

Fluids near a critical point obey a generalized Cox–Merz rule

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Synopsis

Upon approaching the liquid–vapor critical point, the spontaneous density fluctuations in a small-molecule fluid increase in both size and lifetime. Similar increases of the concentration fluctuations occur near the critical mixing point of a binary liquid mixture. The presence of these large fluctuations leads to an increase of the zero-shear viscosity, and their persistence in time leads to viscoelasticity and shear thinning. These rheological phenomena, which are already supported by theory and experiment, are shown here to obey a generalized form of the Cox–Merz rule. This relation formally equates the shear viscosity $\eta(\dot{\gamma})$ measured at shear rate $\dot{\gamma}$ with the magnitude of the linear complex viscosity $|\eta^*(\omega)|$ measured at frequency ω . Comparisons of theoretical results and experimental data obtained elsewhere demonstrate that fluids near a critical point obey the somewhat generalized form $\eta(k_{\text{CM}}\dot{\gamma} = \omega) = |\eta^*(\omega)|$, with $k_{\text{CM}} = 0.4$. The demonstration is simplified by showing that the Carreau–Yasuda model in the form $(1 + bA_{\dot{\gamma}}|\dot{\gamma}\tau|)^{-p}$ represents the theories for $\eta(\dot{\gamma})$ and $|\eta^*(\omega)|$ near critical points. (The product $bA_{\dot{\gamma}}\tau$ is a time constant, and $p = 0.022$ is a universal critical exponent.). © 2004 *The Society of Rheology*.
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I. INTRODUCTION

Even a fluid as simple as xenon exhibits complex rheology near its liquid–vapor critical point. Viscoelasticity, shear thinning, and normal stresses are expected in any small-molecule fluid due to the large, spontaneous fluctuations that occur near the critical point. The density fluctuations have a broad size distribution characterized by a correlation length ξ . The coupling of density fluctuations to velocity fluctuations increases the viscosity near the critical point. (A similar increase due to concentration fluctuations occurs near the critical mixing point of a binary liquid mixture.) As the critical point is approached, ξ increases, which causes the viscosity in the limit of zero frequency and shear rate to increase as

$$\eta = \eta_0(Q_0\xi)^{x_\eta}. \quad (1)$$

The values of the wave vector Q_0 and the “background” viscosity η_0 vary from fluid to fluid; however, the exponent $x_\eta = 0.069$ is universal. Thus, Eq. (1) predicts the same power-law divergence near the liquid–vapor point of a noble gas as it does near the liquid–liquid mixing point of a micellar solution, a polymer solution, or a mixture as simple as methanol and cyclohexane.

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A second universal property relevant to the rheology of critical fluids is the time constant

$$\tau = \frac{6\pi\eta\xi^3}{k_B T} = \text{constant} \times \xi^{3+x} \eta, \quad (2)$$

that characterizes the distribution of the fluctuation lifetimes. (Here, k_B is the Boltzmann constant and T is the temperature.) Dynamic scaling relates the lifetime distribution to the size distribution [Hohenberg and Halperin (1977)]. Viscoelasticity is significant at frequencies such that $\omega\tau > 1$, and shear thinning occurs when $\dot{\gamma}\tau > 1$. Measurements of both phenomena are discussed in a later section. Normal stresses, though predicted to occur, have not yet been measured near the critical point of a small-molecule fluid.

The Cox–Merz rule [Cox and Merz (1958)] equates the viscosity $\eta(\dot{\gamma})$ measured at shear rate $\dot{\gamma}$ with the magnitude of the linear complex viscosity $\eta^*(\omega)$ measured at frequency ω . This empiricism is often used to estimate the shear thinning of polymer melts [Bird *et al.* (1987), Dealy and Wissbrun (1990)]. A slightly generalized form of the rule,

$$\eta(k_{CM}\dot{\gamma} = \omega) = |\eta^*(\omega)|, \quad (3)$$

with $k_{CM} > 1$, has been applied to concentrated suspensions [Gleissle and Hochstein (2003)]. This article will show that, with $k_{CM} \approx 0.4$, the Cox–Merz rule holds near the critical point of a fluid composed of small molecules.

The physical origin of the Cox–Merz rule is not well understood. Marrucci (1996) modified the Rouse model and Ianniruberto and Marrucci (1996) modified the Doi–Edwards model to obtain consistency with the Cox–Merz rule for polymer melts. More generally, Renardy (1997) suggested that three phenomenological assumptions are sufficient to establish a similarity relation consistent with Eq. (3);

- (1) The fluid has many relaxation modes with a broad spectrum.
- (2) Contributions from different modes superpose.
- (3) The stress saturates at large shear rates.

Renardy’s suggestion supports the present result because these assumptions plausibly apply to near-critical fluids.

To demonstrate the validity of the generalized Cox–Merz rule for critical fluids, this article will first show that the Carreau–Yasuda model accurately represents the theories for $\eta(\dot{\gamma})$ and $\eta^*(\omega)$ near critical points. Using that common representation, it will then compare the best available measurements of shear thinning and viscoelasticity.

II. REPRESENTING THEORY WITH THE CARREAU–YASUDA MODEL

Figure 1 plots the Carreau–Yasuda model [Carreau (1968), Yasuda (1979), Yasuda *et al.* (1981), Bird *et al.* (1987)] and compares it with the two best theories for viscoelasticity [Bhattacharjee and Ferrell (1983)] and shear thinning [Oxtoby (1975)]. The Carreau–Yasuda model represents $\eta(\dot{\gamma})$ by an interpolation between the limits of small and large shear rate. Its general form

$$\frac{\eta(\dot{\gamma})}{\eta(0)} = [1 + (\lambda\dot{\gamma})^a]^{(n-1)/a}, \quad (4)$$

has the free parameters n , a , and the time constant λ . (The viscosity at infinite shear rate is approximated by zero here.)

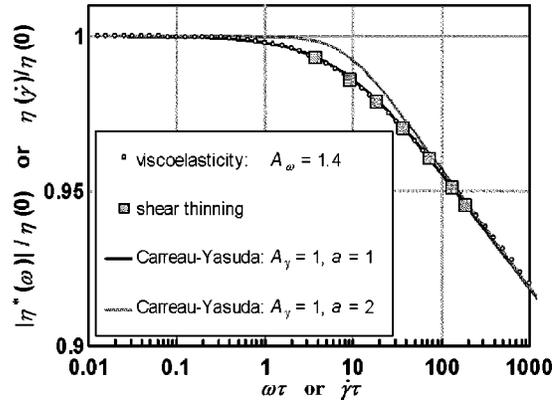


FIG. 1. A comparison of the best theories for viscoelasticity [Bhattacharjee and Ferrell (1983)] and shear thinning [Oxtoby (1975)] demonstrates that small-molecule fluids near the critical point obey the generalized Cox–Merz rule. The shear thinning points were taken from Table I, and the viscoelasticity curve was calculated from Eq. (8) with $A_\omega = 1.4$. The viscoelasticity calculation and the Carreau–Yasuda representations used the exponent value inferred from the shear thinning results at large shear rate, namely $x_\eta = x_{\eta 0} = 0.054$.

Douglas (1992) deduced the form of Eq. (4), with $a = 2$, for near-critical fluids as follows. First, he observed that $\eta(\dot{\gamma})$ is an even function of shear rate because $\eta(\dot{\gamma})$ is invariant to the direction of shear. By assuming that $\eta(\dot{\gamma})$ was also analytic in $\dot{\gamma}\tau$, he inferred the existence of a perturbation expansion for small shear rates

$$\frac{\eta(\dot{\gamma})}{\eta(0)} = 1 - A(\dot{\gamma}\tau)^2 + \dots, \tag{5}$$

where A is an undetermined constant. Resumming this expansion yielded

$$\frac{\eta(\dot{\gamma})}{\eta(0)} = [1 + A_\epsilon(\dot{\gamma}\tau)^2]^{-(x_\eta/2)/(3+x_\eta)}, \tag{6}$$

where $A_\epsilon = 2A(3+x_\eta)/x_\eta$. Douglas deduced the unique exponent $n = 1 - x_\eta/(3+x_\eta)$ based on the physical limit $\eta(\dot{\gamma}) \propto \dot{\gamma}^{-x_\eta/(3+x_\eta)}$ when $\dot{\gamma} \rightarrow \infty$, [see Eq. (2)]. The limit occurs because large shear rates destroy the fluctuations responsible for the near-critical viscosity increase. The asymptotic scaling indicated by this argument is consistent with the exact renormalization group result by Onuki and Kawasaki (1979, 1980).

Equation (6) is plausible for near-critical fluids because the Carreau–Yasuda equation with $a = 2$ successfully describes many polymer liquids [Bird *et al.* (1987)]. However, Fig. 1 shows that it disagrees with Oxtoby’s calculations at intermediate values of $\dot{\gamma}\tau$. The choice $a = 1$ yields the representation,

$$\frac{\eta(\dot{\gamma})}{\eta(0)} = [1 + bA_\gamma|\dot{\gamma}\tau|]^{-x_\eta/(3+x_\eta)}, \tag{7}$$

which also obeys the asymptotic limit but is more accurate. [Equation (7) can be deduced from the same reasoning used to obtain Eq. (6) by allowing the dimensionless shear rate to be the nonanalytic function $|\dot{\gamma}\tau|$ [Douglas (2004)].] Here, the time constant is expressed as the product $\lambda = bA_\gamma\tau$, where b is determined by theory, τ is determined by Eq. (2), and the free parameter A_γ allows for an offset between theory and experiment. Figure 1 shows that Eq. (7) describes the theory for $\eta(\dot{\gamma})$; Oxtoby’s numerical results are

TABLE I. Theoretical values for shear thinning [Oxtoby (1975)].

$\dot{\gamma}\tau$	$\eta(\dot{\gamma})/\eta(0)$
3.770	0.9929
9.42	0.9861
18.85	0.9786
37.70	0.9700
75.4	0.9603
131.1	0.9508
188.5	0.9450

matched to within 0.06%. Furthermore, Eq. (7) matches Bhattacharjee and Ferrell's (modified) theory for $|\eta^*(\omega)|$, which is remarkable given the complexity of the theory.

III. COMPARISON OF THEORIES

Theory predicts the rheology of near-critical fluids to be universal. The two approaches are mode-coupling (not to be confused with Renardy's modes) and the dynamic renormalization group. Calculations have predicted the value of the divergence exponent x_η , the crossover from noncritical to near-critical behavior, and the links among viscosity, thermal conductivity, second viscosity, and diffusion. Reviews have been written by Hohenberg and Halperin (1977), Sengers (1985), Nieuwoudt and Sengers (1987), Onuki (1997, 2002), and Folk and Moser (1998).

In Fig. 1, superposing the theoretical results for $|\eta^*(\omega)|$ and $\eta(\dot{\gamma})$ required two simple modifications to $|\eta^*(\omega)|$. Explaining those modifications first requires a brief discussion of the theoretical results for $\eta(\dot{\gamma})$ as well as $|\eta^*(\omega)|$.

The viscoelasticity curve in Fig. 1 is the magnitude of

$$\eta^*(\omega) = \eta(0)[S(A_\omega z)]^{-x_\eta/(3+x_\eta)}, \quad (8)$$

with $A_\omega = 1.4$. The appendix gives a summary, with corrections of errata, of Bhattacharjee and Ferrell's scaling function $S(A_\omega z)$; its frequency dependence is contained in the dimensionless argument $z \equiv i\omega\tau/2$. Bhattacharjee and Ferrell's original theory (1983) defined $A_\omega = 1$. An improved calculation recently increased the theoretical value of A_ω from 1 to 1.4 [Das and Bhattacharjee (2001)], but the correct value is likely even larger because $A_\omega = 2.0$ describes the only quantitative measurements of $\eta^*(\omega)$ [Berg *et al.* (1999), Flossman *et al.* (2001)].

Bhattacharjee and Ferrell constructed Eq. (8) by assuming that their mode-coupling result

$$\frac{\eta^*(\omega)}{\eta(0)} = 1 - \frac{x_\eta}{3+x_\eta} \ln[S(A_\omega z)], \quad (9)$$

expressed the first terms of an exponential expansion. Thus, in the limit $\omega\tau \gg 1$, where $S(A_\omega z) \propto \ln(z)$, the exponential form of Eq. (8) has the required power-law dependence $(\omega\tau)^{-x_\eta/(3+x_\eta)}$.

The shear thinning points of Fig. 1 represent the only published calculation of shear thinning at intermediate values of $\dot{\gamma}\tau$. Oxtoby's results appeared only as a curve; the values used to draw that curve are listed in Table I.

For large reduced shear rates $\dot{\gamma}\tau$, Oxtoby's results approach

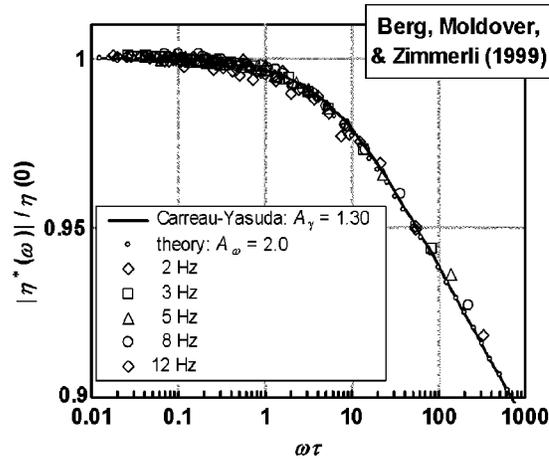


FIG. 2. Viscoelasticity near the liquid–vapor critical point of xenon. The theoretical curve is Eq. (8) with the experimental values $A_\omega = 2.0$ and $x_\eta = 0.069$. The Carreau–Yasuda representation with $A_\gamma = 1.30$ is nearly identical.

$$\frac{\eta(\dot{\gamma})}{\eta(0)} \approx 1 - \frac{x_\eta 0}{3 + x_\eta 0} \ln(b\dot{\gamma}\tau); \quad (10)$$

where b is a universal coefficient. The value of the exponent $x_\eta 0 = 0.054$ reflects the approximations used by Oxtoby; it is smaller than later theoretical values and the accurate experimental value $x_\eta = 0.069$ [Berg *et al.* (1999)]. The value $b = 0.121$ derived from Oxtoby’s results may differ from its true value due to the same approximations; the parameter A_γ in Eq. (7) allows for that possibility.

Two modifications to the analytical expression for $\eta^*(\omega)$ [Eq. (8)] allow it to be compared to the numerical calculations of $\eta(\dot{\gamma})$ [Table I] at the same level of approximation. The first modification, as suggested by comparing Eqs. (9) and (10), is the use of the same approximate exponent $x_\eta 0 = 0.054$. The second modification is an adjustment of the frequency scale factor to $A_\omega = 1.4$. (Generalizing the Cox–Merz rule with $k_{CM} \neq 1$ allows such an adjustment.) Figure 1 shows that the result is in close agreement between $\eta(\dot{\gamma})$ and $|\eta^*(\omega)|$ over the range $4 < \dot{\gamma}\tau < 189$.

IV. COMPARISON OF MEASUREMENTS

This section shows that, within the scale factor A_γ , the Carreau–Yasuda model represents experimental data as well as theoretical results for $\eta(\dot{\gamma})$ and $|\eta^*(\omega)|$. Experimental measurements are possible near the critical mixing point of a binary liquid mixture because careful control of temperature and concentration in the laboratory allows correlation lengths as large as $1 \mu\text{m}$ and fluctuation lifetimes as large as 1 s. Measurements are possible also near the liquid–vapor critical point, but gravitational stratification usually adds a significant complication [Moldover *et al.* (1979)].

Figure 2 shows the data of Berg *et al.* (1999), who measured viscoelasticity in xenon in microgravity. This is the only quantitative measurement of near-critical viscoelasticity. Previous observations of $\eta^*(\omega)$ in carbon dioxide [Bruschi and Santini (1979), Bruschi (1982)], xenon [Izumi *et al.* (1981)], and binary liquid mixtures [Izumi *et al.* (1981), Berg and Moldover (1988)] were only semiquantitative. Figure 2 includes a Carreau–

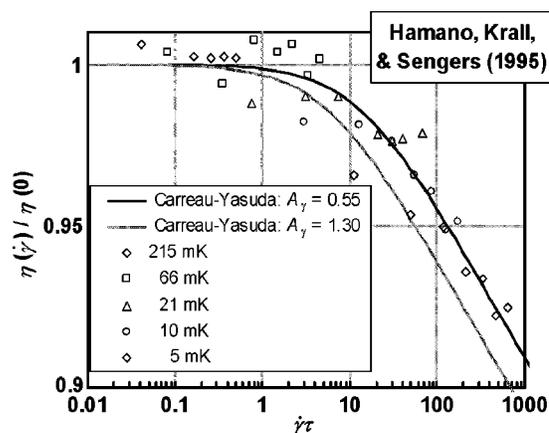


FIG. 3. Shear thinning near the critical mixing point of a micellar solution. The data were taken at five temperature differences from the critical temperature; smaller differences caused larger values of the characteristic fluctuation lifetime τ . Both curves use the experimental value $x_\eta = 0.069$ in the Carreau–Yasuda representation of Eq. (7). The curve using $A_\gamma = 0.55$ represents the shear thinning data shown here, and the curve using $A_\gamma = 1.30$ represents the viscoelastic data of Fig. 2. Therefore, the Cox–Merz rule holds with $k_{CM} = 0.55/1.30 \approx 0.4$.

Yasuda representation that consists of Eq. (7) with the experimentally determined exponent $x_\eta = 0.069$ and the value $A_\gamma = 1.30 \pm 0.02$.

Figure 3 shows the shear-thinning data of Hamano *et al.* (1995), who used a Couette viscometer to create a uniform shear field in a micellar solution. Previous observations of $\eta(\dot{\gamma})$ in capillary viscometers [Allegra *et al.* (1971), Stein *et al.* (1971), Yang and Meeks (1971), Tsai and McIntyre (1974), Hamano *et al.* (1982), Pegg and McLure (1984), McLure and Clements (1997)] were similarly quantitative, but the effective shear rate used to describe the inhomogeneous shear field introduced an ambiguity into the analyses. Shear-thinning capillary data are better analyzed with the Weissenberg–Rabinowitsch equation. (See Example 10-2-32 in [Bird *et al.* (1987)].)

Figure 3 includes two Carreau–Yasuda representations that differ only in the value of A_γ . Using $A_\gamma = 0.55 \pm 0.06$ in Eq. (7) represents $\eta(\dot{\gamma})/\eta(0)$. However, using $A_\gamma = 1.30 \pm 0.02$ in Eq. (7) represents $|\eta^*(\omega)|/\eta(0)$ in Fig. 2. Therefore, the generalized Cox–Merz rule holds with $k_{CM} = 0.55/1.30 \approx 0.4$.

V. CONCLUSION

Three subtleties require mention. First, the understanding of critical fluctuations as physical “clusters” having a size distribution is incomplete. Sator’s helpful review [Sator (2003)] describes the correspondence between the thermodynamics and microscopic morphology of simple fluids in terms of clusters. A recent molecular dynamics simulation of a Lennard-Jones fluid [Campi *et al.* (2001)] yielded distributions of cluster sizes but not cluster lifetimes. Second, dynamic renormalization group theory strictly applies only when the fluid is so close to its critical point that Eq. (1) yields $\eta \gg \eta_0$. That “asymptotic” region is experimentally inaccessible due to the small value of the exponent x_η . Fortunately, there is a broader, accessible region where “crossover” effects are sufficiently small for Eqs. (1), (7), and (8) to be accurate. The multiplicative form of those equations is a postulate [Ohta (1977)] that reconciles the results of mode coupling with those of the dynamic renormalization group [Sengers (1985)].

The third subtlety is that the data of Fig. 3 were not corrected for a shift of T_c caused by shear rate. Theory predicts a shift of

$$[T_c(0) - T_c(\dot{\gamma})]/T_c(0) \propto (\tau_0 \dot{\gamma})^{1/\nu(3+x\eta)}, \quad (11)$$

where τ_0 is the amplitude for the fluctuation decay time τ and ν is the critical exponent for the correlation length ξ [Onuki and Kawasaki (1979), Onuki (1997)]. The simplest application of Eq. (11) is to decrease the time constant that appears in Eq. (7) from $\tau(T - T_c(0))$ to $\tau(T - T_c(\dot{\gamma}))$. That correction would have increased the value of A_γ from 0.55 to 0.85 without changing the general result. The correction was not used because its validity is unclear in the present context. In particular, it makes Eq. (7) independent of shear rate at T_c , a result that disagrees with both theory [Onuki and Kawasaki (1980)] and experiment [Hamano *et al.* (1992)].

At experimentally accessible temperatures the effects of shear thinning and viscoelasticity in near-critical fluids are rather small. Nevertheless, rheological studies near critical points may interest polymer scientists because the associated theories have little empiricism. A detailed explanation of the Cox–Merz rule in near-critical fluids seems feasible as well as desirable. Such an explanation might, for example, calculate the value of k_{CM} , which is presumably universal. More generally, it would add to the connections between near-critical fluids and polymer liquids already pointed out by Douglas (1992).

Improved experiments are also desirable. Ideally, they would measure $\eta(\dot{\gamma})$ and $\eta^*(\omega)$ in the same fluid, and the data would have a span and accuracy comparable to Fig. 2. A rheometer adapted for small viscosity and millikelvin temperature control could measure $\eta(\dot{\gamma})$ and $\eta^*(\omega)$ in a uniform shear field near the critical mixing point of a binary liquid mixture. Measurements of the normal stresses in the same mixture also would be interesting.

APPENDIX: FREQUENCY-DEPENDENT SCALING FUNCTION $S(z)$

This Appendix reproduces the scaling function $S(z)$ derived by Bhattacharjee and Ferrell (1983). Two typographic errors in the original published expressions for $\ln(S_4)$ and for $R(z)$ are corrected.

The dependence of the viscosity on correlation length ξ and frequency ω is

$$\eta(\xi, \omega) = \eta(\xi, 0) S^{-x} \eta^{/(3+x\eta)}, \quad (A1)$$

where the argument of the scaling function $S(z)$ is the scaled frequency defined by $z \equiv -i\omega t/2$. Bhattacharjee and Ferrell used the decoupled-mode theory to calculate $S(z)$ to single-loop order. They accurately approximated their result in closed form by an average of calculations in two and four dimensions

$$S(z) \approx (\tilde{S}_2)^{2/3} (\tilde{S}_4)^{1/3}. \quad (A2)$$

Here, the tilde refers to additional rescalings given by

$$\tilde{S}_2(z) \equiv S_2((2/e)^3 z) \quad \text{and} \quad \tilde{S}_4(z) \equiv S_4((8/e)z). \quad (A3)$$

The scaling functions S_2 and S_4 are given by

$$\ln(S_2) = \left(\frac{z}{z-1} \right) + \left(\frac{z}{z-1} \right)^2 \ln(z) \quad (A4)$$

and

$$\ln(S_4) = \left(-3 + \frac{2}{z}\right) + \left(1 - \frac{3}{z} + \frac{1}{z^2}\right) \ln(z) + \left(5 - \frac{5}{z} + \frac{1}{z^2}\right) R(z), \quad (\text{A5})$$

where

$$R(z) = \left(\frac{1}{(1-4z)^{1/2}}\right) \ln\left(\frac{1+(1-4z)^{1/2}}{1-(1-4z)^{1/2}}\right), \quad |z| < \frac{1}{4},$$

$$R(z) = \left(\frac{1}{(4z-1)^{1/2}}\right) \tan^{-1}[(4z-1)^{1/2}], \quad |z| \geq \frac{1}{4}. \quad (\text{A6})$$

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