Electronic Supplementary Material

Biological systems

The behaviour of human red blood cells (RBC's, or erythrocytes) has received much attention [*e.g.* 26, 164, 165, 166]. Usually they are present in a suspension, even if somewhat aggregated [26, 27, 165, 167], although they are reportedly also able to manifest a yield stress [165]. Aggregation of RBC's into rouleaux appears to be reversible, which is consistent with evidence that the interaction is depletion-mediated (at least initially) [26]. However, coagulation into a clot or formation of a thrombus occurs by an entirely different mechanism, in which the RBC's act more like a 'filler' in a fibrin network [26]. Like mammalian cells in general [25], RBC's are highly deformable under load [26, 164, 168], and furthermore will swell or shrivel in response to changes in ionic strength of the carrier fluid [26, 169].

Bacteria are relatively rigid, but the interactions with their environment are very complicated, and still not fully understood [25, 30, 31]. The interactions of bacteria with inorganic surfaces to form biofilms are already complex, being influenced by 'surface heterogeneities'* and ion-permeability of (at least) their outer layer [31]. However, to form a colloidal network this would have to extend to interaction with other bacteria, either in the form of a biofilm or as a volume-spanning network. In either case there are likely to be biologically-driven spatial gradients across the biofilm or network, which in turn result in different localised behaviour by the bacteria [25, 32] — this is something like a 'reacting' system. In fact, bacteria may even actively migrate (or attempt to migrate) under such a gradient in a process known as chemotaxis, giving rise to the term 'active colloid' to describe such species [32], which are a naturally-occurring subset of the 'internally-driven' class of out-of-equilibrium colloids [29]. The other great difficulty is that many bacteria will be either closely or loosely enveloped by a moderately thick 'slime' coating of various polymers [31], meaning that arguably the network *in extremis* could be described as a polymeric gel that just happens to have bacteria embedded in it, without any direct bacteria–bacteria interaction — mechanically akin to sand particles embedded in jelly. Correspondingly, it is reported that the properties of a biofilm are

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* Of course, real inorganic systems, such as mineral systems, also exhibit surface heterogeneities, but of a different character. Surface roughness and asphericity is an issue for mineral systems, but bacteria can have flagella, fimbriæ or fibrils that look like tendrils or hairs extending out from the surface to distances up to the same scale as the cell body [30-32]. In mineral systems surface chemistry depends upon chemical composition and also crystal plane; in bacteria each region of the surface might have a different biological function, and hence different chemistry [30, 31].

typically "determined predominantly" by the extracellular polymeric substances [25]. A final complexity in the case of biofilms is that a biofilm generally extends no more than 1 mm off a surface, and usually much less [25]. One reason for this is the need to supply nutrients (and possibly expel excretions), which may further constrain the viability of a forming a space-filling network of non-negligible size. Aggregates are much less favoured to form in the bulk than at such interfaces [30].

Other relations derived for viscoelastic fluids

Equation 10 implies that at infinitesimally small deformation rates the slight disturbance from equilibrium of the fluid constituents is the same in either steady shear or oscillatory shear [170].

Coleman & Markovitz [154] also derived a companion relation that can be rearranged as [*cf.* 121, 155]

$$\lim_{\dot{\gamma}\to 0} \dot{\gamma}^2 \Psi_1(\dot{\gamma}) = \lim_{\dot{\gamma}\to 0} N_1(\dot{\gamma}) = \lim_{\dot{\gamma}\to 0} -2\tau^2 J_e\,, \tag{18}$$

in which J_e is the linear-elastic (steady-state) shear compliance. However, equation 18 does not seem to be commonly used.

An alternative expression is provided by the empirical 'rule' of Laun [155]:

$$\Psi_1(\dot{\gamma}) \equiv \frac{N_1(\dot{\gamma})}{\dot{\gamma}^2} = 2\frac{G'(\omega)}{\omega^2}\left[1+\left(\frac{G'(\omega)}{G''(\omega)}\right)^2\right]^b\Bigg|_{\omega=\dot{\gamma}}\,. \tag{19}$$

The exponent b was originally set equal to 0.7, although more recently a value of b closer to 0.5 has been recommended [162, 171]. Applying the limit of small deformation rate (in which $G' \ll G''$) would reduce Laun's 'rule' to equation 10.

Other empirical fits for arbitrarily large $\dot{\gamma}$ and ω have been proposed [*e.g.* 98, 172, 173].

Along with the above limits, an analogous equivalence for the zero-shear-rate viscosity is postulated [41, 66]:

$$\lim_{\dot{\gamma}\to 0} \eta(\dot{\gamma}) = \lim_{\omega\to 0} \eta'(\omega) \equiv \lim_{\omega\to 0} \frac{G''(\omega)}{\omega}\,. \tag{20}$$

with η' being the dynamic viscosity. Equation 20 represents a limiting case of the 'Cox–Merz rule' [174]*, which postulates the equivalence of complex viscosity and steady viscosity

* Cox & Merz [174] also proposed a second relation, between 'consistency' and the dynamic viscosity, but this is seldom mentioned.

for all rates or frequencies [41, 66, 162]. For viscoelastic materials the complex viscosity reduces to the dynamic viscosity in the zero-shear limit [66], and the dynamic viscosity is defined in the same way as the steady viscosity in this limit [121]. For materials with a yield stress these justifications do not hold, and an alternative justification is not immediately obvious.

The limits in the above equations typically require vanishingly small $\dot{\gamma}$. While low shear strain rates can be applied to yield-stress materials, these do not necessarily correspond to a low shear stress. In fact, for typical models $\tau \rightarrow \tau_{\mathrm{y}}^{+}$ under these conditions [*cf.* 143]. According to Larson [41], equations 10 and 20 apply for "a viscoelastic "simple liquid" with fading memory", which implies asymptotically Newtonian behaviour as the shear strain rate goes to zero. Yield-stress materials generally do not satisfy this condition.

Features of the constitutive models for yield-stress materials, and extended discussion

Saramito's first model

Features of Saramito's first model include that:

- the elastic response below the yield stress is damped by a viscous contribution (a later publication [175] removed this feature);
- it has four adjustable parameters — plus one further "arbitrary" constant of integration that arises when the differential equations are solved; and
- the strain and strain rate response under oscillatory simple shear flow is not uniquely known.

Saramito's derivation [47] also explicitly includes the adjustable parameter of the Gordon–Schowalter derivative [see 125, 140]. However, Saramito [47] notes that often the parameter is set so as to reduce the derivative to the limiting case of the 'upper-convected' derivative [*cf.* 140].

For relatively large values of the Bingham number, *e.g.* for large values of the threshold stress and/or at small strain amplitudes, it can be shown that the oscillatory response of Saramito's model material obeys the following equation below the critical stress [47]:

$$\frac{N_1}{\tau_{\mathrm{viscous}}} = G'_{\infty}\frac{c-\cos(2t)}{2}, \tag{21}$$

in which τ_{viscous} is a characteristic viscous stress [*cf.* 65], c is an "arbitrary constant", t is time, and G'_{∞} represents the limiting value of the storage modulus when the Bingham number is larger than a critical value. This last criterion can be interpreted as the condition that the shear strain, γ, is less than a certain threshold, and the material response is viscoelastic. (In the limit in which the Bingham number approaches infinity, the material response becomes purely elastic.) It may be expected that the "arbitrary constant" arises due to a dependence upon the initial stress condition of the loaded material [*cf.* 99].

In comparison, the shear stress experienced under the same conditions can be expressed as [47]:

$$\frac{\tau}{\tau_{\text{viscous}}} = G'_{\infty} \sin(t) \,, \tag{22}$$

Model of Doraiswamy et al.

There are several features of the model of Doraiswamy *et al.*:

- there is no viscous damping below the yield stress;
- it has four adjustable parameters that are readily estimated from oscillatory shear measurements;
- the form of the predicted strain and strain rate response under oscillatory simple shear flow is known; and
- the model exhibits a discontinuity in stress at the critical strain [*cf.* 47].

The elastic response is frequency-independent, while the viscous response depends on the imposed frequency, as in **Figure 11**.

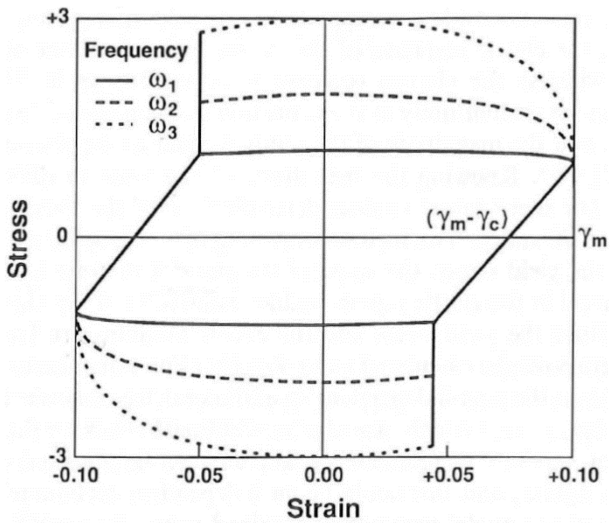

Figure 11: Typical Lissajous plot of dimensionless stress and strain under oscillatory flow at different frequencies ($\omega_1 < \omega_2 < \omega_3$). [Reprinted with permission from Doraiswamy *et al.* [98]. Copyright 1991, The Society of Rheology.]

The oscillatory response of the Doraiswamy *et al.* model material obeys the following equation below the yield stress:

$$N_1 \approx E\,\frac{\gamma_0^{\,2}\cos(2\omega t)}{2}\,, \tag{23}$$

in which E is Young's modulus, and γ_0 is the amplitude of the shear strain. This assumes that the 1,1 element of the upper-convected strain tensor* is the appropriate strain to apply.

For isotropic elastic materials, Young's modulus (the tensile modulus) is related to the shear modulus, G, according to

$$E = 2G(1+\nu)\,, \tag{24}$$

in which is ν Poisson's ratio. The rigorous limits on Poisson's ratio are $-1 \le \nu \le ½$ [176, 177], but commonly the value falls in the range $0 < \nu < ½$ [176], so that $2G \le E \le 3G$. For an incompressible material, conservation of volume requires $\nu = ½$, which gives simply

$$E = 3\,G, \tag{25}$$

which can be inserted into equation 23. However, it must be observed that this is only valid for materials with isotropic properties, whereas the very action of shearing an aggregated, networked suspension can create structures that cause the material properties to become anisotropic.

The elastic shear stress is predicted by

$$\tau \approx G\,\gamma_0 \sin(\omega t)\,. \tag{26}$$

Saramito's second model

Features of Saramito's second model include that:

- the elastic response below the yield stress is damped by a viscous contribution;
- it has five adjustable parameters;
- the strain and strain rate response under oscillatory simple shear flow is not uniquely known; and
- there is no discontinuity in stress at the critical strain.

Again the derivation [65] explicitly includes the adjustable parameter of the Gordon–Schowalter derivative, which is usually set to unity [*cf.* 99].

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* The upper-convected strain tensor is defined in such a way as to neglect strain associated with rigid-body rotations. Given the small shear strains expected for $\tau < \tau_y$ — that is, in the domain $\gamma < \gamma_c$ — the foregoing tensor can safely be taken as approximately equal to the infinitesimal strain tensor, with the 'convected' co-ordinates undergoing negligible rotation [125].

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