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Equilibrium gels of trivalent DNA-nanostars: Effect of the ionic strength on the dynamics

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Abstract. Self-assembling DNA-nanostars are ideal candidates to explore equilibrium gelation in systems composed of limited-valence particles. We present here a light scattering study of the dynamics in a trivalent DNA-nanostars equilibrium gel and of its dependence on ionic strength and concentration. Reversible bonds between different nanostars, whose formation is sensitively dependent on temperature, concentration and ionic strength, are provided by complementary DNA sticky ends. We find that the decay of the density correlations is described by a two-step relaxation process characterised by: i) a slow time scale that varies over nearly four orders of magnitude in a temperature window of less than 30 degrees; ii) an increase of the amplitude (the so-called non-ergodicity factor) of the slow relaxation. The slow process follows an Arrhenius law with temperature. We observe that the activation enthalpy does not depend on the ionic strength and that the dependence of the relaxation time on the ionic strength can be rationalized in terms of the free-energy cost of forming a sticky-end duplex. Finally, we observe that dynamics is insensitive to nanostar concentration, in full agreement with the predicted behaviour in equilibrium gels.

1 Introduction

Colloidal systems are often investigated by soft matter scientists in order to enhance the comprehension of fundamental mechanisms in condensed matter (*e.g.* crystallization, phase transitions, gelation routes) [1–4]. Colloidal dispersions offer the unmatched opportunity of studying samples in which the inter-particle interactions can be tuned, *e.g.* by changing *p*H, composition, ionic strength of the solvent or by functionalizing the colloidal surface. They also offer access to the system collective behaviour in the thermodynamic limit (*i.e.* in bulk). The research on colloidal dispersions has been further fuelled by the development of novel techniques to synthesize particles which has led to the production of an astonishing variety of colloids, differing in size, shape and surface patterning [5–11]. In spite of these outstanding advances, the production of *bulk quantities* of identical particles with specific features and controllable interactions, which could be used to experimentally explore their collective behaviour, remains difficult. One ongoing and promising strategy to achieve bulk production is offered by the possibility of exploiting the programmability of DNA interactions. It is indeed possible to realize high yields of self-assembling nanoconstructs, entirely made of DNA, with highly customized properties. References [12–15] have shown the potential of man-designed DNA-based nanostuctures as a tool to explore open problems in statistical physics. The effectiveness of such approach, which follows the line set by structural DNA nanotechnology [16–22], has recently been proved in the experimental study of the thermodynamic behaviour of limited-valence particles [12]. In ref. [12], particles with controlled valence have been created by designing star-shaped DNA constructs with a fixed number of arms, each one ending with a sticky overhang sequence designed on purpose to provide controllable and reversible mutual interactions. Solutions of such limited-valence DNA-nanostars (NS) have been shown to exhibit a valence-dependent gas-liquid-like phase separation, in agreement with theoretical and numerical investigations [4,23–25].

Besides offering the possibility of realizing bulk quantities of monodisperse particles with the desired valence, the DNA-NS system offers also the possibility to modulate the strength of the sticky overhang interaction by tuning solvent properties, *e.g.* the salt concentration. The possibility of regulating the particle valence, associated to the possibility of finely tuning NS-NS interactions in a reversible and controlled fashion, opens the way to the experimental investigation of equilibrium gelation, the reversible slowing down of the dynamics that is predicted to take place in low-valence systems. Through this article the words "equilibrium gel" are used to define an arrested state of matter in which the progressive slowing down of

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the dynamics is controlled by the continuous formation of a network of bonded (trivalent) particles. Differently from glasses, where excluded-volume interactions are crucial, the onset of a non-ergodic behaviour in equilibrium gels is driven by the increase of the inter particle bond lifetime on cooling. According to numerical predictions [4,23], equilibrium gelation can be achieved only if, at sufficiently low temperatures, colloidal systems are able to form stable networks of bonded particles through a reversible sequence of equilibrium states, without the interference of phase separation. Such condition can be efficiently realized when, as in the case of limited-valence colloids, it becomes possible to confine the phase separation process to a restricted window of densities and temperatures [24].

The dynamics of equilibrium gels in a system of tetravalent DNA-NS has been recently investigated by means of static and dynamic light scattering (DLS) measurements [26]. The DLS correlation functions reported in ref. [26] show a clear two-step relaxation process, with a fast diffusive decay process (essentially temperature independent) and a slow wave vector-independent relaxation process varying over more than four orders of magnitude in temperature on cooling. These results indicate that DNA-NS form reversible equilibrium gels. Differently from limited-valence laponite gels [27], in the DNA-NS case, the valence is controlled by design (the number of NS arms) and the inter-particle interaction is fully reversible. In this article, we perform DLS experiments to show that equilibrium gelation is also clearly observed in trivalent particles (trimers). For all investigated samples, we monitor the continuous transition from an ergodic state of non-interacting NS in solution at high temperatures to the dynamically arrested state (equilibrium gel) at lower temperatures. While ref. [26] focused on the wave vector dependence of tetravalent DNA-NS, here we focus on the dependence of the dynamics in trivalent DNA-NS on the ionic strength with the specific aim of controlling, at fixed temperature T, the decay of the density correlations. Indeed, it is well known that the ionic strength directly affects the binding-unbinding equilibrium of the DNA strands, by modifying their bonding free energy [28–30]. Our measurements provide the possibility to discuss the scenario proposed in previous works [12,26], *i.e.* that the time scale of the decay of density fluctuations is controlled by the thermodynamics of bond formation. In this frame, ionic strength provides a handle to modulate the bond lifetime, a crucial concept in connecting chemical and physical gels [31–34].

2 Methods

Trivalent DNA-NS (fig. 1) result from the programmed self-assembly of three complementary 49-base oligomers:

5'-CTACTATGGCGGTGATAAAAACGGGAAGAG CATGCCCATCCACGATCG-3'

5'-GGATGGGCATGCTCTTCCCGAACTCAACTG CCTGGTGATACGACGATCG-3'

5'-CGTATCACCAGGCAGTTGAGAATTTATCAC CCGCCATAGTAGACGATCG-3'

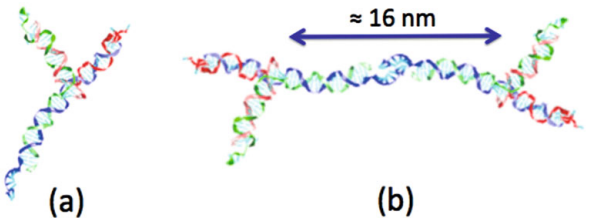

Fig. 1. (a) Pictorial view of a single trivalent DNA-NS. Different colours indicate the different strands forming the nanostar structure. (b) Pictorial view of two bonded DNA-NS. The attractive inter-nanostar interaction is provided by the hybridisation of 6-base-long overhangs on the arm tips, the so-called sticky ends (courtesy of L. Rovigatti).

properly designed to hybridise into star-shaped three-armed particles at a specific temperature of self-assembly $T_{\rm sa}$, with $60\,^{\circ}\mathrm{C} < T_{\rm sa} < 70\,^{\circ}\mathrm{C}$ depending on the salt concentrations here explored. Each strand is designed to specifically bind to two other strands with two 20 bases long segments, leading to the formation of the double helical arms of the structure. Two A bases without complementarity are placed between the arm-forming segments to release angular constraints between the arms arising from the crowding of paired strands at the center of the constructs, thus creating a branch point. With such choice, arms are allowed some flexibility in their mutual angles.

To provide interparticle bondings, each arm of the NS terminates with the same 6-base-long self-complementary single-strand sequence (CGATCG) which allows bond to form with the tips of the neighboring NS via Watson-Crick base pairing. The valence of the NS is thus dictated by the number of arms and equal to three in the present case. An A base with no complementary partner is added before the six bases overhangs. In this way each overhang is allowed to rotate. This minimizes the constraints on the mutual orientation of two bound constructs, since each can freely rotate around the axis connecting the centers of the two structures. Below a specific, salt-dependent, T value (lower than 45 °C for all the salt concentrations here investigated) overhangs on different NS become sticky, providing reversible interparticle bonds. At low enough T, a spanning network of fully bonded NS forms.

DNA is purchased from IDT (Integrated DNA Technologies) with PAGE purification. In previous work [12] we presented results of agarose gel-electrophoresis measurements on tetravalent and trivalent DNA NS (prepared by using the same protocol as in the present study), that showed that $\sim 93\%$ of the total DNA is in properly formed structures. As gel-electrophoresis separates DNA aggregates by size, this provided us with a quantitative indication of the fraction of ill-formed structures in the samples. For the present study, two different batches of NS samples were prepared at two fixed total DNA concentrations, *i.e.* $c_1 \approx 9.0\,\mathrm{mg/ml}$ and $c_2 \approx 12.0\,\mathrm{mg/ml}$, in the region where separation in a nanostar-rich and in a nanostar-poor phase is not present [12].

To investigate the effect of the salt concentration on the dynamics, samples are dissolved using NaCl solutions

with increasing ionic strength (respectively 50, 100, 150 and 250 mM NaCl for each DNA concentration). All the NS solutions are heated to 90 °C for 20 minutes (thermal annealing) and subsequently slowly cooled down to room temperature to allow for NS formation. All samples are then centrifuged (4000 rpm) for 24 h at 42 °C to sediment possible micro-sized impurities (possibly residuals of sample preparation, oligo synthesis or PAGE purification) which can interfere with the light scattering measurements.

Dynamic light scattering measurements provide a powerful technique to explore the dynamics of disordered systems, including gels [35–37]. The present measurements are performed with a custom light scattering setup designed to handle microliter-sized samples and a 633 nm (Newport) He-Ne laser source (17 mW) at a fixed scattering angle $\theta = 90°$. A Brookhaven correlator provides the autocorrelation of the scattered light intensity that, via the Siegert relation, is transformed in the autocorrelation function of the scattered field $g_1(t)$. For each sample, we start measuring at 45 °C (after thermalizing the solution for 1.5 h). We then progressively lower the temperature in steps of few degrees, always allowing an equilibration time of 1.5 h before measuring. For each T, we perform measurements lasting 30 minutes. We cover in this way the interval of T from the temperature at which DNA-NS are formed but weekly interacting down to the T at which the decay of the correlation functions becomes longer than the experimental time scale accessible via DLS (of the order of a few seconds). In the present article we address the onset of gelation, *i.e.* how the system approaches the gel state. All investigated state points refer to ergodic states that show no aging at all. This is equivalent to investigate a supercooled liquid approaching the glass transition.

3 Results and discussion

We start by documenting in fig. 2 the effect of the salt on the system dynamics by comparing the intermediate scattering functions $g_1(t)$ at $T = 20$ °C, for three different ionic strengths (at $c_1 = 9$ mg/ml). All curves show a two-step relaxation decay, with a plateau height f and an average relaxation time strongly depending on salt concentration. To provide a precise characterization of the dependence of the dynamics on T, ionic strength and NS concentration, we show in fig. 3 an exemplifying family of collective intermediate scattering functions measured at various T for the samples at $c_1 = 9$ mg/ml and $c_2 = 12$ mg/ml (both at 150 mM NaCl). Overall, samples at different concentrations show a similar behaviour, *e.g.* a two-step relaxation, with a significant progressive slowing down of the dynamics over nearly four orders of magnitude and a simultaneous increase of the plateau height, similarly to what has been previously observed in gels of valence-four nanostars [26]. We remark that all the investigated samples remain visibly clear over the whole temperature window here explored, showing no sign of opaqueness on cooling, consistent with the equilibrium gel hypothesis [4].

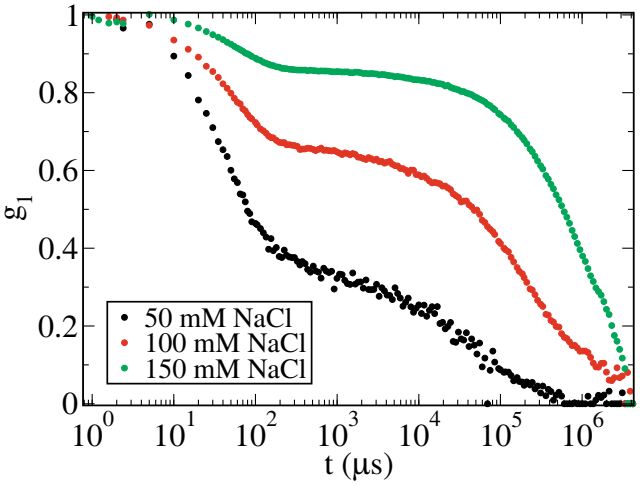

Fig. 2. Intermediate scattering functions measured at $T = 20$ °C for samples at $c_1 = 9$ mg/ml and at different salt concentrations, *i.e.* 50 mM NaCl (black dots), 100 mM NaCl (red dots), 150 mM NaCl (green dots).

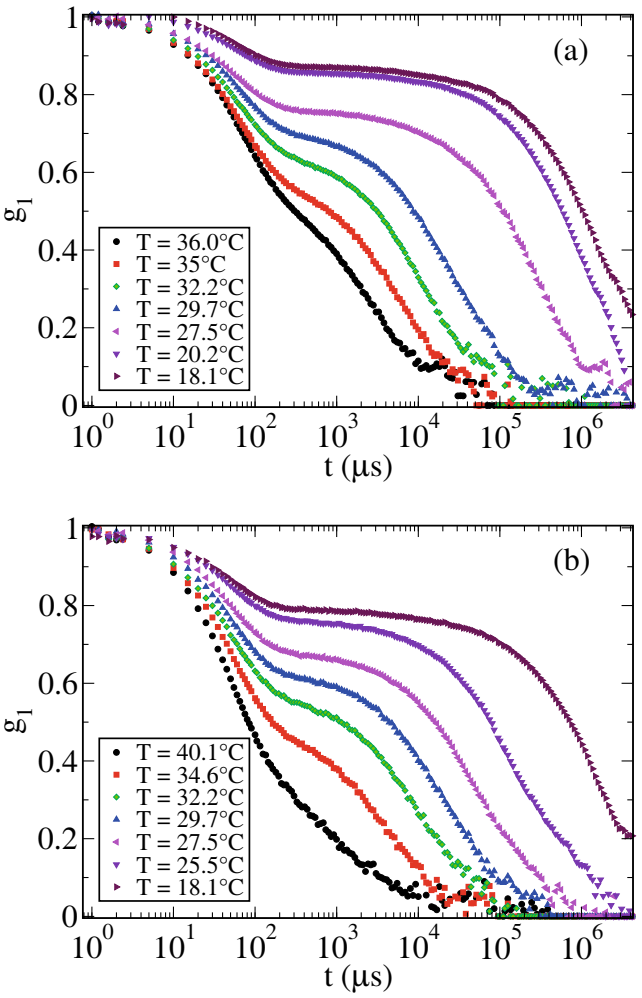

Fig. 3. Intermediate scattering functions measured at various temperatures for samples at $c_1 = 9$ mg/ml (a) and $c_2 = 12$ mg/ml (b), both at 150 mM NaCl.

The presence of a two-step relaxation is characteristic of all systems experiencing slow dynamics. Differently from dynamic arrest driven by packing (glasses), during the formation of an equilibrium gel, the plateau of the correlation function is initially small and increases progressively with the slowing down of the dynamics. This progressive increase of the plateau height f, commonly named in glass physics non-ergodicity factor [38], reflects the progressive formation of a percolating network in the system. As we will discuss in the following, the slowing down mechanisms in glasses and in gels can be discriminated by the different behaviour of the decay of density fluctuations, in particular in the different dependence on cooling of the amplitude of the slow-relaxation mode. Indeed, theoretical and numerical studies [39,32–34,40] of the self-dynamics in chemical gels (infinite bond lifetime) suggest that f is linked to the fraction of particles frozen in the infinite spanning clusters. We note here that a progressive increase in the non-ergodicity factor has been reported in an experimental study of oil in water micro emulsion droplets connected by telechelic polymers [41]. In ref. [41], on varying the polymer concentration the system undergoes a gelation process which appears in g_1 via a progressive increase of the plateau. Differently from the present case, the characteristic decay time does not vary with the polymer concentration and it is thus uncoupled from f.

A convenient quantification of the two-step relaxation can be provided by a non-linear fit of $g_1(t)$ to the function

$$g_1(t) = (1-f)e^{-(t/\tau_f)^{\beta_f}} + fe^{-(t/\tau_s)^{\beta_s}}$$

e.g. to the sum of two stretched exponentials. The parameter $f, \tau_f, \tau_s, \beta_f$ and β_s provide a complete characterization of the dynamic behaviour of the system. The parameter f provides a measure of the amount of correlation that remains in the sample after the fast relaxation process is completed. This amount of correlation relaxes only on the time scale of the slow-relaxation process. The times τ_f and τ_s quantify the time scale of the fast and slow processes and the exponents β_f and β_s their stretching amplitude. The T dependence of the stretching exponent β_s is shown in fig. 4. Despite the significant fluctuations, for both DNA concentrations, the stretching exponent does not show a significant variation with decreasing T, nor with the ionic strength. β_f is always very close to one and it is not discussed further. To incorporate the effect of β_s in the evaluation of the typical times of the system we calculate the so-called average characteristic time, defined as

$$\bar{\tau}_s = \frac{\int_0^\infty t e^{-(\frac{t}{\tau_s})^{\beta_s}} \mathrm{d}t}{\int_0^\infty e^{-(\frac{t}{\tau_s})^{\beta_s}} \mathrm{d}t} = \frac{\tau_s}{\beta_s} \Gamma\left[\frac{1}{\beta_s}\right], \qquad (1)$$

where Γ is the gamma function.

Figure 5 shows the measured $\bar{\tau}_f$ and $\bar{\tau}_s$ decay times for all investigated samples (different salt and different DNA-NS concentration), as a function of the inverse temperature. The fast-relaxation times $\bar{\tau}_f$ are independent of salt concentration as well as of nanostar concentration and T. The T independence of τ_f and its value (approximatively 50 μs) is fully consistent with the trend measured in the case of DNA tetramers [26], suggesting that density (collective) fluctuations associated to the fast process, over the length scale probed by light are independent of the process of gel formation. The slow-relaxation time $\bar{\tau}_s$ slows down by nearly four orders of magnitude as T is lowered, exhibiting an evident Arrhenius behaviour. Addition of salt (at constant T) produces an increase in the relaxation time. Remarkably, the slope of $\ln(\tau_s)$ *vs.* T^{-1} is similar for all the salt concentrations here explored. The effect of salt on the thermodynamic of strand hybridisation has been deeply investigated in the past and it is now routinely implemented in all theoretical modeling of double strand hybridisation. In the SantaLucia approach [42,43], the free-energy change on going from the open (single strand) to the bonded (double strand) state is evaluated as a sum of enthalpy ΔH_{SL} and entropy ΔS_{SL} contributions depending on the base sequence. ΔH_{SL} is independent of T and salt concentration, while ΔS_{SL} is affected by the ionic strength. In the present system, the bonding sequence is GCATGC, resulting in $\Delta H_{\mathrm{SL}} = -44.6\,\mathrm{kcal/mol}$ and $\Delta S_{\mathrm{SL}} = (-125.3 + R\ln c + 0.368\times 6\times \ln[\mathrm{Na}^+])\,\mathrm{cal/(mol\,K)}$

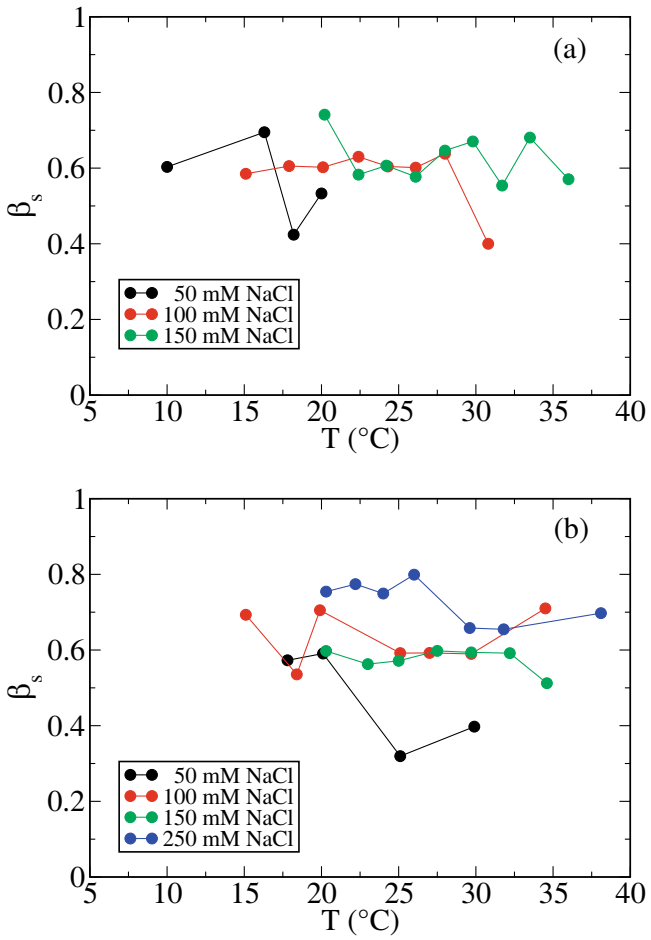

Fig. 4. Temperature dependence of the stretching exponent for the slow process for samples at $c_1 = 9\,\mathrm{mg/ml}$ (a) and $c_2 = 12\,\mathrm{mg/ml}$ (b) at different salt concentrations, *i.e.* 50 mM NaCl (black dots), 100 mM NaCl (red dots), 150 mM NaCl (green dots), 250 mM NaCl (blue dots).

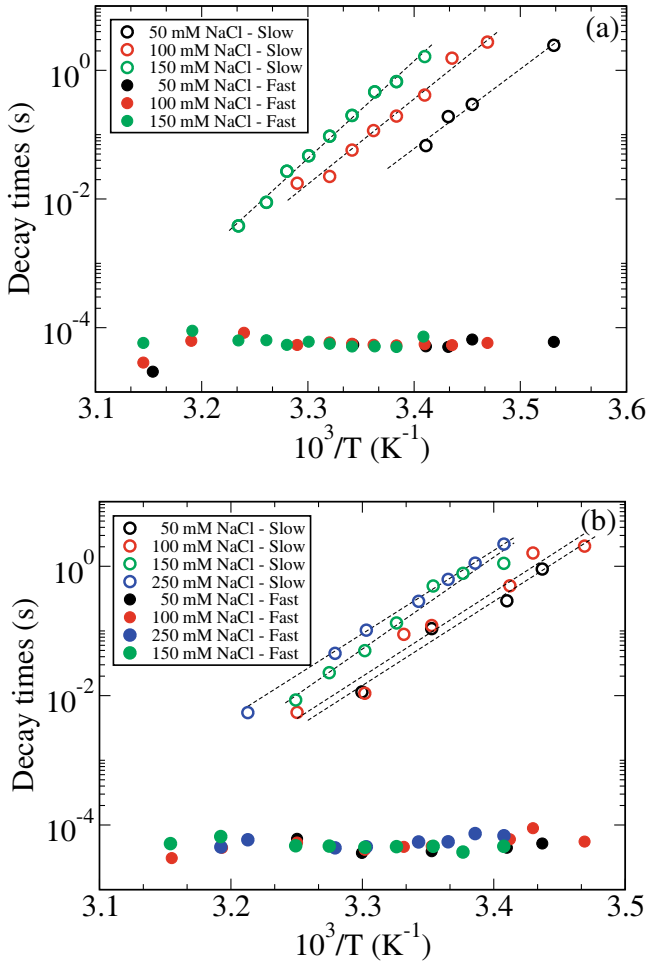

Fig. 5. Temperature dependence of the decay times of the fast (full dots) and slow process (empty dots) for samples at $c_1 = 9\,\mathrm{mg/ml}$ (a) and $c_2 = 12\,\mathrm{mg/ml}$ (b) at different salt concentrations, *i.e.* 50 mM NaCl (black), 100 mM NaCl (red), 150 mM NaCl (green), 250 mM NaCl (blue). The dashed lines indicate the best fitting curves, corresponding to values (from top to bottom) of 1.5, 1.4 and 1.3 ΔH_{SL} (a) and 1.4, 1.5, 1.3 and 1.3 ΔH_{SL} (b).

(where R is the gas constant 1.9872 cal/(mol K) and c and $[\mathrm{Na}^+]$ are, respectively, the total strand concentration and the sodium concentration, both in M units).

In principle, one could also consider the presence of the flexible A base that precede the six basis overhang. In an isolated strand, the presence of a non-paired base modifies the hybridisation free energy significantly [43]. Similarly, it has been recently [44] demonstrated that non-hybridised DNA tails longer than one base can substantially destabilise the DNA duplex. Considering that the flexible A base is not an ending base but is the bridge between the sticky end sequence and the double strand arm, the SantaLucia values for the CGATCG are to be considered indicative.

Figure 5 suggests that the slow-relaxation time follows an Arrhenius T dependence:

$$\tau_s = \tau_0 e^{\Delta G_\tau / RT}, \qquad (2)$$

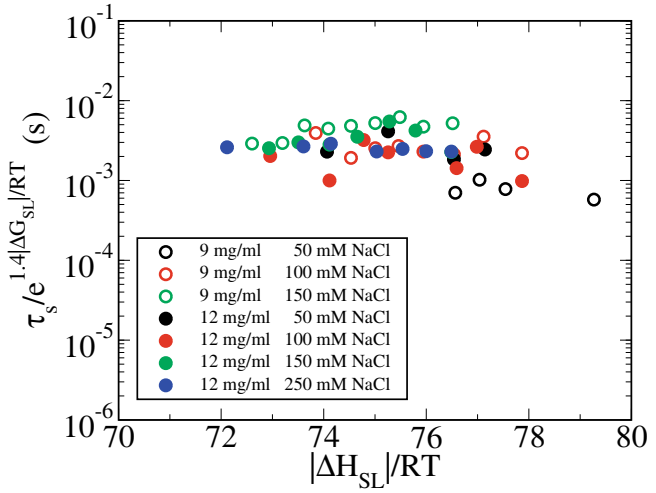

Fig. 6. $\tau_s / e^{1.4|\Delta G_{\mathrm{SL}}|/RT}$ *vs.* $|\Delta H_{\mathrm{SL}}|/RT$ for samples at $c_1 = 9\,\mathrm{mg/ml}$ (empty dots) and $c_2 = 12\,\mathrm{mg/ml}$ (full dots) at different salt concentrations, *i.e.* 50 mM NaCl (black), 100 mM NaCl (red), 150 mM NaCl (green), 250 mM NaCl (blue).

where R is the ideal-gas constant and τ_0 is (the inverse of) the attempt rate to cross the ΔG_τ free energy barrier associated to the slow-relaxation process. Such a functional form has been previously proposed for the case of tetravalent nanostars [26]. As shown in fig. 5, eq. (2) properly describes the experimental data at all salt concentration and densities. A fit of $\ln \tau_s$ *vs.* T^{-1} shows that, in all cases, $\Delta H_\tau \approx 58 \pm 6\,\mathrm{kcal/mol}$, *i.e.* $\Delta H_\tau \approx (1.4 \pm 0.1)|\Delta H_{\mathrm{SL}}|$. The similar value of the slope of $\ln \tau_s$ *vs.* T^{-1} for all samples suggests that ΔH_τ is salt and density independent, in agreement with the SantaLucia modeling of the bonding enthalpy. This further suggests that the decay of the density fluctuations are controlled by the energy scale of the hybridisation process. This suggests that the slow-relaxation time is a function of the variable $|\Delta G_{\mathrm{SL}}|/RT$. According to this assumption, it should be possible to collapse data for different salt concentrations by scaling the measured relaxation time by $e^{1.4|\Delta G_{\mathrm{SL}}|/RT}$. If this is the case, it means that the thermodynamics of bond formation provides the proper estimate of the free-energy barrier controlling the slow dynamics relaxation process. The result of this analysis are reported in fig. 6. We find that within one order of magnitude, data for all salts, temperatures and concentrations follow the relation

$$\tau_s = 3e^{1.4|\Delta G_{\mathrm{SL}}|/RT}\ [\mathrm{ms}].$$

The collapse of the data in fig. 6 supports the possibility that the thermodynamic of sticky-ends hybridisation is indeed the process controlling the time scale of the density relaxation. Given the uncertainty associated to the bonding free energy discussed above, it is impossible to discriminate if the 1.4 factor arises from some kind of cooperativity in bond breaking/reforming or if ΔG_τ coincides with the free energy of one single binding process. Finally, we note that a recent study of the self-dynamics in networks of patchy particles with valence four suggests that the activation energy varies from 2 to 0.5 times the

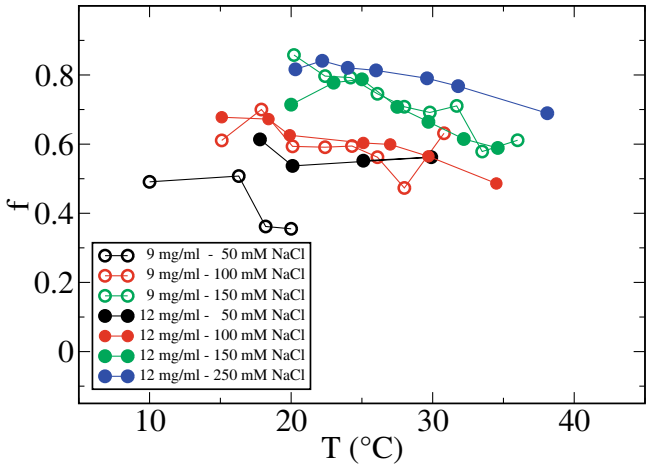

Fig. 7. Temperature dependence of the experimental non-ergodicity factor for samples at $c_1 = 9\,\mathrm{mg/ml}$ (empty dots) and $c_2 = 12\,\mathrm{mg/ml}$ (full dots) at different salt concentrations, *i.e.* 50 mM NaCl (black), 100 mM NaCl (red), 150 mM NaCl (green), 250 mM NaCl (blue).

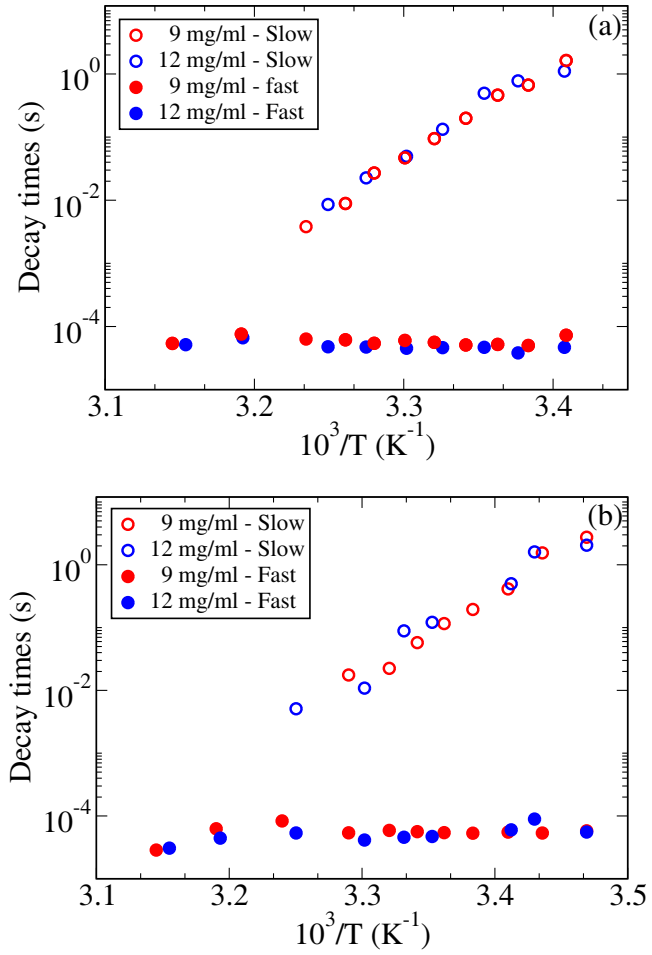

Fig. 8. Temperature dependence of the decay times of the fast (full dots) and slow process (empty dots) for samples at $c_1 = 9\,\mathrm{mg/ml}$ (red) and $c_2 = 12\,\mathrm{mg/ml}$ (blue) at different two diffent salt concentrations, *i.e.* 150 mM NaCl (a), 100 mM NaCl (b).

bond energy on increasing bond flexibility [45], a range of values that includes the 1.4 value here estimated.

Figure 7 shows f as a function of T. Despite the significant uncertainties in the low salt samples, the plateau shows a trend (anticipated in fig. 3): f increases on decreasing T. Differently from supercooled liquids, where the plateau value is T-independent, down to the so-called mode-coupling temperature [46], here we clearly observe a progressive increase of the plateau value on cooling. Such a trend, consistent with what previously found for the related tetravalent DNA gel, has been interpreted as resulting from the progressive onset of the percolating gel clusters that, starting from the percolation transition, incorporates progressively more and more particles. While a theoretical description of the decay of the (collective) density fluctuations in these low-valence network gels is presently missing, one can speculate that the low T value of $1 - f$ (*e.g.* at T where all possible bonds are formed) provides a measure of the decorrelation generated by the breathing modes of the network on the length scale probed by light, in analogy to what has been discussed in the frame of polymeric chemical gels [35].

Comparison between different densities suggests that, within the error, the plateau height is density independent. The density independence of the non-ergodicity factor, associated to the density independence of the relaxation times, suggests that correlation functions g_1 are globally independent of density. This provides further support to the fact that DNA gels provide experimental realizations of equilibrium low-valence gels. Indeed, one of the predictions based on the theoretical and numerical studies of equilibrium gels [4] refers to the slaving of the dynamics to T. Differently from the slowing down associated to the glass transition, the slowing down that accompanies the formation of an equilibrium gel is controlled by the establishment of a network of long-living bonds that inhibit restructuring at the particle level. The time scale of the decay of concentration fluctuations becomes thus slaved to the lifetime of the inter-particle bond. Under these conditions, T as opposed to concentration, becomes the dominant external variable controlling the dynamics. According to the theoretical and numerical studies [4] this results in isochrones (lines of equal relaxation time) that run mostly parallel to the c axis in the equilibrium gel region of the T-c phase diagram.

Figure 8 shows that this is the case for two different salt concentrations. Both the fast and the slow times superimpose, consistent with the hypothesis that T (and not density) is the relevant variable controlling the slow-relaxation process. A similar density independence was also observed in the case of tetravalent nanostars [26].

4 Conclusions

In this article we have investigated the slow dynamics of an equilibrium gel of trivalent DNA-NS and the effect of the ionic strength. To this aim, single-stranded DNA

sequences have been designed to self-assemble into star-shaped particles. Each particle has three double-stranded arms, terminating with six base "palindromic" overhang sequences, acting as sticky terminals. Upon lowering T reversibly bonds form between nearby DNA-NS, giving rise to an infinite spanning network, *e.g.* a thermoreversible equilibrium gel. Interestingly, we find that, in all samples, the free-energy barrier ΔG_τ determining the Arrhenius slowing down of the dynamics is proportional to the hybridisation free energy. The same salt dependence that controls ΔG_τ enters in the thermodynamic description of the paring of the sticky ends, thus suggesting that the density relaxation is slaved to the thermodynamics of bonding. Gels of DNA-NS, both with valence three as in the present study, and with valence four as studied in ref. [26], show a clear independence from the dynamics on NS concentration, as predicted by theoretical and numerical studied for equilibrium gels. Such independence arises from the role played by bonding in controlling the slowing down of the dynamics (different from the role played by packing in the case of the glass transition). Particles are confined in "energetic cages" by the bonds, for times that progressively increase on cooling, enslaved by the growth of the bond lifetime. The presence of a fully bonded network, in which restructuring requires breaking of the individual bonds, is at the origin of the observed Arrhenius behaviour, with an activation enthalpy of the order of the hybridisation enthalpy of the six-bases overhangs. We find that the ionic strength effect on the dynamics can be explained again only in terms of modulation of ΔG_τ. All slow-relaxation times can indeed be made collapse on a master curve assuming that the salt-dependent entropic contribution to bond stability (as modeled by SantaLucia) enters in the barrier controlling the slow dynamics relaxation. Finally, we hope our study will stimulate theoretical investigations of the collective dynamics at low wave vectors in low-valence equilibrium gels.

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