

Scaling of the Viscoelasticity of Weakly Attractive Particles

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The rheological data of weakly attractive colloidal particles are shown to exhibit a surprising scaling behavior as the particle volume fraction, ϕ , or the strength of the attractive interparticle interaction, U , are varied. There is a critical onset of a solid network as either ϕ or U increase above critical values. For all solidlike samples, both the frequency-dependent linear viscoelastic moduli, and the strain-rate dependent stress can be scaled onto universal master curves. A model of a solid network interspersed in a background fluid qualitatively accounts for this behavior.

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Suspensions of colloidal particles exhibit a diverse range of rheological properties, varying from simple viscous fluids to highly elastic pastes; this diversity is one of the key reasons for their widespread technological utility. Control over the rheology is achieved by adjusting the interparticle interactions and the particle volume fraction, ϕ . When the interparticle interactions are attractive, there is a delicate interplay between the magnitude of the attractive energy, U , and ϕ . When U is very large, an elastic gel is formed, even at very low ϕ [1,2]. As U is decreased, the frequency-dependent storage and loss moduli, $G'(\omega)$ and $G''(\omega)$, respectively, can vary rapidly for small changes in either ϕ or U [3–7]. This extreme variability has, to date, defied any general description of the viscoelastic behavior.

In this Letter, we show that the wide variation of $G'(\omega)$ and $G''(\omega)$ exhibited by weakly attractive colloidal suspensions can be dramatically simplified: The moduli can be scaled onto a single master curve. The same scaling is observed as either ϕ or U is varied. Moreover, for non-linear rheology, similar scaling is observed; the stress, σ , as a function of shear rate, $\dot{\gamma}$, can be scaled onto a single master curve. We present a simple model that accounts for the scaling by combining the elasticity of a solid network formed by the particles and the viscosity of the suspending fluid. In addition, we show that the onset of the solid network exhibits critical behavior reminiscent of elasticity percolation [8,9]. These results offer a unified and very general description of the rheology, and, by inference, the structure of weakly attractive colloidal particles.

We investigate the rheological properties of carbon black suspended in base stock oil as a function of particle volume fraction and interaction potential. Carbon black is colloidal carbon formed by insufficient combustion of fuel [10]. Suspensions of carbon black in oil are used as test systems to model the behavior of used motor oils where aggregation of soot leads to an undesired viscosity increase [11,12]. All our samples are prepared using a stock solution made from a paste of carbon black which is milled into the oil at high shear rates. We control the strength of the interparticle interactions with a double-tailed dispersant [13], which acts as a surfactant; a more polar amine group binds to the surface of the carbon black, allowing

the two long hydrocarbon tails to sterically stabilize the particles. Increasing the dispersant concentration in solution leads to an increased density of the surface-adsorbed layer, thereby reducing the attractive interactions between particles. All rheological measurements are performed using a strain-controlled rheometer with Couette geometry. To obtain reproducible results, all measurements are carried out by first preshearing the suspension to break up any large aggregates, then allowing new structures to form for 2000 s. Measurements of all samples were performed at 25 °C; the dispersant samples were also measured at 100 °C.

Electron microscopy reveals that the primary particle size of carbon black is about 30 nm in diameter; however, these particles form larger, fractal clusters that cannot be broken, either through the addition of dispersant or by the application of high shear. These larger clusters, which are about 0.5 μm in diameter as determined by optical microscopy, form the primary particles in our experiments. Their volume fraction is determined by applying a sufficiently large shear to completely break up any larger aggregates, so that the measured viscosity is no longer dependent on the shear rate $\dot{\gamma}$. Then, the effective hydrodynamic volume fraction, ϕ , is estimated using [14] $\eta_\infty/\mu = (1 - \phi/0.71)^{-2}$, where μ is the shear-independent viscosity of the base stock, and η_∞ is the high shear rate viscosity of the suspension. We also determine the fractal dimension of the primary particles to be $d_f \approx 2.2 \pm 0.1$.

With no dispersant, carbon black particles are rather strongly attractive, and small volume fractions are sufficient to transform the suspension into an interconnected network. This is clearly seen by optical microscopy of 23- μm -thick samples of the carbon black; as ϕ is varied, the network becomes increasingly dense and space filling, as seen in the photomicrographs in Fig. 1. At the highest volume fraction shown, $\phi = 0.097$ [Fig. 1(a)], a dense, multiply connected network is observed; as the volume fraction is decreased to $\phi = 0.064$, the network becomes more tenuous and less well connected [Fig. 1(b)]; finally, at even lower volume fractions, $\phi = 0.033$, the clusters no longer form a connected network [Fig. 1(c)].

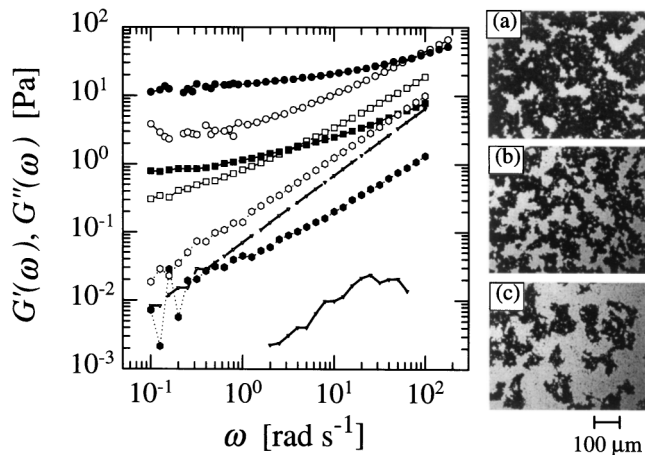


FIG. 1. $G'(\omega)$ (solid symbols) and $G''(\omega)$ (open symbols) for three different volume fractions of carbon black in the solidlike regime, with $\phi = 0.149$ (circles), 0.097 (squares), and 0.064 (hexagons) from top to bottom, and in the fluidlike regime for $\phi = 0.033$, shown by the solid [$G'(\omega)$] and dashed [$G''(\omega)$] lines. The optical micrographs show the weakening network structure as ϕ decreases: (a) 0.097, (b) 0.064, and (c) 0.033. The experimental uncertainty in ϕ is about ± 0.001 .

To characterize the mechanical properties of these suspensions, we measure the frequency-dependent viscoelastic moduli of the suspensions, and plot the results in Fig. 1, using solid symbols for $G'(\omega)$ and open symbols for $G''(\omega)$. At the highest volume fraction, $\phi = 0.149$ (circles), the suspension is clearly elastic, with $G'(\omega)$ nearly independent of ω and larger than $G''(\omega)$. As ϕ is decreased, $G'(\omega)$ decreases dramatically, becoming more dependent on ω ; at $\phi = 0.097$ (squares), $G'(\omega)$ and $G''(\omega)$ cross at intermediate frequencies. Finally, at even lower ϕ , $G''(\omega)$ becomes nearly linear in ω , and greater than $G'(\omega)$ for all frequencies, as shown for $\phi = 0.064$ (hexagons).

Remarkably, despite their marked differences, all the data can be scaled onto a single master curve; this is accomplished by independently scaling both the modulus and the frequency of each data set, by factors a and b , respectively. The resultant master curve is shown by the open symbols in Fig. 2. At low scaled frequencies $\tilde{\omega}$, the scaled storage modulus $\tilde{G}'(\tilde{\omega})$ has nearly no frequency dependence, allowing us to identify a plateau modulus G'_0 ; in addition, $\tilde{G}''(\tilde{\omega})$ exhibits a minimum, rising again at the lowest $\tilde{\omega}$. At intermediate $\tilde{\omega}$, $\tilde{G}'(\tilde{\omega})$ and $\tilde{G}''(\tilde{\omega})$ cross; then $\tilde{G}''(\tilde{\omega})$ asymptotically approaches a linear dependence on $\tilde{\omega}$, while $\tilde{G}'(\tilde{\omega})$ remains smaller. The overall shape of the scaled data is similar to that seen for a wide variety of other soft glassy materials [15]. However, this scaling behavior has never been observed previously.

Data for all $\phi > 0.053$ can be scaled onto the master curve. Data for lower ϕ exhibit a markedly different behavior, as shown for $\phi = 0.033$ in Fig. 1; $G''(\omega)$ (dashed line) is linearly dependent on ω reflecting the viscosity of the suspension. By contrast, $G'(\omega)$ (solid line) is consid-

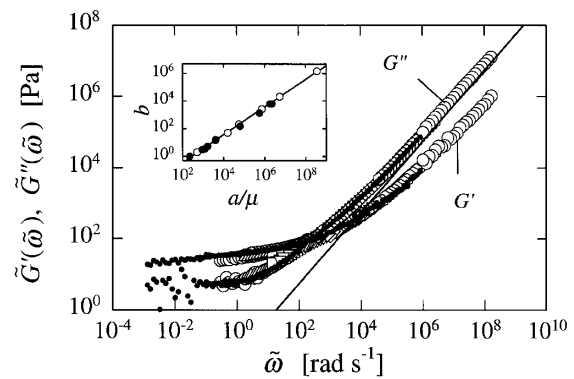


FIG. 2. Master curve showing the scaled moduli for different ϕ (open symbols) and U (solid symbols) as functions of the scaled frequency. The solid line represents the viscosity of the oil. The inset shows the linear relationship between the scaling factors, b and a/μ , for ϕ (open symbols) and U (solid symbols).

erably lower than $G''(\omega)$, and is almost not measurable. This behavior is characteristic of a Newtonian fluid, as expected for a dilute suspension. These data cannot be scaled onto the master curve and are identified as fluidlike.

We can account, at least qualitatively, for the origin of the observed scaling behavior using a simple model which is motivated by the observed structure. We assume that the carbon black forms a solid but tenuous network with a purely elastic, frequency-independent modulus, whose magnitude increases with ϕ as the network becomes more robust. Interspersed throughout this tenuous network is the suspending fluid, which has a purely viscous modulus, with $G''(\omega)$ increasing linearly with ω ; the magnitude of this contribution is independent of ϕ . Thus, at low ω , the elasticity of the network dominates, while, at high ω , the viscosity of the fluid dominates. The crossover occurs when the viscous and elastic contributions are equal: $G'_0 = G''(\omega_c) = \omega_c \mu$. Within this picture, data for different samples will clearly exhibit scaling; normalizing the moduli by the plateau value of the elastic solid, and normalizing the frequency by the crossover frequency will produce a master curve similar to the one observed. This scaling has an essential implication which provides an unambiguous test of the validity of the picture: The shift must be along the viscosity of the fluid; thus plotting the modulus scale factor, b , as a function of the frequency scale factor, a , must yield a linear relationship. To allow for temperature-dependent variations in the fluid viscosity, we normalize a by μ , and plot the results in the inset of Fig. 2; a linear relationship is observed, providing convincing support for our model. Additional support comes from the high frequency behavior of $G''(\omega)$, which asymptotically approaches the linear dependence reflecting the viscosity of the oil (solid line in Fig. 2).

While this simple picture can account for the basic scaling behavior, the physical origin of the scaling is more complex. For example, this picture does not address the behavior of the weaker of the two moduli in each regime.

At low frequencies, $G''(\omega)$ must be determined by the loss modulus of the network, which is larger than that of the suspending fluid. Similarly, at the highest frequencies, $G'(\omega)$ must reflect the storage component of the suspending fluid, with the solid network in it. In the crossover regime, both $G'(\omega)$ and $G''(\omega)$ must reflect contributions of both the elastic network and the viscous fluid. The fact that data scale so well implies that there is a strong similarity in the structures of the networks that form at different ϕ . Based on this observation, and the apparent sudden switch between the scaling behavior and that of a Newtonian fluid, we hypothesize that there is a critical onset of an elastic solid. We can critically test this hypothesis since we are able to determine the plateau modulus of very weak networks from the scale factors, even if we are unable to access sufficiently low frequencies, and therefore torques, to directly measure these values. Thus, we plot G'_0 as a function of the reduced scaling variable, $\delta_\phi = \phi/\phi_c - 1$ using circles in Fig. 3, where we choose $\phi_c = 0.053$; critical behavior is observed, with $G'_0 \sim \delta_\phi^{\nu_\phi}$, where $\nu_\phi = 4.1$. This exponent is consistent with those typically seen for elasticity percolation in three dimensions [8,9]; the high value reflects the strong increase in the modulus that results upon addition of a very small number of new bonds, which significantly increases the elasticity of the network. This critical behavior also implies that the structure of the colloid network is self-similar [8,9], which would help account for the scaling of the rheological data.

The critical onset of a solidlike network is not restricted to a change in volume fraction; it can also occur as the interaction energy between particles, U , is varied by changing the dispersant concentration, $[D]$, while holding ϕ fixed. We use the approximation [16] $U = -h \ln\{[D]/[D]_f\}$, where $[D]_f$ is the concentration for full surface coverage [$U = 0$], and h is a constant which sets the absolute scale of the attraction. The viscoelastic moduli have the same general trend with an increase in U corresponding to an increase in ϕ ; moreover, at sufficiently low values of U , the data exhibit the same, dramatic change to fluidlike behavior. Remarkably,

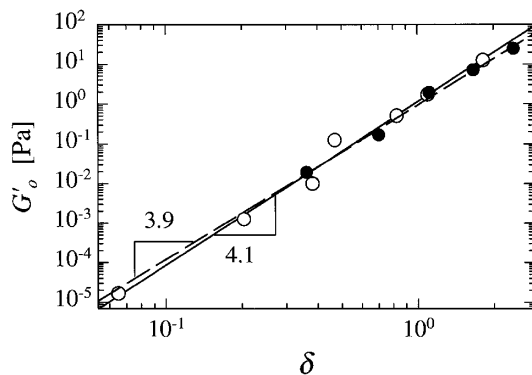


FIG. 3. Critical behavior of the elastic modulus as ϕ (open symbols) and U (solid symbols) are varied.

exactly the same scaling behavior is observed; data for the solidlike samples can be scaled onto exactly the same master curve, as shown in Fig. 2, where the solid symbols are data obtained from samples with $\phi = 0.14$ as U is varied. The scaling factors are again linearly related, and are collinear with the ϕ -dependent data, as shown by the solid symbols in the inset of Fig. 2. Surprisingly, critical behavior is also observed for the modulus as a function of the reduced scaling variable $\delta_U = U/U_c - 1$, as shown by the squares in Fig. 3. In this case, the dependence is $G'_0 \sim \delta_U^{\nu_U}$, where $\nu_U = 3.9$, nearly identical to ν_ϕ . We note that neither $[D]_f$ nor h affect the exponent of the scaling; however, the prefactor is set by $[D]_f$. The scaling allows us to identify a critical value of $[D]$ and, hence, U_c .

The physical picture that emerges from these data is that of a critical onset of a solid network of colloidal particles as either ϕ or U is varied; the value of ϕ_c will depend on U , as will the value of U_c depend on ϕ . Thus, there is a boundary between fluid and solid phases in a U vs ϕ phase diagram [6]. Crossing this boundary from the fluid to the solid phase along either the U or the ϕ axes results in the critical onset of an elastic modulus, similar to the behavior observed for elastic percolation [8,9]. However, the detailed behavior is markedly different from that of standard percolation, as the attractive interaction shifts ϕ_c , changing the nature of the structure. Nevertheless, the resultant networks are scale invariant, even when U changes. Finally, we note that the interparticle bonds are not permanent, and thus the structure may ultimately flow at very low frequencies [7]. This is the likely origin of the rise in $\tilde{G}''(\tilde{\omega})$ at the lowest frequencies. The frequency of this breakup will increase as the network becomes weaker, and thus it is conceivable that a true low frequency modulus would not be observed for the weakest networks, close to ϕ_c , even if the sensitivity and frequency range of the measurements could be extended to probe this. However, the frequency range of the experiments is greater than this breakup frequency for all experimentally accessible ω , ensuring that the network remains intact during each cycle, ω^{-1} , enabling the scaling to be observed.

Our two component model is reminiscent to that of a Bingham solid [17,18], a material that, upon application of a strain, remains elastic up to some yield strain, whereupon it becomes purely viscous and flows like a fluid, $\sigma = \sigma_y + \eta \dot{\gamma}$, where σ_y is the yield stress. Thus, σ remains constant at low applied shear rates until the material yields, and then increases linearly at high $\dot{\gamma}$. Our data represent oscillatory shear measurements for a Bingham solid, and we would expect similar scaling behavior for other Bingham solids. We also test our solidlike samples using steady shear; we obtain reproducible results by applying a high shear to break up any structure, and then measure σ , as $\dot{\gamma}$ is decreased. Data for a series of ϕ are shown in the inset of Fig. 4; in all cases, σ decreases approximately linearly at high $\dot{\gamma}$, but becomes nearly independent of shear rate for low $\dot{\gamma}$. This behavior is characteristic of a solid

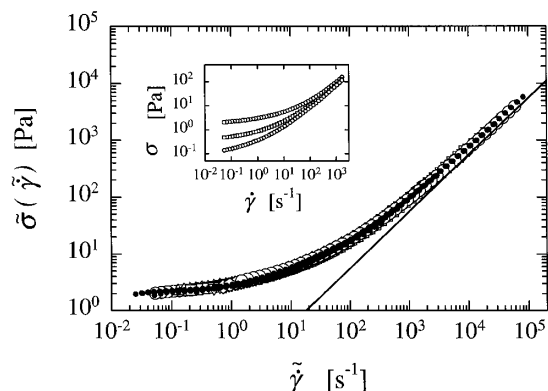


FIG. 4. Scaling behavior of the stress measured as a function of strain rate as ϕ (open symbols) and U (solid symbols) are varied. The solid line represents the viscosity of the oil. The inset shows the unscaled data for $\phi = 0.149$ (circles), 0.097 (squares), and 0.064 (hexagons), from top to bottom.

material with a yield stress, whose magnitude increases with ϕ . However, data for all ϕ can again be scaled onto a single master curve, as shown by the open symbols in Fig. 4. Similar scaling is observed for fixed ϕ as $[D]$ is varied (solid symbols). The scaling factors are again linearly related, consistent with scaling along the fluid viscosity. These data show that the nonlinear viscoelasticity of the network is similar for structures with different ϕ and U , just as the linear viscoelasticity.

Although all the measurements reported here were carried out using carbon black, we expect this scaling behavior to be much more general. Measurements using depletion-induced attraction in colloid-polymer gels confirm this; they yield viscoelastic moduli that can be scaled directly onto the master curve in Fig. 2. Measurements with depletion-induced gels will allow the interparticle interaction to be determined and will enable a full phase diagram to be measured. They will also provide additional input necessary to develop an improved understanding of the origin of the scaling behavior. Nevertheless, even without this detailed understanding, the current data provide a convenient means to summarize a wide range of rheological behavior. Moreover, they provide a valuable predictive

tool for determining the effectiveness of a dispersant to disperse soot.

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