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Tests of dynamical scaling in three-dimensional spinodal decomposition

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We simulate late-stage coarsening of a three-dimensional symmetric binary fluid. With reduced units l,t (with scales set by viscosity, density, and surface tension) our data extends two decades in t beyond earlier work. Across at least four decades, our own and others' individual datasets (<1 decade each) show viscous hydrodynamic scaling ($l \sim a+bt$), but b is *not* constant between runs as this scaling demands. This betrays either the unexpected intrusion of a discretization (or molecular) lengthscale, or an exceptionally slow crossover between viscous and inertial regimes. [S1063-651X(99)51102-1]

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When an incompressible binary fluid mixture is quenched far below its spinodal temperature, it will phase separate into domains of different composition. For symmetric (or nearly symmetric) mixtures, these domains will, at late times, form a bicontinuous structure, with sharp, well-developed interfaces. The late-time evolution of this structure in three dimensions remains incompletely understood despite theoretical [1–3], experimental [4], and simulation [5–8] work over recent years.

In this Rapid Communication, we use the dissipative particle dynamics (DPD) simulation algorithm [9] to access length and time scales far beyond those reached previously. (Details of the simulations will appear elsewhere [10].) When combined with other datasets [5–7] our results allow a severe test of the dynamical scaling ideas, which underlie most theoretical treatments [1–3] and data analyses [4]. We conclude that dynamical scaling is in doubt, perhaps due to the intrusion of a molecular lengthscale through the physics of topological reconnection events. An alternative explanation of the results, based on a universal but extremely slow crossover, is also carefully examined.

As emphasized by Siggia [1], the physics of spinodal decomposition involves capillary forces, viscous dissipation, and fluid inertia. Indeed, assuming that *no other* physics enters, then the parameters governing the behavior are the interfacial tension σ, fluid mass density ρ, and viscosity η. (We now specialize to 50/50 mixtures with complete symmetry of the two species. Any asymmetries in composition, thermodynamics or viscosity [11] provide additional control parameters.) From these three parameters can be constructed only one length, $L_0 = \eta^2/\rho\sigma$ and one time $T_0 = \eta^3/\rho\sigma^2$. We now define the lengthscale $L(T)$ of the domain structure at time T via the structure factor $S(k)$ as [12] $L = (2\pi)[\int kS(k)dk/\int S(k)dk]^{-1}$. The exclusion of other physics in late-stage growth then leads us to the dynamical scaling hypothesis [1,2]:

$$l = a + f(t), \tag{1}$$

where we define reduced time and length variables via $l \equiv L/L_0$ and $t \equiv T/T_0$. Since dynamical scaling should hold only after interfaces have become sharp, and transport by molecular diffusion suppressed, we have allowed for a nonuniversal offset a in Eq. (1). Thereafter the scaling function $f(t)$ should approach a universal form, the same for all (fully symmetric, deep-quenched, incompressible) binary fluid mixtures.

It was argued further by Siggia [1] that, for small enough t, fluid inertia is negligible compared to viscosity, whereas for large enough t the reverse is true. This imparts the following asymptotes to the function f:

$$f \to bt, \quad t \ll t^*, \tag{2}$$

$$f \to ct^{2/3}, \quad t \gg t^*, \tag{3}$$

where, if dynamical scaling holds, the amplitudes b and c must be universal, as must the crossover time t^* (defined, e.g., by the intersection of asymptotes on a log-log plot). Note that the Reynolds number $\mathrm{Re} = (\rho L/\eta) dL/dT = f\dot{f}$, which becomes large in the inertial regime, Eq. (3).

Perfectly symmetrical fluid pairs do not exist in the laboratory, but computer simulations allow us to test the validity of Eq. (1), on which the wider interpretation of experiments crucially depends [4]. In the viscous regime [Eq. (2)], the scaling reduces to $L(T) = A + BT$, where A is nonuniversal and $B = b\sigma/\eta$. This linear law has been reported by several groups [5,13,14] (see also [8,15,16]) but only in two recent cases [6,7] were reliable σ and η values obtained, as are needed to find b. In both of these, the offset A was significant, and the linear regime (the straight part of the curve at late times) spanned much less than a decade. In reduced units [12], we find that the data of Ref. [7] describes times in the range $1 \leqslant t \leqslant 3$ with a value of $b = 0.3$. However, the MD data of Laradji *et al.* [6] has $60 \leqslant t \leqslant 140$ and $b = 0.13$.

The discrepancy over b (see also [5]) cannot simply be brushed aside. For if dynamical scaling [Eq. (1)] applies, and both simulations [6,7] are (as claimed) in the viscous regime [Eq. (2)], then these two b values should both be the same [17]. It is thus premature to conclude that any universal regime of viscous hydrodynamic scaling [Eq. (2)] had yet been observed in computer simulations.

To clarify this important issue, we have conducted several simulations that vastly extend the range of time scales explored: we probe $750 \leqslant t \leqslant 45\,000$. This was done using the DPD algorithm, which combines soft interparticle repulsions with pairwise damping of interparticle velocities and pairwise random forces [9]. The latter conserve momentum, leading to a faithful simulation of the isothermal (and, in this study, effectively incompressible [17]) Navier Stokes equation at large length scales. Among several advantages of DPD over MD, exploited below, is that the viscosity of a DPD fluid can be varied *independently* of its thermodynamics.

To describe our DPD parameters, we briefly switch from reduced physical units (l,t) to ''DPD units'': the range of the repulsive interaction is unity, as is the particle mass. We further set $k_B\mathcal{T}=1$ ($\mathcal{T}$ is temperature). With the form of repulsion used by Groot and Warren [9], we chose a particle density 10 and energy parameters $a_{11}=a_{22}=20$, $a_{12}=100$, which is a deep quench ($\mathcal{T}_c/\mathcal{T}\simeq 80$) [10]. The timestep was 0.01 [9], giving measured $\mathcal{T}$'s within 2% of the nominal value. Integrating the microscopic stress across a flat fluid-fluid interface [18], the interfacial tension was found as 50.6 ± 0.2. For each damping parameter γ the viscosity was found from the mean stress in steady shear under Lees-Edwards boundary conditions [19]; values varied between $\eta=2.6\pm 0.2$ ($\gamma=1$) and $\eta=12.2\pm 0.5$ ($\gamma=30$) [10].

Most runs were performed on a 512 node Cray T3D, with a typical run time of several thousand processor-hours. Resources allowed one or two full-sized runs for each viscosity. The simulation box for these contained 10^6 particles with periodic boundary conditions. Thorough tests of scaling and data collapse for $S(k)$ were made [10]. Finite size effects became apparent when the structural lengthscale L exceeded about half the box size ($L \geqslant \Lambda/2 \simeq 20$); data beyond this was excluded from our fits for $f(t)$. We also excluded an ''early stage'' portion of each run; this was judged by eye from the shape of the $L(T)$ plot. (Possible resulting bias is considered below; little would be changed had we instead applied a sharpness criterion to the observed interfaces.)

The datasets for $L(T)$ (DPD units) are presented in Fig. 1 (inset). Excluded early time data is shown dotted, as is some data for $L \geqslant \Lambda/2$. Slight wobbles in the fitted parts of the curves represent sampling errors in L arising because L/Λ is not small; these vary between duplicate runs and appear distinct from the direct finite size (saturation) effects arising for $L \geqslant \Lambda/2$ [20,21]. Figure 1 shows the same data (with offsets subtracted) on a log-log plot. Note first that, since most of the plots in Fig. 1 show upward curvature at early times, our elimination of early time data will bias *downward* any estimate of the quantity $z = d \ln f/d \ln t$ (a true or effective scaling exponent). Despite this, only for the smallest viscosity run (if that) is there appreciable direct evidence for an exponent $z<1$, as predicted for $t \gg t^*$ [Eq. (3)]. A fit to Eq. (1) with $f=ct^z$ in fact gives $z=0.88$, whereas all but one of the other viscosities give $1.10 \leqslant z \leqslant 1.17$ ($\eta=9.8$ has $z=0.96$). This suggests that our lowest viscosity run ($\eta=2.6$) and it alone, may be approaching the inertial hydrodynamic regime, Eq. (3); for more evidence of this, see [10]. This run covers $20\,000 \leqslant t \leqslant 45\,000$, implying that t^* [the crossover between Eqs. (2) and (3)] is similarly large. A less extreme number is obtained if one quotes instead the equivalent Reynolds number $\mathrm{Re}^* \simeq b^2 t^*$. (This relation applies because in linear scaling, we have $\mathrm{Re} = bl \simeq b^2 t$.) For the middle of the given run, Re is about 20, so Re* need not be much larger than this. Given the smallness of the apparent b values (see below), the largeness of t^* follows, as does the failure to observe a clear inertial scaling regime [Eq. (3)] in previous simulations [6].

Based on these observations, we have fit our remaining 6 datasets to the viscous hydrodynamic scaling form, Eq. (2). In all cases the fits are at least as convincing as those of [6,7]. Despite this, we *definitely cannot* interpret this data

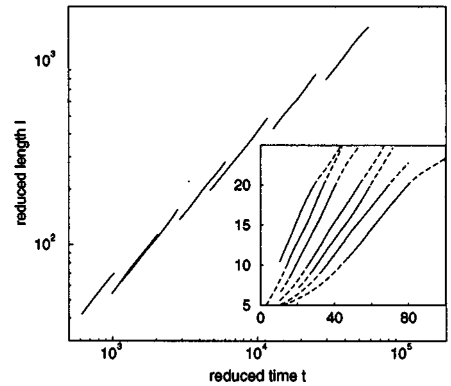

FIG. 1. Inset: Raw DPD data; L vs T for viscosities (left to right) $\eta=2.6$, 3.5, 4.6, 6.2, 8.2, 9.8, and 12.2. The datasets for $\eta=6.2$, 9.8 are averages of two runs. Main figure: the same data in reduced units (log-log) with offsets (found by linear extrapolation to $t=0$) removed.

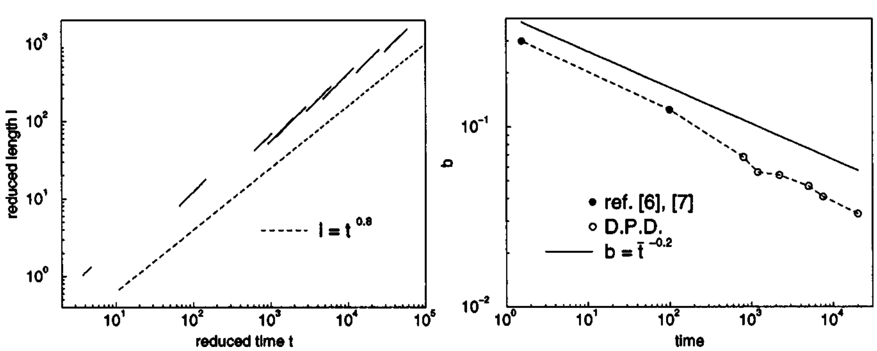

FIG. 2. (a) Fitted functions $f(t)=bt$ for DPD data (rightmost six datasets), that of Ref. [6] (center left), and Ref. [7] (far left). (b) Log-log plot of resulting growth velocities b against the midpoint time $\bar{t}$ of each run.

(nor that of [6,7]) as support for a universal viscous hydrodynamic scaling, Eq. (2). Figure 2(a) shows fits to $f=bt$ (deviations from the data invisible on this scale) including our own and earlier [6,7] datasets. Figure 2(b) shows the fitted b coefficients against the mean time $\bar{t}$, defined by the middle of the fitted section of each run. Obviously, b is not constant as required: it drifts *systematically* toward smaller values at later times $\bar{t}$, a trend representable empirically as a weak power law, $b \simeq \bar{t}^{-0.2}$.

What does all this mean? Clearly, one would expect to measure $b \sim \bar{t}^{-0.2}$ if in fact one had $f=ct^z$ with $z \simeq 0.8$ [see Fig. 2(a)]. We are aware of no theory predicting this value of z, so it would presumably have to be interpreted as an intermediate, *effective* exponent arising in the crossover region between Eqs. (2) and (3). Although possible, at least two arguments counter this interpretation. First, the ''crossover,'' if this is indeed what we are seeing, must be exceptionally broad. Figure 2(b) shows that a single effective exponent governs the entire range of data shown: any ''crossover'' region covers *four decades* in time. The second reason to doubt this explanation is that for all of the DPD datasets shown in Fig. 2, a fit to $f=ct^z$ yields values of z that are not close to 0.8, but close to (and usually slightly larger than) 1.0. Put differently, even after subtraction of the offsets a, our datasets do not join up into a continuous curve on the (l,t) plot as dynamical scaling requires. This is apparent from Fig. 1, and remains true under various replottings we have tried (such as recalculating offsets by imposing $z=0.8$ rather than $z=1$). We therefore ask whether there might be some other physics, playing a role in spinodal decomposition at late times, which could lead to a violation of the dynamical scaling hypothesis itself. One possibility is that the late-stage coarsening velocity b depends on initial conditions, inherited from the nonuniversal early-stage dynamics. (For related ideas, see [22].) This information would have to reside either in the velocity field itself, or in subtle details of the density distribution. The first of these can be tested numerically by reinitializing the fluid velocity field during a late-stage run; we have done this and no significant effect on b was observed.

A more plausible mechanism for the observed nonuniversality of the velocity b could arise from the direct intrusion of physics that the dynamical scaling hypothesis excludes. Thermodynamics (e.g., finite temperature or compressibility [17]) cannot be solely responsible, since all our DPD runs are *identical* thermodynamically. Perhaps the most interesting possibility is that late-stage spinodal decomposition involves a molecular (or, in simulations, discretization) lengthscale which could enter during topological reconnection or ''pinch-off'' events. In such events, without which coarsening of a bicontinuous structure cannot proceed, a fluid neck contracts to (formally) zero width in finite time.

Recent work on a closely related problem (disconnection of a single fluid domain *in vacuo*) suggests that pinch-off processes need not violate dynamical scaling [23]: the asymptotic behavior both before and after the pinch have a universal description in l,t variables (measured from the pinch-off event itself). According to this work, molecular physics intervenes only briefly at pinch-off, and is forgotten soon after. It is not yet known whether similar universality can be recovered for fluid-fluid pinch-offs [23], but crucially, even in the fluid-vacuum case, such universality is *only* expected for large values of the dimensionless quantity

$$\lambda = L_0/h = \eta^2/\rho\sigma h, \tag{4}$$

where h is a molecular (or discretization) length [23,8]. For the fluid-vacuum case, Eggers [23] argues that λ is large enough for some fluids ($\simeq 10^7$ for glycerol) but not others ($\simeq 20$ for water), to recover universal behavior.

If similar ideas govern the fluid-fluid case, and if pinch-off physics remains a controlling factor in late-stage coarsening, then a violation of dynamical scaling could be expected for many real fluids. The same applies for any simulation in which λ is not very large. Taking $h=1$ (DPD units) we find that λ in our runs ranges from $\lambda=0.28$ at $\eta=12.2$ (so that $\bar{t}=800$) to $\lambda=0.014$ at $\eta=2.6$ (so that $\bar{t}=30\,000$). The systematic dependence of b on $\bar{t}$ reported above can, for these DPD runs, equally well be expressed as a dependence on λ. The latter would permit an extended form of dynamical scaling, with $f(t)$ replaced by $f(\lambda,t)$ in Eq. (1); at present this cannot be distinguished from a $\bar{t}$ dependence, because the variations we make through η affect $\bar{t}$ and λ similarly [24].

One speculative possibility is that the time ΔT taken for a fluid neck, of order the domain size L, to reach pinch-off is not linear in L [as Eq. (2) suggests] but varies as $L\ln(L/h)$ [so, in reduced units, $\Delta t \simeq l \ln(l\lambda)$]. In this case, individual runs would show little departure from $f=bt$, yet b would drift slowly downward with $\bar{t}$, and runs of different η would not quite superpose on the (l,t) plot. Such logarithms could conceivably arise from the hydrodynamics of thin fluid cylinders [25]. A fit to $b=\ln\eta$ (not shown) is comparable in quality, for our DPD runs, to that in Fig. 2(b) but less good than the power law shown there, if the data of [6,7] is included.

In conclusion, we have made a careful analysis of our extensive DPD data [10] and of previous simulation results [6,7] on spinodal decomposition in fully symmetric binary fluids. Taken together, these data now cover approximately five decades in reduced physical time units. Contrary to expectation, the data offer no clear support for the hypothesis of a universal dynamical scaling [Eq. (1)] [26]. Such a hypothesis can be sustained, but only [21] by assuming an extremely broad crossover between viscous ($z=1$) and inertial ($z=2/3$) scaling regimes, with an effective exponent $z\simeq 0.8$ spanning about four decades of reduced time t. This ''slow crossover'' interpretation is more plausible when expressed in terms of Reynolds number, which spans only $0.1 \leqslant \mathrm{Re} \leqslant 20$; indeed, experience with turbulence [27] shows that a wide regime of Re might exist in which inertial effects are significant [spoiling Eq. (2)] but not dominant [as required for Eq. (3)]. However, such an interpretation leaves unexplained the facts that (i) almost all our individual simulation runs are better fit by $z \geqslant 1$ than $z \simeq 0.8$, and (ii) even after subtraction of nonuniversal offsets, these runs do not lie on a common curve on the l,t plot [21].

We have therefore put forward a more radical proposal: that the list of physical ingredients (fluid viscosity, density, and interfacial tension), assumed by the dynamical scaling hypothesis to dominate the physics of spinodal decomposition at late times, is incomplete. One possibility is that the ratio $\lambda = L_0/h$ (of continuum to microscopic lengths) remains a relevant parameter: coarsening of a bicontinuous structure is contingent on topological reconnection (pinchoff) events, which could allow the intrusion of microscopic physics no matter how large the mean domain size L.

Note added in proof. Recently, a lattice Boltzmann (LB) study has extended still further the accessible range of l,t. In the range covered by Refs. [6,7], a lower, and constant b value is found. In the l,t range of our DPD study, the LB data lie close to ours on the scaling plot, but is well-fit by $z=0.8$. These LB data support the ''slow crossover'' hypothesis; they suggest that the nonuniversality in our DPD data may be exaggerated by finite size effects, and that in Refs [6,7] by residual diffusion. See V. M. Kendon, J.-C. Desplat, P. Bladon, and M. E. Cates (unpublished).

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