dot{J}_i^\alpha + J_j^\alpha\left(\frac{\partial v_i}{\partial x_j}+\frac{\partial v_e}{\partial x_e}\delta_{ij}\right)-\sum_{\beta=1}^{\nu-1}F_{\alpha\beta}^{-1}\left(\frac{1}{\rho_\beta}\frac{\partial t_{ij}^\beta-\rho_\beta u_i^\beta u_j^\beta}{\partial x_j}-\frac{1}{\rho_\nu}\frac{\partial t_{ij}^\nu-\rho_\nu u_i^\nu u_j^\nu}{\partial x_j}\right)=M_i^\alpha.$$

$F_{\alpha\beta}^{-1}$ is the inverse matrix of $F_{\alpha\beta}$, defined in Section 7, and we may write $F_{\alpha\beta}=\rho_\alpha\delta_{\alpha\beta}-\rho_\alpha\rho_\beta/\rho$. The interaction force M_i^α may be replaced by D_i^α according to the definition of D_i^α in Section 7; D_i^α may be replaced by its constitutive equation. Thus, M_i^α can be expressed as

$$M_i^\alpha=\sum_{\beta=1}^{\nu-1}F_{\alpha\beta}^{-1}\left(T\frac{\partial-\frac{\mu_\beta-\mu_\nu}{T}}{\partial x_i}+\frac{1}{\rho_\beta}\frac{\partial p_\beta}{\partial x_i}-\frac{1}{\rho_\nu}\frac{\partial p_\nu}{\partial x_i}\right)-T\sum_{\beta=1}^{\nu-1}F_{\alpha\beta}^{-1}\left(D_T^\beta\frac{\partial\frac{1}{T}}{\partial x_i}+\sum_{\gamma=1}^{\nu-1}D_J^{\beta\gamma}J_i^\gamma\right),$$

and consequently, the balance of relative momentum reads

$$\begin{aligned}&\dot{J}_i^\alpha + J_j^\alpha\left(\frac{\partial v_i}{\partial x_j}+\frac{\partial v_e}{\partial x_e}\delta_{ij}\right)-\sum_{\beta=1}^{\nu-1}F_{\alpha\beta}^{-1}\left(\frac{1}{\rho_\beta}\frac{\partial\left(t_{ij}^\beta-\rho_\beta u_i^\beta u_j^\beta\right)}{\partial x_j}-\frac{1}{\rho_\nu}\frac{\partial\left(t_{ij}^\nu-\rho_\beta u_i^\nu u_j^\nu\right)}{\partial x_j}\right)\\&\quad=\sum_{\beta=1}^{\nu-1}F_{\alpha\beta}^{-1}\left(T\frac{\partial-\frac{\mu_\beta-\mu_\nu}{T}}{\partial x_i}+\frac{1}{\rho_\beta}\frac{\partial p_\beta}{\partial x_i}-\frac{1}{\rho_\nu}\frac{\partial p_\nu}{\partial x_i}\right)-T\sum_{\beta=1}^{\nu-1}F_{\alpha\beta}^{-1}\left(D_T^\beta\frac{\partial\frac{1}{T}}{\partial x_i}+\sum_{\gamma=1}^{\nu-1}D_J^{\beta\gamma}J_i^\gamma\right).\end{aligned}$$

This is the full balance of relative momentum of constituent α. If $t_{\langle ij\rangle}^\alpha$ are replaced by their phenomenological equations, it is quite explicit except that the phenomenological coefficients $\mu^{\alpha\beta}$, D_T^β and $D_J^{\alpha\beta}$ must be given.

But it is not a simple equation. Usually, it is simplified by a kind of Maxwell iteration whose first step requires that all quantities on the left-hand side are replaced by their equilibrium values J_i^α, and u_i^α are zero in equilibrium and $t_{ij}^\alpha=-p_\alpha\delta^{ij}$. Thus, the first iteration for the right-hand side is given by

$$\sum_{\beta=1}^{\nu-1}F_{\alpha\beta}^{-1}\left(\frac{1}{\rho_\beta}\frac{\partial p^\beta}{\partial x_i}-\frac{1}{\rho_\nu}\frac{\partial p^\nu}{\partial x_i}\right)=\sum_{\beta=1}^{\nu-1}F_{\alpha\beta}^{-1}\left(T\frac{\partial-\frac{\mu_\beta-\mu_\nu}{T}}{\partial x_i}+\frac{1}{\rho_\beta}\frac{\partial p^\beta}{\partial x_i}-\frac{1}{\rho_\nu}\frac{\partial p^\nu}{\partial x_i}\right)-T\sum_{\beta=1}^{\nu-1}F_{\alpha\beta}^{-1}\left(D_T^\beta\frac{\partial\frac{1}{T}}{\partial x_i}+\sum_{\gamma=1}^{\nu-1}D_J^{\beta\gamma}\overset{(1)}{J}{}_i^\gamma\right)$$

or by solving for the first iterate $\overset{(1)}{J}{}_i^\alpha$,

$$\overset{(1)}{J}{}_i^\alpha=\sum_{\beta=1}^{\nu-1}\overset{-1}{D}{}_J^{\alpha\beta}\left(\frac{\partial-\frac{\mu_\beta-\mu_\nu}{T}}{\partial x_i}\right)-\sum_{\beta=1}^{\nu-1}\overset{-1}{D}{}_J^{\alpha\beta}D_T^\beta\frac{\partial\frac{1}{T}}{\partial x_i}.$$

The two expressions with the partial pressures cancel each other.

This is Fick's law as derived by thermodynamics of irreversible processes. It is clearly a strongly mutilated form of the balance of relative momenta of the constituents.

10. Special case

Simplifying assumptions
(i) J_i^α-independent of $\partial T/\partial x_i$,
(ii) $\rho = \text{const}$, $v_i = 0$,
(iii) $t^\alpha_{\langle ij\rangle}$, π_α, $\frac{\partial v_i^\alpha}{\partial x_j}$ – all negligible,
(iv) two phases only, i.e. $v = 2$.
In this case, the final form of Fick's law, derived in Section 9, reduces to a single equation for $J_i^1 \equiv J_i$, viz.

$$J_i = -\frac{\mu_c}{D_J T}\frac{\partial c}{\partial x_i}, \quad \text{where } \mu_c \equiv \frac{\partial \mu_1 - \mu_2}{\partial c}.$$

Hence,

$$J_i = -D\frac{\partial c}{\partial x_i}, \quad D > 0 \text{ is the diffusion constant.}$$

Also, the free energy density reads

$$\rho f = \rho(\varepsilon - Ts)$$

or, by Section 3

$$\rho f = \sum_{\alpha=1}^{2}\rho_\alpha(\varepsilon_\alpha - Ts_\alpha) + \sum_{\alpha=1}^{2}\rho_\alpha \tfrac{1}{2}u_\alpha^2 = \sum_{\alpha=1}^{2}\rho_\alpha(\varepsilon_\alpha - Ts_\alpha) + \tfrac{1}{2}\frac{1}{\rho c(1-c)}J^2.$$

By Section 6, the first term is independent of velocities, and we may denote it by $\rho f_0(c,T)$. The second term represents the kinetic energy of the diffusive motion.

Combining the expressions for the free energy and Fick's law, we obtain

$$\rho f = \rho f_0(c,T) + \frac{D^2}{2\rho c(1-c)}\frac{\partial c}{\partial x_i}\frac{\partial c}{\partial x_i},$$

so that we may now interpret the kinetic energy of the diffusive motion as a gradient term, or vice versa. Infact, this is the main assertion of this paper:

> *The gradient term, usually attributed to a "smeared-out" interfacial energy is nothing else than the kinetic energy of the diffusive motion.*

The partial mass balance – the equation for $\dot{c}_\alpha$ in Section 5 – reads in the present context and with Fick's law and

$$\rho\dot{c} - \frac{\partial}{\partial x_i}\left(D\frac{\partial c}{\partial x_i}\right) = \tau.$$

The mass production τ is given by $M\mu_0\lambda$, according to Section 7, since our "chemical reaction" is merely a phase change in which the molecular mass does not change and where the stoichiometric coefficients are +1 and −1. And the reaction rate is given by the phenomenological equation $\lambda = LM\mu_0(\mu_1 - \mu_2)$, if we ignore the non-linear kinetic energy term. On the other hand, we know from the Gibbs equation that we have to within non-linear terms

$$\frac{\mu_1 - \mu_2}{T} = \frac{\partial f_0}{\partial c}.$$

Therefore, the partial mass balance reads

$$\rho\dot{c} - \frac{\partial}{\partial x_i}\left(D\frac{\partial c}{\partial x_i}\right) = LM^2\ \mu_0^2\ T\ \frac{\partial f_0}{\partial c}.$$

Rearranging and renaming coefficients, we conclude that the partial mass balance has quite the same form as the phase field equations described in Section 1.

With all this, we conclude that the special case of a theory of a phase mixture, which is considered here, does give rise to a phase field equation of the form sketched in Section 1.

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