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Stress Induced Demixing of a Polymer Solution: Mechanic Interpretation with a Suitable Formulation of the Two-Fluid Theory

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ABSTRACT: Stress-induced demixing of a polymer solution is studied in the mainframe of the two-fluid theory. A true phase separation is predicted to take place and the theory has been reformulated so to be able to write the required boundary conditions at the interface between the two phases in terms of stress of the individual fluids. Also the free energy of mixing has been modified so to account for the change of the entropy of mixing due to chain stretching. The predictions of the reformulated theory are compared with experimental data available in the literature showing a fair agreement. All the coupling effects between stress and concentration variations in a polymer solution can be now interpreted within a two-fluid theory framework so to have a universal picture of these phenomena. Indeed, the steady phenomena as the flow induced polymer migration and the enhancement of concentration fluctuations were already predicted in this mainframe, now, in this paper, also the true phase separation induced by steady flow is predicted with the two-fluid theory.

1. Introduction

In the liquid state, coupling effects between stress and concentration are well documented. For instance, an initial homogeneous solution, while sheared, can build up a steady concentration profile that eventually diffuses back to homogeneity when the flow is stopped. Experimental evidence of this behavior can be traced back to the works of Dill and Zimm[1] for flows with curvilinear streamlines and Metzner et al.[2] for flows with a nonuniform shear rate. Similarly, since the pioneering work of Silberberg and Kuhn,[3,4] it is known that the application of shear can induce structural changes in such complex fluids as polymer solutions and polymer blends. Shear can induce, for instance, both reversible mixing and reversible demixing in polymer solutions or blends.[5,6]

Demixing has been repeatedly observed[7–9] and different theoretical approaches have been followed to describe this behavior. From one hand, the first attempt at a quantitative model for reversible demixing of solutions of noncrystallizable polymers assumed that during shear an actual separation in two phases with different concentration took place. Thermodynamic theory were then applied at the steady state. The Gibbs free energy was accordingly modified by adding a term describing the stored elastic energy coming from the long polymer chain stretching due to flow. This term was first obtained phenomenologically,[8,10] then, more recently, a more rigorous theoretical argument was proposed by Chopra et al.[11] who extended the work of Marrucci[12] to obtain the stored elastic free energy in a polymer solution relaxing the dumbbell hypothesis initially proposed by Marrucci.[12] From the other hand, the observed onset of turbidity during flow has also been explained with a kinetic theory describing the enhancement of concentration fluctuations due to flow by Helfand and Fredrickson.[13] The kinetic theory has been then formalized within the framework of a two-fluid theory by several authors.[14–17]

The butterfly patterns predicted by the kinetic theories were, in fact, experimentally observed by Wu et al.[18] and by van Egmond et al.[19] However, increasing the shear rate also some different patterns, not predicted by the kinetic theories, were observed. A vertical streak superimposed on or replacing the butterfly pattern appeared. These optical measurements, together with other signals like a reversal of shear dichroism to a positive value, and a large jump of birefringence have been interpreted as the evidence for actual phase separation where phase separated domains are elongated along the flow direction, rather than temporary fluctuations of concentration.[20–22]

The thermodynamic theories are able to describe phase separation, but not the early stage of the process where only concentration fluctuations appear. Conversely, the kinetic theories are able to describe the enhancement of concentration fluctuations, but not the actual phase separation. The goal of this paper is therefore to predict the actual phase separation within the two-fluid theory framework so to have a universal picture of the coupling effects between stress and concentration in polymer solutions. It should be, indeed, underlined that also polymer migration was described[14,23,24] within the two-fluid theory framework and so it was possible to explain the data of Dill and Zimm[1] and Metzner et al.[2]

The two-fluid theory is here reformulated so to account for phase separation and its predictions are then compared with some data from the literature.

2. Two-Fluid Theory: Reformulation

The basis of the two-fluid theory is the idea that, in addition to the individual mass balances, it is possible to write an individual momentum balance on each of the "two coexisting fluids" constituting the solution. As a consequence each "fluid" flows with its own velocity. If a true phase separation wants to be described, boundary conditions must be written at the interface between the two phases. These are typically written in terms of stresses. In the spirit of the two-fluid theory, among other things, one would impose continuity of the normal stresses of each individual fluid. In the available formulations of the two-fluid theory[14,25–30] this is not possible since the stress carried by each single fluid can not be isolated. Indeed, in all these formulations the individual steady momentum balance is written, e.g., on the inertialess polymer as follows:

$$\boxed{\begin{array}{c}\textit{Mutual Interaction}\\ \textit{Term}\end{array}} + \boxed{\begin{array}{c}\textit{Osmotic Pressure}\\ \textit{Term}\end{array}} - \phi\nabla p + \boxed{\begin{array}{c}\textit{Elastic Stress}\\ \textit{Term}\end{array}} = 0 \qquad (1)$$

Here, the "polymer" contribution to the pressure gradient is $\phi\nabla p$, where ϕ is the polymer volume fraction and p is the

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pressure; this term can not be written as the gradient of a "pressure" since the polymer concentration is in general not uniform. In other words, due to the pressure terms, the individual momentum balances are not written in terms of the divergence of a stress tensor and thus the stress carried by each individual fluid can not be isolated. In all these formulations, the momentum balances have been obtained from a variational principle, and the pressure terms arose from the solution incompressibility constraint that was imposed to the Rayleighian to be minimized. Only in the formulations proposed by Milner[31] and by Minale and Marrucci[32] the stresses of the individual fluids can be isolated; however, the former formulation is limited to dilute solutions, the latter phenomenologically corrects Doi and Onuki theory[25] and, even if less limited than that of Milner,[31] cannot be extended to a concentrated solution, as well.

2.1. Reformulation. If a polymer solution made of components with the same density is considered, the mass balance on the polymer and the solvent can be written as

$$\frac{\partial\phi}{\partial t}=-\nabla\cdot(\phi\mathbf{v}_{\mathrm{p}}) \tag{2}$$

$$-\frac{\partial\phi}{\partial t}=-\nabla\cdot[(1-\phi)\mathbf{v}_{\mathrm{s}}] \tag{3}$$

where $\mathbf{v}_{\mathrm{p}}$ and $\mathbf{v}_{\mathrm{s}}$ are the polymer and solvent velocities, respectively, and t is the time. The velocity, $\mathbf{v}$, of the solution is defined as the volumetric average of $\mathbf{v}_{\mathrm{p}}$ and $\mathbf{v}_{\mathrm{s}}$:

$$\mathbf{v}=\phi\mathbf{v}_{\mathrm{p}}+(1-\phi)\mathbf{v}_{\mathrm{s}} \tag{4}$$

Thus, the sum of eqs 2 and 3 gives $\nabla\mathbf{v}=0$. In other words, while the two fluids are compressible owing to concentration changes, the solution as a whole obeys the classical incompressibility constraint. The momentum balances on the "two fluids" are obtained following Doi and Onuki.[25] In a variational formulation the thermodynamic variable x_i can be obtained from the minimization of a functional $\mathcal{R}$, called the Rayleighian, with respect to $\dot{x}_i$ (the dot stands for time derivative), with x_i held fixed; $\mathcal{R}$ has the general form

$$\mathcal{R}=\frac{1}{2}\sum_{i,j}M_{ij}\dot{x}_i\dot{x}_j+\sum_i\frac{\partial F}{\partial x_i}\dot{x}_i \tag{5}$$

where M_{ij} is the inverse matrix of the kinetic coefficients, and F is the thermodynamic free energy. The first term of the right-hand side (rhs) of eq 5 is the dissipation function W, while the second term is the free energy change due to the time-dependent changes in the thermodynamic variables $\dot{F}$.

In the present problem, $\dot{x}_i$ corresponds to $\mathbf{v}_{\mathrm{p}}$ and $\mathbf{v}_{\mathrm{s}}$ and the dissipation function caused by the relative motion between polymer and solvent can be written as

$$W=\frac{1}{2}\int \mathrm{d}r\,[\zeta(\mathbf{v}_{\mathrm{p}}-\mathbf{v}_{\mathrm{s}})^2] \tag{6}$$

where r is the spatial coordinate and ζ is the friction constant per unit volume. Doi and Onuki showed that the free energy F consists of mixing free energy F_{mix} and elastic free energy F_{e}. The mixing free energy change can be written as

$$\dot{F}_{\mathrm{mix}}=\int \mathrm{d}r\,\frac{\mathrm{d}f_{\mathrm{mix}}}{\mathrm{d}\phi}\frac{\partial\phi}{\partial t} \tag{7}$$

where f_{mix}, the mixing free energy per unit volume, has been considered to be function of the concentration only and the higher order terms in f_{mix} arising from inhomogeneities of the concentration have been neglected. If the "solvent" osmotic pressure, Π_{s}, and the "polymer" osmotic pressure, Π_{p}, are defined as[33]

$$\Pi_{\mathrm{s}}=\phi\frac{\mathrm{d}f_{\mathrm{mix}}}{\mathrm{d}\phi}-f_{\mathrm{mix}};\quad \Pi_{\mathrm{p}}=-(1-\phi)\frac{\mathrm{d}f_{\mathrm{mix}}}{\mathrm{d}\phi}-f_{\mathrm{mix}} \tag{8}$$

using eqs 2 and 3, in agreement with Clarke and McLeish,[27] $\dot{F}_{\mathrm{mix}}$ can be rewritten as:

$$\dot{F}_{\mathrm{mix}}=\int \mathrm{d}r\left[(\Pi_{\mathrm{s}}-\Pi_{\mathrm{p}})\frac{\partial\phi}{\partial t}\right]=\int \mathrm{d}r\,\{\Pi_{\mathrm{s}}\nabla\cdot[(1-\phi)\mathbf{v}_{\mathrm{s}}]+\Pi_{\mathrm{p}}\nabla\cdot[\phi\mathbf{v}_{\mathrm{p}}]\} \tag{9}$$

Concerning the elastic free energy change, for a single homogeneous fluid, one would write

$$\dot{F}_{\mathrm{e}}=\int \mathrm{d}r\,(\boldsymbol{\sigma}:\nabla\mathbf{v}) \tag{10}$$

In a polymer solution, or blend, however, the stress is carried by both fluids; assuming additivity of the stresses, $\boldsymbol{\sigma}=\boldsymbol{\sigma}_{\mathrm{p}}+\boldsymbol{\sigma}_{\mathrm{s}}$ (where $\boldsymbol{\sigma}$ is the total deviatoric stress of the solution, and $\boldsymbol{\sigma}_{\mathrm{p}}$ and $\boldsymbol{\sigma}_{\mathrm{s}}$ are the deviatoric stresses of the polymer and solvent, respectively), eq 10 can be naturally generalized[27,28] as

$$\dot{F}_{\mathrm{e}}=\int \mathrm{d}r\,(\boldsymbol{\sigma}_{\mathrm{p}}:\nabla\mathbf{v}_{\mathrm{p}}+\boldsymbol{\sigma}_{\mathrm{s}}:\nabla\mathbf{v}_{\mathrm{s}}) \tag{11}$$

At this stage, in previous formulations,[25,27–30] the Rayleighian, obtained by summing eqs 6, 9, and 11, was minimized with respect to $\mathbf{v}_{\mathrm{p}}$ and $\mathbf{v}_{\mathrm{s}}$ under the constraint of incompressibility of the whole solution, i.e., adding to the Rayleghian the nil term $-\int \mathrm{d}r\,(p\nabla\cdot\mathbf{v})$, where the pressure p was considered as a Lagrange multiplier. The pressure terms in the polymer and solvent momentum balance arose, using eq 4, from this latter term and, as already discussed in the Introduction, these terms make it impossible to isolate the stress carried by each individual fluid. Though the solution incompressibility constraint is correct, it has not been considered, up to now, that the "polymer" and the "solvent" are, on the contrary, compressible, as stated at the beginning of this section, (see eqs 2 and 3.) When dealing with a compressible fluid also the reversible power converted into internal energy per unit time must be taken into account in the Rayleighian, thus, if p_{p} and p_{s} are the "polymer" and "solvent" pressure, respectively, the following term is added to the Rayleighian, $\mathcal{R}$

$$\dot{F}_{\mathrm{e}}^{\mathrm{rev}}=-\int \mathrm{d}r\,(p_{\mathrm{p}}\nabla\cdot\mathbf{v}_{\mathrm{p}}+p_{\mathrm{s}}\nabla\cdot\mathbf{v}_{\mathrm{s}}) \tag{12}$$

thus obtaining:

$$\begin{aligned}\mathcal{R}=\int \mathrm{d}r\,[\zeta(\mathbf{v}_{\mathrm{p}}-\mathbf{v}_{\mathrm{s}})^2]+&\\ \int \mathrm{d}r\,\{\Pi_{\mathrm{s}}\nabla\cdot[(1-\phi)\mathbf{v}_{\mathrm{s}}]+\Pi_{\mathrm{p}}\nabla\cdot[\phi\mathbf{v}_{\mathrm{p}}]-&\\ (p_{\mathrm{p}}\nabla\cdot\mathbf{v}_{\mathrm{p}}+p_{\mathrm{s}}\nabla\cdot\mathbf{v}_{\mathrm{s}})+(\boldsymbol{\sigma}_{\mathrm{p}}:\nabla\mathbf{v}_{\mathrm{p}}+\boldsymbol{\sigma}_{\mathrm{s}}:\nabla\mathbf{v}_{\mathrm{s}})\}&\end{aligned} \tag{13}$$

$\mathcal{R}$ is then minimized with respect to $\mathbf{v}_{\mathrm{p}}$ and $\mathbf{v}_{\mathrm{s}}$ obtaining

$$-\zeta(\mathbf{v}_{\mathrm{p}}-\mathbf{v}_{\mathrm{s}})+\phi\nabla\Pi_{\mathrm{p}}-\nabla p_{\mathrm{p}}+\nabla\cdot\boldsymbol{\sigma}_{\mathrm{p}}=0 \tag{14}$$

$$\zeta(\mathbf{v}_{\mathrm{p}}-\mathbf{v}_{\mathrm{s}})+(1-\phi)\nabla\Pi_{\mathrm{s}}-\nabla p_s+\nabla\cdot\boldsymbol{\sigma}_s=0 \tag{15}$$

Equations 14 and 15 have the structure of eq 1, but now the pressure terms do not cause trouble anymore. However, p_{p} and p_{s} must be determined to complete the formulation. Considered the work additivity, it can be stated that the reversible power of the solvent ($-p_{\mathrm{s}}\nabla\cdot\mathbf{v}_{\mathrm{s}}$) and that of the polymer ($-p_{\mathrm{p}}\nabla\cdot\mathbf{v}_{\mathrm{p}}$) sum up to the reversible power of the whole solution:

$$p_{\mathrm{p}}\nabla\cdot\mathbf{v}_{\mathrm{p}}+p_{\mathrm{s}}\nabla\cdot\mathbf{v}_{\mathrm{s}}=p\nabla\cdot\mathbf{v} \tag{16}$$

The incompressibility of the whole solution is accounted for by eq 16 in the particular case where the rhs is equal to zero, in this case, eq 16 states that if the polymer gains free energy, the solvent looses it at the same rate, and vice versa. This condition, together with the pressure additivity: $p=p_{\mathrm{s}}+p_{\mathrm{p}}$, can be solved for p_{s} and p_{p}, obtaining:

$$
\begin{aligned}
p_{\mathrm{p}} &= p\frac{\nabla\cdot[\phi(\mathbf{v}_{\mathrm{p}}-\mathbf{v}_{\mathrm{s}})]}{\nabla\cdot(\mathbf{v}_{\mathrm{p}}-\mathbf{v}_{\mathrm{s}})} = p\phi + p\frac{(\mathbf{v}_{\mathrm{p}}-\mathbf{v}_{\mathrm{s}})\cdot\nabla\phi}{\nabla\cdot(\mathbf{v}_{\mathrm{p}}-\mathbf{v}_{\mathrm{s}})}\\
p_{\mathrm{s}} &= p\frac{\nabla\cdot[(1-\phi)(\mathbf{v}_{\mathrm{p}}-\mathbf{v}_{\mathrm{s}})]}{\nabla\cdot(\mathbf{v}_{\mathrm{p}}-\mathbf{v}_{\mathrm{s}})} = p(1-\phi) - p\frac{(\mathbf{v}_{\mathrm{p}}-\mathbf{v}_{\mathrm{s}})\cdot\nabla\phi}{\nabla\cdot(\mathbf{v}_{\mathrm{p}}-\mathbf{v}_{\mathrm{s}})}
\end{aligned}
\tag{17}
$$

The pair of equations that make up eq 17 are, in fact, the required constitutive equations for the pressures p_{s} and p_{p}. The terms correcting the partial pressures ($p\phi$ and $p(1-\phi)$) vanish both in the limit of no flow and when the solution is homogeneous, i.e., when the concentration is uniform and the polymer and the solvent share the same velocity. Notice that the constitutive eqs 17 for the solvent and polymer pressure are frame invariant being function of ϕ and of the relative velocity only.[34]

With the constraint given by eq 16, eqs 14 and 15 sum to the classical Cauchy equation for the whole solution:

$$-\nabla p + \nabla\cdot\boldsymbol{\sigma} = 0 \tag{18}$$

Moreover, they are symmetric with respect to the role of polymer and solvent and, once specified the constitutive choices for the two fluids, together with eqs 2 and 3, form a set of four equations in four unknowns, namely $\mathbf{v}_{\mathrm{p}}$, $\mathbf{v}_{\mathrm{s}}$, ϕ, and p. From eqs 14 and 15, the individual stress of the two fluids can be isolated to obtain

$$
\begin{aligned}
\mathbf{T}_{\mathrm{p}} &= -\left[p_{\mathrm{p}} - \int \mathrm{d}\phi\left(\phi\frac{\mathrm{d}\Pi_{\mathrm{p}}}{\mathrm{d}\phi}\right)\right]\mathbf{I} + \boldsymbol{\sigma}_{\mathrm{p}}\\
&= -\left[p_{\mathrm{p}} + \int \mathrm{d}\phi\left(\phi(1-\phi)\frac{\mathrm{d}^2 f_{\mathrm{mix}}}{\mathrm{d}\phi^2}\right)\right]\mathbf{I} + \boldsymbol{\sigma}_{\mathrm{p}}\\
\mathbf{T}_{\mathrm{s}} &= -\left[p_{\mathrm{s}} - \int \mathrm{d}\phi\left((1-\phi)\frac{\mathrm{d}\Pi_{\mathrm{s}}}{\mathrm{d}\phi}\right)\right]\mathbf{I} + \boldsymbol{\sigma}_{\mathrm{s}}\\
&= -\left[p_{\mathrm{s}} - \int \mathrm{d}\phi\left(\phi(1-\phi)\frac{\mathrm{d}^2 f_{\mathrm{mix}}}{\mathrm{d}\phi^2}\right)\right]\mathbf{I} + \boldsymbol{\sigma}_{\mathrm{s}}
\end{aligned}
\tag{19}
$$

where $\mathbf{I}$ is the identity tensor. In addition, Brochard's theory[35] for mutual diffusivity of the polymer in the solvent is recovered with this formulation. Indeed, let us consider non viscous materials, eq. 18 states $p = p_0$=const, and from eq 15, using eqs 17, we obtain:

$$
\begin{aligned}
(\mathbf{v}_{\mathrm{p}}-\mathbf{v}_{\mathrm{s}}) &= -\frac{(1-\phi)}{\zeta}\frac{RT}{V}\nabla\Pi_{\mathrm{S}}^{*} + \frac{p_0}{\zeta}\nabla\left[(1-\phi) - \frac{(\mathbf{v}_{\mathrm{p}}-\mathbf{v}_{\mathrm{s}})\cdot\nabla\phi}{\nabla\cdot(\mathbf{v}_{\mathrm{p}}-\mathbf{v}_{\mathrm{s}})}\right] \approx\\
&\qquad -\frac{(1-\phi)}{\zeta}\nabla\Pi_{\mathrm{s}}
\end{aligned}
\tag{20}
$$

The second equality is obtained because of the condition $pV/RT \ll 1$ that holds true for all liquids, where V is a molar volume, either of the solvent or of the polymer chain segment, R the ideal gas constant, T the temperature, and Π_{s}^{*} the dimensionless solvent osmotic pressure. Starting from eq 20, Brochard's theory[35] can be derived, as already shown by Doi and Onuki,[25] and once it is generalized to viscoelastic materials, it leads to a diffusion equation that was used, for instance, by Helfand and Fredrickson to predict the enhancement of concentration fluctuations.[13]

So far, inertia forces have been neglected altogether, however, they can be accounted for as in Doi and Onuki[25] paper obtaining eqs 21, instead of eqs 14 and 15

$$
\begin{aligned}
\rho_{\mathrm{p}}\frac{D\mathbf{v}_{\mathrm{p}}}{Dt} &= \rho\phi\frac{D\mathbf{v}_{\mathrm{p}}}{Dt} = -\zeta(\mathbf{v}_{\mathrm{p}}-\mathbf{v}_{\mathrm{s}}) + \phi\Pi_{\mathrm{p}} - \nabla p_{\mathrm{p}} + \nabla\cdot\boldsymbol{\sigma}_{\mathrm{p}}\\
\rho_{\mathrm{s}}\frac{D\mathbf{v}_{\mathrm{s}}}{Dt} &= \rho(1-\phi)\frac{D\mathbf{v}_{\mathrm{s}}}{Dt} = \zeta(\mathbf{v}_{\mathrm{p}}-\mathbf{v}_{\mathrm{s}}) + (1-\phi)\nabla\Pi_{\mathrm{s}} - \nabla p_{\mathrm{s}} + \nabla\cdot\boldsymbol{\sigma}_{\mathrm{s}}
\end{aligned}
\tag{21}
$$

where $D\mathbf{v}_i/Dt = \partial\mathbf{v}_i/\partial t + \mathbf{v}_i\cdot\nabla\mathbf{v}_i$.

3. Demixed Stratified Solution

Minale and Marrucci[32] showed that in steady simple shear when the homogeneous solution becomes unstable a polymer solution with a nonviscous solvent admits only another steady state that we called the stratified demixed solution, characterized by two homogeneous layers, one with high polymer concentration and low shear rate, the other with low concentration and high shear rate. In Minale et al.,[36] the demixed stratified solution was found also for systems with viscous solvents and it will be then looked for also here. Let us impose the shear stress T_0 to the system, thus at the interface between the two homogeneous layers eqs 22 and 23 can be written, where the single apex refers to the dilute layer, and the double apexes to the concentrated one. Continuity of normal stresses are also imposed separately for the solvent and the polymer, or equivalently for the solvent and the whole solution, obtaining eqs 24 and 25

$$\sigma_{xy}^{(\mathrm{p})\prime} + \sigma_{xy}^{(\mathrm{s})\prime} = \sigma_{xy}^{(\mathrm{tot})\prime} = T_0 \tag{22}$$

$$\sigma_{xy}^{(\mathrm{p})\prime\prime} + \sigma_{xy}^{(\mathrm{s})\prime\prime} = \sigma_{xy}^{(\mathrm{tot})\prime\prime} = T_0 \tag{23}$$

$$
\begin{aligned}
T_{yy}^{(\mathrm{s})\prime} &= \sigma_{yy}^{(\mathrm{s})\prime} - p'(1-\phi') + \int \mathrm{d}\phi'\left[(1-\phi')\frac{\mathrm{d}\Pi_{\mathrm{s}}}{\mathrm{d}\phi'}\right] = \sigma_{yy}^{(\mathrm{s})\prime\prime} -\\
&\qquad p''(1-\phi'') + \int \mathrm{d}\phi''\left[(1-\phi'')\frac{d\Pi_{\mathrm{s}}}{d\phi''}\right] = T_{yy}^{(\mathrm{s})\prime\prime}
\end{aligned}
\tag{24}
$$

$$\sigma_{yy}^{(\mathrm{tot})\prime} - p' = \sigma_{yy}^{(\mathrm{tot})\prime\prime} - p'' \tag{25}$$

where x is the velocity direction and y the velocity gradient one. Equation 24 has been obtained using eqs 17 and 19 considering, also, that for a homogeneous layer the solvent pressure reduces to $p(1-\phi)$. In simple steady shear, the reduced pressure, p, of the homogeneous whole solution is uniform, the constant value can be found using the boundary condition at infinity. Noticing that the layers share the same boundary condition at infinity we conclude that $p' = p'' =$ const. In addition, since the condition $pV/RT \ll 1$ holds true for liquids, eqs 24 and 25 simplify to:

$$\sigma_{yy}^{(\mathrm{s})\prime} + \int \mathrm{d}\phi'\left[(1-\phi')\frac{\mathrm{d}\Pi_{\mathrm{s}}}{\mathrm{d}\phi'}\right] = \sigma_{yy}^{(\mathrm{s})\prime\prime} + \int \mathrm{d}\phi''\left[(1-\phi'')\frac{\mathrm{d}\Pi_{\mathrm{s}}}{\mathrm{d}\phi''}\right] \tag{26}$$

$$\sigma_{yy}^{(\mathrm{tot})\prime} = \sigma_{yy}^{(\mathrm{tot})\prime\prime} \tag{27}$$

Once the constitutive equations are specified, eqs 22, 23, 26, and 27 form a set of four equations in four unknowns, namely $\dot{\gamma}',\dot{}\ \dot{\gamma}''$, ϕ', ϕ'' ($\dot{\gamma}$ is the shear rate), that can be solved to find the new steady state. The overall mass balance can also be written ant it determines the relative amount of the dilute and concentrated layer

$$\phi' L + \phi''(1-L) = \phi_0 \tag{28}$$

where L is the thickness of the dilute layer, made dimensionless with the whole sample thickness, and ϕ_0 is the concentration of the initial homogeneous solution.

To find the critical stress above which the homogeneous solution becomes unstable, a stability analysis must be performed and once the demixed stratified solution is found its stability must be checked as well.

4. Linear Stability Analysis

Here the linear stability of the homogeneous solution in simple shear is investigated, and the following quantities are introduced

$$\phi = \phi_0 + \delta\phi; \quad \mathbf{v}_{\mathrm{p}} = \mathbf{v}_0^{(\mathrm{p})} + \delta\mathbf{v}_{\mathrm{p}}; \quad \mathbf{v}_{\mathrm{s}} = \mathbf{v}_0^{(\mathrm{s})} + \delta\mathbf{v}_{\mathrm{s}}; \quad p = p_0 + \delta p \tag{29}$$

where the suffix 0 indicates the ground-state and δ the small perturbation. To study the transition from the homogeneous solution to a state where there is a distribution of all variables in the velocity gradient direction y, the disturbances are assumed to depend on y and t only. The form of the perturbation remains unspecified, in contrast to an analogous analysis performed by Onuki.[15] Equations 2 and 3, together with the y-component of eqs 18 and 15, when linearized in the disturbance, reduce to

$$\frac{\partial \delta\phi}{\partial t} = -\phi_0 \frac{\partial \delta w_\mathrm{p}}{\partial y} \tag{30}$$

$$\delta w_\mathrm{s} = -\frac{\phi_0}{1-\phi_0}\delta w_\mathrm{p} \tag{31}$$

$$\frac{\partial \delta p}{\partial y} = \frac{\partial \delta \sigma_{yy}^{(\mathrm{tot})}}{\partial y} = \frac{\partial \delta \sigma_{yy}^{(\mathrm{p})}}{\partial y} + \frac{\partial \delta \sigma_{yy}^{(\mathrm{s})}}{\partial y} \tag{32}$$

$$\zeta(\delta w_\mathrm{p} - \delta w_\mathrm{s}) = -\frac{\zeta}{1-\phi_0}\delta w_\mathrm{p} = (1-\phi_0)\frac{\partial \delta \Pi_\mathrm{s}}{\partial y} - (1-\phi_0) \times \left(\frac{\partial \delta \sigma_{yy}^{(\mathrm{p})}}{\partial y} + \frac{\partial \delta \sigma_{yy}^{(\mathrm{s})}}{\partial y}\right) + \frac{\partial \delta \sigma_{yy}^{(\mathrm{s})}}{\partial y} \tag{33}$$

where w_i is the y-component of the velocity of the ith fluid. Equation 31 has been obtained from eqs 2 and 3 with some algebraic manipulations invoking the impermeability boundary conditions ($w = w_\mathrm{p} = w_\mathrm{s} = 0$) at the walls, eq 33 has been obtained using eqs 17 and 32 and the condition $p_0 V \ll RT$; it has been considered that $w_0 = w_0^{(p)} = w_0^{(s)} = 0$ and $\Pi_0^{(s)} = \Pi_\mathrm{s}(\phi_0)$. From eqs 30–33, we obtain the following:

$$\frac{\partial \delta\phi}{\partial t} = \frac{\partial}{\partial y}\left\{\frac{\phi_0(1-\phi_0)}{\zeta}\left[(1-\phi_0)\frac{\partial \delta \Pi_\mathrm{s}}{\partial y} - (1-\phi_0)\frac{\partial \delta \sigma_{yy}^{(\mathrm{p})}}{\partial y} + \phi_0 \frac{\partial \delta \sigma_{yy}^{(\mathrm{s})}}{\partial y}\right]\right\} \tag{34}$$

Now, the x-component of the momentum balance of the whole solution ($\sigma_{xy}^{(\mathrm{tot})} = \mathrm{const}$) provides a correspondence between the shear rate and the concentration; we generalize this statement by assuming that also the disturbance of the polymer and solvent shear rate are a function of the concentration only; this is equivalent to assuming that only if there is a concentration profile, then there is a profile of polymer and solvent shear rate. This latter statement is physically sensible. $\delta\Pi_\mathrm{s}$, $\delta\sigma_{yy}^{(p)}$, and $\delta\sigma_{yy}^{(s)}$ are in general function of $\dot{\gamma}$ and ϕ, now, with the latter assumption, they are observed to be a function of ϕ only, and eq 34 can be written as

$$\frac{\partial \delta\phi}{\partial t} = \frac{\partial}{\partial y}\left\{\frac{\phi_0(1-\phi_0)}{\zeta}\left[(1-\phi_0)\left.\frac{d\Pi_\mathrm{s}}{d\phi}\right|_0 - (1-\phi_0)\left.\frac{d\sigma_{yy}^{(\mathrm{p})}}{d\phi}\right|_0 + \phi_0 \left.\frac{d\sigma_{yy}^{(\mathrm{s})}}{d\phi}\right|_0\right]\frac{\partial \delta\phi}{\partial y}\right\} \tag{35}$$

where $\alpha|_0$ indicates that the quantity α is evaluated at the ground state. Equation 35 is a classical diffusion equation in one dimension that is stable whenever the diffusion coefficient is positive, thus if

$$(1-\phi_0)\left.\frac{\mathrm{d}\Pi_\mathrm{s}}{\mathrm{d}\phi}\right|_0 - (1-\phi_0)\left.\frac{\mathrm{d}\sigma_{yy}^{(\mathrm{p})}}{\mathrm{d}\phi}\right|_0 + \phi_0\left.\frac{\mathrm{d}\sigma_{yy}^{(\mathrm{s})}}{\mathrm{d}\phi}\right|_0 > 0 \tag{36}$$

Equation 36 represents the stability condition of the homogeneous solution. There are two contributions to the diffusion coefficient (lhs of eq 36), the first is the classical Brownian diffusivity, while the second term, coming from the polymer and solvent stress, accounts for stress-induced polymer counterdiffusion and is the driving force for demixing.

Concerning the stability analysis of the demixed stratified solution, it is enough to consider that this solution consists of two homogeneous layer stratified, one diluted and the other concentrated. Each homogeneous layer results stable if it fulfils condition 36, then if the two layers are stable also eq 28, determining the relative amount of each layer, results to be stable. To conclude, the stability of the stratified solution is guaranteed if each layer is stable, i.e., if eq 36 is satisfied in each layer.

5. Constitutive Choices

To compare the theoretical predictions with experiments available in the literature, we need the constitutive equations for f_mix, $\sigma_{yy}^{(s)}$ and $\sigma_{yy}^{(p)}$. Actually, since the polymer and solvent stress are deviatoric, $\sigma_{yy}^{(s)}$ and $\sigma_{yy}^{(p)}$ can be obtained from the first and the second normal stress difference, N_1 and N_2 respectively:

$$\sigma_{yy}^{(i)} = -\frac{N_1^{(i)} - N_2^{(i)}}{3} \tag{37}$$

Thus we need the constitutive equations for f_mix, $N_1^{(s)}$, $N_1^{(p)}$, $N_2^{(s)}$, and $N_2^{(p)}$

5.1. N_1 and N_2. The data available in the literature interpreted as originated from phase separated domains elongated along the flow direction refer to polystyrene solutions in dioctyl phthalate.[19–21,36] In this system, the solvent is Newtonian, thus $N_1^{(s)} = N_2^{(s)} = 0$ and so $N_1^{(p)} \equiv N_1^{(\mathrm{tot})}$ and $N_2^{(p)} \equiv N_2^{(\mathrm{tot})}$. From now on the superscript (tot) is omitted for notation simplicity. The first normal stress difference of the whole solution can be estimated, in the linear regime, from compliance data

$$N_1 = 2J(\phi)\sigma_{xy}^{\;2} = 2J(\phi)T_0^{\;2} \tag{38}$$

The second equality has been obtained in view of eqs 22 and 23. In Minale et al.[36] the compliance has been obtained with a best fit of experimental data obtaining

$$J(\phi) = \frac{A\phi}{1 + B\phi^2} \tag{39}$$

with A and B given by

$$\begin{aligned} A &= 1.155 \times 10^{-14} M_\mathrm{w}^{\;2.09} \\ B &= 1.235 \times 10^{-5} M_\mathrm{w}^{\;1.331} \end{aligned} \tag{40}$$

where M_w is the polymer molecular weight. It is then assumed that the parameters A and B here reported are generic for polystyrene solutions in dioctyl phthalate.

The second normal stress difference can be considered to be proportional to N_1

$$N_2 = -k_{N_2} N_1 \tag{41}$$

where k_{N2} is a positive proportionality constant. When N_2 is not experimentally measured, and thus k_{N2} is not known, it can be chosen to be $^1/_7$ as Doi and Edwards[37] predict, or to range from $^1/_4$ to $^2/_7$ as shown by several experiments.[38] With k_{N2} ranging from $^1/_7$ to $^2/_7$, σ_{yy} varies by 10%; this allows us to conclude that the system is not very sensitive to k_{N_2}, and thus all the results presented in the paper are obtained with k_{N_2} arbitrarily set to $^1/_7$.

5.2. Free Energy of Mixing, f_mix. The free energy of mixing per unit volume is given by Flory–Huggins theory:

$$f_\mathrm{mix} = \frac{RT}{V}\left[\frac{\phi \ln(\phi)}{N} + (1-\phi)\ln(1-\phi) + \chi\phi(1-\phi)\right] \tag{42}$$

Here N is the degree of polymerization, i.e., the number of polymer segments per each chain. When the solution is sheared we can imagine that the free energy of mixing, and only it, may vary because of chain stretching. In fact, the enthalpic and entropic contribution to the free energy of mixing may vary since mixing stretched molecules is different from mixing molecules at equilibrium (random coil), and not because there is an elastic energy stored in the molecules (as in Marrucci[12] and in Chopra et al.[11]). It must be underlined that in the two-fluid theory the stored elasticity must not be included in the free energy of mixing since it has been already accounted for in the Rayleyghian that has been minimized. To account for the change of the free energy of mixing only, it should be reminded that the free energy of mixing is defined as the free energy of the polymer solution minus that of the pure components; on the contrary, the elastic energy stored in the molecules due to stretching is related to the difference between the entropy of the polymer molecules in the stretched configuration and that of the random coils (equilibrium). Thus, the free energy of mixing change due to flow will be evaluated as the free energy of the solution in the deformed stretched configuration minus that of the pure components evaluated at the same deformed stretched configuration of the molecules of the solution, so disregarding the stored entropic elasticity. To evaluate how the entropy and enthalpy of mixing change in flow, let us refer to the Flory–Huggins lattice model. Let us first calculate the entropy of mixing when the polymer molecules are fully stretched: Let Ω be the total number of lattice sites per unit volume and n_p the total number of polymer molecules per unit volume, thus the polymer volume fraction is related to the fraction of lattice sites occupied by polymer segments:

$$\phi = \frac{n_p N}{\Omega} \tag{43}$$

To evaluate the entropy of mixing of fully stretched polymer molecules we start evaluating the number of ways of placing the n_p fully stretched polymer molecules in the lattice.[33] The number of ways to place the first fully stretched molecule, w_1, is:

$$w_1 = \Omega \mathbf{1}^{N-1} = \Omega \tag{44}$$

Let us, now, consider the number of ways of laying down the $(j+1)$th polymer when j polymers have been already placed, i.e., Nj lattice sites are already occupied:

$$w_{j+1} = (\Omega - Nj)\mathbf{1}^{N-1} = \Omega\left(1 - \frac{Nj}{\Omega}\right) = w_1\left(1 - \frac{Nj}{\Omega}\right) \tag{45}$$

The total number of ways, W, of placing n_p indistinguishable polymers is

$$W = \frac{1}{n_p!}\prod_{j=1}^{n_p} w_j = \prod_{j=1}^{n_p} \frac{w_j}{j} \tag{46}$$

The entropy, S, per unit volume is then $R/V \ln(W)$; thus

$$\ln(W) = \sum_{j=1}^{n_p} \ln\left(\frac{w_j}{j}\right) \simeq \int_0^{n_p} \mathrm{d}j \left[\ln w_1 + \ln\left(1 - \frac{Nj}{\Omega}\right) - \ln j\right] = -\Omega\left[\frac{\phi}{N}\ln\left(\frac{\phi}{N}\right) + \frac{1-\phi}{N}\ln(1-\phi)\right] \tag{47}$$

Equation 47 is proportional to the entropy of the solution where all the polymer molecules are fully stretched. The entropy of mixing S_{mix} is, then, obtained as the entropy of the mixed status (eq 47) minus the sum of the entropies of the pure fully stretched components, as discussed above:

$$S_{\mathrm{mix}}(\Omega, \phi) = S(\Omega, \phi) - S(\Omega\phi, 1) - S(\Omega(1-\phi), 0) \tag{48}$$

We thus obtain:

$$S_{\mathrm{mix}} = -\frac{R}{V}\left[\frac{\phi}{N}\ln\phi + \frac{1-\phi}{N}\ln(1-\phi)\right] \tag{49}$$

Equation 49 shows that the entropic contribution to the free energy of mixing is reduced with respect to Flory and Huggins predictions, if stretched molecules are considered. The enthalpic contribution to the free energy of mixing can be evaluated analogously for fully stretched molecules and it results to be not affected by the flow, thus the free energy of mixing of the fully stretched case can be written as

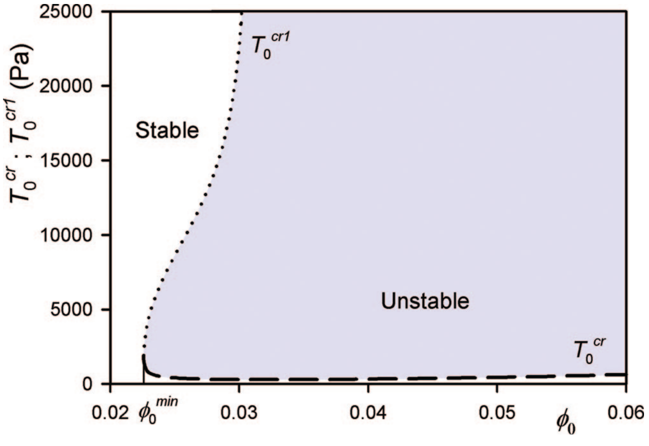

Figure 1. Typical plot of the critical stress vs concentration.

$$f_{\mathrm{mix}}^{\mathrm{str}} = \frac{RT}{V}\left[\frac{\phi\ln(\phi)}{N} + \frac{(1-\phi)}{N}\ln(1-\phi) + \chi\phi(1-\phi)\right] \tag{50}$$

Now, Flory–Huggins theory holds true at equilibrium (eq 42), while the above expression (eq 50) is valid in the limit of infinite flow intensity. We assume that the actual free energy of mixing varies continuously from one asymptote to the other as a function of the degree of stretching, thus, combining eq 42 with eq 50, we assume that the free energy of mixing of a system with a generic degree of stretching is given by

$$f_{\mathrm{mix}} = \frac{RT}{V}\left[\frac{\phi\ln(\phi)}{N} + (1-\phi)\ln(1-\phi) + \chi\phi(1-\phi) - \alpha\frac{N-1}{N}(1-\phi)\ln(1-\phi)\right] \tag{51}$$

where α is a measure of the molecule stretching ranging from 0, for molecules at equilibrium, so to recover the Flory–Huggins theory (eq 42), to 1, for fully stretched polymer molecules, so to obtain eq 50.

The stretch dynamics equation for chain with finite extensivity can be used to estimate α. Let consider the theory developed by Marrucci and Ianniruberto[39] where the dynamic quantity $\mathbf{A} = \langle\mathbf{RR}\rangle/a^2$ is introduced (where $\mathbf{R}$ is the end-to-end vector of the subchains between consecutive entanglements and a is the subchain size under equilibrium conditions.) The chain stretch is proportional to the trace of $\mathbf{A}$, the dynamics equation of which can be obtained taking the trace of eq. 2.9 of the original paper by Marrucci and Ianniruberto[39]

$$\frac{\mathrm{d}(tr\mathbf{A})}{\mathrm{d}t} = 2\mathbf{k}:\mathbf{A} - \frac{1}{\tau_R}\left(\frac{b-1}{b - tr\mathbf{A}}tr\mathbf{A} - 1\right) \tag{52}$$

where $\mathbf{k}$ is the velocity gradient tensor, τ_R is the Rouse relaxation time and b has the meaning of the square of the maximum stretch ratio that is of the order of the number of polymer segments in the subchain $\approx 10 \div 100$. Equation 52 admits an analytical solution for $tr\mathbf{A}$ at steady state, only if the term $\mathbf{k}:\mathbf{A} = \dot{\gamma}A_{12}$ is somehow estimated. The term A_{12}, proportional to the tangential stress, attains different regimes as a function of the shear rate, as it can be seen in Figure 1 of Marrucci and Ianniruberto.[39] In the linear regime it is proportional to $\tau\dot{\gamma}$, where τ is the orientation relaxation time, if the flow strength is increased it passes through a constant plateau and then it becomes proportional to $\tau_R\dot{\gamma}$ to finally evolve toward a second plateau. For the sake of simplicity and in agreement with the constitutive choices of N_1 and N_2, we estimate the term $\mathbf{k}:\mathbf{A}$

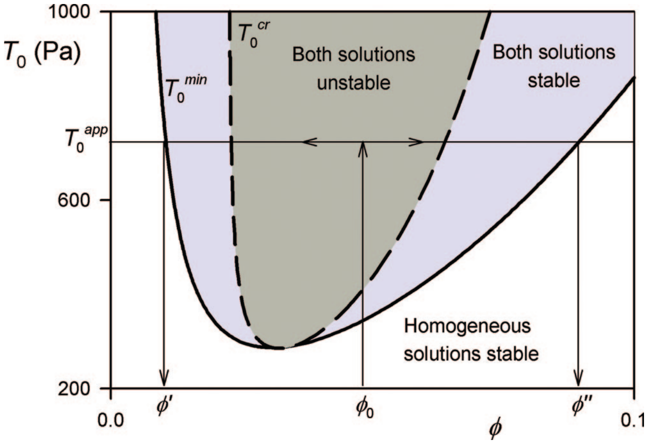

Figure 2. Typical plot where both T_0^{cr} and T_0^{min} are shown. When T_0^{app} is imposed onto the system, the stable steady solution results to be the stratified one, where two layers with concentrations ϕ' and ϕ'' appear.

from the linear regime and thus we assume $\mathbf{k}:\mathbf{A} = \tau\dot{\gamma}^2/3$, as it can be readily obtained with few algebraic calculations from Marrucci and Ianniruberto.[39] If we, now, solve eq 52, at steady state, for $tr\mathbf{A}$, we get:

$$tr\mathbf{A} = \frac{b(1 + 2\tau\tau_R\dot{\gamma}^2/3)}{b + 2\tau\tau_R\dot{\gamma}^2/3} \tag{53}$$

$tr\mathbf{A}$ ranges from 1 (at equilibrium) to b for infinite shear rate (fully stretched molecules). On the contrary, as already discussed, the function α, proportional to $tr\mathbf{A}$, ranges from 0 to 1. $tr\mathbf{A}$ is then rescaled to obtain α

$$\alpha(\phi) = \frac{(\tau\dot{\gamma})^2}{b' + (\tau\dot{\gamma})^2} = \frac{[J(\phi)T_0]^2}{b' + [J(\phi)T_0]^2} \tag{54}$$

where $\tau\dot{\gamma} = J(\phi)T_0$ and $b' = {}^3/_2 k_R b$ with $k_R = \tau/\tau_R$. The constant k_R ranges from 10 to 100; thus, b' ranges from 10^2 to 10^4. In principle, also the parameter b' can be estimated from the linear regime, but to do so the dynamic moduli should be known experimentally for the investigated systems. This happens only seldom, and thus a different argument is proposed.

The parameter b', proportional to b and τ/τ_R, is in principle function of M_w and ϕ, since both b and τ/τ_R are function of ϕ, and τ/τ_R is function of M_w. Concerning the dependence on M_w, it is well-known[40] that $\tau \propto M_w^{3.4}$ and $\tau_R \propto M_w^2$; thus, $b' \propto M_w^{1.4}$. The dependence of b and τ/τ_R on ϕ can also be found in Rubinstein and Colby:[40] $b \propto \phi^{-4/3}$ and $\tau/\tau_R \propto \phi^{4/3}$ for both Θ and good solvents; thus, b' is observed to be independent of ϕ. We then assume b' to be a function of M_w only: $b' = k_{str}M_w^{1.4}$.

To complete the constitutive choices only the constant k_{str} must be assigned. It must be considered that the mathematical problem at hand (eqs 26, 27) can admit two steady state solutions: The homogeneous one and the stratified one. We here require that a stable steady state solution must always exist. From the stability condition, eq 36, it can be seen that the homogeneous solution is stable only if the applied stress is below a critical one: $T_0^{cr}(\phi_0)$. However, the stratified solution, found to solve the set of eqs 22, 23, 26, and 27, exists only if the applied stress is above a minimum value: T_0^{min} (ϕ_0) (see Figure 2). The stratified demixed steady solution will then consist of two homogeneous layers: The dilute one with concentration ϕ' and the concentrated one with ϕ'' and it will be stable only if the applied stress will be smaller than both $T_0^{cr}(\phi')$ and $T_0^{cr}(\phi'')$. To fulfill the condition that a stable solution always exists within an error of 1−2% in the stress values the parameter k_{str} can not be assigned arbitrarily and a value of 1.1×10^{-5} has been then accurately chosen. With this choice the parameter b' ranges, as expected, between 10^2 and 10^4 for a polymer of $M_w = 10^4 - 10^6$ g/mol.

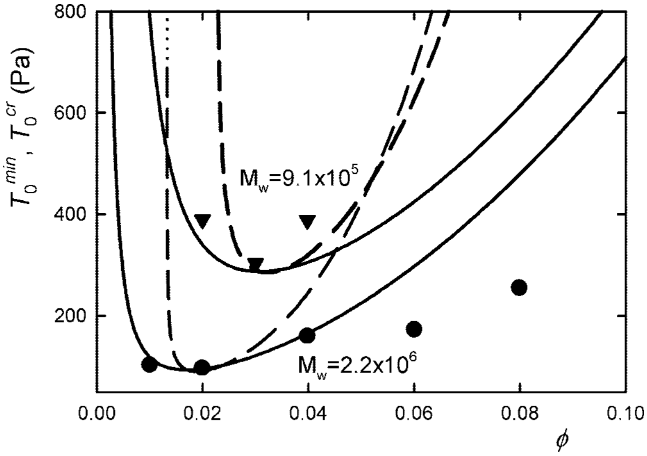

Figure 3. Comparison with demixing data on a polystyrene in dioctyl phtalate solution. Demixing data on two solutions are shown, one with a polystyrene of $M_w = 2.2 \times 10^6$, the other of $M_w = 9.1 \times 10^5$. Solid lines are T_0^{min}, broken lines are T_0^{cr}, and the dotted line is T_0^{cr1}.

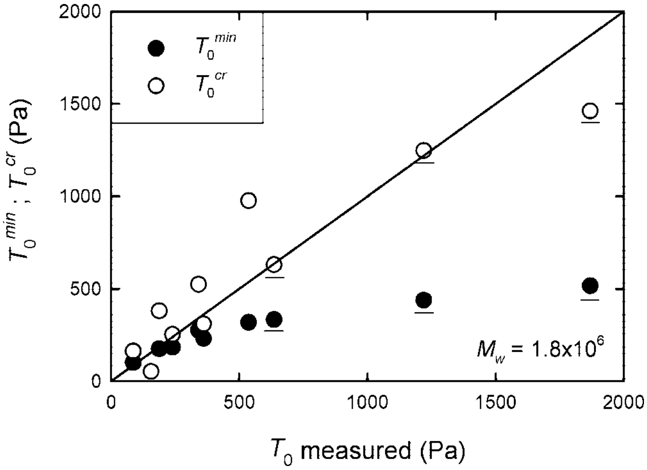

Figure 4. Comparison of predicted stresses with literature data of stresses measured at the onset of demixing for a solution of polystyrene ($M_w = 1.8 \times 10^6$) in dioctyl phtalate. The line is the locus of the points where the predicted and the measured stresses coincide. For the underlined points, the linear regime assumption is no longer valid.

The estimates of both N_1 and N_2, and of the function α from the linear regime, do not limit the theory at all if only qualitative predictions are looked for, indeed the functions chosen are all well behaved. On the contrary, if quantitative predictions are aimed at it should be reminded that since the theory is limited to the linear regime, quantitative predictions can be obtained only for systems for which $\tau\dot{\gamma} < 1$. In the following (Figures 3, 4, and 5) $\tau\dot{\gamma}$ ranges between 0.6 and 3 for the majority of the data shown, and the linear regime has been considered to be always a valid assumption even if it is a bit out of bounds.

6. Theoretical Predictions

The theory here reformulated allows to predict a critical value of the applied stress (T_0^{cr}) above which the homogeneous solution becomes unstable together with a "minimum" value of the applied stress (T_0^{min}) above which the stratified solution exists and is stable. T_0^{cr} is found by solving eq 36 while T_0^{min} is the minimum stress value above which the set of equations eqs 26 and 27 admits a stable solution different from the homogeneous one. In Figure 1, a typical plot of T_0^{cr} vs the concentration is

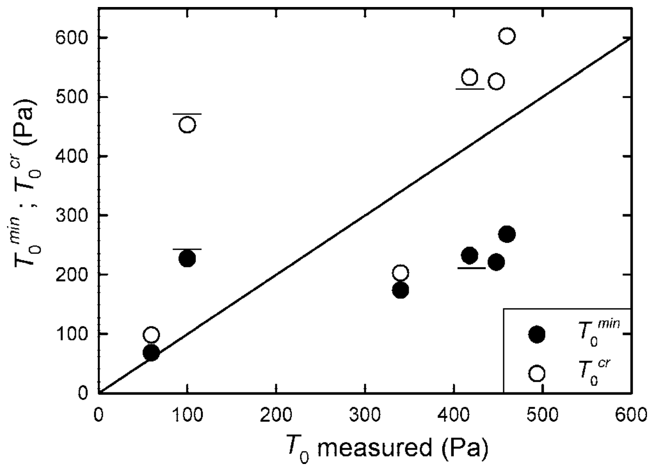

Figure 5. Comparison of predicted stresses with literature data of stresses measured at the onset of demixing for different solutions of polystyrene in dioctyl phtalate (see Table 1). The line is the locus of the points where the predicted and the measured stress coincide. For the underlined points the linear regime assumption is no longer valid. For the points with the over bar, eq 39 does not describe properly the compliance.

Table 1. Experimental Data Available in the Literature

reference	M_w (g/mol)	ϕ_0 (%)	T (°C)	T_0 measured (Pa)
Yanase et al.[20]	1.86×10^6	6	20	≤460
	1.86×10^6	6	15.9	448
Kume et al.[22]	3.84×10^6	6	21	418
	5.48×10^6	3	22	59.5
	5.48×10^6	6	22	100
Migler et al.[21]	1.03×10^6	4	15	340

shown. The dashed line represents $T_0^{cr}(\phi)$, while the dotted line represents the value of the applied stress above which the homogeneous solution regains stability, $T_0^{cr1}(\phi)$. $T_0^{cr1}(\phi)$ is found as a second solution of eq 36 and notice that it shows a vertical asymptote. The homogeneous solution is, then, unstable in the shadowed region, while it is stable in the white region of the plot. It is, then, clear that in a narrow range of concentrations, while increasing the applied stress, the homogeneous solution first becomes unstable and then, at higher stresses, it regains stability. To explain this, let consider that $\partial\sigma_{yy}/\partial\phi \propto -\partial J/\partial\phi$ and that the compliance shows a maximum in correspondence of the vertical asymptote of $T_0^{cr1}(\phi)$ (dotted line). It is, then, clear that for concentrations below the asymptotic one the derivative of the normal stress is negative, while it is positive for higher concentrations. This marks a transition from the dilute regime to a more concentrated one. Looking at the stability condition, eq 36, it is evident that for concentrations below the asymptotic one the normal stress adds stability to the solution while it adds instability when its derivative is positive. Thus, in the dilute regime, while increasing the applied stress the homogeneous solution becomes stable again since the normal stress contribution overcomes the destabilizing effect of the change of the entropy of mixing due to polymer stretching, that, on the contrary, will level off by increasing the applied stress. The observation of a regain of stability is in qualitative agreement with Horst and Wolf[41,42] who predict that a polymer blend first undergoes a shear-induced phase separation and then, for higher stresses, it experiences a flow induced mixing. This behavior was successively also experimentally observed by Fernandez et al.[43] who qualitatively confirmed the predictions of Horst and Wolf. In Figure 1 it is also shown that a homogeneous solution with a concentration below a minimum value (ϕ_0^{min}) can never become unstable.

In Figure 2 the critical stress (dashed line) is plotted together with T_0^{min} (solid line). Notice that the scales are changed with respect to Figure 1. In this graph the dark shadowed area represents the unstable region for both the homogeneous and the demixed stratified solution. Notice that there is a region between T_0^{min} and T_0^{cr} (light shadowed in the graph) where both the stratified solution and the homogeneous one are stable. To better understand the use of the graph, let apply the stress T_0^{app} to a homogeneous solution with concentration ϕ_0, that will then result unstable, the system eventually demixes to give rise to the stratified solution made of two stable homogeneous layers, the dilute one with concentration ϕ' and the concentrated one with ϕ''. If the applied stress is further increased, the stratified solution remains the stable one and the dilute layer becomes more diluted while the concentrated one more concentrated.

7. Comparison with Experimental Data

The data are all taken from the literature[8,19,21,36] and refer to a "real" phase separation of solutions of polystyrene in dioctyl phtalate. In Figure 3 the stress above which the phase separation takes place is plotted as a function of the concentration of the initial homogeneous solution. The data refer to two different solutions, one with a polystyrene of M_w=2.2 × 10^6 g/mol, the other with a polystyrene of $M_w = 9.1 \times 10^5$ g/mol and are taken from Minale et al.[36] Both T_0^{cr} (dashed lines) and T_0^{min} (solid lines) are shown and the agreement between data and predictions is satisfactory.

Rangel-Nafaile et al.[8] measured the stress at the onset of demixing of a solution with a polystyrene of $M_w = 1.8 \times 10^6$ g/mol at several temperatures both in a cone and plate rheometer and in a capillary one. In Figure 4, the data of Rangel-Nafaile et al., reported as the averages between the cone and plate measurements and the capillary ones, are compared with the predicted critical and minimum stress. The measured data are always in between the minimum and the critical stress but are better predicted by the critical stress. The agreement between data and predictions is satisfactory except for the last points obtained at a high temperature and concentration. It should, however, mentioned that the underlined points do not fall into the linear regime, indeed for these experimental points $\tau\dot{\gamma} > 5$. In this case, as expected the theory underestimates the data since N_1, N_2, and the polymer stretching are overestimated by the linear regime assumption. To account for the temperature dependence of the constitutive parameters in the model the following choices have been made, in agreement with Minale et al.[36]

$$\chi = \frac{1}{2} + \psi\left(\frac{\Theta}{T} - 1\right); \quad \psi = 0.5; \quad \Theta = 295 \text{ K} \tag{55}$$

$$A = A_0\frac{T}{\Theta_1}; \quad \Theta_1 = 298 \text{ K} \tag{56}$$

where A_0 is the value of the parameter A at 298 K and is obtained from eq 40. The choices made in eqs 55 and 56 are all that the model requires since with eq 55 the dependence of the free energy of mixing on the temperature is accounted for, and with eq 56, the dependence of the compliance on the temperature is also taken into account.

In the literature some other data on polystyrene/DOP solutions, interpreted as a true phase separation where phase-separated domains are elongated along the flow direction,[20–22] are available. In Table 1, the literature data are summarized together with the experimental conditions and the references where they are taken from. To predict these data all the constitutive choices adopted up to now have been considered valid, even if they are optimized for the data shown in Figure 3 and Figure 4. The demixing shear stresses T_0^{min} and T_0^{cr} have been then calculated for the experimental concentrations and temperatures by the present theory. A comparison of the predicted and experimental results is shown in Figure 5. The predicted values of the demixing stress are reasonably close to the measured values that almost always fall in between the two predicted stresses. The inaccurate prediction of the points with a bar over them is not surprising, because for the corresponding system eq. 39 is no longer a good approximation of the compliance as a function of concentration. Also in this graph the linear regime assumption is no longer valid for the underlined points being for the corresponding solution $\tau\dot{\gamma} > 5$; nonetheless, the theory agrees satisfactorily with the data also in this case.

8. Conclusions and Final Remarks

The two-fluid theory has been reformulated so to individuate the individual stress carried by each coexisting fluid constituting the solution. Each single fluid has been considered compressible, while the whole solution incompressible. The free energy of mixing has been modified so to account for the change of entropy of mixing due to chain stretching. With this reformulation, it has been possible to predict the stress induced demixing in a polymer solution. After demixing the theory predicts that the system can evolve toward a new stable steady state characterized by stratified homogeneous layers with different concentrations and shear rates: Namely two “kind” of layers can be individuated, the first is more diluted and has a higher shear rate, the second is more concentrated and has a lower shear rate. The theory predictions have been compared with data available in the literature on solutions of polystyrene in dioctylphtalate and all the constitutive parameters values required have been estimated from experimental measurements available in the literature. Only one parameter, b', related to the maximum molecule stretch and to the ratio between the Rouse relaxation time and the reptation relaxation time has been assigned autonomously since experimentally only rough estimates of these parameters are available. However, the parameter have been chosen so that the theory predicts the existence of a stable steady state, either the homogeneous one or the demixed one, for any applied shear stress. With this choice, the theory has no adjustable parameters.

The agreement with the data available in the literature is in general satisfactory and in few cases, when the linear regime assumption is not valid anymore, the theory underestimates the experimental data. The constitutve choices have been optimized for the data shown in Figures 3 and 4; nonetheless, the agreement between theory and data remains satisfactory also for the data shown in Figure 5.

The reformulated two-fluid theory allows to have a universal picture of the effects of the coupling between stress and concentration in the liquid state. Indeed, within this framework, it is now possible to predict a true phase separation as well as the enhancement of concentration fluctuations. The latter phenomenon takes place at the early stage of demixing and was already interpreted[14–17] in the two-fluid theory framework, while the former takes place at the end of the process and has been here explained. In addition, it must be said that in the past[23] also polymer migration was predicted with the two-fluid theory. It should also be mentioned that the phase separation here predicted in not conceptually different from a shear banding spaced in the velocity gradient direction. This phenomenon appeared on several systems and also in polystyrene solutions in dioctyl phthalate.[44] In a polymer solution, there is however one more phenomenon related to the coupling between stress and concentration that still deserves an explanation. It has been experimentally observed[45] that when a polymer solution undergoes a large amplitude oscillatory shear flow it can phase separate. The present theory might be applied to model this latter phenomenon in the future.

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