The rheological behaviour of suspensions of fat particles in oil interpreted in terms of a transient-network model

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Abstract: The transient-network model for concentrated dispersions, described in a previous paper, is used to describe the rheological behaviour of dispersions of glyceryl tristearate crystals in paraffin oil. The model prediction of the storage modulus of this system is compared with corresponding expressions given in literature. Model calculations are carried out to fit the linear viscoelastic behaviour of the system as well as its stress response in large amplitude shear experiments. Information is thus obtained about the stiffness and strength of the interparticle bonds, and the chance of them breaking in a state of rest or as the result of flow. It is concluded that the probability of interparticle bond fracture strongly depends on the measure of bond stretching. The general findings link up with the Lennard-Jones potential which is assumed to describe the potential energy of the bonds between the particles. Accurate measurements of the temperature dependence of the dynamic moduli by making use of a torsion resonator lead to the conclusion that the energy dissipation at a high frequency originates mainly from the flow of liquid around the particles.

Key words: Suspension, fat particles, rheological behaviour, structured dispersion, transient-network model.

1. Introduction

Suspensions of fat particles in oil have been the subject of intensive rheological research in the past [1–6]. The purpose was either to obtain more insight into the fundamental relation between structural processes that take place at a microscopical level and the rheological behaviour of concentrated dispersions in general, or to describe the rheological behaviour of these sorts of materials themselves, such as margarine, which are important in the food industry. Thus either the fat particle systems served as model systems for a broad class of concentrated dispersions, or they were the object of the investigation themselves. The systems under consideration exhibit a certain yield stress starting from a crystal phase weight concentration of a few percent. This behaviour can only be explained by the interparticle forces which are apparently of the low-range type, since only van der Waals' attractive and Born's repulsive forces are involved in these systems which consist of nonpolar media. It is generally believed that a three-dimensional particle network is formed, i.e. that there is a nonhomogeneous distribution of crystal particles over the material as a whole. In the systems both domains containing liquid only as well as those containing a relatively large percentage of dispersed material can be distinguished, i.e. holes and conglomerates respectively [1–4, 7]. Conglomerates are assumed to be mutually connected by means of crystal chains (fig. 1).

Theories have been developed to explain the rheological behaviour of concentrated dispersions. Their nature is either phenomenological [6, 8, 9], or they start from the structural processes that take place at a microscopical level if macroscopic deformations are applied to these materials. With regard to the first class of theories we should mention the approach of de Brujine et al. [5], who used a modified Maxwell element to describe the rheological behaviour of fat dispersions at high deformations, and Strivens [8], who used a retarded Maxwell element to describe the

Various structural models explain the effective viscosity of concentrated dispersions from the energy dissipation due to viscous flow between the suspended particles [13, 14]. The elastic-flow model [15-18] was introduced mainly to describe the flow behaviour of coagulated sols. All contributions to energy dissipation were calculated, i.e. those due to liquid flow and bond fracture, and subsequently expressions were obtained for the differential viscosity and the Bingham yield stress in terms of floc size, floc rigidity and medium viscosity. Applications of the model concern stationary flow properties only.

More attempts have been made to relate relevant rheological material properties to both physical and structural properties of the microscopical units building up networks of dispersed material, such as Hamaker's constant and the fraction of particles being absorbed in the chains that connect the conglomerates [1-4, 7, 19]. These models have in common that they calculate the stresses from the deformation of a three-dimensional particle network, which is assumed to exist. However, the effects of the nonlinearity of particle-particle interaction potentials, random structure formations resulting in an infinite number of possible chain shapes, and the basically non-affine network deformation after fracture of stress-carrying network chains, on the rheological behaviour of concentrated suspensions of fat crystals in oil, have not yet been elucidated because a model taking all these effects into account was not available.

Recently a transient-network model designed for describing the rheological behaviour of structured dispersions has been developed which takes the above-mentioned effects into account without being so complicated that numerical analysis is substantially impeded [20]. Stress-tensor components are calculated from the forces in the particle chains that are part of three-dimensional transient network. A set of integral expressions have been derived from which the stresses in transient experiments can be calculated, whereas analytical expressions have been obtained to describe the linear viscoelastic behaviour of the system.

The purpose of this paper is to interpret the rheological behaviour of fat-in-oil dispersions by means of the transient-network model for concentrated dispersions mentioned above. This requires the selection of the correct functions for bond interaction potential and bond fracture chance and the substitution of them in the model equations. Model stress predictions will be compared with rheological measurements on the systems.

The measurements concern both the linear viscoelastic response and the stress response at large shearing deformations. Model parameter values that result in adequate model stress predictions provide information concerning the particle interaction potential and the microstructure. This insight provides the tools to modify the rheological behaviour of the material in some preferred way.

2. Theory

As the model has been described in detail in a previous paper [20], we shall now only give a short description of it and some of the model-stress predictions. A network of chains of dispersed material is assumed to be present in the material (fig. 1). Each chain is represented by a chain vector \( q \) connecting the so-called junction points which are located in the conglomerates. A complexity parameter \( \chi \) is introduced to distinguish chains of different natures. Chains may be created as well as broken during flow and even spontaneously when at rest. Each chain transmits a force \( f \) which parallels \( q \) when the force is of a tensile nature, and opposes \( q \) when it is compressive. The stress ten-
In the case of inception of steady flow, chains that are created during flow are assumed to contribute to the stress in the same way as those chains that were present when the experiment started. It can be proved [20] then that:

\[ T(t) = T_b(t) + \int_0^t T_b(t - t') \frac{\sum_x g(x, q', t') d^3 q'}{n_o} dt', \]  

(5)

where

\[ g(x, q', t') d^3 q' dt' = \phi(x, q', t'|t) d^3 q' dt', \]  

(6)

the number of \( x \)-chains that are created during the time interval \( (t', t' + dt') \) within the configuration range \( d^3 q' \) about \( q' \) and \( n_o \) is the value at rest of the total chain density \( n(t) \).

The density function \( \phi \) in equation (4) is determined by the annihilation function \( h \), which gives its relative decrease per unit of time:

\[ h(x, q', t'|t) = -\frac{\partial}{\partial t'} \phi(x, q', t'|t) \]  

(7)

Integration gives:

\[ \phi(x, q', t'|t) = \phi(x, q', t'|t) \exp \left\{ -\frac{1}{t} \int_0^t h(x, q', t'|t') dt' \right\}. \]  

(8)

By integrating equation (8) for all times \( t' \leq 0 \) for which the system was at rest and by substituting \( h(x, q', t'|t) = h(x, q', 0|t) \) for \( t' \leq 0 \leq t \), we obtain:

\[ \int_{-\infty}^0 \phi(x, q', t'|0) dt' = \int_{-\infty}^0 \phi(x, q', 0|t') dt' \exp \left\{ -\frac{1}{t} \int_0^t h(x, q', 0|t') dt' \right\}. \]  

(9)

Next consider a simple network in which all chains have the same length \( q_o \) in the initial state, while the chain vectors are then isotropically distributed over orientation space, so:

\[ \int_{-\infty}^0 \phi(x, q', t'|0) dt' = \frac{n_o(x)}{4\pi q_o^2} \delta(q' - q_o), \]  

(10)

where \( n_o(x) \) denotes the value at rest of \( n(x, t) \), the number of \( x \)-chains per unit volume and \( \delta \) the delta function.
Expression (4) becomes after substitution of equations (9) and (10):

\[
T_b(t) = \frac{1}{4\pi q_o^2} \sum_x n_o(x) \int g(x, q', 0 | t) f(q', 0 | t) \delta(q' - q_o) 
\times \exp \left[ -\int_0^t h(x, q', 0 | t') dt' \right] d^3 q'.
\]  

The integrations can only be carried out if the dependence of \( q, f \) and \( h \) on time are known. The simplest way to obtain these dependences would be to assume that the junction points move affinely with the applied macroscopic deformation. This would however contradict reality in two ways. First, if \( \epsilon \) depends on \( x \), affine deformation implies that there is an unbalance between forces acting in the network, i.e. condition (2) cannot be fulfilled. Second, there is then no way to take into account the influence of chain fracture, occurring somewhere in the network, on the state of deformation of the rest of the network. Instead, we introduced a vector \( \chi(\vec{x}, \vec{q} | t) \) [20]:

\[
\chi(\vec{q}, \vec{q} | t) = \frac{\sum_x q(x, q', \vec{q} | t) n_o(x)}{n_o} - \frac{q_o}{n_o} \frac{\int_0^t \bar{n}(t' | t) dt'}{n_o},
\]  

where \( E_r(t) \) is the relative macroscopic deformation gradient, and the last term denotes a weighed average state of deformation of part of the network. Thus \( -\chi \) gives the deviation of the average junction flow from the junction flow that would correspond with affine deformation. The function \( \chi \) is believed to represent the effect of the chain fractures on the flow of the remaining part of the network. Therefore \( \chi \) will hang together with the number of fractures. It was argued that in the case of inception of some flow at time \( t = 0 \) which does not allow for any reformation of broken structures:

\[
\chi(\vec{q}, \vec{q} | t) = \lambda q \left( 1 - \frac{\int_0^t \bar{n}(t' | t) dt'}{n_o} \right) f(q', 0 | t) e(q', t' | t),
\]  

for \( t' \leq 0 \leq t \) [20]. The function \( \bar{n}(t' | t) dt' \) denotes the number of chains per unit volume created during the time interval \( (t', t' + dt') \) that is still present at the actual time \( t \). The integral follows from integration of equation (9) over configuration space while equation (10) is taken into account:

\[
\int_0^t \bar{n}(t' | t) dt' = \frac{1}{4\pi q_o^2} \sum_x n_o(x) \int \delta(q' - q_o) 
\times \exp \left[ -\int_0^t h(x, q', 0 | t') dt' \right] d^3 q'.
\]  

A proportionality factor \( \lambda \) with unit \( [kg^{-1} m^{-1} s^{-2}] \) has been introduced in equation (13). The unit vector \( e \) (see also eq. (3)) can be shown to be equal to \( E_r(t) \cdot q' / \|E_r(t) \cdot q'\| \). Equation (13) is also assumed to be valid in the case of cessation of steady flow at some arbitrary time \( t > 0 \). Since equation (2) is valid for all complexities we may express the length of chains of complexity \( x' \) in terms of the length of chains of complexity \( x \):

\[
q(x, q_o, t' | t) = q_o + \frac{c(x, q_o)}{c(x', q_o)} (q(x, q_o, t' | t) - q_o),
\]  

where \( x \) may be equal to \( x' \) or be different.

We shall now derive the chain vectors from the preceding expressions. We may write:

\[
q(x, q_o, t' | t) = \frac{\sum_x q(x', q_o, t' | t) n_o(x)}{n_o(x)} - \frac{\sum_x q(x', q_o, t' | t) n_o(x)}{n_o(x)} \bar{e}(q_o, t' | t).
\]  

Combination of equations (12), (15) and (16) gives:

\[
q(x, q_o, t' | t) = (|E_r(t) \cdot q_o| - \chi(\vec{q}, \vec{q} | t)) \frac{n_o}{n_o(x)}
\times \sum_x \left( q_o + \frac{c(x, q_o)}{c(x', q_o)} (q(x, q_o, t' | t)
- q_o) \right) \bar{e}(q_o, t' | t).
\]  

(17)
After substitution of equations (13) and (2) one finally obtains:

\[
q(x, q', t' | t) = q_o + \left( \frac{|F_o(t) \cdot q_o| - q'_o}{\lambda c(x, q'_o) \left( 1 - \int_0^t \frac{n(t'' | t') dt''}{n_o} + c(x, q'_o) \sum_x n_o(x') \frac{n_o(x)}{c(x', q'_o)} \right)} \right) e(q'_o, t' | t) .
\]  

(18)

Equation (2) then reads:

\[
f(q'_o, t' | t) = \frac{|F_o(t) \cdot q'_o| - q'_o}{\lambda q'_o \left( 1 - \int_0^t \frac{n(t'' | t') dt''}{n_o} + \frac{q'_o}{n_o} \sum_x n_o(x') \frac{n_o(x)}{c(x', q'_o)} \right)} e(q'_o, t' | t) .
\]  

(19)

Expression (11) is solvable after substitution of expressions (18), (19) and subsequently (14), provided that some analytic function is substituted for \( h \).

**Linear viscoelasticity**

The relaxation function corresponding to equation (11) was derived in reference [20]:

\[
G(t) = \frac{T_{b,T}(t)}{\gamma_o} = \frac{q_o A(q'_o, t)}{15} \sum_x n_o(x) e^{-r h_o(x, q'_o)}
\]  

(20)

where \( \gamma_o \) is the applied simple shear and \( h_o \) denotes the rest value of \( h \). Further:

\[
A(q'_o, t) = \frac{B(q'_o)}{1 - \frac{\lambda B(q'_o)}{n_o} \sum_x n_o(x) e^{-r h_o(x, q'_o)}} ,
\]  

(21)

with

\[
B(q'_o) = \frac{1}{\lambda + \frac{1}{n_o} \sum_x n_o(x) \frac{n_o(x)}{c(x', q'_o)}} .
\]  

(22)

We can write \( A(q'_o, t) \) as a series:

\[
A(q'_o, t) = B \left( 1 + \frac{\lambda B}{n_o} \sum_x n_o(x) e^{-r h_o(x, q'_o)} + \left( \frac{\lambda B}{n_o} \sum_x n_o(x) e^{-r h_o(x, q'_o)} \right)^2 + \ldots \right) .
\]  

(23)

Expression (21) can thus be written as a sum:

\[
G(t) = \sum_{i=1}^\infty G_i e^{-t/\tau_i} ,
\]  

(24)

where \( G_i \) is the strength of the mechanism with relaxation time \( \tau_i \). We shall now consider two special types of networks. First a network in which all chains have the same complexity, i.e. in which the number of chain complexities equals one. It then follows that:

\[
\tau_i = \frac{1}{i h_o(1, q'_o)} ,
\]  

(25)

and

\[
G_i = \frac{n_o q'_o (\lambda B)^i}{15 \lambda} .
\]  

(26)

The properties and implications of these results have been extensively discussed in reference [20].

Next we consider the case of two chain complexities, one of which may break spontaneously whilst the other has an infinite lifetime in linear viscoelastic experiments:

\[
h_o(1, q'_o) = 0
\]  

and

\[
h_o(2, q'_o) \neq 0 .
\]  

(27)

The relaxation spectrum of this type of system follows from equations (20)–(24) and (27). The storage moduli at frequency zero and infinity are easily found from the relaxation function:

\[
\lim_{\omega \to 0} G'(\omega) = \lim_{t \to \infty} G(t) = \frac{n_o(1) q'_o B}{15 \left( 1 - \lambda B \frac{n_o(1)}{n_o} \right)} ,
\]  

(28)
\[
\lim_{\omega \to 0} G'(\omega) = \lim_{t \to \infty} G(t) = \frac{n_o \cdot q_o}{15 \sum_{x=1}^{2} c(x, q_o) x(x, q_o)}.
\]

Consider the simple case when \(c(1, q_o) = c(2, q_o)\). The number of chains that contribute to the storage modulus at frequency zero amounts to \(n_o(1)/n_o\) times the number of chains that contribute at frequency infinity. Other network type theories would then predict \(\lim_{\omega \to 0} G'(\omega) = n_0 \lim_{\omega \to 0} G'(\omega)\) [20]. On the other hand, the model presented here states that:

\[
\lim_{\omega \to 0} G'(\omega) \leq \frac{n_o(1)}{n_o} \lim_{\omega \to 0} G'(\omega).
\]

The equality only applies if \(\lambda = 0\). It follows that the effect of network contraction due to the occurrence of fractures elsewhere in the network will cause the storage modulus at low frequency to be lower than one would expect on the basis of just the ratio of the number of permanent chains and the total number of chains.

3. Material functions and parameters of fat particle systems

**Introduction**

In order to calculate stress-tensor components (eq. (5)) we need to specify the time dependence of \(h\), and it is convenient to express the variables \(\lambda\) and \(c\) in terms of physical system parameters. Clearly their values are specific for the material that we intend to describe by means of the model, and we shall accordingly call them material functions and parameters respectively. We have applied our knowledge about the nature of the interactive forces and the processes that lead to chain fracture in fat particle systems in order to select proper expressions for them. The result is given in the following.

**The chain force law**

For the present equation (2) is assumed to apply for fat particle chains. This neglects higher order terms and any dependence upon time. The force-law coefficient \(c\) will now be expressed in terms of physical system parameters. It is evident that also the way in which crystals position themselves inside a chain will affect the value of the resulting force-law constant of the chain. We first consider in detail the forces that act between the fat crystals that are part of the chains. We shall make use of the Lennard-Jones energy equation, which expresses the potential energy content \(\Delta E\) of a bond between two spherical nonpolar particles each having a diameter \(D\) [3]:

\[
\Delta E = \frac{A_H D}{24H} \left[1 - \frac{1}{420} \left(\frac{r_o}{H}\right)^6\right].
\]

In this expression \(A_H\) is Hamaker’s constant, \(H\) the closest sphere surface distance, and \(r_o\) a constant with a value of a few Ångströms. This expression is valid in the case of nonpolar media. On the other hand it can only roughly describe the interaction potential energy between fairly nonspherical particles as in the case of fat dispersions. The interparticle force reads:

\[
f_c = -\frac{\partial \Delta E}{\partial H} = \frac{A_H D}{24H^2} \left[1 - \frac{1}{60} \left(\frac{r_o}{H}\right)^6\right].
\]

At a certain distance \(H_o\) attractive and repulsive forces cancel each other out and the potential energy assumes its minimum value:

\[
H_o = \frac{r_o}{\sqrt{60}}.
\]

(Firth [22] replaced the sixth power in (31) by a variable one, and considered properties of the corresponding potential well, for instance the value of the minimum energy distance \(H_o\)).

When two crystals recede relative to each other, the gap between them is filled with liquid. Papenhuijzen [4] showed that the corresponding hydrodynamic interactive force \(f_h\) can be expressed in \(H, D,\) the relative velocity \(u\) and the viscosity \(\eta_L\) of the medium:

\[
f_h = \frac{3\pi \eta_L D^2 u}{8H}.
\]

This again assumes that the particles can be described as spheres. Basically this equation was derived from a corrected Stokes equation:

\[
f_h = 3\pi \eta_L D u a\alpha,
\]

which gives the force \(f_h\) necessary to move a sphere with diameter \(D\) at speed \(u\) to a flat plate; \(a\) is a correction factor, the value of which depends on the distance between the sphere and the plate [23]. The chain elongation rate is assumed to be very small, i.e.:

\[
u \ll \frac{A_H}{\eta_L D H}.
\]
so that only the Lennard-Jones potential needs to be taken into account. Besides the viscous forces inertial forces are also assumed to be negligible with respect to the interactive forces [20].

By writing:

$$H = H_o + \Delta H,$$

in which $\Delta H \ll H_o$, equations (31) and (32) can be linearized as:

$$\Delta E \approx \frac{A_H D}{28H_o} \left( 1 - \frac{7}{2} \left( \frac{\Delta H}{H_o} \right)^2 \right),$$

$$f_c \approx \frac{A_H D}{4H_o^3} \Delta H.$$  (38)

The force-law coefficient

Next we shall explain the force that is transmitted by a crystal chain in terms of the chain elongation and physical chain properties, i.e. parameter $c$ in equation (2) will be explained in terms of the constants that appear in the Lennard-Jones potential. The force law of the whole chain (eq. (2)) depends not only on the particle-interaction potential but also on the chain structure. We first consider the simplest case, i.e. a straight single chain consisting of an array of linearly arranged identical particles in which expression (32) applies for each of them. The number of crystals along the chain equals $N$. The chain length then reads:

$$q = N(D + H).$$  (40)

After substitution of equation (40) in equation (2) and equating the expressions (2) and (39) it follows that:

$$c \approx \frac{A_H D}{4H_o^3}.$$  (41)

where use is made of the fact that $H_o \ll D$.

It needs to be emphasized that the replacement of the complete expression (32) by the linearized form (2) disregards the high degree of nonlinearity of equation (32). In the case of large deformations this approximation may not be made, since the network elasticity is seen to collapse at shear deformations that exceed $10^{-3}$ (fig. 6). If equation (2) expresses the same force law as equation (32) it follows that the force-law coefficient depends on the actual chain length. We will come back to this point later.

The chain length and crystal separation of a more realistically shaped chain are not necessarily interrelat-

ed through equation (40). It seems to be more likely that the irregularly shaped crystals rotate and reposition somewhat during the process of chain stretching, which may cause the actual crystal surface separation to be far less than one might expect on the basis of equation (40) (see fig. 2).

We therefore write instead of (41) for the force-law coefficient of a single chain:

$$c = e_c \frac{A_H D}{4H_o^3} \theta(q - q_o),$$  (42)

where $e_c$ is a factor that corrects for the non-spherical crystal shape and effects as illustrated in figure 3. Its value is less than unity and may depend on the chain elongation $(q - q_o)/q_o$. Further $\theta$ is the unit step function:

$$\theta(x) = 0 \text{ if } x < 0,$$

$$\theta(x) = 1 \text{ if } x \geq 0,$$  (43)

which takes into account the fact that the chains will bend when being compressed, which results in a spring force of zero in this case. The use of this expression presumes that chains are not bent when being created, i.e. they will carry a force even when $q - q_o$ is very small but positive.

By way of illustration we shall now consider the force law of more complicated chains. Evidently the actual chain shape may differ considerably from that of the single chain. Chains may be built up of one or more parallel subchains, the number of which may be a function of the distance from the closest conglomerate (fig. 3). Since crystal conglomerates are not necessarily rigid, they are assumed to be part of the deformable chains. For the sake of simplicity all conglomerates are assumed to be of equal size. We introduce some parameters that characterize the shape of chains having
in the case of chain elongation. The force-law coefficient for this type of chain finally follows from equations (2), (42) and (44)-(46):

\[ c(x, q') = c_0 \frac{A_H D^2}{4H_0^3} \frac{v_{x,l}}{v_{E}} \theta(q - q'_0). \]  

Figure 4 gives the chain force according to expressions (32) and (45) for both a single chain and one that consists of a single chain for a fraction 0.5 of its length, while the rest consists of three parallel subchains. \( H_m \) denotes the average crystal distance in the direction of the chain vector: \( H_m = (H_E + H_{x,l})/2 \). It can be seen that not only the chain stiffness but also the chain elongation at which the chain force reaches its maximum, depends on the chain shape. When the chain is elongated so much that the crystal distance exceeds the distance is associated with the maximum chain force (fig. 4), the chain becomes unstable and fracture will certainly occur.

**Chain fracture**

Thermal and mechanical actions may bring about the occurrence of chain fracture. Generally mechanical

\[ f_c = v f_v. \]  

At small deformations the crystal distances in different parts of the chain are interrelated through

\[ H_{x,l} = v_{E}/v_{x,l} H_E, \]  

\[ c(x, q'_0) = c_0 \frac{A_H D^2}{4H_0^3} \frac{v_{x,l}}{v_{E}} \theta(q - q'_0). \]  

Figure 4 gives the chain force according to expressions (32) and (45) for both a single chain and one that consists of a single chain for a fraction 0.5 of its length, while the rest consists of three parallel subchains. \( H_m \) denotes the average crystal distance in the direction of the chain vector: \( H_m = (H_E + H_{x,l})/2 \). It can be seen that not only the chain stiffness but also the chain elongation at which the chain force reaches its maximum, depends on the chain shape. When the chain is elongated so much that the crystal distance exceeds the distance is associated with the maximum chain force (fig. 4), the chain becomes unstable and fracture will certainly occur.

**Chain fracture**

Thermal and mechanical actions may bring about the occurrence of chain fracture. Generally mechanical
actions cause chain stretching and thermal actions the final fracture. The annihilation function for a single crystal bond is postulated from absolute reaction rate theory:

\[ h \sim \exp \left( -\frac{\Delta E}{kT} \right), \quad (48) \]

where \( k \) is Boltzmann’s constant, \( T \) the absolute temperature and \( \Delta E \) the free energy for breaking the bond. Chain stretching will cause a decrease in \( \Delta E \) and thus an increase in the probability of fracture. We may write \( \Delta E = (E(x, \infty) - E(x, q')) + (E(x, q') - E(x, q)) \), where \( E(x, \infty) \) is the free energy at infinite stretching, \( E(x, q') \) the free energy in the energy minimum and \( E(x, q) \) the free energy when the chain length is \( q \). The term \( (E(x, q') - E(x, q)) \) can be expressed in terms of the chain elongation, while the other two are constant. We therefore write:

\[ h \sim \exp \left[ \frac{E(x, q') - E(x, \infty)}{kT} \right] \exp \left[ \frac{E(x, q) - E(x, q')}{kT} \right]. \quad (49) \]

In the case of complicated chain structures fracture of one crystal inside a chain does not necessarily lead to fracture of the bond as a whole. The chain fracture mechanism may then be expected to be more gradual, and equation (49) will probably not describe this process adequately. Besides this there will be many sites in a long chain where fracture may occur and \( h \) will therefore also depend on the chain length. A correction factor is introduced to express the influence of the chain’s microstructure on the annihilation function:

\[ h(x, q', t' | t) = h_o(x, q') \exp \left[ \frac{\epsilon h}{kT} \delta(q(x, q', t' | t) - q') \right], \quad (50) \]

where the notation of section 2 has been used. The factor \( h_o(x, q') \) denotes the rest value of the annihilation function of a \( x, q' \)-chain. It contains the term \( \exp ((E(x, q') - E(x, \infty))/kT) \) and therefore depends on temperature. Further \( \epsilon_h \) is the abovementioned correction factor. An expression has to be postulated for the term \( (E(x, q) - E(x, q')) \). As long as the deformation is small we substitute the energy of a chain with linear force law (2). When the chains are more elongated only the attractive term in (31) remains. So in the case of chain stretching:

\[ E(x, q) - E(x, q') = \frac{1}{2} \frac{c(x, q')}{q} (q - q')^2 \]

for small deformations

\[ E(x, q) - E(x, q') \sim \frac{q'}{q - q'} \]

for large deformations. (51)

Instead of using a complete expression that comprises these two limiting cases, the first expression in (51) is substituted in (50) under the restriction that \( \epsilon_h \) must be considered as a factor that also corrects for the error that is caused by the use of the first expression in (51) at large deformations. So:

\[ h(x, q', t' | t) = h_o(x, q') \exp \left[ K_1 \left( \frac{q(x, q', t' | t) - q'}{q} \right)^2 \right] \]

if \( q(x, q', t' | t) \geq q' \), (52)

where \( K_1 \equiv \epsilon_h q' c(x, q')/2kT \).

Parameter \( \lambda \)

The great variety of model parameters compels us to estimate the actual values of as many of them as possible. For this purpose we reconsider the practical significance of the parameter \( \lambda \) that was introduced in equation (13). Take an imaginary case where only one chain breaks in a deformed regular network that consists of one type of chain only. We consider the contraction process of the neighboring chains that follows in more detail and thereby estimate the value of \( \lambda \). Assume that the elongation of the chain that breaks was \( \Delta q/q' \) shortly before fracture occurred. Due to this stretching a force \( c \Delta q/q' \) was acting in the chain which, in turn, was responsible for a total stretching of neighboring chains of approximately \( \Delta q \) as well. We assume that these chains contract themselves over a total distance of \( \Delta q \) after fracture of one of them. Then the average chain length decreases by a total amount of \( \Delta q/n_o \) even at constant macroscopic deformation. Substitution of these estimates in equations (13) and (14) yields the identity:

\[ \frac{\lambda q'}{n_o} \frac{\Delta q}{q'} = \frac{\Delta q}{n_o} \Rightarrow \lambda = \frac{1}{c}. \quad (53) \]
Note that in the case that the chain force is known, equation (2) gives the elongation of chains that are linked in series instead of parallel. In the case of a more complicated type of network, where there is more than just one type of chain, $\lambda^{-1}$ is therefore expected to equal the effective force-law constant of a network of which the chains are linked in series:

$$\lambda = \frac{1}{n_0} \sum_x n_0(x) \frac{c(x, q)}{c(x, q')}. \quad (54)$$

The interpretation of nonlinear data

A straightforward way of performing model calculations would be to derive as many parameters as possible from linear data, to substitute them in expression (5) for the stress tensor and to carry out the integration over time and configuration space. However, the analysis is based upon a linear force law (2), while the actual relation between chain force and length is highly nonlinear (see for instance eq. (32)). When using a series expansion instead of (2) it is difficult to determine its coefficients. They cannot be obtained from equation (32), which is probably only a very rough indication of the true force law of a complicated chain consisting of irregularly shaped crystals. What we will do instead is simply let the value of the force law coefficient $c$ (eq. (2)) depend on the average magnitude of the applied deformation, with the restriction that $c$ is kept constant in one and the same calculation. One of the consequences is that the value of $c$, when obtained from a fit of the (linear) relaxation function, differs from the one that gives the best fit for nonlinear data. On the other hand it is possible to measure the “apparent” moduli at deformations where the response of the system differs from that at infinitely small deformations, but where the stress is still “reasonably” linearly related to the deformation. Parameter values obtained from such measurements fit other nonlinear phenomena in a more satisfactory way. Figure 6 gives an indication of what value to use for $c$ when trying to describe the material deformation at a certain shear $\gamma$.

Since both $K_1$ and $\lambda$ depend on $c$ they are specific for certain experimental conditions. From the values of these parameters that give the best fit of the stresses at a certain deformation one obtains, in return, insight into the dependence of $c$ in equation (2) on the macroscopic deformation, and thus on the individual stretching of the chain.

In addition to effects due to the nonlinearity of the force law at large deformations it is necessary to consider the consequences of the discontinuity of the force law at $q = q'$:

$$f(q', t'|t) = c(x, q') \frac{q(x, q', t'|t) - q'}{q'}$$

$$\theta(q(x, q', t'|t) - q') e(q', t'|t). \quad (55)$$

This affects the analytical results which were derived in section 2 for networks of chains with force laws of type (2). Since now only half of the chains will carry stress in simple-shear flow at small deformations, the denominator 15 in (20) is replaced by 30, while $\lambda$ in (18) and (19) reads $\tilde{\lambda}$, where $\tilde{\lambda} = \lambda$ in the case of chain compression and $\tilde{\lambda} = \lambda$ in the case of chain elongation.

Linear viscoelastic experiments supply information about the values of the parameters in equation (5) or combinations of them. For calculation of the nonlinear stress response, however, we must make use of a large number of so far unknown parameters $(c(x, q_0), n_0(x), q_0', \text{etc.})$. This is the reason why we write $c(x, q_0') = c$ for all $x$. This approximation, identity (54), and the statements made after equation (55) simplify expression (11):

$$T_\infty(t) = \frac{K_2}{4\pi} \sum_x \frac{n_0(x)}{n_0} f(q_0', t) \delta(q' - q_0') \exp \left\{ -\int_0^t h(x, q', 0|t') dt' \right\}$$

$$\times e(q', t'|t) d^3 q', \quad (56)$$

in which $K_2 = n_0 q_0' c$,

$$F(q_0, t) = 0 \text{ if } |F_0(t) : q_0'| \leq q_0',$$

and

$$F(q_0', t) = \left( \begin{array}{c} \frac{|F_0(t) : q_0'|}{q_0'} - 1 \\ 2 - \int_0^\infty \frac{|n(t'|t) dt'|}{n_0} \\ \frac{|F_0(t) : q_0'|}{q_0'} - 1 \\ 2 - \int_0^\infty \frac{|n(t'|t) dt'|}{n_0} \end{array} \right)$$

if $|F_0(t) : q_0'| \geq q_0'$. 

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$$\times e(q', t'|t) d^3 q', \quad (56)$$

in which $K_2 = n_0 q_0' c$,

$$F(q_0, t) = 0 \text{ if } |F_0(t) : q_0'| \leq q_0',$$

and

$$F(q_0', t) = \left( \begin{array}{c} \frac{|F_0(t) : q_0'|}{q_0'} - 1 \\ 2 - \int_0^\infty \frac{|n(t'|t) dt'|}{n_0} \\ \frac{|F_0(t) : q_0'|}{q_0'} - 1 \\ 2 - \int_0^\infty \frac{|n(t'|t) dt'|}{n_0} \end{array} \right)$$

if $|F_0(t) : q_0'| \geq q_0'$.
The relaxation function (20) becomes:

\[ G(t) = \frac{K_2}{60} \sum_x \frac{n_o(x)}{n_o} e^{-\theta_o(x,q_o)} \sum_x \frac{n_o(x)}{n_o} e^{-\theta_o(x,q_o)} - \frac{1}{2} n_o(x) e^{-\theta_o(x,q_o)} \]  

(57)

The stress response can be calculated, provided that \( K_1 \) in equation (52), \( K_2 \) in equation (56), and the values of \( n_o(x)/n_o \) and \( \theta_o(x, q_o) \) for all \( x \) are known. It should be noted again that \( K_1 \) and \( K_2 \) may be deformation dependent, and that this dependence gives information about the true force law and annihilation function. In the case of \( K_2 \), for instance, this is so because it contains \( c \) (see eq. (56)).

4. Some theoretical results

Elastic network properties

We compare the storage modulus as predicted from equations (41) and (57) with expressions proposed in literature. Consider function (57) on the assumption that there is just one type of chain which has an infinite lifetime. Taking the chain length to be equal to the crystal diameter \( D \), i.e. \( q_o = D \), it follows that:

\[ G = \frac{n_o D c}{30} \]  

(58)

where \( G = G'(\omega) = G(t) \) for any \( t > 0 \) and \( \omega < \infty \). By writing:

\[ n_o = \frac{6\Phi}{\pi D^3} \]  

(59)

where \( \Phi \) is the volume fraction of dispersed material, and substitution of equation (41) it follows that:

\[ G = \frac{A_H \Phi}{20\pi H_o^3} \]  

(60)

Nederveen [3] also assumed that the fat particles in this type of system are arranged in permanent chains, all of which have the same stiffness. One third of these chains is believed to be oriented in an arbitrary direction, while the others point perpendicularly. The number of chains that cut through a cross-section of unit area then equals \( 2\Phi/\pi D^2 \) (see ref. [1]). The force \( f_e \) carried by the chains was determined from equation (39) by substitution of the increase in interparticle distance \( cD \) in the case of a relative uniaxial stretching \( c \) of the material. The storage shear modulus was then obtained by multiplication of \( f_e/c \) by the number of chains, and by making use of the relation \( G = E/3 \), where \( E \) is the tensile modulus:

\[ G = \frac{A_H \Phi}{6\pi H_o^3}. \]  

(61)

Papenhuijzen [4], on the other hand, argued that the curvature of the energy curve (31) in the energy minimum just equals the curvature of the Van der Waals contribution at the so-called inflection point of the complete expression (31), where the force attains its maximum value. In that case:

\[ f_e = \frac{A_H D^2}{12H_o^3} \frac{\Delta H}{D}, \]  

(62)

where \( \Delta H \) is about \( 10^\AA \), which differs from the interparticle distance for which \( f_e \) is a minimum, i.e. a few \( \AA \). Subsequently the factor in (62) was multiplied by \( 2\Phi/\pi D^2 \) to obtain the shear modulus:

\[ G = \frac{A_H \Phi}{6\pi H^3}. \]  

(63)

Note the difference between expressions (60), (61) and (63). The expression for the shear modulus that follows from the transient-network model (60) equals a factor 0.3 times Nederveen’s expression (61). The discrepancy between (60) and (63) is also considerable. The explanation is that the moduli of an isotropic network differ from those of a network in which there are only chains in three mutually perpendicular directions.

The Bingham yield stress

Ekdawi and Hunter [18] explained the flow behaviour of coagulated colloidal suspensions at low shear rates by extending the behaviour in the high shear rate region to low shear rate (see also [24]). The Bingham yield stress that follows from this concept equals the amount of energy that is needed to completely separate the network into single units, i.e.:

\[ \tau_b = n_o \Delta E, \]  

(64)

where \( n_o \) is the total number of particle contacts and \( \Delta E \) is the energy required to break each of them.
The network model used in this paper enables us to calculate the real yield stress of systems that exhibit solid-like behaviour at low shear stresses, i.e. the value that the shear stress must exceed before the system will start to flow. We assume that the bonds break when the force that they transmit exceeds the critical value $f_{cr}$:

$$f_{cr} = e \frac{\Delta q_{cr}}{D},$$

(65)

where $\Delta q_{cr}/D$ is the relative chain stretching that matches $f_{cr}$. We may also write:

$$\Delta q_{cr} = \sqrt{\frac{2AE}{c}} \frac{D}{c},$$

(66)

where $AE$ is the bond activation energy. It can be shown that the first chain that breaks in simple-shear flow is oriented in the direction of the principal axis of elongation. For this chain the relative stretching is related to the applied macroscopic shear $\gamma$ as:

$$\frac{\Delta q}{D} = \frac{\gamma}{2}.$$  

(67)

It follows from equations (66) and (67) that the first chain will break when:

$$\gamma = \gamma_{cr} = \sqrt{\frac{8AE}{Dc}}.$$  

(68)

After fracture of this chain the remaining part of the network carries an increasing amount of stress, and network connectivity breakdown is assumed to follow. So the system is believed to start flowing immediately after fracture of the first chain. We shall thus not consider complicated network flow phenomena such as those related to the contraction parameter $\lambda$. The shear stress at deformation $\gamma_{cr}$ follows from multiplication of $\gamma_{cr}$ by expression (58):

$$\tau_{cr} = \frac{\eta_0}{15} \sqrt{2AE Dc}.$$  

(69)

It is seen that not only the activation energy but also the force-law coefficient is taken into account in the expression for the real yield stress. Expression (69) for the real yield stress resulting from network theory, differs considerably from expression (64) for the Bingham stress which is found from the energy dissipation at high shear rates.

5. Materials and methods

Materials

The dispersions were prepared by rapid cooling of 20% hot solutions of glyceryl tristearate (melting point 71°C) in paraffin oil. They were cooled down to 15°C on a plate and subsequently diluted with paraffin oil so that dispersions were obtained containing 5% glyceryl tristearate. The average crystal diameter depends on the crystallization temperature. Generally the crystals are larger when the crystallization temperature is higher. In our case their length was approximately $4 \times 10^{-3}$ m [3]. The particle shape is quite irregular however. Instead of being shaped like spheres they are shaped like rectangles with $L/D$ ratio $4$ [3].

Harmonic oscillations

We made use of two instruments:

- Dynamic measurements at angular frequencies between 0.0628 and 62.8 rad s$^{-1}$ were carried out in the Instron Rheometer Model 3250 using parallel plates of diameter 40 mm at a mutual distance of 1.5 mm. The deformation was 0.004 at the outer rim of the sample.

- We measured the dynamic moduli at a frequency of 1760 rad s$^{-1}$ by means of a torsion pendulum, developed by Blom and Mellem [25], consisting of a cylindrical mass with a moment of inertia, $I$, of $72 \times 10^{-6}$ kgm$^2$ and a torsion rod with spring constant, $k$, of $21 \times 80$ kgm$^{-1}$s$^{-2}$. The resonance frequency of the system lies at $\omega_0 = 1760$ rad s$^{-1}$ (= $\sqrt{k/I}$). The pendulum is excited magnetically. The dynamic moduli are found from the resonance frequency and the damping of the torsion pendulum when immersed in a viscoelastic liquid. The minimum shear that can be imposed on the liquid and still detected is $5 \times 10^{-5}$.

Simple-shear flow

We again made use of two instruments:

- The shear stress after inception and cessation of simple-shear flow was measured in the Rheometrics Mechanical Spectrometer using cone and plate geometry. The cone angle was 0.04 rad, while the diameter of the plate was 50 mm. Microscopical detection of small carbon black particles which were immersed in the dispersion enabled us to visualize the flow pattern inside the sample. It was found to be homogeneous throughout the sample, while there was no slip at the walls. The minimum shear that could be detected was $10^{-1}$.

- We measured the viscosity of the liquid phase by means of the Contraves Low Shear instrument using cylinder geometry. The diameters of the inner and outer cylinders were 11 and 12 mm respectively. The inner cylinder height was 8 mm.

Results and interpretation

Linear viscoelasticity

Figure 5 gives the frequency dependence of the dynamic moduli of the 5% fat dispersion described in the preceding section at 22°C. The behaviour is primarily solid-like. Its elasticity exhibits only a slight dependence on frequency. An arbitrary set of relaxation times $\tau_i$ were chosen, while the corresponding
Fig. 5. Dynamic moduli at 22°C of a 5% dispersion of glyceryl tristearate crystals in paraffin oil that was prepared by rapid cooling of a hot solution down to 15°C. (x): \( G' \); (O): \( G'' \)

strengths \( G_i \) were determined from \( G_{\text{exp}}'(\omega) \) and the expression:

\[
G'(\omega) = \sum_i \frac{G_i \omega^2 \tau_i^2}{1 + \omega^2 \tau_i^2}.
\]  

We applied the method of least squares. From this set \( G_{\text{exp}}(t) = \sum G_i e^{-t/\tau_i} \) has been determined. The fact that \( G_{\text{exp}}' \) hardly depends on frequency allows us to select a discrete number of reciprocal times \( h_0(\tau, q_0') \) and find the corresponding values of \( n_o(\tau)/n_0 \) and \( K_2 \) from fitting expression (57) to \( G_{\text{exp}}(t) \).

It is known that relaxation mechanisms if caused by fractures of this type of network mainly involve long characteristic times [19]. Besides this the model is only valid in creeping-flow conditions, i.e. at deformation rates that are so low that there is enough time during each cycle in oscillatory experiments for the conglom-erated rearrangements that must take place to preserve chain force equilibrium as described by equation (2) [20]. That is why we expect that the shape of the low frequency part of figure 5 can be explained by the transient-network theory and we shall thereby ignore the behaviour at high frequencies (\( \omega \geq 1 \)). A reasonable fit for the low frequency behaviour was obtained for the parameter values given in table 1.

It should be emphasized that the range of linearity of this type of system is very small (\( \leq 10^{-3} \)) (see fig. 6).

When using the apparent moduli that were obtained at larger shear deformations for model fits it was found that the factor \( K_2 \) usually decreases, which we believe is caused by a decrease in the value of the chain-force-law coefficient (see also section 3).

The dependence of the shear stress on shear rate is given in figure 7. The system is seen to behave like a Bingham fluid. The real yield stress, measured by means of a Deer creep rheometer, is \( \sim 8 \text{ Nm}^{-2} \).

### Inception of steady simple-shear flow

Figure 8 gives the shear-stress response of the system after inception of steady simple-shear flow at 22°C. The maximum shear stress is seen to occur at \( \gamma = 0.25 \) independent of the rate of the shear.

We calculate the shear-stress response from equation (56) by substituting equations (14) for \( x = 1, 2 \), (52), and the deformation pattern given by:

\[
F_r(t) = \begin{bmatrix} 1 & \gamma(t', t) & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}
\]
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Fig. 7. Shear stress versus shear rate in steady simple-shear flow of the fat dispersion at 22 °C, measured in the Mechanical Spectrometer using cone-and-plate geometry.

Fig. 8. Shear stress response of the fat dispersion after inception of steady simple-shear flow at 22 °C. Full curves are measurements, broken curves denote the value of $T_{b,xy}$. Parameters used for calculations are listed in Table 2. An extra calculation at $\dot{\gamma} = 0.1$ s$^{-1}$ for $\lambda c = 15$ has been added.

Table 2. Parameter values used for stress calculations in simple-shear flow (Fig. 8).

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$h_0(1,q_o)$ (s$^{-1}$)</td>
<td>$10^{-4}$</td>
</tr>
<tr>
<td>$h_0(2,q_o)$ (s$^{-1}$)</td>
<td>0.1</td>
</tr>
<tr>
<td>$n_o(1)/n_o$</td>
<td>0.9</td>
</tr>
<tr>
<td>$K_1$</td>
<td>740</td>
</tr>
<tr>
<td>$K_2$ (Nm$^{-2}$)</td>
<td>2840</td>
</tr>
<tr>
<td>$\lambda c$</td>
<td>1</td>
</tr>
</tbody>
</table>

We shall now discuss the problem concerning the value to be chosen for $h_0(1,q_o) < 10^{-2}$ in the calculations. If it is zero, it becomes clear from equation (52) that the chain will behave like permanent ones in any experiment. For values that differ from zero, it becomes evident that the chain extension at which considerable fracture occurs is closely related to the values of both $h_0(1,q_o)$ and $K_1$ in (52). Therefore we cannot find a unique value for $K_1$ but only one that is specific for the choice of $h_0(1,q_o)$. The Appendix deals with the relation between $h_0$ and $K_1$. It was found that the shear at which the shear stress attains its maximum value depends strongly on the value of $K_1$ whereas the term $K_2$ determines the maximum shear stress itself. We thus varied $K_1$ and $K_2$ in order to obtain a quantitative fit of both these features of the overshoot curve $\dot{\gamma} = 0.1$ s$^{-1}$. Table 2 summarizes the values of all parameters used in the calculations, the results of which are given in Figure 8.

It is seen that in order to obtain a quantitative fit of the maximum stress in overshoot experiments the modulus $K_2$ must be taken much smaller than the value that was obtained from fitting viscoelastic data (Table 1). The explanation is that the range of linear mechanical responses is very small for this type of material, which is not incorporated in the chain force law (55). Thus at relatively large deformations, such as $\dot{\gamma} = 0.3$, the forces that the chains transmit will be lower than is predicted by equation (55) after substitution of the parameter values that fit the storage moduli. The value given above thus quantifies the relation between chain length and chain force at high deformations. Provided that $n_o$ and $q_o$ are known, for instance from permeametric measurements or Scanning Electron Microscopy, and that all chains are of the so-called single type, one may deduce the value of $\varepsilon_c A H D/H_o^3$ from equation (42) and $K_2$.

All components of the stress tensor $T_b(t)$ in equation (56) fall to zero in the limit $t \rightarrow cs$. This is due to the non-zero values of the annihilation functions $h(x,q_o,0,t)$ in this expression. In shear experiments however the shear stress finally becomes constant. This is due to contributions from chains that are created during flow, i.e. to terms other than $T_b(t)$ in equation (5). The fit of $T(t)$ to experimental results needs the specification of
the creation function $g$ in equation (5). It is seen, however, that we can describe many features of the transient response without taking chain creation into account. The extra shear stress at large deformations can partly be explained by other phenomena than the creation of network chains. If $\lambda c = 15$ is taken instead of 1, as was roughly estimated in the preceding section, the shear stress is seen to decrease much more slowly. This is due to the fact that chains are then not easily extended so far that chain fracture will occur, which, in turn, is due to the fact that an increasing degree of macroscopic deformation is closely related to the growth of holes in the network.

Next we would like to consider the physical consequences of the value of the factor $K_1$ in equation (52). The irregular shape of the chain crystals may cause the separation of their surfaces to be far less than the separation of the centres of gravity of these particles. Rotation of the nonspherical crystals and their gliding along each other may cause the surfaces to remain almost in contact with each other, even with relatively large chain stretching (fig. 2). The chain fracture chance is then considerably smaller than in the case where the closest surface distance is enhanced by an amount that is comparable with chain stretching. The factor $K_1$ quantifies this effect.

Cessation of simple-shear flow

Figure 9 shows the shear stress after a simple-shearing displacement for different values of the applied shear. The curves clearly demonstrate the nonlinearity of the mechanical response of the system. In order to fit these data, different values of $K_2$ must be used in the calculations for any shearing displacement that is applied. When considering the time behaviour, it can be seen that the relaxation times are not greatly altered by the applied deformation, i.e. the characteristic times of network fracture are still close to the equilibrium values $h_o(x, q'_o)$ in equation (52). Model predictions are again obtained from equation (56) on substitution of equations (14), (52), and the deformation gradient

$$ F_r(t) = \begin{bmatrix} 1 & y(t',t) & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}, $$

in which

$$ y(t',t) = 0 \text{ if } t' \leq t < 0 \text{ and } 0 \leq t' < t, $$

and

$$ p(t',t) = y_o \text{ if } t' < 0 \text{ and } t \geq 0. $$

All parameter values are taken from table 2, except $K_2$ which is a function of $y_o$ and therefore has to be deduced from curve fits. Chains are now more elongated than in the case of the harmonic experiments but less than in the case of inception of steady simple-shear flow. Therefore $K_2(y_o)$ adopts values that lie globally between the ones found from fits of these two measurements. The relatively high value of $K_2(y_o = 0.024)$ can be explained by the fact that in start-up experiments the system was first kept at rest so that time hardening took place. The shape of the model curves is seen to be hardly affected by the amount of shear $y_o$. This is explained by the fact that, unlike $K_2$, the annihilation function remains almost unchanged (see expression (52) for $K_1 = 740$).

The temperature dependence of the dynamic moduli

Figure 10 gives the dependence of the dynamic moduli on temperature in the range 20 °C–30 °C at an angular frequency of 1760 rad/sec and deformation $y = 2 \cdot 10^{-4}$.
The measurement was performed in the torsion resonator. The system was kept at rest in the resonator container for 48 hours before the measurement started. Shortly after applying a harmonic oscillation of $\gamma = 2 \times 10^{-4}$ a gradual decrease in the storage modulus of a few percent was observed, which indicates that even at these low amplitudes the system is not yet completely stable. The difference between the storage moduli given in figures 5 and 10 is explained by the difference in time during which the system was at rest before the measurement started, the difference in angular frequency and the difference in applied deformation. Figure 10 also gives the temperature dependence of the liquid phase which was extracted from the fat system by means of a centrifuge. We did not use the pure paraffin oil with which we prepared the samples. This is because the liquid phase in the dispersion may contain glyceryl tristearate crystals which are not part of the network, and which may increase the viscosity of the liquid phase. It is seen from figure 10 that the storage modulus of the dispersion decreases with temperature, and also that $\frac{dG'}{dT}$ decreases with temperature. By considering equation (58), with $D = q'_o$, it is concluded that either the total chain length $n_t q'_o$ decreases (chain fracture), or the force-law coefficients become less. The latter can possibly be explained by the increase of rotational diffusion of crystals in a chain with temperature which prevents them from arranging themselves with respect to each other in such a way that there is maximum surface contact. Figure 10 also shows that the relative decrease in the loss moduli of the dispersion and the liquid phase are of the same order of magnitude, although their absolute values are largely different from each other. There are contributions to the loss modulus from the dissipation of bond energy in the liquid after chain fracture, and the liquid flow through and around the crystal chains and conglomerates. The first contribution does not depend on the liquid viscosity while the second one certainly does. The energy dissipation per unit volume during one cycle ($E_{\text{diss}} = \pi D q'_o G''$) at an angular frequency of 1760 rad s$^{-1}$ and a maximum shear of $2 \times 10^{-4}$ corresponds to the energy contents of $\sim 10^{15}$ crystal bonds with an energy content of say 40 kT each [4]. Since the number of crystals is about $\sim 10^{21}$ m$^{-3}$ only a small part of the available bonds would have to break to explain this value of $G''$. The temperature equivalence of $\frac{dG'_{\text{disp}}}{dT}$ and $\frac{dG''_{\text{disp}}}{dT}$, on the other hand, suggests that at this frequency there is a considerable contribution of viscous dissipation to the loss modulus of the system as a whole. The mechanical behaviour of this type of network at $\omega = 1760$ rad s$^{-1}$ can therefore not be explained by network interactive forces alone.

It should be noted that the model validity is limited to creeping-flow conditions. The analysis for high frequency is not meant to support model assumptions and conclusions, but instead to help unravel the microscopic processes that are responsible for the mechanical behaviour of the system at a high rate of deformation.

Conclusions

It is concluded that the dynamic moduli of the fat crystal system as well as its rheological behaviour in transient shear experiments can be interpreted in terms of a network of crystal particles that is present in the system and that will deform during flow. The storage modulus of the system is correlated to network properties as given indirectly by equation (57), while the shear at which the shear stress maximizes after inception of simple-shear flow is closely related to coefficients that appear in the chain-annihilation function.

It is found that:
- the differences in the behaviour of this system compared with polymer melts and solutions, for instance the occurrence of stress overshoot at (almost)
any rate of shear in simple-shear flow and at almost the same deformation, can be adequately explained by the typical annihilation function (52), which, in the case of low \( h_o \) values, allows for chain fracture only if the chain is elongated up to a certain extent;

— the high degree of nonlinearity of the force law of the individual chain forces us to let the value of the force-law coefficient depend on the average magnitude of the macroscopic deformation. This gives information about the force law of the chains in the network.

Appendix. The relation between \( h_o \) and \( K_2 \)

Below equation (71) it was pointed out that the values of \( h_o(1, q_o') \ll 10^{-2} \text{ s}^{-1} \) and \( K_2 \) to be used in the calculations (see especially eq. (52)) are interrelated. We chose \( h_o(1, q_o') = 10^{-4} \text{ s}^{-1} \) and found that the proper value of \( K_2 \) was then 740 \text{ N m}^{-2}. It is easy to see which other combinations of these coefficients, say \( h_o^* \) and \( K_2^* \), will also result in a reasonable model fit. Figure 8 shows that the maximum shear stress after inception of steady simple-shear flow is reached at \( y = 0.25 \). There is then a considerable amount of chain fracture, and it seems reasonable to postulate:

\[
h(y = 0.25) = h^*(y = 0.25). \tag{A1}
\]

This relation will be worked out for the chain that points in the direction of the principal axis of elongation in simple-shear flow for which \( \Delta q/q' = \Delta y/2 \):

\[
h_o \exp \left( K_1 (0.25)^2 \right) = h_o^* \exp \left( K_1^* (0.25)^2 \right),
\]

i.e.

\[
K_1^* = K_1 + 16 \ln \frac{h_o}{h_o^*}, \tag{A2}
\]

see equation (52). So if \( h_o = 10^{-15} \text{ s}^{-1} \), it follows from equation (A2) that when \( K_1^* = 961 \text{ N m}^{-2} \) the model will again predict that the shear stress maximizes at \( y = 0.25 \).

Acknowledgments

The authors would like to thank Professor P. F. Mijnlieff and Mr. G. Nijman for helpful and inspiring discussion on this subject and Mr. L. L. Hoekstra of the Unilever Research Laboratory, Vlaardingen, the Netherlands, for carrying out part of the experimental work.

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Received July 16, 1985; accepted August 6, 1985

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