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The dynamical fragile-to-strong crossover in attractive colloidal systems

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ABSTRACT

The dynamics of a hierarchical colloid solution, dendrimer in methanol, has been studied using photon-correlation spectroscopy (PCS). The obtained relaxation curves are analyzed according to the mode-coupling theory (MCT). The main results are: i) the occurrence of a fragile to strong dynamical crossover as a function of the packing fraction at $\phi_c \simeq 0.39$, and ii) the observation of a secondary relaxation (β) that has its onset just at the dynamical crossover and is correlated with the primary α-relaxation. Finally we discuss the obtained findings in comparison with recent experiments in similar systems characterized by an attractive interaction obtaining a confirmation on the primary role of the dynamical crossover in the physics of the dynamical arrest.

1. Introduction

The dynamic arrest phenomenon (DA), accompanied by a remarkable dynamic slowing down that marks a dramatic change in the properties of a physical system [1], represents a hot topic in condensed matter research. The phenomenon is customarily studied by exploring the transport coefficients (e.g., viscosity η, self-diffusion constant D_s, and relaxation time τ) as functions of thermodynamical variables (temperature T and concentration C). The dependence of the supercooled liquid dynamics into a metastable state below their melting temperature T_M is well known. The study of the way of their approaching to these limiting values may provide information about the nature of the process. A special situation as regards these coefficients, and τ in particular that, as C increases or T decreases below T_M, can change by several orders of magnitude, eventually surpassing the time required for experimental accessibility. In some cases, this behaves, as proposed by the ideal mode-coupling theory (IMCT) [2], the breaking of the system's ergodicity in the amorphous glass phase at or below the glass transition temperature T_g. This approach has received much attention in the glass-transition literature, but the usual methodology is to explore the T-dependence of these coefficients by supercooling liquids into the metastable state below the melting temperature T_M until they either crystallize or vitrify. Often, the packing fraction (or the volume fraction ϕ) can be the control parameter [2–7], e.g., in complex fluids like polymers and colloids.

Considering the various open questions on the related basic processes, the DA constitutes an exciting and challenging research topic today while strongly debated also with conflicting opinions [8–14]. One of these deals with a possible “DA criticality”: i.e., whether transport parameters reflect an underlying phase transition to a state in which these quantities diverge at a finite temperature (the "dynamic divergence"). Another one instead focuses on the occurrence, or not, of the system non-ergodicity inside the glass phase originally observed in hard colloidal solutions and explained according to the MCT theory [4,5]. For this latter argument it has been recently proposed that grafted polydisperse colloids [15] and molecular liquids with internal degrees of freedom remain ergodic at all temperatures [9,16] and therefore statistical mechanics can be applied to describe the arrest process.

Transport coefficients on approaching DA have been treated by means of the empirical Vogel–Fulcher–Tammann (VFT or super Arrhenius) form: $\tau = \tau_0 exp(BT_0/(T-T_0))$. The significant reason of its extensive use is in the indication of a finite diverging temperature $T_0 \ll T_g$, associated with the Kauzmann temperature T_K [17,8] and for the liquid classification in two separate categories: “fragile” or “strong” glass formers [18]. Whereas “strong” liquids exhibit pure Arrhenius T-dependence: $ln(\tau/\tau_0) = E/k_BT$, the “fragile” ones have a marked VFT behavior. Despite its empiricism, VFT has been treated as a “universal” feature and only recently its validity has been reconsidered because different experimental studies and theoretical reasoning show that it lacks a true physical meaning [9,19,11,12,20].

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Various recent studies [10,12,20] suggest that for the study of liquid dynamics in a broad T-range, at least two dynamic regimes are necessary; the reason lies in an intriguing phenomenon occurring at a temperature (T_B) well above T_g: the so called fragile to strong dynamic crossover (FSDC). Lately, T_B, for the processes disclosing their properties there, has been recognized as a datum point in the DA being the FSDC accompanied by several significant phenomena like: (i) the broadening of the structural relaxation time distribution accompanied in some cases by the loss of ergodicity, conditions for which the scattering functions $F(q, t)$ can be described by means of a stretched exponential $F(q, t) = F_q^c exp[-(t/\tau_\alpha)^\beta]$ and can approach an almost constant value for long times [4,5]; (ii) the splitting of the high-T relaxation into the primary (α) and the Johari–Goldstein β_{JG} relaxation times (also named secondary or β_{slow}) [21]; (iii) the decoupling between the translational and the rotational diffusion (for $T < T_B$) corresponding to a violation of the Stokes–Einstein (SE) relation. In the high T-regime, as evidenced by the SE, the translational diffusion, D_s, tracks the inverse of the shear viscosity (η^{-1}) whereas for $T < T_B$ D_s declines far less rapidly by decreasing T as $D_s \sim \eta^{-\xi}$, with $\xi \simeq 0.75$; instead D_{Rot} (or the rotational correlation time) remains proportional to the inverse of the shear viscosity down to T_g [22–25]. For this reason any experimental technique sensitive only to the D_{Rot} cannot observe the violation; (iv) for a broad set of supercooled systems $\tau(T_B) = 10^{-7 \pm 1}s$ and $\eta(T_B) \approx 10^3$ Pa s are near-universal [20] and if we consider the T–P phase diagram: $\tau(T_B, P_B), \eta(T_B, P_B) = const$ for a given glass former; (v) it is believed that the dynamical crossover is closely related to the appearing of dynamical heterogeneities (DH), although some pure Arrhenius systems show them [26]. DH refers to the presence of transient spatially separated regions with vastly different relaxation times [22,23,27]; (vi) usually a fragile to less fragile (or strong) transformation occurs when passing T_B [20]; (vii) and finally the hopping extended MCT (EMCT) identifies T_B with the MCT critical temperature T_c [2,28,29]. T_B can be evaluated by means of different methods, such as by means of a plot based on the T-derivative of the α-relaxation time [30].

Exploration of all these phenomena can help to stress more the importance of the dynamical crossover [10,31–34], and its universality [20].

Must be noticed that although the FSDC is a datum point for the dynamical arrest, in the case of hydrated proteins the FSDC represents a debated subject with controversial opinions [35–38]. In this latter case it has been proposed that the FSDC may be related to the splitting of a secondary relaxation [36]. Whereas for glass former the transition is related to the molecular cage dynamics [29] for hydrated proteins its origin appears unclear. However, a comparative analysis of the dynamical properties of protein hydration water as far as bulk and confined water coming from many different experimental techniques and proper molecular dynamic simulations (MD) reveals that all the reported data are consistent with the dynamical crossover scenario [37].

Different approaches for estimating T_B have been recently proposed: one is based on the MCT [20,29], the second employs the constraints of the Adam–Gibbs theory [12,31] and the most recent one explores the apparent enthalpy space properties [10]. All of them stress the basic importance of the dynamical crossover in the DA physics. The dynamic crossover concept can be considered of true interest not only for the way in which a system arrests its dynamics but also for the new science frontiers towards the mesoscales. In fact very recently the crossover has been explicitly considered as a way with which multiscale materials can model the mesoscale, i.e. how the understanding of mechanisms at the microscale can enable predictions of functional behavior at the macroscale [31]. For these reasons T_B appears to be of central interest in material science.

We also stress that by considering the relevant results in the field of the dynamical crossover its dependence on the concentration can be a useful test of some important suggestions such as the ϕ-dependence of the β-secondary relaxation strength could be useful to understand if this process has its onset just at the FSDC. Furthermore, in this respect it is noteworthy to verify how the "onset" scenario of this β-process can be related with the crossover scenario for the Johari–Goldstein (β_{JG}) relaxation and γ-secondary relaxations observed in other glass forming materials [32,33].

On the basis of the EMCT generality, the dynamical crossover can be observed also by exploring a system with the volume fraction as the control parameter, rather than T, as customary made, and ϕ_c, like T_c, represents the separation between the two different dynamics. Recently we have substantiated this idea by making use of a copolymer micellar system in which the short-range attraction is due to an effective intermicellar interaction. To be precise we have studied the system viscosity in a large $T - \phi$ range by using separately T and ϕ as control parameters. Fig. 1 evidences the obtained results: whereas the main plot reports the FSDC as a function of ϕ with $\phi_c \simeq 0.37$, the inset reports the FSDC as a function of T with $T_c \simeq 300$ K.

Motivated by these results here we explore, using a photon correlation spectroscopy (PCS or quasi elastic light scattering QELS), the relaxational dynamics of a monodispersed colloidal solution just as a function of the volume fraction. The density–density scattering functions (or correlators) can give, in addition to these viscosity data, more informations on the system properties. The measured correlators are studied in the current MCT frame with the following main objectives: a) to obtain a careful verification of the dynamical crossover in the primary α-relaxation; b) to explore whether the system maintains the ergodicity near and below the glass transition, and whether the dynamical crossover exists with this property; and c) to accurately compare the obtained data with the related findings recently observed in other colloidal systems [15].

2. Experiment and results

It is well known that in the QELS experiment the field autocorrelation function, $S_1(q, t)$, related with the translational and diffusional molecular modes is measured [39]. Just to have only a measure of the density correlations, we worked in a polarized geometry (VV) so that the present PCS experiment measures the correlation function, $g_1(q, t)$.

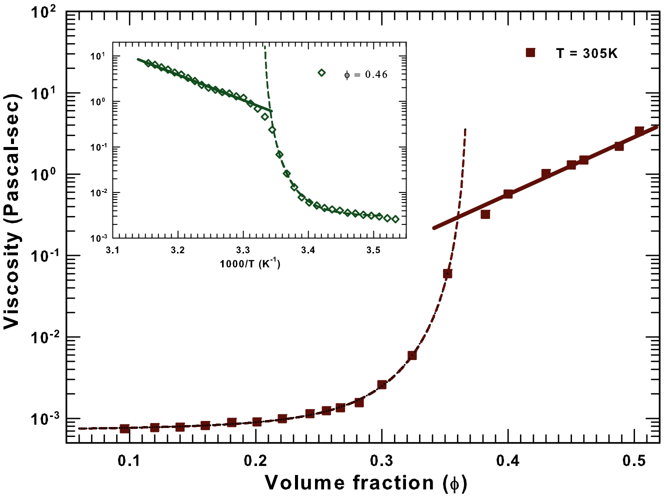

Fig. 1. The viscosity of the $PL64/D_2O$ AHS micellar system measured as a function of the volume fraction at T = 305 K is reported in a log-lin scale. The data are fitted at low ϕ by using the MCT power law (Eq. (2)) with ϕ as the control parameter (short dashed line). The dynamical crossover from a strong to fragile glass former behavior is observable at $\phi_c \simeq 0.37$. In the inset, the log-lin plot of the viscosity of the same micellar system at the volume fraction of 0.46 is reported. The short dashed line represents the data fitting at low T in terms of the MCT power law (Eq. (2)) with T as the control parameter. At this volume fraction the dynamical crossover from super-Arrhenius to Arrhenius behavior (continuous line) can be easily observed. The obtained crossover temperature T_c is about 300 K.