

# The mechanics of fluid suspensions and polymer solutions: a report on Euromech 49

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## 1. Introduction

A European Mechanics Colloquium on fluid suspensions and polymer solutions was held from 2 to 6 April 1974 at Jablonna, Poland, on the invitation of the Polish Academy of Sciences. There were forty-nine participants from thirteen countries, and they came with the different backgrounds of chemical engineers, rheologists, fluid mechanicians and polymer chemists.

Chemical engineers are concerned with the processing of polymer solutions and suspensions of various particles in fluids, and need to be able to predict their flow. Viewed in the bulk as in an engineering material, the heterogeneous fluid suspensions and polymer solutions appear as homogeneous continuum fluids which are usually non-Newtonian, having constitutive equations which are nonlinear and involve non-instantaneous quantities. For some time rheologists have been measuring the mechanical properties of non-Newtonian fluids, including the particular subjects of the conference, and using these measurements to analyse the anomalous flow phenomena of the materials. By studying idealized suspensions and models of polymers in solution, the fluid mechanicians and polymer chemists have been trying to derive theoretically the mechanical properties of their systems.

The purpose of the conference was to allow European researchers to expound and discuss the latest results in their related fields. Recent progress in understanding fluid suspensions suggests improvements to the modelling of polymers. The theoretical calculation of the mechanical properties of some simple systems gives an insight into present and new rheological measures and can suggest better designs of materials for engineering applications. There is also a natural flow of ideas in the opposite direction: engineers are always meeting new and unexplained flow phenomena, while experimental rheologists continue to remind the model builders how real materials behave.

The following sections describe the papers presented at the Colloquium. The fruits of this gathering of the different interests are of course not represented only by the papers, and hopefully will emerge in the future.

## 2. Fluid suspensions

The recent progress in calculating the rheological properties of simple suspensions was reviewed by R. Roscoe (Newcastle). The study of a particular suspension divides into two stages. First, on the microscale of the individual particles, it is necessary to examine the rotation, deformation and interaction of the particles as they respond to a uniform bulk velocity gradient and external fields, such changes being opposed by various internal restoring mechanisms. For these problems a wealth of standard results for low Reynolds number flows can be exploited. The second stage of study is to relate the microscopic examination to the bulk observables, e.g. the bulk velocity gradient and bulk stress tensor, on the macroscale at which the heterogeneous suspension appears as a homogeneous continuum. This relation is made by averaging the randomly varying values of the velocity gradient or stress over a volume which is small compared with the macroscale but large compared with the microscale.

The suspensions which have been investigated have been chosen to isolate different types of particle behaviour. Hydrodynamic interactions have been studied between spheres, as described in the next paper, and aligned rigid rods (Batchelor 1971). The long-range interactions in slow viscous flows result in considerable calculational difficulties. Orientation effects are exhibited by rigid axisymmetric particles. The ability to align the particles with an external magnetic field produces a material with controllable properties (Brenner 1970). Of particular importance to colloid scientists are suspensions of non-spherical particles which are so small that rotary Brownian motion can oppose alignment by the bulk flow (Leal & Hinch 1973). Theories for these suspensions are employed to infer the shape of minute particles from the measured shear-dependent viscosity of the bulk materials. After some discussion strongly influenced by H. Giesekus (Dortmund), the meeting generally agreed that the diffusion stress (the direct contribution to the bulk stress corresponding to the diffusional effective angular velocity) should be included. To understand the effect of deformation of particles, elastic ellipsoids (Roscoe 1967) and liquid droplets (Barthès-Biesel & Acrivos 1973) have been analysed. These two studies have been used as a model of the deformation of polymer molecules in solution. The bursting of liquid droplets when surface tension can no longer resist the stretching of the bulk flow has applications in the preparation of emulsions. Of the original papers contributed in this section, the majority further identified particular particle behaviour.

A sufficient number of results from simple idealized suspensions have recently become available for some generalities to emerge. Nearly always the viscosity thins in simple shear and thickens in pure strain. This, amongst some of the other general rheological properties of the suspensions, is commonly observed in non-Newtonian materials. The suspension studies provide the missing mechanical framework in which to understand at least some non-Newtonian phenomena. As well as supplying physical insight, suspensions of particles of known form are beginning to suggest new mathematical shapes for simple constitutive equations which can describe such phenomena.

G. K. Batchelor (Cambridge) described the calculation of the  $c^2$ -coefficient in the concentration dependence of the viscosity of a suspension of spheres (Batchelor & Green 1972). Earlier attempts at this classical problem failed to remove correctly a divergent integral which sums all possible long-range pair interactions. Variation of the statistics of the relative position of pairs of particles in different flow systems results in a non-Newtonian rheology. Of particular significance is a hydrodynamic indeterminacy in the steady state of shear flow which is resolved only by additionally considering inertia, three-particle interactions, electrical double layers, or Brownian motions.

I. Pieńkowska and R. Herczyński (Warsaw) considered the viscosity of a suspension of rigid spheres at the moderate concentrations which are of practical importance. The hydrodynamic interactions were represented by fluctuations in the linear velocity which was imposed on a spherical boundary surrounding a particle. By assuming particular forms for the statistics of the fluctuations and a particular value of the radius of the spherical boundary, a good fit to the observed concentration dependence of the viscosity could be obtained.

K. Strenge (Berlin) reported some investigations into the elasticity of flocculated dispersions. With volume concentrations of 10%, certain particles attract into long linear chains. Experiments were performed to measure the elastic yield conditions before creep. Simple theoretical considerations of the flocculation energy and bonding separation gave a qualitative interpretation of the experiments, e.g. an increase in electrolyte concentration compressed the double layer and so increased the yield stress.

M. Gosiewski (Warsaw) had tackled the London-Van der Waals interactions in a non-dilute suspension. An expression for the internal energy was derived with the aid of a cell model. This was then used in a phenomenological description of the rheology.

A. Szaniawski and J. Biernacki (Warsaw) were interested in liquid droplets in their own vapour and the calculation of inertial effects, for which the density difference is significant. Using a regular lattice model, they showed that the increase of  $\frac{5}{2}c$  in the effective (relative) velocity of a dilute suspension can be dominated by an  $O(c^{\frac{3}{2}})$  micromomentum flux term (Szaniawski 1972).

H. Giesekus (Dortmund) and L. G. Leal (Pasadena) both talked about their separate work concerning slightly non-Newtonian (second-order fluid perturbation) solvent effects on isolated particle motion. Giesekus considered dumb-bell particles and showed that those in the plane of a shear flow can stop rotating. With long slender particles, Leal showed that particles out of the plane of a shear flow will rotate with a drift until they eventually align with the vorticity axis. Leal showed also that sedimenting particles will slowly rotate so that they fall with their axis vertical.

Y. I. Shmakov (Kiev) noted that the constitutive equations of many suspensions were merely different examples of Ericksen's director equations. He could include rotary inertia of the particles, magnetic and electric couples on dipolar particles, hydrodynamic interactions by Simha's approximate model, and deformable ellipsoidal particles. When rotary Brownian motions were included, it was necessary to supplement Ericksen's equations with an

additional equation for the orientation statistics, and this reduced the simplicity of the structured continuum constitutive equations (Shmakov & Begoulev 1973).

P. Le Roy and J. Pierrard (Grenoble) have obtained a better fit to their different experimental data with the BKZ constitutive equation using a Jaumann time integral instead of an Oldroyd convected integral. In a following discussion it was observed that several suspension studies would support this change from the traditionally favoured time derivative.

### 3. Models of polymer solutions

A survey lecture on dilute polymer solutions was given by E. J. Hinch (Cambridge). The statistics of an undeformed isolated linear macromolecule are determined by the effectively independent bond length, by the excluded volume of the monomers, and by electrostatic forces between ionic subgroups and between the polymer and solvent. As the polymer deforms there are long-range hydrodynamic interactions, difficulties in untying knots, and irreversible losses in straightening the chain. The combination of all these effects is not tractable and it has been necessary to devise simple models. The elastic dumb-bell model of Kuhn with the generalization to a necklace of beads and springs predicts successfully the zero-shear-rate behaviour, in particular the frequency dependence of the viscosity. In the strong flows encountered in chemical engineering there can be large deformations of the polymer. For such conditions a new modified elastic dumb-bell was proposed which had a nonlinear spring of finite maximum length and beads which rotate with the spring and whose friction constant increases with the deformation. There was also an open discussion on the non-zero intrinsic viscosity at high frequencies which favoured the effective bead volume mechanism rather than internal viscosity, the latter having been erroneously incorporated into some models.

An example of a modified elastic dumb-bell model was presented by R. I. Tanner (Providence). The spring is assumed to be linear up to some critical extension and absolutely rigid above this limit. Approximate constitutive equations for dilute solutions containing such modified dumb-bells were derived and some specific effects discussed, e.g. an overshoot in shear stress *vs.* time and normal stresses in shear flow (Tanner 1971).

G. Marucci and D. Acierno (Palermo) analysed theoretically a model of rigid rods connected by freely rotating joints to friction centres (beads) with some hydrodynamic interactions between the beads. The development of the model in time gave some predictions about the transient elongational viscosity (Marucci & Acierno 1974).

C. Wolff (Brest) discussed two experimentally observed effects in very dilute solutions of polymers. For solutions of polyelectrolytes a maximum and a minimum in the specific viscosity *vs.* concentration are observed and are due to electrostatic repulsion between various parts of the same macromolecules leading to extension of the chain (Moan & Wolff 1974). For solutions of uncharged polymers near  $\theta$ -conditions, an upturn of apparent viscosity *vs.* shear rate above some critical rate  $G_m$  can possibly be related to internal viscosity effects (Wolff 1967).

M. Bohdanecky (Prague) reported some investigations into the Flory equation for the viscometric expansion due to polymer-solvent interaction. The excluded-volume effects were determined at different values of the temperature, the molecular weight and the chemical structure of polymer and the solvent power. The results can be interpreted as due to a partial draining of the molecular coil by the solvent.

A. Silberberg (Rehovot) talked about the influence of diffuse macromolecular surface phases on the flow along a liquid/solid interface. The flow of solutions containing flexible macromolecules along a rigid or an elastic gel surface is accompanied by interactions which extend far beyond the thickness of the actual interface layer and which can be important for biological systems in particular (Lahav, Eliezer & Silberberg 1973).

A survey lecture on structural theories of concentrated polymer solutions and melts was presented by A. Ziabicki (Warsaw). He started with simple concepts of intra- and intermolecular forces responsible for the mechanical behaviour. Several fundamental models combining these interactions were described and discussed: a permanent network with chemical cross-links, a temporary network with localized, but dissociable junctions, and entangled systems with non-localized junctions. It has been shown that the temporary network with localized junctions following Yamamoto or Lodge is inherently incapable of describing the molecular-weight effects observed. A model which can account for these effects as well as for steady-state flow, stress relaxation and nonlinear viscoelasticity is provided by a system of entangled flexible chains (Ziabicki 1971, 1974).

Subsequent papers were concerned with various types of molecular networks. W. Klonowski and A. Ziabicki (Warsaw) presented a statistical-thermodynamical theory of cross-linking leading to the thermodynamically most probable structures of localized networks (Ziabicki & Klonowski 1974). G. Ronca (Milan) considered the relaxation of shear and normal components of stress following from various theories of molecular networks. He concluded that an entanglement network rather than a temporary network with localized junctions can account for the observed stress relaxation (Ronca 1974). J. Mewis (Heverlee, Belgium) proposed a theoretical description of entanglement systems based on a modification of the Zimm-Rouse theory for a single macromolecule in dilute solutions. D. Acierno and G. Marucci (Palermo) presented a phenomenological model of an entanglement system (a generalized Maxwell fluid) in which some parameters were interpreted as being related to entanglement density (Marucci & Acierno 1974). D. Acierno (Palermo) and A. Ziabicki (Warsaw) also reported statistical calculations of entanglement density in polymer systems composed of rather rigid slippery chains. They predicted  $2 \times 10^{-3}$  effective entanglements for each chain-chain contact.

#### 4. Mechanical and optical investigation of polymer solutions

A survey lecture about flow birefringence and its relation to rheological properties of polymer fluids was given by H. Janeschitz-Kriegl (Delft) (see Janeschitz-Kriegl & Gortemaker 1974). He discussed the experimental evidence indicating that the deviatoric components of the stress tensor are proportional to the corresponding deviatoric components of the tensor of optical refraction in a wide range of flow conditions and for various polymer melts and concentrated solutions. The stress-optical proportionality coefficient has been found to be a constant independent of time, flow conditions and molecular weight distribution. In particular this holds for transient conditions and for non-Newtonian steady shear flow. Reliable experimental data have been reported by Philippoff (1961) for concentrated polymer solutions and by Wales & Philippoff (1973) for polymer melts. The constancy of the stress-optical coefficient fails, however, when low molecular weight polymers are considered (Janeschitz-Kriegl & Burchard 1968). The importance of the stress-optical law lies in the fact that optical measurements are much more sensitive and easy to perform than stress measurements, especially for the normal stress components.

In the discussion following the lecture it was noted that a constant stress-optical coefficient had been observed for soaps but had not been observed for suspensions of rigid particles. From the theoretical point of view (phenomenological theory of Coleman), proportionality between the stress and the optical tensors can be expected in the linear range of deformation. Extension of this rule beyond the linear region for some systems is not excluded by the theory. The stress-optical law is also inherently included in some special rheological models, e.g. the elastic liquid theory of Lodge.

C. Truchasson (Toulouse) discussed the applicability of birefringence measurements to characterize a flow. For two examples, carboxymethyl cellulose and Milling Yellow in aqueous solutions, the authors showed that flow birefringence is controlled not only by the conditions of flow but also by the thermal history of the system, ageing, rejuvenation, etc. (Jibawi & Truchasson 1974).

Two papers were concerned with studies of the dynamics of macromolecules in solutions using light-scattering methods. M. H. Birnboim (Rehovoth) described the method of studying the optical time autocorrelation function, which is related to rotational and translational diffusion. Experimental data on several biologically important systems (RNA, R 17 phage, Fibrinogen) were given. S. Candau (Strasbourg) has investigated the dynamics of polymer solutions by Rayleigh spectroscopy. He presented experimental data on inelastic light scattering by dilute polystyrene solutions which could show the effects of intramolecular motions.

L. Nicodemo and L. Nicolais (Naples) studied the shear-dependent viscosity of two-phase systems composed of glass beads or short glass fibres suspended in polymer solutions (PIB-decalin, CMC-water, PEO-water). The suspensions exhibited a non-Newtonian behaviour at lower shear rates. Using a double-shift procedure the authors constructed master curves for suspensions with various

polymer and filler concentrations (Nicodemo, Nicolais & Landel 1974). Some empirical formulae were discussed.

D. Bellet (Toulouse) presented theoretical and experimental studies of superposed oscillatory and steady Poiseuille flow. Velocity profiles in a 15% aqueous solution of carboxymethylcellulose (CMC) had been measured with hydrogen bubbles and a laser anemometer. The non-Newtonian behaviour was approximated by an Ostwald-de Waele (power law) model, necessitating numerical solution of their equations of motion (Ply, Bellet & Bousquet 1974).

J. Janáček (Prague) discussed the role of entanglements in lightly cross-linked polymer-diluent systems on the basis of viscoelastic measurements of such systems. The equilibrium modulus, loss compliance, Mooney-Rivlin constants  $C_1$  and  $C_2$  and the ultimate mechanical properties of cross-linked polymethacrylate solutions were studied as functions of the cross-link density, the degree of swelling and the polymer structure (Janáček 1973). The problem of entanglements (both entrapped between chemical cross-links, and temporary ones dissociable under tension) seems to be of considerable importance for the molecular theory of polymer systems.

A. Ziabicki (Warsaw) presented an argument against the widely used approximation in rubber elasticity theory, known as the Mooney-Rivlin equation,

$$W = C_1(I_1 - 3) + C_2(I_2 - 3),$$

where  $W$  is elastic potential,  $I_1$  and  $I_2$  are the first and second invariants of the deformation tensor, and  $C_1$  and  $C_2$  are constants. The Mooney-Rivlin equation does not follow from molecular-thermodynamic considerations. It seems also that it does not provide a consistent second-order approximation for small deformations. A second-order approximation should involve also a square of the first invariant, which is comparable with  $I_2$ , giving

$$W = C_1(I_1 - 3) + C_{21}(I_1^2 - 9) + C_{22}(I_2 - 3).$$

In fact, such an equation was proposed a decade ago by Zahorski (1962). In the discussion following this argument it was noted that the Rivlin treatment is formally correct since it includes an additional assumption about incompressibility of the material. However, this assumption, and consequently also the Mooney-Rivlin approximation, does not follow from molecular considerations, and the full second-order equation seems to be preferable.

## 5. Consequences of non-Newtonian rheology

G. Astarita (Naples) reviewed the wide range of changes in a flow field due to the non-Newtonian properties of a polymer solution. Theoretical difficulties start with irrotational flows which no longer satisfy the momentum equation as they do the Navier-Stokes equation. Some constitutive equations, such as the Maxwell equation, propagate damped elastic waves which would lead to shock waves in the flow around fast-moving bodies. Normal stresses in shear lead to a secondary circulation in flow down pipes. A correct theoretical treatment of secondary circulations is now possible using Pipkin's theory for nearly viscometric flows. A high viscosity in extensional motions is thought to be the cause

of standing vortices upstream of the orifice in converging flows. Some constitutive models suggest there might be a maximum draw velocity in fibre-spinning. Most non-Newtonian materials have a lower critical Reynolds number for the stability of flows such as Couette flow. This destabilization tendency appears curiously to run counter to their reduction of turbulent skin friction.

B. Mena (Manchester) described an experimental study of the flow of a dilute solution of Polyox past spheres and cylinders. At low Reynolds numbers and at moderate Deborah numbers, he and Broadbent had observed an increase in the drag, but no discernible changes in the flow pattern. There was the usual downstream disturbance, instead of the upstream shock waves which had been suggested by the Maxwell equation. The discrepancies between this and similar work by Denn were not resolved.

W. M. Jones (Aberystwyth) discussed micromechanical models of flow through porous media. Polymer solution can be modelled by a suspension of elastic spheres moving from one constriction to another. But to account for the long characteristic time the model has to be modified slightly to one in which there are clumps of temporary networks with interparticle bonds being associated and rebuilt during the flow (Jones & Davies 1972).

J. G. Evans (Cambridge) showed that it was possible to solve for the flow of a rigid-rod suspension which was governed by a highly non-Newtonian constitutive equation. He described various predictions: an oscillatory overshoot in the volume flux at the start of a pipe flow, a slowing down of the collapse of a cavitating bubble, and new boundary layers on a corrugated pipe which were related to standing vortices upstream of an orifice.

Three papers were presented on turbulent drag reduction by polymer additives, and were followed by an inconclusive discussion of this elusive problem. A. Gyr (Zurich) showed a film demonstrating the widening of spanwise structures by polymer additives to wall turbulence. O. Scrivener (Strasbourg) had been using a laser anemometer to measure the mean velocity profile in wall turbulence with polymer additives, and was hoping to investigate turbulent fluctuations. A. B. Metzner (Delaware) reported that the addition of both fibres and polymers to the ambient liquid could reduce turbulent skin friction by 90%, showing that the two drag-reducing agents enhance each other's effect in some way (Lee, Vaseleski & Metzner 1974). Drag reduction due to additives of various kinds is to be the subject of a Euromech Colloquium in Stockholm in August 1974.

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