

Kinetic Glass Transition in a Micellar System with Short-Range Attractive Interaction

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We show that percolation and structural arrest transitions coexist in different regions of the phase diagram of a copolymer-micellar system and relate them to short-range intermicellar attraction. The intermediate scattering function shows a nonergodic transition along a temperature and concentration dependent line. Analyses show a logarithmic time dependence, attributed to a higher-order glass transition singularity predicted by mode-coupling theory, followed by a power law.

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Recently, a number of experiments on colloidal systems have shown the existence of a dynamical structural arrest [1,2], or formation of a gel phase. In many cases the structural arrest has been interpreted in terms of a static percolation (or sol-gel) transition [1], but the interpretation along this line did not always agree with experiments. The general idea is that at certain thermodynamic states colloidal particles tend to form polydispersed aggregates, some of which may span the whole sample, the percolating clusters. Formation of clusters is a result of a short-range attractive tail in the interparticle potential, besides the hard core repulsion. In this Letter we give experimental evidence that structural arrest is a dynamic transition distinct from percolation. We find the structural arrest in a copolymer-micellar system in a region of the phase diagram different from the one where the percolation transition occurs, and we attribute this behavior to a kinetic glass transition. Specifically we observe in the system an ergodic to nonergodic transition in the photon correlation functions on crossing the measured glass transition line as a function of temperature T for concentrations $c > 0.5$. We relate the structural arrest to the attractive tail of the interparticle potential, which is also responsible for the percolation observed in this system. In fact, mode-coupling theory (MCT) of supercooled liquids in the vicinity of a glass transition [3,4] predicts that a system where the interaction potential has repulsive and attractive parts produces two intersecting glass transition lines of the type shown in Refs. [3,4]. Furthermore, the photon correlation functions exhibit a logarithmic time dependence followed by a power-law behavior of the von Schweidler type [3,4], before the structural arrest takes place. The logarithmic time dependence, the limiting case of a power law with vanishing exponent, is due to the existence of a higher-order glass transition singularity of the A3 type, a situation predicted by MCT [3–5]. It is worth stressing that these novel effects of attraction on the nonergodicity transition, which was theoretically predicted, has been experimentally detected in the micellar system we studied.

In this Letter we focus our attention on the high concentration range and temperatures above the room temperature in an adhesive colloidal system. The intermediate scattering function (ISF), as measured by photon correlation spectroscopy (PCS), shows clearly the structural arrest at a series of thermodynamic points. The locus of these ergodic to nonergodic transitions clearly depends on both T and c . We shall explain our results using the idealized MCT [6] which has been used successfully to describe the kinetic glass transition observed in many supercooled liquids [7]. In particular, it has been used to explain dynamic light scattering measurements of a nonergodic transition in a colloidal hard sphere system at high concentrations [8]. In our case, detailed analysis of the ISF's measured by PCS gives various parameters characterizing the two-step relaxation predicted by the MCT. Specifically, the exponent parameter at the transition has a value $\lambda = 0.7$ [9]. The main focus in our interpretation of the structural arrest in terms of the kinetic glass transition is the introduction of the attractive part of the interparticle potential into the MCT, which allows a nonergodic behavior to occur even at low c depending on T . Similarity and difference of this experimentally determined glass transition line to recent theoretical results on the sticky hard sphere model (SHM) and the attractive Yukawa model (AYM) [3,4] are discussed.

The system we study is made of a nonionic triblock copolymer L64 belonging to the Pluronic family [10]. Pluronic is made of polyethylene oxide (PEO) and polypropylene oxide (PPO), with the two PEO chains placed symmetrically on each end of the PPO chain. The chemical structure of L64 is $[\text{PEO}_{13}\text{-PPO}_{30}\text{-PEO}_{13}]$, with a molecular weight of 2900 u and is comprised of 60 wt% PPO. PPO tends to become less hydrophilic than PEO at higher temperatures. Thus the copolymers acquire a surfactant property and self-assemble spontaneously forming spherical micelles in an aqueous solution at sufficiently high temperatures and *above* certain concentrations [11]. The micelles exist in a wide range of copolymer concentrations

from a few wt % up to more than 50 wt % for $T > 30^\circ\text{C}$. We recently investigated by small angle neutron and light scattering [12] the behavior of the disordered micellar phase, the microstructure of the micelles, and their mutual interactions. We also determined that the micelles are essentially monodispersed, with polydispersity below 3%. The phase diagram, shown in Fig. 1, is characterized by an inverted binodal curve with a critical point at $c_c = 5$ wt % and $T_c = 330.3$ K and a percolation line depending on c and T cutting across the phase diagram starting from near the critical point to at least 40 wt %. The percolation locus is determined by the observation that the shear moduli jump by more than 2 orders of magnitude across it, and by a power-law behavior of the frequency-dependent viscosity [12]. It can also be determined by the change of slope of the relaxation time measured by PCS as a function of T at a given c [13]. The PCS data have been taken using a digital correlator with a logarithmic sampling time scale [14] which allows an accurate description of both the short and the long time regions of the ISF, up to times of the order of seconds. Following the method used for colloidal hard spheres [15] we measured the correlation function

$$g^{(2)}(q, \tau) = \langle\langle I(q, 0)I(q, \tau) \rangle\rangle / \langle\langle I(q, 0) \rangle\rangle^2, \quad (1)$$

where $I(q, \tau)$ is the intensity of light scattered at wave vector q at time τ , the second bracket denoting a positional average. Since the system shows a structural arrest, and therefore a nonergodic behavior, particular care has been taken in averaging over many different sample positions in measurements of a long time region of the time correlation function. For each sample and each temperature we

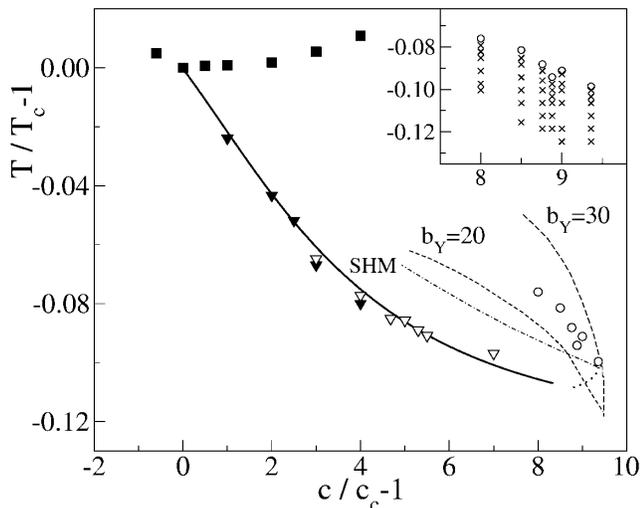


FIG. 1. The phase diagram of the L64/water system showing the binodal line (squares); the percolation line measured through viscoelasticity (full triangles) and PCS (empty triangles); model fit of the percolation locus by SHM (solid line); the measured glass line (circles). The long- and short-dashed lines are the computed glass lines for the AYM with $b_Y = 20$ and $b_Y = 30$, respectively, and the glass line computed by the SHM (dot-dashed line). The inset shows the location of measurements.

have performed from 100 to 200 measurements, observing a larger scattering area corresponding to three or more independent Fourier components and changing the position of the sample in order to observe different scattering volumes. The ISF can be obtained from $g^{(2)}(q, \tau)$ in a straightforward way using the Siegert relation. The measurements have been taken for $c > 40$ wt %, below which no structural arrest has been observed, although the ISF tend to develop a long time tail which can be described by means of a stretched exponential. For $c > 40$ wt %, moving at constant c and increasing T above the percolation line, we observe a progressive slowing down of the decay of the ISF, up to a point where it becomes flat, indicating the structural arrest. The structural arrest is experimentally identified by the breakdown of the Siegert relation and the failure in obtaining reproducible spectra. A typical behavior is shown in Fig. 2 at various concentrations and temperatures. We plotted the ISF for $c = 40$ wt % in order to show that the structural arrest appears only above that threshold. In fact, below it one observes the usual stretched exponential behavior of dense micellar systems but no nonergodicity sets in. The points in the c - T plane where we measured the ISF are indicated in the inset of the phase diagram of Fig. 1.

When the attractive potential has a range short compared to the particle size, it is usually represented by an exponential or a square well interaction. Typical examples are a Yukawa potential or a sticky sphere potential introduced by Baxter [16]. In both cases the Ornstein-Zernike equation for the pair correlation function can be solved in mean spherical approximation or in Percus-Yevick approximation respectively. This type of approach has been successful in interpreting percolation phenomena in microemulsions [17] and in the L64/water system [12]. In particular, the phase diagram can be fairly well described in terms of the SHM [16], i.e., a square well potential of zero range and infinite depth. In order to relate the model

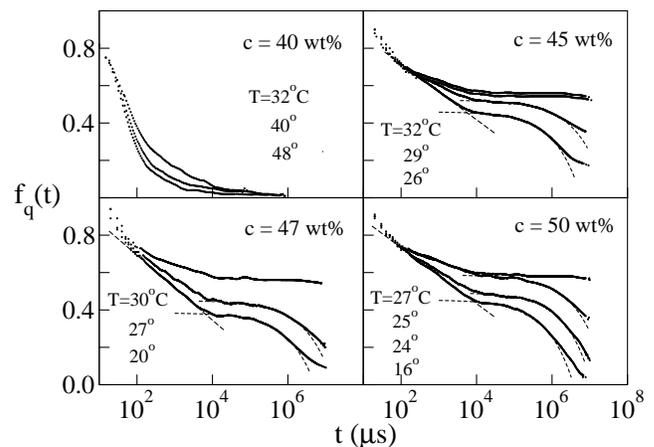


FIG. 2. The ISF for various concentrations and temperatures in the glass region. The short-dashed lines are fits to the von Schweidler law, while the long-dashed lines show the logarithmic decay.

to the thermodynamic properties of the solvent, one has to assume a functional relation between the measured temperature T and the parameter $1/\tau$ which characterize the stickiness in the Baxter model. In our case a simple linear relation $T \approx 1/\tau$ is sufficient to give a fairly good representation of the percolation and binodal lines, once the critical point given by the theory is assumed to coincide with the experimental one. The good agreement with the measured percolation line is clearly seen from Fig. 1. The percolation points, measured through shear viscosity and modulus, and the points marking the structural arrest, measured by dynamic light scattering, cannot easily be explained in terms of other physical phenomena. Following recent suggestions in the literature [3,4], we applied the MCT to model potential possessing a hard core and a short-range attractive tail, in order to describe the structural arrest.

The MCT equations for the normalized ISF $f_q(t) = F_q(t)/S_q$ predict the existence, for a given c , of a critical temperature T_{MCT} where the nonergodic transition takes place, characterized by $f_q(t \rightarrow \infty) = f_q^c > 0$, a finite plateau [9]. The parameter driving the transition is the separation parameter $\sigma \approx 1 - T/T_{\text{MCT}}$. MCT introduces various time regimes in the decay of $f_q(t)$. The short time region $t < t_0$ is dominated by microscopic dynamics and is followed by the β relaxation region close to the plateau f_q^c , characterized by the time scale $t_\sigma = t_0/|\sigma|^{1/2a}$, whose initial part gives the approach to f_q^c while the final one follows von Schweidler's law

$$f_q(t) = f_q^c - h_q(t/t'_\sigma)^b \quad (2)$$

with the second characteristic time scale $t'_\sigma = t_0|\sigma|^\gamma$, $\gamma = (1/2a) + (1/2b)$ and h_q a constant amplitude. a ($0 < a < 0.5$) and b ($0 < b < 1$) are nonuniversal exponents determined solely by the so-called exponent parameter $\lambda = \Gamma^2(1-a)/\Gamma(1-2a) = \Gamma^2(1+b)/\Gamma(1+2b)$ where Γ is the Euler gamma function and λ is in turn determined by the static structure factor S_q . Analyses of the experimental data give the parameters $b = 0.6$ characterizing Eq. (2) [6] and the exponent parameter $\lambda = 0.7$. The universal plot of von Schweidler law is reported in Fig. 3 where the scaling time is also shown and gives the exponent $\gamma = 2.3$. Note that data taken at low T tend to deviate from the power law, indicating that corrections to scaling might be important. The situation is less satisfactory when considering the data above the plateau of the ISF, which should follow a power law with an exponent a . In that region, in fact, the data show a tendency to a logarithmic dependence on time.

Motivated by our previous experience with percolation phenomena in colloidal systems where many phenomena are due to the short-range attractive potential, we have examined a recent version of the MCT applied to these types of systems. In both the SHM and AYM cases the glass transition line in the c - T plane shows two branches, one

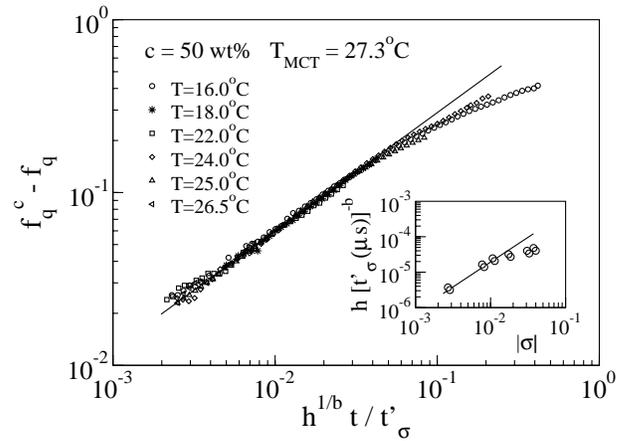


FIG. 3. The fit to the von Schweidler law in terms of the scaling time variable. The line has a slope $b = 0.6$. The inset shows the scaling time as a function of the separation variable which gives the power-law index $\gamma = 2.3$.

essentially corresponding to the glass line of a hard spheres system at high c , the other extending to much lower values of c . The former is attributed, with the usual mechanism due to the excluded volume, to the repulsive part of the interaction, and the latter to the attractive part of the potential. The nonergodicity parameters have a qualitatively different behavior on approaching the two lines. In the case of the sticky hard spheres system a new phenomenon arises, namely, a glass-to-glass transition due to the crossing of the two glass lines. This transition is associated with a higher-order glass transition of type A3 [5]. We use the transformation we adopted to map the binodal and percolation lines of Yukawa or Baxter models, i.e., a linear transformation between the parameter K and T for the AYM [4] and the parameter τ and inverse temperature for the SHM [3]. We then can at least qualitatively plot on the phase diagram of the L64/water system the curves corresponding to the glass transitions in the two models. The two dashed lines in Fig. 1 correspond to the Yukawa attractive potential, $u = -K\sigma \exp[-b_Y(r/\sigma - 1)]/r$ for $r > \sigma$, the hard sphere diameter, with different screening parameters b_Y and inverse temperature proportional to K . The glass line in models with a hard core plus an attractive tail shows a rather steep repulsive part around $c \approx 10c_c$ in the c - T plane. Then there is an attractive part extending smoothly in the direction of the critical point. It is this latter part of the glass line which has a behavior qualitatively similar to the measured locus of structural arrest of our micellar system. The Baxter type glass line is less similar to the measured one. In particular, it shows a *reentrant behavior*, i.e., it reaches values of the concentration higher than the ones corresponding to the hard spheres limit [3,4]. This shows in Fig. 1 as the short-dotted line starting from the measured glass transition point at the lowest T . A square well potential of a narrow but finite width would be in this case more flexible and give a better description

of the measured glass line. Some of our measurements extend in the region of the percolation line but no observable change of the dynamics occurs in the ISF. This is generally expected since percolation is detectable in micellar systems through electrical conductivity and viscoelasticity measurements but not light scattering. The experimental ISF decay also shows a time region with a logarithmic time dependence. This feature is characteristic of a cusp-like singularity of the A3 type [5,6], in the vicinity of which a very slow logarithmic relaxation sets in and influences a large time domain [3]. The logarithmic behavior observed in the ISF could be a manifestation of such an effect.

In conclusion we showed that the micellar system made of a solution of the triblock copolymer L64 in water shows a structural arrest that can be traced to a line in the concentration-temperature phase diagram. In the vicinity of this line the ISF shows the typical two-step decay of the supercooled liquids approaching a kinetic glass transition, and a time region where a logarithmic decay exists. This behavior is related to the existence of an attractive tail of the interparticle potential, which gives rise to a structure factor that, in some approximation can be analytically evaluated. This in turn allows an application of the MCT which is significantly different from the analogous calculations for hard spheres. The kinetic glass transition line is in fact composed of two parts that can be traced to the repulsive and the attractive parts of the potential, the latter being responsible for the structural arrest we have observed experimentally. A confirmation is given by the logarithmic decay of ISF which is a consequence of the short-range attraction, at least in the case of the SHM. The picture that emerges in the case of the micellar system is that the attractive potential is not only the origin of the phase separation, but also of the formation of ramified clusters which then originate the percolation line and finally the structural arrest and the glassy behavior at high concentration of the polymer.

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