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Short Communication

DERIVATION OF THE MARRUCCI MODEL FROM TRANSIENT-NETWORK THEORY

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1. Introduction

Many theories about the rheological behaviour of melts and concentrated solutions of high molecular weight polymers are based upon the transient-network model, originally developed by Green and Tobolsky [1], Lodge [2], and Yamamoto [3]. Among these theories a model proposed by Marrucci and coworkers [4,5] turns out to be rather successful [6—11].

The basic equations of this model, as formulated in ref. [5], are:

$$\boldsymbol{T} = \sum_i \boldsymbol{T}_i \,, \tag{1}$$

$$\lambda_i \frac{\delta}{\delta t}\left(\frac{\boldsymbol{T}_i}{G_i}\right) + \frac{1}{G_i}\boldsymbol{T}_i = 2\lambda_i \boldsymbol{D} \,, \tag{2}$$

$$G_i = G_{0i} x_i \,, \tag{3}$$

$$\lambda_i = \lambda_{0i} x_i^{1.4} \,, \tag{4}$$

$$\frac{\mathrm{d}x_i}{\mathrm{d}t} = \frac{1}{\lambda_i}(1 - x_i) - a x_i \frac{1}{\lambda_i}\sqrt{\frac{\mathrm{tr}\,\boldsymbol{T}_i}{2G_i}} \,, \tag{5}$$

where (1) represents a spectral decomposition of the stress tensor, λ_i and G_i are the i-th relaxation time and elastic modulus, respectively (the same quantities with zero subscript are the corresponding equilibrium values), $\delta/\delta t$ is the contravariant convective derivative (see eqn. (22) below), $\boldsymbol{D}$ is the rate-of-strain tensor and where the dimensionless quantities x_i ($x_i \leqslant 1$) can be regarded as structural variables which describe how far the existing structure is away from equilibrium. They are related to the degree of connectivity of

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the macromolecular network. The constant a is an adjustable parameter.

The model has proven to predict correctly the mechanical response of various polymer melts in different stress and deformation histories. From a physical point of view it is appealing because of the explicit introduction of an expression (eqn. (5)) that describes the change of structure of the system. Despite these attractive features, the derivation of the model, as given in refs. [4] and [5], is not entirely satisfactory. In fact, eqns. (1—6) are introduced in a semi-empirical way: the form of the constitutive equation (2) is suggested by a spring-dashpot model with a variable spring modulus. The contravariant convective derivative is chosen in accordance with results of the network theory for concentrated systems [2,12] and of bead-spring models for dilute polymer solutions [13]. The dependence (eqn. (3)) of G_i on x_i is suggested by the theory of rubber elasticity. The dependence (eqn. (4)) of λ_i on x_i is chosen in such a way that the zero shear viscosity becomes proportional to $c^{3.4}$, where c is the number of macromolecules per unit volume. Finally, the kinetic expression (5) is proposed on the basis of certain microscopic arguments. An objection that may be raised against this procedure is that the constitutive equation (2) and the kinetic equation (5) are not derived from the transient-network model (or any other consistent microscopic model), but, instead, are introduced as separate ad hoc assumptions.

In this note it will be shown that it is possible to derive both the constitutive and the kinetic equations of the Marrucci model from a balance law of the segment-distribution function in the transient-network model. This makes it possible to see which assumptions about this balance law are implicitly made in the Marrucci theory and allows a comparison of this theory with other theories based upon the transient-network model.

2. Distribution functions, balance law

Consider an incompressible fluid with c macromolecules per unit volume. Let N_i be the number per unit volume of segments, consisting of i freely jointed rigid links of length l (segments of this type will be called i-segments), and $\Psi_i(q, t)\, d^3q$ the number of these segments that have their end-to-end vector q in the volume element d^3q in the configuration space. It follows that

$$\int \Psi_i(q, t)\, d^3q = N_i \,. \tag{6}$$

The number of i-segments per molecule will be denoted by n_i, so

$$n_i \equiv N_i/c \,. \tag{7}$$

For highly entangled systems $n_i >> 1$; then the quantity

$$n = \sum_i n_i \tag{8}$$

equals the average number of entanglements per molecule. The equilibrium

value of n_i will be denoted by n_{0i}. Finally we introduce the structural variables [4,5]

$$x_i \equiv n_i/n_{0i} \,, \tag{9}$$

which describe how far the existing structure is away from equilibrium.

Besides the total distribution functions Ψ_i, we also introduce the distribution functions

$$\psi_i(q, t) \equiv (1/N_i)\, \Psi_i(q, t) \,. \tag{10}$$

Assuming Gaussian statistics, in equilibrium we have:

$$\psi_i^0 = (b_i/\pi)^{3/2} \exp(-b_i q^2) \,, \tag{11}$$

where $b_i = 3/2il^2$.

The time dependence of the segment-distribution functions is governed by a balance equation of the following form:

$$\frac{\partial \Psi_i}{\partial t} = -\frac{\partial}{\partial q} \cdot (\Psi_i \dot{q}) + k_i - h_i \Psi_i \,. \tag{12}$$

The first two terms are of the usual form of an equation of continuity in q-space; the terms k_i and $h_i\Psi_i$ represent the formation and annihilation of i-segments respectively. Equation (12) was first derived by Yamamoto [3] and can be shown to be consistent with the theory of Lodge [2,12]. An extensive discussion of (12) can be found in two papers by Wiegel and de Bats [14], [15].

The function $\dot{q} = \dot{q}(q, t)$ in eqn. (12) represents the motion of the segment vectors in the configuration space. If affine deformation of the network is assumed,

$$\dot{q} = L \cdot q \,, \tag{13}$$

where L is the macroscopic velocity gradient of the fluid flow. In this note we will assume that eqn. (13) holds; the subsequent discussion, however, also applies for a special type of non-affine deformation, namely if $\dot{q} = \tilde{L} \cdot q$, where $\tilde{L} = f(L)$ is some effective velocity gradient of the network. In that case one simply has to replace L by $\tilde{L}$ in all our results. A theory of this type has been formulated recently by Phan Thien and Tanner [16,17]. For our purpose it is of interest to note that the assumption of non-affine deformation in this case leads to a constitutive equation which is not of the contravariant Maxwellian type, the form proposed in the Marrucci model.

The creation function k_i and the destruction function h_i will depend [3,15] in general on the variables q and i. Usually certain specific forms of these functions are assumed. The theory of Lodge [12], for instance, essentially corresponds to the assumption that

$$k_i = g_i \psi_i^0(q) \,, \tag{14}$$

where g_i are constants and ψ_i^0 is given by eqn. (11), and that the h_i are constants. The form (14) of the creation functions is a consequence of the assumption that the segments are created at a constant rate, and that they have, at the instant of creation, the same distribution as free chains. The constancy of the h_i means that all i-segments have the same constant probability per unit time of leaving the network *. In more elaborate theories (see for instance [16]) the form (14) is often used in combination with the assumption that g_i and h_i are functions of the mean square extension of the segments, i.e. $g_i = g_i(<q^2>)$ and $h_i = h_i(<q^2>)$.

We shall make no specific assumptions about the functions $k_i(q, t)$ and $h_i(q, t)$ at this stage of the development. For convenience, however, k_i will be written in the form (14), with $g_i = g_i(q, t)$.

Substitution of (14) in (12) and integration over all configurations gives the following differential equations for N_i:

$$dN_i/dt = <g_i>^0 - N_i <h_i> , \tag{15}$$

with

$$<g_i>^0 \equiv \int g_i \psi_i^0 d^3q , \tag{16}$$

and

$$<h_i> \equiv \frac{1}{N_i} \int h_i \Psi_i d^3q = \int h_i \psi_i d^3q . \tag{17}$$

Substitution of (7) and (9) gives the following expression for the rate of change of the structural variables x_i:

$$\frac{dx_i}{dt} = \frac{1}{cn_{0i}} <g_i>^0 - x_i <h_i> . \tag{18}$$

If Ψ_i is written as $\Psi_i = N_i \psi_i$ and substituted in (12), one obtains, using (15):

$$\frac{\partial \psi_i}{\partial t} = -\frac{\partial}{\partial q} \cdot (\psi_i \dot{q}) + \frac{1}{N_i}(g_i \psi_i^0 - <g_i>^0 \psi_i) - (h_i - <h_i>) \psi_i . \tag{19}$$

By multiplying this equation with the diadic qq and integrating over the configuration space, the following expression for the averages

$$<qq>_i \equiv \int qq \psi_i d^3q \tag{20}$$

* In fact, in the theory of Lodge [12] an additional parameter, the complexity, on which the quantities g_i and h_i may depend, is used. This, however, is not essential for the present discussion.

can be obtained:

$$\frac{\delta}{\delta t}\langle qq\rangle_i = \frac{1}{N_i}(\langle g_i qq\rangle^0 - \langle g_i\rangle^0 \langle qq\rangle_i) - \langle h_i qq\rangle + \langle h_i\rangle \langle qq\rangle_i \,, \tag{21}$$

with the contravariant convected derivative $\delta/\delta t$ defined as

$$\frac{\delta}{\delta t}A = \frac{\mathrm{d}}{\mathrm{d}t}A - L \cdot A - A \cdot L^T \tag{22}$$

for an arbitrary second-order tensor A.

3. Specific assumptions

From now on we assume that g_i and h_i do not depend explicitly on q but only on average properties of the state of the fluid. It will be shown that for deriving the Marrucci model this assumption is sufficient. The specific forms of the functions g_i and h_i in that case will be discussed later; at present it is sufficient to know that g_i and h_i do not depend on q. The basic equations (15) and (21) then reduce to

$$\mathrm{d}N_i/\mathrm{d}t = g_i - N_i h_i \tag{23}$$

and

$$\frac{\delta}{\delta t}\langle qq\rangle_i = \frac{g_i}{N_i}(\langle qq\rangle_i^0 - \langle qq\rangle_i) \,, \tag{24}$$

respectively.

4. Constitutive equation

The contribution of the i-segments to the stress tensor is given by the usual expression

$$T_i' = N_i\langle f_i q\rangle \,, \tag{25}$$

in which the entropic force f_i is related to the parameter b_i of the equilibrium distribution (11) in the following way:

$$f_i = 2kTb_i q \,. \tag{26}$$

Here k is the Boltzmann constant and T the absolute temperature. Since the fluid is incompressible, the partial stresses (25) are determined up to an arbitrary isotropic pressure. So we may also use partial stresses T_i defined as

$$T_i = T_i' - p_i 1 \,, \tag{27}$$

where p_i are chosen in such a way that $T_i = 0$ at equilibrium. From (25) and (26) it follows that

$$T_i = 2N_i kTb_i(\langle qq\rangle_i - \tfrac{1}{3}\langle q^2\rangle_i^0 1) \,, \tag{28}$$

where, by (11)

$$\tfrac{1}{3}\langle q^2\rangle_i^0 \mathbf{1} = \langle qq\rangle_i^0 = (1/2b_i)\,\mathbf{1}\,. \tag{29}$$

The total polymer contribution to the stress tensor becomes:

$$\boldsymbol{T} = \sum_i \boldsymbol{T}_i\,. \tag{30}$$

From (24), (28), and (29) we obtain the following expression for the partial stresses:

$$\frac{N_i}{g_i}\frac{\delta}{\delta t}\left(\frac{\boldsymbol{T}_i}{N_i kT}\right) + \frac{\boldsymbol{T}_i}{N_i kT} = 2\frac{N_i}{g_i}\boldsymbol{D}\,. \tag{31}$$

Here $\boldsymbol{D} = \frac{1}{2}(\boldsymbol{L} + \boldsymbol{L}^T) = -\frac{1}{2}\delta\mathbf{1}/\delta t$ is the rate-of-strain tensor. Note that (31) has the form of the constitutive equation (2) assumed in the Marrucci model. This point will be discussed later.

In (31) the quantities N_i/g_i have the meaning of relaxation times. This suggests that the creation parameters g_i and not the annihilation parameters h_i are related to these time constants. Such, however, is not true, for on performing the differentiation in (31) and making use of (23) one obtains the alternative form

$$\frac{1}{h_i}\frac{\delta}{\delta t}\boldsymbol{T}_i + \boldsymbol{T}_i = 2N_i kT\frac{1}{h_i}\boldsymbol{D}\,. \tag{32}$$

This time the quantities h_i^{-1} can be interpreted as relaxation times. The latter interpretation is the usual one in transient-network theories (see for instance refs. [2], [12], [16], [17]).

5. The Marrucci model

On defining the non-linear moduli and relaxation times as

$$G_i \equiv N_i kT \tag{33}$$

and

$$\lambda_i \equiv N_i/g_i\,, \tag{34}$$

respectively, eqn. (31) becomes identical to the constitutive equation (2) of the Marrucci model. With the help of (7) and (9), eqn. (33) may be written in the form (3) with

$$G_{0i} = cn_{0i}kT\,. \tag{35}$$

The assumption (4) of the Marrucci model is consistent with our result (34) if

$$g_i = g_{0i}x_i^{-0.4}\,, \tag{36}$$

where

$$g_{0i} = cn_{0i}/\lambda_{0i} \,. \tag{37}$$

Finally our result (23) should be compared to the kinetic assumption (5) of the Marrucci model. To this end, using (7), (9), and (34), we rewrite (23) as

$$\frac{dx_i}{dt} = \frac{x_i}{\lambda_i} - x_i h_i \,. \tag{38}$$

At first sight, this equation differs from (5), since the creation terms in both equations are not of the same form. Formally, however, (5) may be obtained from (38) by chosing

$$h_i = \frac{1}{\lambda_i}\left(a\sqrt{\frac{\mathrm{tr}\, T_i}{2G_i}} - \frac{1}{x_i} + 2\right). \tag{39}$$

In that case the first term of the right-hand side of eqn. (5) is no longer considered as a creation term but as a combination of the appropriate creation term x_i/λ_i and a part of the annihilation term $x_i h_i$.

6. Discussion

It has been shown that, although introduced originally in a more or less empirical way, eqns. (1—5) of the Marrucci model can be derived from transient-network theory. This makes it possible to give a more complete discussion of some aspects of this model.

First, we see that some specific assumptions about functions k_i and h_i in the general balance equation of the segment-distribution function (12) are needed in order to obtain the results (23) and (24), which have been shown to be in accordance with the Marrucci model. Although it is usual to make assumptions of this kind in transient-network theories, it is still important to realize that in a more general approach, eqns. (15) and (21) should be used instead of (23) and (24). The starting point, eqn. (12) itself, should even be considered as an approximation of a more general balance equation, derived in ref. [14].

A second point of interest is the possibility of non-affine motion of the network. In ref. [18] it is stated that the form (2) of the constitutive equation is retained under suitable assumptions of non-affine motion. This statement was based on the observation that this particular form of the constitutive equation still applies, even in the case of bead-spring models for dilute polymer solutions [13] where the motion of the polymer chains certainly is non-affine. The present derivation, however, shows that the assumption of affine motion is sufficient to obtain (2) from transient-network theory, whereas, in the case of non-affine motion of the type discussed below eqn. (13), a constitutive equation different from (2) will be obtained.

A further interesting result of the present derivation is that it shows that

the kinetic equation (5) should not be considered as an independent assumption but as a special form of the more general equation (38), which, in turn, has been derived from (23), an integrated form of the fundamental balance law (12). We have seen that from this point of view the two terms in the right-hand side of (38) and not the two terms in the right-hand side of (5) should be considered as creation and annihilation terms respectively. This, of course, has consequences for the physical interpretation of eqn. (5). It means, for instance, that in equilibrium ($dx_i/dt = 0$) the creation and annihilation rates of segments are not zero, as is suggested by (5), but instead equal to $h_{0i} = \lambda_{0i}^{-1} \neq 0$.

Finally it should be noted that the present derivation offers the possibility of detailed comparison of the Marrucci model with other transient-network theories based on different forms of the functions g_i and h_i in eqn. (23). It also shows clearly at which points in the development essential assumptions are made, and so in which directions modifications and generalizations are possible.

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