

SIMPLE NON-EQUILIBRIUM THERMODYNAMICS APPLICATIONS TO POLYMER RHEOLOGY

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ABSTRACT

We review here recent developments in non-equilibrium thermodynamics and their applications to rheology.

In particular we review the application of the dissipative Hamiltonian formalism to incompressible, homogeneous and isothermal flows of flexible polymer systems. We show not only the advantages that have been brought up by the non-equilibrium thermodynamics approach but also exactly where the actual contributions are in combination from a variety of specific modeling examples ranging from simple, one-conformation models to most recent coupled multivariable examples. In all cases, special attention is paid to convey the physical significance of the models through a close association to a more detailed microscopic interpretation.

KEYWORDS: Non-equilibrium thermodynamics; Constitutive equations; GENERIC; Polymer rheology

1. INTRODUCTION

In the last 20 years significant progress has been accomplished in establishing a firmer theoretical basis for the description of dynamics in dissipative media (Kauffman [1], Morrison [2], Grmela [3]) upon which transport phenomena and, in particular, rheology can be founded. The new formalisms that have emerged can be described collectively as dissipative Hamiltonian or generalized non-equilibrium (or irreversible) thermodynamics approach as they can be viewed either as extending the traditional Hamiltonian dynamics of conservative (reversible) systems (see, for example, Arnold [4], Abraham and [5], Marsden and Ratiu [6]) by adding dissipation, or (equivalently) as generalizing the more traditional irreversible thermodynamics descriptions (based primarily to the Onsager [7,8] and Onsager-Casimir (Casimir [9]) relations (see, for example, Prigogine [10], de Groot and Mazur, [11]) adding further structure to the velocity-internal variables connection describing convective (in general, reversible) phenomena; i.e. generalizing the material derivative. Either way, the new formalism leads to a beautiful separation of the dynamic equations into a reversible and an irreversible component:

$$\frac{dx}{dt} = \left(\frac{dx}{dt}\right)_{rev} + \left(\frac{dx}{dt}\right)_{irr}, \quad \dots\dots\dots(1)$$

where x represents any variable of the system (like mass, momentum, entropy densities, as well as internal variables) and the subscripts *rev*, *irr* denote reversible and irreversible phenomena, respectively. It is in the structure present in the forms describing those reversible and irreversible changes that the advantage of using non-equilibrium thermodynamics-consistent expressions lies.

The new descriptions incorporate explicitly both reversible (manifested primarily as convective) and irreversible phenomena, as opposed to previous attempts that focused on special limiting cases such as Hamiltonian dynamics (reversible phenomena [Arnold [4], Abraham and Marsden [5]), or irreversible thermodynamics (irreversible phenomena [Onsager [7,8], Prigogine [10], de Groot and Mazur, [11]). Thus, all the structure developed in these formulations can be carried over in the new, while, simultaneously allowing for a wealth of new phenomena to be investigated in a systematic way. Another innovation as opposed to previous attempts to generalize non-equilibrium thermodynamics is that, in general, in the new approaches equal emphasis is placed in the underlying physics as well as in the mathematical formalization (the latter, for example, was the main emphasis of several previous modeling efforts, such as, for example, the axiomatic foundation of continuum mechanics [Truesdell and Toupin [12], Coleman and Noll [13], Truesdell and Noll [14]). Indeed in the dissipative Hamiltonian approach special emphasis is placed in the underlying physics and the desirability to provide results of relevance to the engineering practitioner and therefore to bridge the theory with practice. As such, the new approach in its relatively short time of development has already spread over several levels of description covering anywhere from the atomistic/molecular (Mavrantzas and Öttinger [15]), through the microscopic (Öttinger and Grmela [16], Edwards et al. [17], Öttinger and Beris [18], Öttinger [19], Fang et al [20], Öttinger [21]), to the macroscopic (Grmela, [22,23], Jou et al [24], Jongschaap [25], Beris and Edwards [26], Öttinger and Grmela [16], Jou et al [27]) level. More importantly, these different descriptions are not seen as independent modeling applications but rather as simply representations of the dynamics at different length and time scales, with interesting interconnections and consistency relations --- “coarsening” effects, such as formally achieved, for example, by the general projection operator formalism (Öttinger [28]). To demonstrate the universality of the approach, the theory has even been cast recently at the quantum level of description (Öttinger [29]) as well as in a relativistic form (Öttinger [30,31]) and it has been applied even to cosmology (Ilg and Öttinger [32]). Last, but not least, several monographs have appeared where the details of the various modern non-equilibrium thermodynamics approaches and several of their applications have been exposed (Beris and Edwards [26], Jou et al [33,34], Öttinger [35]). See also the special issue of the *Journal of Non-Newtonian Fluid Mechanics* on this subject (Jongschaap and Öttinger [36]).

All those publications discussed above represent just a small sample of the work that has appeared until now since the original papers of Kauffman [1], Morrison [2] and Grmela [3], appeared in 1984, when for the first time the foundation of the dissipative Hamiltonian approach was laid down. Many more applications can be found among the references of those works, especially the above-mentioned

monographs. In the present review I will try to offer a more end user-oriented description with emphasis on a rather narrow field of applications (but of much interest to rheology!): simple macroscopic applications to polymer rheology with the word “simple” used to describe the incompressible, homogeneous and isothermal assumptions, typical (but not always!) accompanying traditional rheological modeling- (See, for example, Tanner [37]). In particular, what I will like to illustrate here are the main benefits that a rheology-interested end user can draw, not necessarily an expert in microscopic theory and modeling, but rather one who wants to see how the generalized non-equilibrium thermodynamics principles apply into the everyday rheology practice (for example, the experimentalist interested in interpreting his/her results by fitting them to a model). In other words, the question that I would like to address here is if we are interested in developing and using model equations to describe the rheology of a complex polymeric system, to what extent and in what fashion can the application of the above-mentioned new formalism of non-equilibrium thermodynamics help? Hopefully, this modest introduction into the applications of non-equilibrium thermodynamics can provide the motivation for a deeper study of the subject leading to also other, more complex, applications.

One advantage of narrowing purposefully the scope of this review is that within the limit of macroscopic descriptions several of the newly developed non-equilibrium formalisms are in good agreement each other (Edwards et al [38]) or even merge (Edwards [39]), as is the case for the one generator bracket formalism (Beris and Edwards [26]) and the two generator GENERIC formalism (Öttinger and Grmela [16]). In that limit we may therefore use interchangeably the last two formalisms, with the understanding that the latter is more powerful than the former as far as microscopic modeling is concerned (Edwards et al [17]). The other advantage limiting the discussion even more to simple macroscopic models, is that the analysis can be further simplified, thus allowing for a simpler “end-user” presentation of the key concepts behind the modern non-equilibrium thermodynamics theory. The end-user modeler perspective means the discussion on the description of the governing equations will be tailored to be at the more familiar level of the set of partial differential equations typically used to describe transport phenomena, refraining from the use of any higher order mathematical structures (like, for example, Poisson brackets) which, albeit important and necessary in revealing the inner mathematical consistency of the approach, they are not necessarily needed for the theory’s application. If interest arises for a more in depth explanation of the dissipative Hamiltonian description, or when new applications are sought for which the building elements of the governing equations have not yet been developed (for the generation of which a familiarity with a more in depth structural analysis of the formalism is desirable) one is referred to consult one of the monographs mentioned above where a sufficient detailed exposition is available. In any case, the development over the last two decades of many applications, some of which are described here, others in the references supplied, has left us with sufficient thermodynamically-consistent forms so that to allow for a successful implementation of the theory into the engineering rheology practice without the need to assimilate all the details beneath the dissipative Hamiltonian theory.

Without doubt getting the proper form for the governing differential equations for the transport phenomena is the primary benefit to be drawn from non-equilibrium thermodynamics and by “proper” I mean consistent to the principles and constraints

that the extended non-equilibrium thermodynamics corresponding to the dissipative Hamiltonian theory imposes. Much of the debate over the last century or so, has been on the nature and validity of the non-equilibrium principles and indeed some of that carries on to our days (Kestin [40], Muschik [41]). However, we believe that there is already considerable number of successful applications to justify the acceptance, even in an ad hoc basis, of equilibrium thermodynamic quantities, like entropy and temperature, under (mildly) non-equilibrium conditions, as well as accepting the principle of a local non-negative entropy production rate. For example, a working framework can be established for the entropy based on the information at hand; see Jaynes [42] for a very clear description. Also, there is a plethora of applications to “extended” thermodynamic systems (Sieniutycz and Salamon [43]) even to the ecosystem (Sertorio [44]) and non-equilibrium thermodynamics principles have started being discussed in rheology monographs. See also, the Appendix of Leonov and Prokunin [45].

In addition, the new non-equilibrium thermodynamics framework brings in the Poisson structure for the dynamics of the reversible processes (Grmela [3], Beris and Edwards [26], Öttinger and Grmela [16]). Extensive evidence has been collected over the years of the prevalence and ubiquity of the Poissonian structure in all known conservative phenomena ranging from the smallest to the largest scales; especially pertinent for the present discussion is the observation for the prevalence of Poissonian (or, equivalently, symplectic) structure in electromagnetism all the way from subatomic quantum electrodynamics to macroscopic linear optics (Guillemin and Sternberg [46]). In addition, there are now numerous validations of the dissipative Hamiltonian principles against models with good success to engineering practice (and the interested reader is again referred to the references mentioned in the second paragraph above).

As a result, we believe that it is fair to say now that the well established generalized non-equilibrium thermodynamics principles (such as those behind one of the currently accepted formalisms, like GENERIC (Öttinger and Grmela [16])) represent a collective scientific experience. The important thing to notice then, based on numerous applications, is that this collective experience includes in addition to all the previously well established continuum mechanics principles, (such as, for example, the objectivity principle put forward (in rheology) by Oldroyd [47]) additional ones that place further constraints to the accepted forms of the model equations. Those constraints further refine and extend previous ones that have been applied to various limiting cases, such as, as mentioned above, Hamiltonian mechanics and irreversible thermodynamics.

The two key elements on which the application of the dissipative Hamiltonian formulation is based are the Poissonian structure of the reversible dynamics and the Onsager-Casimir structure of the dissipative one (Beris and Edwards [26], Öttinger and Grmela [16]). Then, it is important to realize that those structures do not apply to any single one of the governing equations in isolation, but rather to the whole system of governing equations, for all the variables of the system, that needs to be dealt together. In other words, individual terms in any one of the equations can arise (and usually do) from other principles, like microscopic modeling and continuum mechanics. The main advantage of the dissipative Hamiltonian formalism is in revealing the connection that exists between some of these terms in order to be

consistent with non-equilibrium thermodynamics. For example, there is a close connection between the convective component entering in the description of the evolution dynamics of an inner variable and the dependence of the extra stress of the material on that same internal variable. It is this consistency that brings all the advantage to the end user. It is exactly those items that the present review will tend to emphasize and illustrate in example applications. And, we need to reiterate once more, all this new information, within the most general non-equilibrium thermodynamics context as it is presented here, comes in addition to all the information that was previously generated by applying more limited criteria. Such is the case with the tensor forms that arise by applying the objectivity criterion traditionally developed within continuum mechanics (Oldroyd [47]) or the inequality constraints on various transport coefficients that one usually gets by evaluating expressions of the local entropy production within the context of irreversible thermodynamics and then applying the principle of a non-negative entropy production (de Groot and Mazur [11]).

Moreover, by construction, the theory allows for a smooth extension on whatever equilibrium thermodynamics modeling information one has available into the non-equilibrium regime. (See, for example, the very illuminating first article in the special issue by Jongschaap and Öttinger [36]). This is very important in applications involving polymer systems, for example, where a lot of equilibrium information is already available as a consequence of the substantial previous work performed under equilibrium conditions. Rather than throwing away all that information in order to allow a completely phenomenological transport theory to develop, such as it was the case until recently, the new approach allows for a smooth transition into the non-equilibrium regime preserving and expanding previous equilibrium thermodynamics information. This is only allowed by involving directly thermodynamic potential information into the non-equilibrium transport equations. Last but not least, the new theory allows for a seamless integration of model equations described at two different levels of description. For example, diffusion-type equations governing the evolution of the “propagator” function used to describe the chain conformations down to the repeating segment scale level, have been successfully integrated within the context of the dissipative Hamiltonian approach with phenomenologically-based Oldroyd-B-type macroscopical models in order to describe the flow and surface induced deformation of macromolecular chains and the rheology of dilute polymer solutions next to a surface (Mavrantzas and Beris [48,49]).

However, it is also important to specify here that rather than using the dissipative Hamiltonian formalism to a-priori generate model equations one should try to apply the new ideas in order to shape suitably an independently developed physical understanding (usually arising from a microscopic modeling) building it into the form of evolution equations that are consistent with that formalism. To facilitate that, we provide here several examples where we carefully analyze the physical significance of the various steps involved. It is indeed the close interplay between the formalism and an underlying physical model that allows for the development of the final set of model equations, even if those refer to a macroscopic scale, as we limit to that our discussion in this work. Several stages are involved in the model development process. First, the proper physics is important in order to appropriately define the number of variables, their mathematical type and (very important!) any constraints associated with each one

of them. This information alone is usually sufficient to define the reversible dynamics of the variables. In other cases, more complicated, a suitable approximation from a finer model is needed, but, in return the constraints imposed by the formalism can be used to prune the suitability of approximations so that the resulting approximate equations are still consistent with each other; for a beautiful example of this type of application in selecting closure approximations of fourth order moments for the macroscopic modeling of the second moment dynamics of liquid crystals (See Edwards and Öttinger [50]). Next, it is through typically a microscopic model that we can build up the generalized thermodynamic information needed, in particular the dependency of thermodynamic potentials (usually the Helmholtz free energy) on the system variables. It is exactly at this stage that all previously available equilibrium thermodynamics information can be used, albeit it needs to be extended to also account for non-equilibrium contributions, and this is where we are sometimes missing accurate information and a phenomenological analog mechanical model is often used (see, however, Mavrantzas and Öttinger [15]) for a systematic process to generate that information from atomistic simulation of polymer melts. Finally, additional information needs to be used regarding the nature of the dissipative phenomena that come into play. It is usually there where most of the information is currently lacking with consequence the use of phenomenological formulae depending on adjustable parameters. However, as the system complexity increases, the number of parameters also increases to make the model of little use. This is the weak point of previous modeling attempts established solely at the macroscopic continuum mechanics level. Instead, the newer applications of dissipative Hamiltonian formalism (in particular using the GENERIC formalism (Öttinger and Grmela [16]) circumvent the parameter proliferation problem by operating directly at a microscopic model. Even at the microscopic level use of the dissipative Hamiltonian formalism can be very beneficial, as recent work on various reptation models for polymer melts has shown (Öttinger and Beris [18], Öttinger [19, 21], Fang et al [20]). Again, in these cases, most of the benefit is realized by pruning for the right velocity dependences to describe the reversible (convective) dynamics and by establishing a form for the stress expression that it is consistent with the dynamics of the microscopic internal variables. Eventually one hopes for a systematic transfer of information from the microscopic to the macroscopic level even for the dissipation, exactly as it is established now regarding the reversible dynamics. See Edwards [51] for a recent analysis of a beautiful example of this kind pertaining to polymeric liquid crystals.

For this review, for illustration purposes, we will limit ourselves to a discussion of the application of dissipative Hamiltonian dynamics to the simplest “complex fluid” modeling cases, i.e. for macroscopic models of incompressible isothermal homogeneous polymer systems. Moreover, deliberately we focus our attention to few well studied systems of (flexible) polymer solutions and melts, in an effort to establish patterns and correlations between various models and thus better explain and illustrate the benefits from the application of the dissipative Hamiltonian approach. In so doing, regrettably quite a number of significant advances, of importance to polymer rheology are left out, despite the significant (and many times crucial) contribution taken from non-equilibrium thermodynamics. Such are, for example, the cases of stiff polymeric systems; in particular, polymeric liquid crystals (see chapter 11 in Beris and Edwards [26] and, for more recent contributions, Edwards et al [52]) as well as the cases where multiple transport phenomena such as diffusion and flow (see Beris and Mavrantzas,

[53], El Afif and Grmela [54]). However, discussion also of these issues (some of which are still under active development) would have extended considerably the present review and also increased its level of mathematical sophistication; thus those subjects are deferred for a future separate review. The remainder of the paper is constructed as follows. In the next section, a discussion on the variables selection, the starting point to any modeling effort, is presented. Section 3 then presents a review on applications to single internal mode polymer rheology models. Section 4 reviews multiple internal variable applications to polymer systems rheology with emphasis to cases where the variables are coupled. Finally, section 5 has our conclusions and some thoughts on possible future developments.

2. VARIABLES SELECTION

The starting point of any modeling effort is the identification of the state variables, i.e. the (field) variables used to specify the state of the system under investigation. In traditional transport phenomena, i.e. when a structureless medium is modeled, those variables are the system mass density, ρ , the (mass-averaged) velocity vector, \mathbf{v} , the temperature, T , and N component concentrations, c_i , $i = 1, \dots, N$ for an N -component mixture (Bird et al [55]). However, when a complex medium is to be modeled, such as a polymer solution or melt, additional variables (so-called inner variables (Prigogine and Mazur [56], Muschik [57], Kestin [40]) are necessary in order to describe its inner structure and, in particular, the coupling between the flow-induced structure evolution and the structure-induced changes in the transport phenomena. Depending on the description level (and therefore the complexity) of the modeling effort, those variables can be continuous fields over an extended space. Indeed, at the microscopic level of description, the inner variables span, in addition to the regular 3-dimensional geometrical space and time, an inner conformational space typically of high dimensionality (such is, for example, the case of the distribution function of macromolecular Kramer N -bead/rod chains, spanning a $3*(N-1)$ -dimensional conformational space (Bird et al [58]). On the other hand, under suitable assumptions (for example that of a Gaussian (bell) shape for the distribution function (Sureshkumar and Beris [59]) or when a closure approximation is used to close the first one (or first few) of a set of moment equations, it is sufficient to use as inner variables one (or more) moments of the internal variable distribution function. Those moments then become macroscopic fields extending over space and time alone, exactly like the more traditional field variables (i.e. density, velocity etc) that we discussed above.

Rheological models involving only macroscopic variables are much easier to use in complex flows calculations. However, we should also note here the significant developments which have taken place in mixed finite-element/stochastic numerical methods which have led to efficient computational techniques (Hulslen et al [60]), Wapperom et al [61]) allowing the use of microscopic models for the simulation of complex flows (Wapperom and Keunings [62]). The best current methods, based on the use of configuration fields (Hulslen et al [60]) and/or a backward particle Lagrangian method (Wapperom et al [61]), have substantially refined the CONNFESSIT technique (Laso and Öttinger [63]) which was the first one established within a systematic statistical framework allowing for the solution of microscopic constitutive equations using stochastic methods (Öttinger [64]).

Nevertheless, even if those newer methods allow solutions readily to be obtained in two-dimensional flow geometries of relatively complex shape (Wapperom and Keunings [62]), the computational and memory requirements are still significantly higher than the macroscopic continuum models. Moreover, the additional load makes the use of microscopic models prohibitive for more complex time-dependent and three-dimensional simulations, like the direct numerical simulations of turbulent channel flow which have just started being feasible with current computational resources using macroscopic viscoelastic models (Sureshkumar et al [65]). Indeed, as an indication of the acceptable performance of the macroscopic models there we can note in passing that simulations of a turbulent viscoelastic flow in a channel with the FENE-P model have demonstrated the polymer-induced drag reduction phenomenon and have shown, at least qualitatively, all the experimentally observed effects (like the widening of the streak spacing) associated with it for dilute polymer solutions (Sureshkumar et al [65]). Calculations of this type show that there is strong interest to possess good macroscopic models and justify the emphasis of our discussion here on macroscopic models. Note however, as mentioned above, that even with that goal in mind, the physical basis of any work is most likely on a microscopic model, from which the macroscopic model is systematically constructed, as this represents the most straightforward and least arbitrary (and with the least number of adjustable coefficients!) path for a rational macroscopic model development. It is exactly in this context that the dissipative Hamiltonian formalism finds its most usefulness.

Even focusing on macroscopic models leaves considerable room for discussion as for the nature of the internal variables selected to represent the system structure in a given problem. In particular, it is important to have a clear understanding, based on the physical interpretation of the internal variables, of their exact mathematical nature and of any applicable constraints, as those are crucial in the subsequent development of the theory. For example, exactly as we know that concentration variables make physical sense if and only if they are non-negative scalars, it is also important to specify that, for example, the conformation tensor \mathbf{c} , typically used to characterize the deformation state of flexible chain molecules, makes only physical sense if it is a symmetric and non-negative definite (i.e. with non-negative eigenvalues) second order tensor. This type of information is used in properly shaping the details of the corresponding dynamic evolution equation to consistently preserve the desired structure and, in fact, it is also associated with the well-posedness (i.e. the evolutionary character) of the resulting governing equations (see, for example, Joseph [66], Beris and Edwards [26]). In the past, many numerical schemes failed to provide converged solutions because they led to instabilities which were introduced due to a failure to conserve numerically the proper mathematical character of the internal structural parameters.

At this point, discussing about the nature of the internal variables, it is also appropriate to mention here that in the early years of rheology and under the influence of the analysis of momentum transfer problems within simple (i.e. structureless) media, people used the extra stress tensor as an internal parameter of the system (Oldroyd [47]). Although good insights can lead to equivalent equations in terms of the stress variable as well (such is the case for the Maxwell model, for example) the fact is that the extra stress variable is an intermediate variable of a rheology model, with any internal conformation constraints only implicitly affecting the form of the extra stress tensor. As a consequence, for example, of the fact that when the upper

convected Maxwell model is expressed in terms of the extra stress tensor, the requirements for a non-negative definite conformation tensor translate to a more complex criterion in terms of the values of the eigenvalues of the extra stress tensor, it took a considerable time until those constraints were discovered and as a result it took a long time until the connection was made between the failure to conserve the constraint inequalities numerically and numerical instabilities (Dupret and Marchal [67,68], Joseph [66]). In contrast, in the new non-equilibrium thermodynamics formulations, such as the Hamiltonian bracket formalism (Beris and Edwards [26]), one is practically forced to work directly with the structural parameters and to specify explicitly all the physically imposed constraints.

In addition, we also need to mention here that the nature of the internal variables also may depend on the particular formalism used. Although it is true that there is complete freedom in the variables nature when the most general formalism is used (the GENERIC approach (Öttinger and Grmela [16]), this is not the case with others. In particular, with the most restricted EIT formulation, the internal variables are defined as fluxes (Jou et al. [33]) whereas in the one generator bracket formalism the internal variables are all assumed to be densities (Beris and Edwards [26], Edwards et al [17]). These restrictions are not always limitations but inversely they can be assets as they provide useful guidelines for the construction of the dynamic equations, especially important in complex multivariable representations of many simultaneous transport processes (Beris and Edwards [26]). In addition, for the simpler problems considered here (homogeneous flow problems) any variable characterizing an intensity can be trivially transformed into a density through a multiplication with a constant density. Thus, in the following no special effort will be made to adhere to densities as internal variables, even when the presented equations are derived using the bracket approach.

In the following sections we will illustrate the dissipative Hamiltonian approach starting from the simplest and moving to the more complicated examples. Thus, for convenience the more complicated elements of the theory will be introduced later, as needed. In section 3, we will start by first examining the impact of non-equilibrium thermodynamics to one conformation models of polymeric fluids, where most of the work has so far been accomplished. Then, in section 4, we will address more complex models involving more than one internal variable. Finally, in section 5, we will close our discussion with our conclusions.

3. INCOMPRESSIBLE, ISOTHERMAL AND HOMOGENEOUS FLEXIBLE POLYMERIC SYSTEMS WITH ONE INTERNAL CONFORMATION TENSOR PARAMETER

We follow here the development presented in Chapter 8 of Beris and Edwards [26] as corrected and extended in later works, for example Leygue et al [69]. The general set of variables involves in addition to the velocity a single internal variable, a second order positive definite tensor, the conformation tensor \mathbf{c} . The governing equations involve, in addition to the zero divergence of the velocity:

$$\nabla \cdot \mathbf{v} = 0 \quad \dots\dots\dots(2)$$

due to the incompressibility assumption, a general form for the momentum equation:

$$\rho \frac{D}{Dt} \mathbf{v} = -\nabla p + \eta_s \Delta \mathbf{v} + \nabla \cdot \mathbf{T}^T, \quad \dots\dots\dots(3)$$

where ρ is the (constant) system density, D/Dt represents the substantial (material) time derivative, p is the pressure, η_s is the (non-negative) viscosity of Newtonian stress contribution and \mathbf{T} is the (symmetric) polymeric extra stress. The polymer extra stress is a function of the internal structural parameter, the conformation tensor \mathbf{c} , assumed symmetric and positive definite, which, in turn, follows a dynamic evolution equation of the general form:

$$\frac{D}{Dt} \mathbf{c} - \nabla \mathbf{v}^T \cdot \mathbf{c} - \mathbf{c} \cdot \nabla \mathbf{v} = -\frac{\xi}{2} (\dot{\boldsymbol{\gamma}} \cdot \mathbf{c} + \mathbf{c} \cdot \dot{\boldsymbol{\gamma}}) - \mathbf{g} \quad \dots\dots\dots(4)$$

where ξ is a non affine motion dimensionless parameter, $0 \leq \xi \leq 2$, $\dot{\boldsymbol{\gamma}}$ represents the rate of strain tensor, $\dot{\boldsymbol{\gamma}} \equiv \nabla \mathbf{v} + \nabla \mathbf{v}^T$, and \mathbf{g} is a (symmetric) second order tensor, with units those characteristic of the conformation tensor divided by time, modeling the conformational relaxation. The right hand side of equation (4) represents one of the two available objective formulations of the material derivative for a second order tensor, the upper convected time derivative, first developed for rheology modeling by Oldroyd [47]. The relaxation parameter \mathbf{g} can be interpreted as a restoring force to equilibrium corresponding to the time derivative to the right hand side, and it is a function of the conformation tensor \mathbf{c} .

Continuum mechanics can provide useful information. First, we can easily confirm that equation (4) is consistent to the principle of material objectivity, i.e. we are not introducing any artificial dependence on any particular reference system used to calculate our model equations (Oldroyd [47], Rivlin [70]). Second, continuum mechanics (and tensor calculus) can help us regarding the mathematical interpretation (that can also lead to probable physical interpretations) of the conformation tensor \mathbf{c} and its dynamics as dictated by equation (4). For example, when the dimensionless parameter ξ takes one of its two limiting values (0 or 2), the conformation tensor \mathbf{c} acquires a contravariant or covariant character, respectively, the time evolution of which is described in an Eulerian frame of reference by an upper or lower convected time derivative (Truesdell and Noll [14], Truesdell [71], Jou et al.[34, page 5]), in accordance to equation (4). Based on this mathematical behavior and the connections (through the mathematical properties) to geometry, possible physical interpretations for \mathbf{c} can then be established as either a measure of internal (elastic) strain or an interfacial surface measure, respectively. For most polymeric systems then, it is not a coincidence that it is the first (i.e. the contravariant character, $\xi = 0$) that it is found to be the most appropriate one for applications (see however at the end of section 4 the illustration for an application in blends where the second one, i.e. the covariant, is more appropriate to be used). Finally, we need to mention here that the value of models with $\xi \neq 0, 2$ is still a subject of debate due to the fact that models where such a value is used (for example, the Johnson and Segalman [72]) are found to exhibit Hadamard instabilities (Leonov [73]). However, those may or may not result in a catastrophic material instability in a flow and simply may limit the existence of steady

state solutions (as, for example, associated with the tumbling seen in liquid crystals (Larson [74]; Beris and Edwards [26]).

Kinetic theory (Bird et al [58]) and network theory (Green and Tobolsky [75], Giesekus [76]) have then be used to advantage to connect macroscopic parameters with microscopic ones, for dilute solutions and concentrated solutions and melts, respectively. It is through these works that the bulk of the physics can be introduced into the model, with the internal conformation tensor parameter acquiring a specific physical meaning, that of the second moment of the end-to-end chain distribution (Bird et al [58]) or an elastic deformation strain (Leonov, [77]). Similarly, through the microscopic theories one can build an intuition on the form of the conformational dissipation, \mathbf{g} , and in particular the corresponding effective relaxation time embedded in there and its relation to the (inverse) of the polymer mobility (Giesekus [78,79,80], Bird and DeAguilar [81]). Also pertinent is the insight gained from the microscopic motion within an externally imposed macroscopic flow field of idealized particles, such as rigid particles of ellipsoidal shape. It is through the exact analysis made possible by the model idealization of such cases that an understanding of the non-affine character of the motion (manifested, for example, in the rotational lag between the particle motion and the surrounding fluid local rotation) can be established leading to specific predictions for the value of the non-affine parameter ζ as a function of the particle description and the flow characteristics (Jeffery [82]). It is through these studies that we have learned, for example, to associate the non-affinity to the stiffness of the molecular motion, so this is the reason why this is now primarily used for stiff molecular structures, like liquid crystals (see the discussion in chapter 11 of Beris and Edwards [26]. Also pertinent to this discussion is the work of Edwards and Beris [121], where the connection of the Poissonian structure for liquid crystals to rigid body rotation is made.

However, one has to emphasize here that because of the necessary abstractions and approximations (sometimes known as “projections” from a higher to a lower dimensionality configurational space) required as we move from a microscopic to the more macroscopic model, the correlations between equivalent set of parameters are not always uniquely defined. Instead, what it is most often the most successful strategy is a “renormalization” such as, for example, encountered in the modeling of other physical phenomena, such as in the renormalization of the electron charge in quantum electrodynamics (this is taken to an extreme: the “real” charge cannot be calculated (Feynman [83]). For a more pertinent to rheology example, we can also refer here to the renormalization of the molecular extensibility parameter as we move from the microscopic modeling of the Finite-Elasticity Non-Linear Elastic Dumbbell (FENE), which does not possess a closed form second moment macroscopic model to one of its macroscopic projections, the FENE-P equation. For a range of flows, such as flow past a cylinder, the FENE-P results corresponding to a renormalized extensibility parameter were found much closer to the FENE results, than the results corresponding to the same value of the extensibility parameter (van Heel et al [84]).

Still, there are questions remaining that can only be answered by looking more closely to the local thermodynamics. In particular, it is of usefulness to separate the reversible from the irreversible components of the dynamics, if not for other reason, simply because of the facilitation of further analysis of the structure of the equations

that can lead to a more appropriate and consistent modeling representation (but this is much more useful and fundamental than that, as the following more detailed discussion hopefully will indicate). In this way, we can for example learn to recognize the dissipation components in the governing equations (1)-(3). Those are just three: The viscous contribution in the momentum equation, the non-affine (i.e. with $\zeta \neq 0,2$) interaction of the velocity with the conformation and the relaxation term \mathbf{g} in the evolution equation for the internal structural parameter, \mathbf{c} . In addition to the time irreversibility associated with the phenomena modeled by these terms, one can recognize specific symmetry constraints (see further below) as well as the fact that these are the only terms contributing to the local entropy production. In contrast, the remaining terms in the equations represent reversible effects resulting to a very specific form for the velocity contribution--although in the particular case here this is simply reflected in the use of the appropriate (for the tensorial nature of \mathbf{c}) objective time derivatives, in other cases (see below) this observation can have dramatic consequences in the forms that need to be used.

Let us now discuss these non-equilibrium contributions in more detail. First, the non-equilibrium thermodynamics framework specifies the form of the functional dependence of the tensors \mathbf{T} and \mathbf{g} on the conformation tensor \mathbf{c} in terms of three auxiliary quantities, the elastic contribution to the Helmholtz free energy density, $a_e(\mathbf{c})$, a Newtonian shear viscosity coefficient, η_s , and a fourth order tensor, the normalized relaxation tensor $\Lambda(\mathbf{c})$:

$$\mathbf{T}^T = 2(1 - \zeta)\mathbf{c} \cdot \frac{\partial a}{\partial \mathbf{c}} + \eta_s \dot{\gamma}; \quad \dots\dots\dots(5)$$

$$g_{\alpha\beta} = \sum_{\gamma=1}^3 \sum_{\epsilon=1}^3 \Lambda_{\alpha\beta\gamma\epsilon} \frac{\partial a}{\partial c_{\gamma\epsilon}}, \quad \dots\dots\dots(6)$$

the latter relationship shown here in Cartesian component form for clarity. Notice, for consistency, the appearance of the nonaffine parameter ζ in the stress expression. The auxiliary quantities, a and Λ , have very specific physical (thermodynamic) meaning. The first accounts for the polymer contributions to the (extended; i.e. valid also at non-equilibrium) Helmholtz free energy of the system. Indeed, the total Helmholtz free energy, A , is assumed to have the following form:

$$A = \int_V \left(\frac{1}{2} \rho v^2 + a \right) dV, \quad \dots\dots\dots(7)$$

where V is the volume occupied by the polymer system and the first term in (7) represents the kinetic energy contribution. Various expressions can be assumed to represent the elastic free energy density depending on the nature of the polymer phase (i.e. dilute solution, polymer melt etc). A list of the most widely used ones is supplied in table 1 together, for convenience, with the corresponding expressions for the thermodynamic potential $\frac{\partial a}{\partial \mathbf{c}}$.

In turn, the fourth order relaxation tensor, Λ , accounts for the contribution to the local rate of the entropy production (per unit volume), σ_i , of the polymer relaxation process, a purely dissipative process, assumed to have the following

quadratic form in terms of the gradient of the Helmholtz free energy with respect to the conformation tensor (consistent to the Onsager-Casimir linear irreversibility relations (Onsager [7,8], Casimir, [9]):

$$\sigma_\lambda = \frac{1}{T} \left(\sum_{\alpha=1}^3 \sum_{\beta=1}^3 \sum_{\gamma=1}^3 \sum_{\epsilon=1}^3 \frac{\partial a}{\partial c_{\alpha\beta}} \Lambda_{\alpha\beta\gamma\epsilon} \frac{\partial a}{\partial c_{\gamma\epsilon}} \right), \quad \dots\dots\dots(8)$$

where T is the (assumed constant) temperature. Alternatively, equation (8) can be considered as the starting point for the development of the dissipation terms in the evolution equation of the internal variables---those terms (at least the simple ones, corresponding to quadratic expressions for the local rate of the entropy production in terms of various gradients of the Helmholtz free energy density) can then be easily deduced from equation (8) considering that the entropy production due to relaxation of \mathbf{c} can be also alternatively written as:

$$\sigma_\lambda = \frac{\partial s}{\partial \mathbf{c}} : \mathbf{g} = - \frac{1}{T} \frac{\partial a}{\partial \mathbf{c}} : \mathbf{g} \quad \dots\dots\dots(9)$$

and then deducing \mathbf{g} by comparing equation (9) with equation (8). A similar procedure can also be used to deduce the corresponding terms in the momentum or other internal variables evolution equations, if present, contributed by all present terms to the local rate of entropy production adopted expression. In such a way a more systematic way to develop these terms (and evaluating their consequences to the governing equations) has been developed.

Various models can be generated using different expressions for the relaxation tensor Λ . A compilation of some of the most often employed forms can be found in table 2. The relaxation contribution to the local rate of the entropy production, σ_λ , is one of the two contributions assumed here (in isothermal and homogeneous applications) for the total local rate of the entropy production, σ_s :

$$\sigma_s = \sigma_N + \sigma_\lambda; \quad \dots\dots\dots(10)$$

the other one taken to represent an isotropic viscous (Newtonian) dissipation, σ_N :

$$\sigma_N = \frac{1}{2} \frac{\eta_s}{T} \left(\sum_{\alpha=1}^3 \sum_{\beta=1}^3 \dot{\gamma}_{\alpha\beta} \dot{\gamma}_{\alpha\beta} \right). \quad \dots\dots\dots(11)$$

It is exactly the requirement for a non-negative rate of entropy production which leads to the constraint of non-negative viscosity (from equation (11)) and a non-negative definite relaxation tensor, Λ , from equation (8). Finally we should note here that different models can be constructed by specifying different functional dependences for the scalars η_s , ζ , assumed functions of the conformation tensor \mathbf{c} , primarily (at a higher order there may be a mixing on dependences to the velocity; however, the lower order dependencies are set by the Onsager/Casimir expressions as indicated here).

Model	$a(\mathbf{c})$	$\frac{\partial a}{\partial \mathbf{c}}$
Maxwell Oldroyd-B	$\frac{1}{2}\{\text{tr}(\mathbf{c}) - \ln(\det(\mathbf{c}))\}$ Also called Hookean or Linear Dumbbell model (Bird et al [58])	$\frac{1}{2}\mathbf{I} - \frac{1}{2}\mathbf{c}^{-1}$
FENE-P	$-\frac{1}{2}L^2 \ln\left(1 - \frac{\text{tr}(\mathbf{c})}{L^2}\right)$ $-\frac{1}{2}\ln(\det(\mathbf{c}))$ L represents the dimensionless maximum chain extensibility; L^2 also appears as b (Bird et al [58])	$\frac{1}{2}\left(\frac{1}{1 - \frac{\text{tr}(\mathbf{c})}{L^2}}\right)\mathbf{I} - \frac{1}{2}\mathbf{c}^{-1}$
Bird and DeAguiar (modified)	$\frac{1}{2}\{\text{tr}(\mathbf{c}) - \ln(\det(\mathbf{c}))\}$ $+^{(1-\alpha)}\frac{1}{2}\ln\left(\frac{(\frac{1}{3}\text{tr}(\mathbf{c}))^3}{\det(\mathbf{c})}\right)$ α is an aniso-tropic mobility parameter, (Bird and DeAguiar [81])	$\frac{1}{2}\left(1 - \frac{3(\alpha-1)}{\text{tr}(\mathbf{c})}\right)\mathbf{I}$ $-\frac{1}{2}(2-\alpha)\mathbf{c}^{-1}$
Leonov	$W(a_1, a_{-1});$ $a_1 \equiv \frac{I_1}{I_3^{1/3}}; a_{-1} \equiv I_{-1}I_3^{1/3}; I_{-1} = \frac{I_2}{I_3}$ I_n is the n -th invariant of \mathbf{c} ; in the original model $I_3=1$ (Leonov, [77])	$\frac{\partial W}{\partial a_1} \frac{1}{I_3^{1/3}}(\mathbf{I} - \frac{1}{3}I_1\mathbf{c}^{-1}) +$ $\frac{\partial W}{\partial a_{-1}} \frac{1}{I_3^{2/3}}(I_1\mathbf{I} - \mathbf{c} - \frac{2}{3}I_2\mathbf{c}^{-1})$
Marrucci and Acierno (modified)	$\frac{1}{2}(\chi+1)(\text{tr}(\mathbf{c}) - \ln(\det(\mathbf{c})))$ $-\frac{3}{2}\chi_0 \ln(\chi)$ χ is the number of entanglements per chain (Marrucci et al [85], Acierno et al [86,87])	$\frac{1}{2}(\chi+1)(\mathbf{I} - \mathbf{c}^{-1})$
MGI (modified)	$-\ln\left(\det\left(\frac{\mathbf{c}}{(\text{tr}(\mathbf{c}^{1/2}))^2}\right)\right)$ $= 6\ln(\text{tr}(\mathbf{c}^{1/2})) - \ln(\det(\mathbf{c}))$ (Marrucci et al [88], Leygue et al [69])	$\frac{3\mathbf{c}^{-1/2}}{\text{tr}(\mathbf{c}^{1/2})} - \mathbf{c}^{-1}$
Pompon	$\frac{1}{2}\{3\ln(\text{tr}(\mathbf{c})) - \ln(\det(\mathbf{c}))\}$ $+ \frac{3}{2}\left\{\lambda^{*2} - (\lambda^* - q)^2 H(\lambda^* - q)\right\}$ $\left\{-1 - 2\ln(\lambda^*)\right\}$ λ^* is an extended stretch factor (Öttinger [89], McLeish and Larson [90])	$\frac{3}{2}\frac{\mathbf{I}}{\text{tr}(\mathbf{c})} - \frac{1}{2}\mathbf{c}^{-1}$

Table 1 (Facing page) List of commonly used expressions for the Helmholtz free energy density a and the corresponding thermodynamic potential, $\mathbf{T}_{rev}^T = 2\mathbf{c} \cdot \frac{\partial a}{\partial \mathbf{c}}$, with respect to the conformation tensor, \mathbf{c} . The expressions are provided in dimensionless form. The free energy is made dimensionless with respect to $nk_B T$, where n is a chain number density, k_B is the Boltzmann factor and T the temperature, and \mathbf{c} is made dimensionless with respect to the square of the equilibrium end-to-end chain distance, $k_B T/K$ where K is the (apparent) elastic constant for the chain's elastic energy. In the random flight model, $k_B T/K = l^2/3N$, where N , l is the number, length of repeating (Kuhn) segments (Kuhn and Gr \ddot{u} n [122]).

The fairly simple set of equations described here has still quite powerful predictive capabilities, as it can be judged from the richness of the expressions for the thermodynamic parameters a and Λ that can be used, a sample of which is shown in tables 1 and 2, respectively. Indeed, in this way most of the viscoelastic constitutive models developed over the past several years can be cast in the general form outlined above. For example, using the expression for the Helmholtz free energy, a , corresponding to the linear elastic (Hookean) form from table 1 and choosing the corresponding expression for the relaxation matrix Λ as indicated in table 2, one can recover the Upper Convected Maxwell, the Hookean dumbbell model with hydrodynamic interactions, the Giesekus, the Phan-Thien and Tanner and the Extended White-Metzner models. If in addition to the parameters corresponding to the Upper Convected Maxwell model a non-zero Newtonian viscosity is chosen, we recover the Oldroyd-B model, if in addition we choose a non-zero value for the ζ parameter we recover the Johnson-Segalman model (or the Oldroyd-A model if $\zeta = 2$). Alternatively, keeping the same expression for the relaxation matrix Λ but switching to a different expression for the Helmholtz free energy, a , as shown in table 1, one can also switch to a different model. For example, in this way, one can recover the Finite-Extensible Non-Linear Elastic Dumbbell model with the Peterlin preaveraging approximation (FENE-P) from the Upper Convected Maxwell. Additional applications also exist in the literature following the above exposed approach. Where things become different (and more interesting) is when additional constraints are used to advantage in order to guide tighter restrictions to the models, such as the “volume preserving” constraint, expressed by the requirement that $\det(\mathbf{c})$ remains constant. This has been used originally by Leonov [77] and was later employed within the GENERIC formalism to induce further generalizations of the original Leonov model by Ait-Kadi et al [91]. (See also the corresponding entries in tables 1 and 2).

Going well beyond simply reformulating existing models using the new formalism, the non-equilibrium thermodynamics allows automatically for the generation of new models, simply by mixing and matching different expressions for the model parameters. In this way, for example, a new variant for the Marrucci, Greco and Ianniruberto (MGI) model (Marrucci et al [88]) for entangled linear polymer melts

has been recently developed (Leygue et al [69]) with much improved modeling predictions.

Model	$\Lambda_{\alpha\beta\gamma\epsilon}$
Elastic dumbbell (UCM, OldroydA, B, FENE-P)	$\frac{1}{2} \left(c_{\alpha\gamma} \delta_{\beta\epsilon} + [perm.] \right)$
Elastic dumbbell with hydrodynamic interactions	$\frac{1}{2} \left(c_{\alpha\gamma} \left(\delta_{\beta\epsilon} - \frac{3}{4} h \sqrt{\frac{\pi}{\text{tr}(\mathbf{c})}} \left(\delta_{\beta\epsilon} + \frac{c_{\beta\epsilon}}{\text{tr}(\mathbf{c})} \right) \right) + [perm.] \right)$ $0 \leq h \leq \frac{2}{3} \sqrt{\frac{I_1}{\pi}} ; \text{ (Bird et al [58])}$
Modified encapsulated dumbbell	$\frac{1}{2} \left(\sigma c_{\alpha\gamma} \delta_{\beta\epsilon} + (1 - \sigma) \frac{1}{\text{tr}(\mathbf{c})} c_{\alpha\beta} c_{\gamma\epsilon} + [perm.] \right)$ $\sigma \geq 0, \text{ (Bird and DeAguiar [81])}$
Giesekus	$\frac{1}{2} \left(c_{\alpha\gamma} \left((1 - \alpha) \delta_{\beta\epsilon} + \alpha c_{\beta\epsilon} \right) + [perm.] \right)$ $0 \leq \alpha \leq 1 ; \text{ (Giesekus [78])}$
Leonov	$\left(c_{\alpha\epsilon} c_{\gamma\beta} - \frac{1}{3} c_{\alpha\beta} c_{\gamma\epsilon} + [perm.] \right)$ <p style="text-align: center;">(Leonov, [77])</p>
Phan-Thien/Tanner (linear)	$\frac{1}{2} \left(1 + \epsilon (\text{tr}(\mathbf{c}) - 3) \right) \left(c_{\alpha\gamma} \delta_{\beta\epsilon} + [perm.] \right)$ <p style="text-align: center;">(Phan-Thien and Tanner [92])</p>
Extended White/ Metzner	$\frac{1}{2} \frac{1}{\lambda^*(I_1, I_2, I_3)} \left(c_{\alpha\gamma} \delta_{\beta\epsilon} + [perm.] \right)$ <p>λ^* is a dimensionless, positive function of the invariants of \mathbf{c}; for example, $\lambda^* = K(I_1)^k$ (Souvaliotis and Beris [93])</p>
Leygue, Beris and Keunings	$\frac{1}{2} \left(c_{\alpha\gamma} \left(\alpha c_{\beta\epsilon} + (1 - \alpha) \frac{\text{tr}(\mathbf{c}^{1/2})}{3} c_{\beta\epsilon}^{1/2} \right) + [perm.] \right)$ $0 \leq \alpha \leq 1 ; \text{ (Leygue et al [69])}$

Table 2 (Facing page) List of commonly used expressions for the fourth order relaxation tensor Λ , made dimensionless by $k_B T / \lambda_e n K^2$ where λ_e represents an equilibrium relaxation time and the other parameters have been defined in table 1. Note that only one of four equivalent contributions to the $\partial a / \partial \mathbf{c}$ component is given, the others (represented as [perm.] in the table) arising from the following permutations of the original subscripts: $\alpha\beta\gamma\epsilon \leftrightarrow \beta\alpha\gamma\epsilon \leftrightarrow \alpha\beta\epsilon\gamma \leftrightarrow \beta\alpha\epsilon\gamma$ (this table is adapted from Beris and Edwards [26]. A number of sufficient conditions known to assure the non-negative character of the relaxation dissipation are included (see Beris and Edwards [26] for more details regarding their derivation).

For example, the new expression for the relaxation matrix developed in that model (last entry in table 2) allows (for $\alpha = 1$) for the ratio of the second to the first normal stress coefficients to reach an asymptotic value of 1 at long times after cessation of simple shear flow (Leygue et al [69]), exactly as seen in detailed experimental observations (Kalogianitis and van Egmond [94]). Moreover, the consistency required between the stress and the evolution equation (expressed here in the specific dependence on parameters, like the non-affine parameter ξ (see equations (4) and (5)) also results in a significant improvement of the predictive capabilities of the model, as also demonstrated with the variant of the MGI model developed within the non-equilibrium thermodynamics framework (Leygue et al [69]) as, for example, seen in the comparison for the predictions for the transient expressions for the two normal coefficients in shear flow with experimental data (Kalogianitis and van Egmond [94]). Finally, there is still the possibility for further improvements if the new generalized deformation scale of Milner [95] is employed---however, this still has not been used in connection with the improved MGI model.

With this opportunity we need to note here that a slightly more general form of the evolution equation for the conformation tensor is used in order to represent the Convective Constraint Release (CCR) mechanism incorporated in the MGI model (Marrucci et al [88]) within the non-equilibrium thermodynamics framework (Leygue et al [69]). This more general set for the evolution and stress equations (which also corrects, for the general case where \mathbf{L} lacks the symmetry ($\alpha\beta \leftrightarrow \gamma\epsilon$), an equivalent expression originally proposed in Beris and Edwards [26] has as follows (Leygue et al. [69]):

$$\frac{D}{Dt} \mathbf{c} - \nabla \mathbf{v}^T \cdot \mathbf{c} - \mathbf{c} \cdot \nabla \mathbf{v} = \mathbf{L} : \nabla \mathbf{v} - \Lambda : \frac{\partial a}{\partial \mathbf{c}} \quad \dots\dots\dots(12)$$

and

$$\mathbf{T}^T = 2 \frac{\partial a}{\partial \mathbf{c}} \cdot \mathbf{c} + \mathbf{L} : \frac{\partial a}{\partial \mathbf{c}} + \mathbf{Q} : \nabla \mathbf{v}, \quad \dots\dots\dots(13)$$

where \mathbf{L} and \mathbf{Q} are two new fourth order tensors, in general functions of the conformation tensor \mathbf{c} , also obeying the same symmetry properties as the relaxation

matrix Λ , as indicated in the caption for table 2. The fourth order tensor \mathbf{L} generalizes the non-affine interactions, the previously one (corresponding to the Johnson and Segalman model (Johnson and Segalman [72]) obtained when we adopt the following value for \mathbf{L} (Beris and Edwards [26]) given here in component form:

$$L_{\alpha\beta\gamma\epsilon} = -\frac{\xi}{2} (c_{\alpha\gamma}\delta_{\beta\epsilon} + c_{\beta\gamma}\delta_{\alpha\epsilon} + c_{\alpha\epsilon}\delta_{\beta\gamma} + c_{\beta\epsilon}\delta_{\alpha\gamma}). \quad \dots\dots\dots(14)$$

Notice the similarity between the \mathbf{L} and the Λ tensors (in fact for the Johnson and Segalman model, the two are proportional to each other, $\mathbf{L} = -\xi\Lambda$). Similarly, the tensor \mathbf{Q} generalizes the Newtonian viscous response of the system to an anisotropic one, the previously more common isotropic viscous contribution in equation (5) obtained when we express \mathbf{Q} in terms of the isotropic fourth order tensor obtained by suitable permutations of the diadic \mathbf{II} , where \mathbf{I} is the second order unit (delta) tensor, so as to preserve the symmetries:

$$Q_{\alpha\beta\gamma\epsilon} = \frac{\eta_s}{2} (\delta_{\alpha\gamma}\delta_{\beta\epsilon} + \delta_{\beta\gamma}\delta_{\alpha\epsilon} + \delta_{\alpha\epsilon}\delta_{\beta\gamma} + \delta_{\beta\epsilon}\delta_{\alpha\gamma}) \quad \dots\dots\dots(15)$$

A direct viscous contribution is not necessary for melts, such as that described by the (modified or original) MGI model. There the critical role is played by the CCR mechanism which can be captured if we adopt the following expression for the non-affine fourth order parameter \mathbf{L} (Leygue et al [69]):

$$\mathbf{L} = -J(\mathbf{c}, \nabla\mathbf{v})\Lambda : \frac{\partial a}{\partial \mathbf{c}} \frac{\mathbf{c}^{1/2}}{\text{tr}(\mathbf{c}^{1/2})}, \quad \dots\dots\dots(16)$$

where the scalar function J represents higher order nonlinearities in the model, acting as a switch from 1 to 0 when the prescribed expression for \mathbf{L} risks violating the requirement for a non-negative entropy production (Leygue et al [69]).

The availability of a simple expression for the local entropy production rate is yet another contribution of non-equilibrium thermodynamic considerations to rheology, of importance even to isothermal flows. This expression, provided by equations (8) and (11) for the simple model, generalizes to the following equation when the new equations (12) and (13) are used to replace the simpler previous expressions for the constitutive equation (4) and the stress, equation (5), respectively:

$$\sigma = \frac{1}{T} \Phi^T : \Omega : \Phi, \quad \dots\dots\dots(17)$$

where Φ is a generalized potential forces vector:

$$\Phi^T = \left[\frac{\partial a}{\partial \mathbf{c}}, \nabla\mathbf{v} \right] \quad \dots\dots\dots(18)$$

and Ω is a generalized dissipation matrix

$$\Omega = \begin{pmatrix} \Lambda & -\mathbf{L} \\ \mathbf{L} & \mathbf{Q} \end{pmatrix}. \quad \dots\dots\dots(19)$$

As you can see there is a contribution to the total dissipation from the mixed nonaffine terms only if the fourth order matrix \mathbf{L} is nonsymmetric with respect to an interchange of the first two by the last two indices $\{\alpha\beta\} \leftrightarrow \{\gamma\epsilon\}$ (something which is satisfied by the simpler model, equation (14), but not by the MGI expression, equation (16)). Therefore, the need for the use of the switch function J so as to prevent a potential violation of the non-negative character of the local entropy production. Notice that a similar switch function has also been suggested (Marrucci [96]), from a different ground, namely in order to prevent the appearance of a negative effective relaxation time.

In addition, as it is shown in more detail in the chapter 8 of Beris and Edwards [26], information has been collected there regarding the mathematical well-posedness of the systems of governing equations resulting from the dissipative Hamiltonian formalism and in particular regarding the evolutionary character of the constitutive equations and the preservation (upon integration in time of the constitutive equation) of the positive definite character of the conformation tensor. The latter is necessary especially when the physical interpretation of the conformation tensor requires its positive-definite character. Such is the case for dilute solutions when the conformation tensor is identified with the second moment of the end-to-end distribution function (Bird et al [58]). As shown in section 8.1.6 of Beris and Edwards [26] for most of the models cast in the non-equilibrium thermodynamics formalism described above the well-posedness issues referenced above have been proven to hold whereas it is only with models (such as the White-Metzner fluid [97]) which are inconsistent with the formalism that well-posedness fails. Whether in general the two (i.e. the non-equilibrium thermodynamic consistency and mathematical well-posedness) are always following each other it is not known, but there is plenty of evidence that the two are at least strongly correlated.

Even not considering well-posedness issues (that may or may not be of importance to calculations) there are several advantages already drawn from casting the equations within the general non-equilibrium thermodynamics framework presented here. Some of those have already become evident as we were explaining the proposed equations above. For clarity we repeat them among a more complete list appended below:

1. First of all, it is important to note from the outset that although the formalism-based set of either the set of simpler equations (2) - (4) or even the more general set of equation (2) and equations (12) - (13) is constructed within the rules of traditional continuum mechanics as, for example, those developed by Oldroyd [47], they represent only a small subset of all the possible equations that could have been otherwise constructed based only on the continuum mechanics rules. Non-equilibrium thermodynamics does offer therefore specific constraints and it is in those constraints that most of the usefulness of the formalism can be found. Of special importance is the consistency relationship between the expression for the stress and the evolution equation for the conformation tensor. For some models, such as the MGI and the

Encapsulated Dumbbell, application of that relationship suggests corrective terms to be applied either to the stress or to the evolution equation, respectively. In addition, the formalism provides guidelines for the primary form of the functional dependence of various parameters entering the theory. In particular, excluding a direct dependence on the velocity for the relaxation time and for the elastic part of the Helmholtz free energy, the formalism does not allow the original White-Metzner model (White and Metzner [97], Beris and Edwards [26]). Instead, by suggesting a direct dependence of the parameters only on the conformation tensor, a new model along the same spirit of the original White-Metzner approach has been developed, the so-called extended White Metzner model (Souvaliotis and Beris [93]). This model showed a much better agreement to known experimental trends (among other things, a finite extensional viscosity is predicted) using parametric dependencies on the conformation tensor of the same complexity (like power-law) than the original White-Metzner model has on the velocity gradients. In addition, one can show that this model is devoid of the possible instabilities that can occur as a result of the loss of evolutionarity that can happen with the White-Metzner model (Dupret and Marchal [68], Verdier and Joseph [98]).

2. Second, although other applications of irreversible thermodynamics can lead, usually after considerable manipulation of the formulae, to the same information about the local entropy production (like rational thermodynamics (Truesdell [71])) those expressions are all effortlessly obtained here simultaneously (or even before) with the actual governing equations, since the entropy production terms are an inherent part of the formalism, rather than a product of subsequent form manipulation. The expressions for the local rates of the entropy production allow to obtain, in addition to the standard inequalities for transport phenomena (like a non-negative viscosity) and relaxation processes (non-negative relaxation time) more complex inequalities like the one associated with the non-affine motion accompanying the Convective Constraint Release mechanism accompanying the dynamics of linear polymer melts (Leygue et al [69]). This identification can lead to more physical model descriptions devoid of undesirable mathematical instabilities.
3. Third, the formalism allows for a systematic generation of new model equations through analysis and synthesis. Indeed, by analyzing the governing equations into their convective (reversible) and dissipative (irreversible) parts and by expressing the dependences directly in terms of the (extended) Helmholtz free energy of the system and its derivatives with respect to the field variables as well as in terms of dissipative parameters, one can detect similarities and differences between various previously proposed models, such as shown in the data supplied in tables 1 and 2. Then, through a different combination of those previously identified components, or by suitably modifying them, new models can be constructed that potentially fit better the experimental data. For example, the combination of a sophisticated free energy expression, such, for example, suggested by Marrucci for a linear polymer melt, with a more sophisticated expression for the relaxation tensor suggested originally by Giesekus [78] has led to a better description of transient normal stress data (Leygue et al [69]).

4. Fourth, the formalism lends itself to its generalization to more complex model equations allowing for different measures of deformation (compare, for example, that used in solutions from the melts (see also Milner [95]) or more internal variables (such as, for example, multiple mode models) which also exhibit internal coupling (see the section below for examples). It also becomes indispensable when the complexity of the model increases due to either the presence of multiple transport phenomena (see, for example, chapter 10 in Beris and Edwards [26]) but primarily when the internal structure becomes more complex, due to multiple length (and time) scales (like, for example, with blends (Wagner et al [99], Grmela et al [100]), and flows next to surfaces. (See Mavrantzas and Beris [48,49]).

3. MORE COMPLEX, USING MULTIPLE INTERNAL VARIABLES, MODELS FOR FLEXIBLE POLYMERIC SYSTEMS

One obvious generalization of the models discussed in section 3 involves the use of multiple modes of conformation (Beris and Edwards [26]). Multiple relaxation modes arise naturally from a detailed microscopic analysis of the dynamics of long macromolecular chains due to the natural coupling of the internal degrees of freedom (Bird et al [58]). This analysis is particularly simple in the limit of small deformations and in the absence of hydrodynamic interactions where it can be shown that the overall chain dynamics can be recovered as the linear superposition of a sequence of discrete vibration/deformation modes, each one at specific relaxation time and elastic modulus characteristics (Doi and Edwards [101]). This is the so-called Rouse limit and despite its simplicity it is found to be still pertinent to the dynamics of polymer melts (see, for example, Ferry [102]). In general, one can describe phenomenologically the small deformation dynamics of any viscoelastic system by the superposition of a spectrum of linear viscoelastic responses (Ferry [102]). This spectrum of multiple relaxation modes is theoretically considered continuum but in practice it can be very well approximated as discrete with few modes, of the order of 10 or so. The spectrum has also been shown to be fully compatible with non-equilibrium thermodynamics, which can also be used to infer critical properties (like that of the fading memory, Beris and Edwards [120]).

However, although in a straightforward generalization of linear viscoelasticity to the nonlinear (i.e. large deformations) regime, one could simply replace the linear viscoelastic elements with individual Upper Convected Maxwell (or other more nonlinear) modes, such a description is obviously not unique (Quinzani et al [103]). Moreover, for a general flow it is not even guaranteed that it is going to work, even as we introduce more adjustable parameters to the models, switching to various nonlinear generalizations to the Maxwell model. Nevertheless, the simultaneous use of a series of, configurationally uncoupled (i.e. coupled only through the common flow field), viscoelastic models, is one approach taken in the past in order to represent macroscopically the complicated internal polymer dynamics even in the presence of large deformations, and has seen some success (Quinzani et al [103]). An alternative, but in many ways equivalent approach, is to use an integral model based on the weighting of various deformation measures calculated over the past history of each individual fluid element such as the BKZ (Bernstein et al [104]), Wagner [105], Doi-

Edwards [106] and other integral models. Although some success has also been made following that route as well, these integral generalizations to the finite deformation regime of linear viscoelasticity are also not guaranteed to provide good approximations to arbitrary flow fields. In addition integral models offer, in general, an expensive way of performing simulations in complex flows due to the requirement to keep track of previous particle deformation histories (although some recent work by Wapperom and Keunings [62] has shown promise for two-dimensional flow simulations, using deformation field evaluations).

The reason why we say that both the use uncoupled multiple differential models as well as the single integral models are not guaranteed to work is the neglect of nonlinear interactions that can directly couple the conformations of the individual elements considered in the dynamics. Introducing that coupling restores the generality of the modeling, and in as one gets closer to the most general representation of an arbitrary viscoelastic dynamic behavior, typically represented by a infinite nested integral expression (Truesdell and Noll, [14]). However, the complexity also increases dramatically. In particular, implementing just the next step towards the most general integral expression, necessitate the presence of two nested integral expressions, thus making the already difficult integral calculations even more difficult - see, for example, the work of Vrentas et al [107] on integral models with strain coupling. Therefore, we focus here on the other alternative, the coupled multimode differential models. Introduction of the conformational coupling there is much more straightforward. The first work along those lines is attributed to Giesekus [79] who just stopped short from applying in practice a proposal to examine the possibilities for direct coupling between the multiple conformation tensors. It also arises naturally within the non-equilibrium thermodynamics framework, as more structural parameters are introduced to the model (Edwards et al [108]). Some examples, where non-equilibrium thermodynamics has been applied to, follow.

One of the earlier models where the coupling between two internal structural parameters appears is the Marrucci and Acierno model of entangled polymer melts (Marrucci et al [85], Acierno et al [86,87]). This model possesses two internal variables, the (usual) conformation tensor, meant here to represent the conformation of the entanglement chains, and an additional scalar variable, the number of entanglements per chain, χ . Thus, in constructing the elastic Helmholtz free energy density, we need to make two changes over the more traditional expressions: First, the relevant reference density is that of the entangled chains, thus $n = c(1 + \chi)$, where c is the chain number density. Second, there is an extra contribution due to the entropy of the distribution of the entanglements. Both changes are reflected in the Helmholtz free energy form as it appears in table 1. Where the changes are more interesting is in establishing the right form for the evolution equations for the internal structural parameters. In particular, we have found (Beris and Edwards [26]) that in order to get the right dependence of the evolution equation for χ on the stress, a general form for the relaxation needs to be used corresponding to a symmetric form for the local rate of the entropy production, analogous to the one shown above for the MGM model:

$$\sigma = \frac{1}{T} \Phi^T : \Omega : \Phi, \quad \dots\dots\dots(20)$$

where Φ is a generalized potential forces vector

$$\Phi^T = \left[\frac{\partial a}{\partial \mathbf{c}}, \frac{\partial a}{\partial \chi} \right] \quad \dots\dots\dots(21)$$

and Ω is a generalized dissipation matrix:

$$\Omega = \begin{pmatrix} \Lambda & \Lambda^* \\ \Lambda^* & \Lambda_\chi \end{pmatrix}, \quad \dots\dots\dots(22)$$

where Λ , Λ^* and Λ_χ are relaxation matrices of fourth, second and zero (i.e. scalar) order, respectively. Corresponding to this relaxational entropy dissipation we have now the following evolution equations for the two internal variables, c and χ , developed following a similar procedure to the one described above after equation (9):

$$\frac{D}{Dt} \mathbf{c} - \nabla \mathbf{v}^T \cdot \mathbf{c} - \mathbf{c} \cdot \nabla \mathbf{v} = -\Lambda : \frac{\partial a}{\partial \mathbf{c}} - \Lambda^* \frac{\partial a}{\partial \chi} \quad \dots\dots\dots(23)$$

and

$$\frac{D}{Dt} \chi = -\Lambda^* : \frac{\partial a}{\partial \mathbf{c}} - \Lambda_\chi \frac{\partial a}{\partial \chi} \quad \dots\dots\dots(24)$$

Although specific forms for the relaxation matrices have also been proposed in Beris and Edwards [26] so that the end result is as close to the original model as possible (at least as far as the evolution equation for χ is concerned) the important item to note here is that the coupling correction (through the Λ^* matrix) introduced automatically by the thermodynamic approach to the evolution equation for \mathbf{c} is new. As a consequence of the coupling introduced through this term of the two structural evolution equations (23) and (24), there is an additional term that needs to be introduced into the original evolution equation for \mathbf{c} in order to ensure thermodynamic consistency. This contribution and the possibility for a wider selection for alternative relaxation components for the primary relaxation matrix Λ among the possible choices suggested in table 2, still remain to be tested in practice as far as potentially considerably improving the fit of the Marrucci-Acierno model to experimental data.

A similar in the form differential model for a polymer melt, i.e. based also on two internal parameters, one tensor and one scalar, is the pompon (or pom-pom) model, proposed originally by Bishko et al [109] and McLeish and Larson [90] for branched polymers endowed with the pompon molecular structure, i.e. a main skeleton leading to “fluffy” ends with q side (end) branches each ($q > 1$). The breakthrough in modeling that system came in the development of two special measures for the polymer deformation: a tensor one, \mathbf{S} , representing a scaled polymer skeleton deformation tensor, defined in terms of a (usual) second order and symmetric non-negative definite structural parameter \mathbf{c} as a scaled polymer conformation:

$$\mathbf{S} = \frac{\mathbf{c}}{\text{tr}(\mathbf{c})} \quad \dots\dots\dots(25)$$

of unit trace (by definition), and a scalar parameter representing either the relative deformation, λ , of the skeleton over its equilibrium value if it is smaller or equal than q , or, otherwise, the extent to which side branches penetrate into the overextended tube surrounding the main branch, $2s_c/s_b$, where s_c, s_b are the molecular weights of the arm that penetrates the main tube and the molecular weight of the entire side arm, respectively. Since the meaning of the scalar variable changes depending on whether λ is equal or not to its maximum allowed value, q , it is convenient for modeling to replace it by a more general expression, λ^* , defined as (Öttinger [89]):

$$\lambda^* = \lambda + \frac{s_c}{s_b} H(\lambda - q), \quad \dots\dots\dots(26)$$

where H represents the Heaviside step function defined as zero if the argument is negative and one if it is non-negative. By considering separately the stretching along the main polymer backbone from its overall deformation and by considering the partial retraction of the end arms into the main tube surrounding the polymer, McLeish and Larson [90] have managed to produce a modified reptation model for polymers with the pompon structure that was very successful in reproducing linear viscoelasticity data. The original model was offered in an integral form. However, to allow for an easier handling of complex flows, McLeish and Larson [90] also developed a differential approximation. This is the form that was later cast (Öttinger [89]) into the GENERIC formalism (Öttinger and Grmela [16]), thus ensuring its thermodynamic admissibility.

It is instructive to show here the key elements of the pompon GENERIC reformulation, albeit using a slightly different presentation than in (Öttinger [89]) (to keep the discussion within the simplified non-equilibrium formalism used in this work) that also hopefully allows us to develop a more intuitive understanding of the form of the final equations. Of course, as usual, an additional advantage of the application of the non-equilibrium formalism here, as well as everywhere else, is the potential for an improvement in the model arising through the substitution of the expression used for anyone of its key elements (like the expressions used for the Helmholtz free energy density and the relaxation matrices) with others, potentially more appropriate for a particular application. Indeed, more specifically for the pompon model, generalizations for both these expressions have also been suggested (Öttinger [89], Verbeeten et al [110]).

The starting point of the modeling is to see how to properly describe the reversible (convective) dynamics of the two internal parameters, \mathbf{c} and λ^* . The convective dynamics of the first, the conformation tensor \mathbf{c} , is, as usual, that described by an upper convected derivative:

$$(\dot{\mathbf{c}})_{rev} \equiv \frac{D\mathbf{c}}{Dt} - \nabla\mathbf{v}^T \cdot \mathbf{c} - \mathbf{c} \cdot \nabla\mathbf{v} \quad \dots\dots\dots(27)$$

The second variable, λ^* , needs more care as far as its handling. The important thing here is to realize, guided by its physical meaning, that since it represents a relative deformation measure it is dimensionless and hence modeled by a ratio of the actual length versus a proper reference length. The other piece of information we need to use

is the fact that the only relevant physical length scale in the problem is provided by the conformation tensor, \mathbf{c} , which scales as length square. Therefore, an internal length scale can be constructed by taking the square root of the first invariant of \mathbf{c} , $\text{tr}(\mathbf{c})$. In this way, we can analyze λ^* as the ratio of an absolute length s , (hence representing a proper scalar quantity) and the square root of $\text{tr}(\mathbf{c})$:

$$\lambda^* = \frac{s}{\sqrt{\text{tr}(\mathbf{c})}} \tag{28}$$

Knowing then now that the s as a real scalar obeys a reversible dynamics described simply by the regular material (substantial) time derivative:

$$(\dot{s})_{rev} = \frac{Ds}{Dt} \tag{29}$$

whereas \mathbf{c} , as mentioned above, obeys an upper convected dynamics, it is straightforward to calculate, through application of differentiation by parts, the corresponding reversible dynamics for λ^* :

$$\begin{aligned} (\dot{\lambda}^*)_{rev} &= \frac{(s)_{rev}}{(\text{tr}(\mathbf{c}))^{1/2}} - \frac{s}{2(\text{tr}(\mathbf{c}))^{3/2}} \text{tr}(\dot{\mathbf{c}})_{rev} \\ &= \frac{1}{(\text{tr}(\mathbf{c}))^{1/2}} \frac{Ds}{Dt} - \frac{s}{2(\text{tr}(\mathbf{c}))^{3/2}} \text{tr} \left(\frac{D\mathbf{c}}{Dt} - \nabla\mathbf{v}^T \cdot \mathbf{c} - \mathbf{c} \cdot \nabla\mathbf{v} \right) \\ &= \frac{D\lambda^*}{Dt} - \lambda^* \nabla\mathbf{v}^T : \mathbf{S} \end{aligned} \tag{30}$$

where use was made of the defining relations provided by equations (25) and (28) and the symmetry of \mathbf{S} . It is therefore the *relative* character of λ^* with respect to an invariant of a second order tensor that requires the additional term in the modeling of the reversible (convective) dynamics and this physical understanding is important in order to lead to the proper mathematical description.

The next step in the modeling involves developing an expression for the reversible component for the extra stress, \mathbf{T}_{rev} . For that suffice to use the regular expression developed to model elasticity:

$$\mathbf{T}_{rev}^T = 2\mathbf{c} \cdot \frac{\partial_t a}{\partial \mathbf{c}} \tag{31}$$

where the important item to realize here (emphasized by adding the subscript t to the symbol for the partial derivative) is that the partial derivative in the right hand side is a total partial derivative, i.e. to calculate it one needs to take into account *all* possible dependences, explicit as well as implicit (i.e. through the dependence on parameters which in turn are functions of \mathbf{c}). This last remark is the key to unravel the right stress expression for the pompon model since the assumed expression for the free energy expression there (see last line in table 1) involves an explicit dependence on both \mathbf{c} and λ^* , and we know now, after equation (27), that the later conceals a dependency on \mathbf{c} as

well. Taking that implicit dependency into account, and using differentiation by parts, equation (31) becomes:

$$\begin{aligned} \mathbf{T}_{rev}^T &= 2\mathbf{c} \cdot \left(\frac{\partial a(\mathbf{c}, \lambda^*)}{\partial \mathbf{c}} + \frac{\partial a(\mathbf{c}, \lambda^*)}{\partial \lambda^*} \frac{\partial \lambda^*}{\partial \mathbf{c}} \right) \\ &= 2 \left(\mathbf{c} \cdot \frac{\partial a(\mathbf{c}, \lambda^*)}{\partial \mathbf{c}} + \lambda^* \frac{\partial a(\mathbf{c}, \lambda^*)}{\partial \lambda^*} \mathbf{S} \right) \end{aligned} \tag{32}$$

where use, again, was made of the defining relations provided by equations (25) and (28). Therefore, what we see here is that again all the elastic information is passed through the conformation tensor \mathbf{c} and it is only (again) the relative character of λ^* and, by consequence, its implicit dependence on the $\text{tr}(\mathbf{c})$, that generates an additional contribution to the stress.

The third step in the modeling involves the expression for the elastic contribution of the Helmholtz free energy. The proposed one by Öttinger [89], listed in the last row of table 1, can be explained by resorting again to the physical interpretation of the internal variables. For that purpose, let us start by the simplest expression for a , that for a Hookean (linearly elastic) dumbbell, used in the Upper Convected Maxwell model (first line in table 1). Notice that it has two terms, both expressed in terms of a single second order non-negative-definite tensor internal variable, the conformation tensor \mathbf{c} . The first, proportional to $\text{tr}(\mathbf{c})$, models the entropic contribution of the internal degrees of freedom in a chain; the second one, proportional to $\ln(\det(\mathbf{c}))$, models the group entropy generated by having a (Gaussian) distribution of chains with different conformations. In the pompon model those two effects (internal and group) are represented separately by two different internal variables, the stretching factor λ^* and the strain measure \mathbf{S} . Guided by the similarities we can then interpret the quadratic function of λ^* as replacing the $\text{tr}(\mathbf{c})$ term, and the $\ln(\det(\mathbf{S})) = \ln(\det(\mathbf{c})) - 3\ln(\text{tr}(\mathbf{c}))$ term as equivalent to the $\ln(\det(\mathbf{c}))$, where, again, use is made of the defining equation (25) for \mathbf{S} . If in addition we also see the plausibility of an additional term, proportional to $\ln(\lambda^*)$, in order to model the group entropy contribution for λ^* , and the fact that the quadratic expression for λ^* , could, in general, change discontinuously (as far as the higher than second derivatives are concerned) as λ^* crosses the critical value q , (since then the underlying interpretation for λ^* changes, thus explaining the presence of the Heaviside unit function within the quadratic function), all the terms appearing in the expression for the Helmholtz free energy density can be understood. In particular, the expression appearing in table 1 is the one for which (with suitable choices for the relaxation matrices---see next paragraph below) the original McLeish and Larson [90] model is recovered. Albeit a generalization of that expression is, in principle, also possible (Öttinger [89]), the one chosen there enjoys special properties that can, in a way, justify its selection: the weight of the $\ln(\lambda^*)$ is compatible with that of the $\frac{1}{2}\ln(\text{tr}(\mathbf{c}))$ of the first term, again an indication for the implicit dependence on \mathbf{c} due to the scaling reasons mentioned above; moreover, the quadratic term weighing the heaviside H function is exactly the proper one to allow for the zero and first order continuity of a at $\lambda^*=q$ while

simultaneously the quadratic term on λ^* disappears as $\lambda^* > q$, still preserving the convex character of that expression with respect to λ^* .

The last step in the non-equilibrium modeling involves the introduction of dissipative phenomena. This is typically done, at least for melts, with the selection of the appropriate relaxation matrices to describe relaxation processes of the internal variables. This selection follows the assignment for the local rate of the entropy production, as explained before. In this case, this is represented by a general quadratic form in terms of the thermodynamic potentials that we can form based on the internal variables of the system. For the pompon model, we have (by analogy to the MGM model - see above) the following form for the local rate of the entropy production:

$$\sigma = \frac{1}{T} \Phi^T : \Omega : \Phi, \tag{33}$$

where Φ is a generalized potential forces vector defined as:

$$\Phi^T = \left[\frac{\partial a}{\partial \mathbf{c}}, \frac{\partial a}{\partial \lambda^*} \right] \tag{34}$$

and Ω is a generalized dissipation matrix:

$$\Omega = \begin{pmatrix} \Lambda & \Lambda^* \\ \Lambda^* & \Lambda_\lambda \end{pmatrix}, \tag{35}$$

where Λ , Λ^* and Λ_λ are relaxation matrices of fourth, second and zero (i.e. scalar) order, respectively. The selection of the relaxation matrices, is only limited by the requirement that the corresponding expression to the local rate of entropy production to be non-negative. Several choices are therefore possible, and for each one a different set of constitutive equations arise. (See also Öttinger [89]).

Corresponding to this relaxational entropy dissipation provided by equations (33)-(35) we have now the following evolution equations for the two internal variables, c and λ^* , developed following a similar procedure to the one described above after equation (9):

$$\frac{D}{Dt} \mathbf{c} - \nabla \mathbf{v}^T \cdot \mathbf{c} - \mathbf{c} \cdot \nabla \mathbf{v} = -\Lambda : \frac{\partial a}{\partial \mathbf{c}} - \Lambda^* \frac{\partial a}{\partial \lambda^*} \tag{36}$$

and

$$\frac{D\lambda^*}{Dt} - \lambda^* \nabla \mathbf{v}^T : \mathbf{S} = -\Lambda^* : \frac{\partial a}{\partial \mathbf{c}} - \Lambda_\lambda \frac{\partial a}{\partial \lambda^*} \tag{37}$$

Those reduce to the constitutive equations corresponding to the original McLeish and Larson [90] differential approximation using the following expressions for the relaxation matrices (see also Öttinger [89]):

$$\Lambda = 2(\mathbf{c} - \mathbf{I})(3\mathbf{S} - \mathbf{I})^{-1} \cdot \mathbf{c}; \quad \Lambda^* = \mathbf{0}; \quad \Lambda_\lambda = \frac{1}{3} \frac{\lambda^*}{\lambda^* + 1 - (1+q)\text{H}(\lambda^* - q)} \tag{38}$$

while you should note that different time scales are used in order to render dimensionless the different relaxation matrices in the above expression. Regarding the relaxation matrices, the following remarks may also be added. Although there are choices for the relaxation matrices that can be made in order to recover the McLeish and Larson [90] model, and those choices appear to be thermodynamically admissible, they are marginally so, leading to an almost singular behavior, as the limits $\mathbf{S} \rightarrow \mathbf{I}/3$ and $\lambda^* \rightarrow q+$ are taken, for the relaxation matrices Λ and Λ_λ , respectively. Alternatively, one can use different forms for the relaxation matrices (see also Öttinger [89], Verbeeten et al [110]). An advantage of the use of a more general relaxation is the possibility to obtain more realistic values for the second normal stress coefficient (Öttinger [89], Verbeeten et al [110]). However, we also need to mention here that a drawback to a more conventional dissipation form may be a qualitative different behavior from that of the integral model (the shear viscosity does not exhibit the right asymptotic behavior with increasing shear rate), as the one originally observed with a Maxwellian type dissipation (see the discussion following equation (30) in McLeish and Larson [90]). However, it may be possible to fix that by adding a CCR term, similar to the one seen in the MGI model or further modifying the relaxation matrices, even adding a mixed term. Whether this offers a modeling advantage over the McLeish and Larson model, remains to be seen. In any case, we cannot help but to observe the many possibilities that open once the non-equilibrium formalism is followed, which therefore can make the non-equilibrium thermodynamics formalism beneficial even in cases such as the present one when the original model is amenable from the beginning to a non-equilibrium thermodynamics representation.

A new model that has been developed based on mode coupling is the coupled multimode Upper Convected Maxwell (Edwards et al [108]). This follows an earlier suggestion by Giesekus [79] who examined potentially coupling between multimode models, albeit he did not develop that to any specific model. In Edwards et al [108] this idea is developed through the non-equilibrium thermodynamics formalism by specifically using multiple conformation tensors, \mathbf{c}^i , $i=1,\dots,N$, each one obeying an evolution equation that arises naturally as a generalization of the Upper Convected Maxwell, allowing for each conformation tensor a general relaxation involving, potentially, all modes. In short, the stress is obtained, as in the case of decoupled modes and in linear viscoelasticity, as a linear superposition of elastic contributions from all conformation tensors:

$$\mathbf{T} = 2 \sum_{i=1}^N \frac{\partial a}{\partial \mathbf{c}^i} \cdot \mathbf{c}^i \quad \dots\dots\dots(39)$$

The difference from more traditional (uncoupled) multimode models is in the evolution equation for each one of the conformation tensors, allowing for a more general coupling with all the structural parameters:

$$\frac{D}{Dt} \mathbf{c}^i - \nabla \mathbf{v}^T \cdot \mathbf{c}^i - \mathbf{c}^i \cdot \nabla \mathbf{v} = - \sum_{j=1}^N \Lambda^{ij} : \frac{\partial a}{\partial \mathbf{c}^j} \quad \dots\dots\dots(40)$$

where Λ^{ij} are generalized relaxation (fourth order) matrices, with all the symmetries discussed before and in addition, the symmetry $i \leftrightarrow j$. Another constraint that the

relaxation matrices have to satisfy is that the overall rate for the local entropy production, σ_λ , stays is non negative. This is given as a quadratic form in terms of the thermodynamic potentials $\frac{\partial a}{\partial \mathbf{c}^i}$ (similarly to previous expressions) as:

$$\sigma_\lambda = \frac{1}{T} \left(\sum_{i=1}^N \sum_{j=1}^N \frac{\partial a}{\partial \mathbf{c}^i} : \mathbf{\Lambda}^{ij} : \frac{\partial a}{\partial \mathbf{c}^j} \right) \dots\dots\dots(41)$$

This places additional restrictions, especially to the off-diagonal forms.

In Edwards et al [108] the coupled multimode theory has been worked out in more detail in the limiting case of two coupled modes. There, in addition to the use of two Maxwellian type (i.e. corresponding to the Maxwell model---see first entry in table 2) diagonal elements $\mathbf{\Lambda}^{11}$ and $\mathbf{\Lambda}^{22}$ (with two different relaxation times, λ_1 and λ_2 , respectively), a specific selection for the off-diagonal matrix $\mathbf{\Lambda}^{12} = \mathbf{\Lambda}^{21}$ was proposed:

$$\mathbf{\Lambda}_{\alpha\beta\gamma\epsilon}^{12} = -\frac{\theta}{2\sqrt{n_1 n_2 \lambda_1 \lambda_2}} \left(c_{\alpha\gamma}^1 c_{\beta\epsilon}^2 + c_{\beta\gamma}^1 c_{\alpha\epsilon}^2 + c_{\alpha\epsilon}^1 c_{\beta\gamma}^2 + c_{\beta\epsilon}^1 c_{\alpha\gamma}^2 \right) \dots\dots\dots(42)$$

In particular, it was shown that this selection leads to a thermodynamically admissible model when the coupling parameter θ has an absolute magnitude less or equal than 1. As θ spans its allowed range, the model predictions vary significantly. In particular, shear thinning and non-zero second normal stress coefficients are predicted, as well as a finite extensional viscosity and overshoot of the shear stress in the startup of shear flow (Edwards et al [108]). In addition, the corresponding linear viscoelastic spectrum has relaxation times which are, in general, different than the primary relaxation times of the conformation modes, λ_1 and λ_2 .

Very recently the two coupled Maxwell modes model was used (Edwards et al [52]) to explain the shear thickening behavior occasionally observed in dilute solutions of high molecular weight polymer solutions (Vrahopoulou and McHugh [111], Kishbaugh and McHugh, [112]). In this work of Edwards et al [52], the two conformation tensors, \mathbf{c}^1 and \mathbf{c}^2 , were used to represent the deformed polymer chains and the structures developed in the solution as a result of the association of the macromolecular dynamics, respectively. The primary effect of the supermolecular structures is to reduce the effective shear stress with the reduction being proportional to their size that changes dynamically with the flow. The mechanism offered therefore in this work for the observed shear thickening in two previous experiments, of polypropylene in tetralin (Vrahopoulou and McHugh [111]) and polystyrene in decalin (Kishbaugh and McHugh [112]), is that, due to the coupling of the two structural modes, the size of the structures represented by the second mode goes through a maximum as the shear rate is increased with the consequence that its shear-reducing capability goes through a maximum too, resulting therefore in an overall shear-thickening effect after the maximum has been reached. This is clarifying and considerably refining the previous mechanism based on the development of an internal structure, proposed before by Kishbaugh and McHugh [113]. The innovative component of the Edwards et al [52] work is the use of the structural variables of the model to consistently explain both optical (like dichroism and birefringence) and rheological data with a fairly good success in representing all the major qualitative

trends, provided a mode coupling in used, despite the admittedly crude form of the model involving only 5 parameters. However, clearly due to many phenomenological components in the current model and the complexity of the phenomenon other mechanisms may still be at play and need to be resolved before a truly quantitative understanding emerges. Thus kinetic effects, controlling the creation and distraction of the supermolecular structures may also be important (van Egmond [114]). A qualitative modeling of those effects has also separately been attempted in the past through Brownian dynamics simulations (Hatzikiriakos and Vlassopoulos [115]) with encouraging results. Clearly, as more choices are made to represent the essential components of the model (like the kinetics governing individual population concentrations, as well as for the relaxation, free energy and the coupling between the conformation tensors) and in particular as a more solid foundation of the model is built to the underlying microstructure, the potential of even more successful applications of the coupled modes model seems to be great.

Other examples also exist in the literature, which can also be analyzed following more or less the development put forward before and they keep coming at an accelerating pace. Here, we will only mention one that started from an attempt to use a multimode representation to better capture the behavior of polymer mixtures of two (or more) different polymers represented by two or more internal configuration tensors. However, in the most interesting of those cases, one of the constituents becomes insoluble and forms a separate phase. Then, in order to appropriately handle those cases we also need to follow the structure of the interface and that ended up being the area where most of the effort has so far been spent. See Wagner et al [99] and Grmela et al [100] where the GENERIC framework is used to understand the Doi-Ohta model of immiscible blends (Doi and Ohta [116]) and both the Doi-Ohta and the Maffettone-Minale model of ellipsoid drops (Maffettone and Minale 117)). To successfully pursue that analysis one has to go much more in depth with the underlying microstructure to guide the proper mathematical analysis. It suffices to say here that the internal variables that emerge now involve one scalar field Q (representing the total interfacial area per unit volume) and a symmetric and traceless second order tensor, \mathbf{q} , representing the second moment of the orientation distribution of the surface. The details are complex due to the presence of the constraints and the details of the microscopic interpretation for \mathbf{q} but the important conclusion is that all the physics can properly be taken into account leading again to equations that are consistent with both the physical interpretation of the variables and the principles of non-equilibrium thermodynamics. It is, by the way, interesting enough to note here that due to its very different physical interpretation and in contrast to the cases referring to the conformation tensor \mathbf{c} that we discussed before, it is now the lower convected time derivative that emerges as the dominant part governing the reversible dynamics of the internal structural parameter, \mathbf{q} (the overall reversible dynamics is however more complex than that due to the reasons outlined above). Further extensions have also been worked out within the Poisson bracket and GENERIC formalism, such as the one involving an additional velocity variable to model independently the movement of the interface (Grmela et al [118]).

CONCLUSIONS

In conclusion, it is hoped that through this review I was able to transfer information not only about some of the many results in polymer rheology that have already been established with contributions from the new formalisms of non-equilibrium thermodynamics, but also and most importantly, about what is the exact nature of those contributions. This is why the subject of the review was limited to only “simple” rheological applications in order to allow a more detail description of the modeling process which is necessary in order to appreciate the subtle, but still very decisive, help provided by the new formalisms of non-equilibrium thermodynamics. Those formalisms, by systematically analysis the dynamic equations into a reversible and an irreversible component, allow to exploit all the inherent structural properties imbedded within each one of the two and for which extensive information has already been accumulated to generate a substantial degree of confidence for the results.

But the structural properties represent only a scaffolding to build up the modeling edifice, and one that in many occasions we willingly throw out from the final form of the final equations. I believe that is it exactly based on that allegory that we also need to finally judge the importance of the dissipative Hamiltonian framework. It is there to help build up and in many occasions support the final building model. Without the underlying physics, typically more and more now based on a detailed microscopic model, the building blocks for a robust and efficient macroscopic model simply are not there. But also hopefully we can see that without the right framework acting as a glue to keep together and strengthen the building blocks, the building model may either never be possible to put together or, if it is put together on a flimsy basis, it may altogether collapse.

We have seen here applications of contributions from non-equilibrium thermodynamics in a fairly limited area, that of the macroscopic descriptions of incompressible, isothermal and homogeneous flexible polymer systems. We discussed only macroscopic applications because at the end, for engineering applications, this is what one wants to have, but clearly, the influence of microscopic modeling was clear throughout the review. On the other hand, the limitation in the selection of the applications allowed us to go further in depth in the model development process (while simultaneously keeping the necessary mathematical complexity to a minimum). However, this limited selection of topics prevented us to cover exciting areas of active research (like polymeric liquid crystals, multiple transport processes, non-local (like surface-induced) effects, flow-induced phase transitions etc) where many contributions have also been made. There are nevertheless two issues there that make such a coverage problematic: first, the level of complexity is such that any discussion of those areas can be reduced to either heavy mathematics or some list of final examples. We still need working paradigms to bring the level of difficulty down so that more researchers can take advantage of the developed tools in those important areas. Second, those areas are also heavily dominated by the microstructure; fluctuations are therefore very important and so is the generation and propagation of apparent “discontinuities” (=defects) at the macroscopic scale thus rendering both the modeling but also any simulations a very challenging task.

Although there is a lot of progress in developing microscopic models, where fluctuations are more resolved, we still need to learn how to effectively transfer that

information to more macroscopic levels without increasing to unacceptably high levels the complexity of the approach. Certainly, working on new approximation paradigms, through renormalization (van Heel et al [84]) or additional intermediate macroscopic variables [Ghosh et al., 2002]) is a step in the right direction, however, we are still lacking working examples for most of the problems of interest. I expect most of the future advances in exactly this area where the same principles that have given us the opportunity to construct physically acceptable models at any level can also guide us to efficiently generate bridges between various levels of description.

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