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.

Keywords: Diverging processes, Dynamic Crossover, Fragile to strong transition, Glass forming materials, Soft-matter

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 an hot topic in condensed matter research. The

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5 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 depen-
 dence of the supercooled liquids dynamics into a metastable state below their
 melting temperature T_M is well known. The study of the way of their ap-
 10 proaching to these limiting values may provide information about the nature of
 the process. A special situation 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 acces-
 sibility. In some cases, this behaves, as proposed by the ideal mode-coupling
 15 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 method-
 ology 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
 20 crystallize or vitrify. Often, the packing fraction (or the volume fraction ϕ) can
 be the control parameter [2, 3, 4, 5, 6, 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
 25 debated also with conflicting opinions [8, 9, 10, 11, 12, 13, 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
 30 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.

35 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 liquids classification in two separate categories: "fragile" or "strong" glass formers [18]. Whereas "strong" liquids exhibit pure Arrhenius T -dependence : $\ln(\tau/\tau_0) = E/k_B T$, the "fragile" ones have a marked VFT behavior. Despite of 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 of a true physical meaning [9, 19, 11, 12, 20].

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, 23, 24, 25]. For this reason any experimental technique sensitive only to the D_{Rot} cannot observe the violation; (iv) for a broad set of super-cooled systems $\tau(T_B) = 10^{-7 \pm 1}$ sec and $\eta(T_B) \approx 10^3 Pa \text{ sec}$ are near-universal

[20] and if we consider the $T - P$ phase diagram: $\tau(T_B, P_B), \eta(T_B, P_B) = \text{const}$ 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
70 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
75 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, 32, 33, 34], and its universality [20].

Must be noticed that although the FSDC is a datum poin for the
80 **dynamical arrest, in the case of hydrated proteins the FSDC represents a debated subject with controversial opinions [35, 36, 37, 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 hy-**
85 **drated proteins its origin appears unclear. However, a comparative analysis of the dynamical properties of proteins 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**
90 **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
95 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
100 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 an useful test of some important suggestions such as the ϕ -dependence
105 of the β -secondary relaxation strength could be useful to understand if this process has its onset just at the FSDC. Furthermore, on 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
110 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
115 this idea 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. **Figure 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
120 the FSDC as a function of T with $T_c \simeq 300K$.

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
125 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
 130 with this property; c) to accurately compare the obtained data with the related
 findings recently observed in other colloidal systems [15].

Experiment and Results.

It is well known that in the QELS experiment the field autocorrelation func-
 tion, $S_1(q, t)$, related with the translational and diffusional molecular modes
 135 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 mea-
 sures the correlation function, $g_1(q, t)$.

The colloidal solution we studied is a polyamidoamine (PAMAM, with ethilene-
 diamine central core) dendrimer (or starbust polymers) of generation six (g
 140 $= 6$) in methanol. These macromolecules, synthesized by repeating units in a
 hierarchical self-similar fashion, have a relatively homogeneous radial density
 with flexible end groups (with a certain degree of backfolding). More precisely,
 whereas, the low generations $g < 5$ have a fractal like internal structure, for
 generations $g \geq 5$, the scattering distributions are consistent with an homoge-
 145 neous sphere distribution monodisperse in size [40], a situation confirmed by
 MD simulation [41]; in addition, they can be classified as monodisperse spher-
 ical colloids. Depending on the generation number, their radius ranges from
 5 to $60\text{\AA}$, the molecular weight from some tens to 10^6 Daltons (for $g = 6$,
 $M_W \sim 40.000Da$, and $R_g \sim 22\text{\AA}$, the same order of magnitude of lysozyme
 150 and other small proteins). For moderate and large integer generation, $g > 5$,
 they can be classified as true colloids having a structure characterized by an
 hard core plus a corona region made of the flexible end groups (whose fractional
 depth decreases on increasing g). In principle, these flexible end groups of the
 dendrimer corona can behave like the polymers of the grafted colloids (or the
 155 hydrated corona of copolymer micelles) giving rise to an attractive interparticle
 interaction [40].

We have used only PAMAM dendrimers of generation $g = 6$, with NH_2
 and OH terminal groups, obtained from "Dendritech Inc" as methanol solu-
 tion at the weight concentration of about 10%. The solvent was completely

160 evaporated with a particular care, slightly and at room temperature. After the
measure of the solute volume, sample was prepared at the desired volume frac-
tion by adding the solvent. The studied volume fractions, ϕ , covers a range
from 0.1 to 0.61. PCS measurements were made at a scattering angle $\vartheta_s = 90^\circ$
($|q| = 4\pi n/\lambda_0 \sin(\vartheta_s/2)$ being n the system refractive index and λ_0 the vacuum
165 light wavelength) using a continuous wave solid state laser (Verdi-Coherent) op-
erating at 50mW (5120Å) and an optical scattering cell of a diameter 1 cm in
a refractive index matching bath. The sample is thermostated with a stability
within $\pm 10mK$. The intensity data were also corrected for turbidity and multi-
ple scattering effects [39]. PCS data have been taken using a digital correlator
170 with a logarithmic sampling time scale which allows an accurate description of
both the short- and long- time regions of the intermediate scattering function
from 0.1 μ sec to 100 sec.

The system works in the homodyne mode and measures, at a given wave-
vector q , the intensity correlation function $g_2(q, t) = \langle I(q, 0)I(q, t) \rangle / \langle I \rangle^2$, re-
lated to the scattered electric field normalized autocorrelation function $g_1(q, t) =$
 $S(q, t)/S(q, 0) = \langle E_s^*(q, 0)E_s(q, t) \rangle / \langle |E_s|^2 \rangle$ through the Siegert's relation $g_2(q, t) =$
 $1 + |g_1(q, t)|^2$. To be precise, in order to measure the normalized intensity cor-
relation function we used a method with a special average procedure [5]

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

The first bracket denotes the time average and the second bracket the po-
sitional average over different parts of the sample. The system, in fact, can
175 show a structural arrest, and therefore a non-ergodic behavior, when the cor-
relation functions tend to develop very long time delays. In such a situation a
particular care must be taken in averaging over many different sample positions
for a correct measure of the long time region of the time correlation function.
For each concentration a large number of measurements must be performed,
180 enough for a correct average, 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. By using such

a procedure, that explores many scattering volumes, for each autocorrelation function a typical overall experimental time of about 4 *hours* is necessary in the
185 highest volume fraction regimes. However, for $\phi > 0.3$ we have repeated several times the measuring procedure.

Figure 2 illustrates some measured $g_1(q, t)$ in the range from $\phi = 0.15$ to $\phi = 0.615$ at 293K. All the reported $g_1(q, t)$ curves are characterized by a complex relaxation and the decay to zero in finite times. Besides a very short
190 time contribution, that is well evident for $\phi = 0.15, 0.27$, and identified as the cage relaxation time $\tau_{\beta fast}$, the correlators are characterized by the presence of other two contributions: an intermediate that appears only for $\phi \geq 0.37$ and a long-time tail (the α -decay). Important observations are that the system ergodicity is fully preserved at all the studied concentrations and the presence of
195 the intermediate relaxation that should be the Johari-Goldstein $\tau_{\beta JG}$ relaxation time [21].

In the region $0.11 < \phi < 0.37$ the $g_1(q, t)$ curves have been analyzed (continuous lines in **Figure 2** represent the data fitting) as the superposition of an exponential short-time decay (the $\beta - fast$ contribution) and a long-time
200 stretched tail (the α -decay), weighted for the non-ergodicity factor f_c . As a result we find that whereas the $\tau_{\beta fast}$ results nearly insensitive by increasing ϕ (remains nearly constant, about $0.3 \cdot 10^{-6} sec$) τ_α increases of about four orders of magnitude. For $\phi > 0.37$ in addition to these two mentioned contributions, an intermediate relaxation of the order of some *m* sec appears. Being these three
205 contributions separated by about three orders of magnitude each, we have used, in order to process the data, together with the previous two exponential forms, another stretched exponential. Hence from the data fitting, we obtain the times τ_α , $\tau_{\beta fast}$, and $\tau_{\beta inter.}$, the two stretched exponents β , $\beta_{inter.}$ and finally the non-ergodicity factor f_c .

210 Discussion.

The ideal MCT proposes the existence of a precursor phenomenon characterized by anomalous dynamics, around the critical value of the control parameter T_c or ϕ_c , at the transition from liquid to amorphous solid well prior the

glass transition. Inside this phase the theory interprets experimental data with
215 closed equations of motion obtaining correlators (the density-fluctuation correlation functions $F(q, t)$ at a given wave-vector q [2]). In addition, T_c (or ϕ_c) is explained as a bifurcation singularity in the $F(q, t)$ long- t limit, a reason for which the observables behave differently above and below it; this limit, called glass form factor (or non-ergodicity parameter f_c), is zero in the liquid phase
220 but positive for the ideal glass. In the case of loss of the ergodicity, f_c behaves discontinuously, with a diverging behavior in transport (the MCT divergence) if the control parameter passes its critical value. Thus, f_c exhibits a singularity as a function of the distance $\epsilon = (T - T_c)/T_c$ (or $\epsilon = (\phi - \phi_c)/\phi_c$) for $\epsilon = 0$. Using ϕ as the control parameter, hard (HS) or soft (SS) spheres (like
225 colloidal particles [4, 5, 15]) have been largely used to study the DA by means of the MCT. These systems, at thermal equilibrium have large viscosity (and viscoelastic) and can form an amorphous solid [42] at large ϕ . We note that the HS system has been used as a theoretical paradigm for a simple fluid and that experiments conducted on HS colloids indicate that it can also serve as an accurate test of MCT [4, 5]. Originally it appeared that the ideal glass transition
230 concentration of the MCT was identical to the “calorimetric” glass transition, $\phi_c = \phi_g$. This suggests that studies of colloidal systems can help us understand the conventional glass transition, which is usually studied in molecular liquids.

MCT dynamics is based on the molecular caging for which the correlator behavior is described according to precise scaling laws (also supporting the arrest universality). Below T_c the interactions of density fluctuations arrest the previous region via cage-effects and the molecular origin of the system dynamic evolution represents an open question. The MCT scaling form commonly used to analyze the transport parameters, and to calculate ϕ_c inside the arrest region, is in the $\tau_\alpha(\phi)$ case:

$$\tau_\alpha = \tau_\alpha(\epsilon) = \tau_{\alpha 0} \left[\frac{\phi - \phi_c}{\phi_c} \right]^{-\gamma}, \quad (2)$$

where γ is a non-universal exponent, the same law holds for T . $\phi_c \approx 0.57 -$
235 0.59 are the most accepted values for the location of the colloidal glass transition;

it has been also widely believed that a truly non-ergodic state is obtained at
 larger ϕ . Eq. 3 describes well transport data of fluids in the region $\phi < \phi_c$, and
 thus in the region from the liquid stable phase to the coupled fluid phase. In
 the same region MCT characterizes the measured structural relaxations as the
 240 bimodal decay (primary α - and secondary β -processes) in $F(q, t)$ observing the
 way in which molecules explore all the available cage space. In the quasi-elastic
 scattering (QES) time regime, the two contributions are superimposed, with the
 β contribution at the lowest time (β_{fast}). The IMCT proposes precise scaling
 laws and exponents for both these relaxations. The ideal MCT divergence is
 245 represented by these scaling law forms: designating $\sigma = C\epsilon$ as the separation
 parameter, the β -relaxation is described by $t_\sigma = t_0/|\sigma|^{1/2a}$ ($1/2a > 1.27$).
 In the α - scaling law regime, the IMCT gives another power-law divergence
 (the γ exponent is larger than that of t_σ ($1/2a$), i.e., $\tau_\alpha = B^{-1/b}t_0|\sigma|^{-\gamma}$ and
 $\gamma = [1/(2a) + 1/(2b)]$). The critical exponents $0 < a \leq a_{\max} = 0.395$ and
 250 $0 < b \leq 1$ are related through the system-dependent parameter λ ($1/2 \leq \lambda < 1$)
 as: $\lambda = \Gamma(1 - a)^2/\Gamma(1 - 2a) = \Gamma(1 + b)^2/\Gamma(1 + 2b)$. QES experiments made in
 hard-sphere colloids for $\phi < \phi_c$, which measure both the self-diffusion coefficient
 D_s and τ_α , fully support these suggestions, giving $\gamma = 2.7$ [5]. In polystyrene-
 networked-sphere colloids, however, $\gamma = 3.6$ and $\lambda = 0.88$ [43].

255 The MCT has been intensively studied by means of experimental and simula-
 tion approaches in molecular systems and colloids. There is however a difference
 in these systems: for the same molecular glass formers the transition from an
 ideal MCT regime to an activated one has been experimentally demonstrated.
 Hence, it was possible to consider proper extended MCT models [2]. For col-
 260 loidal hard spheres the situation remains essentially unclear for the limited range
 of the corresponding dynamical data. If compared with the 15 orders of magni-
 tude for which the molecular fluids dynamic data are measurable, for colloids,
 depending on the particle size, is in fact available a much smaller range, typically
 eight decades or less. To be precise, one must note the experimental time win-
 265 dows available for these two classes of systems; whereas in the case of molecular
 materials the α -relaxation can be explored in a time relaxation interval ranging

from 10^{-13} to 10^2 sec, for colloidal systems this range can be actually, by means of a proper use of the dynamical light scattering technique (DLS) [15], 10^{-4} to 10^4 sec. In the past by means of traditional DLS the range for colloids was very limited: 10^{-4} to 1 sec [5], whereas here (see **Figure 2**) we have 10^{-7} to 100 sec.

A special feature of the EMCT is the prediction of a dynamic crossover in the transport parameters occurring just near the critical values of the control parameter associated to the dynamic change in the system, from one determined by the cage effect to one characterized by the hopping processes. It is a FS crossover in which the α -relaxation time and the self-diffusion undergo a crossover from SA to AE behavior. This result, obtained for a Lennard-Jones system, explains the FS crossover observed in a variety of glass-forming fluids [28, 44]. A temperature that marks dynamical changes of fragile supercooled liquids below T_M , has been already considered [11, 12, 45, 46] and from these suggestions started the idea that $T_c \equiv T_B$ [20, 29, 10].

EMCT explains the scale decoupling by assuming two possible diffusional contributions: i.e. a very long time thermally activated hopping process (D^{hop}) and the one typical of the IMCT (D^{id}); hence the total self-diffusion coefficient is $D_s \approx D^{hop} + D^{id}$, characterized by the dynamical crossover at ϕ_c (or T_c) from $D \approx D^{id}$ to D^{hop} . D^{id} , characterizing the kinetic glass transition (the Super-Arrhenius step of the DA) must vanish at $T_c/T = 1$ with a power law $D^{id} \sim |T - T_c|^\gamma$ just reflecting the predictions by the idealized theory. Hence, the dynamical behavior of the system towards the arrest at T_g is dominated by the hopping (Arrhenius) process with only one energy barrier (the second DA step).

The IMCT power law fits the transport parameter data in the SA region and indicates the control parameter value at which the experimental data cross that of the Arrhenius behavior. This analysis indicates the physical significance of the crossover concept in terms of a well-established theory of glass-forming systems, rather than of numerous empirical observations [29].

The FS crossover with ϕ and T as control parameters has been accounted by using copolymer micellar system with short-range attraction intermicellar inter-

action. The system is an aqueous solution of a nonionic, three-block copolymer made of polyethylene and polypropylene oxides (Pluronic L64). This polymer
300 in water is a T -dependent surfactant that forms monodisperse spherical micelles in a wide $T - \phi$ range. The system is widely described in many experiments [47, 42, 48, 49, 50, 6, 51, 7], and the **Figure 1** illustrates the obtained main findings. In this system the attractive interaction gives rise to a complex $(T - \phi)$ phase diagram characterized by the existence of a percolation threshold (PT)
305 line. In this system the super-Arrhenius behavior (described using IMCT) goes from the disordered liquid phase up to the PT line, whereas a strong glass-forming behavior is observable at the highest T and ϕ values going from the PT line (that is also the locus of the T_c and ϕ_c values) to the glass transition line. Due to the attractive interaction, and the clustering process characterizing
310 this system, these critical values are strongly correlated in the sense that at an higher critical temperature value corresponds a lower critical volume fraction value (and viceversa).

Before discussing the relaxation times we measured, we consider, in **Figure 3**, the obtained non-ergodicity factor f_c (inset) and the stretched exponent β .
315 We aim to stress that the overall behavior of these quantities is fully coherent with the theory. It is evident from **Figure 3** that $\beta_{inter.}$ (closed symbols), the stretched exponent of the intermediate relaxation is insensitive to the packing fraction variation with the value, within the experimental error, of $\beta_{inter.} \approx 0.98$ indicating that the corresponding relaxation has practically a pure exponential
320 behavior; on the contrary the β value (open symbols) corresponding to the long-time α -relaxation appears to be strongly ϕ -dependent. As can be observed, β has different behaviors above and below $\phi \approx 0.39$, indicating such a values as the MCT crossover ϕ_c ; more precisely, besides the lowest concentration (about 1) for $\phi < 0.39$ $\beta \simeq 0.7$ whereas in the range $0.39 < \phi < 0.5$ we have $\beta \simeq 0.5$ after that
325 β increases, evolving toward the unity at the highest ϕ . This behavior appears to be consistent with the MCT time-temperature superposition principle [2], no ϕ dependence in this stretching parameter must be observed below the critical value of the control parameter ϕ_c . Above this interval, where β has a constant

behavior, the corresponding stretched exponents are instead characterized by a
330 marked increase towards $\beta \simeq 1$, indicating the recovering of a single exponential temporal behavior. It seems that the relaxation time decays also have to obey to the same precise two-stage activation process indicated by the strong Arrhenius behavior of transport parameters, in a way fully consistent with the hopping process of the EMCT. The f_c behavior for different values of $\phi < \phi_c$ is
335 represented in the range $0.4 < \phi < 0.61$. We found that f_c has a value around to 0.45 and appears to be ϕ -dependent; a behavior also observed in literature [2], in fact the MCT predicts this parameter, as ϕ increases, a behavior according to $|\phi_c - \phi|^{1/2}$. The data reported in the figure appear to agree with such scaling law (dashed line) although the data experimental error is fairly large in order
340 to draw a definitive conclusion on this respect. However, this behavior agrees with the observations on a "strong" molecular glass forming system [52].

Figure 4 reports the relaxation times obtained in our experiments: τ_α , $\tau_{\beta fast}$, and $\tau_\beta = \tau_{\beta inter}$. Also these data confirm that the bifurcation from the α process appears close to $\phi_c \approx 0.39$ (with a value of ~ 0.2 sec). In the same
345 region τ_β seems to have its onset showing an Arrhenius dependence that persists also inside the glass state. The experimental points of the cage relaxation time $\tau_{\beta fast}$, are also reported, and as it can be observed are, on the contrary of the others, nearly ϕ independent. The onset of τ_β for $\phi \geq \phi_c$ suggests that this relaxation time, may represents just the Johari Goldstein relaxation (JGR). This
350 relaxation is basically a molecular process that is supposed to be universal, it seems to be strongly connected to the structural α -relaxation in all glass formers [53]. There is an experimental evidence on its connections in thermodynamic properties to the α -process, as proved by means of the NMR spectroscopy, where it is shown how, in glass forming materials above the critical value of the
355 control parameters, these two relaxations are correlated [54].

Usually the JGR is observed in Dielectric relaxation spectra as a peak, or as an excess wing on the high frequency flank of the primary relaxation when not resolved [53]; although some small molecular glass formers do not evidence such a phenomenon. The instrumental resolution or the thermodynamical conditions

360 (e.g. proper pressure and temperature value) can be e.g. the reasons of this. Eq.
 1 explains why the observed secondary relaxation may be the JGR; as defined,
 the function $g_1(q, t)$ measures the dynamical correlations in both orientation
 and position between all pairs of molecules as due to the interaction processes.
 Whereas the corresponding translational mutual diffusion is reflected in the
 365 α -process, the roto-translational coupling gives rise to the JG contribution.
 The $g_1(q, t)$ contains all the possible molecular dynamics that, depending on
 the probe used, can be (or not) separately measured.

All the PCS data here reported for attractive dendrimers stress the signifi-
 cant role in the dynamical arrest of the dynamical crossover, in agreement with
 370 the same experiment performed in polydisperse grafted colloids also above the
 MCT glass transition concentration (ϕ_c) [15]. It is just this last study that
 gave the first evidence on the preservation of the system ergodicity for $\phi > \phi_c$)
 as shown by our correlation functions (**Figure 2**). The idea that molecular
 glass formers fluids can be characterized by a cutoff mechanism suppressing the
 375 MCT divergence was originally proposed for compressible fluids [55] by means
 of a field-theory approach for which the transition from an IMCT regime to an
 activated one has been demonstrated.

In recent years the viewpoint that colloids posses the property of the MCT di-
 vergence suppressions, has been a subject of special interest and has been widely
 380 discussed especially for systems with different statistics: stochastic, Newtonian
 and Brownian [56, 57]. The main suggestion is that the same behavior must
 hold true for molecular and colloidal systems, whose dynamics takes place in the
 two-steps above described. However, from these studies emerge that the kinetic
 glass transition does not coincide with the ergodicity-breaking and the ergod-
 385 icity is maintained by varying the concentration, also in the activated hopping
 region.

On this subject we have to stress the difference with the findings of previous
 experiments on hard colloids characterized by an evident non-ergodicity [5]. A
 difference that can have two explanations: the first one is that the hard sphere
 390 system is characterized by only a pure repulsive interaction, whereas the grafted

colloid has an interaction with an additional attractive tail; and the second is the difference in the polydispersity. On this issue some discussions [5, 58, 15] must be considered.

In our experiment we have observed the JGR that has its onset at the dynamical crossover ϕ_c . We also have high-lighted that, in the frame of the present scattering experiment, the primary, τ_α , and this latter, $\tau_{\beta,JG}$, are dynamically correlated for the coupling between the rotational and translational motion of the macromolecules. We deal with attractive colloids for which an increase in the packing fraction leads to a clustering process reflected in the measured correlators not only in a pure translational dynamics. From the theoretical point of view, just in the MCT terms, ϕ_c separates two dynamical behaviors before and after it. In the first case the measured τ_α has to obey the MCT scaling law and in the second one a *concentration activated* process takes place. After the critical divergence at ϕ_c , a further compression imposes the crossover to another dynamical stage. Just this dynamical change towards a two energy level activated thermodynamics can be related with the JGR. In fact the JG relaxation, like the primary α -relaxation, involves transitions between different energy basins. Only in these terms the closer connection between these relaxations and the phenomenon of dynamic heterogeneity should be possible [60]. The interbasin transitions for $\phi > \phi_c$ is also accounted by the measured values for the stretched exponents related with the two relaxations τ_α , and $\tau_{\beta,JG}$. As it can be observed in the **Figure 3** whereas all the measured JGR stretched exponent values are about 1, the corresponding value of the α -relaxation increases by increasing ϕ above ϕ_c until the same value.

We conclude observing that our dendrimer system behaves like a grafted colloid [15] suggesting that in the EMCT frame molecular and colloidal systems behave at the same way. From our experiment we also observe in addition with the primary α -relaxation another one that, according to the current models, can represent the Johary Goldstein relaxation. These results give additional supports on the primary importance of the dynamical crossover in the DA.

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Figure 1: The viscosity of the *PL64/D₂O* AHS micellar system measured as a function of the volume fraction at $T = 305K$ is reported in a log-lin scale. The data are fitted at low ϕ by using the MCT power law (Eq.3) 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.3) 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 300K.

Figure 2: The correlator $g_1(t)$ for different values of the volume fraction for PAMAM dendrimer in methanol. The continuous lines represent the best fit obtained by the superposition of an exponential short-time decay (the β -fast contribution) and two stretched tails weighted for the non-ergodicity factor f_c .

Figure 3: The non-ergodicity factor f_c (inset) and the stretched exponent β obtained from the measured correlators of PAMAM dendrimers in methanol. $\beta_{inter.}$ data are reported as closed symbols and the β values as open symbols. The Debye-Waller factor f_c is reported for different volume fractions in the range 0.4-0.65. The dotted line represents the MCT scaling law prediction, as the volume fraction increases above ϕ_c : $f_c \simeq |\phi_c - \phi|^{1/2}$.

Figure 4: The relaxation times here measured in the range $0.11 < \phi < 0.61$ show that a bifurcation from the α process occurs close to ϕ_c (at the relaxation time of about 0.2 sec), where τ_β has its onset with an Arrhenius T-dependence.