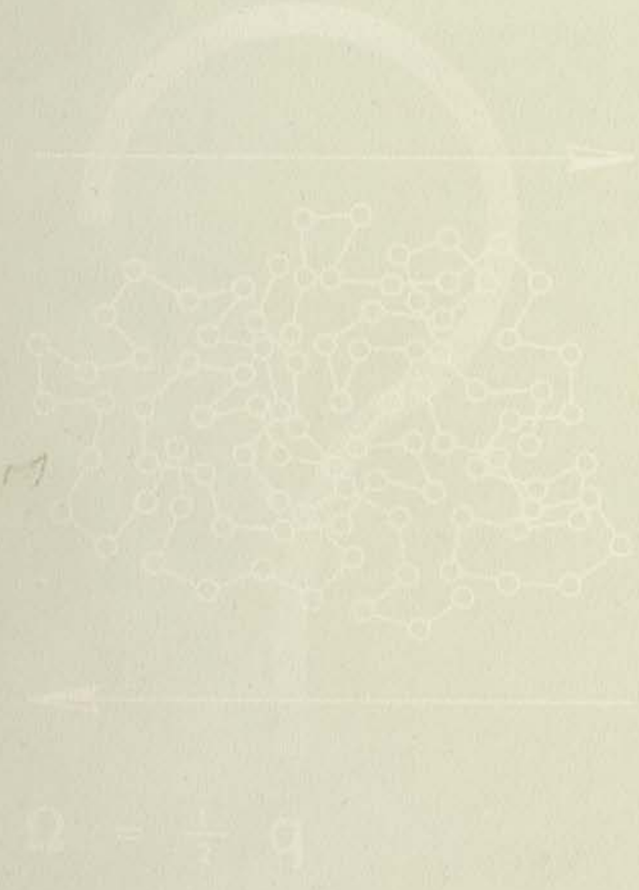
EFFECT OF SUPERIMPOSED STEADY SHEAR FLOW ON DYNAMIC PROPERTIES OF POLYMERIC FLUIDS



H.C. BOOIJ

EFFECT OF SUPERIMPOSED STEADY SHEAR FLOW ON DYNAMIC PROPERTIES OF POLYMERIC FLUIDS

PROEFSCHRIFT

ter verkrijging van de graad van Doctor in de
Wiskunde en Natuurwetenschappen aan de
Rijksuniversiteit te Leiden, op gezag van
de Rector Magnificus Dr. C. Soeteman,
Hoogleraar in de Faculteit der Letteren,
ten overstaan van een commissie uit
de Senaat te verdedigen op
woensdag 18 november 1970
te 16.15 uur

door

HENDRIK CORNELIS BOOIJ

geboren te Achtkarspelen in 1935

Promotor: Prof.Dr. A.J. Staverman

Druk P.M. van Hooren, Heerlen

STELLINGEN

1. De bewering van Makowski e.a., dat gedurende de polymerisatie van butadieen met n-butyllithium de graad van 1,2-additie continu afneemt naarmate de graad van polymerisatie voortschrijdt, is strijdig met hun experimentele gegevens.

H.S. Makowski, M. Lynn en A.N. Bogard, J. Macromol. Sci.-Chem., A2, 665 (1968)

2. Ten aanzien van de frequentie-afhankelijkheid van de dynamische afschuifmoduli van verdunde polymeeroplossingen leiden de berekeningen van Rouse en die van Bueche tot verschillende uitkomsten. Dit heeft twee oorzaken: Rouse verdisconteert de 'diffusie- of Brownse-bewegingskrachten', iets wat Bueche nalaat; bovendien verzuimt Bueche de verandering per tijdseenheid van de vrije energie van de macromoleculen op te nemen in zijn energieberekeningen.

P.E. Rouse, J. Chem. Phys. 21, 1272 (1953)
F. Bueche, J. Chem. Phys. 22, 603 (1954)

3. Gezien de structuur van koolstofvezels dient de term grafietvezels voor deze materialen te verdwijnen.

A. Fourdeux, C. Herinckx, R. Perret en W. Ruland, C.R. Acad. Sc. Paris, C269, 1597 (1969)

4. Het door Overdiep en van Krevelen gegeven criterium voor stromingsinstabiliteit berust op een verkeerd begrip van de verdeling die de afschuifspanning in een stromende vloeistof heeft over de doorsnede van een cilindrische pijp.

W.S. Overdiep en D.W. van Krevelen, J. Appl. Polymer Sci. 9, 2779 (1965)
Zie bijv. J.R. van Wazer, J.W. Lyons, K.Y. Kim en R.E. Colwell, Viscosity and Flow Measurement, Interscience Publ., New York, 1963, p. 189/190

5. Voor niet-newtonse vloeistoffen dient voor de beschrijving van de temperatuurafhankelijkheid van de viscositeit het gebruik van de z.g. Arrhenius-vergelijking ten sterkste te worden ontraden. Een behandeling van de, bij verschillende temperaturen bepaalde, curven van de afschuifspanning en van het eerste normaalspanningsverschil als functies van de afschuifsnelheid analoog aan de gebruikelijke behandeling - met behulp van verschuivingsfactoren - van de curven van de verliesmodulus en van de opslagmodulus als functies van de frequentie, verdient verre de voorkeur en geeft een temperatuurafhankelijkheid die voor de genoemde experimentele grootheden gelijk is.

6. Het door Yamaura voorgestelde mechanisme voor de hydrodynamische inductie van de kristallisatie van polymeren uit geroerde oplossingen is theoretisch onwaarschijnlijk en in strijd met experimentele gegevens.

K. Yamaura, Kolloid-Z.u.Z. Polymere 238, 522 (1970)
A.J. Pennings, J.M.A.A. van der Mark en H.C. Booij, Kolloid-Z.u.Z. Polymere 236, 99 (1970)

7. In de literatuur vindt men vaak schetsmatige curven, die het verband aangeven tussen de vrije mengenthalpie en de samenstelling van een binair vloeibaar mengsel. Het is te betreuren dat in de figuren in leerboeken en naslagwerken, niet altijd rekening wordt gehouden met de eisen waaraan volgens de thermodynamica de vorm van deze curven moet voldoen. Zie bijv.

I. Prigogine, The Molecular Theory of Solutions, North Holland Publ. Comp., 1957, p. 19
G.L. De Haas-Lorentz, De Beide Hoofdwetten der Thermodynamica, Nijhoff, Den Haag, 1942, p. 149
C. Tanford, Physical Chemistry of Macromolecules, John Wiley, New York, 1961, p. 246
M.L. Miller, The Structure of Polymers, Reinhold, New York, 1966, p. 146

8. De consciëntieuse beschouwingen van Dahl en Ballhausen over de diverse quantum-mechanische benaderingsmethoden voor de berekening van energieniveaus in anorganische complexen staan in schril contrast tot het invoeren van het effect van de omgeving bij hun berekening van de energieniveaus in het permanganaat ion.

J.D. Dahl en C.J. Ballhausen, Adv. Quantum Chem. 4, 170 (1968)

9. Naar aanleiding van het door Cox en Merz voor polymere vloeistoffen gevonden empirische verband tussen de viscositeit bij stationaire afschuifstroming en de complexe dynamische viscositeit, stellen Onogi e.a. dat de stationaire viscositeit behalve visceuse effecten ook elastische effecten bevat. Een dergelijke bewering heeft geen betekenis, indien niet gelijktijdig wordt gedefinieerd wat onder elastische effecten bij stationaire afschuifstroming moet worden verstaan.

W.P. Cox en E.H. Merz, J. Polymer Sci. 28, 619 (1958)
S. Onogi, T. Masuda en T. Ibaragi, Kolloid-Z.u.Z. Polymere 222, 110 (1968)

10. Ten aanzien van de aantrekkingskracht van dieren op mensen formuleert Morris de wet: 'De leeftijd van een kind is omgekeerd evenredig met de afmetingen van het dier waaraan het de voorkeur geeft'. Aangezien de aantrekkingskracht van een dier op een kind lineair toeneemt met de aaibaarheidsfactor van het dier voor het kind en deze factor weer lineair van de sterkte van het poppenhuis-syndroom van het kind afhangt, is het ten onrechte dat Morris bij de interpretatie van zijn wet de leeftijdsafhankelijkheid van het poppenhuis-syndroom buiten beschouwing laat.

Desmond Morris, De Naakte Aap, A.W. Bruna & Zoon, Utrecht, 1968, p. 233
Rudy Kousbroek, De Aaibaarheidsfactor, Th. Rap, Amsterdam, 1968

18 november 1970 H.C. Booij

5. Voor [illegible]
[illegible]
[illegible]
lende temperat[illegible]
eerste [illegible]
aan de gebruike[illegible]
van de curven van de verliesmodulus en van de opslagmodulus als functies van de frequentie, verdient verre de voorkeur en geeft een temperatuurafhankelijkheid die voor de genoemde expe[illegible]

[illegible]

6. Het door Yamaura voorgestelde mechanisme voor de hydrodynamische inductie van [illegible] theoretisch onve[illegible]

K. Yamaura, [illegible]
A.J. Pennings, J. [illegible] 36 (1970)

7. In de literatuur vindt men vaak ontmengingscurven, die het verband aangeven tussen de vrije mengenthalpie en de samenstelling van een binair vloeibaar mengsel. Het is te betreuren dat in de figuren in leerboeken en naslagwerken, niet altijd rekening wordt gehouden met de eisen waaraan volgens de thermodynamica de vorm van deze curven moet voldoen. Zie bijv.

I. Prigogine, The Molecular Theory of Solutions, North Holland Publ. Comp., 1957, p. 18
G.L. De Haas-Lorentz, Beknopte Hoofdstukken der Thermodynamica, Nijhoff, Den Haag, 1943, p. 149
C. Tanford, Physical Chemistry of Macromolecules, John Wiley, New York, 1961, p. 248
M.L. Miller, The Structure of Polymers, Reinhold, New York, 1966, p. 196

8. De consciëntieuze beschouwingen van Dahl en Ballhausen over de diverse quantum-mechanische benaderingsmethoden voor de berekening van energieniveaus in anorganische complexen staan in schril contrast tot het invoeren van het effect van de omgeving bij hun berekening van de energieniveaus in het permanganaat ion.

J.P. Dahl en C.J. Ballhausen, Adv. Quantum Chem. 4, 170 (1968)

Aan Margreet en Jan
Aan Ita
Aan mijn ouders

CONTENTS

I. Introduction and survey

II. Survey of published experimental results

III. Summary of published theoretical approaches

IV. Molecular theory

V. Comparison between molecular theory and experiment

CONTENTS

I. Introduction and survey

II. Survey of published experimental results

III. Summary of published theoretical approaches

IV. Molecular theory

Chapter I

INTRODUCTION AND SURVEY

1. Introduction

The terminology used in rheology studies can be defined in a simple way only for strongly idealized experimental circumstances. A mode of definition having more general applicability calls for such a degree of mathematical formalism as will cause the physical nature of the rheological concepts to be masked to a considerable degree. To avoid these two extremes, we shall adopt a middle course in our introductory chapter. For this purpose we shall restrict ourselves in our considerations to isotropic and incompressible media. Further, in defining some rheological concepts, we shall set out from the principle that the definitions should be valid under the most current experimental conditions. Although the definitions may thus lose somewhat in generality and exactness, they will certainly gain in understandability.

Nevertheless, it remains necessary first to make some general remarks about coordinate systems and coordinate transformations. In the following section, several concepts, like shear flow, rate of shear, superposition, stress tensor and dynamic properties, will be introduced. After that, we shall describe the object of our study and, finally, give a survey of the further contents of this thesis.

2. Definition of some rheological quantities

a. Coordinate systems

Every point in the Euclidian space has a *position vector* $\underset{\sim}{r}$, which, in a system of Cartesian coordinates x, y and z, can be decomposed as follows:

$$\underset{\sim}{r} = x\underset{\sim}{e}_x + y\underset{\sim}{e}_y + z\underset{\sim}{e}_z \qquad \text{(I 1)}$$

where $\underset{\sim}{e}_x$, $\underset{\sim}{e}_y$ and $\underset{\sim}{e}_z$ form an orthonormal system of *base vectors.* Any system of three spatial vectors $\underset{\sim}{e}_1$, $\underset{\sim}{e}_2$, and $\underset{\sim}{e}_3$ can be used as basis, provided not all vectors are parallel to any given plane. A spatial point $\underset{\sim}{r}$ can therefore be uniquely described by

$$\underset{\sim}{r} = x^1\underset{\sim}{e}_1 + x^2\underset{\sim}{e}_2 + x^3\underset{\sim}{e}_3 \qquad \text{(I 2)}$$

A *coordinate system* is a reversible one-to-one correspondence between points in the Euclidian space and triples (x^1, x^2, x^3) of numbers, known as *coordinates.*

From Eq. (I 2) it follows that, if the position vector $\underset{\sim}{r}$ is known as a function of the three coordinates x^1, x^2, x^3, the corresponding base can be found from

$$\underline{e}_i = \frac{\partial \underline{r}}{\partial x^i} \quad (i = 1, 2, 3) \qquad \text{(I 3)}$$

Suppose the position of a point in the Euclidian space is denoted by cylindrical coordinates r, φ and z. The position vector $\underline{r}$ can then be written as in Eq. (I 1) and the coordinates are related as follows: $x = r \sin \varphi$; $y = r \cos \varphi$; $z = z$. Eq. (I 3) yields

$$\underline{e}_r = \frac{\partial \underline{r}}{\partial r} = \sin \varphi \, \underline{e}_x + \cos \varphi \, \underline{e}_y$$

$$\underline{e}_\varphi = \frac{\partial \underline{r}}{\partial \varphi} = r \cos \varphi \, \underline{e}_x - r \sin \varphi \, \underline{e}_y \qquad \text{(I 4)}$$

$$\underline{e}_z = \frac{\partial \underline{r}}{\partial z} = \underline{e}_z$$

The *magnitudes* of the base vectors $\underline{e}_i$ are denoted by

$$e_i = | \underline{e}_i | = \sqrt{\underline{e}_i^2} \qquad \text{(I 5)}$$

In the case of cylindrical coordinates, we thus have

$$e_r = 1; \; e_\varphi = r; \; e_z = 1 \qquad \text{(I 6)}$$

Complete analogous reasoning shows that the magnitudes of the base vectors $\underline{e}_r$, $\underline{e}_\varphi$, $\underline{e}_\theta$ in a system of spherical coordinates (Fig. I,1) are:

$$e_r = 1; \; e_\varphi = r \sin \theta; \; e_\theta = r \qquad \text{(I 7)}$$

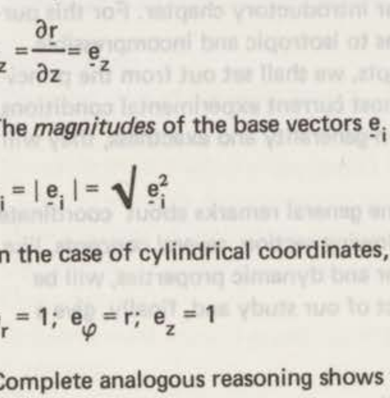


Fig. I,1 System of spherical coordinates

A coordinate system is said to be *orthogonal* if the natural base vectors (I 3) are orthogonal to each other, i.e., if

$$\underline{e}_i \cdot \underline{e}_k = 0 \;\; \text{for } i \neq k \qquad \text{(I 8)}$$

For the basis of such a system to be *orthonormal*, its vectors must satisfy the conditions

$$\underline{e}^{<i>} = \frac{\underline{e}_i}{e_i} \; \text{for } i = 1, 2, 3 \qquad \text{(I 9)}$$

The components of a vector $\underline{v}$ with respect to this orthonormal basis are the *physical components* of the vector; the latter are denoted by

$$v^i = \underline{v} \cdot \underline{e}^{<i>} \;\; \text{for } i = 1, 2, 3 \qquad \text{(I 10)}$$

For the physical components of a position vector $\underset{\sim}{r}$ with respect to a cylindrical coordinate system, Eqs (I 1) and (I 4) consequently give:

$$x^r = x \sin\varphi + y \cos\varphi = r$$

$$x^\varphi = x \cos\varphi - y \sin\varphi = 0$$

$$x^z = z$$

and, hence,

$$\underset{\sim}{r} = r\underset{\sim}{e}^{<r>} + z\underset{\sim}{e}^{<z>} \tag{I 11}$$

We now suppose that the base vectors $\underset{\sim}{e}_i$ are not orthogonal. It is convenient then to introduce a set of *reciprocal base vectors* $\underset{\sim}{e}^j$; these are defined by the equations

$$\underset{\sim}{e}_i \cdot \underset{\sim}{e}^j = \delta_i^j \tag{I 12}$$

from which it follows that $\underset{\sim}{e}^1$ is perpendicular to the plane of $\underset{\sim}{e}_2$ and $\underset{\sim}{e}_3$, and that $\underset{\sim}{e}^2$, and $\underset{\sim}{e}^3$, are perpendicular to the planes of $\underset{\sim}{e}_1$ and $\underset{\sim}{e}_3$, and $\underset{\sim}{e}_1$ and $\underset{\sim}{e}_2$, respectively. Of course the introduction of this reciprocal basis does not serve any useful purpose if the original basis $\underset{\sim}{e}_i$ is orthogonal, because in that case, $\underset{\sim}{e}^j$ is identical to $\underset{\sim}{e}_j$.

Again, any position vector $\underset{\sim}{r}$ can be expressed in terms of the reciprocal base vectors by an equation of the form

$$\underset{\sim}{r} = x_1\underset{\sim}{e}^1 + x_2\underset{\sim}{e}^2 + x_3\underset{\sim}{e}^3 \tag{I 13}$$

where x_1, x_2 and x_3 are now called the *reciprocal coordinates* of $\underset{\sim}{r}$. When $\underset{\sim}{r}$ is known as a function of the reciprocal coordinates, the reciprocal base vectors are obtained from

$$\underset{\sim}{e}^i = \frac{\partial \underset{\sim}{r}}{\partial x_i} \tag{I 14}$$

If the two sets of base vectors $\underset{\sim}{e}_i$ and $\underset{\sim}{e}^j$ do not constitute orthogonal systems, three types of tensors can be constructed from the scalar products of the base vectors. According to the definition equation (I 12), the products of $\underset{\sim}{e}_i$ and $\underset{\sim}{e}^j$ give a diagonal tensor with elements equal to 1. The other two tensors are called the *metric* tensors; the first one is the *metric tensor of Cauchy*, which is defined by

$$\underset{\approx}{C} = \underset{\sim}{e}_i \cdot \underset{\sim}{e}_j \tag{I 15}$$

with elements C_{ij}, the other is the *metric tensor of Finger*

$$\underset{\approx}{B} = \underset{\sim}{e}^i \cdot \underset{\sim}{e}^j \tag{I 16}$$

the elements of which are denoted by B^{ij}.

With non-orthogonal systems, these two tensors are different, and a distinct physical meaning can be attached to them. As demonstrated for example by Lodge1), the quantities C_{ij} can be used for obtaining complete information about the separation of particles of a material, whereas the separation of pairs of parallel material planes can be completely described by means of the quantities B^{ij}. With orthonormal systems, the tensors are equal.

Let us now check up on the *transformation properties* of the various quantities. Suppose a position vector is described by two coordinate systems x'^1, x'^2, x'^3 and x^1, x^2, x^3. From Eq. (I 3) it follows that

$$\underline{e}_i = \frac{\partial \underline{r}}{\partial x^i} = \sum_k \frac{\partial \underline{r}}{\partial x'^k}\,\frac{\partial x'^k}{\partial x^i} = \sum_k \frac{\partial x'^k}{\partial x^i}\,\underline{e}'_k \tag{I 17}$$

and, conversely,

$$\underline{e}'_i = \frac{\partial \underline{r}}{\partial x'^i} = \sum_k \frac{\partial \underline{r}}{\partial x^k}\,\frac{\partial x^k}{\partial x'^i} = \sum_k \frac{\partial x^k}{\partial x'^i}\,\underline{e}_k \tag{I 18}$$

Any vector $\underline{v}$ with the components v'^1, v'^2, v'^3, or v^1, v^2, v^3 can be written as

$$\underline{v} = \sum_i v'^i\,\underline{e}'_i = \sum_i v^i\,\underline{e}_i \tag{I 19}$$

Substitution of Eq. (I 18) yields

$$v^i = \sum_k \frac{\partial x^i}{\partial x'^k}\,v'^k \tag{I 20}$$

The reciprocal base vectors have to satisfy

$$\underline{e}^i = \sum_k \frac{\partial x^i}{\partial x'^k}\,\underline{e}'^k \tag{I 21}$$

as can be easily proved by substitution of Eqs (I 21) and (I 17) in Eq. (I 12). Substitution in equation

$$\underline{v} = \sum_i v'_i\,\underline{e}'^i = \sum_i v'^i\,\underline{e}'_i \tag{I 22}$$

shows that the reciprocal components of $\underline{v}$ transform according to

$$v_i = \sum_k \frac{\partial x'^k}{\partial x^i}\,v'_k \tag{I 23}$$

If three numbers v^i, referred to the system of coordinates x^i, and three numbers v'^k, referred to coordinates x'^k, are related by Eq. (I 20), then the quantities v'^k and v^i are called the *contravariant* components of the vector $\underset{\sim}{v}$, whereas numbers transforming in conformity with Eq. (I 23) are called the *covariant* components of $\underset{\sim}{v}$.

A typical example of components of a contravariant vector is formed by differentials of coordinates. The components of this vector transform according to

$$dx^i = \frac{\partial x^i}{\partial x'^1}\, dx'^1 + \frac{\partial x^i}{\partial x'^2}\, dx'^2 + \frac{\partial x^i}{\partial x'^3}\, dx'^3 \tag{I 24}$$

A prototype of a covariant vector is the gradient of a scalar. The components of this type of vectors obey the following equations

$$\frac{\partial \varphi}{\partial x^i} = \frac{\partial x'^1}{\partial x^i}\,\frac{\partial \varphi}{\partial x'^1} + \frac{\partial x'^2}{\partial x^i}\,\frac{\partial \varphi}{\partial x'^2} + \frac{\partial x'^3}{\partial x^i}\,\frac{\partial \varphi}{\partial x'^3} \tag{I 25}$$

The transformation formulae for the metric tensors are found by substitution of Eq. (I 17) in Eq. (I 15) and Eq. (I 21) in Eq. (I 16). This gives

$$C_{ij} = \sum_k \sum_l \frac{\partial x'^k}{\partial x^i}\,\frac{\partial x'^l}{\partial x^j}\, C'_{kl} \tag{I 26}$$

for the covariant components of the Cauchy tensor, and

$$B^{ij} = \sum_k \sum_l \frac{\partial x^i}{\partial x'^k}\,\frac{\partial x^j}{\partial x'^l}\, B'^{kl} \tag{I 27}$$

for the contravariant components of the Finger tensor.

b. Deformable body

A *deformable body* consists of material points liable to change their relative positions in space under the influence of external forces. If a material point in the Euclidian space occupies a position $\underset{\sim}{r}$ at time t, then it will have occupied a position $\underset{\sim}{r}'$ at time $t' \leqslant t$. The dependence of $\underset{\sim}{r}'$ on $\underset{\sim}{r}$, t and t′ is given by a *displacement function* $\underset{\sim}{r}' = \underset{\sim}{r}'(\underset{\sim}{r}, t, t')$, which also defines the *lines of motion* of the material points.

This use of the vectors $\underset{\sim}{r}$ and $\underset{\sim}{r}'$ differs from that in the preceding section. There, $\underset{\sim}{r}$ and $\underset{\sim}{r}'$ denoted the coordinates of one and the same point in space with respect to different bases, whereas now $\underset{\sim}{r}$ and $\underset{\sim}{r}'$ are used to coordinate a given material point at different positions in space with a basis which may now be regarded as orthonormal. Still, all the formulae given in the preceding section are applicable for describing the deformation of materials, albeit that the interpretation must be slightly modified with the aid of *embedded* or *convected* vectors. These vectors always connect the same material points in the same set. Any three non-coplanar embedded vectors can be taken as an embedded basis, and any position vector of a material point can be expressed by an equation like

$$\underset{\sim}{r}(t) = \xi^1 \underset{\sim}{e}_1(t) + \xi^2 \underset{\sim}{e}_2(t) + \xi^3 \underset{\sim}{e}_3(t) \tag{I 28}$$

During deformation of the body, the embedded base vectors are functions of time, but the coefficients ξ^i are time-independent coordinates associated with the material point considered. At any time t′, the embedded vectors can be related, by means of transformation formulae, with a spatially fixed orthonormal basis $\underline{e}_x, \underline{e}_y, \underline{e}_z$. All the equations of the preceding section remain valid if we replace $\underline{e}'_1, \underline{e}'_2, \underline{e}'_3$ by $\underline{e}_x, \underline{e}_y, \underline{e}_z$, $\underline{e}_i$ by $\underline{e}_i$ (t) (i = 1, 2, 3), x^i by ξ^i and x'^i by x'^i (t′), etc.; after this modification they relate the embedded quantities to the spatial quantities.

For a proper understanding of a few theoretical treatments in Chapter III, some additional attention will now be given to the relations for the metric tensors. Execution of the above-mentioned substitutions, changes Eq. (I 26) into

$$C_{ij}(\xi, t') = \sum_k \sum_l \left(\frac{\partial x'^k}{\partial \xi^i} \frac{\partial x'^l}{\partial \xi^j} \right)_{t'} C'_{kl}(x', t') \qquad \text{(I 29)}$$

Because the spatial basis is taken to be orthonormal, i.e., $C'_{kl}(x', t') = \delta_{kl}$, we have

$$C_{ij}(\xi, t') = \sum_k \left(\frac{\partial x'^k}{\partial \xi^i} \frac{\partial x'^k}{\partial \xi^j} \right)_{t'} \qquad \text{(I 30)}$$

Further, the convected coordinate system is so chosen as to coincide with the spatial system at time t. This gives $\xi^i = x^i$, if x^i are the space coordinates, at time t, of the particle considered. But, since ξ^i are independent of time, we also have $\xi^i = x^i$ at time t′. Hence, Eq. (I 30) takes the form

$$C_{ij}(t') = \sum_k \left(\frac{\partial x'^k}{\partial x^i} \frac{\partial x'^k}{\partial x^j} \right)_{t'} \qquad \text{(I 31)}$$

Similarly, we get

$$B^{ij}(t') = \sum_k \left(\frac{\partial x^i}{\partial x'^k} \frac{\partial x^j}{\partial x'^k} \right)_{t'} \qquad \text{(I 32)}$$

It also follows from these equations that

$$\underline{C}(t) = \underline{B}(t) = \underline{I} \qquad \text{(I 33)}$$

where $\underline{I}$ is the unit tensor.

Still $\underline{C}(t')$ and $\underline{B}(t')$ retain their validity as measures of the separation of material points and parallel material planes. This means that we now have two measures of the strain in the material over the time interval t–t′, namely

a *contravariant strain tensor*

$$\underline{S}(t') = \underline{B}(t') - \underline{B}(t) \qquad \text{(I 34)}$$

and a *covariant strain tensor*

$$\underline{G}(t') = \underline{C}(t') - \underline{C}(t) \tag{I 35}$$

The components of the spatial *velocity* $\underline{v}(\underline{r}, t)$ of a material point at the time t are given by

$$v_i = \left.\frac{\partial x'^i}{\partial t'}\right|_{t'=t} \quad (i = 1, 2, 3) \tag{I 36}$$

if x'^i are the coordinates of the position vector of the material point at t′ with respect to an orthonormal basis.
The components $\dot{\gamma}_{ij} = \dot{\gamma}^{ij}$ of the *velocity gradient tensor* $\underline{\dot{\Gamma}}$ are defined by

$$\dot{\gamma}_{ij}(\underline{r}, t) = \frac{\partial v^j}{\partial x^i} \tag{I 37}$$

The symmetrical part of $\underline{\dot{\Gamma}}$ is the *rate-of-strain tensor* $\underline{\dot{E}}$ with components $\dot{e}_{ij} = \dot{e}^{ij}$ equal to

$$\dot{e}_{ij}(\underline{r}, t) = ½\left[\frac{\partial v^j}{\partial x^i} + \frac{\partial v^i}{\partial x^j}\right] \tag{I 38}$$

while the anti-symmetrical part constitutes the components $\dot{\omega}_{ij} = \dot{\omega}^{ij}$ of the *vorticity tensor* $\underline{\dot{\Omega}}$

$$\dot{\omega}_{ij}(\underline{r}, t) = ½\left[\frac{\partial v^j}{\partial x^i} - \frac{\partial v^i}{\partial x^j}\right] \tag{I 39}$$

These quantities can also be defined with respect to an embedded basis or with respect to the reciprocal embedded basis. This being done, it is seen that e.g. $\underline{\dot{E}}$ provides a measure of the rate at which material points or planes are moving towards or away from each other. In consequence two convected rate of strain tensors can be derived in the same way as the metric tensors. This procedure results in the following transformation formulae for the convected components of

a *contravariant rate-of-strain tensor*

$$\dot{e}^{ij}(t') = \sum_k \sum_l \left(\frac{\partial x^i}{\partial x'^k}\,\frac{\partial x^j}{\partial x'^l}\right)_{t'} \dot{e}^{kl}(\underline{r}', t') \tag{I 40}$$

and a *covariant rate-of-strain tensor*

$$\dot{e}_{ij}(t') = \sum_k \sum_l \left(\frac{\partial x'^k}{\partial x^i}\,\frac{\partial x'^l}{\partial x^j}\right)_{t'} \dot{e}_{kl}(\underline{r}', t') \tag{I 41}$$

c. Shear flow

Continuously varying deformation of a material is referred to as *shear flow* if the material in question comprises a family of surfaces — the *shearing surfaces* — all of which move rigidly in the sense that the separation between any two material points in such a surface remain constant1). These surfaces can be denoted by x^1 = constant in an appropriate coordinate system.

If, considered in an orthogonal coordinate system x^1, x^2, x^3 for which the magnitudes e_i of the base vectors are constant along the lines of flow, the components of the velocity field are

$$v^1 = 0;\ v^2 = u(x^1);\ v^3 = w(x^1) \qquad \text{(I 42)}$$

the shear flow is said to be *curvilinear*2). It is called *laminar* if, measured in Cartesian coordinates, the separation between shearing surfaces is independent of the position on the surfaces, while it is referred to as a *simple shear* flow if, again considered in a Cartesian system,the shearing surfaces are parallel planar surfaces and the lines of flow are straight lines.

Simple shear flow arises when a liquid is sheared between two parallel plates. Examples of cylindrical laminar shear flow are the type of flow produced in rotational Couette-type viscometers and that displayed by the flow pattern of a capillary tube viscometer (telescopic or Poiseuille flow), whereas a more general type of shear flow is encountered in cone-and-plate viscometers, even if the apex of the cone is not in contact with the plate3).

In a curvilinear flow, described by Eq. (I 42), the *rate of shear* $\dot{\gamma}$ is equal to2)

$$\dot{\gamma} = \frac{1}{e_1}\left[e_2^2\left(\frac{du}{dx^1}\right)^2 + e_3^2\left(\frac{dw}{dx^1}\right)^2\right]^{1/2} \qquad \text{(I 43)}$$

The shear flow is said to be *steady* if the shear rate is independent of time. A steady curvilinear flow is called a *viscometric* flow. Hence, the rate of shear in a viscometric shear flow is a constant, which will be denoted by q. In *oscillatory* shear flow, the rate of shear is of the form $\alpha\omega \cos \omega t$, where the amplitude α of the oscillatory shear $\alpha \sin \omega t$ is generally supposed to be small, and ω represents the circular frequency of the oscillation. A liquid can be subjected to various modes of shear flow at the same time. Nevertheless, disregarding all other possibilities, we shall, for brevity, use the term *superposition* when an oscillatory shear is superimposed on a steady shear flow. In case v^2 is proportional to $(q + \alpha\omega \cos \omega t)\, x^1$ and $v^3 = 0$, the mode of superposition will be called *parallel*, whereas we shall speak off *orthogonal* superposition if v^2 is proportional to qx^1 and v^3 to $(\alpha\omega \cos \omega t)\, x^1$.

The definitions given will be illustrated by means of two examples of flow, viz. helical flow between concentric cylinders and cone-and-plate flow.

In a helical flow the components of the velocity field in a cylindrical coordinate system $x^1 = r, x^2 = z, x^3 = \varphi$, are

$$v^r = 0;\ v^z = u(r);\ v^\varphi = w(r) \qquad \text{(I 44)}$$

The rate of shear is given by Eq. (I 43):

$$\dot{\gamma} = \left[\left(\frac{du}{dr}\right)^2 + \left(r\,\frac{dw}{dr}\right)^2 \right]^{1/2} \tag{I 45}$$

We shall now consider a helical flow between two infinite coaxial cylinders – an inner one with radius R_1 and an outer one with radius R_2 – whose angular velocities about their common axis are constant and equal to Ω_1 and Ω_2 respectively, and whose velocities in the direction of this axis are U_1 and U_2 resp. There is evidence2) showing that, if the fluid is assumed to adhere to the cylinders, the velocity profile depends on the rheological properties of the material. However, if the relative gap $(R_2 - R_1)/R_1$ is very small, the velocity gradients will be approximately constant in the gap. We now suppose that the difference in displacement between the two cylinders in the z-direction is an oscillatory function of very small amplitude A, i.e. $U_2 - U_1 = A\omega \cos \omega t$. We are then dealing with orthogonal superposition, and the velocity gradients are equal to

$$\frac{dw}{dr} = \frac{\Omega_2 - \Omega_1}{R_2 - R_1} = \frac{q}{R_1} \quad \text{and} \quad \frac{du}{dr} = \frac{A\omega \cos \omega t}{R_2 - R_1} = \alpha\omega \cos \omega t$$

In this case the rate of shear, determined by means of Eq. (I 45), equals

$$\dot{\gamma} = \left[q^2 + \alpha^2 \omega^2 \cos^2 \omega t \right]^{1/2} \tag{I 46}$$

A parallel mode of superposition exists when

$$\frac{dw}{dr} = \frac{R_1 (\Omega_2 - \Omega_1) + A\omega \cos \omega t}{R_1 (R_2 - R_1)} \quad \text{and} \quad \frac{du}{dr} = 0$$

The shear rate now equals

$$\dot{\gamma} = q + \alpha\omega \cos \omega t \tag{I 47}$$

As regards their basic geometry, the instruments for producing cone-and-plate flow consist of a rigid cone, rotating about its axis with an angular velocity Ω_1, and a rigid disc, rotating about the same axis with angular velocity Ω_2, between which the test fluid is contained. The axis of the cone is taken to be the polar axis of the spherical coordinates θ, φ, r (see Fig. I,1). We suppose that the disc lies in the plane $\theta = \pi/2$, and that the equation for the cone is $\theta = \pi/2 - \theta_o$, which means that the apex of the cone just touches the flat plate. θ_o is the angle between the disc and the cone, the gap angle. It can now be proved4, 5, 6) that the velocity distribution may be approximately described by a space-independent shear rate, on the condition that the quantity $(\Omega_2 - \Omega_1)\,\rho r^2 \theta_o^2\,(3\,\eta)^{-1}$, where ρ and η denote the density and the viscosity of the fluid respectively, is much smaller than unity. This condition is satisfied if the gap angle θ_o is very small. Then, with $\pi/2 - \theta_o \leqslant \theta \leqslant \pi/2$, $\cos\theta \simeq 0$ and $\sin\theta \simeq 1$. Under these circumstances, the surfaces for which θ is constant constitute the shearing surfaces, while the velocity field has the components

$$v^{\theta} = 0;\ v^{\varphi} = \Omega_2 + (\Omega_2 - \Omega_1)\,(\theta - \pi/2)/\theta_o;\ v^{r} = 0 \tag{I 48}$$

The rate of shear found by means of Eqs (I 7) and (I 43), with $\sin\theta = 1$, equals

$$\dot{\gamma} = (\Omega_2 - \Omega_1)/\theta_o \tag{I 49}$$

We are dealing here with parallel superposition if the velocity difference $\Omega_2 - \Omega_1$ is proportional to $q + a\omega \cos \omega t$.

d. Stress tensor

Consider a point A in the interior of a deformable material. Construct a surface element containing A. The orientation of this element in space is characterized by a unit normal vector $\underset{\sim}{n}$ (see Fig. I,2).

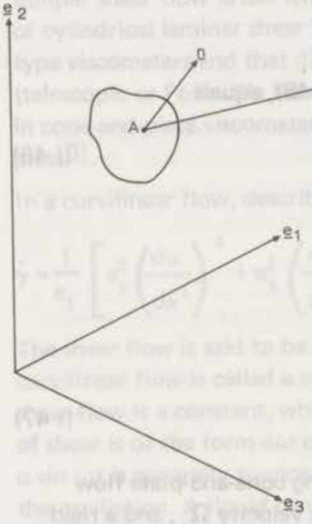


Fig. I,2 Definition sketch for the introduction of the stress tensor

The material on the side to which $\underset{\sim}{n}$ is directed is called 'positive'. Let p be the force per unit area acting across the surface element and exerted by the 'positive' material on the 'negative' material. This stress vector p may be dependent on $\underset{\sim}{n}$, on the location of A and on time.

In every system of base vectors the force p can be written as

$$p = p_{n1}\,\underset{\sim}{e}_1 + p_{n2}\,\underset{\sim}{e}_2 + p_{n3}\,\underset{\sim}{e}_3$$

and the components are denoted by p_{nj}. Index n is linked up with the orientation of the surface element and the index j with the direction of the stress vector. It can be shown that the set of quantities p_{nj} (for any $\underset{\sim}{n}$) can be expressed in terms of nine quantities,

$$p_{ij} = \begin{bmatrix} p_{11} & p_{12} & p_{13} \\ p_{21} & p_{22} & p_{23} \\ p_{31} & p_{32} & p_{33} \end{bmatrix}$$

constituting the *stress tensor* $\underline{P}$. In consequence of the law of balance of angular momentum this stress tensor is symmetric, i.e. $p_{ij} = p_{ji}$.
If the normal $\underset{\sim}{n}$ is in the e_2-direction, then the stresses p_{21} and p_{23} are in the plane of the surface element and p_{22} is normal to it. Conventionally, a tension is represented by a positive p_{22}. p_{11}, p_{22} and p_{33} are *normal stresses,* whereas $p_{11} - p_{22}$ is called the

first normal stress difference, and $p_{22} - p_{33}$ the second normal stress difference. p_{12}, p_{13} and p_{23} are the *shear* or *tangential stresses.* For incompressible liquids the isotropic hydrostatic pressure will be left out of account, and we shall deal only with the extra-stress tensor caused by the deformation of the media.

It is a general result[2, 7, 8] of continuum mechanics that in viscometric flows of incompressible fluids for which the stresses are only determined by the past history of the strain, and which have been in the steady state for a sufficiently long time determined by the material constants (the so-called incompressible simple fluids), all components of the stress tensor are only functions of the steady shear rate. The actual form of these functions is characteristic of the nature of the material. Furthermore, for these types of flow of simple fluids the shear stresses are odd functions of the shear rate, whereas the normal stresses are even functions of this rate of shear.

For non-steady curvilinear flows, the stresses are definitely not unique functions of the value of the shear rate. This can be easily shown for the different cases of superposition. For the case of orthogonal superposition, the rate of shear is given by Eq. (I 46). If ω is of the order of q, or smaller, a good approximation is

$$\dot{\gamma} = q + \frac{a^2 \omega^2}{4q} (1 + \cos 2\omega t)$$

If the shear stresses were unique odd functions of this shear rate, stress components should arise at orthogonal superposition proportional to $a^2 \omega^2$ and of frequency 2ω. In the case of parallel superposition Eq. (I 47) will give for the same reason rise to shear stress components proportional to $a\omega$ and of frequency ω. However, this difference in behaviour is definitely not in comformity with the experimental results, as will be shown later. Moreover, it follows from Eq. (I 47) that in pure oscillation experiments the linear viscoelastic region would be much smaller at high frequencies than at low frequencies, and this is definitely not the case. The length of the linear region proves to be all but independent of the frequency[6].

By means of a first order approximation of the theory of simple fluids Coleman and Markovitz[9] regained the commonly used[10, 11] expressions for the shear stress components in sinusoidal shear of frequency ω and with a small amplitude a. In the stationary state, the shear stresses can be written as

$$p_{ij} = a\,|G^*|\sin(\omega t + \delta_G) = a G' \sin\omega t + a G'' \cos\omega t \qquad \text{(I 50)}$$

The normal stresses are equal to

$$p_{ii} = a^2 (A^0 + A' \sin 2\omega t + A'' \cos 2\omega t) \qquad \text{(I 51)}$$

The quantities G' and G'' are called the storage part, and the loss part of the complex shear modulus G* and the phase angle δ_G between the shear stress and the shear strain is given by $\tan\delta_G = G''/G'$. The stress $a G' \sin\omega t$ is the component of the shear stress in phase with the shear $a \sin\omega t$, and $aG'' \cos\omega t$ represents the shear stress component 90° out of phase with the shear. The normal stresses are proportional to the square of the amplitude of the strain and are sinusoidal functions of the double frequency 2 ω. All quantities G′, G″, A^0, A′ and A″ are functions of the frequency.

If the shear rate $\dot{\gamma}$ is constant and equal to q, the shear stresses are

$$p_{ij} = \eta_{ij}\,(q)\,q \tag{I 52}$$

and the normal stresses

$$p_{ii} = \beta_{ii}\,(q)\,q^2 \tag{I 53}$$

Generally, the viscosity η and the normal stress coefficient β are functions of the shear rate. If η is not a constant, the viscosity function $\eta(q)$ describes the non-newtonian behaviour of the fluid. A fluid, for which β is independent of q, is called a second-order fluid and, hence, the functions $\beta(q)$ describe the deviations of second-order fluid behaviour.

In the case of superposition, the stresses are of the form

$$p_{ij} = \eta q + \alpha\, G'(\omega,q)\sin\omega t + \alpha\, G''(\omega,q)\cos\omega t \tag{I 54}$$

$$p_{ii} = \beta q^2 + 2\,\alpha q\,[N'(\omega,q)\sin\omega t + N''(\omega,q)\cos\omega t] + \\ + \alpha^2\,[A^0 + A'\sin 2\,\omega t + A''\cos 2\,\omega t] \tag{I 55}$$

In the normal stresses there arises a new component, proportional to α and of frequency ω. The quantities 2 q $N'(\omega,q)$ and 2 q $N''(\omega,q)$ may be called the in phase part, and the 90° out of phase part of the normal stress modulus 2 q $N^*(\omega,q)$[12]. (In ref. 12 the notation is somewhat different; there, the normal stress modulus is simply denoted by N^*). The second term in the right-hand member of Eq. (I 55) can also be written as $2\,\alpha q\,|\,N^*(\omega,q)\,|\,\sin(\omega t + \delta_N)$.

Collectively, the quantities G′, G″, N′, N″, A^0, A′ and A″ represent the totality of the dynamic properties of the fluid.

At superposition these dynamic properties are not only functions of the frequency, but also become functions of the steady-shear rate q. How and to what extent this functional relationship has been investigated, both experimentally and theoretically, will be dealt with in the following chapters.

e. Average molecular weights of polymers

Up to now, almost all superposition experiments have been performed on polymer fluids. Different kinds of synthetic polymers will come up for discussion, either as polymer solutions or as non-diluted liquid polymers. All these polymers consist of mixtures of macromolecules of various molecular weights. The distribution of the molecular weights can be described by means of a series of moments of the distribution function.

If a polymer contains a weight w_i of molecules of molecular weight M_i per gram, a series of moments of the function describing the distribution of the weight fractions w_i of the various molecular weights M_i can be defined according to

$$\sum_i w_i\,(M_i)^m \quad (m = 0, 1, 2 \text{ etc.})$$

A series of average molecular weights is obtained by means of the definition

$$\bar{M} = \frac{\sum w_i\,(M_i)^m}{\sum w_i\,(M_i)^{m-1}}\,; \quad m = 0, 1, 2 \text{ etc.}$$

The averages obtained by setting m equal to 0, 1 and 2, are the number average M_n, the weight average M_w and the centrifugal average M_z respectively. Definite values of only M_n, M_w and M_z confine the molecular-weight distribution to a certain region of the multidimensional polymer composition space, but this limitation gives only a very rough characterization of the composition of the mixture. Although it is possible to obtain a much more comprehensive description of the molecular weight distribution, e.g. by equilibrium ultracentrifugation13), the polymers used in this research will only be characterized by at most three average molecular weights.

3. Object of the investigation

The aim of this research is to review and extend the experimental and theoretical work performed on the effect superimposed steady shear flow exercises on the dynamic properties of polymeric fluids. So far, the investigations have been restricted mainly to the linear range of the dynamic properties, i.e. to the range of amplitudes α for which the oscillatory shear stresses are proportional to the oscillatory shear. This has the consequense that stresses proportional to α^2 are very small, and for that reason these stress components have not been investigated experimentally. Hence, the dynamic quantities A^0, A' and A'' will be left out of consideration. The greater part of the experimental work deals merely with the effect of superimposed steady-shear flow on the dynamic quantities $G'(\omega,q)$ and $G''(\omega,q)$.

Polymer melts, or concentrated polymer solutions, generally exhibit a marked non-newtonian viscosity and a great normal stress effect in steady shear flow. On the other hand, the linear viscoelastic behaviour of these fluids can be characterized phenomenologically by a so-called wedge-box type distribution of relaxation times. As seen from the molecular point of view, both features seem to disclose the important role played by the entanglement couplings between polymer chains. The cooperative motions of a multiplicity of molecules joined together by the entanglements give rise to the special shape of the relaxation time distribution11, 14-19). The normal stresses have been accounted for by a large elastic deformation of the quasi-network structure formed by the entanglements20-22), and the non-newtonian flow behaviour can be ascribed to a decrease in the degree of entanglement with increasing rate of shear23-27). It seems obvious therefore to expect that measurements of the complex modulus in superposed steady-shear flow can be used as a tool for analyzing the distribution of characteristic modes of motion associated with the entanglement coupling in polymer fluids subjected to steady shear. However, this train of thought presupposes that as far their effects are concerned, there is no interrelation between the two types of flow used in a superposition experiment, but this is not always born out by reality. In a way superposition experiments come under the category of compounded experiments. As such, they yield more information than simple experiments in which use is made only of either steady-shear flow or oscillatory-shear flow. The interpretation and theoretical description of the experimental results proves to be more difficult than could be expected in view of the additivity of effects. On the other hand, if it were possible to find a theory which describes these results fairly well, this theory would certainly give a good explanation of such effects as non-newtonian viscosity and deviations from second-order fluid behaviour. This is why Huppler et al[28] recommend this type of superposition experiment as a sensitive method for testing the capabilities of model theories.

Various investigators have tried to give a theoretical analysis of the experimental superposition results. Phenomenological theories, as well as theories based on continuum mechanics, were used with varying success. Molecular theories were simply left out of consideration; they were considered useless, because, at least up to some years ago, they were not even capable to describe the non-newtonian behaviour of more concentrated polymer solutions. It is the intention of this thesis to prove that a molecular theory, after being generalized on sensible grounds and after introduction of an energy postulate, certainly gives a qualitative, if not quantitative, description of the majority of experimental results.

4. Survey of the contents

In chapter II the published results of superposition experiments will be treated in chronological order. The object of all investigations was to determine the effect superimposed steady-shear flow has on the dynamic shear properties, hence on $G'(\omega,q)$ and $G''(\omega,q)$. Moreover, in practically all work a parallel mode of superposition has been considered. Only one comprehensive study deals with the case of orthogonal superposition. We shall,of course, not attempt to review all the results, but give the attention mainly to those aspects that play a part in the several investigations.

A recapitulation of the theoretical approaches to the superposition problem will be presented in chapter III. In doing so, we shall have to exercise some restraints, and in some cases shall merely indicate the kind of theory used and the extent to which some theory describes the experimental data. The success of the various approaches will prove to be very different and, particularly in a quantitative respect, not always equally satisfying. The descriptions yielding the best agreement with experimental results have in common that the steady-shear flow somehow introduces a destruction of the liquid structure with the result that the dynamic properties are affected.

A new molecular approach will be presented in chapter IV. This theory is based on Rouse's spring-bead model for macromolecules in dilute solutions. The effect of entanglements on the relaxation time distribution has already been investigated by others, but will now be generalized. Further we shall introduce a postulate stating that the amount of free energy which can be stored in the several modes of motion of entangled macromolecules is limited. By means of this disentanglement theory the stresses arising during superposition will be calculated.

Chapter V will be devoted to a comparison of the theoretical predictions with already published and new experimental results.

5. References

1. A.S. Lodge, Elastic Liquids, Academic Press, London, 1964
2. B.D. Coleman, H. Markovitz and W. Noll, Viscometric Flows of Non-Newtonian Fluids, Springer, Berlin, 1966
3. B.D. Marsh and J.R.A. Pearson, Rheol. Acta 7, 326 (1968)
4. N. Adams and A.S. Lodge, Phil. Trans. Roy. Soc. A256, 149 (1964)
5. K. Walters and N.D. Waters, Polymer Systems, Deformation and Flow, p. 211 and p. 237, Eds. R.E. Wetton and R.W. Whorlow, Macmillan, London, 1968
6. I.F. Macdonald, B.D. Marsh and E. Ashare, Chem. Eng. Sci. 24, 1615 (1969)
7. B.D. Coleman and W. Noll, Arch. Rational. Mech. Anal. 3, 289 (1959)
8. B.D. Coleman and W. Noll, Ann. N.Y. Acad. Sci. 89, 672 (1961)
9. B.D. Coleman and H. Markovitz, J. Appl. Phys. 35, 1 (1964)
10. A.J. Staverman and F. Schwarzl, Die Physik der Hochpolymeren, Vol. IV, Chap. 11, Ed. H.A. Stuart, Springer, Berlin, 1956
11. J.D. Ferry, Viscoelastic Properties of Polymers, Wiley, New York, 1961
12. H.C. Booij, Rheol. Acta 7, 202 (1968)
13. Th.G. Scholte, J. Polymer Sci. A2,6, 91, 111 (1968); European Polymer J. 6, 51 (1970)
14. A.V. Tobolsky, Properties and Structure of Polymers, Wiley, New York, 1960
15. F. Bueche, Physical Properties of Polymers, Interscience, New York, 1962
16. T. Takemura, J. Polymer Sci. 28, 185 (1958)
17. A.V. Tobolsky and J.J. Aklonis, J. Phys. Chem. 68, 1970 (1964)
18. R.S. Porter and J.F. Johnson, Chem. Reviews 66, 1 (1966)
19. R.S. Porter, W.J. MacKnight and J.F. Johnson, Rubber Chem. Techn. 41, 1 (1968)
20. A.S. Lodge, Trans. Faraday Soc. 52, 120 (1956)
21. W. Philippoff, J. Appl. Phys. 27, 984 (1956)
22. M. Yamamoto, J. Phys. Soc. Japan 13, 1200 (1958)
23. M. Yamamoto, J. Phys. Soc. Japan 11, 413 (1956); 12, 1148 (1957)
24. T. Gillespie, Trans. Soc. Rheol. 9:2, 35 (1965)
25. G.V. Vinogradov and I.M. Belkin, J. Polymer Sci. A,3, 917 (1965)
26. W.W. Graessley, J. Chem. Phys. 43, 2696 (1965); 47, 1942 (1967)
27. F. Bueche, J. Chem. Phys. 48, 4781 (1968)
28. J.P. Huppler, I.F. Macdonald, E. Ashare, T.W. Spriggs, R.B. Bird and L.A. Holmes, Trans. Soc. Rheol. 11, 181 (1967)

Chapter II

SURVEY OF PUBLISHED EXPERIMENTAL RESULTS

1. Introduction

More than twenty years ago already Weissenberg[1] formulated the principles of a testing instrument – the 'rheogoniometer' – for measuring the stresses and strains over the entire solid angle at any point in a flowing material. A very preliminary prototype of this instrument was demonstrated by him and Freeman[1-4]. Further essential improvements were introduced particularly by Roberts[5-9], after which the rheogoniometer was brought into production by Farol Scientific Instruments Ltd. (now Sangamo Controls Ltd.) of Bognor Regis, Sussex, England. The theory of the measuring procedure has been described by Weissenberg[10] and more recently, by Walters[11], the latter using a more up-to-date and direct way of approach.

One of the most important geometries that can be used in this instrument is that of the cone-and-plate system. In this system the rate of shear is essentially constant throughout the sample (see chapter I, 2c). The bottom plate can either be rotated continuously for measuring the stresses at steady shear flow, or be oscillated with a variable amplitude for collecting information about the material in its natural, unsheared state. Both the rotational speed and the frequency of oscillation can be varied over a wide range by means of gear boxes and motors. In addition, Weissenberg also introduced the possibility of using this instrument for superposing an oscillatory motion on and parallel to a continuous rotation in order to investigate the material in any sheared state by means of vibration methods.
Still, the first superposition results published were not obtained with a Weissenberg rheogoniometer, but with a coaxial-cylinder rheometer made in Japan.

2. Measurements of dynamic shear moduli by Osaki et al. (parallel)

In 1963, Osaki, Tamura, Kurata and Kotaka[12] were the first to publish the provisional results of a systematic study on the dynamic viscoelasticity of concentrated polymer solutions under conditions of superposed parallel steady shear flow. They studied 15 % w toluenic solutions of polystyrenes differing in average molecular weight at 30 ^{o}C. In the range of newtonian flow no effect of the steady shear rate on the dynamic properties was found. At higher rates of shear, where the viscosity is lower according as the rate of shear q is higher, both G' and G" appeared to be functions of the frequency ω and of q. The values of $G'(\omega,q)$ and of $G''(\omega,q)$ decreased with increasing q, and these effects became more evident at lower frequencies.

In a subsequent paper[13] the number of solutions investigated was extended with a 5 % solution of poly-n-butyl methacrylate in diethyl phthalate and a 10 % solution of polymethyl methacrylate in the same solvent. Both solutions showed a very strong non-newtonian behaviour. Qualitatively, however, all these solutions displayed the same effects. In the range of low frequencies $G'(\omega,q)$ and $G''(\omega,q)$ decreased with increasing rate of shear q, and the effect on $G'(\omega,q)$ was invariably greater than the effect on $G''(\omega,q)$. At high frequencies, however, $G''(\omega,q)$ for the two strongly non-newtonian solutions increased slightly, whereas $G'(\omega,q)$ decreased with increasing q. The instrument used did not permit measurements to be performed at frequencies which are small with respect to q[14]. The range in which the dynamic moduli at constant shear flow could be determined was therefore fairly limited.

3. Dynamic shear moduli experiments by Booij (parallel)

In 1966 the present writer published the results of an investigation into the influence of superposed steady shear flow on the dynamic properties of two kinds of non-newtonian liquids[15]. The measurements were carried out with a Weissenberg rheogoniometer, type R16, provided with a cone-and-plate system. In this investigation, but also in all later work, the cone angle was 1°28′, and the diameter of the plates 7.5 cm. The entire instrument had previously been tested with a newtonian liquid – a low-molecular-weight polyisobutylene. The dynamic viscosity G''/ω of this liquid was found to be independent of the frequency ω, while the rotational viscosity p_{21}/q during shear flow in the 1-direction with a velocity gradient in the 2-direction, proved to be independent of the rate of shear q. Moreover, the two viscosities were equal within the accuracy of measurement and the phase angle between the oscillatory shear stress and the oscillatory shear was 90°. Superposition of the two kinds of shear in this newtonian liquid appeared to have no effect on the dynamic viscosity and the rotational viscosity.

Subsequently, the investigation of two distinctly non-newtonian solutions was described, although, actually, more solutions were studied. Some data on these solutions are listed in the following table. The solvent was invariably decalin.

Sol. no.	Dissolved substance	Conc. % w	Propylene % w	M_w $\times 10^{-6}$	M_n $\times 10^{-4}$	$[\eta]$ dl/g
1	Al. dilaurate	10	–	–	–	–
2	E.P. copolymer	5.0	41	7	6.3	6.7
3	E.P. copolymer	5.85	41	7	6.3	6.7
4	E.P. copolymer	5.0	47	1	5.2	3.6
5	E.P. copolymer	5.0	41	66	5.4	4.0

The intrinsic viscosity $[\eta]$ was measured at 135 °C in decalin, M_n was determined by osmometry and M_w by light scattering.

To give at once some idea of the properties of these solutions, the steady-state values of the rotational viscosity are presented in Fig. II,1 and the normal stress values in Fig. II,2, both as functions of the rate of shear q. All the measurements were carried out at 25 °C.

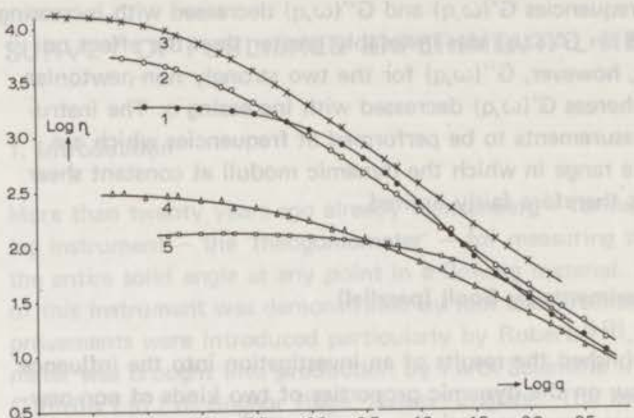


Fig. II,1 Steady-state rotational shear viscosity η, in poises, as a function of the shear rate q, in sec^{-1}, for several solutions

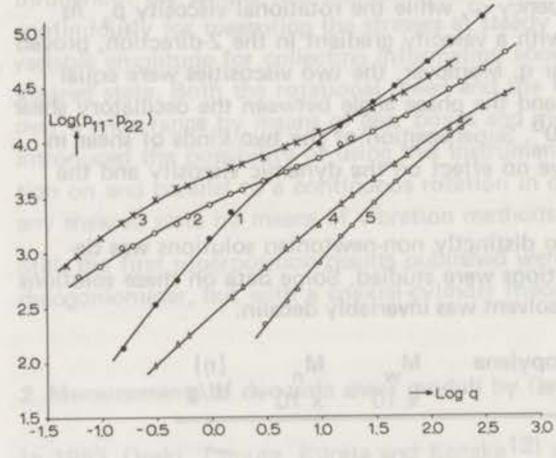


Fig. II,2 Steady-state normal stress difference $p_{11}-p_{22}$, in dynes cm^{-2}, as a function of the shear rate q, in sec^{-1}, for several solutions

It is evident from these figures, that, in a qualitative respect, the solutions all show the same behaviour. They all display non-newtonian viscosity and a departure from 'second-order' behaviour. Only the degree of this departure and the absolute values of the quantities differ from one solution to another.

We shall now broadly recapitulate the results obtained on solution 1. Those relating to solutions of the ethylene-propylene copolymers (rubbers) in decalin will be discussed mainly in a following section of this chapter, and in chapter V.

A solution of aluminium dilaurate in decalin forms a structure of interconnected micelles, which implies that a great many molecules are linked up. Although we are consequently concerned here with a totally different physico-chemical system, this kind of solutions shows many visco-elastic phenomena similar to those of polymer solutions[16]. The viscosity of the solution is fairly high at low rates of shear (about 1800 poises at 27 °C), and strongly decreases at higher rates of shear, as appears from Fig. II,1. The normal stress may rise very high at high q-values, and rapidly decreases at lower q-values (Fig. II,2). At higher rates of shear, both quantities pass through a maximum at the beginning of rotation, but then decrease to constant values. These values are plotted in the figures.

All superposition measurements were evidently carried out in the range of linear visco-elasticity, because, within the error of the measurement, the amplitude of the oscillatory shear stress was found to be proportional to the amplitude of the oscillatory shear. It is always seen that the constant values of the shear stress and of the normal stress caused by the rotation are not affected by the superposed oscillation. What is measured experimentally is the ratio of the amplitudes of the oscillatory parts of the shear stress and of the shear, which gives $|G^*(\omega,q)|$, and the phase angle δ_G between the oscillating components of shear stress and shear. Both quantities are functions of the frequency ω, but upon superposition they also become significant functions of the rate of shear q. Fig. II,3 shows how the phase angle δ_G for solution 1 depends on the two parameters ω and q.

Fig. II,3 Phase difference δ_G between the oscillatory part of the shear stress and the oscillatory part of the shear, as a function of the angular frequency ω, in radians sec^{-1}, for the indicated values of the logarithm of the parallel superimposed steady shear rate q. Solution 1, 27 °C.

The curve marked $-\infty$ shows δ_G as a function of ω for $q = 0$, i.e. for pure oscillation. At low frequencies, the phase angle approaches to 90^o, i.e. to the newtonian region. At high frequencies, δ_G becomes highly dependent on ω, more so than for the majority of polymer solutions. The parameters at the other curves all give the pertinent values of log q. At increasing values of q, the phase angle appears to increase strongly at all frequencies, but particularly at frequencies of the same order as q or smaller. In many experiments it was found that the phase angle δ_G can be even greater than 90^o, although angles larger than 110 °C have never been found. Measurements in this region are not very accurate owing to the low signal-to-noise ratio, and these observations have therefore been omitted in the figure. What is very clear, however, from the variation of δ_G as a function of ω is that these curves intersect the value of $\delta_G = 90^o$ when $q > 0$.

The frequency at which δ_G becomes equal to 90^o is called ω_0. In Fig. II,4 this frequency ω_0 has been plotted against the pertinent value of the superposed rate of shear q, not only for solution 1, but for all solutions investigated.

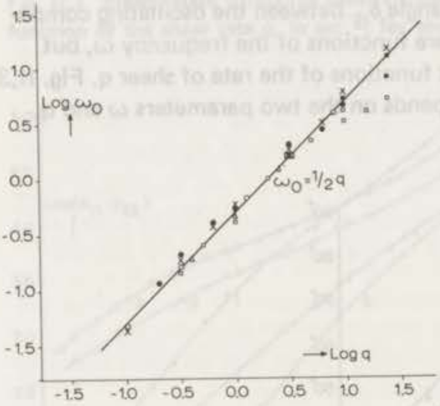


Fig. II,4 Frequency ω_0 at which the phase difference δ_G equals $\pi/2$ as a function of the superimposed rate of shear q for solutions 1 (□), 2 (X), 3 (●), 4 (○) and 5 (△)

The drawn line represents the relation $\omega_0 = ½ q$. It now appears that all solutions examined satisfy this relation within the accuracy of the measurement, irrespective of the temperature at which the measurements were carried out. Solution 1 is an exception, however. At lower temperatures (27^o and 40 °C) and higher q-values ω_0 is lower than would be expected in view of the relation $\omega_0 = ½ q$, but at 52 °C the relation is met again. It is known, however[17), that at higher rates of shear a solution of aluminium dilaurate in toluene displays special inhomogeneous birefringence effects, as are also observed for example upon melt fracturing of polyethene; we shall therefore regard this deviation as an exception to an, apparently, rather universal relation.

The absolute value of the complex shear modulus $G^*(\omega,q)$ is reduced by the superposed steady shear flow, and that increasingly according as q increases. The reduction is largest at the lowest frequencies. Fig. II,5 shows the change of $|G^*(\omega,q)|$ with the

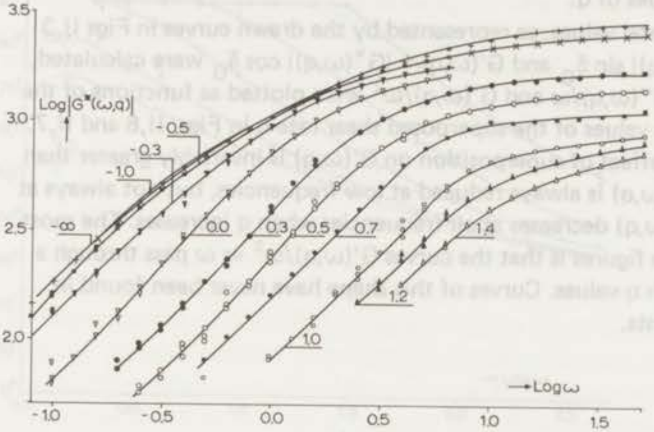


Fig. II,5 Absolute value of the complex shear modulus $G^*(\omega,q)$, in dynes cm^{-2}, as a function of the frequency ω, in radians sec^{-1}, for the indicated values of the logarithm of the superposed steady shear rate q. Solution 1, 27 ^{o}C

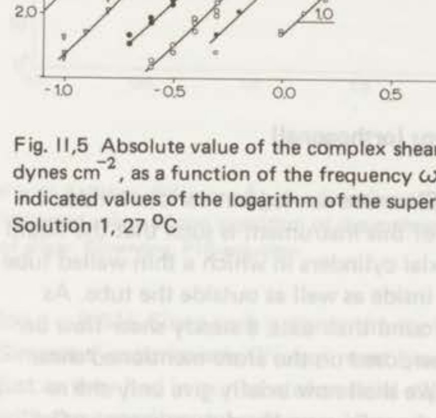


Fig. II,6 Dynamic viscosity $G''(\omega,q)/\omega$, in poises, as a function of the frequency ω for the indicated values of log q. Solution 1, 27 ^{o}C

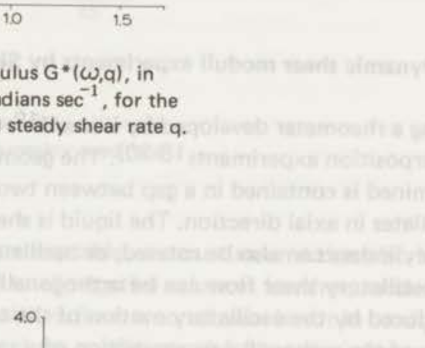


Fig. II,7 Quantity $G'(\omega,q)/\omega^2$, in dynes cm^{-2} sec^{-2}, as a function of the frequency ω for the indicated values of log q. Solution 1, 27 ^{o}C

frequency ω for various values of q.
From the average experimental values, as represented by the drawn curves in Figs II,3 and II,5, $G''(\omega,q) = |G^*(\omega,q)| \sin \delta_G$ and $G'(\omega,q) = |G^*(\omega,q)| \cos \delta_G$ were calculated, after which the quantities $G''(\omega,q)/\omega$ and $G'(\omega,q)/\omega^2$ were plotted as functions of the frequency ω for the various values of the superposed shear rate q in Figs II,6 and II,7. Both figures show that the effect of superposition on $G'(\omega,q)$ is invariably greater than the effect on $G''(\omega,q)$. $G''(\omega,q)$ is always reduced at low frequencies, but not always at high frequencies, while $G'(\omega,q)$ decreases at all frequencies when q increases. The most noteworthy feature of these figures is that the curves $G'(\omega,q)/\omega^2$ vs ω pass through a maximum, especially at high q-values. Curves of this shape have never been found in pure oscillation measurements.

4. Dynamic shear moduli experiments by Simmons (orthogonal)

Using a rheometer developed by himself[18, 19], Simmons carried out various kinds of superposition experiments[18-20]. The geometry of this instrument is such that the liquid examined is contained in a gap between two coaxial cylinders in which a thin-walled tube oscillates in axial direction. The liquid is sheared inside as well as outside the tube. As the cylinders can also be rotated, or oscillated, around their axis, a steady shear flow or an oscillatory shear flow can be orthogonally superposed on the afore-mentioned shear produced by the oscillatory motion of the tube. We shall now briefly give only the results of the orthogonal superposition of a steady shear flow on the dynamic properties of the liquid.

For newtonian liquids it was found that the dynamic viscosity G''/ω is not influenced by the rotation. The non-newtonian liquids investigated consisted for the greater part of solutions of polyisobutylene (PIB) in cetane and, for a smaller part of solutions of carboxymethylcellulose in water. The measurements were all carried out at 25 °C. The amplitude a of the oscillation was taken so small as to ensure that during pure oscillation the measurements would be performed in the linear viscoelastic region. Simmons did not check experimentally whether the dynamic moduli were independent of a also during superposition, but considering the very low values of a, we may suppose that they were.

To permit some comparison of the results for orthogonal superposition with those for parallel superposition, we shall now also give some of Simmons' results, expressed in $|G^*(\omega,q)|$, δ_G, $G''(\omega,q)/\omega$ and $G'(\omega,q)/\omega^2$. This can be done because in Simmons' thesis[19] $G''(\omega,q)/\omega$ and $G'(\omega,q)$ are presented in tabular form. For our purpose we take the experimental values obtained on a 8.54 % solution of PIB in cetane. In Fig. II,8, δ_G has been plotted as a function of log ω for some values of log q.
Simmons mentions the value of $G'(\omega,q) = 0$ for several relatively low frequencies. The corresponding value for δ_G being 90° would imply however, that the curves of δ_G as a function of log ω show a discontinuity at $\delta_G = 90°$ (see for example the curve for

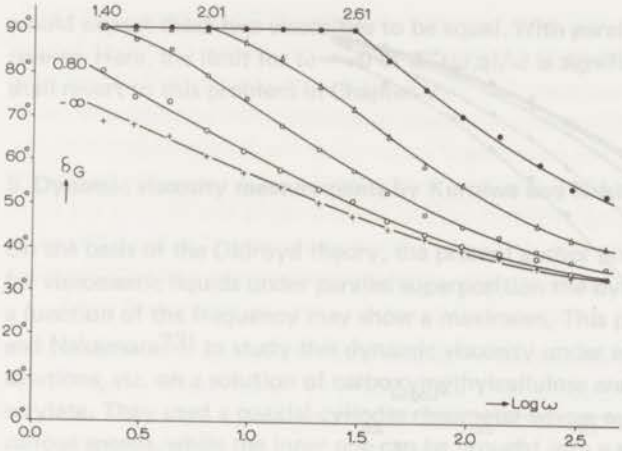


Fig. II,8 Phase difference δ_G as a function of the frequency ω for the indicated values of the logarithm of the orthogonal superimposed rate of shear. Simmons, PIB-solution

$\log q = 2.61$). Since such a discontinuity is not acceptable, we must assume that also in Simmons' experiments $G'(\omega,q)$ must have had small negative values at low frequencies, just as they had in our case of parallel superposition. Such a conclusion is not in conflict with the experimental evidence, because under these conditions also Simmons' rheometer does not give accurate data of $G'(\omega,q)$[21].

If we now compare Fig. II,8 with Fig. II,3, it can be seen from the curves for $\log q = -\infty$ that in the case of pure oscillation the aluminium dilaurate solution shows a much stronger dependence of δ_G on the frequency than the solution of PIB. Qualitatively, however, superposition produces the same effect. In a quantitative respect, on the other hand, orthogonal superposition of a steady rate of shear appears to have a smaller effect on the dynamic shear moduli than parallel superposition. This is particularly clear from the fact that the relation $\omega_o = \frac{1}{2} q$ does not hold in the case of orthogonal superposition. Here ω_o appears to be much smaller than ½ q. Comparison of Figs II,5, II,6 and II,7 with the frequency plots of Simmons' values of $|G^*(\omega,q)|$, $G''(\omega,q)/\omega$ and $G'(\omega,q)/\omega^2$ for orthogonal superposition (Figs II,9, II,10 and II,11, next page) also shows that the effect of parallel superposition is much greater than that of orthogonal superposition.

Another difference between the two types of superposition is that during parallel superposition at high frequencies $G'(\omega,q)$ decreases with increasing q, whilst during orthogonal superposition the effect of q on $G'(\omega,q)$ is negligible at high values of ω. Moreover, Tanner and Simmons[22] point to another peculiar effect. With orthogonal superposition the limit of the dynamic viscosity $G''(\omega,q)/\omega$ for $\omega \rightarrow 0$ appears to be significantly greater than the rotational viscosity $\eta(q)$ at the same value of q. In the first instance, one

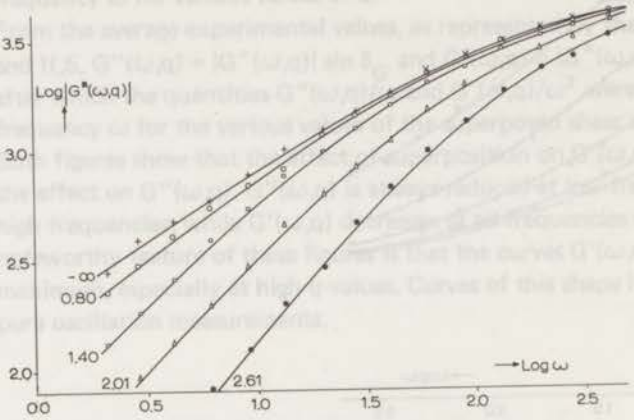


Fig. II,9 Absolute value of the complex shear modulus G*(ω,q) as a function of the frequency ω for the indicated values of log q in the case of orthogonal superposition. Simmons, PIB-solution

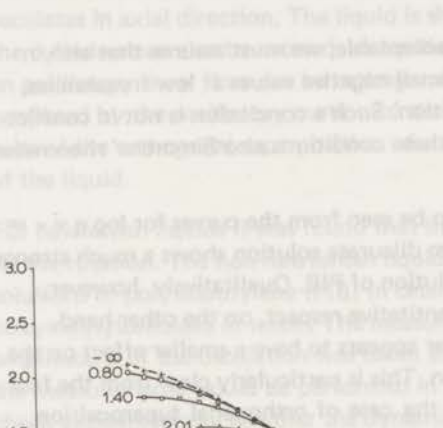


Fig. II,10 Dynamic viscosity G''(ω,q)/ω as a function of ω for the indicated values of log q in the case of orthogonal superposition. Simmons, PIB-solution

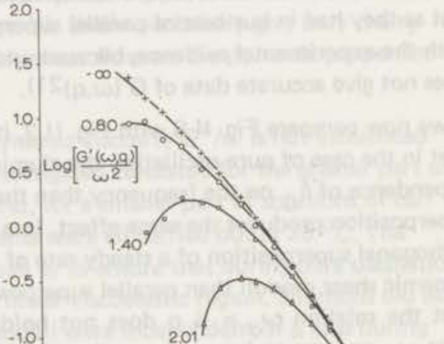


Fig. II,11 Frequency dependence of G'(ω,q)/ω² for the indicated values of log q in the case of orthogonal superposition. Simmons, PIB-solution would expect these two viscosities to be equal. With parallel superposition it is just the reverse. Here, the limit for $\omega \to 0$ of $G''(\omega,q)/\omega$ is significantly lower than $\eta(q)$. We shall revert to this problem in Chapter V.

5. Dynamic viscosity measurements by Kuroiwa and Nakamura (parallel)

On the basis of the Oldroyd theory, the present author predicted (see Chapter III) that for viscoelastic liquids under parallel superposition the dynamic viscosity $G''(\omega,q)/\omega$ as a function of the frequency may show a maximum. This prediction induced Kuroiwa and Nakamura[23)] to study this dynamic viscosity under superposition on two electrolyte solutions, viz. on a solution of carboxymethylcellulose and a solution of sodium polyacrylate. They used a coaxial-cylinder rheometer whose outer cylinder can be rotated at various speeds, while the inner one can be brought into a state of damped oscillation at various frequencies. The dynamic viscosity as a function of the frequency was now measured at various values of the superposed steady rate of shear, particularly at ω-values much smaller than q, i.e. in the range where the investigators mentioned in the previous sections did not succeed in performing measurements. It now appears that for both solutions this dynamic viscosity during parallel superposition is indeed an increasing function of the frequency in the range of frequencies smaller than the value of the steady rate of shear. Besides, this dynamic viscosity during superposition is invariably smaller than the rotational viscosity at the same q-value.

6. Measurements of oscillatory normal stress components by Booij (parallel)

So far we have dealt only with the effect of superposed steady shear flow on the dynamic shear properties. However, the oscillatory normal stress components are also strongly influenced by superposition. Parallel superposition is accompanied by the development of a new normal stress component, whose shape is sinusoidal with the same frequency as the shear and proportional to a. At higher values of the steady rate of shear, this component comes to predominate over the oscillatory terms proportional to a^2 and of frequency $2\,\omega$ (see Eq. (I 55)). The total normal stress at parallel superposition can then be described as

$$p_{11} - p_{22} = (p_{11} - p_{22})_{rot} + 2\,aq\,|N^*(\omega,q)|\,\sin(\omega t + \delta_N) =$$

$$= (p_{11} - p_{22})_{rot} + 2\,aq\,[N'(\omega,q)\sin\omega t + N''(\omega,q)\cos\omega t]$$

in which $(p_{11} - p_{22})_{rot}$ represents the steady normal stress difference resulting from the rate of shear q. As has been established experimentally, the value of $(p_{11} - p_{22})_{rot}$ at a given value of q is not measurably influenced by the superposed oscillation. At low values of q, the second term does not yet predominate, so that this oscillatory component can be determined experimentally only over a limited range of q- and ω-values.

For the solutions 2, 4 and 5 mentioned in the table of section II,3, the normal stress components have been investigated experimentally, and the results have been published24). The constant values of the normal stress and of the viscosity as functions of q were given already in Fig. II,2 and Fig. II,1, respectively. These quantities differ considerably from one solution to another. This is not surprising if we consider the difference between the M_w values for the three rubbers. Still, this is by no means the only cause. The molecular weight distribution and the degree of branching and the branching structure of the three samples are also completely different. All these differences contribute to the difference in the viscoelastic properties of these solutions. As the properties of solution 2 will be further dealt with in Chapter V, we shall restrict ourselves here to solutions 4 and 5.

In measurements of oscillatory normal stress components very stringent demands had to be made on the Weissenberg rheogoniometer, particularly as regards correct alignment, etc.24). Although in the case of superposition we are not concerned with truly viscometric flow, the normal stress is again an even function of the rate of shear q. When the direction of the steady rate of shear q is reversed, the constant component $(p_{11} - p_{22})_{rot}$ remains exactly the same, but the phase angle δ_N turns through exactly 180°, as a result of which the oscillatory component also becomes an even function of q. The experimental value of δ_N at a negative q will be denoted δ_{N-}, that for an equally large, but positive q δ_{N+}. These two phase shifts were measured for many combinations of ω and q; one third of all the observations is represented in Fig. II,12. From 128 observations we found $\delta_{N-} - \delta_{N+} = (180 \pm 1)^{\circ}$ where the error of 1°, which represents the average absolute deviation from the mean, corresponds to the experimental inaccuracy.

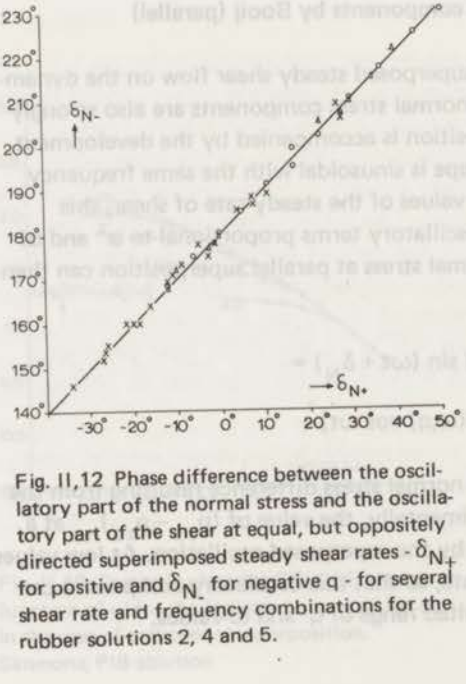


Fig. II,12 Phase difference between the oscillatory part of the normal stress and the oscillatory part of the shear at equal, but oppositely directed superimposed steady shear rates - δ_{N+} for positive and δ_{N-} for negative q - for several shear rate and frequency combinations for the rubber solutions 2, 4 and 5.

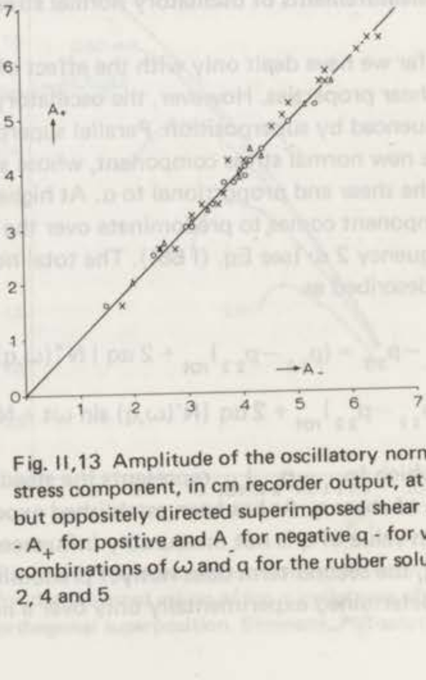


Fig. II,13 Amplitude of the oscillatory normal stress component, in cm recorder output, at equal, but oppositely directed superimposed shear rates - A_+ for positive and A_- for negative q - for various combinations of ω and q for the rubber solutions 2, 4 and 5

The amplitude of the oscillatory part of the normal stress is independent of the direction of q. This is seen in Fig. II,13, where the measured amplitudes, expressed in cm deflection of the UV recorder, are represented for several combinations of ω and q, both for clockwise and counter-clockwise rotation. Averaging over 128 measurements gives

$A_+/A_- = 1.00 \pm 0.03$,

the absolute mean error of 3 % corresponding again to the experimental error.

Figs II,14 and II,15 show how the experimental values of δ_N for the solutions 4 and 5 vary with the frequency at several values of the superposed rate of shear q.

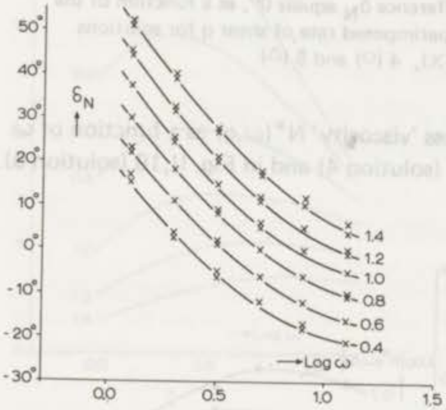


Fig. II,14 Phase difference δ_N as a function of the frequency ω for the indicated values of log q. Solution 4

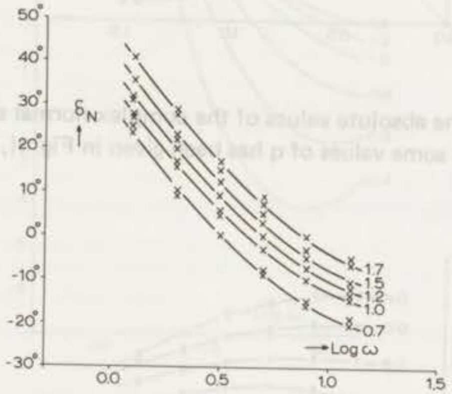


Fig. II,15 Phase difference δ_N as a function of the frequency ω for the indicated values of log q. Solution 5

The phase angle δ_N increases with q. The curves δ_N – log ω are nearly parallel to each other, and demonstrate that, at least in the frequency range examined, δ_N decreases with increasing ω.

The phase angle δ_N can be positive as well as negative, as appeared already from Fig. II,12, and for most values of q one can find a value of ω at which $\delta_N = 0^o$. This value increases with q. The frequency ω_1 at which $\delta_N = 0^o$, has been plotted in Fig. II,16 as a function of the steady rate of shear q for the three solutions 2, 4 and 5.
The three curves thus obtained certainly do not coincide. For the sake of comparison also the line $\omega_0 = ½ q$ has been drawn in this figure. We demonstrated already in Section II,3 that in the case of parallel superposition this line describes the relation between q and the frequency ω_0 at which $\delta_G = 90^o$, and is independent of the other properties of the solution. From Fig. II,16 it appears that the nature of the solution has a pronounced effect on the relation between ω_1 and q. However, what this effect is like, cannot be established from the small number of experiments made.

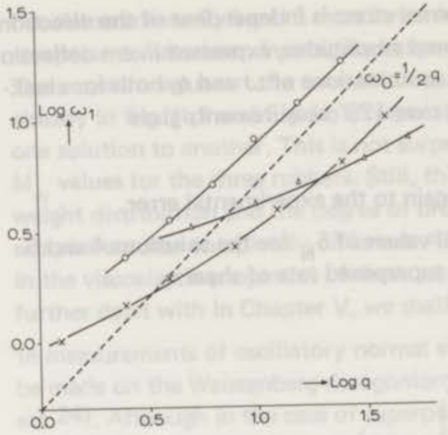


Fig. II,16 Frequency ω_1 at which the phase difference δ_N equals 0^0, as a function of the superimposed rate of shear q for solutions 2 (X), 4 (O) and 5 (△)

The absolute values of the complex normal stress 'viscosity' $N^*(\omega,q)$ as a function of ω at some values of q has been given in Fig. II,17 (solution 4) and in Fig. II,18 (solution 5).

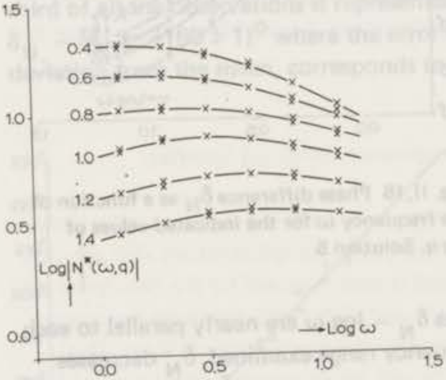


Fig. II,17 Absolute value of the complex normal stress viscosity $N^*(\omega,q)$, in poises, as a function of the frequency ω for the indicated values of log q for solution 4

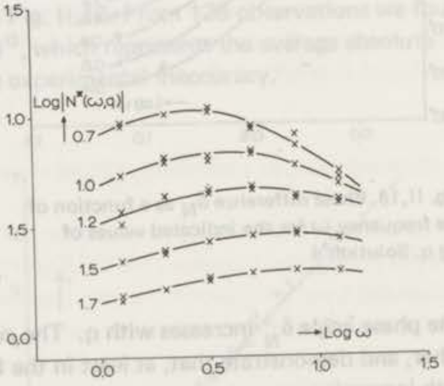


Fig. II,18 Absolute value of the complex normal stress viscosity $N^*(\omega,q)$, in poises, as a function of the frequency ω for the indicated values of log q for solution 5

At a given q the maximum in $|N^*(\omega,q)|$ as a function of ω shifts to higher frequencies at increasing q. The value of the frequency corresponding to this maximum at a given q again depends on the nature of the solution. Furthermore $|N^*(\omega,q)|$ decreases when q increases.

Starting from the curves drawn through the experimental values in the above figures we can now calculate $N'(\omega,q) = |N^*(\omega,q)| \cos \delta_N$ and $N''(\omega,q) = |N^*(\omega,q)| \sin \delta_N$. For solution 4 these quantities are given in Figs II,19 and II,20, and for solution 5 in Figs II,21 and II,22*).

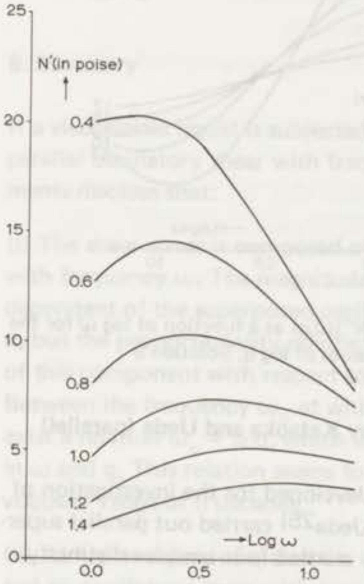


Fig. II,19 Real part of the normal stress viscosity N'(ω,q) as a function of the frequency ω for the indicated values of log q for solution 4

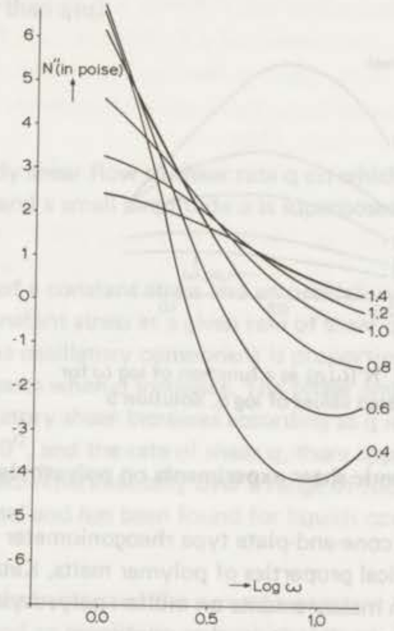


Fig. II,20 Imaginary part of the normal stress viscosity N''(ω,q) as a function of the frequency ω for the indicated values of log q for solution 4

It is evident from these figures that in the range measured N'(ω,q) decreases with increasing q. Further, N'(ω,q) is invariably positive and shows a maximum as a function of ω. This maximum becomes less pronounced and shifts to higher frequencies according as q increases. N''(ω,q) may be positive as well as negative. It is very small at high q values and varies much more according as q is smaller. In the latter case, N''(ω,q) as a function of ω shows a distinct minimum which shifts to higher frequencies with increasing q.

) The shape of all these curves differs from that of the curves plotted in Figs 4 to 7 of ref. 24. This is exclusively due to the fact that the normal stress modulus used in ref. 24 is equal to 2 q times the normal stress 'viscosity' N(ω,q) used here.

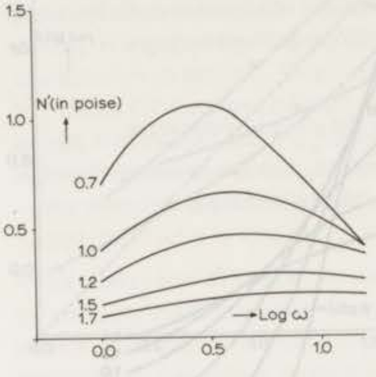


Fig. II,21 N'(ω,q) as a function of log ω for the indicated values of log q. Solution 5

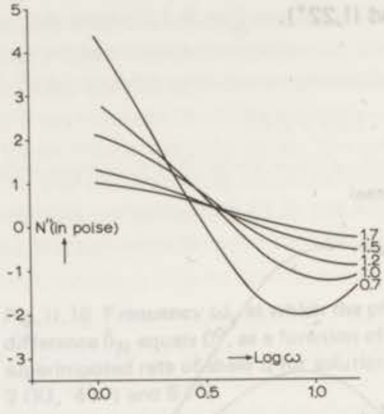


Fig. II,22 N''(ω,q) as a function of log ω for the indicated values of log q. Solution 5

7. Dynamic shear experiments on polyethylene melts by Kataoka and Ueda (parallel)

Using a cone-and-plate type rheogoniometer specially developed for the investigation of rheological properties of polymer melts, Kataoka and Ueda[25)] carried out parallel superposition measurements on molten polyethylenes. They studied four samples distinctly differing in viscosity and normal stress.

All the superposition measurements were performed at fairly low values of ω and of q (ω and q smaller than 2 $\sec^{-1}$). The effect of the steady shear flow on the dynamic properties of these molten polymers appears to be qualitatively the same as the effect on other viscoelastic liquids described in the previous sections. At a fixed value of ω, and increasing values of q, δ_G strongly increases, and $|G^*(\omega,q)|$ strongly decreases. Here again, the equipment used did not permit satisfactory measurements to be carried out at frequencies much lower than q. Also with these melts the frequency ω_0 at which the phase angle δ_G becomes equal to 90° appears to a good approximation to satisfy the relation $\omega_0 = ½ q$.

8. Dynamic shear moduli measurements by Walters and Jones (parallel)

Walters and Jones[26)], using a Weissenberg rheogoniometer, measured the dynamic viscosity and the in-phase modulus of some solutions in water of a polyacrylamide. The solutions show a very strong non-newtonian behaviour and at higher values of q their viscosity is only of the order of 10 poises.

The curves of $G''(\omega,q)/\omega$ and of $G'(\omega,q)$ as functions of ω at various values of q again have the same shape as those for other viscoelastic liquids studied by other investigators. The only difference was that Walters and Jones could also carry out measurements on their solutions at frequencies much lower than q. Their curves clearly show a maximum in the dynamic viscosity as a function of ω and negative values of $G'(\omega,q)$ when $\omega \ll q$. They further show that also for this type of solutions the relation $\omega_0 = \frac{1}{2} q$ is valid. Besides, $\lim\limits_{\omega \to 0} \frac{G''(\omega,q)}{\omega}$ is invariably smaller than $\eta(q)$.

9. Summary

If a viscoelastic liquid is subjected to a steady shear flow of shear rate q on which a parallel oscillatory shear with frequency ω and a small amplitude α is superposed, experiments disclose that:

(i) The shear stress is composed of the sum of a constant stress and an oscillatory stress with frequency ω. The magnitude of the constant stress at a given rate of shear q is independent of the superposed oscillation. The oscillatory component is proportional to α, but the proportionality coefficient decreases when q increases. The phase angle δ_G of this component with respect to the oscillatory shear increases according as q increases. Between the frequency ω_0 at which $\delta_G = 90^\circ$, and the rate of shear q, there appears to exist a relation $\omega_0 = \frac{1}{2} q$, which was observed experimentally over a range of four decades in ω and q. This relation seems to be universal and has been found for liquids covering a viscosity range of 5 decades.

(ii) At higher values of q also the normal stress consists of the sum of a constant stress and an oscillatory stress with frequency ω and an amplitude proportional to αq. The proportionality coefficient decreases according as q increases, and the phase angle between this component and the oscillatory component of the shear is greater according as q increases. Besides, this phase angle shifts by 180°, if the direction of q is reversed. The magnitude of the constant component at a given value of q is not influenced by the superposed oscillation.

If an oscillatory shear is orthogonally superposed on a steady rate of shear q, experiments show that the constant shear stress, resulting from the steady rate of shear is not affected by the oscillation. In a qualitative respect the orthogonal oscillatory shear stress resulting from the superposed oscillation is influenced in the same way by q as the oscillatory component of the stress during parallel superposition but, quantitatively, to a lesser degree. The relation $\omega_0 = \frac{1}{2} q$ is not applicable in the case of orthogonal superposition.

10. References

1. K. Weissenberg, Conf. British Rheologist'Club, p. 36, London, 1946
2. S.M. Freeman, Conf. British Rheologist'Club, p. 68, London, 1946
3. S.M. Freeman and K. Weissenberg, Nature 161, 324 (1948)
4. K. Weissenberg, Proc. Ist Intern. Congr. Rheol., p. II, 114, Scheveningen, 1948

5. J.E. Roberts, Proc. IInd Intern. Congr. Rheol., p. 91, Oxford, 1953
6. A. Jobling and J.E. Roberts in: Rheology, Theory and Application, Vol. II, p. 503, Ed. F.R. Eirich, Academic Press, New York, 1958
7. A. Jobling and J.E. Roberts, J. Polymer Sci. 36, 421 (1959)
8. K.A. Lammiman and J.E. Roberts, Lab. Practice 10, 816 (1961)
9. R.G. King, paper at Meeting British Soc. Rheol., april 1964
10. K. Weissenberg, The Testing of Materials by means of the Rheogoniometer, Farol Ltd, Bognor Regis, 1964
11. K. Walters, Basis Concepts and Formulae for the Rheogoniometer, Sangamo Ltd, Bognor Regis, 1968
12. K. Osaki, M. Tamura, M. Kurata and T. Kotaka, J. Soc. Mat. Sci. Japan 12, 339 (1963)
13. K. Osaki, M. Tamura, M. Kurata and T. Kotaka, J. Phys. Chem. 69, 4183 (1965)
14. K. Osaki, private communication, 1966
15. H.C. Booij, Rheol. Acta 5, 215 (1966)
16. N. Pilpel, Chem. Rev. 63, 221 (1963)
17. F.H. Gaskins, J.G. Brodnyan and W. Philippoff, Trans. Soc. Rheol. 13, 17 (1969)
18. J.M. Simmons, J. Sci. Instrum. 43, 887 (1966)
19. J.M. Simmons, Ph.D. Thesis, Sydney, 1967
20. J.M. Simmons, Rheol. Acta 7, 184 (1968)
21. J.M. Simmons, private communication, 1968
22. R.I. Tanner and J.M. Simmons, Chem. Eng. Sci. 22, 1803 (1967)
23. S. Kuroiwa and M. Nakamura, Kobunshi Kagaku 24, 807 (1967)
24. H.C. Booij, Rheol. Acta 7, 202 (1968)
25. T. Kataoka and S. Ueda, J. Polymer Sci. A2,7, 475 (1969)
26. K. Walters and T.E.R. Jones, Proc. Vth Intern. Congr. Rheol., Vol. IV, Kyoto, 1968

Chapter III

SUMMARY OF PUBLISHED THEORETICAL APPROACHES

1. Introduction

In chapter I, section 3, it was briefly indicated how a number of important properties of polymeric liquids can be considered from a molecular point of view. However, attention may be turned also to other properties of viscoelastic liquids. When a viscoelastic liquid has been deformed, elastic recovery takes place when the forces acting on it are removed. Upon extrusion of these liquids through fine perforations, the diameter of the resulting fibres may well be much larger than that of the perforations. Many other properties of viscoelastic liquids can be mentioned which rather emphasize that the rheological properties are at any moment a function of the recent history of the material. For describing this type of effects, many theories make use of a special system of coordinates, the so-called convected or embedded coordinate system, which has already been discussed in chapter I, section 2b. Rheological equations of state are then defined in this system. In the present chapter we intend to deal merely with those theories which have been used in explaining the results of superposition measurements on polymer systems. The chapter has been subdivided in accordance with the differences in theoretical approach. However, this treatment will be rather brief and not chronological. A molecular-theoretical approach will be discussed fairly extensively in the next chapter.

A very extensive discussion on various kinds of theories, in which special emphasis is given to their suitability for explaining superposition results, can be found in the thesis by Simmons1).

2. Application of Oldroyd's theory

Oldroyd starts from the concept that the rheological properties of a material volume element of a viscoelastic substance, which at a given moment t is located at a position r in space, are determined i.a. by the quantities associated with the same volume element at previous times t', when it was located at positions r'(r,t,t'). As, however, tensor quantities associated with different points in space cannot simply be added up, use is made of convected quantities that remain associated with the same volume element whose coordinates relative to a convected system of base vectors remain constant throughout the deformation history. As we have seen in chapter I, there exist certain transformation rules which express these convected quantities in terms of the fixed coordinates x^i at time t. When all convected quantities occurring throughout the deformation history are transformed back into quantities expressed in the coordinates of a single point x^i in space, summation of these quantities becomes again possible. In 1950, Oldroyd2) gave the various transformation formulas, not only for tensor quantities such as the rate of strain, which is described by formula (I 40) or (I 41), but also for convected integrals, time derivatives, etc.

The procedure presented in the foregoing is useful only if the quantities governing the rheological properties of the volume element at time t are known. In other words, the rheological equation of state, so the relation between stress, strain and time, must be known first. In addition, for application of the procedure to be possible, the deformation history of the volume element must also be known, since it is from this deformation history that the displacement functions $\underline{r}'(r,t,t')$ must be derived.

For the rheological equation of state Oldroyd uses the following differential equation between stress tensor $\underline{P}$ and rate of strain tensor $\underline{\dot{E}}$:

$$(1+\tau_1 \frac{\partial}{\partial t})\, \underline{P} = 2\,\eta_0\, (1+\tau_2 \frac{\partial}{\partial t})\, \underline{\dot{E}} \qquad \text{(III 1)}$$

It contains two characteristic parameters τ_1 and τ_2, both having the dimension of time. In the case of low shear rates Oldroyd[3)] derived this equation for a dilute emulsion of a newtonian liquid in another newtonian liquid; it is equivalent to that derived earlier for a dilute suspension of perfectly elastic spherical particles in a newtonian liquid by Fröhlich and Sack[4)]. Both physical models give $\tau_1 > \tau_2$.

Oldroyd[2)] now supposes that this equation holds for the system of convected coordinates, in which $\partial/\partial t$ becomes equal to the convected time derivative $\delta/\delta t$, and, hence, equal to the rate of change as 'seen' by an observer in a convected coordinate system. Under conditions of simple shear flow in the 1-direction with a constant velocity gradient q in the 2-direction, it appears that the shear stress is proportional to q (and, hence, the viscosity η independent of q) and one normal stress component proportional to q^2. In the co- and contravariant cases we thus have[5)]

A (covariant) $\eta = \eta_0$; $p_{11} = p_{33} > p_{22}$

B (contravriant) $\eta = \eta_0$; $p_{33} = p_{22} < p_{11}$

Hence, with Eq. (III 1) applied in a convected coordinate system, we find a second-order fluid behaviour, while it can also easily be demonstrated that, according to this equation, the dynamic moduli in the case of parallel superposition will be independent of q. Consequently, the equation is unsuited for describing the properties of viscoelastic fluids.

In subsequent considerations, Oldroyd[5, 6)] replaces the derivatives in Eq. (III 1) by other types of time derivatives. In doing so he uses the so-called Jaumann derivative, which makes allowance for the translation and rotation of a material element, but not for the deformation. The results of this approach[5-7)] prove to agree better with the observation that in viscoelastic materials under conditions of simple shear flow there may arise shear stresses and normal stresses whose increase with the rate of shear is neither linear nor quadratic but more complicated. In addition, this theory provides[8, 9)] equations for the dynamic quantities of oscillatory shear which are in good agreement with the phenomenological expressions.

Simultaneously with the first experimental superposition results the author published a theoretical approach[10)] based on the use of the Jaumann derivative in the differential equation (III 1). These calculations will not be repeated here. For the various stress components in the case of parallel superposition the following equations were derived (see also ref. 11):

$$p_{21} = \eta_0 q \, \frac{1 + \tau_1 \tau_2 q^2}{1 + \tau_1^2 q^2} \tag{III 2}$$

$$p_{11} - p_{22} = 2\,\eta_0 q^2 \, \frac{\tau_1 - \tau_2}{1 + \tau_1^2 q^2} \tag{III 3}$$

$$G'(\omega,q) = \frac{\eta_0 \omega^2}{1 + \tau_1^2 q^2} \left[\frac{(\tau_1 - \tau_2)(1 + \tau_1^2 \omega^2 - 3\,\tau_1^2 q^2)}{(1 - \tau_1^2 \omega^2 + \tau_1^2 q^2)^2 + 4\,\tau_1^2 \omega^2} \right] \tag{III 4}$$

$$G''(\omega,q) = \eta_0 \omega \left[\frac{(1 + \tau_1 \tau_2 \omega^2 - \tau_1 \tau_2 q^2)(1 + \tau_1^2 \omega^2 - \tau_1^2 q^2) + 4\,\tau_1 \tau_2 q^2}{(1 - \tau_1^2 \omega^2 + \omega_1^2 q^2)^2 + 4\,\tau_1^2 \omega^2} \right] \tag{III 5}$$

$$N'(\omega,q) = \frac{\eta_0 \omega^2 \tau_1}{1 + \tau_1^2 q^2} \left[\frac{(\tau_1 - \tau_2)(3 + \tau_1^2 \omega^2 - \tau_1^2 q^2)}{(1 - \tau_1^2 \omega^2 + \tau_1^2 q^2)^2 + 4\,\tau_1^2 \omega^2} \right] \tag{III 6}$$

$$N''(\omega,q) = 2\,\eta_0 \omega \left[\frac{\tau_1 - \tau_2}{(1 - \tau_1^2 \omega^2 + \tau_1^2 q^2)^2 + 4\,\tau_1^2 \omega^2} \right] \tag{III 7}$$

Qualitatively, some of these equations are in agreement[10, 11] with certain experimental features, whereas others are definitely not:

i) According to Eq. (III 2), the viscosity is a decreasing function of q. This also appears from experimental data (Fig. II,1).

ii) According to Eq. (III 3), the normal stress increases less than quadratically with q, as is also confirmed experimentally (Fig. II,2).

iii) According to Eq. (III 4), $G'(\omega,q)$ becomes negative if $\omega^2 < 3\,q^2 - 1/\tau_1^2$, whereas the experiments yield negative values of $G'(\omega,q)$ if $\omega < \frac{1}{2}\,q$ (Fig. II,4)

iv) According to Eq. (III 5), with $\tau_2 = 0$, $G''(\omega,q)$ becomes negative if $\omega^2 < q^2 - 1/\tau_1^2$. However, there is no experimental evidence showing that $G''(\omega,q)$ ever becomes negative.

v) Eq. (III 6) predicts negative values for $N'(\omega,q)$ if $\omega^2 < q^2 - 3/\tau_1^2$. The experimental values of $N'(\omega,q)$ are all positive (Figs II,19 and II,21).

vi) Eq. (III 7) predicts positive values for $N''(\omega,q)$ at all values of ω and q, but, as has been found experimentally, $N''(\omega,q)$ can become negative (Figs II,20 and II,22).

Upon a further, more quantitative, comparison with the experimental data these equations moreover appear to have the following drawbacks; these are of a more general nature:

a) The number of parameters is very small. The shape of the curves representing the stress components as a function of ω or of q is, in fact, determined mainly by the one relaxation time τ_1. As a result, the calculated curves show much larger changes in slope than any experimental curve[10)].

b) The expressions for the dynamic quantities have almost a pole. According as ω approaches q, the denominator becomes very small, with the result that all dynamic quantities show a maximum and $G'(\omega,q)$, $G''(\omega,q)$ and $N'(\omega,q)$ pass very sharply through zero. These singularities were pointed out already by Yerushalmi, Katz and Shinnar[12)].

Both drawbacks are clearly evident from the following figures. With the aid of Eqs (III 4) to (III 7) (with $\tau_2 = 0$) the quantities $|G^*| = (G'^2 + G''^2)^{1/2}$, $\delta_G = \arctan (G'/G'')$, $|N^*| = (N'^2 + N''^2)^{1/2}$ and $\delta_N = \arctan (N''/N')$ have been calculated as functions of the frequency for some values of the superposed shear rate expressed as $\tau_1 q$.

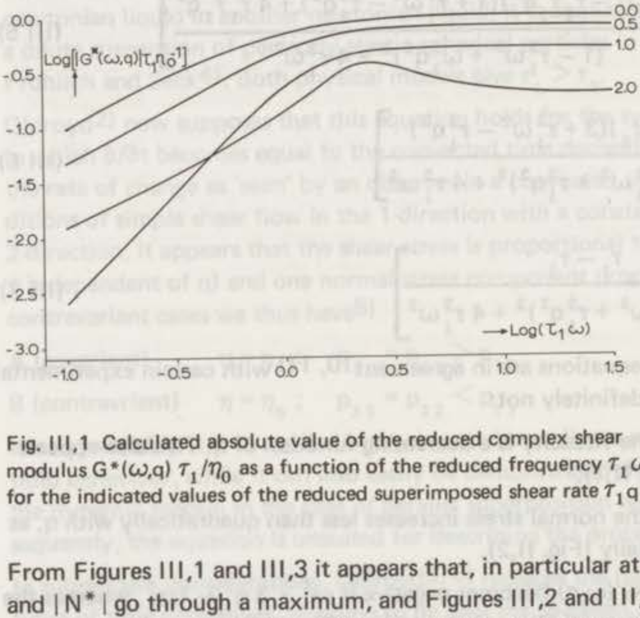


Fig. III,1 Calculated absolute value of the reduced complex shear modulus $G^*(\omega,q)\ \tau_1/\eta_0$ as a function of the reduced frequency $\tau_1\omega$ for the indicated values of the reduced superimposed shear rate $\tau_1 q$

From Figures III,1 and III,3 it appears that, in particular at higher shear rates, both $|G^*|$ and $|N^*|$ go through a maximum, and Figures III,2 and III,4 show that in Oldroyds theory the phase angles δ_G and δ_N are highly dependent on the frequency. In particular, δ_G can assume very high values, while δ_N is always positive and increases to slightly beyond 90° only at higher q-values. These quantities may vary considerably within a fairly narrow frequency range. In a qualitative respect the experimental results presented in the previous chapter show some agreement with this theory; quantitative description, however, cannot be given on this basis.

Another drawback of the differential equation (III 1) to be mentioned is the following. Tanner and Simmons[1, 13)], analyzing various generalized forms of (III 1) for the case of orthogonal superposition, noted an instability. If a disturbance in velocity is orthogonally superposed on a steady flow, it appears that under certain conditions this disturbance is

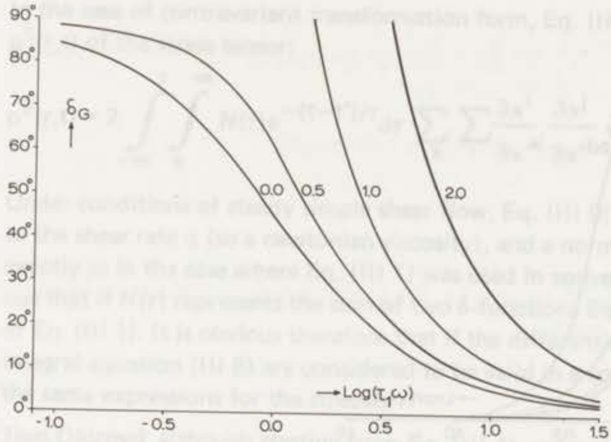


Fig. III,2 Calculated phase difference δ_G as a function of the reduced frequency $\tau_1 \omega$ for the indicated values of the reduced superimposed shear rate $\tau_1 q$

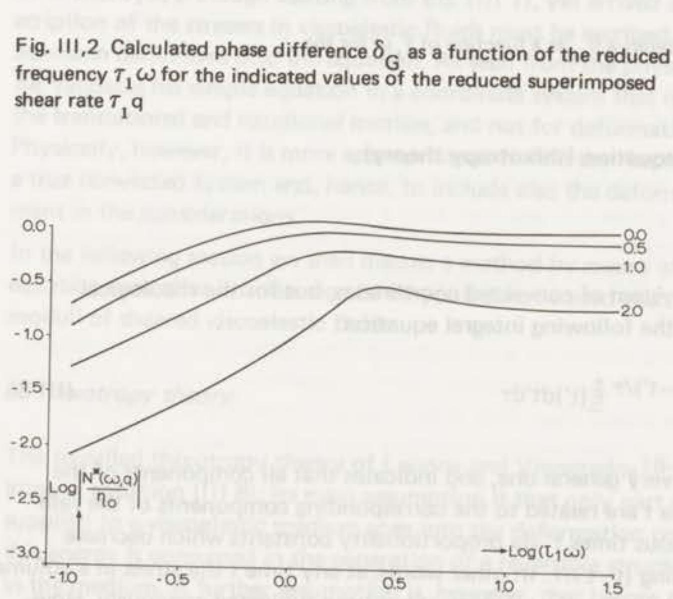


Fig. III,3 Calculated absolute value of the reduced complex normal stress viscosity $N^*(\omega,q)/\eta_0$ as a function of $\tau_1 \omega$ for the indicated values of $\tau_1 q$

not damped, but rather enhanced. A similar flow instability in the Oldroyd model was noted by Pearson and Petrie[14]. These instabilities are inconsistent with the experimental data, which strongly detracts from the value of such differential equations as (III 1).

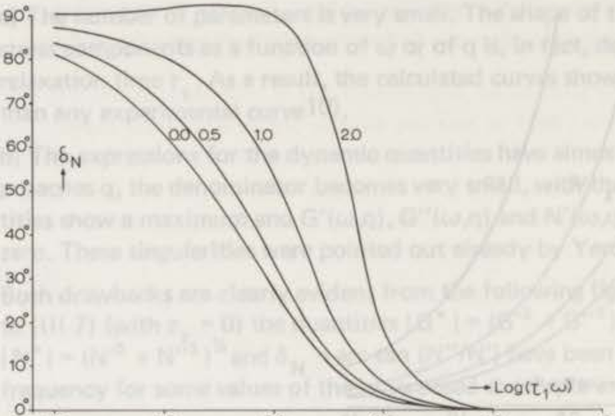


Fig. III,4 Calculated phase difference δ_N as a function of $\tau_1\omega$ for the indicated values of $\tau_1 q$

3. Application of Walters' equation (thixotropy theory)

a. Introduction

Walters[15-17] also uses a system of convected coordinates, but for the rheological equation of state he takes the following integral equation:

$$\underline{P}(t) = 2 \int_{-\infty}^{t}\int_{0}^{\infty} N(\tau)e^{-(t-t')/\tau}\, \dot{\underline{E}}(t')dt'd\tau \qquad \text{(III 8)}$$

This integral equation is a very general one, and indicates that all components of the stress tensor at a given time t are related to the corresponding components of the rate of strain tensor at all previous times t' via proportionality constants which decrease exponentially with increasing $(t-t')/\tau$. In other words, at any time t the stress in a volume element 'remembers' all rates of strain to which it has been subjected previously. However, it remembers less of the previous history according as the time interval t–t' is greater and the relaxation time τ is shorter. Consequently, the stresses in deformation mechanisms with long relaxation times, remember relatively much of the rates of strain that have occurred relatively long ago. For the time being, the distribution function $N(\tau)$ of the relaxation times τ is still an unknown factor. A model for the behaviour of the liquid which obeys Eq. (III 8) is a generalized Maxwell model, consisting of an elastic spring in series with a dashpot of a viscosity equal to the elasticity constant of the spring multiplied by the relaxation time.

It is again assumed that this equation (III 8) holds for a system of convected coordinates. Since integration is a special form of summation, the transformation to the system of fixed coordinates can be carried out in a simple way by means of Eq. (I 40) or (I 41).

In the case of contravariant transformation form, Eq. (III 8) yields for the components $p^{ij}(\underline{r},t)$ of the stress tensor:

$$p^{ij}(\underline{r},t) = 2 \int_{-\infty}^{t} \int_{0}^{\infty} N(\tau) e^{-(t-t')/\tau} d\tau \sum_{k} \sum_{l} \frac{\partial x^{i}}{\partial x'^{k}} \frac{\partial x^{j}}{\partial x'^{l}} \dot{e}^{kl}(\underline{r}',t') dt' \qquad \text{(III 9)}$$

Under conditions of steady simple shear flow, Eq. (III 9) yields a shear stress proportional to the shear rate q (so a newtonian viscosity), and a normal stress proportional to q^2, exactly as in the case where Eq. (III 1) was used in convected coordinates. Walters pointed out that if $N(\tau)$ represents the sum of two δ-functions Eq. (III 8) is the integrated form of Eq. (III 1). It is obvious therefore that if the differential equation (III 1) as well as the integral equation (III 8) are considered to be valid in a convected system, both will yield the same expressions for the stresses.

That Oldroyd, although starting from Eq. (III 1), yet arrived at a more satisfactory description of the stresses in viscoelastic fluids must be ascribed to the fact that he introduced Jaumann derivatives into the equation. As seen from the physical angle, this implies that he validates his simple equation in a coordinate system that makes allowance only for the translational and rotational motion, and not for deformation, of the volume element. Physically, however, it is more appropriate to define the rheological equation of state in a true convected system and, hence, to include also the deformation of the volume element in the considerations.

In the following section we shall discuss a method by means of which Walters' integral equation can, after introduction of a hypothesis, be used even for describing the dynamic moduli of sheared viscoelastic fluids.

b. Thixotropy theory

The so-called thixotropy theory of Leonov and Vinogradov[18-20] is based on Walters' integral equation (III 8); its main assumption is that only part of the mechanical energy supplied to a viscoelastic medium goes into the deformation process. The other part of this energy is consumed in the generation of a reversible structural rupture (thixotropy) in the medium. A further assumption is, however, that before this rupture is initiated, the energy must have reached a certain minimum or critical value. This implies that if the amount of elastic energy stored is below this critical value, no structural breakdown will occur. The latter assumption renders the theory definitily non-linear.

The thixotropy theory will be briefly dealt with below. We point out that, although our way of approach differs rather strongly from that originally followed by Leonov and Vinogradov, the two are in fact equivalent.

Suppose that a liquid for which Eq. (III 8) holds in a system of convected coordinates is subjected for a period t' to a flow field which, in a system of fixed coordinates, is described by a rate of strain tensor $\dot{e}^{kl}(\underline{r}',t')$. If we consider only those Maxwell elements whose relaxation times come between τ and $\tau + d\tau$, and whose collective elasticity modulus equals $N(\tau)d\tau$, it follows from Eq. (III 9) that the stress on these elements is given by:

$$p^{ij}(\tau,t)d\tau = 2 \int_{-\infty}^{t} N(\tau)e^{-(t-t')/\tau} \sum_{k}\sum_{l} \frac{\partial x^i}{\partial x'^k}\,\frac{\partial x^j}{\partial x'^l}\,\dot{e}^{kl}(\underline{r}',t')dt'd\tau \qquad \text{(III 10)}$$

The elastic deformation of these elements at time t then equals:

$$e^{ij}(\tau,t) = \frac{p^{ij}(\tau,t)d\tau}{N(\tau)d\tau} \qquad \text{(III 11)}$$

The amount of work done upon the springs, i.e. the elastic energy stored in one Maxwell element with relaxation time τ, equals:

$$f(\tau,t) = \tfrac{1}{2} \sum_{i}\sum_{j} \left[e^{ij}(\tau,t)\right]^2 \qquad \text{(III 12)}$$

where:

$$e^{ij}(\tau,t) = \int_{-\infty}^{t} e^{-(t-t')/\tau} \sum_{k}\sum_{l} \frac{\partial x^i}{\partial x'^k}\,\frac{\partial x^j}{\partial x'^l}\,\dot{e}^{kl}(r',t')dt' \qquad \text{(III 13)}$$

As we have already seen, a mechanism with a long relaxation time remembers more of a strain rate which occurred a time t–t' ago than does a mechanism with a short τ. Therefore the elastic energy stored over the interval t–t' is also greater for a mechanism with a large τ than for one with a small τ, it being assumed that the deformation history is the same for both mechanisms.

Let us now first calculate the energy for a fairly general flow field, comprising a simple shear flow in the 1-direction with a non-constant velocity gradient $\dot{\gamma}(t)$ in the 2-direction and, superposed thereon, a simple shear flow in the 3-direction with a non-constant velocity gradient $\kappa(t)$ in the 2-direction. For this flow field the displacement functions are:

$$x'^1 = x^1 - x^2 \int_{t'}^{t} \dot{\gamma}(t'')dt'' \qquad \text{(III 14)}$$

$$x'^2 = x^2$$

$$x'^3 = x^3 - x^2 \int_{t'}^{t} \kappa(t'')dt''$$

The components of $\underline{\dot{E}}(r',t')$, which differ from zero, are:

$$\dot{e}^{12} = \dot{e}^{21} = \tfrac{1}{2}\,\dot{\gamma}(t') \qquad \text{(III 15)}$$

$$\dot{e}^{23} = \dot{e}^{32} = \tfrac{1}{2}\,\kappa(t')$$

To calculate the energy we need only the terms:

$$\frac{\partial x^1}{\partial x'^1}\,\frac{\partial x^1}{\partial x'^2} = \frac{\partial x^1}{\partial x'^2}\,\frac{\partial x^1}{\partial x'^1} = \frac{\partial x^1}{\partial x'^2}\,\frac{\partial x^3}{\partial x'^3} = \frac{\partial x^3}{\partial x'^3}\,\frac{\partial x^1}{\partial x'^2} = \int_{t'}^{t} \dot{\gamma}(t'')dt'' \qquad \text{(III 16)}$$

$$\frac{\partial x^1}{\partial x'^1}\,\frac{\partial x^2}{\partial x'^2} = \frac{\partial x^2}{\partial x'^2}\,\frac{\partial x^1}{\partial x'^1} = \frac{\partial x^2}{\partial x'^2}\,\frac{\partial x^3}{\partial x'^3} = \frac{\partial x^3}{\partial x'^3}\,\frac{\partial x^2}{\partial x'^2} = 1$$

$$\frac{\partial x^3}{\partial x'^2}\,\frac{\partial x^3}{\partial x'^3} = \frac{\partial x^3}{\partial x'^3}\,\frac{\partial x^3}{\partial x'^2} = \frac{\partial x^1}{\partial x'^1}\,\frac{\partial x^3}{\partial x'^2} = \frac{\partial x^3}{\partial x'^2}\,\frac{\partial x^1}{\partial x'^1} = \int_{t'}^{t} \kappa(t'')dt''$$

The terms differing from zero in Eq. (III 13) then are:

$$e^{11}(\tau,t) = \int_{-\infty}^{t} e^{-(t-t')/\tau}\,\dot{\gamma}(t') \int_{t'}^{t} \dot{\gamma}(t'')dt''dt' \qquad \text{(III 17)}$$

$$e^{12}(\tau,t) = e^{21}(\tau,t) = \tfrac{1}{2} \int_{-\infty}^{t} e^{-(t-t')/\tau}\,\dot{\gamma}(t')dt'$$

$$e^{23}(\tau,t) = e^{32}(\tau,t) = \tfrac{1}{2} \int_{-\infty}^{t} e^{-(t-t')/\tau}\,\kappa(t')dt'$$

$$e^{33}(\tau,t) = \int_{-\infty}^{t} e^{-(t-t')/\tau}\,\kappa(t') \int_{t'}^{t} \kappa(t'')dt''dt'$$

$$e^{13}(\tau,t) = e^{31}(\tau,t) = \tfrac{1}{2} \int_{-\infty}^{t} e^{-(t-t')/\tau} \left[\kappa(t') \int_{t'}^{t} \dot{\gamma}(t'')dt'' + \dot{\gamma}(t') \int_{t'}^{t} \kappa(t'')dt'' \right] dt'$$

The elastic energy stored per mechanism with relaxation time τ can now be calculated with Eq. (III 12) and, for the present case, equals

$$f(\tau,t) = \tfrac{1}{2}\ \left[(e^{11})^2 + 2\,(e^{12})^2 + 2\,(e^{13})^2 + 2\,(e^{23})^2 + (e^{33})^2 \right] \qquad \text{(III 18)}$$

At this point a simplification is introduced into the original thixotropy theory. For calculating the elastic energy Eq. (III 13), which yields the convected deformation, is displaced by an equation corresponding with Eq. (III 8) which gives the deformations in the fixed system of coordinates. However, the calculation of the stresses is still carried out with Eq. (III 9). Owing to this approximation the terms quadratic in the shear rate are neglected with respect to the linear terms. This is a serious restriction as a result of which the thixotropy theory can be applied only when the normal stresses are small compared with the shear stresses. With this simplification the elastic energy in our example is given by:

$$f(\tau,t) = (e^{12})^2 + (e^{23})^2 \tag{III 19}$$

In what follows it will be assumed as a special case that $\kappa(t') \equiv 0$ and that $\dot{\gamma}(t') = 0$ for $-\infty \leqslant t' < 0$ and $\dot{\gamma}(t') = q$ = constant for $0 \leqslant t' \leqslant t$, or in other words, that the liquid is subjected to a steady simple shear flow from the moment $t' = 0$. Then $e^{23} \equiv 0$ and:

$$e^{12}(\tau,t) = \tfrac{1}{2}\int_0^t e^{-(t-t')/\tau} q\, dt' = \frac{q\tau}{2}\left[1 - e^{-t/\tau}\right] \tag{III 20}$$

This means that the deformation tends exponentially to a final value of $\frac{q\tau}{2}$, which is reached more rapidly according as the relaxation time is shorter, as can be seen in Fig. III,5, which shows the function (III 20) for $q = 2\ \mathrm{sec}^{-1}$ and for τ equal to 1, 2, 3 and 4 sec.

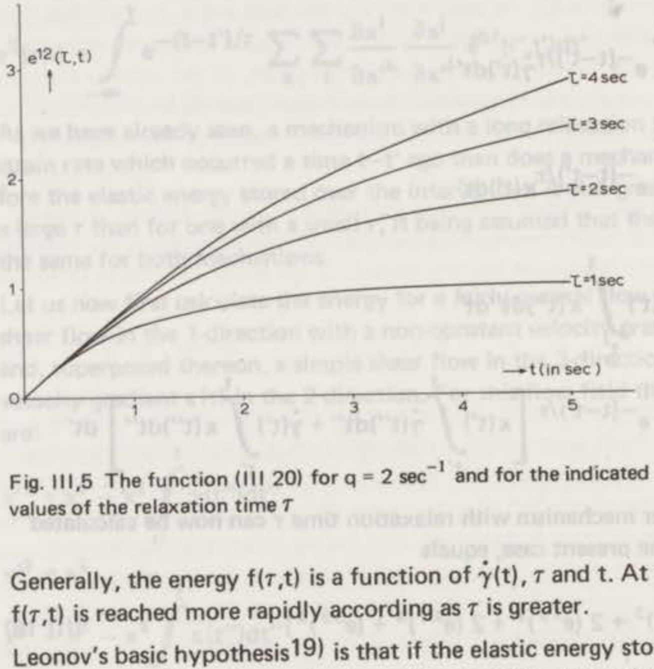


Fig. III,5 The function (III 20) for $q = 2\ \mathrm{sec}^{-1}$ and for the indicated values of the relaxation time τ

Generally, the energy $f(\tau,t)$ is a function of $\dot{\gamma}(t)$, τ and t. At a given q, a given value of $f(\tau,t)$ is reached more rapidly according as τ is greater.

Leonov's basic hypothesis[19)] is that if the elastic energy stored increases beyond a given critical value $f^*(\tau)$, the mechanism with relaxation time τ is broken down. If, however, the elastic energy $f(\tau,t)$ decreases again below the critical energy $f^*(\tau)$, for example owing to a decrease of $\dot{\gamma}(t)$, the structure will be restored. The relaxation time of the mechanism that has just escaped this breakdown is indicated by $\tau_m(t)$. In the case considered here application of Eqs (III 19) and (III 20) then yields the implicit equation

$$\left[\int_{-\infty}^{t} \dot{\gamma}(t')e^{-(t-t')/\tau_m} dt'\right]^2 = \frac{q^2\tau_m^2}{4}\left[1 - e^{-t/\tau_m}\right]^2 = f^*(\tau)\Big|_{\tau=\tau_m} \tag{III 21}$$

from which the maximum relaxation time $\tau_m(t)$ can be calculated.

One consequence of the abovementioned breakdown is that in all formulae, e.g. in the stress equation (III 9), we can no longer integrate from 0 to ∞ but only from 0 to $\tau_m(t)$. From the equations (III 17) and

$$p^{ij} = \int_0^{\tau_m(t)} N(\tau) e^{ij}(\tau,t)\,d\tau$$

it follows that in our special example of steady shear flow starting at time t′ = 0 the normal and shear stresses differing from zero are given by:

$$p^{11} = 2\int_0^{\tau_m(t)} N(\tau)\,d\tau \int_0^t q\,e^{-(t-t')/\tau} \int_{t'}^t q\,dt''dt' =$$

$$= 2\int_0^{\tau_m(t)} N(\tau)\,\tau^2 q^2 \left[1 - e^{-t/\tau} - \frac{t}{\tau} e^{-t/\tau}\right] d\tau \qquad \text{(III 22)}$$

and

$$p^{21} = p^{12} = \int_0^{\tau_m(t)} N(\tau)\,d\tau \int_0^t q\,e^{-(t-t')/\tau} dt' = \int_0^{\tau_m(t)} N(\tau)\tau q \left[1 - e^{-t/\tau}\right] d\tau \qquad \text{(III 23)}$$

which stresses with t → ∞ transform into:

$$p^{11} = 2\,q^2 \int_0^{\tau_m} N(\tau)\tau^2\,d\tau \quad \text{and} \quad p^{21} = q\int_0^{\tau_m} N(\tau)\tau\,d\tau$$

The viscosity $\eta(q)$ during steady shear flow hence equals

$$p^{21}/q = \int_0^{\tau_m} N(\tau)\tau\,d\tau.$$

The value of τ_m can now be determined from the experimental data. Let us suppose that for a given fluid $N(\tau)$ has been established, e.g. by dynamic measurements. The integral

$$\int_0^{\tau_m} N(\tau)\tau\,d\tau$$

can then be calculated for every value of τ_m. Putting these calculated values equal to the experimental values of $\eta(q)$, we find a relation between τ_m and q. From the experimental results18, 20) it now appears that over a fairly wide range of shear rates τ_m for various polymeric liquids is inversely proportional to q, i.e. $\tau_m = a/q$, a being of the order of 1. Substitution of this experimental relation into Eq. (III 21) for t → ∞ gives:

$$f^*(\tau) = a^2/4 \qquad \text{(III 24)}$$

showing that the maximum elastic energy which can be stored in a Maxwell element before rupture occurs is a constant that is independent of the relaxation time. All elements break down at the same value of the stored energy. It also follows from Eq. (III 21) that immediately upon the onset of the shear flow elements with longer relaxation times are liable to rupture sooner than those with shorter relaxation times, whereas elements with relaxation times $\tau < a/q$ are not affected at all. By means of Eqs (III 21), (III 23) and (III 24) Leonov and Malkin[20)] succeeded in describing how, after the start of a high shear rate, the shear stress first rises to a maximum, and then decreases to a constant level.

The thixotropy theory will now be applied to the case of parallel superposition, where:

$$\dot{\gamma}(t) = q + a\omega \cos \omega t; \kappa(t) \equiv 0 \qquad \text{(III 25)}$$

In this case substitution of Eq. (III 25) into Eqs (III 15), (III 16) and (III 19) and various integrations give as stationary stresses (so with t→∞):

$$p^{12} = \int_0^{\tau_m} N(\tau)\tau q d\bar{\tau} + a \sin \omega t \int_0^{\tau_m} \frac{N(\tau)\omega^2\tau^2}{1+\omega^2\tau^2} d\tau + a \cos \omega t \int_0^{\tau_m} \frac{N(\tau)\omega\tau}{1+\omega^2\tau^2} d\tau \qquad \text{(III 26)}$$

$$\begin{aligned} p^{11} = &\int_0^{\tau_m} N(\tau)\tau^2 q^2 d\tau + 2\,aq \sin \omega t \int_0^{\tau_m} \frac{N(\tau)\omega^2\tau^3(3+\omega^2\tau^2)}{(1+\omega^2\tau^2)^2} d\tau + \qquad \text{(III 27)} \\ &+ 2\,aq \cos \omega t \int_0^{\tau_m} \frac{2\,N(\tau)\omega\tau^2}{(1+\omega^2\tau^2)^2} d\tau + a^2 \int_0^{\tau_m} \frac{N(\tau)\omega^2\tau^2}{1+\omega^2\tau^2} d\tau + \\ &+ a^2 \sin 2\,\omega t \int_0^{\tau_m} \frac{3\,N(\tau)\omega^3\tau^3}{(1+\omega^2\tau^2)^2\,(1+4\,\omega^2\tau^2)} d\tau + \\ &+ a^2 \cos 2\,\omega t \int_0^{\tau_m} \frac{N(\tau)\omega^2\tau^2\,(1-2\,\omega^2\tau^2)}{(1+\omega^2\tau^2)\,(1+4\,\omega^2\tau^2)} d\tau \end{aligned}$$

For parallel superposition it follows from Eqs (III 17), (III 19) and (III 24) that under stationary conditions:

$$\tau_m\, q + \frac{a\omega\tau_m}{1+\omega^2\tau_m^2}(\cos \omega t + \omega\tau_m \sin \omega t) = a \qquad \text{(III 28)}$$

Since at all values of ω the coefficient of a in Eq. (III 28) lies between 0 and 1, and a is of the order of 1, we may say that, with $a \ll 1$, the superposed oscillation disturbs the value of τ_m by an amount proportional to a. Eq. (III 28) is obeyed up to the order of a

if we put

$$\tau_m = \tau_o - \frac{1}{\tau_o q} \, \frac{a\omega\tau_o^2}{1+\omega^2\tau_o^2} \left(\cos \omega t + \omega\tau_o \sin \omega t\right) \tag{III 29}$$

where $\tau_o = a/q$.

This equation shows that the value of τ_m varies around the value τ_o determined by the steady-state value of q. The superposed oscillation affects the limit value of τ, and this effect appears to become smaller according as q increases, as is to be expected.

For calculating the stresses with the aid of Eqs (III 26) and (III 27), the upper limit of the integration has to be replaced by Eq. (III 29). The effect of this, e.g. on Eq. (III 26), is that the first integral yields an extra contribution that is proportional to a and negative, whereas the following integrals give additional terms that are proportional to a^2; the latter will be neglected. The additional terms proportional to a indicate the way in which the stresses decrease and increase periodically under the influence of the periodic breakdown and recovery of relaxation mechanisms with relaxation times in the neighbourhood of τ_o. We shall now carry out the integrations in the following way. We first integrate up to τ_o and then replace the integral over the oscillatory part of τ_m by the product of this part and the integrant. For the stresses we thus find, with an accuracy up to the order of a,

$$p^{12} = (p^{12})_{rot} + a\, G'(\omega,q) \sin \omega t + a\, G''(\omega,q) \cos \omega t$$

and

$$p^{11} = (p^{11})_{rot} + 2\,aq\, N'(\omega,q) \sin \omega t + 2\,aq\, N''(\omega,q) \cos \omega t$$

where

$$G'(\omega,q) = \int_o^{\tau_o} \frac{N(\tau)\omega^2\tau^2}{1+\omega^2\tau^2}\, d\tau - \frac{N(\tau_o)\omega^2\tau_o^3}{1+\omega^2\tau_o^2} \tag{III 30a}$$

$$G''(\omega,q) = \int_o^{\tau_o} \frac{N(\tau)\omega\tau}{1+\omega^2\tau^2}\, d\tau - \frac{N(\tau_o)\omega\tau_o^2}{1+\omega^2\tau_o^2} \tag{III 30b}$$

$$N'(\omega,q) = \int_o^{\tau_o} \frac{N(\tau)\omega^2\tau^3\,(3+\omega^2\tau^2)}{(1+\omega^2\tau^2)^2}\, d\tau - \frac{N(\tau_o)\omega^2\tau_o^4}{1+\omega^2\tau_o^2} \tag{III 30c}$$

$$N''(\omega,q) = \int_o^{\tau_o} \frac{N(\tau)\,2\,\omega\tau^2}{(1+\omega^2\tau^2)^2}\, d\tau - \frac{N(\tau_o)\omega\tau_o^3}{1+\omega^2\tau_o^2} \tag{III 30d}$$

The steady stress components equal:

$$(p^{12})_{rot} = \int_{o}^{\tau_o} N(\tau)\tau q \, d\tau \qquad \text{(III 31a)}$$

$$(p^{11})_{rot} = 2\int_{o}^{\tau_o} N(\tau)\tau^2 q^2 \, d\tau \qquad \text{(III 31b)}$$

These formulae, except (III 30c) and (III 30d), are also given by Leonov, Tsiprin and Faitel'son21). Hence, superposition of a steady shear manifests itself in two ways. First the relaxation-time spectrum on the side of the long relaxation times narrows down to a value of τ_o which is characteristic of steady flow. Second, negative terms appear in the expressions for the dynamic quantities; these are to be ascribed to the disturbance of the limit τ_o by the additional small deformations caused by the oscillations.

The above formulae enabled Leonov, Tsiprin and Faitel'son21) to give a very satisfactory description of the results the present author had obtained during superposition on a rubber solution22). The relaxation-time spectrum was calculated from the results obtained with pure oscillation, whereupon the relation between τ_o and q was derived from viscosity measurements with the aid of formula (III 31a). Subsequently, the normal stress was calculated as a function of q by means of Eq. (III 31b), and the dynamic shear moduli $G'(\omega,q)$ and $G''(\omega,q)$ as functions of ω for two values of q, viz. $q = 1\ \text{sec}^{-1}$ and $q = 10\ \text{sec}^{-1}$, by means of Eqs (III 30a) and (III 30b). The calculated normal stress was about 30 % lower than the experimental one, but the difference between the calculated and experimental dynamic modulu was much smaller. Extension of the calculations to cover frequencies lower than those at which experimental measurements could be carried out, predicted that $G'(\omega,q)$ becomes negative at frequencies lower than q, but that $G''(\omega,q)$ remains positive, and that the curve of $\eta_d(\omega,q)$ passes through a maximum. Even the theoretical values of δ_G agreed, within a few degrees, with the experimental values.

Let us now apply this thixotropy theory also to the case of orthogonal superposition. Here, $\dot{\gamma}(t) = q$ and $\kappa(t) = \alpha\omega \cos \omega t$. For the elastic deformations under stationary conditions, Eq. (III 17) then give:

$$e^{11} = 2\,\tau^2 q^2$$

$$e^{12} = e^{21} = \tau q$$

$$e^{23} = e^{32} = \frac{\alpha\omega^2\tau^2}{1+\omega^2\tau^2}\sin \omega t + \frac{\alpha\omega\tau}{1+\omega^2\tau^2}\cos \omega t$$

$$e^{13} = e^{31} = \alpha\tau q\left[\frac{\omega^2\tau^2\ (\omega^2\tau^2-1)}{(1+\omega^2\tau^2)^2}\sin \omega t + \frac{2\,\omega^3\tau^3}{(1+\omega^2\tau^2)^2}\cos \omega t\right]$$

The component e^{33} is proportional to α^2 and will therefore be neglected. Using again the expressions (III 18) or (III 19) for the stored elastic energy, we find that these expressions contain only constant terms or terms proportional to α^2, but no terms that are proportional to α, in contrast to what we have with parallel superposition (see Eq. (III 28)). As a result, the disturbance of τ_m in the case of orthogonal superposition is of the order of α^2, and the integrations needed for calculating the dynamic quantities, do not yield extra terms proportional to α. The formulae for $G'(\omega,q)$ and $G''(\omega,q)$ in the case of orthogonal superposition are equal to (III 30a) and (III 30b) minus the negative terms outside the integral sign. Here again, $\tau_o = a/q$. Hence, according to this theory the effect of superposition on the dynamic quantities is greater with parallel than with orthogonal superposition.

4. Calculations based on Lodge's equation

a. Introduction

The first prediction of the stress components that will arise in the case of superposition was given by Lodge23) on the basis of his theory concerning rubber-like liquids. The rheological equation of state for these liquids has the same form as that derived, i.a. by Lodge24), from a molecular theory for concentrated polymer solutions in which, owing to physical entanglements, a network is formed which, under the influence of thermal motion and external forces, is continuously broken down and rebuilt. The concentration of the network junctions formed in a time interval between t' and t' + dt' and still existing at a later time t is represented by a memory function $\mu(t-t')dt'$, which decreases as the value of t−t' increases.

Now, according to Lodge's theory, all stress components at time t are related, by the same function $\mu(t-t')$, to the corresponding components of the strain tensor at time t' (and not to the rate of strain tensor, as in Walter's equation of state (III 8)). Expressed in fixed coordinates, the following equation holds:

$$\underline{P}(t) = \int_{-\infty}^{t} \mu(t-t')\,\underline{S}(t')\,dt' \tag{III 32}$$

where $\underline{S}(t')$ is the contravariant strain tensor as defined in Eqs (I 34) and (I 32). For the fairly general example of flow treated in the preceding section, we can calculate the components of this strain tensor directly from the displacement functions (III 14). The differential quotients occurring in the Finger tensor $\underline{B}(t')$, which are unequal to zero, are

$$\frac{\partial x^1}{\partial x'^1}\,\frac{\partial x^1}{\partial x'^1} = \frac{\partial x^2}{\partial x'^2}\,\frac{\partial x^2}{\partial x'^2} = \frac{\partial x^3}{\partial x'^3}\,\frac{\partial x^3}{\partial x'^3} = 1 \tag{III 33}$$

$$\frac{\partial x^1}{\partial x'^2}\,\frac{\partial x^2}{\partial x'^2} = \int_{t'}^{t} \dot{\gamma}(t'')dt'';\quad \frac{\partial x^2}{\partial x'^2}\,\frac{\partial x^3}{\partial x'^2} = \int_{t'}^{t} \kappa(t'')dt''$$

$$\frac{\partial x^1}{\partial x'^2}\frac{\partial x^1}{\partial x'^2} = \left[\int_{t'}^{t} \dot{\gamma}(t'')dt''\right]^2 \; ; \; \frac{\partial x^3}{\partial x'^2}\frac{\partial x^3}{\partial x'^2} = \left[\int_{t'}^{t} \kappa(t'')dt''\right]^2$$

$$\frac{\partial x^1}{\partial x'^2}\frac{\partial x^3}{\partial x'^2} = \int_{t'}^{t} \dot{\gamma}(t'')dt'' \int_{t'}^{t} \kappa(t'')dt''$$

Putting $\dot{\gamma}(t)$ equal to $q + a_1 \omega_1 \cos \omega_1 t$ and $\kappa(t)$ to $a_2 \omega_2 \cos \omega_2 t$, this flow corresponds to parallel superposition if $a_2 \equiv 0$, and to orthogonal superposition if $a_1 \equiv 0$. If confusion is excluded, $a_1 = a$, or $a_2 = a$. For simplificity we now put

$$\int_{t'}^{t} \dot{\gamma}(t'')dt'' = q(t-t') + a_1 \; (\sin \omega_1 t - \sin \omega_1 t') \text{ equal to } g_o + a_1 g_1$$

and

$$\int_{t'}^{t} \kappa(t'')dt'' = a_2 \; (\sin \omega_2 t - \sin \omega_2 t') \text{ equal to } a_2 g_2$$

With the aid of Eq. (III 33) we then find for the contravariant strain tensor

$$\underline{S} = \begin{vmatrix} (g_o + a_1 g_1)^2 & g_o + a_1 g_1 & (g_o + a_1 g_1) a_2 g_2 \\ g_o + a_1 g_1 & 0 & a_2 g_2 \\ (g_o + a_1 g_1) a_2 g_2 & a_2 g_2 & a_2^2 g_2^2 \end{vmatrix} \qquad \text{(III 34)}$$

When the rate of shear is constant, i.e. with $a_1 = a_2 = 0$, substitution of Eq. (III 34) in (III 32) gives a shear stress that is proportional to q and a normal stress difference $p_{11} - p_{22}$ that is proportional to q^2, which shows that Eq. (III 32) does not adequately describe the actual viscoelastic behaviour of polymeric liquids. It is evident from Eq. (III 34) for the strain tensor that the shear stress during parallel superposition[23)] is a complete superposition of the separate stresses that would occur with oscillatory shear and with steady shear. A superposed shear rate therefore does not have any effect on the dynamic shear quantities, which is fully incompatible with the experimental results of Chapter II. With parallel superposition this theory will, however, owing to the term $2 a_1 g_o g_1$ in S^{11}, give rise to a new component in the normal stress which is proportional to aq and oscillates with an angular frequency ω.

Eq. (III 32) has been modified in many ways in order to obtain an improved description of the properties of viscoelastic media. Two of these modifications have been applied to superposition and will now be discussed.

b. The WJFLMB model

Ward and Jenkins[25)] extended Eq. (III 32) to

$$\underline{P}(t) = \int_{-\infty}^{t} \left[\mu_1 \underline{S}(t') + \mu_2 \underline{G}(t') \right] dt' \tag{III 35}$$

where both μ_1 and μ_2 are memory functions depending on t–t', and $\underline{G}(t')$ represents the covariant strain tensor as defined by the Eqs (I 35) and (I 31). With the aid of these equations and Eq. (III 14), $\underline{G}(t')$ for the above case of flow can be calculated. The covariant strain tensor then has the following form:

$$\underline{G}(t') = \begin{vmatrix} 0 & -(g_o + \alpha_1 g_1) & 0 \\ -(g_o + \alpha_1 g_1) & (g_o + \alpha_1 g_1)^2 + \alpha_2^2 g_2^2 & -\alpha_2 g_2 \\ 0 & -\alpha_2 g_2 & 0 \end{vmatrix} \tag{III 36}$$

As appears from a comparison of Eqs (III 36) and (III 34), the only effect of introducing this tensor is that in the case of stationary shear there arises a second normal stress difference $p_{22} - p_{33}$, which is proportional to q^2.

Lodge[23] already suggested that the usability of Eq. (III 32) can be considerably improved by making the memory function a function of the shear rate in such a way that at any value of t–t' the function $\mu(t-t')$ will decrease with increasing shear rate. On the basis of this suggestion, Spriggs, Huppler and Bird[26] proposed the WJFLMB model. They started from Eq. (III 35), to which they added elements from various other theories in a more or less empirical manner. The memory functions are made dependent of the absolute value of the shear rate and written as a sum of exponentials with characteristic time constants $\lambda_n = \lambda / n^{\alpha}$, where λ and α represent constants that are to be adapted. In the case of steady shear flow, this model leads to the following formulas for the shear stress and the normal stresses[27]:

$$p_{21} = \frac{\eta_o}{\sum_n \lambda_n} \sum_{n=1}^{\infty} \frac{\lambda_n q}{1 + c^2 \lambda_n^2 q^2} \tag{III 37}$$

$$p_{11} - p_{22} = \frac{2\,\eta_o}{\sum_n \lambda_n} \sum_{n=1}^{\infty} \frac{\lambda_n^2 q^2}{1 + c^2 \lambda_n^2 q^2} \tag{III 38}$$

$$p_{22} - p_{33} = \epsilon\,(p_{11} - p_{22}) \tag{III 39}$$

The constants η_o, c and ϵ may also be obtained by adaptation to experimental results. So, in this theory there are five constants in all. Macdonald and Bird[28] applied this model to the case of parallel superposition, and found for the dynamic shear moduli:

$$G'(\omega,q) = \frac{\eta_o}{\sum_n \lambda_n} \sum_{n=1}^{\infty} \frac{\lambda_n^2 \omega^2 \left[(1 + \lambda_n^2 \omega^2) + c^2 \lambda_n^2 q^2 \; (\lambda_n^2 \omega^2 - 3) \right]}{(1 + \lambda_n^2 \omega^2)^2 \; (1 + c^2 \lambda_n^2 q^2)^2} \tag{III 40}$$

and

$$G''(\omega,q) = \frac{\eta_o}{\sum\limits_n \lambda_n} \sum_{n=1}^{\infty} \frac{\lambda_n \omega \, [(1+\lambda_n^2\omega^2) + c^2\lambda_n^2 q^2 \, (3\lambda_n^2\omega^2 - 1)]}{(1+\lambda_n^2\omega^2)^2 \, (1+c^2\lambda_n^2 q^2)^2} \qquad \text{(III 41)}$$

Comparing these formulae with the expressions (III 4) and (III 5) for $G'(\omega,q)$ and $G''(\omega,q)$ we found on the basis of the Oldroyd theory, one sees that the two objections a) and b) mentioned in section 2, viz. the small number of parameters, and the pole in the expressions (III 4) and (III 5), do not apply to the formulas (III 40) and (III 41). Furthermore, according to Eq. (III 40), $G'(\omega,q)$ may be negative at low values of ω and relatively high values of q. Therefore, Macdonald and Bird, succeeded by means of these expressions in giving a very reasonable description of the influence of q on $G'(\omega,q)$ and $G''(\omega,q)$ measured by Osaki, Tamura, Kurata and Kotaka[29] during parallel superposition.

According to Simmons[1], this model also gives a fairly quantitative description of the experimental results in the case of orthogonal superposition.

c. The network rupture theory

In Lodge's original theory $\mu(t-t')$ is independent of the state of deformation of the network. In the modification discussed above, $\mu(t-t')$ decreases at all values of $t-t'$ at increasing shear rate. Tanner and Simmons[1, 30] introduce a different assumption, viz. that during deformation of the network the function $\mu(t-t')$ in Eq. (III 32) is truncated at a given value of $t-t'$; this value is taken lower according as q is higher.

In the case of, e.g., simple shear flow, old portions of the network, i.e. network linkages that have existed for a long time, are very strongly deformed. Tanner and Simmons now assume that the network will be ruptured after a given time t_R (time to rupture) when a network linkage has been deformed to a given critical degree. This critical degree[31] comes somewhere between 1 and 10 and is indicated by B. At the moment of rupture, the memory function drops to zero. This implies that portions of the network older than a given time t_R will no longer contribute to the stress. In Lodge's theory, the deformation of a network linkage equals the simultaneous macroscopic deformation of the fluid, so that the strain tensors provide a direct measure of the deformation of the network. Tanner and Simmons advanced the rather arbitrary hypothesis that the critical degree of deformation is reached when

$$\mathrm{tr}\, \underline{S}(t') = B^2 \qquad \text{(III 42)}$$

From the matrix (III 34) it follows that for parallel superposition, this condition is

$$(g_o + a_1 g_1)^2 = B^2 \qquad \text{(III 43)}$$

and that for orthogonal superposition we have

$$g_o^2 + a_2^2 g_2^2 = B^2$$

The term $\alpha_2^2 g_2^2$ may be neglected because this term disturbs t_R to a degree proportional to α_2^2. In the case of steady shear flow at a constant rate the following equation must apply

$$q^2 t_R^2 = B^2$$

so that the age t_R of the oldest, still existing junction is given by

$$t_R = B/|q| \tag{III 44}$$

In view of what has been said above, calculation of the stresses with Eq. (III 32) requires that the lower limit of the integral be replaced by $t-t_R$.

The memory function of Eq. (III 32) is often written as a sum of exponential functions

$$\mu(t-t') = \sum_n \frac{a_n}{\tau_n^2} \exp\left[-\frac{t-t'}{\tau_n}\right] \tag{III 45}$$

where a_n and τ_n are constants having the dimensions of viscosity and time, respectively. During rupturing of the network this function becomes suddenly equal to zero, so that $\mu(t-t')$ is given by Eq. (III 45) for $t_R > t-t' \geqslant 0$ and $\mu(t-t') = 0$ for $t-t' \geqslant t_R$.

From Eq. (III 32) it now follows that at a constant rate of shear as well as at orthogonal superposition two stress components are given by1, 30-32)

$$p_{21} = q \sum_n \int_0^{t_R} \frac{a_n}{\tau_n^2} (t-t') \exp\left[-\frac{t-t'}{\tau_n}\right] d(t-t') =$$

$$= q \sum_n a_n \left[1-(1+\frac{t_R}{\tau_n})\, e^{-t_R/\tau_n}\right] = q \sum_n a_n \left[1-(1+\frac{B}{q\,\tau_n})\, e^{-B/(q\,\tau_n)}\right] \tag{III 46}$$

$$p_{11} = 2\, q^2 \sum_n a_n \tau_n \left[1-(1+\frac{t_R}{\tau_n}+\frac{t_R^2}{2\,\tau_n^2})\, e^{-t_R/\tau_n}\right] \tag{III 47}$$

During orthogonal superposition there arises a shear stress which equals1, 30)

$$p_{32} = \alpha \int_0^{t_R} \mu(t-t') \left[\sin\omega t - \sin\omega t'\right] d(t-t') =$$

$$= \alpha\, G'(\omega,q) \sin\omega t + \alpha\, G''(\omega,q) \cos\omega t \tag{III 48}$$

with

$$G'(\omega,q) = \sum_n \frac{a_n}{\tau_n(1+\omega^2\tau_n^2)} \left[\omega^2\tau_n^2 - (1+\omega^2\tau_n^2+\omega\tau_n \sin\omega t_R - \cos\omega t_R) e^{-t_R/\tau_n}\right] \tag{III 49}$$

$$G''(\omega,q) = \sum_n \frac{a_n}{\tau_n(1+\omega^2\tau_n^2)} \left[\omega\tau_n - (\sin\omega t_R + \omega\tau_n \cos\omega t_R)\, e^{-t_R/\tau_n}\right] \qquad \text{(III 50)}$$

In all these formulae t_R is given by Eq. (III 44). As can be seen from the above formulae, it follows from this theory that in the case of orthogonal superposition $G'(\omega,q)$ and $G''(\omega,q)$ remain positive at all values of ω and of t_R, i.e. of q.

With parallel superposition, the situation is slightly more complicated. Eqs (III 34) and (III 42) give

$$|q t_{R'} + \alpha \sin\omega t - \alpha \sin\omega(t - t_{R'})| = B$$

from which it follows[32] that, with an accuracy up to the order of α,

$$t_{R'} = \frac{B}{q} - \frac{\alpha}{q}\left\{\sin\omega t - \sin\omega\left(t - \frac{B}{q}\right)\right\} \qquad \text{(III 51)}$$

Substitution of this expression in the upper limit of the integral (III 46) introduces additional negative terms into the Eqs (III 49) and (III 50) for $G'(\omega,q)$ and $G''(\omega,q)$; a similar feature has been mentioned in our discussion of the thixotropy theory in the preceding section. These terms are equal to

$$\Delta G' = \sum_n \frac{a_n t_R}{\tau_n^2} e^{-t_R/\tau_n} \left[1 - \cos\omega t_R\right] \qquad \text{(III 52)}$$

and

$$\Delta G'' = \sum_n \frac{a_n t_R}{\tau_n^2} e^{-t_R/\tau_n} \sin\omega t_R \qquad \text{(III 53)}$$

Owing to these terms the dynamic moduli in the case of parallel superposition may become negative at low frequencies[32].

Consequently, this theory of the network rupture also discloses a distinct difference between the effects of the two types of superposition.

Simmons and Tanner used the equations (III 49) and (III 50) for $G'(\omega,q)$ and $G''(\omega,q)$ in their description of the results obtained in orthogonal superposition experiments. The constants a_n and τ_n were obtained by adapting the formula for G'' to the experimental results of pure oscillation measurements, while B was found by adapting the theoretical shear stresses as can be calculated as a function of q for various values of B with the aid of Eq. (III 46), to the shear stresses measured during steady rotation. B appears to be not quite independent of q, and the values found are between 2 and 6. By means of Eq. (III 47) the normal stress could then be calculated as a function of the shear stress. This calculated p_{11} was found to increase less sharply with q than had been observed experimentally.

Next, the dynamic moduli in the case of orthogonal superposition were calculated with the aid of Eqs (III 44), (III 49) and (III 50) and the constants found. The agreement with the experimental results is indeed good over the major part of the frequency range measured, but less satisfactory for $G'(\omega,q)$ at lower frequencies. This is because, in theory, the slope of the curves of $\log G'$ as a function of $\log \omega$ is always approximately equal to 2 at low values of ω and high values of q, whereas, as can clearly be seen from Fig. II,11 where $G'(\omega,q)/\omega^2$ vs ω goes through a maximum, the slope found from experiments is occasionally much larger. Furthermore, from a quantitative point of view it is remarkable that at low frequencies and high shear rates the dynamic viscosity found experimentally is always higher than the theoretical value.

5. Considerations on nearly viscometric flows

The treatises in this section are mostly based on Noll's theory of simple fluids33). The often used linearized rheological equations of state can be represented34) in a form analogous to Eq. (III 35), and for this reason the present section might have been added to the previous one. However, in this section we intend to review several theoretical treatments which all lead up to limit relations only.

Superposition flows as dealt with so far can be looked upon as viscometric flows with a constant rate of shear which are disturbed by small time-dependent displacements. As such, flows of this type come exactly under the category of the nearly viscometric flows introduced by Pipkin and Owen35). The theory dealing with flows of this type starts from the covariant strain tensor. The cases of superposition belong in the non-viscometric flow field (III 14) the covariant strain tensor for which is given in Eq. (III 36). The functions $\alpha_1 g_1$ and $\alpha_2 g_2$ are now considered to be disturbances of the viscometric main flow which, with $t-t' = s$, has the strain tensor:

$$\underline{G}^0 = \begin{vmatrix} 0 & -qs & 0 \\ -qs & q^2s^2 & 0 \\ 0 & 0 & 0 \end{vmatrix}$$

The additional strain caused by the disturbance superposed on this viscometric flow is indicated by $\Delta\underline{G} = \underline{G} - \underline{G}^0$, and is equal to

$$\Delta\underline{G} = \begin{vmatrix} 0 & -\alpha_1 g_1 & 0 \\ -\alpha_1 g_1 & 2\alpha_1 g_o g_1 & -\alpha_2 g_2 \\ 0 & -\alpha_2 g_2 & 0 \end{vmatrix} + \begin{vmatrix} 0 & 0 & 0 \\ 0 & \alpha_1^2 g_1^2 + \alpha_2^2 g_2^2 & 0 \\ 0 & 0 & 0 \end{vmatrix} \qquad \text{(III 54)}$$

We assume that the second-order terms in the second tensor may be neglected against the first-order terms in the first tensor. The theory of nearly viscometric flows assumes that the additional stresses Δp_{ij} are linear in the additional deformations ΔG_{ij}, so that they can be written as35):

$$\Delta p_{ij}(t) = \int_0^\infty \sum_k \sum_l S_{ijkl}(q,s)\, \Delta G_{kl}\, ds \qquad \text{(III 55)}$$

Here, S_{ijkl} are material quantities (relaxation moduli) which depend on the shear rate q of the viscometric main flow and on the time lapse s. These quantities must satisfy a few special symmetry rules, viz.

$$S_{ijkl} = S_{jikl} = S_{ijlk} = S_{jilk} \text{ and } \sum_i S_{iikl} = 0 \qquad \text{(III 56)}$$

Moreover, all S_{ijkl} functions disappear if an odd number of indices are equal to 3, while the functions that have an odd, or even, number of indices equal to 1, or 2, are odd, or even, functions of q. Applying formula (III 56) to the case where $\Delta \underline{G}$ is given by Eq. (III 55), then we find for the total stresses in the case of superposition

$$p_{12} = \eta(q)q + \int_0^\infty (S_{1212}\alpha_1 g_1 - S_{1222}\; 2\alpha_1 g_o g_1)\, ds \qquad \text{(III 57a)}$$

$$p_{13} = \int_0^\infty S_{1323}\alpha_2 g_2\, ds \qquad \text{(III 57b)}$$

$$p_{23} = \int_0^\infty S_{2323}\alpha_2 g_2\, ds \qquad \text{(III 57c)}$$

$$p_{ii} = \beta_{ii}(q)\, q^2 + \int_0^\infty (S_{ii12}\alpha_1 g_1 - S_{ii22}\; 2\alpha_1 g_o g_1)\, ds\colon\; i = 1, 2, 3 \qquad \text{(III 57d)}$$

This case of superposition has also been dealt with by Pipkin36) and by Markovitz37), but their results do not contain the products $\alpha_1 g_o g_1$. In my opinion the above authors are wrong in considering these products to be second-order terms. Although the products are proportional to α_1, they also contain the factor q(t–t'), which may assume a large value. Hence, they are certainly of the first order.

The remarkable feature of this theory is that it discloses that stress components Δp_{ij} may occur when the corresponding strain components ΔG_{ij} are equal to zero. For example a superposed orthogonal deformation $\alpha_2 g_2$ will influence not only p_{23} but also p_{13}.

With parallel superposition, the full expressions for the additional stresses read:

$$\Delta p_{12} = \alpha \int_0^\infty (S_{1212} - 2S_{1222}\; qs)\left[(1-\cos\omega s)\sin\omega t + \sin\omega s\cos\omega t\right] ds \qquad \text{(III 58a)}$$

$$\Delta p_{ii} = \alpha \int_0^\infty (S_{ii12} - 2\,S_{ii22}\; qs) \left[(1 - \cos \omega s) \sin \omega t + \sin \omega s \cos \omega t \right] ds \tag{III 58b}$$

so that

$$G'(\omega,q) = \int_0^\infty (S_{1212} - 2\,S_{1222}\; qs)\;(1 - \cos \omega s)\; ds \tag{III 59}$$

$$G''(\omega,q) = \int_0^\infty (S_{1212} - 2\,S_{1222}\; qs) \sin \omega s\; ds \tag{III 60}$$

Analogous expressions are found for $N'(\omega,q)$ and $N''(\omega,q)$. At low values of ω, $\cos \omega s$ and $\sin \omega s$ can be written as power series, from which it follows that at all values of q

$$\lim_{\omega \to 0} \frac{G'(\omega,q)}{\omega^2} = \int_0^\infty (S_{1212} - 2\,S_{1222}\; qs)\; \tfrac{1}{2} s^2\; ds \tag{III 61}$$

$$\lim_{\omega \to 0} \frac{G''(\omega,q)}{\omega} = \int_0^\infty (S_{1212} - 2\,S_{1222}\; qs)\; s\; ds \tag{III 62}$$

Suppose now that αg_1 is not an oscillatory function, but a parallel incremental simple shear. In that case $\alpha g_1 = (\Delta q)s$, where $\Delta q \ll q$. According to Eq. (III 57) the superposed shear stress (see also Eq. (3.3) of ref. 36) is now given by:

$$\Delta p_{12} = \Delta q \int_0^\infty (S_{1212} - 2\,S_{1222}\; qs)\; s\; ds \tag{III 63}$$

The resulting flow is again a viscometric flow, but the shear rate now equals $q + \Delta q$. Hence:

$$\Delta p_{12} = \frac{d(p_{12})_{rot}}{dq}\, \Delta q + \text{terms of higher order in } \Delta q \tag{III 64}$$

From Eqs (III 63) and (III 64) it follows that

$$\frac{d(p_{12})_{rot}}{dq} = \int_0^\infty (S_{1212} - 2\,S_{1222}\; qs)\; s\; ds \tag{III 65}$$

and therefore, in the case of parallel superposition,

$$\lim_{\omega \to 0} \frac{G''(\omega,q)}{\omega} = \eta_d^{\parallel}(0,q) = \frac{d(p_{12})_{rot}}{dq} = \eta(q) \left[1 + \frac{d \ln \eta}{d \ln q} \right] \tag{III 66}$$

For polymeric liquids η usually decreases with q, so that the term d ln η/ d ln q is negative. For this type of non-newtonian liquids it follows from the present theory that in the case of parallel superposition

$$\eta_d^{\|}(o,q) < \eta(q) \tag{III 67}$$

For orthogonal superposition Eq. (III 57c) gives

$$p_{23} = \alpha\, G'(\omega,q) \sin \omega t + \alpha\, G''(\omega,q) \cos \omega t$$

with

$$G'(\omega,q) = \int_o^\infty S_{2323}(q,s)\,(1 - \cos \omega s)\, ds$$

and

$$G''(\omega,q) = \int_o^\infty S_{2323}(q,s) \sin \omega s\, ds \tag{III 68}$$

If αg_2 denotes a small simple shear $(\Delta q)s$ with $\Delta q \ll q$, the overall flow includes a small angle with the direction of the main viscometric flow. The stress

$$p_{23} = \Delta q \int_o^\infty S_{2323}(q,s)\, s\, ds$$

is then found to equal $\Delta q \eta(q)$ with an accuracy up to the order of Δq. In the case of orthogonal superposition this relation, combined with Eq. (III 68), gives:

$$\eta_d^{\perp}(o,q) = \eta(q) \tag{III 69}$$

The main result of this theory on nearly viscometric flows therefore is

$$\frac{d(p_{12})_{rot}}{dq} = \eta_d^{\|}(o,q) < \eta_d^{\perp}(o,q) = \eta(q) \tag{III 70}$$

The theory further contains a large number of unknown functions. However, as there exist many relations like Eq. (III 65) – the so-called self-consistency relations[35] – suitable relations can be found in all kinds of limiting cases.

Another approach starts from the BKZ-fluid theory of Bernstein, Kearsley and Zapas[38]. The rheological equation of state used can again be written in the form of Eq. (III 35) (see ref. 34, p. 120 ff), where the relaxation functions μ_1 and μ_2 are, however, no longer mutually independent and are functions not only of s but also of the invariants of $\underline{G}$, so of the absolute value of the strain. Bernstein[39], applying this equation to the case of parallel superposition, obtained four rheological relations which, expressed in our notation, are of the following form

$$\lim_{\omega\to o} \frac{G''(\omega,q)}{\omega} = \frac{d}{dq}(p_{21})_{rot} \qquad \text{(R-1)}$$

$$\lim_{\omega\to o} \frac{2\,G'(\omega,q)}{\omega^2} = \frac{d}{dq}\,\frac{(p_{11}-p_{22})_{rot}}{q} \qquad \text{(R-2)}$$

$$\lim_{\omega\to o} \frac{2\,q\,N''(\omega,q)}{\omega} = \frac{d}{dq}(p_{11}-p_{22})_{rot} \qquad \text{(R-3)}$$

$$\lim_{\omega\to\infty} 2\,q\,N'(\omega,q) = \frac{d}{dq}\,q(p_{21})_{rot} \qquad \text{(R-4)}$$

The first relation is equivalent to Pipkin's36) equation (III 66) for simple fluids. Bernstein and Fosdick40) demonstrated that the relations (R-2) and (R-4) are valid only in the BKZ-theory, whereas (R-1) and (R-3) hold also for general simple fluids. The right-hand members of (R-1), (R-3) and (R-4) are positive at all values of q, but if the slope of the curve of $\log(p_{11}-p_{22})_{rot}$ versus log q drops below unity, the right-hand member of (R-2) will become negative, with the result that $G'(\omega,q)$ will be negative at sufficiently low frequencies. Bernstein and Fosdick40) state that, as far as they have been able to ascertain, the relation (R-2) does not conflict with the results of superposition studies22) performed by the present author. A more accurate consideration of the normal stress data for the solutions investigated (Fig. II,2) discloses that the slopes of the curves are indeed smaller than unity for the solutions 2, 3 and 4 at all values of q, but larger than unity for the solutions 1 and 5 at log q values smaller than 0.3 and 1.5, respectively. However, all solutions satisfy the relation $\omega_o = ½\,q$. Experiments performed on solution 1 at log q values of −0.5, −0.3, 0.0 and 0.3 and on solution 5 at log q values of −0.4, 0.0, 0.4 and 0.8 confirm this relation, but the slopes of the curves are larger than unity at these rates of shear. This proves that relation (R-2) does conflict with the author's results. Moreover, the other relations can hardly be verified, especially, because it is very difficult on the basis of experimental evidence to say anything definite about the limit values of the normal stress components.

Walters and Jones41) treat superposition with the aid of a third-order integral equation given by Pipkin42), which, however, also comprises many unknown functions. Although their approach will not be discussed further here, it is interesting to note that the above authors also arive at Eq. (III 66) in exactly the same form as given here, and confirm it experimentally.

6. Some entirely different approaches

Overdiep43) describes a mechanical model which, from the mathematical angle, is equivalent to a Maxwell element (spring in series with dashpot) connected in series with a Kelvin-Voigt element (spring parallel to dashpot). The viscosity of the dashpot of the Maxwell element is considered to depend on the deformation of the Kelvin-Voigt element.

This model comprises five parameters in all. It is used successfully for describing some of the experimental relationships between shear stress, shear rate and time given in the literature for some macro-molecular liquids. The dynamic behaviour of the liquid during parallel superposition proves to be given by a second-order differential equation in which two coefficients are dependent on q. By adapting the constants, Overdiep succeeded in giving a very reasonable description of the properties displayed by the solution of aluminium dilaurate mentioned in chapter II. Of course, the model is uni-dimensional. It cannot be transformed into a three-dimensional one, and, in consequence, is unfit for describing normal stresses.

Evans, Warner, Ramakka and Bird[44)] gave a solution for Kirkwood and Plock's rotational diffusion equation for a suspension of rigid dumbbells[45)] in the flow field at parallel superposition. We shall not discuss this model any further here, but merely wish to refer to the work done by others on this point (ref. 46). The above authors have shown that the dynamic viscosity as a function of the frequency passes through a maximum and that, at low frequencies, $G'(\omega,q)$ becomes negative at high values of q. Hence, this model gives a qualitatively correct description of the effect q has on the dynamic shear moduli.

Booij and van Wiechen[47)] tackled the problem of superposition from an entirely different angle. In their approach they started from Rouse's molecular theory, which will be discussed extensively in the next chapter. Since the experimental results clearly demonstrate that in the case of parallel superposition $G'(\omega,q)$ may decrease strongly, they searched for a molecular mechanism that would allow the more or less periodical dilatation a macromolecule undergoes during steady shear flow to interact somehow with the periodical deformation caused by the superposed oscillation. They thought that the concept of the internal viscosity of macromolecules advanced by Kuhn and Kuhn[48)] might come in useful here. Into each segment of the Rouse model they introduced an internal viscosity force acting in the direction of the line connecting the end points of the segment, and being proportional to the rate at which the distance between the end points of the segment is changed. In principle, this modified Rouse model can be treated mathematically in its entirety, but a full calculation was carried out only for a single-segment dumbbell model with a low internal viscosity. This treatment demonstrated that under certain conditions $G'(\omega,q)$ can indeed be negative. However, the most important effect of the internal viscosity proved to be that in the case of superposition $G''(\omega,q)$ increases strongly with increasing values of the steady shear rate q. As this effect is distinctly incompatible with the experimental results, we feel justified in leaving this approach out of consideration in the further part of our study.

7. Discussion

A review of the theoretical treatments of the superposition problem dealt with in this chapter shows that in many theories a viscoelastic liquid is looked upon as an assembly of elements which, after an enforced deformation, relax with different relaxation times τ. The stresses at a given time t are defined by the strains, or rates of strain, of the elements at all previous times t', and by a relaxation function $N(\tau) \exp[-(t-t')/\tau]$, where

$N(\tau)$ denotes the number of elements with relaxation times τ. If, now, this relaxation function is not influenced by the steady shear of the liquid, the system will exhibit a newtonian viscosity and a normal stress proportional to the square of the shear rate q, i.e. a second-order behaviour. In that case, the dynamic properties measured during parallel superposition would be independent of q.

However, as found experimentally, many of the viscoelastic liquids described in the literature have quite different properties. In order to explain these, we have, in this chapter, dealt with various suppositions regarding the effect a steady rate of shear q might have on the relaxation function. The WJFMB model is based on the supposition that, at any value of τ, the number of relaxation mechanisms decreases with increasing q, which would imply that the effect deformations at previous times t' have on the stress at time t, will be smaller at high than at low shear rates. Tanner's theory of network-rupture supposes that a deforming element will rupture the moment the strain of the element exceeds a given value and that, whatever their relaxation time, elements in a steady shear flow will rupture after a deformation time t_R that is inversely proportional to the value of q. This implies that only the deformations of the liquid that took place within the time interval from $(t-t_R)$ to t will contribute to the stresses at time t. Finally, Leonov, who advances the thixotropy theory, supposes that a deforming element will rupture, and no longer make a contribution to the stress, as soon as the stored elastic energy comes to exceed a given critical value. Elements with longer relaxation times break down sooner than those with shorter relaxation times, while elements with relaxation times shorter than τ_m are not affected at all. The maximum relaxation time τ_m of elements that still contribute to the stresses during steady shear flow is found to be inversely proportional to q.

The above assumptions enabled the advocates of the respective theories to describe such phenomena as non-newtonian viscosity and deviations from second-order liquid behaviour in stationary shear flows. Further, these assumtions lead up to the conclusion that during parallel superposition the superposed oscillation will give rise to an additional oscillatory structural breakdown,with the result that negative terms are introduced into the expressions for the dynamic quantities. Another conclusion drawn from all these theories is that the superposed oscillation during orthogonal superposition does not have an additional effect on the structural breakdown.

The way in which the elastic energy is calculated in the thixotropy theory seems rather doubtful, while the network theory uses a fairly arbitrary measure of the maximum strain of the element. A clear shortcoming of all these theories is their lack of a definite physical-molecular basis permitting the derivation of an unambiguous criterion of the influence the deformation history has on the structural breakdown in viscoelastic liquids. In the following chapter we shall attempt, by means of a molecular model, to obtain some more clarity on this point, and, next, to use the theory so developed (the generalized pearl-necklace model or disentanglement theory) in tackling the superposition problem.

8. References

1. J.M. Simmons, Ph.D.Thesis, Sydney, 1967
2. J.G. Oldroyd, Proc. Roy. Soc. **A200**, 523 (1950)
3. J.G. Oldroyd, Proc. Roy. Soc. **A218**, 122 (1953)
4. H. Fröhlich and R. Sack, Proc. Roy. Soc. **A185**, 415 (1946)
5. J.G. Oldroyd, Proc. Roy. Soc. **A245**, 278 (1958)
6. J.G. Oldroyd, Rheol. Acta **1**, 337 (1961)
7. J.G. Oldroyd, Proc. Roy. Soc. **A283**, 115 (1965)
8. M.C. Williams and R.B. Bird, Phys. Fluids **5**, 1126 (1962)
9. M.C. Williams and R.B. Bird, I. & E.C. Fund. **3**, 42 (1964)
10. H.C. Booij, Rheol. Acta **5**, 222 (1966)
11. H.C. Booij, Rheol. Acta **7**, 202 (1968)
12. J. Yerushalmi, S. Katz and R. Shinnar, Chem. Eng. Sci. **24**, 1371 (1969)
13. R.I. Tanner and J.M. Simmons, Chem. Eng. Sci. **22**, 1079 (1967)
14. J.R.A. Pearson and C.J.S. Petrie, Polymer Systems, Deformation and Flow, Eds. R.E. Wetton and R.W. Whorlow, Macmillan, London, 1968, p. 163
15. K. Walters, Quart. J. Mech. Appl. Math. **13**, 444 (1960); **15**, 63 (1962)
16. K. Walters, Journ. de Méc. **1**, 479 (1962)
17. K. Walters, in: Second-order Effects in Elasticity, Plasticity and Fluid Dynamics, Eds. M. Reiner and D. Abir, Pergamon Press, Oxford, 1965, p. 507
18. A.I. Leonov and G.V. Vinogradov, Doklady Akad. Nauk SSSR. **155**, 406 (1964)
19. A.I. Leonov, Zh.P.M.T.F. (J. Appl. Mech. Techn. Phys.) **4**, 78 (1964)
20. A.I. Leonov and A.Ya. Malkin, Zh.P.M.T.F. **5**, 68 (1965)
21. A.I. Leonov, M.G. Tsiprin and L.A. Faitel'son, Mekh. Polim. **5**, 519 (1969)
22. H.C. Booij, Rheol. Acta **5**, 215 (1966)
23. A.S. Lodge, Elastic Liquids, Academic Press, London, 1964
24. A.S. Lodge, Trans. Faraday Soc. **52**, 120 (1956)
25. A.F.H. Ward and G.M. Jenkins, Rheol. Acta **1**, 110 (1958)
26. T.W. Spriggs, J.D. Huppler and R.B. Bird, Trans. Soc. Rheol. **10**, 191 (1966)
27. E. Ashare, Trans. Soc. Rheol. **12**, 535 (1968)
28. I.F. Macdonald and R.B. Bird, J. Phys. Chem. **70**, 2068 (1966)
29. K. Osaki, M. Tamura, M. Kurata and T. Kotaka, J. Phys. Chem. **69**, 4183 (1965)
30. R.I. Tanner and J.M. Simmons, Chem. Eng. Sci. **22**, 1803 (1967)
31. R.I. Tanner, AIChE Journal **15**, 177 (1969)
32. R.I. Tanner, Trans. Soc. Rheol. **12**, 155 (1968)
33. W. Noll, Arch. Rational Mech. Anal. **2**, 197 (1958)
34. S. Middleman, The Flow of High Polymers, Interscience, New York, 1968
35. A.C. Pipkin and D.R. Owen, Phys. Fluids **10**, 836 (1967)
36. A.C. Pipkin, Trans. Soc. Rheol. **12**, 397 (1968)
37. M. Markovitz, Proc. Vth Intern. Congr. Rheol., Vol. I, Kyoto, 1968
38. B. Bernstein, E.A. Kearsley and L.J. Zapas, Trans. Soc. Rheol. **7**, 391 (1963)

39. B. Bernstein, J. Nonlinear Mech. 4 (1968)
40. B. Bernstein and R.L. Fosdick, Rheol. Acta 9, 186 (1970)
41. K. Walters and T.E.R. Jones, Proc. Vth Intern. Congr. Rheol., Vol. IV, Kyoto, 1968
42. A.C. Pipkin, Rev. Mod. Phys. 36, 1034 (1964)
43. W.S. Overdiep, Rheol. Acta 8, 339 (1969)
44. D.C. Evans, H.R. Warner, W.R. Ramakka and R.B. Bird, J. Chem. Phys. 52, 4086 (1970)
45. J.G. Kirkwood and R.J. Plock, J. Chem. Phys. 24, 665 (1956)
46. R.B. Bird, H.R. Warner and W.R. Ramakka, J. Chem. Phys. 52, 2001 (1970)
47. H.C. Booij and P.H. van Wiechen, J. Chem. Phys. 52, 5056 (1970)
48. W. Kuhn and H. Kuhn, Helv. Chim. Acta 28, 1533 (1945); 29, 71 (1946)

Chapter IV

MOLECULAR THEORY

1. Pearl-necklace model

In the pearl-necklace model of a linear macromolecule in solution, inspired by the ideas of Kuhn[1], the molecule is regarded as a chain of submolecules (*segments* or *links*). These segments constitute the connections between *beads* in which the hydrodynamic resistance of the monomers of a segment is supposed to be concentrated. Part of the chain model used is represented in the figure below.

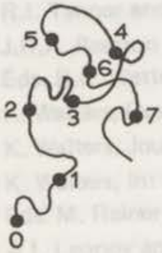


Fig. IV,1 Part of the necklace model used

The length of a segment is determined by the conformation of the monomers within this segment. In principle, the number of monomers comprised in one segment is only limited by the requirement that the segments should not be impeded in rotating with respect to one another.

The position of the centre of gravity of the beads is taken to be an independent variable.

It is further assumed that as long as no external forces act on the solution, the two following conditions will be satisfied:

1) the length of a segment can be described by a, normally gaussian, distribution function ϕ.

2) the length of the various segments and the position of the centre of gravity are mutually independent.

Let us assume that the above conditions can be met by dividing the macromolecule into n segments constituting the links between n + 1 beads. The conformation of the macromolecule can then be described by means of a cartesian coordinate system in which $\underline{r}_o$, $\underline{r}_1, \ldots, \underline{r}_n$ are the position vectors of the beads and every $\underline{r}_i$ has the components x_i, y_i, z_i. Let $\underline{R}$ be a rectangular matrix of n + 1 rows and three columns, with the transposed vectors $\underline{r}_i^T$ forming the rows. The matrix $\underline{R}$ then completely defines the position and the conformation of the macromolecule.

We now introduce the concept of *a complex of macromolecules*. A complex consists of x macromolecules which may be completely independent of each other, entangled or crosslinked. The number x is a parameter determined by the nature of the system considered. For a very dilute solution x can be taken equal to 1, but for a concentrated solution, or a non-dilute polymeric fluid, x may, in principle, be very large. We first suppose that all macromolecules in the complex are equally long. The complex then consists of x(n + 1) beads and xn segments. The location and the whole conformation of the complex can be completely defined by an x(n + 1) x 3 matrix $\underline{R}$, the rows in which represent the coordinates of the beads.

The conformation of a complex can also be defined by giving the dimensionless position vectors of the x centres of gravity of the individual macromolecules and of the xn dimensionless position differences of the successive beads. This is done as follows: number the beads of the first molecules from 0 up to and including n, those of the second from n + 0 up to 2 n, etc, and those of the x-th molecule from (x−1)n + 0 up to xn. Let $3\,b^2$ be the mean square of the segment lengths if no forces are exerted on the fluid*). The coordinates of the x centres of gravity then follow from

$$\underline{s}_p = \frac{1}{b} \sum_{k=(p-1)n+0}^{pn} \underline{r}_k \qquad \text{for } p = 1, 2, \ldots x \qquad \text{(IV 1,1)}$$

and the xn coordinate differences from

$$\underline{s}_i = \frac{1}{b}(\underline{r}_i - \underline{r}_{i-1}) \qquad \text{for} \begin{cases} i = 1, 2, \ldots n, n+1, \ldots xn \\ i-1 = 0, 1, \ldots n-1, n+0, \ldots xn-1 \end{cases} \qquad \text{(IV 1,2)}$$

Denote the components of $\underline{s}_p$ by u_p, v_p, w_p, and those of $\underline{s}_i$ by u_i, v_i, w_i. Let $\underline{S}$ be a rectangular matrix of x(n + 1) rows and three columns. The first x rows are formed by the transposed vectors $\underline{s}_p^T$, and the following xn rows by the vectors $\underline{s}_i^T$. Now the location and the conformation of the complex are completely fixed also by the matrix $\underline{S}$.

$\underline{S}$ and $\underline{R}$ are unambiguously related by the expression

$$\underline{S} = \frac{1}{b}\,\underline{a}\,\underline{R} \qquad \text{(IV 1,3)}$$

where $\underline{a}$ is a square x(n+1) *x* x(n+1) matrix. An example of this transformation matrix for the case x=4 is shown below.

---

*) Under these conditions $3\,b^2$ denotes the average value of $(x_i - x_{i-1})^2 + (y_i - y_{i-1})^2 + (z_i - z_{i-1})^2$ for i = 1, 2, . . . n, n + 1, ... xn and i−1 = 0,1, ... n−1, n + 0, ... xn−1. This value can be related to the monomer length l_m and to the number of monomers in one segment n_m by means of the expression $3\,b^2 = \alpha n_m^{\gamma} l_m^2$. The parameters α and γ denote quantities that are affected by all kinds of refinements of the model, such as the thermodynamic (equilibrium) flexibility of the chain2), the swelling power of the solvent3), the excluded volume effect4-6), the finiteness of n, the concentration of the solution, the temperature, etc. At very large values of $r_i - r_{i-1}$ 7, 8), as well as at small values of n_m 9-11), use has to be made of non-gaussian statistics.

$$\underline{a} = \left[\begin{array}{cccccccccccccccccccccccc}
1 & 1 & 1 & \cdots & 1 & 1 & 0 & 0 & 0 & \cdots & 0 & 0 & 0 & 0 & 0 & \cdots & 0 & 0 & 0 & 0 & 0 & \cdots & 0 & 0 \\
0 & 0 & 0 & \cdots & 0 & 0 & 1 & 1 & 1 & \cdots & 1 & 1 & 0 & 0 & 0 & \cdots & 0 & 0 & 0 & 0 & 0 & \cdots & 0 & 0 \\
0 & 0 & 0 & \cdots & 0 & 0 & 0 & 0 & 0 & \cdots & 0 & 0 & 1 & 1 & 1 & \cdots & 1 & 1 & 0 & 0 & 0 & \cdots & 0 & 0 \\
0 & 0 & 0 & \cdots & 0 & 0 & 0 & 0 & 0 & \cdots & 0 & 0 & 0 & 0 & 0 & \cdots & 0 & 0 & 1 & 1 & 1 & \cdots & 1 & 1 \\
-1 & 1 & 0 & \cdots & 0 & 0 \\
0 & -1 & 1 & & 0 & 0 \\
0 & 0 & -1 & & 0 & 0 \\
\vdots & & & & & \vdots \\
0 & 0 & 0 & & 1 & 0 \\
0 & 0 & 0 & \cdots & -1 & 1 \\
& & & & & & -1 & 1 & 0 & \cdots & 0 & 0 \\
& & & & & & 0 & -1 & 1 & & 0 & 0 \\
& & & & & & 0 & 0 & -1 & & 0 & 0 \\
& & & & & & \vdots & & & & & \vdots \\
& & & & & & 0 & 0 & 0 & & 1 & 0 \\
& & & & & & 0 & 0 & 0 & \cdots & -1 & 1 \\
& & & & & & & & & & & & -1 & 1 & 0 & \cdots & 0 & 0 \\
& & & & & & & & & & & & 0 & -1 & 1 & & 0 & 0 \\
& & & & & & & & & & & & 0 & 0 & -1 & & 0 & 0 \\
& & & & & & & & & & & & \vdots & & & & & \vdots \\
& & & & & & & & & & & & 0 & 0 & 0 & & 1 & 0 \\
& & & & & & & & & & & & 0 & 0 & 0 & \cdots & -1 & 1 \\
& & & & & & & & & & & & & & & & & & -1 & 1 & 0 & \cdots & 0 & 0 \\
& & & & & & & & & & & & & & & & & & 0 & -1 & 1 & & 0 & 0 \\
& & & & & & & & & & & & & & & & & & 0 & 0 & -1 & & 0 & 0 \\
& & & & & & & & & & & & & & & & & & \vdots & & & & & \vdots \\
& & & & & & & & & & & & & & & & & & 0 & 0 & 0 & & 1 & 0 \\
& & & & & & & & & & & & & & & & & & 0 & 0 & 0 & \cdots & -1 & 1
\end{array}\right] \qquad \text{(IV 1,4)}$$

The statistical distribution of the complex over the various conformations is described by a distribution function ψ of the variables $\underline{R}$ or $\underline{S}$. If no external forces are applied to the fluid, the conditions of independence formulated above are applicable. The special distribution function satisfying these conditions is called ϕ. In the absence of external forces, we can therefore put $\psi \equiv \phi$. From what has been said above it follows that in the case of a gaussian distribution, we have

$$\phi = \frac{\prod_{p=1}^{x} g_p(\underline{s}_p)}{(2\pi)^{3xn/2}} \exp\left[-\tfrac{1}{2}\sum_{i=1}^{n} \underline{s}_i^2\right] \qquad \text{(IV 1,5)}$$

where $g_p(\underline{s}_p)$ denotes a, still arbitrary, normalized distribution function for the centre of gravity of the p-th macromolecule. The function ϕ has been normalized over the relevant coordinates, i.e., $\int \phi \, d\underline{S} = 1$.

In the strongly simplified form of a single two-bead segment, the necklace model described above is referred to as the dumbbell model of Kuhn[12)]. Simplification of the complex to one macromolecule yields the necklade model which Rouse[13)] and Bueche[14)] used in 1953/1954 in their first complete description of a polymer molecule in a dilute solution under conditions of simple shear flow. In the following treatise we shall describe a complex of several entangled macromolecules acted upon by various types of flow fields. This treatment, although strongly formal, will prove useful in describing the features of real viscoelastic media.

2. Entropy-elastic forces

If forces are exerted on the fluid, the equilibrium distribution of the complexes will generally be distorted, and, hence, $\psi \neq \phi$. In this section, we shall calculate the force acting on the various beads of the complex as a result of the change of ψ. $\psi(\underline{R}_c)d\underline{R}_c$ is the fraction of complexes with the conformation c, that is to say with a conformation for which the variables $\underline{R}$ assume values between $\underline{R}_c$ and $\underline{R}_c + d\underline{R}_c$. We now introduce an ensemble consisting of υ complexes in a liquid volume V. The number of complexes in this ensemble, which adopts the conformation c, is denoted by m_c and equals

$$m_c = \upsilon\psi(\underline{R}_c)\, d\underline{R}_c \qquad \text{(IV 2,1)}$$

If no external forces are acting on the liquid, and $\psi = \phi$, the number of complexes with conformation c will be

$$m_{oc} = \upsilon\phi(\underline{R}_c)\, d\underline{R}_c \qquad \text{(IV 2,2)}$$

Wall[15)] calculated the difference in entropy between these two states of the ensemble from the difference in the number of possibilities for realization of the two states. According to this author, the difference in entropy is given by

$$\Delta S = k \sum_c m_c \ln (m_{oc}/m_c) \qquad \text{(IV 2,3)}$$

In what follows it will be assumed that during all changes in conformation the internal energy of the ensemble does not vary[*)]. We further suppose the temperature to be constant. The difference in free energy between the two states of the ensemble is then given by

$$\Delta F = -kT \sum_c m_c \ln (m_{oc}/m_c) \qquad \text{(IV 2,4)}$$

[*)] This assumption is certainly not valid for all polymers. For example, in the case of polyethylene, the difference in internal energy during deformation is proportional to the strain[16)]; this may give rise to large energy-elastic forces[17)].

The thermodynamical potential of the complexes with conformation c is equal to

$$\mu_c = \partial\Delta F/\partial m_c = kT\left[1 + \ln(m_c/m_{oc})\right] = kT\left[1 + \ln(\psi(\underline{R}_c)/\phi(\underline{R}_c))\right]$$

and, in general, to

$$\mu = kT\,[1 + \ln(\psi/\phi)] \tag{IV 2,5}$$

ΔF is an extensive quantity for the totality of all complexes in the ensemble. Calling the number of complexes per unit volume $N = \upsilon/V$, we find the free energy difference per unit volume of liquid from:

$$\Delta F = -NkT \int \psi \ln(\phi/\psi)\, d\underline{R} \tag{IV 2,6}$$

The thermodynamical potential μ is a function of the space coordinates of the beads of the complex and, hence, an intensive quantity*).

The gradient of the thermodynamic potential equals the entropy-elastic forces $\underline{F}^e$ acting on the beads of the complex:

$$\underline{F}^e = -\partial\mu/\partial\underline{R} \tag{IV 2,7}$$

where $\underline{F}^e$ is a matrix of $x(n+1)$ rows and three columns. The rows are formed by $x(n+1)$ vectors $\underline{f}_i^{eT}$ ($i = 0, 1, 2, \ldots.\, n, n+0, \ldots.\, xn$), representing the entropy-elastic forces acting on the various beads.

The matrix $\underline{F}^e$ can be transformed by means of the matrix $\underset{-}{a}$ into a new system of forces, according to

$$\underline{H}^e = \frac{1}{b}\, a\, \underline{F}^e \tag{IV 2,8}$$

$\underline{H}^e$ is a matrix with the transposed vectors $\underline{h}_p^{eT}$ as the first x rows and the vectors $\underline{h}_i^{eT}$ as the following xn rows. $\underline{h}_p^e$ represents 1/b times the sum of all forces acting on the beads of macromolecule p (i.e. the force on the centre of gravity p), whereas $\underline{h}_i^e$ ($i = 1, 2, \ldots.\, xn$) denotes 1/b times the difference between the forces on the i-th and the (i−1)-th bead.

Application of Eq. (IV 2,7) changes $\underline{H}^e$ into

$$\underline{H}^e = -\frac{1}{b}\, a\, \frac{\partial\mu}{\partial\underline{R}}$$

With $\underline{S} = 1/b\, \underset{-}{a}\, \underline{R}$, and, hence, with

$$\frac{\partial}{\partial\underline{R}} = \frac{1}{b}\, \underset{-}{a}^T \frac{\partial}{\partial\underline{S}}\,,$$ we get,

---

*) In the treatments of, for instance, DeWames c.s.18) and Blatz19), the free energy is considered to have intensive properties. As seen from the angle of thermodynamics, however, this view is incorrect.

$$\underline{H}^{e} = \frac{1}{b^2}\, \underline{a}\,\underline{a}^{T} \frac{\partial \mu}{\partial \underline{S}} \qquad \text{(IV 2,9)}$$

Substitution of Eq. (IV 2,5) in Eq. (IV 2,9), finally yields

$$\underline{H}^{e} = -\frac{kT}{b^2}\, \underline{a}\,\underline{a}^{T} \frac{\partial}{\partial \underline{S}} \ln \frac{\psi}{\phi} \qquad \text{(IV 2,10)}$$

as the expression for the entropy-elastic force acting on the beads*).

3. Friction forces

Let us suppose that a fluid is exposed to forces producing a macroscopic velocity profile. We shall denote this macroscopic velocity field by a matrix $\underline{V}_o$ the rows in which are constituted by the vectors $\underline{v}_{oi}^{T}$ representing the macroscopic velocity of the fluid at the positions $\underline{r}_i$ ($i = 0, 1, \ldots .n, n+0, \ldots .xn$).

Under conditions of flow, solvent, if present, as well as the other macromolecules will exert friction forces on the beads. An essential contribution to this friction may come from the entanglements between various macromolecules. We now assume that all macromolecules entangled in some way or another constitute a complex as meant above. As entanglement may take place in many ways, we have to give a more precise definition for our ensemble of complexes to which we wish to apply our considerations. For the time being, we shall consider an ensemble consisting of υ identical complexes, all of which comprise the same number (x) of macromolecules of equal length and all being in exactly the same state of entanglement. If the k-th bead contacts the l-th bead in one complex, it will do so in all other (υ–1) complexes.

Two special types of friction can be distinguished. Whereas some friction forces may owe their existence to the friction between solvent and beads, others may be caused by the friction between different macromolecules within one complex. Both types of friction

---

*) This entropy-elastic force is directly opposed to the force referred to in the treatments of e.g. Zimm[20)], DeWames c.s.[18)] and Blatz[19)]. However, since these authors use a wrong sign in drafting the equilibrium of forces, their equation of motion is still approximately identical to that found by us. Many investigators split up Eq. (IV 2,10) into the parts

$$-\frac{kT}{b^2}\, \underline{a}\,\underline{a}^{T} \frac{\partial \ln \psi}{\partial \underline{S}} \quad \text{and} \quad \frac{kT}{b^2}\, \underline{a}\,\underline{a}^{T} \frac{\partial \ln \phi}{\partial \underline{S}},$$

and call these the diffusion, or Brownian motion force, and the entropy-elastic spring force, respectively. Pao[21)] already remarks that this procedure is misleading. The difference between these 'forces' constitutes the total entropy-elastic force. The free energy is minimum if $\psi = \phi$ and, in that case, the beads are not exposed to any forces, except perhaps to fluctuating Brownian motion forces caused by fluctuations in the density of the surrounding medium. However, in view of the short times involved, these may normally be neglected.

forces will now be considered in the extreme cases where friction takes place either only between solvent and macromolecules, or only between macromolecules in the same complex.

The friction between bead i and solvent is supposed to be covered by Stoke's law. The friction force then equals the product of a friction coefficient f_i and the difference between the velocities of the surrounding solvent and the bead. We further assume that all beads have different friction coefficients. The friction forces exerted on the beads can then be written as

$$\underline{F}^f = \underline{f}(\underline{V}'_o - \dot{\underline{R}}) \qquad \text{(IV 3,1)}$$

where $\underline{f}$ is a diagonal matrix with elements f_i, $\dot{\underline{R}}$ is the velocity of the beads expressed in the matrix notation with the transposed velocities $\dot{\underline{r}}_i^T$ serving as the rows, and $\underline{F}^f$ denotes the friction forces acting on the beads. The matrix $\underline{V}'_o$ represents the effective velocity of the solvent at the location $\underline{R}$. The direction and magnitude of this effective velocity are not equal to those of the macroscopic velocity, but vary with the friction forces on all other beads. This hydrodynamic interaction can be accounted for by means of a matrix $\underline{T}$. The effective velocity equals

$$\underline{V}'_o = \underline{V}_o - \underline{T}\,\underline{F}^f \qquad \text{(IV 3,2)}$$

where $\underline{V}_o$ represents the macroscopic fluid velocity at the position $\underline{R}$, and $\underline{T}$ is an $x(n+1) \times x(n+1)$ matrix with regard to which we suppose that the elements T_{ik} are independent of the space coordinates $\underline{R}$ but may be functions of, e.g., the absolute value of the distance between the i-th and the k-th bead. This implies that in very dilute solutions $\underline{T}$ corresponds to the Kirkwood and Riseman[22] approximation of Oseen's interaction tensor[23]. We suppose, however, that also in more concentrated solutions the effect which a force $\underline{f}_k^f$ on the k-th bead exerts on the effective velocity at the i-th bead equals the effect which a force $\underline{f}_i^f$ on the i-th bead has on the velocity at the k-th bead, provided the two forces are equal, i.e., we suppose $\underline{T}$ to be symmetrical. Besides, $T_{ii} = 0$. From Eqs (IV 3,1) and (IV 3,2) it follows that the friction force the solvent exerts on the beads can be written as

$$\underline{F}^f = (\underline{f}^{-1} + \underline{T})^{-1}\,(\underline{V}_o - \dot{\underline{R}}) \qquad \text{(IV 3,3)}$$

where $(\underline{f}^{-1} + \underline{T})^{-1}$ is a symmetrical matrix, because $\underline{f}$ and $\underline{T}$ are symmetrical.

We shall now look at the other limit, namely the case that the friction is exclusively due to friction between entangled macromolecules within one complex. Suppose the beads k and l are in rubbing contact, and call the friction coefficient w. The friction force exerted by bead l on bead k then equals

$$\underline{f}_k^f = w\,(\dot{\underline{r}}_l - \dot{\underline{r}}_k) \qquad \text{(IV 3,4)}$$

where $\dot{\underline{r}}_l$ and $\dot{\underline{r}}_k$ represent the velocities of the l-th and k-th bead. But, because action = – reaction, we further have

$$\underline{f}_l^f = -\underline{f}_k^f = w\,(\dot{\underline{r}}_k - \dot{\underline{r}}_l) \qquad \text{(IV 3,5)}$$

This equation can also be written as

$$-\underline{f}_l^f = +\underline{f}_k^f = w\,(\underline{v}_{ok} - \dot{\underline{r}}_k - \underline{v}_{ol} + \dot{\underline{r}}_l) \qquad \text{(IV 3,6)}$$

because, with the beads k and l being in practically the same position, the macroscopical velocities $\underline{v}_{ok}$ and $\underline{v}_{ol}$ are equal. An identical line of reasoning may be followed with regard to each pair of beads k and l, provided allowance is made for the possibility that the friction coefficient w may differ from one case to the next. Hence, all friction forces between macromolecules within one complex can be represented by

$$\underline{F}^f = \underline{W}\,(\underline{V}_o - \dot{\underline{R}}) \qquad \text{(IV 3,7)}$$

where $\underline{W}$ is an x(n+1) *x* x(n+1) matrix of the friction coefficients. For any value of k and l Eq. (IV 3,6) can be found from Eq. (IV 3,7) by setting the elements W_{kk} and W_{ll} of $\underline{W}$ equal to w, and W_{kl} and W_{lk} equal to −w. This shows that $\underline{W}$ is a symmetrical matrix with equal elements in the diagonal positions (kk) and (ll), and with equally large, but negative, elements in the symmetrical positions (kl) and (lk).

Summarizing, we find that in cases where the friction is due to the solvent, as well as in those where the friction is caused by contact between beads within one complex, the friction forces can be described by a formula like (IV 3,7) in which a symmetric friction matrix occurs. By way of generalization, we may now state that also with the two types of friction occurring simultaneously the friction force is represented by Eq. (IV 3,7), where $\underline{W}$ is then something like the sum of terms appearing in Eqs (IV 3,3) and (IV 3,7).

Using an analogous procedure as in the case of Eq. (IV 2,8), we now introduce a transformed system of friction forces, according to

$$\underline{H}^f = \frac{1}{b}\,a\,\underline{F}^f \qquad \text{(IV 3,8)}$$

and define, in analogy to Eq. (IV 1,3):

$$\dot{\underline{S}}_o = \frac{1}{b}\,a\,\underline{V}_o \quad \text{and} \quad \dot{\underline{S}} = \frac{1}{b}\,a\,\dot{\underline{R}} \qquad \text{(IV 3,9)}$$

where $\dot{\underline{S}}_o$, and $\dot{\underline{S}}$, denote matrices of x(n+1) rows and three columns, with the vectors $\dot{\underline{s}}_{op}^T$ and $\dot{\underline{s}}_{oi}^T$, and $\dot{\underline{s}}_p^T$ and $\dot{\underline{s}}_i^T$, respectively, serving as the rows. Multiplication of Eq. (IV 3,7) by 1/b a gives

$$\underline{H}^f = a\,\underline{W}\,a^{-1}\,(\dot{\underline{S}}_o - \dot{\underline{S}}) \qquad \text{(IV 3,10)}$$

for the friction force on the beads.

4. Equations of motion

In developing the equations of motion, inertia forces are neglected*). Assuming balance of forces on all beads, we have**)

$$\underline{F}^e + \underline{F}^f = 0$$

and, after transformation,

$$\underline{H}^e + \underline{H}^f = 0 \qquad \text{(IV 4,1)}$$

Substitution of Eqs (IV 2,10) and (IV 3,10) gives:

$$-\frac{kT}{b^2}\,\underset{\sim}{a}\,\underset{\sim}{a}^T\,\frac{\partial \ln \psi/\phi}{\partial \underline{S}} + \underset{\sim}{a}\,\underline{W}\,\underset{\sim}{a}^{-1}\,(\dot{\underline{S}}_o - \dot{\underline{S}}) = 0 \qquad \text{(IV 4,2)}$$

which is equivalent to

$$-\frac{kT}{b^2}\,\underset{\sim}{a}\,\underline{W}^{-1}\,\underset{\sim}{a}^T\,\frac{\partial \ln \psi/\phi}{\partial \underline{S}} + \dot{\underline{S}}_o - \dot{\underline{S}} = 0 \qquad \text{(IV 4,3)}$$

The matrix $\underset{\sim}{a}\,\underline{W}^{-1}\underset{\sim}{a}^T$ is a mobility matrix, which, since $(\underset{\sim}{a}\,\underline{W}^{-1}\,\underset{\sim}{a}^T)^T = \underset{\sim}{a}\,\underline{W}^{-1\,T}\underset{\sim}{a}^T$, will be symmetric if $\underline{W}$ is symmetric. The matrix $\partial(\ln \psi/\phi)/\partial\underline{S}$ is an $x(n+1) \times 3$ matrix the first x rows of which represent differentiations to the positions of the centres of gravity of the x macromolecules of the complex. In the next section, it will be proved that, provided the macroscopic flow field meets one special condition, it is always allowed to suppose that the centres of gravity of the molecules are homogeneously distributed through the liquid, both before and after application of the flow field. Then, both ϕ and ψ are independent of $\underline{s}_p$, and $\partial(\ln \psi/\phi)/\partial \underline{s}_p$ is always equal to zero, and the first x rows of the matrix $\partial(\ln \psi/\phi)/\partial\underline{S}$ will contain zero's only. This implies that the first x columns of the matrix $\underset{\sim}{a}\,\underline{W}^{-1}\underset{\sim}{a}^T$ in Eq. (IV 4,3) can be replaced by columns with zero's without affecting the equations.

From Eq. (IV 4,3) it follows that the velocities of the centres of gravity are given by

---

*) This assumption is permissible because the characteristic time associated with the Brownian motion of a mass in a viscous medium -m/f (see refs. 9 and 24) - is very short compared with the experimental times. For a segment, f is of the order $6\,\pi\eta a_h m_m$, and $m = n_m M_m N_a^{-1}$, where M_m denotes the molecular weight of a monomer, N_a the Avogadro number and a_h a measure of the hydrodynamic radius of a monomer. So, $m/f \simeq M_m \times 10^{-25}\, a_h^{-1}\, \eta^{-1}$. For many molecules this quotient comes between $10^{-15}\,\eta^{-1}$ and $10^{-17}\,\eta^{-1}$. At viscosities around 10^{-2} poises, the characteristic time will, therefore, be of the order of 10^{-14} sec. At higher viscosities even shorter times will be found.

**) We suppose that no other external forces are acting on the flowing liquid. For example, if the beads contain electric charges, and an oscillatory electric field is applied to the solution, the dielectric properties of polymeric fluids can be treated by the same theory20, 25, 26).

$$\underline{\dot{s}}_p = \underline{\dot{s}}_{op} - \frac{kT}{b^2} \sum_{k=1}^{xn} (\underline{a}\,\underline{W}^{-1}\,\underline{a}^T)_{pk} \frac{\partial \ln \psi/\phi}{\partial \underline{s}_k} \quad \text{for } p = 1,2, \ldots . x \qquad \text{(IV 4,4}$$

so that the motions of the centres of gravity can be calculated if ψ and all elements of $\underline{W}$ are known.

The velocities of the position differences of the beads are, according to Eq. (IV 4,3), given by

$$\underline{\dot{S}}^* = \underline{\dot{S}}_o^* - \frac{kT}{b^2}\,\underline{B}\,\frac{\partial \ln \psi/\phi}{\partial \underline{S}^*} \qquad \text{(IV 4,5)}$$

In this equation $\underline{S}^*$, $\underline{\dot{S}}^*$ and $\underline{\dot{S}}_o^*$ are identical to the matrices $\underline{S}$, $\underline{\dot{S}}$ and $\underline{\dot{S}}_o$, but for the first x rows with index p. The mobility matrix $\underline{B}$ represents an xn *x* xn matrix, identical to the matrix $\underline{a}\,\underline{W}^{-1}\,\underline{a}^T$, but for the first x rows and the first x columns. Hence, the matrix $\underline{B}$ also equals $\underline{a}^*\underline{W}^{-1}\underline{a}^{*T}$ if $\underline{a}^*$ is the matrix $\underline{a}$ minus the first x rows. The elements of $\underline{B}$ are indicated by B_{ik} (i,k, = 1,2,. . . . xn), and $\underline{B}$ is symmetric if $\underline{W}$ is symmetric. In the special case that x=1, the matrix $\underline{a}^*\underline{a}^{*T}$ equals the n *x* n matrix $\underline{A}$ of Rouse, whereas the (n+1) *x* (n+1) matrix $\underline{a}^{*T}\underline{a}^*$ is then equivalent to Zimm's matrix $\underline{A}^z$.

Although the whole problem has now been reduced by means of Eq. (IV 4,5) to a representation very much analogous to that of Rouse and Zimm, we still want to proceed with the further elaboration of the problem, because there are several points where specific deviations arise, while others permit of a more general or elegant treatment.

We shall first perform a coordinate transformation in which the matrix $\underline{B}$ becomes diagonalized. $\underline{B}$ is a symmetric matrix with xn different real eigenvalues $\lambda_1, \lambda_2, \ldots . \lambda_{xn}$. For very dilute solutions, x=1 and f_i=f for all i's. Using for $\underline{T}$ the pre-averaged representation by Kirkwood and Riseman22) of Oseen's hydrodynamic interaction tensor, we find Rouse's13) eigenvalues if $\underline{T}$ can be ignored, those given by Zimm, Roe and Epstein27) if $\underline{T}$ is dominant, and Tschoegl's28) if $\underline{T}$ comes between these two extremes. Duiser, Staverman, Chömpff and Prins29-33) calculated the eigenvalues for some special modes of crosslinking or entanglement with x=2. In the very general case we are dealing with at the moment, calculation of the eigenvalues of $\underline{B}$ is possible only if all elements of $\underline{W}$ are known. Notwithstanding that the calculation may remain extremely difficult then, all eigenvalues can, in principle, be obtained. The situation becomes somewhat simpler if some elements of $\underline{B}$ are extraordinary small, which may be the case for instance if the friction coefficient w in an equation like (IV 3,6) becomes exceedingly large. The matrix calculus then provides some methods for obtaining a fair approximation of the smallest eigenvalues. As a general rule, it may be stated that when $\underline{W}$ contains several elements that are very much larger than the others, some of the eigenvalues found will be very small. We shall now continue our argument along purely formal lines, and suppose that all eigenvalues of $\underline{B}$ have been established.

Let now $\underline{Q}$ be the matrix which contains the normalized eigenvectors of $\underline{B}$ as the columns. The matrix $\underline{\Lambda} = \underline{Q}^{-1}\,\underline{B}\,\underline{Q}$ will then be a diagonal matrix with elements $\lambda_1, \lambda_2, \ldots . \lambda_{xn}$. Owing to the symmetry of $\underline{B}$, the very important relation $\underline{Q}^T = \underline{Q}^{-1}$ will be valid.

New, so-called *normal*, coordinates are introduced as follows:

$$\underline{P} = \underline{Q}^{-1}\underline{S}^* \qquad \text{(IV 4,6)}$$

which also leads to the definition:

$$\underline{\dot{P}}_o = \underline{Q}^{-1}\underline{\dot{S}}_o^* \qquad \text{(IV 4,7)}$$

$\underline{P}$, and $\underline{\dot{P}}_o$ are matrices with xn rows and three columns, and comprise the vectors ρ_i^T, and $\dot{\rho}_{oi}^T$, respectively, as the rows, which, in turn, are composed of the components ξ_i, η_i, ζ_i, and $\dot{\xi}_{oi}, \dot{\eta}_{oi}, \dot{\zeta}_{oi}$ (i = 1,2, ... xn). It follows from Eq. (IV 4,6) that

$$\partial/\partial\underline{S}^* = (\underline{Q}^{-1})^T \partial/\partial\underline{P} = \underline{Q}\partial/\partial\underline{P} \qquad \text{(IV 4,8)}$$

Multiplication of Eq. (IV 4,5) by $\underline{Q}^{-1}$ yields:

$$\underline{\dot{P}} = \underline{\dot{P}}_o - \frac{kT}{b^2}\,\underline{\Lambda}\,\frac{\partial \ln(\psi/\phi)}{\partial \underline{P}} \qquad \text{(IV 4,9)}$$

As $\underline{\Lambda}$ is a diagonal matrix, this set of equations represents xn separate equations each of which depends on the three variables ρ_i only. This means that the coordinate transformation described above has led to a decoupling of the system of equations (IV 4,5). An essential condition for the introduction of normal coordinates is that the friction forces can be written in a form like (IV 3,7) containing a symmetric matrix $\underline{W}$.

5. Continuity equation and solution for ψ

The rate of change of the distribution function ψ in a given volume element d$\underline{S}$ in the 3xn dimensional space is determined by the flux of ψ across the boundaries of the element d$\underline{S}$. Hence, the law of continuity applies:

$$\frac{\partial\psi}{\partial t} + \operatorname{div}(\underline{\dot{S}}\psi) = 0 \qquad \text{(IV 5,1)}$$

This equation can also be written as

$$\frac{\partial\psi}{\partial t} + \sum_{p=1}^{x} \frac{\partial^T}{\partial \underline{s}_p}(\underline{\dot{s}}_p\psi) + \frac{\partial^T}{\partial\underline{S}^*} : (\underline{\dot{S}}^*\psi) = 0 \qquad \text{(IV 5,2)*)}$$

---

*) An expression like $\underline{A}:\underline{B}$ or $\underline{A}..\underline{B}$, known as the direct or double dot product of two matrices, denotes the sum of the inner products of the rows of the matrix $\underline{A}$ and the corresponding columns of the matrix $\underline{B}$. Written in components, this product is equal to $\sum_i\sum_j a^{ij}b^{ji}$, i.e. equal to tr($\underline{AB}$).

Making allowance for Eqs (IV 4,8) and (IV 4,6) and a special property of direct products

$$\frac{\partial^T}{\partial \underline{S}^*} : (\dot{\underline{S}}^* \psi) = \frac{\partial^T}{\partial \underline{P}} \underline{Q}^T : (\underline{Q}\dot{\underline{P}}\,\psi) = \frac{\partial^T}{\partial \underline{P}} : (\underline{Q}^T \underline{Q}\,\dot{\underline{P}}\,\psi) = \frac{\partial^T}{\partial \underline{P}} : (\dot{\underline{P}}\,\psi) \qquad \text{(IV 5,3)}$$

we can transform Eq. (IV 5,2) into

$$\frac{\partial\psi}{\partial t} + \sum_{p=1}^{x} \frac{\partial^T}{\partial \underline{s}_p}(\dot{\underline{s}}_p\,\psi) + \frac{\partial^T}{\partial\underline{P}} : (\dot{\underline{P}}\,\psi) = 0 \qquad \text{(IV 5,4)}$$

This is a differential equation, in which ψ is a function of the independent variables $\underline{s}_p$, $\underline{P}$ and t. ψ is a distribution function and has to be normalized; which means that every solution of Eq. (IV 5,4) has to meet the following requirement:

$$\int \psi \prod_{p=1}^{x} d\underline{s}_p \, d\underline{P} = 1 \qquad \text{(IV 5,5)}$$

Now, ψ can in principle be solved. To this end, we write ψ as a product of distribution functions

$$\psi = \prod_{p=1}^{x}\psi_p(\underline{s}_p)\prod_{i=1}^{xn}\psi_i(\rho_i) \qquad \text{(IV 5,6)}$$

If every ψ_p or ψ_i in this product satisfies the normalization conditions

$$\int\psi_p(\underline{s}_p)\,d\underline{s}_p = 1 \quad \text{for } p = 1,2, \ldots . x \qquad \text{(IV 5,7)}$$

or

$$\int\psi_i(\rho_i)\,d\rho_i = 1 \quad \text{for } i = 1,2, \ldots . xn \qquad \text{(IV 5,8)}$$

Eq. (IV 5,5) will also be satisfied. Substitution of Eq. (IV 5,6) in Eq. (IV 5,4) then gives

$$\sum_{p=1}^{x}\left[\frac{\partial\psi_p}{\partial t} + \frac{\partial^T}{\partial\underline{s}_p}(\dot{\underline{s}}_p\,\psi_p)\right]\prod_{\substack{q=1\\q\neq p}}^{x}\psi_q\prod_{i=1}^{xn}\psi_i \;+$$

$$+\sum_{k=1}^{xn}\left[\frac{\partial\psi_k}{\partial t} + \frac{\partial^T}{\partial\rho_k}(\dot{\rho}_k\,\psi_k)\right]\prod_{p=1}^{x}\psi_p\prod_{\substack{i=1\\i\neq k}}^{xn}\psi_i = 0 \qquad \text{(IV 5,9)}$$

Eq. (IV 5,9) will apply if

$$\frac{\partial\psi_p}{\partial t} + \frac{\partial^T}{\partial\underline{s}_p}(\dot{\underline{s}}_p\,\psi_p) = 0 \quad \text{for } p = 1,2, \ldots . x \qquad \text{(IV 5,10)}$$

and

$$\frac{\partial\psi_k}{\partial t} + \frac{\partial^T}{\partial\rho_k}(\dot{\rho}_k\,\psi_k) = 0 \quad \text{for } k = 1,2, \ldots . xn \qquad \text{(IV 5,11)}$$

Evidently, all variables are mutually independent, and the distribution function can indeed be factorized as in Eq. (IV 5,6).

Before continuing our argument, we shall have a look at Eq. (IV 5,10) for the centres of gravity. If ψ_p and g_p are constant and independent of $\underline{s}_p$, it follows from Eq. (IV 4,4) that $(\partial^T/\partial \underline{s}_p)\dot{\underline{s}}_p = (\partial^T/\partial \underline{s}_p)\dot{\underline{s}}_{op}$, which means that the divergence of the velocity of the centres of gravity equals the divergence of the macroscopic flow field. However, it then follows from Eq. (IV 5,10) that this divergence is equal to zero. Hence, a homogeneous distribution of the centres of gravity, before as well as after application of a flow field to the liquid, conforms to the Eqs (IV 4,4) and (IV 5,10), on the condition that the flow field is divergence-free. If it is not, a homogeneous distribution of the centres of gravity conflicts with the equations of motion (IV 4,4) and (IV 5,10). Since transition of matrix $\underline{a}\,\underline{W}^{-1}\underline{a}^T$ to matrix $\underline{B}$ requires that $(\partial/\partial \underline{s}_p)\ln\psi_p = 0$, we have to restrict ourselves in the following to a consideration of divergence-free fluid flows.

The equations of continuity (IV 5,11) for the various modes can now be solved for every type of macroscopic flow for which the velocities are linear functions of the coordinates:

$$\underline{v}_{ok} = \dot{\underline{\Gamma}} \cdot \underline{r}_k \quad \text{or} \quad \underline{V}_o = \underline{R}\,\dot{\underline{\Gamma}}^T \tag{IV 5,12}$$

Here, $\dot{\underline{\Gamma}}$ is a 3 x 3 matrix, viz. the velocity gradient matrix, with elements $\dot{\gamma}_{ik}$ (t) which are only functions of time. This type of flow is rather general, and covers not only any time-dependent shear flow but also, for example, linear elongational flow. The additional requirement of non-divergence means that

$$\operatorname{tr}\dot{\underline{\Gamma}} = \dot{\gamma}_{11} + \dot{\gamma}_{22} + \dot{\gamma}_{33} = 0 \tag{IV 5,13}$$

It can be easily demonstrated that the relation between the transformed velocities and coordinates shows the same linearity, for

$$\dot{\underline{S}}_o = \frac{1}{b}\underline{a}\,\underline{V}_o = \frac{1}{b}\underline{a}\,\underline{R}\,\dot{\underline{\Gamma}}^T = \underline{S}\,\dot{\underline{\Gamma}}^T$$

and, hence,

$$\dot{\underline{P}}_o = \underline{Q}^{-1}\dot{\underline{S}}^*_o = \underline{Q}^{-1}\underline{S}^*\,\dot{\underline{\Gamma}}^T = \underline{P}\,\dot{\underline{\Gamma}}^T \tag{IV 5,14}$$

Upon substitution of this expression for the macroscopic flow field in Eq. (IV 4,9), we combine Eq. (IV 4,9) with Eq. (IV 5,11). We further introduce the parameters τ_k defined by

$$\tau_k = b^2/(2\,kT\lambda_k) \qquad k = 1,2,\ldots .\, xn \tag{IV 5,15}$$

and called *relaxation times*. This yields the differential equation

$$\tau_k\frac{\partial\psi_k}{\partial t} + \tau_k\underline{\rho}_k^T\dot{\underline{\Gamma}}^T\frac{\partial\psi_k}{\partial\underline{\rho}_k} - \tfrac{1}{2}\frac{\partial^T}{\partial\underline{\rho}_k}\left(\frac{\partial\psi_k}{\partial\underline{\rho}_k} - \psi_k\frac{\partial\ln\phi}{\partial\underline{\rho}_k}\right) = 0 \tag{IV 5,16}$$

Substitution of the gaussian distribution (IV 1,5) for the equilibrium distribution function ϕ, changes this equation into

$$\tau_k \frac{\partial \psi_k}{\partial t} + \tau_k \underline{\rho}_k^T \, \underline{\dot{\Gamma}}^T \frac{\partial \psi_k}{\partial \underline{\rho}_k} - ½ \frac{\partial^T}{\partial \underline{\rho}_k} \frac{\partial \psi_k}{\partial \underline{\rho}_k} - ½ \, \underline{\rho}_k^T \frac{\partial \psi_k}{\partial \underline{\rho}_k} - 3/2 \, \psi_k = 0 \qquad \text{(IV 5,17)}$$

which completely describes the state of one set of normal coordinates $\underline{\rho}_k$ with the aid of one characteristic time constant τ_k. The function ψ_k describes a so-called *normal mode of motion* of the complex.

The general solution for this equation can be derived34) by means of a Fourier transformation; for simplicity, we shall give it right away. However, before doing so, we must first introduce some moments of the distribution function ψ_k. The moments $\mu_{k\,pqr}$ of ψ_k are defined by

$$\mu_{k\,pqr} = \int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty} \xi_k^p \, \eta_k^q \, \zeta_k^r \, \psi_k(\xi_k, \eta_k, \zeta_k) \, d\xi_k \, d\eta_k \, d\zeta_k \qquad \text{(IV 5,18)}$$

If ψ_k is a normalized distribution function, $\mu_{k\,200}$ denotes the value of ξ_k^2 averaged over ψ_k, $\mu_{k\,020}$ the average value of η_k^2, $\mu_{k\,110}$ the average value of $\xi_k \eta_k$, etc. For these second moments we introduce a new symmetric $3 x 3$ matrix $\underline{M}_k$, which is equal to

$$\underline{M}_k = \begin{bmatrix} \mu_{k\,200} & \mu_{k\,110} & \mu_{k\,101} \\ \mu_{k\,110} & \mu_{k\,020} & \mu_{k\,011} \\ \mu_{k\,101} & \mu_{k\,011} & \mu_{k\,002} \end{bmatrix} \qquad \text{(IV 5,19)}$$

and denote the value of the determinant of this matrix by $|\underline{M}_k|$.

The general normalized solution of Eq. (IV 5,17) is now given by

$$\psi_k = (2\pi)^{-3/2} \, |\underline{M}_k|^{-½} \exp\left[-½ \, \underline{\rho}_k^T \, \underline{M}_k^{-1} \, \underline{\rho}_k\right] \qquad \text{(IV 5,20)}$$

on the extra condition that the moments satisfy the symmetrical matrix equation

$$\tau_k \frac{d\underline{M}_k}{dt} + \underline{M}_k - \tau_k (\underline{\dot{\Gamma}} \, \underline{M}_k + \underline{M}_k^T \, \underline{\dot{\Gamma}}^T) = \underline{I} \qquad \text{(IV 5,21)}$$

$\underline{I}$ is the $3 x 3$ unit matrix. This solution holds for every value of k, so that the distribution function of the whole complex of macromolecules equals the product of all ψ_k's, each with its own relaxation time τ_k and its own moments μ_k.

The solution (IV 5,20) indicates that, whatever the form of the time dependence of the velocity gradient matrix $\underline{\dot{\Gamma}}$, the distribution of the normal coordinates is a time-dependent symmetric normal distribution whose moments have to satisfy a system of six linear differential equations. By solving these equations, one obtains the moments, with the exception of a constant that must be determined from the initial conditions.

As a matter of fact, the Eqs (IV 5,21) are not new. By way of illustration, these equations will be completely written out for two elements of $\underline{M}$, namely for $M_{12} = \mu_{110}$ and

$M_{22} = \mu_{020}$, with omission of the index k:

$$\tau\dot{\mu}_{110} + \mu_{110} - \tau(\dot{\gamma}_{11}\mu_{110} + \dot{\gamma}_{12}\mu_{020} + \dot{\gamma}_{13}\mu_{011} + \mu_{200}\dot{\gamma}_{21} + \mu_{110}\dot{\gamma}_{22} + \mu_{101}\dot{\gamma}_{23}) = 0 \qquad \text{(IV 5,22a)}$$

$$\tau\dot{\mu}_{020} + \mu_{020} - 2\tau(\dot{\gamma}_{21}\mu_{110} + \dot{\gamma}_{22}\mu_{020} + \dot{\gamma}_{23}\mu_{011}) = 1 \qquad \text{(IV 5,22b)}$$

The procedure introduced by Hermans[35)] enables all the equations (IV 5,21) to be obtained in a direct way, viz., by multiplication of Eq. (IV 5,17) by $\xi\eta$, η^2, etc., and subsequent integration over the space of the normal coordinates. For example, multiplication by $\xi\eta$ yields

$$\int\left[\tau\xi\eta\frac{\partial\psi}{\partial t} - \tfrac{1}{2}\xi\eta\left(\xi\frac{\partial\psi}{\partial\xi} + \eta\frac{\partial\psi}{\partial\eta} + \zeta\frac{\partial\psi}{\partial\zeta}\right) - \tfrac{3}{2}\xi\eta\psi + \tau\xi\eta\left(\dot{\xi}_o\frac{\partial\psi}{\partial\xi} + \dot{\eta}_o\frac{\partial\psi}{\partial\eta} + \dot{\zeta}_o\frac{\partial\psi}{\partial\zeta}\right)\right]d\xi d\eta d\zeta =$$

$$= \int \tfrac{1}{2}\xi\eta\left(\frac{\partial^2\psi}{\partial\xi^2} + \frac{\partial^2\psi}{\partial\eta^2} + \frac{\partial^2\psi}{\partial\zeta^2}\right)d\xi d\eta d\zeta$$

Bearing in mind that ψ and all derivatives of ψ decrease exponentially at the boundaries of the integration region, we find that partial integration for divergence-free flows yields

$$\tau\dot{\mu}_{110} + \tfrac{1}{2}(2\mu_{110} + 2\mu_{110} + \mu_{110}) - 3/2\,\mu_{110} - \tau\int(\eta\dot{\xi}_o + \xi\dot{\eta}_o)\,\psi\, d\xi d\eta d\zeta = 0$$

This equation is again equal to Eq. (IV 5,22a). All the Eqs (IV 5,21) can be derived in the same way.

The second-order differential equation (IV 5,17) for the distribution function ψ_k has now been reduced to a system of first-order differential equations for the moments of ψ_k which can be easily solved*). These solutions being known, the expression for ψ_k can be found from Eq. (IV 5,20).

In many cases only the moments of the distribution function need be known**). This will be demonstrated with reference to the calculation of the increase in free energy. Eq. (IV 5,20) yields

---

*) If no external forces are applied to the fluid, so with $\dot{\underline{\Gamma}} = 0$, Eqs (IV 5,21) correspond to Verdier's[5)] auto- and cross-correlation functions for the normal coordinates.

**) For example, in computing the lines of motion of the individual beads, we need the exact solution for ψ_k. This has been demonstrated in the Appendix of ref. 36, where the rates of rotation and deformation of the normal modes are calculated as functions of position, time, and rate of shear in a steady simple shear flow of dilute solutions. The motions of the beads are found through back-transformation.

$$\ln \psi_k = -3/2 \ln (2\pi) - ½ \ln |\underline{M}_k| - ½\, \underset{-}{\rho}_k^T \underline{M}_k^{-1} \underset{-}{\rho}_k$$

and, hence,

$$\int \psi_k \ln \psi_k \, d\underset{-}{\rho}_k = -3/2 \ln (2\pi) - ½ \ln |\underline{M}_k| - ½\, \underline{M}_k : \underline{M}_k^{-1} =$$

$$= -3/2 \ln (2\pi) - ½ \ln |\underline{M}_k| - 3/2 \qquad \text{(IV 5,23)}$$

From Eq. (IV 1,5) it follows, after transformation, that

$$\ln \phi_k = -3/2 \ln (2\pi) - ½\, \underset{-}{\rho}_k^T \underset{-}{\rho}_k$$

and, hence,

$$\int \psi_k \ln \phi_k \, d\underset{-}{\rho}_k = -3/2 \ln (2\pi) - ½ (\mu_{k200} + \mu_{k020} + \mu_{k002}) \qquad \text{(IV 5,24)}$$

Substitution of Eqs (IV 5,23) and (IV 5,24) in Eq. (IV 2,6) gives the following expression for the increase in free energy of a mode with index k:

$$\Delta F_k = \frac{kT}{2} [\mu_{k200} + \mu_{k020} + \mu_{k000} - 3 - \ln |\underline{M}_k|] \qquad \text{(IV 5,25)}$$

Hence, in order to calculate the increase in free energy, we only need the values of the moments, which can be found directly by means of Eq. (IV 5,21).

The purport of the above treatment will be demonstrated with reference to a special macroscopic flow profile: a simple shear flow in the x-direction with a gradient in the y-direction only, plus a superimposed simple shear flow in the z-direction with a gradient in the y-direction only. This flow belongs in the group of curvilinear flows as defined in chapter I, Eq. (I 42), with $x^1 = y$, $x^2 = x$, $x^3 = z$. All elements of $\dot{\underline{\Gamma}}$ are equal to zero, except $\dot{\gamma}_{12}$ and $\dot{\gamma}_{32}$, which, for brevity, will henceforth be denoted by $\dot{\gamma}$ and κ, respectively. For this case, Eqs (IV 5,21) give

$$\tau_k \dot{\mu}_{k200} + \mu_{k200} = 1 + 2\tau_k \dot{\gamma} \mu_{k110} \qquad \text{(IV 5,26a)}$$

$$\tau_k \dot{\mu}_{k110} + \mu_{k110} = \tau_k \dot{\gamma} \mu_{k020} \qquad \text{(IV 5,26b)}$$

$$\tau_k \dot{\mu}_{k101} + \mu_{k101} = \tau_k \dot{\gamma} \mu_{k011} + \tau_k \kappa \mu_{k110} \qquad \text{(IV 5,26c)}$$

$$\tau_k \dot{\mu}_{k020} + \mu_{k020} = 1 \qquad \text{(IV 5,26d)}$$

$$\tau_k \dot{\mu}_{k011} + \mu_{k011} = \tau_k \kappa \mu_{k020} \qquad \text{(IV 5,26e)}$$

$$\tau_k \dot{\mu}_{k002} + \mu_{k002} = 1 + 2\tau_k \kappa \mu_{k011} \qquad \text{(IV 5,26f)}$$

The moment μ_{k020} is independent of $\dot{\gamma}$ and κ, and may be equated to 1. If $\dot{\gamma}$ and κ are further specified, all moments can be calculated straightforwardly. With κ equal to zero, there will be simple shear flow in one direction. In this case, the solutions for the last four equations comprise only damping terms of the form exp $(-t/\tau_k)$, and no loss in generality is involved if we state that $\mu_{k011} = \mu_{k101} = 0$ and $\mu_{k002} = \mu_{k020} = 1$. Consequently, with simple shear flow in one direction, only the moments μ_{k110} and μ_{k200} are dependent on the value of the velocity gradient $\dot{\gamma}$, and for any form of time dependence of $\dot{\gamma}$ these moments can be easily calculated with the aid of Eqs (IV 5,26a) and (IV 5,26b). Once these moments are known, ψ_k follows direct from Eq. (IV 5,20). In this way we arrive at the important conclusion that for any type of simple shear flow in the x-direction with a velocity gradient in the y-direction only, the distribution function ψ_k of the k-th mode is, according to Eq. (IV 5,20), of the form

$$\psi_k = \frac{1}{(2\pi)^{3/2}(\mu_{k200} - \mu_{k110}^2)^{1/2}} \exp\left[-\frac{\xi_k^2 - 2\mu_{k110}\xi_k\eta_k + \mu_{k200}\eta_k^2}{2(\mu_{k200} - \mu_{k110}^2)} - \frac{\zeta_k^2}{2}\right] \qquad \text{(IV 5,27)}$$

Now, the increase in free energy of the k-th mode is given by

$$\Delta F_k = \tfrac{1}{2} kT \,[\mu_{k200} - 1 - \ln(\mu_{k200} - \mu_{k110}^2)] \qquad \text{(IV 5,28)}$$

Although these formulae hold also under starting and transient conditions, we will, for the sake of clarity, leave these conditions out of consideration.

6. Generalization

In the preceding section we dealt with a very definite ensemble of complexes of equally long macromolecules, all being in the same state of friction characterized by a matrix W̲. We proved that the state of this ensemble can be described by a distribution function which is the product of xn distribution functions of the various modes, each with its own characteristic relaxation time τ_k. We further demonstrated that the eigenvalues λ_k for the general case cannot be calculated in a simple manner, but also that strong enlargement of some elements of W̲ will normally give rise to some very small eigenvalues λ_k and, hence, to large values τ_k.

A real polymer solution, or polymer melt, can be conceived as a collection of ensembles of complexes differing both in nature and in state of entanglement. If, moreover, the polymer is polydisperse and the chains vary in length, it is virtually impossible to make any quantitative statement as to the distribution of relaxation times. This distribution depends on the molecular weight distribution and on the distribution of the ensembles over the various complexes that may be present. As a result, the distribution of relaxation times for polymeric fluids can be approximated by a continuous distribution. The number of relaxation times per unit volume of fluid coming between τ and $\tau + d\tau$ is set equal to $N(\tau)d\tau$. Of course, this number is also equal to the number of normal modes, and, hence, to the number of ψ-functions belonging to the τ-values. The distribution function of every normal mode with relaxation time τ is still given by Eq. (IV 5,20) plus Eq. (IV 5,21), in which τ_k should, however, be replaced by τ. The associated moments are denoted by $\mu(\tau)_{200}$, $\mu(\tau)_{110}$, etc.

Suppose we want to calculate the average value of the sum of squared projections in the x-direction of the segment lengths of all molecules per cm^3. We first assume then that the molecular weight distribution is mono-disperse and that there are N_1 complexes per cm^3, all comprising x molecules with n segments and being in the same state of friction characterized by a given $\underline{W}$. The demanded average then equals

$$N_1 \int \sum_{k=1}^{xn} (x_k - x_{k-1})^2 \, \psi(\underline{R}) d\underline{R} = N_1 b^2 \int \sum_{k=1}^{xn} u_k^2 \, \psi(\underline{S}^*) d\underline{S}^* =$$

$$= N_1 b^2 \sum_{k=1}^{xn} \sum_{i=1}^{xn} \sum_{j=1}^{xn} Q_{ki} Q_{kj} \int \xi_i \xi_j \, \psi(\underline{P}) d\underline{P} \qquad \text{(IV 6,1)}$$

The matrix $\underline{Q}$ is formed by the normalized eigenvectors of the symmetric mobility matrix $\underline{B}$ (which, in consequence, are orthonormal), so that

$$\sum_{k=1}^{xn} Q_{ki} Q_{kj} = \sum_{k=1}^{xn} Q_{ik} Q_{jk} = \delta_{ij}$$

where δ_{ij} is the well-known Kronecker delta.

The average value sought for hence equals

$$N_1 b^2 \sum_{k=1}^{xn} \int \xi_k^2 \, \psi(\underline{P}) d\underline{P} = N_1 b^2 \sum_{k=1}^{xn} \mu_{k\,200} \qquad \text{(IV 6,2)}$$

This result holds for any molecular weight and for any ensemble of complexes. If the distribution of the relaxations times is represented by $N(\tau)$, the mean square x-dimension of the segments is equal to

$$b^2 \int_0^\infty N(\tau)\, \mu(\tau)_{200} \, d\tau \qquad \text{(IV 6,3)}$$

In an analogous way we find that

$$\int \sum_k (x_k - x_{k-1})(y_k - y_{k-1}) \, \psi(\underline{R}) d\underline{R} = b^2 \int_0^\infty N(\tau)\, \mu(\tau)_{110} \, d\tau \qquad \text{(IV 6,4)}$$

$$\int \sum_k (y_k - y_{k-1})^2 \, \psi(\underline{R}) d\underline{R} = b^2 \int_0^\infty N(\tau)\, \mu(\tau)_{020} \, d\tau \qquad \text{(IV 6,5)}$$

For the case of simple shear flow, all these averages can be expressed in the parameters $\dot{\gamma}$, τ, and $N(\tau)$.

7. Stress tensor

There appears to be no unanimity in the literature as to the way of assigning a macroscopic state of stress to a system of chain molecules described by a distribution function ψ and exposed to a flow field. The various methods used for the purpose can, in principle, be classified into two categories, according as they are based on

i) additivity of forces or deformations

ii) energetical calculations.

The methods will now be reviewed and applied to a single ensemble of complexes as defined in sections 1 and 3. In doing so, we shall restrict ourselves to the case of simple shear flow.

i) Hermans35), using a model in which only the end-to-end distances of the molecules are taken into consideration and the friction is supposed to be concentrated in these endpoints, concludes on simple geometrical grounds that the extra shear stress in a solution of chain molecules under conditions of shear flow is given by

$$p_{21} = -N < (\underline{f}^{fT} \underline{e}_1)(\underline{r}^T \underline{e}_2) > \qquad \text{(IV 7,1)}$$

where N is the number of molecules per unit volume, $\underline{f}^f$ is the force exerted by the endpoint on the medium, $\underline{r}$ is the end-to-end distance of the molecule, $\underline{e}_1$ and $\underline{e}_2$ are the base vectors in the x_1 and x_2 directions, and $< >$ denotes averaging over the distribution function of the end-to-end distances.

Using an approximation of the Oseen-formula for the perturbation of the velocity field, Kirkwood and Riseman22) arrived at an expression for the extra shear stress in the necklace model at low shear rates:

$$p_{21} = -N \sum_{k=o}^{xn} < (\underline{f}_k^{fT} \underline{e}_1)(\underline{r}_k^T \underline{e}_2) > \qquad \text{(IV 7,2)}$$

where $\underline{r}_k$ is the cartesian position vector of the k-th bead, and $\underline{f}_k^f$ the hydrodynamic force exerted by bead k on the solvent. This expression has been elaborated by Kirkwood37) and used in all the subsequent work done by him and his collaborators38, 39).

The same expression has been found5, 26, 40-42) by using the time-correlation formalism of irreversible statistical mechanics; however, since averaging was performed over the equilibrium distribution, this derivation holds only in the case of low shear rates.

Irving and Kirkwood43, 41) obtained a simular expression for the total stress tensor, expressed in the pair-correlation function, for a homogeneous simple liquid in which the forces between the molecules are only due to intermolecular potentials.

Kotaka44) generalises the formula of Kirkwood37) and defines the stress tensor of a solution of macromolecules as follows:

$$p_{ij} = -N \sum_{k=o}^{xn} < (\underline{f}_k^{fT} \underline{e}_i)(\underline{r}_k^T \underline{e}_j) > ; \qquad i,j = 1, 2, 3 \qquad \text{(IV 7,3)}$$

Williams[45] used this expression to calculate the normal stresses in the pearl-necklace models of Rouse and Zimm.

Another method based on the additivity of deformations, uses the concept of a stress-optical coefficient. In the case of simple shear flow, this coefficient C relates stresses to the flow birefringence Δn and the optical extinction angle χ, according to the relations[46]:

$$\Delta n \sin 2\chi = 2\,C\,p_{21} \quad \text{and} \quad \Delta n \cos 2\chi = C\,(p_{11} - p_{22})$$

where C denotes a characteristic quantity for a type of polymer which, as demonstrated both theoretically and experimentally[47-49], is independent of concentration, molecular weight (distribution), shear stress, etc. However, as demonstrated by Janeschitz-Kriegl[50], there is one definite requirement, viz, that the stresses, as well as the birefringence, must have a purely entropy-elastic source.

For the necklace model we have, according to Zimm[20, 51],

$$\Delta n = NkTC \left[\left\{ \sum_{k=1}^{xn} \mu_{k\,200} - \sum_k \mu_{k\,020} \right\}^2 + 4 \left\{ \sum_k \mu_{k\,110} \right\}^2 \right]^{1/2}$$

and

$$\tan 2\chi = \frac{2 \sum_k \mu_{k\,110}}{\sum_k \mu_{k\,200} - \sum_k \mu_{k\,020}}$$

so that this optical analogon method results in

$$p_{21} = NkT \sum_k \mu_{k\,110} \qquad \text{(IV 7,4)}$$

$$p_{11} - p_{22} = NkT \sum_k \left[\mu_{k\,200} - \mu_{k\,020} \right] \qquad \text{(IV 7,5)}$$

ii) The energetical calculations based on work of Debye[52] start from the fact that in simple shear flow the work per unit time and per unit volume, $p_{21}\dot{\gamma}$, done by the imposed shear stress is equal to the total change per second and per cm^3 of the energy content of the liquid, whatever the time-dependence of $\dot{\gamma}$.

The work done by friction of the liquid on the beads in one second equals[18]

$$-N \sum_{k=o}^{xn} < \underline{f}_k^{fT} (\underline{v}_{ok} - \dot{\underline{r}}_k) > \qquad \text{(IV 7,6)}$$

where $< >$ again denotes averaging over the distribution function ψ of the segment lengths*)). The reversible work done on the dissolved macromolecules is often wrongly left out of consideration in energetic calculations. In the isothermal case, this work is equal to the increase of free energy per cm^3 and per sec. According to Eq. (IV 2,6), this increase is given by

$$\mathrm{NkT}\frac{d}{dt}\int \psi \ln\frac{\psi}{\phi}\, d\underline{R} = \mathrm{NkT}\frac{d}{dt}\left< \ln\frac{\psi}{\phi}\right> \qquad \text{(IV 7,7)**)}$$

The sum of the two types of work must equal the work per cm^3 and per sec. done by the additional external force

$$p_{21}\dot{\gamma} = \mathrm{NkT}\frac{d}{dt}\left< \ln\frac{\psi}{\phi}\right> + N\sum_k \left< \underline{f}_k^{fT}\,(\underline{v}_{ok} - \dot{\underline{r}}_k)\right> \qquad \text{(IV 7,8)}$$

We shall now prove that, applied to the necklace model with a given friction coefficient matrix $\underline{W}$, the various methods yield identical results. In doing so, we may start from Eq. (IV 4,5), preferably after changing over from $\underline{S}^*$-coordinates to $\underline{R}$-coordinates. Eq. (IV 4,5) in $\underline{S}^*$-coordinates is equivalent to the following equation in $\underline{R}$-coordinates

$$\dot{\underline{R}} = \underline{V}_o - \mathrm{kT}\underline{W}^{-1}\frac{\partial \ln \psi}{\partial \underline{R}} - \frac{\mathrm{kT}}{b^2}\underline{W}^{-1}\, \underset{\cdot}{a}^{*T}\, \underset{\cdot}{a}^{*}\, \underline{R} \qquad \text{(IV 7,9)}$$

because multiplication with $1/b\ a^*$ restores Eq. (IV 4,5)***).

After substitution of Eq. (IV 7,9), Eq. (IV 3,7) for the friction forces on the beads changes into

$$\underline{F}^f = \mathrm{kT}\frac{\partial \ln \psi}{\partial \underline{R}} + \frac{\mathrm{kT}}{b^2}\underline{A}^z\underline{R} \qquad \text{(IV 7,10)}$$

if $\underline{A}^z = \underset{\cdot}{a}^{*T}\underset{\cdot}{a}^{*}$, which, in combination with Eq. (IV 7,3) for p_{ij}, gives

---

*) Many investigators (e.g. Rouse[13], Blatz[19], Isihara[53]) have set this friction work equal to

$$-N\sum_{k=o}^{xn} \left< \underline{f}_k^{fT}\ \underline{v}_{ok}\right>$$

The meaning of this expression is not clear. In addition, the expression is not transformation-invariant; for, if the liquid were stagnant and the velocity of a bead $\dot{\underline{r}}_k$, the formula would suggest that no work is done, which is certainly incorrect. The work done by the beads is always nil, because the forces acting on the beads will always be in equilibrium. (This invalidates the theory of Isihara[53]).

**) DeWames et al.[18] take this work into account but, wrongly, define it as

$$\mathrm{NkT}\left< \frac{d}{dt}\ln\frac{\psi}{\phi}\right>$$

Owing to the normalization of ψ, this expression should always be zero.

***) This equation is very similar to the equation of motion used by Zimm[20]. With x=1, the matrix $a^{*T}a^*$ is identical to Zimm's matrix $\underline{A}^Z$. The role of the matrix $\underline{W}^{-1}$ is analogous to that of Zimm's hydrodynamic mobility operator $\underline{H}/f$.

$$p_{ab} = N < kT \sum_{k=o}^{xn} \frac{\partial \ln \psi}{\partial a_k} b_k + \frac{kT}{b^2} \sum_{k=o}^{xn} \sum_{l=o}^{xn} A_{kl}^{z} a_l b_k >; a,b = x,y,z \qquad \text{(IV 7,11)}$$

If ψ is independent of the centres of gravity, we have

$$\frac{\partial \ln \psi}{\partial a_k} = \frac{1}{b} \sum_{j=1}^{xn} a_{jk}^{*} \frac{\partial \ln \psi}{\partial c_j}; c = u,v,w \qquad \text{(IV 7,12)}$$

Eq. (IV 7,11) thus changes into

$$p_{ab} = NkT < \sum_{j=1}^{xn} \frac{\partial \ln \psi}{\partial c_j} d_j + \sum_{j=1}^{xn} c_j d_j >; d = u,v,w \qquad \text{(IV 7,13)}$$

After transformation with the matrix $\underline{Q}$, we thus get:

$$p_{ab} = NkT < \sum_{j=1}^{xn} \frac{\partial \ln \psi}{\partial p_j} q_j + \sum_{j=1}^{xn} p_j q_j >; \; p,q = \xi, \eta, \zeta$$

or

$$p_{ab} = NkT \sum_{j=1}^{xn} \left[-\delta_{pq} + < p_j q_j > \right] \qquad \text{(IV 7,14)}$$

so that

$$p_{21} = NkT \sum_{k=1}^{xn} \mu_{k110}; \; p_{23} = NkT \sum_{k=1}^{xn} \mu_{k011};$$

$$p_{11} = NkT \sum_{k=1}^{xn} \left[-1 + \mu_{k200} \right]; \text{ etc.}$$

and, hence,

$$p_{11} - p_{22} = NkT \sum_{k=1}^{xn} \left[\mu_{k200} - \mu_{k020} \right] \qquad \text{(IV 7,15)}$$

These formulae for the stresses are again identical to the formulae (IV 7,4) and (IV 7,5) obtained by the optical analogon method.

With the energetical method, the different terms in Eq. (IV 7,8) have to be calculated. The rate of change of the total free energy of all normal modes obtained by differentiation of Eq. (IV 5,28) and combination with Eqs (IV 5,26a) and (IV 5,26b) is equal to

$$NkT \frac{d}{dt} < \ln \frac{\psi}{\phi} > = NkT \sum_{k=1}^{xn} \frac{1}{2\tau_k} \left[2 + 2\tau_k \dot{\gamma} \mu_{k110} - \mu_{k200} - \frac{1 + \mu_{k110}^2}{\mu_{k200} - \mu_{k110}^2} \right] \qquad \text{(IV 7,16)}$$

The irreversible work done by friction with the surrounding medium is given by Eq. (IV 7,6), which expression is equal to

$$N < \underline{F}^{fT} : (\underline{V}_o - \underline{\dot{R}}) >$$

The friction force given by Eq. (IV 7,10) can be rewritten as

$$\underline{F}^f = \frac{kT}{b}\,\underline{a}^{*T}\left[\frac{\partial \ln \psi}{\partial \underline{S}^*} + \underline{S}^*\right] = \frac{kT}{b}\,\underline{a}^{*T}\underline{Q}\left[\frac{\partial \ln \psi}{\partial \underline{P}} + \underline{P}\right]$$

so that, using Eq. (IV 3,7), we get

$$\underline{V}_o - \underline{\dot{R}} = \underline{W}^{-1}\frac{kT}{b}\,\underline{a}^{*T}\underline{Q}\left[\frac{\partial \ln \psi}{\partial \underline{P}} + \underline{P}\right]$$

By means of these expressions, the friction work can be defined as follows

$$N < \underline{F}^{fT} : (\underline{V}_o - \underline{\dot{R}}) > = \frac{Nk^2T}{b^2} < \left[\frac{\partial \ln \psi}{\partial \underline{P}} + \underline{P}\right]^T : \underline{\Lambda}\left[\frac{\partial \ln \psi}{\partial \underline{P}} + \underline{P}\right] > =$$

$$= NkT < \sum_{k=1}^{xn} \frac{1}{2\tau_k}\left(\frac{\partial \ln \psi}{\partial \underline{\rho}_k} + \underline{\rho}_k\right)^2 > \qquad \text{(IV 7,17)}$$

as $\underline{a}^*\,\underline{W}^{-1}\,\underline{a}^{*T} = \underline{B}$ and $\underline{Q}^T\underline{B}\,\underline{Q} = \underline{\Lambda}$. Eq. (IV 5,27) for ψ plus some rather lengthy calculations, yields the irreversible friction work

$$N < \underline{F}^{fT} : (\underline{V}_o - \underline{\dot{R}}) > = NkT \sum_{k=1}^{xn} \frac{1}{2\tau_k}\left[-2 + \mu_{k\,200} + \frac{1 + \mu_{k\,110}^2}{\mu_{k\,200} - \mu_{k\,110}^2}\right] \qquad \text{(IV 7,18)}$$

Substitution of Eqs (IV 7,16) and (IV 7,18) into Eq. (IV 7,8) gives

$$p_{21} = NkT \sum_{k=1}^{xn} \mu_{k\,110}$$

It is evident, therefore, that the various methods indeed yield identical expressions for the shear stress and for the first normal stress difference in simple shear flow.

So far, we have dealt again with complexes belonging to a special ensemble, and not with a mixture of ensembles typical of a real polydisperse polymeric fluid. Just as in section 6, a generalization of our results will therefore be the next step. With $N(\tau)d\tau$ again denoting the number of relaxation mechanisms per cm^3 with relaxation times between τ and $\tau + d\tau$, the generalized expressions for the stress components under shear-flow conditions become

$$p_{21} = kT \int_0^\infty N(\tau)\,\mu(\tau)_{110}\,d\tau \qquad \text{(IV 7,19)}$$

$$p_{11} - p_{22} = kT \int_0^\infty N(\tau)\,[\mu(\tau)_{200} - \mu(\tau)_{020}]\,d\tau \qquad \text{(IV 7,20)}$$

For every mode of simple shear flow, the moments in these expressions can be determined by means of Eqs (IV 5,26).

Let us now consider the expression (IV 7,19) for shear stress during stationary parallel superposition. In this case, Eq. (IV 5,26b) has the form

$$\tau \frac{d\mu_{110}}{dt} + \mu_{110} = \tau(q + \alpha\omega \cos \omega t) \qquad \text{(IV 7,21)}$$

with, as stationary solution,

$$\mu_{110} = \tau q + \alpha \frac{\omega\tau}{1+\omega^2\tau^2}(\omega\tau \sin \omega t + \cos \omega t) \qquad \text{(IV 7,22)}$$

Substitution in Eq. (IV 7,19) yields

$$p_{21} = (p_{21})_{rot} + \alpha\, G' \sin \omega t + \alpha\, G'' \cos \omega t \qquad \text{(IV 7,23)}$$

with

$$(p_{21})_{rot} = q\,kT \int_0^\infty N(\tau)\tau\, d\tau$$

$$G' = \int_0^\infty \frac{N(\tau)\,\omega^2\tau^2}{1+\omega^2\tau^2}\, d\tau$$

$$G'' = \int_0^\infty \frac{N(\tau)\,\omega\tau}{1+\omega^2\tau^2}\, d\tau$$

According to this expression, the steady rotational viscosity $(p_{21})_{rot}/q$ equals

$$kT \int_0^\infty N(\tau)\, d\tau$$

for all values of q. Since nowhere in the above treatment any supposition has been made as to an effect of q on the relaxation time distribution N(τ), this theory consequently suggests that the viscosity bears a newtonian character. From the expressions for G′ and G″ it further appears that - again according to this theory - a superposed shear rate q does not have any effect on these dynamic quantities. These two examples already clearly demonstrate that the theory of entangled macromolecules in its present form is unfit for describing polymer fluid properties like non-newtonian behaviour and a strong effect of superposition on the dynamic quantities (see chapter II).
In the next section, we shall introduce an energy postulate by which i.a. the viscosity and the dynamic moduli are, in fact, transformed into functions of q. A quantitative comparison between the predictions of this modified theory and the experimental results will be given in the following chapter.

8. The energy postulate

We have seen that the increase in free energy per unit of volume of an ensemble of complexes (N per cm^3) described by the distribution functions ϕ (undisturbed state) and ψ (disturbed state), is given by

$$\Delta F = NkT \int_{-\infty}^{+\infty} \psi \ln \frac{\psi}{\phi} d\underline{R} \qquad \text{(IV 8,1)}$$

The function ϕ is given by Eq. (IV 1,5), and the function ψ for any type of flow conforming to Eq. (IV 5,12) is defined by Eqs (IV 5,6) and (IV 5,20), while the moments μ_k of ψ_k have to satisfy Eqs (IV 5,21). The increase in free energy for every mode k is represented by Eq. (IV 5,25), and it may be stated as a general rule that every conceivable mode characterized by a distribution function $\psi(\tau)$ and a relaxation time τ will show an increase in free energy by an amount

$$\Delta F(\tau) = \tfrac{1}{2} kT \left[\mu(\tau)_{200} + \mu(\tau)_{020} + \mu(\tau)_{002} - 3 - \ln |\underline{M}(\tau)| \right] \qquad \text{(IV 8,2)}$$

As argued above, the possibility of assigning a difference in free energy to every conceivable mode is bound up with the circumstance that, owing to the symmetry of the friction matrix $\underline{W}$, ψ, as well as ϕ, can be written as the product of different $\psi(\tau)$'s and $\phi(\tau)$'s. As illustrated by the derivation of this formula, $\Delta F(\tau)$ consists of two parts: an increase equal to $\mu(\tau)_{200} + \mu(\tau)_{020} + \mu(\tau)_{002} - 3$ caused by the deformation of the mode, and a decrease $\ln |\underline{M}(\tau)|$ brought about by the normalization condition and consequently related to the increase in volume, or to the decrease in density, of a mode in the deformed state.

We now pose the following *energy postulate:*
A mode characterized by a relaxation time τ can never store an amount of free energy larger than $kT\,a^2(\tau)$. The mode disappears when this limit value is exceeded during the deformation process.

The reasons why we wish to advance this postulate are the following. An entanglement point, or a crosslink point, produces very large or infinite elements in the friction matrix $\underline{W}$. As a result, the transformation to normal coordinates yields very small or even zero eigenvalues (see also Duiser et al.[29-33]), and, in consequence, normal modes of motion with very large or infinite relaxation times, which, during deformation, undergo a considerable increase in free energy. The physical idea underlying the energy postulate now is that if an entanglement of chains is placed in a field of forces, the point of entanglement will shift, or the entanglement will cease to exist altogether, when the chains have deformed to a degree corresponding to a given critical level in the amount of stored elastic energy. Shifting of the entanglement point will cause other elements of $\underline{W}$ to become very large. This produces new modes of motion with relaxation times smaller or larger than the original ones. In these new modes, free energy will again be stored until a new shift sets in. However, if their relaxation times were small enough, these new modes could survive the deformation process. Under conditions of steady shear flow, the net result of the process covered by the above postulate is that many mechanisms with long relaxation times have disappeared and, possibly, have been superseded by new mechanisms with shorter relaxation times. However, since in most stagnant polymeric fluids the number of relaxation times $N(\tau)$ is much larger according as these times are shorter, it is permissable to neglect the relatively small number of new relaxation times with respect to the number already present. This approximation may not be made if, e.g., $N(\tau)$ is nearly independent of τ, but this possibility will be left out of consideration for the time being.

We shall not venture on an opinion as to the energy level where disentanglement takes place. This level is normally denoted by $kTa^2(\tau)$; the factor kT is used here because it also occurs in the expression for the free energy. It is likewise unfeasible to make an apriori statement as to the relation between critical energy and relaxation time τ. However, as will appear from our discussion on the experimental results, this critical energy is practically independent of τ, a circumstance which will be used already in the following calculations.

In formular form, the energy postulate can be written as

$$\mu(\tau)_{200} + \mu(\tau)_{020} + \mu(\tau)_{002} - 3 - \ln |\underline{M}(\tau)| \leqslant 2\, a^2(\tau) \qquad \text{(IV 8,3)}$$

We shall now elaborate this postulate for some special flow fields (IV 5,12), namely for the cases of parallel and orthogonal superposition. Both types of shear flow belong in flow category treated in section 5. Hence, we have

case a) parallel superposition; $\dot{\gamma} = q + a\omega \cos \omega t$, $\kappa = 0$
case b) orthogonal superposition; $\dot{\gamma} = q$, $\kappa = a\omega \cos \omega t$.

With parallel superposition the equations for the moments that are of importance here, viz. Eqs (IV 5,26a) and (IV 5,26b), have the form

$$\tau \frac{d\mu_{200}}{dt} + \mu_{200} = 1 + 2\,\tau\,(q + a\omega \cos \omega t)\, \mu_{110} \qquad \text{(IV 8,4)}$$

$$\tau \frac{d\mu_{110}}{dt} + \mu_{110} = \tau\,(q + a\omega \cos \omega t) \qquad \text{(IV 8,5)}$$

Their stationary solutions are

$$\mu_{110} = \tau q + a \frac{\omega\tau}{1 + \omega^2\tau^2}\,[\omega\tau \sin \omega t + \cos \omega t] \qquad \text{(IV 8,6)}$$

$$\mu_{200} = 1 + 2\,\tau^2 q^2 + 2\,aq \frac{\omega\tau^2}{(1 + \omega^2\tau^2)^2}\,[\omega\tau\,(3 + \omega^2\tau^2) \sin \omega t + 2 \cos \omega t] +$$

$$+ a^2 \frac{\omega^2\tau^2}{1 + \omega^2\tau^2} \left[1 + \frac{3\,\omega\tau}{1 + 4\,\omega^2\tau^2} \sin 2\,\omega t + \frac{1 - 2\,\omega^2\tau^2}{1 + 4\,\omega^2\tau^2} \cos 2\,\omega t \right] \qquad \text{(IV 8,7)}$$

These solutions are not the most general ones; they also contain terms that are proportional to $\exp(-t/\tau)$ but these are of minor importance because they damp out with a relaxation time τ.

The stationary solution for $\psi(\xi,\eta,\zeta,t)$ can be found by substitution of Eqs (IV 8,6) and (IV 8,7) in Eq. (IV 5,27). With constant shear rates ($\alpha = 0$, $q \neq 0$), we find the solution which, according to Hermans[35)], is to be attributed to H.A. Kramers:

$$\psi(\xi,\eta,\zeta,t) = \frac{1}{(2\pi)^{3/2}(1+\tau^2q^2)^{1/2}} \exp\left[-\frac{\xi^2 - 2\tau q\xi\eta + (1+2\tau^2q^2)\eta^2}{2(1+\tau^2q^2)} - \frac{\zeta^2}{2}\right] \qquad \text{(IV 8,8)}$$

Unlike to what is suggested by Zimm[20)], formula (IV 8,8) cannot be applied to the case of oscillatory shear ($q = 0$, $\alpha \neq 0$) after mere replacement of q by $a\omega \cos \omega t$. In fact, the solutions (IV 8,6) and (IV 8,7) with $q = 0$ have to be substituted in Eq. (IV 5,27); this yields a different result – identical to that found by Blatz[19)] – which, for small values of α, can be approximated by[36)]

$$\psi(\xi,\eta,\zeta,t) = \frac{1 + \mu_{110}\,\xi\eta}{(2\pi)^{3/2}} \exp\left[-\frac{\xi^2 + \eta^2 + \zeta^2}{2}\right] \qquad \text{(IV 8,9)}$$

With parallel superposition (case a), the energy postulate (IV 8,3) becomes

$$\mu_{200} - 1 - \ln\left[\mu_{200} - \mu_{110}^2\right] \leqslant 2\,a^2(\tau) \qquad \text{(IV 8,10)}$$

The solutions (IV 8,6) and (IV 8,7) are abbreviated to

$$\mu_{110} = \tau q + \alpha A_1(t) \qquad \text{(IV 8,11)}$$

$$\mu_{200} = 1 + 2\tau^2q^2 + 2\,\alpha\tau q\,A_2(t) + \alpha^2 A_3(t) \qquad \text{(IV 8,12)}$$

Here, $A_1(t)$, $A_2(t)$ and $A_3(t)$ are periodic functions of time with frequency ω and parameter τ; their absolute values come between 0 and 1 at low and high values of ω, respectively. The energy postulate thus changes into

$$2\tau^2q^2 + 2\,\alpha\tau q A_2 + \alpha^2 A_3 - \ln\left[1 + \tau^2q^2 + 2\,\alpha\tau q\,(A_2 - A_1) + \alpha^2\,(A_3 - A_1^2)\right] \leqslant 2\,a^2(\tau) \qquad \text{(IV 8,13)}$$

With orthogonal superposition (case b), the moments are defined by the Eqs (IV 5,26) with $\dot{\gamma} = q$ and $\kappa = \alpha\omega \cos \omega t$. Their stationary solutions are

$$\mu_{020} = 1;\ \mu_{110} = \tau q;\ \mu_{200} = 1 + 2\tau^2q^2;\ \mu_{011} = \alpha A_1;\ \mu_{101} = \alpha\tau q\,A_2;$$

$$\mu_{002} = 1 + \alpha^2 A_3 \qquad \text{(IV 8,14)}$$

which change the energy postulate into:

$$2\tau^2 q^2 + \alpha^2 A_3 - \ln\,[1 + \tau^2 q^2 + \alpha^2 (A_3 - A_1^2) +$$

$$+ \alpha^2 \tau^2 q^2 \left\{A_3 - A_1^2 - (A_1 - A_2)^2\right\}] \leqslant 2\,a^2(\tau) \qquad \text{(IV 8,15)}$$

Eqs (IV 8,13) and (IV 8,15) show that whereas the terms in the energy postulate for parallel superposition are proportional partly to α, partly to α^2, the energy postulate for orthogonal superposition exclusively contains terms that are proportional to α^2. The conclusion drawn from either equation is that during steady rotation ($\alpha = 0$, $q \neq 0$) the stored energy increases about quadratically with τq. As we supposed that $a^2(\tau)$ is practically independent of τ, it follows that the maximum relaxation time τ_m under these conditions must satisfy the relation:

$$2\,\tau_m^2 q^2 - \ln\,(1 + \tau_m^2 q^2) = 2\,a^2(\tau_m) \qquad \text{(IV 8,16)}$$

During superposition, this value of τ_m is influenced by the oscillation, although not in exactly the same way in the two cases. Let us suppose now that α is small with respect to 1. Terms of the order of α^2 will be neglected, but terms of the form $\alpha^2 \tau^2 q^2$ will be maintained, because τq might become very large.

The maximum relaxation time for parallel superposition is found from

$$2\,\tau_m q^2 + 2\,\alpha\tau_m q A_2 - \ln\,[1 + \tau_m^2 q^2 + 2\,\alpha\tau_m q\,(A_2 - A_1)] = 2\,a^2(\tau_m) \qquad \text{(IV 8,17)}$$

that for orthogonal superposition from

$$2\,\tau_m^2 q^2 - \ln\left[1 + \tau_m^2 q^2 + \alpha^2 \tau_m^2 q^2 \left\{A_3 - A_1^2 - (A_1 - A_2)^2\right\}\right] = 2\,a^2(\tau_m) \qquad \text{(IV 8,18)}$$

We suppose that in case a) $\tau_m = \tau_o\,(1 - \alpha P)$ and in case b) $\tau_m = \tau_o\,(1 - \tfrac{1}{2}\alpha^2 Q^2)$. Substitution in Eqs (IV 8,17) and (IV 8,18) leads to the solutions

$$2\,\tau_o^2 q^2 - \ln\,[1 + \tau_o^2 q^2] = 2\,a^2 \qquad \text{(IV 8,19)}$$

$$P = \frac{A_1 + \tau_o^2 q^2 A_2}{\tau_o q\,(1 + 2\,\tau_o^2 q^2)} \qquad \text{(IV 8,20)}$$

$$Q^2 = \frac{A_1^2 - A_3 + (A_1 - A_2)^2}{1 + \tau_o^2 q^2} \qquad \text{(IV 8,21)}$$

These formulae show that P and Q^2 are indeed of the order of 1 or smaller at all values of $\tau_o q$ and, hence, that the above approximation may safely be made. So, according to this theory, the perturbation of τ_o is linear in α in the case of parallel superposition, but proportional to α^2 in the case of orthogonal superposition. Terms of the order of α^2 are negligible during small-amplitude oscillation. It is evident, therefore, that the perturbation of τ_o will have a greater influence on all measurable quantities during parallel superposition than during orthogonal superposition.

With parallel superposition, the energy postulate consequently gives:

$$\tau_m = \tau_o - \frac{a\omega\tau_o^2}{\tau_o q\,(1+\omega^2\tau_o^2)}\left[\frac{\omega\tau_o\,(1+\omega^2\tau_o^2+3\,\tau_o^2q^2+\omega^2\tau_o^4q^2)}{(1+\omega^2\tau_o^2)(1+2\,\tau_o^2q^2)}\sin\omega t + \right.$$

$$\left. + \frac{1+\omega^2\tau_o^2+2\,\tau_o^2q^2}{(1+\omega^2\tau_o^2)(1+2\,\tau_o^2q^2)}\cos\omega t\right] \qquad \text{(IV 8,22)}$$

indicating that the maximum relaxation time varies with time around the maximum existing if only constant shear flow were present ($a = 0$). With parallel superposition, the superposed oscillation contributes to the break-down of the relaxation spectrum. This additional effect varies sinusoidally with time and, as appears from Eq. (IV 8,20), is in phase with the oscillatory component of μ_{110} if $\tau_o q \ll 1$, and in phase with the oscillatory component of μ_{200} if $\tau_o q \gg 1$. Which of the two conditions will be realized fully depends on the value of $a^2(\tau)$, and, hence, on the critical energy; with regard to the latter quantity, however, no theoretical predictions can be made for the time being.

This additional time-dependent break-down effect caused by the superposed oscillation does not occur if the direction of the oscillation is perpendicular to the direction of the steady shear flow.

9. Some consequences of the energy postulate

The most important consequence of the energy postulate discussed in the preceding section is that in the integrations to be performed for calculating the shear stress or normal stress, by means of Eqs (IV 7,19) or (IV 7,20), an upper limit is set to the interval of relaxation times over which the integral can be taken. As a result, the formulae for these stresses now become:

$$p_{21} = kT\int_o^{\tau_m} N(\tau)\,\mu(\tau)_{110}\,d\tau \qquad \text{(IV 9,1)}$$

$$p_{11} - p_{22} = kT\int_o^{\tau_m} N(\tau)\left[\mu(\tau)_{200} - \mu(\tau)_{020}\right]d\tau \qquad \text{(IV 9,2)}$$

where τ_m for any form of $\dot{\underline{\Gamma}}$ follows from the energy postulate (IV 8,3).

Earlier in this chapter, we already calculated the moments for some forms of $\dot{\underline{\Gamma}}$, and it is not much trouble to work out the formulae for the corresponding stresses. In the following, we shall restrict our considerations to the case of parallel superposition. The moments are given by Eqs (IV 8,6) and (IV 8,7), (for divergence free-flows μ_{020} always equals 1), while τ_m – again set equal to $\tau_o(1{-}aP)$ with P smaller than 1 – is given by Eq. (IV 8,22). This expression is accurate up to the order of a, with the result that in the computation of the normal stresses the terms proportional to a^2 cannot be correct. For this reason, and also owing to lack of experimental data, these terms will therefore be omitted.

The integrations in Eqs (IV 9,1) and (IV 9,2) will now be carried out. We first integrate up to τ_o and then set the integration over $aP\tau_o$ equal to the product of $aP\tau_o$ and the integrant. For the stresses in the case of parallel superposition we thus find

$$p_{21} = (p_{21})_{rot} + a\, G'(\omega,q) \sin \omega t + a\, G''(\omega,q) \cos \omega t \qquad \text{(IV 9,3)}$$

and

$$p_{11} - p_{22} = (p_{11} - p_{22})_{rot} + 2\, aq\, N'(\omega,q) \sin \omega t + 2\, aq\, N''(\omega,q) \cos \omega t \qquad \text{(IV 9,4)}$$

where

$$(p_{21})_{rot} = qkT \int_o^{\tau_o} N(\tau)\tau \, d\tau \qquad \text{(IV 9,5)}$$

$$(p_{11} - p_{22})_{rot} = 2\, q^2 kT \int_o^{\tau_o} N(\tau)\tau^2 \, d\tau \qquad \text{(IV 9,6)}$$

$$G'(\omega,q) = kT \int_o^{\tau_o} N(\tau) \frac{\omega^2\tau^2}{1+\omega^2\tau^2} \, d\tau - kT \frac{N(\tau_o)\omega^2\tau_o^3}{1 + 2\,\tau_o^2 q^2} \times$$
$$\times \frac{1 + \omega^2\tau_o^2 + 3\,\tau_o^2 q^2 + \omega^2\tau_o^4 q^2}{(1+\omega^2\tau_o^2)^2} \qquad \text{(IV 9,7)}$$

$$G''(\omega,q) = kT \int_o^{\tau_o} N(\tau) \frac{\omega\tau}{1+\omega^2\tau^2} \, d\tau - kT \frac{N(\tau_o)\omega\tau_o^2}{1 + 2\,\tau_o^2 q^2} \times \frac{1 + \omega^2\tau_o^2 + 2\,\tau_o^2 q^2}{(1+\omega^2\tau_o^2)^2} \qquad \text{(IV 9,8)}$$

$$N'(\omega,q) = kT \int_o^{\tau_o} N(\tau) \frac{\omega^2\tau^3(3+\omega^2\tau^2)}{(1+\omega^2\tau^2)^2} \, d\tau - kT \frac{N(\tau_o)\omega^2\tau_o^4}{1 + 2\,\tau_o^2 q^2} \times$$
$$\times \frac{1 + \omega^2\tau_o^2 + 3\,\tau_o^2 q^2 + \omega^2\tau_o^4 q^2}{(1+\omega^2\tau_o^2)^2} \qquad \text{(IV 9,9)}$$

$$N''(\omega,q) = kT \int_{0}^{\tau_o} N(\tau)\, \frac{2\,\omega\tau^2}{(1+\omega^2\tau^2)^2}\, d\tau - kT\, \frac{N(\tau_o)\omega\tau_o^3}{1+2\tau_o^2 q^2} \times \frac{1+\omega^2\tau_o^2+2\tau_o^2 q^2}{(1+\omega^2\tau_o^2)^2} \qquad \text{(IV 9,10)}$$

According to Eq. (IV 8,19), the upper limit τ_o is now a function of q.

For better conformity with common practice[54, 55], we shall use the logarithms of the relaxation times. If we put kTN(τ) equal to H(τ), H(τ)dlnτ represents kT times the number of relaxation mechanisms per cm^3 whose relaxation times, expressed logarithmically, come between lnτ and lnτ + dlnτ. Using this notation, we have

$$(p_{21})_{rot} = q \int_{-\infty}^{\ln\tau_o} H(\tau)\tau\, d\ln\tau \qquad \text{(IV 9,11)}$$

$$(p_{11}-p_{22})_{rot} = 2\,q^2 \int_{-\infty}^{\ln\tau_o} H(\tau)\tau^2\, d\ln\tau \qquad \text{(IV 9,12)}$$

$$G'(\omega,q) = \int_{-\infty}^{\ln\tau_o} H(\tau)\, \frac{\omega^2\tau^2}{1+\omega^2\tau^2}\, d\ln\tau - \frac{H(\tau_o)\omega^2\tau^2}{1+2\,\tau_o^2 q^2} \times$$
$$\times\, \frac{1+\omega^2\tau_o^2+3\,\tau_o^2 q^2+\omega^2\tau_o^4 q^2}{(1+\omega^2\tau_o^2)^2} \qquad \text{(IV 9,13)}$$

$$G''(\omega,q) = \int_{-\infty}^{\ln\tau_o} H(\tau)\, \frac{\omega\tau}{1+\omega^2\tau^2}\, d\ln\tau - \frac{H(\tau_o)\omega\tau_o}{1+2\,\tau_o^2 q^2} \times \frac{1+\omega^2\tau_o^2+2\,\tau_o^2 q^2}{(1+\omega^2\tau_o^2)^2} \qquad \text{(IV 9,14)}$$

$$N'(\omega,q) = \int_{-\infty}^{\ln\tau_o} H(\tau)\, \frac{\omega^2\tau^3(3+\omega^2\tau^2)}{(1+\omega^2\tau^2)^2}\, d\ln\tau - \frac{H(\tau_o)\omega^2\tau_o^3}{1+2\,\tau_o^2 q^2} \times$$
$$\times\, \frac{1+\omega^2\tau_o^2+3\,\tau_o^2 q^2+\omega^2\tau_o^4 q^2}{(1+\omega^2\tau_o^2)^2} \qquad \text{(IV 9,15)}$$

$$N''(\omega,q) = \int_{-\infty}^{\ln\tau_o} H(\tau)\, \frac{2\,\omega\tau^2}{(1+\omega^2\tau^2)^2}\, d\ln\tau - \frac{H(\tau_o)\omega\tau_o^2}{1+2\,\tau_o^2 q^2} \times \frac{1+\omega^2\tau_o^2+2\,\tau_o^2 q^2}{(1+\omega^2\tau_o^2)^2} \qquad \text{(IV 9,16)}$$

The conclusions that can be drawn from the above formulae are the following: if an oscillatory shear of very small amplitude is superimposed on a steady shear flow, the constant parts of the shear stress and normal stress will not be influenced by it. The dynamic properties, however, are certainly dependent on the value of the steady rate of shear. This dependency is reflected first of all in the fact that the integration on the long-time side of the relaxation spectrum cannot go beyond a value τ_o characteristic of the steady shear rate and, secondly, in the appearance, outside the integral, of a negative term caused by the perturbation of the limit value τ_o under the influence of the small dynamic strains during parallel superposition.

In the case of pure oscillation, so with q = 0, the above equations for the shear moduli change into the well-known formulae obtained from the phenomenologic theories[54, 55]. With q = 0, τ_o becomes equal to ∞ and $H(\tau_o)$ to 0. The negative terms in Eqs (IV 9,13) to (IV 9,16) disappear, so that the dynamic shear moduli are given by

$$G' = \int_{-\infty}^{+\infty} H(\tau) \frac{\omega^2\tau^2}{1+\omega^2\tau^2} \, d\ln\tau \qquad \text{(IV 9,17)}$$

$$G'' = \int_{-\infty}^{+\infty} H(\tau) \frac{\omega\tau}{1+\omega^2\tau^2} \, d\ln\tau \qquad \text{(IV 9,18)}$$

and the normal stress components transform into

$$N' = \int_{-\infty}^{\infty} H(\tau) \frac{\omega^2\tau^3(3+\omega^2\tau^2)}{(1+\omega^2\tau^2)^2} \, d\ln\tau \qquad \text{(IV 9,19)}$$

$$N'' = \int_{-\infty}^{\infty} H(\tau) \frac{2\,\omega\tau^2}{(1+\omega^2\tau^2)^2} \, d\ln\tau \qquad \text{(IV 9,20)}$$

Our next problem is to compare these theoretical results with the experimentally determined stationary properties for each of the three following cases: pure oscillation, pure rotation, and superposition. For the execution of this quantitative comparison we refer to the next chapter; however, the procedure to be followed is briefly indicated below. An extensive part of the relaxation spectrum $H(\tau)$ can be determined from simple oscillation measurements by means of Eqs (IV 9,17) and (IV 9,18). The integral

$$\int_{-\infty}^{\ln\tau_o} H(\tau)\,\tau \, d\ln\tau$$

can then be calculated for many values of $\ln\tau_o$. According to Eq. (IV 9,11) these integrals must be equal to the steady shear viscosity $(p_{21})_{rot}/q$ at various values of q. Equalization of these two quantities yields $\ln\tau_o$ as a function of q. By means of Eq. (IV 8,19) it can now be established how the maximum increase in free energy $kTa^2(\tau)$ will vary as a function of q or τ_o. Eq. (IV 9,12) enables the normal stress to be calculated as a function of the shear rate, and, for our theory to be correct, this function should coincide with the experimentally measured normal stress. By means of Eqs (IV 9,13) to (IV 9,16), it is also possible now to determine theoretically how the dynamic quantities are related to the frequency at different values of the superposed steady shear rate. Comparison of these theoretical predictions with the experimental effect of superposition on the dynamic characteristics provides evidence on the value of the present molecular disentanglement theory.

At this stage, we want to point out that the results obtained in the present chapter are very similar to those of Leonov's thixotropy theory treated in chapter III (see e.g. Eqs (III 29), (III 30) and (III 31)). Whereas the thixotropy theory starts from a generalized Maxwell model, and ours yields the formulae underlying this model, they agree in that both introduce energy postulates which, expressed in the defining parameters of the two theories, are approximately identical in form. Furthermore, it appears that Eqs (IV 9,19) and (IV 9,20) for $N'(\omega,o)$ and $N''(\omega,o)$ can be derived in exactly the same form from Leonov's theory and from the generalized results of the Oldroyd theory (chapter III).

10. Physical interpretation of dynamic moduli

Whereas we have no objection whatsoever against the current terms 'in-phase component' and '90°-out-of phase component' of the complex shear modulus, the reader may have been struck by our consistent use of the symbols $G'(\omega,q)$ and $G''(\omega,q)$ for the concepts normally referred to as storage modulus and loss modulus respectively. Although we must admit that, properly speaking, also the notation $G''(\omega,q)/q$ is not exactly equivalent to the term 'dynamic viscosity' as normally used, we wish to point out that the above terminology is not applicable to the present case. The considerations underlying this statement will now be subjected to some closer scrutiny.

In our calculation of the shear stress we have made use of the fact that the amount of work done by the shear stress per unit time and per unit volume equals $p_{21}\dot{\gamma}$. If $\dot{\gamma} =$ $= q + a\omega \cos \omega t$, then $p_{21} = (p_{21})_{rot} + a\, G'(\omega,q) \sin \omega t + a\, G''(\omega,q) \cos \omega t$, and this work consequently equals

$$(p_{21})_{rot} q + a^2 \omega G''(\omega,q) \cos^2 \omega t + a^2 \omega G'(\omega,q) \sin \omega t \cos \omega t + aq\, G'(\omega,q) \sin \omega t +$$
$$+ aq\, [G''(\omega,q) + \omega \eta_{rot}] \cos \omega t \qquad \text{(IV 10,1)}$$

Suppose now that $a \equiv 0$; we then have $q(p_{21})_{rot} = \eta_{rot} q^2$. This work is always positive and represents the energy dissipation per cm^3 and per sec. With $q = 0$, the work is $a^2 \omega G'' \cos^2 \omega t + a^2 \omega G' \sin \omega t \cos \omega t$. The first term is always positive and represents a dissipated energy. The second term is positive during a certain part of the oscillation period, and negative during an other, the integral over the full period being zero. It shows how energy is stored over a given time lapse and released afterwards. This accounts for the use of the terms storage modulus for G' and loss modulus for G'' in treatises on linear viscoelasticity, and also for certain physical interpretations of these moduli56).

However, the energy stored during superposition is determined by

$$a^2\omega\, G'(\omega,q) \sin \omega t \cos \omega t + a q\, G'(\omega,q) \sin \omega t + a q\, [G''(\omega,q) + \omega \eta_{\mathrm{rot}}] \cos \omega t \qquad \text{(IV 10,2)}$$

and the energy dissipated by

$$\eta_{\mathrm{rot}}\, q^2 + a^2\omega\, G''(\omega,q) \cos^2 \omega t \qquad \text{(IV 10,3)}$$

showing that $G'(\omega,q)$ and $G''(\omega,q)$ are no longer specific measures of the stored energy and the dissipated energy, respectively. This brings us to our conclusion that in the case of superposition the terms storage modulus and loss modulus do not cover the contents of the notations $G'(\omega,q)$ and $G''(\omega,q)$. If during superposition $G'(\omega,q)$ becomes equal to zero, the stored energy is given by $a q\, [G''(\omega,q) + \omega \eta_{\mathrm{rot}}] \cos \omega t$, so that, though the phase angle δ_G equals 90°, the liquid is still not a ideal viscous liquid.

Consequently, the current physical interpretation of the dynamic shear moduli is not valid here. We have not succeeded in conceiving new formulations for these quantities; neither have we been successful in forming a physical picture of the dynamic normal stress quantities $N'(\omega,q)$ and $N''(\omega,q)$, not even in the limiting case $q = 0$ where they are described by the simple formulae (IV 9,19) and (IV 9,20).

11. References

1. W. Kuhn, Kolloid Z. **68**,2 (1934); **76**, 258 (1936)
2. V.N. Tsvetkov, Rubber Chem. Techn. **36**, 337 (1963)
3. A. Peterlin, J. Chem. Phys. **23**, 2464 (1955)
4. P.J. Flory, J. Chem. Phys. **17**, 303 (1949)
5. P.H. Verdier, J. Chem. Phys. **45**, 2118, 2122 (1966)
6. R.J. Fleming, J. Phys. A. (Proc. Phys. Soc.) **1**, 404 (1968)
7. W. Kuhn and F. Grün, Kolloid Z. **101**, 248 (1942)
8. H.M. James and E. Guth, J. Chem. Phys. **11**, 470 (1943)
9. S. Chandrasekhar, Rev. Mod. Phys. **15**, 1 (1943)
10. L.R.G. Treloar, Physics of Rubber Elasticity, Clarendon Press, Oxford, 1949
11. M.V. Volkenstein, Configurational Statistics of Polymeric Chains, Interscience, New York, 1963
12. W. Kuhn, Kolloid Z. **68**, 2 (1934)
13. P.E. Rouse, J. Chem. Phys. **21**, 1272 (1953)
14. F. Bueche, J. Chem. Phys. **22**, 603 (1954)
15. F.T. Wall, J. Chem. Phys. **10**, 132 (1942)
16. U. Bianchi, Polymer Letters **3**, 1079 (1965)
17. T.M. Birshtein and O.B. Ptitsyn, Conformations of Macromolecules, Interscience, New York, 1966
18. R.E. DeWames, W.F. Hall and M.C. Shen, J. Chem. Phys. **46**, 2782 (1967)
19. P.J. Blatz, Rubber Chem. Techn. **40**, 1446 (1967)
20. B.H. Zimm, J. Chem. Phys. **24**, 269 (1956)

21. Y.H. Pao, J. Polymer Sci. **61**, 413 (1962)
22. J.G. Kirkwood and J. Riseman, J. Chem. Phys. **16**, 565 (1948)
23. J.M. Burgers, Kon. Ned. Akad. Wet., Verhand. **16**, no. 4, 113 (1938)
24. M. Fixman, J. Chem. Phys. **42**, 3831 (1965)
25. L.K.H. van Beek and J.J. Hermans, J. Polymer Sci. **23**, 211 (1957)
26. W.H. Stockmayer, W. Gobush, Y. Chikahisa and D.K. Carpenter, Disc. Faraday Soc. **49**, 000 (1970)
27. B.H. Zimm, G.M. Roe and L.F. Epstein, J. Chem. Phys. **24**, 279 (1956)
28. N.W. Tschoegl, J. Chem. Phys. **39**, 149 (1963)
29. J.A. Duiser and A.J. Staverman, in: Physics of non-Crystalline Solids, 376, Ed. J.A. Prins, North Holl. Publ. Cie. A'dam, 1965
30. J.A. Duiser, Ph. D. Thesis, Leiden, 1965
31. A.J. Chömpff, Ph. D. Thesis, Delft, 1965
32. A.J. Chömpff and J.A. Duiser, J. Chem. Phys. **45**, 1505 (1966)
33. A.J. Chömpff and W. Prins, J. Chem. Phys. **48**, 235 (1968)
34. P.H. van Wiechen and H.C. Booij, J. Engng. Math. (to be published)
35. J.J. Hermans, Physica **10**, 777 (1943)
36. H.C. Booij and P.H. van Wiechen, J. Chem. Phys. **52**, 5056 (1970)
37. J.G. Kirkwood, Rec. Trav. Chim. **68**, 649 (1949)
38. J.G. Kirkwood and P.L. Auer, J. Chem. Phys. **19**, 181 (1951)
39. J.G. Kirkwood and R.J. Plock, J. Chem. Phys. **24**, 665 (1956)
40. R. Zwanzig, Ann. Rev. Phys. Chem. **16**, 67 (1965)
41. R.M. Mazo, Statistical Mechanical Theories of Transport Processes, Pergamon Press, Oxford, 1967
42. Y-H. Pao, J. Macromol. Sci. **B1**, 289 (1967)
43. J.H. Irving and J.G. Kirkwood, J. Chem. Phys. **18**, 817 (1950)
44. T. Kotaka, J. Chem. Phys. **30**, 1566 (1959)
45. M.C. Williams, J. Chem. Phys. **42**, 2988 (1965)
46. A.S. Lodge, Nature **176**, 838 (1955); Trans. Faraday Soc. **52**, 120 (1956)
47. R. Pasternak and W. Kuhn, Helv. Chim. Acta **31**, 340 (1948)
48. J.G. Brodnyan, F.H. Gaskins and W. Philippoff, Trans. Soc. Rheol. **1**, 109 (1957)
49. V.N. Tsvetkov, in: Newer Methods of Polymer Characterization, Ed. B. Ke, Interscience, New York, 1964
50. H. Janeschitz-Kriegl, Makromol. Chem. **40**, 140 (1960)
51. A. Peterlin, J. Chem. Phys. **39**, 224 (1963)
52. P. Debye, J. Chem. Phys. **14**, 636 (1946)
53. A. Isihara, J. Polymer Sci. **C23**, 131 (1968); Adv. Polymer Sci. **5**, 531 (1968)
54. A.J. Staverman and F. Schwarzl, in: Physik der Hochpolymeren, Ed. H.A. Stuart, Vol. IV, Springer, Berlin, 1956
55. J.D. Ferry, Viscoelastic Properties of Polymers, Wiley, New York, 1961
56. F. Bueche, Physical Properties of Polymers, Interscience, New York , 1962

Chapter V

COMPARISON BETWEEN MOLECULAR THEORY AND EXPERIMENT

1. Introduction

In the previous chapter certain relations have been derived between the flow gradients applied to a polymeric fluid and the stress tensor occurring in such a fluid; this has been done by means of a generalized pearl-necklace model. A factor of essential importance in our theory is the relaxation spectrum $H(\tau)$, in which any given relaxation time τ pertains to a definite mode of motion of the normal coordinates in a complex of macromolecules. We further introduced an energy postulate stating that only a limited amount of free energy can be stored in a given mode of motion. If this limit is exceeded, the mode disappears, owing to disentanglement of the polymer chains. The postulate yields a relation between velocity gradients, time and maximum relaxation time τ_m. We studied this relation for several flow-fields. It appeared that in the case of parallel superposition τ_m is a function not only of the steady shear rate q, but also of the amplitude and frequency of the superposed oscillatory shear and of the time. This dependence has an effect on the expressions for the stresses produced during parallel superposition; for a description of these stresses we refer to Eqs (IV 9,11) up to and including (IV 9,20) in the previous chapter.

In the present chapter the theoretical predictions will be compared with experimental evidence. For this purpose, however, we need the two quantities introduced into the theory in the form of adaptable parameters, viz. $H(\tau)$ and $\tau_m(q)$.

2. Determination of the relaxation spectra

The actual shape of the relaxation spectra $H(\tau)$ can be derived from experimental data. Eqs (IV 9,17) and (IV 9,18) give the same expressions for G′ and G″ at pure oscillation as have been derived from many phenomenological theories. Ferry[1)] indicates several procedures for calculating an approximate shape of the spectrum from the two shear moduli established over a limited frequency interval. In our approach we primarily used the first-order approximation method suggested by Ninomiya and Ferry[2)]. The rather limited part of the spectrum thus obtained was intuitively extrapolated towards long and short relaxation times; this yielded a spectrum on the basis of which the quantities G′ and G″ were calculated on the computer. Since the first results did not show a close fit with the experimental values of the moduli over the entire measuring range, we modified the spectrum until the computer calculations gave a sufficiently accurate description of the experimental results. We thus determined $H(\tau)$ for the solutions 2 and 3 mentioned in chapter II,3. The spectra are illustrated logarithmically in Fig. V,1. The identity in shape shown by the two spectra is in accordance with the circumstance that the only difference

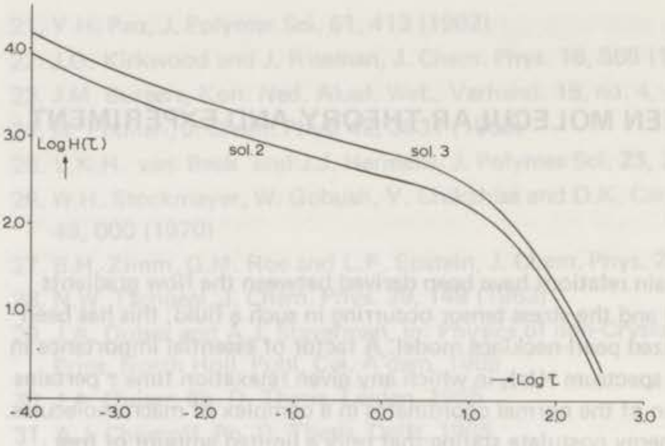


Fig. V,1 Intensity $H(\tau)$ of relaxation mechanisms per unit volume, in dynes cm^{-2}, as a function of the logarithm of the relaxation time τ, in sec, used in the calculations for solutions 2 and 3

between the solutions is a difference in concentration. The two spectra will be used as a basis in our further calculations.

3. Steady stresses and critical energy

For the known spectra the integral

$$\int_{-\infty}^{\ln \tau_o} H(\tau)\tau \, d \ln \tau$$

can be calculated as a function of $\ln \tau_o$. According to Eq. (IV 9,11), the values so found must be equal to those of the steady rotational viscosity $(p_{21})_{rot}/q$ at various values of q. Equating these calculated integrals for various values of τ_o to the experimental viscosity at various values of q, we found a relationship between τ_o and q. For solution 2, as well as for solution 3, this relation can be adeqately described by means of the expression $\tau_o = 2.5/q$, for all q-values used. The validity of this relation is demonstrated in Figs V,2 and V,3. In these figures the shear stresses calculated from the spectra are shown as functions of the shear rate q $(= 2.5/\tau_o)$ for each of the two solutions (drawn lines); in addition, the experimental values of p_{21} have been plotted versus q. It is seen that if the spectrum $H(\tau)$ is known, Eq. (IV 9,11) with $\tau_o = 2.5/q$ gives a good description of the shear stress as a function of the shear rate.

This finding implies that the critical energy $a^2(\tau)$ found from Eq. (IV 8,19) is independent of τ, which confirms the correctness of our assumption in section IV,8 that a^2 is not strongly dependent on τ.

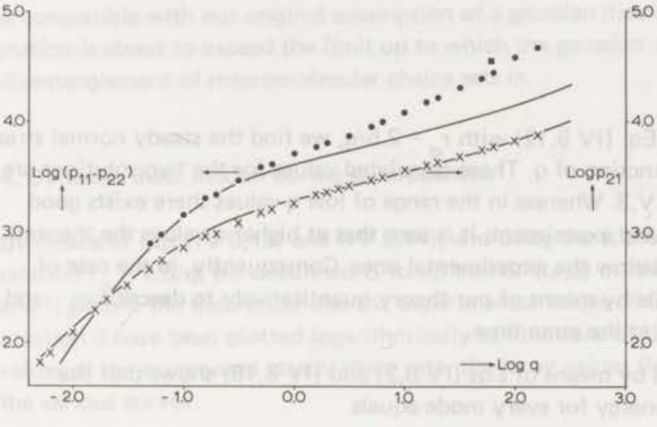


Fig. V,2 Comparison of the calculated shear rate dependence of the shear stress p_{21} and of the normal stress difference $p_{11}-p_{22}$ (drawn lines) with the experimental data (X and ●). Solution 3

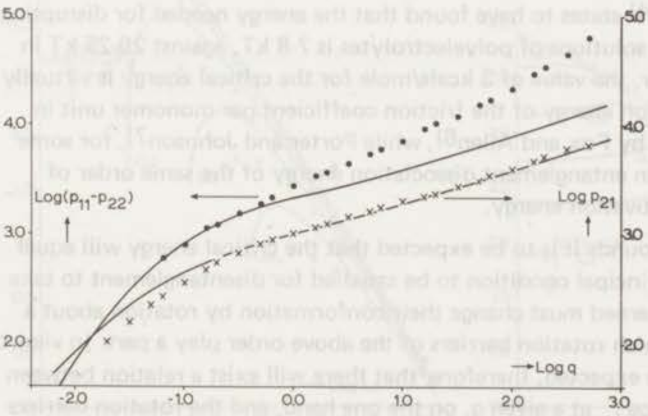


Fig. V,3 Comparison of the calculated shear rate dependence of the shear stress p_{21} and of the normal stress difference $p_{11}-p_{22}$ (drawn lines) with the experimental data (X and ●). Solution 2

Calculating the integrals

$$\int_{-\infty}^{\ln\tau_o} H(\tau)\tau^2 \, d\ln\tau$$

from the spectra and using Eq. (IV 9,12) with $\tau_o = 2.5/q$, we find the steady normal stress difference $p_{11} - p_{22}$ as a function of q. These calculated values for the two solutions are also shown in Figs V,2 and V,3. Whereas in the range of low q-values there exists good agreement between theory and experiment, it is seen that at higher q-values the theoretical results are significantly below the experimental ones. Consequently, in the case of steady shear it is not possible by means of our theory quantitatively to describe p_{21} and $p_{11} - p_{22}$ as functions of q at the same time.

With $\tau_o = 2.5/q$, calculation by means of Eqs (IV 8,2) and (IV 8,19) shows that the maximum increase in free energy for every mode equals

$$\Delta F^* = \tfrac{1}{2} kT \, [2\tau_o^2 q^2 - \ln(1 + \tau_o^2 q^2)] = 5.26\, kT,$$

which value, at room temperature, corresponds to approximately 2.1×10^{-13} ergs per mode. As stated in the previous chapter, this is the energy needed for disentanglement. Expressed in other units, the above energy is approximately equal to 3 kcals per gram-molecule in normal modes, so, much lower than the bond energy of, say, a C-C bond in polymers, which, depending on the further structure of the monomer3), lies between 50 and 70 kcals/mole. Gillespie4) states to have found that the energy needed for disrupting a disentanglement in several solutions of polyelectrolytes is 7-8 kT, against 20-25 kT in polystyrene melts5). Further, the value of 3 kcals/mole for the critical energy is virtually equal to the thermal activation energy of the friction coefficient per monomer unit in several polymers mentioned by Fox and Allen6), while Porter and Johnson7), for some other polymers, calculated an entanglement dissociation energy of the same order of magnitude from the flow activation energy.

Also on purely molecular grounds it is to be expected that the critical energy will equal a few kcals/mole. For, the principal condition to be satisfied for disentanglement to take place is that the chains concerned must change their conformation by rotation about a C-C bond – a process in which rotation barriers of the above order play a part. In view of this interpretation it is to be expected, therefore, that there will exist a relation between the critical energy, and, hence τ_o at a given q, on the one hand, and the rotation barriers in the main chain, on the other. It is evident from this that the solutions 2 and 3, being different in concentration only, will both show the same relation between τ_o and q.

It remains to be pointed out here that a reasonable measure of the deformation experienced by a mode is given by the root mean square of the dimension of the segments parallel to the shear velocity. In the case of simple shear flow this quantity equals $b[\mu(\tau)_{200}]^{1/2}$, as can be calculated by means of Eqs (IV 6,1) and (IV 6,2). Since under critical conditions we have $\tau_o q = 2.5$, the critical deformation calculated by means of Eq. (IV 8,7) equals $b\,(13.5)^{1/2}$, i.e. less than four times the root mean square length at rest. At this value of the end-to-end distance, the gaussian distribution is still a good approximation of the equilibrium distribution function of the segment lengths. This means that our energy postulate is compatible with our original assumption of a gaussian distribution. Before the deformation is about to exceed the limit up to which the gaussian distribution is applicable, disentanglement of macromolecular chains sets in.

4. Dynamic shear moduli during superposition

By means of Eqs (IV 9,13) and (IV 9,14), and using the spectra in Fig. V,1 and the relation $\tau_o = 2.5/q$, we calculated $G'(\omega,q)$ and $G''(\omega,q)$ on the computer. In Figs. V,4 and V,5 both the theoretical and the experimental values of $G'(\omega,q)$ and $G''(\omega,q)$ for solution 3 have been plotted logarithmically as functions of the frequency for some fixed values of the superposed steady shear rate; the latter values (log q) are indicated beside the various curves.

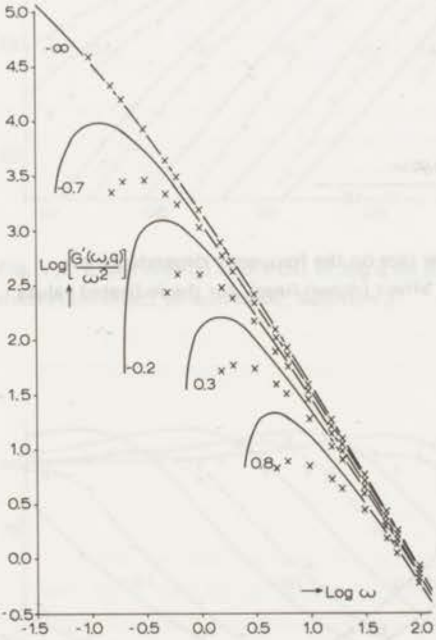


Fig. V,4 Calculated values of $G'(\omega,q)/\omega^2$ (drawn lines) compared with experimental data (X) for the indicated values of the logarithm of the superposed rate of shear q. Solution 3

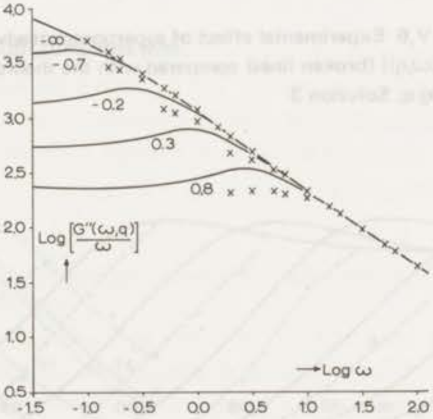


Fig. V,5 Comparison of the calculated frequency dependence of the dynamic viscosity $G''(\omega,q)/\omega$ (drawn lines) with the experimental data (X) for some indicated values of log q. Solution 3

The curve marked log q = −∞ shows that pure oscillation measurements can be very adequately described by means of the spectra given. The effect of q on the moduli is also described in a perfectly satisfactory manner, although, according to theory, the quantitative effect of superposition is slightly smaller than that found experimentally. The deviation between calculated and measured values is greater for $G'(\omega,q)$ than for $G''(\omega,q)$. However, the calculated $G'(\omega,q)/\omega^2$ vs ω curves very clearly display the maxima characteristic of parallel superposition.

A more direct comparison with the experimental quantities relating to some other values of log q for solution 3 is given in Figs V,6 and V,7

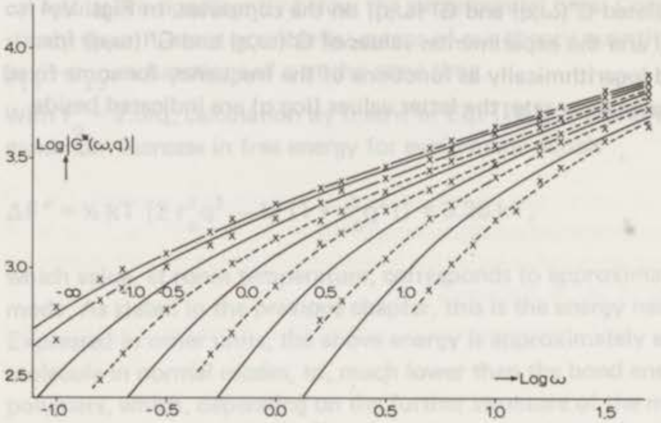


Fig. V,6 Experimental effect of superposed steady shear rate on the frequency dependence of $|G^*(\omega,q)|$ (broken lines) compared with the theoretical effect (drawn lines), for the indicated values of log q. Solution 3

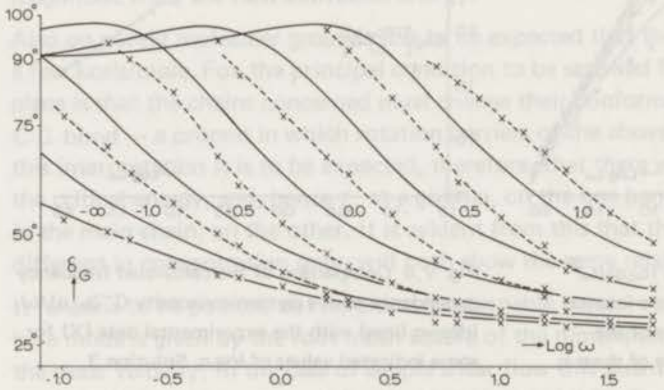


Fig. V,7 Theoretical effect of superposed steady shear rate on the frequency dependence of δ_G (drawn lines) compared with the experimental effect (broken lines), for the indicated values of log q. Solution 3

In these figures the drawn curves show the calculated values of the shear modulus $|G^*(\omega,q)|$ and the phase angle δ_G, while the experimental values are indicated by crosses. It is seen that in all cases the theoretical effect of superposition is again too small. From Fig. V,7 it can be concluded that, theoretically, the phase angle at frequencies lower than q comes to exceed 90^o, but also that at very low frequencies it tends again asymptotically towards this value.

In Figs V,8 and V,9 we have compared the theoretical and experimental values of

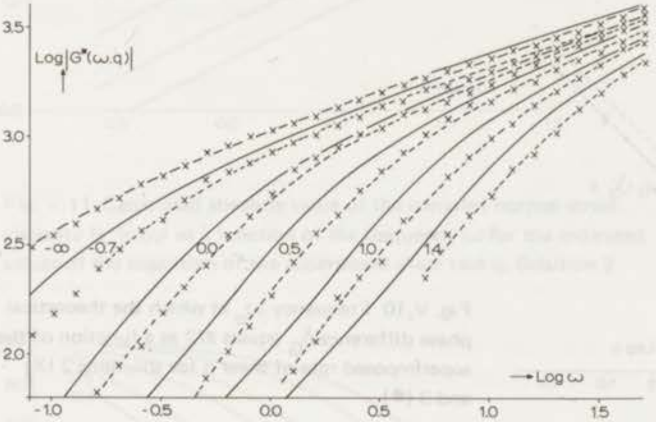


Fig. V,8 Experimental effect (X) of log q on $|G^*(\omega,q)|$ compared with theoretical effect (drawn lines). Solution 2

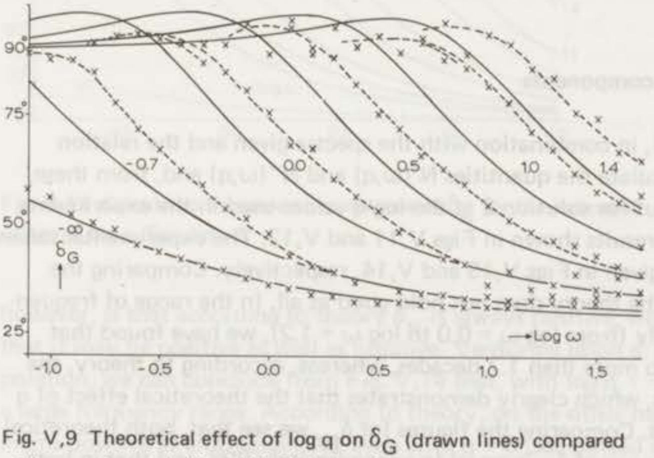


Fig. V,9 Theoretical effect of log q on δ_G (drawn lines) compared with experimental effect (X). Solution 2

$|G^*(\omega,q)|$ and δ_G for solution 2. Here again it is seen that the theoretical effect of superposition is slightly smaller than has been found experimentally.

Experiments with all solutions examined in the present study have shown (Fig. II,4) that in the measuring range employed the frequency ω_o at which the phase difference δ_G equals $\pi/2$ is related with the steady shear rate q via the expression $\omega_o = \frac{1}{2} q$. Calculations at various values of q also yield the frequencies ω_o at which the calculated phase differences equal $\pi/2$. These values, indicated in Fig. V,10, prove to satisfy the relation $\omega_o = 1/3\, q$,

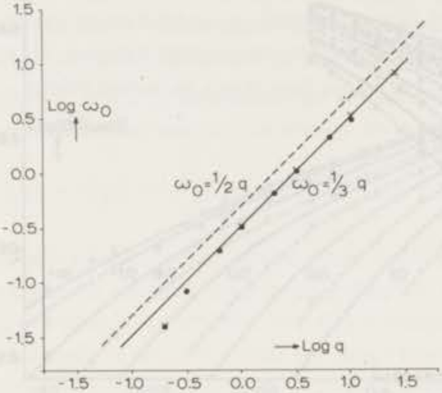


Fig. V,10 Frequency ω_o at which the theoretical phase difference δ_G equals $\pi/2$ as a function of the superimposed rate of shear q for solutions 2 (X) and 3 (●)

and show a tendency to deviate in the low-frequency range. The experimental relation is given for comparison. The difference between the two is not very great but definitely exceeds the experimental inaccuracy. Unfortunately, it is not possible on the basis of Eq. (IV 9,13) for $G'(\omega,q)$ directly to derive a simple theoretical relationship between ω_o and q.

5. Oscillatory normal stress components

Eqs (IV 9,15) and (IV 9,16), in combination with the spectra given and the relation $\tau_o = 2.5/q$, enable us to calculate the quantities $N'(\omega,q)$ and $N''(\omega,q)$ and, from these, $|N^*(\omega,q)|$ and δ_N. Carried out for solution 2 at the log q values used in the experiments, this calculation yielded the results shown in Figs V,11 and V,12. The experimental values of these two quantities are given in Figs V,13 and V,14, respectively. Comparing the various curves, we see that the theory does not hold good at all. In the range of frequencies examined experimentally (from $\log \omega = 0.0$ to $\log \omega = 1.2$), we have found that $\log |N^*(\omega,q)|$ varies over no more than 1.7 decades, whereas, according to theory, the variation covers 2.7 decades, which clearly demonstrates that the theoretical effect of q on $|N^*(\omega,q)|$ is far too great. Comparing the figures for δ_N, we see that, both theoretically and experimentally, the range of δ_N is equal to approximately 90^o, and that in both figures δ_N decreases with the frequency and increases with q. The most notable feature,

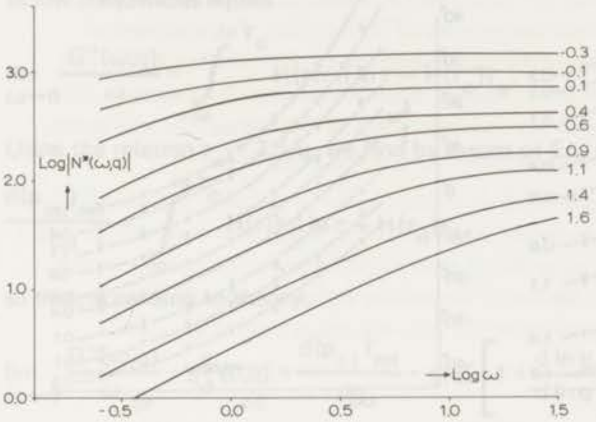


Fig. V,11 Calculated absolute value of the complex normal stress viscosity $N^*(\omega,q)$ as a function of the frequency ω for the indicated values of the logarithm of the superposed shear rate q. Solution 2

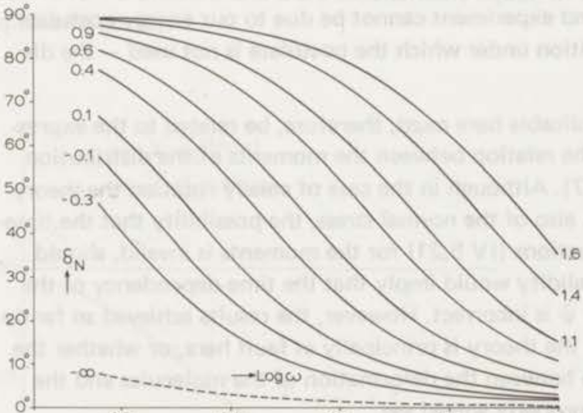


Fig. V,12 Calculated frequency dependence of δ_N for the indicated values of log q. Solution 2

however, is that according to theory δ_N is always positive, whereas experiment has shown that it may be positive as well as negative. Venturing upon a, perhaps inadmissible, extrapolation, we can conclude from Fig. V,14 that, with log q = $-\infty$, δ_N will be negative over a large frequency range. According to theory, on the other hand, the phase angle δ_N remains positive at all frequencies, even with q = 0 (see dotted curve in Fig. V,12). This follows directly from Eqs. (IV 9,19) and (IV 9,20), which indicate that, with q = 0, both N′ and N″, and, hence, also δ_N, are positive at all values of ω. In consequence, the dis-

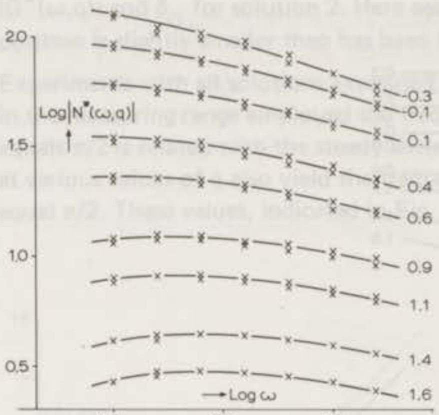


Fig. V,13 Experimental value of the normal stress viscosity $|N^*(\omega,q)|$ as a function of the frequency ω for the indicated values of log q. Solution 2

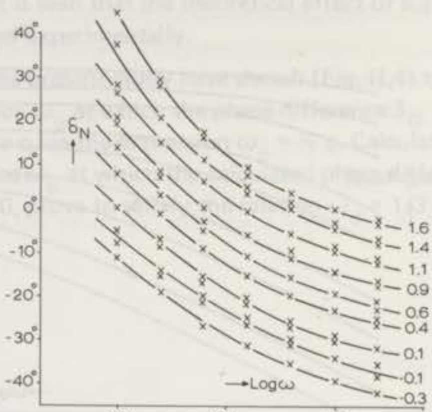


Fig. V,14 Experimental frequency dependence of δ_N for the indicated values of log q. Solution 2

crepancy found between theory and experiment cannot be due to our energy postulate. Also when q equals zero – a condition under which the postulate is not used – the discrepancy is found.

The fact that the theory is not applicable here must, therefore, be related to the expression for the moment μ_{200}, or to the relation between the moments of the distribution and the normal stress (chapter IV,7). Although in the case of steady rotation the theory does give a reasonable description, also of the normal stress, the possibility that the time-dependency of the differential equations (IV 5,21) for the moments is invalid, should certainly not be excluded; this invalidity would imply that the time-dependency of the differential equation (IV 5,17) for ψ is incorrect. However, the results achieved so far do not enable us to establish whether the theory is principally at fault here, or whether the problem regarding the relationship between the deformation of the molecules and the ensuing stress factor has not been properly solved yet.

6. Limiting values for the viscosity

As mentioned several times in chapter II, experiment has revealed that under conditions of superposition and with $\omega \rightarrow 0$, the limiting value of the dynamic viscosity $\eta_d(\omega,q)$ is not equal to the steady rotational shear viscosity $\eta(q)$ at the same q. With orthogonal superposition, it is seen that $\eta_d(\omega,d)$ may come to exceed $\eta(q)$, whereas with parallel superposition the situation is just the reverse.

We shall first subject the limiting values to a theoretical consideration. From formula (IV 9,14) it follows that in the case of parallel superposition the dynamic viscosity limit at low frequencies equals

$$\lim_{\omega \to 0} \frac{G''(\omega,q)}{\omega} = \int_{-\infty}^{\ln \tau_o} H(\tau)\tau \, d \ln \tau - H(\tau_o)\tau_o .$$

Using the relation $\tau_o = 2.5/q$, we find by means of Eq. (IV 9,11)

$$\frac{d(p_{21})_{rot}}{dq} = \int_{-\infty}^{\ln \tau_o} H(\tau)\tau \, d \ln \tau - H(\tau_o)\tau_o ,$$

so that, according to theory,

$$\lim_{\omega \to 0} \frac{G''(\omega,q)}{\omega} = \eta_d^{\parallel}(0,q) = \frac{d(p_{21})_{rot}}{dq} = \eta(q) \left[1 + \frac{d \ln \eta}{d \ln q} \right]$$

The same relation was derived in chapter III,5, where we dealt with various considerations on nearly viscometric flows (Eq. III,66)*). The relative incremental viscosity $[d(p_{21})_{rot}/dq]/\eta(q)$ can now be calculated from both the theoretical and the experimental results. Since the experimental curves for the shear stress can be adequately described by means the theory, the two calculations yield the same result. Moreover, the values found for solutions 2 and 3 are substantially equal. In Fig. V,15 they are plotted versus q (drawn curve).

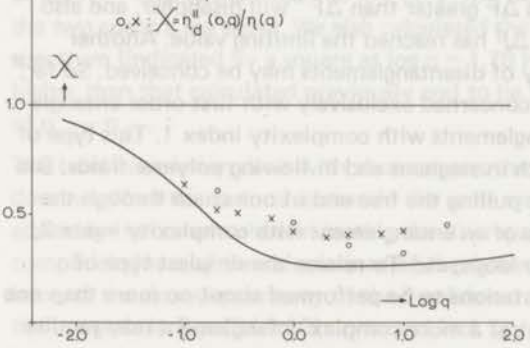


Fig. V,15 Theoretical and experimental values of the relative incremental steady-state viscosity $[dp_{21}/dq]/\eta(q)$ (drawn line) compared with the experimental data of the relative dynamic limit viscosity in the case of parallel superposition $\eta_d^{\parallel}(0,q)/\eta(q)$ for solutions 2 (0) and 3 (X)

---

*) Relations analogous to those derived by Bernstein and Fosdick (see Chapter III,5) also follow from Eqs. (IV 9,11) up to and incl. (IV 9,17), showing that among the four dynamic quantities $G'(\omega,q)$ is the only one that can become negative under certain conditions.

From the experimental values for log $|G^*(\omega,q)|$ as a function of log ω an estimate can be made of the limiting value at very low frequencies of $G''(\omega,q)/\omega$. The quotient of $\eta_d^{\parallel}(0,q)$ and $\eta(q)$ is also plotted versus the superposed shear rate q in Fig. V,15. The quotients for solution 3 are indicated by crosses, those for solution 2 by circlets. It is evident from this figure that, as far as the limiting values of the viscosity is concerned, there exists very reasonable agreement between theory and experiment.

In view of the theory it is to be expected that in the case of orthogonal superposition $\eta_d^{\perp}(0,q)$ will be equal to $\eta(q)$. meaning that the quotient $\eta_d^{\perp}(0,q)/\eta(q)$ must theoretically be equal to 1 at all values of q. A similar conclusion could be drawn from all theories dealt with in chapter III. However, Simmons' experiments have shown that this quotient may be 25 % higher than 1. An explanation for this high value cannot be given.

7. Discussion

The first discrepancy between theory and experiment was encountered when we made a comparison between the normal stresses. Upon proper adaptation of the shear stress as a function of q, we found too low a value for the normal stress.

We postulated that the relaxation mechanisms whose free energy has increased by an amount ΔF greater than a given critical amount ΔF^* are all bound to vanish, whereas all mechanisms that have increased in free energy by less than ΔF^* will remain in existence. This involved that above a given relaxation time τ_o, the relaxation spectrum suddenly fell off to zero. As seen from the physical angle, such an abrupt truncation would be unlikely. For, purely statistical considerations already suggest that, even though ΔF^* has a sharply defined value, not all mechanisms with a ΔF greater than ΔF^* will disappear, and also that a mechanism may disappear before ΔF has reached the limiting value. Another complicating factor is that a wide variety of disentanglements may be conceived. So far, it has been silently assumed that we are concerned exclusively with first-order entanglements, or, to use Bueche's term[8)], entanglements with complexity index 1. This type of entanglement is the most likely one, both in stagnant and in flowing polymer fluids. Disentanglement can be achieved by simply pulling the free end of one chain through the loop in an other one, whereas in the case of an entanglement with complexity index 2, the free end must be pulled through two loops, etc. To release the simplest type of entanglement it suffices for successive rotations to be performed about no more than one main-chain bond, whereas disengagement of a more complex entanglement may require simultaneous rotation about several bonds in the main chain. Such a concerted process calls for more energy, and we may say, therefore, that the value of ΔF^* will, in general, increase with the complexity index of the entanglement. This also explains why ΔF^* will not have a sharply defined value, but cover a whole range of values. This involves that the spectrum $H(\tau)$ will not be abruptly truncated at τ_o, but show a continuous and steep decrease.

In Fig. V,16 we have truncated the spectrum for solution 3 in a rather arbitrary fashion. In the range of low τ-values we have drawn a curve roughly parallel to the spectrum at high τ-values, with the sole intention of examining how a change in truncation manifests itself in the result of the calculations.

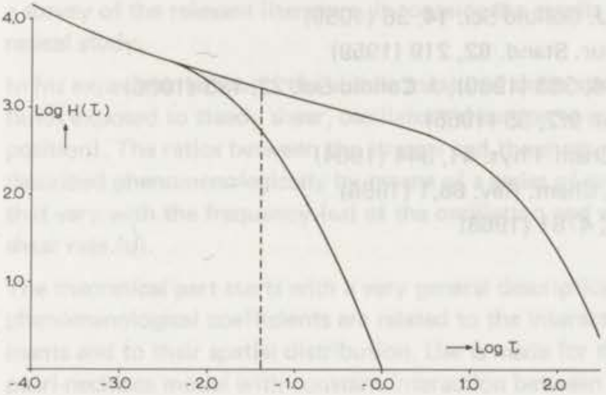


Fig. V,16 Two modes of narrowing the relaxation spectrum, resulting in the same values of the calculated steady-state shear stress p_{21} and in different values of the normal stress difference $p_{11} - p_{22}$ at log q = 1.78.
Solution 3

The value of the shear viscosity for this modified spectrum has been calculated on the computer. It appeared to be equal to that previously calculated for a spectrum truncated at $\log \tau_o = 1.38$ (see dotted line in Fig. V,16). So, at log q = 1.78, the shear stresses for the two spectra are equal. We also calculated the normal stress difference for the new spectrum (indicated by a square at log q = 1.78 in Fig. V,2), and found it to be much higher than that calculated previously and to lie fairly close to the experimental value of $p_{11} - p_{22}$.

The brief calculation dealt with above shows that a change in the shape of the truncation does no affect the various stresses in the same way, a circumstance that may be used to advantage in completely eliminating the discrepancy found. It adds, however, to the complicatedness of the calculations of the dynamic quantities in the case of superposition, because the time-dependency of the breakdown and, hence, the negative terms outside the integrals in Eqs (IV 9,13) up to and incl. (IV 9,16) can then no longer be calculated in a simple way. Moreover, it is not possible to indicate straightforwardly how the truncation should be made. We have therefore not elaborated this refinement of the theory, but only mentioned it as a possible means for arriving at a better description of the experimental results.

There is one point, however, on which the theory falls short very seriously, viz. in the description of the oscillatory normal stress components. As already pointed out in section 5 of the present chapter, this shortcoming has nothing to do with the shape of the relaxation spectrum and the use of the energy postulate. The cause of the discrepancy between theory and experiment on this point must therefore be sought in the basis of the theory.

8. References

1. J.D. Ferry, Viscoelastic Properties of Polymers, New York, 1961
2. K. Ninomiya and J.D. Ferry, J. Colloid Sci. **14**, 36 (1959)
3. S.L. Madorsky, J. Res. Nat. Bur. Stand. **62**, 219 (1959)
4. T. Gillespie, J. Polymer Sci. **46**, 383 (1960), J. Colloid Sci. **22**, 133 (1966)
5. T. Gillespie, Trans. Soc. Rheol. **9:2**, 35 (1965)
6. T.G. Fox and V.R. Allen, J. Chem. Phys. **41**, 344 (1964)
7. R.S. Porter and J.F. Johnson, Chem. Rev. **66**,1 (1966)
8. F. Bueche, J. Chem. Phys. **48**, 4781 (1968)

SUMMARY

The thesis deals with dynamic-mechanical properties of flowing polymeric fluids. Besides a survey of the relevant literature, it contains the results of an experimental and a theoretical study.

In his experimental work, the author measured shear stresses and normal stresses on fluids exposed to steady shear, oscillatory shear, or to a combination of the two (superposition). The ratios between the stresses and the shear rates causing them can be described phenomenologically by means of a series of proportionality coefficients (moduli) that vary with the frequency (ω) of the oscillation and with the value of the steady shear rate (q).

The theoretical part starts with a very general description of the way in which the phenomenological coefficients are related to the interaction between the molecule segments and to their spatial distribution. Use is made for this purpose of a generalized pearl-necklace model with constant interaction between the beads. After that, the author states a postulate about the change in interaction brought about by the shear rate and examines the effect of this change on the measurable quantities.

The principal information obtained from superposition studies by the author and other workers is presented below.

1. All the fluids examined display a distinct decrease in viscosity with the shear rate q, as well as a normal stress whose rate of variation does not keep up with that of q^2. In the case of superposition both shear moduli decrease with increasing q, especially at ω-values that are small compared with q. The in-phase modulus is reduced more strongly than the 90^o-out-of-phase modulus and even becomes negative at low frequencies. Measurements on widely differing viscoelastic fluids reveal that the frequency ω_o at which the in-phase modulus passes through zero is equal to ½ q.

2. All qualitatively satisfying descriptions are based on theories in which a viscoelastic fluid is looked upon as a collection of independent relaxation mechanisms with different relaxation times. In their original form, these theories predict that the viscosity of the fluid is independent of q, that the normal stress increases in proportion to q^2 and, further, that in the case of superposition the moduli are independent of q.

3. The description of the experimental data can be improved by assuming that the relaxation mechanisms are broken down, and no longer contribute to the stresses, as soon as a characteristic quantity comes to exceed a given critical value during the deformation process. The various theories can be differentiated by the type of relaxation mechanism, the nature of the characteristic quantity, and the calculation of the critical value.

a. In his thixotropy theory (chapter III,3) Leonov states that in every relaxation mechanism the stress at any given moment is related via a relaxation function to all previous deformation rates of the liquid regarded as a continuum. As soon as the elastically stored energy surpasses a critical value, the mechanism is broken down. In the calculation of this energy a drastic simplification is made, with the result that the theory loses its validity at high q-values.

b. According to Tanner and Simmons' network rupture theory (chapter III,4) the stress in every network linkage depends on the deformation of the continuous liquid at all previous moments. Network rupture occurs when after a given time lapse the total deformation of the linkage reaches a given critical value. Hence, the contributions to the stress at any given moment can come only from the deformation of network linkages formed within a given previous time interval. However, an unambiguous measure of the total deformation cannot be given, which renders the calculation of the critical deformation rather arbitrary.

c. In the generalized pearl-necklace model (chapter IV) Rouse's theory is extended to cover also concentrated polymer solutions. All sorts of interaction types, such as friction, entanglement, or hydrodynamic interaction between various parts of one or several necklaces, are described by means of a symmetric interaction matrix. It is shown that a polymeric fluid can be characterized as a collection of independent relaxation mechanisms, the so-called normal modes of motion, with relaxation times that can be calculated from the interaction matrix. The distribution function for every mode can be calculated for many types of flow fields, and the distribution moments, which are related to the stresses in a simple manner, must satisfy a set of linear differential equations.
After that, the author introduces the postulate that a given mode of motion vanishes when the increase in free energy of the mode reaches a given critical value. In various polymeric fluids this maximum increase in free energy proves to be approximately 3 kcals/mole, whatever the relaxation time of the mode. It is not unreasonable to suppose that this value is correlated with the energy barrier set to rotation about the main chain bonds.

4. All these theories demonstrate that in the case of parallel superposition the structural breakdown, which is determined by the stationary value of q, is attended by another type of breakdown which, varying with time, is caused by the superposed oscillation. Both types of breakdown have an effect on the dynamic moduli.

5. In the theories referred to under a. and c., the change of the fluid structure with the shear rate finds expression in truncation of the relaxation-time spectrum at the side of the longer relaxation times, and in theory b. in termination of the memory function at the side of longer time intervals.

6. By means of the abovementioned theories a qualitatively satisfying description can be given of the non-newtonian viscosity, the normal stresses and the dynamic shear moduli of sheared viscoelastic fluids. A quantitative comparison of the experimental data with the results of the generalized necklace model is given in chapter V. None of the theories appears to give a fully quantitative description of all the effects measured.

7. Among the theories treated there is not a single one by which the influence of q and ω on the oscillatory components of the normal stress can be described in a qualitatively correct way.

SAMENVATTING

Dit proefschrift behandelt dynamisch-mechanische eigenschappen van stromende polymere vloeistoffen. Naast een overzicht van de literatuur op dit gebied bevat het de resultaten van een experimenteel en van een theoretisch onderzoek.

In het experimentele onderzoek zijn afschuifspanningen en normaalspanningen gemeten in vloeistoffen welke onderworpen zijn aan stationaire afschuifstroming, aan oscillerende afschuifstroming of aan een superpositie van deze beide soorten stromingen. De verhoudingen van de optredende spanningen en de aangelegde afschuifsnelheden kunnen fenomenologisch worden beschreven door een reeks evenredigheidscoëfficiënten (moduli) welke afhankelijk zijn van de frequentie (ω) van de oscillatie en van de waarde (q) van de stationaire afschuifsnelheid.

Het theoretische deel geeft eerst een zeer algemene beschrijving van de verbanden tussen de fenomenologische coëfficiënten en de wisselwerking tussen en de ruimtelijke verdeling van molecuulsegmenten. Hierbij werd gebruik gemaakt van een gegeneraliseerd parelsnoermodel met constante wisselwerking tussen de parels. Vervolgens wordt een postulaat ingevoerd omtrent de verandering van de wisselwerking onder invloed van de afschuifsnelheid en wordt het effect van deze verandering op de meetbare grootheden onderzocht.

De belangrijkste feiten die in superpositieonderzoekingen, uitgevoerd door de auteur en door anderen, naar voren treden, zullen nu worden weergegeven:

1. Alle onderzochte vloeistoffen vertonen een duidelijke afname van de viscositeit met de afschuifsnelheid q en een normaalspanning welke veel minder dan evenredig met q^2 toeneemt. Bij superpositie worden beide afschuifmoduli kleiner naarmate q toeneemt, en wel speciaal bij waarden van ω welke klein zijn t.o.v. q. De in-fase-modulus wordt sterker verlaagd dan de 90°-uit-fase-modulus en wordt bij lage frequenties zelfs negatief. Uit metingen aan zeer verschillende viscoelastische vloeistoffen blijkt dat de frequentie ω_o, waarbij de in-fase-modulus door nul gaat, gelijk is aan ½ q.

2. Alle kwalitatief bevredigende beschrijvingen zijn gebaseerd op theorieën waarin een viscoelastische vloeistof wordt opgevat als een verzameling van onafhankelijke relaxatiemechanismen met verschillende relaxatietijden. In hun oorspronkelijke vorm voorspellen deze theorieën dat de viscositeit van de vloeistof onafhankelijk is van q, dat de normaalspanning evenredig met q^2 toeneemt en dat de moduli bij superpositie onafhankelijk van q zijn.

3. Een betere beschrijving van de experimentele gegevens kan worden verkregen door te veronderstellen dat de relaxatiemechanismen worden afgebroken en niet meer bijdragen tot de spanningen indien gedurende de deformatie een karakteristieke grootheid een bepaalde kritische waarde overschrijdt. De verschillende theorieën onderscheiden zich in het soort relaxatiemechanisme, in de aard van de karakteristieke grootheid en in de berekening van de kritische waarde:

a. In de thixotropie theorie van Leonov (hoofdstuk III,3) is in ieder relaxatiemechanisme de spanning op een bepaald tijdstip via een relaxatiefunctie verbonden met de deformatiesnelheden op alle voorgaande tijden van de als continuum opgevatte vloeistof. Bereikt de elastisch opgeslagen energie een bepaalde kritische waarde, dan wordt het mechanisme afgebroken. Bij de berekening van deze energie wordt een sterke vereenvoudiging toegepast, waardoor de theorie bij grote waarden van q niet meer toepasbaar is.

b. In de netwerkbreuktheorie van Tanner en Simmons (hoofdstuk III,4) is in iedere netwerkverbinding de spanning afhankelijk van de deformaties van de continue vloeistof op voorgaande tijden. Er treedt netwerkbreuk op als na een bepaalde tijd een gegeven kritische grootte van de totale deformatie van de verbinding is bereikt. Tot de spanning op een bepaald moment kunnen daarom alleen maar de deformaties bijdragen van netwerkverbindingen welke minder dan een bepaalde tijd geleden gevormd zijn. Voor de totale deformatie is echter niet een eenduidige maat te geven en de berekening van de kritische deformatie is daardoor vrij willekeuring.

c. In het gegeneraliseerde parelsnoermodel (hoofdstuk IV) wordt de statistische theorie van Rouse uitgebreid tot een theorie voor geconcentreerde polymeeroplossingen. Allerlei soorten wisselwerkingen, zoals wrijving, verstrengeling of hydrodynamische interactie tussen verschillende gedeelten van één of meerdere parelsnoeren, worden beschreven met een symmetrische interactie-matrix. Aangetoond wordt dat een polymere vloeistof te beschrijven is als een verzameling van onafhankelijke relaxatiemechanismen, de z.g. normale modi van beweging, met relaxatietijden welke uit de interactie-matrix kunnen worden berekend. De verdelingsfunctie voor iedere modus kan worden berekend voor velerlei vormen van het stromingsveld, en de momenten van de verdeling, welke op eenvoudige wijze verbonden zijn met de spanningen, moeten voldoen aan een stelsel lineaire differentiaalvergelijkingen.
Als postulaat wordt nu ingevoerd dat een bepaalde modus van beweging verdwijnt als de toename in vrije energie van de modus een bepaalde kritische waarde bereikt. Voor verschillende polymere vloeistoffen blijkt deze maximale toename in vrije energie, ongeacht de relaxatietijd van de modus, gelijk te zijn aan ongeveer 3 kcal/mol. Deze waarde zou wel eens gecorreleerd kunnen zijn met de energiebarriere voor rotatie om hoofdketenbindingen.

4. Volgens al deze theorieën treedt bij parallele superpositie behalve een structuurafbraak welke bepaald wordt door de stationaire waarde van q ook een met de tijd varierende afbraak op als gevolg van de gesuperponeerde oscillatie. Beide soorten afbraak beinvloeden de dynamische moduli.

5. De verandering van de structuur van de vloeistof met de afschuifsnelheid komt in de theorieën a. en c. tot uitdrukking in een afsnijding van het relaxatietijdenspectrum aan de kant van de lange relaxatietijden, en in theorie b. in een afbreking van de herinneringsfunctie aan de kant van de lange tijdintervallen.

6. Met behulp van de genoemde theorieën is het mogelijk een kwalitatief bevredigende beschrijving te geven van de niet-newtonse viscositeit, de normaalspanningen en de dynamische afschuifmoduli van afgeschoven viscoelastische vloeistoffen. Een kwantitatieve vergelijking van de experimentele gegevens met de resultaten van het gegeneraliseerde parelsnoermodel is in hoofdstuk V gegeven. Geen van de theorieën geeft een volledig kwantitatieve beschrijving van alle gemeten effecten.

7. Niet één van de behandelde theorieën is in staat om ook maar op een kwalitatief juiste wijze de invloed van q en ω op de oscillerende componenten van de normaalspanning te beschrijven.

LIST OF USED SYMBOLS

Symbol	Description	Dimension	Page
$\underline{A}$	Rouse matrix	–	77
$\underline{A}^Z$	Zimm matrix	–	77
$\underset{\sim}{a}$	transformation matrix	–	69
$\underline{B}$	mobility matrix	$[m]^{-1}\,[t]$	77
$\underline{B}(t')$	Finger's metric tensor	–	9, 12
b	a dimension factor in macromolecules	$[l]$	69
C	stress-optical coefficient	$[m]^{-1}\,[l]\,[t]^2$	87
$\underline{C}(t')$	Cauchy's metric tensor	–	9, 12
$\dot{\underline{E}}$	rate-of-strain tensor	$[t]^{-1}$	13
$\underset{\sim}{e}$	base vector	$[l]$	7
$\underline{F}^e$	matrix for entropy-elastic forces	$[m]\,[l]\,[t]^{-2}$	72
$\underline{F}^f$	matrix for friction forces	$[m]\,[l]\,[t]^{-2}$	74
$\underset{\sim}{f}^e$	entropy-elastic force vector	$[m]\,[l]\,[t]^{-2}$	72
$\underset{\sim}{f}^f$	friction force vector	$[m]\,[l]\,[t]^{-2}$	74
$\underset{\sim}{f}$	matrix for friction coefficients	$[m]\,[t]^{-1}$	74
$\underline{G}(t')$	covariant strain tensor	–	13
G^*	complex shear-modulus	$[m]\,[l]^{-1}\,[t]^{-2}$	17
G'	storage shear-modulus	$[m]\,[l]^{-1}\,[t]^{-2}$	17
G''	loss shear-modulus	$[m]\,[l]^{-1}\,[t]^{-2}$	17
$G^*(\omega,q)$	complex shear-modulus at superposition	$[m]\,[l]^{-1}\,[t]^{-2}$	18
$G'(\omega,q)$	in-phase component of complex shear-modulus	$[m]\,[l]^{-1}\,[t]^{-2}$	18
$G''(\omega,q)$	90^o-out-of-phase component of complex shear-modulus	$[m]\,[l]^{-1}\,[t]^{-2}$	18
g	distribution function for centre of gravity	–	70
$H(\tau)$	relaxation spectrum	$[m]\,[l]^{-1}\,[t]^{-2}$	98
$\underline{H}^e$	matrix for transformed entropy-elastic forces	$[m]\,[l]\,[t]^{-2}$	72
$\underline{H}^f$	matrix for transformed friction forces	$[m]\,[l]\,[t]^{-2}$	75
$\underset{\sim}{h}^e$	vector of transformed entropy-elastic force	$[m]\,[l]\,[t]^{-2}$	72
$\underset{\sim}{h}^f$	vector of transformed friction force	$[m]\,[l]\,[t]^{-2}$	75

$\underline{I}$	unit matrix	—	12, 81
k	Boltzmann's constant	$[m]\,[l]^2\,[t]^{-2}\,[T]^{-1}$	71
l_m	monomer length	$[l]$	69
M	molecular weight	$[m]$	19
$\underline{M}$	matrix of moments	—	81
N	number of complexes per unit volume	$[l]^{-3}$	72
$N(\tau)$	relaxation-time distribution function	$[m]\,[l]^{-1}\,[t]^{-3}$ or $[l]^{-3}\,[t]$	44 or 85
$2\,q\,N^*(\omega,q)$	complex normal-stress-modulus	$[m]\,[l]^{-1}\,[t]^{-2}$	18
$2\,q\,N'(\omega,q)$	in-phase component of normal-stress-modulus	$[m]\,[l]^{-1}\,[t]^{-2}$	18
$2\,q\,N''(\omega,q)$	90°-out-of-phase component of normal-stress-modulus	$[m]\,[l]^{-1}\,[t]^{-2}$	18
n	number of segments in a macromolecule	—	68
n_m	number of monomers in a segment	—	69
$\underline{P}$	stress tensor	$[m]\,[l]^{-1}\,[t]^{-2}$	16
$\underline{Q}$	transformation matrix	—	77
q	constant shear rate	$[t]^{-1}$	14
$\underline{R}$	matrix for bead coordinates	$[l]$	68
$\dot{\underline{R}}$	matrix for bead velocities	$[l]\,[t]^{-1}$	74
$\underset{\sim}{r}$	position vector (volume element)	$[l]$	7
$\underset{\sim}{r}_i$	position vector bead (i-th bead)	$[l]$	68
$\dot{\underset{\sim}{r}}_i$	velocity vector (i-th bead)	$[l]\,[t]^{-1}$	74
$\underline{S}$	matrix for coordinate differences	—	69
$\underline{S}^*$	matrix for coordinate differences	—	77
$\dot{\underline{S}}$	matrix for coordinate velocities	$[t]^{-1}$	75
$\dot{\underline{S}}_o$	matrix for macroscopic velocity differences	$[t]^{-1}$	75
$\dot{\underline{S}}_o^*$	matrix for macroscopic velocity differences	$[t]^{-1}$	77
$\underline{S}(t')$	contravariant strain tensor	—	12
S_{ijkl}	relaxation moduli	$[m]\,[l]^{-1}\,[t]^{-3}$	60
$\underset{\sim}{s}$	coordinate-difference vector	—	69
$\dot{\underset{\sim}{s}}$	bead-velocity difference vector	$[t]^{-1}$	75
$\dot{\underset{\sim}{s}}_o$	macroscopic velocity difference vector	$[t]^{-1}$	75

s	time difference t−t′	[t]	59
T	absolute temperature	[T]	71
$\underline{T}$	hydrodynamic interaction matrix	$[m]^{-1}\,[t]$	74
t	time	[t]	11
u	component of $\underset{\sim}{s}$	—	69
V	volume	$[l]^3$	71
$\underline{V}_o$	matrix for macroscopic velocities	$[l]\,[t]^{-1}$	73
$\underline{V}'_o$	matrix for disturbed macroscopic velocities	$[l]\,[t]^{-1}$	74
$\underset{\sim}{v}$	velocity vector (volume element)	$[l]\,[t]^{-1}$	13
$\underset{\sim}{v}_o$	macroscopic velocity vector	$[l]\,[t]^{-1}$	73
v	component of $\underset{\sim}{s}$	—	69
$\underline{W}$	matrix for friction coefficients	$[m]\,[t]^{-1}$	75
w_i	weight fraction	—	19
w	component of $\underset{\sim}{s}$	—	69
x	number of macromolecules in a complex	—	68
x_i	component of $\underset{\sim}{r}_i$	[l]	68
y_i	component of $\underset{\sim}{r}_i$	[l]	68
z_i	component of $\underset{\sim}{r}_i$	[l]	68
α	amplitude of oscillation	—	14
β	normal-stress coefficient	$[m]\,[l]^{-1}$	18
$\dot{\underline{\Gamma}}$	velocity-gradient tensor	$[t]^{-1}$	13,80
$\dot{\gamma}$	time-dependent rate of simple shear	$[t]^{-1}$	14
ΔF	free-energy difference	$[m]\,[l]^2\,[t]^{-2}$	71
Δn	flow birefringence	—	87
ΔS	entropy difference	$[m]\,[l]^2\,[t]^{-2}\,[T]^{-1}$	71
δ	phase lag	—	17
ζ	component of $\underset{\sim}{\rho}$	—	78
$\dot{\zeta}_o$	component of $\dot{\underset{\sim}{\rho}}_o$	$[t]^{-1}$	78
η	viscosity	$[m]\,[l]^{-1}\,[t]^{-1}$	15
$\eta(q)$	non-newtonian viscosity function	$[m]\,[l]^{-1}\,[t]^{-1}$	18
$\eta^{\parallel}(\omega,q)$	dynamic viscosity at parallel superposition	$[m]\,[l]^{-1}\,[t]^{-1}$	61
$\eta^{\perp}(\omega,q)$	dynamic viscosity at orthogonal superposition	$[m]\,[l]^{-1}\,[t]^{-1}$	62

η	component of $\underline{\rho}$	—	78
$\dot{\eta}_o$	component of $\dot{\underline{\rho}}_o$	$[t]^{-1}$	78
θ	angle variable	—	8
κ	time-dependent shear rate	$[t]^{-1}$	46, 83
$\underline{\Lambda}$	diagonal matrix for eigenvalues	—	77
λ_k	eigenvalue	—	77
μ	thermodynamic potential	$[m]\,[l]^2\,[t]^{-2}$	72
μ_{pqr}	moments of distribution	—	81
$\mu(t-t')$	memory function	$[m]\,[l]^{-1}\,[t]^{-3}$	53
υ	number of complexes in an ensemble	—	71
ξ	component of $\underline{\rho}$	—	78
$\dot{\xi}_o$	component of $\dot{\underline{\rho}}_o$	$[t]^{-1}$	78
$\underline{P}$	matrix for normal coordinates	—	78
$\dot{\underline{P}}_o$	matrix for macroscopic velocities in normal coordinates	$[t]^{-1}$	78
ρ	density	$[m]\,[l]^{-3}$	15
$\underline{\rho}$	position vector in normal coordinates	—	78
$\dot{\underline{\rho}}_o$	macroscopic-velocity vector in normal coordinates	$[t]^{-1}$	78
τ_k	relaxation time	$[t]$	80
τ_m	maximum relaxation time	$[t]$	48, 95
ϕ	undisturbed distribution function	—	68
φ	angle variable	—	8
χ	extinction angle	—	87
ψ	distribution function	—	70
Ω	angular rotation velocity	$[t]^{-1}$	15
$\dot{\underline{\Omega}}$	vorticity tensor	$[t]^{-1}$	13
ω	circular frequency of oscillation	$[t]^{-1}$	14

Dankwoord

De hoofddirectie van DSM te Heerlen en de leiding van het Centraal Laboratorium te Geleen ben ik zeer erkentelijk voor de ruime mate waarin mij de gelegenheid werd verleend tot het uitvoeren van het onderzoek en het bewerken van dit proefschrift. Meer persoonlijk richt ik deze dank gaarne aan Dr. C. van Heerden en Dr.Ir. R. Koningsveld. Voor zeer vele stimulerende discussies en suggesties ben ik Dr. C. van Heerden, Dr. A.J. Pennings en Ir. P.H. van Wiechen heel dankbaar. De heer C.M.L. Werker dank ik hartelijk voor het uitvoeren van de metingen en voor de hulp bij de berekeningen.

Voor de uiteindelijke vorm van dit werk ben ik veel dank verschuldigd aan de heer P.H. Hermans voor het verzorgen van de Engelse vertaling, juffrouw A.J.M. Rikken voor de wijze waarop zij het typewerk heeft uitgevoerd, de heren G.M.F.X. Baggen en G. Schuler voor het vervaardigen van de illustraties, de heren H.E. Horst, M.A.P. Scholten en J.C.M. Steuns voor de hulp bij vele typografische voorbereidingen, en de drukkerij P.M. van Hooren voor het verzorgen van de off-set.

Levensloop

De schrijver van dit proefschrift werd geboren op 2 december 1935 te Surhuisterveen (gemeente Achtkarspelen). Hij bezocht van 1948 tot 1953 het Christelijk Lyceum voor Zeeland te Goes. Na het eindexamen HBS studeerde hij aan de Vrije Universiteit te Amsterdam, alwaar hij in 1961 het doctoraal examen natuurkunde aflegde. Na het vervullen van de militaire dienstplicht was hij werkzaam op het Centraal Laboratorium van DSM (Afdeling Fundamenteel Polymeer Onderzoek), waar in 1965 een begin werd gemaakt aan het in dit proefschrift beschreven onderzoek.

Dankwoord

De hoofddirectie van DSM te Heerlen en de leiding van het Centraal Laboratorium te Geleen ben ik zeer erkentelijk voor de ruime mate waarin mij de gelegenheid werd verleend tot het uitvoeren van het onderzoek en het bewerken van dit proefschrift. Meer persoonlijk richt ik deze dank gaarne aan Dr. C. van Heerden en Dr.Ir. R. Koningsveld. Voor zeer vele stimulerende discussies en suggesties ben ik Dr. C. van Heerden, Dr. A.J. Pennings en Ir. P.H. van Wiechen heel dankbaar. De heer C.M.L. Werker dank ik hartelijk voor het uitvoeren van de metingen en voor de hulp bij de berekeningen.

Voor de uiteindelijke vorm van dit werk ben ik veel dank verschuldigd aan de heer P.H. Hermans voor het verzorgen van de Engelse vertaling, juffrouw A.J.M. Rikken voor de wijze waarop zij het typewerk heeft uitgevoerd, de heren G.M.F.X. Beggen en G. Schüler voor het vervaardigen van de illustraties, de heren H.E. Horst, M.A.P. Scholten en J.C.M. Steuns voor de hulp bij vele typografische voorbereidingen, en de drukkerij P.M. van Hooren voor het verzorgen van de off-set.

Levensloop

De schrijver van dit proefschrift werd geboren op 2 december 1935 te Surhuisterveen (gemeente Achtkarspelen). Hij bezocht van 1946 tot 1953 het Christelijk Lyceum voor Zeeland te Goes. Na het eindexamen HBS studeerde hij aan de Vrije Universiteit te Amsterdam, alwaar hij in 1961 het doctoraal examen natuurkunde aflegde. Na het vervullen van de militaire dienstplicht was hij werkzaam op het Centraal Laboratorium van DSM (Afdeling Fundamenteel Polymeer Onderzoek), waar in 1965 een begin werd gemaakt aan het in dit proefschrift beschreven onderzoek.