PHYSICAL REVIEW E VOLUME 62, NUMBER 2 AUGUST 2000

Fluctuations in dispersion rheology

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(Received 16 February 2000)

On the basis of the mesoscopic fluctuations of excess density, an experimentally verified model is developed to describe the effective shear viscosity and modulus of complex dispersions as a function of concentration, frequency, and temperature. A stochastic differential equation is used in the derivation of the zero-shear viscosity that shows large viscosity enhancement over a broad range of concentrations. The scaling behavior of shear thinning is determined from an anomalous diffusion equation. We obtain the shear-thinning exponent $1>\beta>\frac{1}{2}$, which depends on the tenuous fractal structure of the complex systems. The divergence of the shear viscosity in the vicinity of a critical temperature is derived as a dynamic critical phenomenon due to thermal fluctuations, and the critical exponent relates directly to the shear-thinning exponent.

PACS number(s): 82.70.Dd, 05.20.−y, 83.50.Fc

I. INTRODUCTION

The viscoelasticity of dispersions exhibits extraordinarily complex phenomena that are of scientific and technological importance because the materials have a wide range of phases from liquid to solid depending on composition, interparticle interactions, and frequency. The physics of hard-sphere dispersion (HSD) has been extensively investigated; in HSD the repulsive interactions between colloidal particles play a key role in establishing structure-property relationships [1–9]. For spherical colloids, explicit expressions for the shear rate and frequency dependence of viscoelasticity have been derived on the basis of the generalized Smoluchowski diffusion equation, in which both the long-range hydrodynamic interactions and the short-range particle interactions are considered [4–8]. A divergence of the effective low-shear limiting viscosity of HSD has been predicted by these mean-field theories [4–7] and verified by experimental data [2]. However, the particles in our complex systems will have very irregular shapes.

When attractive interparticle forces are present, aggregated colloids experience a significant increase in viscosity at low-to-moderate volume concentrations [10–14]. As well as hydrodynamic force and Brownian motion, different repulsive and attractive interactions are expected to exist cooperatively in complex dispersions that consist of polymeric particles, additives, and carrier fluids. This is a real-world problem encountered in many technological applications and presents an interesting scientific challenge. It is unlikely that one can take accurate account of the many-body interactions between different particles and molecules by following the familiar path of studying hard-sphere, aggregated colloids, or polymer gels [15–17]. Therefore, the purpose of this paper is to find an alternative approach for explaining the many unexpected properties of complex dispersions.

A wealth of information is usually associated with the density fluctuations in dynamic shear flow. The evolution of their correlation functions leads to the derivation of the *effective* shear viscosity and modulus. Three types of fluctuation of local density will be considered. The first is the compositional fluctuation that is related to the liquidlike and solidlike fluctuations. The second is the time- and space-dependent dynamic fluctuation. The third is thermal fluctuation in the vicinity of a critical temperature (T_c). The model will then be used to explain the unusual experimental observations in complex dispersions.

The experimental data are obtained from a rheometer manufactured by Rheometrics. The complex fluids consist of filled-polymer particles, rheological additives, and carrier fluids. Colorant, charge-capture additive, and polyester resin are the ingredients of the particles with irregular shapes and surfaces. The carrier fluids have the structure of hydrocarbon isomers. We shall see that the rheological additives influence not only the repulsive but also the attractive forces between particles. Therefore, the structure and properties of the complex dispersions differ completely from those of simple HSD, in which the repulsive forces play a dominant role.

In contrast to the percolation transition of HSD, the composition-dependent transition of the zero-shear viscosity from liquid to solid is soft. In the shear-thinning regime, power-law decay is found to be valid for the real part of the dynamic shear viscosity and modulus over decades of useful frequency range, and a non-mean-field exponent is obtained that is significantly greater than the value $\frac{1}{2}$ for HSD. The dynamic shear viscosity is found to diverge with temperature near T_c, which differs completely from the reported temperature dependence for HSD [18]. In addition, the critical exponent for this transition may be related to the shear-thinning exponent.

II. COMPOSITIONAL FLUCTUATIONS

The inhomogeneity in complex dispersions can be represented by the excess number density of defects, $\delta n=n-\langle n\rangle$, where $\langle n\rangle$ is the homogeneous average. Using the generalized concept of Doolittle [19–20], the shear viscosity (η) is related to the defect volume (v) by

$$\ln\eta\sim\frac{1}{v}\sim\left\langle\frac{1}{n}\right\rangle=\left\langle\frac{1}{\langle n\rangle}\left(1-\frac{\delta n}{\langle n\rangle}+\frac{(\delta n)^2}{\langle n\rangle^2}+\cdots\right)\right\rangle \tag{1}$$

for $\delta n/\langle n\rangle\ll 1$. This microscopic defect is not free volume but is assumed to have heavier mass. Noting that $\langle\delta n\rangle=0$, the relative velocity becomes

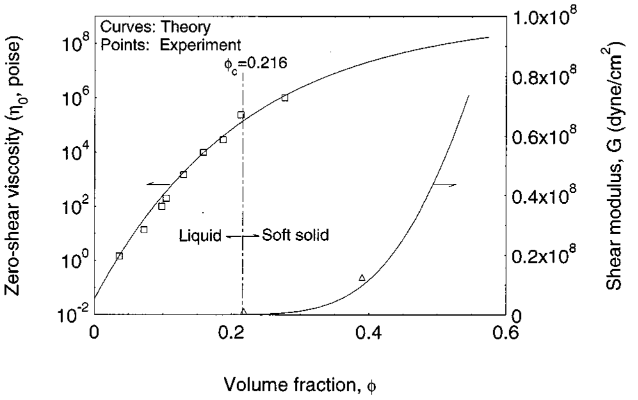

FIG. 1. Calculated zero-shear viscosity and modulus are compared with experimental data measured at 0.1 rad/sec and 23 °C. The viscosity of the carrier fluid is 3.7×10^{-2} P.

$$\ln \eta_r \equiv \ln\left(\frac{\eta}{\eta_2}\right) = \Delta(\ln \eta) \sim \langle(\delta n)^2\rangle, \tag{2}$$

where η_2 is the viscosity of the carrier fluid. The density fluctuations (δn) will be investigated as a function of compositional, dynamic, and thermal fluctuations in the rest of this paper.

In the study of compositional dependence, consider the change of excess number density, which is governed by the Langevin-like stochastic equation

$$\frac{d(\delta n)}{d\phi} = -\frac{\delta n}{2\phi_c} + \mu(\phi), \tag{3}$$

where ϕ is the volume fraction of polymeric particles and μ is the noise term that is the source of fluctuations for δn. The critical volume fraction ϕ_c is identified with the correlation range of the compositional fluctuations [21]. Integrating Eq. (3), squaring it, and taking the mean, we get

$$\langle[\delta n(\phi)]^2\rangle = \exp(-\phi/\phi_c)\int_0^\phi\int_0^\phi \exp\left(\frac{\phi_1+\phi_2}{2\phi_c}\right) \times\langle\mu(\phi_1)\mu(\phi_2)\rangle d\phi_1 d\phi_2 . \tag{4}$$

Assuming the noise is uncorrelated, as in most applications, we have concentration-independent white noise with $\langle\mu\rangle = 0$ and

$$\langle\mu(\phi_1)\mu(\phi_2)\rangle = A\delta(\phi_1-\phi_2). \tag{5}$$

The constant A is determined by treating $\langle\delta n^2(0)\rangle \equiv \langle\delta n_0^2\rangle$ as the variance of the fluctuations. This gives the strength of the noise $A=\sigma^2/\phi_c^2$ and the standard deviation $\sigma = \sqrt{\langle(\delta n_0)^2\rangle}$. Substituting Eq. (5) into Eq. (4) yields

$$\langle[\delta n(\phi)]^2\rangle = \sigma^2[1-\exp(-\phi/\phi_c)]. \tag{6}$$

Combining Eqs. (2) and (6), we obtain

$$\ln \eta_r = B[1-\exp(-\phi/\phi_c)], \tag{7}$$

where B is a constant. Figure 1 shows that Eq. (7) provides a good description of the zero-shear viscosity (η_0) of complex dispersions. We have replaced η in Eq. (7) by η_0, and chosen $B=23.95$ and $\phi_c=0.216$ to fit the experimental data. The intrinsic shear viscosity $[\eta]\equiv\lim_{\phi\to 0}(\eta-\eta_2)/\eta_2\phi = B/\phi_c = 110.9$ of this system is much higher than the value 2.5 of HSD [1]. The rheological additives have significantly enhanced the intrinsic viscosity that may arise from the attractive forces when repulsive forces are present.

Figure 1 also shows the appearance of a measurable shear modulus (G) at the critical volume fraction, which may be interpreted as a soft transition from liquid to solid [22]. The presence of strong attractive interactions inhibits the repulsion-dominated percolation transition observed in hard-sphere dispersion [2–5]. The concentration dependence of the shear modulus can be determined from

$$\eta_0(\phi) = \int_0^\infty G(t,\phi)dt. \tag{8}$$

In measurements, the frequency for the zero-shear viscosity cannot reach zero but is kept very low. The low-shear limit obtained from Eq. (7) can be approximated by a power-law dependence upon the volume fraction ϕ with a power of 8.2 for $0.1<\phi<0.4$. This is much higher than the value of 5.3 for weakly aggregated polystyrene latex dispersions [11]. This result strengthens the idea of strong repulsive and attractive interactions between different particles and molecules that contribute to the large viscosity enhancement over a broad range of volume fractions of complex dispersions.

III. STRONG SHEAR THINNING

The time (t) and spatial ($\vec{r}$) dependence are brought into the excess number density $\delta n(\vec{r},t)$ by

$$n(t)-\langle n\rangle = \int \delta n(\vec{r},t)d\vec{r}, \tag{9}$$

where the integration is taken over a volume element surrounding the defect. $\delta n(\vec{r},t)$ relaxes as time goes on by spreading over the entire medium via diffusion. Let us introduce the density-density correlation function

$$C(\vec{r},t) = \frac{\langle\delta n(\vec{r},t)\delta n(\vec{0},0)\rangle}{\langle\delta n^2\rangle}, \tag{10}$$

which is invariant under translations of $\vec{r}$ and t. It can be treated as the Green's function of anomalous diffusion, which vanishes when $\vec{r}$ and/or t is very large. In the special case of constant diffusion coefficient, $C(\vec{r},t)$ should have the form of the familiar Gaussian spreading. However, a space-dependent diffusion coefficient (D) is expected for complex systems. Using the Fourier transform in space

$$C(\vec{q},t) = \int C(\vec{r},t)\exp(-i\vec{q}\cdot\vec{r})d\vec{r},$$

where $\vec{q}$ is the wave vector of the fluctuation, the anomalous diffusion equation can be written as [20]

$$\left(\frac{\partial}{\partial t} - Dq^{2-\nu}\right)C(\vec{q},t) = \delta(t), \tag{11}$$

where $0 \leqslant \nu < 1$. It produces a fractal dimension d_f, which defines a self-similar scaling between wave numbers by the transformation function

$$q \sim q_\nu^{d_f} \quad \text{with} \quad d_f = \frac{2}{2-\nu}. \tag{12}$$

A fractal is by definition a set made of parts similar to the whole [23]. Self-similarity is the basic notion in fractal structure and is a common feature for all scaling analyses. The fractal dimension d_f is introduced in accordance with the spatial scaling Eq. (12). The $q^{2-\nu}$ dependence in Eq. (11) is an ansatz since the $\vec{r}$ dependence of D is not known. By using Eq. (12), Eq. (11) is transformed to

$$\left(\frac{\partial}{\partial t} - D_\nu q_\nu^2 \right) C(q_\nu, t) = \delta(t), \tag{13}$$

where q_ν is the wave number in the fractal space. Equation (13) reveals that the diffusivity D_ν is a *constant*. Therefore, $C(\vec{q}_\nu, t)$ should exhibit Gaussian characteristics in fractal space. The self-similarity of the fractal has dilation symmetry as shown in Eq. (12).

Taking the Fourier transform in time

$$C(q_\nu, \omega) = \int_{-\infty}^{\infty} C(q_\nu, t) \exp(i\omega t)\, dt,$$

we obtain the solution

$$C(\omega) = \sum_{q_\nu} \frac{1}{D_\nu q_\nu^2 - i\omega} \cong \int_0^{q_C} \frac{\rho(q_\nu)\, dq_\nu}{D_\nu q_\nu^2 - i\omega}, \tag{14}$$

where ρ is the density of states and q_c is the cutoff wave number. The number of modes per unit length along the path of diffusion with wave number between q and $q + dq$ can be expressed in terms of the number of modes in the fractal space. Using Eq. (12), we obtain the density of states,

$$\rho(q_\nu)\, dq_\nu \sim q_\nu^{d_f - 1} dq_\nu \sim \tau_\nu^{-(1 + d_f/2)} d\tau_\nu, \tag{15}$$

where $\tau_\nu = (D_\nu q_\nu^2)^{-1}$ is a local relaxation time. Clearly, the time dependence is diffusive in nature. Substituting Eq. (15) into Eq. (14) leads to the asymptotic solution

$$C(\omega) \sim -\frac{2}{d_f} \frac{\tau^{-d_f/2}}{i\omega} \quad \text{for} \quad \omega\tau_\nu \gg 1, \tag{16}$$

where $\tau = (D_\nu q_c^2)^{-1}$ is the macroscopic relaxation time. On the basis of the fluctuation-dissipation theorem, the real part of the dynamic viscosity is determined from Eq. (16) as $\eta'(\omega) \sim \operatorname{Im} C(\omega) \sim \tau^{-d_f/2}$. Introducing the shear-thinning exponent

$$\beta = d_f/2 = \frac{1}{2-\nu}, \tag{17}$$

we obtain the complex viscosity

$$\eta^*(\omega) = \eta'(\omega) - i\eta''(\omega) \sim (1-i)(\omega\tau)^{-\beta} \quad \text{for} \quad \omega\tau \gg 1. \tag{18}$$

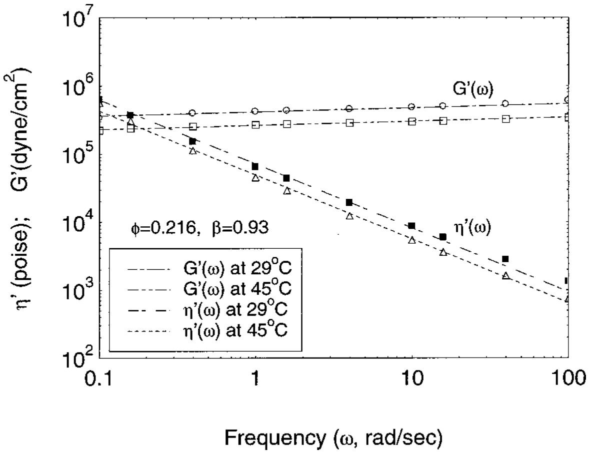

FIG. 2. Experimental data (points) for the real part of the dynamic shear viscosity and modulus are compared with the power laws (dotted lines) given by Eqs. (18) and (19) at two different temperatures. The volume fraction is 0.216.

Because the shear-induced microstructure of HSD has a Gaussian distribution ($\nu = 0$) [4], we can obtain the experimentally [3] verified $\beta = \frac{1}{2}$ from Eq. (17). For complex systems, we are going to have $\frac{1}{2} < \beta < 1$. The corresponding complex shear modulus for Eq. (18) is

$$G^*(\omega) = G'(\omega) + iG''(\omega) = i\omega\eta^*(\omega)$$
$$\sim \frac{1+i}{\tau}(\omega\tau)^{1-\beta} \quad \text{for} \quad \omega\tau \gg 1. \tag{19}$$

Equations (18) and (19) provide the useful scaling laws $\eta' \sim \omega^{-\beta}$ and $G' \sim \omega^{1-\beta}$ over three decades of frequencies measured and shown in Figs. 2 and 3. Interestingly, $\beta = 0.93$ is found to be independent of the volume fraction ϕ and temperature $T < T_c$ (see the next section). This β value is higher than the reported shear-thinning exponents of $\beta = 0.83$ for aggregated colloids [11] and 0.80 for polymer gels [15]. Both attractive and repulsive forces are present in

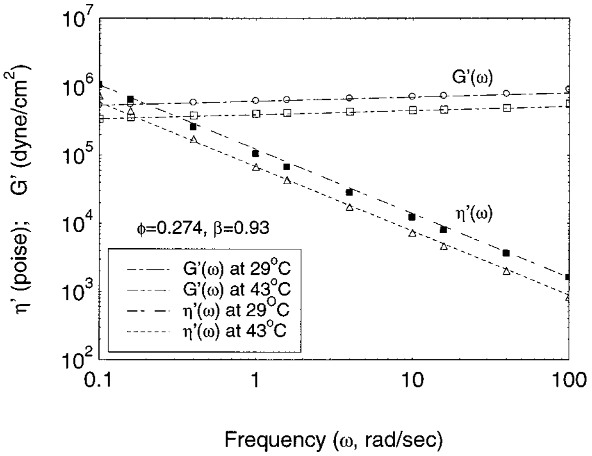

FIG. 3. Experimental data (points) for the real part of the dynamic shear viscosity and modulus are compared with the power laws (dotted lines) given by Eqs. (18) and (19) at two different temperatures. The volume fraction is 0.274.

these systems. The findings reinforce what has been mentioned earlier: we have strongly interacting particles in our systems.

IV. DYNAMIC CRITICAL PHENOMENON

Due to the fractal structure in complex systems, the temperature dependence of the defect volume can be written as

$$v(T) \sim -(T_c - T)^{\alpha} \tag{20}$$

for $T < T_c$, which is the melting temperature of polymeric particles. α is the critical exponent. Since the thermal expansion coefficient of the polymeric particles is lower than that of the carrier fluid, a negative sign is shown in Eq. (20). Substituting Eq. (20) into Eq. (1) yields

$$\ln \eta'(T) \sim -\left(1 - \frac{T}{T_c}\right)^{-\alpha} \quad \text{for } T < T_c. \tag{21}$$

Viscosity is a nonequilibrium property of a flowing fluid. Equation (21) has the form familiar to dynamic critical phenomena [24]. Let us bring in the correlation length of the thermal fluctuations [25]:

$$\xi \sim \left(1 - \frac{T}{T_c}\right)^{-1} \rightarrow \infty \quad \text{as } T \rightarrow T_c. \tag{22}$$

From Eqs. (14), (15), and (17), a scaling law can be written down as

$$\begin{aligned} \operatorname{Im} C(\omega) &\sim \operatorname{Im} \int \frac{q_\nu^{d_f - 1} dq_\nu}{D_\nu q_\nu^2 - i\omega} \sim \operatorname{Im}\left(\int \frac{x^{d_f - 3} dx}{D_\nu (1 - i\omega\tau_\nu)} \right) \xi^{2 - d_f} \\ &\sim \xi^{2(1-\beta)}, \end{aligned} \tag{23}$$

where a substitution of $q_\nu = x/\xi$ has been made, and the integral is a well-defined complex constant. Therefore, we obtain

$$\alpha = 2(1 - \beta). \tag{24}$$

This is a useful relation between the critical exponent and the shear-thinning exponent. With the value of β obtained in Figs. 2 and 3, Eq. (24) gives $\alpha = 0.14$, which provides a good description of the experimental data as shown in Fig. 4. Equation (21) and Fig. 4 differ completely from the reported effect of temperature on the viscosity of HSD [18]. Equations (21) and (24) were derived as a dynamic critical phenomenon due to thermal fluctuations whose correlation length diverges as $T \rightarrow T_c$. For temperatures beyond T_c, the particulate structure of the dispersions break down and the fluctuations are no longer dictated by the short-range interactions.

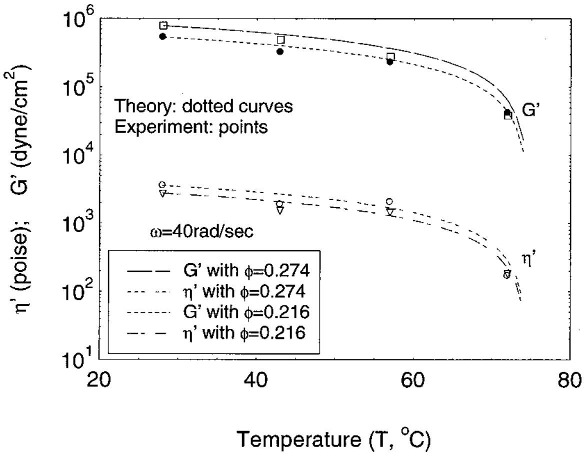

FIG. 4. Comparison of predictions of Eqs. (21) and (24) with experimental data for the real part of the dynamic shear viscosity and modulus as a function of temperature at two different volume fractions. The critical temperature is 75 °C.

V. CONCLUSIONS

An experimentally verified model has been developed to describe the viscoelasticity of complex dispersions as a function of volume fraction, frequency, and temperature by analyzing the excess number density fluctuations that result from the microscopic compositional, dynamic, and thermal fluctuations. On the basis of a stochastic differential equation, the concentration-dependent zero shear viscosity is derived. Strong enhancement of the effective viscosity is found over a broad range of concentrations caused by the depletion-induced attractive force contributions of additives, when repulsive forces are present. This also inhibits the repulsive-dominated percolation transition observed in hard-sphere dispersion.

Strong shear thinning can be explained by solving an anomalous diffusion equation. The solution leads to the derivation of a power-law dependence for the dynamic shear viscosity and modulus on frequency with the shear-thinning exponent $1 > \beta > \frac{1}{2}$ depending on the fractal dimension of the complex system. We have determined $\beta = 0.93$, independent of volume fraction ϕ and temperature. This β value is higher than the reported shear-thinning exponents for aggregated colloids and polymer gels. This result reinforces the assumption that we have strongly interacting particles in the complex dispersions.

The divergence of the shear viscosity in the vicinity of a critical temperature has been analyzed as a dynamic critical phenomenon due to thermal fluctuations. An interesting scaling relation was derived between the critical exponents related to the defect volume and to the shear-thinning behavior of the complex viscosity. The effect of temperature on complex dispersion differs completely from that on hard-sphere dispersions.

ACKNOWLEDGMENTS

The author is indebted to Dr. S. K. Ahuja for his assistance in the rheological measurements of samples provided by Dr. D. H. Pan.

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