Nonequilibrium chemical potential and shear-induced migration of polymers in dilute solutions

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Abstract

We consider the contribution of a nonequilibrium chemical potential depending on the shear rate on shear-induced polymer migration. It is seen that this nonequilibrium contribution strongly enhances, above a threshold of polymer concentration and of shear rate, the migration of the polymer towards the regions with lower stress. This enhancement may explain why the migration rate experimentally observed is much higher than that predicted by constitutive laws where the nonequilibrium effects on the chemical potential are ignored. © 1999 Elsevier Science Ltd. All rights reserved.

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1. Introduction

The coupling between viscous effects and diffusion is one of the most active topics nowadays in rheological analyses. In particular, shear-induced migration of polymers deserves the attention of many researchers, both for its practical aspects (chromatography, separation techniques, and flow through porous media) and for its theoretical implications in nonequilibrium thermodynamics and transport theory. Indeed, this topic is especially attractive, as it deals with the coupling between vectorial fluxes and tensorial forces, which is beyond the usual constitutive equations of classical irreversible thermodynamics, and because it may be a useful testing ground of nonequilibrium equations of state.

Several authors [1–3] have stressed the need for a dynamic analysis to understand the following two points: (a) Polymer diffusivity decreases with increasing flow rate. This has been linked to the change in the shape of the molecules that reduce their ability to diffuse through the solvent. (b) The molecules of the higher-weight species migrate to low shear regions, which requires negative polymer diffusivity [4–6]. It is assumed that the temperature of the solution is above its critical point, that no phase separation occurs upon shearing.

Recently, MacDonald and Muller [7], to whom we refer for a wide bibliography on this topic, have analyzed the observed evolution of the concentration profile of a polymer under the effect of shear in a cone-and-plate configuration. Their conclusions are extremely challenging, as they show a discrepancy in two or three orders of magnitude between theoretical predictions and the observations.

They use as constitutive equation for the diffusion flux J,

$$J = -D\nabla n - \frac{D}{RT}\nabla\cdot\tau_{p}, \tag{1}$$

where n is the polymer concentration (in moles per unit volume), D the translational diffusivity, R the ideal gas constant, T absolute temperature and τ_{p} the symmetric second-order tensor representing the polymeric contribution to the viscous stress. This constitutive equation has been examined from different macroscopic and microscopic points of view by Beris et al. [8,9], and it may be found, for instance, in Ottinger [10], Mavrantzas and Beris [11], and, in a somewhat different form, in Bhave et al. [12]. The reader is referred to Beris and Mavrantzas [13] for details about its microscopic derivation.

MacDonald and Muller have applied Eq. (1) to the analysis of the evolution of the polymer concentration profile in a cone-and-plate configuration, where the only nonzero

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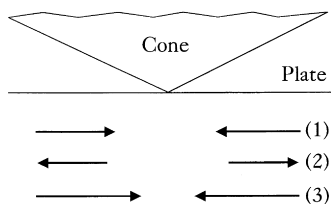*E-mail address:* jou@circe.uab.es (D. Jou)

Fig. 1. The flows of matter are indicated in the cone-and-plate configuration. Arrow (1) shows the shear-induced flow described by the second term in the right-hand-side of Eqs. (1) and (5); arrows (2) and (3) indicate the diffusion flux corresponding to the first term in the right-hand-side of Eq. (5) when the effective diffusion coefficient (10) is positive or negative. When it is positive, the diffusion flux (2) opposes to the shear-induced flow (1), whereas when it is negative, the diffusion flux (3) enhances the shear-induced effects. In contrast with Eq. (5), which uses the nonequilibrium chemical potential, Eq. (1) has only a positive diffusion coefficient, and cannot describe the enhancement of the shear-induced flow far from equilibrium.

components of the stress tensor τ_p are given by

$$\tau_{\phi\phi} = -2RTn(\lambda\dot{\gamma})^2; \quad \tau_{\phi\theta} = -RTn\lambda\dot{\gamma} \tag{2}$$

Here, r, ϕ and θ have the usual meaning, and they refer to the radial, axial and azimuthal directions, respectively, λ is the polymer relaxation time and $\dot{\gamma}$ the shear rate. In fact, the relaxation time λ appearing in Eq. (2) is an average relaxation time, because the actual macromolecules have several (or many) different relaxation times, associated to their different normal modes. Here we will use only one relaxation time, for the sake of simplicity and for comparison with the formulation of MacDonald and Muller.

Combination of Eqs. (1) and (2) and the mass balance equation

$$\frac{Dn}{Dt} = -\nabla \cdot J \tag{3}$$

where D/Dt refers to the usual material convective derivative, yields finally

$$\frac{\partial n}{\partial t} = \frac{D}{r^2} \frac{\partial}{\partial r}\left[r^2 \frac{\partial n}{\partial r} + \beta rn \right] \tag{4}$$

with the parameter β being defined as $\beta = 2(\lambda\dot{\gamma})^2$. To obtain Eq. (4) it has been assumed that the steady viscometric flow has only a nonzero component of the velocity (the ϕ component) which depends on the r and θ coordinates, that the shear-induced flux in the θ direction is negligible when the angle between the cone and the plate becomes small (as it was in the experiments with to which the results are compared), and that the convection of molecules by migration contributes negligibly to the stress. The term in β, arising from the second term in Eq. (1), induces a flux of solute towards the apex of the cone (shown as arrow 1 in Fig. 1) and it is usually believed that this term produces the total induced migration.

But, as it was demonstrated by MacDonald and Muller, this contribution cannot explain by itself the actual rate of migration. In fact, they have obtained a short-time solution

of Eq. (4) for $n(r, t)$ and have compared it with their experimental results for polystyrene macromolecules, nearly monodisperse, of different molecular weights 2.0×10^6 and 4.0×10^6 g/mol (denoted by 2 and 4 M, respectively) in a solvent of oligomeric polystyrene molecules of 500 g/mol, in a cone-and-plate configuration sheared at $\dot{\gamma} = 2 \text{ s}^{-1}$. The initial homogeneous concentration of the molecules of each solution was 0.20 and 0.12 wt.% for the 2 and 4 M solutions, respectively. According to an average value of λ obtained from the steady-state shear data, they obtained for the 2 and 4 M solutions the values $\beta_2 = 240$ and $\beta_4 = 1500$, respectively.

However, when they tried to fit the profile obtained from Eq. (4) with the observed concentration profiles, very severe discrepancies arose, as they found that the migration was much faster than predicted by Eq. (4). They tried to fit the data by allowing either β or D to be adjustable parameters. In this way, they found that to describe the data it is necessary that $\beta_2 = 200\,000$ and $\beta_4 = 1\,100\,000$, instead of the values mentioned previously. It is seen that the discrepancy between the observed and the measured β, which expresses in Eq. (4) the shear-induced flux, is almost of three orders of magnitude.

The aim of this paper is to point out how a simple generalization of Eq. (1) previously used in other contexts (see Refs. [13,14]) may partially alleviate this severe discrepancy, and may at the same time be helpful to understand the nonequilibrium modification of the equation of state of fluids under viscous stress.

2. Nonequilibrium chemical potential

According to classical thermodynamics, it is more fundamental to express the diffusion flux in terms of the gradient of the chemical potential rather than in terms of the concentration gradient. Indeed, it is the chemical potential μ which appears as the quantity conjugated to the variation in the number of moles of the constituents of thermodynamic systems. Thus, by following Jou et al. [13,14], we write instead of Eq. (1)

$$J = -\tilde{D}\nabla\mu - \frac{D}{RT}\nabla\cdot\tau_p \tag{5}$$

where μ is the chemical potential of the solute and $\tilde{D}$ is related to the classical diffusion coefficient D by $D = \tilde{D}(\partial\mu_{eq}/\partial n)$. Here, μ_{eq} is the local-equilibrium chemical potential of the solute. The essential point is that in presence of a nonvanishing τ_p, μ itself may contain contributions of τ_p, thus providing another possible coupling, neglected up to now, between viscous effects and diffusion, besides the term in $\nabla\cdot\tau_p$. Eq. (5), rather than being in contradiction with Eq. (1), is an extension of it to the nonlinear domain, and it reduces to it when one ignores the nonequilibrium (nonlinear) contributions to μ.

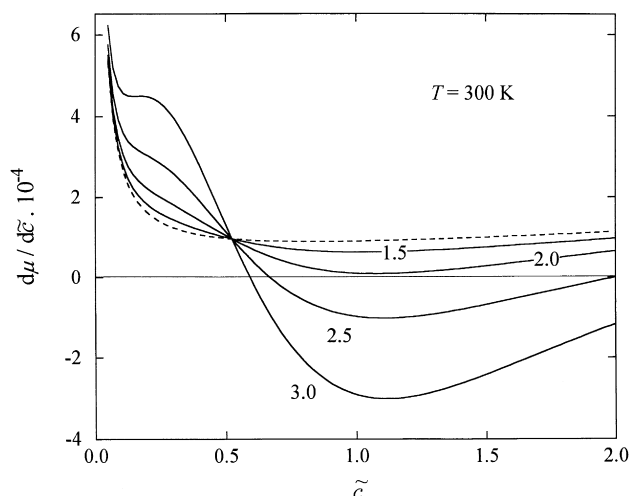In order to be explicit, we use, as in Refs. [13–15], the

Fig. 2. For different Deborah numbers, the variation of $(\partial\mu/\partial\tilde{c})$, which is proportional to the polymer effective diffusivity, in terms of the reduced concentration $\tilde{c}$ is presented, for polystyrene in transdecalin solution. The discontinuous line corresponds to the equilibrium Flory–Huggins contribution. It is seen that for $\tilde{c}$ higher than a critical value approximately equal to 0.5, and for high enough value of the Deborah number, the effective diffusivity becomes negative.

results of extended irreversible thermodynamics, according to which the Gibb's free energy G of a fluid system of volume V in presence of a viscous stress τ_p is

$$G(T,p,N_i;\tau_p) = G_{eq}(T,p,N_i) + \frac{1}{4}JV\tau_p : \tau_p \quad (6)$$

where G_{eq} is the local-equilibrium value of the free energy at the corresponding values of T, p and N_i (we take N for the number of moles of the solute and N_0 the number of moles of the solvent) and J is the so-called steady-state compliance, defined as $J = \lambda/\eta$. The reader interested in the origin and meaning of Eq. (6) will find them extensively discussed in Refs. [13–15]. Here, it is sufficient to know that Eq. (6) is supported by the kinetic theory of polymer solutions, and which it has a rather wide range of applicability, from ideal gases to nuclear matter, provided one identifies in any case the corresponding microscopic expressions for the stress tensor. Furthermore, the idea of a free energy including nonequilibrium contributions appears also in a very natural way in the framework of the Poisson bracket formulation of thermodynamics of flowing systems with internal microstructure [8], which is promising as a rather general framework for the theoretical modeling of the rheological constitutive equations of polymer solutions.

The chemical potential of the solute is defined by $\mu = (\partial G/\partial N)_{T,p,\tau_\pi}$. If we express N in terms of the solute concentration n (moles per unit volume) we have $N = nV$, and μ may be expressed as

$$\mu = \frac{1}{V}(1 - V'n)\left(\frac{\partial G}{\partial n}\right)_{T,p,\tau_p} \quad (7)$$

where $V' = \partial V/\partial N$ is the partial molar volume of the solute.

The term in parentheses in Eq. (7) takes into account the fact that a variation of N at constant p produces a change in the total volume V.

According to Eqs. (6) and (7), the chemical potential of the solute is

$$\mu = \mu_{eq} + \frac{1}{4V}(1 - V'n)\frac{\partial}{\partial n}(JV)\tau_p : \tau_p \quad (8)$$

with μ_{eq} the local-equilibrium chemical potential. The use of the generalized chemical potential leads us to define an effective diffusion coefficient as $D_{ef} = \tilde{D}(\partial\mu/\partial n)$ or, by writing $\tilde{D}$ in terms of the classical diffusion coefficient D,

$$D_{ef} = \frac{D}{(\partial\mu_{eq}/\partial n)}\left(\frac{\partial\mu}{\partial n}\right) \quad (9)$$

Introducing Eq. (8) into Eq. (9) we have

$$D_{ef} = D\left[1 + \frac{1}{(\partial\mu_{eq}/\partial n)}\frac{\partial}{\partial n}\left\{\frac{(1 - V'n)}{4V}\frac{\partial}{\partial n}(JV)\tau_p : \tau_p\right\}\right] \quad (10)$$

If the contribution of the term in $\tau_p : \tau_p$ were negative, it would induce a flow of solute towards higher solute concentrations, i.e. opposite to the usual Fickian diffusion. In the situation being examined here, this would reinforce the contribution of the term in $\nabla\cdot\tau_p$, which yields a migration of the molecules of the solute towards the center, and would render the migration process much faster. The situation is represented in Fig. 1.

3. Results and discussion

To see whether the nonequilibrium contribution to D_{ef} is negative requires a detailed knowledge of μ_{eq}, V' and J on concentration. We do not have enough detailed information about the system studied by MacDonald and Muller, but we may temptatively study from an analogous situation of polystyrene in transdecalin, whose nonequilibrium chemical potential under flow has been studied in detail by Criado-Sancho et al. [13,15]. For this system, the form of $(\partial\mu/\partial n)$ for a given τ_p is plotted in Fig. 2. To obtain this figure we have used for the equilibrium chemical potential the expression from the classical Flory–Huggins model [13,15] and to evaluate the nonequilibrium contribution we have taken for J the formula following from the Rouse–Zimm model, namely

$$J = \frac{CM}{cRT}\left[1 - \frac{\eta_s}{\eta}\right]^2 \quad (11)$$

where c is the polymer concentration expressed in terms of mass per unit volume, η is the viscosity of the solution, η_s the viscosity of the solvent, M the molar mass of the solute, and C a constant which takes the value 0.4 in the Rouse model (which ignores hydrodynamic interactions) and 0.206 in the Zimm model (which includes such interactions). Furthermore, as in [15,16] we have taken for $\eta(c)$ the
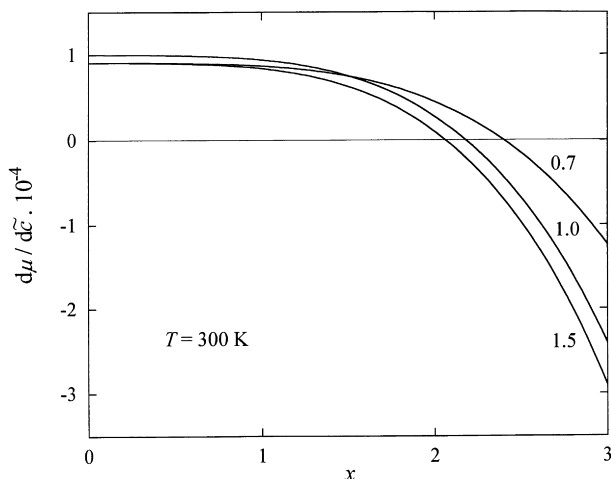
Fig. 3. For different reduced concentrations $\tilde{c}$, it is shown $(\partial\mu/\partial\tilde{c})$, which is proportional to the polymer effective diffusivity, as a function of the Deborah number $x = \lambda\dot{\gamma}$, for polystyrene in transdecalin solution. For $\tilde{c}$ lower than the critical value $\tilde{c} \approx 0.5$ the effective diffusivity is always positive, whereas for values of $\tilde{c}$ higher than the critical one, the effective diffusivity becomes negative far enough from equilibrium (i.e. for sufficiently high shear rates).

usual Huggins expression

$$\frac{\eta}{\eta_s} = 1 + [\eta]c + k[\eta]^2 c^2 \tag{12}$$

The expression for the nonequilibrium contribution to the chemical potential of the solute is thus given, after some tedious calculations which may be found explicitly in Ref. [15]:

$$\frac{1}{RT}\mu_{neq} = \frac{CV_1 M[\eta]}{4R^2 T^2}$$

$$\times \left\{ \frac{M[\eta]}{V_1} \frac{F(\tilde{c})}{\tilde{c}} + 2\left[\frac{M[\eta]}{\tilde{c}V_1} - m\right]\frac{P_5(\tilde{c})}{P_6(\tilde{c})}\right\}\tau_p : \tau_p \tag{13}$$

where m is the ratio between the molar volumes of the solute and the solvent, V_1 the molar volume of the solvent, $\tilde{c}$ the reduced concentration defined by $\tilde{c} = [\eta]c$ (note that $\tilde{c}$ is related to n by means of $\tilde{c} = [\eta]nM$). The functions $F(\tilde{c}), P_5(\tilde{c})$ and $P_6(\tilde{c})$ are auxiliary functions which allow to simplify the notation: in particular, $F(\tilde{c})$ arises from Eqs. (11) and (12) as $J = (CM[\eta]/RT)F(\tilde{c})$, in such a way that

$$F(c) = \tilde{c}\left[\frac{1 + k\tilde{c}}{1 + \tilde{c} + k\tilde{c}^2}\right]^2$$

On the other side, the two other functions $P_5(\tilde{c})$ and $P_6(\tilde{c})$ are related to the derivatives of $F(\tilde{c})$ with respect to the reduced concentration and are defined, respectively, as $P_5(\tilde{c}) = (k - 1)\tilde{c}^2 + (k^2 - 3k)\tilde{c}^3 - 3k^2\tilde{c}^4 - k^3\tilde{c}^5$ and $P_6(\tilde{c}) = (1 + \tilde{c} + k\tilde{c}^2)^3$. These functions do not hide any physical contents but are only a mean to give a compact way to the rather cumbersome expressions. The corresponding results for $(\partial\mu/\partial n)$ for a given τ_p are plotted in

Fig. 2 for the system PS/TD with a polymer molar mass of $520\,\text{kg mol}^{-1}$, where the values $k = 1.40$, $[\eta] = 0.043\,\text{m}^3\,\text{kg}^{-1}$ and $\eta_s = 0.0023\,\text{Pa s}$ are used, as in Refs. [16,17].

It is seen in Fig. 2 that for low enough concentrations $(\partial\mu/\partial n)$, and therefore D_{ef} is positive, whereas for higher concentrations $(\partial\mu/\partial n)$ and consequently D_{ef} is negative. As it is appreciated in Fig. 2, the critical reduced concentration for this transition is given by $\tilde{c} \approx 0.5$. This value corresponds to a volume fraction ϕ (which in the system under consideration is given by $\phi = 2.168 \times 10^{-2}\,\tilde{c}$) of 0.01 and to a corresponding mass percentage of 1.3 wt.%.

It should be also mentioned than in the calculation leading to Fig. 2, use has been made of the Rouse expression for the steady state compliance $J = 0.4(nRT)^{-1}[1 - (\eta_s/\eta)]^2$, instead of the simplest approximation $J = (nRT)^{-1}$, which would yield an opposite sign for the nonequilibrium contributions to the chemical potential. The need of using the rigorous expression for J instead of its simplest scaling law approximation has already been emphasized in Ref. [15] in the different context of shear-induced shift of the critical point in dilute polymer solutions. Here, the need of the use of the rigorous expression for J is confirmed on a different physical situation.

In the cone-and-plate configuration considered by MacDonald and Muller, $\tau_p : \tau_p = \tau_{\phi\phi}^2 + 2\tau_{\phi\theta}^2 = 2(nRT)^2[2(\lambda\dot{\gamma})^4 + (\lambda\dot{\gamma})^2]$, i.e. the dependence of the nonclassical term on $\lambda\dot{\gamma}$ is rather strong. A simple estimation of the order of magnitude of D_{ef}/D for the situations of interest may be obtained from Fig. 2, by taking into account that $D_{ef}/D = (\partial\mu/\partial n)/(\partial\mu_{eq}/\partial n)$ for $\tilde{c} \approx 1.5$ and $x = \lambda\dot{\gamma} \approx 2$, which is of the order of -1, as it may be seen in Fig. 2, and taking into account the dependence of $(\partial\mu/\partial n)$ with respect to $\lambda\dot{\gamma}$ is of the order of $(\lambda\dot{\gamma})^4$. Then, it is obtained that for $\lambda\dot{\gamma} \approx 12$ and $\lambda\dot{\gamma} = 25$, (corresponding to the situations studied by MacDonald and Muller), D_{ef}/D is of order 10^3 and 10^4, respectively. A detailed calculation for the system studied by MacDonald and Muller is up to now not possible with the data available to us, but the order of magnitude of the correction is consistent with their data. Indeed, they refer that the observed effects could be described if one had for the absolute value of the diffusion coefficient $8.1 \times 10^{-10}\,\text{cm}^2\,\text{s}^{-1}$ instead of the experimental value at rest, $6.7 \times 10^{-13}\,\text{cm}^2\,\text{s}^{-1}$, in the solution 2 M, or $5.1 \times 10^{-10}\,\text{cm}^2\,\text{s}^{-1}$ instead of the experimental value at rest, $5.1 \times 10^{-13}\,\text{cm}^2\,\text{s}^{-1}$, in the 4 M solution. In any case, it is seen that the effect proposed here is not at all negligible but dominant.

Therefore, effective polymer diffusivity depends on the shear rate, molecular weight (through the dependence of the relaxation time) and the concentration. In Fig. 3, the corresponding effective polymer diffusivity versus the Deborah number $\lambda\dot{\gamma}$ for the same system of Fig. 2 is presented, for several values of the reduced concentration. For low values of the concentration, the effective diffusivity is always positive and increases with the shear rate and the molecular

weight. In this range of concentration the induced migration seems not possible, or at least very slow. However, for reduced concentrations higher than the critical one, the diffusivity becomes negative for sufficiently high values of the shear rate, the decrease being steeper for higher molecular weights. In the figures, we do not consider reduced concentrations higher than two, since the dilute solution approximation used in Ref. [15] would be no longer valid. Therefore, we will not extrapolate the behavior of the effective polymer diffusivity beyond this value.

We conclude that the stress contribution to the chemical potential of the polymer has important effects with respect to the previous formulation, where the gradient of n rather than the gradient of μ were considered. The following points are especially worth mentioning:

- For a given concentration (higher than a critical value), the effective diffusion coefficient is reduced when the shear stress increases, and it becomes negative. In this regime, the nonequilibrium contribution to the chemical potential considerably enhances the polymer migration. This may explain why the migration observed is much faster than the migration predicted by the simpler Eq. (1). It would be interesting to relate this negative derivative of the generalized chemical potential with concentration to some kind of phase separation. In fact, our description could be interpreted as describing the dynamical aspects of a phase separation in the initially homogeneous and stable mixture. However, it is important to stress that the derivative of the local-equilibrium chemical potential with respect to concentration is positive, and therefore no phase separation would occur from the purely local-equilibrium point of view. It is the nonequilibrium part of the chemical potential which changes sign for sufficiently high value of the shear rate. From this point of view, one would have a shear-induced phase separation: the mixture splits in two different bulk phases with different solute concentrations, one of them (more concentrated) near the apex of the cone and the other one (more dilute) near the edge of the viscometer; and the shear-induced transport would describe the dynamics of this separation from the homogeneous phase to the heterogeneous situation.
- In Fig. 3 we can see that for a given value of the concentration, the effective diffusion coefficient becomes positive for values of the shear rate lower than some critical value. Thus, at low shear rates, the only thermodynamic force leading migration is the coupling of the second term in Eq. (5), and migration is very slow. For higher shear rates, the diffusion coefficient becomes negative and migration is much faster. This feature is also briefly commented by MacDonald and Muller.
- From the point of view of the thermodynamic analysis, a concentration transition is found in the behavior of the polymer diffusivity under flow, which changes sign from positive to negative, depending on the concentration, at a

given value of the shear rate. This point seems a new one and gives the minimum concentration condition to obtain induced migration in a shear flow. This may explain why the polymer concentration in the depletion zone near the edge of the plane–and–cone rheometer does not tend to zero with time, but to a nonvanishing value. Indeed, when the polymer concentration has been reduced, by the migration process, to values lower than the critical one, the effective diffusion coefficient becomes positive, and the influence of the term in $\nabla.\tau_p$ is cancelled by the diffusion term. However, a rigorous analysis of the situation near the walls should take into consideration the possible effects of the interaction between the wall and the polymer, which could contribute to the form of the free energy [18].

To understand better this concentration transition, we think that a combination of macroscopic and microscopic ideas is essential to obtain a fast progress in the field. Essentially, it may be seen as a competition on the influence of two factors on the chemical potential, namely, concentration and shear stress. Indeed, under shear stress, the macromolecules become distorted and aligned by the flow, and therefore their free energy is modified with respect to the equilibrium free energy. This is the intuitive origin of the nonequilibrium contribution to the chemical potential.

The present analysis is qualitative rather than rigorously quantitative. Indeed, we do not know the behavior of μ_{eq}, V' and J on concentration for the solution studied experimentally by MacDonald and Muller, so that we have extracted the qualitative information from the system studied by Criado-Sancho et al. [15], which points, however, the new features that we have just outlined, and which agree qualitatively with the experimental behavior, in contrast with the predictions of Eq. (1), which do not exhibit these previous features. A detailed analysis of the system considered by MacDonald and Muller would be certainly very interesting.

Here, we have adopted a rather macroscopic and phenomenological approach, whose analysis should be complemented in the future by further microscopic studies. Indeed, on the one side, it would be interesting to compare the reduction of the effective diffusion coefficient obtained from our thermodynamic arguments, with the reduction obtained in some microscopic analyses by Ottinger [10]. On the other side, a deeper comparison of the generalized thermodynamic potentials of extended irreversible thermodynamics with those appearing in the generalized Hamiltonian formulation of rheological equations would be also useful.

Thus, in our opinion, the interest of the present work is twofold. On the one side, it allows to compare the effects of a modification of a constitutive Eq. (1), which takes into account a coupling between shear stress and diffusion but ignores the modifications in the equation of state, and Eq. (5), which takes into account both effects. Indeed,

while many authors generalize the transport equations far from equilibrium, most of them do not modify the equations of state. Here it is seen that both changes should be considered far from equilibrium. On the other side, the paper has an experimental interest, as it hints to a possible explanation of the enhancement of shear-induced migration, which has two different contributions: that arising from the coupling term in Eq. (1) and that arising from the nonequilibrium equation of state, considered in this paper.

Before concluding the paper a few useful comments are made here. We must emphasize that the nonequilibrium chemical potential used in this paper has not been built ad hoc for this problem, but that has a macroscopic and microscopic theoretical basis analyzed in detail in Refs. [13,14]. A nonequilibrium chemical potential appears in other analyses of phase separation under flow, as for instance in some approaches which are based on a dynamical analysis of the concentration fluctuations, which may be enhanced due to the flow [19–23]. Such dynamical approaches have been compared in detail with the thermodynamic approach in Ref. [24], in the problem of the shift of the shear-induced spinodal line in polymer solutions, where both approaches coincide—if use is made of the same form for the nonequilibrium chemical potential—in the long-wavelength limit. Of course, the dynamical approach is more general and gives further contributions not included in the thermodynamic approach when the wavelength of the perturbations is comparable to the gyration radius of the polymer. A nonequilibrium chemical potential dependent on the viscous pressure may also arise in a stochastic analysis based on a Langevin equation for the fluctuations of both the concentration and the viscous stress [25], as the total distribution function is projected onto the space of these two variables, in contrast with the classical thermodynamic analysis where the viscous stress is not considered as an independent variable.

It could be argued that, since shear flow is nonintegrable, its dynamics and steady states are generally not described by state functions. We have considered in detail this remark in Ref. [26], where we have considered a statistical description not based on the canonical distribution with only one Lagrange multiplier conjugated to the energy but with a more general description based on two Lagrange multipliers, one conjugated to the energy and the other one to the viscous stress. This is certainly a topic open for discussion in recent nonequilibrium thermodynamics beyond the local-equilibrium approximation. In any circumstance, this paper shows that the inclusion of the nonlinear effects accounted for the present nonequilibrium chemical potential is able to give the correction of two orders of magnitude necessary to agree with the experimental data.

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