Molecular Theory of Transport in Fluid Microstructures: Diffusion in Interfaces and Thin Films

Gradient theory of equilibrium fluid microstructures is extended to nonequilibrium isothermal processes. The theory is applied to steady diffusion across liquid-liquid interfaces. It is shown that local equilibrium across a fluid-fluid interface is maintained even in the presence of very high diffusion fluxes and that the concept of an interface acting as an applied potential energy for a diffusing species is of limited utility. The theory is suited for practical, semiempirical calculations of structure, stress, and isothermal transport in systems containing interfaces.

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SCOPE

Many key problems in chemical engineering revolve around processes that occur in interfacial regions. Adsorption, catalysis, corrosion, detergency, distillation, flocculation, foaming, humidification, membrane transport, and porous media processes are a random sample from a long list (Treybal, 1980). Fluid-solid and fluid-fluid interface processes are both represented frequently in this long list, and in many respects they may be treated similarly.

Much of the chemical engineering literature on interfacial transport phenomena treats interfaces as two-dimensional surfaces. Mathematical analysis using this simple idealization requires further assumptions about concentration profiles in the neighborhood of the interface. In particular, "jump" conditions connecting bulk solute concentrations and fluxes on the two sides of the "surface" are typically applied. These conditions rest on the assertion that, right at the "surface," the two phases in contact are in equilibrium, or, in other words, that the species chemical potentials are continuous across the "surface."

Our objectives in this article are first to study in more detail using a powerful, versatile, and currently rapidly evolving, statistical mechanical molecular theory of inhomogeneous fluids, the nonequilibrium concentration profile in interfacial region. This model, which we term gradient theory, does not treat the interfacial region as a surface, but rather makes complete predictions about density profiles across the region. The present work is the first application of gradient theory to nonequilibrium situations. We are thus able to discuss the validity of the classical equilibrium jump condition in quantitative terms.

A second major question addressed is the utility of trying to improve on the simple two-dimensional singularity picture of the interfacial region by superimposing a spatially varying potential field over the region containing the (still singular) surface, as has been suggested in several recent works (Leal and Brenner, 1977; Brenner and Leal, 1978; Shaeiwitz and Raterman, 1982; Larson, 1982).

The theory as presented is well suited for many practical applications, such as membrane and porous media transport or in the dynamics of separations processes.

CONCLUSIONS AND SIGNIFICANCE

Molecular theory calculations of mass transport across a liquid-liquid interface via gradient theory lead to the conclusion that even for very high rates of interfacial transfer there is very little perturbation of the concentration profile from that obtained under equilibrium conditions. This lends very strong support to the traditionally used but difficult to assess assumption of interfacial equilibrium in mass transfer between phases.

Regarding our examination of the idea of representing some of the nonlocal effects of the interfacial region by some supposedly known potential field, our conclusion is that this is not a very useful picture. In fact we have shown here, via our gradient theory analysis, that there is no true, predeterminable, molecular potential that can represent the interface. There is a quantity that plays the role in the theory of an apparent potential but depends on temperature and bulk compositions of the contacting phases. Several computed density and microstructural potential profiles are given to illustrate these points.

Of most significance in this work is the theory itself, which we feel is quite practical and applicable to a wide range of interfacial transport problems where more rigorous and detailed means of analysis are useful.

INTRODUCTION

Traditionally in engineering applications interfaces are treated as two-dimensional surfaces, films or solids as thin layers of phase, microdrops as spheres of phase, etc. Whereas such an approach may be quite adequate given the proper phenomenological inputs, it ignores the fact that interfacial zones are actually regions of non-infinitesimal width and of continuous density or composition variation, and it provides no insight into the molecular structure of interfacial zones or into the mechanisms of transport operative there. During the last two decades, however, a great deal of progress has been made in the equilibrium statistical mechanical theory of the structure and stress in fluid microstructures. A fluid microstructure is a region in a fluid in which component densities vary appreciably over molecular distances. Examples of fluid microstructures include fluid-fluid interfaces, fluid-solid interfaces, multiphase contact regions, thin films, drops and bubbles, micelles, liquid crystals, and vesicles and bilayers.

Especially potent has been gradient theory, a molecular theory highly receptive to the kind of semiempirical modeling that has proven so powerful for engineers in modeling phase behavior of real multicomponent fluids. The main purpose of the present paper is to extend gradient theory to nonequilibrium isothermal processes in fluid microstructures. By way of illustration, the theory is applied to steady diffusion across a planar liquid-liquid interface. Some aspects of the theory are compared and contrasted with both some older and some more recent treatments of interfacial mass transport situations of interest to chemical engineering.

GRADIENT THEORY OF EQUILIBRIUM MICROSTRUCTURED FLUIDS

In inhomogeneous fluids the Helmholtz free energy and, therefore, the chemical potentials of the components of an inhomogeneous fluid are functionals of the component density distributions. Although exact formal expressions of these functionals have been derived (Yang et al., 1976; Fleming et al., 1976) from statistical mechanics, they are impractical without approximation. Gradient theory, an approximation having its roots in the early works of Lord Rayleigh (1892) and van der Waals (Rowlinson, 1979), has been much applied in recent times to the investigation of spinodal decomposition (Cahn, 1965; Nakanishi and Pincus, 1983), the behavior of surface and interfacial tension (Bongiorno and Davis, 1975; Carey et al., 1978; McCoy and Davis, 1978; Sahimi et al., 1981), wettability and contact angle phenomena (Teletzke et al., to appear, 1981; Benner et al., 1981), the formation of fluid microstructures such as films (Teletzke et al., to appear, 1981; Davis and Scriven, 1981), periodic structures (Davis and Scriven, 1981), drops and bubbles (Falls et al., 1981), and multicomponent polymer systems (Poser and Sanchez, 1981; Klein and Pincus, 1982). Comparisons between tensions predicted by gradient theory and tensions obtained from experiment (Carey et al., 1978a,b), from computer simulation (Bongiorno and Davis, 1975; McCoy and Davis, 1978), and from integral models designed to mimic the rigorous functional equations (Falls et al., 1981) indicate that gradient theory provides a good quantitative approximation for inhomogeneous, microstructured fluids.

In its modern form (Yang et al., 1976; Davis and Scriven, 1981; Bongiorno et al., 1976), the Helmholtz free energy of gradient theory is

$$F = \int \left[f_0(\boldsymbol{n}) + \frac{1}{2} \sum_{i,j}^{\nu} c_{ij} \nabla n_i \cdot \nabla n_j + \sum_{i}^{\nu} n_i u_i^e \right] d^3\boldsymbol{r}, \tag{1}$$

where $\boldsymbol{r}$ denotes position in the fluid, $\boldsymbol{n}$ the focal set $\{n_1, \dots, n_\nu\}$ of component densities, ∇ the gradient operator, u_i^e the external potential energy (e.g., from gravity or from solids contacting the fluid), $f_o(\boldsymbol{n})$ the Helmholtz free energy density of homogeneous fluid in the density state $\boldsymbol{n}$, and the c_{ij} are known as the influence parameters of inhomogeneous fluid ($c_{ij} = c_{ji}$). The quantity $1/2\ (\Sigma_{i,j} c_{ij} \nabla n_i \cdot \nabla n_j)$ is the free energy density of inhomogeneity.

Equation 1 can be rationalized in the following way. In the absence of external fields and compositional or density inhomogeneities, the Helmholtz free energy density is $f_o(\boldsymbol{n})$. Intermolecular interactions between species i and j make a contribution to f_0 of order $u_{ij} n_i n_j$, where u_{ij} is a characteristic interaction energy. The factor $1/2\ n_i n_j$ is a measure of the number of interacting pairs in homogeneous fluid of those component densities. If the fluid is inhomogeneous at position $\boldsymbol{r}$, then the number of interacting pairs in that neighborhood must be corrected by some amount $1/2(\Delta n_i \delta n_j)$. An estimate of δn_i is $r_{ij} \nabla n_i$, where r_{ij} is the range of the intermolecular force between i and j. It follows heuristically then that the local Helmholtz free energy density of inhomogeneous fluid should include a correction for the inhomogeneity of the form $\Sigma_{i,j}^{\nu} 1/2 c_{ij} \nabla n_i \cdot \nabla n_j$ (plus higher-order terms we shall henceforth ignore).

We see that the influence parameters should be proportional to $u_{ij} r_{ij}^2$. More rigorously, the influence parameters are related to homogeneous fluid structure through the formula (Yang et al., 1976; Cahn, 1965)

$$c_{ij} = \frac{kT}{6} \int s^2 C_{ij}^0(s;\boldsymbol{n}) d^3s, \tag{2}$$

where k is Boltzmann's constant, T the absolute temperature, and $C_{ij}^0(s;\boldsymbol{n})$ the direct correlation function of homogeneous fluid in the density state $\boldsymbol{n}$. The direct correlation function is an integral transform of the more familiar pair correlation function $g_{ij}^0(s;\boldsymbol{n})$:

$$C_{ij}^0(s) = g_{ij}^0(s) - 1 - \sum_{k}^{\nu} n_k \int [g_{ij}^0(|s' - s|) - 1] C_{ij}^0(s') d^3s. \tag{3}$$

This transform was introduced by Ornstein and Zernicke (1914) to remove the many-bodied long-range part of the pair correlation function. At large s, $C_{ij}^0(s)$ approaches (March, 1976) $-u_{ij}(s)/kT$, u_{ij} being the pair potential between molecules of species i and j. Thus, kTC_{ij}^0 is asymptotically independent of fluid temperature and density state, a property causing the influence parameters to depend only weakly on temperature and density state. To the extent that kTC_{ij}^0 can be approximated by $-u_{ij}$, c_{ij} has the form arrived at heuristically in the argument given above. The formula given in Eq. 2 is based on the assumption that the C_{ij}^0 exist at all fluid compositions in the microstructure. There is some evidence that the assumption may be false for some unstable fluid compositions (Kerins et al., 1984), in which case the theory of the influence parameters c_{ij} is more complicated. The influence parameters, nevertheless, can be regarded as microstructural parameters to be fitted to semiempirical or empirical expressions using interfacial tension and adsorption data.

At equilibrium the grand potential, Ω,

$$\Omega \equiv F - \sum_{i} \mu_i \int n_i d^3\boldsymbol{r}, \tag{4}$$

is a minimum in closed system. The chemical potential, μ_i, plays the role of a Lagrange multiplier accounting for the constraint that $N_i = \int n_i d^3r$ is fixed for a closed system. It is a straightforward exercise in variational calculus to show that the necessary condition that a given density state $\boldsymbol{n}(\boldsymbol{r})$ be a minimum of Ω is (Davis and Scriven, 1981; March, 1976)

$$\mu_i = u_i^e + \mu_i^0(\boldsymbol{n}) - \sum_{j} \nabla \cdot (c_{ij} \nabla n_j) + \frac{1}{2} \sum_{k,j}^{k} \frac{\partial c_{jk}}{\partial n_i} \nabla n_j \cdot \nabla n_k, \tag{5}$$

for $i = 1, \ldots, \nu$, where $\mu_i^o(\boldsymbol{n})$ is the chemical potential component i in homogeneous fluid in the density state $\boldsymbol{n}$. At equilibrium μ_i is constant and Eq. (5) is a set of nonlinear partial differential equations determining the fluid microstructures allowed for a given set of boundary conditions. Equation 5 is the Euler equation set for the functional Ω. Stability of a given microstructure must be established by considering the second variation, i.e., the Jacobian equations, of Ω.

For some solution models, such as the regular solution and Flory-Huggins models, the fluid component densities obey constraints such as $\Sigma_i n_i v_i = 1$, where the v_i are molecular volume parameters. With such a constraint the condition for stable thermodynamic equilibrium in a closed isothermal condition is that the quantity

$$\Omega - \lambda \sum_i v_i \int n_i d^3 r \tag{6}$$

be a minimum, where λ is a Lagrange multiplier. The Euler equation for the extremum of Eq. 6 is

$$\mu_i = u_i^e + \mu k_i^0 - v_i \lambda - \sum_j \nabla \cdot (c_{ij} \nabla n_j) + \sum_{j,k} \frac{1}{2} \frac{\partial c_{jk}}{\partial n_i} \nabla n_j \cdot \nabla n_k \tag{7}$$

for $i = 1, \ldots, \nu$. λ can be eliminated by multiplying the lth equation by v_i/v_l and subtracting it from the ith to obtain

$$\mu_i - \frac{v_i}{v_l} \mu_l = u_i^e - \frac{v_i}{v_l} u_l^e + \mu_i^o - \frac{v_i}{v_l} \mu_l^o - \Sigma \nabla \cdot \left[\left((c_{ij} - \frac{v_i}{v_l} c_{lj}\right) \nabla n_j\right] + \sum_{j,k} \left(\frac{\partial c_{jk}}{\partial n_i} - \frac{v_i}{v_l} \frac{\partial c_{jk}}{\partial n_l}\right) \nabla n_j \cdot \partial n_k, \tag{8}$$

for $i = 1, \ldots l - 1, l + 1, \ldots \nu$. These $\nu - 1$ equations plus the constraint equation $\Sigma_i n_i v_i = 1$ govern the allowed microstructures in mixtures with such a density constraint.

The theory as outlined thus far is for nonionic fluids. If charged particles are present, then gradient theory, with the approximation that the local dielectric constant equals the dielectric constant $\epsilon^o(\boldsymbol{n}(\boldsymbol{r}))$ of homogeneous fluid in the local density state $\boldsymbol{n}(\boldsymbol{r})$, yields

$$\mu_i = u_i^e + \mu_i^o(\boldsymbol{n}) - \sum_j \nabla \cdot (c_{ij} \nabla n_j) + \sum_{j,k} \frac{1}{2} \frac{\partial c_{jk}}{\partial n_i} \nabla n_j \cdot \nabla n_k + z_i e \psi - \frac{1}{8\pi} \frac{\partial \epsilon^0}{\partial n_i} \boldsymbol{E}^2, \tag{9}$$

where z_i is the valence of the ith component, e the unit electronic charge, ψ the local voltage, and $\boldsymbol{E} \equiv -\nabla \psi$ the local electric field. The local voltage obeys the equation of electrostatics

$$\nabla \cdot (\epsilon^o \nabla \psi) = -4\pi \sum_i z_i e n_i. \tag{10}$$

GRADIENT THEORY OF TRANSPORT IN ISOTHERMAL MICROSTRUCTURED FLUIDS

The continuity equation of species i in a ν component system is

$$\frac{\partial n_i}{\partial t} + \nabla \cdot (n_i \boldsymbol{v}^m) = -\nabla \cdot \boldsymbol{J}_i, \tag{11}$$

where t is the time, $\boldsymbol{v}^m$ is the local molar velocity, and $\boldsymbol{J}_i$ the molar diffusion flux of component i.

The quantity $\boldsymbol{v}^m$ is related to the local mass average velocity $\boldsymbol{v}$ by

$$\boldsymbol{v}^m = \boldsymbol{v} - \sum_i m_i \boldsymbol{J}_i \Big/ \sum_i m_i n_i. \tag{12}$$

where m_i is the molecular mass of species i.

According to linear transport theory (linear in field variables) (de Groot and Mazur, 1962), the diffusion flux for small gradients in chemical potentials is given by the equation

$$\boldsymbol{J}_i = -\sum_{j=1}^{\nu} \boldsymbol{L}_{ij} \cdot \nabla \mu_i, \tag{13}$$

where $\boldsymbol{L}_{ij}$ are the local Onsager coefficients. These coefficients are symmetric, i.e., $\boldsymbol{L}_{ij} = \boldsymbol{L}_{ji}$, and are second rank tensors, because an inhomogeneous fluid is anisotropic. The local anisotropy derives from gradients in local density and so the most general form of $\boldsymbol{L}_{ij}$ is

$$\boldsymbol{L}_{ij} = L_{ij} \boldsymbol{I} + \sum_{k=1}^{\nu} L_{ijk} \nabla\nabla n_k + \sum_{k,l=1}^{\nu} L_{ijkl} \nabla n_k \nabla n_l, \tag{14}$$

where the coefficients L_{ij}, L_{ijk}, and L_{ijkl} are scalar functions of the density distributions. The coefficients do not depend on gradients of local flow velocities, since the theory herein is limited to first order in transport driving forces. In conventional applications of linear transport theory one assumes that the μ_i are the local equilibrium chemical potentials. We shall assume this to be true also when fluid microstructures are present in the system. As an example in a later section suggests, the local equilibrium hypothesis is probably more accurate in the region of a fluid microstructure, where strong forces of inhomogeneity (gradient contributions to the chemical potential) dominate, than in the bulk fluid where it is traditionally used.

The conservation condition $\Sigma_i \boldsymbol{J}_i = 0$ on diffusion fluxes implies the condition

$$\sum_i \mathrm{L}_{ij} = 0. \tag{15}$$

From this result and the symmetry of $\boldsymbol{L}_{ij}$ it follows that $\Sigma_j \boldsymbol{L}_{ij} \cdot \nabla \mu_l = 0$, and, consequently

$$\boldsymbol{J}_i = -\sum_j \boldsymbol{L}_{ij} \cdot \nabla(\mu_j - \mu_l). \tag{16}$$

This form is especially useful for strictly regular solutions ($v_i = v$, $i = 1, \ldots, \nu$), the binary case of which we shall study in subsequent sections.

To put the diffusion flux in a more revealing form, we introduce here the microstructure potential V_j of the jth component of the fluid. It is by definition

$$V_j \equiv \mu_j - \mu_j^o(\boldsymbol{n}) - u_j^e. \tag{17}$$

μ_j is the chemical potential of species J, $u_j^e(\boldsymbol{r})$ the external potential, and $\mu_j^o(\boldsymbol{n}(\boldsymbol{r}))$ the chemical potential of j in homogeneous fluid at composition $n_1(\boldsymbol{r}), \ldots, n_\nu(\boldsymbol{r})$.

For gradient theory

$$V_j = -\sum_k \nabla \cdot (c_{jk} \nabla n_k) + \sum_{k,l} \frac{1}{2} \frac{\partial c_{kl}}{\partial n_j} \nabla n_k \cdot \nabla n_l. \tag{18}$$

The microstructure potential gives rise to the unusual diffusion behavior in spinodal decomposition studied by Cahn (1965). Combining Eqs. 16 and 17, we obtain the basic transport equation for microstructured fluids:

$$\boldsymbol{J}_i = -\sum_k \boldsymbol{D}_{ij} \cdot \nabla n_j - \sum_j \boldsymbol{L}_{ij} \cdot \nabla(V_j + u_j^e), \tag{19}$$

where $\boldsymbol{D}_{ij}$ is the diffusion tensor defined by

$$\boldsymbol{D}_{ij} \equiv \sum_k \boldsymbol{L}_{ik} \frac{\partial \mu_k^o}{\nu n_j} \cdot \tag{20}$$

To apply Eq. 19,the Onsager coefficients L_{ij}, L_{ijk}, and L_{ijkl} must be known. This is not the case presently. However it is known that fluid diffusion and viscosity coefficients are dominated by short-range forces (Alder and Wainwright, 1970; Alder et al., 1974, Chen et al., 1981). From this fact, we believe a reasonable approximation to examine is to neglect L_{ijk} and L_{ijkl} and equate L_{ij} to $L_{ij}^{o}(\boldsymbol{n})$, the ij Onsager coefficient of homogeneous fluid at the local density $\boldsymbol{n}$. In the applications to follow we make this approximation, according to which

$$J_i = -D_{ij}^{o}\nabla n_j - \sum_j L_{ij}^{o}\nabla(V_j + u_j^e). \tag{21}$$

At this point one cannot rigorously go beyond this approximation, since there is presently no theory of transport coefficients in microstructured fluid. This is the approximation, incidentally, on which the theory of spinodal decomposition is based (Cahn, 1965).

In some works (Leal and Brenner, 1977; Brenner and Leal, 1978; Larson, 1982; Shaeiwitz and Raterman 1982) it has been assumed that the fluid microstructure potential V_j is some known function of position $\boldsymbol{r}$ and that it can be used to compute density distributions for a given transport situation. However, V_j is itself a functional of the component density distributions and as such will depend in general on temperature, pressure, and the boundary conditions of each problem. We shall return to this point later.

If the fluid is ionic, to V_j in Eq. 17 or 18 must be added the ionic contribution, an approximation to which has been suggested in the form (Davis and Scriven, 1981)

$$V_j^I \equiv z_j e\psi - \frac{1}{8\pi}\frac{\partial \epsilon^0}{\partial n_j}E^2. \tag{22}$$

The term $z_j e\psi$ is the energy to move a charge $z_j e$ from a voltage of zero to one equal to ψ; the other term is the energy of fluid electrostriction, ϵ^o being the dielectric constant of homogeneous fluid of local composition. The problem with this approximation is that, like the transport coefficients, the dielectric constant of inhomogeneous fluid is not known.

The gradient theoretical pressure tensor in equilibrium microstructures is of the form (Davis and Scriven, 1981)

$$\begin{aligned}\boldsymbol{P} = P_0(\boldsymbol{n})\boldsymbol{I} + \sum_{i,j} [l_{ij}^{(1)}\, n_i\nabla\nabla n_n j + l_{ij}^{(2)}\,(\nabla n_i)(\nabla n_j) \\ + l_{ij}^{(3)}\, n_i\nabla^2 n_j \boldsymbol{I} + {}_{ij}^{l(4)}\,(\nabla n_i)\cdot(\nabla n_j)\boldsymbol{I}],\end{aligned} \tag{23}$$

where $P_o(\boldsymbol{n})$ is the pressure of homogeneous fluid in the density state $\boldsymbol{n}$ and the $l_{ij}^{(\alpha)}$ are functions of the density state $\boldsymbol{n}$ that determine the magnitude of the density gradient contributions to the local pressure state. The general formulas for the $l_{ij}^{(\alpha)}$ are quite unwieldy (Davis and Scriven, 1981) and require for evaluation second-, third-, and fourth-order correlation functions, which are not available even for the simplest fluids. However, the form of the pressure tensor consistent with constant influence parameters is

$$\begin{aligned}\boldsymbol{P} = P_0(\boldsymbol{n})\mathbf{I} - \frac{1}{2}\sum_{i,j} c_{ij}\left\{\left[2[n_i\nabla\nabla n_j - \frac{1}{2}\nabla n_i\nabla n_j\right]\right. \\ \left. - \left[n_i\nabla^2 n_j - \frac{1}{2}(\nabla n_i)\cdot(\nabla n_j)\right]\boldsymbol{I}\right\}\cdot\end{aligned} \tag{24}$$

Until more reliable estimates of the $l_{ij}^{(\alpha)}$ become available, Eq. 24 is our preference for estimating the pressure tensor. Alternatively, structure models (Carey et al., 1978a, 1978b) can be used to estimate the $l_{ij}^{(\alpha)}$. To complete the transport theory of isothermal microstructured fluids we need the momentum balance equation:

$$\rho\frac{d\boldsymbol{v}}{dt} = -\nabla\cdot\boldsymbol{P} + \nabla\cdot\boldsymbol{\tau} + \sum_i m_i n_i \nabla u_i^e. \tag{25}$$

$\boldsymbol{v}$ is the local mass average velocity, ρ the local mass density, $\rho \equiv \sum_i m_i n_i$, and $\boldsymbol{\tau} - \boldsymbol{P}$ the local stress tensor. With the local equilibrium assumption $\boldsymbol{P}$ is the local microstructure pressure tensor given by Eq. 22 or 24 in gradient theory. According to linear transport theory of an anisotropic fluid,

$$\boldsymbol{\tau} = \boldsymbol{M}{:}\nabla\boldsymbol{v}, \tag{26}$$

where $\boldsymbol{M}$ is a fourth rank viscosity tensor and the two dots between $\boldsymbol{M}$ and $\nabla\boldsymbol{v}$ denote a double contraction. In general $\boldsymbol{M}$ has an isotropic part and additive terms proportional to the second- and fourth-order derivatives of the component densities $\nabla\nabla n_j$, $\nabla n_j\nabla n_k$, $\nabla n_j\nabla\nabla n_k, \ldots, \nabla n_j\nabla n_k\nabla n_l\nabla n_m$. In gradient theory, terms of higher than second-order in component density gradients are neglected. In this case $\boldsymbol{M}$ is of the form

$$\boldsymbol{M} = \boldsymbol{M}_I + \sum_{\kappa,\lambda,\nu,\mu} \hat{e}_\kappa\hat{e}_\lambda\hat{e}_\nu\hat{e}_\mu\left[\sum_i M_{\kappa\lambda\nu\mu}^{(i)}\frac{\partial^2 n_i}{\partial x_\nu\partial x_\mu} + \sum_{i,j} M_{\kappa\lambda\nu\mu}^{(ij)}\frac{\partial n_i\partial n_j}{\partial x_\nu\partial x_\mu}\right], \tag{27}$$

where $\boldsymbol{M}_I$ is an isotropic tensor functional and $M_{\kappa\lambda\nu\mu}^{(i)}$ and $M_{\kappa\lambda\nu\mu}^{(ij)}$ are scalar functionals of the component density distributions. $\hat{e}_\nu$ and x_ν are the unit vector and component of $\boldsymbol{r}$ in the νth direction.

Equation (27) brings us once more to the burning need for transport coefficients of microstructured fluids. For those wishing to exploit the theory presently, we agaion intuitively appeal to the dominant role that short-range forces play in the transport coefficients (alder et al., 1974) of Newtonian fluids and recommend that $\boldsymbol{M}$ be approximated by $\boldsymbol{M}_I^0$, the transport coefficients of homogeneous fluid at local composition. The result is

$$\boldsymbol{\tau}(\boldsymbol{r}) = \left[\lambda(\boldsymbol{n}(\boldsymbol{r})) - \frac{2}{3}\mu(\boldsymbol{n}(\boldsymbol{r}))\right]\boldsymbol{I}(\nabla\cdot\boldsymbol{v}) - \mu(\boldsymbol{n}(\boldsymbol{r}))[\nabla\boldsymbol{v} + (\nabla\boldsymbol{v})^T] \tag{28}$$

where $\nu(\boldsymbol{n})$ and $\mu(\boldsymbol{n})$ are the viscosity coefficients of homogeneous fluid at composition $\boldsymbol{n}$.

This completes the elements of the theory for isothermal processes. For nonisothermal processes, an energy balance equation must be added. In the remainder of the paper, we shall discuss a few simple questions regarding diffusion at planar interfaces.

EQUILIBRIUM PLANAR INTERFACE OF A BINARY REGULAR SOLUTION

We consider a binary regular solution in which $v_1^{-1} = v_2^{-1} = n$ = constant. Thus, this is a solution model with a density constraint, and the mole fraction $\phi_1(\equiv n_1/n)$ of component 1 is the only independent compositional variable. The chemical potentials of the model are (Prigogine and Defay, 1965)

$$\mu_1^0(\phi_1) = w(1-\phi_1)^2 + kT\ln\phi_1 \tag{29}$$

and

$$\mu_2^0(\phi_1) = w\phi_1^2 + kT\ln(1-\phi_1), \tag{30}$$

where w is a characteristic energy parameter. The bulk compositions ϕ_1^α and ϕ_1^β of coexisting phases α and β are determined by the equilibrium conditions

$$\mu_1^0(\phi_1^\alpha) = \mu_1^0(\phi_1^\beta), \quad \mu_2^0(\phi_1^\alpha) = \mu_2^0(\phi_1^\beta), \tag{31}$$

from which it follows that

$$\ln[\phi_1^\alpha/(1-\phi_1^\alpha)] = (w/kT)(1-2\phi_1^\alpha), \tag{32}$$

$\phi_1^\beta = 1 - \phi_1^\alpha$. This equation has a two-phase solution for any temperature T below the critical point $T_c = w/2k$. The temperature-composition phase diagram of the binary regular solution given in Figure 1.

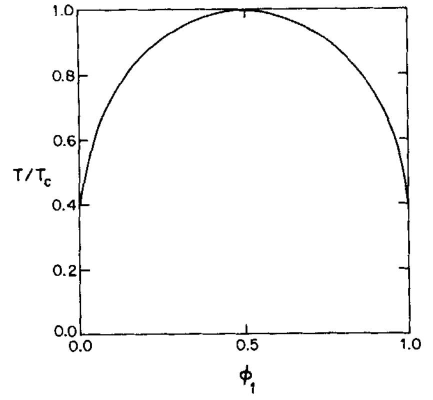

Figure 1. Temperature-composition phase diagram of a binary regular solution.

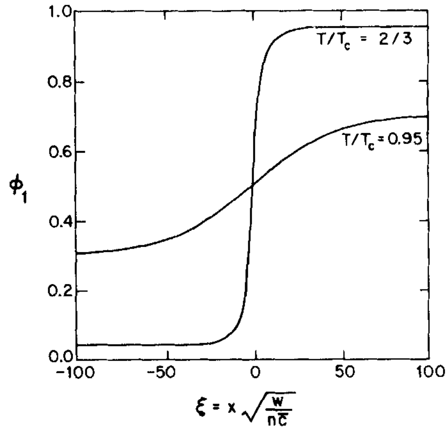

Figure 2. Interfacial composition profiles for component 1 of a binary regular solution at equilibrium for two reduced temperatures, 2/3 and 0.95.

We assume $u_i^e = 0$ and that the c_{ij} are constant. Eq. 8 then becomes

$$\mu_1 - \mu_2 = \mu_1^0(\phi_1) - \mu_2^0(\phi_1) - n\tilde{c}\frac{d^2\phi_1}{dx^2} \tag{33}$$

where

$$\tilde{c} \equiv c_{11} + c_{22} - 2c_{12}. \tag{34}$$

The mole fraction profile $\phi_1(x)$ in the planar interfacial zone is found by solving Eq. 33 subject to the boundary conditions $\phi_1 \rightarrow \phi_1^\alpha$ as $x \rightarrow -\infty$ and $\phi_1 \rightarrow \phi_1^\beta$ as $x \rightarrow \infty$. Equation 33 can be solved by quadrature. The result is

$$x = \sqrt{\frac{n\tilde{c}}{2}} \int_{\phi_1(0)}^{\phi_1(x)} \frac{d\phi_1}{\sqrt{\Delta\omega(\phi_1)}}, \tag{35}$$

where

$$\Delta\omega(\phi) = \phi_1[\mu_1^0(\phi_1^\alpha) - \mu_1^0(\phi_1)] + (1 - \phi_1)[\mu_2^0(\phi_1^\alpha) - \mu_2^0(\phi_1)]. \tag{36}$$

For convenience, we have assumed $\phi_1^\alpha < \phi_1^\beta$ and picked the origin of the coordinate system inside the interfacial zone. Since interfacial zones are only tens or hundreds of angstroms wide except near a critical point, $\nabla_1(x)$ will be approximately equal to ϕ_1^β at quite small values of x. This is illustrated by the predicted profiles in Figure 2. The origin of the coordinate system is placed at the midpoint composition, $\phi_1(x = 0) = 1/2\ (\phi_1^\alpha + \phi_1^\beta) = \underline{1/2}$. The interfacial width is of the order of a few multiples of $\sqrt{\tilde{c}/w}$, even within 5% of the critical temperature. As the quantity $\sqrt{\tilde{c}/w}$ is of the order of a molecular diameter, it is clear that interfacial widths are no more than a few hundred angstroms except very near the critical point [sufficiently near the critical point the interfacial width becomes infinitely wide according to the asymptotic formula (Fisk and Widom, 1969; Huang and Webb, 1969)], $l = l_o/|1 - T/T_c|^{0.62}$, l_o a length parameter of the order of a molecular diameter).

STEADY DIFFUSION ACROSS A PLANAR INTERFACE: BINARY REGULAR SOLUTION RESULTS

We are now prepared to examine the effect of diffusion on the interfacial composition profiles. Detailed results are presented for steady diffusion in a binary regular solution, but guided by these results we can draw some rather general conclusions concerning diffusion across interfaces. We shall examine steady equimolar diffusion in which $v^m = 0$, J_1 is constant, and so

$$J_1 = L_{12}\frac{d}{dx}(\mu_1 - \mu_2) \tag{37}$$

To the order in composition gradients kept in gradient theory

$$L_{12}^N = L_{12}^o + A\left(\frac{d\phi_1}{dx}\right)^2 + B\frac{d^2\phi_1}{dx^2}, \tag{38}$$

when L_{12}^o, A and B are functions of $\phi_1(x)$. From purely dimensional considerations it follows that A and B re of order $L_{12}^o l^2$, where l is a molecular correlation length. This is all one can really claim at this point, since there is no theory for these quantities. Thus, further assumptions must be made in order to proceed. The simplest assumption is that the terms involving A and B are negligible (an assumption that we argued in an earlier section is supported by the fact that the diffusion coefficient is determined primarily by short-range forces) and that L_{12}^o is constant. Generally L_{12}^o will not be constant. However, putting realistic concentration dependence in L_{12}^o would merely add mathematical difficulty without changing the qualitative results. In what follows, we examine in some detail the implications of Eq. 37 with constant L_{12}^N. Then, from insights gained from these implications, we argue that a more realistic approximation to Eq. 38 will lead to similar conclusions. With constant J_1 and L_{12}, Eq. 37 integrates immediately to

$$\mu_1 - \mu_2 = \frac{J_1 x}{L_{12}} + K, \tag{39}$$

which with Eq. 33 yields the following profile equation:

$$n\tilde{c}\frac{d^2\phi_1}{dx^2} = \mu_1^o(\phi_1) - \mu_2^o(\phi_1) - \frac{J_1 x}{L_{12}} + K. \tag{40}$$

Outside the interfacial zone, the derivative $d\phi/dx$ of the mole fraction is of the order of ϕ_1/L (where L is the macroscopic dimension of the system in the x direction) and therefore the term $n\tilde{c}d^2\phi_1/dx^2$ is of the order of $(n\tilde{c}/L^2)\phi_1$, a completely negligible term in Eq. 39 compared to μ_i^o because $n\tilde{c}$ is of the order of kT times the square of the range of intermolecular potential. Thus, outside of the interfacial zone the composition profile is determined by the equation

$$0 = \mu_1^o(\phi) - \mu_2^o(\phi) - \frac{J_1 x}{L_{12}} + K, \tag{41}$$

whereas in the interfacial zone Eq. 40 must be solved.

If we consider situations in which $\phi_1(x) < \phi_1^\alpha(\phi_1^\alpha$ being the mole fraction in equilibrium coexisting phase α, Eq. 32), to the left of the interfacial zone and in which $\phi_1(x)$ increases with x, then $\phi_1(x)$

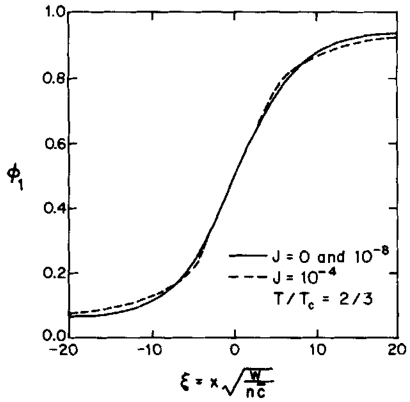

Figure 3. Interfacial composition profiles for component 1 of a binary regular solution with steady, dimensionless diffusive fluxes of 0 (equilibrium), 10^{-8} (normal), and 10^{-4} (extremely large) at a reduced temperature of 2/3.

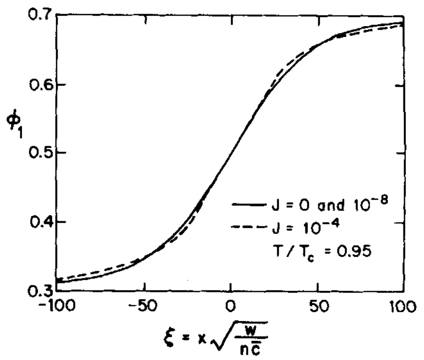

Figure 4. Interfacial composition profiles 1 of a binary regular solution with steady, dimensionless diffusive fluxes of 0 (equilibrium), 10^{-8} (normal), and 10^{-4} (extremely large) at a reduced temperature of 0.95.

has to pass through the value ϕ_1^α at some point. We place the origin of the coordinate system at this point, i.e., $\phi_1(x = 0) = \phi_1^\alpha$. Computing K from Eq. 40 at $\phi_1 = \phi_1^\alpha$ and substituting the result into Eq. 39, we get

$$n\tilde{c}\frac{d^2\phi_1}{dx^2} = \mu_1^o(\phi_1) - \mu_1^o(\phi_1^\alpha) - \mu_2^o(\phi_1) + \mu_2^o(\phi_1^\alpha) - \frac{J_1 x}{L_{12}}. \quad (42)$$

With the dimensionless variables

$$\xi = x\sqrt{w/n\tilde{c}}, \quad J = \frac{J_1\sqrt{n\tilde{c}/w}}{L_{12}w} \quad (43)$$

and the regular solution formulas for μ_1^o and μ_2^o, Eq. 42 becomes

$$\frac{d^2\phi_1}{d\xi^2} = \phi_1^\alpha - \phi_1 + \frac{T}{2T_c}\ln\left[\frac{\phi_1(1-\phi_1^\alpha)}{\phi_1^\alpha(1-\alpha_1)}\right] - J\xi \quad (44)$$

We have solved Eq. 44 numerically by finite differences with the boundary conditions

$$\phi_1(x=0) = \phi_1^\alpha \left.\frac{d\phi_1}{dx}\right|_{x=0} = \frac{(J_1/L_{12})}{\left\{\frac{\partial}{\partial\phi_1}[\mu_1^o(\phi_1) - \mu_2^o(\phi_1)]\right\}} \quad (45)$$

Results for the temperatures $T/T_c = 2/3$ and $T/T_c = 0.95$ are shown in Figures 3 and 4 for a moderate flux condition, $J = 10^{-8}$, and an extremely large flux condition, $J = 10^{-4}$. Note that the origin has been shifted in order to compare more easily the diffusion profiles with the equilibrium profiles. The results are presented in dimensionless form, requiring assignment of values of the parameters of the model. For this purpose we have estimated L_{12} from $L_{12} \simeq nD/2kT$, with the liquidlike data $n = 10^{22}$ molecule/cm^3, $D = 10^{-5}$ cm^2/s, $2kT = 10^{-13}$ erg/molecule. This yields $L_{12} = 10^{30}$ s/cm^{3}g. A moderate flux for this system would be $J = nD/L$ with $L = 10$ cm, which gives $J_i = 10^{16}$ molecules/cm^2·s. Finally, we set $w = 2kT_c = 10^{-13}$ erg/molecule and $\sqrt{n\tilde{c}/w} = 10^{-7}$ cm, values appropriate for small molecule fluids, and estimate a moderate dimensionless flux to be $J = 10^{-8}$.

At the moderate flux level the composition profiles in the interfacial zone are indistinguishable from the equilibrium profiles; and they differ very little from the equilibrium profiles even at the unrealistically high flux level (Figures 3 and 4). This result, which arises from the fact that $J\xi$ is extremely small for ξ of the order of the width of the interfacial zone, justifies the assumption of equilibrium partitioning across an interface that is usually made in analysis of mass transfer across the interfaces.

STEADY DIFFUSION ACROSS A PLANAR INTERFACE: GENERAL RESULTS

From studying a binary regular solution, we have found that interfacial composition profiles vary little from equilibrium when diffusive fluxes are present. The general validity of this conclusion follows from dimensional analysis of the gradient theoretical equations. We rewrite the planar flux equation in terms of the dimensionless variables $\tilde{c}_{ij} \equiv c_{ij}/c_R$, $\tilde{u}_i \equiv \mu_i/kT$, $\tilde{L}_{ij} \equiv L_{ij}/L_R$, and $\tilde{n}_i \equiv n_i v_R$, where v_R, c_R, and L_R are the molecular volume, influence parameter, and Onsager coefficient of a reerence system:

$$\sum_j \tilde{L}_{ij}\frac{d}{dx}\left\{\tilde{u}_j^o - \frac{c_R}{v_R kT}\left[\sum_k \frac{d}{dx}\left(c_{jk}\frac{d\tilde{n}_k}{dx}\right) - \frac{1}{2}\sum_{k,l}\frac{\partial\tilde{c}_{kl}}{\partial n_j}\frac{d\tilde{n}_k}{dx}\frac{d\tilde{n}_l}{dx}\right]\right. = -\frac{J_i}{L_R kT}. \quad (46)$$

If the convection velocity is not zero, then J_i must be replaced by $J_i + n_i v_x$ and the steady state version of Eq. 21 must be solved along with Eq. 46. For zero Reynolds number one-dimensional flow, Eq. 46 becomes P_N = constant, where P_N is the component of P normal to the interface.) In the "bulk region" outside the interfacial zone, the quantity $d\tilde{n}_i/dx$ is of the order of L^{-1}, L being the length of the system in the direction of diffusion. Thus, in the bulk region the microstructure potential terms in Eq. 46 are of order $c_R/(L^2 v_R kT)$. Since $l_m \equiv \sqrt{c_R/v_R kT}$ is a microscopic length of the order of magnitude a molecular diameter, the microstructure potential terms are totally negligible ($\sim O(l_m/L)^2$) compared to $\tilde{\mu}_j^o$. So, in the bulk region, the appropriate diffusion equation is

$$\sum_j L_{ij}\frac{d}{dx}\mu_j^o(n) = -J_i. \quad (47)$$

On the other hand, inside the interfacial region, $d\tilde{n}_i/d\xi$ is of the order of unity, where $\xi \equiv x/\sqrt{c_R/v_R kT}$. Equation 46 can be expressed in the form

$$\sum_j \tilde{L}_{ij}\frac{d}{d\xi}\left[\mu_j^o - \sum_k \frac{d}{d\xi}\left(c_{jk}\frac{d\tilde{n}_k}{d\xi}\right) + \frac{1}{2}\sum_{k,l}\frac{\partial\tilde{c}_{kl}}{\partial n_j}\frac{d\tilde{n}_k}{d\xi}\frac{d\tilde{n}_l}{d\xi}\right] = -J_i, \quad (48)$$

where $\tilde{J}_i \equiv (J_i\sqrt{c_R/v_R kT})/L_R kT$. The range of ξ across the interface is of the order of 10, and for physically realistic fluxes J_i is of the order of 10^{-8}. Thus, the quantity $J_i\xi$ is negligible for the change of ξ across the interface, from which it follows that

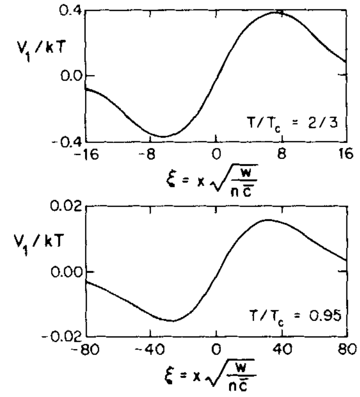

Figure 5. Microstructure potentials for a binary regular solution with a steady, dimensionless diffusive flux of 10^{-8} at two reduced temperatures, 2/3 and 0.95.

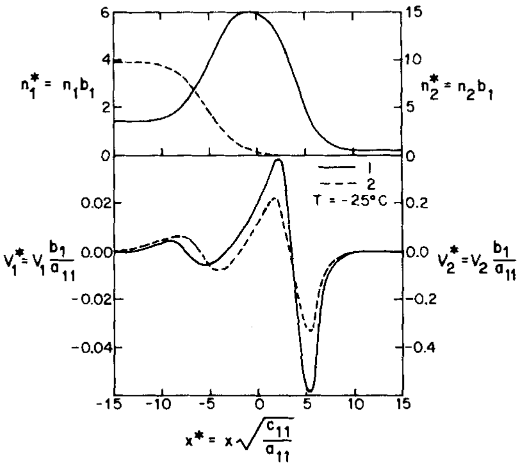

Figure 7. Dimensionless microstructure potentials for a Peng-Robinson CO₂ (component 1)-decane (component 2) fluid at −25°C.

$$\mu_j = \mu_j^o(\boldsymbol{n}) - \sum \frac{d}{dx}\left(c_{jk}\frac{dn_k}{dx}\right) + \frac{1}{2}\sum_{k,l}\frac{\partial c_{kl}}{\partial n_j}\frac{dn_k}{dx}\frac{dn_l}{dx} = \text{constant} \quad (49)$$

in the interfacial zone. As this is the equation for an equilibrium interface, it completes the proof that it is a good approximation to assume that the component density distributions across a planar interface are those of an equilibrium interface even in the presence of steady diffusion. From the dimensional analysis upon which this assertion is based, it will also be valid for curved interfaces if the radii of curvature are large compared to the interfacial width. It will also hold in transient problems when the composition changes in bulk are slow compared to molecular rearrangement in the interfacial zone. This will usually be the case because the interfacial width is so small compared to the length of the system.

A convenient way to find the component density profiles in the presence of an interface is to solve Eq. 47 in the regions $x_\alpha < x < 0$ and $0 < x < x_\beta$ using given compositions and fluxes at the ends x_α and x_β. On the macroscopic scale the interface is located at $x = 0$ and the component densities $\boldsymbol{n}^\alpha$ and $\boldsymbol{n}^\beta$ at $x = 0-$ and $x = 0+$, respectively. $\boldsymbol{n}^\alpha$ and $\boldsymbol{n}^\beta$ are determined by the chemical equilibrium conditions

$$\mu_i^o(\boldsymbol{n}^\alpha) = \mu_i^o(\boldsymbol{n}^\beta), \quad i = 1, \ldots, \nu \quad (50)$$

and the mechanical equilibrium condition

$$P_o(\boldsymbol{n}^\alpha) = P_o(\boldsymbol{n}^\beta) = P_N. \quad (51)$$

This condition is to be added to Eq. 50 follows from dimensional analysis of the momentum balance equation. The mechanical equilibrium condition is not enforced by the density-constraint solution models described earlier. The interface is, of course, not located by the conditions given at the boundaries. An iterative procedure will be necessary to establish the position of the interface and to find the equilibrium solution, $\boldsymbol{n}^\alpha$ and $\boldsymbol{n}^\beta$, to Eq. 50 that are consistent with the boundary conditions and the mass of each component present. Once a consistent solution to Eqs. 47 and 50 has been found, the interfacial component density profiles can be found by solving Eq. 48 for an interface with limiting compositions $\boldsymbol{n}^\alpha$ and $\boldsymbol{n}^\beta$ on sides α and β. Since J_i is so small for realistic fluxes, the composition profiles in the interfacial zone will differ very little from those obtained by solving the equilibrium equation, Eq. 49, with the boundary conditions $\boldsymbol{n} = \boldsymbol{n}^\alpha$ and $\boldsymbol{n}^\beta$ far from the interface. The truth of this claim is exemplified by the computations reported in Figures 2–4 for a binary regular solution.

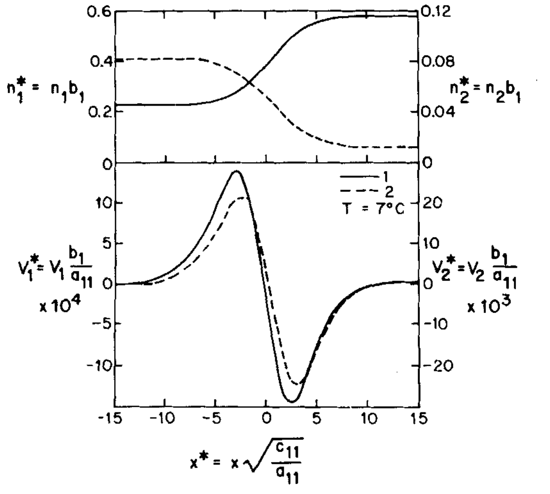

Figure 6. Dimensionless microstructure potentials for a Peng-Robinson CO₂ (component 1)-decane (component 2) fluid at 7°C.

MICROSTRUCTURE POTENTIALS

According to the arguments given above, the microstructure potential V_j, Eq. 17 of a planar interface is well approximated by

$$V_j \approx \mu_j^o(\boldsymbol{n}^\alpha) - \mu_j^o[\boldsymbol{n}(x)] \quad (52)$$

where $\boldsymbol{n}(x)$ is determined by solving Eq. 33 with the boundary conditions $\boldsymbol{n}(x) \to \boldsymbol{n}^\alpha$ as $x \to -\infty$ and $\boldsymbol{n}(x) \to \boldsymbol{n}^\beta$ as $x \to \infty$, $\boldsymbol{n}^\alpha$ and $\boldsymbol{n}^\beta$ being the solution of Eqs. 50 and 51 consistent with Eq. 47 and the boundary conditions of the problem. For the binary regular solution considered above the steady flux equation is

$$J_1 = -D_{12}\frac{d\phi_1}{dx} - L_{12}\frac{dV_1}{dx}, \quad (53)$$

where

$$D_{12} \equiv L_{12} \frac{d}{d\phi_1} [\mu_1^0(\phi_1) - \mu_2^0(\theta_1)] \tag{54}$$

and

$$V_1 \equiv \tilde{c} \frac{d^2\phi_1}{dx^2}$$

$$\simeq \mu_1^0(\phi_1^\alpha) - \mu_1^0[\phi_1(x)] - \mu_2^0(\phi_1^\alpha) + \mu_2^0[\theta_1(x)]. \tag{55}$$

In Figure 5, the microstructure potential is plotted vs. position in the interface for a regular solution under the moderate flux conditions of Figures 3 and 4. The actual potential ($V_1 \equiv \tilde{c}d^2\phi_1/dx^2$ with $\phi_1(x)$ computed from the solution of Eq. 42) is indistinguishable from the approximate potential ($V_1 = \mu_1^0(\phi_1^\alpha) - \mu_1^0(\mathrm{x})) - \mu_2^0(\phi_1^\alpha) + \mu_2^0(\phi_1(x))$) with $\phi_1(x)$ computed from the equilibrium expression Eq. 35), a result verifying the validity of Eq. 52 (or its equivalent for density-constrained solutions).

As a more interesting example, the microstructure potentials V_1 and V_2 are shown in Figures 6 and 7 for a Peng-Robinson fluid of component whose parameters b_i and a_{ij} were adjusted to mimic the CO_2-decane system (Falls et al., 1982). Also plotted are the corresponding density profiles at the two temperatures studied. The equation of state of a homogeneous Peng-Robinson fluid is (Peng and Robinson 1976)

$$P_0 = \frac{nkT}{1 - nb} - n^2a, \tag{56}$$

where $a = \Sigma_{i,j}n_in_ja_{ij}/n^2$ and $b = \Sigma_jn_jb_i/n$. Different curves of V_i vs. interfacial position result for each interfacial boundary set $\boldsymbol{n}^\alpha$ and $\boldsymbol{n}^\beta$ of component densities. The particular set $\boldsymbol{n}^\alpha$ and $\boldsymbol{n}^\beta$ will be determined by the diffusion boundary conditions, but it will correspond approximately to an equilibrium set obeying Eqs. 50 and 51. All of these examples are also a significant dependence of the microstructural potential upon temperature. Thus, although $V_j(x)$ is not a true potential, since it depends on temperature and boundary conditions, all its patterns of behavior for a given set of components can be deduced from the interfacial profiles of all possible pairs of equilibrium phases formed by the set of components. The shape of the V_j vs. x curve is governed by the topography of the homogeneous fluid free energy density $f_o(\boldsymbol{n})$ in component density space. The more the undulations of $f_o(\boldsymbol{n})$ along the interfacial composition path, the more the undulations of one or more of the V_j vs. x curves.

In viewing the complexity of the potential profile that may arise in situations such as Figure 7, one sees the practical difficulty in any attempt to represent the interfacial region by a potential. One cannot determine this potential in advance without a complete calculation of the interface component density profiles at the temperature of interest. In fact, the interfacial density profile must be determined via the methods we have described here (or closely related ones) in order to treat interfacial transport phenomena satisfactorily.

CONCLUDING REMARKS

The theory presented in this article is, as it stands, really on a basic framework for a wide range of potential applications to situations of chemical engineering interest. Examples of problems to which it is being applied currently at Minnesota include polymers in porous media and the dynamics of wetting of solids by liquids. There is much room also for systematic improvements in the theory, such as in the treatment of the transport coefficients themselves in the interfacial regions.

Given a microstructure potential, the Brenner and Leal work (1978) is a useful micromechanical model for the motion of a spherical body in an interfacial region. Our criticism here is simply of the treatment of an interfacial zone as a sharp surface with a known microstructure potential.

ACKNOWLEDGMENT

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NOTATION

a = parameter in Peng-Robinson fluid $a = \Sigma_{i,j}n_in_ja_{ij}/n^2$
b = parameter in Peng-Robinson fluid $b = \Sigma_jn_jb_i/n$
c_{ij} = influence parameters of inhomogeneous fluid
$\tilde{c}_{ij}$ = dimensionless influence parameter $\tilde{c}_{ij} = c_{ij}/c_R$
$C_{ij}^o(s;\boldsymbol{n})$ = direct correlation function of homogeneous fluid in the density state $\boldsymbol{n}$
c_R = influence parameter of reference system
$\tilde{c}$ = combined influence parameter for binary regular solution $\tilde{c} = c_{11} - 2c_{12} + c_{22}$
D_{ij} = diffusion tensor
e = unit electronic charge
$\hat{e}_k$ = unit vector in direction k
$\boldsymbol{E}$ = local electric field
F = Helmholtz free energy
$f_o(n)$ = Helmholtz free energy density of homogeneous fluid in the density state $\boldsymbol{n}$
$g_{ij}^o(s;n)$ = pair correlation function of homogeneous fluid in the density state $\boldsymbol{n}$
$\boldsymbol{I}$ = unit tensor
J = dimensionless diffusion flux
J_i = molar diffusion flux of species i
$\tilde{J}_i$ = dimensionless diffusion flux of species i, $\tilde{J}_i = (J_i\sqrt{c_R/v_RkT})/L_RkT$
k = Boltzmann's constant
K = constant of integration
l = measure of interfacial width
$l_{ij}^{(\alpha)}$ = function of density state $\boldsymbol{n}$
l_m = microscopic length of the order of magnitude of a molecular diameter
l_o = length parameter of order of molecular diameter
L = macroscopic dimension of the system in direction of diffusion
L_R = Onsager coefficient of reference system
$\boldsymbol{L}_{ij}$ = local Onsager coefficients
L_{ijk} = scalar functional of the density distributions
L_{ijkl} = scalar functional of the density distributions
$L_{ij}^o(n)$ = local Onsager coefficient of homogeneous fluid in density state n
$\tilde{L}_{ij}$ = dimensionless Onsager coefficient $\tilde{L}_{ij} = \tilde{L}_{ij}/L_R$
L_{12}^N = constant
m_i = molecular mass of species i
$\boldsymbol{M}$ = fourth rank viscosity tensor
$\boldsymbol{M}_I$ = isotropic tensor functional
$\boldsymbol{n}$ = set of local component densities $(n_1, \ldots, n_\nu)$
$\boldsymbol{n}^\alpha$ = set of density components in phase α in equilibrium with phase β
$\boldsymbol{n}^\beta$ = set of density components in phase β in equilibrium with phase α
$\tilde{n}_i$ = dimensionless density of component i, $\tilde{n}_i = n_iv_R$
N_i = total number of species i particles in the system
$\boldsymbol{P}$ = pressure tensor
P_N = component of pressure tensor normal to interface
$P_o(n)$ = pressure of homogeneous fluid in density state $\boldsymbol{n}$

$\mathbf{r}$ = position in the fluid
r_{ij} = range of intermolecular force between i and j
s = distance between interacting pairs
s' = distance between interacting pairs
t = time t
T = absolute temperature
T_c = critical point
u_i^e = external potential energy on species i
u_{ij} = characteristic interaction energy between i and j
$\mathbf{v}$ = local mass average velocity
$\mathbf{v}^m$ = local molar velocity
v_i = molecular volume parameter of species i
v_R = molecular volume of reference system
v_x = velocity in direction x
V_j^I = approximation to the microstructure potential of species in ionic fluid
V_j = microstructure potential of species i
w = characteristic energy parameter of binary regular solution
x = position variable in one-dimensional problem
x_k = component of $\mathbf{r}$ in direction k
z_i = valence of species i

Greek Letters

δn_j = correction to the density due to inhomogenity
$\Delta\omega(\phi)$ = function of binary regular solution composition
$\epsilon^0(n)$ = dielectric constant of homogeneous fluid in density state n
λ = Lagrange multiplier for constant system volume
$\lambda(n)$ = viscosity coefficient of homogeneous fluid in density state n
μ_i = chemical potential of species i
$\mu_j^0(n)$ = chemical potential of species j in homogeneous fluid in density state n
$\mu(n)$ = viscosity coefficient of homogeneous fluid in density state n
ν = number of system species
ξ = dimensionless position variable
ρ = local mass density
$\boldsymbol{\tau}$ = local viscosity stress tensor
ϕ_i = mole fraction of species i
ϕ_i^α = composition of species i in phase α of binary regular solution in equilibrium with phase β
ϕ_i^β = composition of species i in phase β of binary regular solution in equilibrium with phase α
ψ = local voltage
Ω = equilibrium grand potential

LITERATURE CITED

Alder, B. J., and J. E. Wainwright, "Decay of the Velocity Autocorrelation Function," *Phys. Rev.*, **A1**, 18 (1970).

Alder, B. J., W. E. Alley, and J. H. Dymond, "Studies in Molecular Dynamics. XIV. Mass and Size Dependence of the Binary Coefficient," *J. Chem. Phys.*, **61**, 1,415 (1974).

Benner, R., L. E. Scriven, and H. T. Davis, "Structure and Stress in the Gas-Liquid-Solid Contact Region," Chemical Society II, Faraday Div. (Royal Soc. Chem. Faraday Symp. No. 16, Oxford Univ. (Dec., 1981).

Bongiorno, V., and H. T. Davis, "Molecular Theory of Fluid Interfaces," *Phys. Rev.*, **A12**, 2,213 (1975).

Bongiorno, V., L. E. Scriven, and H. T. Davis, "Molecular Theory of Fluid Interfaces," *J. Colloid Interface Sci.*, **57**, 462 (1976).

Brenner, H., and Lea, L. G., "Interfacial Resistance to Interphase Mass Transfer in Quiescent Two-Phase Systems," *AIChE J.*, **24**, 246 (1978).

Cahn, J. W., "Phase Separation by Spinodal Decomposition in Isotropic Systems," *J. Chem. Phys.*, **42**, 93 (1965).

Carey, B. S., L. E. Scriven, and H. T. Davis, "Semiempirical Theory of Surface Tensions of Pure Normal Alkanes and Alcohols," *AIChE J.*, **24**, 1,076 (1978a).

———, "On Gradient Theory of Interfacial Stress and Structure," *J. Chem. Phys.*, **69**, 5,040 (1978b).

Chen, S.-H., H. T. Davis, and D. F. Evans, "Tracer Diffusion in Polyatomic Liquids. II," *J. Chem. Phys.*, **75**, 1,422 (1981).

Davis, H. T., and L. E. Scriven, "Stress and Structure in Fluid Interfaces," *Adv. Chem. Phys.*, **49**, 357 (1981).

———, "Gradient Theory of Fluid Microstructures," *J. Stat. Phys.*, **24**, 243 (1981).

de Groot, S. R., and P. Mazur, *Non-Equilibrium Thermodynamics*, North-Holland, Amsterdam (1962).

Falls, A. H., L. E. Scriven, and H. T. Davis. "Adsorption, Structure, and Stress in Binary Interfaces," *J. Chem. Phys.*, **78**, 7,300 (1983).

Fisk, S., and B. Widom, "Structure and Free Energy of the Interface Between Fluid Phases in Equilibrium Near the Critical Point," *J. Chem. Phys.*, *fb50*, 3,219 (1969).

Fleming, P. D., III, A. J. M.Yang, and J. H. Gibbs, "A Molecular Theory of Interfacial Phenomena in Multicomponent Systems," *J. Chem. Phys.*, **65**, 7 (1976).

Huang, J. S. and W. W. Webb, "Diffuse Interface in Critical Fluid Mixtures," *J. Chem. Phys.*, **50**, 3,677 (1969).

Kerins, J., H. T. Davis, and L. E. Scriven, "Correlation Functions in Metastable Fluid," *AIChE J.* (to be submitted, 1984).

Klein, J., and P. Pincus, "Interaction Between Surfaces with Adsorbed Polymer: Poor Solvents," *Macromolecules*, **15**, 1,1129 (1982).

Larson, R. S., "Generalized Expressions for Interfacial Resistances to Mass Transfer: Two-Phase Systems," *J. Colloid Interface Sci.*, **88**, 487 (1982).

Leal, L. G., and H. Brenner, "Micromechanical Models for Interfacial Transport Phenomena," in *Physiochemical Hydrodynamics*, D. B. Spalding, Ed., Advance Publ., **II**, (1977).

March, N., *Atomic Dynamics in Liquids*, Wiley, New York (1976).

McCoy, B. F., and H. T. Davis, "Free Energy of Inhomogeneous Fluids," *Phys. Rev.*, **A20**, 120 (1978).

Nakanishi, H., and P. Pincus, "Surface Spinodals and Extended Wetting in Fluids and Polymer Solutions," *J. Chem. Phys.*, **79**, 997 (1983).

Ornstein, L. S., and F. Zernike, "Accidental Deviations of Denisty and Opalescence at the Critical Point of a Single Substance," *Proc. Acad. Sci. Amsterdam*, **17**, 793 (1914).

Peng, D. Y., and D. B. Robinson, "A New Two-Constant Equation of State," *Ind. Eng. Chem. Fund.*, **15**, 59 (1976).

Poser, C. I., and I. C. Sanchez, "Interfacial Tension Theory of Low and High Molecular Weight Liquid Mixtures," *Macromolecules*, **14**, 361 (1981).

Prigogine, I., and R. Defay, *Chemical Thermodynamics*, Longmans, Green, London (1965).

Rowlinson, J. S., "Translation of J. D. van der Waals' 'The Thermodynamic Theory of Capillarity Under the Hypothesis of a Continuous Variation of Density,'" *J. Stat. Phys.*, **20**, 197 (1979).

Sahimi, M., L. E. Scriven, and H. T. Davis. "Thermodynamic Modeling of Phase and Tension Behavior of Carbon Dioxide and Hydrocarbon Systems," *SPE Reprint 10,268*, AIME SPE Meet., San Antonio (Oct., 1981).

Shaeiwitz, J. A., and K. T. Raterman, "Modeling and Calculation of Interfacial Resistances with Energy Profiles," *IEC Fund.*, **21**, 154 (1982).

Teletzke, G. F., L. E. Scriven, and H. T. Davis, "How Liquids Spread on Solids," *J. Colloid Interface Sci.* (to appear).

———, "Patterns of Wetting Behavior in Multicomponent Systems," *SPE Reprint 10,112*, AIME SPE Meet., San Antonio (Oct. 1981).

Treybal, R. E., *Mass Transfer Operations*, 3rd ed., McGraw-Hill, New York (1980).

Yang, A. J. M., P. D. Fleming III, and J. H. Gibbs, "Molecular Theory of Surface Tension," *J. Chem. Phys.*, **64**, 3,732 (1976).

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