

Soft Nanotechnology – from Colloid Physics to Nanostructured Functional Materials

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Abstract: We demonstrate how we can tune the size, shape, surface functionality and properties of nanoparticles and use them as ideal model systems for fundamental investigations as well as for materials applications. In particular we describe ways to create functionalized core-shell particles with various degree of anisotropy and interesting magnetic properties. We show how we can use these particles in order to study the equilibrium and non-equilibrium phase behavior of colloidal suspensions with different interaction potentials and summarize our current understanding of the phenomenon of dynamical arrest, *i.e.* gel and glass formation. While different nanoparticles are vital for fundamental studies of various aspects of soft condensed matter, they also offer fascinating possibilities in materials science. We will demonstrate this with the example of nanocomposites made through an *in situ* polymerization reaction.

Keywords: Colloidal suspensions · Soft nanotechnology

1. Introduction

Colloidal suspensions have frequently been used as ideal model systems to address fundamental issues in condensed matter physics such as liquid ordering, crystallization and glass formation and the corresponding structural and dynamic properties of the various systems as a function of the interaction potential.^[1–3] They offer access to length and time scales that are well suited for experimentalists and allow for a variation of the form, strength and range of the interaction potential almost at will, quite in contrast to the situation encountered when working with atomic or molecular systems.

The possibilities to vary the interaction potential are illustrated in Fig. 1, where we schematically summarize some of the traditionally used classes of interaction poten-

tials in attempts to use colloids as model atoms.

Hard sphere particles created by combining an organic colloid such as polymeth-

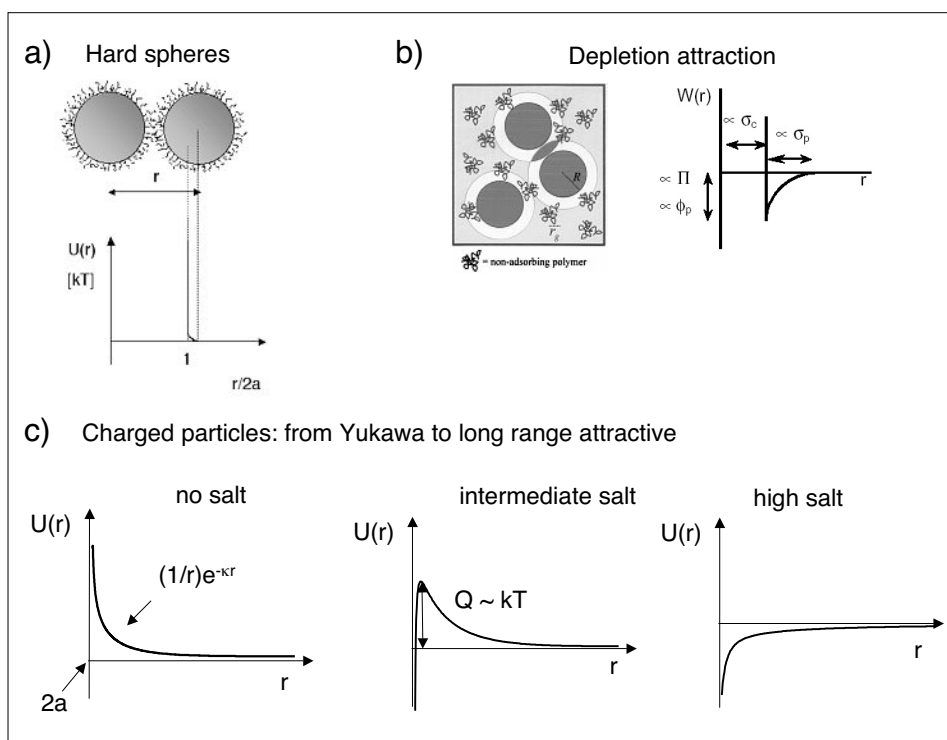


Fig. 1. Schematic description of some of the colloid interaction potentials that can be used to investigate various condensed matter topics with colloids as giant model atoms (see text for details)

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ylmethacrylate (PMMA) with an attached short polymeric hairy layer that provides the hard-sphere-like interaction potential were probably the first type of particles that demonstrated the enormous potential of using colloids as model systems. They were instrumental in experimentally demonstrating the existence of an entropically driven crystallization in a purely hard sphere-like system and thus helped to verify the initial proposal based on computer simulations.^[4] The pioneering work of Pusey and van Meegen was instrumental to establish this line of work, which was then subsequently expanded to encompass also attractive interactions that either mimic a classical atom-like Lennard-Jones potential or helped to investigate the enormous and quite surprising effects that a short range attraction can have.^[3]

Another very interesting class of particles are highly charged colloids, where the additional screening of the Coulomb interactions through counter- and co-ions in solution leads to an effective pair potential at very low ionic strength that is well described by a so-called Yukawa potential, *i.e.* a weakly screened exponential decay with the Debye screening length as the characteristic decay length of the potential.^[2,5] On the other hand we can add salt, which then first leads to a typical mixed interaction potential with a combination of a long range soft potential and a deep attractive well close to the surface, before at even higher ionic strength the attractive van der Waals interactions completely dominate and the particles start to aggregate irreversibly.^[6] It is interesting to point out that careful tuning of the salt concentration permits us to create a potential that almost perfectly matches that of hard spheres even for highly charged particles.^[7]

However, the use of colloids as model atoms has not only resulted in important contributions to our current understanding of phase transitions such as crystallization and melting. The investigation of non-equilibrium phenomena such as gel and glass formation in colloidal suspensions has clearly emerged as one of the most important fields of soft matter research. Areas such as dynamical arrest or jamming in suspensions of (weakly) attractive colloids, the interplay between spinodal decomposition and glass formation or the formation of ordered versus amorphous photonic materials attract considerable attention from the experimental and theoretical soft matter community.^[8] Moreover, the application of the thus generated knowledge and concepts to applied problems from fields as diverse as biology, medicine, food and materials science has already resulted in important progress.^[9] However, numerous intriguing problems remain, and even the understanding of the 'simple' glass transition often en-

countered in hard sphere fluids is far from being complete.^[8,10]

It is clear that many of these fascinating areas of modern colloid science are only possible because of the ever-increasing variety of colloidal model particles with well-defined properties that the colloid chemists are capable of producing. Moreover, the colloidal domain is by no means limited to the use of particles for fundamental studies in condensed matter physics. In particular the combination of the availability of particles with interesting physical properties and our ability to create nanostructured materials with them has opened up fascinating possibilities to create complex materials with novel properties that can be used in a variety of different technological areas. In the remainder of this article we will thus review some of our attempts in following the philosophy schematically drawn in Fig. 2. This Fig. illustrates the potential that the use of functionalized particles combined with our know-how in creating structures with well-defined order and length scales can have in our efforts to create novel materials. A sound knowledge of the interplay between interparticle interaction effects and the resulting phase behavior allows us to create mesoscopic structures with well-defined local order that can be either liquid-like such in colloidal gels and glasses or crystalline. Combined with the possibility to use colloids with well-defined functionalities that include particular magnetic or optical properties or a specific response to a variety of external parameters such as temperature, ionic strength or pH, this then allows us to design and build macroscopic materials that can have interesting and novel properties for a variety of different applications. As illustrated in Fig. 2, such an approach requires both the synthetic capabilities to produce functional and/or responsive par-

ticles with well-defined properties as well as the colloid physics-based experimental infrastructure and knowhow on the characterization, understanding and utilization of interparticle interactions and the creation of solid-like mesoscopic structures with tailored properties.

We therefore first give some selected examples of different routes towards interesting particles with different degrees of functionalization, and then show how these particles can be used to explore fundamental condensed matter phenomena and applications in materials science. Much of what we will present in the following paragraphs is based on pioneering synthetic work from a number of groups such as those led by E. Matijevic, R. H. Ottewill, A. Philipse, or B. Vincent, to name but a few. We do not intend to give a complete survey of the existing literature, but rather try to highlight some select examples of the interplay between particle synthesis and the resulting applications in colloid physics and nanomaterials. These examples were primarily chosen according to our own research interests and are thus completely biased and do not represent a well-balanced view of the current literature. They should nevertheless demonstrate the potential of an approach in which particle synthesis is combined with a soft matter physicists view on fundamental and applied aspects of nanoparticle suspensions.

2. The Synthesis of Particles with Functionalized Surfaces and Tailored Properties

Tuning the size, shape, surface functionalities and other physical properties is essential in using colloidal particles as ideal systems for fundamental investigations as

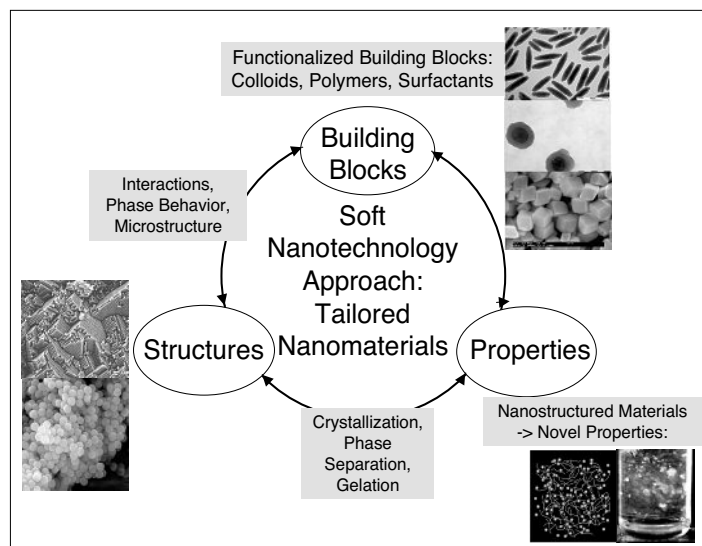


Fig. 2. Schematic description of the basis of our soft nanotechnology approach to create materials with novel and tailored properties

well as for materials applications.^[11] A classical approach for the production of small particles often used in industrial applications is milling of larger solid grains. However, the size distribution of the resulting particles does not fulfill the requirements imposed by their use as model systems. Another industrially relevant production method of colloids is flame synthesis that allows for the production of tonnes of particles, however the dispersion of the nanoparticles thus produced is often difficult and frequently results in dispersions of clusters rather than individual particles. In our attempts to create complex particle architectures with well-defined properties we have thus mostly relied on wet chemistry. We distinguish between particles that can be either organic (*i.e.* based on polymers), inorganic or with core-shell structures (organic, inorganic or hybrid). Our approach is summarized in Fig. 3 where we show a map of particle complexity where we can vary particle size, anisotropy as well as surface functionality. We will illustrate this below in particular with the example of magnetic particles based on hematite, where the pioneering work of Matijevic and coworkers and subsequently the Utrecht group has provided us with a versatile toolbox that is at the origin of Fig. 3.^[12–17]

2.1. Control of Particle Size and Functionality

A particularly important colloid property is the particle-size distribution, where the choice of the particle size for example allows tuning of the characteristic Bragg spots of colloidal crystals. One of the most often studied colloidal model system for which almost perfect control of size ($30 \text{ nm} \leq \sigma \leq 1 \mu\text{m}$) and polydispersity can be achieved is colloidal silica (SiO_2). Silica particles are successfully prepared through a sol-gel process using a synthesis in a basic environment based on Stöber's method.^[18] Fabrication of monodisperse silica particles can be achieved *via* hydrolysis of tetraethylorthosilicate (TEOS) in an ethanol solution in the presence of ammonia. Hydrolysis and condensation of alkoxide silicon lead to monodisperse spheres of silica. Depending on the respective concentrations of TEOS, water, ammonia^[19–21] and temperature of the reaction,^[22] particle size and size distribution can be tuned quite precisely. Silica has another advantage, as its surface can be modified with almost any desired functionality using silane coupling agents.^[23] Different polymerization initiators, aliphatic tails, mercapto and amino groups and more than two thousand different silane coupling agents can be purchased and easily grafted onto the surface of the SiO_2 particles, thus providing us with an enormous flexibility in creating functionalized surfaces for a wide variety of different applications.

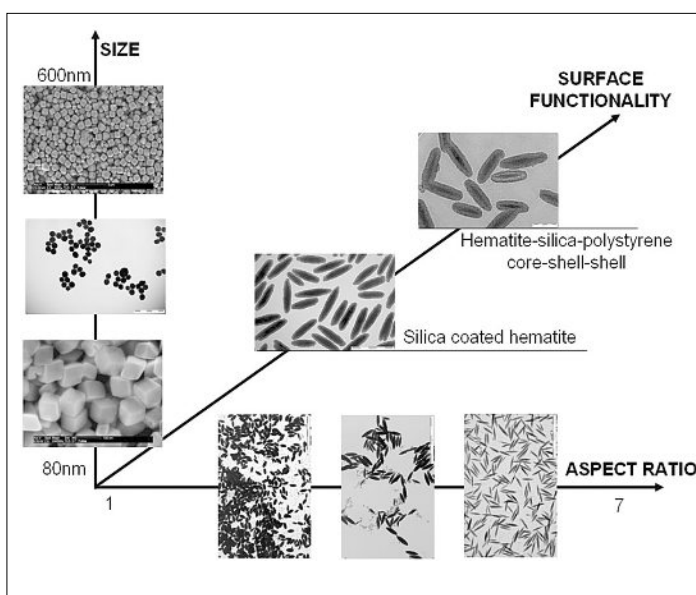


Fig. 3. Complexity map for particle synthesis, where we vary the particle size, the degree of anisotropy and the surface functionality illustrated with the example of magnetic hematite particles. Shown are TEM and SEM images of different hematite particles. They can either have cubic, spherical or rod-like shape, and can also be coated with different inorganic and organic layers.

Another important class of colloids that allow easy control of particle size and polydispersity are organic polymer colloids such as polystyrene (PS) or PMMA. Polystyrene particles can easily be synthesized in water using emulsion polymerization in the presence or absence of a surfactant. Moreover, functionality can be added when block copolymers are used as a stabilizer as described in detail in a recent review of Riess and Labbe.^[24] PMMA particles have been instrumental in most of the previously published investigations of model hard sphere colloids. They can be synthesized almost monodisperse using nonaqueous dispersion polymerization.^[25] Their low refractive index can be optically matched for example using a mixture of decalin and tetralin, which provides an efficient means of suppressing van der Waals attraction and allows experiments at very high volume fractions without loss of transparency.^[4]

While a low index of refraction is often desirable as it allows optical matching and thus an efficient suppression of multiple scattering and van der Waals attraction, in photonic applications one often needs particles with a very high index of refraction instead. This can for example be achieved using inorganic colloids such as TiO_2 or ZnO . Various sol-gel routes for the synthesis of zinc oxide (ZnO) particles have for example been described in the literature.^[26–31] Other interesting options for nanotechnological applications are metallic particles or semiconductor nanocrystals, so-called quantum dots, which can also be coated with a silica shell that provides protection against photochemical degradation and additional

surface functionality that can be explored for example for the creation of organized arrays of metallic cores with well-defined and tailored spacing.^[32]

Magnetic nanoparticles are a particularly interesting class of systems that have become very popular in various applications as well as for fundamental studies. In our work we mainly focus on hematite-based particles, which can be synthesized by forced hydrolysis of iron salts^[33] and exhibit interesting magnetic properties.^[34,35]

Hematite ($\alpha\text{-Fe}_2\text{O}_3$) forms canted ferromagnetic particles with a low remnant moment of about $0.30 \times 10^{-3} \text{ Am}^2/\text{g}$. They have attracted considerable attention due to the existing possibilities to tailor their shape and size by playing with various physical and chemical means such as the precursor concentration^[33] and type,^[36] the variation of the reaction time,^[37,38] the pH,^[39] the temperature, or the ionic strength.^[40] More recently, we demonstrated that the intermediate crystalline structure (akaganeite) formed during the synthesis of hematite can also be used as a starting point to control the monocrystallinity of the subsequently obtained particles.^[41] Fig. 4 illustrates the variation of the hematite nanoparticle size and shape as a function of the Fe^{3+} precursor concentration.^[41–43]

However, while hematite can form well-defined cube-like single crystal nanoparticles, it can also be forced to grow into anisotropic crystalline structures along a distinct axis.^[14,44] Phosphate ions for example are selectively adsorbed perpendicular to the growth axis of hematite (*c*-axis), where they inhibit the growth of the crystal

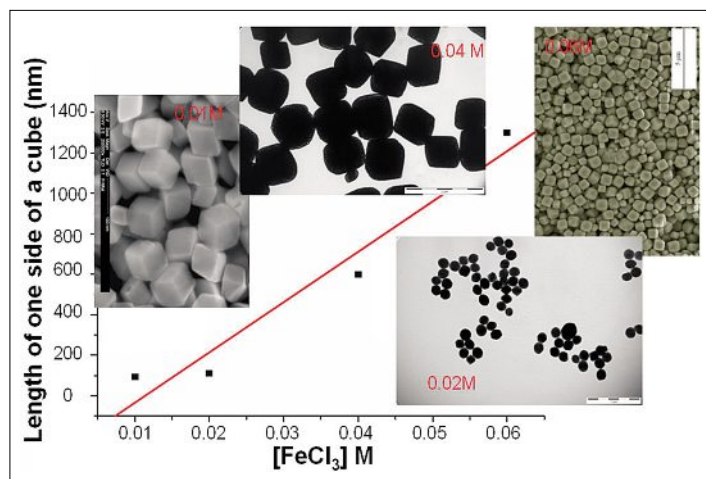


Fig. 4. Variation of hematite particle size and shape as a function of the initial iron precursor concentration (in mol·l⁻¹)

in the perpendicular direction and lead to spindle-shaped particles.^[40] The resulting aspect ratio can be tuned quantitatively and reproducibly with the ionic strength, *i.e.* through an increase of the concentration of NaH₂PO₄^[44] as shown in Fig. 5. The resulting axial ratio follows a simple linear relationship of the form $a/b = 0.57 \times [\text{NaH}_2\text{PO}_4] + 0.93$ (Fig. 5). Even larger values of the axial ratio can be obtained when using Fe(ClO₄)₃ in the presence of urea and NaH₂PO₄^[36] leading to aspect ratios of 6.5–7 with a long axis of about 200 nm. While the low magnetic moment of hematite may not be sufficient for some applications, these particles can be transformed into maghemite ($\gamma\text{-Fe}_2\text{O}_3$) through hydrogenation at 360 °C, which enhances the magnetic moment by a factor of 200.^[45]

2.2. Creating Surface Functionalized and Responsive Particles

We have already seen that we can create a large variety of organic and inorganic nanoparticles with different sizes and shapes that can be used as model systems for fundamental studies in soft condensed matter research as well as ideal building blocks for the preparation of nanostructured materials with interesting optical or magnetic properties. However, in many of these applications a full control of the bulk properties of the particles is not sufficient; we also need to control the surface properties for various reasons. Depending on the solvent or the medium in which the particles have to be dispersed, the particle–particle and particle–medium interactions play an important role in any attempt to avoid aggregation or phase separation. Moreover, frequently we would like to create responsive or adaptive particles that can react to some external stimulus. When working with organic particles prepared using emulsion polymerization, a

certain degree of surface functionality can easily be obtained by using block copolymers as a stabilizer.^[46–48] This allows us for example to prepare either highly charged or sterically stabilized functional core-shell latex particles with a PS core through the use of amphiphilic block copolymers such as the highly charged polystyrene-*block*-polystyrene sulfonate (PS-*b*-PSS) or the non-ionic polystyrene-*block*-polyethylene oxide (PS-*b*-PEO). In both cases we obtain almost monodisperse particles that are either highly charged and capable of crystallizing at volume fractions as low as 5×10^{-4} ,^[48] or possess a temperature-dependent steric stabilization that can be used to investigate the effect of a tunable short range attraction on the phase behavior.^[49,50]

While block copolymers can also be used for surface functionalization of inorganic particles, we generally use a different approach for our work. Here we coat the particles first with a silica layer as a con-

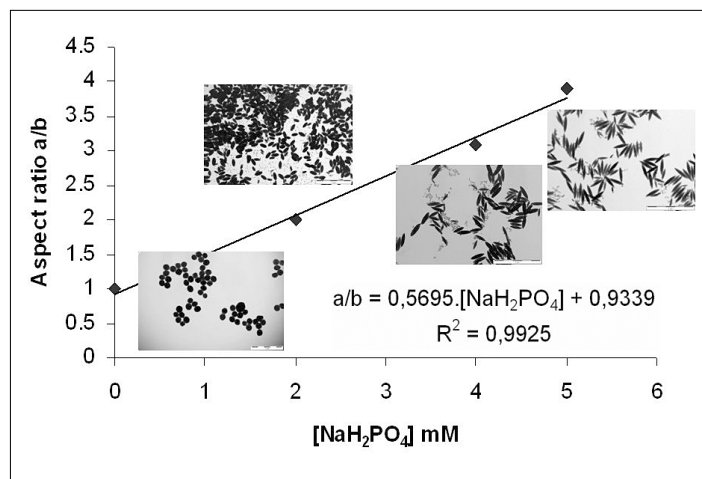


Fig. 5. Variation of the hematite particle size anisotropy as a function of the starting concentration of NaH₂PO₄. The iron (III) chloride precursor concentration is kept constant at a value of 0.02 M.

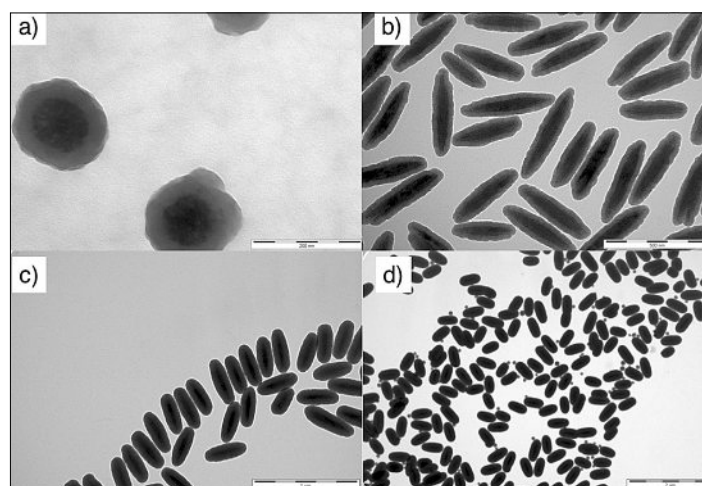


Fig. 6. TEM images of different inorganic core-shell particles. ZnO-SiO₂ core-shell particles (a), and anisotropic magnetic core-shell particles based on a rod-like $\alpha\text{-Fe}_2\text{O}_3$ core with an axial ratio of 7 and a long axis of 200 nm and different silica shell thicknesses of 25 nm (b), 55 nm (c) and 95 nm (d)

venient basis for further surface modifications through silane coupling agents.^[51] The method used follows the general scheme proposed by Graf *et al.*^[16] It consists in adsorbing a non-ionic amphiphilic polymer polyvinylpyrrolidone (PVP) on the surface of our colloidal particles. A modified Stöber approach^[18] then leads to a homogeneous coating with a silica layer of controlled thickness. Some core-shell particles are demonstrated in Fig. 6 with the examples of spherical ZnO particles and rod-like magnetic hematite. Fig. 6 shows that we can create a silica shell with variable and controllable thickness as originally shown with a different approach by Ohmori and Matijevic.^[15]

Subsequent additional synthesis steps furthermore allow us to prepare core-shell particles with a specific surface functionalization that can then be used in various applications.^[52] Moreover, the quite high porosity of the silica layer obtained in this

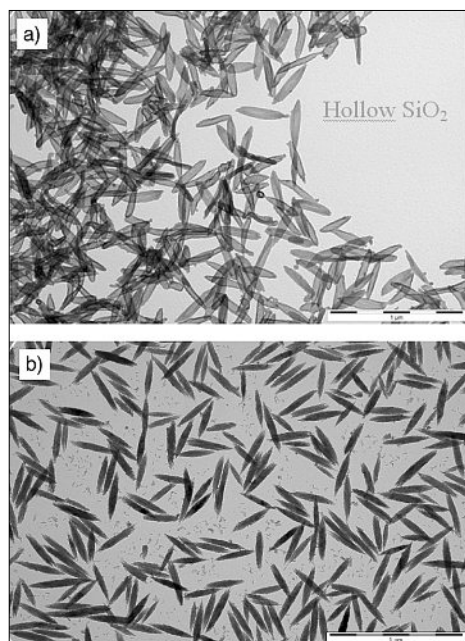


Fig. 7. TEM images of hollow silica particles a) based on the dissolution of the hematite core of the $\alpha\text{-Fe}_2\text{O}_3\text{-SiO}_2$ core-shell particles shown in b)

sol-gel route allows us to create low-density hollow silica rods with an adjustable axial ratio based on the hematite-silica core shell particles shown in Fig. 6. After the initial coating step, the hematite core can be dissolved in a large excess of hydrochloric acid. Fig. 7 shows the resulting hollow spindle-shaped silica particles that now have a low density and low index of refraction in solution due to the fact that the solvent fully penetrates into the particle core.^[17,36]

A particularly interesting and promising type of core-shell particle can be created through a combination of an inorganic core and a thermoresponsive polymeric shell. The thermosensitive polymer poly(N-isopropylacrylamide) (PNIPAM) exhibits a pronounced swelling behavior at lower temperatures, where water is a good solvent, and a dramatic chain collapse at temperature above approximately 33 °C (see reviews by Pelton and Nayak and Lyon for details^[53,54]). Core-shell particles with a polystyrene core and a poly(N-isopropylacrylamide) (PNIPAM) shell have for example already been used as very versatile model systems to investigate the rheological properties of hard sphere suspensions close to the glass transition.^[55] The PNIPAM shell provides the thermosensitive properties and thus allows easy mixing in the collapsed state and subsequent approach of a specific value of the effective volume fraction *via* a temperature-induced swelling. In our own work we concentrate on temperature-sensitive core-shell particles with an inorganic core such as the SiO_2 nanoparticles coated with a PNIPAM shell that have recently been described.^[56] These particles are shown in Fig. 8, which demonstrates the rather monodisperse size

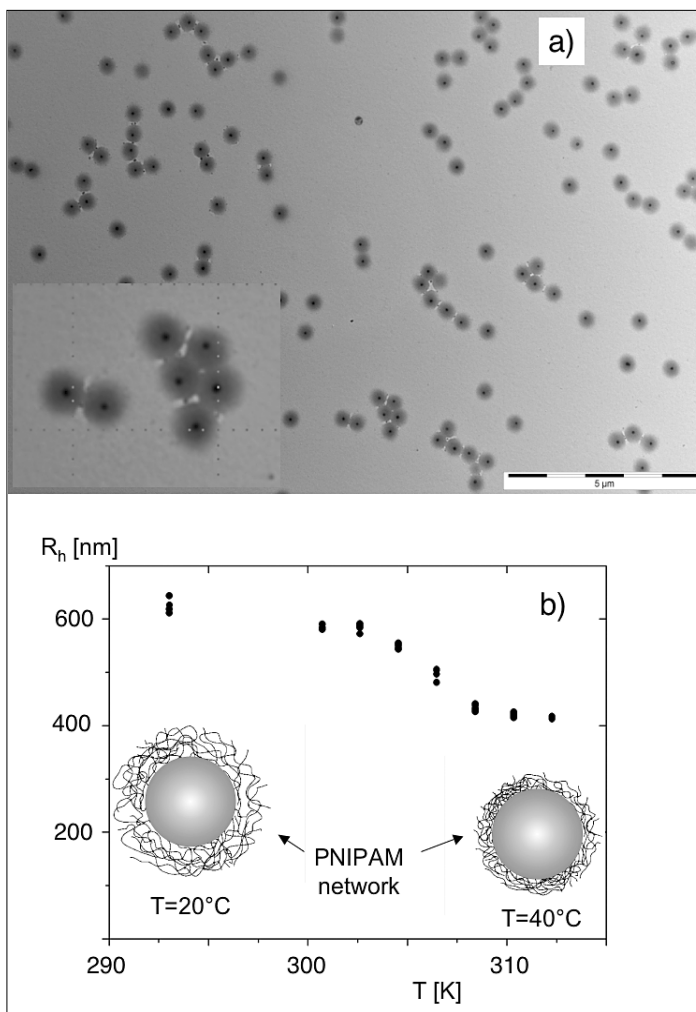


Fig. 8. TEM images of SiO_2 -PNIPAM core shell colloids (inset zoom to demonstrate the core-shell structure of the particles) (a) and an example of the temperature dependence of the particle radius as determined by dynamic light scattering (b)

distribution that can be obtained with SiO_2 -PNIPAM microgel core-shell particles. It is obvious that the combination of inorganic nanoparticles with special optical or magnetic properties combined with an initial coating with a silica shell and a subsequent incorporation into a thermosensitive PNIPAM shell opens up a variety of interesting possibilities in photonics^[57] or other nanotechnology-based materials applications.

3. Equilibrium and Non-equilibrium Phase Behavior of Colloidal Model Systems

3.1. Fluid-Solid Transitions in Colloids with Short Range Attractions

With the enormous variability in particle size, structure and functionality described in the previous section and the resulting exquisite control of the interparticle interaction potential, we now have access to ideal model systems in order to investigate the links between interparticle interactions, particle stability, phase separation, crystal,

gel and glass formation and their potential use in the quest for the creation of novel materials. We have thus started a systematic investigation of the phase behavior of colloidal model systems as a function of the particle shape and for various interaction potentials. Here we not only concentrate on equilibrium properties, but give particular emphasis on non-equilibrium properties and phenomena such as dynamical arrest.

Fluid-solid transitions frequently encountered in colloidal suspensions have moved into the focus of the soft matter community during the last few years.^[8,58-61] It has long been realized that, for some appropriate choice of experimental conditions, particles or macromolecules in a fluid simply stop moving in a quite reproducible manner. This phenomenon has attracted enormous interest, and numerous terms such as 'dynamical arrest', 'jamming' or 'gelation' have been used for it. Sometimes arrested states of colloidal matter are of considerable value, being important in food, biomedical and materials research applications, whereas in other situations (for example in protein crystallization or the

production of photonic crystals on optical length-scales) it is the high quality crystal that we seek to make, overcoming the competition of arrest. It is thus clear that, irrespective of whether we are studying fundamental or industrially oriented topics, it will be instrumental to understand those factors that lead to the onset of dynamical arrest, the properties of that arrested state, and its role in suppressing the crystalline (ordered) state of soft and colloidal matter.

While many of the pioneering studies initially focused either on hard spheres or highly charged particles,^[2] particular attention has recently been devoted to particles with short-range attractions, where a number of intriguing equilibrium and non-equilibrium features have been discovered.^[3] A number of studies have clearly demonstrated that for such systems the topology of the resulting phase diagram is distinctly different from that of classical atomic liquids provided that the range of the potential δ is sufficiently short compared to the particle diameter σ , with $\delta \leq 0.15 \sigma$. Key discoveries for such systems have been the existence of a gas–liquid phase boundary that is now metastable with respect to the liquid–solid phase boundary, and the existence of attractive glasses, where the location of the glass or gel line strongly depends upon the range δ and strength ϵ of the attractive potential.^[3]

Our current state of understanding of the phenomenon of dynamical arrest as a function of the strength of the attractive part of the interparticle interaction potential is schematically summarized in Fig. 9.^[9,61] For ideal hard sphere particles, we observe the formation of colloidal crystals above volume fractions of about 0.49, followed by a transition to a disordered solid phase, a glass, at volume fractions of approximately $\phi \approx 0.58$.^[4] If a weak and short-ranged attraction is now turned on, this leads to the astonishing observation of a melting of the glass, followed by a so-called re-entrant glass or solid formation at even stronger attractions.^[8,58,62]

Despite the fact that dynamic arrest for hard sphere systems has been studied for decades, and been interpreted successfully using analogies to molecular glasses and applying mode coupling theory (MCT),^[63] very recent developments have suddenly questioned our current understanding of these seemingly ‘simple’ systems.^[64] Computer simulations^[65] and experiments under microgravity^[66] had already posed serious doubts on the very existence of a glass transition at $\Phi < 0.64$ for (almost) monodisperse hard spheres in the absence of a gravity field. Recent direct observations of particle motion in dense hard sphere suspensions with various degrees of density matching, *i.e.* at different values of the gravitational length, now provided direct evidence that gravity

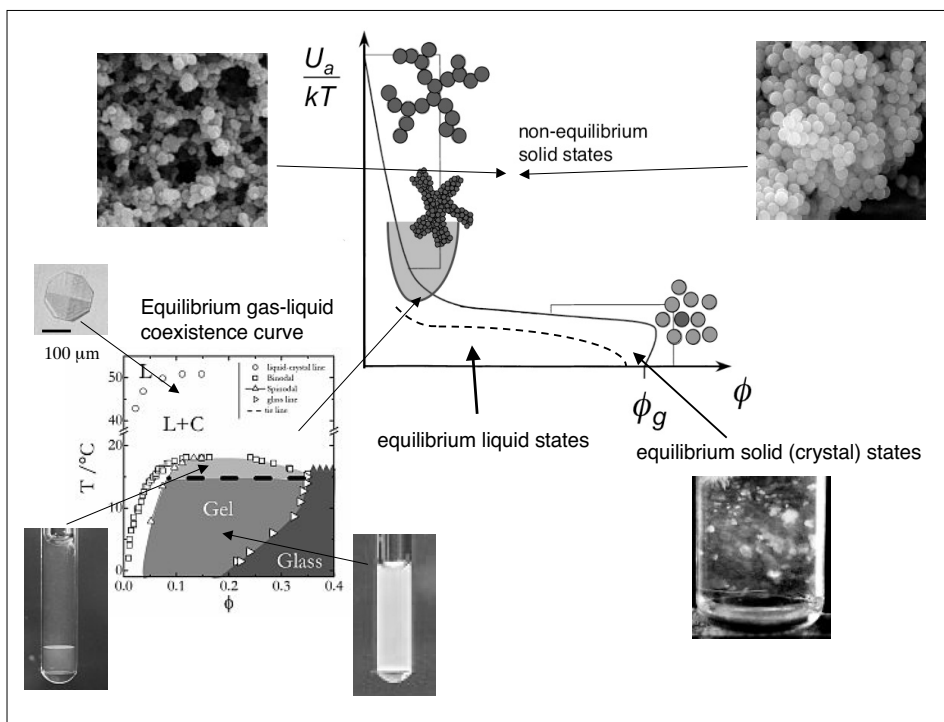


Fig. 9. Schematic state diagram of colloidal particles with short-range attractive interaction potentials, taken from ref. [9] and [49], where different liquid and solid-like states of colloidal suspensions are plotted as a function of volume fraction Φ and strength of the attraction U_a . The solid line in the energy/composition diagram represents the boundary for the formation of disordered solids, the so-called gel or glass line. The dashed line represents the phase boundary for the liquid–crystal transition. Also shown are several examples from the different regions of this state diagram. The two SEM micrographs shown in the upper right and left part illustrate the close analogy between the structure of dense colloidal gels (right, SiO_2 particles) used in sol-gel ceramics production and casein particle gels produced in yoghurt formation (left).^[9] The photograph in the lower right corner illustrates the formation of colloidal crystals made from hard spheres that exhibit a colorful appearance due to the existence of Bragg diffraction peaks when illuminated with white light. Finally, the lower left corner summarizes the phase behavior of a globular protein lysozyme developed in ref. [58]. We see in particular the existence of protein crystals at temperatures above the coexistence curve but below the liquid–solid boundary, and the formation of a macroscopically separated two-phase systems for shallow and an arrested turbid gel for deep temperature quench far below the temperature of 15 °C, where the gel line intersects the coexistence curve.

may dramatically accelerate aging in glassy colloidal systems, thus lowering the glass transition density.^[64] These authors indeed speculated that relaxation of shear inhomogeneities, which always are present upon preparing colloidal systems with very high volume fractions, could be responsible for the dramatic influence of gravity on aging. Thermosensitive core-shell particles that can swell or shrink reversibly upon a variation in temperature may help to shed light on these open questions. They have recently been used to further investigate the flow behavior of concentrated colloidal particle in the vicinity of the glass transition.^[55] Due to the fact that the effective volume fraction can be tuned *via* temperature in a very effective way, these particles allow for an easy and precise adjustment of the volume fraction and thus to the distance to dynamical arrest.

In the other extreme case of very strong attraction, we reach the regime of so-called irreversible aggregation where one observes the formation of soft fractal gels already at

very low volume fractions.^[67,68] The analogy between colloidal glasses at high densities and colloidal gels at low volume fractions has stimulated a considerable effort to explore new ways to characterize, understand and use amorphous solid-like soft matter systems. However, we are still far from having developed a general theoretical framework that is capable of unifying the entire range of concentrations and type of interactions that have been investigated.

At intermediate strength of the attraction, the situation is even more complicated due to the fact that phase separation into a dilute (gas-like) and a concentrated (liquid-like) suspension can occur. The position of the corresponding coexistence curve between the dilute and concentrated suspension can then intersect with the arrest or gel line, and the phase separation can subsequently lead to the formation of a long-lived ‘interaction network’ (a transient gel) of particles, if the attractive interactions between them are strong enough. We have already demonstrated that organic core-shell particles with

a polyethylene oxide-based shell can serve as convenient model systems to investigate gelation in short range attractive particle systems.^[49,50] Subsequently we have used a globular protein, lysozyme, as a model system to investigate in detail the interplay between spinodal decomposition and dynamical arrest for particles with moderate short-range attractions.^[69]

The presence of short-range attractions in protein solutions was first demonstrated *via* the existence of a liquid–liquid coexistence curve that is metastable with respect to the liquid–solid phase boundary.^[70–72] While the exact physical origin of the attractions and their temperature dependence remain obscure,^[73] the resulting phase behavior is indeed equivalent to that found in colloidal suspensions with depletion-induced attractions and in systematic computer simulations of systems with short-range attractions.^[3] This close analogy between the phase behavior of colloids and globular proteins has resulted in a very interesting colloid physics-based approach to protein crystallization. There are strong reasons to believe that the observation that globular proteins sometimes can, and sometimes cannot, easily be crystallized may be linked to the phenomenon of dynamical arrest.^[74] Subsequent investigations have led to a generic state diagram for globular proteins – the zone picture – with a limited region suitable for high-quality crystal growth.^[74–76]

The existence of an arrested state in protein solutions has already been reported by Kulkarni and collaborators.^[75] However, their investigations as well as those conducted with colloidal model systems that possess a short range attractive potential have focused on the existence and location of a glass line at effective temperatures above the metastable binodal. It is only recently that we have been able to unambiguously locate the glass line in the region below the coexistence curve for the globular protein lysozyme.^[69] These findings are summarized in the lower part of Fig. 9, where the lysozyme phase diagram determined in ref. [69] is re-plotted. A lysozyme solution above the coexistence curve quenched down to temperatures within the light gray area above the dashed line undergoes macroscopic phase separation and reaches equilibrium after some time. However, deeper quenches into the dark grey area below 15 °C lead to the formation of a gel due to the interplay between phase separation and glass formation. Here gelation is driven by spinodal decomposition into a space-spanning network of the dense phase, which dynamically arrests due to a local glass transition in this dense phase and gives rise to a finite elastic modulus. The attractive glass line – given by the concentration of the dense phase – is located at lower volume fractions than the high concentration

branch of the coexistence curve and shows a strong temperature dependence.^[69]

The significance of this viscoelastic phase separation in pattern formation in nature and its engineering applications has already been pointed out in the past.^[77] More recently, the importance of the creation of solid-like structures as a result of a competition between phase separation and dynamical arrest in areas as diverse as protein crystallization and food gel formation has also been addressed.^[9,69] It is clear that this topic is far from being fully understood, and important questions in relation to speculations that the phase behavior of colloids should be independent of the exact shape of the potential and depend on the second virial coefficient as an integral measure of the potential only, and that this should most likely also hold for non-equilibrium features such as the arrest line at intermediate and low volume fractions have not yet been answered.^[78] Given the enormous structural and mechanical differences found in colloidal gels and glasses that have formed *via* different routes, a better understanding will undoubtedly open up new avenues towards the formation of solid-like complex fluids that may be extremely interesting for applications in materials or food science.

3.2. Phase Behavior of Anisotropic and Strongly Charged Colloids

While most of the work performed so far has relied on spherical colloids, recently an increasing effort has been devoted to anisotropic particles.^[79] This has opened up a wealth of interesting problems both in fundamental soft matter physics as well as in applications, where anisotropic particles allow us to generate materials with intriguingly different properties. A particularly interesting and controversial class of particles are disk-like clay particles that are both industrially important and of theoretical interest. An interesting feature of clay suspensions is the existence of interactions at different length scales combined with the anisotropic structure of the particles, which lead to a variety of structural and dynamic phenomena such as orientation, ordering and clustering (house of card-like) as a function of the particle concentration C and of the ionic strength I_0 .

For more than 50 years various gelation mechanisms and suspension structures have been proposed for clays.^[70–92] The majority of clay gelation studies have been done with laponite suspensions due to their relatively high longitudinal monodispersity in comparison with natural clays. However, direct observation of laponite with AFM or EM shows that laponite exhibits a considerable polydispersity.^[93–95] At the same time, laponite is chemically unstable at pH below 10. In contrast to laponite, the commercially available natural clay mont-

morillonite is stable even at very low pH, which allows one to study montmorillonite over a wide range of pH and ionic strength. montmorillonite particles have aspect ratios of the order 100:1, which is much higher than for laponite, and therefore the edge area for montmorillonite is typically a very small proportion (<1%) of the total surface area of the particles. The edge surface area is thus expected to be less important in determining the particle interactions in montmorillonite dispersions.

In order to understand the relation between the local and macroscopic properties and the structure of clay suspensions, we have thus systematically investigated the phase and state diagram of clay particles in water.^[96] We in particular focused on sodium cloisite (CNa) particles at concentrations typically used in nanocomposites (concentration from 1 wt% to 4 wt%), and for an extended range of ionic strengths (10^{-5} to 10^{-1} M NaCl). The suspensions have been characterized using rheology and a combination of scattering techniques (neutrons, light) that allowed us to cover an enormous range of length scales from local structural details on almost atomistic resolution to superstructures with many micrometers size. The resulting state diagram is summarized in Fig. 10. We were able to demonstrate the existence of a liquid cluster phase at low clay and intermediate salt concentration, and obtained new insight into the nature of the solid-like dispersions at low and high ionic strength. We have in particular been able to confirm the existence of a repulsive (Wigner) cluster glass, that melts with increasing salt concentration and is finally transformed into an arrested percolated network of concentrated clay domains or a phase separated flocculated phase at high ionic strength. At higher clay concentrations we have been able to directly demonstrate the subtle structural changes that accompany the transition from a repulsive cluster glass at low ionic strength to an attractive glass of percolated individual clay platelets at intermediate ionic strength and finally to a gel formed by an arrested network of percolated small stacks of clay platelets at high ionic strength.

The state diagram in Fig. 10 exhibits a close resemblance to the theoretical diagram previously postulated for laponite suspensions by Abend and Lagaly^[88] and Tanaka and collaborators.^[89] However, while their phase diagram was largely based on indirect evidence from a number of different sets of experimental data from the literature, we have now been able to come up with a rather detailed description of the underlying suspension structure over a very large range of length scales and for a systematic variation of clay and salt concentration. This has also led to a modified picture for the Wigner glass and the

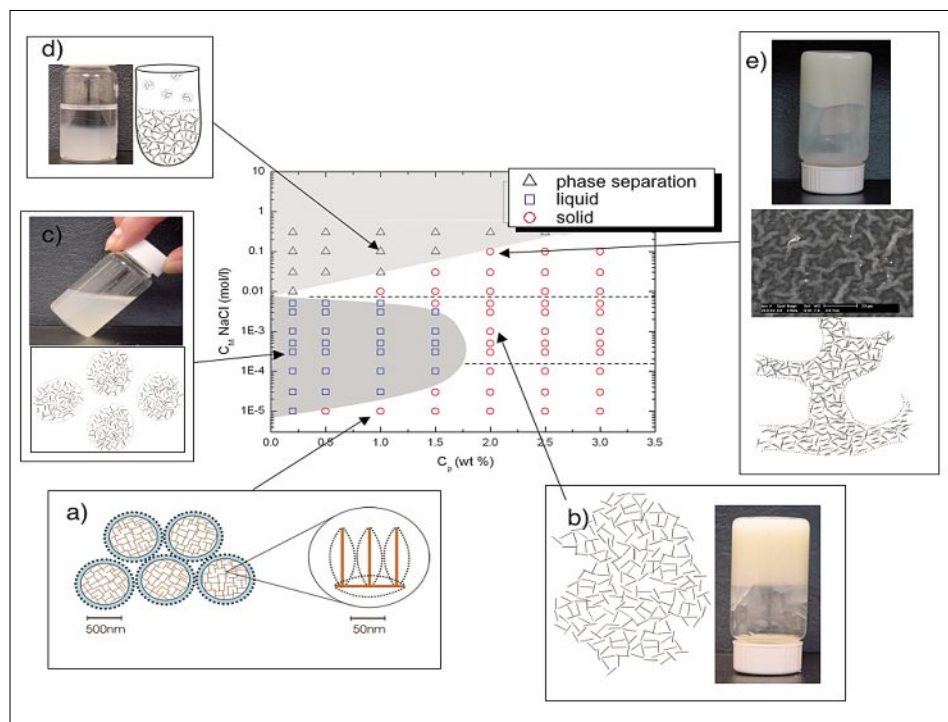


Fig. 10. Schematic representation of the different states of aqueous clay suspensions as a function of ionic strength and clay concentration: a) Wigner glass containing clusters with a size of 400–600 nm and high degree of internal ordering. The right hand side shows a schematic picture of the local structure of the clusters in the Wigner glass where at low ionic strength the individual platelets organize into ordered subunits that are responsible for the weak structure factor peak seen in small-angle neutron scattering experiments [see ref. 96 for details]. b) Continuous percolation gel with random orientation of the individual discs. c) Cluster fluid formed by percolation clusters with a size of 3–5 μm and random orientation of the individual discs. d) Phase separated sample with weak percolation gel formed by small stacks of clay particles on the bottom and a few smaller clusters in the top. e) Transient gel formed by concentrated domains of a percolation gel of small stacks of platelets.

fluid phase observed at low volume fractions and ionic strength, where the building blocks are particle clusters and not individual clay platelets. Moreover, we have also been able to demonstrate the impact of the ionic strength on the local structure, where we observe a transition from ordered to randomly oriented individual platelets and finally to the formation of small stacks of disks with increasing ionic strength.

This investigation once again has demonstrated the quite universal nature of the sequence of arrested states already investigated for spherical colloids.^[8,9,62] It is clear that we still lack additional data on the evolution of the dynamic properties as a function of concentration, ionic strength and aging time for the same system. Moreover, a comparison with detailed computer simulations would also be extremely interesting. Nevertheless, we believe that we have been able to provide further insight into the phenomenon of dynamical arrest in platelet suspensions that are both of considerable interest for the colloid community as well as of enormous technological importance for a wide variety of applications. It will be very interesting to extend these studies to the rod-like particles described above and investigate the influence of particle anisotropy as well as additional non-centro-

symmetric contributions to the interaction potential that can for example be created through the field-dependent magnetic moment of the hematite-based particles.

4. The Creation of Nanostructured Materials with Novel Properties

Given the possibilities to create nanoparticles with tailored functionality and interactions and our advanced understanding of the phase behavior of colloidal model systems, we can now try to use this to create complex materials with improved or novel properties. Nanostructured organic–inorganic hybrid systems represent an exciting class of materials. Nanomaterials fabricated by dispersing nanoparticles in polymer melts have the potential for performances exceeding traditional composites by far.^[97] The combination of nanoscale inorganic moieties with organic polymers allows us to combine the properties of nanoparticles and polymers and thus to design materials with enhanced or even completely new properties. Another important feature is the possibility of tuning the structure and morphology on the nanometric scale, which opens the door to innovative applications in both advanced and conventional technology fields.

Polymers reinforced with nanoscale particles should show vastly improved properties. Yet, experimental evidence suggests that a simple extrapolation of the design paradigms of conventional composites cannot be used to predict the behavior of nanocomposites. A major problem arises from the fact that the control of the mixing between the two dissimilar phases remains a challenging task, and there still is a lack of data on structure–property relationships at a nanoscale level.^[98] We have thus started a systematic study in which we combine synthetic activities with the application of time-resolved scattering methods in order to understand and improve the formation mechanism of polymer–colloid nanocomposites.

We functionalized nanoparticles and thus made them available as crosslinkers for the creation of a polymer gel through *in situ* polymerization. We used a PMMA-based system, since PMMA possesses high optical transparency, exceptional mechanical strength and is thus ideally suited in particular for optical applications. In combination with nanoparticles, it is in addition possible to decrease the gas permeability, and to enhance the physical performance and heat resistance without diminishing the optical transparency.^[99] Optically clear composites of silica–PMMA have been prepared by using silica particles that are much smaller than the wavelength of visible light or by matching the refractive index of the components.^[100,101]

However, the transparency of the composite decreases dramatically if aggregation occurs, since clusters of nanoparticles strongly scatter visible light. Several routes towards stable PMMA–silica-based nanocomposites have been followed in the past. In order to improve the compatibility of silica and vinyl polymer matrices, silane coupling agents have been grafted on colloidal silica surfaces.^[102,103] PMMA-layered silicate nanocomposites were also prepared by *in situ* suspension and emulsion polymerization.^[99]

In our approach for the nanocomposite preparation we used surface-modified silica nanoparticles suspended in a monomer solvent, followed by *in situ* polymerization.^[104] We used 3-(trimethoxysilyl)propylmethacrylate (TPM) surface-modified silica nanoparticles that have a radius of 25 nm. The radical polymerization was performed directly in the monomer solvent. The polymerization process was initiated by an initiator and subsequent UV irradiation. The particles then acted as crosslinkers, and any potential clustering and micro- or macrophase separation due to depletion effects arising from the growing polymer chains could be avoided. The resulting nanocomposites thus remained highly transparent, and no further purification from the solvent

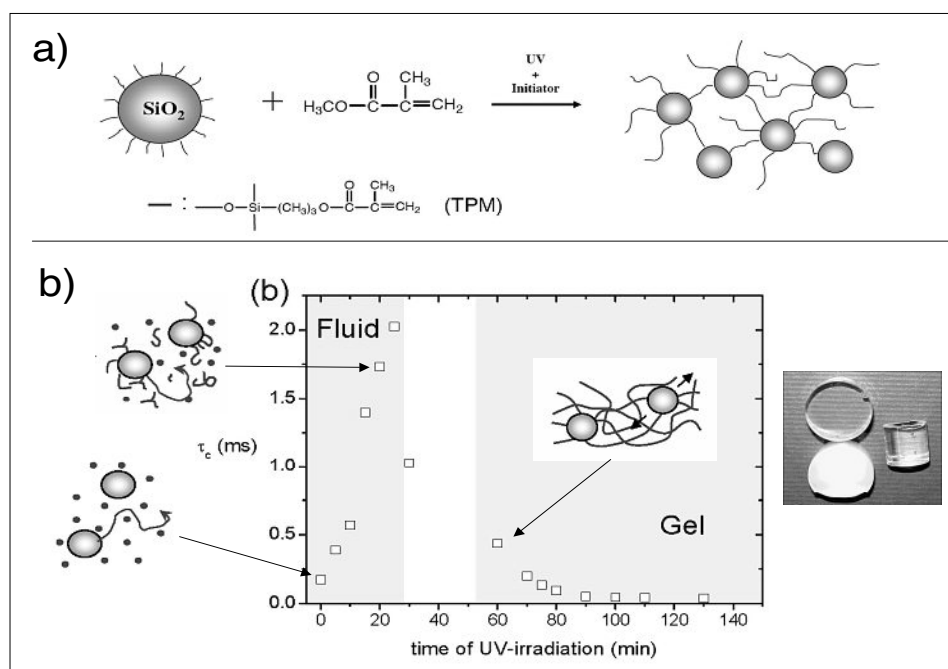


Fig. 11. (a) Schematic representation of the UV-initiated polymerization process, where the particles are initially freely suspended in the monomer solvent. Polymerization then results in growing polymers both in the melt as well as covalently attached to the particle surface. The functionalized particles act as crosslinkers, and a fully crosslinked polymer gel is formed. (b) Characteristic relaxation time τ_c of the motion of the SiO₂ particles as a function of UV irradiation time obtained from dynamic light scattering for the 3.3 wt% TPM-silica nanoparticles in MMA during radical polymerization. Also shown are photographs of PMMA-based nanocomposites prepared with different SiO₂ particle sizes and concentrations (upper left: no added particles; upper right: SiO₂ particles with diameter $d = 50.8$ nm and 13 % by weight; bottom: SiO₂ particles with diameter $d = 515$ nm and 15 % by weight).

was required. Fig. 11 summarizes the approach chosen and provides examples of the resulting nanocomposites formed.

The combination of functionalizing monodisperse silica nanoparticles with TPM and *in situ* polymerization of the monomer solvent resulted in the formation of completely stable and highly transparent nanocomposite materials up to particle concentrations of 13 wt%.^[104] Time-resolved dynamic light scattering and small-angle neutron scattering experiments allowed us to follow the *in situ* polymerization of the nanocomposites in a completely non-invasive way (see Fig. 11 for a summary of the DLS experiments). They provided a quantitative description of the particle dynamics during the polymerization process and the subsequent formation of a chemically crosslinked polymer gel, and they have allowed us to assess the lack of agglomeration and absence of inhomogeneities. Moreover, DLS has yielded additional information on the development of the mechanical properties of the system as the polymers and network form.

This study has already demonstrated the possibilities that such an *in situ* polymerization process combined with functionalized nanoparticles offer. It is clear that this is by no means limited to SiO₂ nanoparticles, but that we could of course use the large variety of silica-coated particles that we have

presented above in order to create various nanocomposites with interesting properties.

5. Conclusions

We have seen that there are a wealth of colloidal model particles with well-defined properties on the basis of an almost unlimited number of building blocks and surface functionalities. This provides us with a fascinating playground for fundamental studies in condensed matter physics. Moreover, our ability to assemble these particles into nanostructured materials opens up new possibilities to create complex materials with novel properties with potential applications in a variety of different technological areas. It has become clear that through a close collaboration between colloid and polymer chemists and soft matter physicists we can successfully create new opportunities in the rapidly expanding area of soft nanotechnology, where in particular the applications of concepts such as self-assembly of complex structures combined with the synthesis and use of adaptive functionalized nanoparticles results in highly promising novel materials.

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