Dynamics of Network Fluids

C. S. Dias, N. A. M. Araújo, and M. M. Telo da Gama

Departamento de Física, Faculdade de Ciências, Universidade de Lisboa, 1749-016 Lisboa, Portugal.
Centro de Física Teórica e Computacional, Universidade de Lisboa, 1749-016 Lisboa, Portugal

Abstract

Network fluids are structured fluids consisting of chains and branches. They are characterized by unusual physical properties, such as, exotic bulk phase diagrams, interfacial roughening and wetting transitions, and equilibrium and nonequilibrium gels. Here, we provide an overview of a selection of their equilibrium and dynamical properties. Recent research efforts towards bridging equilibrium and non-equilibrium studies are discussed, as well as several open questions.

Keywords: Network fluids, Dynamics, Non-equilibrium

1. Introduction

Structured fluids are fluids where the particle-particle correlations extend beyond the molecular scale. Prototypical examples are suspensions of colloidal particles, where the interactions between particles lead to the formation of mesoscopic structures that determine the physical properties of the system (e.g., rheological properties). Among the structured fluids are network fluids, where the anisotropic particle interactions lead to the formation of dynamical network-like structures consisting of chains and branches that are much larger than the individual particles [1, 2]. Such fluids exhibit exotic phase diagrams, including reentrant liquid-vapor or wetting transitions and low density (empty) liquids [3, 4, 5]. Examples of network fluids include, suspensions of cross-linked polymers [6, 7], and dipolar [8, 9, 10, 11, 12], Janus [13, 14, 15, 16, 17, 18], and patchy [19, 20, 21, 22, 23, 24, 25, 26, 27, 28, 29, 30, 31, 32, 33, 34, 35, 36, 37, 38, 39, 40, 41, 42, 43, 44, 45, 46, 47, 48, 49, 50, 51, 52] particles.

Here, we review some of the equilibrium properties of network fluids and focus on their dynamics. We discuss both the bulk [3, 53, 54] and interfacial properties [31, 55, 13]. The manuscript is organized in the following way. The interfacial properties of network fluids are discussed in Sec. 2, including self-assembly on substrates and at interfaces. The submonolayer regime is the focus of Sec. 3. In Sec. 4, the bulk properties are discussed. Experimental and theoretical works on the use of programmed annealing cycles to overcome kinetic barriers are discussed in Sec. 5. Finally, a few concluding remarks are made in Sec. 6.

2. Interfacial properties

The equilibrium and non-equilibrium properties of network fluids close to substrates or interfaces depend on the anisotropy and strength of the interactions, the temperature, and, for non-equilibrium, the overall dynamics. In one example, combining equilibrium Monte Carlo (MC) simulations and density functional theory (DFT) for three-patch colloidal particles near a hard wall, it was found that a contact region of higher density is formed close to the wall, whose maximum density depends on the temperature and bulk density [63]. At high bulk densities, the contact density decreases monotonically with the temperature, as an increase in the bond probability favors a decrease in density, due to the formation of a low density liquid. At sufficiently low bulk densities, the dependence of the contact density on temperature has a minimum at an intermediate temperature, as for very low temperatures, the bond probability approaches unity and an ordered, fully connected, quasi-2d structure is formed near the wall that sets a lower bound for the contact density [63].

Recent studies of the irreversible growth of patchy colloidal particles have uncovered phenomena such as rough-
Figure 1: Self-assembly of network fluids on substrates, or at interfaces, in the limits of irreversible (nonequilibrium) and reversible (equilibrium) binding, both from experiments and theory. (a) Gold and silica Janus particles on a substrate with a strong particle-particle interaction. Reproduced from Ref. [56] with permission from the Royal Society of Chemistry; (b) Functionalized silica particles at the interface of a water drop. Reproduced from Ref. [57]; (c) Simulations (Langevin dynamics) of three-patch colloidal particles at an attractive substrate. Reproduced from Ref. [58] with permission from the Royal Society of Chemistry; (d) Kinetic Monte Carlo simulations of three-patch colloidal particles at an interface. Reproduced from Ref. [59] American Physical Society; (e) Gold and silica Janus particles structure formation. Reproduced from Ref. [60] with permission from the Royal Society of Chemistry; (f) Polystyrene particles with gold patches confined in two dimensions. Reproduced from Ref. [61] with permission from the Royal Society of Chemistry; (g) Pattern obtained from Monte Carlo simulations of Janus particles on a substrate. Reproduced from Ref. [60] with permission from the Royal Society of Chemistry; (h) Monte Carlo simulation of inverse patchy colloidal particles in two dimensions. Reproduced from Ref. [62] with permissions from the American Chemical Society.

Figure 1: Self-assembly of network fluids on substrates, or at interfaces, in the limits of irreversible (nonequilibrium) and reversible (equilibrium) binding, both from experiments and theory. (a) Gold and silica Janus particles on a substrate with a strong particle-particle interaction. Reproduced from Ref. [56] with permission from the Royal Society of Chemistry; (b) Functionalized silica particles at the interface of a water drop. Reproduced from Ref. [57]; (c) Simulations (Langevin dynamics) of three-patch colloidal particles at an attractive substrate. Reproduced from Ref. [58] with permission from the Royal Society of Chemistry; (d) Kinetic Monte Carlo simulations of three-patch colloidal particles at an interface. Reproduced from Ref. [59] American Physical Society; (e) Gold and silica Janus particles structure formation. Reproduced from Ref. [60] with permission from the Royal Society of Chemistry; (f) Polystyrene particles with gold patches confined in two dimensions. Reproduced from Ref. [61] with permission from the Royal Society of Chemistry; (g) Pattern obtained from Monte Carlo simulations of Janus particles on a substrate. Reproduced from Ref. [60] with permission from the Royal Society of Chemistry; (h) Monte Carlo simulation of inverse patchy colloidal particles in two dimensions. Reproduced from Ref. [62] with permissions from the American Chemical Society.

Figure 1: Self-assembly of network fluids on substrates, or at interfaces, in the limits of irreversible (nonequilibrium) and reversible (equilibrium) binding, both from experiments and theory. (a) Gold and silica Janus particles on a substrate with a strong particle-particle interaction. Reproduced from Ref. [56] with permission from the Royal Society of Chemistry; (b) Functionalized silica particles at the interface of a water drop. Reproduced from Ref. [57]; (c) Simulations (Langevin dynamics) of three-patch colloidal particles at an attractive substrate. Reproduced from Ref. [58] with permission from the Royal Society of Chemistry; (d) Kinetic Monte Carlo simulations of three-patch colloidal particles at an interface. Reproduced from Ref. [59] American Physical Society; (e) Gold and silica Janus particles structure formation. Reproduced from Ref. [60] with permission from the Royal Society of Chemistry; (f) Polystyrene particles with gold patches confined in two dimensions. Reproduced from Ref. [61] with permission from the Royal Society of Chemistry; (g) Pattern obtained from Monte Carlo simulations of Janus particles on a substrate. Reproduced from Ref. [60] with permission from the Royal Society of Chemistry; (h) Monte Carlo simulation of inverse patchy colloidal particles in two dimensions. Reproduced from Ref. [62] with permissions from the American Chemical Society.

Figure 1: Self-assembly of network fluids on substrates, or at interfaces, in the limits of irreversible (nonequilibrium) and reversible (equilibrium) binding, both from experiments and theory. (a) Gold and silica Janus particles on a substrate with a strong particle-particle interaction. Reproduced from Ref. [56] with permission from the Royal Society of Chemistry; (b) Functionalized silica particles at the interface of a water drop. Reproduced from Ref. [57]; (c) Simulations (Langevin dynamics) of three-patch colloidal particles at an attractive substrate. Reproduced from Ref. [58] with permission from the Royal Society of Chemistry; (d) Kinetic Monte Carlo simulations of three-patch colloidal particles at an interface. Reproduced from Ref. [59] American Physical Society; (e) Gold and silica Janus particles structure formation. Reproduced from Ref. [60] with permission from the Royal Society of Chemistry; (f) Polystyrene particles with gold patches confined in two dimensions. Reproduced from Ref. [61] with permission from the Royal Society of Chemistry; (g) Pattern obtained from Monte Carlo simulations of Janus particles on a substrate. Reproduced from Ref. [60] with permission from the Royal Society of Chemistry; (h) Monte Carlo simulation of inverse patchy colloidal particles in two dimensions. Reproduced from Ref. [62] with permissions from the American Chemical Society.

Figure 1: Self-assembly of network fluids on substrates, or at interfaces, in the limits of irreversible (nonequilibrium) and reversible (equilibrium) binding, both from experiments and theory. (a) Gold and silica Janus particles on a substrate with a strong particle-particle interaction. Reproduced from Ref. [56] with permission from the Royal Society of Chemistry; (b) Functionalized silica particles at the interface of a water drop. Reproduced from Ref. [57]; (c) Simulations (Langevin dynamics) of three-patch colloidal particles at an attractive substrate. Reproduced from Ref. [58] with permission from the Royal Society of Chemistry; (d) Kinetic Monte Carlo simulations of three-patch colloidal particles at an interface. Reproduced from Ref. [59] American Physical Society; (e) Gold and silica Janus particles structure formation. Reproduced from Ref. [60] with permission from the Royal Society of Chemistry; (f) Polystyrene particles with gold patches confined in two dimensions. Reproduced from Ref. [61] with permission from the Royal Society of Chemistry; (g) Pattern obtained from Monte Carlo simulations of Janus particles on a substrate. Reproduced from Ref. [60] with permission from the Royal Society of Chemistry; (h) Monte Carlo simulation of inverse patchy colloidal particles in two dimensions. Reproduced from Ref. [62] with permissions from the American Chemical Society.

Dynamics of this model, for particles with only one patch, was investigated for diffusive [69] and ballistic transport [70]. By decreasing the size of the patch, an absorbing phase transition was found, also in the Directed Percolation universality class.

Mixtures have been also considered. There are two types of mixtures: mixtures of particle or patch types. The former consists of mixing, at least, two types of particles. A common choice is to consider mixtures of particles of two and more than two patches [3, 71]. The idea is to control the branching rate, since two-patch colloidal particles only form chains and colloidal particles with more patches promote branching. A study based on local density approximation of multilayer stacking of this type of binary mixtures in a gravitational field has shown stacking diagrams with different stacking sequences [72]. The authors studied the effect of the finite thickness of the stacked film on the occurrence of stacks of different layers during sedimentation. A study of the dynamics of sedimentation is...
still lacking. Numerical studies of the dependence on the mechanism of mass transport of binary mixtures towards the substrate have been performed [64]. For diffusive transport, the density of the multilayer film has a non-monotonic dependence on the ratio of two- and three-patch particles, with a maximum at an intermediate ratio. This non-monotonic behavior is a consequence of the competition between the density-reducing mechanism of chain formation and an increase of the number of patch-patch bonds per particle, by reducing the steric effects. For ballistic transport, the density decreases monotonically with the ratio and, intriguingly, it is in the same range as the bulk density at the spinodal [9].

For mixtures of patch types, particles have been considered to have patches of two different interaction energies that are distributed with one type in the poles and the other around the equator. In this case, the competition between branching and chaining depends on the energy ratio between the two types of patches. Using a mesoscopic Landau-Safran theory, Bernardino et al. [5] have shown that the wetting behavior of these network fluids near substrates is characterized by a non-monotonic surface tension, two wetting transitions, and a wetting transition followed by a drying transition. These interfacial properties can be related to the bulk ones for these type of network fluids [74]. Studies of the dynamics have considered 2AnB patchy colloidal particles (2 patches of type A in the poles and n patches of type B along the equator) [73]. The irreversible aggregation on an attractive substrate of 2A9B patchy colloidal particles can lead to non-monotonic behavior of the density near the substrate as a function of the film thickness depending on the number of patches and energy ratio [74]. For two-dimensional 2A2B patchy colloidal particles (disks), the interfacial roughening changes from a Kardar-Parisi-Zhang universality class (KPZ) to a KPZ with quenched disorder for B/A energy ratios much lower than unity [55].

Most studies of the dynamics of interfaces have considered irreversible bonds and neglected relaxation. However, if one waits long enough, the interfaces are expected to relax to equilibrium [5]. The bridge between these two limits is still illusive as it encompasses numerical and theoretical challenges. One step towards closing this gap is the study of the submonolayer regime as discussed in the next section.

3. Submonolayer dynamics

The submonolayer regime is simpler to study, not only from the numerical point of view, but also from the experimental one, as it is possible to follow the dynamics of individual particles using conventional optical techniques. Experimentally, submonolayer studies have considered, for instance, the adsorption on flat and patterned substrates to direct self-assembly into ordered structures [75 76], or the control of the interface curvature to modify the effective interaction between particles [52 77]. From the equilibrium point of view, numerical and mean-field phase diagrams have shown quantitative agreement in certain limits [71 78 43 79]. More recently, it was shown that it is possible to tune the submonolayer assembly of aggregates of heterogeneously charged colloidal particles by confining them between two walls, where one of the walls can be electrically charged to promote adsorption [80 62].

For mixtures of dipolar colloidal particles, in the presence of an external electric field, the submonolayer dynamics is characterized by the formation of a spanning aggregate in both directions parallel and transverse to the field. The dynamics of this aggregate is characterized by a critical slowing down, leading to a power-law decay of the bond correlation function [61 8]. This type of decay is also observed for three-patch colloidal particles on an attractive substrate, which has been related to a percolation transition [55], in the limit where patch-patch bonds are practically irreversible. In this limit, the final arrested structures are significantly different from the thermodynamic ones, and the possible kinetic pathways to overcome them will be discussed in Sec. 5. Also, a study of two systems of three-patch and six-patch colloidal particles, respectively, revealed that the dynamics strongly influences the initial growth regime [51]. The authors compared particles with mobile bonds (no fixed orientation over time) and particles with fixed bonds (fixed orientation over time). They showed that the final cluster is fully connected for the free bonds by contrast to the fixed bonds case, where only a fraction of the total possible bonds are established.

4. Bulk dynamics

The bulk equilibrium phase diagrams of the three models of patchy particles presented in the previous section have been studied in detail [3 52]. For three-patch colloidal particles and mixtures of two- and three-patch colloidal particles, a low density (empty) liquid phase is observed [5]. When the interaction between particles has two energy scales, a competition between chain and branch formation leads to an unconventional phase diagram [52], with a reentrant liquid-vapor phase transition. Noteworthy, if the assembly of rings is taken into account, two critical points may be observed [52]. One of the most exciting features of network fluids is the possibility of obtaining low-density equilibrium gels [54 55 56 57 58], as the percolation line in the phase diagram goes above the coexistence line. This allows for reversible gels outside the phase coexistence region [54]. A relation between temperature, in the reversible limit and time, in the irreversible limit (chemical bonds) was found [90]. This is still a very active field of research, where dynamical properties such as the mean square displacement, intermediate scattering functions, and van Howe function are measured for suspensions of various types of patchy particles [91 92 93 94 95 96 97 98].
All previous results, both for equilibrium and dynamical properties, show that network fluids are very rich systems from the scientific and technological point of view. Despite that, most studies have focused on the mechanisms of reversibility of bond formation and chaining versus branching. This is just one pair of all mechanisms that play a role in the dynamics. Future studies need to consider how the collective motion of particles inside the network can influence structure formation, how the rotational diffusion of patches can affect the relaxation dynamics, how concerted moves and crowding effects can alter the dynamics, and how the effect of large basins on the energy network fluids can trap structures into dynamically arrested configurations. An example of the latter can be found in Fig. 2 where independently of the initial conditions, the dynamics evolves through a configuration that is significantly different from what is predicted from purely thermodynamic arguments [99].

5. Annealing cycles

The idea of performing annealing cycles has been proposed as a kinetic pathway to avoid large kinetic barriers and access thermodynamic structures of micron size and nanoparticles [10]. The necessity to synthesize structures that are mechanically and thermally stable requires strong interparticle bonds. However, the stronger the bonds, the harder it becomes to relax towards thermodynamically stable structures. To surpass this challenge, the idea of the annealing cycles is to perform protocols of switching on and off the bonds to promote the relaxation towards equilibrium. For that end, the particles need to be functionalyzed with different types of molecules that actively react to external perturbations such as, e.g., light and temperature, or changes in pH, oxidation-reduction, and solubility.

One of the most promising routes is the functionalization of colloidal particles with DNA [100, 101, 102, 103, 104, 105, 106]. DNA allows a fine tunning of the interparticle interaction strength, by increasing or decreasing the number of nucleotides, and selectivity of the interactions, by changing the sequence of nucleotides. From a dynamical point of view, the most important characteristic of DNA molecules is the abrupt melting transition at a well defined temperature. This characteristic allows switching on and off bonds through light (UV/blue) [107] or temperature [108, 109, 110, 111] cycles, which can even lead to two melting temperatures due to a competition between inter-particle bonds at intermediate temperatures and intra-particle bonds at low temperature [112]. Numerical results suggest that there is an optimal annealing frequency at which three-patch colloidal particles on a substrate self-assemble into a honeycomb structure [64].

6. Final remarks

In this overview, we discussed recent findings in the field of network fluids, regarding both equilibrium and non-equilibrium properties. The solid framework of equilibrium physics provided the tools to study their equilibrium phase diagrams. However, the lack of an equivalent non-equilibrium framework, requires the development of new methods and tools to analyze the dynamics. Given the typically strong bonds, of the order of several $k_B T$, currently available techniques fail to access the time and length scales at which most relaxation processes occur. Thus, most studies of the dynamics have considered irreversible bond formation or very short time periods. Clearly, there are still many open questions regarding the dynamics of network fluids.

In order to investigate numerically the dynamics it is mandatory to coarse grain the local interactions, averaging the fast processes and following the rare events. A catalog of the relevant processes is needed. Only with such a catalog, will it be possible to investigate the feasibility of the thermodynamically stable structures, identify kinetically trapped structures and their stability, and develop rules to control the dynamics of the self-organization of network fluids.

Acknowledgments

We acknowledge financial support from the Portuguese Foundation for Science and Technology (FCT) under Contracts nos. EXCL/FIS-NAN/0083/2012, UID/FIS/00618/2013, and IF/00255/2013.

References

[1] T. Witten, Structured fluids, Phys. Today 43 (1990) 28.
[2] T. A. Witten, P. A. Pincus, Structured fluids: polymers, colloids, surfactants, Oxford University Press, Oxford, 2004.
[3] E. Bianchi, J. Largo, P. Tartaglia, E. Zaccarelli, F. Sciortino, Directed self-assembly, Soft Matt. 9 (2013) 9039.
[4] S. H. L. Klapp, Collective dynamics of dipolar and multipolar colloids: from passive to active systems, Curr. Op. Coll. Interf. Sci. 21 (2016) 76.
[5] W. H. Stockmayer, Theory of Molecular Size Distribution and Gel Formation in Branched-Chain Polymers, J. Chem. Phys. 11 (1943) 45.
[6] E. M. Furst, Directed self-assembly, Soft Matt. 9 (2013) 9039.
[7] N. R. Bernardino, M. M. Telo da Gama, Reentrant wetting of network fluids, Phys. Rev. Lett. 109 (2012) 114103.
[8] T. A. Witten, Associating polymers and shear thickening, J. Phys. France 49 (1988) 1055.
[9] F. Sciortino, Reentrant phase diagram of network fluids, Phys. Rev. Lett. 106 (2011) 085703.
[10] J. Russo, J. M. Tavares, P. I. C. Teixeira, M. M. Telo da Gama, F. Sciortino, Reentrant phase diagram of network fluids, Phys. Rev. Lett. 106 (2011) 085703.
[11] N. R. Bernardino, M. M. Telo da Gama, Reentrant wetting of network fluids, Phys. Rev. Lett. 109 (2012) 114103.
[12] T. Witten, Structured fluids, Phys. Today 43 (1990) 28.
Figure 2: Snapshots of the time evolution of a network fluid of three-patch colloidal particles starting from two different initial conditions. Top: Fully connected initial state and Bottom: Unconnected random initial state.
chains, rings, and branches: A single component system with two critical points, Phys. Rev. Lett. 111 (2013) 168302.

[84] F. Sciortino, E. Zaccarelli, Reversible gels of patchy particles, Curr. Op. Coll. Interf. Sci. 15 (2011) 246.

[85] B. Ruzicka, E. Zaccarelli, L. Zulian, R. Angelini, M. Sztucki, A. Moussaïd, T. Narayanan, F. Sciortino, Observation of empty liquids and equilibrium gels in a colloidal clay, Nat. Mater. 10 (2011) 56.

[86] E. Zaccarelli, Colloidal gels: equilibrium and non-equilibrium routes, J. Phys.: Condens. Matter 19 (2007) 323101.

[87] E. Zaccarelli, I. Saika-Voivod, A. J. Moreno, P. Tartaglia, F. Sciortino, Gel to glass transition in simulation of a valence-limited colloidal system, J. Chem. Phys. 124 (2006) 124908.

[88] E. Zaccarelli, I. Saika-Voivod, A. J. Moreno, I. Saika-Voivod, F. Sciortino, P. Tartaglia, Modell for reversible colloidal gelation, Phys. Rev. Lett. 94 (2005) 218301.

[89] S. Corezzi, C. De Michele, E. Zaccarelli, P. Tartaglia, F. Sciortino, Connecting irreversible to reversible aggregation: Time and temperature, J. Phys. Chem. B 113 (2009) 1233.

[90] S. Corezzi, C. De Michele, S. Corezzi, D. Fioretto, F. Sciortino, Chemical and physical aggregation of small-functionality particles, Soft Matt. 8 (2012) 11267.

[91] S. Corezzi, C. De Michele, E. Zaccarelli, D. Fioretto, F. Sciortino, A molecular dynamics study of chemical gelation in a patchy particle model, Soft Matt. 4 (2008) 1173.

[92] S. Corezzi, D. Fioretto, C. De Michele, E. Zaccarelli, F. Sciortino, Modeling the Crossover between Chemically and Diffusion-Controlled Irreversible Aggregation in a Small-Functionality Gel-Forming System, J. Phys. Chem. B 114 (2010) 3769.

[93] C. De Michele, S. Gabrielli, P. Tartaglia, F. Sciortino, Dynamics in the presence of attractive patchy interactions, J. Phys. Chem. B 110 (2006) 8064.

[94] S. L. Elliott, R. J. Butera, L. H. Hanus, N. J. Wagner, Fundamentals of aggregation in concentrated dispersions: fiber-optic quasielastic light scattering and linear viscoelastic measurements., Faraday discuss. 123 (2003) 369.

[95] F. Sciortino, C. De Michele, S. Corezzi, F. Sciortino, A parameter-free description of the kinetics of formation of loop-less branched structures and gels, Soft Matt. 5 (2009) 2571.

[96] R. J. Speedy, P. G. Debenedetti, Persistence time for bonds in a tetraevant network fluid, Mol. Phys. 86 (1995) 1375.

[97] S. Roldan-Vargas, L. Rovigatti, F. Sciortino, Connectivity, Dynamics, and Structure in a Tetrahedral Network Liquid, Soft Matt. 13 (2017) 514.

[98] L. Rovigatti, F. Sciortino, Self and collective correlation functions in a gel of tetrahedral patchy particles, Mol. Phys. 109 (2011) 2889.

[99] C. S. Dias, J. M. Tavares, N. A. M. Araújo, M. M. Teló da Gama, Temperature driven dynamical arrest of a network fluid: the role of loops arxiv: 1604.09279.

[100] M. E. Leunissen, D. Frenkel, Numerical study of DNA-functionalized microparticles and nanoparticles: Explicit pair potentials and their implications for phase behavior, J. Chem. Phys. 134 (2011) 084702.

[101] N. Kern, D. Frenkel, Fluid-fluid coexistence in colloidal systems with short-ranged strongly directional attraction, J. Chem. Phys. 118 (2003) 9882.

[102] D. Frenkel, D. J. Wales, Colloidal self-assembly: Designed to yield, Nat. Mater. 10 (2011) 410.

[103] A. Reinhardt, D. Frenkel, Numerical evidence for nucleated self-assembly of DNA brick structures, Phys. Rev. Lett. 112 (2014) 238103.

[104] S. Angioletti-Uberti, P. Varilly, B. M. Mognetti, D. Frenkel, Mobile linkers on DNA-coated colloids: Valency without patches, Phys. Rev. Lett. 113 (2014) 128303.

[105] N. Geerts, E. Eiser, DNA-functionalized colloids: Physical properties and applications, Soft Matt. 6 (2010) 4647.

[106] L. Di Michele, D. Fiocco, F. Varrato, S. Sastry, E. Eiser, G. Foffi, Aggregation dynamics, structure, and mechanical properties of bigels, Soft Matt. 10 (2014) 3633.

[107] A. Bergen, S. Rudik, M. Morel, T. Le Saux, H. Ihmels, D. Baigl, Photodependent Melting of Unmodified DNA Using a Photosensitive Intercalator: A New and Generic Tool for Photoreversible Assembly of DNA Nanostructures at Constant Temperature, Nano Lett. 16 (2016) 773.

[108] J. Maligne, F. Mousseau, D. Zanchi, G. Brun, C. Tribet, E. Marie, Tailored stimul-reversible interaction between particles adjusted by straightforward adsorption of mixed layers of Poly(lysine)-g-PEG and Poly(lysine)-g-PNIPAM on anionic beads, J. Colloid Interf. Sci. 461 (2016) 50.

[109] C. A. Mirkin, R. L. Letsinger, R. C. Muic, J. J. Storhoff, A DNA-based method for rationally assembling nanoparticles into macroscopic materials, Nature 382 (1996) 607.

[110] D. Nykypanchuk, M. M. Maye, D. van der Lelie, O. Gang, DNA-guided crystallization of colloidal nanoparticles, Nature 451 (2008) 549.

[111] S. Angioletti-Uberti, B. M. Mognetti, D. Frenkel, Re-entrant melting as a design principle for DNA-coated colloids, Nat. Mater. 11 (2012) 518.