Strong Critical Enhancement of the Shear Viscosity of Colloidal Systems

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The critical divergence of the shear viscosity of a colloid polymer mixture is experimentally found to be as strong as the divergence of the correlation length. This is in contrast with the divergence of the viscosity in atomic and molecular sytems, which is known to be very weak. The different behavior of the shear viscosity of Brownian systems and molecular systems is believed to be due to the long ranged character of the hydrodynamic interactions between the Brownian particles, a type of interaction absent in molecular systems. [S0031-9007(96)01946-1]

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Critical enhancement of the shear viscosity of atomic and molecular systems is so weak that it is practically impossible to measure anomalous effects of more than about 30% relative to the background viscosity. Proper extrapolation of the background viscosity into the critical region has therefore been of major importance, and often obscured the determination of an accurate value for the very small critical exponent. The critical exponent is now believed to be equal to 0.035 ± 0.003 [1]. This value agrees with some of the theories that have been developed in the past to describe anomalous behavior beyond the mean-field region [1–4]. Mean-field anomalous behavior of the shear viscosity of atomic and molecular systems is probably nonexistent.

In a recent publication, one of the present authors (J. K. G. D.) predicted quite a different critical behavior of the shear viscosity for colloidal systems [5]. In addition to direct interactions, also present in molecular systems, there is another type of interaction particular to colloidal systems. These additional interactions are mediated via the fluid in which the Brownian particles are dispersed. These so-called *hydrodynamic interactions* are the result of scattering of the shear flow field by the Brownian particles, which scattered flow field affects other Brownian particles in their motion. Such interactions are long ranged and are responsible for the much stronger divergence of the shear viscosity as compared to molecular systems.

The theoretical prediction for the critical divergence of the shear viscosity η for Brownian systems is [5]

$$\eta = \eta_B + \eta_A \,, \tag{1}$$

where η_B is the viscosity in the absence of long ranged critical correlations, the so-called background viscosity, and η_A is the *additive* anomalous contribution, which is proportional to the correlation length ξ in the unsheared suspension:

$$\eta_A \propto \xi \,. \tag{2}$$

In this Letter we present experimental results on both the divergence of the correlation length and the viscosity of a colloid polymer mixture. Without polymer the colloidal particles behave as hard spheres. The addition of nonadsorbing polymer induces an effective attraction between the colloidal particles due to a depletion mechanism [6,7]. The magnitude and range of the attractive forces can be tuned by the concentration and size of the polymer. Different size ratios lead to different kinds of phase behavior [8,9]. In our case the size ratio of polymer/colloidal particles is 0.48, which leads to a gas-liquid type of phase separation. Measurements have been performed in the one-phase region approaching the spinodal along so-called dilution lines, where the concentration ratio colloid/polymer is constant and only the amount of solvent is changed, simply by adding or evaporating solvent. The control variable in these systems is not the temperature but rather the chemical potential of the polymer. However, this quantity is not easily accessible experimentally and therefore we will use the relative distance to the spinodal, expressed in concentrations. Since along a dilution line the polymer and colloid concentration are linearly dependent, it suffices to use the colloid volume fraction pertaining to a particular point on the dilution line as the relevant variable. For example, the critical exponent ν' for the correlation length is now defined as

$$\xi = \xi_0 \left(\frac{\varphi_{\text{spin}} - \varphi}{\varphi_{\text{spin}}} \right)^{-\nu'} , \tag{3}$$

where ξ_0 is the length, φ is the volume fraction of colloid, while φ_{spin} is the volume fraction of colloid where the dilution line intersects the spinodal; $(\varphi_{\text{spin}} - \varphi)/\varphi_{\text{spin}}$ is a "reduced volume fraction," analogous to the more conventional reduced temperature. This allows us to express the divergence of the viscosity in terms of the correlation length, for which theoretical values are known. However, the exponents for the viscosity and correlation length as a function of the reduced volume fraction cannot be compared directly with theoretically available exponents (see in this respect Ref. [10]).

The system under study consists of sterically stabilized stearyl-silica particles with a radius of 48 nm, synthesized according to Stöber *et al.* and van Helden *et al.* [11,12], and polydimethylsiloxane (PDMS, Janssen) with a molecular weight of 204 k and a radius of gyration of 23 nm, dispersed in cyclohexane. Measurements were performed at a temperature of 25.0 °C along two different dilution lines: one dilution line which is probably close to intersection with the critical point (after phase separation the volumes of the two phases are approximately equal), and an off-critical dilution line. The colloid/polymer concentration ratios for these dilution lines are 51 g silica/g PDMS and 69 g silica/PDMS, respectively.

Viscosities were measured in the shear rate range of 1 to 10 s^{-1}, using a Contraves LS 40 rheometer. This corresponds to Peclet numbers $Pe < 1$, where the Peclet number is defined as $Pe = \dot{\gamma}\xi^2/2D_0$, which charaterizes the amount of distortion of structures with linear dimension of ξ. These distortions are responsible for shear thinning which is expected to set in at $Pe \approx 1$. Indeed, shear thinning is not observed. The data of the viscosities are presented in Fig. 1. The filled squares are the data for the colloid polymer mixtures. As can be seen, the viscosity dramatically increases in a narrow concentration range on approach of the binodal. In order to determine the background, the viscosity of the pure silica colloid in

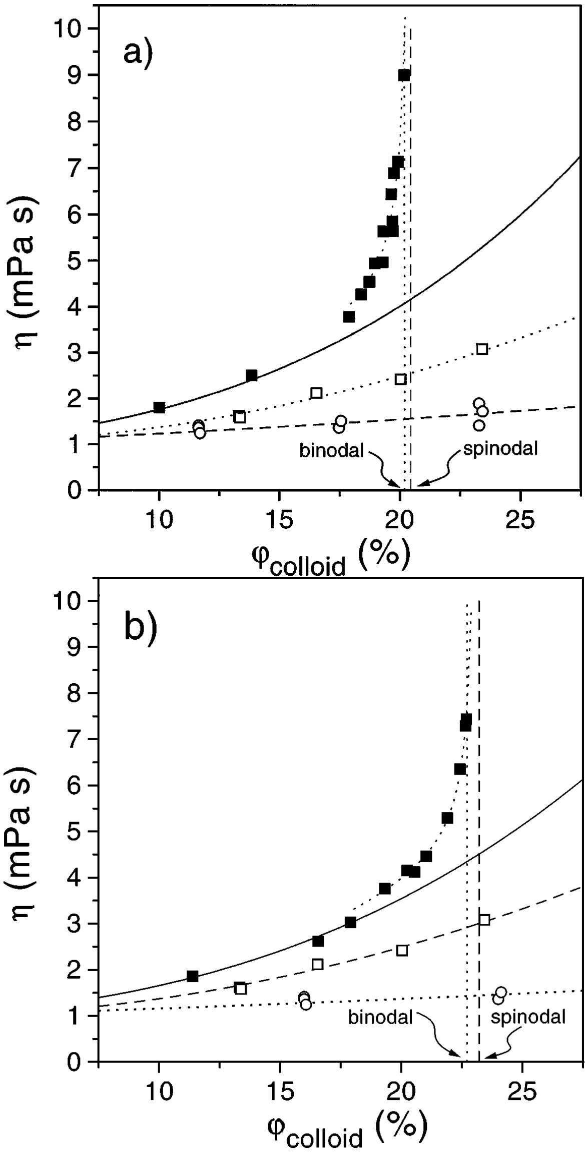

FIG. 1. Results of the viscosity measurements. The upper solid squares represent the viscosity of the colloid polymer mixtures. The dotted line through these points corresponds to the critical exponents as obtained from Fig. 2. The solid line is the estimated background viscosity. The open squares are the viscosities of pure colloid in the absence of polymer, with the dotted line a best fit. The open circles are the measured viscosities of the polymer solution, corresponding to the particular dilution line. (a) refers to the critical dilution line and (b) to the off-critical dilution line.

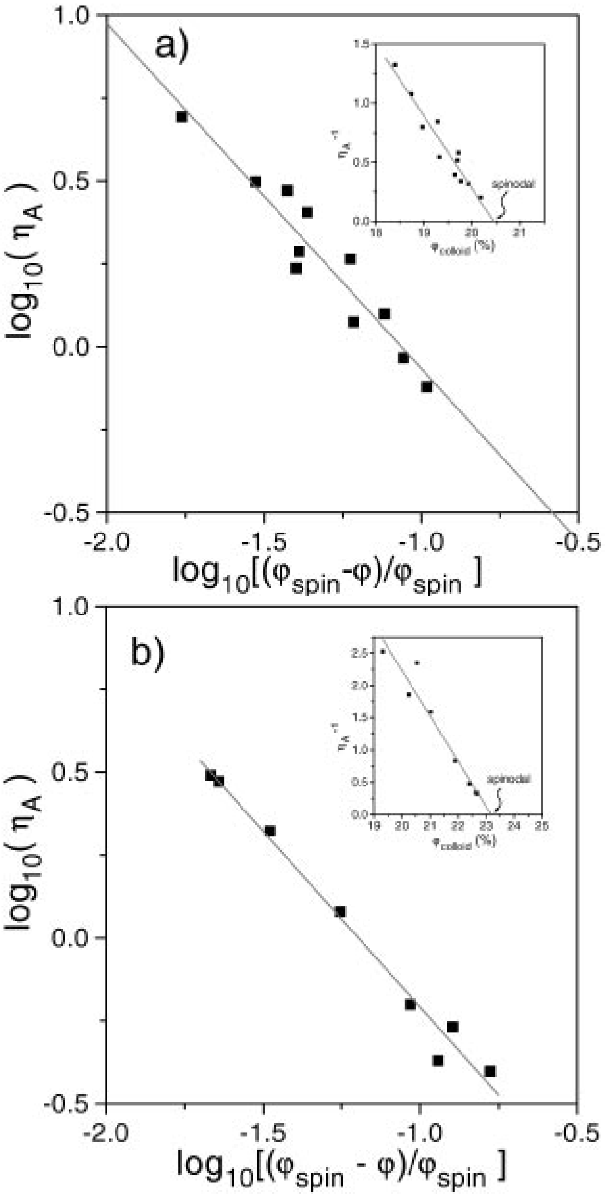

FIG. 2. A log-log representation of the anomalous part of the viscosity vs $(\varphi_{\mathrm{spin}} - \varphi)/\varphi_{\mathrm{spin}}$. (a) refers to the critical dilution line and (b) to the off-critical dilution line. The insets show the linear extrapolation of the reciprocal viscosity vs φ in order to determine the spinodal colloid volume fractions, which are 0.205 ± 0.002 and 0.232 ± 0.002, respectively, rendering values for the critical exponents of 1.04 ± 0.10 and 1.06 ± 0.06.

cyclohexane, without polymer, is measured (the open squares); the dashed line is a best fit to a second order polynomial. The background viscosity is now estimated by multiplying this viscosity by the ratio $\eta_{\mathrm{pol}}/\eta_{\mathrm{CHX}}$, where η_{pol} is the viscosity of the pure PDMS solution, represented in Fig. 1 by the open circles and the dotted line, and η_{CHX} is the viscosity of the solvent cylohexane. The background viscosity is thus assumed to be the result of hard-sphere interacting colloidal particles in a medium with a viscosity equal to that of the PDMS in cyclohexane solution. There are two possible choices for η_{pol} in the calculation of the background viscosity, depending on what is used for the polymer concentration. One can either use the concentration of polymer as such, or the concentration related to the free volume, available to the polymer. We found that the former choice leads to a background that fits the measured viscosities at low concentrations, whereas the latter choice overestimates the viscosity. The background viscosity obtained in this way is represented by the solid line, and agrees with the measured viscosities of the colloid polymer mixture away from the spinodal, as it should. The anomalous part of the viscosity is now simply obtained as the difference between the measured and background viscosity.

The reciprocal of the anomalous part of the viscosity is found to be linearly dependent on the colloid volume fraction, as can be seen from the inset in Fig. 2. Extrapolation of the reciprocal anomalous viscosity to zero yields the corresponding colloid volume fraction of the spinodal. For the critical dilution line it is found that $\varphi = 0.205 \pm 0.002$ and for the off-critical dilution line $\varphi = 0.232 \pm 0.002$.

The log-log plots of the anomalous part of the viscosity versus $(\varphi_{\mathrm{spin}} - \varphi)/\varphi_{\mathrm{spin}}$ are shown in Fig. 2. The critical exponents are found to be equal to 1.04 ± 0.10 and 1.06 ± 0.06 for the critical and off-critical dilution line, respectively.

Correlation lengths were obtained from small angle static light scattering data, using the Ornstein-Zernike expression for the static structure factor [13]. Analogous to the determination of the spinodal from viscosity measurements, the correlation length is found to be linearly dependent on the colloid volume fraction (see inset in Fig. 1), and values for the colloid volume fraction at the spinodal of $\varphi_{\mathrm{spin}} = 0.205 \pm 0.001$ and $\varphi_{\mathrm{spin}} = 0.230 \pm 0.001$ are found for the critical and off-critical dilution lines, respectively, in accordance with those obtained from viscosity measurements. The critical exponents for the correlation length along these dilution lines are found from a log-log representation (see Fig. 3) to be equal to 1.05 ± 0.04 and 1.00 ± 0.07, respectively.

To within experimental errors these exponents are equal to those for the vicosity, in accordance with the theoretical prediction mentioned above. The reduced volume fractions in our experiments span about one decade; a more extended range for the two dilution lines discussed here is not accessible, due to the relatively large distance between the binodal and spinodal, the locations of which are marked in Fig. 1 by vertical lines. It would be worthwhile to more accurately determine the location of the critical point (which is not easy for these systems), so as to have access to a larger range of reduced volume fractions. In addition, there is a need for experiments on colloidal systems where the temperature is the control variable.

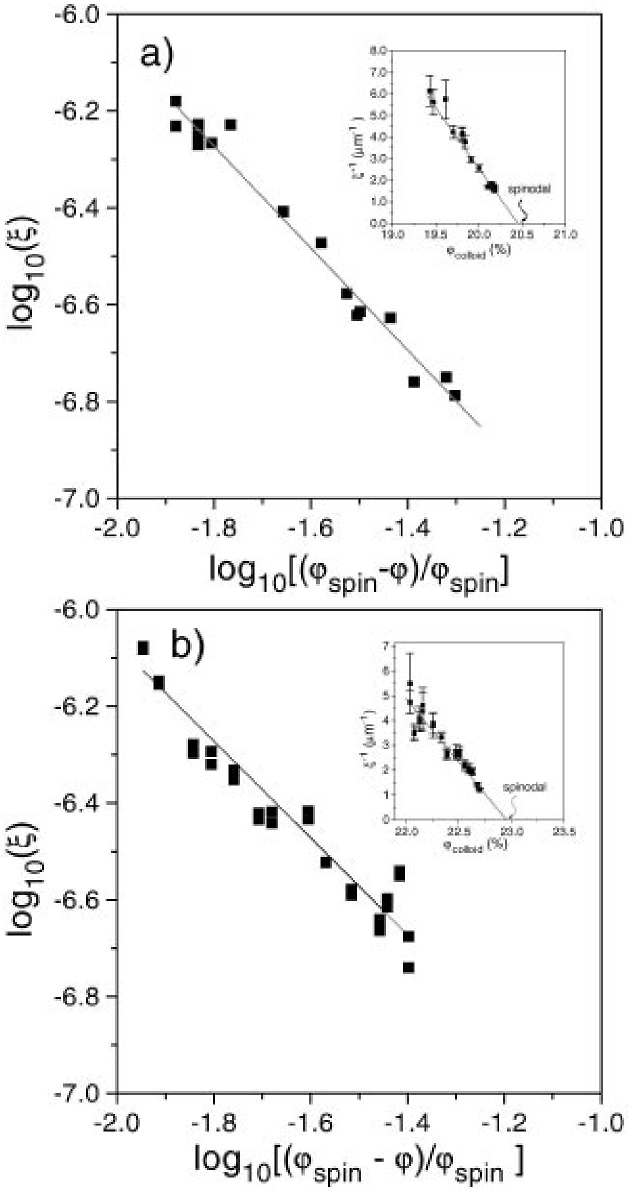

FIG. 3. A log-log representation of the correlation length vs $(\varphi_{\mathrm{spin}} - \varphi)/\varphi_{\mathrm{spin}}$. (a) refers to the critical dilution line and (b) to the off-critical dilution line. The insets show the linear extrapolation of the reciprocal correlation length vs φ in order to determine the spinodal colloid volume fractions, which are 0.205 ± 0.002 and 0.230 ± 0.001 for the critical and off-critical dilution lines, respectively, rendering values for the critical exponents of 1.05 ± 0.04 and 1.00 ± 0.07.

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[1] J. V. Sengers, Int. J. Thermophys. **6**, 203 (1985).

[2] P. C. Hohenberg and B. I. Halperin, Rev. Mod. Phys. **49**, 435 (1977).

[3] T. Ohta, J. Phys. C **10**, 791 (1977).

[4] J. K. Bhattacharjee and R. A. Ferrell, Phys. Rev. A **28**, 2363 (1983).

[5] J. K. G. Dhont, J. Chem. Phys. **103**, 7072 (1995).

[6] S. Asakura and F. Oosawa, J. Chem. Phys. **22**, 1255 (1954).

[7] A. Vrij, Pure Appl. Chem. **48**, 471 (1976).

[8] H. N. W. Lekkerkerker *et al.*, Europhys. Lett. **20**, 559 (1992).

[9] S. M. Ilett, A. Orrock, W. C. K. Poon, and P. N. Pusey, Phys. Rev. E **51**, 1344 (1995).

[10] M. E. Fisher, Phys. Rev. **176**, 257 (1968).

[11] W. Stöber, A. Fink, and E. Bohn, J. Colloid Interface Sci. **26**, 62 (1968).

[12] A. K. van Helden, J. W. Jansen, and A. Vrij, J. Colloid Interface Sci. **81**, 354 (1981).

[13] H. Stanley, *Introduction to Phase Transitions and Critical Phenomena* (Oxford University Press, New York, 1971).