

## Extended irreversible thermodynamics and its relation with other continuum approaches

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Received 15 September 1999

### Abstract

We present an introduction to extended irreversible thermodynamics (EIT) as applied to polymer solutions in the presence of shear flow and of diffusion flux. We discuss with special attention the definition of chemical potential in non-equilibrium situations and its use in the analysis of shear-induced phase transitions. In the second part, we compare EIT with other contemporary continuum approaches: theories with internal variables, the GENERIC approach, and the matrix model. All these theories share an emphasis on the relations between dynamics and thermodynamics at a deeper level than in the classical theory, but each of them has some peculiar advantage in the analysis of some specific aspects of physical problems. © 2001 Elsevier Science B.V. All rights reserved.

**Keywords:** Extended irreversible thermodynamics; Shear-induced phase transitions

### 1. Introduction

The increasing activity on non-equilibrium thermodynamics beyond the local-equilibrium hypothesis strongly demands detailed comparisons of the different current approaches which are being developed nowadays. Each of them may learn from the other ones, and, reciprocally, it may be useful to the others for the understanding of some particular points which find a more explicit or suitable expression in one formulation than in other ones. Polymer solutions are especially relevant systems for analyses beyond the local-equilibrium theory; the memory effects observed in viscoelastic phenomena require to add relaxational terms to the constitutive equation for the viscous pressure tensor, to express the delay of this quantity with respect to changes in the velocity gradient. In this way, the viscous pressure becomes an independent variable with its own evolution equation. Furthermore, from the microscopic point of view, the internal degrees of freedom (orientation and stretching, for instance) of the macromolecules have an influence on the flow and must be taken into account as additional variables besides those describing

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classical fluids of small molecules. Here, as applied to flowing polymer solutions, we present extended irreversible thermodynamics (EIT), a thermodynamic theory which includes relevant fluxes as additional independent variables in the description of the system. Furthermore, we compare it with three other contemporary thermodynamic approaches: internal variables, GENERIC formalism and Matrix Method.

We refer to all these formalisms as continuum approaches, in the sense that they are used at the level on which the state variables are a relatively small number of macroscopic fields (i.e. functions of one position vector). However, some of these approaches (for instance, GENERIC or the Matrix Method) may be used also at a microscopic level, using the distribution function as an independent variable whose evolution equation must be determined. Therefore, when we refer to GENERIC and Matrix Model as continuum approaches we refer to their applications to a macroscopic level of description, rather than meaning that these theories are exclusively macroscopic.

In Section 2, and after a short introduction to some basic rheological concepts, we present extended irreversible thermodynamics, both as an extension of the classical theory [1–3] and of rational thermodynamics [4], and we derive some consequences of the non-equilibrium equation of state for the chemical potential on shear-induced modifications of the phase diagram. In Section 3, we compare it with the three alternative thermodynamic theories mentioned above. In the concluding remarks, we summarise the mutual possible exchanges between these theories.

## 2. Extended irreversible thermodynamics of polymer solutions

### 2.1. Transport equations: thermodynamics and rheology

In this section we provide a short introduction to some rheological concepts and we present EIT as an extension of the classical theory of irreversible processes. A knowledge at least elementary of both topics is necessary since we shall relate rheology and thermodynamics. It must be emphasised that we have pretended to focus our attention on the concepts which are needed for the purposes of this paper, rather than for providing an extensive account of the wide subjects which rheology and extended irreversible thermodynamics have become nowadays.

#### 2.1.1. Review of some basic rheological concepts

The main rheological quantities of interest in steady flows are the 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

$$P_{12}^v = -\eta(\dot{\gamma})\dot{\gamma}, \quad P_{11}^v - P_{22}^v = -\Psi_1(\dot{\gamma})\dot{\gamma}^2, \quad P_{22}^v - P_{33}^v = -\Psi_2(\dot{\gamma})\dot{\gamma}^2, \quad (1.1)$$

where  $P_{ij}^v$  with  $i, j = 1, 2, 3$ , indicate components of the viscous pressure tensor  $\mathbf{P}^v$  related to the total pressure tensor  $\mathbf{P}$  as  $\mathbf{P} = p\mathbf{U} + \mathbf{P}^v$ , with  $p$  the equilibrium pressure and  $\mathbf{U}$  the unit tensor. Furthermore,  $\dot{\gamma}$  denotes the shear rate in a plane Couette flow, i.e.  $\dot{\gamma} = \partial v_x / \partial y$ . In the so-called Newtonian fluids, these normal stress coefficients vanish.

In non-steady situations, some memory effects appear and the rheological properties depend on the frequency of the perturbation: for instance, viscoelastic systems behave as Newtonian liquids at frequencies low in comparison with the inverse of a characteristic relaxation time, and as elastic solids at high frequencies. To account for viscoelastic effects, it is assumed that the viscous pressure tensor depends

not only on the velocity gradient but on its own time rate of change. In the simplest Maxwell model, the viscous pressure tensor is described by the constitutive equation

$$\frac{d\mathbf{P}^v}{dt} = -\frac{1}{\tau}\mathbf{P}^v - 2\frac{\eta}{\tau}\mathbf{V}, \quad (1.2)$$

with  $\mathbf{V}$  the symmetric part of the velocity gradient, whose components are given by  $V_{ij} = 1/2[(\partial v_j/\partial x_i) + (\partial v_i/\partial x_j)]$  where  $\eta$  is the shear viscosity and  $\tau$  the relaxation time. Maxwell's model captures the essential idea of viscoelastic models: the response to slow perturbations is that of a viscous fluid, whereas for fast perturbations, with characteristic time  $t$  of the order of  $\tau$  or less, it behaves as an elastic solid.

However, the material time derivative in (1.2) is not satisfactory, neither from a theoretical basis nor on the practical predictions, as it yields a negative and rather high absolute value of the second normal coefficient, and it must be substituted by some frame-indifferent derivative. We will use here the so-called upper or contravariant convected time derivative [5–7] for which the evolution equation of the viscous pressure tensor  $\mathbf{P}^v$  has the form

$$D^\dagger \mathbf{P}^v \equiv \frac{d\mathbf{P}^v}{dt} - (\nabla \mathbf{v})^T \cdot \mathbf{P}^v - \mathbf{P}^v \cdot (\nabla \mathbf{v}) = -\frac{1}{\tau}\mathbf{P}^v - 2\frac{\eta}{\tau}\mathbf{V}, \quad (1.3)$$

where superscript T indicates transposition. As it is shown below, (1.3) yields a vanishing value for the second normal stress coefficient, which is indeed very small in experiments.

The fluid will be from now on considered as incompressible. This implies that  $\nabla \cdot \mathbf{v} = 0$ ; but this does not mean that  $\text{Tr } \mathbf{P}^v = 0$ , because though the linear contribution to  $\text{Tr } \mathbf{P}^v$ , which is proportional to  $\nabla \cdot \mathbf{v}$ , will be zero, second-order non-linear contributions may give a non-vanishing trace of  $\mathbf{P}^v$ .

For further purposes it will be convenient to have explicit expressions for  $\mathbf{P}^v$ . In a purely shear flow corresponding to  $\mathbf{v} = (v_x(y), 0, 0)$ , introduction of the velocity gradient into (1.3) yields

$$\mathbf{P}^v = \begin{pmatrix} -2\tau\eta\dot{\gamma}^2 & -\eta\dot{\gamma} & 0 \\ -\eta\dot{\gamma} & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}. \quad (1.4)$$

The corresponding steady-state viscometric functions defined in (1.1) are thus

$$P_{12}^v = -\eta\dot{\gamma}, \quad P_{11}^v - P_{22}^v = -2\tau\eta\dot{\gamma}^2, \quad P_{22}^v - P_{33}^v = 0, \quad (1.5)$$

so that the second normal stress is zero and the first normal stress coefficient  $\Psi_1$  is  $\Psi_1(\dot{\gamma}) = 2\tau\eta$ .

In (1.2) and (1.3) we have considered only one relaxation time. In many occasions,  $\mathbf{P}^v$  is the sum of several (or many) independent contributions, i.e.  $\mathbf{P}^v = \sum_j \mathbf{P}_j^v$  with each  $\mathbf{P}_j^v$  obeying a linear evolution equation such as (1.2) or (1.3), characterised by its own viscosity  $\eta_j$  and relaxation time  $\tau_j$ . These independent contributions arise from the different internal degrees of freedom (or the corresponding normal modes) of the macromolecule. These models are known as generalised Maxwell models. The relation between EIT and other kinds of rheological models, as for instance Jeffreys fluids or second-order fluids, has been analysed in [8].

### 2.1.2. Extended irreversible thermodynamics and rheology

After having introduced the rheological equation (1.3), we start the analysis of its thermodynamic aspects. First of all, we recall that the classical formulation of irreversible thermodynamics [1–3], based on the local-equilibrium hypothesis, states that in spite that the system is inhomogeneous the fundamental

thermodynamic relations are still valid locally. In particular, the Gibbs equation expressing the differential form of the entropy in terms of its classical variables (internal energy, volume and number of moles of the chemical components of the system) is locally valid. This is no longer true when viscoelastic effects are considered, and new variables must be added. In EIT, this additional variable is  $\mathbf{P}^v$ , whereas in other theories, it is a tensor related to the microstructure of the fluid.

In this paper we consider not only viscoelastic effects but also relaxational effects in diffusion, in order to be able to analyse the couplings between the diffusion flux and the viscous pressure tensor. For the sake of simplicity, the latter one will be considered as a single independent variable with a single relaxation time. The extension to several independent contributions is straightforward but cumbersome.

As it has been mentioned above, EIT assumes that the entropy may depend, in addition to the classical variables, on the dissipative fluxes as the viscous pressure tensor, the heat flux or the diffusion flux [8–13]. For a wide bibliography on this topic see <http://circe.uab.es/eit> or [14–20]. Its motivation is to make compatible the relaxational transport equations for the fluxes with the positiveness of the entropy production. Here, we consider a binary liquid mixture and, according to the proposals of EIT, we consider the viscous pressure tensor and the diffusion flux as additional independent variables. The corresponding extended Gibbs equation has then the form [8,9,21,22]

$$ds = T^{-1} du + T^{-1} p dv - T^{-1} \tilde{\mu} dc_1 - v\alpha_1 \mathbf{J} \cdot d\mathbf{J} - v\alpha_2 \mathbf{P}^v : d\mathbf{P}^v, \quad (1.6)$$

with  $T, p, u$  and  $v$ , respectively, the temperature, pressure, internal energy and volume,  $c_1$  the concentration (mass fraction) of the solute,  $\tilde{\mu} \equiv \mu_1 - \mu_2$  the difference between the specific (i.e. per unit mass) chemical potentials of the solute and the solvent,  $\alpha_1$  and  $\alpha_2$  coefficients whose form will be identified below, and  $\mathbf{J}$  the diffusion flux. Note that the integrability conditions of (1.6) imply that  $T, p$ , and  $\tilde{\mu}$  depend also on the fluxes  $\mathbf{J}$  and  $\mathbf{P}^v$ , and therefore they do not coincide with the corresponding values of the local-equilibrium quantities defined as functions of only  $u, v$ , and  $c_1$ . In particular, for a discussion of the conceptual differences between  $T$  and  $T_{eq}$ , see [23]. Note finally that in some fluids (micropolar fluids) the viscous pressure tensor has an antisymmetric contribution, which describes a transfer of macroscopic to microscopic angular momentum. We do not consider these effects here, but we refer to [24] for their analysis in the context of EIT.

We assume for the entropy flux the expression

$$\mathbf{J}^s = T^{-1} \mathbf{q} - \tilde{\mu} T^{-1} \mathbf{J} + \beta \mathbf{P}^v \cdot \mathbf{J}. \quad (1.7)$$

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

The energy and the mass balance equations are, respectively,

$$\rho \dot{u} = -\nabla \cdot \mathbf{q} - p(\nabla \cdot \mathbf{v}) - \mathbf{P}^v : (\nabla \mathbf{v}), \quad (1.8)$$

$$\rho \dot{c}_1 = -\nabla \cdot \mathbf{J}. \quad (1.9)$$

Combination of Eqs. (1.7), (1.8) and (1.9) yields for the time derivative of the entropy

$$\rho \dot{s} = -T^{-1} \nabla \cdot \mathbf{q} + T^{-1} \tilde{\mu} \nabla \cdot \mathbf{J} - T^{-1} \mathbf{P}^v : \mathbf{V} - \alpha_1 \mathbf{J} \cdot \dot{\mathbf{J}} - \alpha_2 \mathbf{P}^v : \dot{\mathbf{P}}^v, \quad (1.10)$$

and making use of the general form of the balance equation of entropy  $\rho \dot{s} + \nabla \cdot \mathbf{J}^s = \sigma^s$  one obtains for the entropy production

$$\sigma = \mathbf{q} \cdot \nabla T^{-1} + \mathbf{J} \cdot [-\nabla(T^{-1} \tilde{\mu}) - \alpha_1 \dot{\mathbf{J}} + \nabla \cdot (\beta \mathbf{P}^v)] + \mathbf{P}^v : (-T^{-1} \mathbf{V} - \alpha_2 \dot{\mathbf{P}}^v + \beta \nabla \mathbf{J}). \quad (1.11)$$

From now on, we consider for simplicity isothermal processes allowing us to neglect the heat flux,  $\mathbf{q}$ . This does not mean, of course, that thermal effects are not interesting nor important, but that we focus our analysis on situations in which they are negligible. Under this simplification, the simplest evolution equations for  $\mathbf{J}$  and  $\mathbf{P}^v$  compatible with the positive character of (1.11) are

$$-\nabla(T^{-1}\tilde{\mu}) - \alpha_1 \dot{\mathbf{J}} + \nabla \cdot (\beta \mathbf{P}^v) = \beta_1 \mathbf{J}, \quad (1.12)$$

$$-T^{-1} \mathbf{V} - \alpha_2 \dot{\mathbf{P}}^v + \beta \nabla \mathbf{J} = \beta_2 \mathbf{P}^v, \quad (1.13)$$

with  $\beta_1$  and  $\beta_2$  positive phenomenological coefficients which may be identified in physical terms by comparing (1.12) and (1.13) in the steady state and without couplings with the well-known Newton–Stokes' and Fick's equations, namely

$$\mathbf{P}^v = -2\eta \mathbf{V}, \quad \mathbf{J} = -\tilde{D} \nabla \tilde{\mu}, \quad (1.14)$$

where  $\tilde{D}$  is related to the diffusion coefficient  $D$  as  $D = \tilde{D}(\partial \tilde{\mu} / \partial c_1)$ . Such comparison yields  $\beta_1 = (\tilde{D}T)^{-1}$ ,  $\beta_2 = (2\eta T)^{-1}$ . Furthermore, one may identify the respective relaxation times of  $\mathbf{J}$  and  $\mathbf{P}^v$  as  $\tau_1 = \alpha_1 / \beta_1 = \alpha_1(\tilde{D}T)$ ,  $\tau_2 = \alpha_2 / \beta_2 = \alpha_2(2\eta T)$ .

The evolution equations, (1.12) and (1.13), for  $\mathbf{J}$  and  $\mathbf{P}^v$  may be rewritten more explicitly as

$$\tau_1 \dot{\mathbf{J}} = -(\mathbf{J} + \tilde{D} \nabla \tilde{\mu}) + \beta \tilde{D} T \nabla \cdot \mathbf{P}^v \quad (1.15)$$

and

$$\tau_2 \dot{\mathbf{P}}^v = -(\mathbf{P}^v + 2\eta \mathbf{V}) + 2\beta T \eta \nabla \mathbf{J}. \quad (1.16)$$

In fact, the material time derivatives of  $\mathbf{J}$  and  $\mathbf{P}^v$  in (1.15) and (1.16) should be replaced in general by frame-invariant time derivatives. Eqs. (1.15) and (1.16) exhibit couplings between diffusion and viscous stresses, which are relevant in several physical situations. For instance, in diffusion of small molecules in a polymer matrix, these couplings are due to the swelling due to the solvent, which produces a relative motion between neighbouring polymer chains, whose mutual friction may cause a viscous stress. Other examples of these couplings are shear-induced diffusion and shear-induced phase separation. The couplings between  $\mathbf{J}$  and  $\mathbf{P}^v$  appearing in (1.15) and (1.16) are not exclusive of EIT: in fact, they could follow from simple and general dimensional arguments. What is characteristic of EIT is the relation between the coupling coefficients in (1.15) and (1.16) and the non-classical part of the entropy flux (1.7), and the presence in (1.15) of a generalised chemical potential obtained from (1.8), whose physical relevance is emphasised in Section 2.3.

If one assumed that  $\mathbf{P}^v$  is the sum of several different contributions  $\mathbf{P}_i^v$ , each of them with its own relaxation time  $\tau_{2i}$ , one would have

$$ds = T^{-1} du + T^{-1} p dv - T^{-1} \tilde{\mu} dc_1 - \frac{\tau_1 v}{\tilde{D} T} \mathbf{J} \cdot d\mathbf{J} - \sum_i \left( \frac{\tau_{2i} v}{2\eta_i T} \right) \mathbf{P}_i^v : d\mathbf{P}_i^v. \quad (1.17)$$

If diffusion effects are negligible, integration of (1.17) leads to

$$s(u, v, \mathbf{P}^v) = s_{\text{eq}}(u, v) - \frac{v J}{4T} \mathbf{P}^v : \mathbf{P}^v, \quad (1.18)$$

where subscript eq stands for the local-equilibrium value and  $J (= \tau_2 / \eta)$  is the steady-state compliance in which  $\tau_2$  may be considered as an averaged relaxation time.

Instead of the internal energy, it is very usual to take the temperature as basic variable, because it is more accessible to measurement and control. The thermodynamic potential which has as variables temperature and volume is the Helmholtz free energy  $f$ , defined as  $f = u - Ts$ . The contribution  $\Delta f$  of the flow to the free energy at constant  $T$ , may be written as

$$\Delta f = \Delta u - T \Delta s, \quad (1.19)$$

with

$$\Delta f = f - f_{\text{eq}}, \quad \Delta u = u - u_{\text{eq}}, \quad \Delta s = s(u, v, \mathbf{P}^v) - s_{\text{eq}}(u_{\text{eq}}, v). \quad (1.20)$$

Note that for fixed temperature, the internal energy under flow,  $u$ , is in general different than the internal energy at equilibrium, because the flow may stretch or deform the molecules thus storing internal energy in them.

In order to evaluate the entropic contribution to the free energy we expand  $s_{\text{eq}}(u, v)$  around the equilibrium value  $s_{\text{eq}}(u_{\text{eq}}, v)$  by means of the Taylor expansion

$$s_{\text{eq}}(u, v) = s_{\text{eq}}(u_{\text{eq}}, v) + \left( \frac{\partial s_{\text{eq}}}{\partial u} \right)_{u=u_{\text{eq}}} (u - u_{\text{eq}}) + \cdots, \quad (1.21)$$

which inserted in (1.20) leads to

$$\Delta f = u - u_{\text{eq}} - T \left[ s_{\text{eq}}(u, v) - \left( \frac{vJ}{2T} \right) (P_{12}^v)^2 - s_{\text{eq}}(u_{\text{eq}}, v) \right] = \left( \frac{vJ}{2} \right) (P_{12}^v)^2 \quad (1.22)$$

when use of Eqs. (1.18), (1.19) and (1.20) is made.

It must be finally stressed that (1.18) is only a second order expansion of the entropy in the viscous pressure, but EIT is not limited to this approximation. Indeed, EIT is often complemented with maximum-entropy formalism [25,26], which allows one to obtain more general expressions for the entropy not limited to second order in the fluxes. For instance, if the average values of the internal energy and of the viscous pressure are taken as constraints on the system, the distribution function  $f$  maximising the entropy has the form

$$f = Z^{-1} \exp[-\beta \hat{H} - \Lambda : \hat{\mathbf{P}}^v], \quad (1.23)$$

with  $\hat{H}$  the Hamiltonian,  $\hat{\mathbf{P}}^v$  the microscopic operator for the viscous pressure tensor,  $\beta$  and  $\Lambda$  the corresponding conjugate Lagrange multipliers and  $Z$  the partition function ensuring the normalisation of (1.23). This method has been studied in detail for ideal gases and for polymer solutions [27,28]. The entropy is obtained by introducing (1.23) into

$$s = -k_B \int f \ln f d\Gamma, \quad (1.24)$$

with  $k_B$  the Boltzmann constant and  $d\Gamma$  the volume differential in the phase space of the system.

For dilute polymer solutions, and taking into account the microscopic expression for the viscous pressure tensor [5], one obtains

$$S_p = \frac{1}{2} n_p R \int \left\{ \text{Tr} \left[ \frac{\mathbf{P}^v}{(n_p R T)} \right] + \ln \det \mathbf{U} - \frac{\mathbf{P}^v}{(n_p R T)} \right\}. \quad (1.25)$$

where  $n_p$  is the mole number of the polymer and  $R$  the constant gas. For low values of  $\mathbf{P}^v$  this yields (1.25) provided  $\Lambda$  is identified as  $\Lambda = -(\tau/2\eta k_B T)\mathbf{P}^v$ . We will not discuss in further detail this point in this paper, which is centered on a macroscopic approach, but it will be useful in the comparison with GENERIC approach in Section 3.2.

## 2.2. Rational extended thermodynamics

EIT can be also formulated along the line of thought of rational thermodynamics (RT), a formalism developed by Coleman, Truesdell and Noll in the sixties [4]. Among the basic hypotheses of RT are: (i) absolute temperature and entropy are considered primitive concepts, not restricted to near-equilibrium situations; (ii) it is assumed that systems have memory, i.e. their behaviour at a given instant of time is determined by the past history of the variables; (iii) the second law of thermodynamics, which serves fundamentally as a restriction on the form of the constitutive equations, is expressed in mathematical terms by means of the Clausius–Duhem inequality. In the formulation by Coleman, Truesdell and Noll, the balance equations were combined with the Clausius–Duhem inequality by means of arbitrary source terms in order to avoid such sources, whose physical meaning was much controversial. Liu [29] combined balance equations and Clausius–Duhem inequality by using a more elegant method based on Lagrange multipliers.

Although we borrow some procedures from rational thermodynamics, we depart from it in many aspects and we utilise it as a working method rather than sharing its basic hypotheses as a theory. Essentially, the choice of the independent variables is different: in RT the variables are the histories of the classical state variables  $u, v, \dots$  while here we enlarge the space of independent variables in such a way that the history is no longer needed; accordingly, the response of the system is described by evolution differential equations for the additional independent variables rather than in terms of the constitutive functionals used in RT. However, we keep the idea of combining the entropy inequality with the evolution equations by means of Lagrange multipliers instead of starting directly from a generalised Gibbs equation.

To illustrate this approach, which is often called rational extended thermodynamics (RET) [10], we consider a viscous heat-conducting fluid in motion. The space of the variables is formed by the classical variables (the density  $\rho (= v^{-1})$ , the specific internal energy  $u$ , the velocity  $\mathbf{v}$ ) and the fluxes (here the heat flux  $\mathbf{q}$ , and the viscous pressure  $\mathbf{P}^v$ ), which imply 14 independent variables. We do not include here the diffusion flux as an additional independent variable for the sake of simplicity. In Section 2.1 we considered  $\mathbf{J}$  rather than  $\mathbf{q}$  as independent variable because we were interested in the couplings of  $\mathbf{J}$  and  $\mathbf{P}^v$ . Here, instead, we are mainly interested in providing a simple introduction to the formulation of RET, which is very elegant but rather cumbersome.

The evolution of the classical variables is governed by the balance equations of mass and energy:

$$\rho \dot{v} = \nabla \cdot \mathbf{v}, \quad \rho \dot{u} = -\nabla \cdot \mathbf{q} - \mathbf{P}^v : \mathbf{V} - p\mathbf{U} : \mathbf{V}. \quad (1.26)$$

Concerning the extra variables  $\mathbf{q}$  and  $\mathbf{P}^v$ , we suppose that they obey evolution equations of the rather general form

$$\rho \dot{\mathbf{q}} = -\nabla \cdot \mathbf{Q} + \sigma^q, \quad (1.27a)$$

$$\rho \dot{\mathbf{P}}^v = -\nabla \cdot \mathcal{J}^v + \sigma^v, \quad (1.27b)$$

where  $\mathbf{Q}$  is a tensor of rank two representing the flux of the heat flux,  $\sigma^q$  a vector corresponding to the supply of heat flux,  $\mathcal{J}^v$  a third-rank tensor designating the flux of the viscous pressure tensor, and  $\sigma^v$  its source term. At this stage of the analysis these quantities are not determined and must be specified by means of constitutive relations in terms of the whole set of variables subject to the requirements of positiveness of the rate of entropy production.

To satisfy the second law of thermodynamics, it is assumed that there exists a regular and continuous function  $s$ , called entropy, which obeys a balance law given by

$$\rho \dot{s} + \nabla \cdot \mathbf{J}^s = \sigma^s \geq 0, \quad (1.28)$$

where  $\mathbf{J}^s$  is the entropy flux and  $\sigma^s$  the rate of entropy production. As in rational thermodynamics, the non-negative property of  $\sigma^s$ , calculated by performing the operations indicated in (1.28), is used to place restrictions on the constitutive equations.

To take into account the restrictions placed by the second law — positive entropy production in (1.28) — on the constitutive equations, we follow the well-known method of Lagrange multipliers proposed by Liu and widely used in [10]. According to this technique, we include in (1.35) the constraints introduced by the mass and the energy balances and by the evolution equations of  $\mathbf{q}$  and  $\mathbf{P}^v$  via some Lagrange multipliers  $\Lambda_0$ ,  $\Lambda'_0$ ,  $\Lambda_1$ , and  $\Lambda_2$ , all depending on  $u$ ,  $v$ ,  $\mathbf{q}$ , and  $\mathbf{P}^v$ . Then, the inequality (1.28) takes the form

$$\begin{aligned} \rho \dot{s} + \nabla \cdot \mathbf{J}^s - \Lambda_0(\rho \dot{u} + \nabla \cdot \mathbf{q} + \mathbf{P}^v : \mathbf{V} + p\mathbf{U} : \mathbf{V}) - \Lambda'_0(\rho \dot{v} - \nabla \cdot \mathbf{v}) \\ - \Lambda_1(\rho \dot{\mathbf{q}} + \nabla \cdot \mathbf{Q} - \sigma^q) - \Lambda_2 : (\rho \dot{\mathbf{P}}^v + \nabla \cdot \mathcal{J}^v - \sigma^v) \geq 0. \end{aligned} \quad (1.29)$$

$s$  and  $\mathbf{J}^s$  are, at this stage of the analysis, unknown functions of  $u$ ,  $v$ ,  $\mathbf{q}$ , and  $\mathbf{P}^v$ . By differentiating  $s$  and  $\mathbf{J}^s$  with respect to  $u$ ,  $v$ ,  $\mathbf{q}$ , and  $\mathbf{P}^v$ , and rearranging the various terms one obtains from (1.29)

$$\begin{aligned} \left( \frac{\partial s}{\partial u} - \Lambda_0 \right) \rho \dot{u} + \left( \frac{\partial s}{\partial v} - \Lambda'_0 \right) \rho \dot{v} + \left( \frac{\partial s}{\partial \mathbf{q}} - \Lambda_1 \right) \cdot \rho \dot{\mathbf{q}} + \left( \frac{\partial s}{\partial \mathbf{P}^v} - \Lambda_2 \right) : \rho \dot{\mathbf{P}}^v \\ + \frac{\partial \mathbf{J}^s}{\partial u} \cdot \nabla u + \frac{\partial \mathbf{J}^s}{\partial v} \cdot \nabla v + \frac{\partial \mathbf{J}^s}{\partial \mathbf{q}} : \nabla \mathbf{q} + \frac{\partial \mathbf{J}^s}{\partial \mathbf{P}^v} : \nabla \mathbf{P}^v \\ - \Lambda_0 \nabla \cdot \mathbf{q} - \Lambda_0 \mathbf{P}^v : \mathbf{V} - \Lambda_0 p \mathbf{U} : \mathbf{V} + \Lambda'_0 \nabla \cdot \mathbf{v} - \Lambda_1 \cdot (\nabla \cdot \mathbf{Q}) \\ + \Lambda_1 \cdot \sigma^q - \Lambda_2 : (\nabla \cdot \mathcal{J}^v) + \Lambda_2 : \sigma^v \geq 0. \end{aligned} \quad (1.30)$$

Since the derivatives  $\dot{u}$ ,  $\dot{v}$ ,  $\dot{\mathbf{q}}$  and  $\dot{\mathbf{P}}^v$  are arbitrary, a first requirement for the positiveness of (1.30) is that their respective coefficients in this equation vanish, i.e.

$$\frac{\partial s}{\partial u} = \Lambda_0 = T^{-1}, \quad \frac{\partial s}{\partial v} = \Lambda'_0 = pT^{-1}, \quad \frac{\partial s}{\partial \mathbf{q}} = \Lambda_1, \quad \frac{\partial s}{\partial \mathbf{P}^v} = \Lambda_2, \quad (1.31)$$

where we have identified  $\Lambda_0$  with  $T^{-1}$  and  $\Lambda'_0$  with  $pT^{-1}$  according to the classical interpretation of the derivatives of the entropy.

Omitting second and higher-order terms in the fluxes, the most general expressions of  $\mathbf{Q}$ ,  $\sigma^q$ ,  $\mathcal{J}^v$ , and  $\sigma^v$  are

$$\mathbf{Q} = a_1(u, v)\mathbf{U} + a_2(u, v)\mathbf{P}^v; \quad \sigma^q = -a_3(u, v)\mathbf{q}, \quad (1.32a)$$

$$\mathcal{J}^v = b_1(u, v)\mathbf{q}\mathbf{U} + b_2(u, v)\mathbf{v}\mathbf{U}; \quad \sigma^v = -b_3(u, v)\mathbf{P}^v, \quad (1.32b)$$



with  $a_i(u, v)$  and  $b_i(u, v)$  functions of  $u$  and  $v$ , which are identified below. Calculating the divergence of  $\mathbf{Q}$  and of  $\mathcal{J}^v$ , without including non-linear terms, and substituting into the last three lines of (1.30) (recall that the first line was eliminated according to (1.31)), one has

$$\begin{aligned} & \left( \frac{\partial \mathbf{J}^s}{\partial u} - \frac{\partial a_1}{\partial u} \Lambda_1 \right) \cdot \nabla u + \left( \frac{\partial \mathbf{J}^s}{\partial v} - \frac{\partial a_1}{\partial v} \Lambda_1 \right) \cdot \nabla v + \left( \frac{\partial \mathbf{J}^s}{\partial \mathbf{q}} - b_1 \Lambda_2 - \Lambda_0 \mathbf{U} \right) : \nabla \mathbf{q} \\ & + \left( \frac{\partial \mathbf{J}^s}{\partial \mathbf{P}^v} - a_2 \Lambda_1 \mathbf{U} \right) : \nabla \mathbf{P}^v \\ & - \Lambda_0 \mathbf{P}^v : \mathbf{V} - b_2 \Lambda_2 : \mathbf{V} - a_3 \Lambda_1 \cdot \mathbf{q} - b_3 \Lambda_2 : \mathbf{P}^v \geq 0 \end{aligned} \quad (1.33)$$

after use is made of relation  $\Lambda'_0 = p \Lambda_0$ , obtained from Eq. (1.31), and of the identity  $\nabla \cdot \mathbf{v} \equiv \mathbf{U} : \mathbf{V}$ . As the gradients of independent variables are arbitrary, the coefficients of these quantities in (1.33) must vanish for preserving the inequality. This leads to

$$\frac{\partial \mathbf{J}^s}{\partial u} = \frac{\partial a_1}{\partial u} \Lambda_1, \quad \frac{\partial \mathbf{J}^s}{\partial v} = \frac{\partial a_1}{\partial v} \Lambda_1, \quad (1.34a)$$

$$\frac{\partial \mathbf{J}^s}{\partial \mathbf{q}} = b_1 \Lambda_2 + \Lambda_0 \mathbf{U}, \quad \frac{\partial \mathbf{J}^s}{\partial \mathbf{P}^v} = a_2 \Lambda_1 \mathbf{U}, \quad (1.34b)$$

which suggest for  $\mathbf{J}^s$  the expression

$$\mathbf{J}^s = \beta_1 \mathbf{q} + \beta_2 \mathbf{P}^v \cdot \mathbf{q}, \quad (1.35)$$

where the coefficients  $\beta_i$  are functions of  $u$  and  $v$ . Comparing now (1.34b) and the derivatives of  $\mathbf{J}^s$  with respect to  $\mathbf{q}$  and  $\mathbf{P}^v$  obtained from (1.35) one has

$$\Lambda_0 = \beta_1, \quad \Lambda_1 = \left( \frac{\beta_2}{a_2} \right) \mathbf{q}, \quad \Lambda_2 = \left( \frac{\beta_2}{b_1} \right) \mathbf{P}^v. \quad (1.36)$$

Note that the identification of  $\beta_1$  allows to interpret the first term in (1.35) as a classical term and the second one as an extended contribution. The remaining terms of (1.34) will be analysed below.

In the linear approximation, the evolution equation of  $\mathbf{q}$  given by the first of equations (1.27) can be written as

$$\rho \dot{\mathbf{q}} = - \frac{\partial a_1}{\partial u} \nabla u - \frac{\partial a_1}{\partial v} \nabla v - a_2 \nabla \cdot \mathbf{P}^v - a_3 \mathbf{q}, \quad (1.37)$$

when (1.32a) is taken into account. For the sake of convenience (1.37) may be rewritten as

$$\tau_1 \dot{\mathbf{q}} = -\mathbf{q} - \kappa \nabla u - \delta \nabla v + \alpha \nabla \cdot \mathbf{P}^v, \quad (1.38)$$

where the coefficients are identified as follows  $\tau_i = \rho/a_3$ ,  $\kappa = (a_3)^{-1}(\partial a_1/\partial u)$ ,  $\delta = (a_3)^{-1}(\partial a_1/\partial v)$ ,  $\alpha = -a_2/a_3$ . Eq. (1.38) contains the thermal and viscous contributions to the time evolution of  $\mathbf{q}$ . For  $\tau_1 = \alpha = 0$  one recovers the Fourier law with  $\kappa = \lambda(\partial T/\partial u)$  and  $\delta = \lambda(\partial T/\partial v)$ ,  $\lambda$  being the thermal conductivity. Another result derived from (1.38) when viscous effects are neglected ( $\alpha = 0$ ) is the well-known Maxwell–Cattaneo equation  $\tau_1 \dot{\mathbf{q}} + \mathbf{q} = -\lambda \nabla T$ .

Similarly the evolution equation for  $\mathbf{P}^v$  is obtained from (1.27b) and (1.32b). Thus, in the linear approximation, we have

$$\rho \dot{\mathbf{P}}^v = -b_1 \nabla \mathbf{q} - b_2 \mathbf{V} - b_3 \mathbf{P}^v, \quad (1.39)$$

and putting  $\tau_2 = \rho/b_3$ ,  $2\eta = b_2/b_3$ ,  $\gamma = -(b_1/b_3)$  yields

$$\tau_2 \dot{\mathbf{P}}^v = -\mathbf{P}^v - 2\eta \mathbf{V} + \gamma \nabla \mathbf{q}. \quad (1.40)$$

To derive the generalised Gibbs equation, we write the differential of  $s = s(u, v, \mathbf{q}, \mathbf{P}^v)$  in the form

$$ds = \Lambda_0 du + \Lambda'_0 dv + \Lambda_1 \cdot d\mathbf{q} + \Lambda_2 : d\mathbf{P}^v = T^{-1} du + pT^{-1} dv + \frac{\beta_2}{a_2} \mathbf{q} \cdot d\mathbf{q} + \frac{\beta_2}{b_1} \mathbf{P}^v : d\mathbf{P}^v \quad (1.41)$$

when the equalities in (1.31) are used. To identify  $\beta_2/a_2$  we proceed as follows: from the first of relations (1.34a) and the second of (1.36), one has

$$\frac{\partial \mathbf{J}^s}{\partial u} = \frac{\beta_2}{a_2} \frac{\partial a_1}{\partial u} \mathbf{q}, \quad (1.42)$$

and taking into account the first equality of (1.36), the derivative of (1.35) with respect to  $u$  up to first order in the fluxes gives

$$\frac{\partial \mathbf{J}^s}{\partial u} = \frac{\partial \Lambda_0}{\partial u} \mathbf{q}. \quad (1.43)$$

Equating (1.42) and (1.43) and using that  $(\partial a_1/\partial u) = \rho \lambda \tau_1^{-1} (\partial T/\partial u)$  (see below (1.38)) one is led to  $\beta_2/a_2 = -(\tau_1 v/\lambda T^2)$ . The identification of  $\beta_2/b_1$  is made in a similar way. The four last terms of (1.33) can be written as

$$-(\Lambda_0 \mathbf{P}^v + b_2 \Lambda_2) : \mathbf{V} - a_3 \Lambda_1 \cdot \mathbf{q} - b_3 \Lambda_2 : \mathbf{P}^v \geq 0, \quad (1.44)$$

and preservation of inequality requires that the terms in parentheses vanish, i.e.

$$\Lambda_2 = \frac{\Lambda_0}{b_2} \mathbf{P}^v = \frac{\beta_2}{b_1} \mathbf{P}^v, \quad (1.45)$$

where we have used the third of relations (1.36). From (1.45) and  $b_2 = (2\eta\rho/\tau_2)$  derived from the identification below (1.39) and  $\Lambda_0 = T^{-1}$  according to (1.31), one gets  $\beta_2/b_1 = -(\tau_2 v/2\eta T)$ . Note that the last two terms of (1.44) adopt the quadratic form

$$(\lambda T^2)^{-1} \mathbf{q} \cdot \mathbf{q} + (2\eta T)^{-1} \mathbf{P}^v : \mathbf{P}^v \geq 0, \quad (1.46)$$

which imposes the positiveness of transport coefficients  $\lambda$  and  $\eta$ . Summarising this derivation, the Gibbs equation (1.41) has finally the form [8,9]

$$ds = T^{-1} du + pT^{-1} dv - \frac{\tau_1 v}{\lambda T^2} \mathbf{q} \cdot d\mathbf{q} - \frac{\tau_2 v}{2\eta T} \mathbf{P}^v : d\mathbf{P}^v. \quad (1.47)$$

If the heat flux may be neglected, (1.47) reduces to (1.18) after integration and introduction of the steady-state compliance  $J$ . We have seen here that the main results of Section 2.1 with respect to the entropy, the entropy flux and the evolution equations for the fluxes in EIT are confirmed in RET in the linear approximation.

### 2.3. Equations of state: shear-induced phase transitions

In equilibrium thermodynamics, the chemical potential plays a central role in the analysis of multi-component systems. Since in EIT the free energy depends on the viscous pressure tensor, it follows that the chemical potential in non-equilibrium states should also depend on this quantity. This dependence opens the possibility to generalise the classical analysis of phase diagrams and of reacting systems to non-equilibrium steady states, characterised by a non-vanishing shear rate or shear viscous pressure, which are then expected to influence these phenomena. This is interesting, because it is well-known that a shear viscous pressure implies modifications in the phase diagram of polymer solutions or in the molecular weight distribution of the polymer [21,30–32]. Thus, it is worthwhile to explore the predictions of the non-equilibrium chemical potential and to compare them with the experimental results. Here, we discuss the chemical potential and its application to the analysis of thermodynamic stability in shear flows. It is necessary, however, to stress that such an analysis must not be limited to an uncritical extrapolation of the equilibrium equations, by simply introducing in them the non-equilibrium potential instead of the local-equilibrium one. Each proposition must be carefully and critically examined.

The influence of the shear flow on the phase separation in fluids has been analysed from different points of view. The observations are usually made on the basis of the appearance of turbidity or of changes in the viscosity. These results are interpreted in several different ways: some authors propose that the observed turbidity is due to dynamically enhanced concentration fluctuations, rather than to a true phase separation. Other authors have suggested that there is a true shift of the coexistence line and the spinodal line, leading to turbidity, which may be further enhanced by the dynamical effect of the flow on the concentration fluctuations [21,30–32].

Rangel-Nafaile et al. [31] studied solutions of polystyrene in dioctyl-phthalate and observed a shift of the cloud point curves towards higher temperatures, which could attain 24°C (at  $P_{12}^v = 400 \text{ N/m}^2$ ). Wolf [32] used a thermodynamic theory based on Flory–Huggins equation for the mixing free energy plus a flow contribution. By studying the phase separation of polystyrene solutions in transdecalin, he observed a decrease in the demixing temperature for relatively low-molecular-weight polystyrene and an increase for high-molecular-weight polystyrene. This behaviour may be due to the non-Newtonian effects arising in the latter solutions. The detailed evolution of the separation process has been studied experimentally in [33]; both the time rate and the geometrical structures which appear in the intermediate stages of the separation exhibit a wide variation and a rich phenomenology, which is beyond a purely thermodynamic approach.

We recall that the usual definition of the chemical potential in equilibrium thermodynamics is

$$\mu_i = \left( \frac{\partial G_{\text{eq}}}{\partial n_i} \right)_{T,p,n_j}, \quad (1.48)$$

where  $G_{\text{eq}}$  is the equilibrium Gibbs free energy and  $n_i$  the number of moles of the species  $i$  in the system. The equilibrium Gibbs function for a dilute polymer solution may be expressed by the Flory–Huggins model. The volume of the system is given in such a way that  $V = v_s \Omega$  where the parameter  $\Omega$  is defined as  $\Omega = n_s + mn_p$  with  $n_s$  the number of moles of the solvent,  $v_s$  its molar volume,  $n_p$  the number of moles of the polymer and  $m$  a parameter related to the volume fraction  $\phi$  as  $\phi = mn_p/\Omega$ . The total Gibbs function of the system is given by

$$\frac{G_{\text{eq}}}{RT} = n_s \ln(1 - \phi) + n_p \ln \phi + \chi(1 - \phi)\Omega\phi, \quad (1.49)$$

with  $\chi$  the Flory–Huggins interaction parameter which depends on the temperature as

$$\chi = \frac{1}{2} + \Psi(T^{-1}\Theta - 1), \quad (1.50)$$

where  $\Theta$  is the theta temperature and  $\Psi$  a constant.

From Eqs. (1.48) and (1.49) we can derive the chemical potentials of the solvent,  $\mu_{\text{eq},s}$  and of the polymer,  $\mu_{\text{eq},p}$  which are given, respectively, by

$$\begin{aligned} \frac{\mu_{\text{eq},s}}{RT} &= \ln(1 - \phi) + \left(1 - \frac{1}{m}\right)\phi + \chi\phi^2, \\ \frac{\mu_{\text{eq},p}}{RT} &= \ln\phi + (1 - m)(1 - \phi) + \chi m(1 - \phi)^2. \end{aligned} \quad (1.51)$$

The limit of stability of the homogeneous solution in the plane  $T - \phi$  corresponds to the spinodal line built from the condition

$$\left(\frac{\partial\mu_{\text{eq},s}}{\partial\phi}\right)_{T,p,n_j} = 0. \quad (1.52)$$

When  $(\partial\mu_{\text{eq},s}/\partial\phi)$  is positive, the homogeneous solution is stable; otherwise, it splits into two phases with different polymer concentrations. The critical point corresponds to the maximum of the spinodal line and is specified by the further condition

$$\left(\frac{\partial^2\mu_{\text{eq},s}}{\partial\phi^2}\right)_{T,p,n_j} = 0. \quad (1.53)$$

From (1.52) and (1.53), one obtains that the coordinates of the critical point are the solutions of

$$-(1 - \phi)^{-1} + (1 - m^{-1}) + 2\chi\phi = 0, \quad -(1 - \phi)^{-2} + 2\chi = 0, \quad (1.54)$$

which are given by

$$\phi_c = \frac{1}{1 + m^{1/2}}, \quad \chi_c = \frac{1}{2} + \Psi\left(\frac{\Theta}{T_c} - 1\right) = \frac{1}{2}\left(1 + \frac{1}{m^{1/2}}\right)^2. \quad (1.55)$$

The expression (1.48) can be generalised to non-equilibrium situations by including in  $G$  the non-equilibrium contributions in such a way that the chemical potential of the component  $i$  for a system under flow is defined as

$$\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{T,p,n_j,Z}, \quad (1.56)$$

where  $Z$  is a non-equilibrium variable remaining constant during differentiation. One must be careful to the choice of the variables  $Z$ : indeed, one could perform the differentiation either at constant viscous pressure or at constant shear rate, or at constant molecular conformation. In extended irreversible thermodynamics, we favour the selection of  $\mathbf{P}^v$  as the variable to be kept fixed during the differentiation; not only it is the independent variable of EIT, but furthermore, since the 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 the differentiation

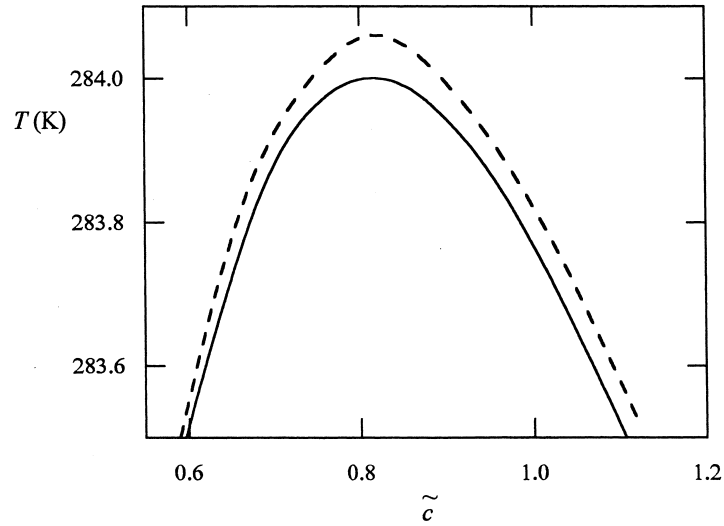


Fig. 1. Spinodal curve of a Rouse–Zimm binary solution at equilibrium (dashed line) and in a non-equilibrium steady state at constant shear rate  $\dot{\gamma} = 1500 \text{ s}^{-1}$  (continuous line) [37].

(1.56) may have a strong influence on the results, as it is shown in Figs. 1 and 2. However, there is still not a definitive answer to this point, neither a complete consensus.

Let us now proceed to evaluate explicitly the flow contribution to the chemical potential. In accordance to Section 2.1, the non-equilibrium contribution to the Gibbs function can be written as

$$\Delta G = VJ(P_{12}^v)^2, \quad (1.57)$$

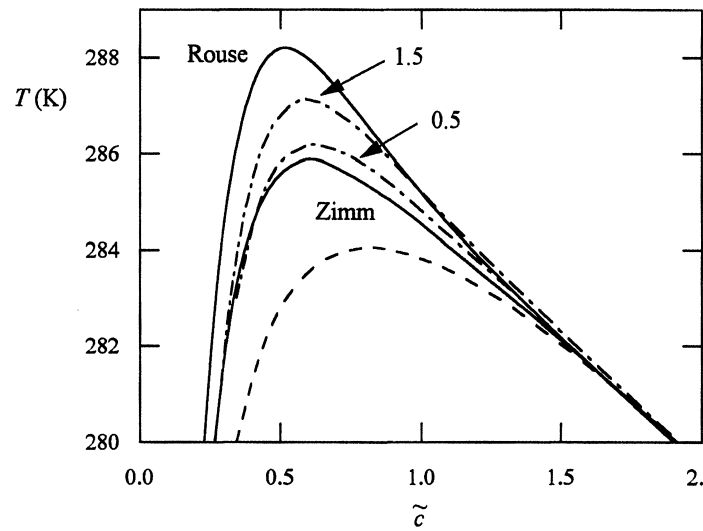


Fig. 2. Spinodal curve of the binary solution at equilibrium (the dashed line corresponds to Flory–Huggins) and in a non-equilibrium steady state at constant shear viscous pressure  $P_{12}^v = 150 \text{ Nm}^{-2}$ . In the figure are shown the lines corresponding to the Rouse model (without hydrodynamic interactions), the Zimm model (which takes into account hydrodynamic interactions) and two intermediate models for the values  $\alpha = 0.5$  and  $\alpha = 1.5$  of the parameter in (1.63) [37].

where  $V$  is the volume of the system and  $J$  the steady-state shear compliance defined below (1.17). Here, we address our attention to the shift of the critical point and the spinodal line in the polymer solution. As a generalisation of the equilibrium situation, we assume that the spinodal line corresponds to the pairs  $(T, \phi)$  satisfying the relation (1.52); note, however, that the classical equilibrium stability condition (1.52) cannot be taken for granted in non-equilibrium steady states, but it must be justified from a dynamical stability analysis [9]. The critical temperature is determined from the additional condition (1.53)

$$\left( \frac{\partial^2 \mu_s}{\partial \phi^2} \right)_{T,p,n_j,Z} = 0. \quad (1.58)$$

We focus our attention to the classical Rouse–Zimm model [9,21,36–38], which leads for  $J(c)$  to

$$J = \frac{CM_p}{cRT} \left[ 1 - \frac{\eta_s}{\eta} \right]^2, \quad (1.59)$$

where  $C$  is a parameter whose value is 0.4 for Rouse model and 0.206 for the Zimm model, and  $M_p$  the molecular weight of the polymer. The latter may be used for low concentrations, whereas when the concentration increases the system tends to the behaviour predicted by Rouse. Therefore, there is a slow shift from Zimm model to Rouse model with increasing polymer concentration.

In order to express  $J$  as a function of the concentration  $c$ , it is necessary to know how  $\eta$  depends on the concentration of the mixture. We have taken the expansion

$$\frac{\eta}{\eta_s} = 1 + [\eta]c + k[\eta]^2 c^2, \quad (1.60)$$

where  $k$  is the so-called Huggins constant, which depends on the solution being analysed, and  $[\eta]$  the intrinsic viscosity. Combining (1.59) and (1.60)  $J$  may be written as a function of the concentration in the form

$$J = \frac{CM_p}{RT} [\eta] \Phi(\tilde{c}), \quad (1.61)$$

with  $\Phi(\tilde{c})$  a function defined as

$$\Phi(\tilde{c}) = \tilde{c} \left[ \frac{1 + k\tilde{c}}{1 + \tilde{c} + k\tilde{c}^2} \right]^2, \quad (1.62)$$

where  $\tilde{c}$  is the reduced concentration, defined as  $\tilde{c} = [\eta]c$ . Note that the simplest scaling law would yield that  $J \approx c^{-1}M$ , which is valid for relatively large concentrations, where the contribution of the polymer to the viscosity is much higher than that of the solvent, but not in the very dilute regime, where the viscosity of the solvent cannot be neglected. The dependence of  $\eta$  on the concentration is crucial in the analysis of the shift of the critical point [35,37].

The transition from the behaviour described by Zimm to that described by Rouse with increasing polymer concentration is monotonous and reflects the fact that with increasing concentration the hydrodynamic effects become less relevant. It may be qualitatively described by assuming that the parameter  $C$  depends on the concentration, as for instance [37]

$$C(\tilde{c}) = 0.206 + \frac{0.194\alpha\tilde{c}}{1 + \alpha\tilde{c}}, \quad (1.63)$$

where  $\alpha$  is a parameter describing how steep is the transition. This expression may be used in the analysis of the influence of the hydrodynamic interactions on the shear-induced shift of the critical point.

When (1.57) and (1.61) are used, the non-equilibrium contribution to  $G$  is given by

$$\frac{\Delta G^{(s)}}{RT} = BC(\tilde{c}) \frac{(P_{12}^v)^2}{T^2} \Omega \Phi(\tilde{c}), \quad (1.64)$$

where  $B = v_s M_p [\eta] / R^2$ .

We have considered two different situations [37]: by keeping constant either  $P_{12}^v$  or  $\dot{\gamma}$  during the differentiation leading to the chemical potential. The corresponding expressions are denoted by  $(\mu_s)_{P_{12}^v}$  and  $(\mu_s)_{\dot{\gamma}}$ , and we have compared their respective predictions for the shift of the spinodal line.

The thermodynamic criterion for the stability limit given by (1.52) yields for the spinodal line

$$\frac{\partial}{\partial \tilde{c}} \left( \frac{\mu_s}{RT} \right) = \frac{\partial}{\partial \tilde{c}} \left( \frac{\mu_{eq,s}}{RT} \right) + \frac{\partial}{\partial \tilde{c}} \left( \frac{(\mu_s)_r}{RT} \right) = 0, \quad r = P_{12}^v, \dot{\gamma}. \quad (1.65)$$

Here,  $(\mu_s)_r$  stands for the chemical potential defined either at constant pressure tensor ( $r = P_{12}^v$ ) or at constant shear rate ( $r = \dot{\gamma}$ ). The explicit cumbersome expressions of the corresponding derivatives are given in full detail in [37], where we have obtained explicit results for a solution of polystyrene of molecular mass  $520 \text{ kg mol}^{-1}$  in transdecalin. The corresponding equilibrium and non-equilibrium spinodal lines are shown in Fig. 1, where it is seen that at constant  $\dot{\gamma} = 1500 \text{ s}^{-1}$  the presence of the shear yields a lowering of the critical temperature.

In contrast, if one takes the derivative at constant  $P_{12}^v$  the conclusion is an increase in the critical temperature, as it is seen in Fig. 2 and consistently with experimental results [31]. An interesting point in the latter figure is the role of hydrodynamic effects: when they are neglected, as in the Rouse model, the shift in the critical point is maximum, and it is minimum in the Zimm model, where hydrodynamic interactions are relevant. The parameter  $\alpha$  in (1.63) plays also an important role in the shift of the critical point.

It must be noted, however, that though the results exhibit the trends observed in experiments, their numerical predictions fall short in comparison with experimental data. We have shown that when the effects of the enhanced hydrodynamic fluctuations are added the quantitative predictions become satisfactory. However, this requires a full dynamical analysis, for which the reader is referred to [38]. Furthermore, it may be shown [21] that the use of the generalised chemical potential  $(\mu_s)_{P_{12}^v}$  in connection with a breaking and recombining mechanism of the macromolecules is able to describe shear-induced polymer degradation.

Another interesting physical situation where the non-equilibrium chemical potential plays a relevant role is the shear-induced polymer migration, in which the presence of a viscous pressure induces migration in an initially homogeneous polymer solution. The most direct and simple way to deal with these effects is through the third term in the right-hand side of the equation for diffusion (1.15), which couples diffusion and viscous pressure. Customarily (1.15) is used with  $\tau_1 = 0$ , and the classical local-equilibrium expression for the chemical potential, so that the term in  $\nabla \cdot \mathbf{P}^v$  provides the only coupling between  $\mathbf{P}^v$  and  $\mathbf{J}$ . In contrast, the generalised chemical potential  $\tilde{\mu}$ , which depends also on  $\mathbf{P}^v$ , sets a further coupling, whose effects may be, in some circumstances, two orders of magnitude higher than those of the term in  $\nabla \cdot \mathbf{P}^v$  [39]. This is in agreement with experimental results [40], which show that the latter coupling, though qualitatively correct, is by far insufficient to describe the observed rate of migration.

### 3. Comparison with other continuum theories

In this part we aim to compare EIT presented above with three other approaches to macroscopic descriptions of continuum systems, namely: internal variables, GENERIC formalism and Matrix Method. All of them are very general formalisms which may be applied to many different physical situations. As in the first part of the paper, we will use them for the description of polymer solutions. For detailed introductions to these approaches the reader is referred to the other contributions to this volume.

#### 3.1. Theories with internal variables

The theories with internal variables [41–44] introduce additional variables related to some relevant details of the microstructure of the system; this allows a more detailed description and enlarges the domain of application of thermodynamics; they have been successfully applied in such fields as rheology or in dielectric and magnetic relaxation, where the structure or the polarisation of the macromolecules plays a relevant role.

EIT may have several connections with these theories, since they also introduce more independent variables and more equations. On the other side, they differ from EIT in the fact that the latter uses the macroscopic fluxes as variables, whereas the internal variables are either unidentified (when they have as the only purpose to provide more general equations for the classical variables rather than being themselves the subject of direct measurement) or, more frequently, motivated by a microscopic modelling of the systems. For instance, when working with polymer solutions the macromolecular configuration of the polymers is incorporated as a supplementary variable described by the configuration tensor

$$\langle \mathbf{R}\mathbf{R} \rangle = \int \psi(\mathbf{R}) \mathbf{R}\mathbf{R} \, d\mathbf{R}, \quad (2.1)$$

with  $\psi$  the configurational distribution function describing the probability distribution of the different values of  $\mathbf{R}$ , the end-to-end vector of the macromolecules. Descriptions including as variable the whole distribution function or the set of tensors  $\langle \mathbf{R}_i \mathbf{R}_i \rangle$  with  $\mathbf{R}_i$  the vector from bead  $i$  to bead  $i + 1$  in a Rouse–Zimm bead-spring description of the macromolecule have been proposed.

As it is well known [5–7,34], the configuration tensors are directly related to the viscous pressure tensor. Indeed, for the contribution of the  $i$ th normal mode to the viscous pressure tensor one has

$$\mathbf{P}_i^v = -nH \langle \mathbf{R}_i \mathbf{R}_i \rangle + nk_B T \mathbf{U}, \quad (2.2)$$

with  $n$  the number of molecules per unit volume,  $H$  the elastic constant characterising the intramolecular interactions, and  $k_B$  the Boltzmann's constant (since in this section we will often refer to microscopic quantities, we use here  $n$  for the number of molecules per unit volume rather than for the number of moles). Thus, introduction of  $\mathbf{P}_i^v$  or of  $\langle \mathbf{R}_i \mathbf{R}_i \rangle$  as independent variables into the free energy is essentially equivalent, in the case of dilute polymer solutions. The use of  $\mathbf{P}_i^v$  or of  $\langle \mathbf{R}_i \mathbf{R}_i \rangle$  as variables has, in both cases, some characteristic advantages. For the analysis of non-equilibrium steady states,  $\mathbf{P}_i^v$  is directly related to the measured and controlled observables. For the microscopic understanding of the macromolecular processes taking place and for the analysis of light-scattering experiments, the use of  $\langle \mathbf{R}_i \mathbf{R}_i \rangle$  is more suitable.



To give an explicit illustration of the theory of internal variables, assume that one includes the configuration tensor  $\mathbf{W} = \langle \mathbf{R}\mathbf{R} \rangle$ , as an independent variable of the theory. The corresponding Gibbs equation would then be

$$ds = T^{-1} du + pT^{-1} dv - \alpha T^{-1} \mathbf{W} : d\mathbf{W}. \quad (2.3)$$

As a consequence, the time derivative of the entropy takes the form

$$\rho \dot{s} = T^{-1} \rho \dot{u} + pT^{-1} \rho \dot{v} - \rho \alpha T^{-1} \mathbf{W} : \dot{\mathbf{W}}. \quad (2.4)$$

Taking into account the mass and energy balance equations (1.26) and (2.4) may be cast in the form

$$\rho \dot{s} + \nabla \cdot (T^{-1} \mathbf{q}) = \mathbf{q} \cdot \nabla T^{-1} - T^{-1} \mathbf{P}^v : (\nabla \mathbf{v})^s - \rho \alpha T^{-1} \mathbf{W} : \dot{\mathbf{W}}. \quad (2.5)$$

We recognise  $T^{-1} \mathbf{q}$  as the entropy flux and the term on the right as the entropy production. The simplest constitutive equations satisfying the positiveness of the entropy production are

$$\mathbf{q} = L \nabla T^{-1}, \quad (2.6)$$

$$\mathbf{P}^v = -L_{00} T^{-1} (\nabla \mathbf{v})^s - L_{01} T^{-1} \rho \alpha \mathbf{W}, \quad (2.7)$$

$$\dot{\mathbf{W}} = -L_{10} T^{-1} (\nabla \mathbf{v})^s - L_{11} T^{-1} \rho \alpha \mathbf{W}, \quad (2.8)$$

with the matrix of the transport coefficients  $L_{ij}$  being definite positive, and with  $L_{10} = -L_{01}$  due to Onsager–Casimir reciprocity relations, due to the opposite parity of  $\nabla \mathbf{v}$  and  $\mathbf{W}$  with respect to time-reversal symmetry.

Eq. (2.6) yields the usual Fourier law provided one identifies  $L = \lambda T^2$ . Eq. (2.7) relates the viscous pressure tensor to the internal variable  $\mathbf{W}$  and (2.8) describes the evolution of the internal variable. If one does not need to measure  $\mathbf{W}$  but only  $\mathbf{P}^v$  and  $\nabla \mathbf{v}$ , one may eliminate  $\mathbf{W}$  by combining (2.7) and (2.8) to obtain an evolution equation for  $\mathbf{P}^v$ . In the simplest linear situation (i.e. assuming the convenient temperature dependence of the transport coefficients in such a way that  $L_{00} T^{-1}$ ,  $L_{10} T^{-1}$ ,  $L_{01} T^{-1} \rho \alpha$  and  $L_{11} T^{-1} \rho \alpha$  are constant) one may differentiate (2.7) and, combining it with (2.8) one obtains an evolution equation of the so-called Jeffreys (or double-lag) form

$$\tau \frac{d\mathbf{P}^v}{dt} + \mathbf{P}^v = -2\eta \left[ (\nabla \mathbf{v})^s + \tau_2 \frac{d(\nabla \mathbf{v})^s}{dt} \right], \quad (2.9)$$

with the relaxation time  $\tau$  given by

$$\tau = (L_{11} T^{-1} \rho \alpha)^{-1}, \quad (2.10)$$

the shear viscosity  $\eta$  expressed as

$$2\eta = -\frac{L_{01} L_{10} - L_{00} L_{11}}{L_{11} T}, \quad (2.11)$$

and the time  $\tau_2$  given by

$$\tau_2 = \frac{L_{00}}{2\eta L_{11} \rho \alpha} = \tau \frac{L_{00} T^{-1}}{2\eta}. \quad (2.12)$$

We recover Maxwell's relation when  $L_{00} = 0$ . In this case we have  $\tau_2 = 0$  and  $2\eta = -(L_{01}L_{10}/L_{11}T) = L_{01}^2/(L_{11}T)$ , and  $\mathbf{W}$  and  $\mathbf{P}^v$  are directly related as  $\mathbf{W} = -\mathbf{P}^v \times (L_{01}T^{-1}\rho\alpha)^{-1}$ . This may be introduced into the Gibbs equation (2.3) and yields, in the linear situation we are considering,

$$ds = T^{-1} du + pT^{-1} dv - \frac{\alpha T^{-1}}{(L_{01}\rho\alpha T^{-1})^2} \mathbf{P}^v : d\mathbf{P}^v, \quad (2.13)$$

which in view of the above identifications of  $\tau$  and  $\eta$  may be rewritten as

$$ds = T^{-1} du + pT^{-1} dv - \frac{\tau}{2\eta\rho T} \mathbf{P}^v : d\mathbf{P}^v, \quad (2.14)$$

which is precisely the Gibbs equation of EIT from which (1.18) is obtained.

This short development shows that when the conformation tensor is directly related to the viscous pressure tensor it is possible, in principle, to directly compare both theories in the linear approach. The choice of variables will depend on the experimental measurements: if one controls the shear pressure, its choice as independent variable, as in EIT, is more convenient, whereas if a more microscopic understanding is wished, the conformation tensor will be more useful.

Other differences between EIT and the usual theories with internal variables are the following ones: (a) in the latter, it is usual to propose purely relaxational equations for the internal variables. In contrast, in EIT one assumes that the fluxes are field variables which satisfy their own balance equations, where a flux of the flux may be present in a rather natural way; (b) theories with internal variables usually associate the additional variables with some structure of underlying molecules, as in the mentioned example of macromolecules. However, in EIT one uses as variables  $\mathbf{P}^v$ ,  $\mathbf{q}$  and other fluxes in spite that the particles composing the fluid are monatomic and without internal degrees of freedom. From this point of view, EIT aims to build a macroscopic formalism which is able to deal with a wide variety of systems, whereas the theories with internal variables refer usually to a given kind of systems, for which the internal variable is explicitly identified.

### 3.2. GENERIC formulation

Hamiltonian formulations express in an elegant way a feature which is common to many different levels of description: the microscopic one (mechanics of the particles), the kinetic theory (based on a distribution function rather than on precise values for the mechanical variables of the particles), and macroscopic approaches (as for instance hydrodynamics or equilibrium thermodynamics). Therefore, it is logical to ask that also mesoscopic intermediate descriptions should have this structure. This compatibility condition among different levels is especially useful in the non-linear domain, where the thermodynamic inequalities do not provide useful restrictions [45–48].

Here, we will follow the so-called GENERIC (General Equation for the Non-Equilibrium Reversible-Irreversible Coupling) formulation by Grmela and Öttinger [45,46], which is especially elegant and powerful. These authors propose that the time evolution equations of the physical systems may be written as

$$\frac{d\mathbf{x}}{dt} = \mathbf{L} \cdot \frac{\delta E}{\delta \mathbf{x}} + \mathbf{M} \cdot \frac{\delta S}{\delta \mathbf{x}}, \quad (2.15)$$

where  $\mathbf{x}$  represents a set of independent variables required for the complete description of the non-equilibrium system (namely, hydrodynamical fields and additional structural variables),  $E$  and  $S$  are

the total energy and entropy of the system expressed in terms of  $\mathbf{x}$ , and  $\mathbf{L}$  and  $\mathbf{M}$  are linear functional operators, commented below. The dot indicates the multiplication of a vector by a matrix and  $\delta/\delta\mathbf{x}$  usually implies functional rather than partial derivatives. The first term in the right-hand-side of (2.15) is purely Hamiltonian and expresses the reversible contribution to the time evolution equations of  $\mathbf{x}$  generated by the energy  $E$  and the entropy  $S$ , whereas the second term is Riemannian and corresponds to the irreversible contributions.

Eq. (2.15) is supplemented by the following degeneracy requirements:

$$\mathbf{L} \cdot \frac{\delta S}{\delta \mathbf{x}} = 0, \quad \mathbf{M} \cdot \frac{\delta E}{\delta \mathbf{x}} = 0. \quad (2.16)$$

The first requirement expresses the reversible contribution of  $\mathbf{L}$  to the dynamics and requires that the functional form of the entropy must be such that it is unaffected by the operator  $\mathbf{L}$  generating the reversible dynamics. The second one expresses the conservation of the total energy by the contribution of the dynamics. Note that these degeneracy requirements express very essential and general physical aspects.

Furthermore, one defines the following brackets

$$\{A, B\} = \left\langle \frac{\delta A}{\delta \mathbf{x}}, \mathbf{L} \cdot \frac{\delta B}{\delta \mathbf{x}} \right\rangle, \quad [A, B] = \left\langle \frac{\delta A}{\delta \mathbf{x}}, \mathbf{M} \cdot \frac{\delta B}{\delta \mathbf{x}} \right\rangle, \quad (2.17)$$

where  $\langle, \rangle$  denotes the scalar product. The bracket  $\{, \}$  extends the usual Poisson brackets of classical mechanics, whereas the  $[, ]$  brackets are intended to describe the dissipative behaviour.

In terms of these brackets, Eq. (2.15) and the chain rule yield the following form for the evolution equation of an arbitrary function  $A$ :

$$\frac{dA}{dt} = \{A, E\} + [A, S]. \quad (2.18)$$

Further conditions for  $\mathbf{L}$  and  $\mathbf{M}$  may be stated as the following properties of the brackets:

$$\begin{aligned} \{A, B\} &= -\{B, A\} \quad (\text{antisymmetry}), \\ [A, \{B, C\}] + \{B, \{C, A\}\} + \{C, \{A, B\}\} &= 0 \quad (\text{Jacobi identity}), \end{aligned} \quad (2.19)$$

from which follows that  $\mathbf{L}$  is antisymmetric, and restrict the possible forms of the connection mechanisms for the structural variables, and

$$[A, B] = [B, A], \quad [A, A] \geq 0, \quad (2.20)$$

which requires that  $\mathbf{M}$  is symmetric (provided that all the variables  $\mathbf{x}$  have the same time-reversal parity) and definite positive. This non-negativeness property guarantees that  $ds/dt \geq 0$  and therefore, together with the degeneracy requirement (2. 16a) expresses a form of the second law.

This form of writing the evolution equations in terms of two generators  $E$  and  $S$  and two matrices  $\mathbf{L}$  and  $\mathbf{M}$  aims to capture the most essential features of the dynamics of the systems, in an analogous way as the fundamental thermodynamic potentials capture all the thermodynamic information into a single potential. The main innovation of GENERIC with respect to previous bracket formalisms [49] is the use of two different generators,  $E$  and  $S$ , instead of a single one: this gives more flexibility in the choice of variables. The matrix  $\mathbf{L}$  is determined by the behaviour of the variables  $x$  under space transformations, whereas the dynamical material information enters in the friction matrix  $\mathbf{M}$  which is related to transport

coefficients. The antisymmetry requirements on  $\mathbf{L}$  are usual in classical mechanics and guarantee the consistency of  $\mathbf{L}$  with the structure of the equivalent Poisson bracket, whereas the symmetry of  $\mathbf{M}$  is directly related to Onsager's reciprocity relations.

The previous formalism may be applied to many physical situations (as for instance polymer solutions, emulsions and blends, polymer melts, ...). Here, we will apply it to polymeric fluids for the sake of comparison. As it will be seen, it relates non-equilibrium expressions for the entropy  $S$ , to the dynamics in a very well specified form through the GENERIC formalism. In fact, entropy appears there as a primitive concept, and its form is only verified a posteriori, after the success of the evolution equations (2.18) has been verified. We follow here the presentation by Öttinger and Grmela [45,46], specified to a dumbbell solution. These authors take as an independent variable the configuration tensor defined as

$$\mathbf{C}(\mathbf{r}) = \frac{1}{n_p} \int \mathbf{R}\mathbf{R} \psi(\mathbf{r}, \mathbf{R}) d\mathbf{R}, \quad (2.21)$$

where  $\psi$  is the configurational distribution function. It must be stressed that in other versions they propose a more detailed description, directly based on the distribution function as internal variable, and their aim is to explore the possible forms of the kinetic equations for  $\psi$  compatible with the general requirements of GENERIC.

They assume that  $E$  and  $S$  are given, respectively, by

$$E = \int \left[ \frac{1}{2} \left( \frac{u^2}{\rho} \right) + \varepsilon + \int V(\mathbf{R}) \psi(\mathbf{R}) d\mathbf{R} \right] d\mathbf{r} \quad (2.22)$$

and

$$S = \int \left[ s(\rho, \varepsilon) - \int \psi [V^{(S)}(\mathbf{R}) + k_B \ln \psi] d\mathbf{R} \right] d\mathbf{r}, \quad (2.23)$$

with  $\varepsilon$  the internal energy per unit volume,  $V(\mathbf{R})$  an interparticle potential energy and  $V^{(S)}(\mathbf{R})$  an entropic potential related to the entropic contribution to the polymer elasticity. Furthermore, they assume that all the dumbbell contribution is of entropic origin, so that they take  $V = 0$  in (2.2) and suppose a quadratic form for  $V^{(S)}(\mathbf{R})$  in (2.23), corresponding to a configurational distribution of the Gaussian type. Then, they obtain that  $S = S_s + S_p$ , with  $S_s$  the solvent entropy and  $S_p$  the polymer entropy, the latter being given by

$$S_p = \frac{1}{2} n_p k_B \int \{ \text{Tr}[\mathbf{U} - \alpha \mathbf{C}(\mathbf{r})] + \ln[\det \alpha \mathbf{C}(\mathbf{r})] \} d\mathbf{r}, \quad (2.24)$$

where  $n_p$  is now the number of polymer molecules per unit volume and the constant  $\alpha$  is chosen such that  $\mathbf{C}(\mathbf{r}) = \mathbf{U}$  at equilibrium (i.e.  $\alpha = H/k_B T$ ). This expression is obtained by integrating over  $\mathbf{R}$  in the entropy given by (2.23) and neglecting the additive constants. Note that

$$\frac{\delta S}{\delta \mathbf{C}} = \frac{1}{2} n_p k_B [\mathbf{C}^{-1}(\mathbf{r}) - \alpha \mathbf{U}]. \quad (2.25)$$

The Hamiltonian theory imposes that the pressure tensor should be chosen in such a way that the gradient of the entropy lies in the null-space of  $\mathbf{L}$  according to the condition (2.16). This matrix is given

by [45,46]

$$\mathbf{L} = \begin{pmatrix} 0 & \nabla \rho & 0 & 0 \\ \rho \nabla & [\nabla \mathbf{v} + \mathbf{v} \nabla]^T & \varepsilon \nabla + \nabla p + \nabla \cdot \mathbf{P} & \mathbf{C} \nabla - \overline{\mathbf{U} \nabla \cdot \mathbf{C}} \\ 0 & \nabla \varepsilon + p \nabla + \mathbf{P} \cdot \nabla & 0 & 0 \\ 0 & \nabla \mathbf{C} - \overline{\mathbf{U} \mathbf{C} \cdot \nabla} & 0 & 0 \end{pmatrix}, \quad (2.26)$$

where  $(\nabla \mathbf{C} - \overline{\mathbf{U} \mathbf{C} \cdot \nabla})_{jkl} \equiv \nabla_l C_{jk} - U_{jl}(\mathbf{C} \cdot \nabla)_k - U_{kl}(\mathbf{C} \cdot \nabla)_j$ .

A possible choice for the pressure tensor  $\mathbf{P}$  is then

$$\mathbf{P} = T \left( 2\mathbf{C} \cdot \frac{\delta S_p}{\delta \mathbf{C}} + S_p \mathbf{U} \right), \quad (2.27)$$

where a divergence-free term may be added to  $\mathbf{P}/T$ . From (2.25) and (2.27) and neglecting the isotropic contributions, one obtains

$$\mathbf{P} = n_p k_B T (\mathbf{U} - \alpha \mathbf{C}), \quad (2.28)$$

which is indeed (2.2). Note that if instead of (2.24) one takes a second-order approximation to the entropy (2.27), would yield instead of the usual form (2.28) the modified form

$$\mathbf{P} = n_p k_B T \alpha \mathbf{C} \cdot (\mathbf{U} - \alpha \mathbf{C}). \quad (2.29)$$

which is not supported by the microscopic theory and which only coincides with (2.28) for small values of  $\mathbf{C}$ . Therefore, the use of the general form (1.25) for the entropy [which is equivalent to (2.24)] is necessary for a fruitful comparison between EIT and GENERIC in general terms. Of course, both theories coincide at second order in the perturbation.

To describe the dynamics of the system, one needs the expressions for the matrices  $\mathbf{L}$  and  $\mathbf{M}$  which appear in (2.15). These are given by [45,46]

$$\mathbf{M} = \begin{pmatrix} 0 & 0 & 0 & 0 \\ 0 & -(\nabla \eta_s T \nabla + \mathbf{U} \nabla \cdot \eta_s T \nabla)^T & \nabla \cdot -\eta_s T \dot{\gamma} & 0 \\ 0 & -\eta_s T \dot{\gamma} \cdot \nabla & \frac{1}{2} \eta_s T \dot{\gamma} : \dot{\gamma} - \nabla \cdot \lambda T^2 \nabla & 0 \\ 0 & 0 & 0 & \frac{2}{n_p k_B c \tau} \mathbf{C} \end{pmatrix}, \quad (2.30)$$

with  $\eta_s$  the solvent viscosity. With these expressions for  $\mathbf{L}$  and  $\mathbf{M}$ , and of the potentials  $E$  and  $S$ , one recovers the balance equations for mass, momentum and energy and the convected Maxwell equation for the viscous pressure tensor.

Thus, the GENERIC formalism constitutes an independent way to assert the consistency between a generalised entropy and the corresponding evolution equations of the system, and it suggests how to generalise the entropy of EIT where terms beyond the second order in the viscous pressure tensor are needed. Instead of a direct formulation of time-evolution equations for the internal variables, GENERIC formalism advocates for their modelling in terms of these four building blocks ( $E$ ,  $S$ ,  $\mathbf{L}$ ,  $\mathbf{M}$ ), which emphasise their connection with thermodynamics. The GENERIC formalism is not exclusive of the

macroscopic level. On the contrary, one of its appeals is precisely that the GENERIC structure of the equations is found at several levels of description. The special strengths of this formalism are: (i) its application up to the level of the microscopic distribution function, thus allowing for the modelling of kinetic equations; (ii) the restrictions imposed by the Jacobi identity; (iii) the ability to identify, through the form of  $\mathbf{L}$ , the microscopic expression for the pressure tensor. A review of recent results on modellisation of polymer solutions in non-isothermal conditions is provided in Ref. [47].

EIT has been compared with GENERIC in the non-linear regime in [48]; it turns out that in the non-linear regime, the extra fields which should extend the classical hydrodynamic variables to have the GENERIC structure are not exactly the viscous pressure tensor and the heat flux, but other closely related variables which are advected with the fluid in the non-linear regime; and advantage of GENERIC with respect to EIT is that the former one has more information in the non-linear regime, where it may deal with some subtleties which are lost in the EIT description at least, in the versions of it formulated up to now. The most interesting example is, in our opinion, the form of the non-equilibrium thermodynamic pressure, which is the subject of discussion in EIT, but which has a clear-cut expression in GENERIC. In this way, the requirement that the evolution equations have a GENERIC structure in the non-linear regime may be very useful to eliminate some hesitations which arise in the formulation of EIT in this regime.

It must finally be mentioned that other formalisms based on a single generator model and Poisson brackets have been used to describe the generalised transport equations (1.57) and (1.58) for the diffusion flux and the viscous pressure tensor, by Beris and Edwards [49]. Another interesting approach is the so-called Matrix Model for thermodynamically driven systems developed by Jongschaap [50,51] and whose relation to GENERIC model has been explored in [52].

### 3.3. Comparison with the matrix model

In the Matrix Model of Jongschaap [50–52], the global thermodynamic system is composed of two separate types of variables (or of distinct physical parts), which may be called the environment and the internal variables. In the system we are studying, we take as internal variables the pressure tensor  $\mathbf{P}^v$ , and as environment variables the classical variables, namely  $\rho$ ,  $\mathbf{v}$  and  $u$ . In EIT there is not necessarily such distinction, but in any way the classical variables are related to general balance laws whereas the evolution equation for  $\mathbf{P}^v$  must be obtained by means of a constitutive equation. In [50,51], Jongschaap has studied the situation where one takes as internal variable the configuration tensor but, since we are interested in comparing with EIT, we take  $\mathbf{P}^v$  instead of the configuration tensor.

The power supplied to the system is characterised in the matrix model by a set of controllable external forces  $\Sigma$  and rate variables  $\dot{\Gamma}$ , and is given by

$$P_w^e = \Sigma \otimes \dot{\Gamma}, \quad (2.31)$$

where  $\otimes$  means full-contracted product. The internal subsystem is characterised by a set of variables  $\mathbf{x}_i$  and a fundamental equation representing the rate of change of energy, i.e. the rate of energy stored in the subsystem, as

$$P_w^i = \Pi \otimes \frac{d\mathbf{x}_i}{dt}, \quad (2.32)$$

where  $\Pi$  indicates the thermodynamic forces conjugated to the respective variables  $\mathbf{x}_i$ . The total dissipation rate is then given by the difference between the rate of power supplied to the system and the internal

rate of storage of energy, namely,

$$\Delta \equiv P_w^e - P_w^i = \Sigma \otimes \dot{\Gamma} - \Pi \otimes \frac{d\mathbf{x}_i}{dt}. \quad (2.33)$$

In the absence of internal variables, the whole supplied power would be dissipated. The dots in (2.33) denote the suitable inner product in the corresponding space of variables.

The matrix model is derived from (2.33) by writing

$$\begin{pmatrix} \Sigma \\ \frac{d\mathbf{x}_i}{dt} \end{pmatrix} = \begin{pmatrix} \eta & -\Lambda^T \\ \Lambda & \beta \end{pmatrix} \begin{pmatrix} \dot{\Gamma} \\ -\Pi \end{pmatrix}. \quad (2.34)$$

This special decomposition is based on the assumption that the variables  $\mathbf{x}_i$  and the dissipation  $\Delta$  remain unchanged under a reversal of sign of the rate variables  $\dot{\Gamma}$ . This is the so-called principle of macroscopic time reversal. Note that this matrix has a well-defined structure. Its upper part defines the flux–force relationships and the bottom part the time-evolution equations for the internal variables. The skew symmetry of the matrix in (2.34) reflects the Onsager–Casimir reciprocity relations for the rate equations obtained from (2.33). Furthermore, the positiveness of the dissipation rate implies that the matrix must be positive definite and, in particular, that the diagonal coefficients must be positive.

Here we specify this general formalism to our physical problem. As mentioned above, we take  $\rho$ ,  $\mathbf{v}$ ,  $u$  as environment variables and  $\mathbf{P}^v$  as internal variable. We have then

$$\Delta = -(\nabla \mathbf{v}) : \mathbf{P}^v + T \mathbf{q} \cdot \nabla T^{-1} - \Pi : \frac{d\mathbf{P}^v}{dt} \geq 0. \quad (2.35)$$

Note that the first two terms in (2.35) are just the entropy production in the local-equilibrium theory (without internal variables) times the absolute temperature (here, the situation is considered isothermal). The last term obviously gives the contribution of the internal variables. It must also be stressed that in (2.35)  $\mathbf{P}^v$  acts both as an internal variable and as a rate variable. This aspect is not typical of the matrix model, but it is due to the special choice of variables in EIT.

By comparing (2.33) and (2.35), we may identify  $\Sigma = \{-\nabla \mathbf{v}\}$ ,  $T \nabla T^{-1}$ ,  $\dot{\Gamma} = \{\mathbf{P}^v, \mathbf{q}\}$ , and  $d\mathbf{x}_i/dt = d\mathbf{P}^v/dt$ . We want to check that the equations relating these quantities may be written in the form (2.34). We have

$$\begin{pmatrix} -\nabla \mathbf{v} \\ T \nabla T^{-1} \\ \frac{d\mathbf{P}^v}{dt} \end{pmatrix} = \begin{pmatrix} \eta' & 0 & -\Lambda \\ 0 & \lambda' & 0 \\ \Lambda & 0 & \beta \end{pmatrix} \begin{pmatrix} \mathbf{P}^v \\ \mathbf{q} \\ -\Pi \end{pmatrix}, \quad (2.36)$$

and we try to identify the coefficients appearing in the matrix.

The equation relating  $\mathbf{q}$  and  $T \nabla T^{-1}$  is, in the situation being analysed here, Fourier's law. Thus,  $\mathbf{q} = -\lambda \nabla T = \lambda T^2 \nabla T^{-1}$  and therefore  $\lambda' = 1/\lambda T$ . The evolution equation for  $\mathbf{P}^v$ , is

$$\frac{d\mathbf{P}^v}{dt} = -\frac{1}{\tau} \mathbf{P}^v - \frac{2\eta}{\tau} (\nabla \mathbf{v})^s. \quad (2.37)$$

It follows from direct comparison of (2.37) with the third equation of (2.36) that  $\Lambda = -1/\tau$ . In this way,

the last equation in (2.36) becomes

$$\frac{d\mathbf{P}^v}{dt} = -\frac{1}{\tau}\mathbf{P}^v - \beta\Pi \quad (2.38)$$

and the first one

$$-(\nabla\mathbf{v})^s = -\frac{1}{\tau}\Pi + \eta'\mathbf{P}^v. \quad (2.39)$$

It follows from (2.37) and (2.38) that  $-\beta\Pi = (2\eta/\tau)(\nabla\mathbf{v})^s$ . Since  $\Pi$  is proportional to  $\nabla\mathbf{v}$  we have from (2.39)  $\eta' = 0$  and  $\Pi = \tau(\nabla\mathbf{v})^s$ . This yields  $\beta = 2\eta/\tau^2$ . Note that the non-zero diagonal coefficients  $\lambda'$  and  $\beta$  are positive, as it was expected. Thus, the equations of EIT may indeed be written in the form proposed by Jongschaap.

In [50,51] Jongschaap has studied several applications of this method to some macroscopic models (Giesekus, Leonov) and to some microscopic models by using the configuration function itself as a variables, as applied to dumbbells and to reptation models. Through its capability of coupling a continuum approach with microscopic rheological models, the matrix formalism is a very flexible tool which enables one to use microscopic information to obtain explicit expressions for the matrix elements in (2.34) and for the thermodynamic functions. In this way, it is possible to relate the expressions of the forces in the microscopic structure to the macroscopic stress tensor, thus providing an explicit microscopic expression for it. This is especially useful to study the consequences of reasonable and appealing modifications of the microscopic models to obtain new macroscopic constitutive equations. In this way, the matrix model outlines the common features of very different rheological models (bead-rod-spring, transient network, reptation and configuration tensor models, for example).

#### 4. Concluding remarks

All the formalisms presented here outline a deep connection between thermodynamics and dynamics. Such a connection is subtler than in the local-equilibrium approach, where thermodynamics is given from the start and it imposes restrictions on the constitutive laws appearing in the dynamical equations. In general, the presence of additional non-equilibrium variables makes that neither the explicit form of the thermodynamics potentials nor the evolution equations of the additional variables are known a priori, and they must be specified simultaneously and in a mutual coherent way. The search of this coherent relation between thermodynamics and dynamics is the common feature of the different approaches commented here.

There are, in this context, two main aspects which particularise EIT with respect to the other approaches: (a) the choice of variables and (b) the emphasis on the exploration of the non-equilibrium equations of state. We briefly comment these two points:

Choice of the variables: in EIT, the variables chosen are the fluxes, which are more macroscopic than the usual internal variables, often related to the microstructure of the system, as for instance the configuration tensor. Of course, the microscopic expression for the fluxes differ from system to system.

Equations of state: they are obtained from the derivatives of the entropy or of the free energy or any other thermodynamic potential being used. It is usually assumed that the aim of non-equilibrium thermodynamics should be to impose restrictions on the constitutive laws. We have seen, however, that



both the thermodynamic potentials and the constitutive equations (evolution equations of the additional variables) must be specified in a joint and coherent way. The attention is usually focused on the constitutive equations, whereas the specific form of the potentials is not completely explored, but considered as an auxiliary tool. In contrast, in EIT we stress the role of the thermodynamic potential through the analysis and interpretation of the non-equilibrium equations of state and the exploration of their physical consequences.

Note that these equations of state correspond to forced systems, i.e. to systems which are subjected to external constraints which impose on them non-vanishing fluxes. This description would be approached by the system, as the time goes to infinity, after starting in an arbitrary state described by many more variables than in usual EIT (for instance, taking into account many higher-order fluxes). When the external non-equilibrium constraints are suppressed, the system would approach equilibrium and the EIT entropy would reduce to the classical equilibrium entropy. The role of entropy in the approach from a more detailed to a more reduced description in the long-time limit after elimination of the corresponding constraints has been emphasised by Grmela in his analyses of the thermodynamics of driven systems [53,54]. Note finally that a completely general treatment of forced systems would require to take into account situations where the system does not reach a stationary state, but dealing with these situations goes beyond the present formulations of EIT.

Of course, these two features do not make EIT a theory disconnected from the other ones. It is possible, for instance, to change variables and to compare with other theories. The most elegant way to proceed would be to establish Legendre transforms with respect to the fluxes and to relate these transformations to the mathematical expression of the external forcing, but this is an aspect which has not been sufficiently explored up to now. Furthermore, the other theories also have non-equilibrium equations of state, but in general they have not paid so much effort in giving a physical interpretation of them or in exploring their physical consequences, but this could (and should) be done. In fact, the comparison with the other theories is very stimulating in pointing new potentialities for each approach. Here are some of the conclusions of the comparison carried out along this paper.

#### 4.1. Comparison with theories with internal variables

The main difference is the choice of variables. We have already commented that the viscous pressure tensor is more general than the configuration tensor, because it is more macroscopic. For instance, it is true that for dilute polymer solutions,  $\mathbf{P}^v$  is directly related to the configuration tensor, but for ideal monatomic gases, a system without internal variables,  $\mathbf{P}^v$  is related to the second moments of the velocity distribution function. In this way, the use of  $\mathbf{P}^v$  as an independent variable allows one to encompass in a single formalism not only the viscoelasticity of polymer solutions, but also that of ideal gases. From a macroscopic point of view, the main difference between both systems is the very different value of the relaxation times of  $\mathbf{P}^v$ , which is of the order of seconds or even minutes in polymers and of picoseconds in gases and liquids of small molecules. For this reason, viscoelastic effects are clearly visible in polymer solutions, but they are only perceptible in ultrasound propagation or in light or neutron scattering experiments in gases and liquids. From the formal point of view, EIT writes the evolution equations of the fluxes as field variables, namely, by considering the fluxes of the fluxes; this allows for the description of non-local effects, instead of assuming purely relaxational equations for the internal variables.

#### 4.2. Comparison with GENERIC

We stress three points in the comparison between EIT and GENERIC. (a) The Jacobi identity arising in the latter approach imposes on the evolution equations some restrictions which are not found in EIT nor on other more classical thermodynamic formalisms. The physical consequences of such restrictions should be explored more explicitly and pedagogically than up to now. (b) GENERIC is especially useful beyond the second order of approximation in non-equilibrium perturbations. Up to the second order, all the approaches coincide. However, the requirement of positive entropy production is not sufficiently restrictive beyond the second order. We have seen that the use of the very non-linear form (2.24) for the entropy is necessary to obtain a general consistency with the microscopic expression (2.28) for the viscous pressure tensor. In EIT, an equivalent expression (1.25) for the entropy is obtained from maximum-entropy methods, but not from internal consistency arguments. (c) In GENERIC, one takes from the start any choice of variables. However, it is well known in thermodynamics that to have the complete thermodynamic information one must use a very precise set of thermodynamic potentials according to the variables used, as for instance  $S(U, V, n)$  or  $G(T, p, n)$ . The connection between the different possibilities is given in classical thermodynamics by Legendre transformations. It would be of interest to deal explicitly with this problem in GENERIC. The consideration of chemical potential  $\mu$  as  $\partial G/\partial n$  at  $Z$  constant may be an interesting situation.

#### 4.3. Comparison with GENERIC and the matrix model

EIT is a macroscopic (or mesoscopic) theory, and it takes from more microscopic theories the microscopic expressions for the entropy, the pressure tensor and the evolution equation for the distribution function. In contrast, GENERIC and the Matrix Model work at different levels, including the microscopic one, by setting consistency restrictions on the admissible form of the evolution equations, the entropy and the pressure tensor. This allows one to obtain in a consistent way constitutive equations from microscopic considerations, for instance, by introducing new features in a partially satisfactory microscopic model in order to improve it. For the moment, this combination of microscopic and macroscopic levels has not been explored in EIT. Note, however, that in EIT there has been a lot effort to compare with microscopic theories, which give a microscopic basis for the macroscopic equations of EIT (see for instance [8,9]). However, the microscopic equations (the Boltzmann equation, the microscopic form of the heat flux or the pressure tensor, ...) are taken as an independent information rather than being obtained from the formalism of EIT itself. In contrast, the formalisms of GENERIC or of Matrix Model often take as internal variable a suitable distribution function and they obtain some coherence relations between the kinetic equation for the distribution function and the microscopic form of the pressure tensor. It must be mentioned, nevertheless, that in some occasions the formalism of EIT has also been applied in this spirit to microscopic level [54,55].

In summary, in our opinion the present comparison of EIT, internal variables, GENERIC and Matrix Method shows that there is a wide common field of interest in these different approaches, and that there are deep relations between them. Furthermore, it points to the need of future developments which could make these relations more evident. We have pointed here the exploration of the consequences of the non-equilibrium equations of state for polymer solutions in the shear-induced phase transitions, which is a very interesting field with an interplay of dynamics and thermodynamics where the combination of the different techniques could probably prove very fruitful.

## Acknowledgements

We want to acknowledge many years of discussion on the foundations of EIT with Prof. G. Lebon, from Liège University (Belgium); the collaboration with Prof. M. Criado-Sancho, from UNED (Madrid, Spain), has been essential in our analyses of shear-induced phase transitions in polymer solutions. Fruitful discussions with Prof. M. Grmela, from Ecole Polytechnique de Montréal (Quebec, Canada) about Hamiltonian methods and Prof. H.C. Öttinger about some aspects of GENERIC are also acknowledged. We have received the financial support of the Dirección General de Investigación Científica y Técnica of the Spanish Ministry of Education under grant PB 94-0718, of European Union in the Program of Human Capital and Mobility (grant EBR-CHR XCT 920 007) and of the Direcció General de Recerca of the Generalitat of Catalonia (grant 1997 — SGR 00387).

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