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Self-organisation of planar and tripod-shaped DNA stars confined to the water–air interface

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ABSTRACT

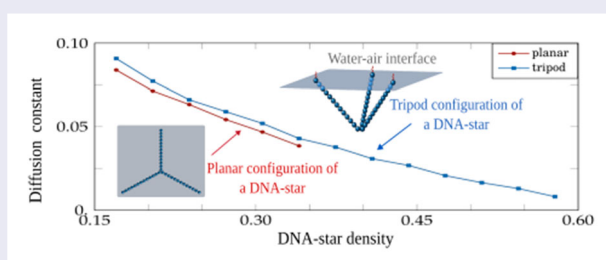
Using molecular dynamic simulations of coarse-grained models, we study the self-organisation of star-shaped all-DNA constructs, composed of suitably intertwined single-stranded DNA chains, confined to water–air interface. Two configurations of DNA stars are considered: planar and tripod with respect to whether the entire star is fixed to an interface or only its terminating nucleotides, while the rest is allowed to dive into a water where high concentration of monovalent salt is dissolved. Calculated structural properties of the solutions they form as well as their dynamical features, investigated in a range from low- to intermediate densities, reveal that both systems stay in liquid state maintaining remarkably similar properties despite striking differences in the conformation of the composing molecules.

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DNA-stars; self-assembly at an interface; diffusion



1. Introduction

The bottom-up approach for surface nano-patterning relies on the self-assembly of two-dimensional confined building blocks. Among the available building materials in this emerging field, DNA holds great promise for the realisation of nano-structured surfaces with arbitrary complexity and spatial addressability at the subnanometer level [1–8], which are of relevance in molecular [9–11] and cellular biophysics [12–14] and materials science [15–17]. Various strategies have been employed for long-range patterning of self-assembled all-DNA nanostructures (DNA tiles and DNA origami structures) on solid substrates [18]. The interfacing of DNA structures with hard surfaces has been achieved in numerous ways, including surfaces that actively influence DNA assembly (such as mica) [19] and selective adsorption on lithographically patterned surfaces [20], which is a characteristic example of a synergy between bottom-up and

top-down fabrication approaches and DNA confinement onto fluid-like two-dimensional (2D) surfaces such as lipid bilayers [21]. The latter type of DNA adsorption can be achieved either by electrostatic binding on an oppositely charged cationic lipid bilayer [22,23] or by a combination of a hydrophobic-mediated DNA anchoring and electrostatic DNA binding to these membranes [24]. The main advantage of this 2D DNA confinement approach over the above-mentioned strategies is that these fluidic 2D surfaces can effectively interface DNA with spherical and planar solid substrates, allowing DNA nanostructures to diffuse freely in-plane. The critical role of the surface-mediated diffusion in the long-range organisation of DNA nano-structures with controlled lateral interactions has been demonstrated, revealing that DNA origami structures [22,23] and star-shaped crossover DNA tiles [24] can self-assemble into a rich assortment of micrometer-sized surface packing morphologies.

From the experimental point of view, the most common tool to access the static structure of these all-DNA 2D assemblies is atomic force microscopy (AFM). A far more difficult task is to probe dynamic processes involved in the formation of these assemblies. High-speed AFM imaging [23] and noninvasive super-resolution microscopy [25] experiments seem to be a promising tool for the direct visualisation of the self-assembly process, however, access to local and fast processes such as the mean squared displacement of the centre of the mass of the adsorbed DNA nanostructures is a major experimental challenge. Molecular dynamics (MD) simulations could be a complementary tool offering structural and dynamical information in an unprecedented level of detail.

Here, we investigate the properties of concentrated adsorbates of a structurally simple yet rich all-DNA construct, the so-called Y-shaped all-DNA [26], i.e. a DNA-based three-arm star. To this end, we employ computer simulation in order to gain a detailed information about DNA-star assemblies confined to an interface. This DNA entity is a three-armed star, consisting of double-stranded helices, 13 base-pairs long, as shown in Figure 1(a), formed in synthesis via hybridisation of three single-stranded DNA chains. Each of these DNAs has partially complementary sequences to the other two DNA chains, leading thus to the formation of base-pairs along the arms. The Y-shaped DNA nanostructure has been used as a building block for the controlled assembly of novel all-DNA dendritic structures [27]. These

novel macromolecules have been modelled in computer simulations [28] *via* a simple bead-spring model, proposed in the context of polyelectrolyte brushes [29,30]. In this contribution, we rely on the proposed model, which was also tested experimentally (see Ref. [28]) for Y-shaped DNA star as well as for higher generations of all-DNA dendrimers with rigid or flexible connecting bonds between the successive generations [31]. Hence, we investigate the self-assembly of all-DNA stars using the tested model, where the each base-pair is represented by a single monomer bead (see Figure 1(b)), which interacts with neighbouring ones via the interactions that recover structural properties of double-stranded DNAs (see also Appendix).

Considering a 2D ensemble of these DNA-stars confined to a water-air interface, we study two different scenarios: one where we have assumed that *all* base-pairs are fixed to an air-water interface, termed the ‘planar configuration’ and shown in Figure 1(b), and the other where the only terminating beads of each arm are fixed to this interface, allowing thus the central monomer of the star to ‘dive’ into the water, termed the ‘tripod configuration’ and shown in Figure 1(c). Particular static and dynamic properties that we have calculated from our simulations, enable us to spot out the characteristic differences between the two scenarios.

Experiments confirmed the importance of a role of DNA stars in the formation of gels [32], liquid crystals [33], cluster crystals [34] in bulk solution. Particularly the bulk solution of 3-arms DNA stars with sticky ends

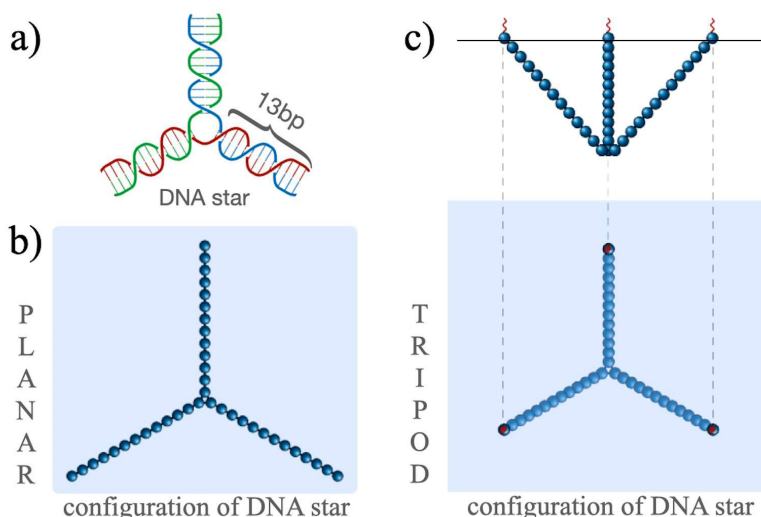


Figure 1. Schematic sketches of: (a) a three-arm DNA star composed of double-stranded helices 13 base-pairs long; and the two configurations it can take when confined to an interface (b) the planar configuration and (c) the tripod configuration with the tip immersed into the fluid. Monomer beads stand for base pairs along DNA strands (not drawn to scale) whereas the blue plane represents the interface to which the macromolecules are confined. In the tripod configuration the ends of the arms of the DNA star are attached to the interface *via* amphiphilic units, depicted by the red appendices, while in the planar configuration the entire DNA star is fixed to the interface *via* amphiphilic units (not shown).

is studied in simulations [35] and in experiment [32] and it is shown that system stays in a disordered state for a wide range of DNA star concentration and temperatures. Concerning all-DNA organisation in two-dimensional confinement, the self-organisation of DNA motifs has also been investigated experimentally [36] showing how DNA tiles can be used for constructing 2D lattices with programmable features of nanometer precision. Nevertheless, the experimental verification of results for the system at hand is still lacking.

In this paper we provide a general description of the model accompanied with details of the set up for the molecular dynamics simulation we use to study two systems of DNA stars confined at the interface, given in Appendix. Section 2 is dedicated to a detailed presentation of the static and of the dynamic properties of the DNA stars in planar and in the tripod configurations respectively. The obtained results for the two aforementioned scenarios are then directly compared with one another. The work is supplemented with results for the effective interactions of the DNA-stars in the planar configuration, given in Section 3, where we discuss how it compares with the data provided in the literature on a closely related model.

2. DNA stars in planar and tripod configurations

As specified in the Introduction, we study self-assembly of DNA stars at water–air interface, focusing on two types of DNA star solutions: one composed of all-DNA stars in planar configuration, Figure 1(b), and the other consisting of all-DNA stars in tripod configuration, Figure 1(c). In experiments, the flat configuration is achieved *via* amphiphilic units [37,38] that decorate DNA chains, so that the whole star is fixed to the surface. For the tripod configuration, amphiphilic units are attached only at the end of the arms, fixing the terminating beads to the interface, Figure 1(c), while the remaining parts of the star are able to dive into the water solution with dissolved monovalent salt. In our model, these amphiphilic units are not considered explicitly. Instead, we fix the star to the interface simply by setting the vertical coordinate of all beads to zero in the case of flat DNA stars while in the case of tripod system only the end monomers are confined to $z = 0$ plane, matching the vertical position of the interface and allowing other monomers to dive into the solvent. The interface itself is not simulated explicitly but is provided by the introduced confinement. DNA stars in both configurations are allowed to move freely in the lateral direction. We employ the same coarse-grained bead-spring model for the DNA stars in both configurations, as stated in Introduction, modelling each base-pair as spherical unit, resulting in a sequence of 13 monomers

per arm of the star whose length amounts to $\simeq 44$ Å. Each monomer interacts with the neighbouring beads with different types of interactions that mimic structural properties of DNA double strand. Salt ions are treated implicitly via a Debye screening parameter. The numerical values of parameters for each potential employed are given in Appendix (for more details see also [28,30]). In our system, DNA helices have blunt ends in contrast to that of Ref. [28], where the arms are terminated with the short sequence of the single-stranded DNA chains that were used as linkers between stars for building higher generation of dendrimers.

The density of 2D solutions of DNA stars is characterised by the (planar) packing fraction,

$$\eta_s = 2\pi R_g^2 \rho_d \quad \text{with } \rho_d = \frac{N_d}{A}. \quad (1)$$

Here, R_g is the radius of gyration of the DNA star. For the flat configuration, it takes the value $R_g = 25.5$ Å. The same value is used for the densities of the tripod system for the reason of an unambiguous comparison of corresponding quantities that follow. Moreover, the stars in the tripod configuration take the planar shape at low star densities. In the above relation, ρ_d is the number density, N_d is the number of stars in a given area A . As discussed in the subsequent subsections, we considered η_s -values up to 0.57. For simplicity, we assume that the permittivity in both media is the same as the stars remain, due to their hydrophilicity, slightly below the interface, in water with dissolved salt of concentration $c = 100$ mM, which represents a typical experimental salinity.

In order to investigate the properties of our systems we have performed standard molecular dynamics simulations in the canonical ensemble, using a Langevin thermostat, fixing the temperature to room conditions, $T = 298$ K and applying the periodic boundary conditions in x and y directions only. We have used the software package ESPResSo [39]. Throughout, ensembles of 400 DNA stars have been considered, corresponding to $400 \times 13 \times 3 = 15600$ monomeric beads. MD simulations were extended over 10^8 time steps, corresponding thus to a total, macroscopic time of $0.25 \mu\text{s}$ (for more details see Appendix). Simulation snapshots for low- and mid-DNA star densities, η_s are shown in Figure 2, for both types of solution – one composed of planar DNA stars (a) and (b) and one consisting of tripod star configuration (c) and (d).

2.1. Systems of planar DNA stars

To study planar (*flat*) all-DNA stars confined to the interface, monomer-resolved MD simulations are performed for the interface density of the DNA stars, η_s , as defined

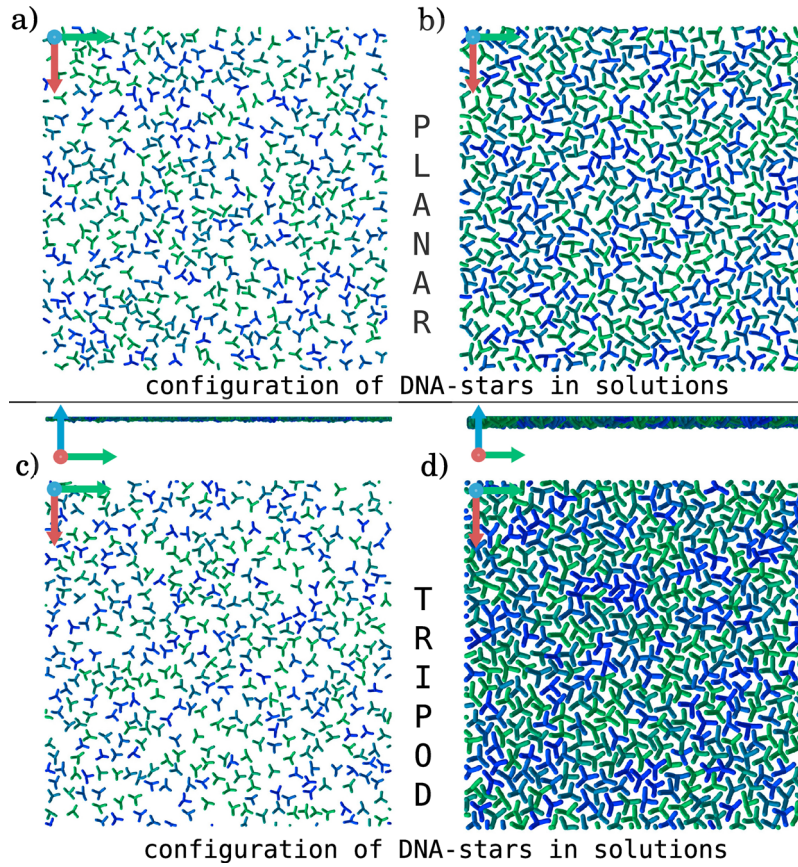


Figure 2. Simulation snapshots of bulk DNA stars solutions confined at the air-water interface at salt concentration $c = 100$ mM and DNA stars' densities (a) $\eta_s = 0.17$ and (b) $\eta_s = 0.34$ for the planar configurations of stars and (c) $\eta_s = 0.17$ and (d) $\eta_s = 0.54$ for the tripod configuration of stars. DNA stars are shown in different colours in order to increase distinguishability between them. The upper panels in (c) and (d) stand for the projection of the simulation box in the yz -plane, whereas the bottom panels show the projection on xy -plane. The orientations of the x -, y - and z -axis are indicated by the red, green and blue arrows, respectively.

in Equation (1) between 0.17 and 0.34. Already for intermediate densities (i.e. for $\eta_s \simeq 0.25$) the particular shape of the stars renders the construction of the initial configurations very challenging. To avoid an overlap of the arms, the stars have to be arranged for their initial configuration in a particularly chosen geometric pattern. With such ordered arrangements one might even proceed to higher η_s -values; however, at these high densities the system would never be able to equilibrate but would rather remain in a trapped configuration. For this reason, we have limited our investigations on the flat stars to $\eta_s \leq 0.34$.

In Figure 3(a), we show the pair correlation function, $g_{yy}(r)$, of our two-dimensional system of flat DNA stars, where r represents the centre-of-mass distance, r_{com} . We find for $g_{yy}(r)$ the typical shape encountered for correlation functions of a disordered state: a main peak with subsequent oscillations, which become more pronounced as the density increases. The distance of closest approach (i.e. below which $g_{yy}(r)$ essentially vanishes) is located at $r \simeq 50$ Å, which corresponds to the length of one arm of the stars. This feature indicates that as a consequence of

the two dimensional confinement, the DNA stars hardly penetrate. The position of the maximum in $g_{yy}(r)$ moves to smaller values with increasing η_s , as expected.

The information about the static structure of the system is supplemented by dynamic properties: to this end we have calculated the mean squared displacement (MSD), denoted by

$$\begin{aligned} \text{MSD}(\Delta t) &= \langle (\Delta \mathbf{r}_{\text{com}}(\Delta t))^2 \rangle \\ &= \langle (\mathbf{r}_{\text{com}}(t + \Delta t) - \mathbf{r}_{\text{com}}(t))^2 \rangle, \end{aligned} \quad (2)$$

where a DNA star is considered to be located at its centre-of-mass, $\mathbf{r}_{\text{com}}$. Averaging the one-particle correlation function independently over each macromolecule and using gliding time windows we can achieve a sufficiently high numerical accuracy of the data. Results for the MSD, calculated for densities within the aforementioned density window, are shown in Figure 3(b) on a double logarithmic scale. At larger times we find a neat diffusive behaviour, where different vertical shifts, corresponding to decreasing diffusion coefficients, are found for different η_s -values, see discussion in the following

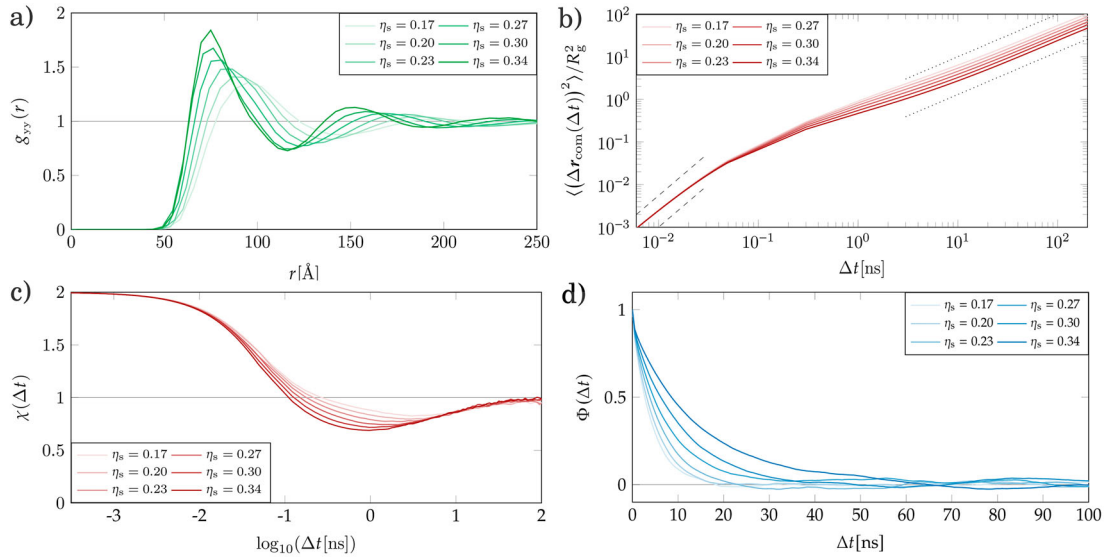


Figure 3. (a) Radial distribution function $g_{yy}(r)$ of a system of planar DNA stars, plotted as a function of centre-of-mass separation r , given in units of Å. (b) Mean squared displacement (MSD) $\langle (\Delta \mathbf{r}_{\text{com}}(\Delta t))^2 \rangle$ of the centres-of-mass, $\mathbf{r}_{\text{com}}(t)$ of DNA stars in the flat configuration, given in units of R_g^2 , as a function of the time lag Δt , given in ns. The dashed lines highlight the ballistic regime (i.e. $\text{MSD} \propto t^2$), while the dotted lines indicate the diffusive regime (i.e. $\text{MSD} \propto t$). (c) Local logarithmic derivative, $\chi(\Delta t)$, of the MSD, related to the centres-of-mass, $\mathbf{r}_{\text{com}}(t)$, of DNA stars in the flat configuration, given in units of the squared radius of gyration R_g^2 , as a function of the logarithmic time lag. (d) Normalised 'orientational' time auto-correlation function $\Phi(\Delta t)$ of DNA stars in the flat configurations as a function of lag time Δt , given in ns. Results are shown for different values of surface density η_s , as labelled.

subsection. To elucidate a possibly sub-diffusive regime, we have calculated the logarithmic derivative of the MSD, $\chi(\Delta t)$, defined *via*

$$\chi(\Delta t) = \frac{d[\log_{10} \langle (\mathbf{r}_{\text{com}}(t + \Delta t) - \mathbf{r}_{\text{com}}(t))^2 \rangle]}{d[\log_{10} \Delta t]} \quad (3)$$

The quantity $\chi(\Delta t)$ is shown in Figure 3(c). We find that this function deviates for $10^{-1} \text{ ns} \leq \Delta t \leq 10^2 \text{ ns}$ from the diffusive behaviour when $\chi(\Delta t)$ assumes values smaller than unity: there, $\chi(\Delta t)$ ranges between $\simeq 0.8$ (for low densities) to $\simeq 0.6$ (at intermediate densities). Obviously, in the latter case, the star-like architecture of the macromolecules renders the system rather bulky, leading to a more pronounced sub-diffusive behaviour than at low densities, where the macromolecules can move around more freely.

Finally, we have investigated the orientational dynamics of the DNA stars, by calculating the (normalised) auto-correlation function of the orientation of the DNA arms. To this end, we have tagged an arbitrarily chosen arm in each DNA star and have connected the centre-of-mass of the star with the end monomer of the same arm *via* the vector $\mathbf{a}(t)$. The orientational correlation function is then given at a lag time Δt by the function $\Phi(\Delta t) = \langle \mathbf{a}(t) \cdot \mathbf{a}(t + \Delta t) \rangle$. The results for the auto-correlation function, obtained *via* a similar averaging procedure as the one mentioned above for the MSD,

are shown in Figure 3(d) for different values of surface density η_s . As expected, the decay of this function is strongly density-dependent: for instance, for the smallest density $\eta_s = 0.17$ and the largest density $\eta_s = 0.34$, the auto-correlation of $\mathbf{a}(t)$ vanishes at lag times ns and ns , respectively. In both cases, at these lag times, the DNA stars have propagated over a distance of only $4R_g$, see Figure 3(b). This finding provides evidence that in this system the orientational correlations decay considerably faster than the spatial correlations.

2.2. Systems of tripod DNA stars

MD simulations have been performed to investigate all-DNA stars in the tripod configuration confined to a water–air interface. The salt concentration was assumed to be *mM* as before. Due to the ability of these DNA stars to immerse their tip (*i.e.* central junctions of the stars) into the fluid, interface densities up to $\eta_s = 0.58$ could now be considered. The z -components of the tips of the tripods in the initial configuration were forced to assume rather large values, rendering thereby the triangular area formed by the end monomers of the arms much smaller (as compared to the case of flat, extended DNA stars). In that way congestion is avoided.

In Figure 4(a), we show the pair correlation function $g_{yy}(r)$ of the system where the distance between two

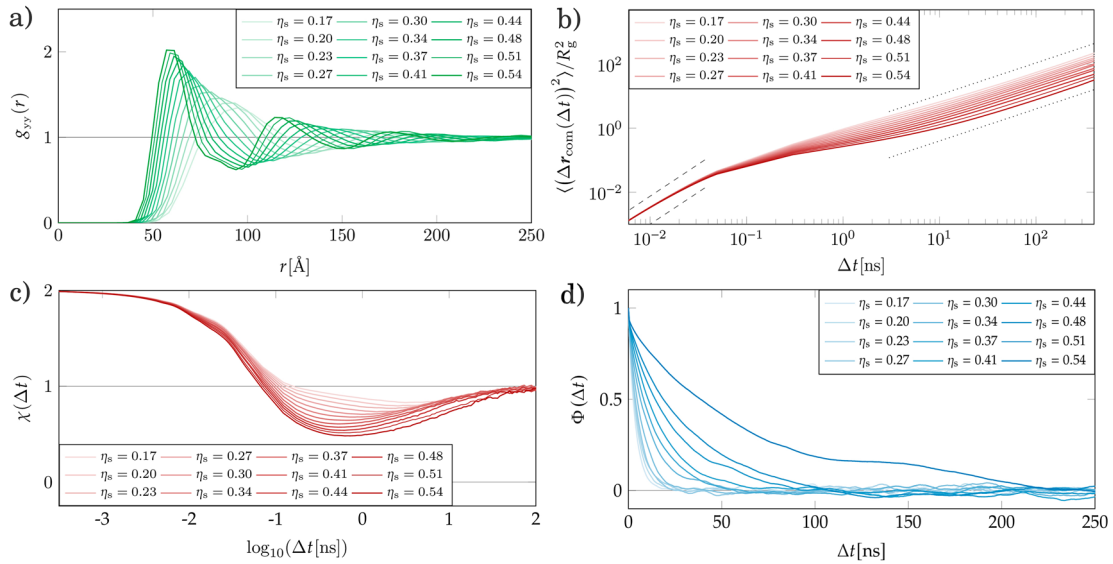


Figure 4. (a) Radial distribution function $g_{yy}(r)$ for the system of DNA stars in the tripod configuration, plotted as a function of the centre-of-mass separation r , given in units of Å. (b) Mean squared displacement (MSD) of the centres-of-mass, $\mathbf{r}_{\text{com}}(t)$ of DNA stars in the tripod configuration, given in units of R_g^2 , as a function of the time lag Δt , given in ns. The dashed lines highlight the ballistic regime (i.e. $\text{MSD} \propto t^2$), while the dotted lines indicate the diffusive regime (i.e. $\text{MSD} \propto t$). (c) Logarithmic derivative, $\chi(\Delta t)$, of the MSD related to the centres-of-mass, $\mathbf{r}_{\text{com}}(t)$, of DNA stars in the tripod configuration, given in units of the squared radius of gyration R_g^2 , as a function of logarithmic time lag. (d) Normalised orientational time auto-correlation function $\Phi(\Delta t)$ of DNA stars in the tripod configurations as a function of lag time Δt , given in ns. Results are shown for different values of surface density η_s , as labelled.

stars, now refers to the projection of the tips onto the interface. Similar to the case of flat DNA stars we find correlation functions which characterise a disordered, fluid state; only for the highest packing fractions one can find minute fingerprints of an evolving side-shoulder of the main peak, close to the first minimum, a feature which might be considered as a precursor of a possible super-cooled state [40–42]. If we consider again the distance beyond which $g_{yy}(r)$ is non-zero, we find a value below 50 Å, providing evidence that in the tripod configuration the DNA stars are able to approach each other more closely than in the case of flat stars. The positions of the maxima in $g_{yy}(r)$ show the expected shift to smaller distances with increasing η_s .

In analogy to the previous subsection we investigated the dynamic translational and orientational correlations by calculating the MSD (now related to the projections of the tips onto the interface), the logarithmic derivative of the MSD, $\chi(\Delta t)$ and the orientational auto-correlation functions $\Phi(\Delta t)$ of the arm vectors $\mathbf{a}(t)$ as functions of the time lag Δt . The results are shown in Figure 4(b–d), respectively, which now extend over a considerably larger range of densities. For each of these functions, findings similar to those made for the planar configuration hold true. The direct comparison of the results obtained for the aforementioned functions, in the planar and in the tripod configurations is presented in the following subsection.

In contrast to the planar DNA stars, the macromolecules in the tripod configuration possess additional degrees of freedom: the vertical position of the central junction of the star Δz , the angle enclosed by the arms and the interface ζ , and the angles formed between the arms θ_i , see the inset of the Figure 5(a).

We calculated the probability distribution $P(\Delta z)$ of the immersion depth of the tip of the stars, Δz (which is simply the orthonormal distance of the central junction from the interface), Figure 5(a), and the probability distribution $P(\zeta)$ of the angle ζ (which is enclosed by the arms of the star and the interface), Figure 5(b), for different densities. For a given density η_s , $P(\Delta z)$ and $P(\zeta)$ are very similar in their shape, a fact which is imposed by the geometry of the tripod configuration. We find a striking change in shape of these functions as the density increases. According to the shape of the distributions we can clearly separate three density regimes: at small densities we find a pronounced peak for rather small Δz values ($\Delta z \simeq 8$ Å) and ζ -values located at $\zeta \simeq 0.05\pi \simeq 10^\circ$: here the majority of the stars show a clear preference for rather flat tripod configurations, made possible by the ample space available at small densities. At high densities, we find again pronounced peaks in the two distributions (for $\Delta z \simeq 25$ Å and $\zeta \simeq 0.2\pi \simeq 36^\circ$); in this context it must be noted (i) that the length of one star arm amounts approximately to 44 Å (to be compared to the aforementioned value of Δz) and (ii) that the steric repulsion

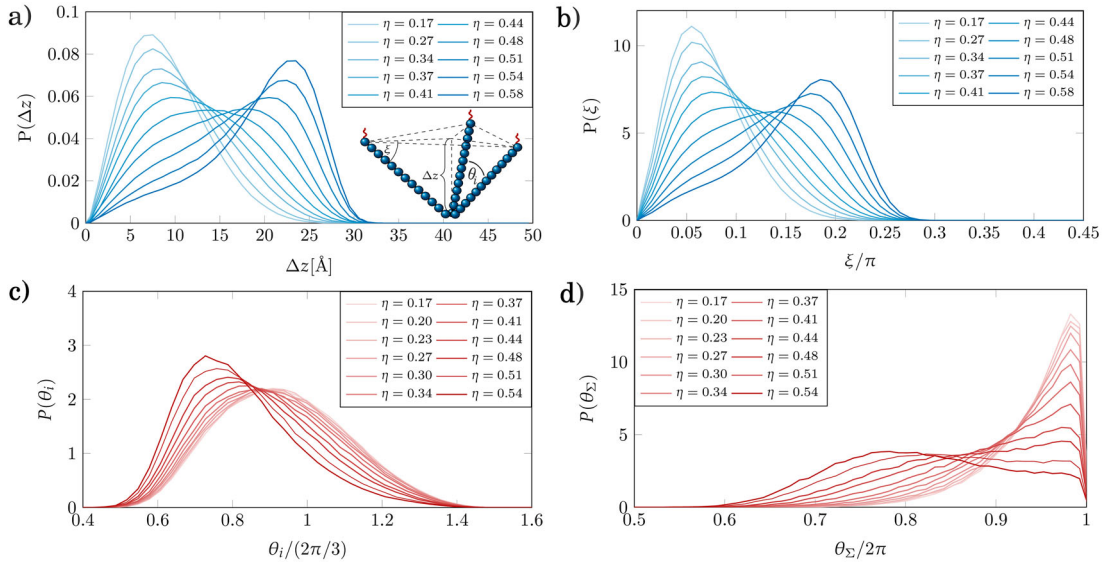


Figure 5. Probability distributions of characteristic length and angles of the tripod DNA star configuration (as indicated at the inset (a)), i.e. (a) $P(\Delta z)$ as a function of the immersion depth Δz given in $\text{\AA}$. (b) $P(\xi)$ as a function of the arm-interface angle ξ given in units of π . (c) $P(\theta_i)$ as a function of the interarm angles θ_i ($i = 1, 2, 3$) given in units of $2\pi/3$. The distributions $P(\theta_i)$ represent the cumulative results over all three interarm angles θ_i , $i = 1, 2, 3$. (d) Probability distribution $P(\theta_\Sigma)$ as a function of the sum over the interarm angles, θ_Σ given in units of 2π . Results are plotted for different values of the surface density η_s , as labelled. The probability distributions are normalised via: $\int_0^\infty P(\Delta z) d(\Delta z) = 1$; $\int_0^{\pi/2} P(\xi) d\xi = 1$; $\int_0^\pi P(\theta_i) d\theta_i = 1$ and $\int_0^{2\pi} P(\theta_\Sigma) d\theta_\Sigma = 1$.

between the DNA arms does not allow angles ξ much larger than $\pi/4 = 45^\circ$, corresponding to a vertical tip position of $31 \text{ \AA}$. At high densities the tripods assume rather sharp tripod configurations, as a consequence of the reduced available space and the mutual repulsion between the stars. The most interesting effects can be found in the intermediate density regime (i.e. around $\eta_s \simeq 0.44$) where both distributions extend over a broad range of the respective variables: to be more specific, a broad ‘maximum plateau’ extends over $\simeq 8 \text{ \AA}$ (in Δz) and over $\simeq 0.08\pi \simeq 14^\circ$ (in ξ) which does not allow to identify a preferred tripod configuration in terms of Δz and ξ . Instead, a large variety of preferred star conformations can be identified. Undoubtedly, in this density range the DNA stars also interpenetrate, and the effects are a consequence of a strong interplay between space optimisation (wide space offered between the arms for interpenetration) on the one hand and mutual repulsion between the end beads of the arms, on the other hand.

Finally, the deviation of DNA stars from the planar configuration can also be analysed *via* the interarm angles θ_i , with $i = 1, 2, 3$, and their sum θ_Σ . The corresponding probability distributions $P(\theta_i)$ with $i = 1, 2, 3$ and $P(\theta_\Sigma)$ are shown in Figure 5(c, d). θ_Σ shows a pronounced peak at low densities for $\theta_\Sigma \simeq 2\pi = 360^\circ$ and $P(\theta_i)$ has a maximum slightly smaller than $2\pi/3 = 120^\circ$, corroborating the emergence of predominantly flat star configurations. At high densities, on the other hand, θ_Σ shows a flat, but well-identifiable maximum for

$\simeq 0.78(2\pi) \simeq 280^\circ$, while $P(\theta_i)$ has a well pronounced maximum for $\simeq 0.75(2\pi/3) \simeq 90^\circ$. In the range of intermediate densities $P(\theta_\Sigma)$ is very broad, indicating that a large variety of tripod configurations can be identified in the system.

To obtain more insights into the conformational changes of the DNA stars as the density is increased, we introduce the concept of a *local* density, η_{loc} : this quantity is defined as the star density within a circular area of radius $r_{\text{loc}} = 200 \text{ \AA}$ (corresponding to roughly 4.5 arm lengths), centred at the projection of the tip of the star onto the interface. In this manner, we obtain a quantitative information about the density fluctuations in a system of given *global* surface density, η_s . The probability distribution of η_{loc} , $P(\eta_{\text{loc}})$, is shown in Figure 6(a) for each of the global densities η_s of the tripod systems investigated. We see that the distributions are very similar in their shape for the different η_s : all of them are centred at the respective η_s -values and have a rather narrow half-width ($\simeq 0.05$), indicating that the local density varies only moderately around the value of the global density. With the concept of the local density in mind, we can now re-consider the immersion depth Δz and analyse it as a function of η_{loc} : in this context, it should be emphasised that – due to the considerable overlap of the $P(\eta_{\text{loc}})$, obtained for different global densities η_s (see Figure 6(a)) – data for a given value of the local density can now originate from simulations carried out for systems with different η_s -values. The corresponding data are shown

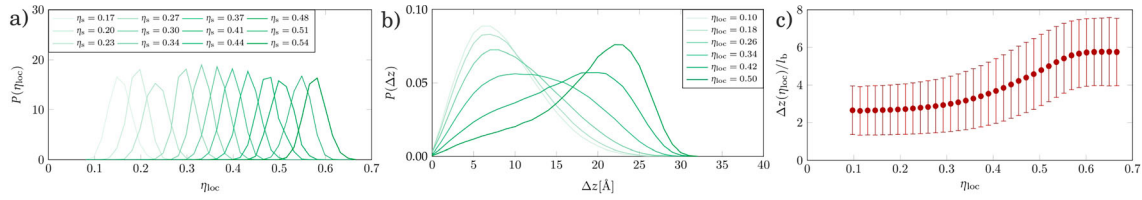


Figure 6. (a) Probability distribution $P(\eta_{loc})$ as a function of the *local* surface density, η_{loc} , of DNA stars in the tripod configuration. Results are plotted for different values of the *global* surface density η_s , as labelled. The probability distributions are normalised via $\int_0^\infty P(\eta_{loc}) d\eta_{loc} = 1$. (b) Probability distribution $P(\Delta z)$ as function of the immersion depth, Δz , of DNA stars in the tripod configuration; Δz is given in Å. Results are plotted for different values of the *local* surface density η_{loc} , as labelled. The probability distributions are normalised via $\int_0^\infty P(\Delta z) d(\Delta z) = 1$. (c) Immersion depth Δz as function of the *local* surface density, η_{loc} , of DNA stars in the tripod configuration; Δz is given in units of l_b , i.e. equilibrium length of the harmonic bond, which for our model is given by $l_b = 3.4$ Å. The vertical bars represent the half-width of the distribution of the Δz .

in Figure 6(b,c) over a representative range of η_{loc} . The probability distributions $P(\Delta z)$, plotted for different *local* densities – see Figure 6(b) – shows essentially the same shape as the related functions, plotted for different *global* densities η_s – see panel (a) of Figure 5. If we now display the tip position as a function of η_{local} , see Figure 6(c), we see that $\Delta z(\eta_{local})$ undergoes a sigmoidal transition from a rather small value of $\Delta z \simeq 2.3l_b$ (corresponding to the left peak in panel (b) of Figure 6) to a considerably larger value of $\Delta z \simeq 5.9l_b$ (corresponding to the right peak in the above-mentioned panel); l_b is the equilibrium length of the harmonic bond (see Appendix), which for our model is given by $l_b = 3.4$ Å. The monotonous increase of $\Delta z(\eta_{loc})$ as a function of η_{loc} provides evidence that it is essentially the local density around a given DNA tripod that imposes the actual value of its tip position.

2.3. Planar DNA stars vs. tripod DNA stars

In this subsection, we present a direct comparison of selected properties, calculated in the previous subsections for the planar, and the tripod configurations of DNA stars confined to the interface and highlight the impact of the additional degrees of freedom for the tripod systems. Of course, this analysis is only possible for surface densities up to $\eta_s = 0.34$.

In Figure 7(a), we present the comparison of the radial distribution functions, $g_{yy}(r)$. At the lowest density ($\eta_s = 0.17$) there is almost no differences between the two scenarios. At $\eta_s = 0.34$, only a minor difference arises indicated by ability of DNA stars in the tripod configuration to arrange closer at the confinement. For the highest investigated density we see a small shoulder close to the first minimum in the $g_{yy}(r)$ of the tripod system, reflecting the aforementioned precursor of a possible supercooled state.

We continue with the comparison of the translational and the rotational correlations as functions of time; these results are presented in Figure 7(b–d). These data reveal

that the differences in the dynamic properties between the two types of systems are marginal. The MSDs in Figure 7(b) shows, although hardly discernible, that flat DNA stars diffuse somewhat slower than the tripod ones. We find that the logarithmic derivative of the MSD displayed in Figure 7(c), provide evidence of only marginal differences between the two types of systems: for DNA stars in the planar configuration the transition from the ballistic to the diffusive regime is somewhat shallower, corresponding to a slightly less pronounced sub-diffusive behaviour. Also, the orientational auto-correlations of the arm vectors, $\mathbf{a}(t)$, shown in Figure 7(d), decay slightly slower for DNA stars in the flat configurations. The tripods at the highest density, $\eta_s = 0.58$ hardly reach the diffusive regime in the time-window simulated and they show signatures of slow dynamics and an incipient glassy state; also the orientational correlation function barely relaxes within the time window of 250 ns.

Finally, we have extracted the diffusion constant, D , from the MSD *via* the Einstein relation for both types of systems as a function of η_s . This quantity is shown in Figure 8. It can be concluded that in the tripod configuration the DNA stars are slightly more diffusive, which is due to their aforementioned ability to evade each other at the interface.

Summarising, it can be concluded that the results for the static and dynamic correlation functions are remarkably similar between the two types of systems, despite their striking difference in their conformations. The reason for an almost identical behaviour could be sought in the range of investigated packing fractions. Namely, the stars in planar configuration are investigated for densities up to only $\eta_s = 0.34$. In that range of densities the available space offers possibility to the DNA star in tripod configuration to spread and take more planar-like shape, which is confirmed by probability distribution functions, see Figure 5. The same figure suggests that the differences between two systems would most likely arise for higher packing fractions, $\eta_s > 0.5$ which is at the moment not

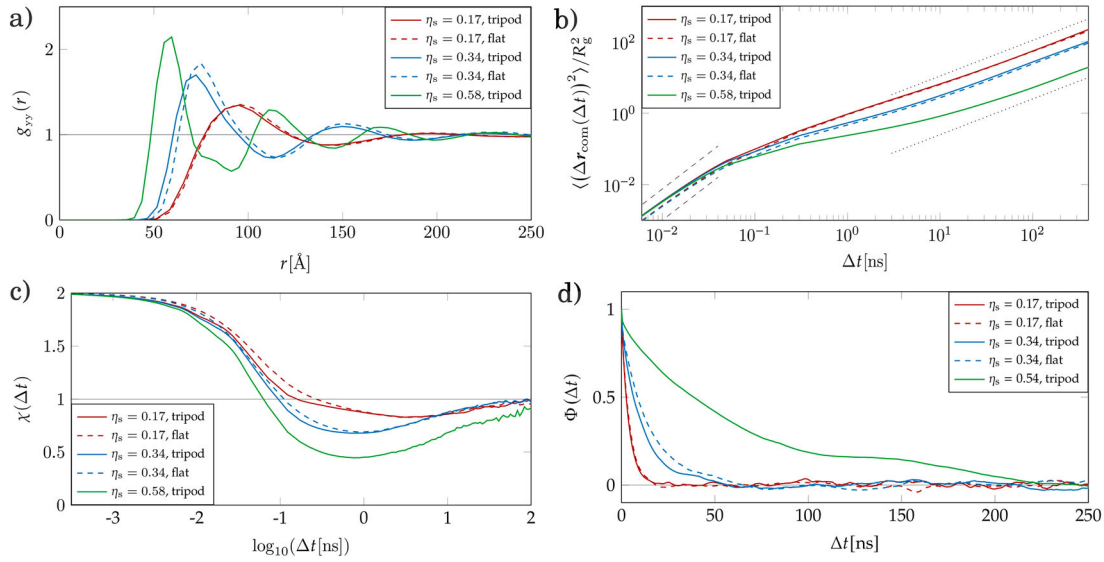


Figure 7. Comparing results between systems of DNA stars in the planar (dashed lines) and in the tripod (solid lines) configurations: (a) Radial distribution function $g_{yy}(r)$, plotted as a function of the centre-of-mass separation r , given in units of Å. (b) Mean squared displacement (MSD), given in units of R_g^2 , as a function of the time lag Δt , given in ns. The dashed black lines highlight the ballistic regime (i.e. $MSD \propto t^2$), while the dotted black lines indicate the diffusive regime (i.e. $MSD \propto t$). (c) Logarithmic derivative, $\chi(\Delta t)$, of the MSD given in units of R_g^2 , and as a function of the logarithm of time lag. (d) Normalised orientational time auto-correlation function $\Phi(\Delta t)$ for the star arm vector $\mathbf{a}(\Delta t)$ as a function of lag time Δt , given in ns. Results are shown for different values of surface density η_s , as labelled.

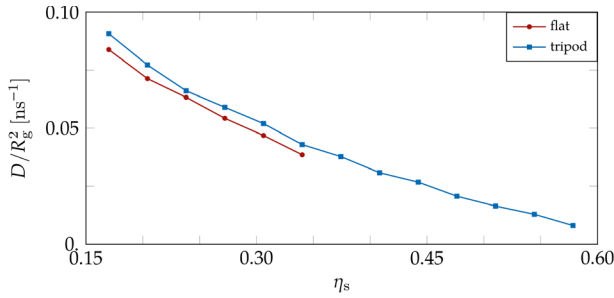


Figure 8. Diffusion constant of DNA stars, D , rescaled by R_g^2 and given in ns^{-1} as a function of the star density η_s . Results are compared between systems of DNA stars in the planar and in the tripod configuration, as labelled.

accessible for our full monomer-resolved simulations of solutions composed of planar DNA stars.

3. Effective interactions of planar DNA stars

To supplement results from the previous sections, we take into a consideration of additional insights to 2D DNA stars self-assembly. We calculate the effective potential between planar DNA stars. The analysis presented in the paper is based on the exact results calculated directly from the full monomer-resolved MD simulations and here we do not tend to use the approximative method of effective interactions to recover them. Instead, we aim to

corroborate the work of Velasco *et al.* [43], who calculated analytically the effective potential between planar Y-shaped DNA stars floating at the interface. The model they used (let us name it: *the reference model*) treats each arm of the DNA star as a stiff rod of the length corresponding to 13 base-pairs as it is the case in our system. Hence we use the Widom insertion (WI) method (see, e.g. [44,45]) to calculate the effective interaction between monomer-resolved model of DNA stars and we check how it compares to the analytical results from the reference model [43]. In both models, the dielectric jump between two interfacing areas is not considered and the stars are immersed in a water solution of the same salt concentration of $c = 100$ mM. It is important to emphasise the differences between the two models: one arises from the description of the charge along the arms – in the reference model it is considered as continuous, while it is discrete in monomer-resolved case; the other refers to the flexibility of the central junction of the star – namely in the reference model the angles enclosed between the rigid arms of the DNA stars were fixed to $\theta_i = \frac{2\pi}{3}i$, $i = 1, 2, 3$ whereas in monomer-resolved model they are allowed to fluctuate. Therefore, in the following subsections, we introduce two types of planar monomer-resolved DNA stars: the one that we already studied in the main text which we will name here as *flat DNA star with flexible junction* and a modified version termed *flat DNA star with a rigid junction* where the angles θ_i are fixed

to match the scenario from the reference model. To gather the data for the related effective potential 2000 independent Widom insertions were performed for each system.

3.1. Planar DNA stars with rigid junction

In this subsection, we discuss our results obtained for the effective potential between two flat DNA stars with rigid junction, $\phi_{\text{eff}}(\alpha; \Delta x, \Delta y)$, which depends both on the inter-star vector, $\mathbf{r} = (\Delta x, \Delta y)$, and on the angle of rotation between the two stars, α , see Figure 9. Due to the symmetry, it is sufficient to limit the investigations to $0 \leq \alpha \leq 60^\circ$. The vector $\mathbf{r}$ connects the centres-of-mass of the stars. We adjusted the respective system so that we consider only DNA stars with rigid (i.e. straight) arms, thus the interarm angles are fixed to $\theta_i = \frac{2\pi}{3}i$ ($i = 1, 2, 3$). This modification allows for a direct comparison between our numerical and the analytic approach [30]. Due to the high internal symmetry, the centre-of-mass of the star, $\mathbf{r}_{\text{com}}$, coincides with three central junction-monomers, $\mathbf{r}_{\text{cj}}$.

We have used the Widom insertion method [44] to calculate $\phi_{\text{eff}}(\alpha; \Delta x, \Delta y)$. Due to the rigidity of the stars, they do not contribute entropically to the effective potential, thus only one single Widom insertion per parameter set $\{\alpha, \Delta x, \Delta y\}$ is required to extract the interaction energy $\phi_{\text{eff}}(\alpha; \Delta x, \Delta y)$ between the two stars; nevertheless, we will keep for consistency's sake the label 'Widom insertion method'.

Results obtained for $\phi_{\text{eff}}(\alpha; \Delta x, \Delta y)$ *via* our numerical procedure (see Figure 10(b, d)) are compared in the following to data originating from the reference model [43], see Figure 10(a, c) at angles $\alpha = 0^\circ$ and $\alpha = 60^\circ$ as indicated at the panels. The potentials are shown both in

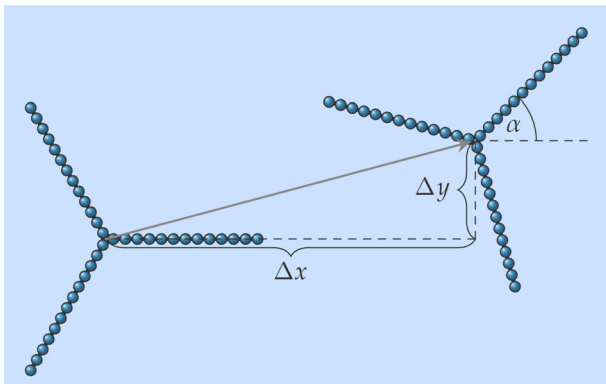


Figure 9. Illustration of the effective interaction parameters between rigid DNA stars in the flat configuration: displacements Δx and Δy and rotation angle α .

two dimensional contour plots as well as in energy profiles, the latter ones being denoted by $\phi_{\text{eff}}(\alpha; \Delta r_i)$, with $i = 1, 2$, along selected slices through these energy landscapes; Δr_1 and Δr_2 are the respective slice coordinates. Additional results for slices through the related energy landscapes for $\alpha = 15^\circ, 30^\circ, 45^\circ$ are shown in Figure 11.

Due to the three-fold rotational symmetry of the internal structure of the DNA stars we expect the effective potential $\phi_{\text{eff}}(\alpha; \Delta x, \Delta y)$ to exhibit a corresponding rotational symmetry. Indeed, all results display such a three-fold symmetry, as can be seen in panels (c) and (d) in Figure 10. For the angle $\alpha = 0^\circ$ even a six-fold symmetry can be identified in the potential $\phi_{\text{eff}}(\alpha = 0^\circ; \Delta x, \Delta y)$, see panels (a) and (b) of Figure 10. We note that the largest values for $\phi_{\text{eff}}(\alpha; \Delta x, \Delta y)$ can be expected for $\alpha = 0^\circ$ and $\alpha = 60^\circ$ due to the parallel alignment of one or more arms of the DNA stars and the resulting high probability for a considerable degree of overlap of the arms.

The comparison of the two sets of data for $\phi_{\text{eff}}(\alpha; \Delta x, \Delta y)$, calculated for $\alpha = 0^\circ$ and $\alpha = 60^\circ$, reflects, on one side differences in the features of the continuous and of the discrete models but provides, on the other side, evidence for a high degree of consistency of the two approaches. As a consequence of the constant charge density along the arms in the model used in Ref. [43], the effective potentials are smooth functions in their arguments, as can be seen both from the contour plots as well as from the energy profiles. In contrast, the effective interactions for the bead model, computed *via* the WI method clearly reflects the internal architecture of the arms, which are composed of essentially impenetrable spherical units: their strong repulsion at short distances is responsible for the pronounced peaks, located at the positions of each of these monomeric units. On the other hand, it can be seen that the peaks in the density profiles $\phi_{\text{eff}}(\alpha; \Delta r_i)$, with $i = 1, 2$, obtained *via* the WI method nicely 'sit' on the smooth curves of the related potential calculated *via* the reference method; this feature demonstrates the consistency of the two approaches.

Finally, we compare the energy profiles $\phi_{\text{eff}}(\alpha; \Delta r_i)$ with $i = 1, 2$, calculated *via* the reference method and *via* the WI method for a broader range of α -values. These energy profiles are obtained by cutting, for a given angle α , a slice through the potential energy landscape $\phi_{\text{eff}}(\alpha; \Delta x, \Delta y)$ along selected lines in the $(\Delta x, \Delta y)$ plane. Our arbitrary choice for these lines are marked in Figure 10 by red and green dashed lines. In Figure 11 we show the energy profiles for $\alpha = 0^\circ, 15^\circ, 30^\circ, 45^\circ$, and 60° . Again we find an excellent agreement between the results for $\phi_{\text{eff}}(\alpha; \Delta r_i)$ with $i = 1, 2$, obtained *via* the two aforementioned methods: the

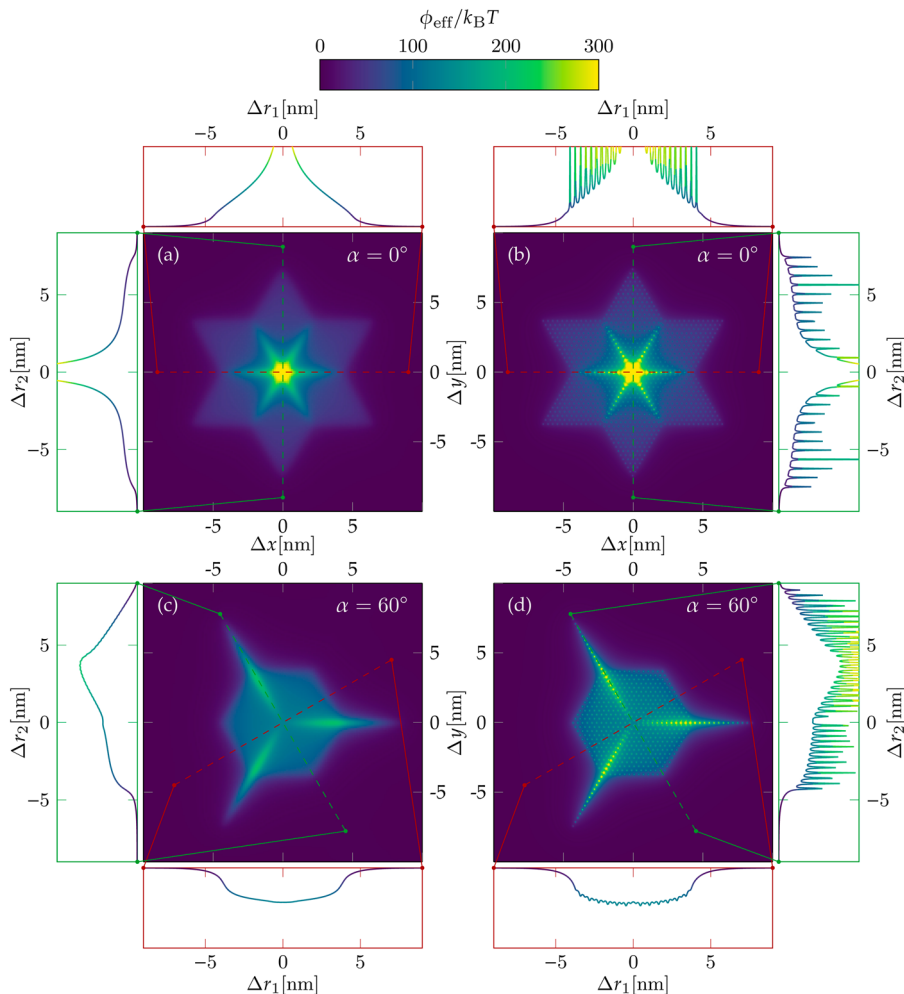


Figure 10. Effective potential, $\phi_{\text{eff}}(\alpha; \Delta x, \Delta y)$, between two flat DNA-stars with *rigid* junction in a contour plot as a function of the centre-of-mass shift Δx and Δy and the relative angle α between the two stars (see Figure 9). $\phi_{\text{eff}}(\alpha; \Delta x, \Delta y)$ is given in units of $k_B T$ (see also colour code at the top of the figure), whereas Δx and Δy are given in nm; α is indicated in the top-right corner of each panel. The interarm angles are fixed to $\theta_i = \frac{2\pi}{3}i$, with $i = 1, 2, 3$. In each of the panels two dashed lines (coloured in red and green) indicate two slices through the energy landscape of $\phi_{\text{eff}}(\Delta x, \Delta y)$. The energy profiles along these slices (in slice coordinates Δr_1 and Δr_2) are shown in the corresponding red- and green-framed plots. The data for the potentials were obtained *via* the reference method [43] (panels (a) and (c)) and *via* the WI method (panels (b) and (d)).

characteristic peaks of the WI-based data nicely ‘sit’ on the smooth curves obtained *via* the reference method. Again, these periodically arranged peaks are induced by the bead structure of our macromolecule, as discussed before.

3.2. Planar DNA stars with flexible junction

We have also calculated the effective potentials for flat stars with *flexible* junction. Of course, for this case no results obtained *via* the reference method are available. Here, the DNA arms are not completely straight and the interarm angles deviate from the ideal values $\theta_i = \frac{2\pi}{3}i$, $i = 1, 2, 3$, thus entropy plays an important role in the calculation of the effective potential. In order to calculate

the effective interactions between two stars, we tag one arm per DNA star to define the rotation angle α between the two stars as the angle between the corresponding arm vectors; the arm vector points from the first to the last monomer of the tagged arm. In contrast to rigid DNA stars, the fluctuations in the conformations of the (equilibrated) DNA stars require now a large number of Widom insertions to average over 2000 pairs of configurations.

The resulting effective potentials are shown in Figure 12 with the centre-of-mass position $\mathbf{r}_{\text{com}}$ as the effective coordinate of the star; results for $\alpha = 0^\circ$ and $\alpha = 60^\circ$ are depicted. As a consequence of the flexibility of the stars the effective potentials are now continuous functions of their variables, a fact which is both visible in the contour plots as well as in the energy profiles,

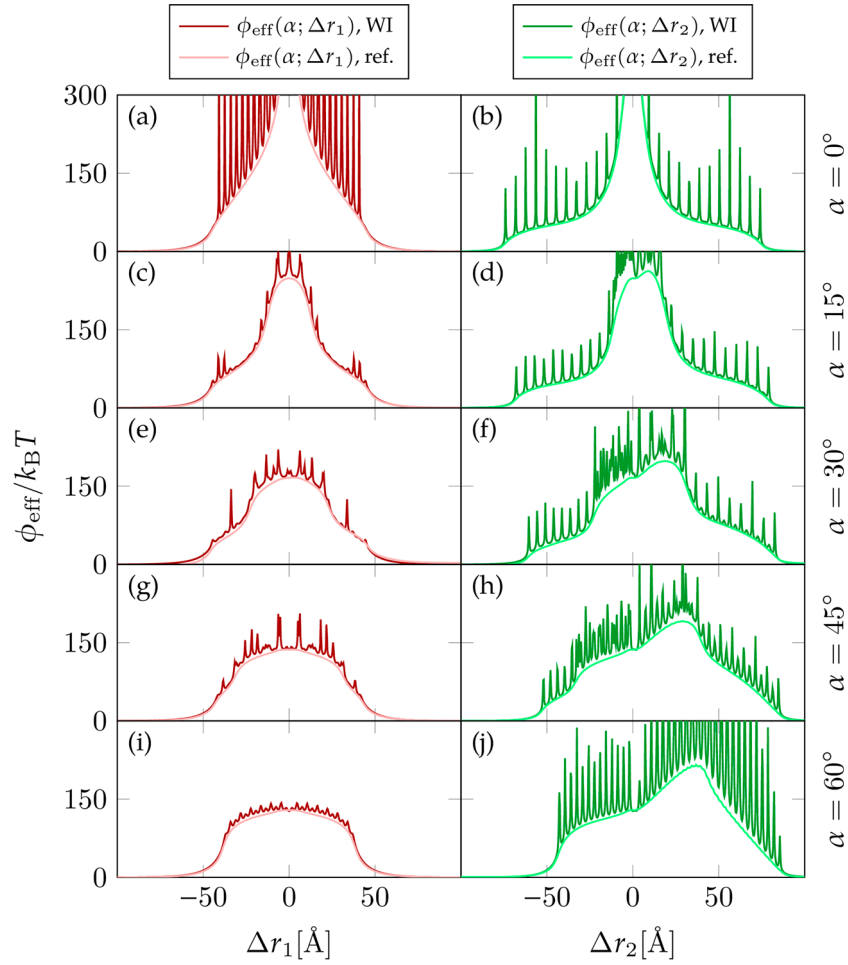


Figure 11. Energy profiles $\phi_{\text{eff}}(\alpha; \Delta r_1)$ and $\phi_{\text{eff}}(\alpha; \Delta r_2)$ of slices through the energy landscapes of the effective potentials $\phi_{\text{eff}}(\alpha; \Delta x, \Delta y)$ as functions of slice coordinates Δr_1 and Δr_2 . The profiles are given in units of $k_B T$, whereas Δr_1 and Δr_2 are given in Å. Panels (a) to (j) show results obtained for rotation angles $\alpha = 0^\circ, 15^\circ, 30^\circ, 45^\circ$, and 60° (as labelled). For each value of α the results for $\phi_{\text{eff}}(\alpha; \Delta r_i)$ ($i = 1, 2$) are shown for two different slices, which correspond to the dashed lines coloured red and green in Figure 10. Data were obtained *via* the Widom insertion method (labeled ‘WI’) and the reference method [43] (labeled ‘ref’).

obtained as slices through this two-dimensional energy landscape. The fingerprints of the granular internal bead-structure of the arms, that is present in the system of planar stars with rigid junctions, Figures 10 and 11, have been completely smeared out.

This insight shows how the introduced minimal flexibility in the model significantly modifies the effective potential of the system. The similar flexibility-induced sensitivity of the effective interaction between all-DNA constructs was also observed in the system of all-DNA dendrimers of the second generation [31] where it was shown how the effective interaction can be fine-tuned with user-prescribed insertion of short flexible segments between stiff DNA arms which further makes strong impact on self-assembly behaviour. The control over self-organisation of DNA constructs in solutions through programmable construction of macromolecules is an application-relevant feature that requires more detailed investigations. These results for the effective potential can

serve for further study of phase diagram of DNA stars in the confinement.

4. Conclusions

In this contribution, we have investigated the self-organisation scenarios of planar and of tripod-shaped all-DNA stars which are fixed via amphiphilic units to an air-water interface: in the planar configurations the entire arms are fixed to this interface while in the tripod configurations, the central monomer of the star is allowed to dive into the water with dissolved monovalent salt. The investigations are based on monomer-resolved simulation with suitable interactions between the beads that have been employed to mimic the structural properties of double-stranded DNA chain. By systematically increasing the planar packing fraction η_s in range from low to mid star densities, we have investigated the static

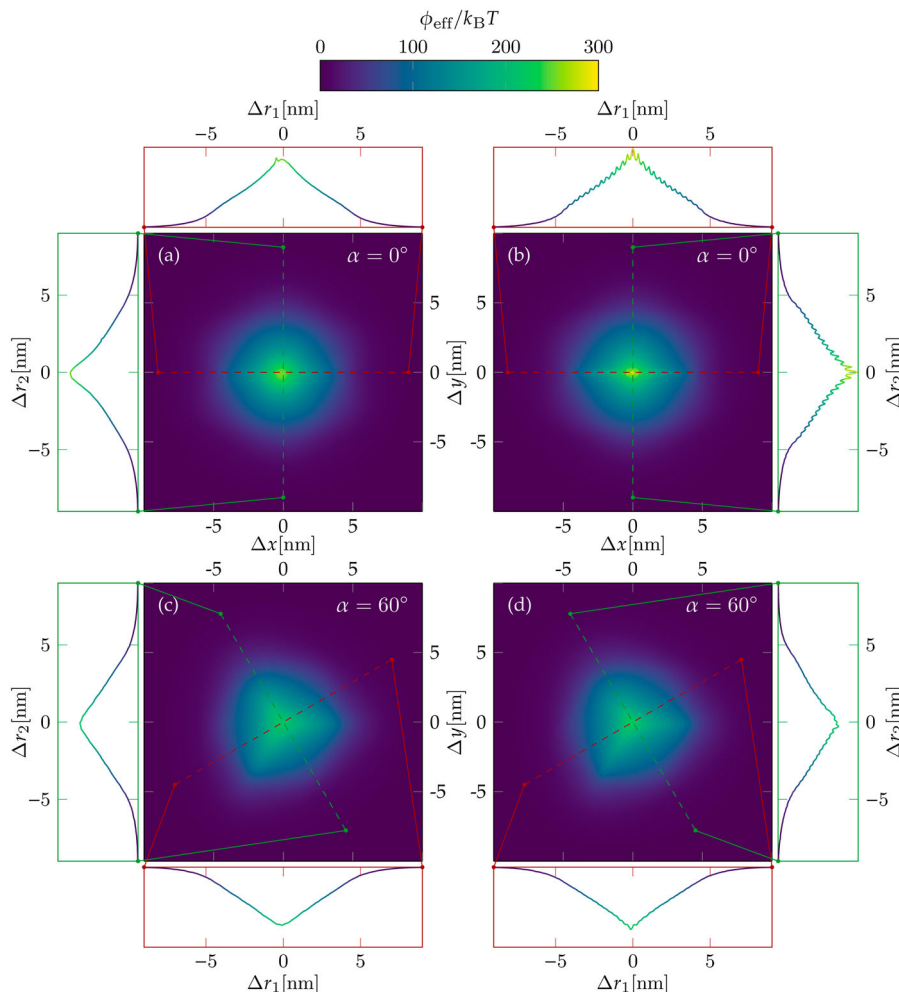


Figure 12. Effective potential $\phi_{\text{eff}}(\alpha; \Delta x, \Delta y)$ between two flat DNA stars with *flexible* junction in a contour plot as a function of the centre-of-mass shift Δx and Δy and the relative angle α between the two stars. $\phi_{\text{eff}}(\alpha; \Delta x, \Delta y)$ is given in units of $k_B T$ (see the colour code at the top of the figure), whereas Δx and Δy are given in nm; α is indicated in the top-right corner of each panel. In each of the panels, two dashed lines (coloured in red and green) indicate two slices through the energy landscape of $\phi_{\text{eff}}(\alpha; \Delta x, \Delta y)$. The energy profiles along these slices (in slice coordinates Δr_1 and Δr_2) are shown in the corresponding red- and green-framed plots. The data for the potentials were obtained *via* the WI method.

and dynamic properties of 2D assembly of all-DNA stars for both configurations.

For the planar configuration of DNA stars investigations could be carried out up to $\eta_s \simeq 0.34$. The radial distribution function shows the typical features of a disordered system; the logarithmic derivative of the mean squared displacement of the star centres reaches values that go down to $\chi(\Delta t) \simeq 0.8$ between the ballistic ($\chi(\Delta t) = 2$) and the diffusive ($\chi(\Delta t) = 1$) regimes. Comparing the time-scales of the auto-correlation function of the arms and of the mean squared displacement we can conclude that the orientational correlations decay faster than the spatial correlations.

In contrast to the planar configurations, the DNA stars in the tripod configuration have an additional degree of freedom, namely the vertical position of their central junction, which increases upon dipping the star

into solvent, shrinking in that way the area spanned by the ending beads of the three arms of a star. That enables denser stars packing in the confinement, so the simulations were extended up to $\eta_s \simeq 0.58$ in this case. From low to mid densities, DNA stars in tripod configuration show an almost identical behaviour as it is the case for the planar DNA stars, whereas for the highest densities, we find an emerging side-shoulder of the main peak in the radial distribution function, indicating the emergence of a supercooled structure.

Particular focus has been put on the probability distributions of the immersion depth of the central monomer, Δz , and of the angle enclosed by the arms and the air-water interface, ζ . As we vary η_s , we find a striking change in the shape of both distribution functions: for small densities the stars prefer to assume flat tripod configurations

while at high densities the stars assume rather sharp tripod configuration, induced by the competition between available space and steric repulsion. In the intermediate density regime, a broad variety of tripod configurations can be found, reflected by rather flat distributions of Δz and ζ . This consequently leads to the cause for obtained similar self-assembly patterns of two systems studied.

The experimental verification of results for the system at hand is still lacking, nevertheless, recently, 2D self-assembly of blunt-ended all-DNA 3-arms stars has been investigated in experiment [24]. The set up is restricted to the assembly on a supported lipid bilayers with cholesterol-mediated DNA anchoring. The research showed the importance of the interaction between DNA duplexes through π -stacking that leads to a long range order in controlled patterned surfaces. That opens the direction in which our further research of denser DNA stars solutions can be conducted to include the interaction between blunt-ends of DNAs that are not neglectable in dense environment and which is not present in our present bead-spring model.

To overcome restrictions of monomer-resolved simulations for studying denser DNA star solutions, one can employ the method of effective interactions and predict theoretically the corresponding phase behaviour. We paved the way for the proposed study by calculating the effective interactions between planar DNA stars, Section 3. In this paper, the emphasis is put on the comparison with the analytically obtained results for similar system of Y-shaped DNA stars [43]. As we have shown good agreement between two models, one can proceed with calculation of effective interaction for the tripod configuration of DNA star and show how the two systems compare in the regime of densities that are not accessible in full monomer-resolved simulations.

Disclosure statement

No potential conflict of interest was reported by the author(s).

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Appendix. Simulation details

The Y-shaped DNA star is approximated with the bead-spring model used in [28] where each nucleotide is represented by a monomer of mass $m = 660$ u, size $d = 18$ Å and charge $q = -e$ that interacts with the Hamiltonian:

$$H_{\text{mm}} = V_{\text{ster}} + V_b + V_{\text{bend}} + V_{\text{el}}. \quad (\text{A1})$$

The steric interaction between monomer beads takes the form

$$V_{\text{ster}}^{\text{mm}} = 4\epsilon \left[\left(\frac{\sigma}{r - r_{\text{mm}}} \right)^{12} - \left(\frac{\sigma}{r - r_{\text{mm}}} \right)^6 + \frac{1}{4} \right] \quad \text{if } r_{\text{mm}} \leq r \leq \sqrt[6]{2}\sigma + r_{\text{mm}} \quad (\text{A2})$$

otherwise for $r < r_{\text{mm}}$ it diverges, while it vanishes for $r > \sqrt[6]{2}\sigma + r_{\text{mm}}$. The input parameters are $\sigma = 4$ Å and $\epsilon = 1$ kJmol⁻¹ and $r_{\text{mm}} = 2r_m - \sigma$, with $r_m = 9$ Å being the radius of monomer, so that the steric interaction acts in the range $r < 18.5$ Å corresponding to the effective diameter of the DNA helix.

The harmonic bonding potential is given

$$V_b = \frac{k_b}{2}(r - l_b)^2 \quad (\text{A3})$$

with the spring constant $k_b = 210$ kJ(molÅ²)⁻¹ and equilibrium bond length $l_b = 3.4$ Å.

The harmonic bending angle potential models the stiffness of a DNA arm by acting on the angle ϕ between bonds connecting neighbouring monomers:

$$V_{\text{bend}} = \frac{k_\phi}{2}(\phi - \pi)^2 \quad (\text{A4})$$

with bending energy $k_\phi = 750$ kJmol⁻¹ chosen to reproduce the typical persistence length of double-stranded DNA chain. The central junction is left fully flexible by setting the bending energy to zero.

All DNA stars systems are studied in high salt concentration, $c = 100$ mM, allowing counterions and salt ions to be implicitly treated through Debye length κ^{-1} . Hence, the electrostatic interaction between charged monomer beads is modelled via a Debye-Hückel interaction

$$\frac{V_{\text{el}}(r)}{k_B T} = \frac{q^2}{4\pi\epsilon_0\epsilon} \frac{e^{-\kappa r}}{r} \quad (\text{A5})$$

with $\kappa = 0.106$ Å⁻¹. The dielectric constant of both media water and air is set to $\epsilon = 80$ assuming that electrostatic effect that arise when the dielectric jump is present in the system can be neglected as subdominant in the case of high salt concentration.

The bulk 2D solutions of both planar and tripod DNA stars are simulated using two-steps procedure. First the system is warmed up using $N_{\text{steps}} = 10^5$ simulation steps with time step $\Delta t = 10^{-15}$ s for a total simulation time $t = 10^{-10}$ s

and then simulated for $N_{\text{steps}} = 2 \times 10^7$ simulation steps with time step $\Delta t = 5 \times 10^{-15}$ s for a total simulation time $t = 10^{-7}$ s for all area densities η_s . Simulations were run in canonical NVT ensembles with periodic boundary conditions at $T = 298$ K using a Langevin thermostat. The number of stars is kept fixed to 400 units (resulting in 15600 monomers) and the length of the quadratic simulation cell

is varied to achieve the following densities of the solutions $\eta_s = 0.17, 0.20, 0.24, 0.27, 0.31$ and 0.34 corresponding to the cell length $l = (2.19, 2.00, 1.85, 1.73, 1.63, \text{ and } 1.55) \times 10^3$ Å respectively. Tripod DNA stars solutions are considered for additional star densities: $\eta_s = 0.37, 0.41, 0.44, 0.48, 0.51, 0.54, \text{ and } 0.58$, setting the cell length $l = (1.48, 1.41, 1.36, 1.31, 1.26, 1.22, \text{ and } 1.19) \times 10^3$ Å accordingly.

Engineering Ultrasoft Interactions in Stiff All-DNA Dendrimers by Site-Specific Control of Scaffold Flexibility

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A combined experimental and theoretical study of the structural correlations in moderately concentrated suspensions of all-DNA dendrimers of the second generation (G2) with controlled scaffold rigidity is reported here. Small-angle X-ray scattering experiments in concentrated aqueous saline solutions of stiff all-DNA G2 dendritic constructs reveal a novel anomalous liquid-like phase behavior which is reflected in the calculated structure factors as a two-step increase at low scattering wave vectors. By developing a new design strategy for adjusting the particle's internal flexibility based on site-selective incorporation of single-stranded DNA linkers into the dendritic scaffold, it is shown that this unconventional type of self-organization is strongly contingent on the dendrimer's stiffness. A comprehensive computer simulation study employing dendritic models with different levels of coarse-graining, and two theoretical approaches based on effective, pair-potential interactions, remarkably confirmed the origin of this unusual liquid-like behavior. The results demonstrate that the precise control of the internal structure of the dendritic scaffold conferred by the DNA can be potentially used to engineer a rich palette of novel ultrasoft interaction potentials that could offer a route for directed self-assembly of intriguing soft matter phases and experimental realizations of a host of unusual phenomena theoretically predicted for ultrasoft interacting systems.

interactions among them is an essential step for designing macroscopic functional soft materials. Different types of ultrasoft interaction potentials have received much attention in the last two decades due to their ability to stabilize novel bulk phase behavior of diverse states of matter,^[1–17] the most prominent of which is the recently experimentally discovered cluster crystal.^[18] To design interactions that promote self-organization into specific equilibrium assemblies requires superior control of the building elements' chemistry and architecture. In this respect, DNA is a versatile nanoscale building block^[19,20] owing to its programmable and fully addressable character, in combination with its unique physico-chemical properties, which allow it to be easily modified and manipulated at the sub-nanometre level (single base level).^[21] Over the last few decades, the remarkable growth of the research field of structural DNA nanotechnology has enabled the fabrication of static and dynamic DNA-based nanoarchitectures of increasing complexity via the robust sequence-complementarity of DNA

strands,^[22–24] the shape-complementarity based on the base-stacking interactions between blunt-ends of DNA helices^[25] and the site-specific decoration of DNA structures with polymers and lipids.^[19,26] This has allowed the emergence of novel

1. Introduction

Establishing a predictive relationship between the collective properties of large assemblies of building blocks and the effective

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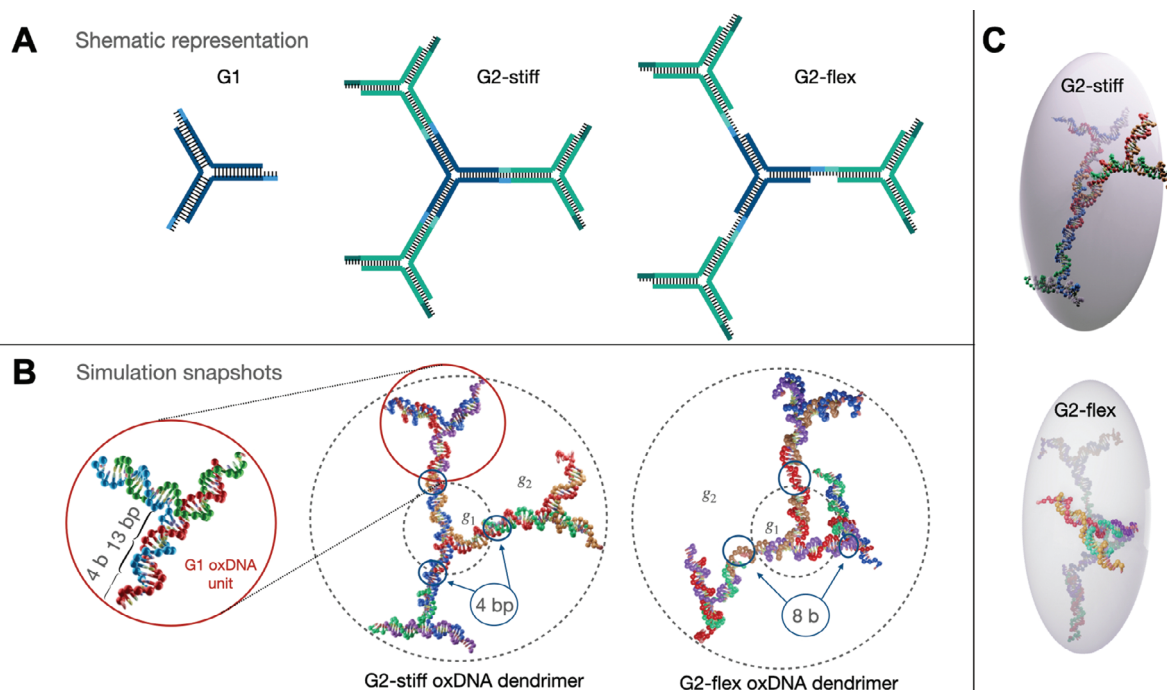


Figure 1. A) Schematic representations and B) simulation snapshots of all-DNA Y-shaped junction (G1) and G2 dendrimers. From left to right: Y-shaped building block; G2-stiff dendrimer with four base-pair long rigid linkers between generations g_1 and g_2 ; and G2-flex dendrimer with eight unpaired bases long flexible linkers between generations g_1 and g_2 . C) Ellipsoid-of-gyration-representation of G2-stiff- and G2-flex-dendrimers. The oxView visualization tool^[38,39] is employed for the demonstration of the all-DNA structures.

applications^[19,27] in diverse areas of research such as biophysics, biomedical engineering, plasmonics, drug delivery, and synthetic biology. Broadly speaking, the traditional engineering approaches focus on altering the building blocks' shape and surface chemistry.^[28–30] Recently, efforts have been shifted toward controlling a significantly less studied structural parameter, namely the internal flexibility of the building block. Control over this structural feature has already enabled the formation of novel crystalline phases, such as the folded smectic phase in all-DNA chain-sticks^[31] and cluster crystals in DNA-based dendritic-linear-dendritic triblocks.^[18]

In this vein, we exploit in this work the large difference in the persistence length L_p between double-stranded DNA (dsDNA, $L_p^{\text{dsDNA}} \approx 50$ nm in 0.15 M NaCl buffer)^[32] and single-stranded DNA (ssDNA, $L_p^{\text{ssDNA}} < 2.0$ nm in 0.15 M NaCl buffer)^[33] in order to engineer the scaffold flexibility of a stiff all-DNA second-generation (G2) dendrimer (G2-stiff).^[34,35] To achieve a flexible all-DNA dendritic version (G2-flex), we modify the internal structure of the G2-stiff by incorporating ssDNA flexible spacers between adjacent generations (core and first layer). These DNA bridges consist of a poly-T sequence, a choice motivated by the significantly reduced propensity of this sequence to form secondary structures.^[36] Key structural quantities of the solutions, namely the total scattering intensities and the structure factors obtained from a range of concentrations, demonstrate that the effective interactions between the dsDNA constructs are ultrasoft. At the same time, this ultrasoftness of the interaction can be further steered through the introduction of flexible bonds. We shall indeed demonstrate that such a structural modification gen-

erates a noticeable decrease in the internal rigidity of the dendrimer's scaffold without, however, altering notably its overall size. Through a combined theoretical and experimental study, we further show that the anomalous liquid-like behavior as reflected in the calculated and measured structure factors emerging from moderately concentrated G2-stiff dendrimers is governed by the scaffold's rigidity. Our results reveal that control over all-DNA dendrimer's stiffness can lead to the realization of ultrasoft particles interacting via tunable repulsive, bounded pair potentials.

2. Results and Discussion

2.1. All-DNA Dendritic Scaffold: Design and Modeling

A fully steerable self-assembled all-DNA dendritic nanostructure with high efficiency is fabricated solely from Y-shaped all-DNA (Y-DNA) building blocks, employing a step-by-step assembly strategy. These three-arm junctions are moderately flexible at the junction point^[37] and they consist of stiff, double-stranded DNA (dsDNA) arms (thirteen (13) base-pair (bp) long), which are terminated with two types of monofunctional single-stranded DNA (ssDNA) dangling tails that are four bases long (4b), allowing other Y-DNA to be covalently connected as each generation is added. A schematic representation of the fundamental Y-DNA building blocks, and a simulation snapshot of the same are shown at the leftmost panels of **Figure 1A,B**, respectively.

In this work, we restricted our studies to the second generation all-DNA dendrimer (G2) with stiff and flexible connectors between the core (Y-DNA, g_1) and the first shell (g_2). The

G2 with stiff dendritic scaffold (G2-stiff) was fabricated following synthetic protocols described in detail in ref. [35]. In short, a combination of a sticky ssDNA dangling tail and enzymatic ligation was used for the formation of 4-bp-long dsDNA stiff bridges between g_1 and the g_2 (Figure 1A,B). For the experimental realization of G2 with flexible dendritic scaffold (G2-flex), we choose a non-sticky ssDNA dangling tail terminated with azide or dibenzylcyclooctyne (dbco) moieties allowing a selective, fast and high-yielding copper-free click chemistry reaction^[40] between the g_1 's Y-DNA and the Y-DNAs belonging to the g_2 (more details in Experimental Section and Note S1, Supporting Information). This design leads to the creation of eight(8)-bases-long (8b) ssDNA bridges without essentially altering the dendrimer's total molecular weight (Figure 1A,B). This structural modification endows the G2 dendrimer with significant internal flexibility, as clearly demonstrated by the decreasing migration mobility of G2-flex compared to the G2-stiff in the polyacrylamide gel electrophoresis experiment, shown in Figure S1, Supporting Information. Strikingly similar flexibility-dependent electrophoretic mobility is also observed in DNA with a linear topology.^[31] The dendrimers' free ends are passivated with poly-T sequences (5T) to minimize aggregation due to base-stacking interaction between blunt-ended DNA helices.^[41,42]

The G2-stiff and G2-flexible all-DNA dendrimers are modeled on the computer using oxDNA2^[43] (see Experimental Section for details). This is a coarse-grained model that has been shown to capture the thermodynamic, structural, and mechanical properties of ssDNA and dsDNA. The basic building block of the model is a rigid nucleotide, and in this model, the DNA molecule is treated as a string of rigid nucleotides that interact through potentials depending on the positions and orientations of the nucleotides. In oxDNA2, the interaction between nucleotides takes into account sugar-phosphate backbone connectivity, sequence-dependent hydrogen-bonding, excluded volume, and different types of stacking strengths (such as nearest neighbor stacking, cross-stacking, and coaxial stacking between non-nearest neighbors), including different interaction strengths for the AA and TT stacking. The latter is particularly useful for capturing the effects of stacking in ssDNA bridges in G2-flex, since the poly-T sequence is used as a flexible linker between g_1 and g_2 . In addition, the oxDNA2 includes different widths for major and minor DNA grooves and a salt-dependent interaction term, in the potential for modeling electrostatic interactions. The base sequences are chosen to match the ones used in experiments, and hydrogen bonding between complementary pairs of nucleotides on opposite strands can spontaneously occur, resulting in the formation of a B-form double-helix. Simulation snapshots of the above-mentioned all-DNA dendrimers using oxDNA2 are presented in Figure 1B; the blue circles in the snapshots indicate the location of the stiff and flexible bridges in the G2 scaffold, respectively.

In this work, we additionally assess the robustness of our simulation results regarding the conformation and unconventional structural correlations of our all-DNA dendrimers by utilizing a bead-spring (BS) model^[44,45] (within the ESPResSo package),^[46,47] which reduces significantly many of the degrees of freedom of the DNA nucleotide compared to the oxDNA2 model (more details about the BS model can be found in Note S2, Supporting Information). This type of coarse-grained approach was successfully employed in previous work of ours in order to cap-

ture the conformational properties of isolated all-DNA stiff dendrimers with generations ranging from G1 to G7.^[35] Most of the simulation work described here focuses on the oxDNA2 model simulation results, unless otherwise stated.

2.2. Conformational Behavior of Rigid All-DNA Dendrimers with Controlled Internal Flexibility

Aiming at obtaining a rigorous insight into the intramolecular structural signatures associated with the site-specific positioning of flexible bridges within the stiff G2 scaffold, we perform a combination of small-angle X-ray scattering (SAXS) experiments in dilute aqueous solutions of G2-stiff and G2-flex molecules and molecular dynamics simulations of one isolated G2-stiff and G2-flex molecule based on the coarse-grained oxDNA2 model at fixed salt (NaCl) concentration ($c = 0.15$ M). The measured and simulated G2-stiff and G2-flex form factors (FF) are shown in Figure 2A–C.

The complete overlap of the experimental FF curves in Figure 2A, at the low scattering wavevector q region ($q \leq 0.02$ nm⁻¹), demonstrates that the overall dimension of the G2 dendrimer is not essentially affected by the replacement of the stiff bridges between the g_1 and g_2 with flexible ones. However, the observed dissimilarities at the intermediate- q region (0.02 nm⁻¹ $\leq q \leq 1.5$ nm⁻¹) highlight the effect of flexibility on the Y-DNA's inter-arm correlation within one single G2 dendrimer. While the FF of the G2-stiff construct shows oscillations in this q region, in the G2-flex case these are noticeable weaker, suggesting a more homogeneous monomer density at the g_1 to g_2 crossover. This effect can be ascribed to the back-folding of the outermost Y-DNA for the G2-flex. The simulated FFs capture rather well the main features of the experimental ones (Figure 2B,C), with a systematic deviation at $q > 1.0$ nm⁻¹. We attribute this discrepancy to the coarse-grained level present in the oxDNA2 model, which deviates from the experimental system on such small length scales. The molecular properties related to the overall size and shape of the simulated G2-stiff and G2-flex at two different salt (NaCl) concentrations (0.15 and 0.5 M) are summarized in the Experimental Section and in Table S1, Supporting Information. Both G2 molecules have similar sizes ($R_g \approx 9$ nm) and a rather disk-like shape, as can be seen from the corresponding ratios between gyration tensor eigenvalues and the relevant simulation snapshot in Figure 1C. In addition, G2-stiff and G2-flex demonstrate resilience in their shapes against increasing the salt concentration. Nevertheless, the data shown in Table S1, Supporting Information, suggests that the presence of the flexible bridges within the dendritic scaffold does result in a minor shrinkage and a tendency to deviate from the planar shape.

The quality of the comparison between simulations and experimental data offers us the possibility to exploit simulations to gain a deeper insight by looking at details of distributions and conformations within the dendritic scaffold. The internal structure of G2-stiff and G2-flex is quantified by obtaining the corresponding radial density distribution function $\rho(r)$ of monomers as a function of the distance r from the center of the mass of the G2-dendrimer. The total g_1 and g_2 monomer density profiles are depicted in Figure 2D. In both G2 molecules, the total monomer profile monotonically drops as one moves from the center of

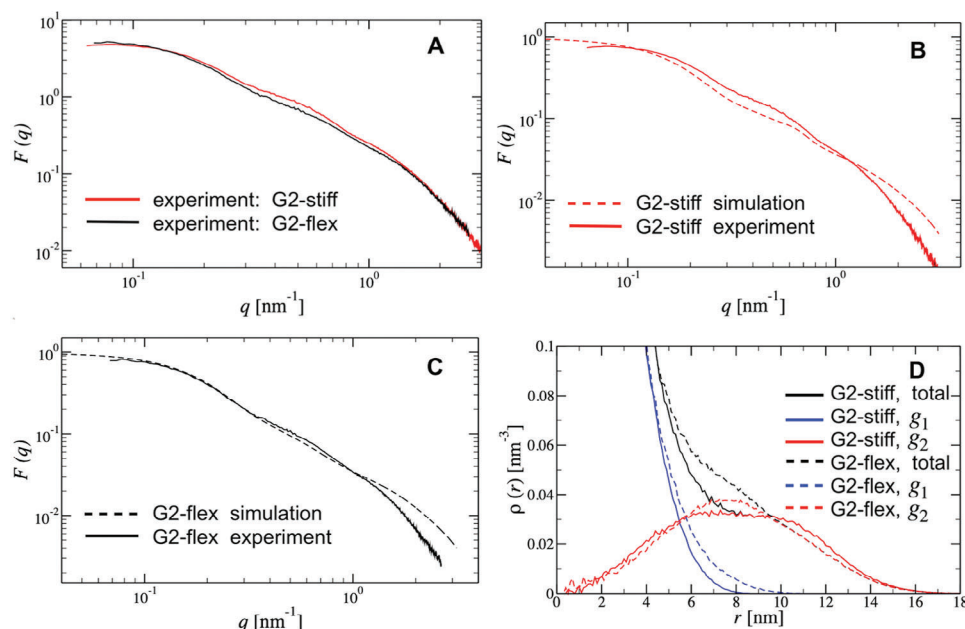


Figure 2. A) Form factor comparison between the G2-stiff and G2-flex measured in the experiment. B,C) Form factor comparison between oxDNA model and experiment for the G2-stiff (B) and G2-flex (C). D) Total density distribution function of nucleic acids, calculated within the oxDNA model for a single G2-stiff (solid lines) and a single G2-flex (dashed lines) dendrimer; together, the density distribution function of their corresponding subgenerations g_1 and g_2 is presented. The salt concentration is kept fixed at $c = 0.15$ M.

the molecule toward its periphery. However, in stark contrast to G2-flex, the G2-stiff exhibits a clear plateau at mid distances (6–10.5 nm), revealing a strong segregation between g_1 and g_2 . This is also manifested in the density profile of monomers belonging to g_2 , which remains rather flat and constant at these interparticle distances. Accordingly, the G2-flex features quite high local monomer packing in its interior compared to the G2-stiff. In addition, the overlap region between the monomer density profiles of g_1 and g_2 is noticeably wider for the G2-flex case, offering clear evidence that the flexible bridges in the G2 scaffold allow significant backfolding of the outer monomers toward the interior of the molecule.

Similar intramolecular correlations and overlap between subsequent subgenerations are also observed by employing the bead-spring model, as evidenced by the computed total g_1 and g_2 monomer density profiles of G2-stiff and G2-flex systems presented in Figure S2, Supporting Information (see also relevant discussion in Supporting Information [Note S2, Supporting Information]). However, contrary to the oxDNA2 model, the corresponding g_2 density profile shows a double-peak feature, suggesting that the spatial distribution of g_1 and g_2 is more coherent. Most probably, the source of this discrepancy can be attributed to the overestimation of the Y-DNA's arm stiffness and of the Y-DNA's junction point flexibility (see the constants of bending energy in the BS model, Note S2, Supporting Information).

2.3. All-DNA Dendrimers as Ultrasoft Colloids

Our previous work^[35] on the structural properties of all-DNA stiff dendrimers at a single particle level with sizes ranging from G1 to G7 revealed that their well-defined branched ar-

chitecture and their inherent rigidity endow these nanostructures with low internal monomer concentration, regular voids in their interior, and, at the same time, a resilience against the addition of salt. These features, together with the DNA's highly charged character, allow us to view these complex macromolecular assemblies as penetrable ultrasoft colloids,^[48] and they are expected to have a significant impact on their collective behavior. In the following sections, we show results on unconventional structural correlations present in concentrated solutions of G2 molecules. Through a combined SAXS and computer simulation study based on effective potentials, the mechanism responsible for the observed anomalous structure factor behavior in the G2-stiff system is identified.

2.3.1. SAXS Apparent Structure Factors

Let us first define a dimensionless measure of dendrimer density by introducing the packing fraction η as

$$\eta = \frac{4\pi N}{3V} R_g^3 \quad (1)$$

where N is the number of dendrimers in the sample volume V , each molecule having a gyration radius R_g . Measured static structure factors at room temperature for the G2-stiff dendrimers are shown in Figure 3A for concentrations below and above their overlap packing fraction. The apparent structure factor $S(q)$, resulting from the interparticle interactions of the G2-stiff molecules, is calculated assuming the validity of the relation $S(q) = I(q)/F(q)$, where $F(q)$ is the experimental form factor (Figure 2A) and $I(q)$ is the measured SAXS intensity by the aqueous saline solutions (0.01 M Tris, pH 8.0, 0.15 M NaCl) of moderately

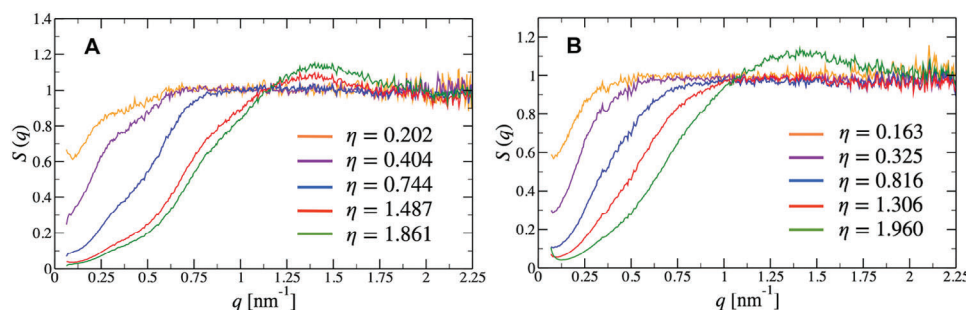


Figure 3. Experimental results for the structure factor $S(q)$ of concentrated solutions of all-DNA G2 dendrimers with A) rigid connections (G2-stiff) and B) flexible connections (G2-flex), at different packing fractions η with fixed salt concentration of $c = 0.15$ M.

concentrated all-DNA dendrimers normalized to the volume fraction. It should be stressed that the factorization of structure- and form-factors above is valid strictly only for systems whose constituent particles are rigid, that is, deprived of any internal fluctuations.

The structure factors of the stiff ds-DNA dendrimer solutions displayed in Figure 3A show the signature of ultrasoft effective interactions, which is the simultaneous suppression of the low- q value of $S(q)$ and the absence of a pronounced peak at finite q -values. Indeed, for the usual, strongly repulsive effective interactions, the two effects appear together since low compressibility (a long-wavelength property) is accompanied by the emergence of strong spatial correlations at finite length scales, whereas ultrasoft repulsive interactions result into incompressible systems lacking a pronounced spatial short-range order.^[1,49–51] For the case at hand, a peak indeed emerges, but the broad character of this peak and the corresponding spatial correlation value ($2\pi/q_{\text{peak}} \approx 4.83$ nm) indicate the presence of just a weak liquid-like positional order between overlapping G2-stiff molecules. Furthermore, the presence of this noticeable correlation peak at a finite wavevector is accompanied by a decrease in osmotic compressibility, given by the $S(q) \rightarrow 0$ limit, of the solution upon increasing the concentration. These characteristics are also present for the structure factors from concentrated flexible ds-DNA solutions shown in Figure 3B; accordingly, both systems are governed by ultrasoft interactions. However, the introduction of flexible junctions allows for further, detailed manipulation of these interactions with visible effects in the form of structural correlations, as we will show below.

The most interesting part of the $S(q)$ is the region of $q \leq 1.2$ nm^{−1}, where for the G2-stiff we observe a strikingly unexpected two-step increase, see Figure 3A. This anomalous structure factor behavior seems to be present already at low packing fractions η of G2-stiff, with the $S(q)$ being more structured for $\eta > 1.0$ as evidenced by the appearance of a broad peak at $q_{\text{peak}} \approx 1.3$ nm^{−1}. To the best of our knowledge, the above-mentioned peculiarity of $S(q)$ at low scattering wavevectors q is absent in traditional neutral or charged dendrimers.^[52–57] The distinctive difference between the low generation of these dendritic structures and our G2-stiff dendrimers is that the former are flexible and the latter are rigid. Therefore, to shed light on the mechanism behind the non-conventional behavior of the resulting $S(q)$ in G2-stiff molecules, their scaffold rigidity is reduced by altering the DNA structure at the interface between subsequent subgenerations. In the G2-stiff case (mid-panels in Figure 1A,B), the dsDNA stiff

bridges between g_1 and g_2 are replaced by ssDNA flexible ones, leading to the formation of its flexible counterpart, which we will refer to as G2-flex (the rightmost panels in Figure 1A,B). The corresponding concentration-dependent static structure factors are shown in Figure 3B. They are calculated following a procedure similar to the G2-stiff case, keeping the same ionic conditions. The results indeed reveal that, for sufficiently flexible bridges between subgenerations, the two-step increase of $S(q)$ disappears without affecting the liquid-like broad peak at high packing fractions ($\eta = 1.96$). To gain a deeper insight to the basic mechanism responsible for the effect of dendritic scaffold rigidity on the stabilization of the aforementioned anomaly in the development of the structure factor, we derive and analyze an effective dendrimer interaction approach to predict the structural correlations of concentrated all-DNA G2 molecules with controlled internal flexibility. Afterward, a direct comparison with experiments is feasible.

2.3.2. Effective All-DNA G2 Dendrimer Interactions

An efficient way to study the collective organization of G2 molecules in concentrated solutions is to render them as effective particles, interacting with a coarse-grained, effective potential that is calculated from the detailed interaction of two molecules under study. In order to calculate this effective interaction, the Widom insertion method is applied to the models of the G2-stiff and G2-flex system (see Experimental Section). In Figure 4, the calculated effective interaction between two G2-stiff dendrimers and as well as between two G2-flex dendrimers at two different salt concentrations ($c = 0.15$ M and $c = 0.5$ M) is presented. All effective potentials are shown as a function of the distance between molecules' centers-of-masses. In marked contrast to the minor overall size difference between the G2-stiff and G2-flex molecules, these two systems have strikingly different behavior in terms of effective interactions. Similar behavior is also observed by employing the significantly less refined coarse-grained BS model (see Figure S3, Supporting Information).

In Figure 4, it can be seen that all calculated potentials, besides being ultrasoft and short-ranged, are also salt- and dendrimer-type-sensitive. The softness of potentials is a direct consequence of the all-DNA-dendrimer's fractal nature, which allows a non-diverging interaction at overlapping separations. The short-range character of the effective interactions is a result of the screened electrostatic interactions between charged DNA segments. In both models studied, these electrostatic interactions are

incorporated through Yukawa screening potentials. This simplification is justified since both salt concentrations used in this work are high enough to allow the Debye–Hückel approximation.^[58] Therefore, the resulting effective interaction of G2-stiff and G2-flex dendrimers vanishes at interparticle distances slightly larger than $2R_g \cong 18$ nm and approaches zero with a Yukawa tail independent of the dendrimer type. Identical behavior is also observed in the bead-spring model, as shown in Figure S3, Supporting Information.

These bounded, ultrasoft interactions can be additionally tuned by solution salinity. The effective potentials for both types of dendrimers at a salt concentration of $c = 0.5$ M (blue curves, Figure 4), are smaller in all inter-dendrimer separations than the corresponding ones calculated at salt concentration of $c = 0.15$ M (red curves, Figure 4). This is rather expected since an increase in the salt concentration results in the screening of the Coulomb interactions between two like-charged objects, yielding to a reduced repulsion. Finally, the observed decrease in effective interactions upon addition of salt becomes more enhanced as the inter-dendrimer separation is decreased, indicating that electrostatics dominate over entropy.

The impact of the internal scaffold flexibility on the effective pair interactions of G2 dendrimers for a fixed salt concentration can be clearly seen in Figure 4. In the case of the dendrimers being in close proximity, the interpenetration of two G2-flex molecules becomes more energetically costly than that of the G2-stiff case. This is a direct consequence of the presence of significant fluctuations in the position and orientation of the outer arms of the G2-flex system. In contrast to the G2-stiff case, this internal flexibility permits the exploration of a wider range of available configurations when inter-penetration begins. Further inter-penetration of G2-flex molecules is accompanied by a significant re-orientation of their outer arms, adapting a more compact structure, which results in a higher energy penalty, whereas in G2-stiff molecules, rigidity prevents significant changes in their conformation. Moreover, since the monomer density in g_2 is low (Figure 2D), there is more available space for interpenetration without significant overlap of G2-stiff's arms, resulting in a smaller energy penalty compared to the G2-flex case. In the oxDNA2 model, the strength of the effective interaction at

the complete overlap of molecules changes and becomes higher for the G2-stiff (Figure 4), in contrast to the BS model case (Figure S3, Supporting Information). This energy difference between G2-stiff and G2-flex molecules becomes more pronounced at lower salt concentrations ($c = 0.15$ M). Apparently, at the complete dendrimer overlap state, the flexible bridges between the g_1 and g_2 in the charged G2-flex molecule play a key role in minimizing the unfavorable monomer contacts at the inter-dendrimer level and therefore the mutual electrostatic repulsion. This situation is clearly not captured by the BS model. However, despite this discrepancy, both the BS and the oxDNA2 model agree fairly well on the shapes and magnitudes of the potentials at both studied salt concentrations ($V_{\text{eff}}(0) \cong 5 \sim k_B T$ at $c = 0.5$ M for G2-stiff and G2-flex and $V_{\text{eff}}(0) \cong 8 \sim k_B T$ at $c = 0.15$ M for G2-flex).

It is particularly important to emphasize that the presence of flexible bridges between g_1 and g_2 (G2-flex system) has a marked effect on the resulting effective potential curves of all-DNA G2 dendrimers (Figure 4). More specifically, the effective interactions of G2-stiff molecules are initially changing slowly for large inter-particle separations, and then as the separation becomes smaller than the dendrimers' radius of gyration, the curves become significantly steeper. This indicates the presence of two characteristic length scales in the effective interaction of G2-stiff molecules, which is absent in the G2-flex case. The microscopic origin of such a behavior can be traced back to the monomer density profiles of G2-dendrimers, presented in Figure 2D. In contrast to the G2-flex case, where the radial monomer density distribution function $\rho(r)$ continuously increases as its center of mass is approached, the G2-stiff case exhibits a stagnation at intra-dendrimer distances between 6–11 nm. As a consequence, the interaction energy of G2-flex molecules is larger than that corresponding to the G2-stiff case in this range of interaction distances. Further approaching the center of the mass of the G2-stiff leads to a faster growth of density distribution function ($\rho(r)$ for $r \leq 6$ nm in Figure 2D) which results in an abrupt increase of the interaction energy ($V_{\text{eff}}(r)$ for $r \leq 6$ nm, see Figure 4). Our results, therefore, reveal that control over the internal flexibility of the dendritic scaffold can lead to the formation of dendrimers with tunable effective potentials, therefore controlling the shape of ultrasoft interactions via targeted flexibility of the intramolecular joints.

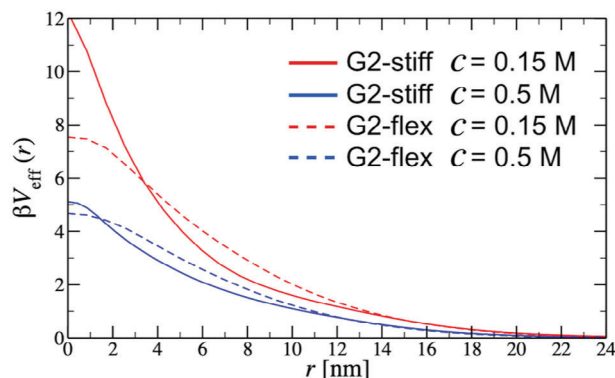


Figure 4. Effective pair interactions between two G2-stiff (solid lines) and between two G2-flex (dashed lines), calculated using Widom insertion method within oxDNA model and shown as a function of center-of-mass-to-center-of-mass separation r , at two different salt concentrations c .

2.3.3. Intermolecular Structural Correlations

The accuracy of the effective pair interaction model was tested in order to employ the calculated effective potentials to study the self-organization of G2-dendrimers in concentrated saline solutions. To achieve this, all-molecules simulations of the dendrimer's solutions are required for calculating the radial distribution functions between the centers of mass, which in turn will be compared with the corresponding radial distribution functions extracted from the effective model. The effective model refers to a system of effective particles that interact through the corresponding effective potentials. This methodology is applied to the oxDNA2 and bead-spring G2 dendrimer model, focusing only on the G2-stiff effective interactions for different salt concentrations and packing fractions η , defined in Equation (1).

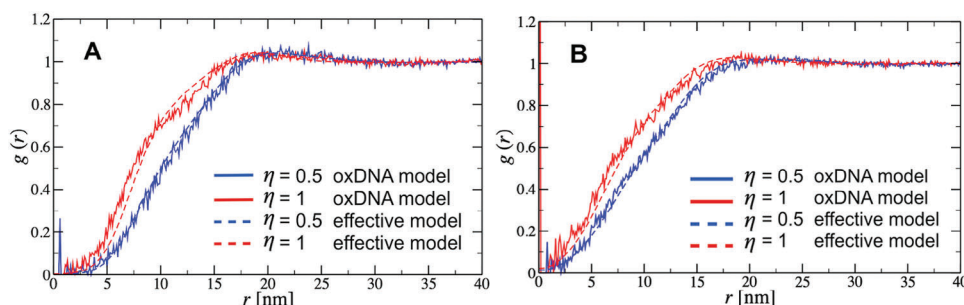


Figure 5. Radial distribution function comparison between explicit (oxDNA) and implicit (effective particles) MD simulations of solutions of G2-stiff simulated for different values of packing fraction η and at two different salt concentrations: A) $c = 0.15$ M and B) $c = 0.5$ M.

The G2-stiff radial distribution function $g(r)$ of the explicit oxDNA2 model and the corresponding implicit effective model at two different salt concentrations is presented in **Figure 5**. A similar comparison for the case of the bead-spring model is shown in **Figure S4**, Supporting Information, where access to high dendrimer packing densities ($\eta > 1$) is attained. A remarkable quantitative agreement between the results of explicit and implicit simulations for $\eta = 0.5$ and $\eta = 1.0$ is found. At this point, it should be stressed that above the dendrimers' overlap packing fraction ($\eta > 1.0$) the many body effects raise serious concerns regarding the effective model validity for accurately predicting the system's collective organization. Previous studies in charged branched macromolecular assemblies with star-like architecture^[59] suggested that three-body forces become important when the star concentration exceeds at least 3–4 times the overlap density. The discrepancy between the radial distribution functions of explicit (BS model) and implicit simulations for $\eta > 1.0$ and salt concentration of $c = 0.15$ M in **Figure S4**, Supporting Information, can be likely ascribed to the above-mentioned effect. In **Figure 5**, explicit $g(r)$ demonstrates the emergence of a characteristic length, $\lambda_c \approx 8$ nm, which corresponds to the position of a “shoulder” and gets more pronounced for higher packing fractions (**Figure S4**, Supporting Information). This feature is found in both salinities and matches nicely with the implicit simulation result for $c = 0.5$ M, however, it is not present in the implicit method for $c = 0.15$ M. Thus, precautions need to be taken when using the effective model to study highly concentrated all-DNA dendrimers at low salinity conditions. In this particular case, the validity of the model will be tested by the comparison between simulation and experimental results; this is discussed in **Section 2.3.5**.

In **Figure 5** and **Figure S4**, Supporting Information, the comparison of the simulation models (oxDNA2 and BS) and the calculated by the effective approach $g(r)$ demonstrates that the latter methodology, which employs a simple Widom insertion approach, can provide reliable results for dendrimer concentrations below the overlap packing value ($\eta = 1.0$). However, the G2-stiff radial distributions functions exhibit a behavior atypical for a normal liquid, in which the well-defined peaks are absent and the shape of $g(r)$ is reminiscent of an ultrasoft particles system. This weakly-correlated-liquid behavior is also encountered for $\eta > 1.0$. In addition, and independently from the coarse-grained level of the employed explicit models, the $g(r)$ shapes at packing fractions close to and above their overlap value reveal the presence of an unconventional structural organization that is more pronounced at the lower salt concentration ($c = 0.15$ M). This is

evidenced by the development of a two-step increase in $g(r)$ for $r < 15.0$ nm, and indicates that G2-stiff dendrimers exhibit an anomalous liquid-like behavior.

Finally, it is imperative to note that for the effective interaction calculation, the isotropy of the potential was presumed when averaging the interaction energy over the solid angles. This is somewhat counter-intuitive, since one would expect that this assumption is not valid for the anisotropic all-DNA G2 dendrimers with a disk-like shape (see **Figure 1**; **Figure S5**, Supporting Information, the simulation snapshots of the G2-stiff BS model at two packing fractions $\eta = 0.5$ and $\eta = 1.0$). Nevertheless, the obtained consistency between the corresponding radial distribution functions in **Figure 5** and **Figure S4**, Supporting Information, confirms the sufficiency of the used assumption. Moreover, when taking into account that those disks are hollow, formed by linear branches of DNA chains that change their orientation, the employment of a spherically symmetric pair potential between disk-like objects is not a rough approximation but becomes rather more reasonable choice.

2.3.4. Calculated Effective Structure Factors

The spherically averaged static structure factor $S(q)$ is calculated from the Fourier transform $\tilde{h}(q)$ of the pair correlation function $h(r) = g(r) - 1$ as $S(q) = 1 + (N/V)\tilde{h}(q)$. The results for increasing packing fractions of G2-stiff and G2-flex ($0.1 \leq \eta \leq 2.0$) at two different salt concentrations are presented in **Figure 6** ($c = 0.15$ M in **Figure 6A** and $c = 0.5$ M in **Figure 6B**). All structure factors are calculated from the coarse-grained model, employing the effective interaction calculated on the basis of the oxDNA2 model of G2 dendrimers. It is evident that for $\eta \leq 1.0$, the $S(q)$ in both types of G2 dendrimers displays the usual liquid-like behavior. The obtained structure factors at a salt concentration of $c = 0.15$ M exhibit a depression of the $S(q \rightarrow 0)$ value (**Figure 6A**), in agreement with a decrease in the osmotic compressibility of the solution upon increasing the concentration. As expected, an increase in salt concentration results in a more compressible system (**Figure 6B**, $c = 0.5$ M) due to the reduction of the inter-dendrimers' Coulomb repulsion. Additionally, at low salt concentrations, a weak and broad but detectable correlation peak at a finite wavevector appears for dendrimer concentrations above their overall packing value ($\eta > 1.0$).

However, in contrast to the G2-flex type of dendrimer, the G2-stiff exhibits an anomaly in the development of the structure

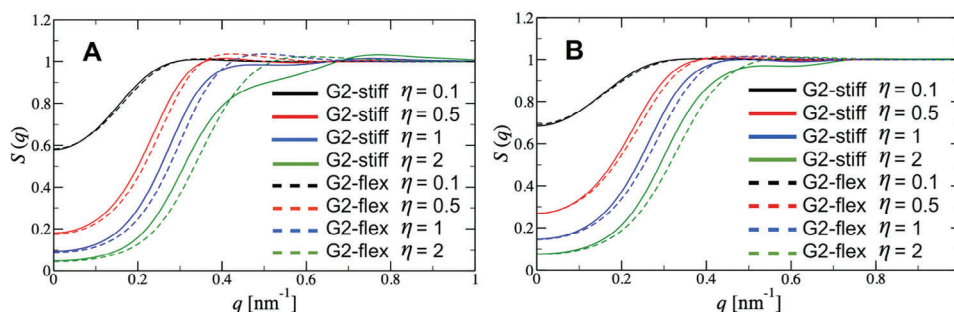


Figure 6. Structure factor of the solution of G2-stiff (solid lines) and G2-flex (dashed lines) calculated for different values of packing fraction η , at two different salt concentrations: A) $c = 0.15$ M and B) $c = 0.5$ M.

factor, namely a two-step increase. Upon increasing the salt concentration, the scattering wavevector q at which this change in the increase of $S(q)$ occurs is slightly shifted toward higher q - and $S(q)$ -values, as can be seen from the comparison between Figure 6A,B. This indicates that the screening of electrostatic interactions allows dendrimers to approach in closer proximity. At both salt concentrations and for packing fractions $\eta > 1.0$, these moderately concentrated G2-stiff solutions are characterized by structure factors whose weak correlation peak corresponds to positional correlations in the range of 7–9 nm, while the q -position of the reported anomaly indicates some level of self-organization in the range of 13–15 nm.

The two well-separated characteristic length scales mentioned above suggest the presence of two types of inter-dendrimer configurations. The longer length scale corresponds to a weak liquid-like positional order between neighboring G2-stiff molecules; the shorter one, however, indicates dendrimer interpenetration at overlapping distances, which correspond to the plateau region in the total density profile of an isolated G2-stiff dendrimer (Figure 2A), where a strong segregation between g_1 and g_2 takes place. This can be intuitively understood from the inherent rigidity of the dendritic arms and the low monomer density close to the dendrimer's center of mass. The energy penalty for the penetration of a G2-stiff dendrimer with a neighboring one is not prohibitively large due to the dendrimer's open-internal structure.

Once a small flexibility is introduced in the G2 system, the observed peculiar self-organization disappears. Driven by the tendency to maximize entropy and avoid high levels of packing frustration, the molecules with flexible connections (G2-flex) undergo shape and size fluctuations in the crowded environment, and therefore the configurations with such organized intertwined structures are prevented. Indeed, at high packing fractions, the G2-flex system does not display such anomalous structure factor behavior but rather an infinite-density ideal gas, where all correlations are smeared out due to the thermal fluctuations. Also, the maximum of the broad peaks in the corresponding $S(q)$ (dashed lines in Figure 6) systematically move toward larger q -values with increasing packing fraction, suggesting that the G2-flex slightly shrinks. Finally, for the same packing fraction, the maximum of these peaks is located at larger q -values compared to the G2-stiff system, implying that upon introducing flexibility in the scaffold of the G2 dendrimer the average inter-particle separation becomes smaller. The above mentioned impact of all-DNA dendritic scaffold rigidity in the calculated effective structure factors is

equally well captured with the significantly higher level of coarse-graining, BS model (see concentration- and salt-dependence of $S(q)$ in Figure S6, Supporting Information). Hence, this model independence in self-organization prediction highlights the robustness of the calculated result regarding the anomaly in the structure factor of G2-stiff and the physical origin of this unconventional behavior.

2.3.5. Experiment Versus Simulation

The comparison between the concentration-dependent structure factors $S(q)$ from SAXS experiments (Figure 3) and simulations (Figure 6) at a salt concentration $c = 0.15$ M NaCl demonstrates that simulation results match fairly well the experimental trends on a qualitative basis. However, in quantitative terms, the anomaly in the development of the structure factor and the weak maxima in the experimental $S(q)$ results occurred at noticeable higher values of the wavevector q compared to theoretical results. Furthermore, even though the correlation peak in $S(q)$ appears for $\eta > 1.0$ in both experiments and simulations, its intensity is significantly larger in the measured case. Similar deviations are also observed between measured and BS-based calculated $S(q)$ (Figure 3A; Figure S6A, Supporting Information, respectively). It should be noted that not only the effective models but also the all-particles-resolved simulations (Figure 5) were unable to accurately predict the height and q -position of the correlation peak in the measured $S(q)$. Most of these discrepancies can be attributed to the factorization approximation of the scattering intensity, $I(q) = F(q)S(q)$, the validity of which is subject to question^[60] once we approach the dendrimers' overlap concentration and diminish the rigidity of the dendritic scaffold (particle deformability). Therefore, in order to avoid a direct yet misleading comparison between these apparent and simulated structure factors from concentrated solutions of G2-stiff and G2-flex dendrimers, a comparison of scattering intensities has to be performed for densities below their overlap value.

In Figure 7, the experimentally measured and theoretically calculated scattering intensities of the G2-stiff and G2-flex dendrimers normalized to volume fraction as a function of q are displayed. The latter are obtained by applying the integral equation theory using the effective potential approach. The structure factor of the G2-stiff and G2-flex systems is extracted using the oxDNA2 model and the corresponding effective

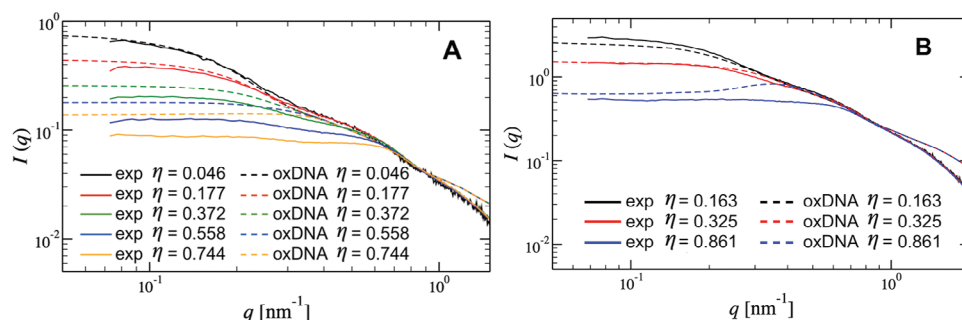


Figure 7. A comparison between total scattering intensities $I(q)$ normalized to the volume fraction η as function of q from experimental (exp) and simulated (oxDNA) A) G2-stiff and B) G2-flex systems, at salt concentration $c = 0.15$ M.

potentials (Figure 4). Together with the calculated form-factor from infinite dilution (Figure 2B,C), the theoretically scattering intensity is derived by the factorization formula. In the G2-stiff case, the agreement between intensities measured in the experiment and calculated in the simulation is excellent for the two lower packing fractions ($\eta < 0.2$) (Figure 7A). However, the onset of the discrepancy in the q -position of the peak in the scattering profiles starts to be detectable as the overlap density is approached. For packing fractions in excess of $\eta = 0.5$, an additional discrepancy regarding the osmotic compressibility is observed, indicating that the repulsion between G2-stiff molecules is significantly underestimated by the simulations. This is an indication that at this packing fraction, when crowding starts, the entropic contribution prevails, short-range, strongly repulsive steric interactions between the DNA strands are not taken into account properly by the oxDNA-model. For $q \geq 1.0 \text{ nm}^{-1}$, simulations fail to describe the measurements, most probably due to the coarse-grained level of the ox-DNA2 model, which affects the calculated form-factor (see also Figure 2C,D for $q \geq 1.0 \text{ nm}^{-1}$). Finally, it can be seen in Figure 7B, that a similar scattering intensity comparison between experiments and simulations is also present in the G2-flex system upon increasing the dendrimer's density. However, in contrast to G2-stiff, a very satisfactory agreement between measured and calculated compressibilities is observed, up to packing fractions of $\eta = 0.816$.

3. Conclusions

In this work, the impact of scaffold rigidity on ultrasoft interactions among all-DNA dendrimers was specifically assessed. In contrast to traditional dendrimers, the all-DNA dendritic construct is a unique, highly charged, void-containing macromolecular assembly^[35] which is afforded by the stiff character of the short dsDNA fragments consisting of the Y-DNA; the only building block from which these dendrimers are built. Through a combined experimental and simulation study, the structural organization of moderately concentrated solutions of all-DNA G2 dendrimers with stiff (G2-stiff) and with flexible patchy (G2-flex) internal structure was contrasted. The key structural investigation here has entailed the precise control of dendritic scaffold rigidity via the insertion of flexible single-stranded DNA domains between the core and the shell and then examining their role in the dendrimers' self-organization behavior.

Unambiguous evidence for the emergence of a novel anomalous liquid-like organization in concentrated aqueous solutions of G2-stiff dendrimers is provided. This is experimentally demonstrated as a two-step increase in the measured structure factors $S(q)$ as extracted from SAXS measurements. Site-specific weakening of dendrimer's scaffold rigidity, resulting in the fabrication of the G2-flex dendrimer, is found to be the key parameter for the complete suppression of this type of structural correlation pinpointing under what conditions this anomaly in the development of the structure factor happens. The experimental findings are in good, semi-quantitative agreement with simulations, despite the notable discrepancy regarding the q -position of this structural anomaly in $S(q)$. The latter seems to be associated with overestimation of the range of the electrostatic interactions in the simulated concentrated solutions of these charged all-DNA dendrimers, resulting in an observed overestimation of the relevant length scale. It nonetheless transpires that the extensive computer simulations performed, employing two G2 dendritic models with different levels of coarse-graining, demonstrate the validity of this unconventional type of self-organization and enable us to identify the interaction mechanisms that are key to the formation of the reported anomaly in the structure factor of G2-stiff dendrimers.

In particular, the structure factor behavior in the G2-stiff and G2-flex systems, which in turn encodes the effective interaction potential between the dendrimers, allows us to clearly distinguish these two types of ultrasoft particles despite the seemingly small internal structural difference. The G2-flex interaction follows a Gaussian core model scenario,^[49] which is driven by the properties of the bounded effective interactions at overlapping distances and follows only one scaling law. However, the G2-stiff interaction, besides being bounded, is also characterized by two length scales, which result in an anomalous structure factor above the overlap concentration. In the context of polymer stars, it has been proven that the existence of two length scales in the interaction energy is the cause of an anomalous structure factor in which the second peak is higher than the first one (see refs. [59, 61, 62]). However, in contrast to the polymer star case, the all-DNA G2 dendrimers experience a bounded interaction, and therefore the system at hand is unique in terms of effective interactions and self-organization behavior.

The intra-structure patterning of a particle with flexible patches at user-prescribed positions could substantially enrich the emerging bottom-up programmable self-assembly platform

based on the control of directionality in the non-covalent interactions between the constituent particles of a self-assembled system. Here, the above self-assembly concept is demonstrated for the all-DNA dendrimer case. The reported synthetic scheme is quite robust and modular since DNA permits profound control over the position and distribution of the flexible single-stranded domains within the dendritic scaffold with sub-nanometer precision. The most prominent examples include the combination of two different Y-DNA building blocks in tandem, one type terminated with sticky ends and the other with biorthogonal reaction pairs from the copper-free click-chemistry toolbox, to realize all-DNA dendrimers with alternate flexible-to-rigid shells. In a similar fashion, combining these two different types of terminal reactivity in a single Y-DNA building block could lead to the development of a new type of dendritic-based Janus particles with distinct softness faces. Further work on exploring the utility of all-DNA dendritic scaffolds toward these endeavors could pave the way to the engineering of novel ultrasoft interaction potentials that are absent in conventional soft-matter particles with isotropic softness.

4. Experimental Section

Synthesis and Characterization of All-DNA G2-Stiff and G2-Flex Dendrimer: Custom and modified (5'-phosphate, 5'-azide-PEG4, 5'-dbco-PEG4) oligonucleotides were purchased from Biomers (www.biomers.net) and purified by HPLC. The DNA concentration was determined by measuring the absorbance at 260 nm with a micro-volume spectrometer (NanoDrop 2000). Following the synthetic protocol described in ref. [35] all-DNA G2-stiff dendrimers were fabricated from double-stranded, three-armed Y-shaped DNA (Y-DNA) with sticky ends by combining a step-by-step base-pairing and enzyme-assisted assembly strategy. A strain-promoted alkyne-azide cycloaddition (SPAAC, copper-free click chemistry) reaction^[40] was employed for the fabrication of the G2-flex construct, using adide- and dbco-functionalized Y-DNA building blocks. The optimal ratio of reacting compounds was determined based on the protocols that were developed in ref. [26]. In the G2-flex case, the optimal ratio at which the electrophoresis experiment did not show any evidence of unreacted azide-Y-DNA was the mixing of dbco-Y-DNA and azide-Y-DNA in ratios of 7:1. The excess dbco-Y-DNA was removed using dialysis (Spectra/Pro, Float-A-Lyzer G2 dialysis device with molecular weight cutoff off 100 kDa). DNA sequences and construction schemes for synthesizing the all-DNA G2-stiff and G2-flex dendrimers are presented in Note S1, Supporting Information. Native polyacrylamide gel electrophoresis (PAGE) experiments were used to characterize the self-assembled G2-stiff and G2-flex dendrimers, an example of which is shown in Figure S1, Supporting Information. Only one band for each Y-DNAs building block involved in the dendrimer construction was detected, suggesting that they were properly formed. The desired all-DNA dendritic constructs migrated as single, sharp bands, with the G2-flex demonstrating undoubtedly slower mobility compared to the G2-stiff.

Experimental Systems Parameters: The all-DNA G2-stiff and G2-flex packing fraction η was estimated, in full agreement with its definition in Equation (1) for the theoretical approach, using the following expression

$$\eta = c_{\text{DNA}} \frac{4\pi N_A}{3M_w} R_g^3 \quad (2)$$

where c_{DNA} is the mass density of dendrimers, M_w represents the molecular weight of the dendrimer, in particular $M_w^{\text{G2-stiff}} = 112.67$ KDa, $M_w^{\text{G2-flex}} = 116.44$ KDa, R_g the radius of gyration from oxDNA-simulations ($R_g^{\text{G2-stiff}} = 9.4$ nm, $R_g^{\text{G2-flex}} = 9.1$ nm), and N_A is Avogadro's number. The

concentrated dendrimer solutions were prepared using Tris-HCl buffer (10 mM), pH 8.0 with 150 mM NaCl.

Small-Angle X-Ray Scattering (SAXS): SAXS experiments were carried out at the high brilliance galium anode low angle X-ray instrument (GALAXI) of the Jülich Center for Neutron Science (JCNS, Germany).^[63] A Dectris-Pilatus 1M detector with a resolution of 981×1043 pixels and a pixel size of $172 \times 172 \mu\text{m}^2$ was employed to record the 2D SAXS scattering patterns. The samples were measured at a sample-to-detector distance of 1.706 m with a flux of 10^9 photons/s/mm² at 0.3 mrad divergence of the beam at the sample position. The 1D-SAXS profiles were obtained by azimuthally-averaged radial scattering intensity of the 2D-SAXS images using the FIT2D software. The solutions were loaded into borosilicate glass capillaries (Hilgenberg) with a thickness of 2.0 mm.

oxDNA Simulations: Coarse-grained molecular dynamics simulations (MD) were carried out with the oxDNA2 simulation platform.^[43,64] To generate the G2-stiff and G2-flex dendrimer configurations, the experimental oligos sequences (Note S1, Supporting Information) were used as input. The single-stranded oligos were hybridized by applying a harmonic potential between complementary bases. A canonical ensemble simulation setup was employed at room temperature $T = 25^\circ\text{C}$ with periodic boundary conditions and a fixed Brownian thermostat. In the MD simulations, the timestep was set to $\Delta t = 0.001$ with a total of 10^9 steps, corresponding to a real time of 3.03×10^{-6} s.

Effective Interaction Simulations: To accelerate and save computational time when studying the all-DNA-dendrimer solutions, the Widom insertion method^[65] is employed to calculate effective interactions between two G2-stiff allDNA dendrimers as well as between G2-flex allDNA dendrimers. For that purpose, a single dendrimer was equilibrated and inserted into a large box in a fixed position. Another dendrimer of the same kind was added, having an uncorrelated configuration with the first one. The MD simulations were then performed keeping one dendrimer fixed while inserting the other one a large number of times, in particular for a total of 5×10^6 Widom insertions, to sample all possible random configurations and orientations for the wide range of center-of mass to center-of-mass separations. Let now s_i^M , $i = 1, 2$ denote the collective coordinates of the M monomers of dendrimers 1 and 2, and $V_{12}(s_1^M, s_2^M; r)$ denote the microscopic interaction potential between the monomers of the two different dendrimers at the instantaneous conformations s_1^M and s_2^M , under the constraint that their centers of mass have a separation r . The effective potential $V_{\text{eff}}(r)$ is obtained as^[65]

$$V_{\text{eff}}(r) = -k_B T \ln \left\langle e^{-\beta V_{12}(s_1^M, s_2^M; r)} \right\rangle_0 \quad (3)$$

where the averaging is performed over a non-interacting Hamiltonian between the two dendrimers. The obtained potential was then used as an effective interaction energy between point particles. The system of point particles interacting with the given potential was employed to mimic the solution of G2-stiff and G2-flex all-DNA-dendrimers.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Author Contributions

N.A. and C.J. performed simulations. C.N.L. co-designed research and supervised the work. E.S. co-designed the research and performed synthesis and experiments. All authors wrote the paper and commented on the manuscript.

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

dendrimers, DNA, DNA nanotechnology, flexible patches, self-assembly, ultrasoft particles

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OePG-CMD-JOINTMEETING 2026

75th Annual Meeting of the Austrian Physical Society
and
32nd Meeting of the Condensed Matter Division
of the European Physical Society

20 - 25 September 2026

University of Graz, Graz Center of Physics, Graz, Austria

Program & Abstracts



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	Monday (21)	Tuesday (22)	Wednesday (23)	Thursday (24)	Friday (25)
	MORNING	MORNING	MORNING	MORNING	MORNING
08:30-09:00	Opening				
09:00-10:00	Plenary 1 Riel	Plenary 4 Bocquet	Plenary 7 Pepper	Plenary 10 Shapiro	Plenary 13 Degerman
09:00-10:00	Plenary 2 Sinova	Plenary 5 Huber	Plenary 8 Seddon	Plenary 11 Gschwendtner	Plenary 14 tba
10:00-10:30	Coffee break	Coffee break	Coffee break	Coffee break	Coffee break
10:30-12:30	Mini-Colloquia Excursions M11 M12/1 M14 M23/1 M03/1 M28/1 M04/1 M32 M10/1 M39/1	Mini-Colloquia Award Ceremony M06/1 M19 M09 M23/2 M10/3 M28/2 M16 M29/1 M17/1	Mini-Colloquia AWS/ERC FAKT/2 M21/1 M01 M25 M05/1 M27/1 M06/2 M30 M12/3 M37/1	Mini-Colloquia OeAW M18/1 NESY/1 PIN M26/2 FAKT/3 M27/3 M05/3 M31/1 M06/3 M37/2 M13/1 M38/1 M42/1	Mini-Colloquia OGD/4 M29/5 COND4 M33/3 YM/3 M36 M37/3 M13/3 M41 M15/2 M42/3
12:30-13:30	Break	Break	Break	Break	Closing Remarks
13:30-14:30	Posters (PS1)	Posters(PS1)	Posters(PS2) OePG General Assembly	Posters (PS2)	
	AFTERNOON	AFTERNOON	AFTERNOON	AFTERNOON	
14:30-15:30	Plenary 3 Maurer	Plenary 6 Coclite	Plenary 9 Gull	Plenary 12 Reichert	
14:30-15:00	Semi-Plenary 1 Geerts	EurophysPrize Jungwirth	Semi-Plenary 3 Akrap	Semi-Plenary 5 Juraschek	
15:00-15:30	Semi-Plenary 2 Kowalczyk	EurophysPrize Šmejkal	Semi-Plenary 4 Giessen	Semi-Plenary 6 Rotter	
15:30-16:00	Coffee break	Coffee break	Coffee break	Coffee break	
16:00-18:00	Mini-Colloquia AKCP/1 M07/1 AMP M10/2 ENS M12/2 GEP M20/1 MBU M22/1 M03/2 M35 M04/2 M39/2	Mini-Colloquia AKCP/2 M08 COND/1 M10/4 FAKT/1 M17/2 LHS M20/2 OGD/1 M22/2 M02/1 M29/2 M07/2 M34/1	Mini-Colloquia COND/2 M21/2 OGD/2 M26/1 YM/1 M27/2 M02/2 M29/3 M05/2 M33/1 M07/3 M34/2 M12/4 M40	Mini-Colloquia COND/3 M18/2 NESY/2 M24 OGD/3 M29/4 YM/2 M31/2 M02/3 M33/2 M05/4 M38/2 M13/2 M42/2 M15/1 M18/2	
Sunday (20)					
Registration and Reception 16:00-20:00		OePG Board Meeting 18:00-19:30	Public Talk 18:30-19:30	Conference Dinner 18:30-22:00	

Poster Session PS1 (RESOWI building B+F):

[AKCP](#) [AMP](#) [MBU](#) [M02](#) [M03](#) [M08](#) [M09](#) [M10](#) [M11](#) [M12](#) [M19](#) [M20](#) [M23](#) [M35](#)

Poster Session PS2 (RESOWI building B+F):

[COND](#) [FAKT](#) [NESY](#) [OGD](#) [YM](#) [M01](#) [M05](#) [M18](#) [M24](#) [M27](#) [M29](#) [M30](#) [M33](#) [M37](#) [M42](#)

Selective formation of a cubic diamond is challenging due to the formation of competing phases possessing similar free energy. Examples of such are: stacking hybrids of interwoven hexagonal and cubic diamonds with (i) its liquid phase, (ii) arrested glasses, or (iii) clathrates, all depending on the relative patch size, despite being within the single association regime [1, 2]. The necessity to selectively achieve cubic diamond is of paramount importance since it exhibits a complete photonic bandgap at lower frequencies than the hexagonal counterpart, making it a promising candidate in view of photonic applications [3].

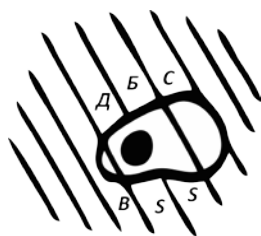
Herein, we demonstrate that due to the presence of an external field and by manipulation of its strength we can attain selectivity in the formation of a cubic diamond in a one-component system comprised of designer tetrahedral patchy particles, despite the formation of stacking hybrids in bulk. The driving force of such a phenomenon is the structure of the first adlayer which is commensurate with the (110) face of the cubic diamond [4].

In contrast, we show that the 1:1 mixture of identical patchy particles cannot selectively form the cubic diamond and always yields a mixture of both diamond phases, however, the emergence of stacking hybrids is observed for a wider range of patch sizes compared to the one-component system [5]. The reason for such a change in the growth mechanism is due to the frustrations present in the system that are manifested in the primary adsorption layer and propagate as the film grows.

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745	Effective interaction between two charged Janus colloids in an asymmetric ionic solution	Natasa Adzic	Contributed talk (11:45-12:00)
Natasa Adzic (1) Emanuela Bianchi (2) (1) Institute of Physics Belgrade, University of Belgrade, Serbia (2) TU Wien Recent studies of electrostatics in colloidal systems have increasingly addressed the complexity that inhomogeneous surface charge distributions introduce into self-assembly processes. However, approaches based on extensions of DLVO-like models remain valid only within the mean-field regime and are therefore mainly applicable to environments dominated by monovalent salts, [1]. In the work we present, we move beyond this limitation by developing a theory for anisotropically charged colloids that is applicable in regimes where mean-field theory fails, such as in salt mixtures containing polyvalent ions. When polyvalent ions are present, strong coupling effects emerge, leading to unconventional electrostatic phenomena such as like-charge attraction. While these effects are well documented for uniformly charged systems, their role in systems with anisotropic charge distributions remains largely unexplored. To address this problem, we consider a simplified model of Janus colloids immersed in a mixed ionic solution containing both monovalent and multivalent salts. Using a field-theoretic, path-integral approach, we derive effective electrostatic interactions that explicitly account for strong correlations and ionic asymmetry. This framework enables exploration of the full orientational dependence of pair interactions and provides a foundation for incorporating these effects into coarse-grained simulations. Our results contribute to a more comprehensive understanding of electrostatic self-assembly in complex ionic environments. [1] A. Gnidovec, E. Locatelli, S. Čopar, A. Božič and E. Bianchi, Natt. Comm., 16, 4277, 2025.			

M37 – Session 3 (Fri 25, 10:30-12:30, HS 15.11, Chair: Sebastian Fürthauer)			
ID	Title	Speaker	Type
80	Embryonic Origami: The forces driving human gastrulation	Diana Pinheiro	Invited talk (10:30-11:00)
Diana Pinheiro (1) (1) Research Institute of Molecular Pathology (IMP), Vienna Gastrulation represents a critical symmetry-breaking event in embryo development, culminating in the specification of all major cell types and the establishment of the body axes. Taking advantage of a two-dimensional (2D) in vitro system derived from human pluripotent stem cells, termed gastruloid discs, we are investigating the molecular and biophysical mechanisms driving human gastrulation. By establishing a high-throughput morphometric pipeline, we found that extraembryonic amnion cells adopt a squamous organization, while the differentiated epiblast remains largely columnar – recapitulating the shape signatures of the 3D human embryo. Through direct force measurements, biophysical modelling, and targeted perturbations, we found that the squamous transition in the amnion is driven by active wetting, i.e. a transition from tension to adhesion dominated cellular states. This is molecularly achieved via the rewiring of cytoskeletal composition in the amnion, from actomyosin to keratin-based networks. We are now investigating whether these shape changes are required for amnion specification and whether they are mechanically transmitted to the embryonic compartment. Overall, this multiscale approach is providing an entry point to understand the regulation and functional role of mechanical forces in human gastrulation.			
133	Phase Separating Nucleator in a Self Straining Active Filament Network	Jakob Schindelwig	Contributed talk (11:00-11:15)
Quentin Bodini-Lefranc (1,2) Sebastian Fürthauer (1) Jakob Schindelwig (1) (1) TU Wien (2) Ecole polytechnique Many membraneless compartments of cells, such as stress-granules, form via liquid-liquid phase separation. In cells many compartments of the same type and similar sizes can coexist. Since this is inconsistent with equilibrium phase separation physics, we ask if active mechanics could explain this observation. We develop a model coupling dynamics of the droplet material to an active self-straining filament network. This model shows (i) arrested coarsening , (ii)			



**11th Regional Biophysics
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BOOK OF ABSTRACTS

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A Dance Story of Two Anisotropically Charged Colloids in an Asymmetric Ionic Solution

Nataša Adžić¹, Emanuela Bianchi²

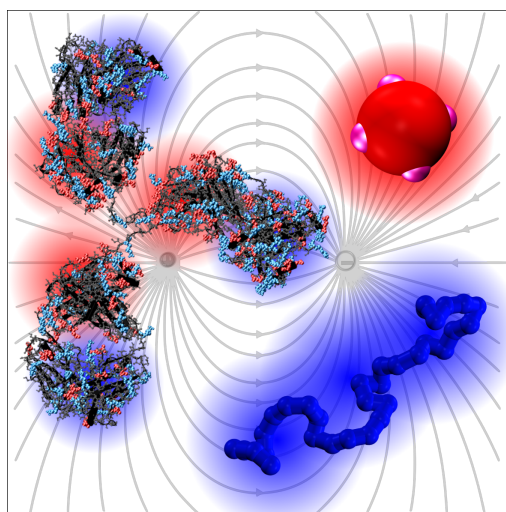
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Biomolecules in polar solutions acquire charge through the dissociation of ionizable groups or the adsorption of ions from the solvent. Their interactions are strongly influenced by the distribution of surrounding ions. Electrostatic interactions between charged colloids in ionic environments have been extensively studied, and most theoretical approaches rely on two key approximations: (i) the assumption of a homogeneous charge distribution on the colloids, and (ii) weak correlations between the colloidal charges and the surrounding ionic cloud. These approximations are typically valid in highly concentrated monovalent salt solutions, where mean-field theories provide an accurate description. Recently, mean-field theories have also been extended to inhomogeneously charged particles. However, a common limitation of these approaches is their inability to accurately predict colloidal interactions when even small amounts of polyvalent salt are added to the solution.

In this work, we address two key complexities that arise in charged biological systems: the anisotropy of colloidal charge and the asymmetry of the ionic environment. We develop a theoretical description based on the path-integral approach for the interaction between two Janus colloids immersed in a mixed ionic solution containing both monovalent and polyvalent salts. The obtained results provide insights beyond the mean-field approximation into the full orientational interaction landscape of two charged Janus particles.

Charged Soft Matter: Bridging Theory and Experiment



Erwin Schrödinger Institute
Vienna, Austria

September 8, 2025 – September 12, 2025

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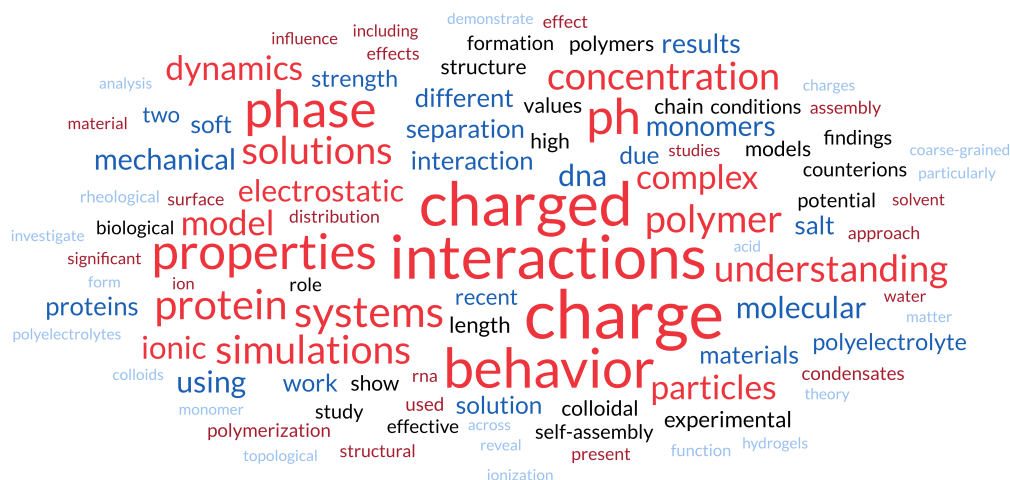
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Word cloud showing 100 most frequent words across all of the submitted abstracts, summing up to ~ 11000 words in total. The font size is proportional to the occurrence. Stop words, numerals and special symbols were removed.

Schedule

Monday, September 8

12:00 – 14:00	Registration
14:00 – 14:15	Opening & Information for the Participants
	Chair: Christos N. Likos
14:15 – 14:45	Peter Schurtenberger : Exploring charge effects in soft matter: responsive particles, shape anisotropy and the role of charge patches
14:45 – 15:15	Ilja Voets : On Complex(ed) Relations: the Power and Peculiarities of Nanoscopic Polyelectrolyte-based Particles
15:15 – 15:45	Jeetain Mittal : Wiggles to Flow: Multiscale Dynamics of Charged Protein Condensates
15:45 – 17:30	Welcome Reception

Tuesday, September 9

	Chair: Christos N. Likos
09:00 – 09:30	David Andelman : Remembering Rudi Podgornik: Charged liquids, electrified interfaces and more
09:30 – 10:00	Anže Božič : Evolutionary changes in charge on spike protein of SARS-CoV-2
10:00 – 10:30	Nataša Adžić : Field-theoretic approach to charged Janus colloids beyond mean field
10:30 – 11:00	Coffee Break
	Chair: Peter Košovan
11:00 – 11:30	Andreas Walther : Phase Separation of DNA: From Fundamentals to Artificial Cells
11:30 – 12:00	Ronald Larson : pH and Salt-Dependent Charging and Coacervation of Weak Polyelectrolytes: Hydrophobic Effects
12:00 – 12:30	Stefanie Schneider : Monte Carlo Simulations of pH-sensitive polyelectrolyte microgels
12:30 – 14:00	Lunch Break
	Chair: Roman Staňo
14:00 – 14:30	Matthias Ballauff : Driving Forces in the Formation of Biocondensates of Highly Charged Proteins
14:30 – 15:00	Hannes Ausserwöger : Biomolecular condensates sustain pH gradients at equilibrium through charge neutralisation
15:00 – 15:30	Coffee Break
	Chair: Emanuela Bianchi
15:30 – 16:00	Jeffrey Everts : The interplay between electric double layers and nematic order
16:00 – 16:30	Vitja Beltram : Charged Active Nematics

Talks

Field-theoretic approach to charged Janus colloids beyond mean field

Nataša Adžić (Institute of Physics Belgrade)

The self-assembly of charged biological entities is a topic of fundamental importance in both fundamental and applied sciences. Our current understanding of how uniformly charged particles, ranging from the nano- to micron-scale, interact in polar solvents with dissolved salts largely relies on the mean-field framework, i.e. DLVO theory. While recent extensions of DLVO-like models have incorporated particles with non-uniform charge distributions, their applicability remains limited primarily to conditions involving higher concentrations of monovalent salts.

This talk aims to address the self-assembly behavior of anisotropically charged colloids in solutions that also contain polyvalent ions. It is well established that the strong coupling between polyvalent salts and macroions can give rise to unusual electrostatic phenomena, such as like-charge attraction. However, the impact of these interactions on the phase behavior of anisotropically charged colloidal suspensions remains poorly understood.

To tackle this complex problem, we begin with a simplified model of charged Janus colloids immersed in an asymmetric ionic environment. By employing a field-theoretic approach, we derive the effective electrostatic interactions, which can then be incorporated into coarse-grained models suitable for simulation studies.

Remembering Rudi Podgornik: Charged liquids, electrified interfaces and more

David Andelman (Tel Aviv University)

The purpose of this talk is twofold. First, to highlight the significant contributions of the late Professor Rudolf Podgornik in five research areas: physics of DNA, virus capsids, Casimir effect, fluctuation-induced interactions, and the role of electric charge in soft matter systems. Second, to introduce two projects related to charged soft matter. (i) The surface tension of electrolytes has a history spanning a century, beginning with Onsager's groundbreaking work. This topic will be examined again using a field-theoretical approach that incorporates ionic specificity based on the Hofmeister series. (ii) The idea of charge regulation provides a more realistic way to understand biomolecules with charges that can dissociate into the surrounding water. Recent modeling of charge regulation will be presented, along with its applications to proteins, polyelectrolytes, and membranes.

Biomolecular condensates sustain pH gradients at equilibrium through charge neutralisation

Hannes Ausserwöger (University of Cambridge)

Electrochemical gradients are essential to the functioning of cells and form across membranes using active transporters. Here, we show in contrast that condensed biomolecular systems sustain significant pH gradients without any external energy input. By studying individual condensed droplets on the micron scale using a microdroplet platform, we reveal dense phase pH shifts towards conditions of minimal electrostatic repulsion. We demonstrate that by doing so protein condensates can drive substantial alkaline and acidic gradients which are compositionally tuneable and can extend to complex architectures sustaining multiple unique pH conditions simultaneously. Through in silico characterisation of human proteomic condensate networks, we further highlight potential wide ranging electrochemical properties emerging from condensation in nature, while correlating intracellular condensate pH gradients with complex biomolecular composition. Together, the emergent nature of condensation shapes distinct pH microenvironments, thereby creating a unique regulatory mechanism to modulate biochemical activity in living systems.

**21. СИМПОЗИЈУМ ФИЗИКЕ
КОНДЕНЗОВАНЕ МАТЕРИЈЕ**
**THE 21st SYMPOSIUM ON
CONDENSED MATTER PHYSICS**

BOOK OF ABSTRACTS



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14:30 — 15:00	Group-IV SiGeSn Alloys For Photonics and Electronics – Recent Progress	Z. Ikonić
15:00 — 15:30	Effect of Large Quantum Correlations in “Russian Doll” Quantum Dots: Impact on MEG Solar Cells	S. Tomić
15:30 — 15:45	A Nonequilibrium-Thermodynamics Perspective on Charge Separation in Organic Solar Cells	V. Janković
15:45 — 16:00	Soft Cluster Crystals in Simulation and Experiment	N. Adžić
16:00 — 16:30	How Can We Benefit From The Optical Properties Of Mn ⁵⁺ To Make Pigments And Near-Infrared Phosphors?	M. Dramićanin
16:30 — 16:50	Coffee break	

Chair***Stanko Tomić***

16:50 — 17:20	Fabrication of hybrid Janus particles and their application as light-driven micromotors	V. Djoković
17:20 – 17:50	Designing of a “perfect” porphyrin molecule for the Mechanically Controllable Break Junction Experiments	D. Dulić

Soft Cluster Crystals in Simulation and Experiment

N. Adžić^a, E. Stiakakis^b and C. N. Likos^c

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Abstract. Soft cluster crystals are unconventional state of matter, characterized with ordered periodic structures with multiple site occupancy. The number of overlapping building blocks in a cluster at each lattice site is not fixed but its expectation value depends on thermodynamic conditions, which makes this exotic phase to be a hybrid of solidity and fluidity. Soft cluster crystals were first discovered in a model of penetrable spheres [1] and their first experimental realization is achieved two decades later [2]. Here we show that experimental system that undergoes a phase transition from a cluster fluid to a body-centered-cubic cluster crystal and we discuss theoretical background of its self-assembly processes [3,4].

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1. Likos, C. N., Watzlawek, M. and Löwen, H. *Phys. Rev. E* **58**, 3135 (1998).
2. Stiakakis, E., Jung, N., Adžić, N., Balandin, T., Kentzinger, E., Rucker, U., Biehl, R., Dhont, J., Jonas, U., and Likos, C.N., *Nat. Commun.* **12**, 7167 (2021).
3. Likos, C. N., Lang, A., Watzlawek, M. and Löwen, H. *Phys. Rev. E* **63**, 031206 (2001).
4. Likos, C. N., Mladek, B.M. Gottwald, D. and Kahl, G. *J. Chem.Phys.* **126**, 224502 (2007).

**Coarse-graining the finer structure
of macromolecular interactions
Ljubljana, August 27–30, 2023**

About the symposium

The symposium "Coarse-graining the finer structure of macromolecular interactions," will take place in the vibrant city of Ljubljana, Slovenia, from August 27 to 30, 2023. This event aims to gather distinguished researchers, both experimentalists and theorists, from across the globe to delve into the most exciting prospects and challenges in the field. The main objective of the symposium is to foster an environment of intellectual exchange and collaboration, where the participants can share their insights and discoveries concerning macromolecular interactions. The symposium will feature a series of 30-minute talks, which will serve as the backbone of the event. Alongside the scheduled talks, plenty of time will be left for participants to engage in in-depth conversations, allowing for the exploration of ideas, novel approaches, and potential collaborations. Apart from the scientific program, attendees can enjoy the charming atmosphere of Ljubljana. The city's mix of history and modernity provides a perfect environment for networking and socializing.

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KEMIJSKI INŠTITUT

PROGRAM

Monday, August 28		
09:00	Matej Kanduč	Opening remarks
09:15	David Andelman	One Hundred Years of Modeling Electrolytes: What's New with the Theories of Debye and Onsager?
09:45	Vincent Démery	Pair Correlation in Out of Equilibrium Mixtures
10:30	<i>coffee break</i>	
	<i>(chair: X. Man)</i>	
11:00	Christian Holm	Simulating Acid-Base Equilibria in Polymeric Systems
11:30	Jalal Sarabadani	Polymer Translocation in an Environment of Active Rods
12:00	Daniel Harries	Determination of Thermodynamic Parameters in Molecular Simulations: Insights into Lipid Nanodiscs and Sugar Glass
12:30	<i>lunch break</i>	
	<i>(chair: G. Pabst)</i>	
14:00	Achille Giacometti	On the Effects of Chirality and Charge on the Stability of Liquid Crystal Phases
14:30	Ali Naji	Highly Tunable Casimir Interactions Mediated by Ferrofluids
15:00	Horacio V. Guzman	RNA Adsorption onto Flat and Membranous Substrates from Multiscale Models
15:30	<i>coffee break</i>	
	<i>(chair: A. Naji)</i>	
16:00	Şahin Büyükdaglı	Self-Consistent Analysis of Electrostatic Correlation Effects in Bulk and Nano-Confined Liquids with Composite Structure
16:30	Yevgeniy Mamasakhlisov	The Polyelectrolyte with a Disorder Over Short-Range Interactions
Tuesday, August 29		
	<i>(chair: M. Praprotnik)</i>	
09:00	Kurt Kremer	Playing with Entanglements to Structure Polymer Materials
09:30	Cristian Micheletti	Designed Self-Assembly of Molecular Knots, Links and Topological Gels
10:00	Xingkun Man	Onsager Variational Theory of Gel Swelling
10:30	<i>coffee break</i>	
	<i>(chair: L. Tubiana)</i>	
11:00	Roya Zandi	Virus Symmetry-Breaking, Elasticity and Self-Assembly
11:30	Nataša Adžić	All-DNA Constructs in a Construction of Unconventional State of Matter
12:00	Jure Dobnikar	Self-Assembly of Viral Capsids and Packing of Genome
12:30	<i>lunch break</i>	

ALL-DNA CONSTRUCTS IN A CONSTRUCTION OF UNCONVENTIONAL STATE OF MATTER

Nataša Adžić

Institute of Physics, Belgrade, Serbia

All-DNA constructs are macromolecules that are solely composed of short segments of DNA chains joined together to form dendrimeric structures [1]. We first take a look at equilibrium properties of a single molecule of various dendrimer generations immersed in an ionic solution at room temperature. The results extracted from simulation and experiment show how the given macromolecules exhibit a behavior atypical for other dendrimer families, classifying all-DNA constructs as good candidates for nanocarriers [2]. Then we delimit our study on the second generation of all-DNA constructs only and we investigate self-assembly of these molecules in dense solutions. Both theoretic and experimental results demonstrate that the system stays in a liquid phase characterized by an anomalous structure factor behavior. Last, we modify the structure of all-DNA constructs of the first and the second generation by inserting a polymer chain as a connector between two all-DNA building blocks. We show that self-assembly of these molecules leads to the formation of soft cluster crystals, periodic structures with multiple site occupancy [3].

- [1] Y. Li, Y. Tseng, and D. Luo, *Nat. Mater.* **3**, 38 (2004).
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- [3] E. Stiakakis, N. Jung, N. Adžić, T. Balandin, E. Kentzinger, U. Rucker, R. Biehl, J. Dhont, U. Jonas, and C. N. Likos, *Nat. Commun.* **12**, 7167 (2021).