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# ON THE USE OF FICK'S LAW IN REGIONS OF MIXED PHASE

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## ABSTRACT

This note has the sole purpose of highlighting the fundamental inconsistency that arises when Fick's law is invoked to describe the diffusion of constituents in a region of mixed phase.

The purpose of this note is to draw attention to a disturbing inconsistency in some theoretical arguments that have been used to determine the evolution of regions of mixed solid and liquid phase. The inconsistency, elaborated in precision by the mathematics that follows, results from a very simple physical idea. The distribution of solid in a mixed phase region in complete equilibrium is arbitrary, that is, each point  $\mathbf{x}$  in space can equally well be occupied by solid or by liquid. Thus, although pressure,  $p$ , and temperature,  $T$ , are uniform in the equilibrium state, the mass fraction of solid phase,  $\phi(\mathbf{x})$ , is an arbitrary (and possibly discontinuous) function of position.

When a two-phase region is modelled by a mixture,  $\phi(\mathbf{x})$  is allowed to take any value from 0 to 1. Any attempt to introduce a physical process that evens out  $\phi(\mathbf{x})$ , making it uniform across the system, strikes at the very heart of the thermodynamic basis of phase equilibrium. Thus, to be viable, a system of equations that purports to describe a mixed phase state must *not* predict that  $\phi$  becomes uniform when an isolated system is allowed to come to equilibrium. Thus, in particular, the mass flux of solid may not include a Fickian type of diffusion term, proportional to  $\nabla\phi$ .

This demand, couched above in terms that apply to the freezing of a pure substance, has equal force for mixed phase regions of alloys. Fixing attention on a single binary alloy, there is a simple relation

$$\xi = \phi\xi^S + (1 - \phi)\xi^L, \quad (1)$$

between  $\phi$  and the mass fraction,  $\xi$ , of the light constituent of the alloy; here  $\xi^S$  and  $\xi^L$  are the mass fractions of the light constituent in solid and liquid phases, respectively. Since  $\phi$  can take any value between 0 and 1,  $\xi$  can, in a system in thermodynamic equilibrium, take any value between  $\tilde{\xi}^S$  and  $\tilde{\xi}^L$ , the solidus and liquidus concentrations of  $\xi$  [see equ. (11) below]. Thus, while  $p$ ,  $T$ ,  $\tilde{\xi}^S$ ,  $\tilde{\xi}^L$  are uniform in the final state,  $\phi$ ,  $\xi$ ,  $\rho$ ,  $S$  all vary with  $\mathbf{x}$ ; here  $\rho$  is density and  $S$  specific entropy. Thus the system of equations that govern the mixed phase region out of equilibrium, must not predict that  $\xi$  becomes uniform when an isolated system is allowed to equilibrate. The mass flux of the light component may not include a Fickian type diffusion term proportional to  $\nabla\xi$ .

In more detail, the specific internal energy,  $U$ , of a binary alloy in mixed phase is a function of  $S$ ,  $\xi^S$ ,  $\xi^L$ ,  $\phi$ , and the specific volume,  $V$

$$U = U(V, S, \xi^S, \xi^L, \phi). \quad (2)$$

Differentiating (2) we have

$$dU = -pdV + TdS + \phi\mu^S d\xi^S + (1 - \phi)\mu^L d\xi^L + \psi d\phi, \quad (3)$$

where

$$\begin{aligned} p &= -\frac{\partial U}{\partial V}, & T &= \frac{\partial U}{\partial S}, & \phi\mu^S &= \frac{\partial U}{\partial \xi^S}, \\ (1 - \phi)\mu^L &= \frac{\partial U}{\partial \xi^L}, & \psi &= \frac{\partial U}{\partial \phi}. \end{aligned} \quad (4)$$

Here,  $\mu^S$ ,  $\mu^L$  and  $\psi$  are chemical potentials.

Consider a static binary alloy contained within a fixed boundary that is impermeable to mass and heat flux. Then the total volume, total internal energy,  $E$ , and total masses  $M_1$ ,  $M_2$  of the two constituents are constant where

$$\int \rho U d^3x = E, \quad \int \rho \xi d^3x = M_1, \quad \int \rho d^3x = M_1 + M_2, \quad (5)$$

$\rho = 1/V$ . This system will attain thermodynamic equilibrium only when the total entropy,

$$\mathfrak{R} = \int \rho S d^3x,$$

attains its maximum. In that state,  $\delta \mathfrak{R} = 0$  for all variations  $\delta S(\mathbf{x})$ ,  $\delta V(\mathbf{x})$ ,  $\delta \xi^S(\mathbf{x})$ ,  $\delta \xi^L(\mathbf{x})$ ,  $\delta \phi(\mathbf{x})$  consistent with the constraints (5). From Euler's rule for isoperimetric problems we require

$$\delta [\rho S - T_0^{-1}(\rho U - \tilde{\mu}_0 \rho \xi - \mu_0 \rho)] = 0,$$

for independent variations of  $\delta S$ ,  $\delta V$ ,  $\delta \xi^S$ ,  $\delta \xi^L$ ,  $\delta \phi$ , where  $T_0$ ,  $\tilde{\mu}_0$ ,  $\mu_0$  are *constant* Lagrangian multipliers. We obtain

$$\mu^S = \mu^L = \tilde{\mu}_0, \quad \psi = \tilde{\mu}_0(\xi^S - \xi^L), \quad (6)$$

$$T = T_0, \quad \Phi - \tilde{\mu}_0 \xi = \mu_0, \quad (7)$$

where

$$\Phi = U + pV - TS, \quad (8)$$

is the specific Gibbs' potential. According to (3)

$$d\Phi = V dp - S dT + \phi \mu^S d\xi^S + (1 - \phi) \mu^L d\xi^L + \psi d\phi, \quad (9)$$

where

$$\begin{aligned} V &= \frac{\partial \Phi}{\partial p}, & S &= -\frac{\partial \Phi}{\partial T}, & \phi \mu^S &= \frac{\partial \Phi}{\partial \xi^S}, \\ (1 - \phi) \mu^L &= \frac{\partial \Phi}{\partial \xi^L}, & \psi &= \frac{\partial \Phi}{\partial \phi}, \end{aligned} \quad (10)$$

and it follows from (6) and (7) that in equilibrium,  $p$  is constant across the system with value  $p_0$ , say. By employing the Gibbs' function,  $\Phi$ , the constant  $\mu_0$  can be eliminated in favour of  $p_0$  for (6) and (9) *apparently*

give three equations for determining  $\xi^S$ ,  $\xi^L$  and  $\phi$  as functions of  $p_0$ ,  $T_0$  and  $\tilde{\mu}_0$ . These constants can themselves be determined (if necessary) in terms of  $E$ ,  $M_1$  and  $M_2$  by substitution in (5).

We say *apparently* since, by eliminating  $\tilde{\mu}_0$ , the solution gives  $\xi^S$  and  $\xi^L$  which depend on  $p$ ,  $T$  and  $\phi$ :

$$\xi^S = \tilde{\xi}^S(p, T, \phi), \quad \xi^L = \tilde{\xi}^L(p, T, \phi). \quad (11)$$

But it is known to an excellent approximation that  $\tilde{\xi}^S$  and  $\tilde{\xi}^L$ , the so-called "solidus" and "liquidus" phase curves are *independent of  $\phi$* . For this to be true it is *necessary* that the total Gibbs' potential  $\Phi$  for the two phases is linear in  $\phi$ :

$$\Phi = \phi\Phi^S(p, T, \xi^S) + (1 - \phi)\Phi^L(p, T, \xi^L). \quad (12)$$

By (10),  $V$  and  $S$  obey similar "lever rules" and the chemical potentials,

$$\mu^S = \frac{\partial\Phi^S}{\partial\xi^S}, \quad \mu^L = \frac{\partial\Phi^L}{\partial\xi^L}, \quad \psi = \Phi^S - \Phi^L, \quad (13)$$

are all independent of  $\phi$ . Then, in the static equilibrium state of maximum  $\mathfrak{R}$ ,  $p$  and  $T$  are uniform leading to spatially uniform mass fractions  $\xi^S (= \tilde{\xi}^S)$  and  $\xi^L (= \tilde{\xi}^L)$  also. But with the choice (12),  $\phi$  is unrestricted by equilibrium considerations and so is free to take arbitrary values in the range  $[0,1]$ . Physically this reflects the thermodynamic indifference of a mixed phase as to whether the solid or liquid state is formed. It means that spatial non-uniformity in  $\phi$  is possible with a concomitant non-uniformity for the fields  $\xi$ ,  $S$  and  $V$  also. In short, once we demand that  $\tilde{\xi}^S$  and  $\tilde{\xi}^L$  are independent of  $\phi$ , we are *forced* to assume the lever rule (12) and we are *forced* to admit that in a phase mixture there is an infinity of possible maximum entropy states corresponding to the arbitrariness of  $\phi$ . Most importantly we are *forced* to reject any theory for the mixed phase region that prefers one of these maximum entropy states over the others, *e.g.* that requires the system to equilibrate to a state of uniform  $\phi$  (or  $\xi$ ). The last of these conclusions has implications in respect of Fick's law for  $\xi$ . If  $\Phi$  is not additive as in (12), then we should expect that  $\xi$  and  $\phi$  will evolve to uniform states, but then the solidus and liquidus will depend upon  $\phi$ , an effect which is generally rejected as negligible.

To return to Fick's law and the evaluation of  $\xi$ , the conservation of mass of constituents 1 and 2 lead to continuity equations of the form

$$\rho \frac{D\xi}{Dt} = -\nabla \cdot \mathbf{i}, \quad \frac{D\rho}{Dt} = -\nabla \cdot (\rho\mathbf{v}), \quad (14,15)$$

where  $D/Dt$  is the motional derivative based on the barycentric (mass centre) velocity,  $\mathbf{v}$ , and  $\mathbf{i}$  represents the mass flux of constituent 1 relative to that motion. Equation (15) is the usual continuity equation, and we focus on (14). This is supplemented by a constitutive law for  $\mathbf{i}$ , the simplest form of which is a linear combination of gradients:

$$\mathbf{i} = -k_p \nabla p - k_T \nabla T - k_S \nabla \xi^S - k_L \nabla \xi^L - k_\phi \nabla \phi, \quad (16)$$

where the  $k$ -coefficients are functions of the state variables. When (12) holds,  $k_\phi$  must vanish in all states of thermodynamic equilibrium, since otherwise  $\phi$  would become uniform in an isolated system, and we have seen that  $\phi$  can be an arbitrary function of  $\mathbf{x}$  (where  $0 \leq \phi \leq 1$ ).

Most theories of evolving regions of mixed phase assume local phase equilibrium, and take for the Gibbs' energy

$$\tilde{\Phi}(p, T, \xi) = \Phi(p, T, \tilde{\xi}^S(p, T, \phi), \tilde{\xi}^L(p, t, \phi), \phi), \quad (17)$$

where, by (6) and (9),

$$d\tilde{\Phi} = \tilde{V} dp - \tilde{S} dT + \tilde{\mu} d\xi. \quad (18)$$

Here, by (2)

$$\xi = \phi \tilde{\xi}^S(p, T, \phi) + (1 - \phi) \tilde{\xi}^L(p, T, \phi), \quad (19)$$

and the tildes on  $\tilde{V}$  and  $\tilde{S}$  signify, as in (17), that  $\tilde{\xi}^S$  and  $\tilde{\xi}^L$  have replaced  $\xi^S$  and  $\xi^L$  in (10)<sub>1</sub> and (10)<sub>2</sub>. [Loper and Roberts [1] called this "the fast melting approximation" so recognizing that it should be acceptable whenever the time taken by the system to reach local phase equilibrium is short compared with the time scales over which the system evolves.] In this approximation (16) reduces to

$$\mathbf{i} = \tilde{k}_p \nabla p - \tilde{k}_T \nabla T - \tilde{k}_\xi \nabla \xi. \quad (20)$$

Whether the full theory or this reduced local equilibrium form of the theory is adopted, it remains true that, when  $\Phi$  is determined by the lever rule (12)

$$\Phi = [\xi^S - \xi^L]^{-1} [(\xi - \xi^L)\Phi^S(p, T, \xi^S) + (\xi^S - \xi)\Phi^L(p, T, \xi^L)], \quad (21)$$

where  $\xi^S = \tilde{\xi}^S(p, T)$ ,  $\xi^L = \tilde{\xi}^L(p, T)$ , then any function  $\xi(\mathbf{x})$  should be possible in the final state of uniform  $T$  and  $p$  to which an isolated system

equilibrates, the only restrictions being that  $\xi$  everywhere lies between  $\tilde{\xi}^S$  and  $\tilde{\xi}^L$  and that  $\rho\xi(\mathbf{x})$  integrates to give the total mass of the light constituent. The presence of the last term in (20) would, however, cause  $\xi$  to become uniform. It follows that

$$\tilde{k}_\xi = 0. \quad (22)$$

In other words, once we demand that  $\tilde{\xi}^S$  and  $\tilde{\xi}^L$  are independent of  $\phi$  (the generally accepted view), we are *forced* to assume (12), *compelled* to admit an infinity of possible maximum entropy states corresponding to this arbitrariness of  $\phi$  and  $\xi$ , and we are therefore *driven* to reject the “normal” diffusive coefficient  $\tilde{k}_\xi$ , of Fick’s law when postulating a constitutive law (20).

The inconsistency on which we have focussed in this note is an ever-present danger in applications of the so-called “entropy method” for determining the structure of an evolving region of mixed phases. See, for example, Alexiades *et. al.* [2, eqs. (3.6), (5.1)], Alexiades *et. al.* [3, eqs. (2.20), (2.22)], Solomon *et. al.* [4, eqs. (2), (4)], Wilson *et. al.* [5, eq. (17)] and Wilson *et. al.* [6, eqs. (1), (3)]. It is possible for a “weak solution” formulation to be so enfeebled that it becomes totally impotent as far as representing physical reality.

The inconsistency is not present in the papers of Loper and Roberts [1], [7], Hills, Loper and Roberts [8] and Hills and Roberts [9] – [11].

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