Rheol Acta (2012) 51:487–495
DOI 10.1007/s00397-011-0612-8

RAPID COMMUNICATION

An intriguing empirical rule for computing the first normal stress difference from steady shear viscosity data for concentrated polymer solutions and melts

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Received: 17 August 2011 / Revised: 30 November 2011 / Accepted: 5 December 2011 / Published online: 22 January 2012

Abstract The Cox–Merz rule and Laun's rule are two empirical relations that allow the estimation of steady shear viscosity and first normal stress difference, respectively, using small amplitude oscillatory shear measurements. The validity of the Cox–Merz rule and Laun's rule imply an agreement between the linear viscoelastic response measured in small amplitude oscillatory shear and the nonlinear response measured in steady shear flow measurements. We show that by using a lesser-known relationship also proposed by Cox and Merz, in conjunction with Laun's rule, a relationship between the rate-dependent steady shear viscosity and the first normal stress difference can be deduced. The new empirical relation enables a priori estimation of the first normal stress difference using only the steady flow curve (i.e., viscosity vs shear rate data). Comparison of the estimated first normal stress difference with the measured values for six different polymer solutions and melts show that the empirical rule provides values that are in reasonable agreement with measurements over a wide range of shear rates, thus deepening the intriguing connection between linear and nonlinear viscoelastic response of entangled polymeric materials.

Keywords Cox–Merz rule · First normal stress difference · Normal stresses · Third-order fluid · Nonlinear viscoelasticity · Shear viscosity

The Cox–Merz rule and Laun's rule

The empirical Cox–Merz rule (Cox and Merz 1958) which states that

$$\left|\eta^*(\omega)\right| \equiv \eta(\dot{\gamma})|_{\dot{\gamma}=\omega} \tag{1}$$

is obeyed by many polymeric melts (Booij et al. 1983; Cox and Merz 1958; Dealy and Larson 2006; Kulicke and Porter 1980; Laun 1986; Winter 2009) and also semi-dilute and concentrated polymer solutions (Al-Hadithi et al. 1992; Kulicke and Porter 1980; Laun 1986; Yasuda et al. 1981) with a wide range of chemical structures and molecular weight. The Cox–Merz rule establishes a connection between the magnitude of the complex viscosity $|\eta^*(\omega)|$ measured in an oscillatory frequency sweep (at a fixed strain amplitude within the linear viscoelastic regime) and the steady shear viscosity $\eta(\dot{\gamma}) = \sigma/\dot{\gamma}$ measured as a function of shear rate $\dot{\gamma}$. In 1958, Cox and Merz communicated this empirical rule as a Letter to the Editor (Cox and Merz 1958), and in the last 50 years, the rule has been widely applied (the letter has over 900 citations) and discussed by a number of researchers (Booij et al. 1983; Dealy and Larson 2006; Ianniruberto and Marrucci 1996; Larson 1999; Laun 1986; Marrucci 1996; Mead 2011; Renardy 1997; Winter 2009) and is often used by industrial rheologists for obtaining estimates of the high shear rate viscosity for samples that show edge fracture or other elastic flow instabilities at high deformation rates. The Cox–Merz rule often fails for complex fluids that exhibit deformation-dependent microstructure (e.g., for associating polymers, suspensions or hydrogen-bonding polysaccharides; Al-Hadithi et al. 1992; Annable et al. 1993; Kulicke and Porter 1980; Lapasin and Pricl 1995;

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Larson 1999), though various extensions of the Cox–Merz rule have been proposed for suspensions and thixotropic/yielding materials as well as shear thickening materials (Doraiswamy et al. 1991; Gleissle and Hochstein 2003; Mujumdar et al. 2002; Raghavan and Khan 1997).

In their letter, Cox and Merz initially compare the apparent shear viscosity $\eta_a(\dot{\gamma}_a)$ computed from pressure-drop/flow rate measurements in a capillary extrusion viscometer for two polystyrenes with the magnitude of the complex viscosity measured in oscillatory shear. Larson and Dealy note that a computation of true viscosity implies that Cox and Merz actually found an equivalence of $|\eta^*(\omega)|$ with $\eta\,(\dot{\gamma} = 0.79\omega)$ or $|\eta^*(\omega)|$ with $\eta_a\,(\dot{\gamma}_a)$ where the subscript denotes an apparent or nominal measure (Dealy and Larson 2006), suggesting that the familiar Cox–Merz rule defined by Eq. 1 is somewhat different from what Cox and Merz initially obtained. Though Cox and Merz graphically compared the magnitude of the complex viscosity $|\eta^*(\omega)|$ with the apparent viscosity $\eta_a\,(\dot{\gamma}_a)$, the text mentions that a comparison was also carried out with true viscosity (after using the Rabinowitsch correction (Walters 1975)), Cox and Merz note "The general shape, on a log–log plot, of apparent viscosity vs shear rate remains virtually unchanged for these polystyrenes if $\dot{\gamma}_a$ in Eq. 1 (defined as $\eta_a = \sigma_w/\dot{\gamma}_a$ or ratio of wall shear stress σ_w to apparent shear rate $\dot{\gamma}_a$) is replaced by the shear rate at the wall as suggested by Rabinowitsch". Further, in the second figure of their letter, Cox and Merz compare the magnitude of the complex viscosity $|\eta^*(\omega)|$ with steady shear viscosity $\eta\,(\dot{\gamma})$ data of polyisobutylene–decalin solutions, measured using cone and plate geometry by DeWitt et al. (1955) and also show a good agreement. Thus Eq. 1 is the Cox–Merz rule both as defined by the authors in their 1958 article and as used in practice. Interestingly though, while Cox and Merz used a simplified superposition captured by Eq. 1, they were motivated by experimental and theoretical arguments provided by DeWitt and coworkers (Dewitt 1955; DeWitt et al. 1955; Markovitz 1975; Padden and DeWitt 1954). Dewitt and coworkers were probably the first to show that suitably normalized measures of $|\eta^*(\omega)|$ and $\eta\,(\dot{\gamma})$ data can be successfully superimposed on each other.

In steady shear viscosity measurements carried out on torsional rheometers, concentrated polymer solutions and melts exhibit edge fracture at shear rates as low as 10 s^{-1}. Though capillary extrusion rheometers can extend the measurements to comparatively higher shear rates, extrusion instabilities, viscous heating and wall slip can all serve to limit the overall shear rate range (Macosko 1994; Walters 1975). In such systems, the Cox–Merz rule provides valuable estimates of the steady shear viscosity from the small amplitude high frequency oscillatory shear viscosity measurements at $\dot{\gamma} \equiv \omega$. The particular utility of oscillatory shear measurements lie first in the ability to use a smaller sample volume compared to conventional capillary rheometers, and second in the great precision and wide dynamic range of modern torsional rheometers. However, the nonlinear elastic properties of polymeric systems which are manifested as normal stress effects, and which lead to rod climbing (Weissenberg 1947), die swell, and elastic instabilities (Barnes et al. 1989; Bird et al. 1987; Harris 1973; Larson 1992; Macosko 1994; Walters 1975), cannot be directly measured using oscillatory shear measurements.

In 1986, Laun went on to describe another empirical rule that interrelates the first normal stress difference $N_1\,(\dot{\gamma})$ measured using steady shear flow to the storage modulus $G'(\omega)$ and loss modulus $G''(\omega)$ measured in oscillatory shear (Laun 1986):

$$N_{1,\mathrm{Laun}}\,(\dot{\gamma})\big|_{\omega=\dot{\gamma}} \cong 2G'\,(\omega)\left\{1+\left(\frac{G'\,(\omega)}{G''\,(\omega)}\right)^2\right\}^{0.7} \tag{2}$$

Laun's rule is found to work for melts and concentrated solutions of many commercial polymers (polyethylene, polypropylene, polystyrene, polybutadiene) and again emphasizes the relationship between the linear and nonlinear response of polymeric fluids (Laun 1986; Winter 2009). The present communication is motivated by an intriguing extension of the arguments presented by Cox and Merz and by Laun to deduce a relationship between the steady shear viscosity $\eta\,(\dot{\gamma})$ and the first normal stress difference $N_1\,(\dot{\gamma})$. Before describing the new result, we define the notation used to represent the various rheological measures in the following section, and then introduce the less well-known empirical rules that are also part of the letter in which the famous Cox–Merz rule was first proposed.

Linear and nonlinear viscoelasticity: definitions

The relevant stress distribution for Non-Newtonian fluids in response to a steady simple shear flow given by $v_x = \dot{\gamma}y$, $v_y = v_z = 0$ is expressed using three viscometric measures of the non-zero stress components; the shear stress $\sigma_{xy} \equiv \sigma = \eta\,(\dot{\gamma})\,\dot{\gamma}$ and two normal stress differences (N_1 and N_2) defined as follows $\sigma_{xx} - \sigma_{yy} = N_1\,(\dot{\gamma})$ and $\sigma_{yy} - \sigma_{zz} = N_2\,(\dot{\gamma})$. All the other components of the stress tensor are zero. The normal stress differences are associated with nonlinear viscoelastic effects, and are identically zero for Newtonian fluids.

They also become vanishingly small in linear viscoelastic measurements (Bird et al. 1987). They first appear as second-order effects, such that $N_1(\dot{\gamma}) = \Psi_1\dot{\gamma}^2$, $N_2(\dot{\gamma}) = \Psi_2\dot{\gamma}^2$ where Ψ_1 and Ψ_2 are called the first and second normal stress coefficients, respectively (Barnes et al. 1989; Larson 1988). At high shear rates, N_1 values can be comparable or even larger than the shear stress, σ; however $N_1(\dot{\gamma})$ is typically difficult to measure for many complex fluid systems and requires very sensitive (and expensive) force rebalance transducer technology.

Laun's relationship provides an approximate relationship between the first normal stress difference (N_1) and the two components of the complex modulus defined by $G^*(\omega) = G'(\omega) + iG''(\omega)$, that are measured when a small amplitude oscillatory shear is imposed on the sample, with $\gamma(t) = \gamma_0 \sin \omega t$ and $\gamma_0 \ll 1$. The real and imaginary parts of the complex modulus represent elastic and viscous contributions and are referred to as the storage modulus and loss modulus respectively. Alternatively, the response in oscillatory shear can be expressed in terms of the complex viscosity (Gemant 1935), and the components of complex viscosity are given by $\eta^*(\omega) = -i\omega G^*(\omega) = \eta'(\omega) - i\eta''(\omega)$. The two moduli are related to the two viscosities through the expressions $G''(\omega) = \eta'\omega$; $G'(\omega) = \eta''\omega$.

The forgotten Cox–Merz rules of elasticity and consistency

Interestingly, even though the Cox–Merz rule $|\eta^*(\omega)| \equiv \eta(\dot{\gamma})|_{\dot{\gamma}=\omega}$ for viscosity is used often to extract estimates of steady shear viscosity from oscillatory shear data, two additional empirical rules for the dynamic viscosity and the elastic modulus, also postulated in the original letter by Cox and Merz (1958) are now, to the best of our knowledge, largely ignored by the rheological community (based on a survey of many papers and books that invoke the Cox–Merz rule (Al-Hadithi et al. 1992; Barnes et al. 1989; Bird et al. 1987; Doraiswamy et al. 1991; Ianniruberto and Marrucci 1996; Kulicke and Porter 1980; Larson 1999; Laun 1986; Marrucci 1996; Mead 2011; Venkatraman et al. 1990; Winter 2009; Yasuda et al. 1981)).

Cox and Merz related the dynamic viscosity $\eta'(\omega)$ to a quantity defined as the consistency $\eta_c \equiv d\sigma \big/ d\dot{\gamma}$, i.e., a tangent viscosity that can be computed directly from the flow curve measured in steady shear. They graphically showed that

$$\eta'(\omega) \cong \eta_c(\dot{\gamma})|_{\dot{\gamma}=\omega} \tag{3}$$

The equivalence is shown on the two plots in their 1958 paper that also showed the well-known equivalence of Eq. 1. We refer to this empirical rule as the *forgotten Cox–Merz rule of consistency*. Booij et al. (1983) considered the internal consistency of the two rules originally proposed by Cox and Merz. By considering a class of integral models that satisfy time-strain factorizability, they showed that to exactly satisfy either rule requires an oscillatory and unphysical strain-dependent damping function. They also showed that it is not formally possible to exactly satisfy both the Cox–Merz rule and the forgotten consistency rule at the same time. Nonetheless, experimental data for a range of entangled polymeric materials (which are described by molecularly motivated damping functions of markedly different functional form to those determined by Booij et al. (Dealy and Larson 2006; Doi and Edwards 1986; Renardy 1997)) are repeatedly found to be in good agreement with Eq. 1. Furthermore, Cox and Merz presented results for a polystyrene (PS) melt ($M_n = 79$ kg/mol, $M_w = 340$ kg/mol) and 13% and 20% solutions of polyisobutylene (PIB) in decalin and found that both Eq. 1 and the forgotten consistency rule were both equally valid.

In the original letter, Cox and Merz (1958) also introduced the following equation for estimation of elastic modulus from steady shear viscosity data:

$$G'(\omega)\big|_{\omega=\dot{\gamma}} \cong \dot{\gamma}\left(\eta^2 - \eta_c^2\right)^{1/2} \tag{4}$$

Following Cox and Merz, we note that Eq. 4 formally follows from the use of the *forgotten Cox–Merz*

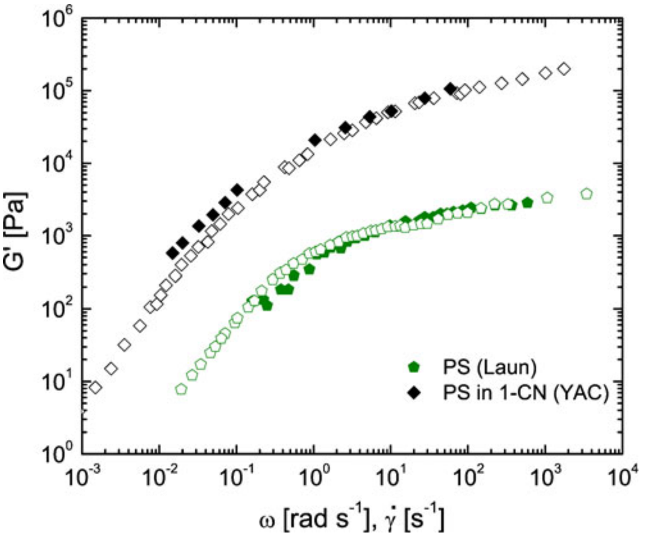

Fig. 1 Comparison of storage modulus (*filled squares*) measured by Laun (replotted from (Laun et al. 1979; Laun 1986)), and by Yasuda et al. (replotted from Yasuda et al. 1981) in oscillatory shear and the values computed using the *forgotten Cox–Merz rule of elasticity* (Eq. 4), using steady shear viscosity data from the quoted papers

rule of consistency (Eq. 3) in conjunction with Eq. 1 and the identity $|\eta^*(\omega)|^2 = (\eta')^2 + (G'/\omega)^2$. While Cox and Merz noted that the measured values of storage modulus for polystyrene and high-density polyethylene (HDPE) matched the value obtained by using Eq. 4, no plots were provided.

Figure 1 shows a comparison of the frequency dependent storage modulus $G'(\omega)$ measured in small amplitude oscillatory shear (SAOS) and the values computed by using Eq. 4 for two canonical materials: a commercial polystyrene melt (Larson 1988; 1999; Laun 1986; Laun et al. 1979; Macosko 1994) and a concentrated polystyrene/1-chloronapthalene (PS/1-CN) solution (Bird et al. 1987; Yasuda et al. 1981). Additional details about experimental methods and materials are summarized in Table 1. It is clear from the Fig. 1 that the estimated values, computed using this *forgotten Cox–Merz rule for elasticity*, are in close agreement with the experimentally measured values.

For calculating the consistency from the experimental data, we have first fitted the rate-dependent viscosity using a Cross model (Cross 1965)

$$\eta(\dot{\gamma}) = \eta_\infty + \frac{\eta_0 - \eta_\infty}{1 + (\dot{\gamma}/\dot{\gamma}_c)^m} \tag{5}$$

The Cross model incorporates four parameters: the zero shear viscosity η_0, the critical strain rate $\dot{\gamma}_c$ and an exponent m were used as fitting parameters; the high shear rate viscosity was taken to be either the solvent viscosity for the solutions or alternately set to $\eta_\infty = 0$ for the melts. Table 1 lists the fit parameters extracted from the original data in the cited papers.

Table 1 Summary of the molecular weight and molecular weight distribution of polymers, corresponding measurement techniques and conditions, cross model parameters corresponding to each system and reference(s) corresponding to each dataset

Material M_w, M_w/M_n	Method and comments	Cross model parameters, η_0, $\dot{\gamma}_c$ m	S (Laun) Eq. 2	S Eq. 7	Ref.
LDPE Melt 1 $M_w = 460$ kg/mol $M_w/M_n = 22$ $T = 150°$C, tTs	N_1 and η with WRG, RSR; CR	53079.95 Pa s 0.57 s^{-1} 0.74	3.7	1.86	(Laun 1986)
HDPE I $M_w = 98$ kg/mol $M_w/M_n = 10$ $T = 150°$C	N_1 and η with WRG, RSR; Capillary rheometer (plus tTs)	7215.08 Pa s 0.31 s^{-1} 0.50	1.17	1.13	(Laun 1986)
PS II $M_w = 240$ kg/mol $M_w/M_n = 2.76$ $T = 170°$C, tTs	N_1 and η with WRG, RSR; CR	98827.04 Pa s 0.16 s^{-1} 0.67	3.35	1.75	(Laun 1986; Laun et al. 1979)
PS (Linear) in 1-Chloronaphthalene (1-CN) $M_w = 2000$ kg/mol $M_w/M_n = 1.3$ $T = 25°$C, tTs $c/c^* = 66$; 0.15 g/ml	G', G'': eccentric rotating disk on (RMS) η: C&P on RMS; IRR; CR	1587.29 Pa s 0.63 s^{-1} 0.85	–	–	(Yasuda et al. 1981)
Polyisobutylene in Decalin $M_w = 400$ kg/mol $T = 21$–$25°$C $c = 10$ wt %	N_1 and η with C&P on WRG; PPG: TSR; Slit die on Lodge Stressmeter	3.11 Pa s 175.44 s^{-1} 0.57	–	1.51	(Lodge et al. 1987)
Viscarin in distilled water $c = 2\%$ $T = 20°$C	C&P (3.75 cm / 1.5° and 1.25 cm/ 2°) on WRG, model R 16	4.22 Pa s 3.03 s^{-1} 0.57	–	1.89	(Al-Hadithi et al. 1992)
PP copolymer melt $T = 260°$C	C&P (3.75 cm / 1.5° and 1.25 cm/ 2°) on WRG, model R 16	386.053 510.2 s^{-1} 0.53	–	1.8	(Al-Hadithi et al. 1992)

C&P Cone and Plate; *WRG* Weissenberg Rheogoniometer; *RMS* Rheomatrics Mechanical Spectrometer; *RSR* rheometrics stress rheometer; *IRR* Instron Rotatory Rheometer, *tTS* time Temperature superposition; *CR* capillary rheometer

The first normal stress difference and the AbNormal rule

An interesting corollary follows if we combine Laun's rule for the first normal stress difference (Eq. 2) along with the forgotten Cox–Merz rules for elasticity and consistency (or Eqs. 3 and 4). This results in a new empirical rule (we call it, somewhat colloquially, the *AbNormal rule*) that can be written as follows (using Eqs. 2 and 3):

$$N_{1,\mathrm{AbNormal}}(\dot{\gamma}) \cong 2\dot{\gamma}\left(\eta^2-\eta_c^2\right)^{0.5}\left\{1+\frac{\left(\eta^2-\eta_c^2\right)}{\eta_c^2}\right\}^{0.7} \tag{6}$$

which then simplifies to the following equation:

$$N_{1,\mathrm{AbNormal}}(\dot{\gamma}) \cong 2\dot{\gamma}\,\eta\left(1-\frac{\eta_c^2}{\eta^2}\right)^{0.5}\left(\frac{\eta_c^2}{\eta^2}\right)^{-0.7} \tag{7}$$

where the shear viscosity is $\eta = \sigma/\dot{\gamma}$ and the consistency is $\eta_c = d\sigma/d\dot{\gamma}$. This expression provides an a priori estimate of the first normal stress difference based exclusively on the shape of the steady flow curve $\sigma(\dot{\gamma})$. Interestingly, Eq. 7 involves the ratio of the consistency and the steady shear viscosity, which is quite reminiscent to experimental rheologists from the correction term $d\log\sigma/d\log\dot{\gamma} \equiv \eta_c/\eta$ that appears in the well-known Weissenberg–Rabinowitsch–Mooney equation (Macosko 1994) and which is used to calculate the true viscosity for non-Newtonian fluids in capillary flow measurements. It must be remarked here that the AbNormal rule is limited to shear-thinning fluids (with $\eta_c < \eta$) such as entangled solutions and melts with a broad spectrum of relaxation times. It cannot be used for estimating the first normal stress difference for dilute solutions, or Boger fluids (Boger 1977), i.e., highly elastic fluids engineered to have rate-independent, Newtonian viscosity response (i.e., with $\eta_c / \eta \to 1$) or for viscoelastic fluids such as telechelic polymer solutions (Annable et al. 1993) that display a single exponential Debye–Maxwell relaxation.

The N_1 data obtained by Laun (Laun 1986; Laun et al. 1979) for three commercial, polydisperse polymer melts: HDPE 1, PS, and LDPE (closed symbols) are compared to the N_1 values computed using Eq. 7 (open symbols) in Fig. 2. Also shown (as a dotted line) are the N_1 values estimated by Laun using Eq. 2 (in conjunction with small amplitude oscillatory shear data). Visually, the measured N_1 values seem to be in closer agreement with the AbNormal rule (Eq. 7) than with Laun's rule. To quantify this, we introduce a parameter S to characterize the goodness of the estimate over the entire dataset, defining S by

$$S = \exp\left(\sqrt{\frac{1}{k}\sum_{j=1}^{k}\left(\log N_{1,\mathrm{computed}}^{(j)} - \log N_{1,\mathrm{measured}}^{(j)}\right)^2}\right)$$
$$= \exp\left(\sqrt{\frac{1}{k}\sum_{j=1}^{k}\left(\log\frac{N_{1,\mathrm{computed}}^{(j)}}{N_{1,\mathrm{measured}}^{(j)}}\right)^2}\right) \tag{8}$$

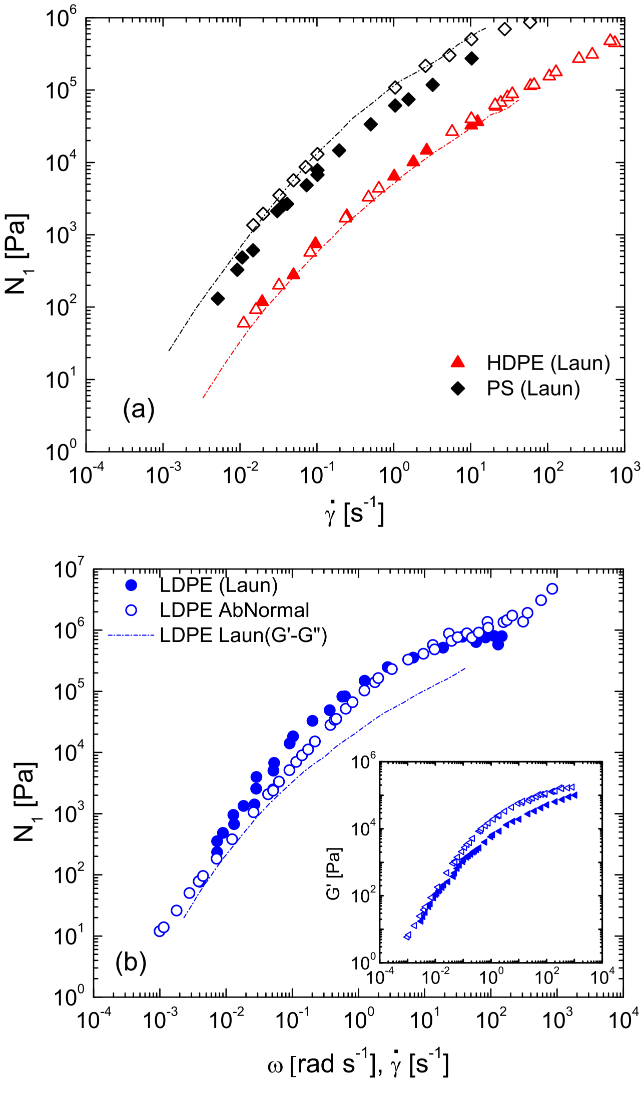

Fig. 2 Measured first normal stress difference data (*filled symbols*) is compared to the values (*open symbols*) computed using the *AbNormal rule* (Eq. 7) using Laun's data (adapted from Laun et al. 1979 and Laun 1986). The results obtained using Laun's rule and oscillatory shear data are also shown by *dotted lines*. **a** Comparison of N_1 values (measured, Laun's rule, *AbNormal rule*) for PS and HDPE melts. **b** Comparison of the corresponding N_1 values for LDPE is shown with an inset plot that compares the measured (*filled triangles*) and the computed values (*open triangles*) of G' (the x-axis in the inset has the same label as x-axis on the main plot)

where $N^{(j)}_{1,\mathrm{computed}}$ is the jth element of the dataset, computed using Eq. 7 at $\dot{\gamma}_j = \omega_j$ which is compared to the corresponding measured value of the first normal stress difference. A value of $S = 1$ is obtained when the computed values agree exactly with the measured values, and $S = 2$ when on an average every computed value is within a factor of two of the measured values. The values of S(AbNormal) for each data set are listed in Table 1. For the melts and solutions that follow the Cox–Merz rule (Eq. 1), application of the AbNormal rule consistently estimates the measured values of N_1 within a factor of two, whereas the corresponding measures from application of Laun's rule (obtained by using Eq. 2 and plotted as a dotted line in Fig. 2a and b) are consistently worse than the new rule and correspond to S(Laun) $= 3.71$ for LDPE, 1.17 for HDPE and 3.35 for PS.

In Fig. 2b, the measured N_1 data (filled circles) for the well-known LDPE Melt I data set are compared with values obtained using Eq. 7 (hollow circles); again the first normal stress difference is approximated better by the AbNormal rule than by Laun's original rule, even through the agreement between the estimated storage modulus $G'(\omega)$, computed using Eq. 4 (open triangles), and the actual oscillatory data (filled triangles, inset in Fig. 2b) is not as good as we obtained for the PS melt in Fig. 1.

We note that the polymeric fluids listed in Table 1 are relatively high molecular weight and entangled and have a large polydispersity. Also, a large shear rate or frequency range was accessed for these samples by the use of time–temperature superposition (tTs), implying that most of the systems described here also exhibit thermorheological simplicity, i.e. the molecular mechanisms underlying the relaxation processes accessed using this range of oscillation frequencies show a similar temperature dependence (Ferry 1980; Markovitz 1975). Additional comparisons of measured and computed N_1 values using the new rule of Eq. 7 are shown in Fig. 3, including the classical data from Lodge et al. (1987) that established that N_1 values measured by different methods coincide for a PIB/Decalin system (10% by weight, PIB $M_w = 400{,}000$ Daltons). The two datasets acquired by Al-Hadithi et al. (1992) for a polypropylene copolymer melt and an aqueous solution of a polysaccharide called vascarin (2% by weight) are also shown. In their paper, these authors (Al-Hadithi et al. 1992) also proposed an alternate relationship between oscillatory shear measurements and N_1 (obtained "after much trial and error", and by including zero shear viscosity, η_0):

$$N_{1,\mathrm{AhBW}}(\dot{\gamma}) \cong 2G'(\omega)\left\{1+\frac{(\eta_0+\eta')\,G'(\omega)}{2\omega\eta'^2}\right\}^{0.5} \qquad (9)$$

It is possible to again invoke the forgotten Cox–Merz rules of elasticity and consistency and write an alternate version of Eq. 9 to estimate the first normal stress difference from the steady flow curves, but a quantitative comparison of the datasets listed in Table 1 over an extended shear rate range, show that the AbNormal rule (based on Laun's rule) gives uniformly better agreement with the experimental data (i.e., lower values of S) than Eq. 9.

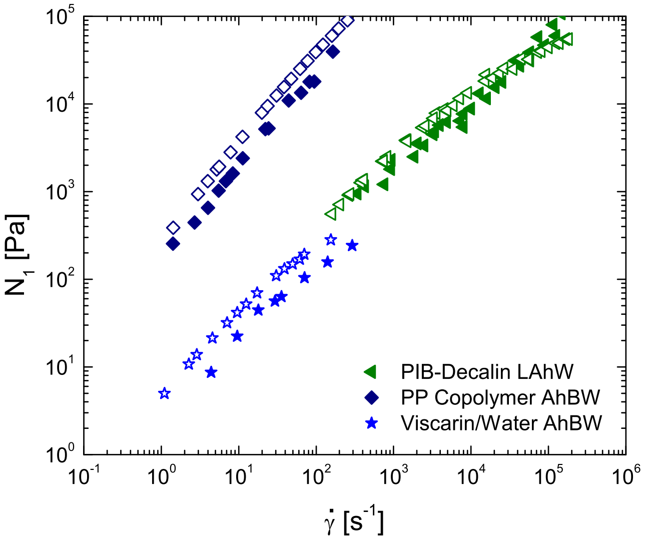

Fig. 3 Measured first normal stress difference data (*filled symbols*) is compared to the values (*open symbols*) computed using the *AbNormal rule* (Eq. 7); using data reported by Lodge et al. (1987) and Al-Hadithi et al. (1992) (see text and Table 1 for details)

Discussion and outlook

The validity of the Cox–Merz rule, Laun's rule and the AbNormal rule (Eq. 7) all imply an interconnection between the linear viscoelastic response measured in small amplitude oscillatory shear and the nonlinear viscometric response measured in steady shear flow. Normal stress measurements are relatively difficult to perform and the dynamic range of deformation rates accessible is typically limited (due to the quadratic scaling of the measured normal force with imposed shear rate). By contrast, measurements of the complex viscosity/modulus (in oscillatory shear) or steady flow curves are now relatively straightforward with modern rheometric instrumentation, are far more accurate and can be performed over a very wide dynamic range. This new rule may thus find applicability in making a priori estimates of the relative magnitude of the first normal stress difference from knowledge of the flow curve of a polymeric material. While complex correlations (based on sophisticated memory kernels and/or constitutive equations) that relate first normal stress difference to steady shear viscosity data exist in literature (Stastna and De Kee 1982; Wagner 1977); Eq. 7 presents the simplest, a priori estimate of the first normal stress difference that is independent of the choice of a constitutive model.

Linear viscoelasticity describes the response to small amplitude deformations under conditions where the imposed strain causes only vanishingly small chain stretch and increase in local segmental orientation (Dealy and Larson 2006). By contrast, the appearance of elastic normal stresses and the onset of shear thinning in steady shear flow both arise from the distortion of the microstructure or from a change in the effective drag acting on chain segments (this is typically diminished as the chains deform and orient with flow). Connecting the underlying polymer physics of nonlinear viscoelasticity (which is dominated by dynamics such as chain orientation, chain stretching and convective constraint release) to linear viscoelasticity (which is a result of diffusive dynamics) is still an unresolved challenge that has attracted much theoretical attention (Ianniruberto and Marrucci 1996; Marrucci 1996; Mead 2011; Milner 1996). Several groups have emphasized that a superposition of a broad spectrum of relaxation modes allows a closer agreement with the Cox–Merz rule (Dewitt 1955; Giacomin et al. 2011; Mead 2011; Milner 1996; Renardy 1997). An important recognition is that measurements of the nonlinear rate-dependent shear viscosity include both a dissipative contribution and also a contribution related to the effective recoverable strain (i.e., a manifestation of elasticity), as described by Laun (1986) and others (Barnes et al. 1989; Cross 1979; Doraiswamy et al. 1991; Mead 2011). The challenge is to describe the time-dependent and strain-dependent contributions to the relaxation modulus (and the corresponding memory function) in a self-consistent manner to capture both linear and nonlinear effects, and relate these contributions to constitutive equations based on either continuum mechanics (Bird et al. 1987; Larson 1988) or molecular viscoelasticity (Doi and Edwards 1986).

The canonical model for consistently capturing the first onset of nonlinear viscoelastic effects is the third-order fluid (Bird et al. 1987) in which the shear stress and first normal stress difference in steady simple shear flow are given respectively by

$$\begin{aligned} \sigma_{xy} &= b_1\dot{\gamma} - 2(b_{12} - b_{1:11})\dot{\gamma}^3 + O(\dot{\gamma}^5)\ldots \\ \sigma_{xx} - \sigma_{yy} &= -2b_2\dot{\gamma}^2 + O(\dot{\gamma}^4)\ldots \end{aligned} \tag{10}$$

It is well known that the material coefficients that appear at first and second order interconnect the viscometric properties and moments of the linear viscoelastic relaxation spectrum; $b_1 \equiv \eta_0 = \int G(s)ds$ and $-2b_2 \equiv \Psi_{10} = \int_0^\infty sG(s)\,ds$ (Bird et al. 1987). It can also be shown that the grouping of coefficients $(b_{12} - b_{1:11}) > 0$ (Bird et al. Chap 6) and this term describes the first onset of shear-thinning in steady shear flow. From the definitions of the viscosity and the consistency it is clear that at third order $\eta_c \leq \eta(\dot{\gamma})$. Substituting the expressions in Eq. 10 into (respectively) the right- and left-hand sides of Eq. 7 we obtain, at leading order (within the domain of validity of this model (Bird et al. 1987))

$$\Psi_{10}\dot{\gamma}^2 \cong 4\left(2\eta_0(b_{12} - b_{1:11})\right)^{1/2}\dot{\gamma}^2 \tag{11}$$

The AbNormal rule thus encompasses the correct quadratic asymptotic scaling at low shear rates that is expected theoretically for a simple fluid and that is also observed in the experimental data sets shown in Figs. 1 and 2. Validity of the rule also implies a new inter-relationship (given by $-2b_2 = 4\left(2b_1(b_{12} - b_{1:11})\right)^{1/2}$) between all of the independent material coefficients obtained at third order in the Ordered Fluid expansion.

Looking ahead, a deeper understanding of the relationship between steady shear viscosity and material measures of the rheological response in large amplitude oscillatory shear (LAOS) is likely to provide the basis for distinguishing strain-dependent and time-dependent effects that simultaneously contribute to the rate-dependence of the shear viscosity and the first normal stress difference, in addition to any interconnections between the three viscometric measures. Indeed very recently Giacomin et al. (2011) have shown that the Cox–Merz rule is not obeyed for the corotational

Maxwell model; but instead a nontrivial alternate expression is obtained;

$$\left.\frac{|\eta^*(\omega)|}{\eta_0}\right|_{\omega=\dot{\gamma}} = \sqrt{\frac{\eta(\dot{\gamma})}{\eta_0}} \tag{12}$$

We note that Eq. 12 given above should replace Eq. (87) in the paper by Giacomin et al. (2011), as η_0 is required in the denominator on both sides (of Eq. (87) of their original paper) to make the equation dimensionally consistent. Much closer agreement with the Cox–Merz rule is recovered, however, when the corotational Maxwell model is generalized to include a spectrum of relaxation times (Giacomin et al. 2011). This model is arguably the simplest canonical nonlinear viscoelastic equation of state that incorporates linear viscoelasticity, rheological invariance as well as shear-thinning material functions. It will be interesting to explore more complex constitutive models derived from both continuum mechanics and from molecular theory within the LAOS framework.

We expect that the use of the forgotten Cox–Merz rule of elasticity to obtain G' from steady shear viscosity data (Eq. 3) and the new AbNormal rule, Eq. 7, for estimating N_1 from steady shear data will be successful only for a limited class of fluids (i.e., entangled polymer melts and solutions) in which both the Cox–Merz rule and Laun's rule are valid. Yet, as an experimentally motivated correlation, the use of the forgotten Cox–Merz rule of elasticity is arguably just as justified as the use of the conventional Cox–Merz rule or Laun's rule; and quantitative comparison shows that it performs equally well (cf. Fig. 1). Furthermore, the AbNormal rule that directly follows from combining these well-tested rules can be used for estimating the first normal stress difference from a simple measurement of the steady flow curve $\sigma_{xy} = \eta(\dot{\gamma})\,\dot{\gamma}$. The apparent validity of the AbNormal rule documented in the present work is an interesting and intriguing result, and we hope our note will stimulate further comparisons and discussions.

Acknowledgements VS wishes to acknowledge AkzoNobel for funding support, and discussions with Gareth McKinley's NNF group, especially with Chirag Kalelkar and Marc Fardin. The authors would also like to thank A. J. Giacomin for a careful reading of the manuscript.

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