Electronic Supplementary Material (ESI) for Soft Matter.

Supplementary Information

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This document contains the supplementary information for the article: "A comprehensive constitutive law for waxy crude oil: A thixotropic yield stress fluid"

1 Effect of rheological aging on G' and G''

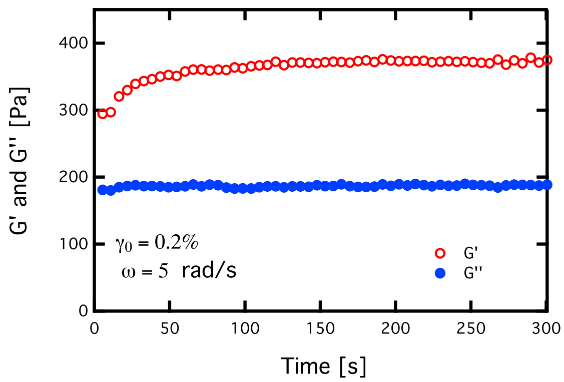

Figure A: G' and G'' in a 10% wax in oil system after shear rejuvenation. The fluid is shear rejuvenated through application of an apparent shear rate of $\hat{\dot{\gamma}} = 50\ \mathrm{s}^{-1}$ shear rate for 5 minutes. As can be seen in the figure, G' and G'' increase by 20% or less after the subsequent cessation of steady shear at $t = 0$.

2 Effect of IKH parameter values on LAOS data fitting

As discussed in the text, the simple model which describes the evolution in the material microstructure through the scalar variable $\lambda(t)$, and the back strain A, captures the correct qualitative form of the Bowditch-Lissajous figures observed in LAOS. To achieve quantitative agreement with experimental data, it is necessary to fine tune the yielding parameter C/q and the modulus k_3. We illustrate the sensitivity of the model predictions to changes in these values using the two illustrative figures below. In Fig. B, we show predictions using the same values of the model parameters as those in Fig. 13 of the manuscript. For comparison, in Fig. C, the values of C/q and $k3$ are changed to 0.85 Pa and 1.5 Pa respectively (note that these are the same values used to fit the model to steady shear data and startup of steady shear in Figs. 11 and 12). Some quantitative differences are apparent between Figs. B and C, however overall the qualitative features of the curves are the same.

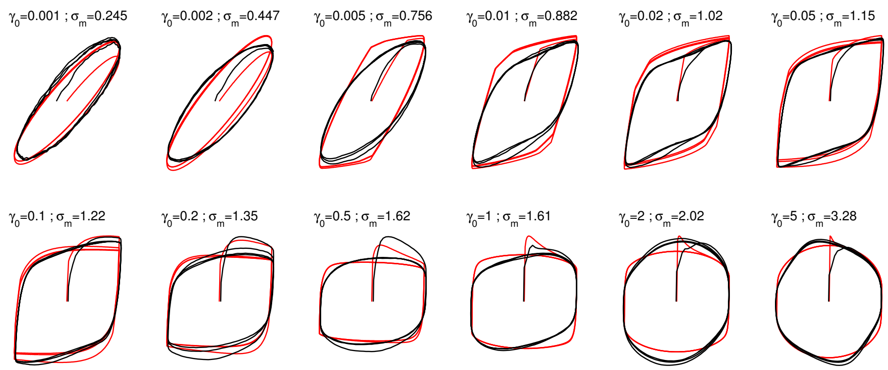

Figure B: Fitting of LAOS data for the model waxy crude oil to the MIKH model. Model parameter values are the same as they are in Fig. 13 of the manuscript ($C/q = 0.7$ Pa, $\mu_p = 0.42$ Pa.s, k_3=0.7 Pa, $k_1/k_2 = 0.033$ s^{-1}, $G = 250$ Pa, $\eta = 500$ Pa.s, $k_1 = 0.1$ s^{-1}, $C = 70$ Pa, $m = 0.25$).

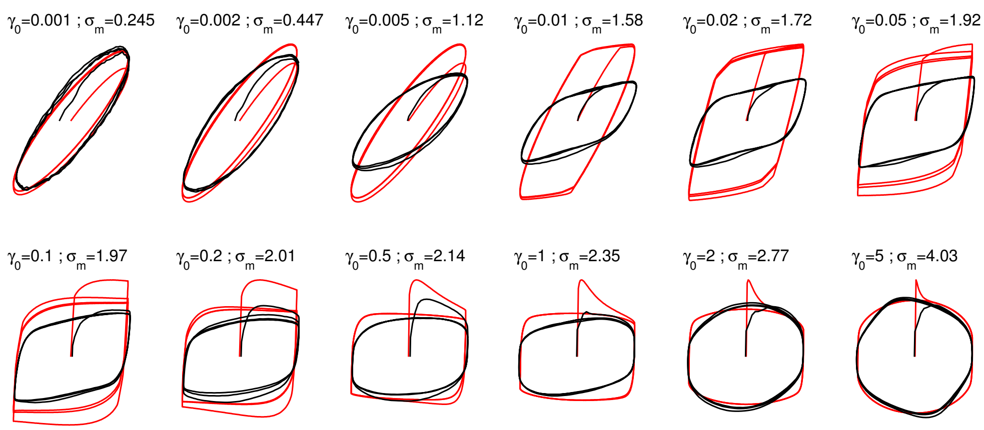

Figure C: Fitting of LAOS data for the model waxy crude oil to the MIKH model. Model parameter values are the same as they are in Fig. 11 and 12 of the manuscript ($C/q = 0.85$ Pa, $\mu_p = 0.42$ Pa.s, k_3=1.5 Pa, $k_1/k_2 = 0.033$ s^{-1}, $G = 250$ Pa, $\eta = 500$ Pa.s, $k_1 = 0.1$ s^{-1}, $C = 70$ Pa, $m = 0.25$).

3 Avalanche effect

In Fig. D below, we illustrate the prediction of delayed yielding (or avalanche effect [1]) predicted by the MIKH model. The response to creep of the model is simulated for three different applied stresses ($\sigma_0 = 1.9$ Pa, $\sigma_0 = 1.96$ Pa, and $\sigma_0 = 2.1$ Pa). For consistency, the values of the model parameters for these simulations are the same as those in Sec. 4.3.2 of the manuscript ($G = 250$ Pa, $\eta = 500$ Pa.s, $\mu_p = 0.42$ Pa.s, $k_1 = 0.1$ s^{-1}, $k_2 = 3$, $k_3 = 1.5$ Pa, $C = 70$ Pa, $q = 82$ and $m = 0.25$).The particular values of the applied stress σ_0 are chosen so that they are just below the static yield stress $\sigma_s \simeq 2$ Pa, just above the static yield stress, and as close to the static yield stress as possible. As is clear from the figure, when $\sigma_0 = 1.96$ Pa, the model predicts an initial slow creeping behavior for the first 1 second, followed by a sudden yielding beyond a critical strain where the shear rate increases dramatically and the material flows

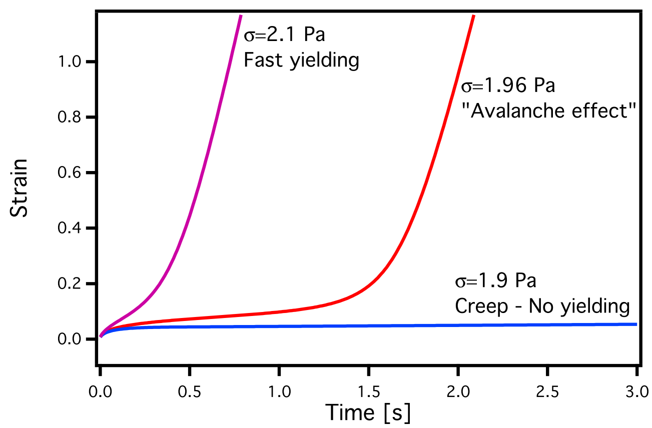

Figure D: Delayed yielding (or avalanche effect) predicted by the MIKH model. Values of the model parameters are the same as those used in Fig. 17 of the manuscript.

4 Three-Dimensional form of the EIKH model

Below we outline a three-dimensional, frame-invariant form of the elastic isostropic-kinematic hardening model (EIKH). This three-dimensional form of the model will be analogous to the 1D model shown in Fig. 10 and described in Sec. 4.1.2, for the case when $m = 1$ (i.e. a linear function in the recovery term of the evolution equation for A) and $\eta \to \infty$ (i.e. purely Hookean elastic response before yielding). The model discussed here is the same as the three-dimensional form of the KH model discussed in the work by Dimitriou et. al. [2] with one key difference: The scalar flow law is modified to include an isotropic yield stress, and this yield stress is a function of the micro structural parameter λ. The nomenclature used here is the same as that of Gurtin et. al. [3].

The model formulation begins by specifying the Kroner decomposition in which the deformation gradient, $\mathbf{F}$, is multiplicatively decomposed into elastic and plastic components, $\mathbf{F}^e$ and $\mathbf{F}^p$ respectively.

$$\mathbf{F} = \mathbf{F}^e\mathbf{F}^p \tag{1}$$

This plays the same role that the additive decomposition of strain plays for the 1-D case. The polar decomposition of the elastic component of the deformation gradient is as follows:

$$\mathbf{F}^e = \mathbf{R}^e\mathbf{U}^e \tag{2}$$

With $\mathbf{R}^e$ representing a rotation and $\mathbf{U}^e$ a stretch. The stretch $\mathbf{U}^e$ has the following spectral representation:

$$\mathbf{U}^e = \sum_{i=1}^{3} \lambda_i^e \mathbf{r}_i^e \otimes \mathbf{r}_i^e \tag{3}$$

Where λ_i^e are the principal values and $\mathbf{r}_i^e$ are the principal directions of $\mathbf{U}^e$. From the stretch $\mathbf{U}^e$ we can therefore define the logarithmic elastic strain (Hencky strain) which is as follows:

$$\mathbf{E}^e \equiv \ln \mathbf{U}^e = \sum_{i=1}^{3} (\ln \lambda_i^e) \mathbf{r}_i^e \otimes \mathbf{r}_i^e \tag{4}$$

The use of the logarithmic elastic strain is typically preferred in order to approximately capture elastic behavior at large strains. In addition to the definition of $\mathbf{E}^e$, we can define the right ($\mathbf{C}^e$) and left ($\mathbf{B}^e$) elastic Cauchy-Green tensors as follows:

$$\mathbf{C}^e = (\mathbf{F}^e)^{\intercal}\mathbf{F}^e \tag{5}$$

$$\mathbf{B}^e = \mathbf{F}^e(\mathbf{F}^e)^{\intercal} \tag{6}$$

The left Cauchy-Green tensor is also sometimes referred to as the Finger tensor.

The plastic velocity gradient $\mathbf{L}^p$ is related to $\mathbf{F}^p$ as follows:

$$\mathbf{L}^p = \dot{\mathbf{F}}^p(\mathbf{F}^p)^{-1} \tag{7}$$

$\mathbf{L}^p$ can be split into its symmetric and skew (antisymmetric) components, such that $\mathbf{L}^p = \mathbf{D}^p + \mathbf{W}^p$. One of the assumptions that goes into this model is that of plastic irrotationality, which assumes $\mathbf{W}^p = 0$, i.e. there is no plastic spin. We can then write the plastic stretching $\mathbf{D}^p$ as a product of its magnitude, $d^p = |\mathbf{D}^p|$, and its direction $\mathbf{N}^p = \mathbf{D}^p/d^p$, so that

$$\mathbf{D}^p = d^p\mathbf{N}^p \tag{8}$$

We next define the free energy Ψ as follows:

$$\Psi = G|\mathbf{E}^e|^2 + \frac{1}{2}\Lambda|\mathrm{tr}\mathbf{E}^e|^2 + \underbrace{\Psi^p(\mathbf{A})}_{\text{defect energy}} \tag{9}$$

Where G is the shear modulus and Λ is an additional material parameter which was not needed for the one-dimensional case of the model. It is related to the bulk modulus K through $K = \Lambda + 2G/3$. The form of the free energy Ψ above results (through differentiation of Ψ with respect to $\mathbf{E}^e$) in the following form for the second Piola elastic stress $\mathbf{T}^e$:

$$\mathbf{T}^e = 2G\mathbf{E}^e + \Lambda\left(\text{tr}\mathbf{E}^e\right)\mathbf{1} \tag{10}$$

Where $\mathbf{T}^e$ is defined as follows:

$$\mathbf{T}^e = J(\mathbf{F}^e)^{-1}\mathbf{T}(\mathbf{F}^e)^{-\intercal} \tag{11}$$

Where $\mathbf{T}$ is the Cauchy stress and $J = \det(\mathbf{F})$.

The form of the free energy equation above in Eq. 9 also introduces a defect energy, Ψ^p, which depends on the tensor $\mathbf{A}$ (which is the three-dimensional generalization of the parameter A. $\mathbf{A}$ is symmetric and unimodular (i.e. $\det(\mathbf{A}) = 1$), and has the following spectral representation:

$$\mathbf{A} = \sum_{i=1}^{3} a_i \mathbf{l}_i \otimes \mathbf{l}_i \tag{12}$$

Where the $\mathbf{l}_i$ are the principal directions of A. The following simple form of Ψ^p is used to model the defect energy:

$$\Psi^p = \frac{1}{4}C\left[(\ln a_1)^2 + (\ln a_2)^2 + (\ln a_3)^2\right] \tag{13}$$

In Eq. 13 the back stress modulus C has been introduced. By differentiation of Ψ^p with respect to $\mathbf{A}$, Eqns 9 and 13 above result in the following equation for the back stress, $\mathbf{M}^e_{\text{back}}$:

$$\mathbf{M}^e_{\text{back}} = C\ln\mathbf{A} \tag{14}$$

The parameter $\mathbf{A}$ is then defined through the following evolution equation:

$$\dot{\mathbf{A}} = \mathbf{D}^p\mathbf{A} + \mathbf{A}\mathbf{D}^p - q\mathbf{A}(\ln\mathbf{A})d^p \tag{15}$$

i.e., the defects in the microstructure are convected by the plastic deformation rate $\mathbf{D}^p$ and also consumed or destroyed by the flow at a rate proportional to the product of the back stress and the current level of defects in the microstructure. Here we introduce the material constant q. The value of the parameter q determines the dynamic recovery of $\mathbf{A}$. The effective stress driving the plastic flow, $\mathbf{M}^e_{\text{eff}}$, is then given by:

$$\mathbf{M}^e_{\text{eff}} = \mathbf{M}^e_0 - \mathbf{M}^e_{\text{back}} \tag{16}$$

Where $\mathbf{M}^e_0$ is the deviatoric Mandel stress, and it is associated with an intermediate "structural" space in the material [3]. The Mandel stress ($\mathbf{M}^e$) is defined as:

$$\mathbf{M}^e = \mathbf{C}^e\mathbf{T}^e \tag{17}$$

With kinematic hardening we assume that the plastic flow $\mathbf{D}^p$ is codirectional with the effective stress $\mathbf{M}^e_{\text{eff}}$, so we have the following additional relation for the direction tensor $\mathbf{N}^p$:

$$\mathbf{N}^p = \frac{\mathbf{M}^e_{\text{eff}}}{|\mathbf{M}^e_{\text{eff}}|} \tag{18}$$

We can then define an equivalent plastic strain rate and equivalent shear stress:

$$\dot{\bar{\gamma}}^p = \sqrt{2}d^p \qquad \text{Equivalent plastic strain rate} \tag{19}$$

$$\bar{\sigma} = \frac{1}{\sqrt{2}}|\mathbf{M}^e_{\text{eff}}| \qquad \text{Equivalent shear stress} \tag{20}$$

Finally, the flow rule is introduced, which gives the relation between the stress $\bar{\sigma}$ and the plastic rate of strain $\dot{\bar{\gamma}}^p$:

$$\dot{\bar{\gamma}}^p = \left(\frac{\bar{\sigma} - \sigma_y}{\mu_p} \right) \tag{21}$$

In the above equation, the isotropic part of the yield stress σ_y has been introduced, which is related to the internal scalar structural parameter λ through $\sigma_y = k_3 \lambda$. The internal scalar parameter λ is then defined through the following evolution equation:

$$\frac{d\lambda}{dt} = k_1 (1 - \lambda) - k_2 \lambda |\dot{\bar{\gamma}}^p| \tag{22}$$

Which is identical to the evolution equation for λ in the 1-dimensional form of the model in the manuscript.

To summarize the three-dimensional form of the EIKH model involves 8 parameters. Two elastic moduli below yield G and Λ, a rate constant k_1 that describes recovery of the internal microstructure variable λ, and a nonlinear coefficient k_2 that describes the flow induced destruction of the isotropic part of the microstructure. The isotropic part of the yield stress is related to the microstructure by a modulus k_3, such that $\sigma_y = k_3 \lambda$. Beyond yield the flow is controlled by the plastic viscosity μ_p. Furthermore, there are the kinematic hardening parameters: the back stress modulus C, and the parameter q which controls the recovery of the back stress.

Finally, for illustrative purposes, the table below compares the analog equations of the one-dimensional and three-dimensional forms of the EIKH model.

	3D EIKH	1D EIKH
Strain decomposition	$\mathbf{F} = \mathbf{F}^e \mathbf{F}^p$	$\gamma = \gamma^e + \gamma^p$
Elastic stress-strain relation	$\mathbf{T}^e = 2G\mathbf{E}^e + \Lambda \left(\mathrm{tr} \mathbf{E}^e \right) \mathbf{1}$	$\sigma = G\gamma^e$
Flow rule	$\mathbf{D}^p = \underbrace{\frac{\dot{\bar{\gamma}}^p}{\sqrt{2}}}_{\text{magnitude}} \underbrace{\frac{\mathbf{M}_0^e - C \ln \mathbf{A}}{\lvert \mathbf{M}_0^e - C \ln \mathbf{A} \rvert}}_{\text{direction}}$	$\dot{\gamma}^p = \lvert\dot{\gamma}^p\rvert \frac{\sigma - CA}{\lvert\sigma - CA\rvert}$
Magnitude of strain rate	$\dot{\bar{\gamma}}^p = \frac{\frac{1}{\sqrt{2}} \lvert \mathbf{M}_0^e - C \ln \mathbf{A} \rvert - k_3 \lambda}{\mu_p}$	$\lvert\dot{\gamma}^p\rvert = \frac{\lvert\sigma - CA\rvert - k_3 \lambda}{\mu_p}$
λ evolution eq.	$\dot{\lambda} = k_1(1 - \lambda) - k_2 \lambda \dot{\bar{\gamma}}^p$	$\dot{\lambda} = k_1(1 - \lambda) - k_2 \lambda \lvert\dot{\gamma}^p\rvert$
$A/\mathbf{A}$ evolution eq.	$\dot{\mathbf{A}} = \mathbf{D}^p \mathbf{A} + \mathbf{A} \mathbf{D}^p - q \mathbf{A} (\ln \mathbf{A}) \frac{\dot{\bar{\gamma}}^p}{\sqrt{2}}$	$\dot{A} = \dot{\gamma}^p - qA\lvert\dot{\gamma}^p\rvert$

References

[1] M. Denn and D. Bonn. Issues in the flow of yield-stress liquids. *Rheologica Acta*, 50:307–315, 2011.

[2] C. J. Dimitriou, R. H. Ewoldt, and G. H. McKinley. Describing and prescribing the constitutive response of yield stress fluids using large amplitude oscillatory shear stress (laostress). *Journal of Rheology*, 57(27):1–44, 2013.

[3] M. Gurtin, E. Fried, and L. Anand. *The Mechanics and Thermodynamics of Continua*. Cambridge, 2010.