Hydrodynamic crossovers in surface-directed spinodal decomposition and surface enrichment

Prabhat K. Jaiswal\(^1\), Sanjay Puri\(^1\)(a) and Subir K. Das\(^2\)

\(^1\) School of Physical Sciences, Jawaharlal Nehru University - New Delhi, 110067, India
\(^2\) Theoretical Sciences Unit, Jawaharlal Nehru Centre for Advanced Scientific Research Jakkur, Bangalore, 560064, India

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Abstract – We present comprehensive molecular dynamics results for the kinetics of surface-directed spinodal decomposition and surface enrichment in binary mixtures at wetting surfaces. We study the surface morphology and the growth dynamics of the wetting and enrichment layers. The growth law for the thickness of these layers shows a crossover from a diffusive regime to a hydrodynamic regime. We provide phenomenological arguments to understand this crossover.

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A rich class of physical phenomena occurs when a homogeneous binary (AB) mixture is placed in contact with a surface (S). In many cases, the surface has a preferential attraction for one of the components of the mixture (say A). If the mixture is immiscible, the homogeneous bulk is unstable to phase separation and segregates into growing A-rich and B-rich domains. The surface becomes the origin of surface-directed spinodal decomposition (SDSD) waves which propagate into the bulk [1–11]. The system evolves into a partially wet (PW) or completely wet (CW) equilibrium morphology, depending upon the relative interaction strengths among A, B and S [12–15]. In the PW morphology, the interface between the A-rich and B-rich domains meets the surface at a contact angle determined by Young's condition [16]. In the CW morphology, the A-rich phase expels the B-rich phase from the surface, and the AB interface is parallel to the surface. On the other hand, if the mixture is miscible, the emergent morphology consists of a thin surface enrichment (SE) layer followed by an extended depletion layer [17–20]. The kinetics of SDSD and SE are of great technological and scientific importance, and find application in the fabrication of nanostructures, layered materials, composites, etc.

Many experiments on SDSD and SE involve polymer or fluid mixtures, where hydrodynamic effects play an important role. For bulk phase-separation kinetics, it is well known that hydrodynamics has a drastic effect on the intermediate and late stages [21,22]. The coarsening domains with size \(L(t)\) show a power-law growth, \(L(t) \sim t^{\phi}\), with the exponent \(\phi\) changing from \(1/3\) (diffusive regime) to \(1\) (viscous hydrodynamic regime) to \(2/3\) (inertial hydrodynamic regime) [23–25]. However, there is no analogous understanding of the role of fluid velocity fields in SDSD and SE [26,27]. In this paper, we present comprehensive molecular dynamics (MD) results for the kinetics of SDSD and SE. Our MD simulations show the first clear evidence for a sharp crossover from a diffusive regime to a viscous hydrodynamic regime in both SDSD and SE. We also provide arguments to determine growth laws of the wetting and enrichment layers in the hydrodynamic regime. Our results provide a novel framework for the interpretation of experiments, and will also stimulate further experiments in this area.

We consider a binary (AB) fluid mixture of point particles confined in a box of volume \(V = L \times L \times D\). Periodic boundary conditions are applied in the \(x\) and \(y\) directions. An impenetrable surface is present at \(z = 0\), which gives rise to an integrated Lennard-Jones (LJ) potential \((\alpha = A, B)\):

\[
u_w(z) = \frac{2\pi n \sigma^3}{3} \left\{ \frac{2\epsilon_r}{15} \left( \frac{\sigma}{z} \right)^9 - \delta_{\alpha} \epsilon_a \left( \frac{\sigma}{z} \right)^3 \right\},
\]

where \(n\) is the fluid density, and \(\sigma\) is the LJ diameter. In eq. 1, \(\epsilon_r\) and \(\epsilon_a\) are the strengths of the repulsive and

\(^{(a)}\)E-mail: purijnu@gmail.com
attractive parts of the surface potential. We set $\delta_A = 1$ and
$\delta_B = 0$, i.e., $A$ particles are attracted at large distances,
whereas $B$ particles are only repelled. Further, $z' = z + \sigma/2$
so that the singularity of $u_s(z)$ occurs at $z = -\sigma/2$ (outside
the box). A similar surface is present at $z = D$ with $z' = D + \sigma/2 - z$, and $\delta_A = \delta_B = 0$, i.e., both $A$ and
$B$ particles are repelled. The simulation box corresponds
to a semi-infinite geometry [7]: the generalization to any
other geometry is straightforward.

The particles in the system interact with LJ potentials
$(\alpha = A, B)$:

$$u(r_{ij}) = 4\epsilon_{\alpha\beta} \left[ \left( \frac{\sigma}{r_{ij}} \right)^{12} - \left( \frac{\sigma}{r_{ij}} \right)^6 \right],$$

(2)

where $r_{ij} = |\vec{r}_i - \vec{r}_j|$. We set the interaction parameters as
$\epsilon_{AA} = \epsilon_{BB} = 2\epsilon_{AB} = \epsilon$. The bulk phase diagram for this
potential is well known [28–30]. We use the truncated LJ
potential with $r_t = 2.5\sigma$ — this potential is shifted and
force-corrected [31]. We consider a critical composition
with phase separation in the bulk. This wetting layer
has been studied by Das and Binder [33], who observed a first-order
wetting transition at the temperatures of interest.

The order parameter $\psi(z,t)$ is defined as the first zero-crossing of the
laterally averaged density profile $\langle n_A - n_B \rangle / (n_A + n_B)$. The density
and velocity fields are obtained by averaging over $A$ and
$B$ particles contained in coarse-graining boxes of size
$(2\sigma)^3$. The quantity $\psi_{av}(z,t)$ is obtained by averaging
$\psi(\vec{r},t)$ in the $x, y$ directions (parallel to the surface), and
further averaging over 50 independent runs. In the bulk, the
spinodal decomposition wave vectors are randomly
oriented — the above procedure yields $\psi_{av} \approx 0$. Near the
surface, we see a structured morphology consisting of a
wetting layer at the surface, depletion layer adjacent to it, etc. This layered structure propagates into the bulk. These
SDSD profiles have been observed in many experiments on
this problem [1–5].

An important characteristic of the SDSD profiles is the
time dependence of the wetting-layer thickness $R_1(t)$. This
is defined as the first zero-crossing of the laterally averaged
depth profiles in fig. 1. In fig. 2, we plot $R_1(t)$ vs. $t$ for the
evolution shown in fig. 1, for two different system
sizes. The growth dynamics shows a power law behavior,
$R_1(t) \sim t^{\theta}$, with $\theta \approx 1/3$ for $t \lesssim 2000$ and $\theta \approx 1$ for $t \gtrsim 2000$. Note that the results from both the system sizes overlap
(within statistical error) for the whole time range. This
indicates only weak finite-size effects. This is expected for
a first-order wetting transition like ours, where $R_1$ will
have only a finite value (of the order of a few atomic
diameters) in the equilibrium limit. In this context, the
linear dimension of our system in the $z$-direction is large
enough that no size effects are expected to be seen all the
way up to the equilibrium limit.
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How can one understand this crossover? At early times, the wetting layer grows by the diffusive transport of $A$ from bulk domains of size $R \sim (\sigma t)^{1/3}$ (with chemical potential $\mu \approx \sigma/R$, $\sigma$ being the surface tension) to the flat surface layer of size $\sim \infty$ (with $\mu \approx 0$). If we neglect the very early potential-dependent growth regime [34], we have

$$\frac{dR_1}{dt} \approx \frac{\sigma}{R h} \approx \frac{\sigma}{R R_1},$$

(3)

where $h \sim R_1$ is the thickness of the depletion layer (see fig. 1). From eq. (3), we readily obtain the Lifshitz-Slyozov (LS) growth law: $R_1 \sim (\sigma t)^{1/3}$. At later times, bulk tubes establish contact with the wetting layer and material is pumped hydrodynamically to the surface. The subsequent growth is analogous to that in phase separation of fluids—we expect $R_1(t) \sim t$ (viscous hydrodynamic regime) which crosses over to $R_1(t) \sim t^{2/3}$ (inertial hydrodynamic regime). The latter stage is presently not accessible via MD simulations [25], due to computational limitations. However, our results for wetting-layer dynamics in fig. 2 appear to access the viscous regime, albeit in a limited time-window. We remark that the crossover time ($t_\text{c} \approx 2000$) is consistent with that reported by Ahmad et al. [25] in an MD simulation of bulk phase separation with similar parameter values. Clearly, we need substantially larger system sizes to obtain an extended regime of linear growth in the viscous regime. Notice that the crossover in fig. 2 is quite sharp, suggesting that there is a rapid pumping of material to the wetting layer when the bulk tubes first make contact.

Second, we present results for the kinetics of SE. In this case, the system size was $L^2 \times D$, with $L = 32, D = 64$ ($N = 66536$). As the bulk remains homogeneous, the lateral size $L$ (in the $x,y$ directions) is not severely constrained. However, in the direction perpendicular to the surface at $z = 0$, we need sufficiently large $D$ to ensure decay of the enrichment profiles as $z \to D$. For the range of times studied here ($t \leq 7000$), test runs with other linear dimensions showed that $D = 64$ is large enough to eliminate finite-size effects. In fig. 3, we show the laterally averaged profiles and an evolution snapshot (inset) for the kinetics of SE. The coarse-graining procedure is the same as that for SDSD. The quench temperature was $T = 2.0 \pm 1.41T_c$. The depth profiles were obtained using the same procedure as for SDSD, as an average over 50 independent runs. The surface potential parameters were $\epsilon_r = 0.5$ and $\epsilon_a = 3.0$.

As expected, the morphology for SE is quite different from that in the SDSD case (cf. fig. 1). There is a thin enrichment layer of $A$ at the surface. Due to the conservation of the order parameter, there must be a corresponding depletion layer which decays to $\psi_{av} \approx 0$ in the bulk. These profiles are in agreement with the experimental observations of Jones et al. [18] on blends of deuterated and protonated polystyrene, and the experimental results of Mouritsen [35] on biopolymer mixtures. Notice that similar profiles are seen for SDSD if the system is quenched to the metastable region of the phase diagram [34]. The evolution dynamics in that case is analogous to the SE problem, as long as droplets are not nucleated in the system.

For the case with diffusive dynamics, Binder and Frisch [36] and Frisch et al. [37,38] have studied the morphology of SE profiles in the framework of a linear

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theory. They find that the SE profiles have a double-exponential form:

\[ \psi(z, t) \approx B_-(t) e^{-z/\xi_-(t)} - B_+(t) e^{-z/\xi_+(t)}, \]

with amplitudes \( B_-(t), B_+ > 0 \). The quantities \( B_-(t) \) and \( \xi_-(t) \) rapidly saturate to their equilibrium values \( a_1 \) and \( b_1 \), which depend on the surface potential. The other length scale \( \xi_+(t) \) grows diffusively with time, and \( B_+(t) \) shows a corresponding decay:

\[ B_+(t) \approx a_2 t^{-1/2}, \quad \xi_+(t) \approx b_2 t^{1/2}. \]

The conservation constraint requires that \( B_- \xi_+ = B_+ \xi_- \).

In fig. 3, we see that the double-exponential function in eq. (4) describes the SE profiles very well.

What about the parameters of the double-exponential profile? As for the dissipative case, we find that \( B_- \) and \( \xi_- \) rapidly saturate to their equilibrium values and may be treated as static quantities. The growing length scale \( \xi_+(t) \) we plot \( \xi_+ \) vs. \( t \) for different surface field strengths in fig. 4(a). The early-time dynamics is consistent with diffusive growth \( \xi_+ \sim t^{1/2} \), but again there is a crossover at \( t \sim t_c \) to a hydrodynamic regime \( \xi_+ \sim t \). The crossover is also seen in the thickness of the SE layer. For the profile in eq. (4), the zero is located at \( z_0(t) \approx \ln(B_-/B_+) \). Thus, we expect \( Z_0(t) \approx \ln \) in both the time regimes of fig. 4(a), but the slope should be steeper for \( t > t_c \). This is precisely the behavior seen in fig. 4(b), where we plot our MD results for \( Z_0(t) \) vs. \( t \) on a log-linear scale. This confirms that there is a crossover in the growth exponent from the diffusive regime \( (\theta \approx 0.5) \) to the hydrodynamic regime \( (\theta \approx 1.0) \).

To understand the crossover in fig. 4, consider the dimensionless evolution equation for the order parameter in the presence of a fluid velocity field \( \vec{v}(\vec{r}, t) \) [21,22]:

\[ \frac{\partial}{\partial t} \psi(\vec{r}, t) = \nabla^2 \mu - \vec{v} \cdot \nabla \psi, \]

where the chemical potential (for \( T > T_1 \)) is \( \mu = \psi + \psi^3 - (1/2) \nabla^2 \psi \). For \( T > T_c \), the bulk is approximately homogeneous and there is no large-scale structure formation in the composition or velocity fields. We have examined the structure of the vector velocity field \( (v_x, v_y, v_z) \) in planes parallel and perpendicular to the surface. We have also studied the laterally averaged components:

\[ v_i^{av}(z, t) = \frac{1}{L^2} \int dx \int dy \: v_i(x, y, z, t), \quad i = x, y, z. \]

The velocity field shows an interesting structure, which we will discuss in detail elsewhere. There is a high density of vortices and anti-vortices, which do not show a coarsening behavior [25]. As expected from the symmetry of the system, \( v_i^{av}(z, t) \) and \( v_i^{av}(z, t) \) show random fluctuations about a zero average. The laterally averaged \( x \)-component \( v_x^{av}(z, t) \) also consists of random fluctuations, but about a non-zero average \( v_x^{av}(t) \) which very slowly reduces with time. These observations motivate the following arguments. We consider the laterally averaged version of eq. (6) and set \( \psi(r, t) \approx \psi(z, t) \) and \( v_x(r, t) \approx v_x^0(t) \):

\[ \frac{\partial}{\partial t} \psi(z, t) = \frac{\partial^2 \mu}{\partial z^2} - v_x^0 \frac{\partial \psi}{\partial z}. \]

We use the functional form of \( \psi(z, t) \) in eq. (4) to estimate the dominant contribution to the various terms in eq. (8) at \( z \sim O(\xi_+) \), i.e., far from the surface [39]. We have

\[ \frac{\partial \psi}{\partial t} \sim \frac{1}{\xi_+^2} \frac{\partial \xi_+}{\partial t}, \quad \frac{\partial^2 \mu}{\partial z^2} \sim \frac{1}{\xi_+^3}, \quad v_x^0 \frac{\partial \psi}{\partial z} \sim \frac{v_x^0}{\xi_+}. \]

Notice that \( v_x^0 < 0 \), so there is a net hydrodynamic current towards the enrichment layer. This current is dissipated at the surface by the formation of locally inhomogeneous structures. At early times, the dissipative term in eq. (8) dominates, yielding \( \xi_+ \sim t^{1/2} \). At late times, the convective term in eq. (8) is dominant, giving a crossover to \( \xi_+ \sim v_x^0 t \).

The precise dependence of the crossover time on various physical parameters can be estimated by considering the dimensional version of eq. (6) in conjunction with the Navier-Stokes equation for the velocity field [21,22].

In summary, we have presented comprehensive MD results for the kinetics of SDS and SE in binary mixtures at wetting surfaces. Both the SDS wetting layer and the SE layer show a crossover from a dissipative regime (with \( R_1 \sim t^{1/3} \) and \( \xi_+ \sim t^{1/2} \)) to a hydrodynamic regime (with \( R_1 \sim t \) and \( \xi_+ \sim t \)). These crossovers can be understood by simple phenomenological arguments. Our MD results are of great experimental relevance as most studies of these problems are done on polymer or fluid mixtures. We hope that our results in this paper will provoke fresh experimental interest in this problem, and our theoretical results will be subjected to experimental confirmation.

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