White Rose Research Online

eprints@whiterose.ac.uk
https://eprints.whiterose.ac.uk
Universities of Leeds, Sheffield and York

Deposited via The University of Leeds.

White Rose Research Online URL for this paper:
https://eprints.whiterose.ac.uk/id/eprint/179454/

Version: Accepted Version

Article:
Hinch, J and Harlen, O (2021) Oldroyd B, and not A? Journal of Non-Newtonian Fluid Mechanics, 298. 104668. ISSN: 0377-0257

https://doi.org/10.1016/j.jnnfm.2021.104668

© 2021, Elsevier. This manuscript version is made available under the CC-BY-NC-ND 4.0 license http://creativecommons.org/licenses/by-nc-nd/4.0/.

Reuse
This article is distributed under the terms of the Creative Commons Attribution-NonCommercial-NoDerivs (CC BY-NC-ND) licence. This licence only allows you to download this work and share it with others as long as you credit the authors, but you can't change the article in any way or use it commercially. More information and the full terms of the licence here: https://creativecommons.org/licenses/

Takedown
If you consider content in White Rose Research Online to be in breach of UK law, please notify us by emailing eprints@whiterose.ac.uk including the URL of the record and the reason for the withdrawal request.

UNIVERSITY OF LEEDS
University of Sheffield
UNIVERSITY of York

Oldroyd B, and not A?

John Hinch[a], Oliver Harlen[b,*]

[a]*Department of Applied Mathematics and Theoretical Physics, University of Cambridge, Cambridge, CB3 0WA*
[b]*School of Mathematics, University of Leeds, Leeds, LS2 9JT*

Abstract

Highlights

- Oldroyd's 1950 paper
- Derivation of upper and lower convected time-derivatives
- Choice between Oldroyd-B and Oldroyd-A
- Insights from micro-structural studies
- Refinements from elastic-dumbbell model

We examine Oldroyd's 1950 paper *On the Formulation of Rheological Equations of State* [1] in which he introduced the upper and lower convected time-derivatives, along with the Oldroyd-A and Oldroyd-B model fluids. Those developments are placed in context of prior ideas and his own subsequent papers on constitutive equations. The choice between the A and B models is addressed by looking at micro-structural studies, finding that something in between is appropriate. Finally some refinements are discussed in terms of the elastic-dumbbell model.

Keywords:
Oldroyd-B, convected time-derivative, microstructure, elastic-dumbbell, FENE

*Corresponding author

1. Introduction

Mainly due to the large rise in activity in computational rheology, the Oldroyd-B model has featured frequently in recent years. According to the Web of Science there are about 2000 papers that reference Oldroyd-B in either the title or abstract, around 100 a year in the last 12 years. In contrast Oldroyd-A brings up just 6 papers since 1950. We need to explain this discrepancy.

The focus of this article is Oldroyd's 1950 paper [1] in which he argued that time-derivatives must be evaluated in a frame moving with the material, and by moving he included translation, rotation and (unusually) deformation. This leads to the upper and lower convected time-derivatives. In particular, Oldroyd claimed that the simple time-derivatives in a Jeffreys model of Fröhlich and Sack (1946) [2] would produce different results in different frames. Applying his upper and lower time-derivatives to the Jeffreys model gave the Oldroyd-B and Oldroyd-A models respectively, which would produce the same results in all frames.

However, the problem is how to choose between these two possible good models, A and B. Oldroyd commented that it depends on the physics, but frustratingly offered no example nor any suggestion on detecting which flavour of physics this might be. At the end of his 1950 paper Oldroyd calculated the flow around a rotating rod, where he found the B-model would climb the rod, as Weissenberg had observed, whereas the A-model would descend, which had not been observed. Hence the Oldroyd-B is to be favoured. In fact 'rod-dipping' has been observed in dense suspensions of non-Brownian particles by Boyer, Pouliquen and Guazzelli (2011) [3].

We start this article with an extended section §2 on Fröhlich and Sack's paper, because it motivated Oldroyd's creation of convected time-derivatives, and because later we use its physics to discuss the choice of A or B. In section §3 we present the work in Oldroyd's 1950 paper. In the following section §4 we look at his other publications on constitutive equations, including some interesting insights from his thesis written three years before the publication of the 1950

paper. To settle the choice between Oldroyd-A and Oldroyd-B, section §5 looks at the physics involved in the rotation and deformation of the micro-structure, this physics having been studied over 20 years after the 1950 paper. That section concludes with the radical suggestion that Oldroyd himself could have made the choice between A and B had he fully adopted his philosophy of watching how the stress was convected. We then present in section §6 the elastic-dumbbell model, which leads directly to the Oldroyd-B model. Additionally the simplicity of elastic-dumbbell model allows one to see potential refinements such as FENE, which are presented in section §7.

2. H. Fröhlich & R. Sack (1946)

Working in Bristol, Fröhlich & Sack (1946) [2] sought differential equations that would describe the visco-elastic behaviour of bitumen that had been observed by Lethersich (1942) [4], namely that, when a constant load was applied, strain would build up, eventually increasing linearly in time, and when the load was removed, the strain would relax. Fröhlich & Sack investigated a very simple model system — a dilute suspension of stiff elastic spheres in a viscous liquid; dilute means that hydrodynamic interactions between the spheres could be neglected, stiff elastic means that the spheres were only slightly deformed, and viscous means that Stokes flow could be applied. They considered a uni-axial straining motion and used a cell-model adapted from a previous calculation of dielectric polarisation to evaluate the properties of the effective visco-elastic material. This cell model is different to Einstein's dissipation method, and they checked that it gave the same answer for rigid spheres.

Fröhlich & Sack derived a linear visco-elastic constitutive equation described, in a slightly different notation, by

$$\sigma + \tau_1 \dot{\sigma} = 2\mu^*(E + \tau_2 \dot{E}), \tag{1}$$

with a relaxation time τ_1 for the relaxation of stress at zero strain-rate, a retardation time τ_2 for the relaxation of strain-rate at zero stress, and an effective

viscosity μ^*, given respectively by

$$\tau_1 = \frac{3\mu}{2G}\left(1+\tfrac{5}{3}\phi\right), \quad \tau_2 = \frac{3\mu}{2G}\left(1-\tfrac{5}{2}\phi\right), \quad \text{and} \quad \mu^* = \mu\left(1+\tfrac{5}{2}\phi\right).$$

Here σ is the stress, E is the strain-rate, μ is the viscosity of the liquid, G the elastic shear modulus of the spheres, and ϕ the volume concentration of the spheres. The condition that the elastic deformation of the spheres is small requires that $\mu E/G \ll 1$. Fröhlich & Sack's constitutive equation (1) is that of a Jeffreys (1929) [5] model.

Their cell model gives the correct result for both the effective viscosity μ^* and for the difference between the two times $\tau_1 - \tau_2 = 25\mu\phi/4G$. The numerical coefficients of the ϕ-terms in the two times are, however, incorrect, because they depend on hydrodynamic interactions which are treated incorrectly in the cell-model.

Seventy-five years after Fröhlich & Sack's original long derivation, it is possible to give a more concise derivation using the linearity of the Stokes equations, a known result for the stress inside a rigid sphere in a straining motion, and volume-averaging to evaluate the bulk stress.

Consider a small sphere placed in a general linear straining motion $\mathbf{u} = \mathbf{E}\cdot\mathbf{x}$. Vorticity just spins the sphere, so we can ignore it here, but not later. The sphere deforms linearly, with internal elastic displacements $\mathbf{D}(t)\cdot\mathbf{x}$ and velocities $\dot{\mathbf{D}}\cdot\mathbf{x}$. Write the flow outside the sphere as $\mathbf{u} = \dot{\mathbf{D}}\cdot\mathbf{x} + \mathbf{u}'$. The disturbance flow $\mathbf{u}'$ then satisfies the Stokes equations, in the far field tends to $(\mathbf{E}-\dot{\mathbf{D}})\cdot\mathbf{x}$, and vanishes on the sphere. Thus the disturbance flow is that outside a rigid sphere with a reduced strain-rate at infinity. It is known that such a flow produces a uniform stress inside the rigid sphere equal to $5\mu(\mathbf{E}-\dot{\mathbf{D}})$, the 5μ being Einstein's $\frac{5}{2}$ multiplied by 2μ. Adding the stress from the $\dot{\mathbf{D}}\cdot\mathbf{x}$ first part of the flow, and then equating to the elastic stress inside gives

$$2\mu\dot{\mathbf{D}} + 5\mu(\mathbf{E}-\dot{\mathbf{D}}) = 2G\mathbf{D}.$$

Rearranging, we have the evolution equation for the micro-structure

$$\mathbf{D} + \tau\dot{\mathbf{D}} = \tfrac{5}{3}\tau\mathbf{E}, \tag{2}$$

with micro-structural relaxation time

$$\tau = \frac{3\mu}{2G}.$$

Note that the coefficient on the right-hand side of equation (2) is $\frac{5}{3}$ and not 2. This will be important later.

The local stress in the suspension can be constructed from that given by the viscous liquid, $2\mu\mathbf{e}(\mathbf{x})$, plus something extra, $(2G\mathbf{D} - 2\mu\dot{\mathbf{D}})$, inside the particles, from which one can make a volume-average to obtain the bulk stress

$$\boldsymbol{\sigma} = 2\mu\mathbf{E} + \phi(2G\mathbf{D} - 2\mu\dot{\mathbf{D}}).$$

It is possible to eliminate $\mathbf{D}$ and $\dot{\mathbf{D}}$ from this expression using the evolution equation for the micro-structure (2), with a result similar to Fröhlich & Sack's equation (1) but with slightly different numerical coefficients of the ϕ-terms in the relaxation and retardation times. Alternatively one can eliminate just $\dot{\mathbf{D}}$ to obtain

$$\boldsymbol{\sigma} = 2\mu(1 - \tfrac{5}{3}\phi)\mathbf{E} + \tfrac{10}{3}\phi G\mathbf{D}. \tag{3}$$

3. Oldroyd 1950

The rheological equation of state, or constitutive equation, for visco-elastic liquids needs to incorporate past values of the stress and strain. This can be achieved using integration and/or differentiation with respect to time. In his 1950 paper [1] *On the Formulation of Rheological Equations of State*, Oldroyd recognised that time-integration and time-differentiation of a tensor depends not only on the changing values in time of the components but also on the changing basis vectors of the reference frame. In order for the equation of state to express physics totally independent of the observer's frame of reference, Oldroyd argued that one must use the frame of reference experienced by the material, i.e. the frame *moving* with the material.

There are three parts to the *movement* of the material:– a local velocity, a local rotation, and a local deformation. The time-derivative seen translating

with the local velocity is the familiar advected time-derivative for transforming between the moving Lagrangian frame and a fixed laboratory Eulerian frame,

$$\frac{D}{Dt} = \frac{\partial}{\partial t} + \mathbf{u} \cdot \boldsymbol{\nabla}.$$

The time-derivative seen rotating with the material is the co-rotational derivative suggested by Zaremba (1903) [6] and Jaumann (1911) [7]. For a second order tensor $\mathbf{A}$, it is

$$\overset{\circ}{\mathbf{A}} = \frac{D\mathbf{A}}{Dt} - \mathbf{A} \cdot \boldsymbol{\Omega} + \boldsymbol{\Omega} \cdot \mathbf{A}, \tag{4}$$

where $\boldsymbol{\Omega}$ is the vorticity tensor

$$\boldsymbol{\Omega} = \tfrac{1}{2} \left(\boldsymbol{\nabla}\mathbf{u} - \boldsymbol{\nabla}\mathbf{u}^T \right). \tag{5}$$

The most important and original contribution of Oldroyd's 1950 paper was to form the time-derivatives deforming with the material. Hencky (1925) [8] briefly suggested using a frame deforming with the material, but it was Oldroyd who fully formulated the idea and worked out the details — and the details are somewhat complicated. An initial Cartesian frame deforms into a skew non-orthogonal coordinate frame. There is then a question of whether components of tensors are co-variant or contra-variant. For a vector $\mathbf{x}$, one can take components parallel to the non-orthogonal basis vectors, the contra-variant components x^i, or take components perpendicular to the coordinate planes (parallel to the reciprocal basis vectors), the co-variant components x_i. If the physics is to be formulated in terms of how the co-variant components A_{ij} of a second order tensor $\mathbf{A}$ evolve in the material frame, Oldroyd showed, see *crash course* below, that one should use the lower convected time-derivative,

$$\overset{\triangle}{\mathbf{A}} = \frac{D\mathbf{A}}{Dt} + \mathbf{A} \cdot (\boldsymbol{\nabla}\mathbf{u})^T + \boldsymbol{\nabla}\mathbf{u} \cdot \mathbf{A}. \tag{6}$$

On the other hand, if the physics is formulated in terms of the contra-variant components A^{ij}, then one should use the upper convected time-derivative,

$$\overset{\triangledown}{\mathbf{A}} = \frac{D\mathbf{A}}{Dt} - \mathbf{A} \cdot \boldsymbol{\nabla}\mathbf{u} - (\boldsymbol{\nabla}\mathbf{u})^T \cdot \mathbf{A}. \tag{7}$$

Oldroyd applied his new time-derivatives deforming with the material to generalise Fröhlich & Sack's linear visco-elastic constitute equation (1). That linear equation was derived under the condition of small deformations of the elastic sphere, $\mu E/G \ll 1$. When this restriction on the flow is relaxed, the simple time-derivatives are not independent of the frame of the observer. Oldroyd offered two possible generalisations that would be valid for all observers,

$$\text{Oldroyd A:} \qquad \boldsymbol{\sigma} + \tau_1 \overset{\triangle}{\boldsymbol{\sigma}} = 2\mu^* (\mathbf{E} + \tau_2 \overset{\triangle}{\mathbf{E}}), \tag{8}$$

$$\text{Oldroyd B:} \qquad \boldsymbol{\sigma} + \tau_1 \overset{\triangledown}{\boldsymbol{\sigma}} = 2\mu^* (\mathbf{E} + \tau_2 \overset{\triangledown}{\mathbf{E}}), \tag{9}$$

To choose between these two possibilities, Oldroyd said that further examination of structural models or experiments was necessary. The choice depends on whether the physics is formulated in co-variant or contra-variant components. As we shall see later, for physics involving material area-elements like rotating discs, which are co-variant, one should use the lower convected derivative and Oldroyd-A. While for physics involving material line-elements like rotating fibres, which are contra-variant, one should use the upper convected derivative and Oldroyd-B. Oldroyd gave no illustrations of physics requiring a co-variant or contra-variant formulation of the physics, nor hints of how one might know which formulation was appropriate for a particular material.

At the end of his 1950 paper, Oldroyd calculated the flow between vertical concentric rotating cylinders for his A- and B-fluids. He found that the A-fluid would fall near the inner cylinder, while the B-fluid would rise up. As rod-climbing had been observed by Weissenberg (1947) [9], the option Oldroyd-B might be favoured.

In steady simple shear, both the Oldroyd-A and Oldroyd-B fluids have a viscosity which is independent of the shear-rate, and a first normal stress difference which is quadratic in the shear-rate. The second normal stress difference vanishes for Oldroyd-B, and for the Oldroyd-A is negative and equal in magnitude to the first normal stress difference. In uni-axial extensional flow, the extensional viscosity becomes infinite at $\lambda_1 E = \frac{1}{2}$ for Oldroyd-B and $\lambda_1 E = 1$ for Oldroyd-A, and vice-versa in bi-axial extension.

Oldroyd's idea of using coordinates fixed in the deforming material was taken up later by Lodge (1951) [10] and Truesdell (1952) [11]. Making the rheological equation of state independent of the observer was later called *Material Frame Indifference*.

3.1. Crash course on convected time-derivatives

The question is how to express a time-derivative of a tensor as seen by the deforming material in terms of changes of the tensor seen in the fixed laboratory frame. Consider a transformation from (Lagrangian) coordinates ξ^α in the deforming material frame to (Eulerian) coordinates x^i in the fixed laboratory frame

$$x^i = x^i(\xi^\alpha, t).$$

We shall use Greek letters for the material frame and Roman for the laboratory frame. While the laboratory coordinates should be orthogonal, the deforming material coordinates will be non-orthogonal (skew) with a difference between contra-variant and co-variant components of tensors.

Let us start with the co-variant components of a vector $\mathbf{a}$, such as for a gradient $\nabla\phi$, and also for material area-elements. The transformation of the components is

$$a_\alpha = \frac{\partial x^i}{\partial \xi^\alpha} a_i, \qquad \text{as in} \qquad \frac{\partial \phi}{\partial \xi^\alpha} = \frac{\partial x^i}{\partial \xi^\alpha}\frac{\partial \phi}{\partial x^i}.$$

Differentiating this transformation with respect to time, we form the lower convected time-derivative

$$\overset{\triangle}{a}_\alpha = \frac{\partial x^i}{\partial \xi^\alpha}\dot{a}_i + \left(\frac{\dot{\partial x^i}}{\partial \xi^\alpha}\right) a_i = \frac{\partial x^i}{\partial \xi^\alpha}\dot{a}_i + \frac{\partial v^j}{\partial \xi^\alpha} a_j = \frac{\partial x^i}{\partial \xi^\alpha}\left(\dot{a}_i + \frac{\partial v^j}{\partial x^i} a_j\right).$$

So we have the lower convected derivative for the vector $\mathbf{a}$,

$$\overset{\triangle}{\mathbf{a}} = \dot{\mathbf{a}} + (\boldsymbol{\nabla}\mathbf{u}) \cdot \mathbf{a},$$

and equation (6) for the second order tensor $\mathbf{A}$.

For the contra-variant components of a vector $\mathbf{a}$, such as for a material line-element $\delta\boldsymbol{\ell}$, the transformation of components is

$$a^\alpha = \frac{\partial \xi^\alpha}{\partial x^i} a^i, \qquad \text{as in} \qquad \delta\ell^\alpha = \frac{\partial \xi^\alpha}{\partial x^i}\delta\ell^i.$$

Differentiating this transformation with respect to time, we form the upper convected time-derivative

$$\overset{\triangledown}{a}{}^{\alpha} = \frac{\partial \xi^{\alpha}}{\partial x^{i}} \dot{a^{i}} + \left(\frac{\partial \dot{\xi}^{\alpha}}{\partial x^{i}} \right) a^{i} = \frac{\partial \xi^{\alpha}}{\partial x^{i}} \dot{a^{i}} - \frac{\partial \xi^{\alpha}}{\partial x^{i}} \frac{\partial v^{i}}{\partial x^{j}} a^{j} = \frac{\partial \xi^{\alpha}}{\partial x^{i}} \left(\dot{a^{i}} - \frac{\partial v^{i}}{\partial x^{j}} a^{j} \right),$$

where we have used

$$\left(\frac{\partial \dot{\xi}^{\alpha}}{\partial x^{j}} \right) \frac{\partial x^{j}}{\partial \xi^{\beta}} + \frac{\partial \xi^{\alpha}}{\partial x^{j}} \frac{\partial v^{j}}{\partial \xi^{\beta}} = \frac{d}{dt} \left(\frac{\partial \xi^{\alpha}}{\partial x^{j}} \frac{\partial x^{j}}{\partial \xi^{\beta}} = \delta^{\alpha}_{\beta} \right) = 0.$$

So we have the upper convected derivative for a vector

$$\overset{\triangledown}{\mathbf{a}} = \dot{\mathbf{a}} - (\boldsymbol{\nabla} \mathbf{u})^{T} \cdot \mathbf{a},$$

and equation (7) for the second order tensor $\mathbf{A}$.

4. Related papers by Oldroyd

Before looking at Oldroyd's subsequent papers about rheological equations, it is interesting go back to his earlier thesis. Oldroyd was an undergraduate at Trinity College in Cambridge University from 1939 to 1942. He then spent 3 years working for the Ministry of Supply on rocket research at Aberporth near Aberystwyth. In 1945 he was recruited to the Fundamental Research Laboratory of Courtaulds Ltd. in Maidenhead by A.H. Wilson, who had been one of his mathematics teachers at Cambridge and after the war had become the research director of Courtaulds. He spent part of the academic year of 1945 in Cambridge as a research scholar. In August 1947, after just two years of research, Oldroyd wrote a thesis, a very full thesis[1]. Oldroyd acknowledged 'most helpful suggestions and criticism throughout the course of this work' from A.H. Wilson and W.R. Dean, neither of whom ever worked on visco-elastic fluids. Dean is the Dean of secondary flow in curved pipes, and was another of his Cambridge teachers. Part I of the thesis has seven chapters about 'Bingham

[1] On the basis of the thesis, Oldroyd was elected to a Fellowship at Trinity College from 1947 to 1951. Probably the same thesis was used for the Cambridge University PhD, awarded in May 1949. Elected to Junior Research Fellowships at Trinity in the same year as Oldroyd were George Batchelor, Thomas Gold and Fritz Ursell.

solids', with six chapters the basis of papers published in the *Proceedings of the Cambridge Philosophical Society* that year or the following. These papers, and more on Bingham fluids, will be considered in another article in this special issue by Balmforth, Craster and Hewitt [12].

Part II of Oldroyd's 1947 thesis gives his first thoughts on what will become his famous 1950 paper, and there are some interesting differences. Aware of the work of Murnaghan (1937) [13] on finite strains in elasticity theory, Oldroyd argues that time-derivatives should be evaluated in the 'proper' coordinates (of the deforming material) and not in 'fixed' coordinates (of the laboratory). The calculus of taking the first and higher time-derivatives is developed in terms of the strain, and only in the last few pages applied to stress. Also in the last few pages, an application is made to the Jeffreys model proposed by Fröhlich and Sack just a year earlier. There is a very honest statement that the generalisation to convected derivatives is ambiguous, because one does not know if the physics demands that the stress be described by a co-variant or contra-variant tensor: one sentence says that there is a 'need to establish the co-variant, contra-variant or mixed nature of any physical quantity before differentiating it'. By the time of the 1950 paper, Oldroyd had calculated the Weissenberg effect and was able to conclude that Oldroyd-B would climb while Oldroyd-A would do the opposite.

In 1953 Oldroyd [14] revisited Fröhlich and Sack's calculation, but now for a dilute emulsion of liquid drops of a different viscosity $\lambda\mu$ to that of the suspending liquid μ, and with a surface tension γ sufficiently strong to keep the drops effectively spherical, with radius a. Oldroyd showed that the emulsion was described by the same Jeffreys equation (1) with different expressions for the parameters. The relaxation and retardation times and the effective viscosity are

$$\tau_1 = \frac{a\mu}{\gamma} A\left(3 + 2\lambda + 8A\phi\right), \qquad \tau_2 = \frac{a\mu}{\gamma} A\left(3 + 2\lambda - 12A\phi\right),$$
$$\mu^* = \mu\left(1 + \frac{2+5\lambda}{2(1+\lambda)}\phi\right), \qquad \text{where} \qquad A = \frac{16+19\lambda}{40(1+\lambda)}.$$

Because the deformation of the drops was not included, the response is lin-

ear visco-elasticity with no nonlinear terms; nonlinear terms that would have determined which convected derivative should be used.

In a 1951 paper [15], Oldroyd introduced his 5-constant model by adding two terms to his Oldroyd-A, additional symmetric quadratic terms,

$$\boldsymbol{\sigma} + \tau_1 \overset{\triangle}{\boldsymbol{\sigma}} - 2\kappa_1(\mathbf{E}\cdot\boldsymbol{\sigma} + \boldsymbol{\sigma}\cdot\mathbf{E}) = 2\mu_0(\mathbf{E} + \tau_2 \overset{\triangle}{\mathbf{E}}) - 8\mu_0\kappa_2\mathbf{E}\cdot\mathbf{E}. \tag{10}$$

He found that in the steady flow between two rotating concentric cylinders the fluid had a shear viscosity

$$\mu(\gamma) = \mu_0 \frac{1+\sigma_2\gamma^2}{1+\sigma_1\gamma^2}, \tag{11}$$

where γ is the shear-rate and

$$\sigma_1 = 4\kappa_1(\tau_1 - \kappa_1) \quad \text{and} \quad \sigma_2 = 2(\tau_1\kappa_2 + \kappa_1\tau_2 - 2\kappa_1\kappa_2).$$

He noted that the shear viscosity would be constant independent of the shear-rate in the special cases of his A-fluid with $\kappa_1 = \kappa_2 = 0$ and his B-fluid with $\kappa_1 = \tau_1$ and $\kappa_2 = \tau_2$. The paper goes on to consider linearised small amplitude oscillations, in which the nonlinear κ terms play no role. There is a discussion on how best to estimate the relaxation time τ_1 and the retardation time τ_2 from oscillating experiments. The two additional terms in the 5-constant model permit a smooth transition between the A- and B-fluids, and that gives the shear-thinning.

A longer paper published in 1958 [16], five years after Oldroyd had moved to Swansea University, introduces his 8-constant model

$$\begin{aligned}\boldsymbol{\sigma} + \tau_1 \overset{\circ}{\boldsymbol{\sigma}} - \tau_3(\mathbf{E}\cdot\boldsymbol{\sigma} + \boldsymbol{\sigma}\cdot\mathbf{E}) + \tau_5(\boldsymbol{\sigma}:\mathbf{I})\mathbf{E} + \tau_6(\boldsymbol{\sigma}:\mathbf{E})\mathbf{I} \\ = 2\mu_0\left(\mathbf{E} + \tau_2\overset{\circ}{\mathbf{E}} - 2\tau_4\mathbf{E}\cdot\mathbf{E} + \tau_7(\mathbf{E}:\mathbf{E})\mathbf{I}\right).\end{aligned} \tag{12}$$

Oldroyd labelled the terms differently, with $\tau_1 = \lambda_1$, $\tau_2 = \lambda_2$, $\tau_3 = \mu_1$, $\tau_4 = \mu_2$, $\tau_5 = \mu_0$, $\tau_6 = \nu_1$ and $\tau_7 = \nu_2$. In steady simple shear he found a shear-rate dependent viscosity following (11) with

$$\sigma_1 = \tau_1^2 + \tau_5(\tau_3 - \tfrac{3}{2}\tau_6) - \tau_3(\tau_3 - \tau_6),$$

$$\sigma_2 = \tau_1\tau_2 + \tau_5(\tau_4 - \tfrac{3}{2}\tau_7) - \tau_3(\tau_4 - \tau_7).$$

He also found similar expressions for the normal stresses. The shear-rate dependent viscosity was applied to flow down a circular pipe, and rectilinear flow down a pipe with an arbitrary cross-section. The normal stresses were applied to the Weissenberg effect in the flow between rotating vertical cylinders. Oldroyd also found a very restrictive condition on the normal stresses such that they would not induce a secondary flow in the pipe with an arbitrary cross-section. The paper ends with a preliminary investigation of the cone and plate rheometer, a new device at the time to measure normal stress differences.

The additional terms in the 8-constant model, beyond those of the Oldroyd-B model, are the only permitted terms that are either bilinear in the stress and the strain-rate or quadratic in the strain-rate. The 1958 paper has no discussion of any physics that might require these additional terms. On the one hand, it is unclear how the many parameters could be estimated from experiments. On the other hand, it is clear today that terms that are more nonlinear than quadratic are needed in order to describe certain rheological behaviour, notably the response in extensional flows.

In a paper published in 1965 [17], the year that he moved to Liverpool University, Oldroyd showed how in some simple flows that the kinematics of the convected coordinates could be calculated. He looked at steady simple shearing, steady 'pure shearing' which we now call pure straining, general rectilinear flow under a constant pressure gradient, flow caused by the steady rotation of solids of revolution (cylinders and cones), and rotational and axial flow combined. No constitutive equations are considered. The corresponding form of the stress is given using just the symmetry of the flow.

In 1964 Oldroyd won the Adams Prize for his essay entitled *An approach to non-Newtonian fluid mechanics*. The Adams Prize is awarded jointly by the Faculty of Mathematics and St. John's College in Cambridge. Two chapters of the essay were selected by Ken Walters and published in 1984 [18], two years after Oldroyd's death. The 1984 paper gives a careful and extended account of

his famous 1950 paper.

5. Micro-structure

Now it is time for some physics. Oldroyd fully appreciated that a consideration of the physics was necessary to resolve the choice between the possible permitted time-derivatives. He himself has only one paper in which he examined the physics involved, and that is his 1953 paper on dilute emulsions, which led to the Jeffreys model. However by neglecting the small deformations of the spherical drops, he could not see the nonlinear effects that determine the type of time-derivative.

It is rarely possible to make a theoretical study of the physics of a realistic micro-structure. Various limiting approximations must be applied, such as the diluteness of an emulsion in which interactions between the drops can be ignored. With computer simulations it is possible to lift some restrictions. The hope is always that an idealised study will reveal the form of the constitutive equation, a form which might also apply beyond the limiting conditions. Thus although Fröhlich and Sack found that a dilute emulsion is described by the Jeffreys model with the two time-constants very nearly equal, the model has been applied to non-dilute emulsions with the two time-constants no longer close.

One immediately apparent feature of any study of a micro-structure is that the resulting constitutive equation is not a single simple relation between the stress and the strain and their time-derivatives. As discussed by Hinch and Leal (1975) [19], there is always another variable involved that describes the state of the micro-structure, and which has its own evolution equation. In Fröhlich and Sack's calculation, the variable is the deformation of the elastic sphere $\mathbf{D}(t)$, governed by equation (2). It is unwise to eliminate such hidden variables. So for Fröhlich and Sack, the Jeffreys model (1) requires boundary conditions on the the stress and strain-rate, which are far from obvious, while the equivalent evolution equation (2) obviously needs just the value of $\mathbf{D}$ to be specified on inflow boundaries.

5.1. Rotation

The question as to which convected time-derivative should be used is rapidly answered by considering a suspension of elongated rigid particles. Jeffery (1922) [20] showed that spheroids (ellipsoids with an axis of symmetry) rotate in a general linear flow with all of the vorticity and only a fraction of the strain-rate, the fraction $(r^2-1)/(r^2+1)$, where r is the aspect ratio of the spheroids. Thus one should use a Gordon-Schowalter (1972) [21], or Johnson-Segalman (1977) [22], convected time-derivative with a non-affine slip parameter of this fraction. Thus

$$\overset{\square}{\mathbf{A}} = \overset{\circ}{\mathbf{A}} - \tfrac{r^2-1}{r^2+1}\,(\mathbf{E}\cdot\mathbf{A} + \mathbf{A}\cdot\mathbf{E}) \equiv \tfrac{r^2}{r^2+1}\overset{\triangledown}{\mathbf{A}} + \tfrac{1}{r^2+1}\overset{\triangle}{\mathbf{A}}. \tag{13}$$

This non-affine time-derivative is within the Oldroyd 5-constant model. Both Gordon & Schowalter and Johnson & Segalman offered no argument based on physics to support their time-derivative. Jeffery offered no constitutive equation.

Fibres and long thin rods, $r \gg 1$, behave like material line-elements (of zero thickness) which are convected like contra-variant vectors, so that the upper convected derivative and Oldroyd-B are appropriate. Clay platelets and flat discs, $r \ll 1$, behave like material area-elements which are convected like co-variant vectors, so that the lower convected derivative and Oldroyd-A are appropriate. In between these limits, the appropriate derivative is a mixture of upper and lower convected.

A simple suspension of elongated rigid particles does not have a fading memory until one adds Brownian rotations. Adding Brownian rotations leads to a Fokker-Plank description. The reduced efficiency of the straining motion at rotating the particles is not however changed, so that the selection of the convected time-derivative is unaffected. For early solutions of the Fokker-Plank description giving a shear-thinning viscosity see Burgers (1938) [23] and Peterlin (1938) [24], and for approximate constitutive equations see Hinch and Leal (1976) [25].

5.2. Deformation

After Fröhlich and Sack's 1946 study of elastic spheres with small deformations, R. Cerf (1951) [26] observed that large deformations could be tackled because a homogeneous elastic sphere would deform into an ellipsoid, and the Stokes flow outside an ellipsoid was available in Jeffery (1922) [20]. This idea was exploited later by Roscoe (1967) [27] to evaluate the rheology of a dilute suspension of visco-elastic spheres. He found a shear-thinning viscosity, normal stresses, and in pure straining motion a critical strain-rate above which no steady solution existed.

Similarly, Oldroyd's small deformation study of drops in an emulsion was extended to larger deformations by Barthès-Biesel and Acrivos (1973) [28] and surveyed by Rallison (1984) [29].

A key conclusion from these large deformation studies is that the microstructure is rotated fully by the vorticity and stretched by only a fraction of the strain-rate, i.e. a non-affine convected time-derivative is appropriate. It is interesting that these large deformation studies are not in fact needed to determine the nature of the non-affine slip, that the answer is all in the small deformation studies of Fröhlich and Sack (1947) and Oldroyd (1953) if the physics is correctly interpreted.

The evolution equation (2) for Fröhlich and Sack's elastic spheres says that the internal elastic displacements $\mathbf{D}$ are created by the strain-rate $\mathbf{E}$ as a source term. In his 1950 paper Oldroyd wished to express the physics differently, in terms of the deforming convected material coordinates. The displacements $\mathbf{D}$ are a result of deforming an isotropic base state $\mathbf{I}$. We therefore need to introduce a new variable $\mathbf{A}$ to describe the state of the micro-structure, combining the isotropic state and the small displacements,

$$\mathbf{A} = \mathbf{I} + \mathbf{D}.$$

The evolution equation (2) then becomes, with neglect of terms of $O(DE)$

$$\frac{1}{\tau}(\mathbf{A} - \mathbf{I}) + \left(\overset{\circ}{\mathbf{A}} - \tfrac{5}{6}\left(\mathbf{E}\cdot\mathbf{A} + \mathbf{A}\cdot\mathbf{E}\right)\right) = 0, \tag{14}$$

a nearly Oldroyd-B fluid but with a small non-affine slip. The constitutive equation is a pair, this evolution equation for the micro-structure, taken with an expression, effectively equation (3), for the stress

$$\boldsymbol{\sigma} = 2\mu(1 - \tfrac{5}{3}\phi)\mathbf{E} + \tfrac{5}{3}\phi 2G(\mathbf{A} - \mathbf{I}). \tag{15}$$

Similarly for the dilute emulsion, Oldroyd's 1953 analysis contains all the information to see that the emulsion is a nearly Oldroyd-B fluid with a non-affine slip coefficient $5/(2(2\lambda + 3))$.

6. The elastic-dumbbell model

There are perhaps four reasons for the enduring use of the Oldroyd-B model. First, the model has only three parameters to be fitted to experimental data. Second, the model represents fairly well many aspects, but not all, of the flow behaviour of some polymer solutions, such as Boger fluids. Third, really a result of the first two reasons, the Oldroyd-B equations are a sensible choice for numerical calculations of flows. And finally fourth, the elastic-dumbbell model is a simple micro-structural model of polymer solutions which is governed by the Oldroyd-B equation. The Oldroyd-B model has a constant shear viscosity, a quadratic first normal stress difference and zero second normal stress difference, reasonably approximating a Boger fluid. These rheological responses predict the behaviour in viscometric flows, in particular the many phenomena explained by a tension in the streamlines from the first normal stress differences. However, the Oldroyd-B model has a problem in steady pure straining flows, with an infinite extensional viscosity at a finite strain-rate. It would seem that Oldroyd himself, in print, was unaware of this problem. While there is this problem in steady extensional flows, sometimes the Oldroyd-B model can reasonably predict some transient extensional flows. Keiller (1992) [30] was able to predict the curious observations in four different stretching flows of the M1 Boger fluid using an Oldroyd-B with the three parameters of the relaxation time, solvent viscosity and elastic modulus found from shear-flow data.

Working in Basel in 1945, Werner Kuhn and student Hans Kuhn (no relation) proposed in a long 46-page paper [31] a simple elastic-dumbbell model of a thread (linear) polymer molecule in a shearing flow. While this simple model cannot describe many details of the macro-molecular behaviour, it does expose clearly the key issues which determine how much distortion can be expected when the polymer is placed in a particular flow.

The gross distortion of the random walk of the chain, e.g. the separation of the monomers at the ends of the chain, is represented by a single vector $\mathbf{r}$ which becomes the extension of a spring separating two beads. Now Brownian fluctuations in the configuration of the chain produce a relaxation of the distortion $\mathbf{r}$. This entropic desire to return to the most probable, spherically symmetric, randomly coiled state is modelled by the elasticity of the spring. The Hookean linearised spring constant κ is usually taken to be $3kT/Nb^2$, in which kT is the Boltzmann temperature, N the number of monomers and b their length.

Under flow the polymer chain is distorted by the velocity gradient, because there is a velocity difference between the two sides of the random walk. In the elastic-dumbbell model this is represented by a hydrodynamic drag acting on the spherical beads with friction constants $6\pi\mu a$ according to Stokes law, where μ is the solution viscosity and a the size of beads. The size can be taken to be the equilibrium radius of gyration r_0 of the random coil $a = r_0 = b(N/6)^{1/2}$. A force balance on the two beads yields an evolution equation,

$$\dot{\mathbf{r}} = \mathbf{r} \cdot \boldsymbol{\nabla}\mathbf{u} - \frac{\kappa}{3\pi\mu a}\mathbf{r}. \tag{16}$$

Finally one adds a Brownian motion of the beads. The state of the polymer coil is then described by a Fokker-Planck equation for the probability density for $\mathbf{r}$. For the simple model, it is possible to form a closed equation governing the expected second moment of the distortion $\langle \mathbf{rr} \rangle$,

$$\frac{D}{Dt}\langle \mathbf{rr} \rangle = \langle \mathbf{rr} \rangle \cdot \boldsymbol{\nabla}\mathbf{u} + \boldsymbol{\nabla}\mathbf{u}^T \cdot \langle \mathbf{rr} \rangle - \frac{1}{\tau}\left(\langle \mathbf{rr} \rangle - \frac{r_0^2}{3}\mathbf{I} \right), \tag{17}$$

with relaxation time $\tau = 3\pi\mu a/2\kappa$. The constitutive equation for a dilute

polymer solution is completed with an expression for the bulk stress

$$\boldsymbol{\sigma} = -p\mathbf{I} + \mu(\boldsymbol{\nabla}\mathbf{u} + \boldsymbol{\nabla}\mathbf{u}^T) + n\kappa\langle\mathbf{rr}\rangle, \tag{18}$$

where n is the number density of the polymers. These two equations, (17) and (18), govern an Oldroyd-B fluid.

Why does the elastic-dumbbell model deliver Oldroyd-B rather not Oldroyd-A? An initial answer comes from equation (16), which shows that the chain's end-to-end vector $\mathbf{r}$ is convected by the flow like a material line-element, which leads to the upper convected time-derivative and so Oldroyd-B. But why is $\mathbf{r}$ convected like a material line-element? The answer to that deeper question lies in the modelling of the hydrodynamic forces distorting the chain. These forces are calculated as the drag on the spherical beads, which in turn just uses the undisturbed velocity at the centre of the sphere, a single point. For example, if a couple balance were made with the beads required to rotate with the spring, then the strain-rate would have the reduced efficiency of $3r^2/(3r^2+16a^2)$ on the rotation, although this is probably not a sensible model of the internal modes of the coiled chain.

7. Refinements

The elastic-dumbbell model represents only the gross distortion of the polymer chain. It has a single relaxation time, so poorly fits linear visco-elastic experimental data. An early refinement proposed by Rouse (1953) [32] was to consider a linear chain of connected elastic-dumbbells. The normal modes of which yield a spectrum of relaxation times $\tau_n \propto n^{-1}$. Later Zimm (1956) [33] included some hydrodynamic interactions between the beads on the chain. Previously Kirkwood and Riseman (1948) [34] had considered hydrodynamic interactions between beads on a chain, in which the beads were connected by rigid links. The hydrodynamic interactions in the chain of elastic-dumbbells improves the spectrum to $\tau_n \propto n^{-0.6}$. In linear visco-elasticity, the internal modes are independent, so that one might think of using a spectrum of Oldroyd-B models, each with their own relaxation-time and contribution to the stress. Nonlinear

effects, however, mix the modes, in ways that remain poorly understood. When computing a flow, viscoelastic effects come only from the modes where the product of relaxation time and the velocity gradient is of order unity or higher, so that the dynamics tends to be controlled by the lowest, slowest decaying mode, with the higher (more expensive to compute) modes just contributing to an enhanced viscosity of the solvent.

A known deficiency of the Oldroyd-B fluid is that in a steady pure straining motion, the stress and hence the extensional viscosity diverges to infinity at a finite strain-rate. The elastic-dumbbell model explains what is going wrong, and thereby suggests a small modification to rectify the misbehaviour. In the evolution equation (16) the distortion $\mathbf{r}$ will increase without bound if the strain-rate, measured as the largest eigenvalue of $\boldsymbol{\nabla}\mathbf{u}$, exceeds $1/2\tau$, i.e. the flow is so-called 'strong'. However, there is an obvious limit to the end-to-end length, $|\mathbf{r}|$, that of the contour length of the chain Nb. As $\mathbf{r}$ approaches this maximum length the entropic spring force becomes nonlinear. Whilst it is easy to incorporate a nonlinear spring into equation (16) only a linear spring allows a closed form for the second moment equation (17). Peterlin (1966) [35] limited the distortion by using the inverse Langevin force-law, which he evaluated with the expected (pre-averaged) distortion $r = \sqrt{\mathrm{Tr}(\langle \mathbf{rr} \rangle)}$. Later Bird's student Harold R. Warner (1972) [36] coined the name *Finite-Extensible-Nonlinear-Elastic* (FENE) connector for a spring force $-\kappa\mathbf{r}/(1 - r^2/N^2b^2)$. Following Peterlin's use of the pre-averaged distortion, one has the FENE-P modification of Oldroyd-B

$$\boldsymbol{\sigma} = -p\mathbf{I} + \mu(\boldsymbol{\nabla}\mathbf{u} + \boldsymbol{\nabla}\mathbf{u}^T) + Gf\mathbf{A}, \tag{19}$$

$$\overset{\triangledown}{\mathbf{A}} = \frac{1}{\tau}\left(f\mathbf{A} - \mathbf{I}\right), \tag{20}$$

$$\text{with} \quad f = -\frac{1}{1 - \mathrm{Tr}(\mathbf{A})/L^2}, \tag{21}$$

where $\mathbf{A} = 3\langle \mathbf{rr} \rangle / r_0^2$ and the limiting stretch is now non-dimensionalised by the equilibrium coil size, $L = \sqrt{3}Nb/r_0$. In steady shear flow FENE-P shows some shear-thinning. Chilcott and Rallison (1988) [37] suggested a small modification to equation (20), that gives the FENE-CR model which has a constant steady

viscosity,

$$\overset{\triangledown}{\mathbf{A}} = -\frac{f}{\tau}\left(\mathbf{A}-\mathbf{I}\right). \tag{22}$$

The hydrodynamic stretching is more effective on a nearly fully extended polymer compared with that on the equilibrium coiled state. De Gennes (1974) [38] and independently Hinch (1974) [39] proposed increasing the bead friction appropriately, by increasing the relaxation time from τ to $\tau\sqrt{\mathrm{Tr}(\mathbf{A})}$ in equations (20) and (22). This produces a hysteresis in steady straining flows, in which a much smaller strain-rate is required to maintain full extension compared with the larger strain-rate required to produce the full extension. Such a hysteresis may be useful in turbulent drag reduction. Harlen, Hinch and Rallison (1992) [40] found that the nonlinear bead-friction was needed to explain some birefringence lines seen experimentally in stagnation flows.

Turning to polymer melts, several other modifications of Oldroyd-B are preferred over FENE. Polymer melts show a large shear-thinning, and the Oldroyd-B does not shear-thin. The Oldroyd-B can be made to have some shear-thinning by moving to a Gordon-Schowalter (Johnson-Segalman) time-derivative, which also gives a negative second normal stress difference. Phan Thien and Tanner (1977) [41] studying network models proposed two modification. They replaced the upper convected derivative by a Gordon-Schowalter (Johnson-Segalman) time-derivative to a give a second normal stress difference and included a quadratic term to control the extensional viscosity, giving an equation of the form

$$\overset{\square}{\mathbf{A}} = -\frac{1+\alpha\,\mathrm{Tr}(\mathbf{A})}{\tau}\left(\mathbf{A}-\mathbf{I}\right). \tag{23}$$

Later Phan Thien (1978) [42] proposed an exponential decrease in the relaxation time

$$\overset{\square}{\mathbf{A}} = -\frac{1}{\tau}\exp(\alpha\,\mathrm{Tr}(\mathbf{A}))\cdot\left(\mathbf{A}-\mathbf{I}\right). \tag{24}$$

Using a different reasoning, Giesekus (1982) [43] suggested including a quadratic term to account for the effects of anisotropic drag,

$$\overset{\triangledown}{\mathbf{A}} = -\frac{1}{\tau}(\mathbf{I}+\alpha\mathbf{A})\cdot\left(\mathbf{A}-\mathbf{I}\right). \tag{25}$$

A better fit to experimental data is possible by adopting a spectrum of such modified Oldroyd-Bs, each with a different relaxation time, although computing with a spectrum becomes more expensive. A simpler fix is the White-Metzner (1963) [44] version of Oldroyd-B

$$\boldsymbol{\sigma} + \tau(\dot{\gamma}) \overset{\triangledown}{\boldsymbol{\sigma}} = 2\mu(\dot{\gamma})\mathbf{E}, \quad \text{where} \quad \dot{\gamma} = \sqrt{\tfrac{1}{2}\mathbf{E} : \mathbf{E}}. \tag{26}$$

One can use the experimentally observed shear-thinning viscosity for $\mu(\dot{\gamma})$, and the experimentally observed first normal stress difference $N_1(\dot{\gamma})$ to determine the shear-dependent relaxation time $\tau(\dot{\gamma}) = N_1(\dot{\gamma})/2\mu(\dot{\gamma})\dot{\gamma}^2$.

For polymers with long side-chain branches, which is typical of some industrial polymers such as low density polyethylene, McLeish and Larson (1998) [45] suggested a model based on tube-theory of an idealised branched polymer, the *pom-pom* model in which the backbone sections of chain between branches behave as dumbbells constrained to tubes formed from entanglements with other molecules, giving rise to different relaxation times for stretching and orientation. In the simplified version of the model, the orientation is characterised by a normalised tensor $\mathbf{S}$ calculated from the usual micro-structural part of Oldroyd-B with a relaxation time τ_b

$$\overset{\triangledown}{\mathbf{A}} = -\frac{1}{\tau_b}(\mathbf{A} - \mathbf{I}) \quad \text{and then} \quad \mathbf{S} = \mathbf{A}/\operatorname{Tr}(\mathbf{A}). \tag{27}$$

Given the orientation, a scalar stretch λ is calculated with similar equation with a relaxation time τ_s up to a limit of q to the stretch

$$\frac{D\lambda}{Dt} = \lambda(\boldsymbol{\nabla}\mathbf{u} : \mathbf{S}) - \frac{1}{\tau_s}(\lambda - 1) \quad \text{for} \quad \lambda < q, \tag{28}$$

and then $\lambda = q$ while the above gives $D\lambda/Dt > 0$. The stress is given by

$$\boldsymbol{\sigma} = -p\mathbf{I} + 3G\lambda^2\mathbf{S}. \tag{29}$$

More recently for entangled linear polymers Likhtman and Graham (2003) [46] developed a single mode approximation to their full chain constitutive model that includes three distinct relaxation mechanisms: reptation, retraction and

convective constraint release. Unlike the pom-pom model the *Rolie poly* model uses a single equation to describe the polymer configuration,

$$\overset{\triangledown}{\mathbf{A}} = -\frac{1}{\tau_d}\left(\mathbf{A}-\mathbf{I}\right) - \frac{2(1-\sqrt{3/\operatorname{Tr}(\mathbf{A})})}{\tau_R}\left[\mathbf{A} + \beta\left(\frac{\operatorname{Tr}(\mathbf{A})}{3}\right)^{\delta}\left(\mathbf{A}-\mathbf{I}\right)\right], \qquad (30)$$

where τ_d and τ_R are the relaxation times for reptation and retraction respectively. The parameter β controls the rate of convective constraint release while δ controls how this is suppressed by chain stretch.

References

References

[1] J. G. Oldroyd (1950) *On the Formulation of Rheological Equations of State.* Proc. Royal Soc. **A200**, 523—541.

[2] H. Fröhlich & R. Sack (1946) *Theory of the rheological properties of dispersions.* Proc. Royal Soc. **A185**, 415–430.

[3] F. Boyer, O. Pouliquen & E. Guazzelli (2011) *Dense suspensions in rotating-rod flows: normal stresses and particle migration.* J. Fluid Mech. **686**, 5–25.

[4] W. Lethersich (1942) *The mechanical behaviour of bitumen.* J. Soc. Chem. Ind., Lond., **61**, 101–108.

[5] H. Jeffreys (1929) *The Earth, its origin, history and physical constitution* 2nd ed. (Cambridge University Press).

[6] S. Zaremba (1903) *Remarques sur les travaux de M. Natanson relatifs à la théorie de la viscosité.* Bull Int Acad Sci Cracovie 85–93.

[7] G. Jaumann (1911) *Geschlossenes System physikalischer und chemischer Differentialgesetze.* Sitxber. Akad. Wiss. Wein (Ila) **120**, 385–530.

[8] H. Hencky (1925) *Die Bewegungsgleichungen beim nichtstationären Fliessen plastischer Massen (The equation of motion in the non-stationary deformation of plastic masses).* Z. angew. Math. Mech., **5**, 144–146.

[9] K. Weissenberg (1947) *A continuum theory of rheological phenomena.* Nature **159**, 310–311.

[10] A.S. Lodge (1951) *On the use of convected coordinate systems in the mechanics of continuous media.* Proc. Camb. Phil. Soc., **47**, 575–584.

[11] C. Truesdell (1952) *The mechanical foundations of elasticity and fluid dynamics.* J. Rat. Mech. Anal., **1**, 125–291.

[12] N.J. Balmforth, R.V. Craster and D.R. Hewitt (2021) *Building on Oldroyd's viscoplastic legacy: Perspectives and new developments.* J. Non-Newtonian Fluid Mech. **294**, 104580.

[13] F.D. Murnaghan (1937) *Finite deformations of an elastic solid.* Amer. J. Maths. **59**, 235–260.

[14] J. G. Oldroyd (1953) *The elastic and viscous properties of emulsions and suspensions.* Proc. Royal Soc. **A218**, 122–132.

[15] J. G. Oldroyd (1951) *The motion of a visco-elastic liquid contained between coaxial cylinders 1.* Quart. J. Mech. and Appl. Math. **4**, 271–282.

[16] J. G. Oldroyd (1958) *Non-Newtonian Effects in Steady Motion of Some Idealized Elastico-Viscous Liquids.* Proc. Royal Soc. **A245**, 278–297.

[17] J. G. Oldroyd (1965) *Some steady flows of the general elastico-viscous liquid.* Proc. Royal Soc. **A283**, 115–133.

[18] J. G. Oldroyd (1984) *An approach to non-Newtonian fluid mechanics.* J. Non-Newtonian Fluid Mech. **14**, 9–46.

[19] E.J. Hinch & L.G. Leal (1975) *Constitutive equations in suspension mechanics. Part 1. General formulation.* J. Fluid Mech. **71**, 481-–495.

[20] G.B. Jeffery (1922) *On the motion of ellipsoidal particles in a viscous fluid.* Proc. Royal Soc. **A102**, 161–179.

[21] R.J. Gordon and W.R. Schowalter (1972) *Anisotropic fluid theory: A different approach to the dumbbell theory of dilute polymer solutions.* Trans. Soc. Rheol. **16**, 79—97.

[22] M.W. Johnson, and D. Segalman (1977) *A model for viscoelastic fluid behavior which allows non-affine deformation.* J. Non-Newtonian Fluid Mech. **2**, 255-–270.

[23] J.M. Burgers (1938) in the *Second Report on Viscosity and Plasticity*, chapter 3. Kon. Ned. Akad. Wet. Verhard. **16**, 113– .

[24] A. Peterlin (1938) *The viscosity of dilute solutions and suspensions as a function of particle shape.* Z. Physik **111**, 232–263.

[25] E.J. Hinch & L.G. Leal (1976) *Constitutive equations in suspension mechanics. Part 2. Approximate forms for a suspension of rigid particles affected by Brownian rotations.* J. Fluid Mech. **76**, 187–208.

[26] R. Cerf (1951) *Recherches théoriques et expérimentales sur l'effet Maxwell des solutions de macromolécules déformables - I. — Théorie de l'effet maxwell des suspensions de sphères élastiques.* J. Chim. Phys. **48**, 59–84.

[27] R. Roscoe (1967) *On the rheology of a suspension of viscoelastic spheres in a viscous liquid.* J. Fluid Mech. **28**, 273–293.

[28] D. Barthès-Biesel and A. Acrivos (1973) *Deformation and burst of a liquid droplet freely suspended in a linear shear field.* J. Fluid Mech. **61**, 1–21.

[29] J.M. Rallison (1984) *The deformation of small viscous drops and bubbles in shear flows.* Ann. Rev. Fluid Mech. **16**, 45–66.

[30] R.A. Keiller (1992) *Modelling the extensional flow of the M1 fluids with the Oldroyd equation.* J. Non-Newtonian Fluid Mech. **42**, 49-–64.

[31] W. Kuhn and H. Kuhn (1945) *Bedeutung beschränkt freier Drehbarkeit für die Viskosität und Strömungsdoppelbrechung von Fadenmolekellösungen*

I (Significance of limited free rotation for the viscosity and flow birefringence of thread molecule solutions I). Hel. Chim. Acta **28**, 1533–1579.

[32] P.E. Rouse (1953) *A Theory of the Linear Viscoelastic Properties of Dilute Solutions of Coiling Polymers .* J. Chem. Phys. **21**, 1272-1280.

[33] B.H. Zimm (1956) *Dynamics of Polymer Molecules in Dilute Solution: Viscoelasticity, Flow Birefringence and Dielectric Loss.* J. Chem. Phys. **24**, 269–278.

[34] J.G. Kirkwood and J Riseman (1948) *The Intrinsic Viscosities and Diffusion Constants of Flexible Macromolecules in Solution.* J. Chem. Phys. **16**, 565–573.

[35] A. Peterlin (1966) *Hydrodynamics of linear macromolecules.* Pure Appl. Chem. **12**, 563–586.

[36] H.R. Warner (1972) *Kinetic Theory and Rheology of Dilute Suspensions of Finitely Extendible Dumbbells.* Ind. Eng. Chem. Fundementals **11**, 9–37.

[37] M.D. Chilcott and J.M Rallison (1988) *Creeping flow of dilute polymer solutions past cylinders and spheres.* J. Non-Newtonian Fluid Mech. **29**, 381–432.

[38] P.G. de Gennes (1974) *Coil-stretch transition of dilute flexible polymers under ultrahigh velocity gradients.* J.Chem. Phys. **60**, 5030–5042.

[39] E.J. Hinch (1974) *Mechanical models of dilute polymer solutions for strong flows with large deformations.* in *Polymères et Lubrification*, Colloques Internationaux du CNRS **233**, 241–247.

[40] O.G. Harlen, E.J. Hinch and J.M. Rallison *Birefringent pipes: the steady flow of a dilute polymer solution near a stagnation point.* J. Non-Newtonian Fluid Mech. **44**, 229–265.

[41] N. Phan Thien and R.I. Tanner (1977) *A new constitutive equation derived from network theory.* J. Non-Newtonian Fluid Mech. **2**, 353—365.

[42] N. Phan Thien (1978) *A nonlinear network viscoelastic model.* J. Rheol. **22**, 259–283.

[43] H. Giesekus (1982) *A simple constitutive equation for polymer fluids based on the concept of deformation-dependent tensorial mobility,* J. Non-Newtonian Fluid Mech **11**, 69—109.

[44] J.L. White and A.B. Metzner (1963) *Rheological equations from molecular network theories.* J. App. Poly. Sci. **7**, 1867–1889.

[45] T.C.B. McLeish and R.G. Larson (1998) *Molecular constitutive equations for a class of branched polymers: The pom-pom polymer.* J. Rheol. **42**, 81-–110.

[46] A.E. Likhtman and R. S. Graham (2003) *Simple constitutive equation for linear polymer melts derived from molecular theory: Rolie poly equation.* J. Non-Newtonian Fluid Mech **114**, 1–12.