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From evaporation-induced self-assembly to shear-induced alignment†

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The functionality of compact nanostructured thin films depends critically on the degree of order and hence on the underlying ordering mechanisms during film formation. For dip coating of rigid nanorods the counteracting mechanisms, evaporation-induced self-assembly (EISA) and shear-induced alignment (SIA) have recently been identified as competing ordering mechanisms. Here, we show how to achieve highly ordered and homogeneous thin films by controlling EISA and SIA in dip coating. Therefore we identify the influences of the process parameters including temperature, initial volume fraction and nanorod aspect ratio on evaporation-induced convective flow and externally applied shear forces and evaluate the resulting films. The impact of evaporation and shear can be distinguished by analysing film thickness, surface order and bulk order by careful *in situ* SAXS, Raman and SEM-based image analysis. For the first time we derive processing guidelines for the controlled application of EISA and SIA towards highly ordered thin nematic films.

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Introduction

The long-range and defect-free organization of nanomaterials to macroscopic structures on a substrate is a major challenge in colloidal science. Ordered nanostructures are favourably formed *e.g.* by soft methods such as self-assembly.¹ In self-assembly particle interactions are tailored to trigger the spontaneous formation of ordered structures. Size and shape dependent particle interactions include non-covalent interactions such as hydrogen bonding, van der Waals forces, electrostatic forces, π - π interactions and capillary forces.^{2,3} An even higher degree of control and especially an acceleration of the ordering processes can be achieved by superimposing additional external fields, *e.g.* magnetic, electric or flow fields.⁴

Particularly in drop casting, spin coating, dip coating or doctor blading flow fields are induced.^{5–7} For spherical particles the aforementioned deposition methods have been well

investigated. Yu *et al.* investigated the drying of dropcast dispersions of colloidal spheres by video microscopy.⁸ The authors showed that the particles are driven to the contact line by convective flow. This was followed by dewetting and breakdown of the pinned liquid layer. The colloidal spheres were simultaneously packed into 2D colloidal crystals.⁸ This phenomenon has also been described as a convective influx of spherical particles from the suspension to the contact line by Dushkin *et al.*⁹ However, the formation of colloidal crystals in bulk solution has not been detected.¹⁰ In all cases the particles are found to consolidate at the contact line as reported by Deegan *et al.* (coffee-stain effect).^{11,12} Detailed analysis of self-assembly of colloidal spheres in dip-coating was conducted by Li *et al.*¹³ Particle jamming under the effect of repulsive interactions between the particles occurred and was followed by ordered aggregation until a cohesive wet solid was obtained. The convective flow responsible for the mass transport towards the contact line and especially for self-assembly into organized colloids was found to be driven by evaporation of the solvent. This process is commonly known as evaporation-induced self-assembly (EISA).¹⁴ Free evaporation and constrained evaporation in confined geometries were utilized by Han *et al.* and Byun *et al.* to produce hierarchical structures and microchannels.^{15–17} Besides evaporation-induced flow, a directed flow can be utilized to align nanoparticles on a substrate: highly ordered thin films comprised of viruses, micelles or nanowires have been realized by flow-enabled self-assembly.^{18–21}

Evaporation and shear are known to affect film formation in dip coating.²² In the literature EISA is frequently utilized to

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assemble elongated particles mainly parallel to the contact line: commonly, low evaporation rates or very slow withdrawal velocities in combination with low volume fractions are used. Thiemann *et al.* showed ZnO nanorods of different aspect ratios ranging from 9.5 to 37.5 and a nematic alignment parallel to the contact line.²³ At a low evaporation rate of $2 \mu\text{m min}^{-1}$ and a low volume fraction of 0.007 vol% they achieved different zones of alignment. Shimoda *et al.* used this method to self-assemble carbon nanotubes parallel to the contact line. They explained the self-assembly by heterogeneous nucleation of a locally super-saturated suspension.²⁴ Russell *et al.* self-assembled carbon nanotubes from even lower concentrated dispersions by dip coating with withdrawal velocities between 1.2 mm min^{-1} and 15.8 mm min^{-1} .²⁵ At the middle withdrawal velocity of 8.6 mm min^{-1} they achieved compact uniform alignment of the carbon nanotubes parallel to the contact line presumably caused by evaporation. At the maximum withdrawal velocity sparse alignment of the tubes in the direction of withdrawal was observed.

Anisotropic colloidal particles such as nanorods allow distinguishing the impact of evaporation-induced flow and externally applied shear flow for microstructure formation. We have recently identified evaporation-induced self-assembly and shear-induced alignment (SIA) as ordering mechanisms in dip coating. At low withdrawal velocities EISA and SIA are competing and counter-acting mechanisms.²⁶ In dip coating a substrate is withdrawn from a colloidal reservoir at a constant velocity. This results in a parabolic dependency of the film thickness on the withdrawal velocity. In total, three deposition regimes, namely the capillary, the intermediate and the viscous drag regime can be discriminated.^{27,28} In the evaporation dominated capillary regime, which is found at low withdrawal velocities, the film thickness increases with decreasing velocity. The dispersed particles are transported and accumulated at the contact line by an evaporation-induced convective liquid flow: since the evaporation rate is constant the particle flux increases with decreasing withdrawal velocity. Compared to the dispersion in the reservoir the evaporation rate at the contact line between the substrate, the solvent and air is enhanced due to the curvature effects. Formation of the microstructure occurs at the three phase contact line near the meniscus (solid–liquid–gas interface) due to evaporation. The meniscus is dynamically moving since the solvent front is drawing back while the substrate is withdrawn and a stick-slip motion is observed.^{29–32} Thereby undesirable stripes are formed in the thin film. In the viscous drag regime, *i.e.* at high withdrawal velocities, the film thickness is again increasing with the withdrawal velocity: above the liquid bath surface, the moving substrate entrains the liquid in a boundary layer that splits into two layers (withdrawn layer and drained layer). The draining layer returns to the dispersion reservoir at the stagnation point, where the receding drying line velocity equals the withdrawal velocity. In the case of high withdrawal velocities the substrate is fully withdrawn from the bulk liquid and is coated with a wet film. The withdrawn wet film dries homogeneously over the whole liquid–gas interface. The reversed

evolution of the film thickness in both regimes results in a minimum film thickness in the so-called intermediate regime.³³ With respect to the dip coating of nanorods we have recently reported that the capillary regime is EISA dominated and SIA prevails in the viscous drag regime.²⁶ For EISA a critical nanorod volume fraction in the suspension is required. From a theoretical point of view this critical volume fraction can be described for monodisperse spherocylinders on the basis of the Onsager theory. However, this theory is only valid for long rods with high L/D values around 100.³⁴ Lower volume fractions for phase transitions are calculated by other groups.^{35–40}

In this study we combine *in situ* SAXS to study structure formation with *ex situ* SEM-based image analysis and Raman analysis. This allows us to tailor highly ordered nematic thin films by influencing the relative impact of the resulting evaporation-induced convective flow and externally applied shear forces.

The withdrawal velocity, temperature, solid concentration and aspect ratio are systematically varied. We derive for the first time processing guidelines for the controlled application of EISA and SIA in dip coating. Furthermore, the influence of the governing process parameters on the surface and the bulk order of the resulting thin films are quantified. With optimized process parameters homogeneous nematic thin films with high bulk and surface order can be achieved by dip coating. Highly ordered dense films could also be prepared solely by evaporation. However, significantly longer process times are needed and detrimental stripes are formed due to the stick-slip effect during evaporation. Furthermore, a direct comparison of an EISA-assisted thin film and a SIA-assisted thin film of comparable thicknesses ($\sim 100 \text{ nm}$) and high BO is conducted. Special emphasis is placed on the role of the nanorod aspect ratio. It is shown that already for a very narrow range of the aspect ratio limitations in nematic film formation prevail: in EISA-assisted thin film formation a critical nanorod volume fraction for phase transition exists which is predominantly dependent on the aspect ratio. The phase transition in solution is investigated by SAXS measurements and rheology analysis. Additionally, the aspect ratio dependent shear-alignment is shown.

Experimental

Preparation and characterization of ZnO nanorods

Zinc oxide (ZnO) nanorods were obtained by precipitation from solutions of zinc acetate dihydrate ($\text{ZnAc}_2 \cdot 2\text{H}_2\text{O}$, $\geq 99\%$ purity, VWR, Germany) and potassium hydroxide (KOH, $\geq 85\%$ purity, Carl Roth, Germany) in methanol (99.5% purity, Carl Roth, Germany) following the protocol given by Pacholski *et al.*⁴¹ and Voigt *et al.*⁴² It is well known that the aspect ratio (AR, length/diameter) of the precipitated nanorods increases with synthesis time: the mean AR can be tuned between 2 and 8 by adjusting the synthesis time from 1 day to 14 days. The particle size distributions of the ZnO nanorod synthesis were characterized by using a field emission scanning electron

microscope (SEM, ULTRA 55, Carl Zeiss NTS, Germany). For each sample the lengths and the diameters of up to 500 individual rods were measured by using the software ImageJ provided by the National Institutes of Health (USA). ZnO nanorods with low AR (<5) and high AR (>5) were compared and the AR was identified as a critical parameter for film formation. On the basis of the simulation conducted by Veerman and Frenkel the threshold for low and high AR was chosen to be 5: numerically Veerman and Frenkel found that spherocylinders with higher AR than 5 form stable nematic phases.⁴³ The ZnO nanorod AR is adjusted by the synthesis time (see S1†).

Preparation and characterization of well-stabilized nanorod dispersions

ZnO nanorod dispersions with different solid concentrations were obtained by transferring the ZnO particles into appropriate amounts of absolute ethanol. Stabilization was achieved by adding 20 wt% (related to the ZnO mass) of TODA [2-(2-(2-methoxyethoxy)ethoxy)acetic acid] purchased from VWR (Germany).^{26,44} To qualify primary particle stabilization sufficiently diluted dispersions (0.01 wt%) were analysed by dynamic light scattering (DLS) using a Zetasizer ZEN3600 (Malvern Instruments, UK). SAXS measurements were conducted using a unique and highly customized instrument developed by SAXSlab (Denmark) which is described elsewhere.⁴⁵ In brief the collimated Cu-K α X-ray beam has a size of $150 \times 150 \mu\text{m}^2$ at the sample position and the sample to detector distance is 2068 mm. Due to the increasing absorption of the highly concentrated samples, the measurement times were chosen between 3600 s for the lower concentrated samples and up to 36 000 s for the highly concentrated samples. To determine the different scattering contributions of form factors and structure factors all samples were additionally diluted to a concentration of approximately 0.042 vol% and were measured for 3600 s. Rheology measurements were performed using a cone/plate system in a MC 200 rotational rheometer (Physica, Anton Paar, Germany) at 20 °C using a 50 mm plate and a cone angle of 2°. A solvent trap was used to minimize solvent evaporation during the measurements.

Preparation and characterization of ZnO nanorod thin films

ZnO nanorod thin films were prepared either by dip coating or solely by evaporation under controlled conditions in a climate chamber.²⁶ For all experiments the relative humidity was set to 10%. Pre-cleaned silicon wafer slides coated with 20 nm Ti, 100 nm TiN and 500 nm Al were used as substrates. The coating omits the superimposing effect of the silicon signal during Raman measurements of the ZnO layers. The surface orders (SO) were obtained by screening angle distributions of individual nanorods in SEM images: the measured angles (θ) of individual rods were normalized in between +90° and -90° by setting the maximum occurring frequency in the angle distribution to zero. For each sample the area in the range of +15° to -15° of the resulting angle distribution was integrated and compared to the integrated area in the range of +90° to -90°.

To determine the SO in the resulting films, the angle of at least 200 individual nanorods measured in three different SEM images were analysed for each sample. The three images were used to calculate the mean value and the standard deviation of the SO. To exclude the effects of the substrate edge and the preliminary contact line, only SEM images from the centre of the films were evaluated. Film thicknesses were measured by using a tactile profilometer (DektakXT, Bruker Nano Surfaces Division, Germany): to measure the film thickness each sample was screened along three independent lines in the direction of the substrate withdrawal. Averaging was performed along each line and the mean value of the three lines and its standard deviation were calculated. Bulk order (BO) was analysed by polarized and orientation-dependent Raman spectroscopy: Raman spectra were recorded using a confocal Raman spectrometer (LabRAM HR Evolution, Horiba, Germany). A He-Ne laser ($\lambda = 633 \text{ nm}$) was used. The laser beam was focused on the thin film with a 100-fold objective (numerical aperture 0.9, laser spot size $\approx 0.85 \mu\text{m}$). The hole and slit were fully opened at $1200 \mu\text{m}$ to record the maximum signal intensity over the bulk film. The grating was set to 1800 gr per mm. The polarization was realized by using a half-wave plate so that the incident light polarization could be rotated by an angle θ . The scattered light passed through an analyser to efficiently detect the phonons polarized parallel or perpendicular with respect to the optical axis of the sample. A scrambler was installed to remove polarization effects which were caused by the diffraction grating by transforming the linear polarization into a circular polarization. Phonons parallel to the *c*-axis of the ZnO nanorod enhance the intensity of $A_1(\text{TO})$ at about 378 cm^{-1} . In EISA-assisted thin films scattering intensities parallel to the contact line were analysed since the *c*-axes of the ZnO nanorods predominantly align parallel to the contact line. In SIA-assisted films scattering intensities perpendicular to the contact line (parallel to the withdrawal direction) were analysed, since the *c*-axes of the ZnO nanorods predominantly align in the direction of withdrawal. All relevant phonon mode frequencies of wurtzite ZnO in the measured range of 175 cm^{-1} and 475 cm^{-1} are in summary: $2\text{-E}_2(\text{M})$ at 331 cm^{-1} , $A_1(\text{TO})$ at 378 cm^{-1} , $E_1(\text{TO})$ between $413\text{--}420 \text{ cm}^{-1}$ and E_2^{high} at 438 cm^{-1} . After baseline correction the spectra were normalized to $2\text{-E}_2(\text{M})$ at 331 cm^{-1} since this peak is indifferent to polarization. The spectra were fitted by Lorentzian functions and the integrated band intensity of $A_1(\text{TO})$ was compared to the sum of all other relevant modes.²⁶ 100 individual spectra were analysed in order to obtain a mean value and a standard deviation for the BO. Further details can be found elsewhere.²⁶

Results and discussion

Analysing the critical volume fraction for phase transition by SAXS

The critical nanorod concentration for isotropic-anisotropic phase transition was determined by SAXS measurements.

The scattering intensity for SAXS measurements is given by:

$$I(Q) = n(\Delta\rho)^2 \cdot V^2 \cdot F(Q)^2 \cdot S(Q) \quad (1)$$

where n is the particle number, $\Delta\rho$ is the scattering contrast, V is the particle volume, $F(Q^2)$ is the form factor and $S(Q)$ is the structure factor.

In the case of high dilution the inter-particle distance is large and thus in the given Q -range the structure factor can be assumed to be $S(Q) = 1$. This allows extracting the structure factor of the concentrated samples without additional parameters by simply dividing the normalized scattering patterns of the concentrated and the respective diluted sample:

$$S(Q) = \frac{I(Q)_{\text{conc}}}{I(Q)_{\text{diluted}}} = \frac{n(\Delta\rho)^2 \cdot V^2 \cdot F(Q)^2 \cdot S(Q)}{n(\Delta\rho)^2 \cdot V^2 \cdot F(Q)^2} \quad (2)$$

The scattering patterns for the concentrated and diluted samples are shown in S2† exemplarily for 3.4 vol% and 36 vol% at $AR > 5$ and $AR < 5$. The results for the resulting $S(Q)$ are depicted for the different concentrations from 1.5 vol% to 36 vol% in Fig. 1.

For all concentrations of low AR and high AR, peaks of the structure factor at high Q -values can be found ($Q > 0.35 \text{ nm}^{-1}$). These peaks represent a d -spacing, which is close to the diameter of the ZnO nanorods. Thus, it might indicate the existence of a few small agglomerates for all samples as the centres of the rods can only come as close together as their particle diameter. In the synthesis the nanorods exist as agglomerates. After adding the stabilizer most of the nanorods are primary particle stabilized. In addition to the peak at high Q -values,

another peak is seen for all samples at small Q -values, which shifts from $Q = 0.08 \text{ nm}^{-1}$ for 1.5 vol% to $Q = 0.18 \text{ nm}^{-1}$ for 36 vol% for high AR. The respective d -values decrease from about 75 nm to 35 nm and indicate the changing mean distance between the rods in solution for the different concentrations. This distance is smaller in the case of low AR due to the higher number of nanorods in comparison with high AR at a given volume fraction. Interestingly, the second order of this peak can be seen for samples with concentrations higher than 5 vol%, which first appears as a small shoulder and forms a small peak for the highest concentrated samples. This second order shows a long-ranged ZnO nanorod order for very high sample concentrations. Additionally, for concentrations exceeding 25 vol% liquid crystalline features through anisotropic scattering patterns are observed as depicted in Fig. 1 for 36 vol% at the right bottom. In contrast, for low AR nanorods at the same concentrations an isotropic pattern was observed (Fig. 1, right top).

Evaporation-induced self-assembly of ZnO nanorods

In the following, the substrate is not withdrawn and the movement of the contact line occurs only due to evaporation and lowering of the dispersion level in the storage container to omit shear forces. The H , the SO and the BO of ZnO nanorod thin films obtained by EISA are analysed. In the EISA regime the c -axis of the ZnO nanorods align parallel to the contact line in order to maximize the interfacial coverage per particle, which in turn minimizes the Helmholtz free energy of the system.²⁶ Low volume fractions were selected to ensure Brownian motion for free diffusion of the ZnO nanorods to the

Fig. 1 Left: Scattering factor $S(Q)$ versus scattering vector Q for low (dashed lines) and high AR nanorods (solid lines). The first peak at small Q -values shifts for increasing ZnO concentrations and gives the mean rod distance. Smaller peaks at $Q > 0.35 \text{ nm}^{-1}$ are observed, which indicate the formation of few dimers or small oligomers for all samples. Right: Scattering patterns of ZnO dispersions at 36 vol% for low AR < 5 (top) and high AR > 5 (bottom) nanorods.

Fig. 2 On the left: Film height over the receding speed of the dispersion level is assigned. On the right: SO (closed symbols) and BO (open symbols) over receding speed of the dispersion level are outlined.

contact line. If the nanorod diffusion is constrained as realised in high volume fractions, rather unordered and thick films are formed (see S3†). Temperatures of 10 °C, 20 °C and 40 °C were set in the climate chamber to increase the evaporation rate. Increasing evaporation rates led to increasing receding speeds of the dispersion level (r). The receding speed of the dispersion level was estimated by the measured length in the direction of withdrawal on the covered substrate divided by the deposition time. With increasing temperature, the receding speed of the dispersion level increases leading to an increase of film height. This is due to the increasing mass flow of nanorods to the contact line (Fig. 2, left).

Thereby the effect is enhanced at increased volume fractions in the initial dispersion. An exception is seen for low AR nanorods at comparable concentrations (Fig. 2, left, upward triangles). Low AR nanorods fail to form compact thin films. This is visualized by the high standard deviation in H (see Fig. 2, left, upward triangles). Low AR nanorods resemble spherical particles which have a lower contact area and lower affinity to the substrate, so that a planar coverage is not possible by diluted dispersions as used for EISA. This results in ZnO nanorod deposition only in the stripe and not in the spacing during stick-slip deposition.⁴⁶ Therefore non-compact sparse stripes with substrate coverages below 80% form (see S4†).

An increase of SO is achieved by increasing r (Fig. 2, right, filled symbols). The trend in SO is somewhat similar to the trend in H (see Fig. 2, left). The BO (open symbols) does not show the same trend as the SO. For high AR nanorods it shows a maximum at a moderate deposition rate of $26 \mu\text{m min}^{-1}$ (20 °C). At comparable concentrations SO and BO are clearly lower for low AR nanorods than for high AR nanorods. This is also attributed to non-complete coverage. Lower concentrations at the same AR result in lower BO.

As long as the wet solvent film of the meniscus is thick enough, particles can diffuse and align at the contact line. As soon as evaporation thins the meniscus to a critical thickness, which is in the range of the particle diameter, the particles

cannot rotate or diffuse anymore. Thus, the particles are frozen at their positions by particle interactions and capillary forces. EISA relies on the increase of the ZnO nanorod volume fraction prior to drying which results in an isotropic-anisotropic phase transition. In order to achieve high BO the critical concentration for phase transition has to be reached before the meniscus thickness falls below the critical thickness (see Fig. 1). At lower r (corresponding to 10 °C) the particle mass flow is decreased. Additionally, since the surface tension is a function of temperature, the meniscus height is thin. Thus, a full phase transition does not occur. At high r (40 °C) the increased mass flow supports a quick phase transition in the meniscus. Convective flow rotates the ordered nanorod structures parallel to the contact line in order to reduce the Helmholtz free energy. However, the meniscus thickness is so high that as observed from SEM imaging in most cases the aforesaid rotation is not completed prior to drying. The resulting structure is thus comparable to EISA assisted ZnO nanorod films produced by using extremely high initial volume fractions (3.4 vol%, see S3†). In comparison, at lower volume fractions lower mass flow results in incomplete phase transition (Fig. 2, right, open downward triangle). At 20 °C and AR > 5 the BO is high: the evaporation rate is low enough to allow for the phase transition and, at the same time, fast enough so that a sufficient amount of nanorods is being transported to the contact line (Fig. 2, right, open circles). The volume fraction exceeded the critical volume fraction of 25 vol% for AR > 5 prior to drying as analysed by *in situ* SAXS measurements (see Fig. 1).

Shear-induced alignment of ZnO nanorods by dip coating

To reduce process time and to omit detrimental stripe formation by the stick-slip effect, we placed special emphasis on SIA assisted thin films by dip coating. Densely packed nanorods in the direction of withdrawal are formed with higher volume fractions. For the shear-induced alignment of ZnO nanorods we utilize the shear forces induced by substrate withdrawal. In order to optimize the degree of order in SIA assisted

thin films the film height, the surface order and the bulk order are analysed as a function of the AR, the dispersion concentration, the temperature and the withdrawal velocity.

The results are given in Fig. 3 (film height), 4 and 5 (surface and bulk order). At a constant temperature of 40 °C and a similar volume fraction (3.4 vol%) high and low AR nanorods show a similar parabolic evolution of the film thicknesses over the withdrawal velocity (Fig. 3, left, boxes and circles). A minimum thickness is observed around 30 mm min⁻¹. Processing of the lower volume fraction for high AR nanorods (upward triangles) again follows the above mentioned para-

bolic evolution of the film thickness. However, reducing the nanorod concentration reduces the overall film thickness in all three regimes. A similar result has been shown by Grosso for sol-gel particles.²⁷ Additionally the minimum film thickness is shifted to higher velocities (around 60 mm min⁻¹).

Changes in the temperature from 40 °C to 20 °C reduce the film thickness only in the capillary regime (Fig. 3, right, downward triangles and diamonds): the viscosity is increased by reducing the temperature. Furthermore, surface tension and density are increased, which are counter-acting on the viscosity-effect. Hence, the film thickness in the viscous drag

Fig. 3 Height of the dried film *versus* withdrawal velocity. In the left diagram (constant temperature of 40 °C) high (boxes) and low (circles) AR nanorods are compared at the same volume fractions. Furthermore, for high AR nanorods (boxes), high and low (upward triangles) volume fractions are compared. In the right diagram for constant AR different processes' temperatures of 40 °C (downward triangle) and 20 °C (diamonds) at the same volume fractions are compared. Furthermore at a constant temperature of 20 °C volume fractions of 3.4 vol% (diamonds) and 5.7 vol% (stars) are compared.

Fig. 4 SO (left) and BO (right) *versus* withdrawal velocity. At a constant temperature of 40 °C high (boxes) and low (circles) AR nanorods at the same volume fractions are compared. Furthermore, at AR > 5 high volume fraction (boxes) and lowered volume fraction (upward triangles) are compared.

Fig. 5 SO (left) and BO (right) versus withdrawal velocity. At high AR 40 °C (downward triangles) and 20 °C (diamonds) process temperatures are compared. Furthermore at 20 °C a higher volume fraction of 5.7 vol% (stars) is compared to a lower volume fraction of 3.4 vol% (diamonds).

regime is not influenced by temperature. At lower temperature the particle deposition rate by evaporation-induced convective liquid flow is reduced in the capillary regime. Thus, the thickness of the deposited film is reduced. Temperature plays only a minor role on film thickness in the shear-induced regime. At a constant temperature of 20 °C for high AR nanorods, an increase in volume fraction shifts the minimum thickness to a lower withdrawal velocity of 6 mm min⁻¹ (Fig. 3, right, stars). Compared to the films obtained from processing lower volume fractions the overall film thickness in the capillary and viscous drag regime is higher. In the intermediate regime, however, even thinner films are achieved (Fig. 3, right, stars). The increase in viscosity, which is associated with the increasing suspension concentration, might change the conditions in the boundary layer. Thus, the gravitational impact on the draining layer is enhanced.

The SO and BO of the resulting films processed at a constant temperature of 40 °C are depicted in Fig. 4. High and low concentrations of AR > 5 nanorods show high SO in the capillary regime (Fig. 4, left, boxes and upward triangles). Low AR nanorods at the same concentration show slightly lower SO in the capillary regime (Fig. 4, left, circles).

Remarkably, a parabolic evolution comparable to the film thickness is observed only for the SO over the withdrawal velocity for high AR nanorods at 3.4 vol% (Fig. 4, left, boxes). The SO at lower volume fraction and AR < 5 is not increasing in the viscous drag regime. Instead a plateau is reached (Fig. 4, left, circles and upward triangles). The BO (Fig. 4, right) does not follow the trend of the SO. This is also the case for EISA-assisted thin films (see Fig. 2, right). The BO at AR > 5 and 3.4 vol% is at the maximum in the intermediate regime (see Fig. 4, right, boxes). At low AR and lower volume fractions the BO is significantly reduced in all three regimes (Fig. 4, right, circles and upward triangles). In order to understand the results of SO and BO not only evaporation but also the competing effect of shear has to be discussed. For the presented

experiments, solvent evaporation is assumed to be constant. Additional substrate withdrawal during dip coating introduces shear forces. The shear effects are increasing with increasing withdrawal velocities. The withdrawal velocity is linked to the film thickness in a parabolic manner. The film thickness itself is directly linked to the critical thickness at the meniscus. At the same temperature the particle flux to the meniscus is constant. In the capillary regime at low withdrawal velocities the critical particle volume fraction for phase transition will be exceeded. Highly ordered nematic thin films at the substrate surface are formed. Nanorods with AR < 5 have more freedom to rotate prior to drying, so that less SO is achieved (see Fig. 4, left). The nanorods at the substrate-solvent interface are, however, shear-aligned by the substrate withdrawal. Between the highly ordered top and bottom layers the nanorods are gradually reoriented. Thus, the overall BO is at a minimum in the capillary regime (see Fig. 3, right). Therefore the SO is high and the BO is low in the capillary regime.

Shear-induced alignment caused by the substrate at the solid-solvent interface enhances the effect of SIA with increasing velocity. As a consequence a predominant nanorod orientation in the direction of substrate withdrawal is evidenced in the intermediate regime. In contrast, the SO is at minimum, since the critical concentration for the phase transition is not reached before the substrate is withdrawn. The nanorods at the surface are randomly oriented. In the viscous drag regime the substrate is withdrawn fully and is not in contact with the dispersion reservoir. EISA at the solvent-air interface controls the surface ordering and tends to reorient the nanorods parallel to the contact line. Thus, the overall BO in the viscous drag regime is disturbed by the effect of EISA. In the case of high AR and high volume fraction the position of the nanorods is too inert for a reorientation by EISA, thus the SO is increasing.

The SO and BO of the resulting films processed at a constant AR > 5 are depicted in Fig. 5. For the same volume frac-

tion processed at 40 °C and 20 °C a parabolic evolution of the SO with increasing withdrawal velocity is observed (see Fig. 5, left, downward triangle and diamonds). At 20 °C (diamonds) an overall higher SO is achieved in the viscous drag regime due to relatively low evaporation rates: the pre-aligned nanorods are rarely reoriented by EISA. An increase in volume fraction to 5.7 vol% at 20 °C (stars) shows almost a constant SO of around 70% for withdrawal velocities exceeding 3 mm min⁻¹. The high SO is achieved due to rare reorientation by EISA due to the relatively high viscosity in the initial dispersion. At 40 °C the SO and BO (downward triangle in Fig. 5 left and right) show a reverse trend. The reduction of the temperature to 20 °C at the same concentration results in the formation of two maxima for the BO (Fig. 5, right, diamonds). The maxima are found at the intersections from the capillary to intermediate and the intermediate to viscous drag regime, respectively (compare Fig. 3, right). At a higher volume fraction processed at 20 °C (Fig. 5, right, stars) the maximum in BO is shifted in the direction of the capillary regime.

Compared to the SO, a reverse trend is expected at 3.4 vol% and 40 °C (Fig. 5, right, downward triangles) for the BO: EISA is dominating at low withdrawal velocities and SIA is dominating at higher withdrawal velocities. In the viscous drag regime high temperatures favour a reorientation by EISA. Reduction of the temperature (Fig. 5, right, diamonds) leads to reduction of evaporation and minimization of the reorientation effect by EISA. A shift of the maximum in BO to higher velocities exceeding 60 mm min⁻¹ and a smaller minimum is found for the BO at 3 mm min⁻¹. Film thicknesses at both velocities are at minimum as seen in Fig. 2(right): the effect of SIA is at

maximum. At 3 mm min⁻¹ EISA has a counter-acting effect on the SO; at 60 mm min⁻¹ the influence of EISA is low, which leads to a high SO. Higher volume fractions of 5.7 vol% at 20 °C (Fig. 3 right, stars) shift the maximum BO to lower withdrawal velocities due to lower diffusional freedom of the nanorods in the initial dispersion. This is clearly related to the earlier initiating effect of SIA at the substrate–solvent interface due to higher viscosities. Increasing withdrawal velocities should further increase the effect of SIA. However, compared to higher temperature and lower volume fraction (see Fig. 3, right, downward triangle) the film thickness is increasing more steeply (see Fig. 3, right, stars). The entrained thick wet film is affected by convective flow. In the resulting films we observed shear-aligned domains which were reoriented by EISA (see S5†). Conclusively, the increased height of the wet film enables an evaporation-induced reorientation, which leads to a reduced BO at high withdrawal velocities.

Large scale bulk order in EISA and SIA evidenced by Raman mapping

EISA-assisted thin films show periodic alternation in film thickness due to the stick-slip effect. Additionally long process times are needed for the phase transition at the contact line. In comparison, for SIA-assisted thin films the process time is noticeably reduced from μm min⁻¹ to mm min⁻¹. Moreover, a homogeneous film height is achieved, since the withdrawn film dries homogeneously at the liquid–air interface. In order to compare EISA- and SIA-assisted thin nematic films Raman maps with a size of 60 μm × 60 μm were analysed. The bulk order is visualized in Fig. 6. A ZnO nanorod thin film pro-

Fig. 6 Raman map of a ZnO nanorod thin film processed by EISA with high BO parallel to the contact line (left) and a ZnO nanorod thin film processed by dominating SIA forces with high BO in the direction of withdrawal (right). On the bottom the cross-sectional view of the ZnO nanorod thin films, which were broken along the withdrawal direction, in the EISA and SIA thin films are depicted.

cessed by EISA at 20 °C and 0.146 vol% (cf. Fig. 2) is compared to a SIA dominated dip coated thin film processed at 40 °C from a dispersion with a high volume fraction of 3.4 vol% (cf. Fig. 5). The ZnO nanorods align parallel to the contact line in the purely EISA processed thin film as depicted in Fig. 6 (bottom, right). Nanorod alignment in the direction of substrate withdrawal was achieved by shear effects at the substrate–solvent interface (Fig. 6, bottom, left). The ZnO nanorod thin film obtained by EISA comprises a film thickness of only 185 nm and an extremely high BO of $91 \pm 13\%$. The ZnO nanorod thin film obtained by SIA at optimized parameters shows a comparable BO of $83\% \pm 11\%$ and an even lower film thickness of 136 nm.

From the conducted systematic process parameter study above, we derive that the interplay of nanorod diffusional freedom and the wet film thickness at the meniscus or the thickness of the entrained film are the crucial factors for film formation. Pre-confinement of the nanorods in the dispersion support shear forces. However, wet films that are too thick allow reorientation by evaporation. Liquid films which are too thin do not allow phase transition and are not affected by shear forces.

For Newtonian and non-evaporating liquids the Landau–Levich principle holds in the viscous drag regime, *i.e.* the film thickness scales with $H \sim v^{2/3}$.⁴⁷ As can be seen in Fig. 3 the aforementioned power law is only true for ZnO nanorods processed from ethanol at high volume fractions of 5.7 vol% and 20 °C, presumably due to the low evaporation rates. Under all other processing conditions the experimentally obtained power law scales with an exponential factor of around 0.25. The latter finding might be due to the evaporation and the relatively low viscosity. At low withdrawal velocities the film thickness is dominated by evaporation and has been modelled for aqueous systems by Dimitrov and Nagayama as well as Berteloot *et al.*^{48,49} According to the literature the film thickness in this regime scales with $H \sim v^{-1}$ or $H \sim v^{-2}$. Again this holds only for a high volume fraction of 5.7 vol% and 20 °C (Fig. 3, right, stars). For all other conditions exponents around 0.58 were found for the processed ZnO nanorod suspensions. We suggest that the higher evaporation rates and the lowered surface tension of ethanol compared to water might be the reason: the low contact angle of ethanol limits the particle flux to the contact line and the meniscus area.

AR dependent shear response and structure formation

In order to investigate the influence of nanorod AR on the shear-alignment, rheology measurements were conducted. In the literature it was shown that shear rates in dip coating can vary between 50 s^{-1} and 1000 s^{-1} depending on the position in the wet film. At the stagnation point maximum shear rates around 1000 s^{-1} were measured.²²

In order to study the shear response of the ZnO nanorod dispersions different concentrations (similar to the SAXS measurements – see Fig. 1) were used. In Fig. 7 the viscosity as a function of the volume fraction of ZnO at a fixed shear rate of 1000 s^{-1} is depicted for low $AR < 5$ and high $AR > 5$ ZnO

Fig. 7 Viscosity versus ZnO nanorod volume fraction for $AR > 5$ and $AR < 5$.

nanorods. The viscosity is increasing with the volume fraction independent of the AR. At high volume concentrations between 12 and 25 vol% the viscosity for high AR nanorods is lower than for low AR nanorods. The hydrodynamic forces at high AR and high volume fractions are strong enough to align the long axis of the rods in the direction of the flow and therefore the dispersion shows a shear thinning effect (see S6†).⁵⁰ Shear thinning has also been observed in ethylene glycol-titanate nanotube nanofluids by Chen *et al.* or in aqueous suspensions of carbon nanotubes.^{51,52} This means that at the same volume fraction nanorods with $AR > 5$ are likely to align in the direction of the shear, while nanorods with $AR < 5$ are randomly oriented. The rheology measurements support the SAXS measurements and the dip coating results. In SAXS anisotropic structure formation (see Fig. 1) for nanorods with $AR > 5$ above 25 vol% is observed, which fits well to the shear thinning effect. The dip coating result shows that nanorods with $AR > 5$ are more appropriate for shear-alignment and hence result in highly ordered nematic thin films.

For further verification the rotational Péclet number Pe_{rot} was calculated, which gives the ratio between hydrodynamic forces and Brownian diffusion:

$$Pe_{rot} = \frac{\dot{\gamma}}{D_{ro}} \quad (3)$$

with the rotational diffusion coefficient D_{ro}

$$D_{ro} = \frac{3k_B T \left(\ln \left(\frac{L}{D} \right) - 0.8 \right)}{\pi \eta_s L^3}$$

where η_s is the solvent viscosity, T the temperature set at 20 °C and k_B the Boltzmann constant.⁵⁰

At a high shear rate of 1000 s^{-1} $Pe_{rot} > 1$ holds true for higher concentrations of high AR nanorods due to the dominating hydrodynamic forces. The equilibrium self-assembled

anisotropic phase at high concentration (see Fig. 1) is disturbed by shearing, but the network is not fully destroyed. Vermant and Solomon concluded that the microstructure is strongly influenced by interparticle forces, Brownian motion and hydrodynamic interactions. They highlighted that dispersions with repulsive interactions readily form ordered crystalline structures upon application of steady-shear flow.⁵³ Examples are given in various studies of one-dimensional nanostructures, where shearing implemented by screen printing, spin coating or manual shearing by a cover slip, enhances the overall alignment in the microstructure.^{54–58}

The shear thinning effect is seen most strongly for ZnO nanorod volume fractions exceeding 25 vol% with high AR nanorods (see S6†). Direct deposition of this highly concentrated dispersion is not possible, since the resulting film will exceed the critical cracking thickness. Reduced Brownian motion or nanorod confinement is achieved by varying the number density ν . As defined by Doi and Edwards the system is dilute for $\nu < \frac{1}{L^3}$ and concentrated for $\nu > \frac{1}{DL^2}$. The regime in between is defined as semi-dilute:⁵⁹

$$\frac{1}{L^3} \ll \nu \ll \frac{1}{DL^2} \quad (4)$$

High AR nanorods ($AR > 5$) are pre-confined in the semi-dilute regime at 3.4 vol%, while the short nanorods ($AR < 5$) are still in the dilute regime at the same volume fraction. The pre-confinement of the ZnO nanorods in the semi-dilute region enhances the order in the dip coated film as seen in Fig. 4 (right) for 3.4 vol% (boxes) compared to 1.5 vol% (upward triangles). And as expected from the above calculations the nanorods with $AR < 5$ show also low BO (see Fig. 3, right circles). Above 12 vol% the dispersions are in the concentrated regime for high AR nanorods according to the Doi and Edwards theory. Above this volume fraction a beginning of the shear-thinning effects are observed (see S6†). At low AR the shear thinning effect is not observed at comparable high concentrations, although the dispersion is in the concentrated regime according to eqn (4). Therefore, low order is achieved, when using dispersions with low AR as seen in Fig. 4 (right, circles).

Phase transition compared to theory and experiment

For spherocylinders the volume fractions (Φ) where the phase transitions from isotropic to biphasic and biphasic to nematic should occur can be calculated theoretically according to the Onsager theory.

The first phase transition from an isotropic to a biphasic system occurs at $\Phi_I = 3.34(\frac{D}{L})$. The second phase transition from the biphasic to the nematic system occurs at $\Phi_N = 4.49(\frac{D}{L})$.³⁴ For the investigated aspect ratios (high AR 6.6 and low AR 3.7) the volume fractions for the biphasic transition are calculated to be around $\Phi_{I, \text{high AR}} = 51 \text{ vol\%}$ and $\Phi_{I, \text{low AR}} = 100 \text{ vol\%}$, respectively. For the nematic phase transition the volume fractions are $\Phi_{N, \text{high AR}} = 69 \text{ vol\%}$ and over $\Phi_{N, \text{low AR}} = 100 \text{ vol\%}$. We observe a phase transition already at a volume fraction of about 25 vol% (see Fig. 1) which is much

lower than the calculated values. Strictly speaking, however, the Onsager theory holds for monodisperse spherocylinders with hard-rod interactions and is only valid for long rods with ARs around 100.³⁴ Thus, the classical Onsager theory only gives qualitative explanations for our findings.

In order to consider one-dimensional nanostructures of a low aspect ratio and particle–particle interactions, expansion of the Onsager theory has been continuously performed over the last few decades. Beside van der Waals interactions, the effects of electrostatic interactions were studied.^{38,39} Furthermore, attractive interactions between the spherocylinders by depletion forces were considered by Bolhuis *et al.*⁴⁰ Attractive interactions support the parallel orientation of the rods, so that the anisotropic phase starts to appear already at lower volume fractions as observed by Li *et al.*³⁵ Bolhuis and Frenkel have simulated spherocylinders of low AR and found that the lower limit for nematic phases is at $AR > 3.7$.³⁶ From the calculated phase diagram of Bolhuis and Frenkel it is read for our system that already at a concentration of 32 vol% an isotropic–nematic phase transition occurs for the rods with an AR of 6.6. For the AR of 3.7 the isotropic–nematic phase transition is simulated to occur around 40 vol%.

In addition to the AR the polydispersity in length of the nanorods has been identified as a crucial factor: based on Monte Carlo simulations Bates and Frenkel limited the maximum allowed polydispersity in length to 18% for a smectic phase to occur. In polydisperse systems the longer rods readily undergo the phase transition already at lower volume fractions and thus the biphasic region is broadened. The polydispersity for low AR ZnO nanorods in this study is around 20%, while the polydispersity for high AR is around 40%. For the calculation of the polydispersity the normalized standard deviation was taken, based on the ratio of the mean value and the standard deviation of the distribution length (L) as proposed by Bates and Frenkel.³⁷ Consequently, the formation of smectic phases is inhibited, nematic phases form at lower volume fractions and the biphasic region is broadened.

Lemaire *et al.* synthesized goethite nanorods with an AR between 5 and 10 and observed the phase transition at lower values than the theoretical one, which is explained by the polydispersity, the relatively low AR and electrostatic interactions.^{60,61} Similar experimental observations, where the Onsager theory is overestimating the isotropic–nematic phase transition, are noticed for SiO₂ nanorods, TiO₂ rutile nanorods and CdSe nanorods.^{54,55,62} Further studies on the phase behaviour of one-dimensional nanostructures, as for example cellulose, carbon nanotubes and Ag nanowires have also been published.^{56,63–66} Both, advanced simulations and the experimental studies prove the occurrence of isotropic–nematic phase transitions at significantly lower volume fractions than predicted by Onsager theory. This is also the case in our system as proven by the SAXS measurements (see Fig. 1). As seen in the EISA films (see Fig. 2) the AR is a crucial factor in the isotropic–anisotropic phase transition. The maximum BO of 91% at 20 °C is achieved since the phase transition has exceeded the critical concentration of 25 vol% (see Fig. 1)

when evaporation thins the meniscus to the critical meniscus height. Thus, the phase transition has to be controlled mainly by the AR, the initial volume fraction and the drying time, which can be influenced by temperature.

Conclusions

Within this account the relative influences of evaporation-induced convective flow and externally applied shear forces on film thickness, surface order and bulk order of thin nematic films obtained from dip coating of ZnO nanorods, which exhibit different AR, were systematically analysed. The relative influences of the two counteracting mechanisms were varied by carefully adjusting the process parameters. In thin films, which are prepared solely by evaporation, the critical volume fraction for phase transition has to be overcome in the meniscus prior to drying. At 20 °C in nanorod-ethanol dispersions the meniscus thickness is high enough for a complete phase transition. The critical volume fraction for the phase transition is found to be above 25 vol% for nanorods with $AR > 5$. Nanorods with $AR < 5$ do not undergo a phase transition at the same volume fraction. In order to minimize the necessary process times and to avoid the detrimental stripe formation thin films can be formed by shear-induced alignment. Homogeneous thin nematic films are formed. In dip coating shear flow benefitting from high AR and high viscosities at high withdrawal velocities are utilized. Comparably high BOs and low film thicknesses can be achieved in EISA- and SIA-assisted thin films by optimizing the process conditions. We derive that the impact of evaporation-induced convective flow and externally applied shear forces is determined by the interplay of critical wet film thickness and nanorod diffusional freedom.

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Notes and references

- 1 C. J. Brinker, Y. Lu, A. Sellinger and H. Fan, *Adv. Mater.*, 1999, **11**, 579–585.
- 2 A. V. Titov and P. Král, *Nano Lett.*, 2008, **8**, 3605–3612.
- 3 P. A. Kralchevsky and N. D. Denkov, *Curr. Opin. Colloid Interface Sci.*, 2001, **6**, 383–401.
- 4 M. Grzelczak, J. Vermant, E. M. Furst and L. M. Liz-Marzán, *ACS Nano*, 2010, **4**, 3591–3605.
- 5 H. Dai, R. Ding, M. Li, J. Huang, Y. Li and M. Trevor, *Sci. Rep.*, 2014, **4**, 6742.
- 6 A. Dessombz, C. R. Pasquier, P. Davidson and C. Chanéac, *J. Phys. Chem. C*, 2010, **114**, 19799–19802.
- 7 H. Yang and P. Jiang, *Langmuir*, 2010, **26**, 13173–13182.
- 8 J. Yu, L. Gao, Q. Yan, D. Shen and C. Wong, *J. Cryst. Growth*, 2011, **318**, 1129–1133.
- 9 C. Dushkin, H. Yoshimura and K. Nagayama, *Chem. Phys. Lett.*, 1993, **204**, 455–460.
- 10 C. Querner, M. D. Fischbein, P. A. Heiney and M. Drndić, *Adv. Mater.*, 2008, **20**, 2308–2314.
- 11 R. D. Deegan, O. Bakajin, T. F. Dupont, G. Huber, S. R. Nagel and T. A. Witten, *Nature*, 1997, **389**, 827–829.
- 12 A. F. Routh, *Rep. Prog. Phys.*, 2013, **76**, 46603.
- 13 J. Li, B. Cabane, M. Sztucki, J. Gummel and L. Goehring, *Langmuir*, 2012, **28**, 200–208.
- 14 Z. Lin, *Evaporative Self-assembly of Ordered Complex Structures*, World Scientific, Singapore, 2012.
- 15 W. Han, M. He, M. Byun, B. Li and Z. Lin, *Angew. Chem. Int. Ed.*, 2013, **52**, 2564–2568.
- 16 W. Han, B. Li and Z. Lin, *ACS Nano*, 2013, **7**, 6079–6085.
- 17 M. Byun, W. Han, B. Li, X. Xin and Z. Lin, *Angew. Chem. Int. Ed.*, 2013, **52**, 1122–1127.
- 18 S. P. Wargacki, B. Pate and R. A. Vaia, *Langmuir*, 2008, **24**, 5439–5444.
- 19 J. Kim, J. Peretti, K. Lahlil, J.-P. Boilot and T. Gacoin, *Adv. Mater.*, 2013, **25**, 3295–3300.
- 20 B. Li, W. Han, B. Jiang and Z. Lin, *ACS Nano*, 2014, **8**, 2936–2942.
- 21 B. Li, C. Zhang, B. Jiang, W. Han and Z. Lin, *Angew. Chem. Int. Ed.*, 2015, **54**, 4250–4254.
- 22 S. F. Kistler, *Liquid film coating. Scientific principles and their technological implications*, Chapman & Hall, London, 1997.
- 23 S. Thiemann, M. Gruber, I. Lokteva, J. Hirschmann, M. Halik and J. Zaumseil, *ACS Appl. Mater. Interfaces*, 2013, **5**, 1656–1662.
- 24 H. Shimoda, S. J. Oh, H. Z. Geng, R. J. Walker, X. B. Zhang, L. E. McNeil and O. Zhou, *Adv. Mater.*, 2002, **14**, 899.
- 25 J. M. Russell, S. Oh, I. LaRue, O. Zhou and E. T. Samulski, *Thin Solid Films*, 2006, **509**, 53–57.
- 26 R. Srikantharajah, K. Gerstner, S. Romeis and W. Peukert, *Nanoscale*, 2016, **8**, 7672–7682.
- 27 D. Grosso, *J. Mater. Chem.*, 2011, **21**, 17033.
- 28 M. Le Berre, Y. Chen and D. Baigl, *Langmuir*, 2009, **25**, 2554–2557.

- 29 M. Ghosh, F. Fan and K. J. Stebe, *Langmuir*, 2007, **23**, 2180–2183.
- 30 H. Bodiguel, F. Doumenc and B. Guerrier, *Langmuir*, 2010, **26**, 10758–10763.
- 31 J. Huang, R. Fan, S. Connor and P. Yang, *Angew. Chem.*, 2007, **119**, 2466–2469.
- 32 W.-J. Chung, J.-W. Oh, K. Kwak, B. Y. Lee, J. Meyer, E. Wang, A. Hexemer and S.-W. Lee, *Nature*, 2011, **478**, 364–368.
- 33 M. Faustini, B. Louis, P. A. Albouy, M. Kuemmel and D. Grosso, *J. Phys. Chem. C*, 2010, **114**, 7637–7645.
- 34 L. Onsager, *Ann. N. Y. Acad. Sci.*, 1949, **51**, 627–659.
- 35 L.-s. Li, M. Marjanska, G. H. J. Park, A. Pines and A. P. Alivisatos, *J. Chem. Phys.*, 2004, **120**, 1149.
- 36 P. Bolhuis and D. Frenkel, *J. Chem. Phys.*, 1997, **106**, 666–687.
- 37 M. A. Bates and D. Frenkel, *J. Chem. Phys.*, 1998, **109**, 6193.
- 38 G. J. Vroege and H. N. W. Lekkerkerker, *Rep. Prog. Phys.*, 1992, **55**, 1241–1309.
- 39 A. Stroobants, H. N. W. Lekkerkerker and T. Odijk, *Macromolecules*, 1986, **19**, 2232–2238.
- 40 P. G. Bolhuis, A. Stroobants, D. Frenkel and H. N. W. Lekkerkerker, *J. Chem. Phys.*, 1997, **107**, 1551.
- 41 C. Pacholski, A. Kornowski and H. Weller, *Angew. Chem., Int. Ed.*, 2002, **41**, 1188–1191.
- 42 M. Voigt, M. Klaumünzer, H. Thiem and W. Peukert, *J. Phys. Chem. C*, 2010, **114**, 6243–6249.
- 43 J. A. C. Veerman and D. Frenkel, *Phys. Rev. A*, 1990, **41**, 3237–3244.
- 44 S. Schäfer, R. Srikantharajah, M. Klaumünzer, V. Lobaz, M. Voigt and W. Peukert, *Thin Solid Films*, 2014, **562**, 659–667.
- 45 T. Schindler, J. Walter, W. Peukert, D. Segets and T. Unruh, *J. Phys. Chem. B*, 2015, **119**, 15370–15380.
- 46 S. Watanabe, K. Inukai, S. Mizuta and M. T. Miyahara, *Langmuir*, 2009, **25**, 7287–7295.
- 47 L. Landau and B. Levich, *Acta Physicochim. URSS*, 1942, **17**, 42–54.
- 48 A. S. Dimitrov and K. Nagayama, *Langmuir*, 1996, **12**, 1303–1311.
- 49 G. Berteloot, A. Daerr, F. Lequeux and L. Limat, *Chem. Eng. Process.*, 2013, **68**, 69–73.
- 50 U. Bröckel, W. Meier and G. Wagner, *Product Design and Engineering. Formulation of Gels and Pastes*, Wiley-VCH, Weinheim, 2013.
- 51 H. Chen, Y. Ding, A. Lapkin and X. Fan, *J. Nanopart. Res.*, 2009, **11**, 1513–1520.
- 52 Y. Ding, H. Alias, D. Wen and R. A. Williams, *Int. J. Heat Mass Transfer*, 2006, **49**, 240–250.
- 53 J. Vermant and M. J. Solomon, *J. Phys.: Condens. Matter*, 2005, **17**, R187–R216.
- 54 T. Xu and V. A. Davis, *Langmuir*, 2014, **30**, 4806–4813.
- 55 A. Dessombz, D. Chiche, P. Davidson, P. Panine, C. Chanéac and J.-P. Jolivet, *J. Am. Chem. Soc.*, 2007, **129**, 5904–5909.
- 56 S. Murali, T. Xu, B. D. Marshall, M. J. Kayatin, K. Pizarro, V. K. Radhakrishnan, D. Nepal and V. A. Davis, *Langmuir*, 2010, **26**, 11176–11183.
- 57 C. Zamora-Ledezma, C. Blanc, M. Maugey, C. Zakri, P. Poulin and E. Anglaret, *Nano Lett.*, 2008, **8**, 4103–4107.
- 58 H. Zhou, P. Heyer, H.-J. Kim, J.-H. Song, L. Piao and S.-H. Kim, *Chem. Mater.*, 2011, **23**, 3622–3627.
- 59 M. Doi and S. F. Edwards, *J. Chem. Soc., Faraday Trans. 2*, 1978, **74**, 918.
- 60 B. J. Lemaire, P. Davidson, J. Ferre, J. P. Jamet, D. Petermann, P. Panine, I. Dozov and J. P. Jolivet, *Eur. Phys. J. E*, 2004, **13**, 291–308.
- 61 B. J. Lemaire, P. Davidson, D. Petermann, P. Panine, I. Dozov, D. Stoenescu and J. P. Jolivet, *The Eur. Phys. J. E*, 2004, **13**, 309–319.
- 62 L.-S. Li and A. P. Alivisatos, *Adv. Mater.*, 2003, **15**, 408–411.
- 63 E. E. Ureña-Benavides, G. Ao, V. A. Davis and C. L. Kitchens, *Macromolecules*, 2011, **44**, 8990–8998.
- 64 V. A. Davis, L. M. Ericson, A. N. G. Parra-Vasquez, H. Fan, Y. Wang, V. Prieto, J. A. Longoria, S. Ramesh, R. K. Saini, C. Kittrell, W. E. Billups, W. W. Adams, R. H. Hauge, R. E. Smalley and M. Pasquali, *Macromolecules*, 2004, **37**, 154–160.
- 65 V. A. Davis, A. N. G. Parra-Vasquez, M. J. Green, P. K. Rai, N. Behabtu, V. Prieto, R. D. Booker, J. Schmidt, E. Kesselman, W. Zhou, H. Fan, W. W. Adams, R. H. Hauge, J. E. Fischer, Y. Cohen, Y. Talmon, R. E. Smalley and M. Pasquali, *Nat. Nanotechnol.*, 2009, **4**, 830–834.
- 66 V. A. Davis, *J. Mater. Res.*, 2011, **26**, 140–153.