Shear thinning of a critical viscoelastic fluid

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The frequency and shear dependent critical viscosity at a correlation length $\xi=\kappa^{-1}$ has the form $\eta=\eta_0\kappa^{-x_\eta}G(z_1,z_2)$, where z_1 and z_2 are the independent dimensionless numbers in the problem defined as $z_1=-i\omega/2\Gamma_0\kappa^3$ and $z_2=-i\omega/2\Gamma_0\kappa_c^3$. The decay rate of critical fluctuations of correlation length κ^{-1} is $\Gamma_0\kappa^3$ and k_c is the effective wave number for which $\Gamma_0 k_c^3=S$, the shear rate. The function $G(z_1,z_2)$ is calculated in a one-loop self-consistent theory.

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Response functions, in general, tend to diverge near a second-order phase transition point. As the fluctuations become more long range and drive the system toward the transition, the response functions in the thermodynamic limit (if static) and in the hydrodynamic limit (if dynamic) diverge. Some, such as the susceptibility (static) and thermal diffusivity (dynamic) [1], diverge strongly with an exponent near one, others, such as the specific heat (static) and shear viscosity (dynamic) [2–4], diverge weakly with an exponent close to zero. The small exponents have always provided an interesting challenge for theorists and experimentalists. The shear viscosity of ordinary fluids or binary mixtures, in particular, has been a favorite candidate for pushing theory and experiment to the limit. The exponent is small but over the last two decades the experiments [5,6] have increased the accuracy of the measurements so strongly that theorists have had to worry about higher loops [7,8], something, which is rarely done.

The critical divergence is masked if the system is not in the hydrodynamic limit. Hydrodynamic limit implies the wavelength is larger than the critical correlation length and all frequencies are lower than the rate of decay of critical fluctuations. While wavelengths are always larger than the critical correlation length, critical slowing down may imply that frequencies may not be smaller than the fluctuation relaxation rate. The frequency of an oscillating viscometer used to measure the critical viscosity can, in that case, determine the viscosity of the sample, and the fluid will become viscoelastic.

The frequency dependence of the viscosity has been predicted [9,10] and measured over the last two decades. It has been recognized by Oxtoby [13] and others [9–12] that a shear rate will also introduce a time scale in the problem, and, if the fluctuations are more long lived than this time scale, then experiments on this time scale will not feel the longest-lived fluctuations and the viscosity will be limited by the shear rate—a phenomenon known as shear thinning. The dependence of various static quantities on the shear rate as well as its effect on light scattering has been considered by Onuki [14] as well as Onuki and Kawasaki [15]. With so much information available on both theoretical and experimental fronts, experiments have been designed to test the shear thinning of critical viscoelastic fluids. The only previous measurement of shear thinning near a critical point is that of Hamano *et al.* [16], which was carried out on a micellar solution. We have carried out a one-loop calculation of the frequency and shear dependent critical viscosity and present our results in this paper.

It should be noted that the physical effect of both finite frequency and finite shear are similar. They both inhibit the divergence of the hydrodynamic shear viscosity because they produce an effective low-momentum cutoff to the continuous distribution of modes in the system. This has prompted the recent observation by Berg [17] that there should be a Cox-Merz [18] rule for the critical fluid. The Cox-Merz rule equates the viscosity $\eta(S)$ measured at a shear rate S and zero frequency to the viscosity $\eta(\omega)$ measured at some frequency ω and zero shear. This observation is often used to estimate shear thinning of polymer melts [19], and a slightly generalized form has been applied to concentrated suspension [20]. The physical origin of the Cox-Merz rule has been explored by Renardy [21]. It is clear that this empirical observation will be correct in a general sense, but a complete description of the shear thinning and especially shear thinning in the presence of viscoelasticity (on this issue the Cox-Merz rule is not applicable) can be had only on the basis of a detailed calculation. This is the aim of our paper.

We begin by discussing the effect of critical fluctuations on the shear viscosity of a fluid near its critical point. First, we consider the proper hydrodynamic limit, i.e., wave vector (k) and frequency (ω) tend to zero.

In the hydrodynamic regime, characterized by the sole length scale, the correlation length $\xi=\kappa^{-1}=\xi_0[(T-T_c)/T_c]^{-\nu}$ with $\nu\simeq\frac{2}{3}$, the shear viscosity diverges as

$$\eta(\kappa)=\eta_0\kappa^{-x_\eta}, \tag{1}$$

where x_η is the small exponent discussed above which is found to be around 0.068. The decay time of the critical fluctuations τ is given by

$$\tau^{-1}=\Gamma(k,\kappa)=\frac{L}{\chi}k^2, \tag{2}$$

where L is the Onsager coefficient and χ is the static susceptibility. The critical susceptibility can, to a very good accuracy, be taken as $\chi^{-1}(k,\kappa)=k^2+\kappa^2$, and the Onsager coefficient or thermal diffusivity diverges at the critical point. The behavior of wavelength and correlation length dependent diffusivity is governed by the Kawasaki function [1], which was simplified for practical use by Ferrell [22] and can be used in the form

$$L = \Gamma_0(k^2 + \kappa^2)^{-1/2} \tag{3}$$

in $D=3$, where D is the spatial dimensionality. The characteristic decay time of a fluctuation of wavelength equal to the correlation length is given by

$$\tau^{-1} = \Gamma(\kappa) = \Gamma_0\kappa^3. \tag{4}$$

Hydrodynamic regime implies that frequencies are such that $\omega\tau \ll 1$. However, at a fixed frequency ω, as κ decreases on approaching the critical point, τ diverges and it is not possible to satisfy $\omega\tau < 1$. In that situation Eq. (1) cannot hold, and, if $\tau^{-1} \simeq 0$, the response is limited by the frequency ω. Since ω scales as κ^3, it is clear that the limiting viscosity will be of the form

$$\eta(\omega) = \eta_0(-i\omega)^{-x_\eta/3} \tag{5}$$

and the full viscosity will be governed by

$$\eta(\kappa,\omega) = \eta_0\kappa^{-x_\eta}F(z)^{-x_\eta/3}, \tag{6}$$

where $F(z)$ is a function of the dimensionless variable $z = -i\omega/2\Gamma_0\kappa^3$. For $z \to 0$, $F(z) \to 1$ and if $z \gg 1$, $F(z) \propto z$. The simplest possible functional representation of $F(z)$ is

$$F(z) = 1 + \beta z. \tag{7}$$

Now, β is a number of $O(1)$, which can be found from the small z form of the one-loop integral or from the $z \gg 1$ form. If determined from the low-frequency end $\beta = 3\pi/16 \simeq 0.59$. From the high-frequency end $\beta \simeq 0.2$. The two-loop calculation is found to enhance β by about 30% to 0.8 at the low-frequency end. The experimental value found by Berg *et al.* [6] is about 1.2.

If a shear rate S is now switched on, which results in a mean flow in (say) the x direction, then the velocity can be written as

$$\vec{v} = Sy\hat{e}_x. \tag{8}$$

The shear rate S introduces a length scale k_c^{-1} defined by

$$S = \Gamma k_c^3. \tag{9}$$

Strong shear implies $k_c > \kappa$, while the reverse is the case of weak shear. Our primary interest will be in strong shear, which will always be the case, sufficiently close to the critical point. For the shear thinning of a viscoelastic fluid we now have two dimensionless numbers in the problem $z_1 = \omega/2\Gamma_0\kappa^3$ and $z_2 = \omega/2\Gamma_0 k_c^3$ and Eq. (6) is generalized to

$$\eta = \eta_0\kappa^{-x_\eta}[G(z_1,z_2)]^{-x_\eta/3} \tag{10}$$

Our purpose is to find an expression for $G(z_1,z_2)$ at the one-loop level.

The equation of motion for the order parameter is nonlinear. The effect of the nonlinearity is to make the transport coefficient divergent in the absence of the shear. The contribution of the shear to the equation of motion is a linear term. Consequently, we will work with an effective equation of motion where the effect of the nonlinear terms will be handled by a dressing of the transport coefficient. Consequently, in momentum space, the order parameter $\phi(\vec{k})$ satisfies

$$\frac{\partial\phi(\vec{k})}{\partial t} + S\frac{\partial}{\partial k_y}\phi(\vec{k}) = -\frac{Lk^2}{\chi}\phi(\vec{k}) + \eta, \tag{11}$$

where $\chi^{-1} = k^2 + \kappa^2$ and $L = \Gamma_0\chi^{1/2}$ as explained in Eq. (3). We now need to work out the susceptibility in the presence of S, and this is simply retracing Onuki's calculation with the present L. This leads in a straightforward fashion to

$$\chi^{-1} = k^2 + \kappa^2 + k_c^2\left(\frac{|k_x|}{k_c}\frac{2}{\pi}\right)^{1/2}. \tag{12}$$

The effect of the changed diffusion coefficient shows up in the slightly different k_x dependence in the last term on the right-hand side. In the expression for viscosity, the susceptibility will be averaged over all directions, and, for that specific case, we will use an angle averaged form of χ^{-1}, where we replace $|k_x|^{1/2}$ by $k^{1/2}\langle\sin^{1/2}\theta\cos^{1/2}\theta\rangle = \frac{2}{3}k^{1/2}$. The one-loop shear viscosity is now given by

$$\begin{aligned}
\eta(\kappa,\omega,S) &= \frac{\eta_0}{4\pi}\int d^3p\frac{\chi^2(p,\kappa,S)p^4}{-i\omega + 2\Gamma_0 p^2[\chi(p,\kappa,S)]^{1/2}} \\
&= \frac{\eta_0}{4\pi}\int d^3p\frac{p^4}{\left[p^2 + \frac{2}{3}\left(\frac{2}{\pi}\right)^{1/2}k_c^2\left(\frac{p}{k_c}\right)^{1/2} + \kappa^2\right]^2}\frac{1}{\left[-i\omega + 2\Gamma_0 p^2\left[p^2 + \frac{2}{3}\left(\frac{2}{\pi}\right)^{1/2}k_c^2\left(\frac{p}{k_c}\right)^{1/2} + \kappa^2\right]^{1/2}\right]} \\
&= \frac{\eta_0}{8\pi\Gamma_0}\int d^3p\frac{p^4}{\left[p^2 + \frac{2}{3}\left(\frac{2}{\pi}\right)^{1/2}\left(\frac{z_1}{z_2}\right)^{1/2}p^{1/2} + 1\right]^2}\frac{1}{\left[z_1 + p^2\left[p^2 + \frac{2}{3}\left(\frac{2}{\pi}\right)^{1/2}\left(\frac{z_1}{z_2}\right)^{1/2}p^{1/2} + 1\right]^{1/2}\right]}.
\end{aligned} \tag{13}$$

It is the characterization of this one-loop integral that has to be carried out. The limit $z_2 \to \infty$ (or $k_c \to 0$, i.e., no shear) has already been treated, and this is what we represent to the lowest order by Eq. (7). It should be noted that Eq. (13) has a logarithmic divergence rather than a power-law divergence. To extract $G(z_1,z_2)$ from Eq. (15), we use the fact that $x_\eta \ll 1$ and expand Eq. (10) as

$$\eta = \eta_0 \kappa^{-x_\eta}[G(z_1,z_2)]^{-x_\eta/3} \simeq \eta_0\left[1 - x_\eta \ln \kappa - \frac{x_\eta}{3}\ln G(z_1,z_2)\right] = \eta_B + \eta_0\left[\ln\frac{\Lambda}{\kappa} - \frac{1}{3}\ln G(z_1,z_2)\right], \tag{14}$$

where η_B is a background viscosity and the part within the square brackets emerges from the loop calculation. Here we anticipate the emergence of a cutoff wave number Λ and include it in the definition of the background viscosity.

For $z_2 \to \infty$, Eq. (13) becomes

$$\eta(\omega,\kappa) = \frac{\eta_0}{2\Gamma_0}\int_0^{\Lambda/\kappa} dp \frac{p^6}{(1+p^2)^2}\frac{1}{[z_1 + p^2(1+p^2)^{1/2}]} = \frac{\eta_0}{2\Gamma_0}\left[\ln\frac{\Lambda}{\kappa} + \ln 2 - 2 + \frac{\pi}{4} - \frac{\pi}{16}z_1 + \cdots\right] \tag{15}$$

for $z_1 \ll 1$. On the other hand for $z_1 \gg 1$, $\eta(\omega,\kappa)=(\eta_0/2\Gamma_0)\times[\ln \Lambda/\kappa - \frac{1}{3}\ln z_1 + \cdots]$, which when combined with Eq. (15), leads to the approximation shown in Eq. (7).

Another limit that can be similarly explored is $\omega \to 0$ (i.e., $z_1 \to 0$ and $z_2 \to 0$, but $z_1/z_2 \neq 0$) in which case, Eq. (13) becomes

$$\eta(S,\kappa) = \frac{\eta_0}{2\Gamma_0}\int_0^{\Lambda/\kappa} dp \frac{p^4}{\left[p^2 + \frac{1}{2}\left(\frac{z_1}{z_2}\right)^{1/2} p^{1/2} + 1\right]^{5/2}}. \tag{16}$$

For $z_1/z_2 \ll 1$, an expansion similar to Eq. (15) obtains. For $(z_1/z_2) \gg 1$, we scale momenta by $(z_1/z_2)^{1/3}$ to find

$$\eta(S,\kappa \to 0) = \frac{\eta_0}{2\Gamma_0}\int_0^{\Lambda/k_c} dp \frac{p^4}{\left[p^2 + \frac{1}{2}p^{1/2} + \left(\frac{z_2}{z_1}\right)^{2/3}\right]^{5/2}} \simeq \frac{\eta_0}{2\Gamma_0}\left[\ln\frac{\Lambda}{k_c} + \frac{4}{3}\ln 2 - \frac{8}{3} + \frac{2\pi}{3} + \cdots\right]. \tag{17}$$

Combining Eq. (17) with the small z_1/z_2 form,

$$G(z_1 \to 0, z_2 \to 0) = \left[1 + 0.3\left(\frac{z_1}{z_2}\right)^{1/2}\right]^2. \tag{18}$$

Finally, as $\kappa \to 0$, $z_1 \to \infty$ with finite z_2 and Eq. (15) reduces to

$$\eta(\omega,S) = \frac{\eta_0}{2\Gamma_0}\int_0^{\Lambda/k_c} dp \frac{p^6}{\left[p^2 + \frac{1}{2}p^{1/2}\right]^2\left[z_2 + p^2\left(p^2 + \frac{1}{2}p^{1/2}\right)^{1/2}\right]}. \tag{19}$$

For $z_2 \to 0$, we recover Eq. (19), while for $z_2 \to \infty$,

$$\eta(\omega,S) = \frac{\eta_0}{2\Gamma_0}\left[\ln\frac{\Lambda}{k_c} - \frac{1}{3}\ln z_2 - \frac{3\pi}{8z_2^{1/2}} + \cdots\right]. \tag{20}$$

We thus obtain the following limiting forms:

$$G(z_1,z_2) \to 1 + 0.6z_1 \quad \text{if } z_2 \to \infty,$$

$$G(z_1,z_2) \to 0.6z_1\left[1 + \frac{3}{2}\frac{1}{z_2^{1/2}}\right]^2 \quad \text{if } z_1 \to \infty,$$

$$G(z_1,z_2) \to \left[1 + 0.3\left(\frac{z_1}{z_2}\right)^{1/2}\right]^2 \quad \text{if } z_1, z_2 \to 0. \tag{21}$$

The form of $G(z_1,z_2)$, taking into account all the above constraints, is given by the interpretation formula

$$G(z_1,z_2) = [1 + 0.6z_1]\left[1 + \frac{3}{2z_2^{1/2}} \times \frac{1 + 0.2/z_1^{1/2}}{1 + \frac{1}{z_1}}\right]. \tag{22}$$

This is the desired one-loop result. A phenomenological improvement can be obtained by going to the zero shear limit at finite frequency. This implies $z_2 \to \infty$, while z_1 is finite. In this limit, accurate measurements [6] have been made and we know from these results that the first factor on the right-hand side of Eq. (22) represents the data very well, provided 0.6 is replaced by 1.2. As already explored, part of this can be accounted for by a two-loop calculation [23], and, hence, a phenomenological improvement of Eq. (22) would be to replace the coefficient 0.6 by 1.2.

In closing we note that the details of $G(z_1,z_2)$ differ in one essential way from what could be learned on the basis of a Cox-Merz rule. This has to do with the nonanalytic behavior in z_2 and z_1 in the second factor of the right-hand side of Eq. (22). This nonanalytic behavior is a direct reflection of the form of the static susceptibility in Eq. (12). The $k_x^{1/2}$ behavior shown in Eq. (12) leads to the corresponding nonanalytic behavior in Eq. (22). This would be an important issue in any forthcoming experiment.

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