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**THERMODYNAMIC INSTABILITY OF POLYMERIC LIQUIDS
IN LARGE-AMPLITUDE OSCILLATORY SHEAR FLOW
FROM COROTATIONAL MAXWELL FLUID**

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ABSTRACT

When polymeric liquids are subjected to oscillatory shear flow, if the amplitude of the shear rate is high enough, the shear stress response will become aperiodic. This has been variously attributed to fracture, common line ingress, slip, shear-banding and phase change, however, the underlying causes for these is unclear. In this paper we explore the creation of new thermodynamic phases as the trigger for these phenomena. Specifically, we examine two thermodynamic instability criteria that have been suggested for large-amplitude oscillatory shear flow (LAOS). One of these criteria is based on non-equilibrium thermodynamics (the Ziegler criterion), and the other, on equilibrium thermodynamics (the free energy criterion). The advent of exact solutions for stress responses to LAOS provokes this investigation. We use one such exact solution to evaluate these criteria for the simplest relevant constitutive model, the corotational Maxwell fluid. By *relevant*, we mean at least predicting higher harmonics in LAOS. Applying our results to instability measurements on dissolved polybutadiene, we find the Ziegler criterion to be useful at low frequency, and the free energy criterion to be useful elsewhere.

Keywords: Ziegler instability criterion; free energy instability criterion; dissolved polybutadiene; large-amplitude oscillatory shear flow; LAOS.

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I INTRODUCTION

If the shear rate amplitude is sufficiently low, after just a few cycles, the shear stress response of a polymeric liquid to the sudden inception of oscillatory shear flow reaches periodicity, and we call this alternance. The number of cycles to reach alternance can even be estimated approximately from Eq. (112) of [1] or exactly from Eq. (65) of [2]. However, if oscillatory shear experiments are conducted one after another, with increasing shear rate amplitude, one eventually traverses one or more critical conditions for aperiodicity. These aperiodicities have been variously attributed to fracture ([3]; Eq. (7-14) of [4], common line ingress [5,6,7], slip [8,9,10], shear-banding [11,12,13] or to phase change [14,15]. The criteria for aperiodicity are the focus of this investigation.

Conceived in 1935 [16,17,18], oscillatory shear flow, when performed at small amplitude, has become the most popular experiment for exploring the physics of elastic liquids. We generate the velocity field in oscillatory shear flow:

$$\mathbf{v} = [v_x, v_y, v_z] = [\dot{\gamma}^0 y \cos \omega t, 0, 0] \quad (1)$$

by confining the fluid to a simple shear apparatus, and then by subjecting one solid-liquid boundary to a coplanar sinusoidal displacement (see this flow field, and the corresponding coordinate system, illustrated in FIG. 1. of [19]). Hence, the corresponding cosinusoidal shear rate is:

$$\dot{\gamma}(t) = \dot{\gamma}^0 \cos \omega t \quad (2)$$

which can be nondimensionalized, using the fluid relaxation time, λ , to:

$$\begin{aligned} \lambda \dot{\gamma}(t) &= \lambda \dot{\gamma}^0 \cos \lambda \omega (t / \lambda) \\ &\equiv \text{Wi} \cos \text{De}(t / \lambda) \end{aligned} \quad (3)$$

in which the Deborah and Weissenberg numbers are given by:

$$\text{De} \equiv \lambda \omega, \quad \text{Wi} \equiv \lambda \dot{\gamma}^0 \quad (4)$$

where De and Wi are each both functions of the fluid and the flow. Whereas De reflects the amount of elasticity, Wi reflects the amount of nonlinearity. In oscillatory shear flow, elastic liquids respond with both a shear stress, and also two normal stress differences (see Fig. 13 of [20] or Fig. 14 of [21]). For fluency, we gather all dimensional variables in Table I, and dimensionless ones in Table II. We also alert our readers to errata to [14] and [15] in Table III, and other useful errata to cited articles in this paper that we collected in TABLE I of [22].

For polymeric liquids in oscillatory shear flow, when the following condition applies (see Eq. (11) of [22], Figure 14 of [22]):

$$[\text{Wi} > 1] \cap \left[\frac{\text{Wi}}{\text{De}} > 1 \right] \quad (5)$$

higher harmonics in oscillatory stress responses are commonly observed. By *higher harmonics*, we mean the harmonics higher than the first for shear stress response, and the harmonics higher than the second for normal stress differences. Eq. (5) is thus a useful working definition for *large-amplitude oscillatory shear flow* (LAOS).

A few cycles after startup, when the stress waveforms reach *alternance*, we can then represent these stress responses with Fourier series:

$$\frac{\tau_{yx}(\omega, \dot{\gamma}^0, \tau)}{\dot{\gamma}^0} = - \sum_{\substack{n=1 \\ \text{odd}}}^{\infty} \left[\eta'_n(\omega, \dot{\gamma}^0) \cos n\tau + \eta''_n(\omega, \dot{\gamma}^0) \sin n\tau \right] \quad (6)$$

$$\frac{N_1(\omega, \dot{\gamma}^0, \tau)}{(\dot{\gamma}^0)^2} \equiv \frac{\tau_{xx} - \tau_{yy}}{(\dot{\gamma}^0)^2} = - \sum_{\substack{n=0 \\ \text{even}}}^{\infty} \Psi'_{1,n}(\omega, \dot{\gamma}^0) \cos n\tau + \Psi''_{1,n}(\omega, \dot{\gamma}^0) \sin n\tau \quad (7)$$

$$\frac{N_2(\omega, \dot{\gamma}^0, \tau)}{(\dot{\gamma}^0)^2} \equiv \frac{\tau_{yy} - \tau_{zz}}{(\dot{\gamma}^0)^2} = - \sum_{\substack{n=0 \\ \text{even}}}^{\infty} \Psi'_{2,n}(\omega, \dot{\gamma}^0) \cos n\tau + \Psi''_{2,n}(\omega, \dot{\gamma}^0) \sin n\tau \quad (8)$$

where $\tau \equiv \omega t$. By contrast, when the higher harmonics do not appear, the stress responses reduce to (Eq. (64) of [23]; Eqs. (6.39)–(6.44) of [24] and after Ref. 33 of [2]; [25]; APPENDIX B of [26]):

$$\frac{\tau_{yx}(\omega, \dot{\gamma}^0, \tau)}{\dot{\gamma}^0} = - \left[\eta'(\omega) \cos \tau + \eta''(\omega) \sin \tau \right] \quad (9)$$

$$\frac{N_1(\omega, \dot{\gamma}^0, \tau)}{(\dot{\gamma}^0)^2} \equiv \frac{\tau_{xx} - \tau_{yy}}{(\dot{\gamma}^0)^2} = - \left[\Psi_1^d(\omega) + \Psi'_1(\omega) \cos 2\tau + \Psi''_1(\omega) \sin 2\tau \right] \quad (10)$$

$$\frac{N_2(\omega, \dot{\gamma}^0, \tau)}{(\dot{\gamma}^0)^2} \equiv \frac{\tau_{yy} - \tau_{zz}}{(\dot{\gamma}^0)^2} = - \left[\Psi_2^d(\omega) + \Psi'_2(\omega) \cos 2\tau + \Psi''_2(\omega) \sin 2\tau \right] \quad (11)$$

in which $\Psi_1^d \equiv \Psi'_{1,0}$ and $\Psi_2^d \equiv \Psi'_{2,0}$, called the *displacement* coefficients, reflect time averages of the alternant normal stress difference responses.

II THERMODYNAMIC INSTABILITY CRITERIA

We begin with the mechanics of free surface fracture in LAOS, impressively photographed in **Figs. 6.** and **13.** of [27], or Fig. 2. of [28] (see also Section 6.2.1 of [29]) and simulated in [30]. The criterion for the inward propagation of a Mode I fracture of the free surface of an elastic liquid is given by (see Eq. (12) of [3], see also Eq. (7-14) of [4]):

$$|N_2| > \frac{2\Gamma}{3a} \quad (12)$$

where a is the crack tip radius, and Γ , the surface tension between the fluid and air. By Mode I fracture we mean the *crack-opening displacement* mode (see Section 2.2 of [31]). For the fracture of the free surface (of constant spherical radial coordinate $r = R$) of an elastic liquid, loaded into a cone-plate or parallel-disk rheometer, Mode I fracture propagation generates new, topologically distinct, surface of constant θ .

If we improve on Eq. (12) by including fluid inertia, we get (see Eq. (18) of [32]):

$$|N_2| \left(1 - \frac{\text{Re}^2 \eta_0^2 a}{3\rho R^3 |N_2|} \right) > \frac{2\Gamma}{3a} \quad (13)$$

where:

$$\text{Re} \equiv \frac{\rho \Omega R^2}{\eta_0} \quad (14)$$

Simplifying Eq. (13) gives:

$$|N_2| > \frac{2\Gamma}{3a} + \frac{\rho \Omega^2 a R}{3} \quad (15)$$

from which we learn that fluid inertia stabilizes the edge fracture to Mode I propagation. Nondimensionalizing Eq. (15) gives:

$$\frac{a}{\Gamma} |N_2| > \frac{2}{3} \left(1 + \frac{\rho \Omega^2 a^2 R}{2\Gamma} \right) \quad (16)$$

which uncovers the Keentok number:

$$\text{Ke} \equiv \frac{\rho \Omega^2 a^2 R}{2\Gamma} \quad (17)$$

so that:

$$\frac{a}{\Gamma} |N_2| > \frac{2}{3} (1 + \text{Ke}) \quad (18)$$

By contrast with Eq. (12), from elastic energy considerations, Hutton derived and verified it experimentally ([33,34,35]; Eq. (1) of [3]):

$$-N_1 > \frac{k\Gamma}{H} \quad (19)$$

where H is the shear flow gap and k is a dimensionless material constant such that $k\Gamma \approx 0.05 \text{ dynes/cm}$ (Fig. 2. of [33]). For fluids for which $N_2 \propto N_1$, such as the corotational Jeffreys fluid (see Eqs. (64) and (65) of [23], corotational Maxwell fluid (see Eq. (34) of [2]), or the arbitrary normal stress ratio (ANSR) fluid [36], Eq. (19) reduces to Eq. (12).

More recently, edge fracture has been explained by applying perturbation theory to the leading or trailing edges of a parallelepipedal sample in oscillatory sliding plate flow. This study spawned the new criterion for edge fracture (Eq. (8) of [30]):

$$\Delta \tau_{yx} \frac{d|N_2|/d\dot{\gamma}}{d\tau_{yx}/d\dot{\gamma}} > \frac{4\pi\Gamma}{H} \quad (20)$$

where $\Delta \tau_{yx}$ is the jump interface condition between the fluid and the outside air.

Taking the air viscosity as negligible with respect to the polymer, $\Delta \tau_{yx} = \tau_{yx}$, so that:

$$\frac{d|N_2|/d\dot{\gamma}}{d \log \tau_{yx}/d\dot{\gamma}} > \frac{4\pi\Gamma}{H} \quad (21)$$

which can be nondimensionalized to:

$$\frac{H}{4\pi\Gamma} \frac{d|N_2|/d\dot{\gamma}}{d \log \tau_{yx}/d\dot{\gamma}} > 1 \quad (22)$$

Furthermore, if $\tau_{\theta\theta}$ exceeds the critical value for the inward propagation of a Mode III fracture of the free surface of an elastic liquid. By Mode III fracture we mean the *tearing* mode (see Section 2.2 of [31]. For the fracture of the free surface (of constant r) of an elastic liquid, loaded into a cone-plate or parallel-disk rheometer, propagation also generates new, topologically distinct, surface of constant θ . To our knowledge, the criterion for the tearing mode has not been derived.

The simplest criterion for aperiodicity attributed to slip in LAOS is [37]:

$$\tau_{yx} > \tau_c \quad (23)$$

where the critical shear stress, τ_c , is a constant. Thus, the periodicity envelope on a Pipkin diagram (see Figure 12.4 of [38]) corresponds to a contour of constant shear stress amplitude (see Figs. 3. and 4. of [37]).

a Point-Wise

Aperiodicity in LAOS has also been ascribed to *thermodynamic instability*, by which we mean, that the fluid will tend to produce one or more new phases (see Section A.5 of [39]). For aperiodicity in LAOS, two such criteria have been proposed, one from equilibrium thermodynamics (Eq. (13) of [14] or [15]), and another from non-equilibrium (Eq. (10) of [14] or [15]). Recently, the new theory for non-equilibrium has developed to study the flow to capture specifically for no delay feedback control [40].

In this paper, we study the simplest non-equilibrium thermodynamic criterion, called the *Ziegler instability*. This criterion is given by (Eq. (9.5) of [14] or [15]; Eqs. 4.9 of [41]):

$$\frac{\partial D}{\partial \dot{\gamma}^0} \geq \frac{D}{\dot{\gamma}^0}, \quad D < 0 \quad (24)$$

in which D is the *non-equilibrium dissipative function* (see Section 4.1 of [41]), which is defined by (unnumbered equation on the last paragraph of p. 544 of [14]):

$$D \equiv \boldsymbol{\tau} : \dot{\boldsymbol{\gamma}} \quad (25)$$

and which has dimension of M/Lt^3 . For oscillatory shear flow, be it large-amplitude or small-amplitude, Eq. (25) becomes:

$$D = \begin{bmatrix} \tau_{xx} & \tau_{yx} & 0 \\ \tau_{yx} & \tau_{yy} & 0 \\ 0 & 0 & 0 \end{bmatrix} : \begin{bmatrix} 0 & \dot{\gamma}^0 \cos \tau & 0 \\ \dot{\gamma}^0 \cos \tau & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} = 2\tau_{yx} \dot{\gamma}^0 \cos \tau \quad (26)$$

which is true regardless of any fluid constitutive model being used.

In Eq. (25), D is not to be confused with $\boldsymbol{\tau} : \nabla \mathbf{v}$ of the equation of change (see Eqs. (B.8-1)–(B.8-3) of [61,62]), which is used to calculate temperature rise, as in oscillatory shear flow [42,43,44]. We can deepen our understanding of the *Ziegler instability* criterion by rewriting it as:

$$\frac{\partial \log D}{\partial \log \dot{\gamma}^0} \geq 1 \quad (27)$$

from which we learn that, whenever the slope of $\log D$ versus $\log \dot{\gamma}^0$ is too gentle, we can expect the fluid to produce one or more new phases.

By contrast, from equilibrium thermodynamics, we get the *free energy instability* criterion (Eq. (13) of [14]):

$$\frac{\partial^2 F}{(\partial \dot{\gamma}^0)^2} < 0 \quad (28)$$

and which has dimension of L^2/t^2 . The free energy function in Eq. (28) is defined by:

$$F \equiv \frac{\lambda(N_1^2/2 + 2\tau_{yx}^2)}{4\rho\eta_0} \quad (29)$$

The free energy instability criterion applies in tandem with its non-equilibrium counterpart, Eq. (27).

The criteria for aperiodicity in LAOS given by Eqs. (12), (15), (19), (22), (23), (24) and (28) each apply point-wise. By point-wise, we mean at every value of ωt . For oscillatory shear flow, from symmetry, each criterion for aperiodicity can only be satisfied in pair of subintervals $(\omega t_1 + n\pi, \omega t_2 + n\pi)$ where $0 < \omega t_1 < \omega t_2 < \pi$ and $\pi < \omega t_1 + \pi < \omega t_2 + \pi < 2\pi$, and where $n = 0, 1, 2, \dots$ is the half-cycle number. If, for instance, Eqs. (12) or (15) or (19) are satisfied over any pair of subintervals, then, over these subintervals, the edge fracture advances. If Eq. (22) is satisfied over any pair of subintervals, then, over these subintervals, the edge perturbation examined in [30] will grow. If Eq. (23) is satisfied any pair of subintervals, then, over these subintervals, the fluid will slip at the boundary. If either Eqs. (24) or (28) is satisfied any pair of subintervals, then, over these subintervals, the fluid will tend toward producing one or more new phases. Outside the unstable subinterval pairs, the polymer would tend to revert to its stable phases. This reciprocation between stable and unstable phases may or may not be alternant. If not alternant, this phase reciprocation might explain the aperiodic or quasiperiodic responses that have been reported in LAOS [10]. Any production of new unstable phases, if this phase forms one or more less viscous bands, might also lead to shear-banding in oscillatory shear flow. When the phase reciprocation is not alternant, aperiodic shear-banding would result [30].

b Cycle-Average

Instability criteria apply point-wise, but they can also be simplified by averaging over any integer number of cycles [14]. By *simplified*, we mean that ωt is removed from the mathematics.

Cycle-averaging and nondimensionalizing the Ziegler instability criterion, Eq. (24), yields (Eq. (10) of [14]):

$$\frac{\partial \bar{\mathbb{D}}}{\partial \text{Wi}} \geq \frac{\bar{\mathbb{D}}}{\text{Wi}} \quad \text{where} \quad \bar{\mathbb{D}} < 0 \quad (30)$$

in which:

$$\bar{\mathbb{D}} \equiv \frac{1}{2\pi} \int_0^{2\pi} \frac{\lambda^2 D}{\eta_0} d\tau = \frac{\lambda^2 \dot{\gamma}^0}{\eta_0 \pi} \int_0^{2\pi} \tau_{yx} \cos \tau d\tau \quad (31)$$

Eq. (30) can be generalized to multimode fluid as:

$$\sum_{k=1}^{\infty} \bar{D} \equiv \frac{1}{2\pi} \int_0^{2\pi} \sum_{k=1}^{\infty} D^{(k)} d\tau = \frac{\dot{\gamma}^0}{\pi} \int_0^{2\pi} \sum_{k=1}^{\infty} \tau_{yx}^{(k)} \cos \tau d\tau \quad (32)$$

For brevity, for the rest of this paper, we leave out the second condition in Eq. (30), $\bar{D} < 0$, because the dissatisfied ones are not in the scope of this paper.

Cycle-averaging and nondimensionalizing the free energy instability criterion, Eq. (28), yields:

$$\frac{\partial^2 \bar{F}}{\partial Wi^2} < 0 \quad (33)$$

where:

$$\bar{F} \equiv \frac{\rho \lambda \bar{F}}{\eta_0} = \frac{1}{2\pi} \int_0^{2\pi} \frac{\rho \lambda F}{\eta_0} d\tau \quad (34)$$

We consider Eqs. (30) and (33) to be the simplest thermodynamic instability criteria for LAOS.

III COROTATIONAL MAXWELL FLUID

The corotational framework has been studied extensively, both in theory [1,2,19,23] and in its applications [22,45,46,47,48,49]. The simplest special case of this framework is the corotational Maxwell fluid:

$$\boldsymbol{\tau} + \lambda \frac{\mathcal{D}\boldsymbol{\tau}}{\mathcal{D}t} = -\eta_0 \dot{\boldsymbol{\gamma}} \quad (35)$$

where λ is the characteristic time of the fluid, and η_0 is its zero shear viscosity. In Eq. (35) the corotational derivative of the extra stress tensor is:

$$\frac{\mathcal{D}\boldsymbol{\tau}}{\mathcal{D}t} \equiv \frac{D\boldsymbol{\tau}}{Dt} + \frac{1}{2} \{ \boldsymbol{\omega} \cdot \boldsymbol{\tau} - \boldsymbol{\tau} \cdot \boldsymbol{\omega} \} \quad (36)$$

where $D\boldsymbol{\tau}/Dt$ is the substantial derivative (see Eq. 3.5-2ff. of [61]) and:

$$\dot{\boldsymbol{\gamma}} \equiv \nabla \mathbf{v} + (\nabla \mathbf{v})^\dagger, \quad \boldsymbol{\omega} \equiv \nabla \mathbf{v} - (\nabla \mathbf{v})^\dagger \quad (37)$$

are the rate of strain, and vorticity tensors. The corotational derivative measures change with respect to a coordinate frame that both translates and rotates with the fluid element. We find this corotational derivative to be easier to teach and to learn than its codeformational counterparts (compare [51] with [50]). For an extensive discussion of corotational models and their applications, see Chapters 7 and 8 of [51], and also [52,53,54,55,56].

For any simple shear flow (see Eq. (19) of [57]), the rightmost term in Eq. (36) is given by:

$$\frac{1}{2} \{ \boldsymbol{\omega} \cdot \boldsymbol{\tau} - \boldsymbol{\tau} \cdot \boldsymbol{\omega} \} = \frac{1}{2} \begin{bmatrix} -2\tau_{yx} & \tau_{xx} - \tau_{yy} & 0 \\ \tau_{xx} - \tau_{yy} & 2\tau_{yx} & 0 \\ 0 & 0 & 0 \end{bmatrix} \dot{\gamma}_{yx}(t) \quad (38)$$

and with the use of Eq. (1), we can nondimensionalize Eq. (37) as:

$$\lambda \dot{\gamma} = \begin{bmatrix} 0 & \text{WicosDe}(t/\lambda) & 0 \\ \text{WicosDe}(t/\lambda) & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} \quad (39)$$

where De and Wi are the Deborah and Weissenberg numbers. Whereas De reflects the amount of elasticity in both the fluid and the flow, Wi reflects the amount of nonlinearity. Eq. (39) corrects Eq. (8) of [14] for its correction to steady shear flow predictions from Ziegler instability criterion (see Eq. (70)ff.).

In oscillatory shear flow, when $\omega \rightarrow 0$, we get steady shear flow. The shear stress and normal stress difference responses are given by (see Eqs. (4.3–1)–(4.3–3) of [51] with Eqs. (14) and (22) [with Eq. (24)] of [58]):

$$\tau_{yx} = \frac{-\eta_0 \dot{\gamma}}{1 + (\lambda \dot{\gamma})^2}, \quad N_1 = -2N_2 = \frac{-2\eta_0 \lambda (\dot{\gamma})^2}{1 + (\lambda \dot{\gamma})^2} \quad (40),(41)$$

For simplicity, throughout this paper, the second normal stress difference for the corotational Maxwell fluid can be easily evaluated from the first normal stress difference, i.e., $N_2 = -\frac{1}{2}N_1$ (see Eq. (34) of [2]).

In small-amplitude oscillatory shear (SAOS), the stress responses take the form of:

$$\tau_{yx} = -\dot{\gamma}^0 [\eta'(\omega) \cos \tau + \eta''(\omega) \sin \tau] \quad (42)$$

$$N_1 = -(\dot{\gamma}^0)^2 [\Psi_1^d(\omega) + \Psi_1'(\omega) \cos 2\tau + \Psi_1''(\omega) \sin 2\tau] \quad (43)$$

where (Eqs. (17)–(21) of [22] with $\lambda_1 = \lambda$ and $\lambda_2 = 0$):

$$\eta' = \frac{\eta_0}{1 + (\lambda \omega)^2}, \quad \eta'' = \frac{\eta_0 \lambda \omega}{1 + (\lambda \omega)^2} \quad (44)$$

$$\Psi_1^d = \frac{\eta_0 \lambda}{1 + (\lambda \omega)^2}, \quad \Psi_1' = \frac{\eta_0 \lambda (1 - 2(\lambda \omega)^2)}{(1 + (\lambda \omega)^2)(1 + 4(\lambda \omega)^2)}, \quad \Psi_1'' = \frac{3\eta_0 \lambda^2 \omega}{(1 + (\lambda \omega)^2)(1 + 4(\lambda \omega)^2)} \quad (45)$$

If $\dot{\gamma}^0$ is large enough, we call the oscillatory shear flow *large-amplitude*, and the alternant part of the stress responses take the form of Fourier series:

$$\tau_{yx} = -\dot{\gamma}^0 \sum_{n=1}^{\infty} [\eta'_{2n-1}(\omega, \dot{\gamma}^0) \cos(2n-1)\tau + \eta''_{2n-1}(\omega, \dot{\gamma}^0) \sin(2n-1)\tau] \quad (46)$$

$$N_1 = -(\dot{\gamma}^0)^2 \sum_{n=0}^{\infty} [\Psi'_{1,2n}(\omega, \dot{\gamma}^0) \cos 2n\tau + \Psi''_{1,2n}(\omega, \dot{\gamma}^0) \sin 2n\tau] \quad (47)$$

where:

$$\begin{aligned}\tilde{\eta}'_{2n-1} \equiv \frac{\eta'_{2n-1}}{\eta_0} = & -\sum_{p=1}^{n-1} \frac{4(n-p)\text{De} J_{2p-1} J_{2n-2p}}{\text{Wi}(1+4(n-p)^2 \text{De}^2)} + \sum_{k=1}^{\infty} \frac{4k \text{De} J_{2k} J_{2k+2n-1}}{\text{Wi}(1+4k^2 \text{De}^2)} + \frac{J_{2n}(J_2 + J_0)}{1 + \text{De}^2} \\ & + \frac{J_0(J_{2n} + J_{2n-2})}{1 + (2n-1)^2 \text{De}^2} + \sum_{p=1}^{n-1} \frac{J_{2p}(J_{2n-2p} + J_{2n-2p-2})}{1 + (2n-2p-1)^2 \text{De}^2} + \sum_{k=1}^{\infty} \frac{4(k+n-1)\text{De} J_{2k-1} J_{2k+2n-2}}{\text{Wi}(1+4(k+n-1)^2 \text{De}^2)}\end{aligned}\quad (48)$$

$$\begin{aligned}\tilde{\eta}''_{2n-1} \equiv \frac{\eta''_{2n-1}}{\eta_0} = & -\sum_{k=1}^{n-1} \frac{8(n-k)^2 \text{De}^2 J_{2k-1} J_{2n-2k}}{\text{Wi}(1+4(n-k)^2 \text{De}^2)} - \sum_{k=1}^{\infty} \frac{\text{De}(2k+1) J_{2k+2n}(J_{2k+2} + J_{2k})}{1 + (2k+1)^2 \text{De}^2} - \frac{\text{De} J_{2n}(J_2 + J_0)}{1 + \text{De}^2} \\ & + \frac{\text{De}(2n-1) J_0(J_{2n} + J_{2n-2})}{1 + (2n-1)^2 \text{De}^2} + \sum_{k=1}^{\infty} \frac{8(k+n-1)^2 \text{De}^2 J_{2k-1} J_{2k+2n-2}}{\text{Wi}(1+4(k+n-1)^2 \text{De}^2)} - \sum_{k=1}^{\infty} \frac{8k^2 \text{De}^2 J_{2k+2n-1} J_{2k}}{\text{Wi}(1+4k^2 \text{De}^2)} \\ & + \sum_{k=1}^{\infty} \frac{\text{De}(2k+2n-1) J_{2k}(J_{2k+2n} + J_{2k+2n-2})}{1 + (2n+2k-1)^2 \text{De}^2} + \sum_{k=1}^{n-1} \frac{\text{De}(2n-2k-1) J_{2k}(J_{2n-2k} + J_{2n-2k-2})}{1 + (2n-2k-1)^2 \text{De}^2}\end{aligned}\quad (49)$$

$$\tilde{\Psi}'_{1,0} \equiv \frac{\dot{\gamma}^0 \Psi'_{1,0}}{\eta_0} = \sum_{q=1}^{\infty} \frac{16q^2 \text{De}^2 J_{2q}^2}{\text{Wi}(1+4q^2 \text{De}^2)} + \sum_{q=1}^{\infty} \frac{2(2q-1)\text{De} J_{2q-1}(J_{2q} + J_{2q-2})}{1 + (2q-1)^2 \text{De}^2}\quad (50)$$

$$\begin{aligned}\tilde{\Psi}'_{1,2n} \equiv \frac{\dot{\gamma}^0 \Psi'_{1,2n}}{\eta_0} = & \frac{16n^2 \text{De}^2 J_0 J_{2n}}{\text{Wi}(1+4n^2 \text{De}^2)} + \sum_{p=1}^{n-1} \frac{16(n-p)^2 \text{De}^2 J_{2p} J_{2n-2p}}{\text{Wi}(1+4(n-p)^2 \text{De}^2)} + \sum_{q=1}^{\infty} \frac{16(q+n)^2 \text{De}^2 J_{2q} J_{2q+2n}}{\text{Wi}(1+4(q+n)^2 \text{De}^2)} \\ & + \sum_{q=1}^{\infty} \frac{16q^2 \text{De}^2 J_{2q+2n} J_{2q}}{\text{Wi}(1+4q^2 \text{De}^2)} - \sum_{p=1}^n \frac{2\text{De} J_{2p-1}(2n-2p+1)(J_{2n-2p+2} + J_{2n-2p})}{1 + (2n-2p+1)^2 \text{De}^2} \\ & + \sum_{q=1}^{\infty} \frac{2\text{De} J_{2q-1}(2n+2q-1)(J_{2n+2q} + J_{2n+2q-2})}{1 + (2n+2q-1)^2 \text{De}^2} + \sum_{q=1}^{\infty} \frac{2\text{De} J_{2n+2q-1}(2q-1)(J_{2q} + J_{2q-2})}{1 + (2q-1)^2 \text{De}^2}\end{aligned}\quad (51)$$

$$\begin{aligned}\tilde{\Psi}''_{1,2n} \equiv \frac{\dot{\gamma}^0 \Psi''_{1,2n}}{\eta_0} = & -\frac{8n \text{De} J_0 J_{2n}}{\text{Wi}(1+4n^2 \text{De}^2)} - \sum_{p=1}^{n-1} \frac{8(n-p)\text{De} J_{2p} J_{2n-2p}}{\text{Wi}(1+4(n-p)^2 \text{De}^2)} - \sum_{q=1}^{\infty} \frac{8(n+q)\text{De} J_{2q} J_{2n+2q}}{\text{Wi}(1+4(n+q)^2 \text{De}^2)} \\ & + \sum_{q=1}^{\infty} \frac{8q \text{De} J_{2q} J_{2q+2n}}{\text{Wi}(1+4q^2 \text{De}^2)} + \sum_{p=1}^n \frac{2J_{2p-1}(J_{2n-2p+2} + J_{2n-2p})}{1 + (2n-2p+1)^2 \text{De}^2} + \sum_{q=1}^{\infty} \frac{2J_{2n+2q-1}(J_{2q} + J_{2q-2})}{1 + (2q-1)^2 \text{De}^2} \\ & - \sum_{q=1}^{\infty} \frac{2J_{2q-1}(J_{2q+2n} + J_{2q+2n-2})}{1 + (2q+2n-1)^2 \text{De}^2}\end{aligned}\quad (52)$$

The single-mode corotational Maxwell fluid usually succeeds in predicting the qualitative behavior of elastic liquids. However, for accurate prediction of measured behaviors of molten polymers (see Figure 23 of [2]), we must generally generalize to multimode:

$$\tau_{yx}(\omega, \dot{\gamma}^0; t; \eta_0, \lambda) = \sum_k \tau_{yx}^{(k)}(\omega, \dot{\gamma}^0; t; \eta_k, \lambda_k), \quad N_1(\omega, \dot{\gamma}^0; t; \eta_0, \lambda) = \sum_k N_1^{(k)}(\omega, \dot{\gamma}^0; t; \eta_k, \lambda_k) \quad (53)$$

Simply put, all η_0 and λ in the single-mode equations, Eqs. (40), (41), (42), (43), (46) and (47), are replaced by η_k and λ_k . One simple way to generalize to multimode is by using the Spriggs relations (Eqs. (6.1-14) and (6.1-15) of [51]; [59]):

$$\eta_k = \frac{\eta_0 k^{-\alpha}}{\zeta(\alpha)}, \quad \lambda_k = \lambda k^{-\alpha} \quad (54)$$

where $\zeta(\alpha)$ is the Riemann zeta function (see Eq. (6.2-11a) of [51]). When $\alpha \rightarrow \infty$, the Spriggs relations reduce to single-mode, where $\lambda_1 = \lambda$ and where $\lambda_k = 0$ for $k > 1$.

For a multimode fluid in steady shear flow we get:

$$\tau_{yx}^{(k)} = \frac{1}{\zeta(\alpha)} \frac{-k^{-\alpha} \eta_0 \dot{\gamma}}{1 + k^{-2\alpha} (\lambda \dot{\gamma})^2}, \quad N_1^{(k)} = \frac{1}{\zeta(\alpha)} \frac{-2k^{-2\alpha} \eta_0 \lambda (\dot{\gamma})^2}{1 + k^{-2\alpha} (\lambda \dot{\gamma})^2} \quad (55), (56)$$

For a single-mode corotational Maxwell fluid, non-monotonicity of the shear stress arises in steady shear flow (see FIG. 3 of [19]; Eq. (141)ff. of [1]). However, generalizing the stress response as in Eq. (55) pushes the local maximum further away from the origin. We can find the extrema associated with this non-monotonicity by substituting Eq. (55) into Eq. (53), nondimensionalizing, and differentiating to get:

$$\frac{\partial \bar{\tau}_{yx}}{\partial (\lambda \dot{\gamma})} = \frac{1}{\zeta(\alpha)} \sum_{k=1}^{\infty} \frac{k^{\alpha} (\lambda \dot{\gamma})^2 - k^{3\alpha}}{(k^{2\alpha} + (\lambda \dot{\gamma})^2)^2} \quad (57)$$

which we then set to zero:

$$\sum_{k=1}^{\infty} \frac{k^{\alpha} \text{Wi}_e^2 - k^{3\alpha}}{(k^{2\alpha} + \text{Wi}_e^2)^2} = 0 \quad (58)$$

The **red** contour in Figure 1 shows $\text{Wi}_e(\alpha)$ predicted by Eq. (58). We find that, when $\alpha < 3.457$, as is normally the case, our generalization, Eq. (55), eliminates the non-monotonicity.

We next consider SAOS. The shear stress and normal stress difference in SAOS are given by (Eqs. (72) and (73) of [22]):

$$\sum_{k=1}^{\infty} \tau_{yx}^{(k)} = -\frac{\dot{\gamma}^0 \eta_0}{\zeta(\alpha)} \sum_{k=1}^{\infty} \left[\frac{k^{\alpha}}{k^{2\alpha} + (\lambda \omega)^2} \cos \tau + \frac{\lambda \omega}{k^{2\alpha} + (\lambda \omega)^2} \sin \tau \right] \quad (59)$$

$$\sum_{k=1}^{\infty} N_1^{(k)} = -\frac{(\dot{\gamma}^0)^2 \eta_0 \lambda}{\zeta(\alpha)} \sum_{k=1}^{\infty} \left[\frac{1}{k^{2\alpha} + (\lambda \omega)^2} + \frac{(k^{2\alpha} - 2(\lambda \omega)^2) \cos 2\tau + 3k^{\alpha} \lambda \omega \sin 2\tau}{(k^{2\alpha} + (\lambda \omega)^2)(k^{2\alpha} + 4(\lambda \omega)^2)} \right] \quad (60)$$

and finally for LAOS:

$$\sum_{k=1}^{\infty} \tau_{yx}^{(k)} = -\dot{\gamma}^0 \sum_{k=1}^{\infty} \sum_{n=1}^{\infty} \left[\eta_{2n-1}^{(k)}(\omega, \dot{\gamma}^0) \cos(2n-1)\tau + \eta_{2n-1}^{\prime\prime(k)}(\omega, \dot{\gamma}^0) \sin(2n-1)\tau \right] \quad (61)$$

$$\sum_{k=1}^{\infty} N_1^{(k)} = -(\dot{\gamma}^0)^2 \sum_{k=1}^{\infty} \sum_{n=0}^{\infty} \left[\Psi_{1,2n}^{(k)}(\omega, \dot{\gamma}^0) \cos 2n\tau + \Psi_{1,2n}^{\prime\prime(k)}(\omega, \dot{\gamma}^0) \sin 2n\tau \right] \quad (62)$$

where:

$$\tilde{\eta}_{2n-1}^{(k)} = \frac{k^{-\alpha}}{\zeta(\alpha)} \left[-\sum_{p=1}^{n-1} \frac{4(n-p) \text{De} J_{2p-1} J_{2n-2p}}{\text{Wi}(1+4(n-p)^2 k^{-2\alpha} \text{De}^2)} + \sum_{m=1}^{\infty} \frac{4m \text{De} J_{2m} J_{2m+2n-1}}{\text{Wi}(1+4m^2 k^{-2\alpha} \text{De}^2)} + \frac{J_{2n}(J_2 + J_0)}{1+k^{-2\alpha} \text{De}^2} \right. \\ \left. + \sum_{m=1}^{\infty} \frac{4(m+n-1) \text{De} J_{2m-1} J_{2m+2n-2}}{\text{Wi}(1+4(m+n-1)^2 k^{-2\alpha} \text{De}^2)} + \sum_{m=1}^{\infty} \frac{J_{2m}(J_{2m+2n} + J_{2m+2n-2})}{1+(2m+2n-1)^2 k^{-2\alpha} \text{De}^2} \right. \\ \left. + \frac{J_0(J_{2n} + J_{2n-2})}{1+(2n-1)^2 k^{-2\alpha} \text{De}^2} + \sum_{p=1}^{n-1} \frac{J_{2p}(J_{2n-2p} + J_{2n-2p-2})}{1+(2n-2p-1)^2 k^{-2\alpha} \text{De}^2} + \sum_{m=1}^{\infty} \frac{J_{2m+2n}(J_{2m+2} + J_{2m})}{1+(2m+1)^2 k^{-2\alpha} \text{De}^2} \right] \quad (63)$$

$$\tilde{\eta}_{2n-1}^{\prime\prime(k)} = \frac{k^{-\alpha}}{\zeta(\alpha)} \left[\sum_{m=1}^{\infty} \frac{8(m+n-1)^2 k^{-\alpha} \text{De}^2 J_{2m-1} J_{2m+2n-2}}{\text{Wi}(1+4(m+n-1)^2 k^{-2\alpha} \text{De}^2)} - \sum_{p=1}^{n-1} \frac{8(n-p)^2 k^{-\alpha} \text{De}^2 J_{2p-1} J_{2n-2p}}{\text{Wi}(1+4(n-p)^2 k^{-2\alpha} \text{De}^2)} \right. \\ \left. - \sum_{m=1}^{\infty} \frac{8m^2 k^{-\alpha} \text{De}^2 J_{2m+2n-1} J_{2m}}{\text{Wi}(1+4m^2 k^{-2\alpha} \text{De}^2)} + \frac{(2n-1)k^{-\alpha} \text{De} J_0(J_{2n} + J_{2n-2})}{1+(2n-1)^2 k^{-2\alpha} \text{De}^2} - \frac{k^{-\alpha} \text{De} J_{2n}(J_2 + J_0)}{1+k^{-2\alpha} \text{De}^2} \right. \\ \left. + \sum_{p=1}^{n-1} \frac{(2n-2p-1)k^{-\alpha} \text{De} J_{2p}(J_{2n-2p} + J_{2n-2p-2})}{1+(2n-2p-1)^2 k^{-2\alpha} \text{De}^2} - \sum_{m=1}^{\infty} \frac{(2m+1)k^{-\alpha} \text{De} J_{2m+2n}(J_{2m+2} + J_{2m})}{1+(2m+1)^2 k^{-2\alpha} \text{De}^2} \right. \\ \left. + \sum_{m=1}^{\infty} \frac{(2m+2n-1)k^{-\alpha} \text{De} J_{2m}(J_{2m+2n} + J_{2m+2n-2})}{1+(2n+2m-1)^2 k^{-2\alpha} \text{De}^2} \right] \quad (64)$$

$$\tilde{\Psi}_{1,0}^{(k)} = \frac{k^{-\alpha}}{\zeta(\alpha)} \sum_{m=1}^{\infty} \left[\frac{16m^2 k^{-\alpha} \text{De}^2 J_{2m}^2}{\text{Wi}(1+4m^2 k^{-2\alpha} \text{De}^2)} + \frac{2(2m-1)k^{-\alpha} \text{De} J_{2m-1}(J_{2m} + J_{2m-2})}{1+(2m-1)^2 k^{-2\alpha} \text{De}^2} \right] \quad (65)$$

$$\tilde{\Psi}_{1,2n}^{(k)} = \frac{k^{-\alpha}}{\zeta(\alpha)} \left[\frac{16n^2 k^{-\alpha} \text{De}^2 J_0 J_{2n}}{\text{Wi}(1+4n^2 k^{-2\alpha} \text{De}^2)} + \sum_{p=1}^{n-1} \frac{16(n-p)^2 k^{-\alpha} \text{De}^2 J_{2p} J_{2n-2p}}{\text{Wi}(1+4(n-p)^2 k^{-2\alpha} \text{De}^2)} + \sum_{m=1}^{\infty} \frac{16m^2 k^{-\alpha} \text{De}^2 J_{2m+2n} J_{2m}}{\text{Wi}(1+4m^2 k^{-2\alpha} \text{De}^2)} \right. \\ \left. + \sum_{m=1}^{\infty} \frac{16(m+n)^2 k^{-\alpha} \text{De}^2 J_{2m} J_{2m+2n}}{\text{Wi}(1+4(m+n)^2 k^{-2\alpha} \text{De}^2)} - \sum_{p=1}^n \frac{2(2n-2p+1)k^{-\alpha} \text{De} J_{2p-1}(J_{2n-2p+2} + J_{2n-2p})}{1+(2n-2p+1)^2 k^{-2\alpha} \text{De}^2} \right. \\ \left. + \sum_{m=1}^{\infty} \frac{2(2n+2m-1)k^{-\alpha} \text{De} J_{2m-1}(J_{2n+2m} + J_{2n+2m-2})}{1+(2n+2m-1)^2 k^{-2\alpha} \text{De}^2} + \sum_{m=1}^{\infty} \frac{2(2m-1)k^{-\alpha} \text{De} J_{2n+2m-1}(J_{2m} + J_{2m-2})}{1+(2m-1)^2 k^{-2\alpha} \text{De}^2} \right] \quad (66)$$

$$\tilde{\Psi}_{1,2n}^{(k)} = \frac{k^{-\alpha}}{\zeta(\alpha)} \left[-\frac{8n \text{De} J_0 J_{2n}}{\text{Wi}(1+4n^2 k^{-2\alpha} \text{De}^2)} - \sum_{p=1}^{n-1} \frac{8(n-p) \text{De} J_{2p} J_{2n-2p}}{\text{Wi}(1+4(n-p)^2 k^{-2\alpha} \text{De}^2)} + \sum_{m=1}^{\infty} \frac{8m \text{De} J_{2m} J_{2m+2n}}{\text{Wi}(1+4m^2 k^{-2\alpha} \text{De}^2)} \right. \\ \left. - \sum_{m=1}^{\infty} \frac{8(n+m) \text{De} J_{2m} J_{2n+2m}}{\text{Wi}(1+4(n+m)^2 k^{-2\alpha} \text{De}^2)} + \sum_{p=1}^n \frac{2J_{2p-1} (J_{2n-2p+2} + J_{2n-2p})}{1+(2n-2p+1)^2 k^{-2\alpha} \text{De}^2} + \sum_{m=1}^{\infty} \frac{2J_{2n+2m-1} (J_{2m} + J_{2m-2})}{1+(2m-1)^2 k^{-2\alpha} \text{De}^2} \right. \\ \left. - \sum_{m=1}^{\infty} \frac{2J_{2m-1} (J_{2m+2n} + J_{2m+2n-2})}{1+(2m+2n-1)^2 k^{-2\alpha} \text{De}^2} \right] \quad (67)$$

The Spriggs generalization has played an important role in the analyses of polymeric liquids [59]. In Sections IV and V, we will analyze the effect of the Spriggs exponent, α , on the stability of steady shear flow, SAOS and of LAOS.

IV ZIEGLER CRITERION

We deepen our understanding of thermodynamic instability of three kinds of flow: (i) steady shear, (ii) SAOS and (iii) LAOS. We will first use the stress responses given in Section III to study the non-equilibrium thermodynamic criterion, due to Ziegler criterion (Eq. (4.9) of [41]; Eq. (10) of [14]). For each kind of flow, we examine instability for both single-mode fluid and multimode corotational Maxwell fluids.

a Steady Shear

The shear stress response in steady shear flow is given by Eq. (40). Substituting Eq. (2) into Eq. (40), and then the result, into Eq. (31):

$$\bar{\mathbb{D}} = \frac{2}{\sqrt{1+\text{Wi}^2}} - 2 \quad (68)$$

and then differentiating gives:

$$\frac{\partial \bar{\mathbb{D}}}{\partial \text{Wi}} = \frac{-2 \text{Wi}}{(1+\text{Wi}^2)^{3/2}} \quad (69)$$

Substituting Eqs. (69) and (68) into the Ziegler instability criterion, Eq. (30), gives:

$$\text{Wi} \geq \sqrt{\frac{1+\sqrt{5}}{2}} \cong 1.27 \quad (70)$$

from which we learn that, in steady shear flow, the single-mode fluid will become thermodynamically unstable when $\text{Wi} \geq 1.27$. In other words, when $\text{Wi} \geq 1.27$, the fluid will tend to produce one or more new phases. We consider Eq. (70) to be a correction to Burlii's work, which gives $\text{Wi} = 0$ in steady shear flow.

Proceeding with the multimode corotational Maxwell fluid, we substitute Eqs. (3) and (55) into Eq. (32), integrate the result and then nondimensionalize to get:

$$\bar{\mathbb{D}} \equiv \sum_{k=1}^{\infty} \frac{\lambda^2 \bar{D}^{(k)}}{\eta_0} = \frac{-2}{\zeta(\alpha)} \sum_{k=1}^{\infty} \left[k^{\alpha} - \frac{k^{2\alpha}}{\sqrt{k^{2\alpha} + \text{Wi}^2}} \right] \quad (71)$$

Differentiating this:

$$\frac{\partial \bar{\mathbb{D}}}{\partial \text{Wi}} = \frac{-2}{\zeta(\alpha)} \sum_{k=1}^{\infty} \left[\frac{k^{2\alpha} \text{Wi}}{(k^{2\alpha} + \text{Wi}^2)^{3/2}} \right] \quad (72)$$

and then substituting Eqs. (71) and (72) into the Ziegler instability criterion, Eq. (30), gives:

$$\sum_{k=1}^{\infty} \left[\frac{k^{2\alpha} \text{Wi}}{(k^{2\alpha} + \text{Wi}^2)^{3/2}} \right] - \frac{1}{\text{Wi}} \sum_{k=1}^{\infty} \left[k^{\alpha} - \frac{k^{2\alpha}}{\sqrt{k^{2\alpha} + \text{Wi}^2}} \right] \leq 0 \quad (73)$$

Figure 2 to illustrate the thermodynamic stability map implied by Eq. (73).

b SAOS

The shear stress response in SAOS is given by Eq. (42) [with Eq. (44)]. Substituting Eq. (42) into Eq. (31):

$$\bar{\mathbb{D}} = \frac{-\text{Wi}^2}{1 + \text{De}^2} \quad (74)$$

and then differentiating gives:

$$\frac{\partial \bar{\mathbb{D}}}{\partial \text{Wi}} = \frac{-2 \text{Wi}}{1 + \text{De}^2} \quad (75)$$

Substituting Eqs. (74) and (75) into the Ziegler instability criterion, Eq. (30), gives:

$$2 \leq 1 \quad (76)$$

from which we learn that SAOS never satisfies the Ziegler instability criterion, Eq. (30). In other words, SAOS is always thermodynamically stable from the Ziegler perspective.

Proceeding with the multimode corotational Maxwell fluid, we generalize Eq. (74) to get:

$$\bar{D} = \sum_{k=1}^{\infty} \bar{D}^{(k)} = \sum_{k=1}^{\infty} \frac{-\eta_k (\dot{\gamma}^0)^2}{1 + (\lambda_k \omega)^2} \quad (77)$$

Substituting the Spriggs relations, Eq. (54), into Eq. (77), and then nondimensionalizing gives:

$$\bar{\mathbb{D}} = \frac{-1}{\zeta(\alpha)} \sum_{k=1}^{\infty} \frac{k^{\alpha} \text{Wi}^2}{k^{2\alpha} + \text{De}^2} \quad (78)$$

Differentiating Eq. (78), and then substituting the result into the Ziegler instability criterion, Eq. (30), gives:

$$\sum_{k=1}^{\infty} \frac{-k^{\alpha} \text{Wi}}{k^{2\alpha} + \text{De}^2} \geq 0 \quad (79)$$

from which we learn that SAOS never satisfies the Ziegler instability criterion. In other words, SAOS is always thermodynamically stable from the Ziegler perspective, be it single or multimode.

c LAOS

For single-mode corotational Maxwell fluid in LAOS, the shear stress response is given by Eq. (46) [with Eq. (48) and (49)]. We derive the corresponding expression for

non-equilibrium dissipative function for LAOS by substituting Eq. (46) into Eq. (31) to get:

$$\bar{\mathbb{D}} = -Wi^2 \tilde{\eta}'_1 \quad (80)$$

Differentiating Eq. (80), and then nondimensionalizing gives:

$$\frac{\partial \bar{\mathbb{D}}}{\partial Wi} = - \left[Wi^2 \frac{\partial \tilde{\eta}'_1}{\partial Wi} + 2 Wi \tilde{\eta}'_1 \right] \quad (81)$$

where $\tilde{\eta}'_1$ is given by Eq. (48). Substituting Eqs. (80) and (81) into Eq. (30) gives:

$$- Wi \frac{\partial \tilde{\eta}'_1}{\partial Wi} - \tilde{\eta}'_1 \geq 0 \quad (82)$$

where the left side depends only upon De and Wi . Figure 3 explores the behavior of the Ziegler instability criterion in LAOS from the single-mode corotational Maxwell fluid by mapping the left side Eq. (82) onto Pipkin space.

When generalized to multimode, the Ziegler criterion is given by Eq. (32). Substituting Eq. (61) into Eq. (32):

$$\bar{D} = \sum_{k=1}^{\infty} \bar{D}^{(k)} = -(\dot{\gamma}^0)^2 \sum_{k=1}^{\infty} \eta'^{(k)}_1 \quad (83)$$

and nondimensionalizing gives:

$$\bar{\mathbb{D}} \equiv \sum_{k=1}^{\infty} \bar{\mathbb{D}}^{(k)} = -Wi^2 \sum_{k=1}^{\infty} \tilde{\eta}'^{(k)}_1 \quad (84)$$

Differentiating Eq. (84) gives:

$$\frac{\partial \bar{\mathbb{D}}}{\partial Wi} \equiv \sum_{k=1}^{\infty} \frac{\partial \bar{\mathbb{D}}^{(k)}}{\partial Wi} = - \left[Wi^2 \sum_{k=1}^{\infty} \frac{\partial \tilde{\eta}'^{(k)}_1}{\partial Wi} + 2 Wi \sum_{k=1}^{\infty} \tilde{\eta}'^{(k)}_1 \right] \quad (85)$$

Substituting Eqs. (84) and (85) into Eq. (30) then gives:

$$- Wi \sum_{k=1}^{\infty} \frac{\partial \tilde{\eta}'^{(k)}_1}{\partial Wi} - \sum_{k=1}^{\infty} \tilde{\eta}'^{(k)}_1 \geq 0 \quad (86)$$

where the left side depends upon De , Wi and the Spriggs exponent, α . Figure 4 explores the behavior of the Ziegler instability criterion in LAOS from the multimode corotational Maxwell fluid by mapping the left side of Eq. (86) onto Pipkin space.

V FREE ENERGY CRITERION

For the corotational Maxwell fluid, the cycle-average free energy (Eq. (14) of [14]) is given by:

$$\bar{F} \equiv \frac{\lambda}{4\pi\rho\eta_0} \int_0^{2\pi} \left(\tau_{yx}^2 + \frac{N_1^2}{4} \right) d\tau \quad (87)$$

which can be generalized to multimode using the Spriggs relations, Eqs. (54), as:

$$\bar{F} = \sum_{k=1}^{\infty} \bar{F}^{(k)} = \frac{\lambda\zeta(\alpha)}{4\pi\rho\eta_0} \sum_{k=1}^{\infty} \int_0^{2\pi} \left(\tau_{yx}^{(k)2} + \frac{N_1^{(k)2}}{4} \right) d\tau \quad (88)$$

We will use Eq. (87) and (88) in the following subsections to examine thermodynamic instability of three kinds of flow: (i) steady shear, (ii) SAOS and (iii) LAOS.

a Steady Shear

The shear stress and first normal stress difference in steady shear flow are given in Eqs. (40) and (41). Substituting these into Eq. (87):

$$\bar{F} = \frac{\eta_0}{\rho\lambda} \frac{(1 + Wi^2)^{3/2} - Wi^2 - 1}{2(1 + Wi^2)^{3/2}} \quad (89)$$

and then differentiating twice gives:

$$\frac{\partial^2 \bar{F}}{\partial (\dot{\gamma}^0)^2} = \frac{\eta_0 \lambda}{\rho} \frac{1 - 2 Wi^2}{2(1 + Wi^2)^{5/2}} \quad (90)$$

which can be nondimensionalized to:

$$\frac{\partial^2 \bar{F}}{\partial Wi^2} = \frac{1 - 2 Wi^2}{2(1 + Wi^2)^{5/2}} \quad (91)$$

Substituting this into the free energy criterion, Eq. (33), gives:

$$Wi > \sqrt{1/2} \approx 0.7071 \quad (92)$$

which is the region of non-equilibrium thermodynamic instability in steady shear flow for a single-mode fluid.

Substituting Eq. (2) into Eqs. (55) and (56), and then the result, into Eq. (88):

$$\bar{F} = \sum_{k=1}^{\infty} \bar{F}_k = \frac{\eta_0}{2\rho\lambda\zeta(\alpha)} \sum_{k=1}^{\infty} \left[\frac{(1 + k^{-2\alpha} Wi^2)^{3/2} - k^{-2\alpha} Wi^2 - 1}{(1 + k^{-2\alpha} Wi^2)^{3/2}} \right] \quad (93)$$

and then differentiating twice gives:

$$\sum_{k=1}^{\infty} \frac{\partial^2 \bar{F}_k}{\partial Wi^2} = \frac{\eta_0}{2\rho\lambda\zeta(\alpha)} \sum_{k=1}^{\infty} \left[\frac{k^{-2\alpha} (1 - 2k^{-2\alpha} Wi^2)}{(1 + k^{-2\alpha} Wi^2)^{5/2}} \right] \quad (94)$$

Nondimensionalizing:

$$\bar{F} = \sum_{k=1}^{\infty} \frac{\partial^2 \bar{F}_k}{\partial Wi^2} = \frac{1}{2\zeta(\alpha)} \sum_{k=1}^{\infty} \frac{k^{-2\alpha} (1 - 2k^{-2\alpha} Wi^2)}{(1 + k^{-2\alpha} Wi^2)^{5/2}} \quad (95)$$

and substituting this into Eq. (33) yields:

$$\sum_{k=1}^{\infty} \frac{k^{-2\alpha} (1 - 2k^{-2\alpha} Wi^2)}{(1 + k^{-2\alpha} Wi^2)^{5/2}} < 0 \quad (96)$$

which we use to plot Figure 5 to illustrate the effect of the Spriggs exponent, α , on the free energy thermodynamic instability criterion of a multimode fluid in steady shear flow.

b SAOS

The shear stress and normal stress differences in SAOS are given in Eq. (42) and (43) [with Eqs. (44) and (45)]. Substituting Eqs. (42) and (43) into Eq. (87):

$$\bar{F} = \frac{\lambda(\dot{\gamma}^0)^2}{4\rho\eta_0}(\eta'^2 + \eta''^2) + \frac{\lambda(\dot{\gamma}^0)^4}{16\rho\eta_0} \left(2(\Psi_1^d)^2 + (\Psi_1')^2 + (\Psi_1'')^2 \right) \quad (97)$$

and then differentiating twice, substituting the result into Eq. (33) gives:

$$\frac{\partial^2 \bar{F}}{(\partial \dot{\gamma}^0)^2} = \frac{\lambda(\eta'^2 + \eta''^2)}{2\rho\eta_0} + \frac{3\lambda(\dot{\gamma}^0)^2}{4\rho\eta_0} \left[2(\Psi_1^d)^2 + (\Psi_1')^2 + (\Psi_1'')^2 \right] \quad (98)$$

Substituting Eqs. (44) and (45) into Eq. (98), and then nondimensionalizing gives:

$$\frac{\partial^2 \bar{\mathbb{F}}}{\partial \text{Wi}^2} = \frac{1}{2(1 + \text{De}^2)} + \frac{3 \text{Wi}^2 (2 + 5 \text{De}^2)}{4(1 + \text{De}^2)^2 (1 + 4 \text{De}^2)} \quad (99)$$

Substituting this into Eq. (33) then gives:

$$3 \text{Wi}^2 (2 + 5 \text{De}^2) + 2(1 + \text{De}^2)(1 + 4 \text{De}^2) < 0 \quad (100)$$

which is never satisfied. In other words, for the single-mode fluid, SAOS is always thermodynamically stable from the free energy perspective.

When generalized to multimode, the free energy criterion is given by Eq. (88). Substituting Eq. (59) and (60) into Eq. (88).

$$\bar{F} = \frac{\eta_0(\lambda\dot{\gamma}^0)^2}{4\rho\lambda\zeta(\alpha)} \left[\sum_{k=1}^{\infty} \frac{1}{k^{2\alpha} + (\lambda\omega)^2} + \frac{(\lambda\dot{\gamma}^0)^2}{4} \sum_{k=1}^{\infty} \frac{2(k^{2\alpha} + 4(\lambda\omega)^2)^2 + (k^{2\alpha} - 2(\lambda\omega)^2)^2 + 9k^{2\alpha}(\lambda\omega)^2}{(k^{2\alpha} + (\lambda\omega)^2)^2 (k^{2\alpha} + 4(\lambda\omega)^2)^2} \right] \quad (101)$$

and differentiating this twice, and then nondimensionalizing gives:

$$\frac{\partial^2 \bar{\mathbb{F}}}{\partial \text{Wi}^2} = \frac{1}{2\zeta(\alpha)} \sum_{k=1}^{\infty} \frac{1}{k^{2\alpha} + \text{De}^2} + \frac{3 \text{Wi}^2}{4\zeta(\alpha)} \sum_{k=1}^{\infty} \frac{2(k^{2\alpha} + 4 \text{De}^2)^2 + (k^{2\alpha} - 2 \text{De}^2)^2 + 9k^{2\alpha} \text{De}^2}{(k^{2\alpha} + \text{De}^2)^2 (k^{2\alpha} + 4 \text{De}^2)^2} \quad (102)$$

Substituting Eq. (102) into Eq. (33) gives:

$$\sum_{k=1}^{\infty} \frac{1}{k^{2\alpha} + \text{De}^2} + \frac{3 \text{Wi}^2}{2} \sum_{k=1}^{\infty} \frac{2(k^{2\alpha} + 4 \text{De}^2)^2 + (k^{2\alpha} - 2 \text{De}^2)^2 + 9k^{2\alpha} \text{De}^2}{(k^{2\alpha} + \text{De}^2)^2 (k^{2\alpha} + 4 \text{De}^2)^2} < 0 \quad (103)$$

which is never satisfied. Combining the results from Eqs. (100) and (103), we learn that, from the free energy perspective, SAOS is always thermodynamically stable for both single-mode or multimode.

c LAOS

The shear stress and normal stress difference in LAOS are given in Eqs. (46) and (47) [with Eqs. (48)–(52)]. Substituting Eqs. (46) and (47) into Eq. (87):

$$\bar{F} = \frac{\lambda(\dot{\gamma}^0)^2}{4\pi\rho\eta_0} \left[\sum_{n=1}^{\infty} \eta'_{2n-1} \eta'_{2n-1}(\pi) + \sum_{n=1}^{\infty} \eta''_{2n-1} \eta''_{2n-1}(\pi) \right. \\ \left. + \frac{(\dot{\gamma}^0)^2}{4} \left[\Psi_{1,0}'^2(2\pi) + \sum_{n=1}^{\infty} \Psi_{1,2n}' \Psi_{1,2n}'(\pi) + \sum_{n=1}^{\infty} \Psi_{1,2n}'' \Psi_{1,2n}''(\pi) \right] \right] \quad (104)$$

and differentiating twice, and then nondimensionalizing gives:

$$\begin{aligned}
\frac{\partial^2 \bar{\mathbb{F}}}{\partial \text{Wi}^2} = & \frac{\text{Wi}^2}{2} + \frac{1}{2} \left[\check{\Psi}_{1,0} \frac{\partial^2 \check{\Psi}'_{1,0}}{\partial \text{Wi}^2} + \left(\frac{\partial \check{\Psi}'_{1,0}}{\partial \text{Wi}} \right)^2 \right] + \frac{1}{4} \sum_{n=1}^{\infty} \left[\check{\Psi}_{1,2n} \frac{\partial^2 \check{\Psi}'_{1,2n}}{\partial \text{Wi}^2} + \left(\frac{\partial \check{\Psi}'_{1,2n}}{\partial \text{Wi}} \right)^2 \right] \\
& + \frac{1}{4} \sum_{n=1}^{\infty} \left[\check{\Psi}''_{1,2n} \frac{\partial^2 \check{\Psi}''_{1,2n}}{\partial \text{Wi}^2} + \left(\frac{\partial \check{\Psi}''_{1,2n}}{\partial \text{Wi}} \right)^2 \right] \\
& + \text{Wi} \left[2 \sum_{n=1}^{\infty} \check{\eta}'_{2n-1} \frac{\partial \check{\eta}'_{2n-1}}{\partial \text{Wi}} + 2 \sum_{n=1}^{\infty} \check{\eta}''_{2n-1} \frac{\partial \check{\eta}''_{2n-1}}{\partial \text{Wi}} + 2 \check{\Psi}_{1,0} \frac{\partial \check{\Psi}'_{1,0}}{\partial \text{Wi}} + \sum_{n=1}^{\infty} \check{\Psi}_{1,2n} \frac{\partial \check{\Psi}'_{1,2n}}{\partial \text{Wi}} \right. \\
& \left. + \sum_{n=1}^{\infty} \check{\Psi}''_{1,2n} \frac{\partial \check{\Psi}''_{1,2n}}{\partial \text{Wi}} \right] \\
& + \frac{1}{2} \left[\sum_{n=1}^{\infty} \check{\eta}_{2n-1}'^2 + \sum_{n=1}^{\infty} \check{\eta}_{2n-1}''^2 + 3 \check{\Psi}_{1,0}'^2 + \frac{3}{2} \sum_{n=1}^{\infty} \check{\Psi}_{1,2n}'^2 + \frac{3}{2} \sum_{n=1}^{\infty} \check{\Psi}_{1,2n}''^2 \right]
\end{aligned} \tag{105}$$

Substituting this into Eq. (33) gives:

$$\begin{aligned}
& \left[\frac{\text{Wi}^2}{2} + \frac{1}{2} \left[\check{\Psi}_{1,0} \frac{\partial^2 \check{\Psi}'_{1,0}}{\partial \text{Wi}^2} + \left(\frac{\partial \check{\Psi}'_{1,0}}{\partial \text{Wi}} \right)^2 \right] + \frac{1}{4} \sum_{n=1}^{\infty} \left[\check{\Psi}_{1,2n} \frac{\partial^2 \check{\Psi}'_{1,2n}}{\partial \text{Wi}^2} + \left(\frac{\partial \check{\Psi}'_{1,2n}}{\partial \text{Wi}} \right)^2 \right] \right. \\
& \left. + \frac{1}{4} \sum_{n=1}^{\infty} \left[\check{\Psi}''_{1,2n} \frac{\partial^2 \check{\Psi}''_{1,2n}}{\partial \text{Wi}^2} + \left(\frac{\partial \check{\Psi}''_{1,2n}}{\partial \text{Wi}} \right)^2 \right] \right] < 0 \tag{106} \\
& + \text{Wi} \left[2 \sum_{n=1}^{\infty} \check{\eta}'_{2n-1} \frac{\partial \check{\eta}'_{2n-1}}{\partial \text{Wi}} + 2 \sum_{n=1}^{\infty} \check{\eta}''_{2n-1} \frac{\partial \check{\eta}''_{2n-1}}{\partial \text{Wi}} + 2 \check{\Psi}_{1,0} \frac{\partial \check{\Psi}'_{1,0}}{\partial \text{Wi}} + \sum_{n=1}^{\infty} \check{\Psi}_{1,2n} \frac{\partial \check{\Psi}'_{1,2n}}{\partial \text{Wi}} \right. \\
& \left. + \sum_{n=1}^{\infty} \check{\Psi}''_{1,2n} \frac{\partial \check{\Psi}''_{1,2n}}{\partial \text{Wi}} \right] \\
& + \frac{1}{2} \left[\sum_{n=1}^{\infty} \check{\eta}_{2n-1}'^2 + \sum_{n=1}^{\infty} \check{\eta}_{2n-1}''^2 + 3 \check{\Psi}_{1,0}'^2 + \frac{3}{2} \sum_{n=1}^{\infty} \check{\Psi}_{1,2n}'^2 + \frac{3}{2} \sum_{n=1}^{\infty} \check{\Psi}_{1,2n}''^2 \right]
\end{aligned}$$

Figure 6 shows the behavior of the free energy instability in LAOS from the single-mode corotational Maxwell fluid, Eq. (106), mapped onto Pipkin space.

When generalized to multimode, the free energy criterion is given by Eq. (88). Substituting Eq. (61) and (62) into Eq. (88) yields:

$$\begin{aligned} \sum_{k=1}^{\infty} \bar{F}^{(k)} = & \frac{\lambda \zeta(\alpha) (\dot{\gamma}^0)^2}{4\pi\rho\eta_0} \sum_{k=1}^{\infty} \left[\int_0^{2\pi} \left(\sum_{n=1}^{\infty} \left[\eta_{2n-1}^{(k)} \cos(2n-1)\tau + \eta_{2n-1}^{(k)} \sin(2n-1)\tau \right] \right)^2 d\tau \right] \\ & + \frac{\lambda \zeta(\alpha) (\dot{\gamma}^0)^4}{16\pi\rho\eta_0} \sum_{k=1}^{\infty} \left[\int_0^{2\pi} \left(\sum_{n=0}^{\infty} \left[\Psi_{1,2n}^{(k)} \cos 2n\tau + \Psi_{1,2n}^{(k)} \sin 2n\tau \right] \right)^2 d\tau \right] \end{aligned} \quad (107)$$

Next, following our steps to get Eq. (106) for single-mode, we get:

$$\sum_{k=1}^{\infty} \left[\begin{aligned} & \frac{\zeta(\alpha) \text{Wi}^2}{2} + \frac{1}{2} \tilde{\Psi}_{1,0}^{(k)} \frac{\partial^2 \tilde{\Psi}_{1,0}^{(k)}}{\partial \text{Wi}^2} + \frac{1}{2} \left(\frac{\partial \tilde{\Psi}_{1,0}^{(k)}}{\partial \text{Wi}} \right)^2 + \frac{1}{4} \sum_{n=1}^{\infty} \tilde{\Psi}_{1,2n}^{(k)} \frac{\partial^2 \tilde{\Psi}_{1,2n}^{(k)}}{\partial \text{Wi}^2} + \frac{1}{4} \sum_{n=1}^{\infty} \left(\frac{\partial \tilde{\Psi}_{1,2n}^{(k)}}{\partial \text{Wi}} \right)^2 \\ & + \frac{1}{4} \sum_{n=1}^{\infty} \tilde{\Psi}_{1,2n}^{(k)} \frac{\partial^2 \tilde{\Psi}_{1,2n}^{(k)}}{\partial \text{Wi}^2} + \frac{1}{4} \sum_{n=1}^{\infty} \left(\frac{\partial \tilde{\Psi}_{1,2n}^{(k)}}{\partial \text{Wi}} \right)^2 \\ & + \zeta(\alpha) \text{Wi} \left[2 \sum_{n=1}^{\infty} \tilde{\eta}_{2n-1}^{(k)} \frac{\partial \tilde{\eta}_{2n-1}^{(k)}}{\partial \text{Wi}} + 2 \sum_{n=1}^{\infty} \tilde{\eta}_{2n-1}^{(k)} \frac{\partial \tilde{\eta}_{2n-1}^{(k)}}{\partial \text{Wi}} \right. \\ & \quad \left. + \tilde{\Psi}_{1,0}^{(k)} \frac{\partial \tilde{\Psi}_{1,0}^{(k)}}{\partial \text{Wi}} + \frac{1}{2} \sum_{n=1}^{\infty} \tilde{\Psi}_{1,2n}^{(k)} \frac{\partial \tilde{\Psi}_{1,2n}^{(k)}}{\partial \text{Wi}} + \frac{1}{2} \sum_{n=1}^{\infty} \tilde{\Psi}_{1,2n}^{(k)} \frac{\partial \tilde{\Psi}_{1,2n}^{(k)}}{\partial \text{Wi}} \right] \\ & + \frac{\zeta(\alpha)}{2} \left[\sum_{n=1}^{\infty} \tilde{\eta}_{2n-1}^{(k)2} + \sum_{n=1}^{\infty} \tilde{\eta}_{2n-1}^{(k)2} + \frac{1}{2} \tilde{\Psi}_{1,0}^{(k)2} + \frac{1}{4} \sum_{n=1}^{\infty} \tilde{\Psi}_{1,2n}^{(k)2} + \frac{1}{4} \sum_{n=1}^{\infty} \tilde{\Psi}_{1,2n}^{(k)2} \right] \end{aligned} \right] < 0 \quad (108)$$

Figure 7 shows the behavior of the free energy instability in LAOS from the multimode corotational Maxwell fluid, generalized using Spriggs relations, mapped onto Pipkin space [Eq. (108)].

VI DISCUSSION

For the special case of a single-mode fluid ($\alpha \rightarrow \infty$), the system is unstable when $\text{Wi} > \sqrt{(1+\sqrt{5})}/2 \cong 1.272$ from the Ziegler criterion (see Eq. (70) and ordinate of Figure 2). By contrast, the system is unstable when $\text{Wi} > \sqrt{1/2} \cong 0.707$ from the free energy criterion (see Eq. (92) ordinate of Figure 5). Thus, in steady shear flow, we learn that free energy criterion overrides the Ziegler. By *override*, we mean that it happens at the lower shear rate, and thus that it happens first (see **black** and **blue** envelope in Figure 9b).

Proceeding to multimode, from the Ziegler perspective, Figure 2 shows that decreasing the Spriggs exponent, α , stabilizes steady shear flow. The **red** curve in Figure 2 plateaus at $\text{Wi} \cong 1.272$ when $\alpha \rightarrow \infty$ for single-mode, as it should [see Eq. (70)]. This serves as a consistency check on our Eq. (73). Moreover, when $\alpha < 3.711$, as is normally the case for polymeric liquids, we learn that the flow is always thermodynamically stable from the Ziegler perspective. For the free energy criterion, Figure 5 shows that decreasing α destabilizes steady shear flow. The **red** curve in

Figure 5 plateaus at $Wi \cong 0.707$ when $\alpha \rightarrow \infty$ for single-mode, as it should. This serves as a consistency check on our Eq. (96).

In SAOS, we found that the flow is always stable [Eqs. (76) and (103)]. Predictions from both the Ziegler and free energy criteria agree on this, for both single-mode and multimode fluids. These results agree with the experimental observations, since slip, shear-banding and edge-fracture are never observed in SAOS experiment (see for example Fig. 4 of [14]).

Next, using the Ziegler criterion, we analyze the stability of LAOS for the single-mode corotational Maxwell fluid in Figure 3. This figure shows that increasing De stabilizes the flow, which agrees with experimental observation (see for example Fig. 4 of [14]). We also see that when $De < 1$, the instability branch approaches the value for steady shear flow, $Wi \cong 1.272$, as it should. This serves as a consistency check on our Eq. (82).

Next, still using the Ziegler criterion, we analyze the stability of LAOS for the multimode corotational Maxwell fluid, generalized using the Spriggs relations, in Figure 4. From this figure, we learn that decreasing the Spriggs exponent, α , stabilizes LAOS by both shrinking the instability envelope, and by raising its lower branch. In other words, in these two ways, broadening the relaxation time distribution stabilizes LAOS. The unstable envelope almost vanishes when $\alpha = 2$.

Finally, using the free energy criterion, we analyze the stability of LAOS for single-mode corotational Maxwell fluids in Figure 6, and for multimode, in Figure 7. From these two figures, we see that in the nonlinear viscoelastic region, the instability boundary is further from both axes. We also learn that generalizing the fluid using the Spriggs relations shrinks the unstable region on the Pipkin map. In other words, in these two ways, broadening the relaxation time distribution stabilizes LAOS.

We close this subsection with a comment on computational cost. Normally, an exact solution to a set of differential equations gives us a significant advantage in computational cost over a numerical solution, by finite difference for instance. In this paper, we have used exact solutions to calculate derivatives, both first (Ziegler criterion) and second (free energy criterion). Indeed, the advent of the exact solution that we have used is what made this investigation possible. However, Bessel functions appear 42 times in Eqs. (48) and (49), and each of these Bessel functions appears within a summation to infinity. This is why, despite our use of an exact solution, the computational cost of our investigation is not low.

Consider, for instance, our computation of the Ziegler instability envelopes in Figure 4. To minimize our computational cost, we continue k and n in our sums in Eqs. (86)

until $|\bar{\mathbb{D}}^{(\text{end})}/\bar{\mathbb{D}}^{(1)}| < 10^{-15}$. We coded Eq. (86) into MATLAB (Version R2017b) on a Macbook Pro (3.1 GHz Intel Core i7 processor with 16GB 1867 MHz DDR3 memory) employing the OS High Sierra (Version 10.13.3) operating system. For each cell in Figure 4, where $\Delta De = \Delta Wi = 0.1$, we consume roughly 30 seconds of CPU time, and thus, for the whole figure, we consume 12 hours.

Similarly, for our computation of the free energy instability envelopes in Figure 7, to minimize our computational cost, we continue k and n in our sums in Eq. (108) until $|\bar{\mathbb{F}}^{(\text{end})}/\bar{\mathbb{F}}^{(1)}| < 10^{-15}$. We coded Eq. (108) into MATLAB (Version R2017b) on the Macbook Pro. For each cell in Figure 7, where $\Delta De = \Delta Wi = 0.4444$, we consume roughly 15 min

of CPU time, and thus, for the whole figure, we consume 24 hours. The computational cost of the free energy instability criterion is thus twice that of the Ziegler criterion.

VII APPLICATIONS: DISSOLVED POLYBUTADIENE

In this section, we apply both the Ziegler and free energy instability criteria to compare with observations of dissolved polybutadienes (PB) in LAOS by Burlii *et al.* [14]. We begin by fitting the multimode corotational Maxwell fluid, generalized using the Spriggs relations, to SAOS measurements of PB, reported by Vinogradov (see FIG. 1 of [60]). From Eq. (59), we deduce (see also Eqs. (6.2–10) and (6.2–11) of [51]):

$$\frac{\eta'}{\eta_0} = \frac{1}{\zeta(\alpha)} \sum_{k=1}^{\infty} \frac{k^\alpha}{k^{2\alpha} + (\lambda\omega)^2}; \quad \frac{\eta''}{\eta_0} = \frac{1}{\zeta(\alpha)} \sum_{k=1}^{\infty} \frac{\lambda\omega}{k^{2\alpha} + (\lambda\omega)^2} \quad (109)$$

From the model fitting, illustrated in Figure 8a, we get: $\lambda = 0.350\text{ s}$, $\eta_0 = 1.87 \times 10^6 \text{ Pa}\cdot\text{s}$ and $\alpha = 4.00$. Using these fitted parameters in our main results for multimode fluids, Eq. (86) for Ziegler, and Eq. (108) for free energy instability criteria, we identify the instability regions in Pipkin space. From Figure 9a, we learn that the Ziegler instability criterion agrees qualitatively with the reported values by Burlii *et al.* (see Fig. 4 of [14]) for low to moderate ranges of De . From Figure 9a, we also learn that the ranges of moderate to high Wi are covered by the free energy instability criterion. Although we find η' and η'' to be fit accurately with multimode (Figure 8a), Figure 9a shows the instability predictions to be inaccurate for multimode. In Figure 9a, near $(De, Wi) = (0, 6)$, we identify the second islet of thermodynamic instability well above the first, from the Ziegler perspective.

Just for completeness, we illustrated the predictions from the single-mode corotational Maxwell fluid ($\alpha \rightarrow \infty$). For this, we start over again using $\lambda = 0.350\text{ s}$, $\eta_0 = 1.87 \times 10^6 \text{ Pa}\cdot\text{s}$ in our main results for single-mode fluids, Eq. (82) for Ziegler, and Eq. (106) for free energy instability criteria. From Figure 9b, we learn that the Ziegler instability criterion covers qualitatively all ranges of De , be they low, moderate or high. From Figure 9b, we also learn that the ranges of moderate to high Wi are still covered by the free energy instability criterion.

Thus, surprisingly, although we find η' and η'' to be fit more accurately with multimode (compare Figure 8a with Figure 8b), we find that the stability of LAOS is governed by the longest relaxation time, $\lambda = \lambda_1$ (compare Figure 9a with Figure 9b). We consider this to be the main finding of this work.

VIII CONCLUSION

In this work, we study the thermodynamic instability of single-mode (Eq. (82) for Ziegler, and Eq. (106) for free energy) and multimode (Eq. (86) for Ziegler, and Eq. (108) for free energy) corotational Maxwell fluids. We arrive at the latter by generalizing the single-mode fluid using the Spriggs relations. We consider cycle-average non-equilibrium and equilibrium instability criteria, both Ziegler and free energy. We discover that, be it single or multimode, SAOS is always stable. We also discover that, when the fluid is generalized using the Spriggs relations, the unstable region in Pipkin space shrinks. This is true for both steady shear flow and LAOS. Surprisingly, we find that the stability of LAOS is predicted much more accurately by just considering the single-mode corotational Maxwell fluid. In other words, the thermodynamic stability of

LAOS appears to be governed by the stability of the portion of the fluid contributing to the longest relaxation time, $\lambda = \lambda_1$. Our theories agree qualitatively with the experimental LAOS instability measurements of dissolved PB reported by Burlii *et al.* [14].

We close our conclusion with remarks on discrepancies between the predictions from two theories, Ziegler and free energy instability criteria, and the reported values by Burlii *et al* [14] in Section VII. Specifically, we find our theory to overpredict the stability of LAOS (see Figure 9). We attribute this overprediction to the use of cycle-average instability theories. In other words, we speculate that advancing to point-wise instability theories would solve this discrepancy issue, and we leave this higher cost computation for another day.

IX DATA ACCESSIBILITY

This paper has no data

X COMPETING INTERESTS

We have no competing interests’.

XI AUTHORS’ CONTRIBUTIONS

All contribute to this work equally.

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Table I: Dimensional Variables

Name	Unit	Symbol
Angular velocity [Eqs. (1) or (2)]	t^{-1}	ω
Cartesian coordinates	L	x, y, z
Complex first normal stress difference, displacement, real and minus the imaginary parts, SAOS [Eq. (45)]	M/L	$\Psi_1^d, \Psi_1', \Psi_1''$
Complex first normal stress difference, displacement, real and minus the imaginary parts, n th harmonic [Eqs. (50)–(52)]	M/L	$\Psi_{1,n}', \Psi_{1,n}''$
Complex viscosity, real and minus the imaginary parts, SAOS [Eq. (44)]	M/Lt	η', η''
Complex viscosity, real and minus the imaginary parts, n th harmonic [Eqs. (48) and (49)]	M/Lt	η_n', η_n''
Crack tip radius [Eq. (12)]	L	a
Critical shear stress [Eq. (23)]	M/Lt^2	τ_c
Dissipative function and its cycle-average [Eqs. (25), (31)]	M/Lt^3	$D, \bar{D}$
Extra stress tensor [Eq. (35)]	M/Lt^2	τ
Extra stress tensor, ij th component [Eq. (35)]	M/Lt^2	τ_{ij}
Extra stress tensor, ij th component, k th spectrum [Eq. (53)]	M/Lt^2	$\tau_{ij}^{(k)}$
Fluid density	M/L^3	ρ
Free energy function and its cycle-average [Eq. (29), (34)]	L^2/t^2	$F, \bar{F}$
Gap between two parallel plates [Eq. (19), (20)]	L	H
Normal stress differences, first and second [Eqs. (10) and (11)]	M/Lt^2	$N_1 \equiv \tau_{xx} - \tau_{yy}$ $N_2 \equiv \tau_{yy} - \tau_{zz}$
Normal stress differences, first and second, k th spectrum [Eqs. (53)]	M/Lt^2	$N_1^{(k)} \equiv \tau_{xx}^{(k)} - \tau_{yy}^{(k)}$ $N_2^{(k)} \equiv \tau_{yy}^{(k)} - \tau_{zz}^{(k)}$
Radius position at free surface of polymeric sample [Eq. (17)]	L	R
Rate-of-strain tensor [Eq. (37)]	t^{-1}	$\dot{\gamma}$
Relaxation time, longest and k th spectrum [Eqs. (35) and (54)]	t	λ, λ_k
Shear rate [Eq. (2)]	t^{-1}	$\dot{\gamma}$
Shear rate, amplitude [Eq. (2)]	t^{-1}	$\dot{\gamma}^0$
Shear stress, yx -component, jump interface between fluid and air [Eq. (20)]	M/Lt^2	$\Delta\tau_{yx}$
Surface tension between fluid and air [Eq. (12)]	M/t^2	Γ
Velocity vector, and its i th component [Eq. (1)]	L/t	$\mathbf{v}, v_i$
Vorticity tensor [Eq. (37)]	t^{-1}	ω
Zero-shear viscosity, longest and k th spectrum [Eqs. (35) and (54)]	M/Lt	η_0, η_k

Legend: $M \equiv$ mass; $L \equiv$ length; $t \equiv$ time; $T \equiv$ temperature

*Where τ_{ij} is the force exerted in the j th direction on a unit area of fluid surface of constant x_i by fluid in the region lesser x_i on fluid in the region greater x_i (see “Note on the Sign Convention for the Stress Tensor” on pp. 19–20 of [61], or pp. 24–25 of [62]).

Table II: Dimensionless Variables and Groups

Name	Symbol
Dissipative function, cycle-average, longest and k th spectrums [Eq. (31)]	$\bar{\mathbb{D}} \equiv \lambda^2 \bar{D} / \eta_0, \bar{\mathbb{D}}^{(k)} \equiv \lambda^2 \bar{D}^{(k)} / \eta_0$
Complex viscosity, real and minus the imaginary parts, n th harmonic, longest and k th spectrums [Eqs. (48) and (49)]	$\tilde{\eta}'_n \equiv \eta'_n / \eta_0, \tilde{\eta}''_n \equiv \eta''_n / \eta_0$ $\tilde{\eta}'^{(k)}_n \equiv \eta'^{(k)}_n / \eta_0, \tilde{\eta}''^{(k)}_n \equiv \eta''^{(k)}_n / \eta_0$
Complex first normal stress difference, displacement, real and minus the imaginary parts, n th harmonic, longest and k th spectrum [Eqs. (50)–(52) and (65)–(67)]	$\tilde{\Psi}'_{1,2n} \equiv \dot{\gamma}^0 \Psi'_{1,2n} / \eta_0$ $\tilde{\Psi}''_{1,2n} \equiv \dot{\gamma}^0 \Psi''_{1,2n} / \eta_0$ $\tilde{\Psi}'^{(k)}_{1,2n} \equiv \dot{\gamma}^0 \Psi'^{(k)}_{1,2n} / \eta_0$ $\tilde{\Psi}''^{(k)}_{1,2n} \equiv \dot{\gamma}^0 \Psi''^{(k)}_{1,2n} / \eta_0$
Free energy function, cycle-average [Eq. (34)]	$\bar{\mathbb{F}} \equiv \rho \lambda F / \eta_0$
Deborah number [Eq. (4)]	$\text{De} \equiv \lambda \omega$
Weissenberg number [Eq. (4)]	$\text{Wi} \equiv \lambda \dot{\gamma}^0$
Weissenberg number at extrema [Eq. (58)]	$\text{Wi}_e \equiv \lambda \dot{\gamma}_e^0$
Raynolds number [Eq. (14)]	Re
Keentok number [Eq. (17)]	Ke
Spriggs exponent [Eq. (54)]	α
Shear stress	$\tilde{\tau}_{yx} \equiv \lambda \tau_{yx} / \eta_0$
Time	$\tau \equiv \omega t$

Table III: Errata to Cited References [14] and [15].

[14]	In the abscissa label to Fig. 1., “ $ \alpha_{12} $ ” should be “ $ \sigma_{12} $ ”; “BP-7” should be “PB-7”; “ $\bullet$) Frequency of 5 Hz” should be “o) Frequency of 5 Hz”; and “o $\rightarrow$) instability...” should be “ $\bullet \rightarrow$) instability...”. The line above CONCLUSIONS, “PB-7” should be “PB-6”
[15]	In the abscissa label to the first figure, <i>Puc. 1.</i> , $\lg \sigma_{12} $ should be $\lg_{10} \sigma_{12} $, where $ \sigma_{12} $ represents the amplitude of the first harmonic

Figure 1: Surface of $\zeta(\alpha) \partial \tilde{\tau}_{yx} / \partial Wi$ [right side of Eq. (58)]. **Red** curve illustrates the zero contour of $\zeta(\alpha) [\partial \tilde{\tau}_{yx} / \partial Wi]$. Monotonicity vanishes when $\alpha < 3.457$.

Figure 2: Contours of $(\partial \bar{\mathbb{D}}/\partial \text{Wi} - \bar{\mathbb{D}}/\text{Wi})$ mapped onto Pipkin space for steady shear flow of generalized corotational Maxwell fluid [Eq. (73)]. The **red** contour, where $\partial \bar{\mathbb{D}}/\partial \text{Wi} - \bar{\mathbb{D}}/\text{Wi} = 0$, circumscribes the unstable region. For multimode, when $\alpha < 3.711$, the flow is always stable. For single-mode ($\alpha \rightarrow \infty$), when $\text{Wi} < \sqrt{\frac{1}{2}(1+\sqrt{5})} \cong 1.272$ the flow is also always stable.

Figure 3: Contours of $(\partial \bar{D}/\partial Wi - \bar{D}/Wi)$ mapped onto Pipkin space for LAOS of single-mode corotational Maxwell fluid [Eq. (82)]. The **red** contour, where $\partial \bar{D}/\partial Wi - \bar{D}/Wi = 0$, circumscribes the unstable region.

Figure 4: Contours of $(\partial \bar{\mathbb{D}} / \partial Wi - \bar{\mathbb{D}} / Wi) = 0$ mapped onto Pipkin space for LAOS of generalized corotational Maxwell fluid [Eq. (86)] for three values of the Spriggs exponent, $\alpha = 2, 4, \infty$ (single-mode). Each of which contour circumscribes the unstable for corresponding α .

Figure 5: Contours of $\partial^2 \mathbb{F} / \partial Wi^2$ mapped onto Pipkin space for steady shear flow of generalized corotational Maxwell fluid [Eq. (96)]. The **red** contour, where $\partial^2 \mathbb{F} / \partial Wi^2 = 0$, circumscribes the unstable region.

Figure 6: Contours of $\partial^2 \bar{\mathbb{F}} / \partial \text{Wi}^2$ mapped onto Pipkin space for LAOS of single-mode corotational Maxwell fluid [Eq. (106)]. The **red** contour, where $\partial^2 \bar{\mathbb{F}} / \partial \text{Wi}^2 = 0$, circumscribes the unstable region.

Figure 7: Contours of $\partial^2 \bar{\mathbb{F}} / \partial \text{Wi}^2 = 0$ mapped onto Pipkin space for LAOS of generalized corotational Maxwell fluid [Eq. (108)] for three values of the Spriggs exponent, $\alpha = 3, 4, \infty$ (single mode). Each of which contour circumscribes the unstable for corresponding α .

Figure 8: SAOS measurements of dissolved polybutadienes at 22°C from Fig. 1 of [60] fitted to multimode corotational Maxwell fluid generalized by the Spriggs relations [Eq. (109)]. Best fit is $\lambda = 0.3500\text{s}$, $\eta_0 = 1.87 \times 10^6 \text{ Pa}\cdot\text{s}$, (a) $\alpha = 4.00$ and (b) $\alpha = \infty$.

Figure 9: Region of instability for dissolved polybutadienes ($\lambda = 0.350s$, $\eta_0 = 1.87 \times 10^6 \text{ Pa}\cdot\text{s}$, (a) $\alpha = 4.00$ and (b) $\alpha = \infty$) mapped onto Pipkin space. **Black** surface is when the cycle-average Ziegler instability criterion satisfies [Eq. (86)], and **blue** surface, when the free energy instability criterion satisfies [Eq. (108)]. **Magenta** surface, extrapolated from dots, is reported values by Burlii *et al.* (Fig. 4 of [14]).

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