Andrzej Ziabicki

STRUCTURAL THEORIES
IN POLYMER RHEOLOGY

32/1968

WARSZAWA

C O N T E N T S

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I. INTRODUCTION

There are two, basically different, though complementary ways of attack the main task of rheology - building-up a constitutive equation. The first approach, phenomenological (macroscopical) is based on general laws of mechanics and phenomenological thermodynamics, like conservation laws, law of material objectivity etc. on one side, and some model assumptions concerning the material (e.g. isotropy, elasticity, fading memory) on the other side. In one of more general at the present day phenomenological treatments, viz. that by N_0ll[1] the stress tensor at the instant t, $p(t)$, of an isotropic "simple material" may be expressed as a tensor-valued functional of the deformation gradient $\underline{A}$ taken over the time interval from $-\infty$ up to t

$$p(t) = \underset{s=0}{\overset{\infty}{H}} [\underline{A}(t - s)] \qquad (1)$$

So, for a "simple material" defined through eq.(1) the stress at any instant is determined by the entire history of strain.

For practical purposes more simple than eq.(1) (while

less general) models are used. To build-up a constitutive
equation for a particular material on a phenomenological ba-
sis one should: i) make some model assumptions about the ma-
terial involved, ii) derive the constitutive equation for
the corresponding class of materials, and iii) determine the
material functions appearing in the equations in properly
planned experiments.

When the model assumptions are specific enough there ap-
pear only few material functions in the constitutive equation
and these can be found from simple experiments. The more ge-
neral is the phenomenological model the more material func-
tions appear and the more complex is their experimental mea-
surement. So, for instance, the constitutive equation of a
non-linear viscous fluid (Reiner-Rivlin fluid) involves only
3 material functions, whereas that for a second-order "diffe-
rential" fluid (Rivlin-Ericksen fluid) involves 9 functions
etc. It should be emphasized that the model assumptions made
in the deriving of a phenomenological theory are in princip-
le quite arbitrary; they require an experimental proof a po-
steriori consisting of determination of the material functi-
ons. While such a proof is easily available for very simple
models, it is practically inaccessible in more general cases.
Therefore the phenomenological approach, yielding many valu-
able informations in general understanding of mechanical be-
havior, seems to be not very promising in building-up cons-
titutive equations for particular materials with more comp-

lex properties.

The other, structural (microscopical) approach consi-
ders discontinuous structure of matter and expresses its ma-
croscopical properties through averaged microscopical chara-
cteristics. The characteristics specifical for a given sys-
tem are physical parameters of the structural units involved
(atoms, molecules, molecular clusters) and in principle can
be found from independent sources. Unlike in the phenomeno-
logical treatment (eq.1) the macroscopic stress tensor at
the moment t, $p(t)$ can be. expressed as a function (rather
than functional) of some configurational variables ξ for the
individual structural elements, averaged over the whole en-
semble according to the statistical distribution function Ψ

$$p(t) = <F(\xi_1,\xi_2, \ldots \xi_n,t)> \tag{2}$$

$$<F>(t) = \int_{\xi_1} d\xi_1 \ldots \int_{\xi_n} F \; \Psi(\xi_1,\xi_2, \ldots \xi_n,t)d\xi_n \tag{3}$$

The time-dependent distribution function Ψ describes the ac-
tual at t structure of the system. This structure depends on
the actual deformation, deformation rate, etc. acting as bo-
undary conditions as well as on the past history of the sys-
tem. However the stress tensor as written in eq.(2) depends
explicitly only on the actual structure no matter how this
particular structure has been reached; the "history" has on-
ly an indirect, implicit effect on the physical behavior via
structure (distribution function Ψ). It is important to note

that the distribution function Ψ, having a clear physical sense, can in principle be found from independent measurements, if not in a complete form, then in form of some moments.

Since all the molecular parameters appearing in a structural theory have clear physical sense, the microscopical constitutive equations have an absolute character and do not involve constants which must be found empirically. Also the choice of a molecular model for microscopical considerations may be examined <u>a priori</u> if only molecular structure of the system involved is known.

The structural approach was used by Kirkwood[2] to the calculation of the stress tensor in monoatomic liquids and then by Dahler and Scriven[3] for polyatomic liquids. The microscopical stress tensor in both these theories consists of two parts: <u>kinetic</u>, resulting from thermal fluctuations (particularly important in gases), and <u>interaction</u>, associated with the intermolecular potential, U. It was shown, that so calculated stress tensor is not necessarily symmetrical[3]: it is symmetrical only when the intermolecular potential U is central and when ∇U is collinear with the intermolecular vector $\underline{R}$.

In the above theories the averaging of the kinetic term was accomplished according to the density distribution function $f^{(1)}$, that in the interaction term, according to the pair distribution function $f^{(2)}$. Both these functions appear

in many problems of the molecular physics and can be studied independently, using, e.g. optical methods.

There are several factors which distinguish systems containing large structural units from low-molecular ones.

a) Large macromolecules built of many repeating units have a great number of degrees of freedom and many possible conformations differing in molecular dimensions and thermo--dynamic properties. Therefore structural effects associated e.g. with deformation or spatial orientation of macromolecules are of primary importance affecting non-linear behavior strongly dependent on the geometry of deformation. An example of such an effect is provided by shear and extensional viscosities, essentially different in polymer systems (cf.[4,5]).

Figure 1. presents non-linear flow curves of molten polystyrene[4] in two principally different geometries.

b) In the systems containing both very large and small molecules (solvent) the interactions "solvent-solvent" can usually be neglected as compared with those "polymer-solvent" and "polymer-polymer" and the solvent can be considered a viscous continuum what considerably simplifies the theoretical treatment.

c) The consequence of large molecular dimensions is also long relaxation times of structural transformations what leads to strongly pronounced viscoelasticity, transient effects etc. Moreover, for the same reason polymer systems of-
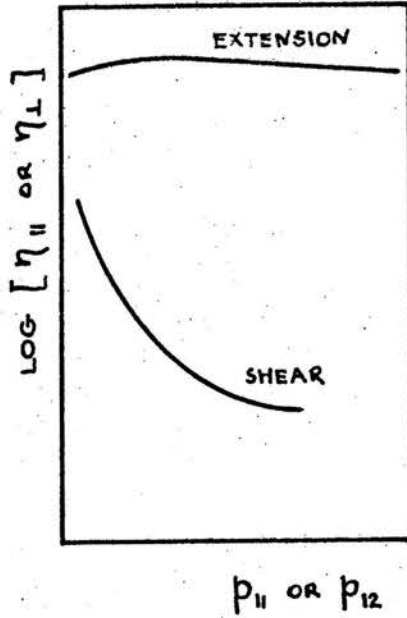
Fig.1.

Non-linear flow behavior of molten polystyrene
in extensional and shear flow. After Ballman[4].

ten exist in states far from thermodynamic equilibrium, though more or less stable kinetically. Slow structural changes (affecting also mechanical behavior) may proceed in isothermal conditions of steady-state flow. Examples of such changes are commonly met in polymer science. We will name e.g. an isothermal increase of zero-shear viscosity of PVA solutions due to molecular aggregation[6] (fig.2) and isothermal increase of shear modulus of concentrated PAN solutions resulting from network formation (gelation)[7] (fig.3.). Such a non-equilibrium behavior, common in polymer systems can hardly be treated in terms of purely phenomenological theory. On the other hand it will be shown that the structural approach offers relatively simple possibility of describing isothermal, non-equilibrium, as well as non-isothermal situations.

In the next section (II) of this paper we will discuss general requirements and the construction of a polymer rheological theory on a structural basis. Section III will include a brief review of the results and possibilities of the existing theories for various polymer systems.

II. CONSTRUCTION OF A STRUCTURAL RHEOLOGICAL THEORY FOR POLYMER SYSTEMS

General requirements

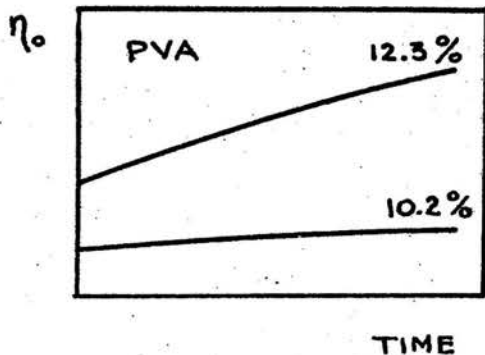We will discuss here several conditions which, in our

Fig.2.

Variation of zero-shear-rate viscosity η_0 of polyvinylalcohol solutions with time as the result of molecular aggregation. (reference[4])
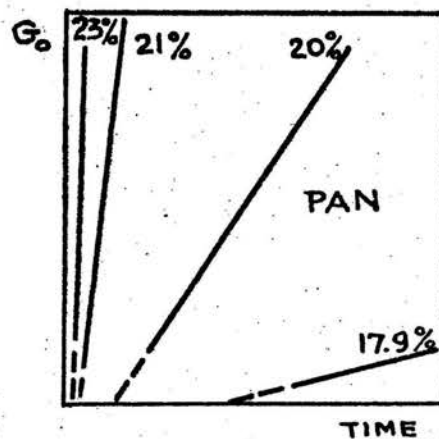

Fig.3.

Variation of zero-shear modulus G_0 of polyacrylonitrile solutions with time as the result of network formation (gelation). (ref.[6]).

belief, should be satisfied by any purely structural rheolo-
gical theory. At the same time these conditions define   the
range of theories which will be reviewed in this paper.

i. The molecular model making basis of the theory,
should be physically realistic and founded on the   physical
knowledge about the real system involved. No assumptions   or
parameters lacking clear physical sense are admissible.

ii. The molecular model chosen for the description   of
a real system should be consistent in all aspects of its phy-
sical behavior with experimental facts commonly observed   in
such systems.

iii. The theory should consider the entire macroscopi-
cal system with proper boundary conditions rather   than   an
isolated structural element.

iv. The theory should be so formulated that it be ca-
pable of discussing three-dimensional deformations in any
geometry and non-steady-state processes.

The above conditions may seem to be quite trivial   and
in fact they are so. It is therefore surprising how few theo-
ries considered as molecular do conform to these require-
ments.

The first condition confines the range of theories
which have a "purely structural" character. It is obvious
that only the models which conform to i) can be discussed in
purely molecular terms and their applicability verified   on
the basis of the structural data. There are numerous rheolo-

gical theories which are either based on combined molecular-and phenomenological assumptions (e.g.[8,9,66]), or, basing on a purely phenomenological ground, ascribe a posteriori some molecular significance to phenomenological constants (e.g.[10]). We will not discuss such theories in this paper.

The second condition is specific for purely structural theories and does not apply to phenomenological treatments. Its significance can be explained on the example of concentrated polymer solutions. It is well known that the rheological behavior of such systems strongly depends on the molecular weight of the dissolved polymer. So, e.g. the zero-shear viscosity is often found to be proportional to $M^{3.4}$. One of the molecular models proposed for such systems is a "temporary energetical network" with dissociating and reforming junctions[11,12]. It can be shown quite generally[13] that this model is in principle incapable of predicting any molecular weight effects, and, according to condition ii) we will consider this model generally improper for polymer solutions, even if it predicts correctly some other phenomena observed in solutions like streaming birefringence or non-linear flow[11,12].

The third condition is important for concentrated systems with intermolecular interactions. In the case of infinitely diluted suspensions or solutions, solvent is usually considered a Newtonian continuum which transmits affinely the macroscopic boundary conditions to individual structural ele-

ments. In consequence, non-interacting structural units in dilute systems can be treated as isolated and a single element can be analyzed. The situation is quite different in more concentrated systems with interactions however. The boundary conditions are defined only for the macroscopic volume and the kinematic and dynamic behavior of the individual structural elements results from the interactions in the entire system. There are theories which, assuming strongly interacting (entangled) macromolecular systems, ignore the system as such and consider only single macromolecules. So, e.g. Bueche[14] and Middleman[15] transmit to such systems the concepts developed for dilute polymer solutions changing only the "effective" friction factor. More recent analysis of entangled systems[13] shows that such systems should in principle be treated as a whole and the resulting distribution of deformation and velocities among the individual structural elements is of first order importance.

The last condition arises from the importance of non-linear and non-equilibrium effects in polymer systems. Nearly all the early structural theories in polymer rheology were confined to one-dimensional problems of shear flow. Now it seems necessary to require that the modern structural theory be more general. Some of the early one-dimensional theories can easily be generalized (e.g.[16,17]) but others do not offer such a possibility. For this reason we will not discuss in the present review the, otherwise interesting, viscosity

theories of Eyring and his followers[18-21] which hardly can be generalized as required in condition iv).

Fundamental equations of the structural theory

Now we will discuss a general scheme of a structural polymer theory. As noted above in such a theory the kinetic contribution to the stress tensor can be neglected and there will be considered only interactions of the type "polymer-polymer" and "polymer-solvent".

Consider the system which at the instant t consists of N structural elements (macromolecules, sub-chains, aggregates, etc.) with average number concentration $\nu(t)$. Assume that any k-th element can be characterized by some vector R_k (e.g. end-to-end vector of a flexible macromolecule, symmetry axis of an ellipsoid, etc.) and the forces acting on the element from the side of other elements and of the solvent can be represented by the tension f_k between the peripheral points of the vector R_k. It is easy to show that in the vicinity of the k-th element appears then the "local" stress p_k involving the dyadic $(R_k f_k)$ (eq.4)

$$p_k(t) = \nu(t) \, (R_k f_k) \tag{4}$$

The macroscopical stress in the system may be expressed as an average over the entire ensemble of structural elements (eq.5).

$$\underset{\sim}{p}(t) = (\nu/N) \sum_{k=1}^{N} (\underset{\sim}{R}_k \underset{\sim}{f}_k) = \nu(t) <(\underset{\sim}{R} \ \underset{\sim}{f})> \qquad (5)$$

The first step in building-up a structural theory is to define the tension $\underset{\sim}{f}_k$ through corresponding configurational variables ς. In general, when there is N structural elements each having n degrees of freedom we will have the dynamic equation in the form of eq.(6)

$$\underset{\sim}{f}_k = \underset{\sim}{\mathcal{L}}(\varsigma_1^1, \varsigma_2^1, \ldots, \varsigma_1^2, \ldots, \varsigma_n^N, t) \qquad (6)$$

The form of the dynamic equation (6) depends on the molecular model involved (character of structural units, interactions etc.).

The second step involves determination of the concentration of structural units, ν, in given conditions. In some systems ν is constant and predetermined (dilute suspensions and solutions), in others (entangled systems, temporary networks, etc.) the concentration ν can strongly depend on the external conditions and time. Generally speaking, the function $\nu(t)$ is determined by the kinetics of dissociation and reformation processes.

The third step is associated with the averaging of the dyadic in the eq.(5) with the aid of the distribution function Ψ^N

$$<(\underset{\sim}{R} \ \underset{\sim}{f})> (t) = \int_{\varsigma_1^1} d\varsigma_1^1 \ldots \int_{\varsigma_n^N} (\underset{\sim}{R} \ \underset{\sim}{f}) \ \Psi^N(\varsigma_1^1, \ldots \varsigma_n^N, t) \ d\varsigma_n^N \qquad (7)$$

In the general case, Ψ^N is the distribution density function in an (Nn)-dimensional configurational space, but for particular cases the problem can often be reduced to more simple distributions. The function Ψ^N is to be found from the equation of continuity:

$$\frac{\partial \Psi^N}{\partial t} + \underset{\sim}{\nabla}^N \cdot (\Psi^N \underset{\sim}{\dot{\xi}}) = \dot{\Psi}^N_{kin} \tag{8}$$

where
$$\underset{\sim}{\nabla}^N = (\partial/\partial\xi_1^1, \ \ldots \ \partial/\partial\xi_n^N)$$
and $\underset{\sim}{\dot{\xi}} = (\dot{\xi}_1^1, \ \ldots \ \dot{\xi}_n^N)$

denote, respectively, the divergence operator and the velocity vector in the (Nn)-dimensional space, and $\dot{\Psi}^N_{kin}$ - the kinetical term i.e. the net rate of formation and dissociation of various structural elements. Like the total concentration of elements, ν, the kinetic term $\dot{\Psi}^N_{kin}$ should be found from proper kinetical equations.

To solve eq.(8) it is also necessary to define the set of kinematical equations for the components of the velocity vector $\dot{\underset{\sim}{\xi}}$, which involve the macroscopic boundary conditions.

So, any structural theory comprises a set of simultaneous differential (or integro-differential) equations: dynamic equation (eq.6), equation of continuity (eq.8), kinetic equations (defining the ν and $\dot{\Psi}^N_{kin}$ terms) and kinematic equations for the velocity vector $\dot{\underset{\sim}{\xi}}$. The stress tensor $\underset{\sim}{p}(t)$ results in the form given by eq.(5).

Non-steady-state, non-homogeneous
and non-isothermal conditions

When the macroscopic flow is steady-state and the velocity gradient $q = \underline{\nabla V}$ is homogeneous, the distribution function may be assumed constant and eq.(8) reduces to the form:

$$\underline{\nabla}^N_{\cdot}(\Psi^N \dot{\underline{\xi}}) = \dot{\Psi}^N_{kin} \tag{9}$$

At the same time the concentration of structural elements, ν and the velocity gradient are constants:

$$\nu(t) = \text{const.}$$
$$\underline{q} = \text{const.} \tag{9a}$$

If the flow is non-steady-state or/and non-homogeneous, the distribution function must be considered time-dependent and full continuity equation should be solved. In the case of non-homogeneous velocity field it seems to be reasonable to follow some macroscopical volume element along its (macroscopical) trajectory. Then the total time-dependence of the velocity gradient (appearing as a boundary condition in the kinematic equations) may be written in the form:

$$\frac{d\underline{q}}{dt} = \frac{\partial \underline{q}}{\partial t} + V \cdot \nabla \underline{q} \tag{10}$$

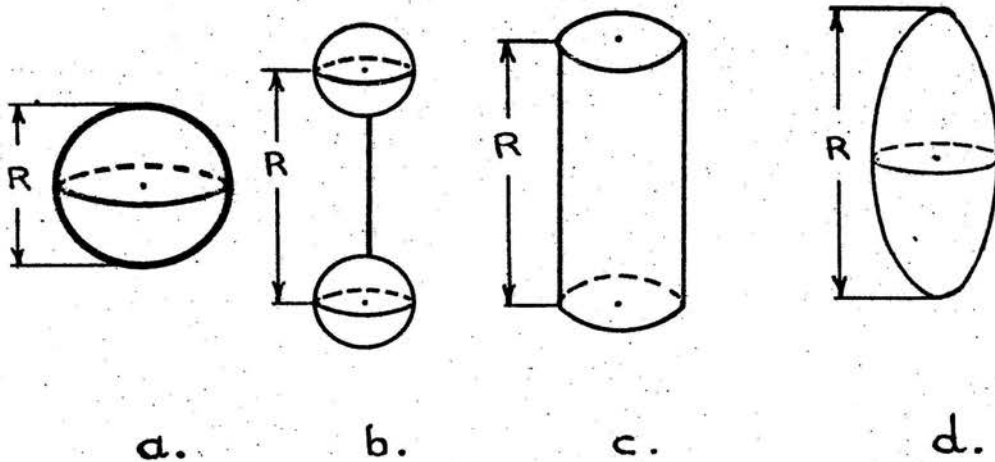Such an approach has been successfully applied by Prager in his theory of dilute suspensions.

Fig.4.

Molecular models of rigid particles.

a)sphere,   b) rigid dumbbell, c) cylinder, d) ellipsoid of revolution

If flow is accompanied by any variations of the variables of state (temperature, composition, ambient pressure, etc.) also those effects can be taken into account through properly defined time-dependencies of the molecular parameters involved in the theory. If some molecular parameter, α (molecular friction coefficient, internal viscosity, etc.), depends on several variables of state, x_i, then it can be written:

$$\frac{d\alpha}{dt} = \sum_i \frac{\partial \alpha}{\partial x_i} \frac{dx_i}{dt} \tag{11}$$

At the same time the former equations (4 - 8) do not lose their validity, no matter how complex are external conditions.

The structural approach offers therefore the possibility of treating rather complex situations (not rare in polymer systems) which hardly can be solved in other way.

III. RESULTS OF STRUCTURAL THEORIES FOR INDIVIDUAL POLYMER SYSTEMS

Dilute suspensions

The molecular model of a dilute suspension consists of rigid, non-interacting particles suspended in a Newtonian solvent where velocity field is homogeneous. The most often analyzed particle shapes comprise sphere, dumbbell, cylindri-

cal rod and ellipsoid (fig.4.). In non-interacting systems
the distribution function Ψ can be defined for a single par-
ticle and the degrees of freedom reduce to the spatial orien-
tation of the particle axes.

An early analysis by Einstein[22] considering spherical
particles yielded Newtonian behavior, observed in fact in
very dilute spherical suspensions. Extension of the analysis
onto anisodiametrical forms led to non-linear viscosity and
normal stress effects in shear flow, a different non-linear
behavior in extensional flow and stress relaxation effects.
In all cases the microscopical stress tensor was symmetrical
as defined through the dyadic ($\underline{RR}$) formed by the characteri-
stical particle vector $\underline{R}$.

The structural analysis of rigid dumbbells in simple
shear flow was made by Kuhn and Kuhn[23], Kirkwood and Plock[24]
and Kotaka[25]. More recently a general theory of rigid dumb-
bells was formulated by Giesekus[25] and Prager[17]. Jeffery[27]
solved the hydrodynamical part of the structural theory of
ellipsoids which made basis of further studies by Peterlin[28],
Giesekus[29] (shear flow) and Takserman-Krozer and Ziabicki[30]
(extensional flow). An orientation distribution function for
rotational ellipsoids in a general velocity field was recent-
ly calculated by Pokrovskii[31].

In a steady-state shear flow as characterized by the ve-
locity vector:

$$\underline{V} = (qy, 0, 0) \tag{12}$$

the excess stress tensor for dilute suspension of rigid
dumbbells results in the form[17]

$$
\underset{\sim}{p} - \underset{\sim}{p}^o = Kqc
\begin{pmatrix}
\dfrac{1}{5}(q/D)+ \ldots & 1 - \dfrac{1}{60}(q/D)^2+ \ldots & 0 \\[2ex]
1 - \dfrac{1}{60}(q/D)^2+ \ldots & 0 & 0 \\[2ex]
0 & 0 & 0
\end{pmatrix} \quad (13)
$$

where q - perpendicular velocity gradient, D - diffusion con-
stant, c - volume concentration, K - constant.

   As evident in eq.(13) there appears only one non-zero
normal stress component in shear flow (Weissenberg effect).
A different result obtained for the same molecular model by
Giesekus[26] was evidently due to some numerical error as the
author admits himself[29]. In a steady extensional flow   with
the velocity vector:

$$
\underset{\sim}{V} = (q^*x, \; -\tfrac{1}{2}q^*y, \; -\tfrac{1}{2}q^*z) \quad (14)
$$

the stress tensor predicted by Prager[17] reads:

$$
\underset{\sim}{p} - \underset{\sim}{p}^o = Kq^*c \; \times
$$

$$
\times
\begin{pmatrix}
1 + \dfrac{1}{5}(q^*/D) - \dfrac{1}{70}(q^*/D)^2+\ldots & 0 & 0 \\[2ex]
0 & -\dfrac{1}{2} + \dfrac{1}{20}(q^*/D) + \dfrac{1}{280}(q^*/D)^2+\ldots & 0 \\[2ex]
0 & 0 & -\dfrac{1}{2} + \ldots
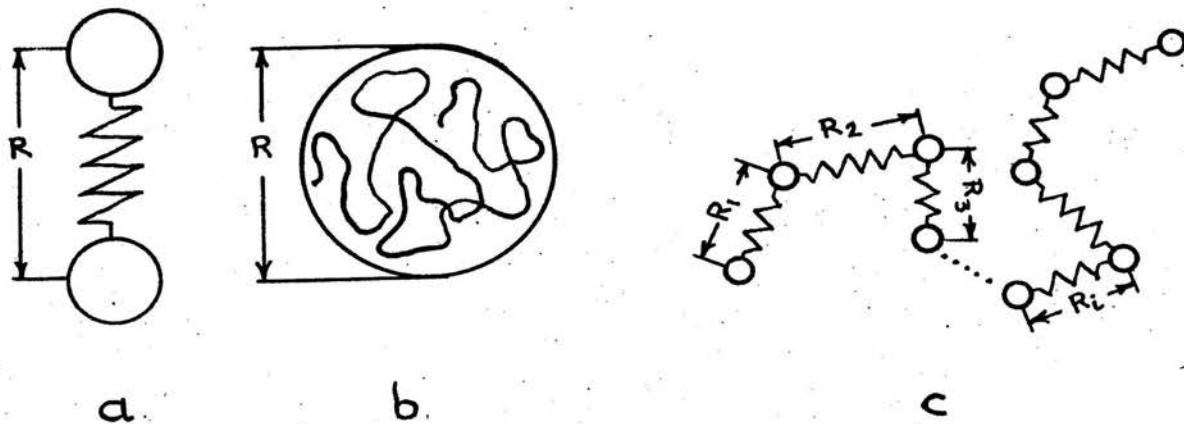\end{pmatrix} \quad (15)
$$

Fig.5.

Molecular models of flexible macromolecules.

a) elastic dumbbell, b) semi-penetrable sphere, c) system of sub-chains

where q^* is the parallel velocity gradient.

Two different normal stress components in shear flow appear in the structural theory when various parts of the particle are allowed to exhibit hydrodynamic interactions through viscous medium. This is clearly evident in the theory of Kotaka[25] who analyzed the "necklace" model, as well as in the theories of ellipsoids by Giesekus[29] and Pokrovskii[31]. Supposedly the same effect would be obtained if non-linear particle-solvent interactions were considered. At the present moment it seems that the existing structural theories of dilute suspensions rather well describe their rheological behavior. It should be noted that the structural theory, combined with rheological and optical measurements is also widely used for characterization of the suspended particles (cf. e.g.[32]).

Dilute solutions of flexible, chain-macromolecules

Like in the preceding case the structural theories consider independent macromolecules in a Newtonian solvent. The molecular models of a chain-macromolecule comprise elastic dumbbell[33], elastic, deformable sphere[34] and a system of elastic dumbbells, socalled "sub-chain" model[35] (fig.5.). The tension f appearing in the dynamic equation comprises elastic-, diffusional, solvent friction- and internal viscosity terms.

The early structural analysis of shear viscosity was

due to Kuhn and Kuhn[33], Hermans[36] and Kramers[37] who analyzed ideally elastic dumbbells and to Rouse[38], Zimm[39] and Kirkwood and Riseman[40] using more sophisticated sub-chain model. Cerf[41] introduced to the sub-chain model the internal viscosity of macromolecular chains, a concept used by Kuhn and Kuhn[42] in the analysis of elastic dumbbells. Structural analysis of elastic dumbbells in steady extensional flow was made by Rivlin[43] and, independently, by Takserman-Krozer[44] who considered more exact sub-chain system. More recently this analysis was extended onto non-Gaussian chains by Peterlin[45]. Behavior of elastic dumbbells in a general velocity field was studied by Giesekus[46] and by Takserman-Krozer[16].

Also in the theories of elastic macromolecules the excess stress tensor is always symmetrical. In the absence of internal viscosity and with assumed linear elasticity of the macromolecular chain (sub-chain) the stress tensor for steady shear flow as calculated by Takserman-Krozer[16] reads:

$$\underset{\sim}{p} - \underset{\sim}{p^0} = kTq\nu \begin{pmatrix} 2q \sum_i k_i \tau_i^2 & \sum_i k_i \tau_i & 0 \\ \sum_i k_i \tau_i & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \tag{16}$$

and that for extensional flow[16]:

$$p - p^0 = kTq^*\nu \begin{pmatrix} 2 \sum_i \dfrac{k_i \tau_i}{1 - 2q^*\tau_i} & 0 & 0 \\[2ex] 0 & -\sum_i \dfrac{k_i \tau_i}{1 + q^*\tau_i} & 0 \\[2ex] 0 & 0 & -\sum_i \dfrac{k_i \tau_i}{1 + q^*\tau_i} \end{pmatrix} \quad (17)$$

where ν - number of macromolecules in unite volume, k - Boltzmann constant, T - absolute temperature, τ_i - relaxation time in i-th mode of deformation, k_i - i-th eigenvalue of the problem.

As evident from eq.(16) the theory predicts one non-zero normal stress component and constant viscosity coefficient in shear flow; the elongational viscosity (eq.17) increases with parallel velocity gradient, q* and tends to infinity at $q^*\tau_i = \frac{1}{2}$. The latter result is a consequence of assumed linear elasticity (Gaussian chain statistics) which naturally fails at higher deformations. Application of more exact non-linear model by Peterlin[45] removed this singularity. The theory of ideally flexible chains predicts also stress relaxation effects and the existence of relaxation time spectra (many relaxation times τ_i for the individual modes of deformation).

The constant shear viscosity as predicted by all the above theories contradicts the experimental facts commonly observed in dilute polymer solutions. Shear-dependent visco-

sity was obtained first in more complex theories involving limited flexibility of macromolecular chains (internal viscosity)[41,42], anisotropical diffusion of solvent within the macromolecular coil[47-49] or non-Gaussian chain statistics[50]. Bueche[51] obtained non-linear viscosity in steady shear flow analyzing ideally flexible, Gaussian chains, i.e. the model for which all other theories yielded constant viscosity values[16,38-40]. He neglected however the diffusional term in the dynamic equation and made some arbitrary assumptions concerning the periodicity of forces acting on the macromolecule, assumptions which do not follow from boundary conditions.

Consideration of the internal viscosity in the behavior of dilute solutions in a general velocity field led Takserman-Krozer[16] to somewhat striking conclusion that the stress tensor can be asymmetrical, the antisymmetrical components vanishing for ideally flexible chains. It can be shown that this result is incorrect and follows from the kinematical assumptions made by Cerf[41] in the introducing of the internal viscosity. Quite generally the internal viscosity term cannot produce any asymmetrical stress effects. In view of this fact it seems that also other conclusions following from the Cerf method (e.g. non-linear shear viscosity) should be reexamined.

The theory of dilute polymer solutions explaining satisfactorily zero-shear viscosity and relaxation spectra, requires further studies on other aspects of rheological behavior,

first of all on non-linear flow.

Moderately concentrated suspensions and solutions

There is no adequate structural theory of moderately concentrated systems with interacting elements. In finitely concentrated suspensions and solutions the stress is no more a linear function of concentration as predicted for dilute systems. The effect of molecular weight is also more complex and non-linear and elastic effects are strongly pronounced even in suspensions of spherical particles.

There have been published several attempts to explain the behavior of concentrated suspensions in shear flow[52-56]; they predict non-linear concentration dependence and non-Newtonian shear viscosity. So, e.g. hydrodynamic interactions between spherical particles as considered by Krieger and Dougherty[52], and Gillespie[53], lead to non-Newtonian viscosity resulting from formation of asymmetrical doublets or triplets (see fig.6.).

The concentration effects were analyzed, among others by Robinson[54], Brinkman[55] and Mooney[56] who derived non-linear theories of suspensions. A complete theory of such systems however is still not available.

Similar situation may be observed in the theory of polymer solutions with such concentrations that the intermolecular contacts are probable but do not guarantee formation of continuous network system. From the molecular point of
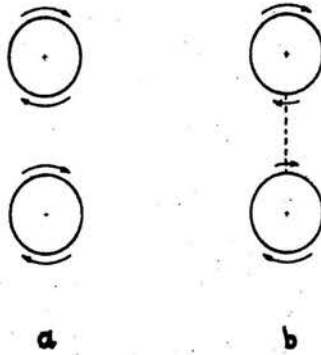
Fig.6.

Hydrodynamic interaction between two spheres suspended
in a viscous medium.

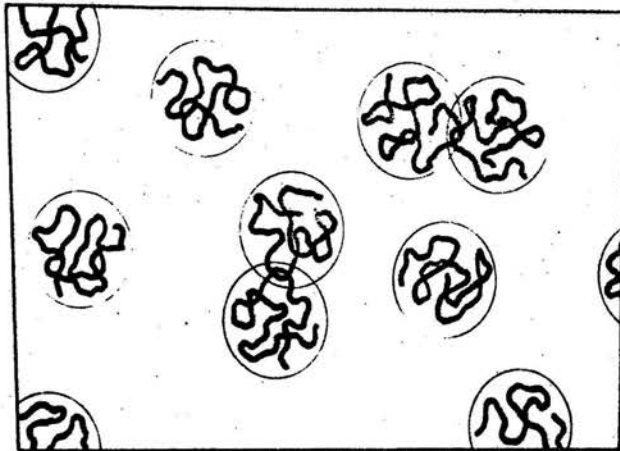a) rotation without interactions, b) interacting pair

Fig.7.

Model of a moderately concentrated solution
containing partially entangled macromolecular coils

view one may expect long, flexible chains in such systems to
entangle and disentangle one with another forming temporary
"entangled clusters" (fig.7.).

Also in the case of solutions of chains polymers the
existing theories were confined to one-dimensional problems
of shear viscosity. Several authors[14,15,57-60] based their
considerations of "entangled systems" on the models apparen-
tly more or less resembling our figure 7. although some of
them speak about "infinite entangled networks"[14,57]. Since
all these theories are based with some modifications on the
approach used in viscosity calculations for dilute solutions
. the applicability of their results to very concentrated sys-
tems is rather dubious.

The theory of Graessley[57] predicts shear-dependent vis-
cosity as based on variable equilibrium of the entangling-
disentangling processes, explains some "elasticity" and non-
linear effect of molecular weight. The other theories by
Bueche[14,60], Middleman[15], Merker[58] and Nakagaki[59] are confi-
ned to the prediction of the effects of molecular weight-
and molecular weight distribution on zero-shear viscosity.
All these theories involve some arbitrary assumptions (e.g.
"slaloming" of macromolecules through entanglement contacts[57]
or rigid rotations[60]) and do not satisfy most of our condi-
tions. A consequent structural theory of partially entangled
systems, badly needed in polymer rheology, is not available
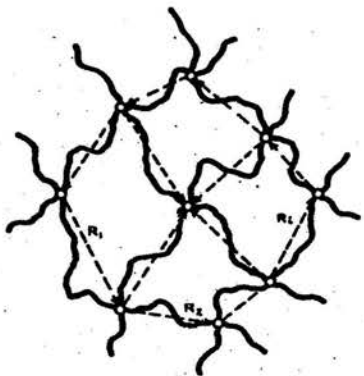at the present moment.

Fig.8.

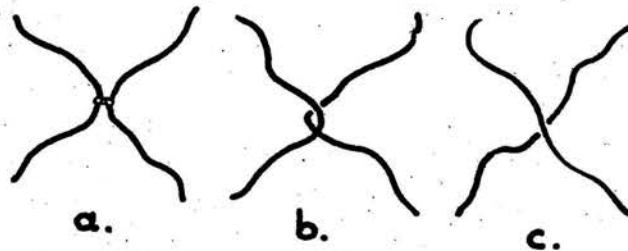A tetrafunctional network
composed of flexible chains

Fig.9.

Three types of network junctions
a) an energetic junction, b) a topological
(entanglement) junction, c) a contact junction

Amorphous bulk polymers, melts and very concentrated solutions

If volume fraction of polymer exceeds some critical va-
lue the probability of intermolecular contacts becomes so
high that the entire system can be considered a continuous,
"instantaneous" network. Such a continuous, often fluctua-
ting, network seems to make the most appropriate and promi-
sing structural model for condensed polymer systems (fig.8).
The structural element involved in this model is now a "net-
work chain" i.e. a portion of the macromolecule contained
between two adjacent junctions.

According to the nature of interactions between macro-
molecules in the system and to the character of network junc-
tions, 3 classes of macromolecular networks can be distingui-
shed[61].

Energetical networks (fig.9a) are formed by chemical or
quasi-chemical (van der Waals) cross-links. An energetical
junction is localized in a definite part of the macromolecu-
le and does not slide; it can dissociate when enough energy
is supplied, and eventually reform in another place. Hence -
the "temporary" character of the structural units (network
chains) and variable concentration v. An asymptotic case
(infinite dissociation energy, no junction breaking) consti-
tutes socalled permanent network - the model widely used in
the theory of vulcanized rubbers.

The second class of networks results of topological in-
teractions of long, flexible chains capable of forming loops
and entanglements (fig.9b). Junctions in the entanglement
networks are no more localized but can slide along the cha-
ins, the sliding being associated with some friction and dis-
sipation of energy. The existence of free chain ends leads
to some probability of sliding-in and sliding-out of the en-
tanglements thus making source of variation of the concentra-
tion v.

Contact networks (fig.9c) form the third class. They
result from mere contacts of impenetrable structural ele-
ments with frictional interactions. The formation and break-
age of such junctions is controlled by thermal motions which
determine their average lifetimes. Also these junctions are
not localized and chain-chain friction contributes to the
mechanical behavior.

The concept of a permanent, ideally flexible macromole-
cular network was introduced in early thirties[62,63] to ex-
plain the elasticity of vulcanized rubber. With the assump-
tion of constant chain concentration v, (typical for perma-
nent networks), and linear behavior of an individual network
chain, the theory yields the constitutive equation of a Hoo-
kean solid, what agrees with mechanical behavior of chemical-
ly cross-linked systems at not too high deformations. Appli-
cation of non-linear elasticity of network chains leads to
the equation of non-linear elastic solid[64,65].

The recent analysis of the theory of networks[13] shows that in permanent networks also two other effects should be taken into account. First effect is internal viscosity of network chains as introduced in dilute solutions[42]. Some attempts to apply this concept were made by Halpin[66] and Pokrovskii[9], they were not lacking some arbitrariness however. The other effect, not recognized in the earlier theories, is associated with intermolecular friction of the portions of macromolecules between network junctions. It may be shown[13,67] that the assumption of an affine displacement of the network junctions, made as a rule in all theories, is not generally true, and local deviations from this affinity can contribute to the stress tensor and dissipation of energy. The theory of permanent networks completed with the above two effects is capable of predicting retarded elasticity but excludes relaxation and flow.

To account for the latter effects, Green and Tobolsky[68] introduced the concept of a "temporary" network (in our nomenclature: energetical network with finite dissociation energy). The theory of this model was further developed by Scott and Stein[69], Furukawa[70], Lodge[11] and Yamamoto[12].

The most complete and general among existing theories of temporary energetical networks, viz.that by Yamamoto[12] predicts non-linear elasticity, stress relaxation and non-linear steady-state flow in various flow geometries. The non-linear viscosity is controlled by variable probability of

junction breakage, β, and, to less extent, by non-Gaussian statistics of the individual network chains. When the chains are Gaussian and the probability β is constant (what corresponds to the earlier theories of Green and Tobolsky[68] and Lodge[11]) the theory predicts for steady shear flow[12]

$$\underset{\sim}{p} - \underset{\sim}{p}^o = kTq\nu \begin{pmatrix} 2\,q\tau^2 & \tau & 0 \\ \tau & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \qquad (18)$$

and for steady extensional flow

$$\underset{\sim}{p} - \underset{\sim}{p}^o = kTq^*\nu \; \times$$

$$\times \begin{pmatrix} 2\tau[1 + q^*\tau + 3(q^*\tau)^2+\dots] & 0 & 0 \\ 0 & \tau[-1 + \dots] & 0 \\ 0 & 0 & \tau[-1 + \dots] \end{pmatrix}. \quad (19)$$

where $\tau = 1/\beta$ - relaxation time.

Eqs.(18-19) are almost identical with the results for dilute polymer solutions modelled by elastic dumbbells (cf. eqs. 16-17 with i = 1 and k_i = 1). The matrix in eq.(18) is identical with that in eq.(16) and predicts the same behavior in steady shear flow: constant shear viscosity and only one non-zero normal stress component. Components of the matrix in eq.(19) slightly differ from series expansion of the corresponding closed expressions in eq.(17). Probably this discrepancy is due to some numerical error, since also asymptotical behavior of the both theories for extensional flow

(singularity at $q^*\tau = \frac{1}{2}$) is identical.

The formal consistency of the theory of energetical networks with that of dilute solutions containing flexible chains is not surprising. In fact, both these theories consider the same molecular model – Gaussian chain, and differ only in the significance of the concentration parameter ν (concentration of macromolecules in dilute solutions and concentration of network chains in the other case). Introduced by Yamamoto more general assumptions: variable breakage probability, β, and/or non-linear elasticity of the network chains led to non-Newtonian shear viscosity and to the appearance of two different normal stress components[12]. So, in temporary energetical networks appears an additional source of non-linear behavior: kinetics of breaking process which did not exist in dilute solutions.

The model of temporary energetical networks, possibly completed with internal viscosity and intermolecular friction terms (cf.[13]) can explain retarded elasticity as well as stress relaxation. It should be emphasized here that in energetical networks with localized junctions (both permanent and temporary) the network chain constitutes an independent structural unit and characteristics of the primary macromolecule do not appear in the theory (to speak nothing about the minor effect of free ends). Therefore this theory cannot predict any effects of molecular weight and as such it is inapplicable for polymer melts and concentrated solu-

tions. Apparently applicability of this theory is confined
to amorphous rubbers with breaking chains, polar gels and
similar systems where effects of molecular weight do not
play any important role.

Structural theory of entanglement networks at the pre-
sent moment does not exist. Some attempts of discussing such
systems were made by several authors. The considerations of
Bueche[14,60], Middleman[15] and Graessley[57] as noted above, are
more appropriate for moderately concentrated systems than to
infinite networks. At the same time the works of Hayashi[71]
and Hoffmann[72] dealing directly with entanglement networks
involve some serious incorrectnesses. Both the authors neg-
lect chain sliding in the entanglement junctions and contact
points - perhaps the most important mechanism of energy dis-
sipation. Hayashi, applying the sub-chain formalism of the
theory of dilute solutions made also several arbitrary as-
sumptions (e.g. the molecular weight-dependent friction fac-
tor) and mathematical errors (diagonalization of several dif-
ferent matrices with the same linear transformation, Q).
Hoffmann, discussing a one-dimensional deformation, neglects
in the kinetical considerations formation of new network cha
ins due to sliding-in into the entanglement, what excludes
the possibility of a real steady-state flow with a constant
concentration of network chains, ν.

Still less has been made in the theory of contact net-
works. Apparently the molecular models assumed in the papers

of Takemura[73] and Chömpff and Duiser[74] correspond to what we
define as "contact networks", but the authors themselves use
the term "entanglement networks". Both the papers mentioned
were confined to the analysis of stress relaxation and no
dynamic analysis was ever made.

The general considerations of Takserman-Krozer and the
author[13] give some outlines of the theory of entanglement-
and contact networks. It was shown that both these models
are capable of predicting non-linear viscoelasticity, steady-
state flow, stress relaxation, retarded elasticity as well
as non-linear effects of molecular weight of primary macro-
molecules. It seems that development of these models should
explain many features of the rheological behavior of concen-
trated polymer solutions and melts.

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