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CONSTITUTIVE EQUATIONS FROM GAUSSIAN MOLECULAR NETWORK THEORIES IN POLYMER RHEOLOGY

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CONSTITUTIVE EQUATIONS FROM GAUSSIAN MOLECULAR NETWORK THEORIES IN POLYMER RHEOLOGY

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Abstract - With the aim of facilitating discussion of the molecular basis of rheological behavior in polymer liquids, several of the published molecular network theories which have led to the formulation of constitutive equations are considered. The main emphasis here is on the summarizing and comparing of assumptions used in the different theories, not with their comparison with experimental data. Equations considered include those due to James, Green & Tobolsky, Yamamoto, Lodge, Carreau, Meister, Kaye, Marrucci et al., Wagner, Phan-Thien & Tanner, and Johnson & Segalman. New assumptions are introduced in order to describe a possible dependence of network strand creation and loss rates on polymer molecular weight and temperature.

INTRODUCTION

Recent years have seen increasing activity devoted to the goal of relating rheological properties of polymer liquids to their known molecular structure. We believe that the aim of increasing understanding of these relations is of particular importance: not only does the variety of pronounced rheological properties make the subject one of fundamental scientific interest, but also the possible varied applications to practical flow situations make the subject one of considerable technological importance in several industries.

Predictions of published molecular theories are widely used in comparisons made with experimental data. We believe that the value of such theories rests not only on the extent of agreement found in such comparisons, but also on the logical foundations of the theory. In some cases, it seems that progress in comparing predictions with data has outstripped progress in understanding both the logical foundations and the steps taken to derive useful equations from the molecular model used. The aim of the present paper is to take a modest step towards restoring the balance: we have selected a few related theories and have simply listed what we believe to be a complete set of underlying assumptions made in each case. We hope that this will serve as a helpful starting point for future critical assessment of the value of these theories. We do not give derivations of final equations, since these are available in the original papers, nor do we give comprehensive comparisons with experimental data. We recognize that a thorough assessment of any one molecular theory should make use of all available structural information obtainable from "non-rheological" techniques of characterization.

The present paper is the outcome of a cooperative effort by members of the IUPAC Working Party on "Structure and Properties of Commercial Polymers" who formed a "Molecular Theory Discussion Sub-Group" in 1976. Out of a large number of important molecular theories that have been published, a few were selected for first consideration on the grounds that they should lead to constitutive equations for molten polymers (reflecting the predominant interests of Working Party members) rather than dilute polymer solutions.

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The use of a single, tensor, constitutive equation is a convenient way of giving a compre-
hensive mathematical description of rheological properties of a given material; comparison
of constitutive equations derived from different but related molecular theories can be help-
ful. The theories considered here have a common link with the molecular network theory
(in the Gaussian approximation) of rubberlike elasticity which has enjoyed some success for
describing elastic behavior of crosslinked elastomers above the glass transition temperature,
T_g. We have not included the alternative theories of Ziabicki, of Doi and Edwards, and of
Curtiss and Bird in this study because of time limitations.

In comparison with "pure" molecular theories of macroscopic properties of condensed phases,
the present theories must be regarded as "hybrid" because of the nature of some of the
assumptions made. Molecular theories might reasonably be called "pure" if the seemingly
unavoidable idealizations involved are confined to the model used for the molecules and their
interactions; well-defined approximations may be introduced in the mathematical analysis of
the model. The present theories, however, invoke certain additional *ad hoc* assumptions
about the response of the molecules to macroscopically imposed disturbances, instead of
deriving these responses from a clearly defined molecular model. It is certainly desirable
ultimately to remove the more useful of these *ad hoc* assumptions by deriving their conse-
quences from purely molecular arguments. However, we feel that in view of the extraordinary
difficulties associated with constructing a 'pure' theory, the 'hybrid' theories can play a
constructive role in the early stages of developing a molecular understanding of rheology
and provide direction for the 'pure' theories.

It is sufficient for the present purpose to confine the discussion to isothermal homogeneous
deformations and flows of incompressible materials. Cartesian space vectors and tensors
will be used.

2. NETWORKS OF CONSTANT CONNECTIVITY

For convenience, we summarize briefly the features of the well-known Gaussian network theory
for cross-linked elastomers above T_g. The form of the theory used is essentially that of
James[1], recently reformulated by Lodge[2] to allow for compressibility. Definitions of terms
together with an alternative formulation using body tensors components were given by Lodge[3].
In the present paper, Cartesian space vectors and tensors are used throughout, partly to
facilitate comparisons between affine- and non-affine motion theories.

Assumptions

(2.1)   The elastomer consists of a single "coherent" network of linear macromolecules,
         crosslinked at certain points, together with unattached molecules. ("Coherent"
         means that each network point is connected by at least two unbroken network paths
         to the bounding surface of a physically infinitesimal material element).

(2.2)   The points of intersection of the network with the bounding surface of a physically
         infinitesimal material element (the "boundary points") can be given arbitrary
         affine motions and can thus coincide with particles of the equivalent macroscopic
         continuum. (i.e., Boundary point thermal motion is suppressed).

(2.3)   The canonical ensemble in the classical approximation is adequate to calculate the
         equilibrium behavior of the elastomer (i.e., for a given temperature T and for given
         positions of the boundary points).

(2.4)   The elastomer partition function Z can be expressed as a product

         $$Z = Z_1(V,T)\ \Omega,$$

         where $\Omega := \int \exp(-\phi/kT)\ dq$ (the "network configuration integral"); ϕ is the sum
         of all bond potential energies in the network; the integration extends over all
         network configuration space; V denotes the elastomer volume; k is Boltzmann's
         constant.

The factorization of the partition function places the chain-chain interactions (except
those that occur at junctions) in the Z_1 term. This may be regarded as serious inasmuch
as the Z_1 term always contributes isotropically to the bulk stress regardless of the
deformation of the network.

(2.5) Ω can be evaluated in the "Gaussian approximation" e.g., as if each stand (the part
         of a macromolecule joining consecutive crosslinks) were modelled as a linear array
         of a large number of point masses connected by freely-jointed rigid)or non-rigid[2])
         bonds, with neglect of mutual interactions between strands and of other than
         nearest-neighbor interactions along a strand.

(2.6) $\partial Z_1/\partial V$ has a unique value at zero stress at any given temperature.

Deductions

(2.7)   Ensemble-average positions of crosslinks move affinely and can be identified with particles of the equivalent macroscopic continuum. In particular, if the elastomer is given a time-dependent <u>homogeneous</u> deformation, we have

(2.8) $\dot{R} = R \cdot \tilde{\boldsymbol{v}}$

where R denotes an ensemble-average strand end-to-end vector, and $\boldsymbol{v}(\boldsymbol{x}, t)$ denotes the elastomer velocity at the place of position vector $\boldsymbol{x}$ and time t. The superior dot denotes a time derivative. It is implied in writing the ensemble average strand motion in terms of the macroscopic velocity gradient that the time τ_1 for a macromolecular strand to pass through most of its configurations is small compared to the bulk flow time scale, i.e., $\tau_1 \ll \|\tilde{\boldsymbol{v}}\|^{-1}$.

We emphasize in connection with (2.8) that all of the network theories are developed for homogeneous flows or deformations. The resulting predictions (primarily the constitutive equations) are, however, frequently used for non-homogeneous deformations. This use implies an additional working assumption, which we do not use in this paper, that the homogeneous flow theory applies without change to inhomogeneous flows. We would expect this assumption to be reasonable as long as a molecular length scale, such as the average distance between junctions, is smaller than a macroscopic length scale, such as the distance over which changes in deformation gradient occur.

The extra-stress tensor P is given by the equation

(2.9) $P(t) = 3kT \ \Sigma' R(t)R(t)/\hat{R}^2$,

where Σ' denotes a sum over all strands in a unit volume, and $\hat{R}^2$ ($=n l^2$ for a strand composed of n rigid bonds, each of length l), defined[2] in terms of bond potentials for the strand, can be regarded as a mean square end-to-end distance for a free strand.

(2.10)   At any given temperature, there is a unique stress-free state t_0, and we have

(2.11) $P(t) = g_0 kTN \ B(t_0 \to t)$,

where N is the strand concentration, B is the Finger strain tensor, and

(2.12) $g_0 = N^{-1} \ \Sigma' R^2(t_0)/\hat{R}^2$.

R denotes the magnitude of R.

It should, perhaps, be noted that the shear modulus $g_0 kTN$ involves three different averages (the "front factor" g_0 is a network average of the ratio of an ensemble average for a strand in the network and an average for the same strand freed from the network; g_0 is not, in general, a ratio of two averages, as is often incorrectly stated in the polymer literature). Crosslink functionality does not enter explicitly in the above expression for the shear modulus.

For extensions of the theory of temporary-junction networks, it is important to note that (provided the various assumptions are not violated) the above results are applicable whether the network is formed by addition of crosslinks in one or in several states of the elastomer. In the latter case ("composite networks"), the stress-free state t_0 is often called the "state of ease"; it and the front factor g_0 depend on the states in which crosslinks are added, but the form of the above equations does not.

For later extensions, it is also of interest to note that, from (2.8) and (2.9) with Σ' independent of time for constant connectivity, it follows that

(2.13) $P_{(1)} := \partial P/\partial t + \boldsymbol{v} \cdot \tilde{\boldsymbol{v}} - (\tilde{\boldsymbol{v}}) \cdot P = 0.$ (Gaussian network; constant connectivity; affine motion)

This states that the contravariant time derivative of the extra stress tensor is zero. The term involving ∇P vanishes in the present context (because the deformations are restricted to be homogeneous) and is included merely for completeness. Equation (2.11) is an integral[4] of the differential equation (2.13). The result (2.13) is the Cartesian space tensor version of the result[5] the the contravariant extra stress body tensor is constant for any isothermal deformation of a Gaussian network material at constant connectivity.

In the present context, the materials are assumed to be incompressible, and the extra stress tensor $P = \boldsymbol{p} + pI$, where $\boldsymbol{p}$ is the stress tensor, I is the unit tensor, and p is a scalar determined by the constant volume condition taken with boundary conditions and the other equations. For the compressible case[2], we have an equation of the same form but with p replaced by $-\rho kT \ \partial \ln Z_1/\partial \ln V$; ρ denotes the density.

3. NETWORKS WITH TIME-DEPENDENT CONNECTIVITY; AFFINE MOTION

In the hope of obtaining a molecular theory applicable to molten (or undiluted) polymers and to concentrated polymer solutions, it is asked whether the foregoing network theory can be utilized in any form for a polymeric material which has no (permanent) chemical crosslinks. This might be possible provided that one could find a polymeric material for which the following two assumptions were valid.

Assumptions

(3.1)   The extra stress is determined by the thermal motion of the strands of a "temporary-junction" network.

(3.2)   The processes of macroscopic polymer flow and of junction creation and loss are slow enough on the time scale of strand thermal motion so that, each instant t, the network can be treated by the methods of equilibrium statistical mechanics (as in §2 above). ("Quasistatic network deformation and quasistatic changes in network connectivity").

The concept of entanglements is widely used in the polymer literature, and more than one meaning can be distinguished[6]; only one is appropriate to the temporary junction concept described above. It is conceivable that in certain systems temporary junctions could occur, whether from physical knots, weak chemical bonds, secondary forces, small crystalline regions, or from small glassy regions in block copolymers. All that seems to be required for the validity of the above assumptions is that, in a temporary junction, "small" parts of macromolecules should move together during a period of some order of magnitude τ^* which is large enough for the network to pass through almost all of its available configurations. Such temporary junctions should be, or course, at least trifunctional.

It will be convenient to use the phrase "Gaussian network material" to refer to an (idealized) polymeric material for which assumptions (2.1) - (2.6), (3.1), and (3.2) are valid (with the understanding that, for temporary-junction materials, the term 'crosslink' shall be understood to mean 'temporary junction' in the sense described above). It follows at once that, for such a material, we have

(3.3) $\boldsymbol{P}(t) = g^*(t)kTN(t)\boldsymbol{B}(t^* \rightarrow t),$ (Gaussian network material)

where t^*, the stress-free state at time t, the front factor g^*, and possibly also the strand concentration N, must be expected to depend on the flow history. Until this unknown dependence on flow history can be replaced with definite equations - at least for the stress-free state - equation (3.3) cannot be regarded as a constitutive equation. It is interesting nevertheless that (3.3), incomplete though it is, does lead to definite predictions which should, in principle, be testable if, for example, the values of shear stress and first normal stress difference could be measured immediately before and after a jump shear strain[7]. Although it is outside the scope of the present paper, it is of great importance to note that the well-known linear relation between refractive index and stress tensors can be derived for a Gaussian network material, provided that the ususal simplifying assumptions concerning additivity of bond polarizability tensors and about the local field are made[8]. The importance of both these sets of predictions lies partly in the fact that they do not depend on the validity of various additional assumptions introduced below in order to get constitutive equations; for example, for the validity of these predictions, it is necessary that junction ensemble-average positions should move affinely during the jump shear strain (which is assumed to take place at constant connectivity); such affine motion is not required, however, during the period of changing connectivity (when the affine motion assumption made later is most questionable) associated with any prior unidirectional shear flow.

The temporary-junction hypothesis simplifies the mathematical analysis of polymer liquids, but it must be admitted that we do not yet know whether or not it represents a valid idealization for real polymeric liquids.

To obtain constitutive equations, the following additional assumptions have been introduced[3,9-12]:

Assumptions

(3.4)   At any instant t, the set of network strands in a unit volume may be regarded as mutually exclusive, mutally independent subsets labelled by discrete values $(1,2,...)$ of a suffix i; the probability per unit time that any $(\boldsymbol{R}, i, n)$-strand shall leave the network is a function $1/\tau_{in}(t)$, say, of t, i, and n, where n denotes the number of equivalent random links (or of freely-jointed non-rigid bonds) in the strand.

(3.5)   (i, n)-strands are created with a spherically symmetric distribution of R-vectors: i.e. at a rate which can be expressed as a function $L_{in}(R, t)$ of i, n, t, and the magnitude of R alone.

The assumption of spherical symmetry in assumption (3.5) is made for mathematical convenience; it is not known how serious the physical implications of this assumption are. The time dependence of creation and loss rates, omitted in some of the earlier theories, is here introduced in order to develop a formalism which will include theories which allow these rates to depend on macroscopis variables (such as strain rate invariants).

These assumptions may be questionable from a "pure molecular theory" standpoint, because (i) the fundamental processes of loss and creation involve junctions, not strands, in the first instance, and (ii) these processes may generate interdependence between sets of strands because the loss of one tetrafunctional junction results in the loss of two strands. These facts are glossed over in the present theories, but not in certain more detailed calculations[13-15] of the closely related problem of composite networks.

It is clear that eventually the functions $\tau_{in}(t)$ and $L_{in}(R, t)$, or appropriate replacements, should be obtained from detailed molecular calculations of the motions of the constituent macromolecules. In this way the dependence of the measurable predictions (obtained from the theory) on molecular structure (e.g., molecular weight), which is presently missing in the network models, could be determined. Although it is beyond the scope of this paper to obtain the connections, we can note a few features of the structure dependence. First, to the extent that loss and creation of junctions are produced by thermal motions of the macromolecules (and we believe this is the dominant mechanism at least for small deformations), $1/\tau_{in}$ and L_{in} should depend on the number of equivalent random links (molecular weight) and temperature in the same way. One simple way to indicate this dependence is to let

(3.6)
$$\tau_{in} \propto M^{\beta} a_T$$
$$L_{in} \propto M^{-\beta} a_T^{-1}$$

where β is an unknown constant and a_T is a function of temperature. The function a_T is the "shift factor" in the principle of time-temperature superposition[6] and its inclusion in (3.6) is consistent with its normal use to scale time constants. The exponent β is expected to be positive since the time required for overall macromolecular configuration changes increases with molecular weight. It can be shown that constitutive equations obtained from the network theory, with (3.6) included, follow the time-temperature superposition priciple and give

$$\eta_o \propto M^{\beta}$$
$$\Psi_{1,0} \propto M^{2\beta}$$

A value of β equal to 3.4 thus gives good agreement with structure/property data on these material functions.

For a Gaussian network material satisfying (3.4) and (3.5), it follows from (2.9) that

(3.7) $P(t) = 3kT \sum_n \hat{R}_n^{-2} \sum_i [RR]_{in},$

where

(3.8) $[RR]_{in} := \iiint_{-\infty}^{\infty} f_{in}(R, t) \, d^3R$

and $f_{in}(R, t) \, d^3R$ denotes the concentration at time t of (R, i, n)-strands (i.e., of (i,n)-strands having ensemble-average end-to-end vectors within d^3R of R). We also have

(3.9) $\partial f_{in}/\partial t = -\nabla \cdot (\dot{R} f_{in}) + L_{in}(R, t) - f_{in}/\tau_{in}(t),$

expressing the rate of change of strand concentration as a sum of three terms which arise from changes in the ensemble average end-to-end vector of the strands, from creation, and from loss, respectively. Because of (2.8), we can regard the first term on the right side as being produced by the macroscopic liquid flow.

By using these equations together with the affine motion equation (2.8), the constant volume condition ($\nabla \cdot v = 0$), and the reasonable assumption that f_{in} tends to zero fast enough for large R to enable Green's theorem to be used, we obtain the following expression for the contravariant time derivative at t:

(3.10) $[RR]_{in(1)} = \bar{L}_{in}(t) \mathbf{1} - [RR]_{in}/\tau_{in}(t),$ where

(3.11) $\bar{L}_{in}(t) := (4\pi/3) \int_0^{\infty} R^4 L_{in}(R, t) \, dR.$

The integral of (3.10) may be written in the form

(3.12) $[RR]_{in}(t) = \int_{-\infty}^{t} \bar{L}_{in}(t') B(t' \to t) \exp\{\int_t^{t'} dt''/\tau_{in}(t'')\} \, dt'',$

and hence the constitutive equation may be written in the form

(3.13) $P(t) = \int_{-\infty}^{t} m(t, t') B(t' \to t) dt'$,   (Gaussian material, affine
                                                                 motion, creation & loss
                                                                 assumptions (3.4) & (3.5)

(3.14) $m(t, t') := 3kT \sum_{n}\sum_{i} \hat{R}_n^{-2} \overline{L}_{in}(t') \exp \int_{t}^{t'} dt''/\tau_{in}(t'')$.

If, further, at the instant of creation, all (i, n)-strands have R - vectors that are not only
spherically symmetrically distributed (as already assumed) but also have the same distribution
as that of a set of free n-strands (the "Wall distribution"), then the memory function in
(3.14) can be written in the slightly simpler form

(3.15) $m(t, t') = kT \sum_{j} \hat{L}_j(t') \exp \int_{t}^{t'} dt''/\tau_j(t'')$,   (Wall distribution on creation)

where $\hat{L}_j(t')$ denotes the creation rate for all (i, n)-strands at time t', and $\sum_j$ is written as
an abbreviation for $\sum_{in}\sum$. In this case, it can be seen that $m(t, t') dt' = kT \times$ (the
concentration at time t of strands created during the interval t', $t' + dt'$).

Equations (3.13) and (3.15) can be seen to include, as special cases, several of the
constitutive equations derived in the literature from Gaussian molecular network arguments.
If all creation and loss rates are constant, we obtain the "rubberlike liquid" of Lodge [10, 11]
which generalized the single-exponential equation of Green and Tobolsky[9]. If creation and
loss rates are functions of instantaneous values of strain rate invariants, we obtain various
equations including those of Meister [16] and Carreau [17]. If the creation and loss rates are
functions of the instantaneous values of stress invariants, we obtain the equation of Kaye [18].
These and other related equations have been tabulated elsewhere in a common notation[5] and
need not be relisted here. Comparisons of rheological predictions for many of these
constitutive equation have been given by Carreau and De Kee [19].

The equation of Marrucci et al.[20] is of the form (3.13) but the memory function does not
appear on first inspection to be of the form (3.15); it is given instead by an equation
of the form

(3.16) $m(t, t') = \sum_{j} m_j(t, t')$

              $= \sum_{j} \dfrac{G_j(t)}{\lambda_j(t')} \exp \int_{t}^{t'} dt''/\lambda_j(t'')$,

where $G_j(t)$ is a functional of strain on the interval $(-\infty, t)$ and $\lambda_j(t')$ is a functional of
strain on the interval $(-\infty, t')$:

(3.17) $G_j(t) = G_{oj} x_j(t)$

(3.18) $\lambda_j(t) = \lambda_{oj}\{x_j(t)\}^{1.4}$

The time dependence of the two functionals is described by scalar differential equations for
the "structural variables" x_j

(3.19) $\lambda_j \dfrac{dx_j}{dt} = 1 - x_j - ax_j (trP'_j/2G_j)^{1/2}$

where P'_j is the non-equilibrium part of the jth contribution to P given by

              $P'_j = P_j - \int_{-\infty}^{t} m_j(t, t') dt' \, 1$

and P_j is computed from (3.13) with $m(t,t')$ replaced by $m_j(t, t')$.

It would appear that (3.15) and (3.16) are of different form, because $G_j(t)$ has t instead of
t'. It is thus not easy to see how the equation of Marrucci et al. can be interpreted in
terms of a Gaussian network. Jongschaap[21] showed that this connection can be made if we take
the segment loss probability function τ_j^{-1} in the network model to be

(3.20) $\dfrac{1}{\tau_j} = \dfrac{1}{\lambda_j}\left(a\sqrt{\dfrac{trP'_j}{2G_j}} - \dfrac{1}{x_j} + 2 \right)$.

When (3.20) is combined with (3.19), x_j replaced by N_j/N_{jo}, and the result multiplied by
N_{jo} we obtain

(3.21) $\dfrac{dN_j}{dt} = \dfrac{N_j}{\lambda_j} - \dfrac{N_j}{\tau_j}$

Here $N_j \equiv \int f_j(\boldsymbol{R}, t)d^3R$ is the total concentration of j-segments at time t, and N_{jo} is the equilibrium value of N_j. If in (3.21) we identify N_j/λ_j with the creation rate $\hat{L}_j(t) = \int L_j(\boldsymbol{R}, t)d^3R$, then we have

$$(3.22) \qquad dN_j(t)/dt = \hat{L}_j(t) - N_j(t)/\tau_j(t) ,$$

which is simply the integral of (3.9) over all configuration space. Thus the differential equations of the structure variables in the Marrucci model are directly related to the segment balance equations in the network model.

To see why $G(t)$ and not $G(t')$ occurs in (3.16), let $G_j = N_j kT$ and intergrate (3.21) to give

$$(3.23) \qquad G_j(t) = G_j(t') \exp \int_{t'}^{t} \left\{ \frac{1}{\lambda_j(t'')} - \frac{1}{\tau_j(t'')} \right\} dt''$$

When (3.23) and (3.16) are combined, we obtain exactly (3.15) since $G_j(t')/\lambda_j(t') = kT\hat{L}_j(t')$. Finally, to complete the interrelation of the network model with Marrucci's model we note that in (3.17) $G_{oi} = N_{oi}kT$ and for (3.18) to be satisfied we must take $\hat{L}_j = \hat{L}_{oj}x^{-0.4}$.

The equation of Marrucci et al. is seen to allow the segment creation and loss rates to depend on the deformation through the trace of the non-equilibrium part of the stress tensor. In the context of the network model discussion, it is not at all clear why the particular form used for this dependence was chosen or why it is so successful. The model of Phan-Thien and Tanner[27] also allows segment creation and loss rates to vary with trP'_j, but in a much more straightforward manner. This latter model has also been fairly successful in describing rheological data on polymer melts.

An even more successful equation of the form (3.13) for describing molten polymers is one in which the memory function includes a scalar function of strain $t' \to t$ as a factor. Recent step-strain data have given compelling evidence for such a "strain/time" factorization (at least in the terminal zone of the relaxation spectrum)[22,23], which had also previously been rather widely used to describe data, for example in rubber elasticity.

Wagner[24] uses an equation of the form (3.13) with a memory function of the form

$$(3.24) \qquad m(t, t') = kT \sum_j \hat{L}_j h(I_w(t' \to t)) \exp (t'-t)/\tau_j ,$$

for a Gaussian network material with the following assumptions:

(3.25)   Strand creation rates $\hat{L}_j$ are constant.

(3.26)   There are two independent mechanisms for strand loss: one, due to thermal motion, with constant loss probabilities $1/\tau_j$, and

(3.27)   another, due to 'disentanglement by deformation': the probability that a strand will survive from the instant t' of creation to the instant t at which the extra stress is measured is the same for all such strands and is denoted $\frac{1}{\tau_d(t',t)}$.

In (3.24), $I_w(t' \to t)$ is a scalar invariant of the macroscopic continuum strain from the state t' to the state t. By virtue of the fact that mechanisms (3.26) and (3.27) are independent, we have the total strand loss probability expressed as

$$(3.28) \qquad \frac{1}{\tau_j(t', t)} = \frac{1}{\tau_j} + \frac{1}{\tau_d(t', t)} .$$

Note that (3.28) differs from (3.4) in the appearance of two times t and t' in the argument for the loss rates.

Since the thermal motions determine τ_j and not $\tau_d(t',t)$, then the τ_j (and $\hat{L}_j$) would depend on the structure as in (3.6), but the τ_d would be structure independent. Equation (3.24) is obtained by combining (3.15) and (3.28) and by taking

$$(3.29) \qquad h(I_w(t' \to t)) := \exp \int_t^{t'} \frac{1}{\tau_d(t'', t)} dt''$$

For Small strains, $h = I$, and the constants $\hat{L}_j$ and τ_j have been chosen empirically to fit linear viscoelastic data (e.g., for the dynamic modulus $G'(\omega)$ and dynamic viscosity $\eta'(\omega)$) for a low-density polyethylene at 150°C[23]. The 'damping function' h was then chosen empirically to fit stress relaxation data for single-jump shear strain experiments and stress growth data in step-function elongation rate experiments; for the particular sample used, the following form for h gave a good fit:

(3.30) $\log_e h = -n\{\alpha I_1 + (1-\alpha)I_2 - 3\}^{0.5}$ ($n = 0.18$, $\alpha = 0.032$). Note that h in (3.30) is equivalent to a deformation loss probability $(1/\tau_d(t',t)) = -(n/2)I_w^{-\frac{1}{2}}\, dI_w/dt'$ where $I_w = \alpha I_1 + (1-\alpha)\,I_2 - 3$. The resulting constitutive equation, a particular case of the K-BKZ class of equations, gave a good description of data from a variety of experiments in shear and in elongation, but significantly overestimated the elastic recovery following elongation at constant rates[25]; the agreement with shear recovery data (following shear flow) was satisfactory, however.

To rectify this situation, Wagner and Stephenson[26] note (i) that recoverable strains are much larger for elongation than for shear, and (ii) that network strands lost during elongation from mechanism (3.27) would not be expected to be recreated during recovery. Accordingly, (3.27) is replaced by the following "irreversibility" assumption:

(3.31) Strands are lost irreversibly during a non-decreasing deformation and are not recreated during a subsequent decreasing deformation; the deformation-governed survival probability function h in (3.24) should be replaced by a functional H of strain given by the equation

(3.32) $$H(t,t') = \underset{t''=t'}{\overset{t''=t}{\text{Min}}} \{\, h(I_w(t',\, t'')) \},$$

where 'Min' denotes the minimum value assumed by the function h in the interval shown. The terms 'decreasing' and 'non-decreasing' as applied to deformations here are defined as follows:

(3.33) A deformation is $\{\begin{smallmatrix}\text{non-decreasing}\\\text{decreasing}\end{smallmatrix}\}$ throughout an interval (t',t) (where $t' < t$)

according as $h(I_w(t' \to t''))$ is $\{\begin{smallmatrix}\text{increasing}\\\text{non-increasing}\end{smallmatrix}\}$ for $t' < t'' < t$.

One interesting consequence of the use of two times in $\tau_.(t',t)$ in the Wagner model is that it is not in general possible to find an equivalent differential form for the constitutive equation (cf. (3.10) and (3.12)). For some applications, it appears to be helpful to have a differential equation for the stress tensor.

4. TIME-DEPENDENT CONNECTIVITY; NON-AFFINE MOTION

The modifications to the simplest form of network theory considered above have retained the affine motion assumption and have altered the assumption of constant creation and loss rates; the tensor character of the integrand in the constitutive equation is thereby retained, but the scalar memory function is made to depend on additional variables. Phan-Thien and Tanner[27] and Johnson and Segalman[28] simultaneously and independently altered the affine motion assumption in similar ways. Phan-Thien and Tanner, in addition, allow creation and loss rates to vary.

The Gaussian network formalism is used with the single change that the affine motion equation (2.8) be replaced by

(4.1) $$\dot{R} = R \cdot \hat{\nabla v} \,,$$

where

(4.2) $$\hat{\nabla v} = \nabla v - \frac{1}{2}\,\xi(\nabla v + \hat{\nabla v}),$$

where ξ is a constant (whose value is assigned empirically for a given material) and $\hat{v}(x,t)$ can be regarded as the velocity field of a fictitious continuum whose particles include ensemble-average positions of network junctions.

The analysis given above can be carried through for this case simply by replacing v by $\hat{v}$ at the appropriate places (i.e., in (2.13), (3.10), (3.12), and (3.13)), resulting in the replacement of the constitutive equation (3.13) by

(4.3) $$P(t) = \int_{-\infty}^{t} m(t,\, t')\, \hat{B}(t' \to t)\, dt',$$

where the new strain tensor $\hat{B}$ differs from the Finger tensor B only in that it is computed from the velocity $\hat{v}$ instead of v.

Phan-Thien and Tanner also include an additional term $-\sigma R$ on the right-hand side of (4.1); it turns out, however, that this can be omitted without loss of generality (it becomes absorbed in other terms in the subsequent analysis) and in any case appears to us to be inadmissible if the theory is to describe a network of changing connectivity: if the macroscopic material is

at rest (i.e., if $\boldsymbol{v}$ = 0), it is clear that $R \to 0$ or ∞ according as $\sigma > 0$ or $\sigma < 0$; both alternatives are physically unreasonable, so we must take $\sigma = 0$.

It is certainly reasonable to challenge the affine motion assumption in the context of Gaussian networks of changing connectivity: it is well known [1] that for certain purposes a Gaussian network of constant connectivity can be replaced by an equivalent system of "Gaussian springs" whose points of connection coincide with the ensemble-average positions of junctions in the real network; a Gaussian spring has a constant modulus (depending on the number of equivalent random links and on the temperature) and zero natural length. If one removes a junction, then the local force balance suggests that there will be an instantaneous rearrangement of nearby springs resulting almost certainly in non-affine motion of ensemble-average junction positions by an amount which would be expected to be greatest near the site of the lost junction and less further away. It is not clear, however, whether the particular form (4.2) of non-affine motion represents a valid description of this kind of behavior. (4.2) was presumably introduced on grounds of mathematical simplicity.

5. CONCLUSIONS AND RECOMMENDATIONS

The main result of this study has been to delineate carefully the underlying assumptions of the network theory for polymer rheology and to show to what extent a number of current theories for the stress tensor of molten polymers share this set of assumptions or differ from them. It seems that since the original formulations of the network theory, little has been done to develop our molecular understanding of the model. Most changes in the theory have been *ad hoc* modifications to the junction kinetics; some recent changes have been made in the affine motion assumption, but these, too, do not provide further structural basis to the theory. Thus the weakest aspect of the network theories remains their lack of structural basis. Certainly it would be worthwhile to have future work in the area that attempts to obtain the equations presented here from a full phase-space kinetic theory treatment.

There are several specific areas in which we wish to recommend further work. These are:

(5.1)   Incorporation of molecular variables, such as molecular weight dependence, into the network model. We have indicated in (3.6) what form results from this effort might take.

(5.2)   Extensive calculations of model predictions of various network models. It would have been nice at the end of this study to say not only what assumptions are involved in the various models, but also what predictions these lead to. In this way we could assess which assumptions are important for obtaining realistic rheological equations of state. Unfortunately, most authors do not present evaluations of constitutive equations that are as extensive as we feel necessary. We recommend that the following properties be computed for the models in this study and any new constitutive equations:

$\eta(\dot{\gamma})$, $\Psi_1(\dot{\gamma})$, $\Psi_2(\dot{\gamma})$, $G'(\omega)$, $G''(\omega)$, $G(t;\gamma)$, $E(t,\epsilon)$, $\eta^+(\dot{\gamma};t)$, $\eta^-(\dot{\gamma};t)$, Ψ_1^+, Ψ_1^-, Ψ_2^+, Ψ_2^-,

$\bar{\eta}^+(t;\dot{\epsilon})$, $\bar{\eta}^-(t,\dot{\epsilon})$, $\bar{\eta}(\dot{\epsilon})$, (for $\dot{\epsilon} > 0$ and $\dot{\epsilon} < 0$), $\gamma(t)$ and $N_1(t)$ in creep and creep recovery, and $\epsilon(t)$ in recovery after elongation.

(5.3)   It is important to compare the predictive success of the physical ideas underlying the network model with those of alternate theories for polymer melt rheology. Specifically, the recent theories of Doi and Edwards[29] and of Curtiss and Bird[30] model polymer-polymer interactions with a polymer diffusion tensor whose components for motion perpendicular to the chain backbone are much smaller than components for parallel motion. In future work we want to study these theories with the idea of comparing this physical picture of molten polymers with the network model in which polymer-polymer interactions are localized at junctions.

(5.4)   A critical set of experiments needs to be performed on small samples of well-defined polymers. This is needed to allow assessment of structure/property relations produced by molecular theories, as they become available. We think that optimum use of small samples would be made by performing

a. Non-linear step shear strain stress relaxation.
b. Non-linear step elongation stress relaxation.
c. Recovery following elongation flow and steady shear flow.
d. Linear viscoelastic properties $G(0)$, J_e^o, η_o, $G(t)$.
e. Steady shear flow properties $\eta(\dot{\gamma})$, $\Psi_1(\dot{\gamma})$.
f. Transient stress growth properties $\bar{\eta}^+$, η^+.

(5.5)   Finally we think that, to be as useful as possible, molecular theories need to predict mixing rules.

Notation

$A := B$	A is defined by the equation $A = B$.
$\underset{\sim}{\nabla v}$	Cartesian 2nd rank tensor represented by the matrix $[\partial v_c / \partial x_r]$, where r labels rows and c columns.
$\overset{\sim}{\nabla v}$	Transpose of the above tensor
$u \cdot v$	Scalar product of u and v.
$B(t_o \rightarrow t)$	Finger strain tnesor for the deformation $t_o \rightarrow t$; the components are given by $B_{rc} = \sum_i (\partial x_r / \partial x_i^o)(\partial x_c / \partial x_i^o)$, where x_i^o and x_i are the rectangular Cartesian coordinates of places occupied at times t_o and t by a typical particle of the macroscopic continuum
p	Cartesian space stress tensor; $p_{11} > 0$ for a tensile component.
P	extra-stress tensor.
R	ensemble-average strand end-to-end vector.
$d^3 R$	$dX\ dY\ dZ$, where X, Y, and Z are rectangular Cartesian components of R.
$I_1(t' \rightarrow t)$	$\sum \lambda_i^2$; λ_i ($k = 1,2,3$) are principal elongation ratios for the deformation $t' \rightarrow t$.
$I_2(t' \rightarrow t)$	$\sum \lambda_i^{-2}$.

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