

Unraveling the equilibrium chain exchange kinetics of polymeric micelles using small-angle neutron scattering – architectural and topological effects

Reidar Lund,^{a*} Lutz Willner,^b Dieter Richter,^b Hermis Iatrou,^c Nikos Hadjichristidis^c and Peter Lindner^d

^aDonostia International Physics Center, Paseo Manuel de Lardizabal 4, 20018 Donostia-San Sebastián, Spain, ^bInstitute of Solid State Research, FZ-Jülich, D-52425, Jülich, Germany, ^cLaboratory of Industrial Chemistry, Department of Chemistry, National and Kapodistrian University of Athens, Zografou 157 71, Greece, and ^dInstitute Laue–Langevin, BP 156X, Avenue des Martyrs, F-38042 Grenoble Cedex 9, France. Correspondence e-mail: reidar_lund@ehu.es

In this paper, we present a study of micellar structures formed by poly(styrene)-poly(butadiene) (PS10-PB10; the numbers indicate the molecular weight in kg mol^{-1}) diblock copolymers and PB10-PS20-PB10 triblock copolymers in different *n*-alkane solvents. Particular emphasis is placed on the dynamic properties of these micelles under equilibrium which are studied using a novel time-resolved small-angle neutron scattering technique. The results show that the structures of the micelles are very similar for both the diblock and triblock copolymers, which allows a direct comparison of the dynamic properties. A novel logarithmic relaxation is found for both the triblock and the diblock micelles which is not consistent with theoretical expectations. However, for the diblock micelles, the relaxation kinetics seem to approach the rate and the single exponential decay predicted by Halperin & Alexander [*Macromolecules*, (1989), **22**, 2403–2412] when the micellar cores are strongly swollen with solvent. For the triblock micelles a logarithmic relaxation is found for all cases as an effect of additional topological knots present even in highly swollen micellar cores. This behavior is assigned to an increased coupling of chain motion within the dense confined core – an effect which seems to vanish in diblock micelles when the core is sufficiently swollen.

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1. Introduction

Equilibrium kinetics of molecular exchange between low molecular weight surfactant micelles have been studied extensively during the 1970s and 1980s and are known to occur on a relatively fast timescale of the order of μs to ms (Wennerström & Lindman, 1979). In a similar fashion a dynamic equilibrium, although much slower, may also be formed for diblock copolymer micelles. Unfortunately, the exchange kinetics between block copolymer micelles are generally very difficult to assess under equilibrium conditions. In addition to the inherently very slow exchange kinetics, the origin for this difficulty is that significant chemical or physical perturbations need to be imposed in traditional techniques such as fluorescence spectroscopy (Wang *et al.*, 1995) or temperature jump experiments (Waton *et al.*, 2001). Consequently, the kinetic mechanism governing the real dynamic equilibrium of such systems is poorly understood.

In recent studies we have circumvented this problem by employing a novel time-resolved small-angle neutron scattering (TR-SANS) technique that simply takes advantage of the large difference in scattering length between hydrogen (h) and deuterium (d) (Willner *et al.*, 2001; Lund, Willner, Stellbrink *et al.*, 2006; Lund, Willner, Dormidontova & Richter, 2006a). The idea is based on mixing micelles consisting of two differently labeled but otherwise identical polymer chains. The technique is illustrated in Fig. 1. Two reservoirs

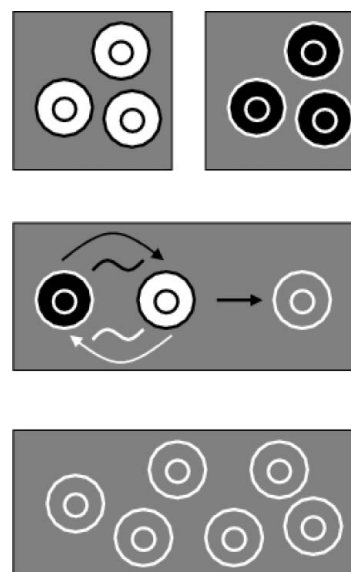


Figure 1

Illustration of the TR-SANS experiment for the determination of the chain exchange kinetics in block copolymer micelles.

Table 1

Number average molecular weights, M_n , in kg mol^{-1} , and degrees of polymerization, N , of the PS-PB/PB-PS-PB block copolymers.

| Polymer | M_n | M_n (PS) | N_{PS} | M_n (PB) | N_{PB} |
|----------------------|-------|------------|-----------------|------------|-----------------|
| h-PS10-d-PB10 | 22.2 | 10.5 | 100 | 11.7 | 195 |
| h-PS10-h-PB10 | 22.2 | 10.5 | 100 | 11.7 | 216 |
| d-PS10-d-PB10 | 21.6 | 9.9 | 88 | 11.7 | 194 |
| d-PB10-h-PS20-d-PB10 | 45.4 | 24.2 | 233 | 10.6 | 177 |
| h-PB10-h-PS20-h-PB10 | 39.6 | 21.0 | 202 | 9.3 | 172 |
| d-PB10-d-PS20-d-PB10 | 43.8 | 22.6 | 202 | 10.6 | 177 |

consisting of deuterated (black) and protonated (white) micelles are prepared in an isotopic solvent mixture (grey) which exactly matches the average scattering length density of the two constituent block copolymers. As the chains exchange, the overall scattering length density of the micelles will tend towards that of the solvent (grey) and consequently the intensity decreases. The average excess fraction of chains residing in the micelles, $R(t)$, is then simply related to the observable intensity, $I(t)$, by

$$R(t) \equiv \left[\frac{I(t) - I_\infty}{I(t=0) - I_\infty} \right]^{1/2}, \quad (1)$$

where I_∞ is the scattering intensity of the randomized blend of the two polymers and $I(t=0)$ is the intensity at time zero, which is taken as the mean normalized intensity of the two reservoirs at low concentrations where there is no influence of structure factors.

As the probability of exchanging a deuterated or a hydrogenated chain is equal to 1/2 and constant for all times, this function will tend to zero only when all chains have escaped their respective micelle at least once.

Previously, this technique has been employed for an aqueous system consisting of poly(ethylene-*alt*-propylene)-poly(ethylene oxide) (PEP-PEO) in water/dimethylformamide (DMF) mixtures. These studies showed that the interfacial tension γ represents a key tuning parameter for the timescale of exchange kinetics, which can be varied between less than minutes to practically infinity (Lund, Willner, Dormidontova & Richter, 2006a). It has also been shown that the exchange kinetics of diblock copolymer micelles are described by a characteristic logarithmic decay (Lund, Willner, Stellbrink *et al.*, 2006). This is in sharp contrast to existing theories (Halperin & Alexander, 1989) which all predict a single relaxation time for the expulsion process and thereby a single exponential decay.

In the previous work, the logarithmic decay has been rationalized in terms of a strong coupling between the chains owing to topological interactions and the confinement within the core. Since a core chain experiences an increasing expulsion as it approaches the surface, the probability of escape is strongly correlated with the conformational state of the chain and will only be significant if the chain has a compact conformation near the surface. Whenever the core is rather dense, such a pathway is likely to be cooperative (involving successive movement of several chains) and thus leading to a logarithmic relaxation in nature as pictured in models for hierarchical constrained dynamics (Brey & Prados, 2001). Hence the key parameter here is topological constraints. Whenever such effects are not present, *e.g.* in low molecular weight surfactant micelles, the single chain activated diffusion process as anticipated by Halperin and Alexander is expected to be valid.

In this paper, we present first results of the effect of architecture on the exchange kinetics in order to probe the effect of topological interactions. We compare the results from two different block copolymers [one diblock copolymer, poly(styrene)-poly(butadiene) (PS10-PB10) (the numbers indicate the molecular weight in

kg mol^{-1}), and a triblock copolymer which is a ‘double diblock’ (PB10-PS20-PB10)] in different *n*-alkane solvents which are selective for the PB block. Since the composition and corona block are equal for both polymers, the aggregation behavior and micellar dimensions are similar. However, a single but important difference between the resulting micelles will be the connectivity between the two PB blocks present only in the triblock micelle, which may lead to additional topological interactions of chains. Thus, by comparing the results from the two micellar systems the effect of chain ‘knotting’ and topological interactions inside the core can be directly studied.

2. Synthesis

All polymers employed in this study were synthesized by anionic polymerization using high vacuum/breakseal techniques. The procedures were similar to those described in the literature (Hadjichristidis *et al.*, 2000). The PS-PB diblocks were prepared by sequential addition of styrene and butadiene monomers. For high comparability, the h-PS blocks in h-PS10-h-PB10 and h-PS10-d-PB10 are identical since they were made from one batch. The triblock structure was obtained by coupling a living PB-PS diblock with dichlorodimethylsilane. Excess diblock was removed by fractionation. This method yields triblocks with identical outer PB blocks. Moreover, in analogy to the diblock synthesis, the d-PB10 blocks were also made from one batch such that the triblocks obtained have very similar molecular weight characteristics. All polymers including homo and diblock precursors were characterized by size exclusion chromatography (SEC). Relative to PS standards, the polydispersity was smaller than 1.05 in all cases. No homo polymers and/or diblock copolymer impurities were finally found in the SEC chromatograms. Absolute molecular weights and block compositions were determined by a combination of membrane osmometry, ^1H NMR and low-angle laser scattering. The important characteristics are given in Table 1.

3. Results and discussion

3.1. Structure

Micellar structure – SANS. The SANS measurements were performed at the KWS2 instrument at the research reactor FRJ2 at Forschungszentrum Jülich GmbH, Germany, and the D11 instrument at Institute Laue–Langevin, Grenoble, France. Raw data were collected and reduced to radially averaged, calibrated data using standard data evaluation tools provided on site. The structure of the micelles has been extensively studied and will be published in detail in a later paper. We will therefore only give a brief summary of important results here.

The structure of the micelles was determined in detail by contrast variation experiments on the partially labeled diblock and triblock copolymers h-PS10-d-PB10 and d-PB10-h-PS20-d-PB10 in isotopic *n*-alkane mixtures as solvents. Three contrasts were employed: core contrast (d-PB matched out), shell contrast (h-PS matched out) and an intermediate contrast (the interference between h-PS and d-PB visible). Corresponding partial scattering functions are shown in Fig. 2 for the triblock copolymer in hexadecane as a function of the modulus of the scattering vector Q , given by $Q = 4\pi \sin(\theta/2)/\lambda$, where θ is the scattering angle and λ the wavelength.

The data have been fitted with a core-shell model described in detail in a previous work (Lund *et al.*, 2004). All model curves were convoluted with a resolution function describing the experimental spread of the scattering vector of the instrument. The experimental

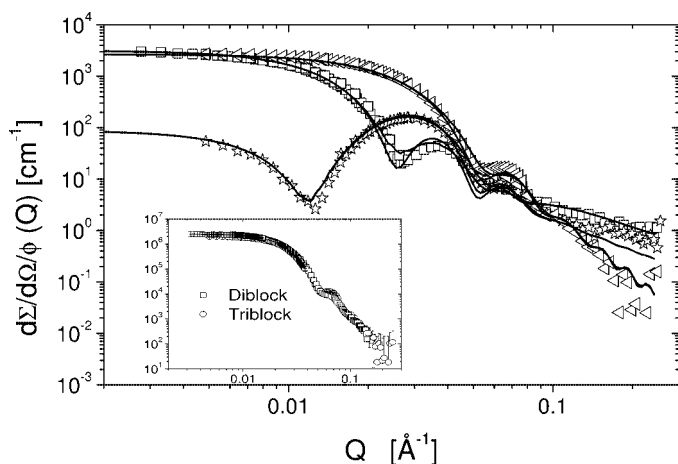


Figure 2 Partial scattering functions of d-PB10-h-PS20-d-PB10 in hexadecane at 293 K showing the core (triangles), shell (squares) and an average contrast (stars). The lines display a simultaneous fit to the experimental data using the core-shell model convoluted with the experimental resolution. Inset: comparison of the core scattering of the diblock and triblock micelles.

curves could be best fitted with a uniform, constant density profile for both the PS core and the PB corona. Fits are shown as solid lines in Fig. 2. For the PS10-PB10 data at higher temperatures, only the core scattering was measured and the fits were performed using a combination of the spherical form factor and single chain scattering (Lund, Willner, Dormidontova & Richter, 2006b). Some selected fits are given in Table 2.

An important observation is the decrease of the aggregation number with the *n*-alkane length of the solvent, while the solvent fraction, Φ_0 , in the core decreases. It should be noted at this point that although PS exhibits a rather high glass transition temperature in bulk (approximately 373 K), the core of the micelles is not vitrified owing to the presence of the large fraction of solvent. This has been confirmed by differential scanning calorimetry on a PS sample swollen with only 7% hexadecane. This sample already showed that T_g is drastically shifted to lower temperatures by almost 50 K. Thus, in this case when the PS cores contain 30–60% solvent, we do not expect any complications of glassy dynamics on the kinetics.

A comparison of the data for the d-PB10-h-PS20-d-PB10 and h-PS10-d-PB10 micelles reveals very similar micellar size characteristics. The aggregation number, on the other hand, was found to be 53, which almost perfectly corresponds to half of the aggregation number of the diblock. This is rather intuitively reasonable as the triblock chain exhibits twice the volume compared to the diblock, leading to identical volumes of the micellar cores. In fact, the scattering curves in core contrast fall perfectly on top of each other as displayed in the inset plot in Fig. 2. Both the forward scattering as well as the minimum coincide very well, indicating the same micellar volume and core radius. A more quantitative rationalization is offered by a scaling model proposed in an earlier work on the micellization of block copolymers with different architectures (Iatrou *et al.*, 1996). According to this work, the aggregation number for micelles with comparable core and corona sizes should scale as

$$P \sim f^{-3} N_{PS}^2 N_{PB}^{-18/11}, \quad (2)$$

where f is the functionality taking the value $f = 1$ for diblocks and $f = 2$ for triblock copolymers. Nominally one expects $P^{\text{triblock}}/P^{\text{diblock}} = 1/2$. However, more thoroughly, by inserting the values from Table 2 we obtain $P^{\text{triblock}}/P^{\text{diblock}} \simeq 0.7$, which is slightly larger than what we found experimentally, $P^{\text{triblock}}/P^{\text{diblock}} \simeq 0.48$. In any case, from the

Table 2 Micellar characteristics of diblock (h-PS10-d-PB10) and triblock (d-PB10-h-PS20-d-PB10) copolymers in *n*-alkanes.

R_c and R_m are the core and the overall micellar radii, respectively. P is the aggregation number and Φ_0 is the volume fraction of solvent in the micellar core.

| Polymer, <i>n</i> -alkane | T (K) | R_c (Å) | R_m (Å) | P | Φ_0 |
|---------------------------|---------|-----------|-----------|-----|----------------|
| Diblock, C ₁₀ | 293 | 91 | 144 | 85 | 0.5 (1) ± 0.05 |
| Diblock, C ₁₀ | 303 | 80 | — | 53 | 0.6 (0) ± 0.05 |
| Diblock, C ₁₂ | 293 | 88 | 148 | 100 | 0.4 (0) ± 0.08 |
| Diblock, C ₁₄ | 293 | 90 | 154 | 106 | 0.4 (1) ± 0.04 |
| Diblock, C ₁₆ | 293 | 87 | 150 | 110 | 0.3 (9) ± 0.07 |
| Triblock, C ₁₆ | 293 | 89 | 142 | 53 | 0.3 (0) ± 0.07 |

structural characterizations we can conclude that the micelles formed by the triblock and the diblock are very similar. Very importantly, the micellar cores are essentially identical (see inset plot in Fig. 2), thus allowing a direct comparison without any size-dependent influence on the kinetics.

3.2. Chain exchange kinetics

From the theory of Halperin and Alexander, the relaxation kinetics are controlled by the expulsion rate constant, k , which is given by

$$k = \frac{1}{\tau_0} f(N_A, N_B) \exp(-E_a/k_b T), \quad (3)$$

with k_b the Boltzmann constant and T the absolute temperature. τ_0 is a characteristic diffusion time, $f(N_A, N_B)$ is a pre-factor that only depends on the number of repeat units of the insoluble, N_B , and the soluble, N_A , blocks. E_a is the activation energy given by

$$E_a = \gamma(N_B v_B)^{2/3}, \quad (4)$$

where v_B is the molecular volume of the monomer unit of the insoluble block. Again, since the insertion rate as well as the diffusion time is much faster than the expulsion rate, the relaxation function should simply be given by

$$R(t) = \exp(-kt). \quad (5)$$

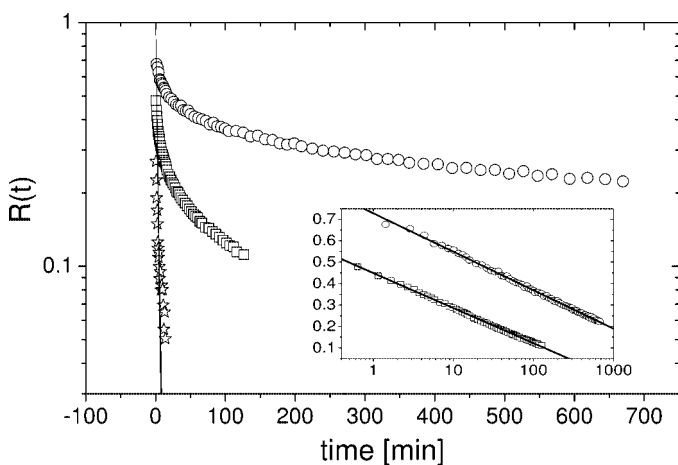


Figure 3 Chain exchange kinetics of the PS10-PB10 diblock micelles in hexadecane (C₁₆) at 293 K (spheres), 303 K (squares) and 313 K (stars). The data are displayed in a semi-logarithmic representation. The solid line displays a simultaneous fit according to Halperin and Alexander including the experimental polydispersity. Inset plot: the same data at 293 and 303 K on a logarithmic timescale. The lines represent the best least-squares linear fits.

In the following paragraph we will compare this prediction with experimental results to explore its validity.

Diblock copolymer micelles – effect of temperature. Fig. 3 shows the measured relaxation function, $R(t)$, for PS10-PB10 diblock copolymer micelles in hexadecane at different temperatures.

At the two lowest temperatures the data display a very broad heterogeneous decay that deviates strongly from a single exponential decay. As the relaxation rate given by Halperin and Alexander is very sensitive to the molecular weight of the core-forming polymer block, it is crucial to carefully take into account the polydispersity. Since the polymers are made with controlled anionic polymerization techniques, the resulting size distribution is very narrow and given by the Poisson distribution

$$P(N_{PS}) = \frac{(\langle N_{PS} \rangle - 1)^{N_{PS}-1} \exp[-(\langle N_{PS} \rangle - 1)]}{\Gamma(N_{PS})}, \quad (6)$$

where $\Gamma(x)$ is the Gamma function. The resulting relaxation can then be calculated using k from equations (3) and (4) and inserting the relevant systems parameters. $R(t)$ can then be estimated according to

$$R(t) = \int_1^{\infty} P(N_{PS}) \exp(-kt) dN_{PS}. \quad (7)$$

However, as seen in Fig. 3, such an approach does not describe the data at all except at the highest temperature, 313 K, which is reasonably well described by this approach. Since the interfacial tension between PS and hexadecane is very low ($\gamma \approx 2.1 \text{ mN m}^{-1}$),

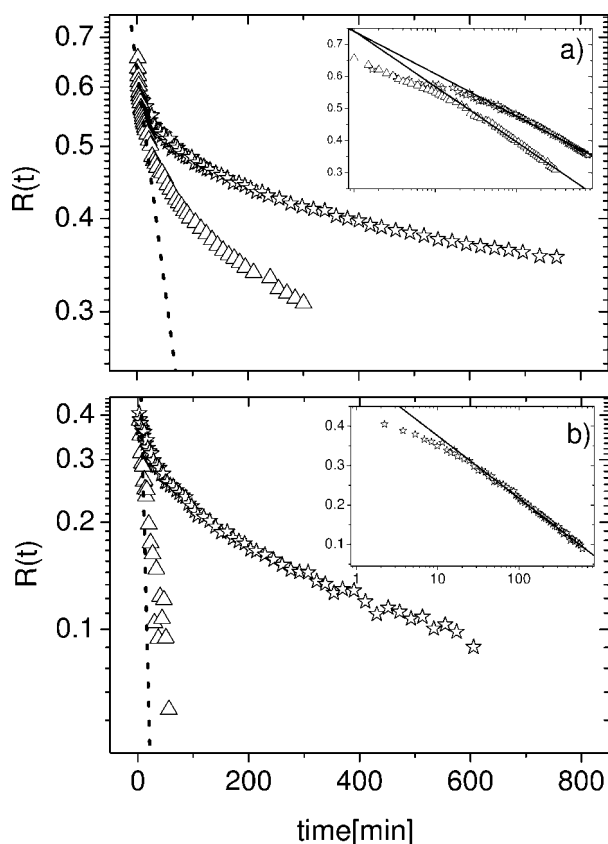


Figure 4 Semi-logarithmic representation of the relaxation curves of PS10-PB10 diblock (triangles) and PB10-PS20-PB10 triblock (stars) micelles in (a) tetradecane (C_{14}) and (b) dodecane (C_{12}) and at 293 K. The dotted lines represent fits using equations (3) and (4) taking into account the Poisson distribution for polydispersity. Inset plots: triblock data on a logarithmic timescale including a linear fit.

the fitted lines are very close to that of a single exponential. Instead, as seen in the inset plot, the relaxation curves at 293 and 303 K can be accurately described with a logarithmic law:

$$R(t) \approx -\ln t. \quad (8)$$

As previously discussed (Lund, Willner, Stellbrink *et al.*, 2006; Lund, Willner, Dormindontova & Richter, 2006a), this is likely to be an effect of the constrained chain dynamics within the micellar cores. The volume fraction of solvent in the core is small for PS10-PB10 in hexadecane at low temperatures, giving rise to strong interchain correlations. At higher temperatures, however, for example at 313 K, the core is strongly swollen leading to a reduction of these effects. This can be seen nicely in the data in Fig. 3: the relaxation curve approaches the predicted relaxation at higher temperatures. Thus, at this temperature the experimental data nicely compare with the activation energy and corresponding rate constant expected from the theory of Halperin and Alexander.

Hence, the results seem to demonstrate that when the micellar core is sufficiently swollen at higher temperatures correlations between chains gradually disappear, the expulsion process can be pictured as a simple single chain activated diffusion process and the theory of Halperin and Alexander is applicable.

Effect of chain architecture – triblock copolymer micelles. Fig. 4 shows the relaxation curves for the diblock and triblock micelles in both dodecane (C_{12}) and tetradecane (C_{14}).

The kinetics observed are generally much faster in the diblock micelles than in the corresponding micelles consisting of the triblock copolymers. This can be attributed to either (i) the increased activation energy because of the double length of the PS block in the triblock; and/or (ii) chain connectivity between the two PB blocks present in the triblock but not in the diblock. However, while the former effect certainly will be present, this will only lead to a shift in the timescale. This is indeed observed in Fig. 4(a), where we just see that the relaxation is faster in one case while the shape of the relaxation curve is similar and logarithmic, at least at long times. Now, considering point (ii), this will certainly lead to less trivial topological effects inherent for the triblock micelles. In order to liberate one chain from the micelle, either one PB chain has to pass through the PS-rich core leading to an extra energy penalty and thus a slowdown of the timescale and/or the test chain as well as the neighboring chains have to rearrange in such a way that the chain can pass out to the core-corona interface and later be expelled. The latter effect is more prominent for the micelles in dodecane in Fig. 4(b). Here the triblock copolymer exhibits a logarithmic relaxation indicating some cooperative behavior, while the diblock system exhibits a close to single exponential decay signifying single chain behavior. This clearly demonstrates the importance of topological interaction: while for the PS10-PB10 system the micellar core is sufficiently swollen such that the internal correlations have nearly vanished, there are still topological ‘knots’ present for the PB10-PS20-PB10 system. Thus, in conclusion it seems that the logarithmic relaxation is caused by cooperative effects (involving several chains).

4. Summary and outlook

In summary, we have presented novel experimental results using time-resolved small-angle neutron scattering that elucidate the role of architecture and topological interactions on the exchange kinetics of polymeric micelles. Two types of micellar systems have been studied and compared, one consisting of a PS10-PB10 diblock copolymer and another of triblock copolymer PB10-PS20-PB10 in different n -alkane solvents. As has been verified experimentally, both

micelles have nearly the same micellar characteristics since both the composition and corona-forming PB blocks have been made equal. This has the important implication that the micellar core characteristics are the same and the topological interactions can be studied. The results show that logarithmic relaxation is a prominent feature for micelles having dense cores and for the triblocks where topological knots may form between the polymer chains. Thus, the results highlight the important effect of topological constraints which lead to an increased degree of cooperativity of the chains within the micellar cores. This needs to be carefully taken into account in future theoretical and experimental works. In a forthcoming full paper the relaxation curves will be analyzed in more detail, presenting a more quantitative analysis.

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