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Spinodal decomposition of asymmetric binary fluids in a micro-Couette geometry simulated with molecular dynamics

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The spinodal decomposition of quenched polymer/solvent and liquid-crystal/solvent mixtures in a miniature Taylor–Couette cell has been simulated by molecular dynamics. Three stacking motifs, each reflecting the geometry and symmetry of the cell, are most abundant among the fully phase separated stationary states. At zero or low angular velocity of the inner cylindrical drum, the two segregated domains have a clear preference for the stacking with the lowest free energy and hence the smallest total interfacial tension. For high shear rates, the steady state appears to be determined by a minimum dissipation mechanism, i.e., the mixtures are likely to evolve into the stacking demanding the least mechanical power by the rotating wall. The partial slip at the polymer-solvent interfaces then gives rise to a new pattern: A stack of three concentric cylindrical shells with the viscous polymer layer sandwiched between two solvent layers. Neither of these mechanisms can explain all simulation results, as the separating mixture easily becomes kinetically trapped in a long-lived suboptimal configuration. The phase separation process is observed to proceed faster under shear than in a quiescent mixture. © 2008 American Institute of Physics.

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I. INTRODUCTION

Phase separation is a common phenomenon in mixtures of liquids and in liquids dispersed with buoyant bodies, such as colloids, polymers, or surfactants, where small differences between the mutual attractions of the various molecules are capable of separating like molecules from unlike molecules, thus driving the formation of clusters or extended patterns. Phase separation may occur in many industrial processes dealing with compound fluids, such as paints, foods, and health-care products, where it often has undesired detrimental effect and shortens the shelf life of many products.¹ The kinetics of phase separation has therefore attracted the attention of many researchers over the years and still remains a topic of intense study to date.

A central quantity in the study of spinodal decomposition—the system-wide phase separation immediately following a quench in one of the system parameters—is the evolution of the average domain size $R(t)$ of the emerging patterns or aggregates, with t denoting the time since the quench. Theoretical models of the growth process, such as the “model H ” for fluid-fluid phase separation, combine a Ginzburg–Landau-type expression for the free energy as a functional of the fluid composition field with a Navier–Stokes expression for the hydrodynamic flow field, compounded with cross terms coupling the dynamics of the fields.^{2,3} Although this model is beyond analytic solution, it is generally accepted that the domains formed in the spinodal decomposition of a symmetric binary fluid follow a scaling

law, i.e., the patterns at early and late times are statistically similar in structure and differ by a scale factor only. The evolution of the single relevant length scale is believed to follow a power law, $R(t) \propto t^\alpha$, where the growth exponent α is determined by equating the dominant terms in model H . Since the importance of the various terms in this model depends on R and $\dot{R}$, it follows that the growth exponent passes through three consecutive regimes: An initial diffusion-dominated $\alpha=1/3$ period,⁴ a regime of interfacial-driven viscous growth where $\alpha=1$,⁵ and a late stage of interfacial-driven inertial growth with $\alpha=2/3$.^{6,7} The linear regime is ubiquitous in the experiments,^{1,8,9} diffusive growth has been observed for shallow quenches near the critical point,^{10,11} while the existence of the late stage has only been confirmed recently in lattice Boltzmann (LB) simulations.¹² The two earlier stages have also been studied in computer simulations by using dedicated Navier–Stokes solvers, such as LB and lattice gas automata,^{13–15} and by off-lattice particle-based methods including molecular dynamics (MD) and dissipative particle dynamics (DPD).^{16–21}

Other spinodal decomposition processes are less well understood than the idealized situation outlined above, although the basic principles guiding the ongoing investigations remain the same. Dynamical asymmetry of the two mixed fluids, meaning that their viscosities differ significantly or that one component shows viscoelastic behavior, explains the complex phase separation processes and the “phase inversion” phenomenon observed in polymer-solvent mixtures and colloidal suspensions.^{22–24} In these systems the “slow” component cannot keep up with the growth rate imposed by the “fast” component; hence, a network enriched in the slow component forms and subsequently succumbs to

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internal stresses to arrive again at a regular phase separated final configuration. An externally imposed shear flow both accelerates and hinders the phase separation process by the continuous transport, elongation, and resulting ruptures of the domains.^{25,26} In combination with the interfacial driving force, these give rise to anisotropic growth of the domains, with two linear growth processes in the flow-vorticity plane and a possibly supralinear growth, $\alpha > 1$, in the shear-gradient direction.^{25,27,28} The domains cannot grow indefinitely in the shear-gradient direction but can attain a rate-dependent nonequilibrium steady state; it is not clear whether the growth in the two perpendicular directions also saturates.^{25,29} Shear may also be applied to induce phase separation in dynamically asymmetric mixtures.^{30,31} Deviations from the ideal case also occur in the presence of walls and other fixed obstacles, which limit the attainable domain size, interfere with the buildup of a hydrodynamic flow field, and may have a preference for wetting by either constituent of the mixture.^{32–34} Another interesting spinodal decomposition process has been reported for rodlike colloids, where the nematic (dis)ordering enslaves the spatial ordering into dense and less dense phases.^{35,36}

Experimental investigations of spinodal decomposition are traditionally aimed at studying one of the above decomposition processes by specifically designing the equipment and conditions such as to eliminate or minimize perturbing side effects. Occasionally two factors are taken into account in one experiment, e.g., dynamically asymmetric mixtures under shear,^{30,37} to study the synergy or competition between the two mechanisms involved in these phase separation processes. However, with the rapid advances in “microfluidics”—the field studying the flow processes in individual liquid droplets and extremely narrow channels^{38,39}—there are many conceivable experiments in which several of the aforementioned mechanisms are simultaneously involved in the spinodal decomposition process. In a microfluidic rheology experiment on a polymer-solvent mixture using a miniaturized Taylor–Couette cell, for instance, the kinetics of the phase separation process is determined by dynamic asymmetry, nonuniform shear, confinement, and wetting, in addition to the unequal attractions between the molecules. Computer simulations provide a preview on the intricate phase separation processes that arise under these complex conditions.

In this work we study the phase separation of polymer-solvent and rod-solvent mixtures in a miniature Taylor–Couette cell, extending our previous simulations on binary fluids in the same geometry.³⁴ Details on the employed models and simulation techniques are summarized in Sec. II. The simulation results, both for stationary walls and for a rotating inner wall, are presented and discussed in Sec. III for a wide range of systems. By necessity, our results and the deliberations will mostly be of a qualitative nature. The main conclusions distilled from the simulations are summarized in Sec. IV.

II. SIMULATION DETAILS

In the current simulation study, the nonbonded interaction between two like particles i and j with relative positions $\mathbf{r}_i - \mathbf{r}_j = r_{ij}\hat{\mathbf{r}}_{ij}$, with the hat indicating a unit vector, is modeled by the usual Lennard-Jones potential,

$$U_{\text{LJ}}(r_{ij}) = 4\epsilon \left[\left(\frac{\sigma}{r_{ij}} \right)^{12} - \left(\frac{\sigma}{r_{ij}} \right)^6 \right], \quad (1)$$

where ϵ and σ are the strength and range, respectively. Discontinuities in the potential and force close to the cut-off distance, $r_c = 2.5\sigma$, are removed by a smooth truncation of the potential. A purely repulsive Weeks–Chandler–Andersen (WCA) potential, $U_{\text{WCA}}(r_{ij}) = U_{\text{LJ}}(r_{ij}) + \epsilon$ for $r_{ij} \leq 2^{1/6}\sigma$ and $U_{\text{WCA}}(r_{ij}) = 0$ for $r_{ij} > 2^{1/6}\sigma$, acts between pairs of unlike particles. A polymer P_n is created by the expedient of stringing n solvent particles S together via a finitely extensible nonlinear elastic (FENE) potential,

$$U_b(r_{i,i+1}) = -\frac{1}{2}k_b r_\infty^2 \ln \left[1 - \left(\frac{r_{i,i+1}}{r_\infty} \right)^2 \right]. \quad (2)$$

With the bond constant set to $k_b = 30\epsilon/\sigma^2$ and the maximum length of the bond limited to $r_\infty = 1.5\sigma$, the resulting polymers are very flexible, as shown by their persistence length of nearly 1σ . A more rigid chain, R_n , resembling a polymeric liquid crystal, is made by introducing a stiffening potential between the next-nearest neighbors in a chain,

$$U_s(r_{i,i+2}) = \frac{1}{2}k_s(r_{i,i+2} - r_s)^2. \quad (3)$$

For $k_s = 10\epsilon/\sigma^2$ and $r_s = 4\sigma$, the persistence length of the chain increases to 17σ , which amounts to about three times the chain length of R_7 . The classical mechanics equations of motion are integrated numerically using the Verlet leap-frog algorithm^{40,41} with a time step $\Delta t = 0.002\tau$, where the unit of time is defined by $\tau = \sqrt{m\sigma^2/\epsilon}$. All particles have the same mass m .

A thermostat^{40,41} is employed to maintain a steady temperature $T = 1\epsilon/k_B$, with k_B the Boltzmann constant. Without a thermostat the system would gradually heat up due to the energy released during phase separation and the work exerted on the system by the rotating wall. Since hydrodynamic interactions are essential in the proper simulation of the later stages of spinodal decomposition, as well as in the simulation of flow phenomena, care was taken to select a hydrodynamics conserving thermostat. Such a thermostat was introduced as part of the DPD method^{42–44} by implementing friction and random forces as momentum conserving interactions between pairs of particles. In short, these forces are expressed as

$$\mathbf{F}_{ij}^{d+r} = -\frac{\kappa^2}{2k_B T} \left(1 - \frac{r_{ij}}{r_c} \right)^2 (\hat{\mathbf{r}}_{ij} \cdot \Delta \mathbf{v}_{ij}) \hat{\mathbf{r}}_{ij} + \frac{\kappa}{\sqrt{\Delta t}} \left(1 - \frac{r_{ij}}{r_c} \right) \zeta_{ij} \hat{\mathbf{r}}_{ij}, \quad (4)$$

where $\kappa = 3.0\epsilon\tau^{1/2}\sigma^{-1}$ determines the strength of the thermostat, $r_c = 2.5\sigma$ is the cut-off distance, and $\Delta \mathbf{v}_{ij}$ is the velocity difference between two particles. The $\zeta_{ij}(t)$ denotes a random number with zero mean and unit variance, sampled independently and without correlation for every pair at every time

step. A fluctuation-dissipation theorem, relating the dissipative first term to the stochastic second term via the temperature T , is usurped in the above expression. The effectiveness of the thermostat was verified by calculating local velocity distributions, which indicate that the average temperature typically overshoots the desired temperature by some 2%. This slight excess temperature is due to the heat produced by the phase separation process, the work done by the externally imposed shear flow, and the simplified implementation of friction and random forces in the standard DPD algorithm.^{43,45}

A Taylor–Couette geometry is created by confining the fluid particles between two coaxial cylindrical walls. In the simulations presented here, the outer wall is always stationary while the inner wall is either stationary or rotating at a constant angular velocity ω_i . For any particle i crossing a wall during the integration time step, the velocity $\Delta \mathbf{v}_i$ of the particle relative to that wall is reversed at the moment of collision, $\Delta \mathbf{v}_i \mapsto -\Delta \mathbf{v}_i$, before executing the remainder of the time step. This bounce-back rule is introduced with the aims of restricting the particles to the Couette cell and creating stick boundary conditions at both walls, but in the simulations, especially those at high angular velocities or with viscous fluids, some slippage remains. It is therefore augmented with a scheme to resample the velocities of all particles within 1σ of a wall from a Maxwell–Boltzmann distribution, offset by the rotational velocity of the wall; by applying this procedure every time step, the desired nonslip boundary conditions are recovered.

In order to reduce the computational demands of the simulation, we do not simulate the entire Taylor–Couette cell but a section amounting to one-sixth of the cell, i.e., a segment covering an angle $\Theta_i = \pi/3$, with periodic boundary conditions^{40,41} applied along the azimuthal direction. These corrections are readily implemented in a Cartesian-coordinate based simulation code,³⁴ the only minor complication is that any calculation involving a boundary crossing term now involves a rotation over $\pm \Theta_i$ around the central axis of the Couette cell. Regular periodic boundary conditions apply along the axial direction.

The inner wall radius R_i is set at either 25σ or 40σ , the outer wall radius R_o takes on a range of values from 40σ to 75σ . The systems with the smaller inner radius contain $N=10\,500$ particles, simulations with 15-bead chains are executed with 30 000 particles, while all other systems contain 21 000 particles. Both solvent and polymer particles are always present in equal numbers. The particle density was fixed at $\rho=0.7\sigma^{-3}$, resulting in box heights $h=2N/[\rho\Theta_i(R_o^2 - R_i^2)]$ varying from 15.3σ to 31.2σ .

In rheological experiments employing a Couette cell, the obvious quantities of interest are the total torque exerted by the rotating inner wall and the amount of work required to maintain its steady angular velocity. The relevant shear stress at the inner wall is calculated in our simulations from

$$\tau_{r\theta}(R_i) = -\frac{1}{\Theta_i h R_i^2} \left\langle \sum_i m_i r_i v_{i\theta} v_{ir} + \sum_i \sum_{\substack{j \\ j>i}} \bar{\mathbf{r}}_{ij}(r_i - r_j) [\mathbf{F}_{ij}^{c+d} \cdot \hat{\mathbf{e}}_\theta(\bar{\mathbf{r}}_{ij})] \right\rangle, \quad (5)$$

where the pointed brackets denote a temporal average, $v_{ir} = \mathbf{v}_i \cdot \hat{\mathbf{e}}_r(\mathbf{r}_i)$ the radial velocity, $v_{i\theta} = \mathbf{v}_i \cdot \hat{\mathbf{e}}_\theta(\mathbf{r}_i)$ the azimuthal velocity of particle i , and $\bar{\mathbf{r}}_{ij} = (\mathbf{r}_i + \mathbf{r}_j)/2$. The superscript to the pair force emphasizes that both conservative and dissipative forces are needed in the stress calculation. The power supplied by the inner wall in the steady state is given by $P = \omega_i \Theta_i h R_i^2 \tau_{r\theta}(R_i)$ and equals the rate of energy dissipation by viscous effects in the sheared fluid. A derivation of these expressions is presented in the Appendix.

III. RESULTS

In this section an extensive survey of the simulated phase separation processes in a Couette geometry is given. To structure the discussion, the fluid properties will be analyzed first. Next comes phase separation in a quiescent mixture, studying the final stable states and their rates of formation. We end with phase separation under shear, again describing both the stationary states and the evolutions bringing the mixed systems to these states.

A. Characterization of the fluids

The most important fluid parameters in the simulations of phase separation in a Couette flow are the interfacial tensions and the viscosities; these parameters are easiest calculated from simulations of cubic boxes. A system with regular three-dimensional (3D) periodic boundary conditions then phase separates into two parallel flat layers, and one readily shows, from the free energy change under a volume-conserving area variation, that the interfacial tension γ follows from

$$\gamma = \left(\frac{\partial F}{\partial L_\parallel^2} \right)_{NVT} = \frac{1}{2} (p_\parallel - p_\perp) L_\perp. \quad (6)$$

Here p denotes the pressure, with the subscripts $\perp$ and $\parallel$ indicating the directions perpendicular and parallel to the interface, respectively, and L is the edge length of the box. The factor of $1/2$ on the right hand side arises because a 3D periodic box contains two interfaces. Fluid-wall interfacial tensions are calculated in a similar way using a two directional periodic box with hard walls in the third direction. The surface tensions of the various interfaces are summarized in Table I. Visual inspection of the fluid-fluid simulations using the Visual Molecular Dynamics (VMD) program⁴⁶ reveals that the polymer and rod phases are denser than their coexisting solvent phases by some 10%. A similar observation is made in the Couette geometry. We attribute this increased density to the bonds between the particles, which reduce the nearest neighbor distances between particles in the same polymer. In order to correct for the possible effects of these density differences, the fluid-wall interfacial tensions listed

TABLE I. Surface tensions γ_{SX} of the solvent-fluid interface and γ_{WX} of the wall-fluid interface, and the fluid viscosities η_X , as obtained from simulations of cubic systems. Columns four and five contain the densities ρ_S of the solvent and ρ_X of the fluid in the solvent-fluid systems. All wall-fluid interfacial tensions are calculated at the denoted fluid density ρ_X . The solvent-wall interfacial tensions for the two relevant solvent densities are reported in the first two rows.

X	$\gamma_{SX}/\epsilon\sigma^{-2}$	$\gamma_{WX}/\epsilon\sigma^{-2}$	ρ_S/σ^{-3}	ρ_X/σ^{-3}	$\eta_X/\epsilon\tau\sigma^{-3}$
S	1.23 ^a	0.53	0.70	0.70	8.4
S	...	0.41	...	0.64	6.4
P_7	1.40	0.64	0.64	0.78	36 ^b
P_{15}	1.38	0.69	0.64	0.78	
R_7	1.37	0.39	0.64	0.78	55 ^b
R_{15}	1.28	0.51	0.64	0.78	

^aInterfacial tension with repulsive interactions between the two solvent phases.

^bViscosity in the zero-shear limit. The polymer and rod fluids are shear thinning, see text.

in Table I have been calculated at the specific densities found in the fluid-solvent simulations.

The viscosities of the various fluids are readily obtained from shear simulations in conventional rectangular boxes as the proportionality constant relating the shear stress τ_{xz} to the shear rate $\dot{\gamma}$. Linear shear flows $\mathbf{v}(\mathbf{r}) = \dot{\gamma}z\hat{\mathbf{e}}_x$ are introduced by applying Lees-Edwards moving boundary conditions,⁴⁰ as well as by placing a two directional periodic fluid between one stationary and one linearly moving wall. In the latter case, the stress tensor is calculated excluding the regions within 2σ of the walls to avoid complications from the stick-wall procedure. Both sets of simulations yield similar results, indicating that the stick conditions at the walls are working satisfactorily. The viscosities are listed in Table I. Both the polymers and rods exhibit shear thinning over the applied range of $(1-50) \times 10^{-3} \tau^{-1}$ of shear rates. The flow curves are well fitted by the four-parameter Carreau equation,⁴⁷ $\eta(\dot{\gamma}) = \eta_\infty + (\eta_0 - \eta_\infty)[1 + (\zeta\dot{\gamma})^2]^\delta$, with $\eta_\infty = 11\epsilon\tau\sigma^{-3}$, $\eta_0 = 35\epsilon\tau\sigma^{-3}$, $\zeta = 96\tau$, and $\delta = -0.30$ for the P_7 polymers and $\eta_\infty = 10\epsilon\tau\sigma^{-3}$, $\eta_0 = 55\epsilon\tau\sigma^{-3}$, $\zeta = 210\tau$, and $\delta = -0.28$ for the R_7 rods. The exponents δ agree with the typical experimental values for polymers,⁴⁷ while the remaining three parameters are specific for the employed polymer. Clearly, shear thinning further complicates the nature of the phase separation process under shear, as it may have consequences for both the growth rate and the resulting steady state.

In their homogeneous phase, the stiff R_7 and R_{15} chains show a hallmark of liquid crystals: The rods spontaneously

align to establish a nematic ordering. The order parameter S_2 , defined as the largest eigenvalue of the matrix

$$\mathbf{S} = \frac{3}{2} \left(\langle \hat{\mathbf{u}}_i \hat{\mathbf{u}}_j \rangle - \frac{1}{3} \mathbf{I} \right), \quad (7)$$

where $\hat{\mathbf{u}}_i$ denotes the bond vectors in the rods and $\mathbf{I}$ is the unit matrix, increases to about 0.6 on a scale from 0 for purely random to 1 for completely aligned. No such ordering was observed in the homogeneous solvent-rod systems with Lennard-Jones interactions between all particles because the isotropic phase is either stable or a long-lived metastable state.

B. Steady state at zero shear

Based on the geometry of the Couette cell, the orientations of the fluid-fluid interfaces in a fully phase separated state are likely to correspond to the basis vectors in cylindrical coordinates. Stable states with interfacial normals along the radial direction $\hat{\mathbf{e}}_r$ will henceforth be denoted as r -stacks, states with normals parallel to the axial axis $\hat{\mathbf{e}}_z$ are called z -stacks, and normals in the azimuthal direction $\hat{\mathbf{e}}_\theta$ are θ -stacks. Snapshots illustrating these stacks are shown in Fig. 1. The calculated surface tensions then permit a straightforward approximate determination of the thermodynamically stable state by finding the stack with the lowest free energy among the anticipated optimum configurations. Here it is implied that interfacial contributions dominate the free

FIG. 1. (Color) Snapshots of four typical phase separated final configurations showing (from left to right) a z -stack, an r -stack, a θ -stack and a droplet attached to the inner wall. The z stack is shown in a side view with the rotation axis of the Couette cell running vertically, while the other configurations are top views looking down along the rotation axis of the cell. Because of the Couette cell's rotational symmetry, we simulate a segment amounting to one-sixth of the entire cell by using periodic boundary conditions in the axial and azimuthal directions. Polymer particles are colored green, solvent particles are blue; note that the particles are not drawn to scale and that the dimensions of the cell vary in the four systems.

FIG. 2. (Color online) The total interfacial energies of three different stackings in a phase separated polymer-solvent system, P_7-S , as a function of the radius R_o of the outer wall. All parameters entering the calculation of these theoretical curves are based on the simulated system with an inner wall radius $R_i=40\sigma$.

energy differences between the various stackings of a given mixture, while variations in the bulk contributions are deemed negligible. A simple surveying of the various surface contributions, where one may conveniently assume idealized flat or uniformly curved interfaces, then yields the free energies for every mixture and stacking. Corrections for the density differences between the coexisting fluids are readily implemented. The example depicted in Fig. 2 concerns one of the simulated systems, namely, the P_7-S system containing 21 000 particle and a cell with an inner wall radius $R_i=40\sigma$. On the basis of this plot, we expect the simulations of this system to yield z -stacks for outer wall radii of up to 52σ , r -stacks beyond approximately 69σ , and θ -stacks in the intermediate region. A comparison with the simulation results is described in Sec. III C.

Due to the different fluid-wall interfacial tensions (see Table I), most fluid-fluid interfaces will impinge on the wall under a nonperpendicular contact angle, following Young's law,⁴⁸ and the fluid-fluid interfaces will consequently be non-uniformly curved. Theoretical expressions for the interfacial shape in a Couette cell have been derived in Ref. 34, where it was found that the surface tensions consistently enter the expressions in the form $\Gamma=(\gamma_{AW}-\gamma_{BW})/\gamma_{AB}$, with A , B , and W denoting the two fluids and the wall, respectively. For a θ -stack, for instance, the interface is described by

$$\theta(r) = \theta(R_i) + \int_{R_i}^r \frac{C + \lambda x^2}{\sqrt{x^4 - x^2(C + \lambda x^2)^2}} dx, \quad (8)$$

where $\lambda=\Gamma/(R_i-R_o)$ and $C=\Gamma R_i R_o/(R_o-R_i)$. Note that density differences between the two fluids affect the location of the interface, i.e., $\theta(R_i)$, but have no influence on the shape of the interface. The predicted interface is depicted in Fig. 3, for $\Gamma=0.16$, along with the actual interface of a polymer-solvent system. We have calculated this profile by using a 2D grid to establish the average densities $\rho_P(r, \theta)$ and $\rho_S(r, \theta)$ of polymer and solvent particles, respectively. The order parameter field for a given grid value of r ,

$$\phi_r(\theta) = \frac{\rho_P(r, \theta) - \rho_S(r, \theta)}{\rho_P(r, \theta) + \rho_S(r, \theta)}, \quad (9)$$

is then numerically fitted with a sum of two theoretical interfacial profiles,

FIG. 3. (Color online) The profile of the polymer-solvent interface obtained from simulations (circles) of a P_7-S system ($R_i=25\sigma$, 21 000 particles). The theoretical curve (dashed line) of Eq. (8) is calculated with $\Gamma=0.16$ based on the interfacial tensions in Table I, while the optimum fit (solid line) is achieved at $\Gamma=0.31$.

$$\phi_r^{\text{theo}}(\theta) = \alpha_r \tanh[\beta_r r(\theta - \theta_1)] - \alpha_r \tanh[\beta_r r(\theta_2 - \theta)], \quad (10)$$

to yield the profiles $\theta_1(r)$ and $\theta_2(r)$ of the two polymer-solvent interfaces. Figure 3 shows the moderate agreement of their average with the predicted interfacial shape, suggesting that other factors, such as the connectivity of the beads in the polymers, might play subtle roles as well. The deviations from a flat interface are small, however, and of little consequence in the area-based free energy calculations of Fig. 2. As concerns the remaining two fitting parameters, α_r approximately equals unity, while $\beta_r^{-1} \approx 2\sigma$ measures the combined effects of the interfacial width and temporal variations in the location of the interface.

The simulations of spinodal decomposition of binary fluid mixtures in a Couette geometry are first performed for stationary walls, i.e., without the added complications of a nonuniform shear flow. For each mixture, a start configuration is created by randomly placing the fluid particles in the simulation box, subject to the conditions imposed by bonds between connected particles; trial positions resulting in significant pair overlaps are rejected. The systems are then equilibrated by running extensive simulations at the desired equilibrium temperature using regular Lennard-Jones interactions between all particles to suppress phase separation of the two fluid components. A subsequent deep quench to an unstable state is created by instantaneously introducing purely repulsive WCA interactions between unlike particles, thus initiating the spinodal decomposition of a homogeneous mixture. Visual inspection of the ensuing simulation dynamics clearly shows the formation of a fine bicontinuous network of regions rich in either of the fluids. The network gradually coarsens as the domains grow in size, and the connections between the domains break one by one until the system eventually arrives at a steady state consisting of two fully separated regions. The final states of some 30 systems, varying in fluid-fluid compositions and Couette geometry, are collected in Table II, with snapshots of typical end configurations shown in Fig. 1. In most cases the orientations of the fluid-fluid interfaces correspond to one of the basis vectors in cylindrical coordinates, i.e., $\hat{e}_r$ for r -stacks, $\hat{e}_z$ for z -stacks, or $\hat{e}_\theta$ for θ -stacks. A significant fraction of the simulations has ended up in less regular states: Several runs

TABLE II. Phase separated steady states in a stationary nanoscopic Taylor–Couette cell for various drum geometries (collected in rows, with R_i and R_o as the inner and outer radii of the cell) and various binary fluid mixtures (sorted in columns, with S for solvent, P for polymer, and R for rod). Each state is coded according to the direction of its fluid-fluid interfacial normals, which predominantly point in the radial (r), azimuthal (θ), or axial (z) direction with snapshots illustrating these stacks given in Fig. 1. Subscripts to r -stacks indicate the sequential order of layers traversed when going from the inner to the outer wall of the Couette cell. Droplets are marked d , with the superscript distinguishing between droplets attached to the inner (i) or outer (o) wall, and the subscript giving the composition of the droplet. Long-lived bicontinuous networks spanning the entire cell are registered as n . Three systems in the top-left corner of the table were run four times each, with the results of these independent simulations collected in a comma-separated list to give an impression of the repeatability of the final state. Bracketed entries showing the stable state according to a free energy calculation, as discussed in Sec. III B, are included if the predicted state differs from the observed final state.

R_i/σ	R_o/σ	P_7-S	R_7-S	P_7-R_7	R_7-R_7	$P_{15}-S$	$R_{15}-S$
25	40	z, z, z, z (θ)	z, z, z, θ (θ)		z (θ)		
25	50	d_P^i, d_P^i, n, r_{SPS} (r_{PS})	r_{RS}				
40	60	z (θ)	θ	θ			
40	65	θ	θ	d_P^o (θ)	θ	r_{PS} (θ)	n (θ)
40	70	θ (r_{PS})	θ (r_{RS})	d_R^o (θ)		r_{PS}	n (r_{RS})
40	75					d_P^o (r_{PS})	n (r_{RS})

duced a droplet (d) attached to a wall, while still other runs appear stuck in an intermediate bicontinuous network state (n) attached to both walls at multiple positions.

Table II shows a moderately satisfactory agreement between the steady states in the simulations and the predictions based on the interfacial free energies. Several factors may contribute to the deviations, which are more abundant here than for previous simulations of a fluid-fluid mixture in a micro-Couette cell.³⁴ The assumption that the surface tensions dominate the free energy, ignoring all other contributions, is approximate by nature, and bending contributions to the interfacial free energy are neglected. The surface tensions have been calculated for flat interfaces and are perhaps less suited for the current curved interfaces, as exemplified by the interfacial profile in Fig. 3. A recalculation using the fitted Γ in combination with γ_{SW} and γ_{SP} does not significantly alter the predictions. It is well conceivable that the walls steer the initial phase separation in a certain direction, thereby setting the system onto a path toward a suboptimal final state. Lastly, since the emerging decomposition pattern varies with the quenched start configuration, the final state is to a certain degree inherently unpredictable: In periodic simulation boxes this indeterminism manifests itself in the apparently random locations of the domains and in variations of the domain sizes,⁴⁹ but perhaps the chaotic origin suffices in the current cell geometry to codetermine the shape of the final state. To assess the reproducibility of the separation process, three systems have been simulated four times each using independently generated homogeneous starting configurations. The results (see Table II) indicate that one system consistently arrives at the same final state, while the two other systems yield multiple steady states. In conclusion, the thermodynamically optimum state yields a moderately accurate prediction, but it cannot be completely relied on for a number of reasons.

In the case of r -stacks, both the flexible and rigid chains systematically cover the inner wall with the solvent occupying the outer region of the cell. This configuration is stabilized by a minimization of the total fluid-wall interfacial en-

ergy, which drives the chains with their higher surface tensions, $\gamma_{WP} > \gamma_{WS}$, to the wall with the smaller area. Since the densities of the chain fluids are higher than the density of the solvent, the configuration with the chains on the inside also has the smallest chain-solvent interfacial area, which further contributes to the stability of this configuration.

Besides the three expected types of stacks, Table II also includes a number of additional long-lived conformations. Several simulations ended with a droplet of the dense polymer or rod phase attached to either the inner or the outer wall of the Couette cell. These droplets are always oriented parallel to the drum axis and span the entire height of the simulation box, suggesting that the periodic boundary condition along z contributes to their stability⁵⁰ and, hence, that droplets are less likely in experiments. Droplets surrounded by a solvent phase prove to be very stable in our simulations, indicating a high activation barrier for the eventual transition to a regular stacked configuration, which most likely will be a θ -stack. The droplets observed in the polymer-rod mixtures are larger than those exposed to solvent because here both separated phases have approximately equal densities. These droplets resemble metastable states, which can evolve either into a θ -stack, by stretching in the radial direction toward the opposite wall, or into an r -stack, by bridging the gap separating the droplet from its periodic image. In the simulations with the long R_{15} rods, the mixture forms an irregular bicontinuous network within about $4 \times 10^3 \tau$ and remains unchanged until the termination of the run some $6 \times 10^3 \tau$ later. This suggests that the rod fluids relax relatively slowly, compared to the polymer melts, which will be the topic in Sec. III C.

C. Decomposition dynamics at zero shear

In order to get a first impression of the rates of domain formation, we have simulated spinodal decomposition in a periodic cubic box of sides $L = 48\sigma$ using the procedures outlined above. The employed binary mixtures are $S-S$, P_7-S , and R_7-S , again with equal numbers of each type of particle.

FIG. 4. (Color online) Average domain size R as a function of time t for spinodal decomposition in three fluid mixtures. The P_7 - S curve (dashed) is scaled (indicated by the arrow) along the horizontal axis by a factor of 4 and along the vertical axis by a factor of 2 to make the curve coalesce with the S - S curve (dash-dotted). Scaling factors of 7 and 2 for t and R , respectively, have been applied to the R_7 - S curve (solid).

Time-dependent average domain sizes $R(t)$ have been determined by means of structure factor calculations using the procedure outlined in Ref. 21. Figure 4 shows the growth curves of the three mixtures, as obtained by averaging five independent simulations for each mixture. It is evident that the binary liquid mixture separates much faster than the polymer and liquid-crystal mixtures, and that the curves are all fairly similar in shape. Since the growth curves $R(t)$ of symmetric binary mixtures are believed to coalesce to a master curve after appropriate adjustments of the time and length scales, we have followed a similar procedure to maximize the agreement between the current three curves. From optimizing the scaling factors, it follows that the P_7 - S mixture separates about $1\frac{3}{4}$ times as fast as the R_7 - S mixture. This difference is most likely caused by the rigidity of the rods, which may hinder their motions, since both mixtures have comparable interfacial tensions. In addition, the stiff polymers show signs of nematic ordering in the dense polymer phase. Based on the three curves, we estimate the transition from diffusive growth $R \propto t^{1/3}$ to interfacial-driven viscous growth $R \propto t$ to happen around a time t_{dv} of about 10τ for the binary solvent mixture, about 40τ for the polymer-solvent mixture, and about 70τ for the rod-solvent mixture.

The limitation of conventional structure factor calculations to periodically continued rectangular systems prevents this method from being applied to determine the growing average domain size in the current cell with two curved bounding walls. In the absence of a sound alternative mea-

surement procedure, we resort to visual inspection of the emerging patterns to get an impression of the relative growth rates. By comparing movies⁴⁶ of phase separation in a Couette cell against movies of the same binary mixture in a cubic periodic box, we are led to the conclusion that the initial growth rates are similar in both cases, suggesting that the domains developing in the bulk of the Couette cell are not yet influenced by the walls. Only in the latter stages, when the domain sizes approach the cell dimensions, does the geometry of the cell start to affect the domain growth by preferentially driving the system to the state with the lowest interfacial free energy. The differences between domain growth in an infinite cell and domain growth in a finite cell, including the partiality of the wall toward either fluid, appear to be of little impact until the domain sizes correspond to a significant fraction of the smallest cell dimension. However, at this late stage these effects are often not sufficiently persuasive to prevent the system from becoming trapped in a suboptimal state, explaining the modest agreement between simulations and theory in Table II. A quantitative analysis of the growth rate of the domains and the role played herein by the geometry of the cell requires a large number of independent phase separation simulations⁴⁹ preferably with a larger cell to widen the range of length scales separating the molecular dimensions from the cell dimensions.

Two series of snapshots of phase separations in P_7 - S and R_7 - S are collected in Fig. 5. Because of the anticipated scaling factor of $1\frac{3}{4}$ (see Fig. 4), the snapshots of the liquid-crystal system are taken at correspondingly later times than those of the polymer system. By comparing the two series, it appears that the growth rates indeed differ by a factor of about $1\frac{3}{4}$ during the initial stages of phase separation. For later times, however, the rod mixture is clearly lagging behind even more: The connected network of rod domains survives much longer than the network of polymer domains. A similar slowing down arises for the longer R_{15} rods, which are still in a network phase by the time the corresponding P_{15} polymers have already fully phase separated into their steady state.

D. Steady state under shear

The binary fluid mixtures and cell geometries in Sec. III B have also been simulated with a rotating inner wall. The final steady states observed in these simulations,

FIG. 5. (Color) Side views of polymer-solvent (top, at $t=100\tau$, 500τ , 1500τ and 2500τ) and rod-solvent (bottom, at $t=175\tau$, 875τ , 2625τ and 4375τ) mixtures showing various stages during their respective phase separations in Couette cells with $R_i=25\sigma$ and $R_o=40\sigma$. The difference in the time scaling by a factor of $1\frac{3}{4}$ compensates for the anticipated slower segregation of the rods in a cubic periodic box (see Fig. 4).

TABLE III. Steady states of phase separated binary mixtures in a nanoscopic Taylor–Couette cell for inner walls rotating at an angular velocity $\omega_i=0.001$ rad/ τ (top half of the table) or $\omega_i=0.01$ rad/ τ (bottom half of the table) and a stationary outer wall. See Table II for an explanation of the notation. Double and triple banded r -stacks are distinguished by their number of subscripts. The steady states marked $r_{XS}+d_X^o$ comprise a layer of polymers or rods (X) covering the inner wall and a droplet of the same composition attached to the outer wall.

R_i/σ	R_o/σ	P_7-S	R_7-S	P_7-R_7	R_7-R_7	$P_{15}-S$	$R_{15}-S$
25	40	z	z		z		
25	50	d_P^o	$r_{RS}+d_R^o$				
40	60	r_{PS}	r_{RS}	d_R^o			
40	65	r_{PS}	d_R^o	r_{PRP}	z	r_{PS}	z
40	70	d_P^o	r_{SRS}	r_{PR}		r_{PS}	r_{RS}
40	75					r_{SPS}	r_{RS}
25	40	z	z		z		
25	50	$r_{PS}+d_P^o$	$r_{RS}+d_R^o$				
40	60	r_{SP}	r_{SR}	r_{PR}			
40	65	r_{SPS}	r_{SRS}	r_{PR}	z	r_{SP}	r_{SR}
40	70	r_{SPS}	r_{SRS}	r_{PR}		r_{SP}	r_{SR}
40	75					r_{SPS}	r_{SRS}

which again started from a homogeneously mixed initial state, are summarized in Table III for inner wall angular velocities ω_i of 10^{-3} and 10^{-2} rad/ τ . Several trends stand out in Table III and these will be discussed in this subsection in some detail. We start by noting that a rough indication of the corresponding shear rates is given by $\dot{\gamma} \approx \omega_i R_i / (R_o - R_i)$ and ranges from $10^{-3} \tau^{-1}$ to $2 \times 10^{-2} \tau^{-1}$, while the actual shear rate is, of course, nonuniform in a Couette cell. The shear rates are therefore relatively small compared to the transition times between consecutive growth regimes, with $\dot{\gamma} t_{dv} < 1$ for most systems, implying that the spinodal decompositions reach a growth regime driven by interfacial tension. Consequently, we find large domains whose dimensions are not limited by the shear even at the highest attempted drum velocity of $\omega_i = 5 \times 10^{-2}$ rad/ τ .

From Table III it is clear that θ -stacks, which are abundant in the absence of shear, are not formed under shear. An existing θ -stack connecting the two opposing walls will, under the influence of a rotating inner cylinder, be wrapped around the inner drum and simultaneously be stretched thin, and subsequently be torn apart under the mounting elongational strain. It is not surprising, therefore, that θ -stacks are not spontaneously formed in the phase separating mixtures. Networklike structures are suppressed on similar grounds. Only rotationally symmetric stacks, i.e., the r and z -stacks, are expected to be stable against the continuous deformations brought upon the fluid mixture by the shearing Couette cell. Interestingly, the simulations under shear also yield a structure that was not previously observed, namely, an r -stack with three bands.

All double-banded r -stacks at the lower shear rate have the dense polymer or liquid-crystal fluid on the inside and the less dense solvent on the outside. This distribution is inline with the theoretical predictions and the simulation results for the quiescent system. For the double-banded r -stacks at the higher shear rate, however, we observe that the order of the bands has reversed, with the solvent now consistently covering the inner wall and the fluid of chains

occupying the outer wall. Three underlying mechanisms are hypothesized to explain this inversion of the steady state:

- (1) Following a thermodynamical line of thought, any system strives to minimize its free energy within the restrictions set by the externally imposed conditions. In the absence of shear, this free energy is dominated by the interfacial contributions, as discussed in Secs. III A and III B. The flow field $v_\theta(r)$ may be accounted for, in a casual approach inspired by statistical mechanics, by extending the free energy with a kinetic term,

$$F_{\text{kin}} = \frac{1}{2} \int_V \rho(\mathbf{r}) v_\theta^2(\mathbf{r}) d\mathbf{r} = \frac{1}{2} m \sum_i v_{i\theta}^2 - \frac{1}{2} N k_B T. \quad (11)$$

In the last step, a Maxwell–Boltzmann distribution of $v_{i\theta}$ centered around $v_\theta(r_i)$ is assumed to arrive at a computationally attractive expression, which avoids the analytic solution of the flow fields of shear-thinning fluids in various stackings. The extended free energy may explain some transitions with varying drum velocity, as illustrated by the examples in Table IV, but the overall agreement with the simulations remains wanting.

- (2) Based on the minimum dissipation theorem in fluid dynamics,⁵¹ the steady state may be identified as the configuration requiring the least power by the rotating wall in the stationary state. The power is calculated from the shear stress $\tau_{r\theta}$ on the inner wall using the expressions derived in the Appendix. The results in Table IV suggest that this mechanism is becoming important at the high shear rate, especially in the larger simulation boxes, while there is little correlation at the low shear rate. Of course, for stationary walls the power is zero and the mechanism holds no predictive power.
- (3) As noted earlier, a system can become kinetically trapped during the phase separation process. The centrifugal forces experienced by the rotating mixture may then explain the preference of the denser polymer and

TABLE IV. Differences in free energies and shear powers for binary P_7 - S systems, comparing four stacks in three Couette geometries (with inner radius R_i and outer radius R_o) at two angular velocities ω_i of the inner wall. The free energies are based on the interfacial free energy and augmented with a kinetic term accounting for the flow field [see Eq. (11)]. The power required to rotate the inner wall is calculated using the expressions derived in the Appendix. Within each row the lowest free energy and the lowest shear power are taken as the reference points for all entries in that row—these minima therefore appear as zeros in the table. The steady states obtained from the phase separation simulations of these systems (see Table III) are marked with an asterisk.

Free energy (ϵ)					Shear power (ϵ/τ)				
R_i/R_o	$\omega_i/\text{rad } \tau^{-1}$	z	r_{PS}	r_{SP}	r_{SPS}	z	r_{PS}	r_{SP}	r_{SPS}
25/40	10^{-3}	$10^{1.5*}$	0	$10^{2.0}$	$10^{3.1}$	$10^{3.1*}$	$10^{2.1}$	$10^{0.7}$	0
25/40	10^{-2}	0*	$10^{1.9}$	$10^{1.4}$	$10^{3.1}$	$10^{3.9*}$	$10^{2.5}$	$10^{2.5}$	0
40/60	10^{-3}	$10^{2.9}$	0*	$10^{2.3}$	$10^{3.3}$	$10^{3.5}$	$10^{2.8*}$	$10^{2.1}$	0
40/60	10^{-2}	$10^{2.7}$	$10^{2.4}$	0*	$10^{3.2}$	$10^{4.3}$	$10^{3.3}$	$10^{3.1*}$	0
40/65	10^{-3}	$10^{3.3}$	0*	$10^{2.2}$	$10^{3.1}$	$10^{3.2}$	$10^{2.6*}$	$10^{2.6}$	0
40/65	10^{-2}	$10^{3.2}$	$10^{2.6}$	0	$10^{3.0*}$	$10^{4.1}$	$10^{3.3}$	$10^{3.0}$	0*

liquid-crystal fluids to gyrate to the outer wall with the less dense solvent moving to the inner wall. Once a nascent metastable structure has formed, it will be difficult for the preceding two mechanisms to drive the system away from the metastable state to a state of minimum free energy or minimum work.

More generally, the abovementioned three mechanisms may be invoked to explain the steady states of the other systems as well, both under shear and at zero shear. The data in Tables II–IV suggest, however, that none of these mechanisms describes all final states correctly. Most likely, the thermodynamic argument presides at zero and small shear rates, the flow argument becomes increasingly important with rising shear rates, and the trapping argument repeatedly frustrates these mechanisms by capturing the system in a long-lived suboptimal state.

A typical flow profile $v_\theta(r)$ and the corresponding angular velocity distribution $\dot{\theta}(r)=v_\theta(r)/r$ are shown in Fig. 6 for an r -stack with the polymers on the inside and the solvent on the outside. Because of the high viscosity of the polymeric fluid, this melt hardly flows under the applied shear and the azimuthal velocity v_θ even increases with r in this section of the Couette cell. The angular velocity $\dot{\theta}$ slightly decays, confirming that the melt behaves as a viscous fluid rather than a plug flow. At the polymer-solvent interface, for $r \approx 52\sigma$, the velocity profile shows a steep drop, indicative of a significant degree of slippage. Rod-solvent and even solvent-solvent³⁴ systems show similar hallmarks of slippage at their interfaces. It might be argued that the partial nonstick boundary

FIG. 6. (Color online) The flow profile $v_\theta(r)$ (solid line, left axis) and angular velocity profile $\dot{\theta}(r)=v_\theta(r)/r$ (dashed line, right axis) for an r -stack with the rigid polymer R_7 on the inside and the solvent on the outside.

condition is exacerbated by the purely repulsive interactions between unlike particles, which weakens the mutual grip of the two fluids. The width of the decay region results from slight undulations in the interface, which is not perfectly smooth. In the solvent region of the Couette cell, beyond the slip layer, the flow profile continues to gradually decay until reaching zero at the outer wall. We note that at high shear rates a solitonlike perturbation appears at the interface, which appears to orbit the inner wall indefinitely.³⁴

A number of simulations, especially at elevated drum velocities, yield r -stacks with three bands (see Fig. 7). These systems invariably consist of a central layer of polymer sandwiched between two layers of solvent. The location of the central band, which is virtually impermeable to the solvent particles, varies from simulation to simulation, with typically about 40%–50% of the solvent particles caught in the inner band. It might be argued that these triple r -stacks are kinetically trapped but their abundance in Table III suggests oth-

FIG. 7. (Color) Top view of the steady state for a solvent (blue)-polymer (P_7 , green) mixture in a Couette cell of dimensions $R_i=40\sigma$ and $R_o=65\sigma$, with the inner wall rotating at $0.05 \text{ rad}/\tau$.

FIG. 8. (Color) Snapshots of four phase separating polymer-solvent mixtures at 800τ after the quench for inner wall angular velocities of $\omega_i = (0, 1, 10, 50) \times 10^{-3} \text{ rad}/\tau$ (from left to right) in Couette cells with $R_i = 25\sigma$ and $R_o = 40\sigma$. These side views, with the drum axis vertically and the shear flow running from left to right, highlight the acceleration of the decomposition process under shear.

erwise. The extra interfacial area discards the minimum free energy mechanism, leaving the minimum dissipation mechanism as the most likely explanation. A calculation of the power required to rotate the inner wall (see Table IV) supports this conclusion. Note that an equivalent power must be extracted by the thermostat in order for the system to reach a steady state. To ascertain the impact of a high shear rate and two slipping interfaces on the temperature in the system, we have calculated radial temperature profiles from the velocity distributions along $\hat{e}_r$ and $\hat{e}_z$, i.e., the two directions perpendicular to the shear flow. Even for a very high angular velocity $\omega_i = 0.05 \text{ rad}/\tau^{-1}$ of the inner wall, the thermostat proves capable of maintaining a relatively constant temperature, varying from $1.02k_B/\epsilon$ near the walls and in the slip layers to $1.05k_B/\epsilon$ at the center of the cell.

In several simulations a droplet of the denser chain phase is formed. Sometimes a single large droplet contains all chains, while in other cases the droplet is accompanied by an r -stack. All observed droplets under shear are attached to the outer wall, and the occasional r -stack of chains covers the inner wall. At the higher shear rate, this ordering of the r -stack contrasts with the regular double-banded r -stack at high shear rates and the triple-banded r -stack, which both expose a solvent layer to the inner wall. The droplet gradually moves along the outer wall by following the flow in the surrounding solvent. By tracking individual chains in the droplet, the droplet is found to slowly roll along the wall.

E. Decomposition dynamics under shear

In addition to its impact on the final stationary state, the shear also appears to promote the phase separation process. This acceleration is clearly recognizable in the snapshots in Fig. 8, showing the progression of the decomposition at a fixed time lapse of 800τ for a number of inner wall velocities. At zero and low shear rate the growing domains are significantly smaller than at the high shear rates, where the formation of z -stacks has nearly reached the steady state at 800τ . Inspection of movies generated from the stored trajectories suggests that the nonuniform shear flow assists the separation process both by bringing separate domains together and by pulling domains apart. The latter mechanism, which at first sight might appear to slow down the separation, advances the rupture of thin necks connecting large domains—these necks would have survived longer in the absence of shear—and thus also prevents the system from becoming trapped in an intermediate network configuration. It is impossible, at this stage of the research, to make a more

quantitative assessment of the contributions of the various mechanisms to the overall acceleration. An acceleration of the phase separation under shear has also been reported in previous experimental and simulation studies.^{27,28} The breakup of domains under shear is also expected to introduce a maximum attainable domain size, but this limit is apparently not reached under the current simulation conditions.

Visualization of the simulations also reveals that the final state of an r -stack coexisting with a droplet can be formed along two distinct kinetic pathways. In the first route, a homogeneously mixed state evolves a cell-spanning structure akin to a θ -stack, which subsequently is twisted, stretched, and torn apart under the stresses imposed by the ongoing rotation of the inner wall. The fragment attached to the inner wall forms an r -stack, while the remainder at the outer wall compacts into a droplet. In the second route a mixed state appears to evolve into a triple-banded r -stack, consisting of a solvent layer between two polymer layers. The metastable outer layer eventually ruptures and contracts into a single droplet.

IV. CONCLUSIONS

The spinodal decompositions under shear of polymers and polymer liquid crystals solvated in a simple liquid have been studied by MD simulations of a miniaturized Taylor–Couette rheometer. Most mixtures phase separate into radial, azimuthal, or axial stacks reflecting the geometry of the confining walls (see Fig. 1), but we also observed a number of exceptions. The phase behavior of the system is fairly complex as the steady state configuration is determined by a number of parameters, including the dimensions of the cell and the angular velocity of the rotating inner drum. We believe that the current simulations give a qualitatively realistic impression of the phase behavior to be expected in microfluidic experiments on polymer-solvent mixtures, which constitutes an interesting experimental challenge.

The simulations strongly suggest that the equilibrium and nonequilibrium steady states formed by the phase separating mixtures are determined by a balance between two mechanisms, namely, the minimalization of free energy and the minimalization of viscous dissipation. It is obvious that the thermodynamic mechanism rules in a quiescent mixture, implying that the preferred phase separated state is the configuration with the lowest total interfacial energy. The induced flow field at low angular velocity of the inner wall is already sufficiently strong to suppress the formation of θ -stacks, yet the thermodynamic mechanism appears to be

still capable of selecting the configuration with the lowest interfacial energy among the remaining allowed stacks, i.e., the rotational symmetric and therefore shear-resistant stacks. At high shear rates, the hydrodynamic flow field emerges as the dominant factor by preferentially establishing the configuration requiring the lowest work from the rotating drum wall in the steady state. These global trends are extracted from the simulation results but are by no means conclusively proven at this stage. A number of simulations deviate from this model, e.g., the steady states with a droplet attached to a wall, which we currently attribute to kinetic trapping during phase separation. Nor is it clear at what shear rate the hydrodynamic mechanism takes precedence over the thermodynamic mechanism; the suppression of θ -stacks at the lowest shear rate may be interpreted to suggest that the transition depends on the stack (or effectively, on the torque needed to shear the stack).

A second important property that surfaced during the simulations is the significant slippage of two fluids at their joint interface. The partial slip is clearly visible in the plots of the azimuthal velocity versus the radius (see Fig. 6) and is also manifest from visualizations of the simulations by following individual particles near the interface. Indications of slippage are even detectable at the macroscopic level in the form of an additional third layer in the radial stacks at high shear rate (see Fig. 7). We speculate that the formation of this extra layer is instigated by the hydrodynamic mechanism outlined above, as the slippage at the thermodynamically unfavorable extra interface reduces the viscous dissipation in the system. Conversely, thermodynamic arguments may have prevented the formation of even more radial bands. One should keep in mind that the purely repulsive potential between unlike particles contributes to the slippage at the interface and, hence, that a real fluid-fluid interface is expected to show a less pronounced sliding of the interfaces. The multiple radial bands in shear experiments are therefore more likely explained by incomplete phase separation and by shear-limited domain growth than by slip at the interfaces.

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APPENDIX: SHEAR TRESS $\tau_{r\theta}$ IN A COUETTE GEOMETRY

The relevant shear stress in the Couette geometry is $\tau_{r\theta}$, the stress acting along the azimuthal direction on a plane whose normal points in the radial direction. In the steady state this stress will be a function of r only. A conceptually appealing way of deriving an expression for $\tau_{r\theta}$ starts by looking at the axial component of the total angular momentum of all particles outside a coaxial cylinder of radius r ,

$$L_z(r) = \sum_i m_i (\mathbf{r}_i \times \mathbf{v}_i)_z \Theta(r_i - r), \quad (\text{A1})$$

where Θ denotes the Heaviside step function. The time derivative of this angular momentum, i.e., the torque exerted by the interior of the cylinder on the exterior, reads as

$$\begin{aligned} \dot{L}_z(r) &= \sum_i (\mathbf{r}_i \times \mathbf{F}_i)_z \Theta(r_i - r) \\ &+ \sum_i m_i (\mathbf{r}_i \times \mathbf{v}_i)_z \delta(r_i - r) \dot{r}_i \end{aligned} \quad (\text{A2})$$

$$\begin{aligned} &= \sum_i \sum_j (\mathbf{r}_i \times \mathbf{F}_{ij})_z \Theta(r_i - r) \Theta(r - r_j) \\ &+ \sum_i m_i (\mathbf{r}_i \times \mathbf{v}_i)_z \delta(r_i - r) \dot{r}_i. \end{aligned} \quad (\text{A3})$$

In the second line we have expressed the total force $\mathbf{F}_i$ on particle i as a sum of pair forces $\mathbf{F}_{ij}$, where j lies either inside or outside the cylinder of radius r ; in the latter case, the pair force makes no contribution to the torque and can be omitted. The average torque is expressed mesoscopically as shear stress times lever arm integrated over the surface S of the cylinder of height h ,

$$\langle \dot{L}_z(r) \rangle = \left(\int_S \mathbf{r} \times \boldsymbol{\tau} \cdot d\mathbf{S} \right)_z = -2\pi r^2 h \tau_{r\theta}(r), \quad (\text{A4})$$

where the stress matrix is assumed independent of θ in the last step. The power corresponding with this torque reads as

$$P(r) = \int_S \mathbf{v} \cdot \boldsymbol{\tau} \cdot d\mathbf{S} = 2\pi r h v_\theta(r) \tau_{r\theta}(r) \quad (\text{A5})$$

in the stationary state, when the velocity field has converged to $\mathbf{v}(\mathbf{r}) = v_\theta(r) \hat{\mathbf{e}}_\theta$ and $\boldsymbol{\tau}$ has become rotation symmetric.

In the stationary state the axial angular momentum $L_z(r, \Delta r)$ of any concentric cylindrical shell with inner radius r and thickness Δr must be constant; hence, its time derivative must vanish,

$$0 = \frac{d}{dt} L_z(r, \Delta r) = \frac{d}{dt} [L_z(r) - L_z(r + \Delta r)]. \quad (\text{A6})$$

Consequently, the torque acting in every coaxial cylindrical plane will be identical and the product $r^2 \tau_{r\theta}(r)$ will be independent of r . We take advantage of this property to reduce the noise level by averaging the shear stress over all cylinders with radii between r and $r + \Delta r$,

$$r^2 \tau_{r\theta}(r) = - \frac{1}{2\pi h \Delta r} \int_r^{r+\Delta r} \langle \dot{L}_z(r') \rangle dr' \quad (\text{A7})$$

$$\begin{aligned}
&= -\frac{1}{2\pi h} \frac{1}{\Delta r} \left\langle \sum_{\substack{i \\ r \leq r_i < r+\Delta r}} m_i r_i v_{i\theta} v_{ir} \right. \\
&\quad \left. + \sum_i \sum_{\substack{j \\ r_j \leq r_i \\ r_j \leq r+\Delta r}} f_{ij}(r, r+\Delta r) r_i [\mathbf{F}_{ij} \cdot \hat{\mathbf{e}}_\theta(\mathbf{r}_i)] \right\rangle, \quad (\text{A8})
\end{aligned}$$

where the weight factor is given by

$$f_{ij}(r_1, r_2) = \int_{r_1}^{r_2} \Theta(r_i - r) \Theta(r - r_j) dr. \quad (\text{A9})$$

The only nonzero values to this integral are found when all three conditions in the double summations are met, i.e., $r_i \geq r_1$, $r_j \leq r_2$, and $r_i > r_j$, in which case

$$f_{ij}(r_1, r_2) = \begin{cases} r_2 - r_1 & \text{if } r_i > r_2 \text{ and } r_1 > r_j \\ r_i - r_1 & \text{if } r_1 \leq r_i \leq r_2 \text{ and } r_1 > r_j \\ r_2 - r_j & \text{if } r_i > r_2 \text{ and } r_1 \leq r_j \\ r_i - r_j & \text{if } r_1 \leq r_i \leq r_2 \text{ and } r_1 \leq r_j \leq r_i \end{cases}. \quad (\text{A10})$$

Simulations under shear, of both simple liquids and r_{PS} -stacks, confirm that the right hand side of Eq. (A8) is indeed independent of r .

We end this appendix with three brief comments on the stress expression. (i) A related expression has been used before to calculate stress profiles in flat geometries, for instance, the pressure profile in a lipid bilayer,⁵² based on a more general derivation of the stress tensor by Schofield and Henderson.⁵³ Following analogies with the above derivation, one readily obtains the appropriate stress expressions from the time derivative of the total linear momentum of all particles at one side of a flat plane. (ii) The change in the angular momentum $L_z(r)$ or the corresponding change in the linear momentum is readily seen to require a summation over all pair forces acting between pairs on either side of the dividing plane. We therefore conclude that the dissipative and random pair forces introduced by the DPD thermostat also have to be included in the stress calculation, although the random forces are easily shown to average out to zero. This situation is in contrast to Brownian dynamics simulations, where the friction and random forces are implemented as self-interactions of the particles and therefore do not contribute to the stress. (iii) The above stress expressions, especially Eqs. (A3) and (A8), contain a peculiar asymmetric treatment of the particles i and j . In both expressions, the pair force $\mathbf{F}_{ij}$ is projected on the $\hat{\mathbf{e}}_\theta$ direction at the position of particle i , subject to the restriction that i is the *outermost* particle, $r_i > r_j$. An alternative derivation, based on the angular momentum of the particles inside a cylinder of radius r , even yields a final expression in which the pair-force projection is made with respect to the *innermost* particle. Both seemingly distinct expressions yield identical results, however, since $\mathbf{r}_i \times \mathbf{F}_{ij} = \mathbf{r}_j \times \mathbf{F}_{ji}$ for pair forces acting along $\hat{\mathbf{r}}_{ij}$.

Equation (5) is finally obtained by symmetrizing the stress expression with respect to the particles i and j and by extending the average in Eq. (A8) to include the entire Couette cell.

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