Diffusion-Limited Growth of Wetting Layers

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In binary liquid mixtures, the growth of wetting layers can be limited by diffusion. At complete wetting, the distance l between the interfaces bounding the layer is shown to grow as $l(t) \approx A_* t^\theta$ for large times t where A_* increases near the consolute point. In three dimensions where this growth behavior should be accessible to experiments, $\theta = \frac{1}{8}$ and $\frac{1}{10}$ for nonretarded and retarded van der Waals forces, respectively. The interfacial motion resulting from diffusion-limited growth is studied for general interactions, and a planar interface is found to be stable for $\theta < \frac{1}{2}$.

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Let us consider a binary mixture of two liquids A and B in contact with a third phase which we will take to be a solid wall. Below the temperature T_c of the consolute point of the mixture,[1] an A-rich phase, α, can coexist with a B-rich phase, β. One of those phases, say β, may completely wet the wall.[2] In thermal equilibrium at or near $\alpha\beta$ coexistence, a wetting layer of the β phase intrudes between the bulk phase α of the mixture and the solid. During the growth of such a wetting layer, the region of α phase adjacent to the layer becomes depleted of B molecules. If there is no flow or convection, further growth of the wetting layer can occur only by diffusion of B molecules through the depleted region. Such diffusion-limited growth will be studied here. As shown below, the corresponding motion of the $\alpha\beta$ interface bounding the layer is rather slow.

The dynamics of interfaces resulting from diffusion-limited growth has been studied previously in various contexts such as precipitation,[3] crystal growth,[4] and aggregation.[5] Here, we investigate the *effect of interactions on the interfacial dynamics.* In the context of wetting, the two interfaces bounding the layer can interact by direct microscopic or by fluctuation-induced forces. Our approach is, however, more general and applies to the interfacial motion in any interface potential [see (8) and (14) below].

Let us assume that the binary mixture is initially in the one-phase region with an equilibrium composition (= fraction of B molecules) $X = X_\alpha$ corresponding to the A-rich phase α. In such a situation, there is no wetting layer of the β phase or only a thin one consisting of a few atomic layers. Then, suppose that the mixture is quenched by a change of pressure or temperature to reach the boundary of the two-phase region at temperature $T = T_*(X_\alpha)$. Since the β phase is assumed to wet the solid wall completely, the equilibrium thickness of the wetting layer is macroscopic. After the quench, the wetting layer thickens continuously. In fluids, the thermal diffusivity is usually large compared to the chemical diffusivity, and the thickening of the wetting layer is limited by mass transport. The early stages of this process are presumably governed by microscopic kinetics which are outside the scope of this paper. Here, we are concerned with the later stages of this thickening when initial transients have died out and the layer thickness is already large compared to the bulk correlation length. We find that, for nonretarded van der Waals interactions between the molecules, these later stages are characterized by the growth law

$$l(t) \approx A_* t^{1/8}, \quad T = T_*, \tag{1}$$

for the layer thickness l as a function of time t. An explicit expression for A_* [see (11) below] leads to the rough estimate $A_* \simeq 10$ nm/sec$^{1/8}$ for temperatures T_* away from T_c. Closer to T_c, this amplitude is found to diverge as $A_* \propto (T_c - T_*)^{-\phi}$, with $\phi \simeq 0.31$. Note that this behavior is contrary to the usual expectation of critical slowing down. For thick layers with $l \gtrsim 50$ nm, retardation effects are important and the growth law (1) is predicted to cross over to a $t^{1/10}$ behavior.

These estimates indicate that the growth behavior (1) should be accessible to experimental observation. Very fast pressure-quench techniques have been developed[6] for bulk spinodal decomposition of binary mixtures. These techniques should also be useful in the present context. Furthermore, the wetting of a solid by one liquid phase of a binary mixture has already been studied experimentally by Wu *et al.*[7] In their experiments, the equilibrium thickness l_{eq} of the wetting layer was finite either because the layer was thinned by gravity[8] or because the bulk mixture was near but not at $\alpha\beta$ coexistence. If such a layer grows isothermally by diffusion, its equilibration time $t_{\rm eq}$ can be roughly estimated from (1) via $l(t_{\rm eq}) \simeq A_* t_{\rm eq}^{1/8} \simeq l_{\rm eq}$ which gives $t_{\rm eq} \simeq (l_{\rm eq}/A_*)^8$. For $t \gtrsim t_{\rm eq}$, the final approach to $l_{\rm eq}$ is given by $l_{\rm eq} - l(t) \sim 1/\sqrt{t}$ [see (10) below].

The growth law (1) can be most easily obtained from the following heuristic argument. First, let us assume that the composition gradients within the bulk phase α are characterized by a single length scale, the diffusion length

$$\delta(t) \sim (Dt)^{1/2}, \tag{2}$$

where D is the diffusion coefficient for B molecules in the α phase. In this case, the total amount of depletion of B molecules per unit area within the spectator phase is of order $\rho[X_\alpha - X(l)]\delta$, where ρ is the total number density of the mixture[9] and $X(l)$ is the composition in front of the $\alpha\beta$ interface. Then conservation of the number of B molecules implies that

$$[X_\beta - X_\alpha][l(t) - l(0)] \sim [X_\alpha - X(l)]\delta(t). \tag{3}$$

Now, we anticipate that $l(t) << \delta(t)$, i.e., that the relaxation of composition gradients is fast compared to the motion of the $\alpha\beta$ interface.[3,10] Thus, we assume *local* equilibrium on length scales comparable to $l(t)$. This implies that $X(l)$ has the same value as when l is the layer thickness in equilibrium. It is convenient to express the small difference $X_\alpha - X(l)$ in terms of the relative chemical potential $\mu(X,T) = \mu_B(X,T) - \mu_A(X,T)$ for B and A molecules:

$$X_\alpha - X(l) = [\mu(X_\alpha,T) - \mu(X(l),T)](\partial X/\partial\mu)_\alpha, \tag{4}$$

where the derivative is taken in the α phase. The chemical potential difference can be related to the interface potential $V(l)$ which is the free energy per unit area of a film of thickness l[2,11]:

$$\rho(X_\beta - X_\alpha)[\mu(X_\alpha,T) - \mu(X(l),T)] = -\partial V/\partial l. \tag{5}$$

If l is large compared to the bulk correlation length and if the fluid and solid molecules interact via nonretarded van der Waals forces, then

$$V(l) \approx \rho\Delta\mu l + W/l^2, \tag{6}$$

where W is the Hamaker constant. The linear term in (6) describes the deviation of $\mu(X_\alpha,T)$ from $\alpha\beta$ coexistence at T. For gravity-thinned layers,

$$\rho\Delta\mu = (\bar\rho_\alpha - \bar\rho_\beta)gL, \tag{7}$$

where $\bar\rho_\alpha$, $\bar\rho_\beta$, g, and $L >> l$ are the mass densities of the α and β phases, the gravitational acceleration, and the thickness of the α phase, respectively. Now, a combination of (2)–(6) leads to

$$[l(t) - l(0)]/(Dt)^{1/2} \sim -(K/\Sigma)\partial V/\partial l, \tag{8}$$

with

$$K/\Sigma = (\partial X/\partial\mu)_\alpha/\rho(X_\beta - X_\alpha)^2. \tag{9}$$

The parameters K and Σ are a capillary length[4] and the tension of the $\alpha\beta$ interface, respectively.

For $\Delta\mu > 0$, the equilibrium thickness $l_{\rm eq}$ is finite, and (8) implies that

$$l_{\rm eq} - l(t) \sim [l_{\rm eq} - l(0)]/(\omega t)^{1/2} \tag{10}$$

for large times, with $\omega \equiv [D(\partial^2 V/\partial l^2)_{\rm eq} K/\Sigma]^2$. For $\Delta\mu = 0$, on the other hand, the solution of (8) is $l(t) \approx A_* t^{1/8}$ as in (1) with

$$A_* \sim (D^{1/2} W K/\Sigma)^{1/4}. \tag{11}$$

Note that for $\Delta\mu$ small and $l_{\rm eq}$ large, $l(t)$ will obey (1) until it becomes of order $l_{\rm eq}$ after which (10) holds.[12]

Away from T_c, typical values for the parameters in (11) are $D \simeq 10^{-5}$ cm^2/sec, $W \simeq 10^{-14}$ erg, and $K/\Sigma \simeq 10^{-8}$ cm^3/erg. As a result, one obtains $A_* \simeq 10$ nm/sec$^{1/8}$ as mentioned. For $T = T_* \rightarrow T_c$, we have $D \sim (T_c - T)^{\nu(1+x_\eta)}$, where $\nu \simeq 0.63$ and[13] $x_\eta \simeq 0.06$ are the critical exponents for the bulk correlation length and dynamic viscosity, respectively; $W \sim (T_c - T)^\beta$, where $\beta \simeq 0.33$ is the order-parameter exponent; and $K/\Sigma \sim (T_c - T)^{-(2\beta+\gamma)}$, with $\gamma \simeq 1.24$. This results in $A_* \sim (T_c - T)^{-\phi}$, with $\phi \simeq 0.31$.[14]

Let us now proceed to a more systematic derivation of the growth laws (1) and (10). We denote the coordinate perpendicular to the solid wall by z and consider a planar $\alpha\beta$ interface at distance $z = l(t)$ from the wall. Furthermore, we introduce the equilibrium composition profile $X_{\rm eq}(z|l)$ which has its $\alpha\beta$ interface at the same position $z = l(t)$. If the instantaneous composition profile $X(z,t)$ were identical with $X_{\rm eq}(z|l)$, no diffusion would occur. Therefore, the diffusive current is taken to be proportional to the gradient of the excess quantity $X(z,t) - X_{\rm eq}(z|l)$, and

$$\frac{\partial}{\partial t}X(z,t) = D\frac{\partial^2}{\partial z^2}[X(z,t) - X_{\rm eq}(z|l)]. \tag{12}$$

On length scales large compared to the bulk correlation length, the equilibrium composition profile may be written, for $z \geqslant l$, as

$$X_{\rm eq}(z|l) = X(l) + a(X_\beta - X_\alpha)/(z - l + b)^3, \tag{13}$$

with $X(l) = X_{\rm eq}(\infty|l)$, $a/b^3 << 1$, and b of the order of the bulk correlation length. The power-law tail in (13) arises from the long-range van der Waals forces.[8]

In accordance with the local-equilibrium assumption, $X(z,t)$ is now taken to be identical with $X_{\rm eq}(z|l)$ for $z \leqslant l$, i.e., within the wetting layer. This assumption implies two boundary conditions at the $\alpha\beta$ interface. First, it follows that $X(z=l+,t)=X_{\text{eq}}(l+|l)$. In addition, conservation of the total amount of B relates dl/dt to the diffusive current at $z=l+$. Starting from these boundary conditions and the diffusion equation (12), one can derive an integral equation for $l(t)$ using Green's-function techniques.[4,15] As a result we obtain

$$-\frac{K}{\Sigma}\frac{\partial V}{\partial l}=\int_0^t dt'\, G(l,t|l',t')\left[\Delta\frac{dl'}{dt'}-\frac{K}{\Sigma}\frac{\partial V(l')}{\partial l'}\frac{l-l'}{2(t-t')}\right]+I_0(l,t)+I_S(l,t), \tag{14}$$

with $l'=l(t')$, $\Delta=1-a/b^3$, and

$$G(l,t|l',t')=\theta(t-t')\exp[-(l-l')^2/4D(t-t')]/[4\pi D(t-t')]^{1/2}. \tag{15}$$

The term $I_0(l,t)$ depends on the initial composition profile at $t=0$. The term $I_S(l,t)$ arises from the inhomogeneity in (12) which acts as a source term.

We now make the *Ansatz* $l(t)\approx A_*t^\theta$ for large t, and insert the form (6) for the effective interface potential $V(l)$ with $\Delta\mu=0$ into (14). The term $\propto a/b^3$ contained in $\Delta dl'/dt'$ is exactly canceled by the leading contribution from $I_S(l,t)$. As a result, we recover the growth law (1) with $\theta=\frac{1}{8}$, and the amplitude (11). In the same way, (10) is recovered from (14) when the equilibrium thickness is finite.

The growth law (1) holds for the effective interface potential (6) (with $\Delta\mu=0$) which is appropriate for three-dimensional systems governed by nonretarded van der Waals forces. We will now briefly discuss the corresponding behavior for the general potential

$$V(l)\approx Ul^{-p} \tag{16}$$

for large l, with $p\geq -1$ and $Up>0$. Such a potential, when used in (14), leads to

$$l(t)\sim t^\theta,\quad \theta=1/2(p+2). \tag{17}$$

For d-dimensional systems with long-ranged interactions between the molecules which decay as $1/r^{d+\sigma}$ for large separations r, one has[11] $p=\sigma-1$ for $d>d^*(\sigma)=(3\sigma-1)/(\sigma+1)$ and $p=2(d-1)/(3-d)$ for $d<d^*(\sigma)$, where the latter value for p can be obtained from the overall loss of entropy[16] of the $\alpha\beta$ interface due to the presence of the solid wall. For retarded van der Waals forces, one has $\sigma=4$ and, thus, $\theta=\frac{1}{10}$ in $d=3$ as mentioned. For short-range forces with $V(l)\approx\exp(-l)$, one has $\theta=0$ (logarithmic divergence). If the wall is charged with ions, the counterions in the fluid lead to[17] $p=1$ in $d=3$ and, thus, $\theta=\frac{1}{6}$. Furthermore, for $d=2$ and $\sigma>2$, one obtains the universal growth law $l(t)\sim t^{1/8}$. This behavior should be accessible to Monte Carlo simulations of two-dimensional lattice models with spin-exchange dynamics.[18]

It is instructive to compare the exponent θ as given by (17) with the corresponding exponent for a one-component system where a liquid or solid layer is deposited from the vapor phase.[19] For such systems, the chemical potential is determined by the pressure which is a propagating mode, and, thus, mass transport is not limited by diffusion. Then one may assume that the deposition rate from the vapor phase onto the interface is proportional to the pressure while the evaporation rate depends on the binding energies within the condensed phase but not on the pressure.[20] This leads to the equation $dl/dt\propto -\partial V/\partial l$ which has been studied before.[19] As a result, one finds that $l(t)\propto t^{\theta'}$, with[19] $\theta'=2\theta$.[21]

It turns out that the above analysis leads to the growth behavior (17) even for interface potentials (16) with $U<0$ and $-1\leq p<0$, i.e., for potentials which are not bounded from below. However, we have assumed so far that the $\alpha\beta$ interface has a *planar* geometry. Such an interface could be unstable with respect to the diffusive Mullins-Sekerka[22] instability. In order to investigate this possibility, we have performed a linear stability analysis of the planar interface. This analysis starts from a generalization of (14) for $l=l(\mathbf{x},t)$, where $\mathbf{x}$ are the coordinates parallel to the solid wall. Within the quasistationary approximation,[4] we find that a perturbation of the form $e^{i\mathbf{q}\cdot\mathbf{x}}\eta(\mathbf{q},t)$ behaves as

$$\eta(q,t)=\eta(q,0)\exp[E_1(q,t)+E_2(q,t)], \tag{18}$$

with

$$E_1(q,t)=-(p+1)C'q(Dt)^{1/2}-2Kq^3Dt \tag{19}$$

and

$$E_2(q,t)=(pUK/\Sigma)^{2\theta}[C''q^2(Dt)^{\theta+1/2}+C'''q(Dt)^{\theta}], \tag{20}$$

with p and θ from (16) and (17), and positive numerical coefficients C', C'', and C'''.[23] The negative term E_1 stabilizes the planar interface whereas the positive term E_2 destabilizes it. As long as $p>-1$ in (16) which implies that the planar interface moves out with $\theta<\frac{1}{2}$, the time dependence of all perturbing modes $\eta(q,t)$ is governed by E_1 both for short and for long times. Thus, all perturbations will eventually decay and we conclude that the long-time behavior of the mean interfacial position is correctly described by the planar geometry studied above. On the other hand, for $p=-1$ in (16), i.e., for an interfacial potential $V(l)=-|U|l$, the time dependence of perturbations

$\eta(q,t)$ with small q is controlled by E_2 as given by (20) since $\theta + \frac{1}{2} = 1$ for $p = -1$. Therefore, the planar interface is *unstable* for $p = -1$ with respect to the Mullins-Sekerka instability and the long-time behavior cannot be deduced from the planar interface.[24]

The interface potential $V(l) = -|U|l$ does, in fact, correspond to a physical situation, namely to a quench *into* the two-phase region [compare (6) with $\Delta\mu < 0$]. If one stays close to the boundary of this region, the bulk of the mixture is metastable as a result of nucleation barriers. In contrast, there are usually no such barriers[25] for the formation of the wetting layer near the solid wall which means that this layer starts to grow even though the bulk remains in its metastable state. The above stability analysis implies, however, that the interface will be convoluted as a result of the Mullins-Sekerka instability, and that its mean position $l(t) \sim t^{\theta}$ could grow superdiffusively with $\theta > \frac{1}{2}$. Experimental studies of this growth behavior would be very interesting.

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[1] We do not explicitly discuss binary mixtures with an inverted coexistence curve. Our results apply, however, equally well to such mixtures.

[2] A recent review on wetting is by D. Sullivan and M. M. Telo da Gama in *Fluid Interfacial Phenomena,* edited by C. A. Croxton (Wiley, New York, to be published).

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[12] Here, we have ignored finite-size effects resulting from a finite extent L of the bulk phase α. For a finite system, (1) and (10) hold as long as the diffusion length $\delta(t) \lesssim L$. The case $\delta(t) >> L$ and $L(t) >> L_{\rm eq}$ has been discussed, for gravity-thinned layers, by R. F. Kayser, M. R. Moldover, and J. W. Schmidt, Faraday Symp. Chem. Soc. (to be published), who argue that, in this case, the diffusive current across the interface is a time-independent constant.

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[14] This result applies to a semi-infinite geometry as studied here. For a finite system, the asymptotic regime with $l(t)$ large compared to the bulk correlation length will not be accesssible sufficiently close to T_c.

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[17] This follows from the Langmuir equation; see, e.g., R. F. Kayser, Phys. Rev. Lett. **56**, 1831 (1986).

[18] For two-dimensional lattice models, the overall loss of entropy leads to $p = 2$ and $U \simeq (k_B T)^2/\tilde{\Sigma}$ in (16), where the interfacial stiffness $\tilde{\Sigma} \sim \exp(\mathrm{const}/T)$ for $T \to 0$ (see Ref. 16). Therefore, U rapidly decreases for $T \to 0$. For $T \to T_c$, on the other hand, $U \sim 1/\tilde{\Sigma}$ becomes large and $A_* \sim (T_c - T)^{-\phi}$, with $\phi = \frac{17}{32}$ for the two-dimensional Ising model.

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[20] Compare J. D. Weeks and G. H. Gilmer, in *Advances in Chemical Physics,* edited by I. Prigogine and S. A. Rice (Wiley, New York, 1979), Vol. 40, where these assumptions are discussed in the context of crystal growth.

[21] In principle, the layer growth in a one-component system could be limited by the diffusion of heat. In this case, the growth law would eventually cross over to the form (17).

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[23] Power-law tails in the equilibrium composition profile [compare (13)] lead to higher-order corrections not displayed in (19) and (20).

[24] It is interesting to note that the same approach can be applied to diffusion-limited aggregation with the boundary condition $X = 0$ at the interface. This leads again to $\theta = \frac{1}{2}$ and, thus, to an unstable planar interface.

[25] Nucleation barriers for wetting layers do occur near a first-order wetting transition.