

Two Mechanisms and a Scaling Relation for Dynamics in Ferrofluids

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Two relaxation peaks were found in the complex susceptibility of ferrofluids. Both can be described by the Vogel-Fulcher law $\tau = \tau_0 f(T) \exp[E/k(T - T_0)]$. Nevertheless, the physical origins for these two relaxations are quite different. We found that Néel relaxation strongly depends on the dipole-dipole interaction. The dramatic dependence can be described by a surprisingly simple scaling relation: $\tau = \tau_0 \exp[E/k(T - a\phi^{0.8})]$, where ϕ is the volume fraction of the dipoles. In contrast, Brownian relaxation is much less sensitive to the concentration of magnetic moments because the interparticle force is mainly hydrodynamic in nature. [S0031-9007(96)00634-5]

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Slow relaxation is a common feature in disordered materials such as glasses, spin glasses, and other complex systems [1]. Despite extensive effort a complete understanding of the mechanisms governing the dynamics is still lacking. Instead, phenomenological formulas such as the Vogel-Fulcher law have been used to describe relaxations in many different materials. So far, there is hardly any experiment available to provide the mechanism for the Vogel-Fulcher relation.

In this Letter, we report the observation of two relaxation mechanisms in the same ferrofluid and, more importantly, their dissimilar dependence on interaction between magnetic dipoles. We found that although both relaxations can be described by the Vogel-Fulcher law, Néel relaxation—the motion of a magnetic moment relative to the particle—is much more sensitive to the interparticle force than Brownian relaxation—the rotation of the moment through the particle's movement. We will report that, for the first time, the strong dependence of Néel relaxation on the dipole-dipole interaction can be characterized by an amazingly simple scaling relation. With the scaling law, all the data for Néel relaxation from samples with different concentrations of magnetic particles can be superimposed onto a master curve. This result provides an intimate relation between the relaxation time and the dipole force. For Brownian relaxation, on the other hand, the hydrodynamic interaction dominates the dipole interaction. Distinguishing these two mechanisms not only can help one to understand the complex dynamics in colloidal systems but also can provide some insight into relaxation phenomena of disordered systems in general.

Experiments were performed on ferrofluid [2] samples consisting of magnetite particles suspended in kerosene, abbreviated as KBF. Each particle has a mean diameter of $90 \pm 20 \text{ \AA}$. Particles are coated with surfactant to avoid agglomeration. The average moment is $2.5 \times 10^4 \mu_B$. Particles interact with each other through the long range dipole force [3]. The sample was sealed inside a small quartz tube. All the data have been corrected for the demagnetizing effect. The ac susceptibility measure-

ments were performed with a SQUID ac susceptometer. Although some work has been done on susceptibility of ferrofluids, the distinction between the effect of polydispersity and that of interaction is not clear [4]. To address the problem, we made samples with different concentrations by changing the amount of the solvent, thus the size distribution is unchanged. To check the universality of the scaling law, we also performed a similar experiment on samples with different solvent, particle size, and size distribution. We found that the scaling relation holds as long as we are in the weak interaction regime, independent of materials and the size distribution. Therefore one of the important consequences of our experiments is that *we are able to separate the physical effect of interparticle force from the effect of the polydispersity.*

Figure 1 shows the imaginary part of susceptibility, $\chi''(T)$, for frequencies $f = 0.01$ and 100 Hz. For each frequency, two peaks were observed [5]: T_{p1} and T_{p2} . Both maxima shift to higher temperatures with increasing frequency. In order to understand the mechanisms

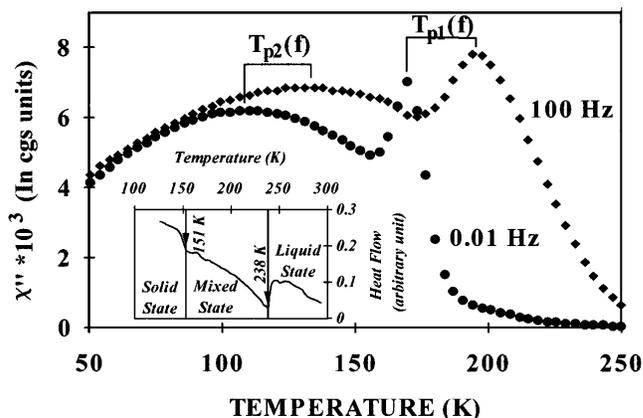


FIG. 1. χ'' vs T (volume fraction $\phi = 6\%$) for $f = 0.01$ and 100 Hz for sample KBF. The amplitude of the ac field is 1 Oe. The inset is the phase diagram for the same sample determined from DSC experiment. T_{p2} and T_{p1} are in the solid and mixed phases, respectively.

for these two relaxation peaks, we performed differential scanning calorimetry (DSC) measurements on both pure kerosene and the ferrofluid. Three distinct phases were found as shown in the inset of Fig. 1 for the same ferrofluid: a liquid phase for $T > T_{\text{pour}}$, where T_{pour} is the pour point, the temperature above which the system can flow like a fluid; a solid phase in the lowest temperature region, and a “mixed” state in the range of $T_{s-m} < T < T_{\text{pour}}$, where T_{s-m} is the transition temperature from the solid to the mixed phase. In the mixed phase, the viscosity is high. For pure kerosene, $T_{\text{pour}} = 233$ K and $T_{s-m} = 145$ K. For a ferrofluid with $\phi = 6\%$, $T_{\text{pour}} = 238$ K and $T_{s-m} = 151$ K, as shown in the inset of Fig. 1 [6].

Because the system is a rigid solid at low temperature, particles cannot move for $T < T_{s-m}$. Therefore, the peak at T_{p2} must be due to the relaxation of the magnetic moment relative to the particle—the Néel relaxation. Néel pointed out [7] that the moment of a single-domain magnetic particle relaxes via an activated process $\tau = \tau_0 \exp(E/kT)$, i.e., the Arrhenius law, where E is the barrier due to the anisotropy energy, τ is the relaxation time, and τ_0 is the characteristic time of the system. At the temperature where the relaxation time τ is comparable with the experimental time scale, a spin will look “frozen” or “blocked.” Apparently, the blocking temperature depends on the observation time $1/f$, f is the frequency of the experiment. If we take T_{p2} in Fig. 1 as the blocking temperature, $1/2\pi f$ as the time τ , we get a relation between T_{p2} and the frequency f . We found that $T_{p2}(f)$ can be described reasonably well by the Arrhenius law. However, parameters for the fit are unphysical: The characteristic time $\tau_0 = 1/2\pi f_0 = 4.6 \times 10^{-24}$ sec for $\phi = 6\%$. The shortest time scale in magnetism is the spin-flip time of a single atom, $\tau_s \sim 10^{-13}$ sec. No time scale should be shorter than τ_s . Therefore, the Arrhenius law does not describe the physics of the relaxation peak at T_{p2} .

This conclusion leads to the speculation that T_{p2} might not be attributed to single particle relaxation. To verify this, we investigated the frequency dependence of T_{p2} for samples with different ϕ as plotted in Fig. 2(a). The concentration dependence, thus the effect of interparticle force on the dynamics, is very clear. We notice that different curves are nearly parallel to each other, suggesting that all the data can be superimposed onto a master curve by simply shifting them along the temperature axis to the curve for the most dilute sample as illustrated in Fig. 2(b). We found that for the most diluted sample ($\phi = 0.12\%$) τ can be described by the Vogel-Fulcher (VF) law: $\tau = \tau_0 \exp[E/k(T - T_0)]$ with $\tau_0 = (2 \pm 1) \times 10^{-9}$ sec, $E/k = (5.9 \pm 0.4) \times 10^2$ K, and $T_0 = 3 \pm 1$ K. Then the master curve in Fig. 2(b) can be described by $\tau = \tau_0 \exp(E/kT')$, with the same τ_0 and E/k , while $T' = T_{p2} - T_0$, $T_0 = 3, 12, 50, 82$ K, for $\phi = 0.12\%, 0.6\%, 3\%$, and 6% , respectively, with an error of ± 1 K for T_0 . To verify the universality of the scaling curve, we performed a similar experiment on a

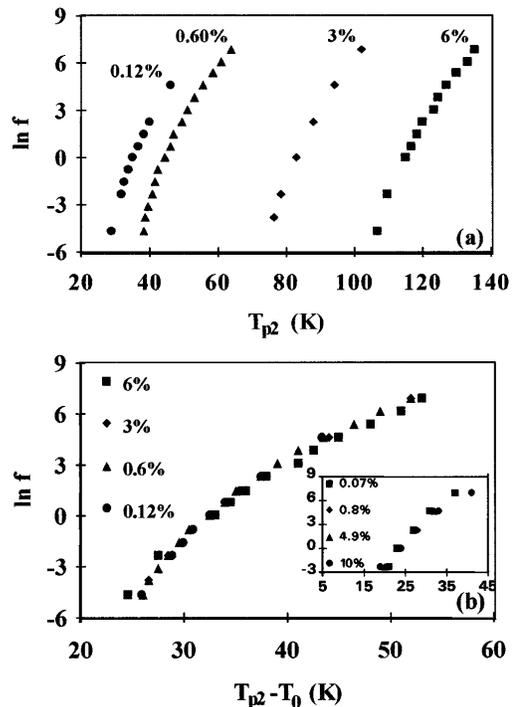


FIG. 2. (a) $\ln f$ vs T_{p2} for four different concentrations of KBF. (b) Scaling of data from all concentrations of KBF by shifting the curves in (a) along the temperature axis by various amounts. Inset: Scaling curve for ABF samples.

completely different system—alkyl-nthalene based magnetic fluid, “Marpomagna FV-42,” abbreviated as ABF. The particles are magnetites. The mean diameter is 70 \AA with standard deviation of 10 \AA [8]. We found that the scaling is still valid as shown in the inset of Fig. 2(b) for $\phi = 0.07\%, 0.8\%, 4.9\%$, and 10% . The fact that dissimilar systems, with different carrier, particle size, and size distribution, obey the same relation for a wide range of concentration and frequency indicates a universal physical origin.

In Fig. 3 we plot T_0 obtained in Fig. 2 versus the volume fraction ϕ for KBF. The line is the least squares fit of the data to a power law of ϕ and we get $T_0 \propto \phi^{0.8 \pm 0.1}$. Because the volume fraction is proportional to the dipole interaction between particles, the sublinear dependence of T_0 on ϕ suggests that T_0 is directly related to this interaction. Now the frequency dependence of relaxation peaks for various concentrations in Fig. 2(a) can be described by a universal relation $\tau = \tau_0 \exp[E/k(T - a\phi^{0.8})]$, with $a = 8 \times 10^2$ K. This result clearly indicates that the effect of interparticle force is simply to introduce a temperature scale T_0 so that the relaxation time diverges at $T = T_0$ instead of zero temperature as in the Arrhenius law. From Fig. 3 we realize that when $\phi = 0$, we get $T_0 = 0$. Then the activated dynamics for independent dipoles, i.e., the Arrhenius law, is recovered. Therefore the physical meaning of T_0 in the VF law describing Néel relaxation is that for temperature T above T_0 the thermal

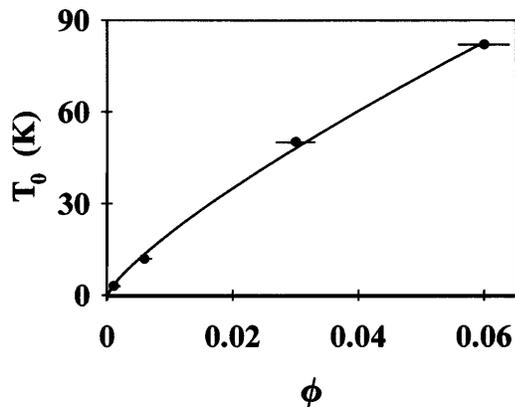


FIG. 3. T_0 obtained from the Vogel-Fulcher fit as a function of ϕ . $T_0 \propto \phi^{0.8 \pm 0.1}$.

energy dominates, while below T_0 , the interaction energy wins. Because τ_0 and E were obtained from fitting the data for the most diluted sample, they should be very close to values for single particle dynamics. We found that τ_0 agrees with Néel's prediction [7] and the value from the Mössbauer [9] experiment, i.e., 10^{-9} sec. We want to point out that the scaling relation works for the concentration range discussed here. For higher volume fraction, the energy barrier is no longer independent of the concentration of the particles. Then the scaling law breaks down (slight deviation from the scaling can be seen for $\phi = 10\%$ of ABF as shown in the inset of Fig. 2). From our preliminary data, it is possible that we start to see the formation of structures [10] and possibly the onset of magnetic ordering for higher volume fractions [11,12].

The VF law has been found to describe the temperature dependence of the relaxation times for many glass-forming liquids and some spin glasses [1,13]. However, the transition temperature of glass-forming liquids usually shows a linear concentration dependence [14]. In fact, the power law dependence of T_0 on the concentration is similar to that in spin glasses with similar exponents [15]. Additional similarities between frozen ferrofluids and spin glasses have been reported recently [3,16]. This suggests that the Néel dynamics in ferrofluids might relate more closely to a spin glass more than to a glass-forming liquid. The divergence of the relaxation time τ at T_0 indicates that the system enters a glassy state at T_0 . Therefore, T_0 here may have a similar significance as the spin glass transition temperature T_g . Further experiments are needed to explore this similarity.

The high temperature peak at T_{p1} in Fig. 1 is in the mixed state where the system is no longer a rigid solid. Consequently, it is possible for particles to move locally. Brownian relaxation, in which a moment responds to the external field through the particle movement, plays an important role. Since both Néel and Brownian relaxations can exist in this region, the maximum at T_{p1} in Fig. 1 does not represent a single relaxation. To separate these

two channels, we plot both the real and the imaginary part of susceptibility, χ' and χ'' , versus frequency for fixed temperature in the mixed state in Fig. 4(a). The main peak of χ'' in Fig. 4(a) comes from particle rotation and the rising of χ'' at the high frequency part is due to the Néel relaxation since Néel dynamics is faster than Brownian relaxation when both channels coexist [17]. We can single out the Brownian contribution by studying the main peak of χ'' in Fig. 4(a). We found that Brownian susceptibility can be described by the generalized Debye [18] formula

$$\chi(\omega) = \chi_\infty + (\chi_0 - \chi_\infty)/[1 + (i\omega\tau_B)^{1-\alpha}], \quad (1)$$

where $0 < \alpha < 1$, χ_∞ and χ_0 represent high frequency and dc susceptibility, respectively. τ_B is the Brownian relaxation time. By fitting the real and imaginary parts of Eq. (1) to the experimental χ' and χ'' independently for different temperatures we can obtain $\tau_B(T)$. The solid lines in Fig. 4(a) are the fits to only the Brownian relaxation (lower frequency part). At $T = 178$ K, $\tau_B = 0.1$ s and $\alpha = 0.7$ for fits from both real and imaginary parts.

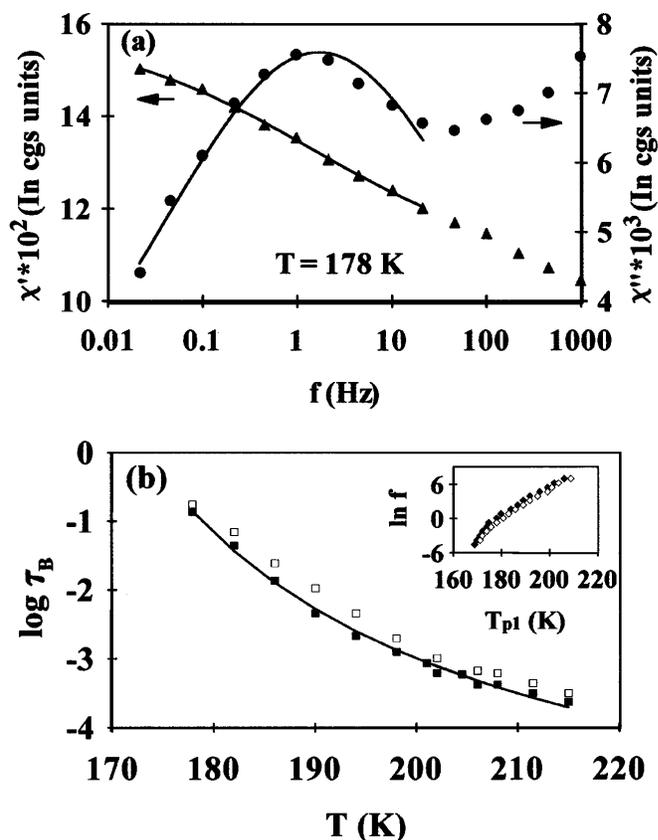


FIG. 4. Brownian relaxation in the "mixed" phase for KBF. (a) χ' and χ'' vs $\log f$. The high frequency tail is due to Néel relaxation. The solid lines are the fits to Eq. (1) for Brownian relaxation only; (b) $\tau_B(T)$, for two concentrations. The solid line is the VF fit. The inset shows that $T_{p1}(f)$ vs $\ln f$. In both plots the filled symbols are for $\phi = 6\%$ and the empty symbols are for $\phi = 3\%$.

In Fig. 4(b) we plot $\log \tau_B$ vs T for two KBF samples. We found again that the relation obeys the VF law as indicated by the solid lines in Fig. 4(b) for $\phi = 6\%$. In this case, however, the VF law has a quite different origin. Frenkel pointed out that Brownian rotational diffusion time τ_B depends on the viscosity of the fluid η as: $\tau_B = 3V\eta/kT$, where V is the particle volume [19]. The exponential temperature dependence of τ_B is attributed to the divergence of the viscosity at the temperature T_0 as found in many glassy systems [1]. Using the relation $\eta = \eta_0 \exp[E'/k(T - T'_0)]$ we get $\tau_B = \tau'_0 f(T) \exp[E'/k(T - T'_0)]$, where $f(T) = E'/kT$, $\tau'_0 = 3V\eta_0/E' = (2.8 \pm 0.1) \times 10^{-7}$ sec, $E'/k = (4.2 \pm 0.2) \times 10^2$ K, and $T'_0 = (144 \pm 3)$ K for the sample with $\phi = 6\%$. Because T'_0 is the same as T_{s-m} , the transition temperature from the mixed to the solid phase, we believe that the transition is the origin of the divergence in the viscosity, similar to the glass-transition temperature for the glass-forming liquids [1]. In contrast to the Néel peak, T_{p1} is much less sensitive to the volume fraction of the magnetic particles as demonstrated in Fig. 4(b) and the inset in it—the differences between the results for different concentrations are much smaller than that in Fig. 2(a). Because Brownian relaxation dominates at T_{p1} , it is not hard to understand this difference when one realizes that the effect of dipole interaction on Brownian relaxation occurs indirectly through the viscosity of the fluid. As a consequence, the hydrodynamic interaction dominates the magnetic dipole interaction which only contributes a small correction in the viscosity of the fluid [2,20].

In conclusion, two relaxations were found in the same ferrofluid, both of them can be described by the VF law. The dipole interaction has a dramatic consequence on Néel relaxation. The scaling relation for various concentrations suggests that as a result of the dipole interaction the relaxation time diverges at a finite temperature which has a power law dependence on the concentration of dipoles. For Brownian relaxation, the VF law originates from the temperature dependence of the viscosity, thus the magnetic dipole interaction is secondary to the hydrodynamic interaction. We found that, regardless of the relaxation channels, the Arrhenius law cannot apply to our system as long as the interaction between magnetic moments is not negligible. We want to mention that although the generalized Arrhenius law $\tau = \tau_0 \exp(E/kT^\alpha)$ has been used to describe relaxations in other materials [21], it does not give physical parameters for our systems.

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