International Journal of Non-Linear Mechanics 44 (2009) 727–734

Contents lists available at ScienceDirect

International Journal of Non-Linear Mechanics

journal homepage: www.elsevier.com/locate/nlm

On Hadamard stability and dissipative stability of the molecular stress function model of non-linear viscoelasticity

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ARTICLE INFO

Article history:
Received 5 December 2007
Received in revised form 31 December 2008
Accepted 11 March 2009

Keywords:
Hadamard stability
Dissipative stability
Molecular stress function (MSF) theory
Non-linear viscoelasticity
Constitutive equation
Simple shear
Simple elongation

ABSTRACT

We study the stability characteristics of the molecular stress function (MSF) model, i.e., a molecular constitutive theory for stress that extends the original Doi–Edwards model for linear polymers to the case of branched polymers, by repeating the assumption that the tension in the deformed chain is equal to its equilibrium value. We derive analytical, closed-form conditions for Hadamard stability under general 3-D high-frequency, short-amplitude wave disturbances in bi-quadratic form, which reduce to simple algebraic criteria for the cases of 1-D and 2-D disturbances. Application of the derived conditions in the case of general biaxial extension, which provides a simplified description of many processes encountered in industry and nature, shows that the MSF is Hadamard unstable for strains beyond 2. This casts doubts on its ability in predicting correct elastic response under rapid extensional deformations. The region of instability widens with the strengthening of network connectivity or the alignment strength of the flow. Dissipative stability of the MSF is examined using two necessary criteria: the first and less restrictive criterion requires the stress to be monotonically and unboundedly increasing function of strain in uniaxial elongation and simple shear. The second criterion requires the free energy and the rate of energy dissipation to be bounded functions of deformation. We find that while MSF satisfies the first stability criterion, violates the second, thus revealing thermodynamic inconsistencies in formulating the dissipative terms of the constitutive equation.

1. Introduction

The apparent success of the Doi–Edwards constitutive theory in explaining non-linear viscoelasticity of entangled *linear* polymer fluids 30 years ago sparked a still ongoing flurry of activity aiming in providing molecular explanations in rheology modeling. A large part of this activity is motivated by the realization that in polymers the dependence of the viscoelastic (VE) memory on deformation is not "universal" but depends on the macromolecular architecture: strain-thinning is diminished with the extent of long chain branching, especially when this is due to the formation of internal (double-crosslinked) branches. The reason is that, following a sudden deformation, the presence of appropriately positioned chemical bonds (branch end points) contributes to some remaining segmental stretching, which along with segmental orientation, accentuates stress survival. Therefore, the type and degree of branching as well as the branch length and location (internal vs. external, i.e., crosslinked on both ends vs. tethered) improve the connectivity of the temporary (since we are dealing with liquids) polymer network, reduce entanglement destructibility upon deformation and, therefore, *smoothout* the non-linear viscoelastic character of the fluid. Consequently, molecular or phenomenological constitutive models owe to accommodate a range of network connectivity strengths; in both flexible polymer liquids [1–14] and solids [15–18] this increases with the ratio of permanent crosslinks over temporary entanglements.

One such constitutive equation (CE) is the molecular stress function (MSF) model, proposed by Wagner et al. [40] which is especially developed to calculate the elongational stresses of entangled polymers; it is derived by generalizing the strain energy function of the Doi–Edwards model in a way that covers a wide spectrum of degrees of polydispersity and branching (Br), starting from a purely linear chain where $Br = 0$. Unlike Doi–Edwards, MSF takes into account the change of the tension in the ends of the deforming molecular chains and the decrease of the tube diameter with increasing deformation. In the tube concept for extensional flows, the extension of a network strand can only be achieved by reduction of the tube diameter. The functional form of the MSF model consists the basis for many recently proposed CEs [8,10,11], also developed for the description of extensional flows. These flows are particularly useful in modelling processes such as melt spinning, blow molding, sheet

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0020-7462/$ - see front matter © 2009 Elsevier Ltd. All rights reserved.
doi:10.1016/j.ijnonlinmec.2009.03.002

stretching, tube inflation, vacuum molding, extrusion coating and foaming.

The proposed CEs have been developed and established by comparison with experimental data for simple flows and low Deborah (*De*) numbers (*De* ∼ the product of deformation rate times relaxation time), which they can describe accurately. Nevertheless, in real polymer processes, complex and *three-dimensional* (3-D) flows, in the region of high Deborah numbers, are encountered. Employment of the constitutive theories in such cases has been hindered by the appearance of several types of instabilities, not observed in real life, during numerical simulation, reflecting the poor formulation of the CEs. The purpose of this paper is to study the stability of the MSF, which is a quite versatile constitutive scheme.

As explained by Kwon and Leonov [19], VE CEs, may be plagued by two types of mathematical instabilities: the Hadamard and the dissipative instability. The Hadamard instability means the ill-posedness of the solution under sudden or high frequency wave disturbances and, therefore, addresses the elastic character of a CE. The dissipative instability addresses its viscous character; for differential CEs is caused by improper formulation of dissipative terms which, in an integral CE, are hidden inside the "hereditary functional". Testing a score of CEs [19] showed that few fulfil the tough constraints for both Hadamard and dissipative stability. Unless one neglects inertial terms (and sometimes even then), unstable CEs lead to unphysical prediction of flow properties and implementation problems in trying to solve them numerically; these are especially true in high Deborah number (*De*) flows.

The set of a CE concerning a VE liquid plus the continuity equation and equation of motion with which it is coupled may be defined as Hadamard stable (or evolutionary stable, or well posed) when its solution at any time provides the complete initial conditions for determining the solution at subsequent times [23]. Thus, Hadamard stability allows solutions to propagate in the positive direction of the time axis. Otherwise, blow-up instability occurs very quickly, even with extremely short wave disturbances. This results in progressive failure of numerical calculations; the finer the mesh, the worse will be the degradation of the results [34–36]. In many cases, one can treat the Hadamard instability as a blow-up type increase in the amplitude of initially infinite small waves of disturbances as the wavelength tends to zero. This type of instability can be associated with a non-linear rapid response of the CE; i.e., the CE should possess a perfect elastic limit and, furthermore, its elastic potential should be thermodynamically stable. Therefore, Hadamard instability depends on such quasi-equilibrium properties as the differential operator in the evolution equation of a differential CE model or the elastic potential of an integral model. Moreover, Hadamard stability is closely related with thermodynamic admissibility constrains, such as the Baker–Ericksen inequality and the strong ellipticity condition [47,48]. If a CE is Hadamard stable then it follows that

- the greater principal force corresponds always to the greater principal stretch;
- the curve of principal stretch against the corresponding principal force, when the other principal forces are kept constant, slopes upward;
- the curve of principal force against the corresponding principal stretch, when the other principal stretches are kept constant, slopes upward;
- the force–stretch relations are uniquely invertible.

In some cases, regularization of ill-posedness may be achieved. The most common remedy is the addition of a small newtonian term to the stress. However, in complex flow simulation, this may not be enough to suppress numerical instability, and when the newtonian term becomes larger, the description of the CE deviates from the experimental data of VE liquids.

Dissipative instabilities, on the other hand, result from the poor formulation of the viscous terms of the CE, and may occur even if the rate of energy dissipation is positive definite. Their study was initiated by Leonov [20] and was based on the general Maxwell fluid. The motivation was that the upper convected Maxwell model, although globally Hadamard stable, displays the unbounded growth of stress in simple extension, when the elongation rate exceeds the half of the reciprocal relaxation time. For VE fluids describable by a differential CE, subject to any regular flow with a given history, Leonov [20] proposed a sufficient condition (close to the necessary one) for dissipative stability. The corresponding conditions for a single integral time–strain separable with exponential type memory CE fluid were derived in [21]. It is noticeable that, in many VE flows the knowledge of both strain and stress history is necessary for a proper dissipative stability analysis [20,21]. Several patterns of pathological behavior related to dissipative instability predicted for *one-dimensional* (1-D) flow by some popular variations of Maxwell-like CEs are exposed in [22]. For stability, it is necessary that both the steady flow curves in simple shear and simple elongation are monotonically and unboundedly increasing [22].

By *reviewing the literature*, one discovers that Hadamard stability (the most studied of the two types) was initiated for VE fluid models by Rutkevich [23] and Godunov [24]. Significant results obtained until the late 1980s are summarized by Joseph [25]. These studies dealt with Hadamard stability of specific differential VE CEs, both time–strain separable and non-separable, for specific flows, employing the method of characteristics to derive the stability criteria. They had also focused on specifying the functional form of the evolution operator of the Cauchy tensor for these CEs.

Kwon and Leonov [19,21,26] have studied Hadamard stability of a variety of both differential and time–strain factorable integral Kaye–Bernstein Kearsley Zapas (K–BKZ) VE CEs. The strain measure of the fluid models is the Cauchy tensor, which is supposed to be positive definite and its time evolution is described by a linear differential operator. Their results were obtained by employing standard perturbation analysis of small amplitude and extremely short and high frequency waves of disturbances imposed on a basic flow. They have shown that this technique, called the method of "frozen coefficients", is equivalent to the more general method of characteristics.

Kwon and coworkers [27,28] have studied both Hadamard and dissipative stability of two CEs based on molecular arguments: the Doi–Edwards and the differential pom-pom models. They have derived criteria for Hadamard stability in the general case of 3-D disturbances for both models. An attempt has also been made to derive Hadamard stability for the original, integral version of the pom-pom model. However, it failed to provide any such criteria. Instead of deriving criteria for dissipative stability, they have considered the limiting case of creep shear flow and have shown that the conformation tensor eventually becomes negative.

Rajagopal and Wineman [46] put forward a general theory to describe the mechanics of solid materials in which microstructural changes are induced due to deformations. Contrary to classical theories, they considered the possibility that as the material is deformed more than a single micromechanism determine the Cauchy stress. The creation of the second micromechanism is given by an activation criterion similar to a yield condition in plasticity, which is fixed once and forever and there is no evolution of a yield surface. "Inelastic" behavior of materials can be explained within the context of such a theory. Following a more general approach based on thermodynamics, Dunn and Rajagopal [29] performed a stability analysis of incompressible VE fluids of differential type. A dissipation principle and the assumption that the stored energy should reach an extremum at equilibrium constitute the cornerstones of their study. Rajagopal and Srinivasa [30] continued by developing a thermody-