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Thermodynamics and dynamics of flowing polymer solutions and blends

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Abstract

We review the basic ideas and main results of our analysis of shear-induced effects in polymer solutions and blends. The analysis combines thermodynamic and hydrodynamic descriptions. The flow contribution to the free energy of the solution is described in the framework of extended irreversible thermodynamics, which relates the viscoelastic constitutive equations to a non-equilibrium entropy that depends on the viscous pressure tensor. This yields, by differentiation, the corresponding non-equilibrium equation of state for the chemical potential, which couples diffusion flux to viscous pressure in the presence of a flow. In some conditions, the one-phase system becomes unstable and splits into two phases, leading to a shift in the spinodal line. The theoretical analysis is based on the stability of the mass and momentum balance equations, the constitutive equations for viscous pressure tensor and diffusion flux, and the equation of state for the chemical potential. The resulting predictions corroborate qualitatively the known experimental observations. Results for dilute and entangled polymer solutions and for polymer blends are given.

Resum

Passem revista a les idees bàsiques i els principals resultats dels nostres estudis sobre els efectes induïts per gradients de velocitat en dissolucions i mescles de polímers, en què es combinen les descripcions hidrodinàmica i termodinàmica. La contribució del flux hidrodinàmic a l'energia lliure de la dissolució és descrita en el marc de la termodinàmica irreversible estesa, que estableix una relació entre les equacions constitutives viscoelàstiques i una entropia de no-equilibri que depèn del tensor de pressions viscoses. Per diferenciació d'aquesta, s'obté l'equació d'estat per al potencial químic de no-equilibri, el qual, en presència de gradients de velocitat, acobla el flux de difusió amb la pressió viscosa. En certes condicions, aquesta influència fa que un sistema que en repòs seria unifàsic esdevingui inestable i es descompongui en dues fases, tot provocant, així, un desplaçament de la línia espinodal en el diagrama de fases. L'anàlisi teòrica està basada en l'estabilitat de les equacions de balanç de massa i de quantitat de moviment, de les equacions constitutives per al flux de difusió i el tensor de pressions viscoses, i de l'equació d'estat per al potencial químic de no-equilibri. Les prediccions concorden qualitativament amb les observacions experimentals conegudes. Presentem resultats per a dissolucions polimèriques diluïdes i concentrades i per a mescles de polímers.

Keywords: Non-equilibrium thermodynamics, polymer solutions, shear-induced effects, phase diagram, migration, spinodal line.

1. Introduction

The thermodynamics of fluids under flow is an active and very challenging topic in modern non-equilibrium thermodynamics and statistical mechanics [1-6]. In theoretical terms, the influence of flow on thermodynamic potentials requires going beyond the local-equilibrium hypothesis, which opens many questions and fosters an active dialogue between macroscopic and microscopic theories. It also means the relations between thermodynamics and hydrodynamics have to be discussed, because in general there will be an interplay of the two approaches. To clarify the formulation of non-equilibrium thermodynamics beyond local equilibrium and its relationship with both microscopic and hydrodynamic theories is currently an important frontier of science. This as-

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pect is often neglected in rheology, which focuses its attention on the constitutive equations but assumes that the equations of state keep their local-equilibrium form. In the present approach, the equations of state contain flow contributions that are related to some terms of the viscoelastic equations by means of a non-equilibrium entropy.

Modifications in the thermodynamic equations of state and the conditions of chemical equilibrium and stability imply changes in the phase diagram of substances in non-equilibrium states. Much study has been devoted to flow-induced changes in the phase diagram of polymer solutions and blends. The practical importance of the problems arising under flow is easily understood, as most industrial processing (pumping, extruding, injecting, molding, mixing, etc.) and many biological processes (those in flowing blood) take place under flow, in which the polymer undergoes shear and elongational stresses. Thus, flow-induced changes of phase may take place, affecting both rheological and structural properties of the materials. These effects are important, too, in flows of polymer solutions through packed porous beds, as in membrane permeation or flow of oil through soil and rocks.

Another field of application for these analyses is provided by some of the main current experiments in nuclear and particle physics searching for the transition from nuclear matter to a quark–gluon plasma through highly energetic collisions of heavy nuclei. Since the total duration of these collisions is of the order of a few times the mean time between successive collisions amongst nucleons in the nuclei, the latter are far from equilibrium during the collision. Thus, it is conceivable that an analysis based on the local-equilibrium equations of state for nuclear matter and quark–gluon plasma is not a fully reliable way to describe the transition. Thus, a more general theory than the local-equilibrium one would be useful.

A decisive step in the thermodynamic understanding of these phenomena is to formulate a free energy depending explicitly on the characteristics of the flow and to establish its role in transport phenomena, thus intimately linking hydrodynamics and thermodynamics. In Section 2, we provide the basis in macroscopic terms, from the perspective of extended irreversible thermodynamics, and we compare it with other macroscopic theories, such as rational thermodynamics, theories with internal variables and Hamiltonian formulations. Section 3 is devoted to the application of the formalism to the analysis of the phase diagram of dilute and entangled polymer solutions and polymer blends under flow. Section 4 analyses the flow-induced diffusion that results from couplings between mass transport and viscous pressure and its consequences for polymer migration, shear-induced concentration banding and chromatography.

2. Non-equilibrium thermodynamics and rheology

Local-equilibrium thermodynamics assumes that the thermodynamic potentials and, consequently, the equations of state retain the same form out of equilibrium as in equilibrium, but with a local meaning [7-10]. According to this view, thermodynamics is not modified by flow, since flow does not change the equations of state, though it may modify the transport equations. This approach is insufficient to deal with systems with internal degrees of freedom, so that on some occasions [11-14] one includes in the set of thermodynamic variables several internal variables describing some details of the microstructure of the system, such as, for instance, polymeric configuration. In this case, flow may affect the thermodynamic equations of state through its action on such internal variables.

In the 1960s, another non-equilibrium theory, known as rational thermodynamics, was proposed [15-17]. This theory assumes that entropy and (absolute) temperature are primitive quantities, not restricted to situations near local equilibrium. Instead of a local-equilibrium assumption, it is assumed that entropy, or free energy, depends on the history of the strain, which allows for an explicit influence of flow on the thermodynamic analysis. The theory developed a powerful formalism to obtain thermodynamic restrictions on the memory functions relating viscous stress to the history of the strain. However, the analysis centred on the constitutive equations, but paid little attention to the non-equilibrium equations of state.

At the end of the 1960s, a new approach, called extended irreversible thermodynamics (EIT) [5, 18-31] was proposed. This has been developed considerably since 1980. This theory assumes that entropy depends on, as well as the classical variables, dissipative fluxes, such as the viscous pressure tensor, the heat flux or the diffusion flux. Its motivation is to make the relaxational transport equations for the heat flux or the viscous pressure tensor compatible with the positiveness of entropy production, which is not satisfied when such general transport equations are combined with local-equilibrium entropy. The direct influence of the viscous pressure tensor and other fluxes on the thermodynamic potentials opens a way towards thermodynamics under flow, whose equations of state incorporate non-equilibrium contributions.

2.1 Rheology: viscoelastic constitutive equations

Before going into thermodynamics, which is the main subject of this review, we wish to summarise some of the basic concepts of rheology that will appear throughout the paper. The main rheological quantities of interest in steady flows are shear viscosity and the first and second normal stress coefficients $\eta(\dot{\gamma})$, $\Psi_1(\dot{\gamma})$ and $\Psi_2(\dot{\gamma})$, respectively, which are defined as [32-36]

$$\begin{aligned} P^{\mathrm{v}}_{12} &= -\eta(\dot{\gamma})\dot{\gamma}, \\ P^{\mathrm{v}}_{11} - P^{\mathrm{v}}_{22} &= -\Psi_1(\dot{\gamma})\dot{\gamma}^2, \\ P^{\mathrm{v}}_{22} - P^{\mathrm{v}}_{33} &= -\Psi_2(\dot{\gamma})\dot{\gamma}^2, \end{aligned} \tag{2.1}$$

in which P^{v}_{ij} indicates components of the viscous pressure tensor $\mathbf{P}^{\mathrm{v}}$ and $\dot{\gamma}$ the shear rate in a planar Couette flow, i.e. $\dot{\gamma} = \partial v_x / \partial y$. Recall that $\mathbf{P}^{\mathrm{v}}$ is related to the total pressure tensor $\mathbf{P}$ as $\mathbf{P} = p\mathbf{U} + \mathbf{P}^{\mathrm{v}}$, with p the equilibrium pressure and $\mathbf{U}$

the unit tensor. In what are known as Newtonian fluids, normal stress coefficients vanish and viscosity does not depend on the shear rate. In non-steady situations, some memory effects appear and the rheological properties depend on the frequency of perturbation: for instance, viscoelastic liquids behave as Newtonian liquids under low-frequency perturbations (low in comparison with the inverse of a characteristic relaxation time), and as elastic solids at high frequencies.

The simplest description of these memory effects in the study of polymeric systems is to assume that the viscous pressure tensor depends not only on the velocity gradient but also on its own time rate of change by means of a relaxational term. In the simplest Maxwell model, the viscous pressure tensor is described by the constitutive equation

$$\frac{\mathrm{d}\mathrm{P}^{v}}{\mathrm{d}t} = -\frac{1}{\tau}\mathrm{P}^{v} - 2\frac{\eta}{\tau}\mathrm{V}, \qquad (2.2)$$

with $\mathbf{V}$ being the symmetric part of the velocity gradient, η the shear viscosity and τ the relaxation time. Maxwell's model captures the essential idea of viscoelastic models: the response to slow perturbations is characteristic of a viscous fluid, whereas for fast perturbations it behaves as an elastic solid. However, the material time derivative in (2.2) is not satisfactory, neither in theoretical terms nor in the practical predictions, and it must be replaced by some frame-indifferent derivative, as in the upper-convected Maxwell model [32-36] for which the evolution equation for the viscous pressure tensor has the form

$$\frac{\mathrm{d}\mathrm{P}^{v}}{\mathrm{d}t} - (\nabla\mathbf{v})^{T}\cdot\mathrm{P}^{v} - \mathrm{P}^{v}\cdot(\nabla\mathbf{v}) = -\frac{1}{\tau}\mathrm{P}^{v} - 2\frac{\eta}{\tau}\mathrm{V}, \qquad (2.3)$$

In a pure shear flow corresponding to $\mathbf{v} = (\mathrm{v}_x(y), 0, 0)$, the velocity gradient is

$$\nabla\boldsymbol{v} = \begin{pmatrix} 0 & 0 & 0 \\ \dot{\gamma} & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}. \qquad (2.4)$$

Introduction of (2.4) into (2.3) yields, in the steady situation,

$$\mathrm{P}^{v} = \begin{pmatrix} -2\tau\eta\dot{\gamma}^{2} & -\eta\dot{\gamma} & 0 \\ -\eta\dot{\gamma} & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}. \qquad (2.5)$$

The viscometric functions are thus $P^{\nu}{}_{12} = -\eta\dot{\gamma}$, $P^{\nu}{}_{11} - P^{\nu}{}_{22} = -2\tau\eta\dot{\gamma}^{2}$, $P^{\nu}_{22} - P^{\nu}_{33} = 0$, so that the second normal stress is zero and the first normal stress coefficient Ψ_1 is $\Psi_1(\dot{\gamma}) = 2\tau\eta$. However, if equation (2.2) is used, all the diagonal components in the viscous pressure vanish and normal stresses are absent, unlike in experiments.

In usual rheological studies, equations (2.2) or (2.3) are combined with the local-equilibrium equations of state. For instance, the equilibrium Gibbs function for a dilute polymer solution may be expressed according to the Flory–Huggins model. The volume of the system is given by $V = \upsilon_1\Omega$, with υ_1 being the molar volume and Ω a parameter defined as $\Omega = N_1 + mNp$,where N_1 is the number of moles of the solvent, Np the number of moles of the polymer and m a new parameter, which allows the volume fraction ϕ to be expressed as $\phi = mNp/\Omega$ [2, 5]. The total Gibbs function of the system is given by

$$\frac{G}{RT} = N_1\ln(1-\phi) + N_p\ln\phi + \chi(1-\phi)\Omega\phi, \qquad (2.6)$$

with χ being the Flory–Huggins interaction parameter which depends on the temperature as

$$\chi = \tfrac{1}{2} + \Psi\left(T^{-1}\Theta - 1\right) \qquad (2.7)$$

where Θ is the theta temperature (at which the repulsive excluded volume effects balance the attractive forces between the segments and the polymer has the behaviour of an ideal chain) and Ψ is a parameter which does not depend on T.

From equation (2.6), one can derive the chemical potentials of the solvent, μ_1, and of the polymer, μ_p, which are given, respectively, by

$$\frac{\mu_1}{RT} = \ln(1-\phi) + \left(1 - \frac{1}{m}\right)\phi + \chi\phi^{2},$$
$$\frac{\mu_p}{RT} = \ln\phi + (1-m)(1-\phi) + \chi m(1-\phi)^{2}. \qquad (2.8)$$

However, equations (2.2) and (2.3) are not compatible with local-equilibrium entropy. Indeed, the classical entropy production is $\sigma_{CIT} = -T^{-1}\mathbf{P}^{\mathrm{v}}{:}\mathbf{V}$, in such a way that constitutive equation (2.2) yields for it

$$\sigma_{CIT} = 2\eta T^{-1}\mathrm{V}{:}\mathrm{V} + \tau T^{-1}\mathrm{V}{:}\frac{\mathrm{d}\mathrm{P}^{v}}{\mathrm{d}t}. \qquad (2.9)$$

The first term is always positive but the second may be positive or negative, and may overcome in value the first term. This inconsistency leads us to investigate in greater detail the foundations of non-equilibrium thermodynamics.

2.2 Extended Irreversible Thermodynamics: non-equilibrium equations of state

First, we recall that the classical formulation of irreversible thermodynamics [7-10] is based on the local-equilibrium hypothesis. It states that, despite the non-homogeneous nature of the system, fundamental thermodynamic relations are still valid locally. In particular, the Gibbs equation expressing the differential form of entropy in terms of its classical variables (internal energy, volume and number of moles of the chemical components of the system) is locally valid.

By combining the Gibbs equation and the evolution equations for mass, momentum and energy, one obtains an expression for the evolution equation of entropy. This expression provides with an explicit form for entropy flux and entropy production in terms of the fluxes (heat flux, diffusion flux, viscous pressure tensor, reaction rates,...) and of the conjugate thermodynamical forces (the gradients of temperature, chemical potential, velocity and the chemical affinities of the reactions, respectively).

Finally, the fluxes are related to the forces by means of constitutive equations that must obey the positive character of entropy production. In the simplest but most usual versions, one assumes linear constitutive equations in which the fluxes are linear combinations of the thermodynamic forces. In this case it may be shown that the matrix of the transport coefficients relating the fluxes to the forces obeys the reciprocity relations established by Onsager and Casimir [7-10]. As explained in the previous section, local-equilibrium entropy production is not definitely positive if constitutive equations with memory, like (2.2) or (2.3) for the viscous pressure tensor, are used.

EIT, which has been widely reviewed in [5, 18-20], assumes that entropy may depend on dissipative fluxes, in addition to classical variables. First, we take a one-component fluid, neglect thermal conduction and assume that the only non-equilibrium independent thermodynamic variable is the viscous pressure tensor. Then, we consider a two-component mixture and incorporate the effects of the diffusion flux and its couplings with viscous pressure.

2.2.1 Viscous pressure

According to EIT, the generalised Gibbs equation for a simple unicomponent fluid in the presence of a non-vanishing viscous pressure tensor is, up to the second order in $\mathbf{P}^v$ [5, 18-20]

$$\mathrm{d}s = T^{-1}\mathrm{d}u + T^{-1}p\,\mathrm{d}v - \frac{\tau^{(2)}v}{2\eta T}\mathbf{P}^v\!:\!\mathrm{d}\mathbf{P}^v, \qquad (2.10)$$

with u and v being the specific internal energy and the specific volume, respectively, and T and p the absolute temperature and the thermodynamic pressure. The first two terms on the right-hand side in (2.10) correspond to the classical Gibbs equation, whereas the third term is characteristic of EIT and is related to the non-vanishing character of the relaxation time $\tau^{(2)}$. When $\tau^{(2)}$ tends to zero, both the relaxational terms in the constitutive equations (2.2) and (2.3) and the non-equilibrium contribution to the entropy in (2.10) tend to zero; thus, the constitutive equations (2.2) and (2.3) tend to the usual Newton–Stokes law and (2.10) reduces to the classical Gibbs equation. Thus, the presence of relaxational terms in the constitutive equations implies the presence of a non-equilibrium contribution to the Gibbs equation. The advantage of (2.10) over local-equilibrium entropy is that its production is given by [5, 18-20]

$$\sigma_{EIT} = -T^{-1}\mathbf{P}^v : \left(\mathrm{V} + \frac{\tau^{(2)}}{2\eta}\frac{\mathrm{d}\mathbf{P}^v}{\mathrm{d}t}\right). \qquad (2.11)$$

When (2.2) is introduced into this expression, it reduces to $\sigma_{EIT} = (2\eta T)^{-1}\mathbf{P}^v\!:\!\mathbf{V}$, which is definite positive.

In polymer solutions, where the macromolecules have several internal degrees of freedom, each with its own contribution $\mathbf{P}_i^v$ to the viscous pressure and η_i to the viscosity, and its own relaxation time $\tau_i^{(2)}$, the Gibbs equation (2.10) is generalised to

$$\mathrm{d}s = T^{-1}\mathrm{d}u + T^{-1}p\,\mathrm{d}v - \sum_i \left(\tau_i^{(2)}v/2\eta_i T\right)\mathbf{P}_i^v:\mathrm{d}\mathbf{P}_i^v. \qquad (2.12)$$

Thus, $\tau^{(2)}$ in (2.10) may be considered an average relaxation time. It is useful, furthermore, to rewrite (2.10) in terms of steady-state compliance J ($J = \tau^{(2)}/\eta$) as

$$\mathrm{d}s = T^{-1}\mathrm{d}u + T^{-1}p\,\mathrm{d}v - \frac{v}{2T}J\mathbf{P}^v:\mathrm{d}\mathbf{P}^v. \qquad (2.13)$$

In the case of several degrees of freedom, J is an effective quantity, which is a function of the several relaxation times and viscosities, given explicitly in (3.15).

2.2.2 Viscous pressure and diffusion flux

When we consider a binary mixture instead of a single fluid, it is natural to introduce diffusion flux as a further independent variable, because it plays an important role in the phase separation and migration processes we are interested in describing. Instead of (2.10), we write now the extended Gibbs equation in the form [5, 18-20]

$$\mathrm{d}s = T^{-1}\mathrm{d}u + T^{-1}p\,\mathrm{d}v - T^{-1}\tilde{\mu}\,\mathrm{d}c_s - \frac{v\tau^{(1)}}{\tilde{D}T}\mathbf{J}\cdot\mathrm{d}\mathbf{J} - \frac{v\tau^{(2)}}{2\eta T}\mathbf{P}^v:\mathrm{d}\mathbf{P}^v, \qquad (2.14)$$

with c_s being the concentration (mass fraction) of the solute, $\mu \equiv \mu_s - \mu_1$ the difference between the specific chemical potentials of the solute and the solvent, $\tilde{D}$ is related to the usual diffusion coefficient D as $D = \tilde{D}(\partial\tilde{\mu}/\partial c_s)$ and $\tau^{(1)}$ and $\tau^{(2)}$ are the relaxation times of $\mathbf{J}$ and $\mathbf{P}^v$, respectively. Furthermore, we assume for the entropy flux the expression

$$\mathbf{J}^s = T^{-1}\mathbf{q} - \tilde{\mu}T^{-1}\mathbf{J} + \beta\mathbf{P}^v\cdot\mathbf{J}. \qquad (2.15)$$

The first two terms are classical; the latter one is characteristic of EIT, and β is a phenomenological coefficient coupling $\mathbf{P}^v$ and $\mathbf{J}$.

The energy and the mass balance equations are, respectively,

$$\rho\dot{u} = -\nabla\cdot\mathbf{q} - p(\nabla\cdot\mathbf{v}) - \mathbf{P}^v:\mathrm{V}, \qquad (2.16)$$

$$\rho\frac{\mathrm{d}c_s}{\mathrm{d}t} = -\nabla\cdot\mathbf{J}. \qquad (2.17)$$

The corresponding evolution equations for the fluxes are [5, 18-20]

$$\tau^{(1)}\frac{\mathrm{d}\mathbf{J}}{\mathrm{d}t} = -(\mathbf{J} + \tilde{D}\nabla\tilde{\mu}) + \beta\tilde{D}T\nabla\cdot\mathbf{P}^v \qquad (2.18)$$

and

$$\tau^{(2)}\frac{\mathrm{d}\mathbf{P}^v}{\mathrm{d}t} = -(\mathbf{P}^v + 2\eta\mathrm{V}) + 2\beta T\eta(\nabla\mathbf{J})^s \qquad (2.19)$$

where $(\nabla \boldsymbol{J})^s$ stands for the symmetric part of $\nabla \boldsymbol{J}$. These equations exhibit couplings between diffusion and viscous stresses whose relevance will be illustrated in Section 5. The material time derivatives of $\boldsymbol{J}$ and $\mathbf{P}^v$ in these equations should be replaced, in general, by frame-invariant time derivatives, as in (2.3). When the coupling coefficient β and the relaxation times vanish, these equations reduce to the well-known Navier–Stokes and Fick equations, namely

$$\mathrm{P}^v = -2\eta \mathrm{V}\,, \quad \mathbf{J} = -\tilde{D}\nabla\tilde{\mu}\,. \tag{2.20}$$

It should be emphasised that the chemical potential appearing in (2.18) is not the local-equilibrium one, but is obtained by differentiation of (2.14) and therefore contains contributions from the fluxes, which will be discussed in length in Section 3.

2.3 Other approaches

EIT is not the only theory going beyond local equilibrium. Rational thermodynamics, theories with internal variables, and formulations based on Hamiltonian methods also aim to go beyond this hypothesis, and allow exploration of more general possibilities in the thermodynamic analysis of polymer solutions and other complex systems.

2.3.1 Rational thermodynamics

The formalism of rational thermodynamics [15-17] offers an approach to deriving constitutive equations that is radically different from that of classical irreversible thermodyamics. Among the basic hypotheses underlying the earliest versions of this theory we can outline: (i) absolute temperature and entropy are considered primitive concepts, not restricted to near-equilibrium situations; (ii) systems under study have memory, i.e. their behaviour at a given time is determined by their past history; (iii) the second law of thermodynamics, which serves as a restriction on the form of constitutive equations, is expressed by means of Clausius–Duhem inequality. To obtain restrictions on the memory functionals an elaborate mathematical theory is required. As well as these ideas, rational thermodynamics makes use of some auxiliary "principles", namely those of equipresence (all variables are assumed to be present, in principle, in all equations, and some of them may be eliminated by using the restrictions of the second law), of fading memory (the memory is assumed to be evanescent, i.e. to be stronger for recent times than for old ones) and of frame-indifference (constitutive equations are assumed to be invariant under Euclidean transformations). Rational thermodynamics involves a more general entropy than the local-equilibrium entropy. It may depend on non-equilibrium variables, such as, for instance, the gradients of temperature and velocity, but the equations of state obtained as derivatives of the entropy are usually not explored, unlike in EIT, one of whose objectives is precisely the full exploration of such equations.

Some aspects of rational thermodynamics were reformulated at the beginning of the 1970s. One especially interesting reformulation, by Shi-Liu, is based on the use of Lagrange multipliers to include the restrictions of the balance equations as admissible processes. This method is widely used, for instance, by Müller and Ruggeri [30] in their formulation of extended thermodynamics. It is interesting to consider EIT from perspectives of both classical and rational irreversible thermodynamics because EIT provides a common ground for comparison despite their appearing unrelated original formulations. A comparison of rational thermodynamics with extended irreversible thermodynamics in the linear domain may be found in [18, 20].

2.3.2 Theories with internal variables

Another interesting and useful perspective on the thermodynamics of systems with microstructure, such as polymer solutions, is provided by theories with internal variables [11-14, 37, 38]. These theories, by introducing additional variables, allow a more detailed description of the system and enlarge the domain of application of thermodynamics. They have been successfully applied in such fields as rheology and dielectric and magnetic relaxation. They have several connections with EIT, since they introduce more variables and more equations. However, they differ from EIT since it uses the macroscopic fluxes as variables, whereas the internal variables are either unidentified (when they have as their sole purpose to provide more general equations for the classical variables) or motivated by a microscopic modelling of the systems.

Indeed, when applied to polymer solutions, the average molecular configuration of the macromolecules is incorporated as a supplementary variable. One usually takes as a description of the configuration the so-called configuration tensor $\mathbf{W}$

$$\mathrm{W} = \langle \boldsymbol{QQ} \rangle = \int \Psi(\boldsymbol{Q})\boldsymbol{QQ}\mathrm{d}\boldsymbol{Q}, \tag{2.21}$$

with ψ being the configurational distribution function and $\boldsymbol{Q}$ the end-to-end vector of the macromolecules. Other more detailed descriptions are possible in terms of $\langle \boldsymbol{Q}_i\boldsymbol{Q}_i \rangle$, with $\boldsymbol{Q}_i$ the vector from bead i to bead $i + 1$, or the vector related with the ith normal mode in a Rouse–Zimm description [33-36].

The configuration tensors are directly related to the viscous pressure tensor. Indeed, for the contribution of the ith normal mode to the viscous pressure tensor, one has [33-36]

$$\mathrm{P}_i^v = -nH\langle \boldsymbol{QQ} \rangle + nk_B T\mathrm{U}, \tag{2.22}$$

n being the polymer molecules per unit volume of the solution, H an elastic constant characterizing the intramolecular interactions, and k_B the Boltzmann constant. Thus, introduction of $\mathbf{P}_i^v$ or of $\langle \boldsymbol{Q}_i\boldsymbol{Q}_i \rangle$ into free energy as independent variables is essentially equivalent in the case of dilute polymer solutions (this is not so in the case of ideal gases, where there are no internal degrees of freedom). The use of $\mathbf{P}_i^v$ or of $\mathbf{W}_i$ as variables has, in both cases, some characteristic advantages. For the analysis of non-equilibrium steady states, $\mathbf{P}_i^v$ is directly controlled from the outside, whereas for the microscopic understanding of the macromolecular processes and for the analysis of light-scattering experiments, the use of $\mathbf{W}_i$ is more suitable though it cannot be directly controlled. The dynamical equations for the configuration tensor thus provide evolution equations for the viscous pressure tensor and reciprocally. A problem not sufficiently studied in the framework of internal variables is the proper definition of the chemical potential.

2.3.3 Hamiltonian approach

A third approach relating dynamics and thermodynamics of complex systems is provided by Hamiltonian formulations [39-42] which require the evolution equations for the variables of the system (which are not specified a priori) to have a form dictated by some very general principles: (i) energy conservation, (ii) entropy generation, (iii) Hamiltonian character for the reversible part and (iv) Onsager-Casimir reciprocity relations for the irreversible part. The requirement of Hamiltonian character follows from the observation that not only the microscopic dynamics of the constituent particles is Hamiltonian, but also the hydrodynamics of perfect fluids may be cast into Hamiltonian form. Thus, it is tempting to assume that the reversible part of the dynamics of the systems is Hamiltonian at all levels of description (for instance, mechanical description of particles, kinetic theory, hydrodynamics). This imposes on the convective reversible part of the evolution equations some valuable requirements (coming from Jacobi identity) which are satisfactory for the description of the experiments but which cannot be obtained from purely thermodynamic arguments.

When applied to polymer solutions, the configuration tensor is usually taken as an additional variable describing the internal degrees of freedom of macromolecules. The evolution equations of extended irreversible thermodynamics are found to satisfy the Hamiltonian restrictions, in the linear approximation, and may be given a generalised nonlinear form by following the Hamiltonian requirements [18, 43, 44].

3. Non-equilibrium chemical potential and its physical consequences

In equilibrium thermodynamics, chemical potential is important in the analysis of multicomponent systems. In particular, it is the most useful tool for studying phase coexistence and the equilibrium conditions in chemical reactions. Since free energy under flow may depend on the viscous pressure tensor, the configuration tensor or the velocity gradient, this implies, quite naturally, that chemical potential in non-equilibrium states should also depend on these quantities. The definition of the chemical potential for non-equilibrium situations opens up the possibility of generalising the classical analysis of phase diagrams and of reacting systems to non-equilibrium steady states, provided it is suitably complemented with dynamical considerations. It follows that viscous pressure is expected to have an influence on these phenomena.

Indeed, non-equilibrium conditions, such as a shear or an extensional viscous pressure, imply modifications in the phase diagram of polymer solutions, for which the application of a viscous shear stress may induce phase segregation or modification of the molecular weight distribution of the polymer because of shear-induced degradation. Thus, it is worth studying in detail the predictions of the non-equilibrium chemical potential to compare them with the experimental results.

The phenomena we want to describe are the shear-induced effects on the phase diagram of polymer solutions. Observations are usually based on the appearance of turbidity in the solution under flow as compared with the solution at rest, on the analysis of light scattering or on changes in viscosity. Changes in solubility of polymers due to the presence of a flow have been reported many times in the literature. The papers by Rangel-Nafaile *et al.* [45] and of Wolf [46] as well as the reviews [1-6] make up a wide bibliography on the subject. A clear polymer solution upon passing from a reservoir into a capillary (a region of high shear rate) becomes turbid in the capillary. After leaving it, the solution becomes clear again. This phenomenon is exhibited only above a certain shear rate or shear stress which depends on the polymer, solvent concentration and temperature. The visual observation of the cloud points, always made in laminar flow, shows an increase in cloud point temperature, i.e. the turbidity curves are shifted to higher temperatures for increasing values of shear stress.

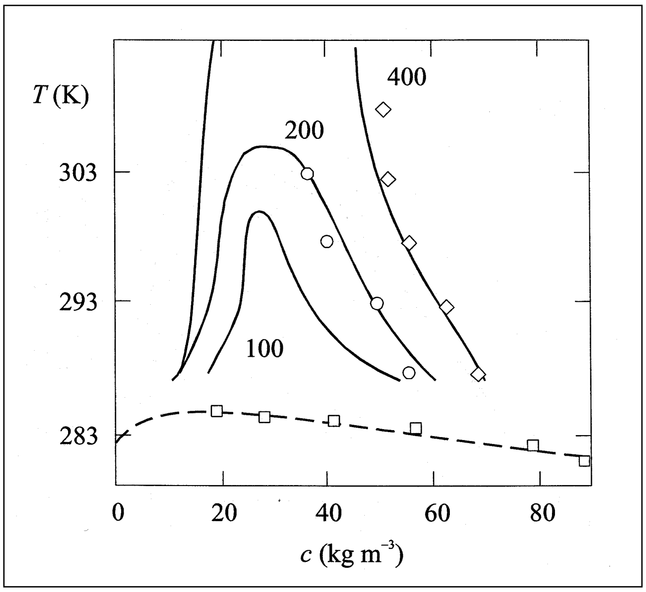

Figure 1. Shear-induced shift of the coexistence line of polymer solutions. Results reported by Rangel-Nafaile *et al.* [45] in which the dashed line corresponds to the equilibrium solution.

In 1984, Rangel-Nafaile *et al.* [45] studied solutions of polystyrene in dioctyl-phthalate and observed a shift of the cloud point curves towards higher temperatures (Fig.1). The shift in the critical temperature can reach 24 °C (at P^v_{12} = 400 N/m^2). They also used a thermodynamic expression based on Marrucci's formula for excess free energy. Also in 1984, Wolf [46] used a thermodynamic theory based on the Flory–Huggins equation for mixing free energy and Marrucci's formula for the change in free energy due to flow. By studying the phase separation of polystyrene solutions in transdecalin, Wolf observed a decrease in the demixing or cloud point temperatures for relatively low-molecular-weight polystyrene and an increase for high-molecular-weight polystyrene. The detailed evolution of the separation process has been studied experimentally (see bibliography in [5]); the time rate and the geometrical structures which appear in the intermediate stages of the separation are rich in phenomena [6, 47-50]. Note that a decrease in flow rate at constant stress, or an increase in shear stress at constant shear rate, may be attributed either to a change of phase induced by the flow or to the formation of an adsorption entanglement layer, the first being a bulk and the second a boundary phenomenon. The origin of turbidity could, in principle, be attributed to both phenomena. To distinguish the two situations, one could perform experiments under an oscillatory flow, in which the adsorption layer effects could be much less than in a steady-state experiment, whereas the shear stress in the bulk would be maintained.

3.1 Chemical potential

First of all, we recall that the usual definition of the chemical potential in equilibrium thermodynamics is [51]

$$\mu_i = \left(\frac{\partial G}{\partial N_i}\right)_{T,p,N_j}, \tag{3.1}$$

where G is the Gibbs free energy and N_i the number of moles of the species i in the system. We also note that in equilibrium situations, the condition of stability of the homogeneous phase is given by [51]

$$\left(\frac{\partial \mu_1}{\partial \phi}\right)_{T,p,N_j} > 0. \tag{3.2}$$

When $(\partial\mu_1/\partial\phi)$ is positive, the homogeneous solution is stable; otherwise, the solution splits into two phases with different polymer concentrations. The line separating the stable and unstable regions in the plane T–ϕ is the so-called spinodal line, built from the condition $(\partial\mu_1/\partial\phi) = 0$.

From the expression (2.8) and the condition (3.2) one immediately finds that the spinodal line in the temperature-concentration plane in equilibrium (i.e. in the quiescent fluid) is defined by the following equation

$$-(1-\phi)^{-1} + (1-m^{-1}) + 2\chi\phi = 0. \tag{3.3}$$

Now, we want to explore how the presence of a flow modifies equation (3.3), which defines the spinodal line. In this case, condition (3.2) can no longer be used a priori, but the stability condition must be derived by studying the stability of the solutions of the mass and momentum balance equations

$$\rho\frac{\mathrm{d}c_1}{\mathrm{d}t} = -\nabla\cdot\mathbf{J}, \tag{3.4}$$

$$\rho\frac{\partial\mathbf{v}}{\partial t} + \rho\mathbf{v}\cdot\nabla\mathbf{v} = -\nabla p - \nabla\cdot\mathbf{P}^v, \tag{3.5}$$

in addition to the constitutive equations for the diffusion flux and the viscous pressure tensor, namely,

$$\mathbf{J} = -\tilde{D}\nabla\mu - \frac{D}{RT}\nabla\cdot\mathbf{P}^v, \tag{3.6}$$

$$\frac{\mathrm{d}\mathbf{P}^v}{\mathrm{d}t} - (\nabla\mathbf{v})^T\cdot\mathbf{P}^v - \mathbf{P}^v\cdot(\nabla\mathbf{v}) = -\frac{1}{\tau^{(2)}}\mathbf{P}^v - 2\frac{\eta}{\tau^{(2)}}\mathrm{V}. \tag{3.7}$$

To close these equations, the explicit expression for the non-equilibrium chemical potential appearing in (3.6) must be used. Often, however, the local-equilibrium chemical potential is used [52], though in a rigorous sense this is only an approximation. Other authors use the local-equilibrium form for the chemical potential but take for $\mathbf{P}^v$ a constitutive equation different from (3.7) [53].

To define the chemical potential under flow, we generalise the expression (3.1) by including in the free energy G the non-equilibrium contributions due to the flow. Thus, the chemical potential of component j for a system out of equilibrium is defined as [2, 5, 54, 55]

$$\mu_j = \left(\frac{\partial G}{\partial N_j}\right)_{T,p,N_i,Z}, \tag{3.8}$$

where Z is a non-equilibrium variable which is kept constant during differentiation. Out of equilibrium the differentiation occurs either at constant viscous pressure or at constant shear rate or at constant molecular conformation. This diversity of choice has been a source of misunderstandings. In extended irreversible thermodynamics, we favour the selection of $\mathbf{P}^v$ as the variable to be kept fixed during differentiation. Indeed, since pressure p is a natural variable of G in equilibrium, it seems tempting to take the total pressure tensor (i.e. both p and $\mathbf{P}^v$) as a natural variable for G in non-equilibrium states.

The non-equilibrium parameter Z kept constant in differentiation (3.8) may affect results markedly. The choice of this parameter does not depend on the experimental conditions, but on general arguments. Indeed, remember that in equilibrium $\mu_i = (\partial G/\partial N_i)_{T,p}$, but $\mu_i \neq (\partial G/\partial N_i)_{T,V}$, i.e. given a thermodynamical potential, the quantities to be kept constant during differentiation are not arbitrary, but are the proper variables of the thermodynamic potential being used. However, for the moment there is no consensus on the non-equilibrium variable to be kept fixed under flow: for instance, Rangel-Nafaile *et al.* [45] have used a definition at constant P^v_{12}, Wolf [46] at constant $\dot{\gamma}$, and Onuki [56] at constant macromolecular configuration $\mathbf{W}$ or at constant molecular extension [57]. The first variable is more macroscopic than $\mathbf{W}$, and is especially suited to the description of non-equilibrium steady states, whereas the configuration tensor $\mathbf{W}$ is more useful for a microscopic understanding of the problem.

To clarify the relation between the different choices, it is appropriate to recall the analogous problem in equilibrium thermodynamics, where several choices of variables may contain all the information on the system, provided that one uses the suitable thermodynamic potential [51]: internal energy $U(S, V, N)$, when S (entropy), V (volume) and N (number of moles) are taken as variables; Helmholtz free energy $F(T, V, N)$ when T (absolute temperature) is used as variable instead of S; or Gibbs free energy $G(T, p, N)$, when S and V are replaced by T and p (pressure). These thermodynamic potentials are connected to each other by means of Legendre transforms, which allow one to pass from one choice of variables to another without losing information. However, information is lost if thermodynamic functions are not expressed in terms of their natural variables, such as $S(T, p, N)$, or $F(T, p, N)$.

A Legendre transform connecting non-equilibrium free energy $F_1(T, V, N, V\mathbf{P}^v)$ depending on the viscous pressure tensor $\mathbf{P}^v$ and non-equilibrium free energy $F_2(T, V, N, \mathbf{W})$ depending on the macromolecular configuration tensor $\mathbf{W}$ can be found [58]. To simplify the analysis, we take only one normal mode of the macromolecule and a dilute polymer solution. According to EIT, the Gibbs equation (2.13) in non-equilibrium may be written in the form

$$\mathrm{d}U = T\mathrm{d}S - p\mathrm{d}V + \mu\mathrm{d}N - \tfrac{1}{2}\mathrm{W}:\mathrm{d}(V\mathrm{P}^v) \tag{3.9}$$

where we have used the relation $\mathbf{P}^v = -J^{-1}\mathbf{W}$ to write explicitly the conjugate of $V\mathbf{P}^v$. We can thus write for the free energy $F_1(T, V, N, V\mathbf{P}^v)$ the expression

$$F_1(T,V,N,V\mathrm{P}^v) \equiv U - \frac{\partial U}{\partial S}S = U - TS\ , \tag{3.10}$$

in which S has been replaced by T as independent variable. If, instead of $V\mathbf{P}^v$, $\mathbf{W}$ is preferred as independent variable, the corresponding free energy $F_2(T, V, N, \mathbf{W})$ would be

$$F_2(T,V,N,\mathrm{W}) \equiv U - \frac{\partial U}{\partial S}S - \frac{\partial U}{\partial (V\mathrm{P}^v)}:V\mathrm{P}^v = F_1(\mathrm{W}) + \frac{1}{2}\mathrm{W}:V\mathrm{P}^v, \tag{3.11}$$

which is seen to be different from $F_1(\mathbf{W})$.

The use of the right expression for free energy is essential to obtaining correct results for the chemical potential. In the presence of a viscous flow, the chemical potential is given by

$$\mu = \left(\frac{\partial F_1}{\partial N}\right)_{T,V,V\mathrm{P}^v} = \left(\frac{\partial F_2}{\partial N}\right)_{T,V,\mathrm{W}}, \tag{3.12}$$

but differentiation of F_1 at constant $\mathbf{W}$ should not be used, because

$$\mu \neq \left(\frac{\partial F_1}{\partial N}\right)_{T,V,\mathrm{W}}\ . \tag{3.13}$$

It follows that both $V\mathbf{P}^v$ and $\mathbf{W}$ can play the role of independent variables in the definition of the chemical potential, provided one uses a correct expression for free energy. Unfortunately, misunderstandings about the definition of μ in non-equilibrium situations are so abundant in the literature, that the incorrect definition (3.13) is sometimes used.

The form of the Gibbs free energy in the presence of a viscous pressure is, according to the Gibbs equation (2.12)

$$G = G_{eq} + \sum_{i=1}^{N-1}\left[\frac{\tau_i^{(2)}}{4\eta_i}\mathrm{P}_i^v:(V\mathrm{P}_i^v)\right] \equiv G_{eq} + \frac{1}{4}J\mathrm{P}^v:(V\mathrm{P}^v)\ . \tag{3.14}$$

Note that the steady state compliance J on the right-hand side of (3.14) is an effective quantity and includes the influence of the different normal modes of the macromolecules.

On the right-hand side of (3.14) $\mathbf{P}^v$ is the total viscous pressure of the solution, given by $\mathbf{P}^v = \sum_{i=0}^{N-1}\mathbf{P}_i^v$, where the contribution of the solvent (i = 0) is included. After writing $\mathbf{P}_i^v = -2\eta_i(\nabla v)$ and $\mathbf{P}^v = -2\eta(\nabla v)$, where η is the total viscosity given by the sum of solvent viscosity and the contributions corresponding to all normal modes, and using the expressions of $\mathbf{P}_i^v$ and $\mathbf{P}^v$, as given in terms of the velocity gradient, in both sides of (3.14), one obtains [5, 59]

$$J = \left(\sum_{i=1}^{N-1}\tau_i^{(2)}\eta_i\right)\Bigg/\left(\sum_{i=0}^{N-1}\eta_i\right)^2, \tag{3.15}$$

where the sum in the denominator must include the solvent viscosity η_0.

3.2 Phase diagram under flow for several polymer solutions

We will study here several different systems, which will be reflected in different choices of the steady-state compliance J. In particular, we will consider dilute polymer solutions described by the Rouse-Zimm model, entangled polymer solutions described by the reptation model, and polymer blends. The corresponding expressions for the steady-state compliance J, obtained from (3.15), are as follows:

3.2.1 Dilute polymer solutions

In the dilute regime, the several macromolecules are well separated from each other. They are not entangled with each other and behave fairly independently, except for hydrodynamic interactions. The form of J in the context of Rouse and Zimm bead-and-spring models for dilute polymer solutions is [5, 59, 60]

$$J = \frac{CM}{ck_BT}\left(1 - \frac{\eta_0}{\eta}\right)^2, \tag{3.16}$$

where c is the polymer concentration expressed in terms of mass per unit volume of the solution, M the mass of a macromolecule and C a constant which in Rouse model is $C = 0.4$ and in Zimm model $C = 0.206$. Remember that the main difference between Rouse and Zimm models is that the second one includes hydrodynamic interactions amongst the several parts of the macromolecule, which are neglected in the first model. On some occasions, a scaling relation of the form $J \sim c^{-1}$ is used, whereas the term in parentheses is ignored, leading to incorrect results for J at small values of the concentration. The dependence of viscosity on concentration plays too a relevant role, which will be discussed in (3.19).

3.2.2 Entangled polymer solutions

In the concentrated regime, the molecules are entangled with each other. In a mean-field approach, the effect of the remaining molecules on one given molecule is described by means of the formation of a tube in which the macromolecule describes a random longitudinal motion which is graphically called reptation. In the reptation model [35, 36], one has for the steady-state compliance J [61]

$$J = \frac{C_{rep} M_e(c)}{c k_B T}\left(1 - \frac{\eta_0}{\eta}\right)^2 , \tag{3.17}$$

with $M_e(c)$ being the average molecular weight between consecutive entanglements of the macromolecules and the constant C_{rep} = 2. The main difference between (3.16) and (3.17) is the appearance in the latter of $M_e(c)$ instead of M. This modifies the scaling laws of J in terms of c, since M_e depends on the concentration, i.e. it becomes smaller when c increases since the average length between successive entanglements is shorter for higher concentrations. The dependence is of the order of c^{-2}; or more explicitly, it may be written as $M_e(\phi) = M_e^0[\rho(\phi_p)/\rho_p^0]\phi_p^{-2}$, where ϕ_p is the volume fraction of the polymer, M_e^0 the value of M_e for the melt of the pure polymer, ρ_p^0 the mass density of the pure melt and $\rho(\phi_p)$ the density of the solution with polymer volume fraction ϕ_p. Since for entangled solutions the viscosity of the solution is much higher than that of the solvent, the term in parentheses in (3.17) may be equated to 1. In the reptation regime, the concentration is high enough to neglect the solvent contribution to viscosity, and then (3.17) can be written in the approximate form as

$$J = \frac{C_{rep} M^*}{RT}\left(\frac{M[\eta]}{m v_1}\right)^2 [\eta]\,\tilde{c}^{-3} \tag{3.18}$$

where $M^* = M_e^0[\rho(\phi)/\rho_p^0]$ and υ_1 is the molar volume of the solvent.

3.2.3 Polymer blends

In polymer solutions, it is assumed that the solute consists of long polymeric macromolecules, whereas the solvent is a fluid made of relatively small molecules. Instead, polymer blends are composed of two kinds, A and B, of polymer macromolecules. In the so-called double-reptation model [53], the steady-state compliance of the blend is related to the respective volume fractions ϕ_i, relaxation times τ_i and plateau moduli G_i (where $G_i \equiv J_i^{-1}$) of the polymer A and B as [62]

$$J = \frac{\phi_A^2 \tau_A^2 G_A + \phi_B^2 \tau_B^2 G_B + 2\phi_A\phi_B\tau_C^2 (G_A G_B)^{1/2}}{[\phi_A^2 \tau_A G_A + \phi_B^2 \tau_B G_B + 2\phi_A\phi_B\tau_C (G_A G_B)^{1/2}]^2} \tag{3.19}$$

with $\tau_C^{-1} \equiv 2(\tau_A^{-1} + \tau_B^{-1})$. This non-linear mixing rule is the simplest one describing the details of coupled stress relaxation in polymer blends.

3.2.4 Concentration dependence of viscosity

To express J as a function of the concentration c, we need an expression for viscosity as a function of concentration in (3.16). For the sake of illustration, we consider the truncated expansion $\eta(c)$

$$\eta / \eta_s = 1 + [\eta]c + k_H[\eta]^2 c^2 , \tag{3.20}$$

where k_H is what is known as Huggins constant, whose numerical value depends on the solution [2, 5, 33]. Combining this expression with (3.16) we may write J as a function of the concentration in the form

$$J = \frac{CM^*}{RT}[\eta]\Phi(\tilde{c}) , \tag{3.21}$$

where $[\eta]$ is the intrinsic viscosity of the solution, M^* is equal to the polymer mass in the Rouse-Zimm model or to $M_e^0[\rho(\phi_p)/\rho_p^0]$ in the reptation model, and $\Phi(\tilde{c})$ is a function defined as

$$\Phi(\tilde{c}) = \frac{\tilde{c}^2}{\tilde{c}^n}\left(\frac{1 + k_H\tilde{c}}{1 + \tilde{c} + k_H\tilde{c}^2}\right)^2 , \tag{3.21}$$

where $\tilde{c}$ is the reduced concentration, defined as $\tilde{c} = [\eta]c$. The exponent n in the denominator is 1 for the Rouse-Zimm model and between 2.25 and 3 in the reptation model.

The flow contribution ΔG to Gibbs free energy according to EIT has the form $\Delta G = VJP_{12}^{v2}$. By introducing into it the expressions for the steady state compliance J (3.20-21) (dilute and entangled solutions) or (3.19) (polymer blends) one may obtain by differentiation the non-equilibrium contribution to the chemical potential. In the figures of the next subsection, we specify the results both under conditions of constant viscous pressure and constant shear rate, which are indeed two well-defined physical situations that differ in the boundary conditions on the walls.

3.2.5 Polymer solutions: results

We studied shear-induced effects in dilute polymer solutions in [60, 63-66] and entangled polymer solutions in [61]. Here, we summarize our main results. We took a solution of poly-

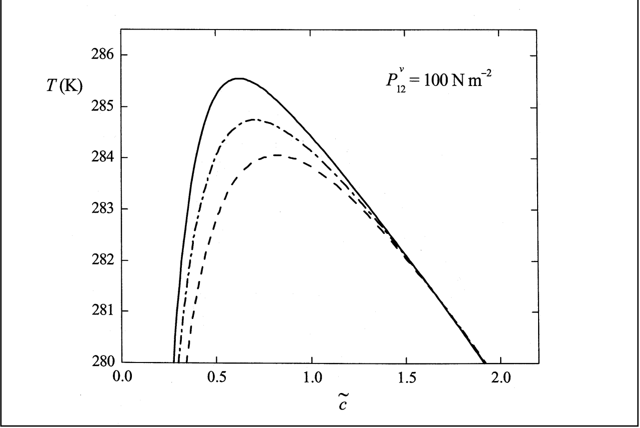

Figure 2. Shift of the spinodal line for a dilute solution of polystyrene in transdecalin at constant viscous pressure P_{12}^v = 100 Nm–^{2} predicted by the Rouse (continuous curve) and Zimm (dot and dashed curve) models [61]. The dashed curve corresponds to the equilibrium situation (Flory-Huggins model).

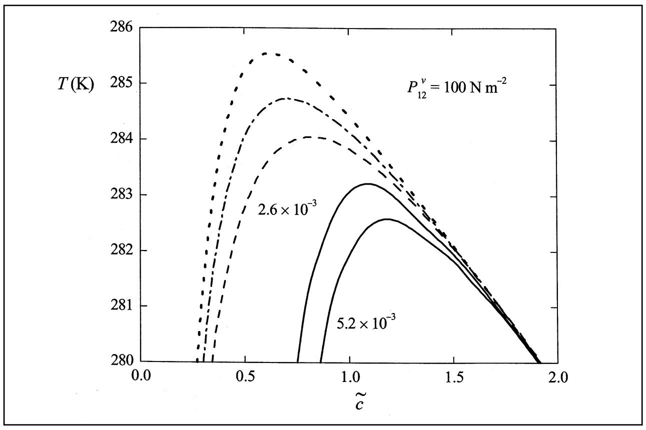

Figure 3. Shift of the spinodal line for an entangled solution of polystyrene in transdecalin at constant viscous pressure $P^{v}_{12} = 100$ Nm–^{2}. The label in continuous curves indicates the value of the parameter M^* in Eq. (3.17) and the dashed curve represents equilibrium conditions [61]. The other two curves show, for comparison, the shifts, if the Rouse (dotted line) or the Zimm (dotted and dashed lines) models were used for this solution.

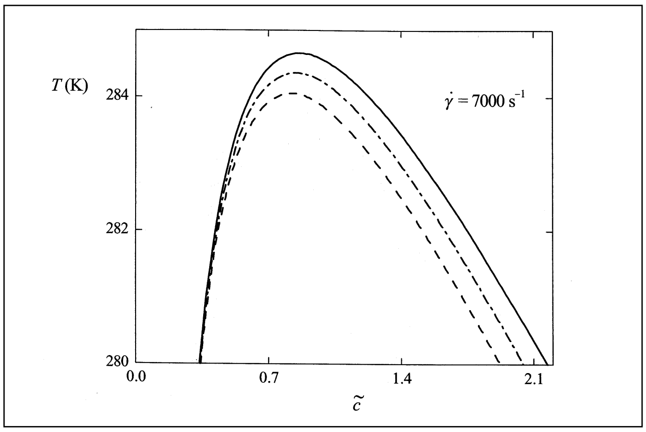

Figure 4. Shift of the spinodal line for a dilute solution of polystyrene in transdecalin at constant shear rate $\dot{\gamma} = 7000$ s^{-1} predicted by the Rouse (continuous curve) and Zimm (dotted and dashed curves) models [61]. The dashed curve portrays equilibrium conditions.

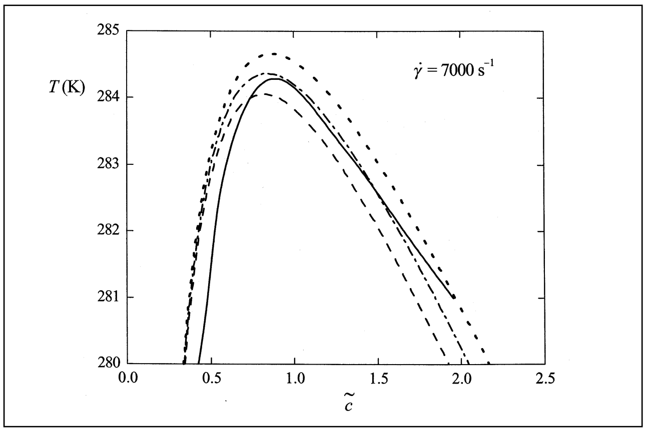

Figure 5. Shift of the spinodal line for an entangled solution of polystyrene in transdecalin at constant shear rate ˙ = 7000 s^{-1} calculated when the parameter M^* in (3.17) takes the value 2.6×10^{-3} kg mol^{-1} (continuous line) [61]. The dashed curve portrays the equilibrium situation. Note that the shift coincides with the one predicted by the Zimm model for the concentration range $0.9 < \tilde{c} < 1.6$. The other two curves show, for comparison, the shifts if the Rouse (dotted line) or the Zimm (dotted and dashed line) models were used for this solution.

styrene of molecular mass 520 kg mol^{-1} in transdecalin, taking for the parameters the same values used in [5, 60], and for M^* appearing in (3.20) the estimated values 2.6×10^{-3} and 5.2×10^{-3} kg mol^{-1}.

The results for the spinodal line for the Rouse and Zimm models at constant P^{v}_{12} are given in Fig. 2. Note that the spinodal line (and therefore the critical point) in the presence of the shear flow is higher than in the equilibrium situation, i.e. it is shifted towards higher values of temperature. This means that the homogeneous solution is less stable in the presence of the flow, i.e., that the flow induces phase separation. In contrast, in the reptation model, the spinodal line in the presence of the flow, shown in Fig. 3, is shifted towards lower temperatures than in the equilibrium situation. This means that the flow stabilises in this case the homogeneous solution, and contributes to the mixing of small inhomogeneities arising as perturbations. This result is a consequence that the derivative $\partial\mu_1/\partial\tilde{c}$ is negative for all values of $\tilde{c}$. In the other cases considered here, the sign of the respective derivatives depends on the concentration. The value of the concentration at which there is a crossover from less to more stability depends solely on the value of k_H. For instance, on the right-hand side of Eq. (3.21), corresponding to Fig. 2, this crossover value is $\tilde{c} = 1.64$. For higher values of $\tilde{c}$, there is an increase in stability and the spinodal line in the Rouse–Zimm model remains below that in equilibrium, but this effect is almost imperceptible in Fig. 2.

The results for the spinodal line at constant $\dot{\gamma}$, for the Rouse–Zimm model are given in Fig. 4. The spinodal line is shifted to higher temperatures. However, there is a difference between this behaviour and the shift at constant P^{v}_{12}. In the latter, the shift is higher for lower values of concentration, whereas at constant shear rate the shift is higher at higher values of concentration. Accordingly, at constant P^{v}_{12} the value of the critical concentration is lowered, but at constant $\dot{\gamma}$ shows the opposite trend. The results for the reptation model at constant shear rate are shown in Fig. 5. As can be seen in this Figure, for low concentrations, the spinodal line is shifted to lower temperature than in the equilibrium conditions, whereas for high ones (where the reptation model is more useful), the shift towards higher temperature occurs. The upper limit of concentration for which non-equilibrium effects increase stability is calculated at $\tilde{c} = 0.79$.

Another interesting point is the role of hydrodynamic effects in the shift of the critical point. It is seen that the value of this shift is higher in the Rouse model, where hydrodynamic interactions are neglected, than in the Zimm model, where they are taken into account. Further, our model shows that the role of hydrodynamic interactions is more relevant in the shift (increase) of the critical temperature T_c than in the shift (decrease) of the critical concentration.

It is also worth mentioning that the behaviour of the spinodal line in the Rouse-Zimm model at constant shear rate would decrease the critical temperature if the chemical potential was obtained by differentiating G at constant shear rate $\dot{\gamma}$ instead of at constant viscous pressure. Therefore, to derive the spinodal line, either at constant pressure or at constant shear rate, one must obtain the chemical potential by differentiation of G at constant P_{12}^{v}, whereas the subsequent differentiation of the chemical potential must be carried out either at constant P_{12}^{v} or at constant $\dot{\gamma}$, depending on the conditions to which the system is submitted.

3.2.6 Polymer blends: results

The results for polymer blends can be seen in Figures 6 and 7. We examined one isotopic blend of polydimetylsiloxane (PDMS) [62]. Our results were compared with those of Clarke and McLeish (CM) [53]. They used a local-equilibrium chemical potential but modified the rheological equation for the viscous pressure, by taking a model different from the upper Maxwell model. Note in Fig. 6 that both the CM and EIT models predict an increase in critical temperature of the same order. However, the shift of the value of the critical concentration is opposite in both models: positive in CM and negative in EIT.

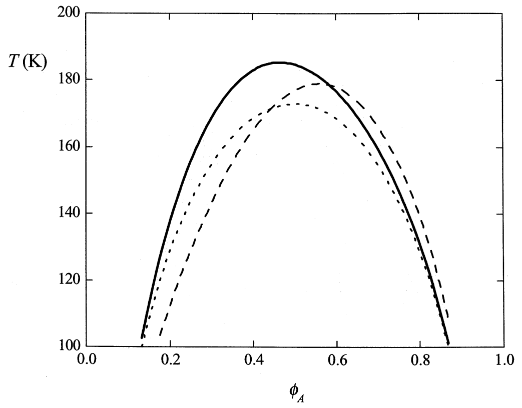

Figure 6. Spinodal lines predicted for the isotopic blend of hydrogenous PDMS with degree of polymerization 964 and deuterated PDMS of degree of polymerization 957 [62]. The dotted curve shows the Flory-Huggins model without interfacial contribution. The other curves show fluctuations in the y direction when the system is submitted to a shear stress of 250 Pa. The continuous curve and the dashed curve are for the EIT [62] and CM [53] models, respectively.

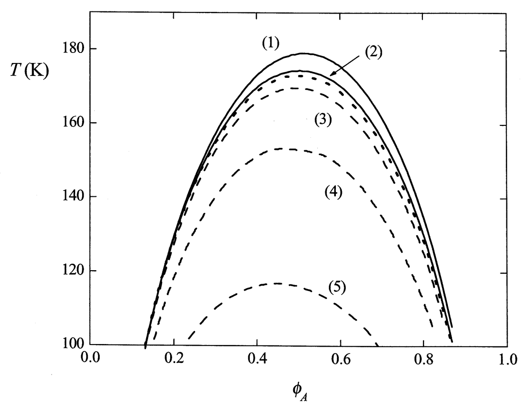

Figure 7. Spinodal lines predicted for the isotopic blend mentioned in Figure 6 [62]. The dotted curve is for the Flory–Huggins model without interfacial contribution. The other curves are for fluctuations in the z direction when the system is submitted to a constant shear rate. The continuous curves are for the EIT model [62] with two shear rates (10 s^{-1}, curve 1 and 5 s^{-1}, curve 2). All dashed lines correspond to the CM model [53] (at shear rates 5 s^{-1}, curves 3 and 4, for different lengths of the molecules, and shear rate 10 s^{-1}, curve 5).

In Fig. 7, EIT predicts a shear-induced increase in critical temperature whereas the CM model predicts a decrease. Further, the shift predicted by CM is more sensitive to the value of the shear rate than the shift predicted by EIT. Detailed experimental results are not yet currently available, but they very much help to establish which of these theoretical models is more suitable.

In summary, the combination of thermodynamic arguments with the Rouse and Zimm and the reptation models for polymer solutions and the double reptation model for polymer blends allows one to obtain values for the shift in the critical point which are qualitatively consistent with those found in experiments, when these are available. The phase diagram at constant shear rate is rather different from the phase diagram at constant shear viscous pressure: in the first case the flow produces a decrease in the critical temperature, whereas in the second one it yields a shift towards higher values of the critical temperature.

4. Shear-induced migration of polymers

In previous sections we have outlined the role of the non-equilibrium part of the chemical potentials in (2.18) or (3.6) in the study of the shear-induced shift of the spinodal line. In this section, it will be seen that this non-equilibrium contribution may be relevant in dynamical terms, and may help clarify problems that arise when the local-equilibrium chemical potential is used. In so doing, we will also pay detailed attention to the coupling between viscous effects and diffusion, which is one of the most active topics nowadays in rheological analyses [68]. In particular, shear-induced migration of polymers deserves the attention of researchers, both for its practical aspects (chromatography, separation techniques, flow through porous media) and for its theoretical implications in non-equilibrium thermodynamics and transport theory. Indeed, this topic implies the coupling between vectorial fluxes and tensorial forces, and is also a useful testing ground of non-equilibrium equations of state.

4.1 Non-equilibrium chemical potential and the rate of migration

The simplest constitutive equation coupling the diffusion flux J and the viscous pressure tensor $\mathbf{P}^{v}$ is

$$\mathbf{J} = -D\nabla n - \frac{D}{RT}\nabla \cdot \mathbf{P}^{v}, \qquad (4.1)$$

where n is the polymer concentration, i.e. the mole number of the polymer per unit volume. This constitutive equation has been examined in both macroscopic and microscopic terms [5, 69-72].

MacDonald and Muller [73] have applied (4.1) to the analysis of the evolution of the polymer concentration profile in a cone-and-plate configuration (see Fig. 8), where the only non-zero components of $\mathbf{P}^{v}$ are given by

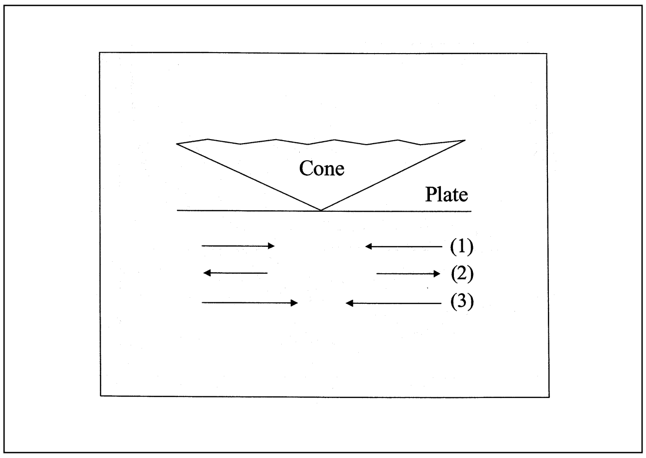

Figure 8. Flows of matter are indicated in the cone-and-plate configuration. Arrow (1) shows the shear-induced flow described by the second term on the right-hand side of (4.1) and (4.5); arrows (2) and (3) indicate the diffusion flux for the first term on the right-hand side of (4.5) when the effective diffusion coefficient (4.8) is positive or negative. When the diffusion coefficient is positive, the diffusion flux (2) opposes the shear-induced flow (1); whereas when it is negative, the diffusion flux (3) enhances the shear-induced effects.

$$P^v_{\phi\phi} = -2RTn(\tau\dot{\gamma})^2; \qquad P^v_{\phi\theta} = -RTn\tau\dot{\gamma}\cdot \tag{4.2}$$

Here, r, ϕ and θ refer to the radial, axial and azimuthal directions, respectively, τ is the polymer relaxation time and $\dot{\gamma}$ the shear rate. Combination of (6.1) and (6.2) yields for the radial component of the diffusion flux

$$J_r = -D\frac{\partial n}{\partial r} - D\beta\frac{n}{r}, \tag{4.3}$$

with the parameter β being defined as $\beta = 2(\tau\dot{\gamma})^2$ and where the rotational symmetry of the situation has been taken into account.

Combination of (4.3) and the mass balance equation yields

$$\frac{\partial n}{\partial t} = \frac{D}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial n}{\partial r} + \beta rn\right) - D\beta\frac{n}{r^2}. \tag{4.4}$$

The term in β, arising from the second term in (4.1), induces a flux of polymer towards the apex of the cone (shown as arrow 1 in Fig. 8) which is usually believed to produce the total induced migration. However, as demonstrated by MacDonald and Muller [73], this contribution cannot explain by itself the actual rate of migration; it falls two or three orders of magnitude short in comparison with observations. MacDonald and Müller compared it with their experimental results for polystyrene macromolecules, nearly monodisperse, of molecular weights 2.0×10^6 and 4.0×10^6 g mol^{-1} (denoted by 2M and 4M, respectively) in a solvent of oligomeric polystyrene molecules of 500 g mol^{-1}, when the cone is rotated to produce a shear $\dot{\gamma} = 2s^{-1}$. The initial homogeneous concentration of the molecules of each solution was 0.20 and 0.12 wt % for the 2M and 4M solutions, respectively. According to an average value of τ obtained from the steady-state shear data, they obtained for the 2M and 4M solutions the values $\beta_2 = 240$ and $\beta_4 = 1\,500$, respectively. However, when they tried to fit the profile obtained from (6.4) to the observed concentration profiles by allowing β to be an adjustable parameter, they found that it was necessary that $\beta_2 = 200\,000$ and $\beta_4 = 1\,100\,000$, instead of 240 and 1 500. Thus, the discrepancy between observed and measured β, which expresses the shear-induced flux in (4.1), is almost three orders of magnitude.

Instead of (4.1), we use for the diffusion flux the equation (2.18), which in the steady state reduces to [5, 74]

$$\mathbf{J} = -\tilde{D}\nabla\mu - \frac{D}{RT}\nabla\cdot\mathbf{P}^v, \tag{4.5}$$

where $\tilde{D}$ is related to the classical diffusion coefficient D by $D = \tilde{D}(\partial\mu_{eq}/\partial n)$ and μ_{eq} is the local-equilibrium chemical potential of the solute. The essential point in (4.5) is that the non-equilibrium chemical potential μ contains contributions of $\mathbf{P}^v$, thus providing an additional coupling between viscous effects and diffusion, besides the term in $\nabla\cdot\mathbf{P}^v$.

To be explicit, we use for the Gibbs free energy G in presence of $\mathbf{P}^v$ the expression (3.14). If we write N in terms of the polymer concentration n (moles per unit volume) as $N = nV$, chemical potential μ may be expressed as [5, 75-76]

$$\mu = \mu_{eq} + \frac{1}{4V}(1 - V'n)\frac{\partial}{\partial n}(JV)\mathbf{P}^v : \mathbf{P}^v, \tag{4.6}$$

where $V' = \partial V/\partial N$ is the partial molar volume of the polymer. The generalised chemical potential leads us to define an effective diffusion coefficient as $D_{eff} = \tilde{D}(\partial\mu_{eq}/\partial n)$ or, by writing $\tilde{D}$ in terms of the classical diffusion coefficient D, $D_{eff} = \tilde{D}\Psi(n,\dot{\gamma})$, where Ψ is defined as

$$\Psi(n,\dot{\gamma}) = \frac{(\partial\mu/\partial n)}{(\partial\mu_{eq}/\partial n)}, \tag{4.7}$$

which, using (4.6), takes the explicit form [76, 77]

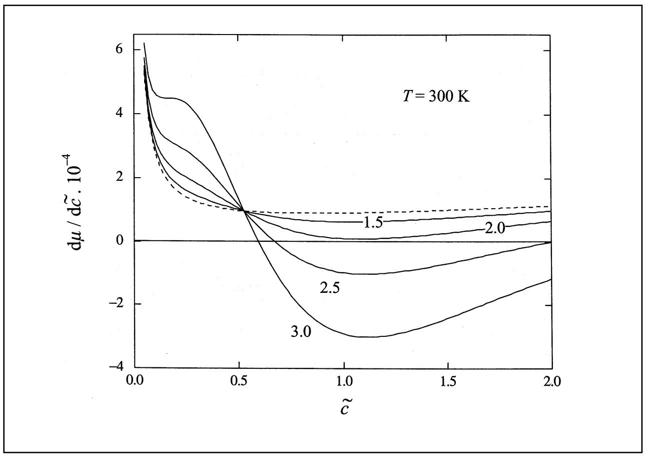

Figure 9. Ratio of the effective diffusion coefficient defined in (4.7) over the usual diffusion coefficient as a function of the concentration for three values of the shear rate (continuous curve 1.5 s^{-1}, dashed and dotted curve 1.0 s^{-1} and dashed curve 0.5 s^{-1}). The system considered is polystyrene with a molecular mass of 2000 kg mol^{-1} dissolved in oligomeric polystyrene of molecular weight 0.5 kg mol^{-1} [75].

$$\Psi(n,\dot{\gamma}) = 1 + \frac{1}{(\partial\mu_{eq}/\partial n)}\frac{\partial}{\partial n}\left[\frac{(1-V'n)}{4V}\frac{\partial}{\partial n}(JV)\mathrm{P}^{v}:\mathrm{P}^{v}\right] . \quad (4.8)$$

When the contribution of the term in $\mathbf{P}^v$:$\mathbf{P}^v$ is negative, it induces a flow of solute towards higher solute concentrations, i.e. contrary to the usual Fickian diffusion. This reinforces the contribution of the term in $\nabla\cdot\mathbf{P}^v$, which yields a migration of the molecules of the solute towards the centre, and speeds up the migration process, as sketched in Fig. 8.

To determine in which circumstances D_{eff} is negative, a detailed knowledge of μ_{eq}, V' and J as a function of concentration is required. As an example, we plot the results for a solution of polystyrene in transdecalin. For this system, the derivative of chemical potential for different values of $\tau\dot{\gamma}$ is plotted in Fig. 9. To obtain this Figure we used for the equilibrium chemical potential the expression from the Flory–Huggins model and we took for J the formula (3.16) from the Rouse–Zimm model combined with the Huggins expression (3.19) for $\eta(c)$. The numerical values of this derivative for the system PS/TD with a polymer molar mass of 520 kg mol^{-1} are plotted in Fig. 9, where the values k = 1.40, $[\eta]$ = 0.043 m^3 kg^{-1} and η_s = 0.0023 Pa s are used. It is seen in Fig. 9 that for low enough concentrations $(\partial\mu/\partial\tilde{c})$, and therefore *Deff*, is positive, whereas for higher concentrations , and consequently *Deff*, is negative [5, 75, 76].

Therefore, effective polymer diffusivity depends on the shear rate, molecular weight (through the dependence of the relaxation time) and concentration. Fig.10 shows the corresponding effective polymer diffusivity versus $\tau\dot{\gamma}$ for the same system as in Fig. 9, for several values of the reduced concentration. For low values of the latter, effective diffusivity is always positive and increases with the shear rate and molecular weight. In this range of concentrations, induced migration is expected to be very slow. However, for reduced concentrations higher than the critical one, diffusivity becomes negative for sufficiently high values of the shear rate, the decrease being steeper for higher molecular weights.

Thus, it is seen that the stress contribution to the chemical potential of the polymer in (4.5) has important effects on the formulation (4.1), where the gradient of n rather than the gradient of μ appears. For a given concentration (higher than a critical value), the effective diffusion coefficient decreases when the shear stress increases, and it becomes negative. In this regime, the non-equilibrium contribution to the chemical potential considerably enhances polymer migration. This may explain why the migration observed is much faster than that predicted by (4.1). However, at low shear rates, the only thermodynamic force leading migration is the coupling of the second term in (4.5), and migration is very slow. For higher shear rates, the diffusion coefficient becomes negative and migration is much faster.

4.2 Shear-induced concentration banding

As well as the dynamical effects related to the rate of migration, analysed in the previous subsection, the final non-equilibrium state under the action of the rotation of the cone needs to be analysed. When there is no rotation, the system is homogeneous and polymer concentration is constant everywhere. Under rotation, a concentration gradient toward the axis appears. When the rotation rate is small, the concentration profile is smooth. However, when the rotation rate exceeds some threshold value, the system splits into two different regions with different values of the polymer concentration, separated by a thin layer with a steep concentration gradient.

The main questions which arise in this situation are: what is the threshold value of the rotation rate (correspondingly, of the shear rate) beyond which the system splits into two different concentration bands, and what are the quasi-homogeneous values of the polymer concentration at each of these bands?. A further question of practical importance is how this banding phenomenon depends on the macromolecular mass; if dependence on the concentration of the bands is sufficiently sensitive to such mass, this phenomenon could provide the basis for a chromatographic separation method. Indeed, an initially homogeneous solution con-

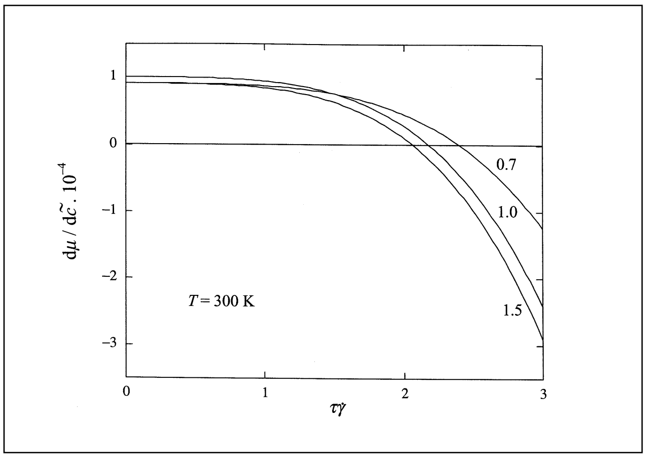

Figure 10. Ratio of the effective diffusion coefficient defined in (4.7) over the usual diffusion coefficient as a function of the Deborah number $\tau\dot{\gamma}$ for three values of the reduced concentration, for the same system as in Figure 9 [75]. Diffusivity becomes negative for sufficiently high values of the shear rate.

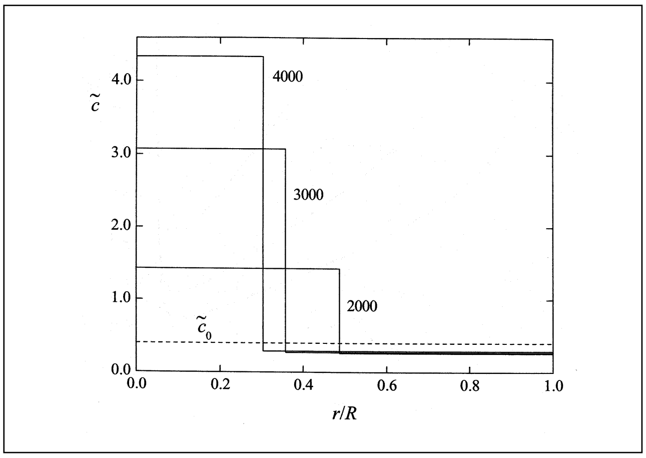

Figure 11. Sketch of the concentration profiles of polystyrene macromolecules of molecular weight M = 2,000, 3,000 and 4,000 kg mol^{-1} under shear pressure in a rotating cone-and-plate device. The dotted line corresponds to the homogeneous initial conditions at rest [77].

taining solutes of different molecular mass becomes separated if the rotation exceeds a threshold value, in different bands corresponding to different macromolecules.

As rigorous analysis of this phenomenon is very complicated, we devised a simplified procedure based on the approach presented in the previous subsection on the properties of the effective diffusion coefficient [77, 78]. When D_{eff} is everywhere positive, the concentration profile is smooth but when D_{eff} becomes negative, the system splits into two different regions, whose respective concentrations correspond to the values of the concentration where $D_{eff} = 0$, as shown in Figure 11. The values of this concentration are plotted in Fig 12 as a function of the shear rate, for different values of the macromolecular mass. At a given value of the shear rate, the concentration values correspond to the intersection of the corresponding curve with the horizontal line at the corresponding value of the shear rate. Note that for small enough values of the shear rate, the system does not split into different bands; thus, the minimum of the curve in 12 indicates the threshold value at which banding appears. It is interesting to outline that the concentration of the bands is rather sensitive to the macromolecular mass, in such a way that this procedure provides indeed the basis of a chromatographic method [77, 78].

The concentration-banding phenomenon is also found in cylindrical tubes, where the polymer tends to concentrate near the axis [69, 78]. In this geometry, the contribution of the divergence of the viscous pressure from the diffusion flux (i.e. the second term in (4.5)) is zero. The entire separation is due to the dependence of the non-equilibrium chemical potential on the viscous pressure in the first terms of (4.5).

The reader should be warned that another banding phenomenon appearing in liquid crystals is often studied in the literature [79, 82]. In this case, the bands are related to the orientation of the macromolecules rather than to their concentration, in such a way that viscosity is lower in the more oriented phase. Submitted to a given shear stress, the system splits into two bands with shear rate, unlike the situation examined here, where a homogeneous shear rate is imposed on the system and two bands of different concentrations (and therefore different shear viscosity and different shear stress) appear. Since several features of both banding phenomena are different, it is important to not confuse them.

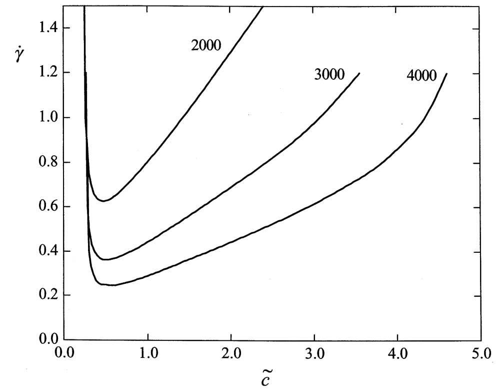

Figure 12. For values of shear rate and concentration in the region above the curve in this figure, the effective diffusion coefficient D_{eff} is negative, for solutions of macromolecular polystyrene with M = 2,000, 3,000, and 4,000 kg mol^{-1}, dissolved in oligomeric polystyrene of 0.5 kg mol^{-1} [77].

5. Concluding remarks

In this review, we outline recent progress towards the combined use of thermodynamics and hydrodynamics to describe polymer solutions and blends under shear flow. The basic idea is that thermodynamic functions must incorporate non-equilibrium contributions, thus going beyond the local-equilibrium approximation. The results of the approach are presented in various geometries (plane shear flow, Poiseuille flow and cone-and-plate flow) and for three kinds of physical systems (dilute solutions, entangled solutions and blends). The main trends of the results, which are mathematically cumbersome, are shown in several Figures, for two given systems: polystyrene in dioctylphthalate and polystyrene in transdecalin, for which the values of the physical parameters appearing in the theory are known.

The central quantity in the present approach is the non-equilibrium chemical potential provided by extended irreversible thermodynamics. It contains contributions from the flow, linked to the viscoelastic effects through a generalised non-equilibrium entropy dependent on the viscous pressure tensor, which makes compatible the viscoelastic constitutive equations with the restrictions of the second law of thermodynamics.

The flow contributions to the chemical potential have several physical consequences. In particular, they modify stability conditions, thus yielding shear-induced changes in the phase diagram of polymer solutions, and they couple diffusion to viscous pressure. In some situations, this coupling yields a fast polymer separation in two different phases, and a splitting of the system in bands characterized by different values of the macromolecular concentration. We have outlined the main results and some possible applications.

We will mention four kinds of difficulties currently facing theoreticians in this subject. These relate to: (1) the various sets of possible non-equilibrium variables; (2) the possible overlapping of contributions coming from constitutive equations of the viscous pressure tensor and from non-equilibrium equations of state; (3) the influence of the geometry of the flow, and (4) the lack of sufficient information on the values of physical parameters.

Some approaches include viscoelastic contributions to the flow, but instead of taking viscous pressure as an independent variable, they use the conformation tensor. Though this choice is completely legitimate, results of these theories in several situations contradict experiments, because they do not pay enough attention to the suitable thermodynamic potentials and to the variables kept constant during the differentiation that yields the chemical potential. Furthermore, the expression considered for steady-state compliance is often too simplistic and yields results at variance with experiments.

We hope that the present approach contributes to the clarification of these points: it considers in detail the problems related to the definition of chemical potential in the presence of the flow, and it studies the Legendre transform between viscous pressure and conformation tensor. It also justifies the stability criteria on a dynamical basis, and analyses the detailed form of the dependence of steady-state compliance on the concentration in the dilute and the entangled regimes. Finally, it shows that the thermodynamic predictions qualitatively coincide with the observations and suggests the experimental information needed to improve quantitatively the relationship between theoretical predictions and observations.

A second difficulty concerns the overlapping of effects from the rheological constitutive equations and from the equations of state. In fact, it is possible to obtain shifts of the spinodal line by modifying both kinds of equations. Consequently, in order to decide the best alternative, different kinds of fluids and of geometries should be compared in experiment. For instance, flows with straight lines of flow do not have some couplings between the divergence of $\mathbf{P}^v$ and the diffusion flux J, which are relevant, however, in situations with curved lines of flow. Thus, whether a model is satisfactory or not cannot be decided unless it has been tested in several kinds of flows. For example, in Poiseuille flow, the divergence of the viscous pressure does not contribute to polymer migration, and non-equilibrium contributions must be used in the chemical potential, whereas in cone-and-plate flows migration can be produced by means of this coupling.

More experimental information is needed before it can be decided which of the several approaches is the best way of describing the observations. We have outlined some differences between the predictions of an approach incorporating non-equilibrium contributions to the chemical potential and using the upper-convected Maxwell model for the viscous pressure tensor and of another approach with local-equilibrium chemical potential but a modified form of the constitutive equations for the viscous pressure tensor. In the near future, this line of research could profitably be developed in the following directions: incorporation of macromolecules of biological interest, mainly proteins and DNA, and detailed study of the perspectives of the banding process as the basis of chromatographic methods. Analysis of polyelectrolites instead of neutral macromolecules would make the analysis of proteins and DNA more realistic. Study of micelles [81, 83, 84] under flow would also broaden the applications of this formalism and its possible connections with biological problems. The study of chemical reactions under flow [85] could help in the analysis of polymer degradation and of immunological processes in the blood flow. Other topics worth including in future studies are the influence of the walls of the ducts for tubes of diameter comparable to the giration radius of the macromolecules, and of the diffusion-induced migration in arteries and in veins, which may be of clinically relevant interest to the study of deposition of macromolecules on the walls of the ducts. Finally, the dynamics and geometry of the separating process need to be examined in greater detail [47-50, 86]. Thus, we feel that, apart from the theoretical interest in the basis of non-equilibrium thermodynamics beyond local equilibrium, the study of solutions under flow is pertinent to real problems.

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