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An Intriguing Empirical Rule for Computing The First Normal Stress Difference from Steady Shear Viscosity Data for Polymer Solutions and Melts

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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 polymeric materials.

Introduction: The Cox-Merz rule and Laun's rule

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

$$\left|\eta^*(\omega)\right| \cong \eta(\dot{\gamma})\Big|_{\dot{\gamma}=\omega} \qquad (1)$$

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 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 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 fifty 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, Renardy 1997, Winter 2009) and is often used by industrial rheologists for obtaining estimates of high shear rate viscosity. The Cox-Merz rule often fails for complex fluids that exhibit deformation-dependent microstructure (e.g. for associating polymers, suspensions, hydrogen bonding polysaccharides)(Al-Hadithi et al. 1992, Annable et al. 1993, Kulicke and Porter 1980, Lapasin and Pricl 1995, 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 compared apparent shear viscosity measured in capillary extrusion viscometer for two polystyrenes with 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 $\eta_{app}(\dot{\gamma}_{app})$ where subscript denotes apparent measure (Dealy and Larson 2006), suggesting that Cox-Merz rule defined by eq. (1) is somewhat different from what Cox and Merz found. Though Cox and Merz graphically compared $\eta^*(\omega)$ with the apparent viscosity, the text mentions a comparison was carried out with true viscosity (after using the Rabinowitz correction), The authors noted that on a log-log plot, the difference between the apparent and true viscosity is no longer perceptible. Further, in the second figure of their letter, Cox and Merz compare $\eta^*(\omega)$ with steady shear viscosity data of polyisobutylene-decalin solutions, measured using cone and plate geometry by DeWitt and coworkers (DeWitt et al. 1955). Thus eq. (1) is Cox-Merz rule both as defined by the authors 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 the suitably normalized $\eta^*(\omega)$ and $\eta(\dot{\gamma})$ data can be 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 extend the measurements to comparatively higher shear rates, extrusion instabilities limit the overall shear rate range. In such systems, Cox-Merz rule provides valuable estimate of viscosity from small amplitude oscillatory shear viscosity measurement. 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 manifested as normal stress effects, 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):

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

Laun's rule is found to work for melts and 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 and the first normal stress difference. 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-discussed empirical rules that are also part of the paper where 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 stress; the shear stress $\sigma_{xy} = \sigma = \eta(\dot{\gamma})\dot{\gamma}$ and normal stress differences (N_1 & N_2) defined as follows $\sigma_{xx} - \sigma_{yy} = N_1(\dot{\gamma}),\ \ \sigma_{yy} - \sigma_{zz} = N_2(\dot{\gamma})$. 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 and 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 $\Psi_1,\ \Psi_2$ 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 $\gamma_0 << 1$. 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 $G'' = \eta'\omega;\ G' = \eta''\omega$.

The Forgotten Cox-Merz Rules of Elasticity and Consistency

Interestingly, even though the Cox-Merz rule $|\eta^*(\omega)| \cong \eta(\dot{\gamma})\big|_{\dot{\gamma}=\omega}$ for viscosity is used often to extract estimates of steady shear viscosity from the oscillatory shear data, two additional empirical rules for the dynamic viscosity and the elastic modulus, also postulated in the original article by Cox and Merz (1958) are now largely ignored by the rheological community (to the best of our knowledge and 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 consistency $\eta_c = d\sigma/d\dot{\gamma}$, i.e. a tangent viscosity that be computed directly from the flow curve measured in steady shear. They graphically showed that

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

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 and coworkers (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 1988, Renardy 1997)) are repeatedly found to be in good agreement with eq. (1). Furthermore, Cox & 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 (Cox and Merz 1958) also introduced the following equation for estimation of elastic modulus from steady shear viscosity data:

$$G'(\omega) \cong \dot{\gamma}\left(\eta^2 - \eta_c^2\right)^{1/2} \qquad (4)$$

Following Cox and Merz, we note that eq. (4) formally follows from the use of the *forgotten Cox-Merz rule of consistency* (eq. (3)) in conjunction with eq. (1) and the identity $\left|\eta^*(\omega)\right|^2 = (\eta')^2 + (G'/\omega)^2$. 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, Larson 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, the rate-dependent viscosity was first fit using a Cross model (Cross 1965)

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

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.

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 eq. (3) and eq. (4)). This results in a new empirical rule (we call it the *AbNormal rule*) that can be written as follows (using eq. (2) & (3)):

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

which then simplifies to the following equation:

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

This expression provides an *a priori* estimate of the first normal stress difference based exclusively on the shape of the steady flow curve $\sigma\left(\dot{\gamma}\right)$. 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-Rabinowitch-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 non-zero consistency) and cannot be used for estimating the first normal stress difference for dilute solutions, or for viscoelastic fluids (like telechelic polymer solutions) that display a single exponential Debye-Maxwell relaxation, or Boger fluids i.e. elastic fluids engineered to have rate-independent, Newtonian viscosity response.

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 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

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

where $N_{1,\text{computed}}^{(j)}$ is the j^{th} 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 & 2b;) 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 figure 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. molecular mechanisms underlying relaxation processes accessed using a range of oscillation frequencies show similar temperature dependence (Ferry 1980). 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 & coworkers (Lodge et al. 1987) that established that N_1 values measured by different methods coincide for a PIB/Decalin system. The two datasets acquired by Al-Hadithi and coworkers (Al-Hadithi et al. 1992) for a polypropylene copolymer melt and an aqueous solution of a polysaccharide called vascarin 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):

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

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 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).

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 complicated memory kernels and/or constitutive equations) that relate first normal stress difference to steady shear viscosity data exist in literature (Stastna and Dekee 1982, Wagner 1977); eq. (7) presents the simplest, constitutive model-independent estimate of the first normal stress difference.

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 in 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 non-linear viscoelasticity (which is dominated by dynamics such as chain orientation 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 (Iannirubertо and Marrucci 1996, Marrucci 1996, Mead 2011, Milner 1996). 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 (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 1988).

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

$$\begin{aligned} \sigma_{yx} &= b_1\dot{\gamma} - 2(b_{12} - b_{1:11})\dot{\gamma}^3 + O(\dot{\gamma}^5)... \\ \sigma_{xx} - \sigma_{yy} &= -2b_2\dot{\gamma}^2 + O(\dot{\gamma}^4)... \end{aligned} \tag{9}$$

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 $\eta_c \le \eta(\dot{\gamma})$. Substituting the expressions in eq. (10) into (respectively) the righthand and lefthand side of eq. (7) we obtain, at leading order (within the domain of validity of this model (Bird et al. 1987))

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

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, 2. Validity of the rule also implies a new interrelationship (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 3rd 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 and to any interconnections between the three viscometric measures. Indeed very recently Giacomin and coworkers (Giacomin et al. 2011) have shown that for the corotational Maxwell model the Cox-Merz rule is not obeyed; but instead a nontrivial alternate expression is obtained;

$$\left|\eta^*(\omega)\right|/\eta_0\Big|_{\omega\to\dot{\gamma}} = \sqrt{\eta(\dot{\gamma})/\eta_0} \qquad (12)$$

We note that the eq. (12) given above should replace the eq. (87) in the paper by Giacomin and coworkers(Giacomin et al. 2011), as η_0 is required in denominator on the both sides (in eq. (87) of their paper) to make the equation dimensionally consistent. Much closer agreement with the Cox-Merz rule is recovered, however, when the co-rotational 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/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 with 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.

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References

Al-Hadithi TSR, Barnes HA, Walters K (1992) The relationship between the linear (oscillatory) and nonlinear (steady-state) flow properties of a series of polymer and colloidal systems. Colloid and Polymer Science 270: 40-46. DOI 10.1007/bf00656927

Annable T, Buscall R, Ettelaie R, Whittlestone D (1993) The rheology of solutions of associating polymers: comparison of experimental behavior with transient network theory. Journal of Rheology 37: 695-726

Barnes HA, Hutton JF, Walters K (1989) An Introduction to Rheology. Elsevier Science Publishers B. V., Amsterdam

Bird RB, Armstrong RC, Hassager O (1987) Dynamics of Polymeric Liquids. John Wiley & Sons, New York

Booij HC, Leblans P, Palmen J, Tiemersmathoone G (1983) Nonlinear viscoelasticity and the Cox-Merz relations for polymeric fluids. Journal of Polymer Science Part B-Polymer Physics 21: 1703-1711. DOI 10.1002/pol.1983.180210910

Cox WP, Merz EH (1958) Correlation of dynamic and steady flow viscosities. Journal of Polymer Science 28: 619-622. DOI 10.1002/pol.1958.1202811812

Cross MM (1965) Rheology of non-Newtonian fluids - A new flow equation for pseudoplastic systems. Journal of Colloid Science 20: 417-437. DOI 10.1016/0095-8522(65)90022-x

Cross MM (1979) Relation between viscoelasticity and shear thinning behavior in liquids. Rheol Acta 18: 609-614. DOI 10.1007/bf01520357

Dealy JM, Larson RG (2006) Structure and Rheology of Molten Polymers. Hanser Gardner Publications, Cincinnati

Dewitt TW (1955) A rheological equation of state which predicts non-Newtonian viscosity, normal stresses, and dynamic moduli. Journal of Applied Physics 26: 889-894. DOI 10.1063/1.1722114

DeWitt TW, Markovitz H, Padden FJ, Zapas LJ (1955) Concentration dependence of the rheological behavior of the polyisobutylene--decalin system. Journal of Colloid Science 10: 174-188

Doi M, Edwards SF (1988) The Theory of Polymer Dynamics. Oxford University Press, New York

Doraiswamy D, Mujumdar AN, Tsao I, Beris AN, Danforth SC, Metzner AB (1991) The Cox-Merz rule extended: A rheological model for concentrated suspensions and other materials with yield stress. Journal of Rheology 35: 647-685. DOI 10.1122/1.550184

Ferry JD (1980) Viscoelastic Properties of Polymers. Wiley, New York

Gemant A (1935) The conception of a complex viscosity and its application to dielectrics. Trans Faraday Soc 31: 1582-1589. DOI 10.1039/tf9353101582

Giacomin AJ, Bird RB, Johnson LM, Mix AW (2011) Large-amplitude oscillatory shear flow from the corotational Maxwell model. Journal of Non-Newtonian Fluid Mechanics. DOI 10.10116/j.jnnfm.2011.04.002

Gleissle W, Hochstein B (2003) Validity of the Cox-Merz rule for concentrated suspensions. Journal of Rheology 47: 897-910. DOI 10.1122/1.1574020

Harris J (1973) The Karl Weissenberg 80th birthday celebration essays. East African Literature Bureau, Kampala

Ianniruberto G, Marrucci G (1996) On compatibility of the Cox-Merz rule with the model of Doi and Edwards. Journal of Non-Newtonian Fluid Mechanics 65: 241-246. DOI 10.1016/0377-0257(96)01433-4

Kulicke WM, Porter RS (1980) Relation between steady shear flow and dynamic rheology. Rheol Acta 19: 601-605. DOI 10.1007/bf01517513

Lapasin R, Pricl S (1995) Rheology of Industrial Polysaccharides: Theory and Applications. Chapman & Hall, London

Larson RG (1988) Constitutive Equations for Polymer Solutions and Melts. Butterworth Publishers, Boston

Larson RG (1992) Instabilities in viscoelastic flows. Rheol Acta 31: 213-263. DOI 10.1007/bf00366504

Larson RG (1999) The Structure and Rheology of Complex Fluids. Oxford University Press, New York

Laun HM (1986) Prediction of elastic strains of polymer melts in shear and elongation. Journal of Rheology 30: 459-501. DOI 10.1122/1.549855

Laun HM, Wagner MH, Janeschitz-kriegl H (1979) Model analysis of nonlinear viscoelastic behavior by use of a single integral constitutive equation: stresses and birefringence of a polystyrene melt in intermittent shear flows. Rheol Acta 18: 615-622. DOI 10.1007/bf01520358

Lodge AS, Al-Hadithi TSR, Walters K (1987) Measurement of the 1st normal stress difference at high shear rates for a polyisobutadience decalin solution D2. Rheol Acta 26: 516-521. DOI 10.1007/bf01333735

Macosko CW (1994) Rheology: Principles, Measurements and Applications. VCH Publishers Inc, New York

Markovitz H (1975) Superposition in rheology. Journal of Polymer Science Part C-Polymer Symposium: 431-456

Marrucci G (1996) Dynamics of entanglements: A nonlinear model consistent with the Cox-Merz rule. Journal of Non-Newtonian Fluid Mechanics 62: 279-289. DOI 10.1016/0377-0257(95)01407-1

Mead DW (2011) Analytic derivation of the Cox–Merz rule using the MLD "toy" model for polydisperse linear polymers. Rheol Acta. DOI DOI 10.1007/s00397-011-0550-5

Milner ST (1996) Relating the shear-thinning curve to the molecular weight distribution in linear polymer melts. Journal of Rheology 40: 303-315. DOI 10.1122/1.550742

Mujumdar A, Beris AN, Metzner AB (2002) Transient phenomena in thixotropic systems. Journal of Non-Newtonian Fluid Mechanics 102: 157-178. DOI 10.1016/s0377-0257(01)00176-8

Padden FJ, Dewitt TW (1954) Some rheological properties of concentrated polyisobutylene solutions. Journal of Applied Physics 25: 1086-1091. DOI 10.1063/1.1721819

Raghavan SR, Khan SA (1997) Shear-thickening response of fumed silica suspensions under steady and oscillatory shear. Journal of Colloid and Interface Science 185: 57-67

Renardy M (1997) Qualitative correlation between viscometric and linear viscoelastic functions. Journal of Non-Newtonian Fluid Mechanics 68: 133-135. DOI 10.1016/s0377-0257(96)01466-8

Stastna J, Dekee D (1982) On the prediction of the primary normal stress coefficient from shear viscosity. Journal of Rheology 26: 565-570. DOI 10.1122/1.549678

Venkatraman S, Okano M, Nixon A (1990) A comparison of torsional and capillary rheometry for polymer melts: The Cox-Merz rule revisited. Polymer Engineering and Science 30: 308-313. DOI 10.1002/pen.760300508

Wagner MH (1977) Prediction of primary normal stress difference from shear viscosity data using a single intergral constitutive equation. Rheol Acta 16: 43-50. DOI 10.1007/bf01516928

Walters K (1975) Rheometry. Chapman Hall, London

Weissenberg K (1947) A continuum theory of rheological phenomena. Nature 159: 310-311. DOI 10.1038/159310a0

Winter HH (2009) Three views of viscoelasticity for Cox-Merz materials. Rheol Acta 48: 241-243. DOI 10.1007/s00397-008-0329-5

Yasuda K, Armstrong RC, Cohen RE (1981) Shear flow properties of concentrated solutions of linear and star branched polystyrenes. Rheol Acta 20: 163-178. DOI 10.1007/bf01513059

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 & 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 ^oC, tTs	N_1 & 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 ^oC	N_1 & 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 ^oC, tTs	N_1 & 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 ^oC, 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 ^oC c = 10 wt %	N_1 & 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 ^oC	C&P (3.75 cm / 1.5^o & 1.25 cm/ 2^o) 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^oC	C&P (3.75 cm / 1.5^o & 1.25 cm/ 2^o) 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; Weissenberg Rheogoniometer (WRG); Rheomatrics Mechanical Spectrometer (RMS); Rheometrics Stress Rheometer (RSR); Instron Rotatory Rheometer (IRR), tTS: time Temperature superposition

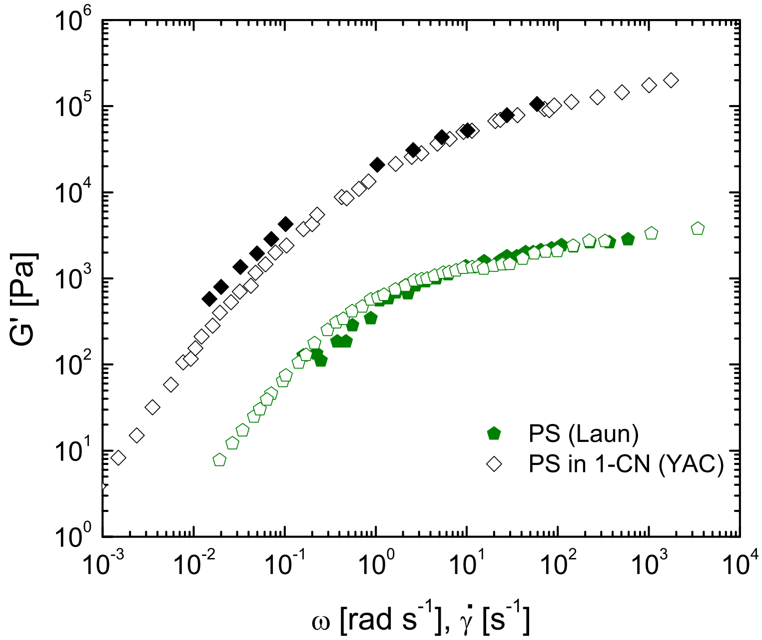
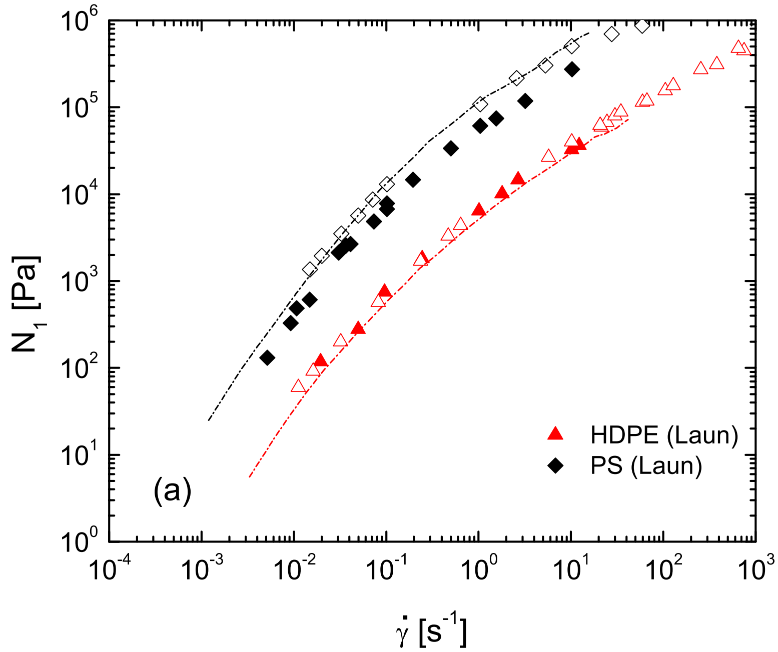


Figure 1 Comparison of storage modulus (filled squares) measured by Laun (replotted from (Laun, 1979, 1986)), and by Yasuda et al (replotted from Yasuda et al, 1981) in oscillatory shear and the values computed using the *forgotten Cox-Merz rule of elasticity* (eq. (4)), using steady shear viscosity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



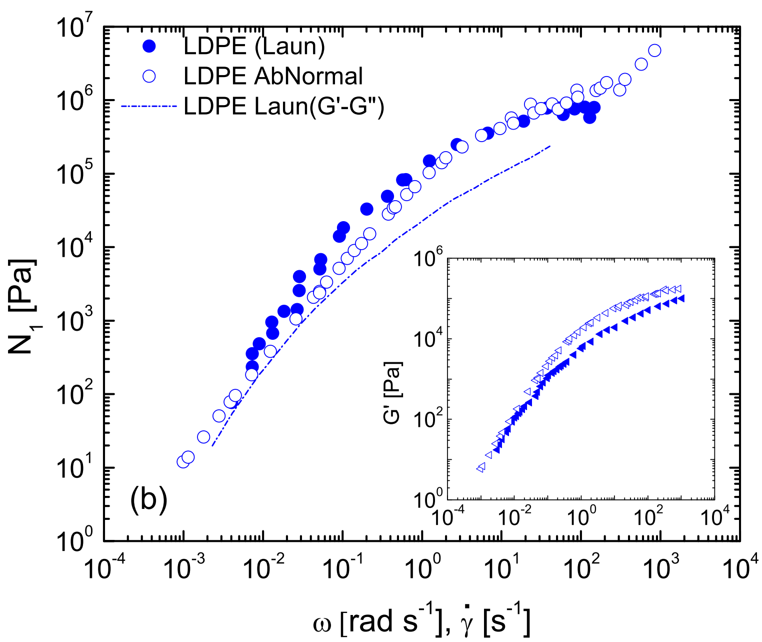


Figure 2 Measured first normal stress difference data (filled symbols) is compared to the values (open symbols) computed using the *AbNormal Rule* (eq. (7)) using Laun's data (adapted from Laun, 1986 and Laun, 1979). Laun's formula that uses oscillatory shear data is also shown (as dotted line. (a) Comparison 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 computed values (open triangles) of G' (the x-axis in inset has same label as x-axis on the main plot).

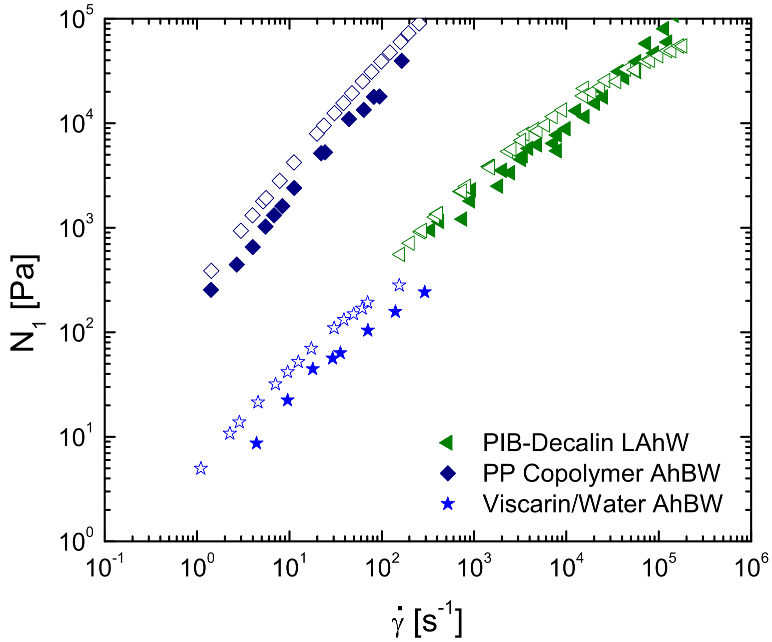


Figure 3 Measured first normal stress difference data (filled symbols) is compared to the values (open symbols) computed using the *AbNormal Rule* (eq. (7)); using data reported by Lodge et al (1987) and Al-Hadithi et al (1992) (see text and Table 1 for details).