ORIGINAL CONTRIBUTIONS

A transient-network model describing the rheological behaviour of concentrated dispersions

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Abstract: Attractive forces acting between particles in dispersions may cause a three-dimensional structure to be built up. A temporary-network model is postulated that describes the rheological behaviour of such systems. Chains of particles are assumed to be created and broken by thermal actions and by applied deformation. The relation between the network structure and the macroscopic stress tensor is deduced. One of the main model features is that no use is made of the common assumption of affinity of the motion of the chain vectors with the gradient of the macroscopic velocity field. Instead, the chain deformations are assumed to depend on the forces acting on them, i.e. their deformations depend on their stiffness and on the applied deformation, whereas fracture of chains may cause stress relaxation in the rest of the network. The chains may behave as highly non-linear springs, whereas the probability that the chains will break in some time interval may be an explicit function of the chain length itself. Integral equations are derived, from which the stress-tensor components can be calculated in any flow experiment, that obeys creeping-flow conditions. Analytical expressions are obtained for the relaxation spectrum of such systems in terms of the microscopic parameters.

Key words: Transient-network model, stress tensor, relaxation spectrum, concentrated dispersion, conglomerate

1. Introduction

A material containing particles of colloidal dimensions embedded in a liquid may show viscoelastic properties. When the concentration of the dispersed phase is higher than a certain critical value, a network of particles may be formed that take up the total available space [1].

Much theoretical work has been carried out to explain the typical rheological properties of such systems. The resulting theories can be classified either as phenomenological or structural. An example of the first class of theories is the approach of De Bruijne et al. [2], who modified the constitutive equation according to the Maxwell model in such a way that it became more suitable for describing the rheological behaviour of dispersions of fat crystals in oil. They observed that in this kind of system the shear stress mainly depends on the shear itself and very little on the shear rate. The modification was to let the relaxation time that appears in the constitutive equation be proportional to the inverse of the shear rate, starting from a constant level. In general, the parameters that appear in such phenomenological expressions cannot be easily connected with microscopic properties of the system.

In the structural theories various approaches have been used. Much attention was paid to the fall of the steady-shear

viscostiy with increasing shear rate, and its relation to the number of links between particles. Chaffey [3] gave an extensive survey of these types of theories in all of which the density of particle links is calculated in relation with formation and destruction of links between particles under the influence of Brownian motion or applied flow. The stationary link density is found by means of kinetic expressions. Subsequently the steady-shear viscosity is derived by using expressions originating from macromolecular theories [4, 5], from the number of links that transverse shear planes [6], from the energy dissipation due to the presence of aggregates [7], or from the Mooney equation for the viscosity of a suspension of spheres [8]. Hudson et al. [9] studied the shear-stress relaxation in sheared pigment suspensions after a step of the shear rate from the change of the effective volume fraction of dispersed material as a function of time. Van de Ven, Firth and Hunter [10, 11] investigated the effect of both structural changes and energy dissipation due to the flow of the liquid phase through and around aggregates, on the characteristic flow parameters of sheared coagulated sols. The equations that result from these theories contain information about microscopic parameters.

Not only the particle-link density but also the link-orientation distribution function, together with the forces transmitted by these links can play a role in the rheological behaviour of dispersed systems. Takano [1] and Van den Tempel [12] explain the rheological behaviour of certain dispersions in terms of the stretching and breaking of so-called

primary and secondary bonds that are part of a particle network; this results in expressions for the dynamic and steady-state viscosity and for the creep behaviour of these systems, respectively. An extensive investigation of the rheological behaviour of fat dispersions was carried out by Papenhuijzen [13]. In his model creation and annihilation of bonds between crystals which are part of a three-dimensional network, together with viscous effects due to liquid flow, are responsible for the viscoelastic properties of these materials. The structural effects that take place when network chains break and reform as well as the time effects related to the motion of particles in a viscous medium are taken into accout in his considerations. In the model a distribution of strengths is adopted for the available chains and all stress carrying chains are assumed to be oriented along the principal axis of elongation in simple shear. The storage modulus of disperse systems in which the network deviates strongly from the so-called single-chain network was given in a generalized form by Van den Tempel [14]. These types of theories show resemblance to transient-network models originally proposed by Green and Tobolsky [15], Lodge [16], and Yamamoto [17] for the description of the rheological behaviour of polymer melts and polymer solutions. The following assumptions are fundamental for these polymer network theories:

(i) Inertial effects are ignored.
(ii) The system is incompressible.
(iii) Network chains may be created as well as annihilated during flow.
(iv) The stress is the sum of the contributions from all chains that were created in the past and still exist at the present time.
(v) There is no hydrodynamic interaction between chains.
(vi) Chains are characterized by a single complexity parameter $\varkappa$.

Polymer chains are generally modelled as Gaussian springs. All network chains of the same complexity have the same chance to be lost in some time interval. The chain-length distribution for network chains at the time of their creation is assumed to be identical to the equilibrium distribution of freely jointed polymer molecules. The junctions move as if they were particles of an equivalent macroscopic homogeneous continuum (affine deformation assumption).

In the present paper a transient-network model is introduced that contains some of the elements of molecular-network theories, but that is so far generalized that it becomes applicable to concentrated dispersions. It describes the rheological behaviour of that kind of system in terms of interactions between network particles. A distribution function of particle-chain vectors analogous to that in molecular-network theories mentioned above is introduced. The time dependence of this function due to creation and fracture of particle links and due to the macroscopic flow is evaluated. However, the nature of chains that consist of dispersed material is far different from the nature of polymer chains. The force law that is valid for the individual chains in concentrated dispersions is generally non-Hookean. Besides, when considering systems that display yield phenomena, the probability for chains to break may depend on their lengths much more strong-

ly than in the case of polymer chains. In that case, it is not allowed to assume all chains of the same complexity have the same probability to break in some interval without taking their lengths into consideration. The non-linearity of the force law and effects due to chain fracture imply that the affine-deformation assumption is not generally valid. The deformation of an individual chain may be affected by fracture occurring somewhere in its neighbourhood. Clearly classical polymer-network theories cannot be used in their original form for describing the rheological behaviour of concentrated dispersions. Assumptions (i) − (vi) are assumed valid also for networks in concentrated dispersions. The following assumption is added:

(vii) Network-chain forces are in mutual equilibrium.

The network topology is explained in section 2. The relation between the volume-averaged stress tensor and the forces transmitted by network chains is derived in the Appendix. Integral equations containing both physical and structural parameters are found, which can be used to evaluate the stress tensor in rheological experiments (section 3). A simple expression for the relaxation spectrum is obtained for some classes of materials (section 4). The model is meant to be valid for various types of systems, such as those in which the dispersed phase consists of non-deformable particles between which a time-independent force-distance relation prevails, like suspensions of fat crystals in oil, and systems in which the dispersed phase is a continuum itself, transmitting forces that originate from a transient network on molecular scale and that are time-dependent themselves (f. i. denatured protein dispersions in water).

2. Terminology and definitions

The stresses that act in concentrated dispersions are closely connected with the state of deformation of the network. We therefore start with the introduction of some terms which are helpful in describing the network structure and the forces it carries (see figure 1).

Conglomerate   – an amount of dispersed material, closely packed together in a more or less spherical way and possibly connected with other conglomerates by chains.

Chain   – dispersed material that is distributed over the space between two conglomerates, being so close together that the interactive force holds it together.
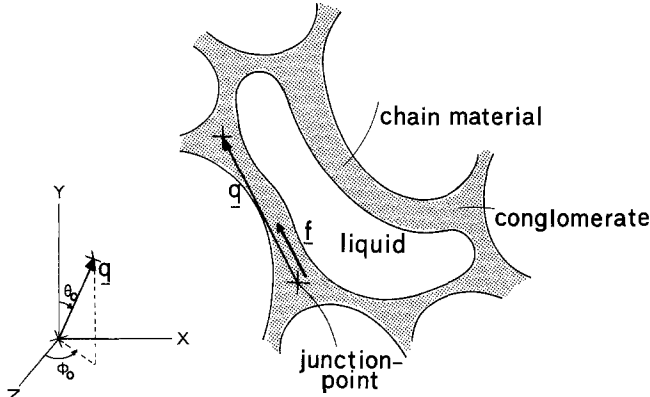
Fig. 1. Network structure in concentrated disperse systems

Junction point — a point in space where at least three chains can be thought to be connected together. Since connected chains move together, the points act as constraints on the motions of the chains that come together in it. Every junction point is situated within a conglomerate.

Chain vector (q) — a vector that represents the direction and length of a chain. It connects the junction point at one end of the chain with the junction point at the other end of it.

Interactive force — the force acting between units of dispersed material or within the dispersed material itself, in so far as it is not of a hydrodynamic nature.

Complexity ($\varkappa$) — a parameter that distinguishes all chains that have certain properties, such as the stress-strain relaton.

Several density functions need to be introduced to describe structural effects due to flow, i.e. structural breakdown and creation:

$\Phi(\varkappa, q', t' \mid q, t)$
$\cdot d^3 q \, d^3 q' \, dt'$
— the concentration of $\varkappa$-chains that were created in the time interval $(t', t' + dt')$ within the configuration range $d^3 q'$ about q' and which are still present at time. $t \geqq t'$ within the configuration range $d^3 q$ about q.

$\varphi(\varkappa, q', t' \mid t) \, d^3 q' \, dt'$ — the concentration at time $t \geqq t'$ of $\varkappa$-chains that were created in the time interval $(t', t' + dt')$ within the configuration range $d^3 q'$ about q'.

$\Psi(\varkappa, q, t) \, d^3 q$ — the concentration at time t of $\varkappa$-chains within the configuration range $d^3 q$ about q.

$n(\varkappa, t)$ — the concentration at time t of $\varkappa$-chains.

$\tilde{n}(\varkappa, t' \mid t) \, dt'$ — the concentration at time $t \geqq t'$ of $\varkappa$-chains that were created in the time interval $(t', t' + dt')$.

Derived definitions:

$$n(t) \equiv \sum_{\varkappa} n(\varkappa, t), \tag{1}$$

$$\tilde{n}(t' \mid t) \equiv \sum_{\varkappa} \tilde{n}(\varkappa, t' \mid t). \tag{2}$$

From these equations the following equalities follow directly:

$$\tilde{n}(\varkappa, t' \mid t) = \int \varphi(\varkappa, q', t' \mid t) \, d^3 q', \tag{3}$$

$$n(\varkappa, t) = \int_{-\infty}^{t} \tilde{n}(\varkappa, t' \mid t) \, dt' \tag{4}$$

$$\varphi(\varkappa, q', t' \mid t) = \int \Phi(\varkappa, q', t' \mid q, t) \, d^3 q, \tag{5}$$

$$\Psi(\varkappa, q, t) = \int_{-\infty}^{t} \int \Phi(\varkappa, q', t' \mid q, t) \, d^3 q' \, dt'. \tag{6}$$

$f(\varkappa, q', t' \mid q, t)$ — the force that is transmitted at time $t \geqq t'$ through a $\varkappa$-chain that was created at time t' with chain vector q', the actual chain vector of which reads q. It is assumed to point from one junction to the other. The force vector is parallel to q when the force is of a tensile nature and opposite when it is compressive.

The subscript zero indicates that a quantity adopts its rest value. We may then omit the time t, i.e. write n_0, $n_0(\varkappa)$ and $\psi_0(\varkappa, q)$ instead of the notations used in eqs. (1) and (6).

Brackets denote averaging over q with respect to Φ:

$$\langle A \rangle (\varkappa, q', t' \mid t) \equiv \frac{\int A(\varkappa, q', t' \mid q, t) \, \Phi(\varkappa, q', t' \mid q, t) \, d^3 q}{\int \Phi(\varkappa, q', t' \mid q, t) \, d^3 q}, \tag{7}$$

in which A is any vector or tensor function of one or more of the given variables.

Integration involves the whole configuration space when not marked otherwise. The magnitudes of vector functions are symbolized by writing them light face.

3. The transient-network model

3.1 Introduction

Our aim is to derive an equation from which the stress behaviour of concentrated dispersions can be

predicted for a variety of deformation histories; furthermore, the parameters in this equation should preferably be connected with microscopic parameters.

In attempting to derive such an equation we were forced to introduce a number of simplifications. We tried, however, to do so without bypassing the complicating fact that the stress-strain relation of the chains may be far from linear and not the same for all chains either, that is, chains of all kinds of complexity may be present. This fact has an immediate consequence for the "affinity" of the motion of junction points in deformation. Provided inertia is negligible, the total force that acts on a conglomerate is zero at any moment. This total force is the sum of the forces exerted on it by the surrounding liquid and network chains. Only when the chains behave like linear Gaussian springs (as they do in an ideal polymer network), is affine motion accompanied by force equilibrium, for any topology of the network. This can be realized by considering a Gaussian network in the junctions of which there is force equilibrium. Simple calculations show that the equilibrium is preserved if all junctions move affinely with the applied deformation. But when the chains are no longer Gaussian springs, affine motion of the junction points does not necessarily correspond with force equilibrium (it will only be so for very regular networks, containing chains of just one complexity). This implies that the displacement of the individual junction points diverges from the displacement in accordance with the macroscopically imposed one.

From energy considerations it follows that the work of deformation as calculated when assuming affine displacement of all individual junction points, when this violates local force equilibrium, is always larger than the actual work, that is the work done when local force equilibrium is preserved. Thus, chain-force equilibrium leads to a lower increase in the Helmholtz free energy per unit volume of the network than calculated on assuming affine junction motion. A similar statement holds for the stress tensor, which is closely connected with the Helmholtz free energy [18].

A special case arises when a force-carrying chain becomes detached from a junction. Then the force first transmitted by the chain is temporarily not compensated by forces exerted on the conglomerate by other chains, but by viscous forces. As a consequence, junction-point positions change until equilibrium between forces of chains attached to a junction point is established again. During this process some of the elastic energy stored in the network is dissipated and the total elastic energy that is stored in the network decreases slightly. It should be noticed that this rearrangement – which represents a non-affine motion of junction points

– also takes place in temporary networks of linear Gaussian chains. When this rearrangement is taken into account, a relaxation function is found that differs from previously proposed ones. We will return to this point in section 3.4.

3.2 The stress tensor

Knowledge of the density function $\Psi(\varkappa, q, t)$ alone does not generally suffice for evaluating components of the stress tensor, because the relation between the chain length and the chain force may involve time effects. The required information about the chain-deformation history is supplied by $\Phi(\varkappa, q, t' \mid q, t)$. An expression for the volume-averaged stress tensor is derived in the Appendix. From eq. (A.11) it follows that the contribution at the present time to the macroscopic stress tensor from a $\varkappa$-chain that was created within the time interval $(t', t' + dt')$ within the range d^3q' about q', of which the actual chain vector lies within the range d^3q about q reads $qf(\varkappa, q', t' \mid q, t)$. The number of these chains equals $\Phi(\varkappa, q', t' \mid q, t) \, d^3q \, d^3q' \, dt'$, so

$$dT_{\varkappa, q', t', q, t}$$
$$= qf(\varkappa, q', t' \mid q, t) \, \Phi(\varkappa, q', t' \mid q, t) \, d^3q \, d^3q' \, dt'. \quad (8)$$

The average stress tensor itself follows by summation of eq. (8) over all complexities and by integrating over configuration space and time:

$$T = -p\mathbf{1} + \sum_{\varkappa} \int_{-\infty}^{t} \int \int qf(\varkappa, q', t' \mid q, t)$$
$$\cdot \Phi(\varkappa, q', t' \mid q, t) \, d^3q \, d^3q' \, dt'. \quad (9)$$

Unlike in the Appendix T is now considered as a quantity that follows from ensemble averaging. That is why no upper dash is used.

An ambient pressure term $-p\mathbf{1}$ has been added since both phases are assumed incompressible (see eq. (A.11)).

For $\varkappa$-chains created at the same time t' with chain vector q', one may assume that their deformation histories will not differ too much from each other; this implies that the chain forces that are transmitted through them are about the same for all of them. The narrowness of the distributions of the q-vectors of these chains justifies the following approximation:

$$\langle qf \rangle (\varkappa, q', t' \mid t) \cong \langle q \rangle (\varkappa, q', t' \mid t) \langle f \rangle (\varkappa, q', t' \mid t). \quad (10)$$

From now on we use the notations:

$$q(\varkappa, q', t' \mid t) = \langle q \rangle (\varkappa, q', t' \mid t), \quad (11)$$

$$f(\varkappa, q', t' \mid t) = \langle f \rangle (\varkappa, q', t' \mid t). \quad (12)$$

Expression (9) for the average stress tensor can then be written as:

$$T(t) \cong -p\mathbf{1} + \sum_\varkappa \int_{-\infty}^{t} \int q(\varkappa, q', t'\,|\,t)\, f(\varkappa, q', t'\,|\,t)$$

$$\cdot\, \varphi(\varkappa, q', t'\,|\,t)\, d^3q'\, dt'. \qquad (13)$$

The following aim is to evaluate the functions q and f that appear in eq. (13). We first consider the equilibrium of forces acting in the chains.

3.3 Equilibrium of chain forces

The magnitude of any specific chain force depends on the chain's deformation history following from the time of its creation and on the force it transmitted at the time of its creation. We now consider the displacements of junction points in more detail. Conglomerates in which chains with different stiffnesses come together will move in such a way that the stiffest chains are elongated least. The ratio of the magnitudes of the forces that are transmitted by chains with low and high moduli, respectively, is always closer to unity than it would be in the case of affine junction motion. The preceding considerations suggest that the averaged forces carried by $\varkappa$-chains at time t depend mainly on the interval $t - t'$ and the chain vector q' at the time of creation rather than on the chain complexity; therefore, we adopt the following approximation which is assumed to be valid for any specific flow:

$$f(1, q', t'\,|\,t) = f(2, q', t'\,|\,t) = \ldots \equiv f(q', t'\,|\,t). \qquad (14)$$

Though not explicitly indicated, the deformation history of individual chains may also affect the actual value of f. However when the nature of the network chains is purely elastic, the chain force depends only on the actual chain length. We assume the average chain force then to depend on the average chain vector:

$$f(q', t'\,|\,t) = f(\varkappa, q(\varkappa, q', t'\,|\,t)), \qquad (15)$$

which is the same for every $\varkappa$. The average stretching of the various types of chains can be found by inverting eq. (15).

Eqs. (14) and (15) state that not the forces transmitted by the individual chains, but only their averages, defined by eq. (7), are equal. In addition they express the force that appears in eq. (13) in terms of the chain elongations.

The force transmitted by the chains may be given by some time-independent particle-interaction potential, e.g. by the Lennard-Jones potential in the case of non-polar and non-deformable particles. On the other hand, in the case of continuous structures, the dispersed
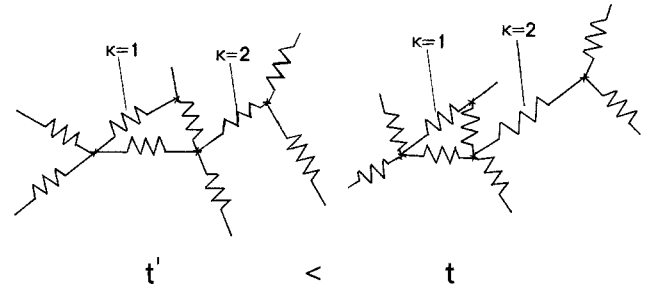

Fig. 2. Chain stretching in a network undergoing shear

phase may be a non-permanent molecular network in which bonds are created and annihilated on a molecular scale, thus causing the chain itself to behave as a viscoelastic material. In this case the chain-force magnitudes depend on the chain-deformation histories. This dependence can be evaluated as a function of time by means of a constitutive equation that is valid for the dispersed material itself and allows for both elastic and dissipative behaviour.

Figure 2 illustrates the microscopic-flow processes described by eqs. (14) and (15). Attention is focussed on two chains, being of different stiffnesses, but which were both created at time t' with orientation vector q'. At time t both chains are stretched, but the amount of stretching will depend on the chains' moduli.

3.4 Average junction flow

We now closely investigate the consequence of non-affine junction motion, in particular in so far as it is caused by chain fracture. In order to specify the non-affinity of the motion of chains that were created at time t' with chain vector q' we define a vector:

$$z(q', t'\,|\,t) \equiv F_{t'}(t) \cdot q'. \qquad (16)$$

In this definition $F_{t'}(t)$ is the relative deformation gradient that corresponds with the macroscopic deformation. The vector z does not generally coincide with the average chain vectors of chains that were created at time t' with chain vector q'. This is due to the fact that the stretching of chains depends on the chain stiffness and the network configuration. In addition, conglomerates may drift apart after fracture of the chain that previously interconnected them. This will affect the amount of stretching of the neighbouring chains. It is a special case of non-affine motion, generally accompanied by some relaxation of the stress in the remaining network, see figure 3.

A vector function is introduced, as a measure for the average state of deformation at time t of chains present
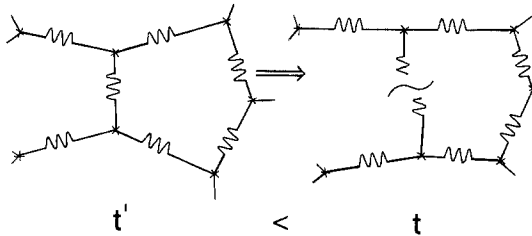
Fig. 3. Network contraction due to chain fracture

at time t' with chain vector q', that still exist at time t:

$$q_{av}(q', t' \mid t) = \frac{\sum_{x} q(x, q', t' \mid t)\, \Psi(x, q', t')}{\sum_{x} \Psi(x, q', t')}. \qquad (17)$$

In the case when the network structure is not disturbed too much and the fraction of x-chains is about the same for every q' we approximate:

$$q_{av}(q', t' \mid t) = \frac{\sum_{x} q(x, q', t' \mid t)\, n_0(x)}{n_0}. \qquad (18)$$

We now introduce the vector function χ, defined as:

$$\chi(q', t' \mid t) \equiv z(q', t' \mid t) - q_{av}(q', t' \mid t). \qquad (19)$$

The physical significance of this function can be clarified by considering a simple one-dimensional network.

From the equilibrium of forces it can be shown that z and q_{av} are equal in the case of sets of interconnected permanent q'-chains of different moduli that are arranged along straight lines. When chains break χ will deviate from zero, so χ is a measure for the non-affinity of the junction flow in so far as resulting from chain fracture. Though not necessarily correct, we assign the same physical meaning to χ in the case of flow of a three-dimensional network. A non-zero value of χ can thus only be caused by chain fracture. To be exact, χ is a measure of the network rearrangement which is likely to follow chain fracture. It is not so that χ being equal to zero implies that the junctions move affinely with the macroscopic flow. Condition (14) or (15) implies that chains with the highest moduli deform less than the others, which produces non-affine junction flow even when the network is permanent. According to eqs. (18) and (19) the elongation of the remaining part of the network will become somewhat less when χ differs from zero due to fracture of some chains, provided that the magnitude and direction of χ are such that q_{av} shows some decrease. The stress in the network may relax as a result of this effect. Since fracture of chains may be caused by the stress in the network, it is very well thinkable that the process of breakdown of the network is delayed when the stress relaxes. It is thus

seen that fracture processes occurring in different parts of the network are coupled, the stronger the higher the value of χ. This interplay is generally not taken into account in molecular-network theories.

The deformation of the network chains in relation to the macroscopic flow can in principle be determined from eqs. (14) or (15), (16), (18) and (19), provided that function χ is known. What follows now is an attempt to quantify this function.

We wish to express χ in terms of microscopic system parameters and flow properties. Primarily, if fracture occurs, χ must be of the order of z in the case of very large deformations. However, we now focus our attention on small deformations when the network originally present in the system still exists for the major part. First of all microscopic fracture mechanisms need to be considered in more detail. What happens to the network when a chain breaks, followed by a drifting apart of the junctions?

In some previous molecular-network theories the network deformation is assumed to deviate from affine deformation only in so far as the symmetrical part of the velocity gradient tensor that describes network flow is concerned. The angular velocity of the motion of molecular chains is then assumed to be given by the vorticity of the velocity field in the macroscopic continuum [19]. In our case we assume that the directions of the q- and z-vectors are the same. So for every x:

$$\frac{z(q', t' \mid t)}{z(q', t' \mid t)} = \frac{q(x, q', t' \mid t)}{q(x, q', t' \mid t)} \equiv e(q', t' \mid t). \qquad (20)$$

From eq. (18) it then follows that q_{av} and z have the same direction as well. Therefore:

(i) $\chi(q', t' \mid t)$ is a vector that parallels $e(q', t' \mid t)$.

It seems plausible that the fracture of chains will cause network contraction to an amount that is related to the initial chain lengths. We assume proportionality:

(ii) $\chi(q', t' \mid t) \sim q'$.

We first consider the case of very small deformations. It is assumed that both the number of fractures and the excess force that is transmitted by a q', t'-chain at time $t \geq t''$ linearly affect the deformation of the network in the case of an infinitesimal stepwise deformation at time $t = t''$:

(iii) $\partial \chi(q', t' \mid t) \sim \dfrac{n_0 - \displaystyle\int_{-\infty}^{t''} \tilde{n}(t''' \mid t)\, dt'''}{n_0}$

$$\underbrace{\frac{\partial}{\partial z}[f_s(q', t'' \mid t)]\,(z(q', t' \mid t) - q')}_{\text{excess chain force}},$$

where $t' \leqq t'' \leqq t$ and f_s denotes the chain force in this type of experiment.

Statements (i) – (iii) can be combined for the type of flow that can be considered as a superposition of equivalent stepwise deformations each of which leading to an extra force f_s (see eq. (iii)). The above expression thus needs to be integrated over time:

$$\chi(\boldsymbol{q}', t' | t) = \lambda\, q' \int_{t'}^{t} \frac{n_0 - \int_{-\infty}^{t''} \tilde{n}(t''' | t)\, dt'''}{n_0} \qquad (21)$$

$$\cdot \underbrace{\frac{\partial}{\partial z}[f_s(\boldsymbol{q}', t'' | t - t'')] \frac{\partial}{\partial t''} z(\boldsymbol{q}', t' | t'')\, dt''}_{\text{excess chain force}}\, e(\boldsymbol{q}', t' | t),$$

where f_s is the same function as the one that was used in (iii), i.e. the chain force after an infinitesimal deformation, and λ is a proportionality factor $[\text{kg}^{-1}\,\text{m}^{-1}\,\text{s}^2]$. It is seen that the rearrangement of q', t'-chains due to an applied deformation ∂z at time t'' depends not on the total number of fractures between t' and t but, instead, only on the number of fractures between t'' and t. The underlying thought is that chains are being created as quickly as they are broken down. In the case when the applied deformation is much more intense, we expect chain fracture to affect the state of deformation of the network more. This can be achieved by letting χ be proportional to the total number of broken chains. For such a flow starting at time $t = t''$ we assume:

$$\chi(\boldsymbol{q}', t' | t) = \lambda\, q' \frac{n_0 - \int_{-\infty}^{t''} \tilde{n}(t''' | t)\, dt'''}{n_0}$$

$$\cdot (f(\boldsymbol{q}', t'' | t) - f(\boldsymbol{q}', t'' | t''))\, e(\boldsymbol{q}', t' | t)$$

if $t' \leqq t'' \leqq t$,

and

$$\chi(\boldsymbol{q}', t' | t) = \lambda\, q' \frac{\tilde{n}(t' | t') - \tilde{n}(t' | t)}{\tilde{n}(t' | t')}$$

$$\cdot (f(\boldsymbol{q}', t' | t) - f(\boldsymbol{q}', t' | t'))\, e(\boldsymbol{q}', t' | t) \qquad (22)$$

if $t'' < t' \leqq t$.

As a chain fracture causes a decrease of the elastic energy content of the rest of the network, λ is taken positive. Its magnitude is a measure of the mutual interference of kinetic processes taking place in different parts of the network.

3.5 Network kinetics

Expressions for network-chain creation and fracture functions are very specific for the nature of the dispersed system considered and need to be based on physical system properties, such as the nature of the interactive forces, and on flow characteristics, such as the shear rate in simple-shear flow.

a) Creation of chains

When created, the chains are assumed to be isotropically distributed over orientation space and may carry a chain force, while the chance of chain creation is assumed to depend on the probability that conglomerates collide and interconnect. For the creation function we write:

$$\varphi(\varkappa, \boldsymbol{q}', t' | t') \equiv g(\varkappa, \boldsymbol{q}', t'), \qquad (23)$$

where g may depend on the individual chain variables $\varkappa$ and $\boldsymbol{q}'$ and on global flow variables as well. Generally g will contain terms based on collisions induced by diffusion and by applied flow [1]. It will thus depend on the conglomerate density, on properties of the deformation history and on the actual rate of deformation. The latter may introduce a dependence on the principal invariants $II_{D(t')}$ and $III_{D(t')}$ of the rate-of-strain tensor of the macroscopic deformation. The first invariant is excluded, since only isochoric flows are considered. Function g generally adopts its minimum value after a long period of rest, when the network connectivity has often reached its maximum value.

b) Network fracture

In order to describe the network breakdown, the annihilation function $h(\varkappa, \boldsymbol{q}', t' | t)$ is introduced to give the relative decrease of the density of $\varkappa$-chains created at time t' with orientation $\boldsymbol{q}'$:

$$\frac{\partial}{\partial t} \varphi(\varkappa, \boldsymbol{q}', t' | t) = - h(\varkappa, \boldsymbol{q}', t' | t)\, \varphi(\varkappa, \boldsymbol{q}', t' | t), \qquad (24)$$

where we have again only indicated the chain variables.

Also the annihilation function needs to be specified for any dispersed system one wishes to describe with the model. It may be so formulated that the chain breaks when some critical length or transmitted force is exceeded. When the chains break by thermal and mechanical actions, an Arrhenius-type equation may be used [1, 12]. It is advantageous that one can let the annihilation function adopt different values when considering chains of different age and thus, in general, chains that transmit different forces.

In most molecular theories the fracture function is assumed to depend on some invariant flow property, which is the same in every chain of the same complexity, irrespective of its elongation. This approach seems reasonable when fracture is induced mainly by thermal

actions. However, in the more general situation, one needs to take into account that the chance of a chain breaking also depends on its deformation history, and thus on the original orientation q' and the time that has passed since the moment of creation.

By integrating eq. (24) and substituting eq. (23) we get:

$$\varphi(x, q', t' \mid t) = g(x, q', t') \exp\left\{-\int_{t'}^{t} h(x, q', t' \mid t'') \, dt''\right\}.$$

(25)

Instead of eq. (13), eqs. (14) and (25) allow us to write:

$$T(t) = -p\mathbf{1} + \sum_{x} \int_{-\infty}^{t} \int q(x, q', t' \mid t) f(q', t' \mid t) g(x, q', t')$$

$$\cdot \exp\left\{-\int_{t'}^{t} h(x, q', t' \mid t'') \, dt''\right\} d^3q' \, dt'. \quad (26)$$

3.6 Some final remarks

It should be noted that the use of eq. (15) can lead to erroneous results in the case of a part of the network chains having very low moduli. It is not realistic to expect that these chains will be stretched to such an extent as is predicted by this equation. Chains that are connected to those with low moduli will prevent this from happening. The analysis presented in this paper enables us to take into account a distribution of chain moduli. However, these chains having moduli that differ considerably from the average chain modulus should be disregarded. It should also be noted that the value of the vector function q in eq. (26) cannot be determined when all chains of a certain complexity have been annihilated (see eq. (7)). Whenever this is the case, junction displacements cannot be expressed by a function of the type (19). Then one has to look for other ways to take chain fracture into account.

4. Model stress predictions

4.1 Flow starting at t = 0

In this section we present model predictions for some classes of flow and some types of materials. In the case of flow experiments starting at time $t = 0$ after a long period of rest, eq. (26) can be simplified by carrying out the integration from $t' = -\infty$ to $t' = 0$ and from $t' = 0$ to $t' = t$ separately:

$$T(t) = -p\mathbf{1} + T_b(t) + \sum_{x} \int_{0}^{t} \int q(x, q', t' \mid t)$$

$$\cdot f(q', t' \mid t) g(x, q', t')$$

$$\cdot \exp\left\{-\int_{t'}^{t} h(x, q', t' \mid t'') \, dt''\right\} d^3q' \, dt', \quad (27)$$

where $T_b(t)$ is the contribution at time t to the stress from chains that were present at time $t = 0$. It seems reasonable to postulate that all chains present at $t = 0$ will contribute to the actual stresses independent of the time of their creation (in so far as they have not been broken). This means that $q(x, q', t' \mid t)$ and $f(q', t' \mid t)$ do not depend on t' if $t' \leq 0 \leq t$. Accordingly we may replace t' by zero and write for $T_b(t)$:

$$T_b(t) = \sum_{x} \int q(x, q', 0 \mid t) f(q', 0 \mid t) \int_{-\infty}^{0} \varphi(x, q', t' \mid t) \, dt' \, d^3q'.$$

(28)

The density of x, q'-chains that were created at times $t' \leq 0$ is given by:

$$\int_{-\infty}^{0} \varphi(x, q', t' \mid t) \, dt' = \int_{-\infty}^{0} \varphi(x, q', t' \mid 0) \, dt'$$

$$\cdot \exp\left\{-\int_{0}^{t} h(x, q', 0 \mid t'') \, dt''\right\}.$$

(29)

4.2 Linear viscoelasticity

We consider a network of chains which may be treated as springs with properties that do not depend on time. The force law for the individual chain is then written as eq. (15). We assume that the average force that is transmitted by x-chains of any initial length q' is given in first order by:

$$f(x, q', t' \mid t)$$

(30)

$$= \left(f(q') + c(x, q') \frac{q(x, q', t' \mid t) - q'}{q'}\right) e(q', t' \mid t).$$

In this equation $c(x, q')$ is a constant with unit $[\text{kg m s}^{-2}]$ and $f(q')$ is the force that is transmitted by the chains at the time of their creation (figure 4). All network chains are assumed to be of equal length q_0'
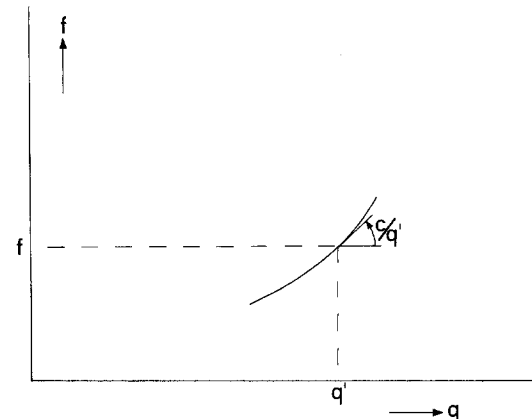

Fig. 4. Force law for an individual x-chain

and isotropically distributed over orientation space at time $t = 0$ when the system is at rest. The density function is normalized such that eq. (4) is satisfied:

$$\int_{-\infty}^{0} \varphi(\varkappa, q', t' \mid 0) \, dt' = \frac{n_0(\varkappa)}{4 \pi q_0'^2} \delta(q' - q_0').$$ (31)

Later on, the results are generalized for distributions of initial chain lengths. The relaxation spectrum of the dispersion is found by calculating the shear-stress relaxation following an infinitesimal shearing displacement γ_0 at time $t = 0$. This is effected by substitution in

$$q(\varkappa, q_0', t' \mid t) = \left[q_0' + \frac{|F_{t'}(t) \cdot q_0'| - q_0'}{\lambda c(\varkappa, q_0') \left(1 - \dfrac{\int_{-\infty}^{t''} \tilde{n}(t''' \mid t) \, dt'''}{n_0}\right) + \dfrac{c(\varkappa, q_0')}{n_0} \sum_{\varkappa'} \dfrac{n_0(\varkappa')}{c(\varkappa', q_0')}} \right] e(q_0', t' \mid t).$$ (37)

Eq. (30) then reads:

$$f(q_0', t' \mid t) = \left[f_0(q_0') + \frac{|F_{t'}(t) \cdot q_0'| - q_0'}{\lambda q_0' \left(1 - \dfrac{\int_{-\infty}^{t''} \tilde{n}(t''' \mid t) \, dt'''}{n_0}\right) + \dfrac{q_0'}{n_0} \sum_{\varkappa} \dfrac{n_0(\varkappa')}{c(\varkappa', q_0')}} \right] e(q_0', t' \mid t).$$ (38)

eq. (16) of:

$$F_{t'}(t) = \begin{bmatrix} 1 & \gamma_0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \quad \text{if} \quad t' \leq 0 < t$$

and

$$F_{t'}(t) = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \quad \begin{array}{l} \text{if} \quad t' \leq t \leq 0 \\ \text{and if} \quad 0 < t' \leq t. \end{array}$$ (32)

In the case of linearity, the value of the chain annihilation function does not differ from its value at rest. It depends only on $\varkappa$ and q'. Therefore, the density of $\varkappa, q'$-chains that were present at rest follows from:

$$\int_{-\infty}^{0} \varphi(\varkappa, q', t' \mid t) \, dt' = \frac{n_0(\varkappa)}{4 \pi q_0'^2} \delta(q' - q_0') e^{-t h_0(\varkappa, q_0')}.$$ (33)

Since eq. (15) is valid for all complexities we may express the elongation of chains of complexity $\varkappa'$ in terms of the elongation of chains of complexity $\varkappa$:

$$q(\varkappa', q_0', t' \mid t) = q_0' + \frac{c(\varkappa, q_0')}{c(\varkappa', q_0')} (q(\varkappa, q_0', t' \mid t) - q_0'),$$ (34)

where $\varkappa$ may be equal to $\varkappa'$ or be different (see eq. (30)).

We shall now derive the chain vectors from the preceding expressions. We start by writing:

$$q(\varkappa, q_0', t' \mid t) = \left(\frac{\sum_{\varkappa'} q(\varkappa', q_0', t' \mid t) n_0(\varkappa')}{n_0(\varkappa)} \right.$$

$$\left. - \frac{\sum_{\varkappa' \neq \varkappa} q(\varkappa', q_0', t' \mid t) n_0(\varkappa')}{n_0(\varkappa)} \right) e(q_0', t' \mid t).$$ (35)

The unit vector e has been introduced in eq. (20). Combination of eqs. (18), (19), (34) and (35) gives:

$$q(\varkappa, q_0', t' \mid t) = \left((|F_{t'}(t) \cdot q_0'| - \chi(q_0', t' \mid t)) \frac{n_0}{n_0(\varkappa)} \right.$$

$$\left. - \sum_{\varkappa' \neq \varkappa} \left(\left(q_0' + \frac{c(\varkappa, q_0')}{c(\varkappa', q_0')} (q(\varkappa, q_0', t' \mid t) - q_0') \right) \frac{n_0(\varkappa')}{n_0(\varkappa)} \right) \right)$$

$$\cdot e(q_0', t' \mid t).$$ (36)

After substitution of eqs. (22) for $t' \leq t'' \leq t$ and (30), one finally obtains:

Note that the use of eq. (21) instead of eq. (22) in deriving q and f leads to the same expressions. Expressions (37) and (38) can be simplified for $t' = t'' = 0$:

$$q(\varkappa, q_0', 0 \mid t) = \left(q_0' + \frac{\lim_{t \downarrow 0} z(q_0', 0 \mid t) - q_0'}{c(\varkappa, q_0')} A(t) \right)$$

$$\cdot e(q_0', 0 \mid t)$$ (39)

and

$$f(q_0', 0 \mid t) = \left(f_0(q_0') + \frac{\lim_{t \downarrow 0} z(q_0', 0 \mid t) - q_0'}{q_0'} A(t) \right)$$

$$\cdot e(q_0', 0 \mid t),$$ (40)

where

$$A(t) \equiv \frac{B}{1 - \dfrac{\lambda B}{n_0} \sum_{\varkappa} n_0(\varkappa) e^{-t h_0(\varkappa, q_0')}}$$ (41)

with

$$B \equiv \frac{1}{\lambda + \dfrac{1}{n_0} \sum_{\varkappa} \dfrac{n_0(\varkappa)}{c(\varkappa, q_0')}}.$$ (42)

The density function was found by integrating eq. (33) over configuration space. Further we made use of eq. (16).

The vector functions can be expressed in terms of polar coordinates (Fig. 1):

$$q_0' = q_0' \begin{pmatrix} \sin \theta_0 \sin \varphi_0 \\ \cos \theta_0 \\ \sin \theta_0 \cos \varphi_0 \end{pmatrix},$$ (43)

$$z\,(q_0', 0 \mid t) = q_0' \begin{pmatrix} \sin\theta_0 \sin\varphi_0 + \gamma_0 \cos\theta_0 \\ \cos\theta_0 \\ \sin\theta_0 \cos\varphi_0 \end{pmatrix}. \qquad (44)$$

For small deformations we find:

$$q\,(\varkappa, q_0', 0 \mid t) \qquad\qquad\qquad\qquad (45)$$

$$\cong q_0' \left(1 + \frac{\gamma_0}{c\,(\varkappa, q_0')} \cos\theta_0 \sin\theta_0 \sin\varphi_0 A\,(t)\right) e\,(q_0', 0 \mid t),$$

$$f\,(q_0', 0 \mid t) \qquad\qquad\qquad\qquad (46)$$

$$\cong (f_0\,(q_0') + \gamma_0 \cos\theta_0 \sin\theta_0 \sin\varphi_0 A\,(t))\, e\,(q_0', 0 \mid t),$$

which are in fact first-order approximations of eqs. (39) and (40). On substituting eqs. (33), (45) and (46) in eq. (28) and carrying out the integration over configuration space, the relaxation function can be shown to read:

$$G(t) \equiv \frac{T_{b,xy}(t)}{\gamma_0} = \frac{q_0'}{15} \left\{ \sum_{\varkappa} \left(3 f_0\,(q_0')\right.\right.$$

$$\left.\left. + \left(1 + \frac{f_0\,(q_0')}{c\,(\varkappa, q_0')}\right) A\,(t)\right) n_0\,(\varkappa)\, e^{-t h_0(\varkappa, q_0')}\right\}. \quad (47)$$

We can write $A\,(t)$ as a series:

$$A(t) = B\left(1 + \frac{\lambda B}{n_0} \sum_{\varkappa} n_0\,(\varkappa)\, e^{-t h_0(\varkappa, q_0')}\right.$$

$$\left. + \left(\frac{\lambda B}{n_0} \sum_{\varkappa} n_0\,(\varkappa)\, e^{-t h_0(\varkappa, q_0')}\right)^2 + \dots\right). \quad (48)$$

Eq. (47) can thus be written as a sum:

$$G(t) \equiv \sum_i G_i\, e^{-t/\tau_i}, \qquad\qquad (49)$$

where G_i is the strength of the mechanism with relaxation time τ_i. In case all chains have the same complexity, it follows that

$$\tau_i = \frac{1}{i\, h_0\,(1, q_0')} \qquad\qquad (50)$$

and

$$G_i = \begin{cases} \dfrac{n_0 q_0'}{15} \left(3 f_0\,(q_0') + \left(1 + \dfrac{f_0\,(q_0')}{c\,(1, q_0')}\right) B\right) & \text{if } i = 1, \\[2ex] \dfrac{n_0 q_0'}{15} \left(1 + \dfrac{f_0\,(q_0')}{c\,(1, q_0')}\right) B\,(\lambda B)^{i-1} & \text{if } i > 1. \end{cases} \qquad (51)$$

The relaxation spectrum is visualized in figure 5. It is seen that, by introducing the effect of network contraction due to chain fracture by means of assigning a non-zero value to the parameter λ in eq. (51), the single relaxation mechanism with characteristic time $1/h_0\,(1, q_0')$ is replaced by a whole set of relaxation mechanisms. The shear stress following an instantane-
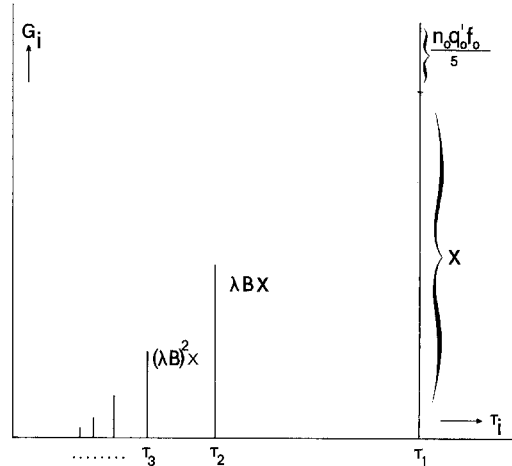

Fig. 5. Relaxation moduli according to the network model for a structure that consists of one type of chain only;

$$x \equiv \frac{n_0 q_0'}{15}\left(1 + \frac{f_0\,(q_0')}{c\,(1, q_0')}\right) B$$

ous shearing displacement at the beginning approaches zero faster than it would do if chain fracture would not be followed by some network relaxation, i.e. $\lambda = 0$. The distribution of relaxation strengths over the relaxation mechanism strongly depends on λ. However, the sum of the strengths does not, as can be seen from eq. (51).

The important thing to note is that the model predicts linear viscoelastic behaviour that is described by an infinite number of relaxation mechanisms, even for a simple network consisting of identical chains throughout the whole sample. If one sets $\lambda = 0$, the relaxation spectrum of a system of identical chains contains one relaxation time only. This corresponds to the simplest case of elementary transient-network theories [18], i.e. in which the number of relaxation mechanisms is set equal to one. Most systems, however, display a rheological behaviour that is much more complicated and that can only be described by a *set* of relaxation mechanisms. One way to do so is to assign different properties, i.e. probability of breaking to chains of different complexities, each of which being responsible for one independent relaxation mechanism [20]. Physical interpretation of data obtained from this method becomes difficult when there are plausible grounds for believing that all chains have the same physical properties. This may be so when the system is monodisperse. The model proposed in this paper enables one to relate the possibly complicated relaxation spectrum of such homogeneous systems to individual and collective properties of network elements, which may be identical or may have only a few complexities. The physical significance of the relaxa-

tion function is clarified in terms of bond stiffnesses, lifetimes, etc., by means of eqs. (50) and (51), in the case of one chain complexity. The relaxation spectrum that results when more than one chain complexity is assumed to exist is found from eqs. (47) and (48) in a similar way. The complex shear modulus is related to the relaxation function (49) in the following way:

$$G^*(j\omega) = \int_{-\infty}^{\infty} e^{-j\omega\tau} \dot{G}(\tau) \, d\tau, \tag{52}$$

where j is the imaginary number, ω the angular frequency, and $\dot{G}(\tau)$ the time derivative of the relaxation function. The complex shear modulus of a system that consists of one type of chains only can be expressed in terms of the relaxation times and moduli introduced in eqs. (50) and (51):

$$G^*(j\omega) = \sum_{i=1}^{\infty} \frac{j\omega\tau_i \, G_i}{1+j\omega\tau_i}. \tag{53}$$

4.3. Distributions of initial chain lengths

At rest the chains need not all be of the same initial length q_0'; instead, an isotropic distribution of chain vectors may be expected. We consider such a network in a state of rest and write for the initial number of $\varkappa$-chains of length q_0':

$$N(\varkappa, q_0') = \iint_{-\infty}^{0} \varphi(\varkappa, q', t' \mid 0) \, dt' \, \delta(q' - q_0') \, d^3q'. \tag{54}$$

The relaxation function of systems in which the chains assume distinct initial end-to-end distances is found simply by integrating eq. (47) over the initial chain lengths:

$$G(t) = \frac{1}{15} \sum_{\varkappa} \int_0^{\infty} q_0' \left(3f_0(q_0') + \left(1 + \frac{f_0(q_0')}{c(\varkappa, q_0')}\right) A(q_0', t) \right)$$
$$\cdot N(\varkappa, q_0') \, e^{-t h_0(\varkappa, q_0')} \, dq_0', \tag{55}$$

where:

$$A(q_0', t) \equiv \frac{B(q_0')}{1 - \frac{\lambda B(q_0')}{n_0} \sum_{\varkappa} \int_0^{\infty} N(\varkappa, q_0') \, e^{-t h_0(\varkappa, q_0')} \, dq_0'}. \tag{56}$$

Take $h_0 = 0$ for any $\varkappa$, i.e. the network behaves as a permanent one. We assume chain force equilibrium to hold below some angular frequency ω_1. The elastic modulus then equals $\lim_{t \downarrow 0} G(t)$, so:

$$G'(\omega_1) = \frac{1}{15} \sum_{\varkappa} \int_0^{\infty} q_0' \left(3f_0(q_0') \right. \tag{57}$$
$$\left. + \left(1 + \frac{f_0(q_0')}{c(\varkappa, q_0')}\right) \frac{n_0}{\sum_{\varkappa} \frac{n_0(\varkappa)}{c(\varkappa, q_0')}} \right) N(\varkappa, q_0') \, dq_0'.$$

This expression does not show any frequency dependence, because the effects of inertia and liquid phase displacement are not taken into account. However, at an angular frequency $\omega_2 \gg \omega_1$, for which liquid drag forces constrain the conglomerates to move affinely with applied shear, the chain vectors read:

$$q(\varkappa, q_0', t' \mid t) = F_{t'}(t) \cdot q_0'. \tag{58}$$

The chain force equilibrium given by eq. (15) can then no longer be satisfied. This implies that the chain forces depend on the chain moduli. From eqs. (28), (30), (32), and (58) it follows:

$$G'(\omega_2) = \frac{1}{15} \sum_{\varkappa} \int_0^{\infty} q_0' \left(4f_0(q_0') + c(\varkappa, q_0')\right) \\ \cdot N(\varkappa, q_0') \, dq_0'. \tag{59}$$

The difference between the elastic moduli of permanent networks as calculated on the basis of different assumptions with respect to the conglomerate flow, eqs. (57) and (59) reads:

$$G'(\omega_2) - G'(\omega_1) = \frac{1}{15} \sum_{\varkappa} \int_0^{\infty} q_0' \left(1 + \frac{f_0(q_0')}{c(\varkappa, q_0')}\right)$$
$$\cdot \left(c(\varkappa, q_0') - \frac{n_0}{\sum_{\varkappa} \frac{n_0(\varkappa)}{c(\varkappa, q_0')}} \right) N(\varkappa, q_0') \, dq_0', \tag{60}$$

which equals zero when all chains have the same force constant. It is an estimate of the frequency dependence of the elastic modulus of a permanent network, the chains of which having different complexities. Next consider a permanent network of identical polymer molecules modelled as linear springs which adopt an isotropic Gaussian chain-vector distribution at rest:

$$N(\varkappa, q_0') = 4\pi q_0'^2 \, n_0 \left[\frac{3}{2\pi(v-1) L^2} \right]^{3/2} e^{-3q_0'^2/2(v-1) L^2}, \tag{61}$$

where q_0' is the end-to-end vector of a freely jointed chain with $(v-1)$ links of length L [21]. At temperature T the forces transmitted by the chains equal:

$$f(q_0', t' \mid t) = \frac{3kT}{(v-1) L^2} \, q(q_0', t' \mid t), \tag{62}$$

where k is Boltzmann's constant. On inserting $c = f_0 = \dfrac{3kT}{(v-1) L^2} \, q_0'$ it follows from either eqs. (57) or (59) and (61) that the storage modulus $G'(\omega) = n_0 kT$, a well-known result from the rubber-elasticity theory. It is noted that all results derived so far that assume

chain force equilibrium are valid under creep conditions only. At chain fracture the network remaining adopts a new configuration within a time scale that is small compared to time scales connected to network-fracture processes themselves. However, when the product λB is in the order of unity, the fastest relaxation processes may occur within time scales that are in the order of network-contraction characteristic times (figure 5). This interferes with one of the main assumptions underlying the model, namely that network-chain forces are in mutual equilibrium at any time. Thus, one has to restrict the interpretation of relaxation

h-functions, this can be true only if the value of h does not depend on $\varkappa$. Further we assume that h does not depend on global network and flow properties, i.e. its value depends only on individual chain properties, such as the length of the chain under consideration. It then follows from eqs. (19) and (22) that all chains with the same $\varkappa$ and q' undergo the same average deformation during flow irrespective of the time of their creation $t' \geqq 0$, so:

$$q\,(\varkappa, q', t' \mid t)\,f\,(q', t' \mid t)$$
$$= q\,(\varkappa, q', 0 \mid t - t')\,f\,(q', 0 \mid t - t')\,, \qquad (64)$$

for any $t \geqq t'$, while the ratio:

$$\frac{\varphi\,(\varkappa, q', t' \mid t)}{\int\limits_{-\infty}^{0} \varphi\,(\varkappa, q', t'' \mid t - t')\,dt''} = \frac{g\,(\varkappa, q', t')\,\exp\left\{-\int\limits_{t'}^{t} h\,(\varkappa, q', t' \mid t'')\,dt''\right\}}{\int\limits_{-\infty}^{0} g\,(\varkappa, q', t'')\,\exp\{h_0\,(\varkappa, q')\,t''\}\,dt''\,\exp\left\{-\int\limits_{0}^{t-t'} h\,(\varkappa, q', 0 \mid t'')\,dt''\right\}} \qquad (65)$$

spectra in terms of model constants to the relaxation-time interval that coincides with this condition.

Both results (57) and (59) differ from expressions for the elastic moduli of a permanent network used in literature, as derived from special chain arrangements by Nederveen [22] on applying Poisson's rule.

4.4. Inception of steady flow

Eq. (27) together with eqs. (15) and (36) and the kinetic equation (25) can, in principle, be solved numerically for the inception of any steady flow. Not only chains that are present at the time the flow starts but also chains that are created during flow will, sooner or later, contribute to the macroscopic stress. Under certain conditions it is possible to express the stress contribution of these chains in terms of the chain creation function and the stress $T_b(t)$ that is carried by these chains that were present at the beginning. It is an important consideration that $T_b(t)$ is proportional to the number of chains that were present at the inception of flow, say $t = 0$, provided the ratio $n_0(\varkappa)/n_0$ is kept constant. This is so, because only ratios of chain densities are taken into account in eqs. (18–22).

We consider the special case that the distribution of chain vectors of chains created at time $t' \geqq 0$ is the same as the initial one, apart from a constant factor, i.e.:

$$\frac{g\,(\varkappa, q', t')}{\sum\limits_{\varkappa} g\,(\varkappa, q', t')} = \frac{\int\limits_{-\infty}^{0} \varphi\,(\varkappa, q', t' \mid 0)\,dt'}{\sum\limits_{\varkappa} \int\limits_{-\infty}^{0} \varphi\,(\varkappa, q', t' \mid 0)\,dt'} \qquad (63)$$

for any value of $\varkappa, q'$ and t'. Since the values of the density functions follow from the ratio of the g- and

$$= \frac{g\,(\varkappa, q', t')}{\int\limits_{-\infty}^{0} g\,(\varkappa, q', t'')\,\exp\{h_0\,(\varkappa, q')\,t''\}\,dt''}\,,$$

does not depend on $\varkappa, q'$ and t (see eq. (63)). We may then write for (27):

$$T(t) = -p\mathbf{1} + T_b(t)$$
$$+ \int\limits_{0}^{t} T_b(t - t')\,\frac{\varphi\,(\varkappa, q', t' \mid t)}{\int\limits_{-\infty}^{0} \varphi\,(\varkappa, q', t'' \mid t - t')\,dt''}\,dt'$$
$$= -p\mathbf{1} + T_b(t)$$
$$+ \int\limits_{0}^{t} T_b(t - t')\,\frac{\sum\limits_{\varkappa} \int g\,(\varkappa, q', t')\,d^3q'}{n_0}\,dt'\,. \qquad (66)$$

Use was made of eqs. (63) and (65) in the second step, while integration was carried out over q'. The chain-density function which may appear in the expression for g in eq. (66) can be deduced in an analogous way:

$$n(t') \equiv \sum\limits_{\varkappa} \int\limits_{-\infty}^{t'} \int \varphi\,(\varkappa, q', t'' \mid t')\,d^3q'\,dt'' \qquad (67)$$
$$= n_b(t') + \int\limits_{0}^{t'} n_b(t' - t'')\,\frac{\sum\limits_{\varkappa} \int g\,(\varkappa, q', t'')\,d^3q'}{n_0}\,dt''_t$$

where

$$n_b(t') = \begin{cases} n_0 & \text{if } t' < 0\,, \\[6pt] \sum\limits_{\varkappa} \int\limits_{-\infty}^{0} \int g\,(\varkappa, q', t'') \\[6pt] \cdot \exp\left\{-\int\limits_{t''}^{t'} h\,(\varkappa, q', t'' \mid t''')\,dt'''\right\} d^3q'\,dt'' \\[6pt] \qquad\qquad \text{if } t' \geqq 0\,. \end{cases} \qquad (68)$$

The functions $T_b(t)$ and $n_b(t)$ are found from eqs. (28) and (68) on substituting the proper annihilation func-

tion. Subsequently, the stress-tensor components, when taking the creation of chains during flow into account, are found from eqs. (66) and (67).

4.5. An illustrative stress calculation

As an illustration the stress response to the inception of steady simple-shear flow ($v_x = \dot{\gamma} y$) is calculated for a certain choice of the chain stiffness and chain-annihilation function that is typical for a dispersed-particle network. All chains have the same length q'_0 and are isotropically distributed over orientation space at the beginning (eq. (33)). All chains have the same complexity. When the chain end-to-end distance is less than the initial length q'_0, the transmitted force equals zero:

$$f(1, q'_0, t' \mid t) = \begin{cases} 0 & \text{if } q(1, q'_0, t' \mid t) \leq q'_0, \\ c(1, q'_0)\dfrac{q(1, q'_0, t' \mid t) - q'_0}{q'_0} e(q'_0, t' \mid t) & \\ & \text{if } q(1, q'_0, t' \mid t) \geq q'_0. \end{cases} \quad (69)$$

When the chains deform, the potential energy stored in the bonds inside the chains increases with a total amount:

$$\Delta E(q(q'_0, t' \mid t)) = \begin{cases} 0 & \text{if } q(1, q'_0, t' \mid t) \leq q'_0, \\ \frac{1}{2} c(1, q'_0) q'_0 \left(\dfrac{q(1, q'_0, t' \mid t) - q'_0}{q'_0}\right)^2 & \\ & \text{if } q(1, q'_0, t' \mid t) \geq q'_0. \end{cases} \quad (70)$$

The annihilation function is approximated by an Arrhenius-type expression:

$$h(1, q'_0, t' \mid t) = h_0(T) \exp\left\{\dfrac{\Delta E(q(1, q'_0, t' \mid t))}{kT}\right\}. \quad (71)$$

The factor $h_0(T)$ denotes the rest value of the annihilation function. It depends on the total potential energy available in particle bonds within the chain that must be overcome before chain fracture occurs, k is Boltzmann's constant and T the absolute temperature.

Structural build-up by means of peri- and orthokinetic coagulation is assumed to be negligible since model calculations are carried out for high rates of shear only ($\dot{\gamma} h_0^{-1} \cong 10$) and because the shear itself is taken to be so small that network breakdown and hence the number of freely diffusing conglomerates are limited. Under these assumptions the components of $T_b(t)$ in eq. (27) are approximately equal to the components of the stress tensor itself.

The relative deformation gradient reads:

$$F_{t'}(t) = \begin{bmatrix} 1 & \gamma(t', t) & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}, \quad (72)$$

in which

$$\gamma(t', t) = 0 \qquad \text{if } t' \leq t < 0,$$
$$\gamma(t', t) = \dot{\gamma} t \qquad \text{if } t' \leq 0 < t,$$
$$\gamma(t', t) = \dot{\gamma}(t - t') \quad \text{if } 0 \leq t' \leq t.$$

The shear stress and first normal-stress difference that follow upon the inception of steady simple-shear flow are calculated from $T_b(t)$ (eqs. (28), (29) and (31)):

$$T_b(t) = \frac{n_0}{4\pi q_0'^2} \int q(1, q'_0, 0 \mid t) f(q'_0, 0 \mid t) \delta(q' - q'_0)$$
$$\cdot \exp\left\{-\int_0^t h(1, q', 0 \mid t') dt'\right\} d^3q'. \quad (73)$$

The chain vector follows from eq. (37):

$$q(1, q'_0, 0 \mid t) \qquad\qquad\qquad (74)$$
$$= \left[q'_0 + \dfrac{\mid F_0(t) \cdot q'_0 \mid - q'_0}{1 + \tilde{\lambda} c(1, q'_0) \left(1 - \dfrac{\int_{-\infty}^0 n(t'' \mid t) dt''}{n_0}\right)}\right]$$
$$\cdot e(q'_0, 0 \mid t),$$

where $\tilde{\lambda} = 0$ and $\tilde{\lambda} = \lambda$ in the case of chain bending and chain stretching, respectively, and

$$\int_{-\infty}^0 n(t'' \mid t) dt'' = \frac{n_0}{4\pi q_0'^2} \int \delta(q' - q'_0)$$
$$\cdot \exp\left\{-\int_0^t h(1, q', 0 \mid t'\right\} d^3q'. \quad (75)$$

These equations are solved numerically on substituting eqs. (69–72), see figures 6–8. Parameter values used for calculations are listed in table 1.

The elastic response at the beginning of the experiment is seen to correspond to an elastic modulus that is half the one that follows from eq. (49) on substituting $f_0 = 0$ and the parameter values listed in table 1. This is due to the fact that, according to eq. (69) the chains bend when they are compressed. The non-zero value of h_0 causes the responses to diverge somewhat at low shears. At larger shears the curves are seen to diverge further as a result of chain fracture, as predicted by eq. (71). The shear at which the stress components reach their maximum is determined mainly by cq'_0 and h_0, i.e. by the maximum elongation that the individual chains are able to stand. The divergence of the curves is governed by the steepness of the fracture function (71). If the chain-annihilation chance would rise from zero to infinity after exceeding a certain critical length, there would be no $\dot{\gamma}$-dependence left at all in the stress overshoot curve. In figure 8 the effect of varying λc on
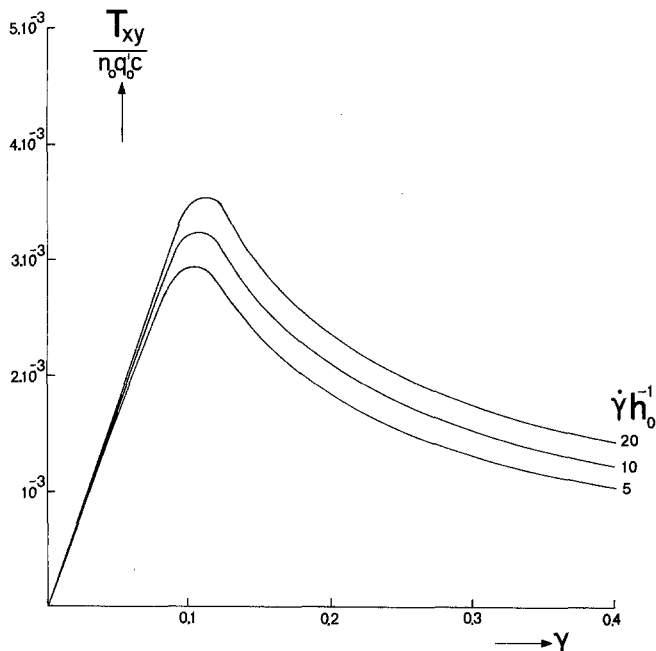
Fig. 6. Model calculations; shear stress versus shear after inception of steady simple-shear flow for different values of the shear rate. See table 1; $\lambda c = 5$
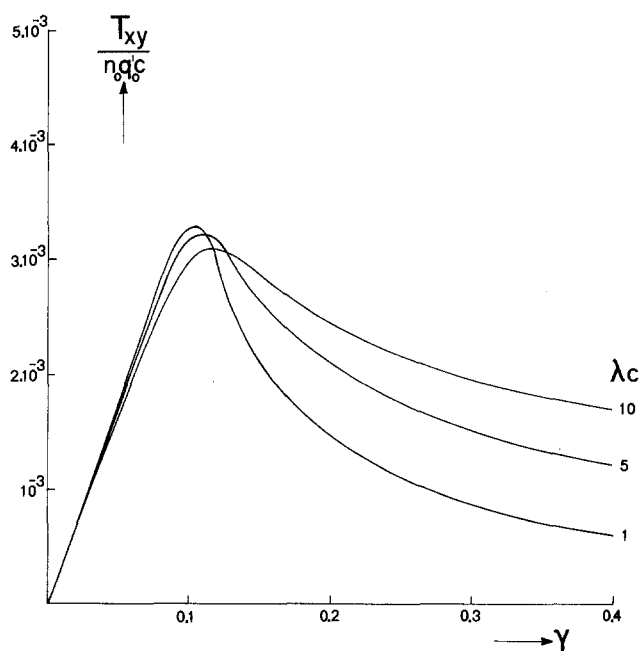

Fig. 8. Model calculations; shear stress versus shear after inception of simple-shear flow for different values of the contraction parameter λc. See table 1; $\dot{\gamma} h_0^{-1} = 10$
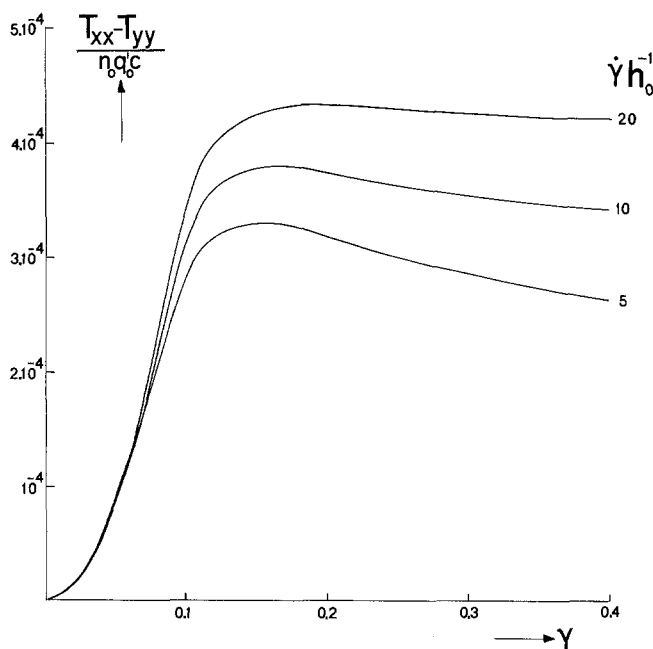
the shape of the overshoot curve is illustrated. With λc increasing, chain fracture occurring somewhere in the sample causes an increase of contraction of the remaining part of the network, implying that the process of network-connectivity breakdown is delayed. The first normal-stress difference is naturally somewhat smaller than the shearing stress. The ratio of maximum shearing stress versus maximum first normal-stress difference depends on the value of the parameter λc. By means of assigning the proper values to the system parameters in eqs. (69−71), the shear-stress overshoot response can be adjusted so as to have a region in which the material behaves primarily elastically with a slight shear-rate dependence only, and a region in which time effects affect the stress response more intensely, i.e. at the maximum shearing stress, where the chains carry about all the maximum force they can bear. The shape of the stress-overshoot curves can thus

Fig. 7. Model calculations; first normal-stress difference versus shear after inception of steady simple-shear flow for different values of the shear rate. See table 1; $\lambda c = 5$

Table 1. Parameter values used for model calculations

$\lambda c (1, q_0')$	$1 - 5 - 10$
$c (1, q_0') \, q_0'$ (kg m^2 s^{-2})	$2 \cdot 10^{-17}$
T (K)	293
$\dot{\gamma} h_0^{-1}$	$5 - 10 - 20$

be established to be in qualitative agreement with masurements on classes of dispersed materials in which network-interaction forces are of dominating importance to the system's rheological properties, such as dispersions of fat crystals in oil [2, 13, 23].

5. Conclusions

The transient-network model for concentrated dispersed systems introduced in this paper explains the relation between typical rheological properties of these types of systems and the microscopical parameters, both structural and physical, that are responsible for them. For instance, the initial slope of the stress-shear curve in the case of inception of simple-shear flow, i.e. the elastic part of the response, the shear at which the shear stress passes through its maximum, the influence of the shear rate, and other phenomena, can all be modelled by substituting the proper chain moduli, kinetic functions, and structural parameters in eqs. (14), (19), (23) and (24). Conversely, by fitting model-stress curves to experimental data, information is obtained about both structural build-up of dispersed-particle networks and interaction forces between the particles themselves. When either the three-dimensional structure of the system or the nature of the interaction potential is known, either the interaction potential or the structural parameters can be obtained separately by fitting rheological data, provided the kinetic functions (23) and (24) are known. The three-dimensional structure can sometimes be determined for example by Scanning Electron Microscopy.

Once the relation between the microscopic properties of the system and its rheological behaviour under varying circumstances is known, tools are available for modifying the network structure and the physical properties of the dispersed particles in such a way that the rheological behaviour of dispersed systems is altered in a predetermined way.

Appendix: An expression for the stress tensor

A network consisting of conglomerates of dispersed material connected by chains is visualized in figure 9. The volume in so far as occupied by the dispersed phase is subdivided into small volume elements, which contain only one conglomerate each, supplemented by half of all the dispersed material
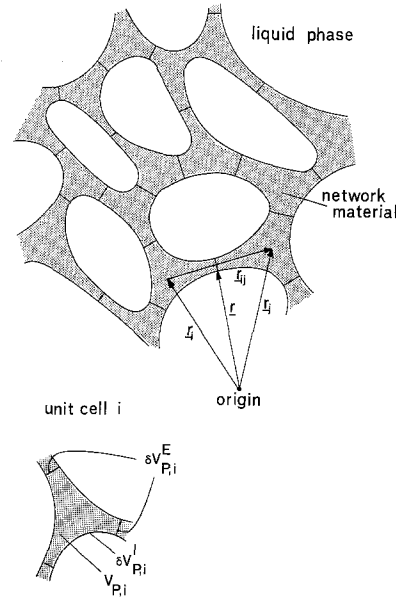

Fig. 9. Network structure subdivided into unit cells

chains that are connected with these conglomerates. The number of volume elements equals the number of conglomerates. Each cell is identified by the index i. The value of the y-component of the Cartesian coordinates of the conglomerates is a continuously increasing function of i. The volume of the cell is given by $V_{P,i}$. The total volume occupied by the liquid phase in a volume V of the dispersion is given by V_F, so:

$$V \equiv V_F + \sum_i V_{P,i}.$$ (A.1)

Summation is carried out over all conglomerates in volume V. The contact surface of the dispersed phase and the liquid phase is given by $\partial V^I_{P,i}$ for each cell, while $\partial V^E_{P,i}$ denotes the intersections of the chains at the cell walls.

The local stress tensor reads:

$$T = -p\mathbf{1} + T_E,$$ (A.2)

where p equals the ambient pressure in the liquid phase, due to the incompressibility of both phases, and T_E the extra stress. Body and inertial forces are assumed to be absent, so:

$$\text{div } T = 0.$$ (A.3)

Viscous forces are assumed to be negligible in magnitude with respect to the interactive forces. Then p is a uniform pressure anywhere in the liquid phase and T_E equals zero in the liquid phase.

The volume-averaged stress tensor is marked by an upper bar:

$$\bar{T} \equiv \frac{1}{V} \int_V T \, dV = \frac{1}{V} \left\{ \int_{V_F} T \, dV + \sum_i \int_{V_{P,i}} T \, dV \right\}$$

$$= -p\mathbf{1} + \frac{1}{V} \sum_i \int_{V_{P,i}} T_E \, dV.$$ (A.4)

Again the summation is carried out over all conglomerates in a volume V. It can be seen from eqs. (A.3) and (A.4) that the

contribution of the extra stress in the i-th cell to the volume-averaged stress tensor can be written as:

$$\bar{T}_i = \frac{1}{V} \int_{\partial V_{P,i}} r \, T_E \cdot n \, dS , \qquad (A.5)$$

where r is a vector that points from the origin to the surface $\partial V_{P,i}$, n the external unit normal on dS, and

$$\partial V_{P,i} \equiv \partial V^I_{P,i} + \partial V^E_{P,i} . \qquad (A.6)$$

It follows from eq. (A.3) and the boundary condition $T_E \cdot n = 0$ at $\partial V^I_{P,i}$ that, instead of eq. (A.5), we may write:

$$\bar{T}_i = \frac{1}{V} \int_{\partial V^E_{P,i}} (r - r_i) \, T_E \cdot n \, dS , \qquad (A.7)$$

in which r_i is a vector that points from the origin to the junction position in the i-th conglomerate.

The vector $r - r_i$ is related to the vector r_{ij}, that points from the junction in the i-th conglomerate to the junction in the j-th conglomerate. Therefore we write:

$$r - r_i \cong \xi_{ij} \cdot r_{ij}, \quad r_j - r \cong (1 - \xi_{ij}) \cdot r_{ij} = \xi_{ji} \cdot r_{ij}, \qquad (A.8)$$

where ξ_{ij} is a tensor.

The force, f_{ij}, transmitted by the chain that connects the conglomerates i and j on omitting the liquid pressure term is given by:

$$f_{ij} = \int_{S_{ij}} T_E \cdot n \, dS , \qquad (A.9)$$

where S_{ij} is the surface area of the ij-chain at the site where it is intersected by the wall between the i-th and j-th cell. If the i-th and the j-th cells are not interconnected by chains, S_{ij} equals zero, so $f_{ij} = 0$.

The following expression is found from eqs. (A.7–9) for the contribution of the i-th cell to the volume-averaged stress tensor:

$$\bar{T}_i = \frac{1}{V} \sum_{j \neq i} \xi_{ij} \cdot r_{ij} f_{ij}, \qquad (A.10)$$

where the summation is carried out over all unit cells j for which $j \neq i$. The force f_{ij} equals zero for all values of j that represent a unit cell that is not connected with the i-th cell by a chain. Summation over i and taking the liquid pressure into account yields the total stress:

$$\bar{T} = -p\mathbf{1} + \sum_i \bar{T}_i = -p\mathbf{1} + \frac{1}{V} \sum_i \sum_{j > i} r_{ij} f_{ij}. \qquad (A.11)$$

If, however, the dispersed phase is built up of discrete particles rather than continuous structures, possibly not even making contact, the surface enclosing a unit volume may only involve the liquid phase at the sites where it cuts the particle chains. This would lead to ambiguous results when eq. (A.5) is used, since the local stress tensor is assumed to have only ambient pressure terms in the liquid phase.

Jongschaap and Doeksen [24] have illustrated the use of a fictitious stress field T^I describing the interactive forces. The divergence of this field equals zero in the liquid phase and it equals the interactive force field inside the particles. On imposing proper boundary conditions to T^I the contributions of the chain forces to the macroscopic stress tensor can be shown to be given by an expression analogous to eq. (A.11). This prompts us to use eq. (A.11), even if the dispersed phase consists of discrete particles.

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