On shear-rate dependent relaxation spectra in superposition rheometry: A basis for quantitative comparison/interconversion of orthogonal and parallel superposition moduli

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Abstract and Kinematics

Abstract:

(i) Expressions for determining rate-dependent relaxation spectra directly from parallel superposition rheometry data.
(ii) Expressions to convert from parallel to orthogonal dynamic moduli in a stable manner.
(iii) The real and imaginary parts of $G^*_{||}$ do satisfy the Kramers-Krönig relations.

Kinematics of PSR and OSR:

$$x_1(t) = x_1(t') + [\dot{\gamma}(t - t') + a(e^{i\omega t} - e^{i\omega t'})]x_2(t'),$$
$$x_2(t) = x_2(t'),$$
$$x_3(t) = x_3(t') + b(e^{i\omega t} - e^{i\omega t'})x_2(t'),$$

where $a = \gamma_0$ and $b = 0$ for PSR, whilst for OSR $a = 0$ and $b = \gamma_0$

The subscripts || and $\perp$ serve to distinguish between the superposition.

Linear relaxation spectrum

$$\sigma(t) = \int_{-\infty}^{t} G(t-t')\dot{\gamma}(t')dt' \longrightarrow \sigma(t) = \int_{-\infty}^{t} M(t-t')\gamma(t,t')dt'.$$

Where $G(t)$ denotes the modulus and $M(t)$ the memory function.

$$G(t) = G_e + \int_0^{\infty} H(\tau)e^{-\frac{t}{\tau}}\frac{d\tau}{\tau} = G_e + \mathcal{L}[\tau H(\tau)](t),$$

where L denotes Laplace transformation with respect to the variable τ^{-1} , and G_e is a material constant given by $G_e = \lim_{t\to\infty} G(t).$

$H(\tau)$ is the relaxation spectrum associated with distribution of relaxation times τ.

Similarly, memory function can be written as,

$$M(t) = \int_0^{\infty} \frac{H(\tau)}{\tau}e^{-\frac{t}{\tau}}\frac{d\tau}{\tau} = \mathcal{L}[H(\tau)](t), \longrightarrow H(\tau) = \tau^{-1}\mathcal{L}^{-1}[G(t)](\tau) = \mathcal{L}^{-1}[M(t)](\tau).$$

$$G^*(\omega) = G'(\omega) + iG''(\omega) = G_e + i\omega\int_0^{\infty}[G(t) - G_e]e^{-i\omega t}dt, \longrightarrow$$

$$G'(\omega) - G_e = \int_0^{\infty}\frac{\omega^2\tau^2}{1+\omega^2\tau^2}H(\tau)\frac{d\tau}{\tau} \equiv (\mathcal{T}H)(\omega),$$ → elastic [E]

$$G''(\omega) = \int_0^{\infty}\frac{\omega\tau}{1+\omega^2\tau^2}H(\tau)\frac{d\tau}{\tau} \equiv (\mathcal{S}H)(\omega).$$ → viscous [V]

Superposition rheometry and rate dependent relaxation spectra

Lodge-type constitutive model
$$\boldsymbol{\sigma} = -p\mathbf{I} + \int_{-\infty}^{t} M(t-t', II_{\mathbf{2D}}(t'))(\mathbf{C}^{-1}(t,t') - \mathbf{I})dt',$$

where $C^{-1}(t,t')$ is the relative Finger strain tensor, II_{2D} is the second invariant of the rate of deformation tensor 2**D** at time t'. we define $II_{2D} = \frac{1}{2}tr(2D)^2$.

$$H(\tau, II_{\mathbf{2D}}(t')) = \mathcal{L}^{-1}[M(t-t', II_{\mathbf{2D}}(t'))], \qquad G(t, II_{\mathbf{2D}}(t')) = G_e(\dot{\gamma}) + \mathcal{L}[\tau H(\tau, II_{\mathbf{2D}}(t'))],$$

In steady shear flow, $II_{\mathbf{2D}} = \dot{\gamma}^2,$ With a small amplitude oscillatory shear super imposed, $II_{\mathbf{2D}}(t') = \dot{\gamma}^2 + 2ia\gamma_0\dot{\gamma}\omega e^{i\omega t'} + O(\gamma_0^2)$

where the constant a takes the value $a = 1$ in PSR and $a = 0$ in OSR.

Expanding $H(\tau, II_{2D}(t'))$ about $II_{2D} = \dot{\gamma}^2$

$$H(\tau, II_{\mathbf{2D}}(t')) = H(\tau, \dot{\gamma}^2) + 2ia\gamma_0\dot{\gamma}\omega e^{i\omega t'} \frac{\partial}{\partial \dot{\gamma}^2} H(\tau, \dot{\gamma}^2) + O(\gamma_0^2),$$

where

$$\frac{\partial}{\partial \dot{\gamma}^2} H(\tau, \dot{\gamma}^2) = \left[\frac{\partial}{\partial II_{\mathbf{2D}}} H(\tau, II_{\mathbf{2D}}(t'))\right]_{II_{\mathbf{2D}} = \dot{\gamma}^2}$$

Orthogonal and parallel superposition

Orthogonal superposition:

$$\sigma_{23}(t) = G_{\perp}^{*}(\omega)\gamma_0 e^{i\omega t}$$

$$G_{\perp}'(\omega) - G_e(\dot{\gamma}) = \int_0^{\infty} H(\tau, \dot{\gamma}^2)\frac{\omega^2\tau^2}{1+\omega^2\tau^2}\frac{d\tau}{\tau},$$

$G(\omega, \dot{\gamma}^2)$

$H \equiv H_{\perp}$

$$G_{\perp}''(\omega) = \int_0^{\infty} H(\tau, \dot{\gamma}^2)\frac{\omega\tau}{1+\omega^2\tau^2}\frac{d\tau}{\tau}.$$

Parallel superposition:

$$\sigma_{12}(t) = \dot{\gamma}\eta(\dot{\gamma}) + G_{\parallel}^{*}(\omega)\gamma_0 e^{i\omega t},$$

$$G_{\parallel}'(\omega) = \int_0^{\infty}\left[H(\tau, \dot{\gamma}^2)\frac{\omega^2\tau^2}{1+\omega^2\tau^2} + \frac{4\dot{\gamma}^2\omega^2\tau^2}{(1+\omega^2\tau^2)^2}\frac{\partial}{\partial\dot{\gamma}^2}H(\tau, \dot{\gamma}^2)\right]\frac{d\tau}{\tau},$$

$$G_{\parallel}''(\omega) = \int_0^{\infty}\left[H(\tau, \dot{\gamma}^2)\frac{\omega\tau}{1+\omega^2\tau^2} + \frac{2\dot{\gamma}^2\omega\tau(1-\omega^2\tau^2)}{(1+\omega^2\tau^2)^2}\frac{\partial}{\partial\dot{\gamma}^2}H(\tau, \dot{\gamma}^2)\right]\frac{d\tau}{\tau}.$$

$$\tau\frac{\partial}{\partial\tau}\left(\frac{\omega^2\tau^2}{1+\omega^2\tau^2}\right) = \frac{2\omega^2\tau^2}{(1+\omega^2\tau^2)^2},$$

$$\tau\frac{\partial}{\partial\tau}\left(\frac{\omega\tau}{1+\omega^2\tau^2}\right) = \frac{\omega\tau(1-\omega^2\tau^2)}{(1+\omega^2\tau^2)^2},$$

Parallel superposition

Parallel superposition:

$$U = \frac{\omega^2\tau^2}{1+\omega^2\tau^2}, \qquad V = \frac{\partial}{\partial\dot{\gamma}^2} H(\tau,\dot{\gamma}^2).$$

$G_e(\dot{\gamma}) = \{0\}$

→ may not be true!

$$\int_0^\infty \frac{2\omega^2\tau^2}{(1+\omega^2\tau^2)^2} \frac{\partial}{\partial\dot{\gamma}^2} H(\tau,\dot{\gamma}^2) \frac{d\tau}{\tau} = \int_0^\infty \tau \frac{\partial U}{\partial\tau} V \frac{d\tau}{\tau} = \int_0^\infty \frac{\partial U}{\partial\tau} V \, d\tau.$$

$$\int_0^\infty \frac{\partial U}{\partial\tau} V \, d\tau = [UV]_0^\infty - \int_0^\infty U \frac{\partial V}{\partial\tau} d\tau,$$

$$\int_0^\infty \frac{\partial U}{\partial\tau} V \, d\tau = -\int_0^\infty U\tau \frac{\partial V}{\partial\tau} \frac{d\tau}{\tau},$$

$$\int_0^\infty \frac{2\omega^2\tau^2}{(1+\omega^2\tau^2)^2} \frac{\partial}{\partial\dot{\gamma}^2} H(\tau,\dot{\gamma}^2) \frac{d\tau}{\tau} = -\int_0^\infty \left[\tau \frac{\partial^2}{\partial\tau\partial\dot{\gamma}^2} H(\tau,\dot{\gamma}^2)\right] \frac{\omega^2\tau^2}{1+\omega^2\tau^2} \frac{d\tau}{\tau}$$

Following the same arguments for $G''_{||}$, we obtain $H_{||}$

$$\frac{\partial}{\partial\dot{\gamma}^2} \equiv \frac{\partial^2}{\partial\tau\partial\dot{\gamma}^2}$$

$$G'_{||}(\omega) = \int_0^\infty \left[H(\tau,\dot{\gamma}^2) - 2\dot{\gamma}^2\tau \frac{\partial^2}{\partial\tau\partial\dot{\gamma}^2} H(\tau,\dot{\gamma}^2)\right] \frac{\omega^2\tau^2}{1+\omega^2\tau^2} \frac{d\tau}{\tau},$$

$$G''_{||}(\omega) = \int_0^\infty \left[H(\tau,\dot{\gamma}^2) - 2\dot{\gamma}^2\tau \frac{\partial^2}{\partial\tau\partial\dot{\gamma}^2} H(\tau,\dot{\gamma}^2)\right] \frac{\omega\tau}{1+\omega^2\tau^2} \frac{d\tau}{\tau}.$$

Parallel superposition

Hence,

$$G'_{\parallel}(\omega) = \int_0^\infty H_{\parallel}(\tau, \dot{\gamma}^2)\frac{\omega^2\tau^2}{1+\omega^2\tau^2}\frac{d\tau}{\tau},$$

$$G''_{\parallel}(\omega) = \int_0^\infty H_{\parallel}(\tau, \dot{\gamma}^2)\frac{\omega\tau}{1+\omega^2\tau^2}\frac{d\tau}{\tau},$$

where,

$$\boxed{\underset{\perp}{H}(\tau, \dot{\gamma}^2) - 2\dot{\gamma}^2\tau\frac{\partial^2}{\partial\tau\partial\dot{\gamma}^2}\underset{\perp}{H}(\tau, \dot{\gamma}^2) = H_{\parallel}(\tau, \dot{\gamma}^2)}$$

→ OBR ≡ RSR

$\int H \tau$, dt $d\tau$

$\eta = \int G(s)\, ds$.

Some exact solutions: $0 < \dot{\gamma}_a < \dot{\gamma} < \dot{\gamma}_b < \infty,$

$$H_{\parallel}(\tau, \dot{\gamma}^2) = \lambda H(\tau, 0) + \bar{H}_{\parallel}(\tau, \dot{\gamma}),$$

$$H_{\perp}(\tau, \dot{\gamma}^2) = \lambda H(\tau, 0) + \bar{H}_{\perp}(\tau, \dot{\gamma}), \longrightarrow \eta(\dot{\gamma}) = \int_0^\infty H_{\perp}(\tau, \dot{\gamma}^2)d\tau = \lambda\eta_0 + \bar{\eta}(\dot{\gamma}), \quad \text{where} \quad \bar{\eta}(\dot{\gamma}) = \int_0^\infty \bar{H}_{\perp}(\tau, \dot{\gamma})d\tau,$$

Some exact solutions

$$\eta(\dot\gamma) = \bar\eta(\dot\gamma) + \lambda\eta_0 \geq 0, \quad \dot\gamma_a < \dot\gamma < \dot\gamma_b.$$

If shear thinning: $\bar\eta > 0$

$$\lambda < 1 \quad \text{and} \quad \frac{d}{d\dot\gamma}\bar\eta(\dot\gamma) = \int_0^\infty \frac{\partial \bar H}{\partial \dot\gamma}(\tau,\dot\gamma)d\tau < 0, \quad \dot\gamma_a < \dot\gamma < \dot\gamma_b.$$

On the other hand, if $\bar\eta < 0$, at least one of the inequalities is reversed

$\dot\gamma\tau \Rightarrow$ better

We. no.

$$\boxed{H(\tau,\dot\gamma^2) - 2\dot\gamma^2\tau\frac{\partial^2}{\partial\tau\partial\dot\gamma^2}H(\tau,\dot\gamma^2) = H_\parallel(\tau,\dot\gamma^2)}$$

$$\xrightarrow{\partial/\partial\dot\gamma^2 = (2\dot\gamma)^{-1}\partial/\partial\dot\gamma,} \quad -\bar H_\perp(\tau,\dot\gamma) + \tau\dot\gamma\frac{\partial^2}{\partial\tau\partial\dot\gamma}\bar H_\perp(\tau,\dot\gamma) = -\bar H_\parallel(\tau,\dot\gamma).$$

Introducing $\xi = \tau\dot\gamma^\alpha$ where α is a constant $\longrightarrow$ $\bar H_\perp(\tau,\dot\gamma) = \bar H_\perp(\xi)$, with $\bar H_\parallel(\tau,\dot\gamma) = \bar H_\parallel(\xi)$, $\xi = \tau\dot\gamma^\alpha$.

$$\eta(\dot\gamma) = \lambda\eta_0 + \kappa\dot\gamma^{-\alpha}, \quad \dot\gamma_a < \dot\gamma < \dot\gamma_b, \qquad \kappa = \int_0^\infty \bar H_\perp(\xi)d\xi$$

$$\boxed{H(\tau,\dot\gamma^2) - 2\dot\gamma^2\tau\frac{\partial^2}{\partial\tau\partial\dot\gamma^2}H(\tau,\dot\gamma^2) = H_\parallel(\tau,\dot\gamma^2)} \longrightarrow \boxed{-\bar H_\perp(\xi) + \alpha\xi\bar H_\perp'(\xi) + \alpha\xi^2\bar H_\perp''(\xi) = -\bar H_\parallel(\xi),}$$

$$\bar H_\perp(\xi) = \beta\int^{\ln\xi} \sinh[\beta(\ln x - \ln\xi)]\bar H_\parallel(x)d(\ln x). \qquad \beta = 1/\sqrt{\alpha},$$

Boundary conditions

For viscosity to remain finite, $\bar{H}_{\perp}(0) = 0, \quad \text{and} \quad \lim_{\xi \to \infty} \bar{H}_{\perp}(\xi) = 0.$ The same conditions are asked for $\bar{H}_{||}$ as well.

To ensure regularity,

$$\lim_{\xi \to \infty} \xi \bar{H}'_{\perp}(\xi) = \lim_{\xi \to \infty} \xi^2 \bar{H}''_{\perp}(\xi) = 0.$$

Also, if $\alpha < 0$

$$\boxed{\bar{H}_{\perp}(\xi) = |\beta| \int^{\ln \xi} \sin[|\beta|(\ln \xi - \ln x)] \bar{H}_{||}(x) d(\ln x).}$$

Result: *In a shear-thinning region, $\bar{H}_{||}(\xi)$ must be negative for some values of the relaxation time τ.*

This allows $G'_{||}(\omega)$ to become negative for a certain range of frequencies ω. Differnentiating the above equation gives us

$$\bar{H}'_{\perp}(\xi) = -\beta^2 \xi^{-1} \int^{\ln \xi} \cosh[\beta(\ln x - \ln \xi)] \bar{H}_{||}(x) d(\ln x).$$

always +ve

$\bar{H}_{||} \to$ must?

It is clear that if $\bar{H}_{||}$ is everywhere positive then $\xi \bar{H}_{\perp}{}'(\xi)$ is everywhere negative. Furthermore, either there exists a finite constant c < 0 such that $\xi \bar{H}_{\perp}{}'(\xi) \to c$ as $\xi \to \infty$ or $\xi \bar{H}_{\perp}{}'(\xi) \to -\infty$ as $\xi \to \infty$. Hence the above result follows immediately.

Discrete and semi-discrete response spectra

Let us first examine the spectral representation for $\overline{H}_{\perp}$ resulting from a single constituent mode in $\overline{H}_{||}$. Consider

$$\bar{H}_{\|}(\xi) = c_1\delta(\xi - \xi_1), \quad + \quad \xrightarrow{\tau_1 = \xi_1\dot{\gamma}^{-\alpha}} \quad \bar{H}_{\|}(\xi) = c_1\dot{\gamma}^{-\alpha}\delta(\tau - \tau_1),$$

Solution:

$$\bar{H}_{\perp}(\xi) = -\beta c_1\xi_1^{-1}\sinh[\beta(\ln\xi - \ln\xi_1)]\mathscr{H}(\xi - \xi_1),$$

This does not satisfy all the boundary conditions. $|\overline{H}_{\perp}(\xi)| \rightarrow \infty$ as $\xi \rightarrow \infty$.
Clearly, therefore, the representation of $\overline{H}_{||}$ by a single discrete mode is *not compliant* with a finite shear viscosity. We shall show that this situation can easily be rectified by constructing a triplet of Dirac functions with coefficients whose values alternate in sign.

Definition:

Let ξ_1, ξ_2, ξ_3 be three positive constants with $0 < \xi_1 < \xi_2 < \xi_3$. We define a compliant Dirac triplet as a triplet of the form

$$D(\xi; \xi_1, \xi_2, \xi_3) = c_1\delta(\xi - \xi_1) + c_2\delta(\xi - \xi_2) + c_3\delta(\xi - \xi_3),$$

$$c_1 : c_2 : c_3 = \xi_1 \sinh\left[\beta\ln\left(\frac{\xi_2}{\xi_3}\right)\right] : \xi_2 \sinh\left[\beta\ln\left(\frac{\xi_3}{\xi_1}\right)\right] : \xi_3 \sinh\left[\beta\ln\left(\frac{\xi_1}{\xi_2}\right)\right].$$

Solution for Dirac triplet

Result: The compliant Dirac triplet has a corresponding orthogonal response spectrum $E(\xi;\xi_1,\xi_2,\xi_3)$,

$H_\perp$

$$E(\xi;\xi_1,\xi_2,\xi_3)=\begin{cases}0, & 0\le\xi\le\xi_1,\\ -\beta c_1\xi_1^{-1}\sinh\left[\beta\ln\left(\frac{\xi}{\xi_1}\right)\right], & \xi_1\le\xi\le\xi_2,\\ -\beta\left\{c_1\xi_1^{-1}\sinh\left[\beta\ln\left(\frac{\xi}{\xi_1}\right)\right]+c_2\xi_2^{-1}\sinh\left[\beta\ln\left(\frac{\xi}{\xi_2}\right)\right]\right\}, & \xi_2\le\xi\le\xi_3,\\ 0, & \xi\ge\xi_3.\end{cases}$$

This solution is compliant with all the boundary conditions.

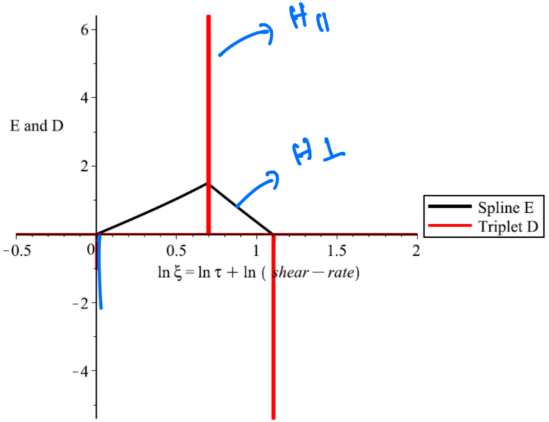


Fig. 1. A compliant Dirac triplet, D, and its corresponding hyperbolic spline, E, with $\beta=1;c_1=-1;(\xi_1,\xi_2,\xi_3)=(1,2,3)$. E is doubled in scale for clarity.

$$H_\perp(\tau,\dot\gamma^2)=\lambda H(\tau,0)+\bar H_\perp(\tau,\dot\gamma).$$

δC

If the linear spectrum $H(\tau,0)$ is represented as a conventional discrete spectrum and the response spectrum $\bar H_{||}(\tau,\dot\gamma)$ is represented by Dirac triplets, then the corresponding spectrum $H_\perp(\tau,\dot\gamma)$ will be semi-discrete, i.e. a combination of the discrete linear spectrum and continuous hyperbolic splines of order 2.

$H_\perp \equiv \delta C$ → discrete

$\bar H$ → continuous

$H_\perp$ = semi

Interconversion of complex moduli

$G_{\parallel} \rightarrow G_{\perp}$

The integral operators T and S introduced earlier have a special property:

$$\left(\mathcal{T}\tau\frac{d}{d\tau}A\right)(\omega) = -\omega\frac{d}{d\omega}(\mathcal{T}A)(\omega) \quad \text{and} \quad \left(\mathcal{S}\tau\frac{d}{d\tau}A\right)(\omega) = -\omega\frac{d}{d\omega}(\mathcal{S}A)(\omega).$$

$\dot{\gamma} \rightarrow x_1$

G' $\quad \omega \rightarrow x_3$ or x_1

$$H_{\perp}(\tau,\dot{\gamma}^2) - \dot{\gamma}\tau\frac{\partial^2}{\partial\tau\partial\dot{\gamma}}H_{\perp}(\tau,\dot{\gamma}^2) = H_{\parallel}(\tau,\dot{\gamma}^2).$$

Applying $T + iS$ on both sides of the above equation and with the use of special property of T and S, we get

$$G^*_{\perp}(\omega) + \cancelto{0}{\dot{\gamma}\omega\frac{\partial^2}{\partial\omega\partial\dot{\gamma}}G^*_{\perp}(\omega)} = G^*_{\parallel}(\omega).$$

Result: Since $\displaystyle \lim_{\omega\to\infty}\omega\frac{\partial^2 G'_{\perp}(\omega)}{\partial\omega\partial\dot{\gamma}} = \lim_{\omega\to\infty}\int_0^{\infty}\frac{2\omega^2\tau^2}{(1+\omega^2\tau^2)^2}\frac{\partial H_{\perp}}{\partial\dot{\gamma}}\frac{d\tau}{\tau} = 0,$ The plateau moduli in OSR and PSR, derived from the Lodge-type model are equal, (i.e.)

$$\lim_{\omega\to\infty}G'_{\perp}(\omega) = \lim_{\omega\to\infty}G'_{\parallel}(\omega), \quad \text{or} \quad G'_{\perp}(\infty) = G'_{\parallel}(\infty).$$

Interconversion of complex moduli

$\zeta = \omega \dot{\gamma}^{-\alpha}$

$$G^*_{\perp}(\omega) = \lambda G^*(\omega) + \bar{G}^*_{\perp}(\zeta),$$

$$G^*_{\parallel}(\omega) = \lambda G^*(\omega) + \bar{G}^*_{\parallel}(\zeta),$$

$$\beta = 1/\sqrt{\alpha},$$

Following the same way we calculated the spectrum for orthogonal spectrum, we obtain the relationship between orthogonal and parallel moduli as,

$$G^*_{\perp}(\omega) = \lambda G^*(\omega) + \bar{G}^*_{\perp}(\zeta_1) + \beta \int_{\ln \zeta_1}^{\ln \zeta} \sinh[\beta(\ln z - \ln \zeta)] \bar{G}^*_{\parallel}(z) d(\ln z).$$

The requirements necessary in the practical implementation of the conversion formula:

(i) the collection of possibly negative parallel moduli, $G^*_{||}(\omega)$;
(ii) the estimation of a low frequency initial value $G^*_{\perp}(\zeta_1)$;
(iii) sufficiently many sampled frequencies to enable the accurate evaluation of the integrals by numerical quadrature; and
(iv) a flow curve to enable the determination of the parameter β.

A spectral representation approach.

→ SAOS

$H(0,\tau)$

$$H_{\parallel}(\tau,\dot\gamma^2) = \lambda \sum_k c_{k0}\delta(\tau-\tau_{k0}) + \sum_k D(\tau\dot\gamma^{\alpha};\xi_{k1},\xi_{k2},\xi_{k3}),$$

$$H_{\perp}(\tau,\dot\gamma^2) = \lambda \sum_k c_{k0}\delta(\tau-\tau_{k0}) + \sum_k E(\tau\dot\gamma^{\alpha};\xi_{k1},\xi_{k2},\xi_{k3}),$$

$H(0,\tau)$

→ $c_{k0}\ \tau_0$

G'_0

$$G'_{\parallel}(\omega) = \lambda G'(\omega) + \bar G'_{\parallel}(\omega\dot\gamma^{-\alpha}),$$

$$= \lambda \sum_k c_{k0}\frac{\omega^2\tau_{k0}}{1+\omega^2\tau_{k0}^2} + \sum_k\sum_{m=1}^{3} c_{km}\frac{\omega^2\xi_{km}}{\dot\gamma^{2\alpha}+\omega^2\xi_{km}^2}, \quad 1$$

$$G''_{\parallel}(\omega) = \lambda G''(\omega) + \bar G''_{\parallel}(\omega\dot\gamma^{-\alpha}),$$

$$= \lambda \sum_k c_{k0}\frac{\omega}{1+\omega^2\tau_{k0}^2} + \dot\gamma^{\alpha}\sum_k\sum_{m=1}^{3} c_{km}\frac{\omega}{\dot\gamma^{2\alpha}+\omega^2\xi_{km}^2}, \quad 2$$

The linear spectrum $\{c_{k0}, \tau_{k0}\}$ has been predetermined from a pure oscillatory shear experiment.

With $\{c_{k0}, \tau_{k0}\}$ predetermined, the remaining constants $\{c_{km}, \tau_{km}\}$ are determined by fitting the models 5.12 and 5.13 to the available PSR experimental data at a fixed shear-rate $\dot\gamma$. The constants c_{k1}, c_{k2}, c_{k3} must be chosen in the ratio as we discussed before, so only one in three of these constants is a free parameter

G' $H\perp$

$$G'_{\perp}(\omega) = \lambda G'(\omega) + \bar G'_{\perp}(\omega\dot\gamma^{-\alpha}),$$

$$= \lambda \sum_k c_{k0}\frac{\omega^2\tau_{k0}}{1+\omega^2\tau_{k0}^2} + \sum_k [\mathcal{T}E(\tau\dot\gamma^{\alpha};\xi_{k1},\xi_{k2},\xi_{k3})](\omega),$$

τE

$''$ $H\perp$

$$G''_{\perp}(\omega) = \lambda G''(\omega) + \bar G''_{\perp}(\omega\dot\gamma^{-\alpha}),$$

$$= \lambda \sum_k c_{k0}\frac{\omega}{1+\omega^2\tau_{k0}^2} + \sum_k [\mathcal{S}E(\tau\dot\gamma^{\alpha};\xi_{k1},\xi_{k2},\xi_{k3})](\omega).$$

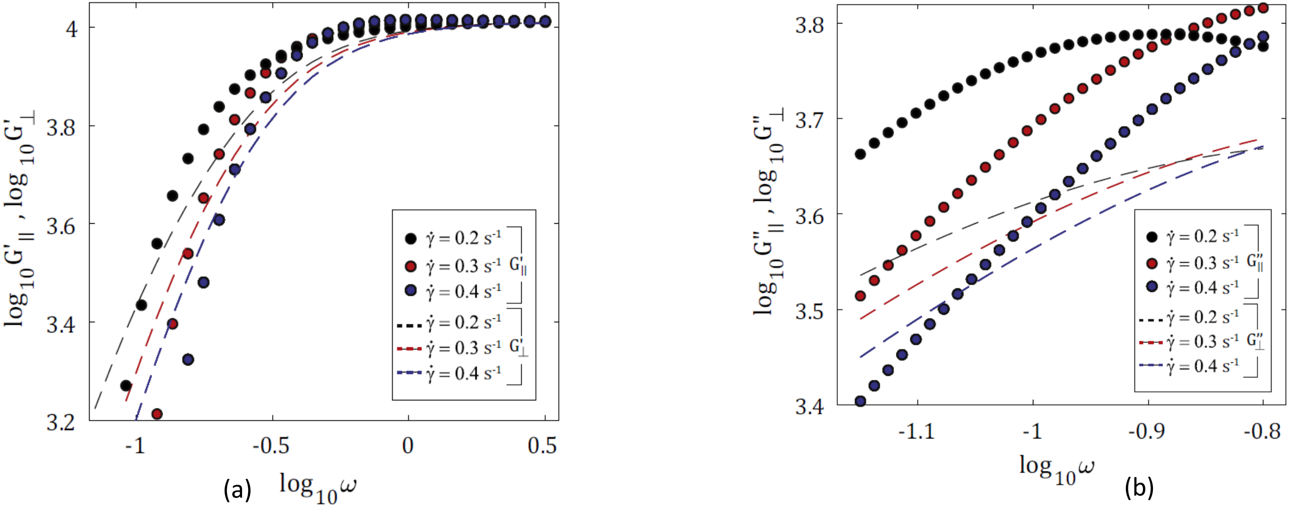
$$\tau = \int H \frac{\omega^2}{1+\omega^2}$$

Model

+ - +

- + -

$$\lambda c_0 = 25000; \tau_0 = 4; \beta = 1; (c_1, c_2, c_3) = (-1, 6.4, -5.4) \times 10^4; \; (\xi_1, \xi_2, \xi_3) = (1, 2, 3)$$



→ Fig. 2 instead

(a) Comparison of $G'_{||}$ and $G'_{\perp}$ for different shear rates. (b) Comparison of $G''_{||}$ and $G''_{\perp}$ for different shear rates.

Thank you

Thank you for your attention