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# Thermodynamics of Fluids Under Flow

*Second Edition*

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# Preface

The thermodynamics of flowing fluids is an active and very challenging topic in modern non-equilibrium thermodynamics and statistical mechanics. After ten years of publication of the first edition of this book, we felt that a fully renewed, updated and enlarged edition was necessary to cover some of the progress made in these fields. A book on the thermodynamics of flowing fluids was published in 1994 by A. N. Beris and S. J. Edwards, *Thermodynamics of Flowing Fluids with Internal Microstructure*, Oxford University Press, New York, 1994: it was based on the Poisson bracket formalism and focused on fluids with internal microstructure. The books by D. J. Evans and G. P. Morriss, *Statistical Mechanics of Nonequilibrium Liquids* (Australian National University E Press, 2007), A. Onuki, *Phase Transition Dynamics* (Cambridge University Press, 2002) and V. Garzó and A. Santos, *Kinetic theory of gases in shear flow* (Kluwer, Dordrecht, 2003) have also been useful and important contributions to a global vision of this field, the first with more emphasis on molecular dynamical simulations, the second one with special attention on critical phenomena, and the third one from the perspective of the kinetic theory of gases. The central perspective of the present book is, instead, on non-equilibrium thermodynamics beyond local equilibrium. The more macroscopic and phenomenological character of this approach allows to deal with a wider range of systems, going from ideal gases and phonon hydrodynamics to polymer solutions and melts, and to laminar and turbulent superfluids.

The interest of the thermodynamics of flowing fluids is both theoretical and practical. From the theoretical point of view, the influence of the flow on the thermodynamic potentials requires the formulation of thermodynamic theories beyond the local-equilibrium hypothesis; this is a field with many open challenges, which fosters an active dialogue between macroscopic and microscopic theories, the latter based either on the kinetic theory of gases, or on molecular dynamical simulations of fluids. Furthermore, it also requires an open discussion between thermodynamics and hydrodynamics, because some of the observed phenomena may have a purely thermodynamic origin (due to the modification of some equations of state) or a purely hydrodynamic origin, but in general there will be an interplay of both thermodynamics beyond the local-equilibrium regime, and its relationship with microscopic theories and with hydrodynamic theories currently represents an important frontier

of research. In our book by G. Lebon, D. Jou and J. Casas-Vázquez, *Understanding Non-equilibrium Thermodynamics. Foundations, Applications, Frontiers* (Springer, Berlin, 2008) we have discussed and examined in detail several different avenues towards the formulation of such thermodynamics beyond local equilibrium.

From the practical point of view, many situations of technological interest are present in flowing systems. Indeed, the modification of the thermodynamic equations of state for the chemical potential imply modifications in the phase diagram of substances in non-equilibrium steady states, or on the conditions of chemical equilibrium and stability. The ability to control the thermodynamic state of the system is essential in technology and also in fundamental science. For instance, much study has been devoted to flow-induced changes in the phase diagram of polymer solutions or in shear-induced flow of macromolecules. The practical importance of the problems arising under flow is easily understood. Most industrial processes take place in flowing fluids (pumping, extruding, injecting, molding, mixing...), in which the polymer macromolecules undergo different shear and elongational stresses, depending on the position. Thus, a flow-induced change of phase could take place in some positions and not in others, affecting both rheological and structural properties of the flow. The materials formed in these processes may be very sensitive to the extent of the phase transitions occurring in the fluids previous to solidification.

Other related fields of interest are the thermodynamically induced polymer degradation under flow, which may be important in viscous drag reduction, or in flows of polymer solutions through packed porous beds, as in membrane permeation or flow of oil through soil and rocks. Also, in biological experiments shear-induced precipitation and degradation of proteins has been observed, and new separation techniques have been devised on the effects of the interaction between viscous pressure and diffusion. Microfluidics and nanofluidics have experienced a strong development in the last ten years, opening new and surprising applications of flowing fluids at a minuscule scale. In particular, phonon hydrodynamics provides a useful phenomenological basis to analyze heat transport from the diffusive to the ballistic regimes, with application to nanosystems and nanowires, thin layers, tubular layers, porous superlattices and so on.

From a more fundamental point of view, some of the main experiments in nuclear and particle physics refer to the transition from nuclear hadronic to a quark-gluon plasma. This is pursued through very energetic ultrarelativistic collisions of heavy nuclei. The total duration of such collisions is of the order of five to ten times the mean time between successive collisions amongst nucleons in the nuclei. Therefore, the nuclei are rather far from local equilibrium during the collision and it is problematic to what extent an analysis based on the local-equilibrium equations of state for nuclear matter and for quark-gluon plasma and normal hydrodynamics may be sufficient to provide a reliable description of the transition. Efforts towards using more general non-equilibrium thermodynamic and hydrodynamic theories are a challenge in this field. Another topic where the flow has a deep influence on the fluids is in turbulent superfluids, where a tangle of quantized vortex filaments appears for sufficiently high values of the heat flow or of the relative

velocity between normal and superfluid components. This vortex tangle contributes to the internal friction of the fluid, and it is by itself an interesting phase of matter, constituted of vortex loops and filaments. Finally, at a more abstract level, understanding the meaning and the mutual relationships between several definitions of temperature and entropy finds in flowing fluids an interesting benchmark where explicit illustrations are possible.

From a thermodynamic perspective, the already mentioned book by Beris and Edwards was based on Hamiltonian formalisms, as Poisson brackets, which has achieved a more general and elegant formulation in the so-called GENERICS, which has been presented in detail by H. C. Öttinger in the book *Beyond Equilibrium Thermodynamics* (Wiley, New York, 2005). Here, instead, we adopt extended irreversible thermodynamics as our general framework, and we try to emphasise both the general thermodynamic structure underlying fluids without internal structure (namely, ideal gases, phonons, real gases, simple fluids) as well as fluids with internal structure (namely, polymer solutions and blends, and turbulent superfluids). In this way, this volume may be seen as a complement of our monograph D. Jou, G. Lebon and J. Casas-Vázquez, *Extended Irreversible Thermodynamics* (fourth edition, Springer, Berlin, 2010), dealing with a variety of problems that were not included in that volume for the lack of space.

A decisive step in the thermodynamic understanding of flowing fluids is to formulate a free energy depending explicitly on the characteristics of the flow. This important problem in non-equilibrium thermodynamics has not yet received as much attention as it deserves. It must be noted that several authors have preferred to follow another method, to analyse the phase separation or phase homogenization under shear from a dynamical point of view, i.e. by writing dynamical equations for the behaviour of concentration and velocity fluctuations and analysing the stability of the corresponding set of equations. Of course, the dynamical procedure has a wider range of potentialities than the pure thermodynamic analysis: the latter may be able to set the spinodal line limiting the regions of stability, but it certainly cannot give a detailed view of the processes of segregation of both phases, or about the changes in viscosity observed during the segregation. However, the existence of both methods is not contradictory, e.g., the dynamical method may describe the instability through the change of sign of an effective diffusion coefficient, but this change of sign is produced at the spinodal line, and this fact is related, in many situations, to the vanishing of the first derivative of an effective chemical potential with respect to the composition. Furthermore, the dynamical analysis cannot avoid the use of equations of state of the flowing fluid; therefore, to find and analyse equations of state in non-equilibrium conditions is always of interest. Thus, although there is a common ground for thermodynamical and dynamical analyses, both methods have their own advantages and disadvantages, so that it would be unwise to dismiss a priori either of them.

Here, we give a brief description of the contents of the book, and point to the changes made with respect to the first edition. In Chap. 1, we provide the general basis from a macroscopic point of view, or more precisely from the perspective of extended irreversible thermodynamics, and we compare it with other macroscopic

theories, as rational thermodynamics, theories with internal variables, and Hamiltonian theories. Chapters 2 and 3—the much enlarged outcomes of the Chap. 2 of the first edition—deal with ideal gases: in Chap. 2 we use information theory to describe the steady state of flowing ideal gases under Couette flow, and we explore in depth how several definitions of temperature behave in the presence of a non-vanishing viscous pressure, and how they relate to each other. Of course, in the absence of the viscous pressure all of them tend to the same value, identical to the local-equilibrium temperature. In Chap. 3 we remind the basic concepts of the kinetic theory description of flowing ideal gases, and we discuss with some detail the application of thermodynamic ideas to the flow of phonons in the so-called phonon hydrodynamics, with special emphasis on the application of this formalism to heat transfer in nanosystems. This requires taking into detailed consideration the boundary conditions for the slip heat flow along the walls of the system. This topic was not considered in the second edition.

Chapter 4 is devoted to non-ideal gases, with a comparison with some results of molecular dynamical simulations, and with an application to some thermodynamic and hydrodynamic aspects of relativistic ion collisions. Chapter 5 discusses the microscopic description of polymer solutions, as kinetic theory of dilute solutions, reptation model for concentrated solutions, and double-reptation model for polymer blends, to which much attention is devoted in further chapters. Chapter 6 analyzes the influence of a shear flow on the phase diagram of polymer solutions, and shear-induced phase transitions; the first edition was limited to dilute solutions whereas the present one incorporates also concentrated solutions and polymers blends. Chapter 7 considers dynamical effects, the role of hydrodynamically enhanced fluctuations, and provides an understanding of the range of application of the thermodynamic formalism. Chapters 8 and 9 enlarge the contents of Chap. 7 of the first edition. Chapter 8 deals with the couplings of viscous pressure and diffusion; in particular, much attention is devoted to shear-induced diffusion and its applications to macromolecular separation in cone-and-plate and in tube configurations. Chapter 9 is also devoted to diffusion in the presence of a velocity gradient, with special attention to Taylor dispersion and its applications, and to anomalous diffusion, both in a system at rest as in a fluid with a velocity gradient. Chapter 10 deals with chemical reactions under flow, both for ideal gases and polymer solutions; the latter case is applied to the analysis of polymer degradation due to the flow. Chapter 11 discusses the thermodynamics of flowing superfluids, not only in the well-known laminar regime, but also in the more intriguing and challenging turbulent regime, with quantized vortices. Appendix A is devoted to a survey of experimental information on the relevant material functions used for the evaluation of the non-equilibrium chemical potential in the examples considered in the book, and Appendix B briefly describes the results on the influence of a shear flow on the isotropic-nematic transition in liquid crystals. Appendices C–E contain other useful information related to mathematical results.

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# Contents

<b>1</b>	<b>Non-equilibrium Thermodynamics and Rheology</b>	1
1.1	A Short Review of Rheological Concepts	2
1.1.1	Basic Rheological Quantities	3
1.1.2	Basic Rheological Models	4
1.2	Extended Irreversible Thermodynamics	10
1.2.1	Viscous Pressure	11
1.2.2	Viscous Pressure and Diffusion Flux	14
1.3	Rational Extended Thermodynamics	17
1.4	Theories with Internal Variables	23
1.5	Hamiltonian Formulations	26
1.5.1	Microscopic Level: Distribution Function as an Internal Variable	28
1.5.2	Mesoscopic Level: Configuration Tensor as an Internal Variable	29
<b>2</b>	<b>Non-equilibrium Temperature and Entropy in Flowing Ideal Gases: Maximum-Entropy Approach</b>	33
2.1	Review of Some Basic Concepts	34
2.2	Information Theory: General Formalism	35
2.3	Information Analysis of an Ideal Gas Under Viscous Pressure	39
2.3.1	Non-equilibrium Entropy and Chemical Potential: General Formalism	42
2.3.2	Analysis of Plane Couette Flow: Pure Shear Effects	44
2.3.3	Plane Couette Flow: Shear and Normal Effects	47
2.4	Non-equilibrium Temperatures in Flowing Gases and Mixtures	50
2.5	Partition Function for a Flowing Relativistic Ideal Gas	54
<b>3</b>	<b>Kinetic Theory of Flowing Gases and Phonons. Phonon Hydrodynamics and Heat Transport in Nanosystems</b>	57
3.1	Kinetic Theory: Basic Concepts	57
3.1.1	H Theorem	58
3.1.2	Non-equilibrium Distribution Function	60

3.2	Grad's Approach .....	61
3.3	Comparison with Exact Results .....	63
3.4	Kinetic Theory of Phonons and Phonon Hydrodynamics .....	65
3.5	Poiseuille Phonon Flow and Heat Transport in Nanosystems .....	69
3.6	Boundary Conditions and Effective Thermal Conductivity in Smooth and Rough Nanowires .....	70
3.6.1	Heat Transfer in Thin Smooth Nanowires .....	71
3.6.2	Heat Transfer in Thin Rough Nanowires .....	72
3.7	Thermal Conductivity of Porous Silicon .....	74
<b>4</b>	<b>Non-ideal Fluids and Nuclear Collisions .....</b>	<b>79</b>
4.1	Modified Equations of State and Shift of Critical Point .....	80
4.1.1	Van der Waals Fluids .....	80
4.1.2	Regular Binary Solutions .....	83
4.1.3	Experimental Results .....	84
4.2	Kinetic Theory of Dilute Non-ideal Gases .....	85
4.3	Comparison with Computer Simulations .....	90
4.4	Nuclear Collisions .....	95
4.4.1	Internal Collective Flows and Information Theory .....	95
4.4.2	Generalised Gibbs Equation .....	96
4.4.3	Causal Dissipative Hydrodynamics .....	99
<b>5</b>	<b>Polymeric Solutions and Blends .....</b>	<b>101</b>
5.1	Kinetic Theory of Dilute Polymeric Solutions .....	102
5.1.1	Freely Jointed Chain .....	102
5.1.2	The Bead-and-Spring Rouse–Zimm Model .....	105
5.2	Derivation of the Steady-State Compliance .....	113
5.3	Maximum-Entropy Approach .....	115
5.4	Entangled Solutions. Reptation Model .....	116
5.5	Polymer Blends. Double Reptation Model .....	119
<b>6</b>	<b>Non-equilibrium Chemical Potential and Shear-Induced Effects in Polymer Solutions and Blends .....</b>	<b>123</b>
6.1	Survey of Experimental Results .....	124
6.2	Equilibrium Chemical Potential and Stability Analysis .....	127
6.3	Non-equilibrium Chemical Potential and Stability Analysis .....	129
6.3.1	The Choice of Non-equilibrium Variables: Viscous Pressure or Configuration Tensor .....	129
6.3.2	Stability Analysis .....	132
6.3.3	Two-Fluids Model .....	133
6.4	Phase Diagram of Polymer Solutions Under Shear Flow .....	134
6.4.1	Dilute and Semidilute Polymer Solutions .....	135
6.4.2	Entangled Solutions .....	138
6.5	A Practical Illustration: Flow Effects in Polymer Extraction from a Porous Matrix .....	141

6.6	Flow-Induced Effects in Polymer Blends: Two-Fluid Approach and Extended Approach .....	144
6.6.1	Two-Fluid Approach .....	145
6.6.2	Extended Approach .....	147
6.7	Non-Newtonian Effects in Phase Separation .....	149
6.8	Other Approaches: Flexibility and Droplet Approaches .....	151
6.8.1	The Flexibility Approach .....	151
6.8.2	The Droplet Approach .....	152
<b>7</b>	<b>Comparison of Thermodynamical and Dynamical Approaches .....</b>	<b>155</b>
7.1	Dynamical Derivation and Generalization of Thermodynamical Stability Criteria .....	156
7.1.1	Situations Without Coupling Between Diffusion and Shear .....	157
7.1.2	Situations with Coupling Between Diffusion and Shear .....	159
7.2	Structure Factor .....	161
7.2.1	Generalized Ginzburg–Landau Potential in Flowing Systems .....	162
7.2.2	Dynamical Contributions to the Chemical Potential .....	164
7.3	Derivation of the Structure Factor .....	165
7.3.1	Evolution Equations .....	165
7.3.2	Equations of State .....	166
7.3.3	Flow Contribution to the Structure Factor .....	167
<b>8</b>	<b>Shear-Induced Migration and Flow Chromatography .....</b>	<b>171</b>
8.1	Shear-Induced Migration of Polymers .....	171
8.1.1	The Simplest Model for Shear-Induced Migration .....	172
8.1.2	Non-equilibrium Chemical Potential and Effective Diffusion Coefficient .....	174
8.2	Shear-Induced Concentration Banding and Macromolecular Separation in Cone-and-Plate Flows .....	180
8.3	Shear-Induced Migration and Molecular Separation in Tubes .....	184
<b>9</b>	<b>Taylor Dispersion and Anomalous Diffusion .....</b>	<b>187</b>
9.1	Brownian Motion in Shear Flow .....	188
9.2	Taylor Dispersion and Microfluidics .....	190
9.3	Taylor Dispersion for Short and Intermediate Times .....	192
9.3.1	Evolution Equation for the Flow of Matter .....	193
9.3.2	Evolution of Effective Diffusion Coefficient: From Reversible to Irreversible Behaviours .....	193
9.3.3	Entropy and Entropy Flux: From Exhaustive Information to the Relevant Information .....	194
9.4	Anomalous Diffusion and Non-equilibrium Thermodynamics .....	197
9.4.1	Classical Irreversible Thermodynamics and Diffusion .....	197

9.4.2	Non-conventional Statistical Mechanics .....	198
9.4.3	Generalized Thermodynamics and Anomalous Diffusion .....	200
9.5	Anomalous Diffusion in Flowing Systems .....	203
9.6	Taylor Dispersion and Anomalous Diffusion .....	205
9.7	Diffusion on Fractals .....	206
<b>10</b>	<b>Chemical Reactions and Polymer Degradation Under Flow .....</b>	<b>211</b>
10.1	Thermodynamic Formulation .....	211
10.2	Shear-Induced Polymer Degradation: Kinetic Analysis .....	214
10.3	Shear-Induced Polymer Degradation: Thermodynamic Analysis .....	218
10.4	Kinetic Theory of Chemical Reactions .....	222
10.5	Recurrence Method for Probability Weight Distribution Under Viscous Pressure .....	225
<b>11</b>	<b>Non-equilibrium Thermodynamics of Laminar and Turbulent Superfluids .....</b>	<b>229</b>
11.1	Essential Concepts and Phenomena of Superfluids .....	230
11.2	The Two-Fluid Model and Second Sound .....	231
11.2.1	Evolution Equations and Wave Propagation .....	232
11.2.2	Thermodynamics of Superfluid Helium .....	235
11.3	The Extended One-Fluid Model of Liquid Helium II .....	236
11.4	Quantized Vortices in Rotation and Counterflow .....	239
11.4.1	Macroscopic Description of Vortex Friction .....	241
11.4.2	Rotating Frame .....	242
11.4.3	Counterflow Turbulence .....	242
11.5	Second Sound Propagation in the Presence of Quantized Vortices .....	244
11.5.1	Rotating Cylinders .....	244
11.5.2	Second Sound and Counterflow Turbulence .....	245
11.6	Evolution Equation for the Vortex Line Density .....	246
11.6.1	Transition from the Laminar to the Turbulent Regime .....	247
11.6.2	Simultaneous Rotation and Counterflow .....	249
11.6.3	Non-equilibrium Thermodynamics of Vortex Tangles ...	250
11.7	Hydrodynamics of Turbulent Superfluids .....	253
<b>Appendix A</b>	<b>Experimental Data on Polymer Solutions .....</b>	<b>257</b>
A.1	Polystyrene in Dioctyl-Phthalate (PS/DOP) .....	257
A.2	Polystyrene in Transdecalin (PS/TD) .....	258
A.3	Polystyrene Dissolved in Oligomeric Polystyrene .....	260
<b>Appendix B</b>	<b>Liquid Crystals .....</b>	<b>263</b>
B.1	Equilibrium Thermodynamics and the Isotropic-Nematic Phase Transition .....	263

- B.1.1 Phase Transition Induced by Temperature Changes ..... 264
- B.1.2 Phase Transition Induced by Density Changes ..... 265
- B.2 Dynamic Equations in the Presence of a Flow ..... 266
- B.3 Thermodynamic Formulation ..... 269
- B.4 Maximum-Entropy Approach ..... 270
  
- Appendix C Summary of Vector and Tensor Notation ..... 273**
  - C.1 Symmetric and Antisymmetric Tensors ..... 273
  - C.2 Decomposition of a Tensor ..... 273
  - C.3 Scalar (or Dot) and Tensorial (Inner) Products ..... 274
  - C.4 (Inner) Tensorial Product (Also Named Dyadic Product) ..... 274
  - C.5 Cross Multiplication Between Two Vectors and Between  
a Tensor and a Vector ..... 275
  - C.6 Differentiation ..... 275
  - C.7 Tensor Invariants ..... 276
  
- Appendix D Useful Integrals in the Kinetic Theory of Gases ..... 277**
  
- Appendix E Some Physical Constants ..... 279**
  
- References ..... 281**
  
- Index ..... 297**

# Chapter 1

## Non-equilibrium Thermodynamics and Rheology

Local-equilibrium thermodynamics assumes that the equations of state retain the same form out of equilibrium as in equilibrium, but with a local meaning (Prigogine 1961; De Groot and Mazur 1962; Gyarmati 1970). According to this point of view, there is not strictly any especial thermodynamic features characteristic of flowing fluids, since the 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, in which case the flow may influence the thermodynamic equations of state through its action on such internal variables. In such occasions (Meixner 1949, 1954; Verhas 1997; Lhuillier and Ouibrahim 1980; Maugin and Drouot 1983; Maugin and Muschik 1994a, b, Maugin 1999) one includes in the set of thermodynamic variables some internal variables describing the relevant details of the microstructure of the system, such as, for instance, the polymeric configuration.

In the 1960s was proposed the so-called rational thermodynamics (Truesdell 1971, 1984), which assumes that the entropy and the (absolute) temperature are primitive quantities, not restricted to situations near local-equilibrium. Instead of a local-equilibrium assumption, it was assumed that the entropy, or the free energy, could depend on the history of the strain, or of the rate of strain, or of the temperature gradient, thus allowing for an explicit influence of the flow on the thermodynamic analysis through the history of these non-equilibrium variables. The theory developed a powerful and elegant formalism to obtain thermodynamic restrictions on the memory functions relating viscous stress to the history of the strain. However, the analysis was centred on the constitutive equations, but it paid little attention to the consequences of the generalised entropy on the non-equilibrium equations of state.

At the end of the 1960s, a new approach, called extended irreversible thermodynamics (EIT) (Jou et al. 1988, 1992, 1996, 1998, 1999, 2010; Müller and Ruggeri 1998; Sieniutycz and Salamon 1992; Eu 1992, 1998, 2002; Wilmanski 1998; Nettleton and Sobolev 1995a, b, 1996), was proposed and it was much developed during the 1980s and 1990s. (For a wide bibliography on this topic see <http://telemaco.uab.es> or Nettleton and Sobolev 1995a, b, 1996; Jou et al. 1988, 1992, 1998, 1999, 2010). This theory assumes that the entropy depends, besides the classical variables, on the 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 (Maxwell–Cattaneo equation) or the viscous pressure tensor (Maxwell viscoelastic fluids) compatible with the positiveness of the entropy production, which is not satisfied, in general, when such generalised transport equations are combined with the local-equilibrium entropy. The direct influence of the viscous pressure tensor and other fluxes on the thermodynamic potentials clearly opens a way towards a thermodynamics under flow.

Once the expression of the entropy is known, there is no difficulty in deriving the corresponding equations of state, which are directly obtained as the first derivatives of the entropy with respect to the basic variables. Thus, EIT links the generalised transport equations with generalised equations of state which contain non-equilibrium contributions. A natural question concerns the physical meaning of these equations of state which, of course, depend on the fluxes and therefore differ from their analogous local-equilibrium expressions. Recall that in classical thermodynamics, the first derivatives of the entropy with respect to the internal energy, the volume and the number of moles are related to the absolute temperature, the pressure, and the chemical potential, respectively. At this point, it may be asked whether the derivatives of the generalised entropy introduced in EIT still enable one to define an absolute non-equilibrium temperature as well as a non-equilibrium pressure and a non-equilibrium chemical potential. This is a very subtle question which has, however, received partial answers in recent years, after that some specific thought experiments were proposed (Casas-Vázquez and Jou 1994) a real experiment was interpreted (Luzzi et al. 1997) and non-equilibrium molecular dynamics simulations were carried out (Baranyai 2000a, b; Daivis 2008). Here, we will mainly concentrate our attention on the equation of state for the chemical potential at a given temperature and pressure; this will play a central role in Chaps. 6–10.

In this chapter, we provide a short introduction to the basic rheological concepts. Furthermore, we present EIT, both as an extension of the classical theory and of the rational thermodynamics, and we compare it with two alternative thermodynamic theories: the internal variable approach and the Hamiltonian formalisms. We have not aimed to be exhaustive, but only to provide the necessary basis to work out the consequences of the non-equilibrium equations of state; therefore, we have omitted a comparison with other valuable theories, such as the matrix model of irreversible processes (Jongschaap 1990), or variational approaches (Sieniutycz 1994). Sections 1.3 and 1.5 correspond to a slightly more advanced and specialised level: they may be skipped in a first reading, but will be stimulating to the researcher interested in going beyond the linear approximation presented in Sects. 1.2 and 1.4.

## 1.1 A Short Review of Rheological Concepts

Since we are dealing with flowing fluids, it is not surprising that in our analysis we will often find rheological quantities, rheology being the science of flow. Here, we provide a short review of some basic rheological concepts and of the most



widely used rheological models. The knowledge of these is necessary since we will often relate rheology and thermodynamics. It must be emphasized that we have attempted to focus our attention on the concepts necessary for the purposes of the present monograph, rather than to provide an extensive account of the wide topic of rheology.

### 1.1.1 Basic Rheological Quantities

A central quantity in fluid mechanics and rheology is the viscous pressure tensor  $\mathbf{P}^v$ , which describes the forces between neighbouring fluid elements moving at different speeds. The knowledge of these forces is necessary to describe the evolution of the flow. The relation between the viscous pressure tensor and the velocity gradient, the tensor describing the local features of the flow, plays an essential role in rheology. The coefficients relating these tensors depend on the fluid being considered and are the basic quantities of interest in rheology. The main coefficients are defined by considering the simplest flow exhibiting a velocity gradient, namely, the plane Couette flow, i.e. the flow between two plane parallel layers moving at different speeds.

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

$$P_{12}^v = -\eta(\dot{\gamma})\dot{\gamma}, \quad (1.1a)$$

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

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

where  $P_{ij}^v$ , with  $i, j = 1, 2, 3$  indicate components of the viscous pressure tensor  $\mathbf{P}^v$  and  $\dot{\gamma}$  the shear rate in a planar Couette flow, i.e.  $\dot{\gamma} = \partial v_x / \partial v_y$ . We will often take as component  $x$  or 1 the component along the velocity,  $y$  or 2 the component along the velocity gradient, and  $z$  or 3 the component orthogonal to the two previous ones. In the so-called Newtonian fluids, the normal stress coefficients vanish. Recall that  $\mathbf{P}^v$  is 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.

In non-steady situations some memory effects, such as those described in viscoelastic models, appear. The rheological properties thus depend on the frequency of the perturbation: for instance, viscoelastic liquids are materials which 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 shear linear viscoelastic effects are usually summarized in terms of a complex viscosity  $\eta^*(\omega)$ , or, alternatively, in terms of two other complex functions: a

complex stress–strain modulus  $G^*(\omega)$ ; or a complex compliance  $J^*(\omega)$ . Assuming the simplest oscillatory behaviour for the shear strain  $\gamma$  and the shear stress  $P_{12}^v$

$$\gamma = \gamma^0 \cos \omega t, \quad P_{12}^v = P_{12}^{v0} \cos \omega t, \quad (1.2)$$

with  $\gamma^0$  and  $P_{12}^{v0}$  the amplitudes of the respective oscillations, the coefficients  $\eta^*(\omega)$ ,  $G^*(\omega)$  and  $J^*(\omega)$  are defined as (Ferry 1980; Coleman et al. 1966; Tanner 1988; Bird et al. 1987a)

$$P_{12}^{v0} = -\eta^*(\omega)\dot{\gamma}^0, \quad (1.3a)$$

$$P_{12}^{v0} = -G^*(\omega)\gamma^0, \quad (1.3b)$$

$$\gamma^0 = -J^*(\omega)P_{12}^{v0}, \quad (1.3c)$$

where  $\gamma^0$  and  $\dot{\gamma}^0$  are the amplitudes of the oscillatory shear strain and shear rate, respectively. These three functions are closely related to each other, stemming from their definition, by means of

$$\eta^*(\omega) = (i\omega)^{-1}G^*(\omega), \quad J^*(\omega) = 1/G^*(\omega), \quad (1.4)$$

where  $i$  is the imaginary unit.

The three mentioned quantities are often split in their real and imaginary parts as

$$J^*(\omega) = J' - iJ'', \quad G^*(\omega) = G' + iG'', \quad \eta^*(\omega) = \eta' - i\eta''. \quad (1.5)$$

Complex quantities are used here to account both for the response in phase with the perturbation (real part) as the response 90° out of phase (imaginary part). Note that  $J'(\omega)$  is the strain in phase with stress divided by the stress, so that it is a measure of the energy stored and recovered per cycle, while  $J''(\omega)$  is the strain 90° out of phase with the stress divided by the stress, and it is a measure of the energy lost into heat per cycle. It is not then surprising that the compliance will play an important role in the connection between thermodynamics and rheology.

### 1.1.2 Basic Rheological Models

In the study of polymeric systems it is assumed 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, which will account for the different behaviours observed at low and high frequency. Such a relaxational contribution is usually written in terms of a frame-indifferent time derivative (Ferry 1980; Coleman et al.

1966; Tanner 1988; Bird et al. 1987a), as the co-rotational derivative or the upper convected derivative, rather than in terms of the material time derivative. We will discuss here these different time derivatives, leading to different rheological models.

### 1.1.2.1 Linear Viscoelastic Models

In the simplest Maxwell model, the viscous pressure tensor is described by the constitutive equation

$$\frac{d\mathbf{P}^v}{dt} = -\frac{1}{\tau}\mathbf{P}^v - 2\frac{\eta}{\tau}\mathbf{V}, \quad (1.6)$$

with  $\mathbf{V}$  the symmetric part of the velocity gradient, whose components are given by  $V_{ij} = (1/2)[(\partial v_j/\partial x_i) + (\partial v_i/\partial x_j)]$ , and 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 characteristic of a viscous fluid, namely  $\mathbf{P}^v = -2\eta\mathbf{V}$ , whereas for fast perturbations, with characteristic time  $t$  of the order of  $\tau$  or less, it behaves as an elastic solid with  $\mathbf{P}^v$  standing for the elastic pressure,  $\mathbf{P}^v = -2G(\nabla\mathbf{X})^s$ ,  $\mathbf{X}$  being the deformation vector field, and  $G = \eta/\tau$  being related to the elastic Young modulus of the material.

However, the material time derivative used in (1.6) is not very satisfactory, neither from a theoretical viewpoint, since it is not invariant under rigid rotations, nor on the practical predictions, and it must be substituted by some frame-indifferent derivatives which are invariant under rigid motions of the system. The simplest example of such derivatives is the co-rotational time derivative

$$\frac{D\mathbf{P}^v}{Dt} = \frac{d\mathbf{P}^v}{dt} + \mathbf{W} \cdot \mathbf{P}^v - \mathbf{P}^v \cdot \mathbf{W}, \quad (1.7)$$

where  $\mathbf{W}$  is the antisymmetric part of the velocity gradient, whose components are given by  $W_{ij} = (1/2)[(\partial v_j/\partial x_i) - (\partial v_i/\partial x_j)]$ . This derivative describes the rate of change of  $\mathbf{P}^v$  as seen in a local reference system which rotates with the fluid. Other widely used frame-indifferent time derivatives are the upper or contravariant convected time derivative, namely

$$D^\uparrow\mathbf{P}^v = \frac{d\mathbf{P}^v}{dt} - [(\nabla\mathbf{v})^T \cdot \mathbf{P}^v + \mathbf{P}^v \cdot (\nabla\mathbf{v})], \quad (1.8a)$$

or the lower or covariant convected time derivative

$$D_\downarrow\mathbf{P}^v = \frac{d\mathbf{P}^v}{dt} + (\nabla\mathbf{v}) \cdot \mathbf{P}^v + \mathbf{P}^v \cdot (\nabla\mathbf{v})^T, \quad (1.8b)$$

where superscript  $T$  indicates transposition.

If one uses (1.8a) instead of the material time derivative, one has the upper-convected Maxwell model (Ferry 1980; Coleman et al. 1966; Tanner 1988; Bird et al. 1987a) for which the evolution equation for the viscous pressure tensor  $\mathbf{P}^v$  has the form

$$\frac{d\mathbf{P}^v}{dt} - (\nabla\mathbf{v})^T \cdot \mathbf{P}^v - \mathbf{P}^v \cdot (\nabla\mathbf{v}) = -\frac{1}{\tau}\mathbf{P}^v - 2\frac{\eta}{\tau}\mathbf{V}. \quad (1.9)$$

If, instead of (1.8a), the time derivative (1.8b) is used, one has the so-called lower-convected Maxwell model.

The fluid will be considered as incompressible from here on. This implies that  $\nabla \cdot \mathbf{v} = 0$  and since  $\nabla \cdot \mathbf{v}$  is the trace of the  $\nabla\mathbf{v}$  tensor one could think that this will mean that the trace of the viscous pressure tensor will also vanish, i.e.  $\text{Tr}\mathbf{P}^v = 0$ . However, though it is true that 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 appear, giving a non-vanishing trace of  $\mathbf{P}^v$ .

For further discussions it will be convenient to have explicit expressions for  $\mathbf{P}^v$  in some steady flows. In a purely shear flow corresponding to  $\mathbf{v} = (v_x(y), 0, 0)$ , the velocity gradient tensor, is

$$\nabla\mathbf{v} = \begin{pmatrix} 0 & 0 & 0 \\ \dot{\gamma} & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}, \quad (1.10)$$

where  $\dot{\gamma}$  is the shear rate. Introduction of (1.10) into (1.7) yields, in the steady situation, for the co-rotational Maxwell model

$$\mathbf{P}^v = \begin{pmatrix} -\tau\eta\dot{\gamma}^2(1 + \tau^2\dot{\gamma}^2)^{-1} & -\eta\dot{\gamma}(1 + \tau^2\dot{\gamma}^2)^{-1} & 0 \\ -\eta\dot{\gamma}(1 + \tau^2\dot{\gamma}^2)^{-1} & \tau\eta\dot{\gamma}^2(1 + \tau^2\dot{\gamma}^2)^{-1} & 0 \\ 0 & 0 & 0 \end{pmatrix}, \quad (1.11)$$

and therefore the steady-state viscometric functions are

$$P_{12}^v = -\eta\dot{\gamma}(1 + \tau^2\dot{\gamma}^2)^{-1}, \quad (1.12a)$$

$$P_{11}^v - P_{22}^v = -2\tau\eta\dot{\gamma}^2(1 + \tau^2\dot{\gamma}^2)^{-1}, \quad (1.12b)$$

$$P_{22}^v - P_{33}^v = \tau\eta\dot{\gamma}^2(1 + \tau^2\dot{\gamma}^2)^{-1}. \quad (1.12c)$$

For the upper-convected Maxwell model (1.9), one has

$$\mathbf{P}^v = \begin{pmatrix} -2\tau\eta\dot{\gamma}^2 & -\eta\dot{\gamma} & 0 \\ -\eta\dot{\gamma} & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}. \quad (1.13)$$

The corresponding steady-state viscometric functions are thus

$$P_{12}^v = -\eta\dot{\gamma}, \quad P_{11}^v - P_{22}^v = -2\tau\eta\dot{\gamma}^2, \quad P_{22}^v - P_{33}^v = 0, \quad (1.14)$$

so that the second normal stress is zero and the first normal stress coefficient  $\Psi_1$  is

$$\Psi_1(\dot{\gamma}) = 2\tau\eta. \quad (1.15)$$

For the lower-convected Maxwell model, the viscous pressure tensor in the steady state is given by

$$\mathbf{P}^v = \begin{pmatrix} 2\tau\eta\dot{\gamma}^2 & -\eta\dot{\gamma} & 0 \\ -\eta\dot{\gamma} & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}. \quad (1.16)$$

and therefore, the viscometric coefficients are given by

$$P_{12}^v = -\eta\dot{\gamma}, \quad P_{11}^v - P_{22}^v = 2\tau\eta\dot{\gamma}^2, \quad P_{22}^v - P_{33}^v = 0. \quad (1.17)$$

It turns out that the upper-convected model agrees rather satisfactorily with a wide range of experimental results, while the predictions (1.17) of the lower-convected model or (1.12) of the co-rotational model are at variance with experiments.

Another flow of much viscometric and practical interest is the planar extensional flow, in which the velocity field has two components  $\mathbf{v} = (v_x(x), v_y(y), 0)$ , such that its gradient takes the form

$$\nabla\mathbf{v} = \begin{pmatrix} \dot{\epsilon} & 0 & 0 \\ 0 & -\dot{\epsilon} & 0 \\ 0 & 0 & 0 \end{pmatrix}, \quad (1.18)$$

with  $\dot{\epsilon} (= \partial v_x / \partial x = -\partial v_y / \partial y)$  the extensional rate. In the steady state, (1.6) yields

$$\mathbf{P}^v = \begin{pmatrix} -2\eta\dot{\epsilon}(1 - 2\tau\dot{\epsilon})^{-1} & 0 & 0 \\ 0 & 2\eta\dot{\epsilon}(1 + 2\tau\dot{\epsilon})^{-1} & 0 \\ 0 & 0 & 0 \end{pmatrix}. \quad (1.19)$$

The expressions of  $\mathbf{P}^v$  for the other viscoelastic models may easily be obtained.

In the previous Maxwell models we have considered only one relaxation time. In many cases, one must consider that  $\mathbf{P}^v$  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 (1.6) or (1.9), characterized by its own viscosity  $\eta_j$  and relaxation time  $\tau_j$ . These independent contributions arise from the different internal degrees of freedom of the macromolecule, as will be explained in detail in Chap. 5. These models are known as generalised Maxwell models.

It is often useful, in linear models for viscoelasticity, to write the viscous pressure tensor in terms of a memory function as

$$\mathbf{P}^v = - \int_{-\infty}^t G(t-t') \dot{\gamma}(t') dt' \quad (1.20)$$

where the memory function  $G(t-t')$  is known as the relaxation modulus, and  $\dot{\gamma}$  as the rate-of-strain tensor, which is twice  $\mathbf{V}$ . The Fourier transform of  $G(t-t')$  is the complex strain–stress modulus  $G^*(\omega)$  defined in (1.3). In a generalised Maxwell model, one has for  $G(t-t')$

$$G(t-t') = \sum_j (\eta_j / \tau_j) \exp[-(t-t') / \tau_j], \quad (1.21)$$

with  $\eta_i$  and  $\tau_i$  the different viscosities and relaxation times corresponding to the different degrees of freedom of the macromolecules (see Chap. 5). If one has only one relaxation time, this expression is the one corresponding to the simple Maxwell model (1.6). Note that for  $t=t'$  one has  $G(0) = \eta/\tau$  and therefore, according to (1.4b) the compliance is  $J(0) = \tau/\eta$ . The value  $J(0)$  is usually called the steady-state compliance, and it will appear in the generalised Gibbs Eq. (1.31).

In a small-amplitude oscillatory motion, integration of (1.20) and the use of the definitions (1.3–1.5) of  $\eta^*$  and  $G^*$  yields

$$\eta'(\omega) = \sum_j \eta_j [1 + (\tau_j \omega)^2]^{-1}, \quad \eta''(\omega) = \sum_j \eta_j \tau_j \omega [1 + (\tau_j \omega)^2]^{-1}, \quad (1.22)$$

or

$$G'(\omega) = \sum_j \eta_j \tau_j \omega^2 [1 + (\tau_j \omega)^2]^{-1}, \quad G''(\omega) = \sum_j \eta_j \omega [1 + (\tau_j \omega)^2]^{-1}, \quad (1.23)$$

where  $\eta_i$  and  $\tau_i$  now correspond to the  $i$ th degree of freedom.

### 1.1.2.2 Non-linear Viscoelastic Models

In the models defined by (1.6) or (1.9), the viscometric coefficients do not depend on the shear rate. However, there are many phenomena which show that, in general, the viscometric functions depend in a complicated way on the shear rate and which require non-linear constitutive equations for their description. For instance, many fluids exhibit a decrease in viscosity with increasing shear rate, an effect known as “shear thinning” (or pseudoplasticity). A few fluids (usually concentrated suspensions of very small particles) exhibit the opposite behaviour, namely, an increase of viscosity with shear rate, which is known as “shear thickening” (or dilatancy).

Still another non-linear effect is viscoplasticity, which is shown by fluids (such as paints and pastes) which do not flow unless they are acted on by a shear higher than a threshold value.

A well known and rather general non-linear model is the so-called eight-constants Oldroyd model (Ferry 1980; Coleman et al. 1966; Tanner 1988; Bird et al. 1987a), defined by the following constitutive equation

$$\begin{aligned} \mathbf{P}^v + \lambda_1 \mathbf{P}_{(1)}^v + \frac{1}{2} \lambda_3 (\mathbf{V} \cdot \mathbf{P}^v + \mathbf{P}^v \cdot \mathbf{V}) + \frac{1}{2} \lambda_5 (\text{Tr} \mathbf{P}^v) \mathbf{V} + \frac{1}{2} \lambda_6 (\mathbf{P}^v : \mathbf{V}) \mathbf{U} \\ = -\eta_0 \left[ \mathbf{V} + \lambda_2 \mathbf{V}_{(1)} + \lambda_4 \mathbf{V} \cdot \mathbf{V} + \frac{1}{2} \lambda_7 \mathbf{V} : \mathbf{V} \mathbf{U} \right] \end{aligned} \quad (1.24)$$

where  $\mathbf{U}$  is the unit tensor and  $\mathbf{V}_{(1)}$  is the convected time derivative of  $\mathbf{V}$ , the symmetric part of the velocity gradient, and  $\mathbf{P}_{(1)}^v$  is the convected time derivative of  $\mathbf{P}^v$ . For a steady shear flow, its explicit form is

$$\mathbf{V}_{(1)} = \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \frac{d\dot{\gamma}}{dt} - 2 \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \dot{\gamma}^2. \quad (1.25)$$

It follows from (1.24) and (1.25), after a cumbersome but straightforward calculation, that in steady-state shear flow the viscometric functions are

$$\frac{\eta}{\eta_0} = \frac{1 + \sigma_2 \dot{\gamma}^2}{1 + \sigma_1 \dot{\gamma}^2}, \quad (1.26)$$

with  $\sigma_i = \lambda_i(\lambda_3 + \lambda_5) + \lambda_{i+2}(\lambda_1 - \lambda_3 - \lambda_5) + \lambda_{i+5}(\lambda_1 - \lambda_3 - \frac{3}{5}\lambda_5)$ , and

$$\frac{\psi_1}{2\eta_0\lambda_1} = \frac{\eta(\dot{\gamma})}{\eta_0} - \frac{\lambda_2}{\lambda_1}, \quad (1.27)$$

$$\frac{\psi_2}{\eta_0\lambda_1} = -\frac{\psi_1}{2\eta_0\lambda_1} + \frac{\lambda_1 - \lambda_3}{\lambda_1} \frac{\eta}{\eta_0} - \frac{\lambda_2 - \lambda_4}{\lambda_1}. \quad (1.28)$$

The 8-constants Oldroyd model is very general, and we recover from it several especially interesting and widely used models. Indeed, the linear model (1.9) is obtained from (1.24) when  $\lambda_2 = \dots = \lambda_7 = 0$ . Furthermore, other well known non-linear models which are special cases of (1.24) are:

- the second-order Rivlin–Ericksen fluid ( $\lambda_1 = \lambda_3 = \lambda_5 = \lambda_6 = \lambda_7 = 0$ ), for which the viscometric functions are  $\eta = \eta_0$ ,  $\Psi_1 = -2\eta_0\lambda_2$ ,  $\Psi_2 = \eta_0\lambda_4$ ;
- the co-rotational Jeffreys model, for which  $\lambda_3 = \lambda_1$ ,  $\lambda_4 = \lambda_2$ ,  $\lambda_5 = \lambda_6 = \lambda_7 = 0$ , for which the viscometric functions are  $\eta(\dot{\gamma})$ ,  $\psi_1(\dot{\gamma})$  and  $\Psi_2 = -\frac{1}{2}\Psi_1$ ;
- the convected Jeffreys model ( $\lambda_3 = \lambda_4 = \lambda_5 = \lambda_6 = \lambda_7 = 0$ ), and, therefore, the viscometric functions are  $\eta = \eta_0$ ,  $\Psi_1 = 2\eta_0(\lambda_1 - \lambda_2)$  and  $\Psi_2 = 0$ .

In fact, the Oldroyd model is not truly universal, because the variation in viscosity predicted by (1.26) is too low to describe some real materials, in which the viscosity changes a hundred-fold in a finite range of shear rate. In (1.24), the coefficients  $\lambda_i$  are assumed not to depend on the shear rate. In more general situations, they could be functions of the scalar invariants of the velocity gradient. In some situations described below we will mention some of these non-linear models, but, in general, our analysis will be restricted to linear situations.

## 1.2 Extended Irreversible Thermodynamics

After having reviewed the most usual constitutive equations for viscoelastic fluids, we start the analysis of the thermodynamic aspects. First of all, we recall the basic ideas of the classical formulation of irreversible thermodynamics (Prigogine 1961; De Groot and Mazur 1962; Gyarmati 1970), which is based on the local equilibrium hypothesis. It states that, despite the inhomogeneous nature of the system, i.e. the values of its physical quantities differ from place to place, 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.

By combining the Gibbs equation and the evolution equations for mass, momentum and energy, one obtains an expression for the evolution equation for the entropy, with explicit forms for the entropy flux and the entropy production in terms of the fluxes (heat flux, diffusion flux, viscous pressure tensor, reaction rates) and of the conjugated thermodynamic forces, which are expressed as functions of the gradients of temperature, chemical potential, velocity, and of the chemical affinities of the reactions.

Finally, one relates the fluxes to the forces by means of constitutive equations which are required to obey the positive character of the 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 must obey the reciprocity relations established by Onsager and Casimir.

In this book, we want to focus our attention on the characteristic new aspects that the flow implies on the thermodynamics. As has been said, the classical theory retains the classical Gibbs equation, and therefore the thermodynamic relations are not changed by the presence of a flow. Therefore, instead of presenting all the details of the classical theories, we will directly write the main ideas and concepts of extended irreversible thermodynamics (EIT), which will be the basis of the analyses in this monograph, and we will explain how they reduce to the corresponding local-equilibrium expressions.

EIT, which has been widely discussed in the companion volume (Jou et al. 2010), assumes that the entropy may depend, in addition to the classical variables, on the



dissipative fluxes. In Sect. 1.2.1, we discuss a one-component fluid, in which we neglect thermal conduction and consider that the only non-equilibrium quantity in the space of independent thermodynamic variables is the viscous pressure tensor (Jou et al. 2010; Lebon et al. 1986, 1988). In Sect. 1.2.2, we consider a two-component mixture and incorporate the effects of the diffusion flux, which will play an important role in Chaps. 7–10.

### 1.2.1 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  $\mathbf{P}^v$

$$ds = T^{-1}du + T^{-1}pdv - \frac{\tau v}{2\eta T} \mathbf{P}^v : d\mathbf{P}^v, \quad (1.29)$$

with  $u$  and  $v$  the specific internal energy and the specific volume,  $T$  and  $p$  the absolute temperature and the thermodynamic pressure,  $\eta$  the shear viscosity and  $\tau$  the relaxation time of  $\mathbf{P}^v$  as defined in (1.6) or (1.9). To avoid unnecessary formal complications we use as a variable the whole tensor  $\mathbf{P}^v$ , instead of splitting it into the trace and the corresponding traceless part. In Sect. 1.2.2, a derivation of (1.29) will be presented. The first two terms on the right-hand side on (1.29) correspond to the classical Gibbs equation, whereas the third term is characteristic of EIT. It is related to the non-vanishing character of the relaxation time  $\tau$ . When  $\tau$  tends to zero, both the relaxational terms in the constitutive Eqs. (1.6) and (1.9) and the non-equilibrium contribution to the entropy in (1.29) tend to zero, in such a way that the constitutive equations tend to the usual Newton–Stokes law for the viscous pressure tensor and (1.29) reduces to the classical Gibbs equation. Thus, we stress that the presence of relaxational terms in the constitutive Eqs. (1.6) or (1.9) implies the presence of a non-equilibrium contribution to the Gibbs Eq. (1.29).

In general one could take, instead of a single relaxation time, several relaxation times and one could assume that  $\mathbf{P}^v$  is the sum of several different contributions  $\mathbf{P}_i^v$ , each of them with its own relaxation time  $\tau_i$  and its own viscosity  $\eta_i$ , as in the generalised Maxwell models introduced in (1.21). In this case, one would have instead of (1.29)

$$ds = T^{-1}du + T^{-1}pdv - \sum_i (\tau_i v / 2\eta_i T) \mathbf{P}_i^v : d\mathbf{P}_i^v. \quad (1.30)$$

The total viscosity  $\eta$  is  $\eta = \sum_i \eta_i$ . Consequently,  $\tau$  in (1.29) may be considered as an averaged relaxation time, defined as  $\tau = (\sum_i \tau_i \eta_i) (\sum_i \eta_i)^{-1}$ . Note that in terms of the steady-state compliance introduced after (1.21) ( $J = \tau/\eta$ ), one may write the generalised Gibbs Eq. (1.29) as

$$ds = T^{-1}du + T^{-1}pdv - \frac{vJ}{2T} \mathbf{P}^v : d\mathbf{P}^v, \quad (1.31)$$

which, after integration, becomes

$$s(u, v, \mathbf{P}^v) = s_{\text{eq}}(u, v) - \frac{\nu J}{4T} \mathbf{P}^v : \mathbf{P}^v, \quad (1.32)$$

where subscript eq stands for the equilibrium value.

For shear flow, the generalised entropy (1.32) reduces to

$$s(u, v, P_{12}^v) = s_{\text{eq}}(u, v) - \frac{\nu J}{4T} \left[ 2(P_{12}^v)^2 + 2(P_{12}^v)^4 \right], \quad (1.33)$$

if one takes into account that for the model described by (1.13)  $P_{11}^v = -2J(P_{12}^v)^2$ . Notice that  $P_{12}^v$  is of the order of  $\dot{\gamma}$ , and for low values of  $\dot{\gamma}$  we may neglect the contribution of  $P_{12}^v$  of order higher than two and write

$$s(u, v, P_{12}^v) = s_{\text{eq}}(u, v) - \frac{\nu J}{2T} (P_{12}^v)^2. \quad (1.34)$$

Instead of the internal energy it is usual to take as an independent variable the temperature, because it is more accessible to direct measurement. The thermodynamic potential which has as variables temperature and volume is the Helmholtz free energy  $f$ , defined as

$$f = u - Ts, \quad (1.35a)$$

where we are using values per unit mass. In view of its interest we comment also on the corresponding non-equilibrium contributions of a viscous pressure tensor. We are interested in the contribution  $\Delta f$  of the flow to the free energy, for which we write, at constant  $T$ ,

$$\Delta f = \Delta u - T \Delta s, \quad (1.35b)$$

with

$$\Delta f = f - f_{\text{eq}}, \quad \Delta u = u - u_{\text{eq}}, \quad \Delta s = s(u, v, \mathbf{P}^v) - s_{\text{eq}}(u_{\text{eq}}, v). \quad (1.35c)$$

Note that for fixed temperature, the internal energy under flow  $u$  is in general not equal to 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, as given in (1.36), we expand  $s_{\text{eq}}(u, v)$  around the equilibrium value  $s_{\text{eq}}(u_{\text{eq}}, v)$  as

$$s_{\text{eq}}(u, v) = s_{\text{eq}}(u_{\text{eq}}, v) + \left( \frac{\partial s_{\text{eq}}}{\partial u} \right)_{u=u_{\text{eq}}} (u - u_{\text{eq}}) + \dots \quad (1.36a)$$

which when inserted in (1.35b) leads to

$$\Delta f = u - u_{\text{eq}} - T \left[ s_{\text{eq}}(u, v) - (\nu J/2T)(P_{12}^v)^2 - s_{\text{eq}}(u_{\text{eq}}, v) \right] = \frac{1}{2} \nu J (P_{12}^v)^2, \quad (1.36b)$$

when use of (1.34) and (1.36a) is made.

In a more general situation, when one is not restricted to second order in shear rate, one assumes that the energy contribution, proportional to  $(P_{12}^v)^2$ , is much higher than the entropic one. We will comment on this point later from a microscopic point of view. One should thus have

$$\Delta f = \Delta u = vJ(P_{12}^v)^2. \quad (1.37)$$

This is consistent with the meaning of  $J(P_{12}^v)^2$  as stored energy. An expression slightly more general than (1.29) has been derived by Daivis (2008) using the shear rate  $\dot{\gamma}$  instead of the viscous pressure as independent variable. His derivation is based on the analysis of the work stored in a viscoelastic fluid when it is brought from the equilibrium state to a shearing steady state. This author writes the generalized Helmholtz free energy as

$$df = -sdT - pdv + \zeta d\dot{\gamma}, \quad (1.38)$$

with  $\zeta$  the corresponding conjugate parameter to  $\dot{\gamma}$ , from which it is obtained the Maxwell relation

$$\left(\frac{\partial \zeta}{\partial v}\right)_{T, \dot{\gamma}} = -\left(\frac{\partial p}{\partial \dot{\gamma}}\right)_{T, v} = \frac{\partial^2 f}{\partial v \partial \dot{\gamma}}. \quad (1.39)$$

He carried out non-equilibrium molecular dynamics simulations of a simple shearing fluid, but these Maxwell relations were not verified. Daivis saw as a possible source of disagreement the sensibility of these quantities with temperature, and the fact that out of equilibrium one may define several different temperatures. Indeed, he used for  $T$  the kinetic temperature instead of the thermodynamic non-equilibrium temperature depending on  $\dot{\gamma}$ , which should be used for the sake of internal consistency. Analyses of Maxwell relations stemming from non-equilibrium potentials seem worth to be pursued.

In our formalism, and in the steady state, (1.29) could be rewritten as

$$dS = T^{-1}dU + T^{-1}pdV + T^{-1}\tau\mathbf{V} : d(V\mathbf{P}^v), \quad (1.40a)$$

where we have written  $\mathbf{P}^v = -2\eta\mathbf{V}$  and the symbol of entropy, energy and volume as capital letters in order to stress that (1.29) is not restricted to values per unit mass  $s$ ,  $u$  and  $v$ , but for total volume  $V$ , entropy  $S$  and internal energy  $U$ . Thus,  $T^{-1}\tau\mathbf{V}$  may be considered as the intensive variable conjugate to the extensive quantity  $V\mathbf{P}^v$  whose preferable use as variable rather than  $\mathbf{P}^v$  will be commented in Chaps. 2 and 6. Consequently, we may go from the extensive variable  $V\mathbf{P}^v$  to the intensive variable  $\tau\mathbf{V}$  through a Legendre transform. In particular, we may rewrite (1.40a) in terms of  $U$  as

$$dU = TdS - pdV - \tau\mathbf{V} : d(V\mathbf{P}^v), \quad (1.40b)$$

and write the corresponding Legendre transforms for  $F_1(T, V, VP^v)$  or  $F_2(T, V, \tau\mathbf{V})$  as

$$dF_1 = -SdT - pdV - \tau\mathbf{V} : d(V\mathbf{P}^v), \quad (1.41a)$$

and

$$dF_2 = -SdT - pdV + VP^v : d(\tau\mathbf{V}). \quad (1.41b)$$

The latter expression would be the generalization of Davis expression (1.38). These Legendre transforms show that it is possible to go from the viscous pressure tensor to the velocity gradient as independent variables. Analogously, in Chap. 5 it will be considered another Legendre transform going from the viscous pressure tensor to the macromolecular configuration tensor, which will be introduced in Chap. 4. However, these Legendre transforms may be carried out in steady states, where  $\mathbf{P}^v$  and  $\mathbf{V}$  are univocally related, but in general they are not expected to be valid in fast varying states, where  $\mathbf{P}^v$  and  $\mathbf{V}$  behave in a completely independent way.

Note that an analogous analysis could be carried out for the Gibbs free energy, which has as basic variables the temperature and pressure instead of temperature and volume, and which plays a central role in physico-chemical thermodynamics, in the analysis of phenomena at constant temperature and constant pressure.

## 1.2.2 Viscous Pressure and Diffusion Flux

In this subsection we consider a binary mixture and introduce the diffusion flux as a further independent variable, because it will play an important role in several of the phenomena studied in this monograph (Nettleton 1988; Jou et al. 1991, 2010; Goldstein and García-Colín 1993, 1994; Pérez-Guerrero and García-Colín 1991; Pérez-Guerrero 1997; Nettleton 1993, 1996a, b). Furthermore, we carry out a detailed justification of the generalised form of the entropy, which was presented in (1.29) without derivation. Our aim is to analyse the couplings between the diffusion flux and the viscous pressure tensor. For the sake of simplicity, the latter will be considered here as a single independent variable with a single relaxation time instead of the addition of several independent contributions, each with its own relaxation time. The extension to the latter situation is straightforward but cumbersome. We will use the coupled evolution equations for the diffusion flux  $\mathbf{J}$  and  $\mathbf{P}^v$  in Chaps. 6–8.

Instead of (1.29), we write now the extended Gibbs equation in the form

$$ds = T^{-1}du + T^{-1}pdv - T^{-1}\tilde{\mu}dc_1 - v\alpha_1\mathbf{J} \cdot d\mathbf{J} - v\alpha_2\mathbf{P}^v : d\mathbf{P}^v, \quad (1.42)$$

with  $c_1$  the concentration (mass fraction) of the solute,  $\tilde{\mu} \equiv \mu_1 - \mu_2$  the difference between the specific chemical potentials of the solute and the solvent, and  $\alpha_1$  and  $\alpha_2$  coefficients whose form will be identified below. We neglect here the effects of the bulk viscous pressure, for the sake of simplicity. Note the third and fourth terms on

the right-hand side of (1.41), related to changes in composition and to the diffusion flux, which were absent from (1.29).

We assume for the entropy flux the expression

$$\mathbf{J}^s = T^{-1}\mathbf{q} - T^{-1}\tilde{\mu}\mathbf{J} + \beta\mathbf{P}^v \cdot \mathbf{J}. \quad (1.43)$$

The first two terms are classical; the latter one is characteristic of EIT, and it is of second order in the fluxes:  $\beta$  is a phenomenological coefficient characterizing the coupling of  $\mathbf{P}^v$  and  $\mathbf{J}$ .

The energy and the mass balance equations are, respectively,

$$\rho\dot{u} = -\nabla \cdot \mathbf{q} - p(\nabla \cdot \mathbf{v}) - \mathbf{P}^v : \mathbf{V}, \quad (1.44)$$

$$\rho\dot{c} = -\nabla \cdot \mathbf{J}. \quad (1.45)$$

Combination of (1.42), (1.44) and (1.45) yields for the time derivative of the entropy

$$\rho\dot{s} = -T^{-1}\nabla \cdot \mathbf{q} + T^{-1}\tilde{\mu}\nabla \cdot \mathbf{J} - T^{-1}\mathbf{P}^v : \mathbf{V} - \alpha_1\mathbf{J} \cdot \dot{\mathbf{J}} - \alpha_2\mathbf{P}^v : \dot{\mathbf{P}}^v. \quad (1.46)$$

It is convenient to rewrite the two first terms of the right-hand side of (1.46) as

$$T^{-1}\nabla \cdot \mathbf{q} = \nabla \cdot (T^{-1}\mathbf{q}) - \mathbf{q} \cdot \nabla T^{-1}, \quad (1.47)$$

$$T^{-1}\tilde{\mu}\nabla \cdot \mathbf{J} = \nabla \cdot (T^{-1}\tilde{\mu}\mathbf{J}) - \mathbf{J} \cdot \nabla (T^{-1}\tilde{\mu}). \quad (1.48)$$

Then, taking into account (1.43), one obtains for the entropy production

$$\begin{aligned} \sigma &= \mathbf{q} \cdot \nabla T^{-1} + \mathbf{J} \cdot [-\nabla (T^{-1}\tilde{\mu}) - \alpha_1\dot{\mathbf{J}} + \nabla \cdot (\beta\mathbf{P}^v)] \\ &\quad + \mathbf{P}^v : (-T^{-1}\mathbf{V} - \alpha_2\dot{\mathbf{P}}^v + \beta\nabla\mathbf{J}), \end{aligned} \quad (1.49)$$

where use has been made of the general form of the balance equation of entropy

$$\rho\dot{s} + \nabla \cdot \mathbf{J}^s = \sigma. \quad (1.50)$$

From now on, we consider an isothermal situation and neglect the heat flux. This does not mean, of course, that thermal effects are not important, but that we will focus our analysis on situations in which they are negligible, only for the sake of simplicity. Under this simplification, the simplest evolution equations for  $\mathbf{J}$  and  $\mathbf{P}^v$  compatible with the positive character of (1.49) are

$$-\nabla (T^{-1}\tilde{\mu}) - \alpha_1\dot{\mathbf{J}} + \nabla \cdot (\beta\mathbf{P}^v) = \beta_1\mathbf{J}, \quad (1.51)$$

$$-T^{-1}\mathbf{V} - \alpha_2\dot{\mathbf{P}}^v + \beta(\nabla\mathbf{J})^s = \beta_2\mathbf{P}^v, \quad (1.52)$$

where  $(\nabla \mathbf{J})^s$  stands for the symmetric part of  $\nabla \mathbf{J}$ . The positive phenomenological coefficients  $\beta_1$  and  $\beta_2$  may be identified in physical terms by comparing (1.51) and (1.52) in the isothermal steady state and without couplings with the well known Navier–Stokes and Fick’s equations, namely

$$\mathbf{P}^v = -2\eta \mathbf{V}, \quad \mathbf{J} = -\tilde{D} \nabla \tilde{\mu}, \quad (1.53)$$

where  $\tilde{D}$  is a coefficient related to the usual diffusion coefficient  $D$  by means of  $D = \tilde{D}(\partial \tilde{\mu} / \partial c_1)$ . 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  $\tau_1 = \alpha_1 / \beta_1 = \alpha_1(\tilde{D}T)$ ,  $\tau_2 = \alpha_2 / \beta_2 = \alpha_2(2\eta T)$ . This allows one to identify in physical terms the coefficients  $\alpha_1$  and  $\alpha_2$  appearing in the extended Gibbs Eq. (1.42) and yields for it the explicit form

$$ds = T^{-1}du + T^{-1}pdv - T^{-1}\tilde{\mu}dc_1 - \frac{v\tau_1}{\tilde{D}T} \mathbf{J} \cdot d\mathbf{J} - \frac{v\tau_2}{2\eta T} \mathbf{P}^v : d\mathbf{P}^v. \quad (1.54)$$

Note that the latter term has the form given in the last term of (1.29), which appears now explicitly justified, as well as its deep and direct relation with the relaxational terms in the constitutive Eq. (1.51).

It is also worthwhile to note that in the absence of viscous pressure and in a steady state, where  $\mathbf{J} = -D\nabla c_1$ , (1.54) may be integrated to give

$$s = s_{\text{eq}}(u, v, c_1) - l^2 \nabla c_1 \cdot \nabla c_1, \quad (1.55)$$

with  $l$  a correlation length defined by  $l = v\tilde{D}\tau_1/T$ . The contribution of the density gradients to the entropy, or to the free energy, is usually known as a Ginzburg–Landau contribution, and will be discussed in Chap. 7.

The evolution equations for  $\mathbf{J}$  and  $\mathbf{P}^v$  may be rewritten as

$$\tau_1 \dot{\mathbf{J}} = -(\mathbf{J} + D\nabla c_1) + \beta \tilde{D}T \nabla \cdot \mathbf{P}^v \quad (1.56)$$

and

$$\tau_2 (\mathbf{P}^v)^\cdot = -(\mathbf{P}^v + 2\eta \mathbf{V}) + 2\beta T \eta (\nabla \mathbf{J})^s. \quad (1.57)$$

Equations (1.56) and (1.57) clearly exhibit the couplings between diffusion and viscous stresses. 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.

The material time derivatives of  $\mathbf{J}$  and  $\mathbf{P}^v$  in (1.56) and (1.57) should be replaced, in general, by frame-invariant time derivatives, as mentioned in Sect. 1.1. Their form for tensors has already been discussed in (1.7–1.8). The corresponding form for the frame-indifferent derivative of  $\mathbf{J}$  is

$$\frac{D\mathbf{J}}{Dt} = \dot{\mathbf{J}} + \mathbf{W} \cdot \mathbf{J}. \quad (1.58)$$