

Temperature-induced flocculation of colloidal particles immersed into the isotropic phase of a nematic liquid crystal

A. Borštnik,^{1,2} H. Stark,¹ and S. Žumer²

¹*Institut für Theoretische und Angewandte Physik, Universität Stuttgart, D-70550 Stuttgart, Germany*

²*Department of Physics, University of Ljubljana, 1000 Ljubljana, Slovenia*

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The aim of our theoretical study is to investigate the stability of a liquid crystal colloidal dispersion, i.e., a suspension of rigid spherical particles in the isotropic phase of a nematic liquid crystal. We pay special attention to a temperature dependent liquid crystal mediated attraction between particles which originates in a surface-induced nematic order localized to the vicinity of particles. The attraction strongly increases as the temperature of the nematic-isotropic phase transition (T_{NI}) is approached. In real systems this interaction is accompanied by electrostatic and steric repulsion and by the attractive van der Waals interaction. The major part of our work is dedicated to colloidal dispersions that are stabilized by a screened electrostatic repulsion of charged particles in the presence of counter ions in the solvent. We demonstrate that close to T_{NI} a decrease of temperature for about 1 K can induce a sudden transition of the system from a dispersed to a flocculated state. This transition can only take place if the electrostatic repulsion is sufficiently weak. We present a “phase diagram” where we show how the temperature that separates a flocculated from a dispersed state depends on the surface charge density and Debye length.

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I. INTRODUCTION

Colloidal dispersions are materials where particles, whose radii range from 10 nm to 10 μm , are dispersed in a solvent. The characteristics of colloidal dispersions change significantly when a transition from a dispersed to an aggregated state occurs. This is the reason why the stability of colloidal dispersions against flocculation presents a key issue in colloidal physics [1]. The aggregation of particles is determined by an attractive two-particle potential. If the attraction is strong compared to the thermal energy kT , a relatively long-living nonequilibrium phase occurs. On the other hand, attractions that are weak compared to kT lead to an equilibrium phase separation. A system is considered to be in a phase equilibrium if it attains equilibrium in the period of interest of, e.g., several hours. Single particles in a colloidal dispersion perform Brownian motion. Once they approach each other they form aggregates due to the attractive potential. In the nonequilibrium phase, they cannot leave the aggregates in the period of interest. In the case of equilibrium, particles coexist with equal chemical potentials in the dispersed and in the aggregated state. The higher interaction energy of the dispersed particles is compensated by their larger contribution to entropy.

The first explanation of the aggregation process in colloidal dispersions was given by Smoluchowski in 1917 [2]. He derived expressions for the rates of doublet formation in unstable dispersions due to Brownian motion and shear-induced collisions without taking into account particle interactions which were later introduced by Fuchs [3]. However, a comparison with experiments only became possible when Derjaguin and Landau [4] and Verwey and Overbeek [5] presented more sophisticated theories of colloidal stability where they specified the origins of attraction and repulsion between particles. In standard colloidal dispersions a repul-

sion between particles originates from an electrostatic interaction and from the interaction due to soluble polymers adsorbed at the surface of particles, while dispersion forces are always attractive. The theory of Derjaguin and Landau and Verwey and Overbeek was improved by Spielman [6] and Honig, Roebersen, and Wiersema [7] in the early 1970s. Following a suggestion by Derjaguin [8], they included hydrodynamical interactions in the calculation of the rate of flocculation.

Lately, special attention was paid to liquid crystal colloidal suspensions and emulsions, i.e., dispersions of solid particles or liquid droplets in a liquid crystal, respectively. In particular, interactions between micron-size water droplets immersed into a liquid crystal deep in the nematic phase were investigated [9–11]. Aggregates of latex particles were observed below the nematic-isotropic phase transition [12–15], and the Brownian motion of silica particles in the isotropic phase of a nematic liquid crystal was investigated [16]. The theoretical study of interactions between spherical particles immersed into a liquid crystal concentrated both on temperatures below and above the nematic-isotropic phase transition T_{NI} . At temperatures below T_{NI} , the liquid crystal mediates a relatively strong long-range interaction which overwhelms further interactions present in the dispersions, e.g., the van der Waals attraction [17–19]. In the isotropic phase, on the other hand, the liquid crystal mediates a short-range interaction whose magnitude is much smaller than the one in the nematic phase [20,21]. (The existence of such an interaction was also suggested by Löwen in a more general context [22].) In order to describe the relevant two-particle potential in the isotropic phase, one has to take into account van der Waals, electrostatic, and steric interactions, as well.

In our previous study [20], we developed a simple description of the liquid crystal mediated interaction above T_{NI} . The description is performed within mean-field approximation, neglecting order fluctuations which only yield a

minor correction to the mean-field values. Our approximate analytical approach uses ansatz functions for the surface-induced liquid crystalline order. A homeotropic alignment of the molecules at the particle surfaces is assumed. The two-particle interaction, which results from our analytical study, is strongly attractive for small particle separations. The deep potential well of this attraction is followed by a weak repulsive barrier as the particles are moved further apart. At distances large compared to the nematic coherence length, which for a typical liquid crystal material close to T_{NI} is of the order of 10 nm, the interaction vanishes exponentially. Both the depth of the potential well and the height of the repulsive barrier are strongly temperature dependent. They decrease with temperature approximately exponentially, and only a few Kelvin above the nematic-isotropic phase transition they become negligible relative to kT . The liquid crystal mediated interaction can therefore be ‘‘switched off’’ by raising the temperature by a few degrees.

The experimental studies of interactions in liquid crystal colloidal dispersions stimulated us to perform a theoretical study of all relevant interactions in such systems above T_{NI} . In order to determine the conditions for the stability of a colloidal dispersion, which is the main purpose of the present work, one has to fine-tune the parameters which substantially influence the van der Waals, electrostatic, and liquid crystal mediated interactions. The most crucial parameters are the temperature through which the liquid crystal mediated interaction is controlled, the surface charge density of particles, and the concentration of ions in the solvent which determine, respectively, the strength and the range of the electrostatic repulsion. We assume that the surface charge density and concentration of ions can be varied independently. The latter can, e.g., be controlled by adding salt to the solvent.

The paper is organized as follows. In Sec. II we describe our system. We pay special attention to the relevant two-particle interactions, i.e., van der Waals, electrostatic, steric, and liquid crystal mediated interactions. We also introduce a criteria which enables us to distinguish between the dispersed and flocculated state of the system. In Sec. III we mainly concentrate on electrostatic stabilization. We present the interactions as a function of particle separation for various temperatures, surface charge densities, and concentrations of ions. A ‘‘phase diagram,’’ illustrating the ‘‘flocculation transition’’ temperature as a function of surface charge and ion density, sums up the results. We conclude with remarks concerning steric stabilization. Finally, in Sec. IV, we discuss our results.

II. DESCRIPTION OF THE MODEL

The subject of our investigation is a dilute dispersion of rigid spherical particles in the isotropic phase of a nematic liquid crystal. We limit our discussion to surfaces that prefer homeotropic, i.e., perpendicular anchoring of the liquid crystalline molecules. Furthermore we assume that smectic layers are not formed at the surfaces. This seems to be reasonable for a liquid crystal such as the compound 5CB in which only rarely surface induced smectic layers are found in contrast to 8CB or 12CB in which pretransitional smectic layering is often observed [23,24]. In the case of electrostatic stabilization, we assume that all the spherical particles in our

model carry the same amount of surface charge. Together with ions which are dissolved in the liquid crystal they form the so-called double layer [1]. To study steric stabilization, we concentrate on organic molecules grafted on the particle surface. Their length is comparable to the liquid crystalline molecules, i.e., approximately 2 nm [16]. Such a coating still allows for a well-defined homeotropic boundary condition.

To estimate the stability of dispersions we pay special attention to the region where the two-particle interaction is attractive. Namely, if the attractive potential is strong compared to kT , Brownian motion mediates fast aggregation of particles. On the other hand, attraction potentials comparable to kT lead to an equilibrium phase separation in which particles coexist in two different phases, in a dispersed and in an aggregated state. We refer to the process of aggregation in either limit of the interaction strength as to *flocculation* [1].

The most commonly used criterion for the distinction between the completely aggregated state and the equilibrium phase separation is the escape time needed by a doublet to break up into single particles. It should be longer than the observation time if a system is to be considered as a non-equilibrium system. The escape time can be easily estimated as the time a particle needs to leave the potential well of the two-particle interaction [25]

$$t_{\text{esc}} \sim \frac{6\pi\eta R^3}{kT} e^{-\Phi_{\text{min}}/kT}, \quad (1)$$

where η is the viscosity of the solvent, R is the radius of the particle, and Φ_{min} is the depth of the potential minimum. More sophisticated methods [26,27] suggest that the complete potential curve, not only its minimum value, has to be taken into account when estimating the escape time. For a particle which is caught in a potential minimum at r_{min} in the vicinity of another particle of radius R , the escape time equals [26]

$$t_{\text{esc}} \sim \frac{1}{D} \int_{r_{\text{min}}}^{\infty} dr \frac{1}{r^2} e^{\Phi(r)/kT} \int_R^r dr' r'^2 e^{-\Phi(r')/kT}. \quad (2)$$

Using Eqs. (1) or (2), one can make a crude estimate for the depth of a potential minimum that corresponds to a reasonable escape time. For a repulsive barrier of the order of kT or less, which is the case for our system, one can conclude that $|\Phi_{\text{min}}/kT| \approx 1-3$ leads to phase equilibrium while in the case $|\Phi_{\text{min}}/kT| \approx 5-10$ particles are completely aggregated. The existence of a large repulsive barrier ($\approx 10kT$, e.g.), increases the escape time by several orders of magnitude. It also plays an important role in the process of aggregation. A large repulsive barrier increases considerably the time that two particles need to form a doublet. A weak repulsive barrier ($\approx 1kT$) on the other hand changes the doublet formation time only slightly.

In our study we introduce the term ‘‘flocculation transition temperature’’ T_{FD} that characterizes the temperature at which the system switches from a flocculated (below T_{FD}) to a dispersed state (above T_{FD}). To be more precise, we choose T_{FD} as the temperature below which aggregates of particles are stable. Above T_{FD} aggregates can be, depending on temperature, metastable or unstable. We would like to stress that the ‘‘flocculation transition’’ is not an ordinary phase transi-

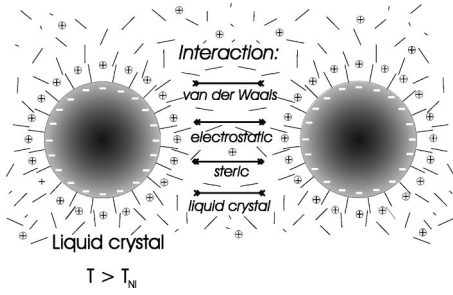


FIG. 1. Charged spherical particles are immersed into a liquid crystal at temperature above the nematic-isotropic phase transition. The surface of the particles induces partial nematic ordering of molecules which results in an attractive contribution to the net interaction of a pair of particles. Surface charge screened by a group of dissipated ions induces a repulsive electrostatic interaction. A van der Waals interaction yields an attraction. If in addition a polymer brush is added to the surface of the particles, it gives rise to a hard core repulsion.

tion. When analyzing the results of our study we also distinguish between *slow* and *rapid flocculation*. Slow flocculation refers to the situation where particles flocculate into a potential minimum over a repulsive barrier while rapid flocculation denotes the case where such a barrier does not exist.

For the interpretation of our results we introduce another term, “*flocculation end line*.” Beyond this line the dispersed states are absolutely stable for all temperatures above T_{NI} . The line is determined by the two relevant parameters of the electrostatic repulsion, i.e., the surface charge density of particles and the concentration of ions in the solvent. For example, if the surface charge density is sufficiently large, the electrostatic repulsion always compensates the liquid crystal mediated attraction and an aggregation of particles above T_{NI} does not occur.

In the following we first present all relevant contributions to the two-particle interaction of our system (see Fig. 1), i.e., van der Waals, electrostatic, steric, and liquid crystal mediated interactions. We introduce the determining parameters for each type of interaction. Since we are interested in very dilute systems only, we limit our description to pair interactions. (Note when we discuss the explicit expressions for the interaction potential, we often skip the term “potential” and just use “interaction” for short.)

van der Waals interaction. The van der Waals potential of two thermally fluctuating electric dipoles that are close together ($d \ll 10$ nm) decays with the sixth power of their inverse distance, $1/d^6$. However, at separations of about 5 nm retardation effects of the electromagnetic field become apparent which ultimately result in a $1/d^7$ dependence of the potential. Moving the dipoles even further apart, the zero-frequency polarizabilities become important and the potential decays again as $1/d^6$ [31]. The effective van der Waals interaction of two macroscopic particles is obtained by a summation over all pairwise interactions of fluctuating charge distributions what in the case of two spherical particles of equal radii R yields [1]

$$U_{vw} = -\frac{A(d)}{6} \left[\frac{2R^2}{d(d+4R)} + \frac{2R^2}{(d+2R)^2} + \ln \frac{d(d+4R)}{(d+2R)^2} \right]. \quad (3)$$

Here d is the closest distance between the surfaces of the two particles, and $A(d)$ is generalization of the Hamaker constant which now depends on the particle separation. In the case of equal particles made of material 1 embedded in the medium 2, $A(d)$ is given by

$$A(d) = \frac{3}{4} kT \left(\frac{\epsilon_1 - \epsilon_2}{\epsilon_1 + \epsilon_2} \right)^2 + \frac{3h\nu_e}{16\sqrt{2}} \frac{(n_1^2 - n_2^2)^2}{(n_1^2 + n_2^2)^{3/2}} \times \left[1 + \left(d \frac{\pi^2 \nu_e n_2}{2\sqrt{2}c} (n_1^2 + n_2^2)^{1/2} \right)^{3/2} \right]^{-2/3} \quad (4)$$

[1,31], where ϵ_1 and ϵ_2 are the zero-frequency dielectric constants of the two materials, and n_1 and n_2 are the corresponding refractive indices. The frequency ν_e refers to the dominant ultraviolet absorption in the dielectric spectrum of the embedding medium 2. It depends on electronic transitions in the atoms and is typically around $3 \times 10^{15} \text{ s}^{-1}$. For separations $d \gg R$, particles are pointlike, and the van der Waals interaction ultimately decays as $1/d^6$ when the retardation effects become negligible [31].

Electrostatic interaction. We are interested in charged particles dispersed in a liquid crystal which contains a small amount of ionic impurities. We assume that the particles are made of a dielectric material and that they all carry the same uniform surface-charge distribution which does not change under the influence of the two-particle interaction. The ionic impurities in the solvent tend to screen the surface charges of particles. Together with the surface charges they form the so-called electrostatic double layer. For equal particles of radii R and fixed surface charge density q_s , the electrostatic interaction is described by the following expression [1]:

$$U_E/kT = -\pi R \frac{q_s^2}{e_o^2 z^2 n_p} \ln(1 - e^{-\kappa d}). \quad (5)$$

Here, e_o is the fundamental charge, and z and n_p are the valence and concentration of the dissolved ions, respectively. The range of the repulsive interaction is determined by the Debye length

$$\kappa^{-1} = \sqrt{\epsilon \epsilon_o kT / 2e_o^2 z^2 n_p}, \quad (6)$$

whereas the surface charge density q_s controls its strength. The expression (5) was derived via the *Derjaguin approximation* and is therefore valid only for $\kappa R > 30$ [28]. In our case, this condition is fulfilled. The interaction is strongly repulsive in comparison to kT at small particle separation and exponentially decays to zero for large d .

Steric interaction. Steric repulsion is realized by attaching polymers to the surface of particles. Here, we assume relatively short polymer fibers or simply organic molecules which have the same length l as the liquid crystalline molecules, i.e., $l \approx 2$ nm. They prevent two particles from approaching each other closer than the separation $d = 2l$. For simplicity we model the interaction by a hard-core repulsion at $d = 2l = 4$ nm.

Liquid crystal mediated interaction. The description of the liquid crystal mediated interaction is based on our theoretical study in Ref. [20]. There, we derive an analytical expression for the interaction of two spherical particles immersed in a liquid crystal above the nematic-isotropic

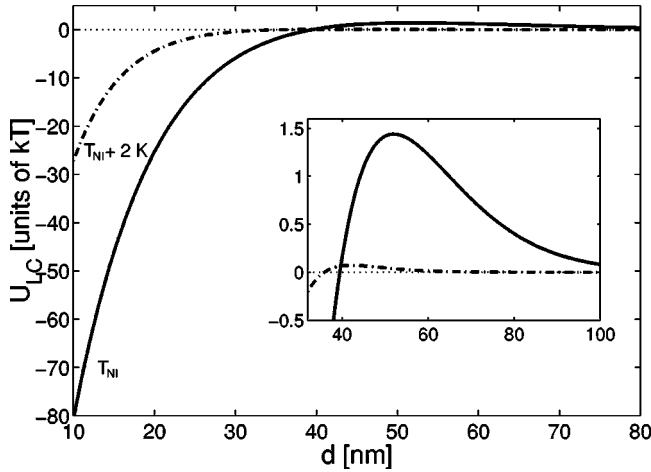


FIG. 2. The two-particle interactions mediated by a liquid crystal as a function of distance d between the particles at various temperatures. A magnified part of the figure is shown as inset.

phase transition, and we show that the interaction is a sum of a repulsive and an attractive contribution. Every single particle carries with it a layer of surface-induced nematic order which decays exponentially in the radial direction on a characteristic length scale given by the nematic coherence length ξ_N . If the layers overlap, the volume of nematic order, which possesses a larger free energy density than the isotropic liquid, is reduced. That means, the free energy of the system decreases with the separation of particles which results in an attractive interaction. On the other hand, a repulsion originates in the elastic distortion of the director field lines connecting the two particles. It is increased as particles approach each other.

The analytical expression for the interaction is cited in the appendix. There, we also introduce the parameters which describe the material properties of liquid crystal as well as the surface coupling of molecules. We illustrate the interaction as a function of particle separation for two different values of temperature in Fig. 2. At the nematic-isotropic phase transition, the interaction is strong in comparison to kT for small particle separations, $d \sim \xi_N$, and it exhibits a weak repulsive barrier of the order of kT as the particles are moved further apart, $d \sim 50$ nm (see inset). For large distances d , the interaction exponentially approaches zero. If the temperature is increased by a few Kelvin the attraction at $d \approx 10$ nm becomes much weaker and the repulsion barrier is decreased considerably as well. Since the strength of the interaction depends strongly on temperature, it becomes almost negligible if the temperature is increased further by some degrees.

III. RESULTS

In the presentation of the discussed interactions, we focus our attention on spheres of radii 250 nm. The magnitude of liquid crystal mediated interaction is varied by changing the temperature of the system in the interval $T_{NI} \leq T \leq T_{NI} + 10$ K, where T_{NI} is the temperature of the nematic-isotropic phase transition in a bulk liquid crystal. To specify the Hamaker constant which strongly influences the van der Waals interaction the following dielectric constants and refractive indices corresponding to silica particles immersed in

a typical nematic liquid crystal will be taken into account [29–31]: $\epsilon_1 = 3.8$, $n_1 = 1.45$, $\epsilon_2 = 11$, $n_2 = 1.57$, and $\nu_e = 3 \times 10^{15} \text{ s}^{-1}$. As a result, the Hamaker ‘‘constant’’ equals $A(d) = \{0.18 + 0.87[1 + (0.11d)^{3/2}]^{-2/3}\}kT$, where d is in nm. The parameters of the steric interaction were already introduced in the last section. The electrostatic interaction is specified by the valence and the concentration of the ions dissolved in a liquid crystal, the dielectric constant of the liquid crystal, and the surface charge density. We assume that the ions are monovalent, i.e., $z = 1$ with a concentration, n_p , varying between 10^{-4} and 10^{-3} mol/l. Taking into account that the dielectric constant of the liquid crystal equals $\epsilon_2 = 11$, the corresponding Debye length at room temperature varies between 3.5 and 10 nm. A typical value of the surface charge density q_s is of the order of $10^4 e_o / \mu\text{m}^2$ [32]. In our study we vary q_s between 10^3 and $10^4 e_o / \mu\text{m}^2$. We point out that the range of the surface charge densities and concentrations of ions that are taken into account in our study is small in comparison to all values which can be achieved in experiments with polar solvents. In organic solvents, however, it is generally difficult to dissolve ions. This creates problems in achieving Debye lengths of the order of 10 nm. Furthermore, ionogenic groups attached to the surface of the suspended particles do not dissociate into ions very easily, and as a result, reasonable surface charge densities cannot be obtained. Liquid crystal compounds consist of organic molecules which do, however, contain polar groups. It seems that the ionic concentrations and surface charge densities which we employ in our study can hardly be realized. However, in Ref. [33] complex salt is dissolved in nematic liquid crystals and ionic concentrations of up to 10^{-4} mol/l are reported. Furthermore, when silica spheres are coated with silan, the ionogenic group $\text{NH}_2^+ \text{OH}^-$ occurs at the particle surface with a density of 3×10^6 molecules/ μm^2 . It dissociates to a large amount even in a liquid crystal [34]. In addition, the silan coating provides the required homeotropic boundary condition for the liquid crystal molecules. These two examples illustrate that our parameters of the electrostatic interparticle potential should be accessible in conventional thermotropic liquid crystals. They are achievable with no problem in lyotropic liquid crystals [35]. Amphiphilic molecules in water form rodlike or disclike micelles which exhibit liquid crystalline phases as a function of the micelle concentration. However, there are lyotropic systems where the transition from the isotropic to the nematic phase is also controlled by temperature [12,15]. Our investigation applies to such systems as well.

In the following we consider two different types of dispersions. In the first type, which we refer to as *electrostatically stabilized*, particles carry a surface charge whereas a polymer brush is not grafted on their surface. We will thoroughly investigate the total two-particle interaction U which is a sum of the van der Waals (U_{VW}), electrostatic (U_E), and the liquid crystal mediated (U_{LC}) interaction: $U = U_{LC} + U_E + U_{VW}$. In the second type of dispersion, referred to as *sterically stabilized*, particles are basically neutral, however a coating of organic molecules gives rise to a hard core repulsion U_S . The total interaction $U = U_{LC} + U_S + U_{VW}$ again consists of three parts.

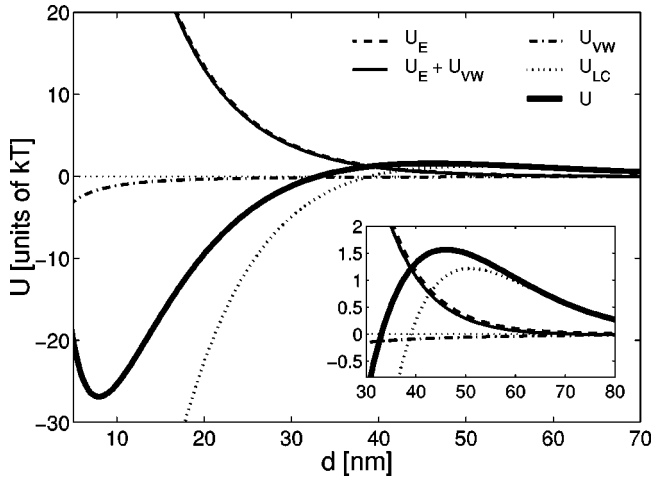


FIG. 3. Electrostatic (U_E), van der Waals (U_{VW}), the sum $U_E + U_{VW}$ and liquid crystal mediated (U_{LC}) and total ($U = U_{LC} + U_{VW} + U_E$) interaction are plotted as a function of the particle separation. The surface charge density and Debye length are chosen to be $0.45 \times 10^4 e_o / \mu\text{m}^2$ and 8.3 nm, respectively, while $T = T_{NI} + 0.1$ K. A magnified part of the figure is shown as an inset.

A. Electrostatic stabilization

Liquid crystal, electrostatic, and van der Waals contribution. To show how van der Waals, electrostatic, and liquid crystal contributions influence the total two-particle interaction, we present in Fig. 3 U_{LC} , U_E , U_{VW} , the sum $U_E + U_{VW}$, and the net interaction U as a function of particle separation. The temperature is $T_{NI} + 0.1$ K, and the surface charge density and Debye length are taken to be $0.45 \times 10^4 e_o / \mu\text{m}^2$ and 8.3 nm, respectively. The electrostatic interaction exhibits a strong repulsion at small distances d and decays exponentially for large d . The van der Waals interaction, on the other hand, yields an attraction of some kT at $d = 5$ nm—much weaker than the electrostatic interaction—and decays as $1/d^6$ for large d . A sum of these two contributions is strongly repulsive at small d , exhibits a shallow potential minimum of $1/3 kT$ at $d \approx 70$ nm and approaches zero for large d . The liquid crystal mediated interaction U_{LC} is strongly attractive for small particle separations and weakly repulsive at $d \approx 50$ nm. It approaches zero for large d . If this interaction is added to $U_E + U_{VW}$, an interaction exhibiting a deep potential minimum and a weak repulsive barrier is obtained. The minimum and the barrier appear at $d \approx 10$ nm and $d \approx 50$ nm, respectively.

Flocculation transition. In Fig. 4 we show the two-particle interaction $U = U_{LC} + U_{VW} + U_E$ as a function of particle separation for various values of temperature. For $T = T_{NI}$, the interaction curve exhibits a minimum with a depth of the order of $20kT$ at $d \approx 10$ nm. The minimum is followed by a small potential barrier of $\approx 1kT$. As the temperature is raised, the depth of the minimum decreases, and already 0.3 K above T_{NI} it becomes very shallow. At $T_{NI} + 0.54$ K, the minimum still exists but belongs to a metastable state, only. We call the temperature at which the interaction at the minimum equals zero the temperature of the *flocculation transition*, T_{FD} . Namely, above this temperature the probability of finding two particles in an aggregated state becomes smaller than the probability that they are dispersed. Above T_{FD} aggregates of particles are unstable or meta-

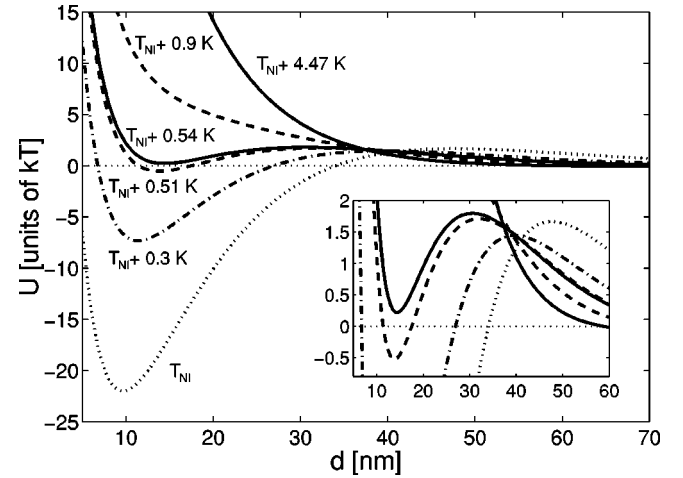


FIG. 4. Interaction U as a function of distance between the particles for various temperatures. Surface charge density equals $0.5 \times 10^4 e_o / \mu\text{m}^2$ while $\kappa^{-1} = 8.3$ nm. A magnified part of the figure is shown as an inset.

stable. When the temperature is raised even further, the interaction minimum disappears completely. That means, within a temperature range of a few tenth of a Kelvin there is a sudden change from a fully aggregated to a completely dispersed state, reminiscent to the critical flocculation transition in polymer stabilized colloidal dispersions [1,36].

Beyond the flocculation end line. Since the electrostatic interaction depends on the square of the surface charge density q_s , a strong electrostatic repulsion can easily be achieved. If the surface charge is large enough, the interaction at the potential minimum exceeds zero even at T_{NI} . This case is presented in Fig. 5, where one can see a shallow minimum at T_{NI} which disappears as the temperature is increased by 0.1 K. The surface charge density and Debye length equal $q_s = 0.63 \times 10^4 e_o / \mu\text{m}^2$ and $\kappa^{-1} = 8.3$ nm, respectively. We define the flocculation end line as the border line in a q_s, κ^{-1} diagram beyond which the flocculated state is never absolutely stable for all temperatures (see Fig. 9).

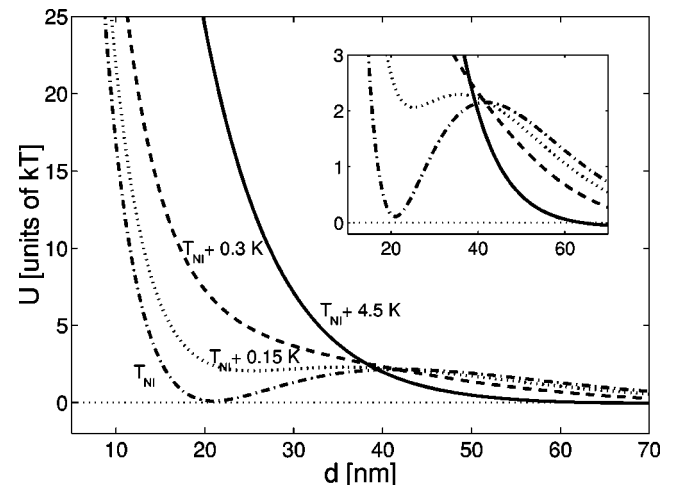


FIG. 5. Interaction U as a function of distance between the particles for various temperatures. Surface charge density equals $0.63 \times 10^4 e_o / \mu\text{m}^2$ while $\kappa^{-1} = 8.3$ nm. A magnified part of the figure is shown as an inset.

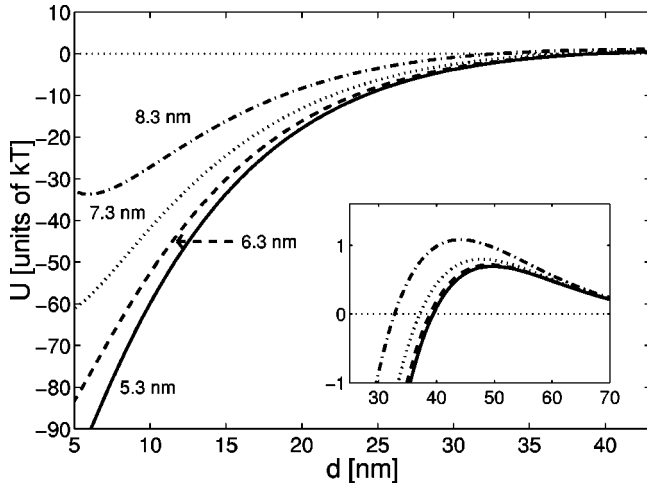


FIG. 6. Interaction U as a function of particle separation for various values of Debye length, i.e., various n_p . Surface charge density equals $0.4 \times 10^4 e_o / \mu\text{m}^2$, $T = T_{\text{NI}} + 0.3$ K. A magnified part of the figure is shown as an inset.

Influence of the Debye length. In Fig. 6 we illustrate how the concentration of the dissolved ions in the liquid crystal n_p and herewith the Debye length κ^{-1} , defined via Eq. (6), influences the depth of the interaction minimum and the height of the repulsive barrier of U close to T_{NI} . The surface charge density is chosen to be $0.4 \times 10^4 e_o / \mu\text{m}^2$ while $T = T_{\text{NI}} + 0.3$ K. The primary minimum becomes deeper as the Debye length is decreased, and the repulsive barrier is reduced and moved to larger distances.

Rapid flocculation. Figure 7 shows the interaction U as a function of particle separation for various temperatures. This plot is similar to the one in Fig. 4, however, here the Debye length is decreased to 4.3 nm, and the surface charge density equals $1 \times 10^4 e_o / \mu\text{m}^2$. As expected, the interaction minimum is deeper than in the case of $\kappa^{-1} = 8.3$ nm while the repulsive barrier is decreased. It is interesting to note that at $T = T_{\text{NI}} + 1.8$ K the repulsive barrier disappears completely. At this temperature, a rapid flocculation occurs. Furthermore,

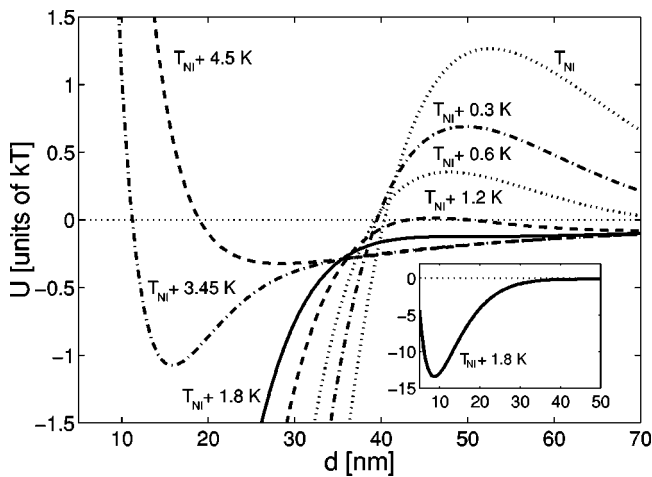


FIG. 7. Interaction U as a function of particle separation for various temperatures. The surface charge density equals $1 \times 10^4 e_o / \mu\text{m}^2$ while $\kappa^{-1} = 4.3$ nm. The interaction curve for d from the interval $[5, 50$ nm] and $T = T_{\text{NI}} + 1.8$ K is shown as an inset.

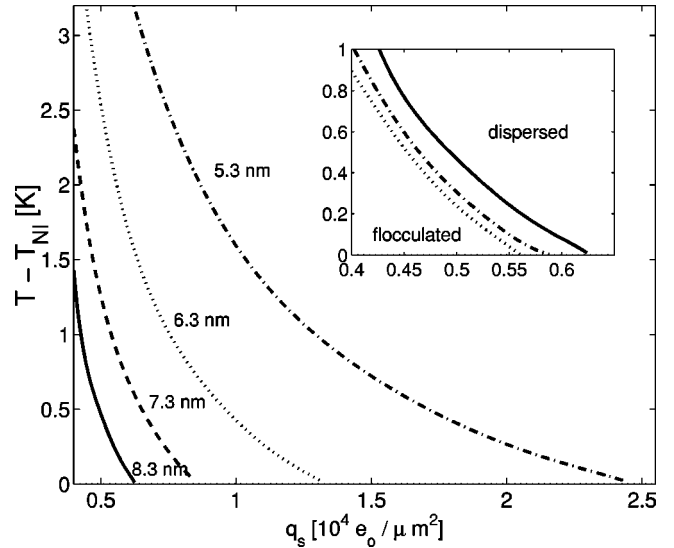


FIG. 8. Temperatures of flocculation transition for different values of Debye length. A flocculation phase diagram for $\kappa^{-1} = 8.3$ nm is shown as an inset. Temperatures above the temperature of flocculation transition (solid line) correspond to dispersed state while for those below T_{FD} doublets are formed. Dashed lines represent the temperatures at which the escape time is ten (dash-dotted) or one hundred (dotted) times larger than in the case of zero interaction.

we point out that the characteristic time for a doublet formation [1,32] is not dramatically changed when the repulsive interaction barrier is reduced from $1.5 kT$ to zero, i.e., to the point where rapid flocculation occurs. It is only decreased by a factor of 3.

Flocculation phase diagram. In Fig. 8 we present flocculation phase diagrams as a function of temperature and surface-charge density, indicating the dispersed or the flocculated state of particles. The inset corresponds to the phase diagram for $\kappa^{-1} = 8.3$ nm. The solid line represents the temperatures of the ‘‘flocculation transition’’ T_{FD} . For temperatures above T_{FD} , particles stay dispersed while for temperatures below T_{FD} the system is flocculated. To obtain a feeling for the stability of the aggregated state at temperatures below T_{FD} , we have determined lines in the phase diagram, where the escape time from the minimum of the interparticle potential is, respectively, ten (dash-dotted) or one hundred (dotted) times larger than in the case of zero interaction. Note that these lines are rather close to the line of the flocculation transition. In the large plot of Fig. 8, the temperatures of the flocculation transition are shown for different values of the Debye length. A decrease of the surface charge density results in a higher transition temperature. A larger concentration of dissolved ions, i.e., a smaller Debye length causes the same effect. The qualitative feature of the transition lines can be easily understood. A smaller surface charge decreases the strength of the electrostatic repulsion which is then compensated by a weaker attraction of the liquid crystal mediated interaction. Thus the flocculation occurs at a higher temperature.

Flocculation end line. In Fig. 9 we present the flocculation end line. At a given Debye length, it indicates the smallest value of the surface charge density, which is still large enough to prevent a flocculation of particles for all tempera-

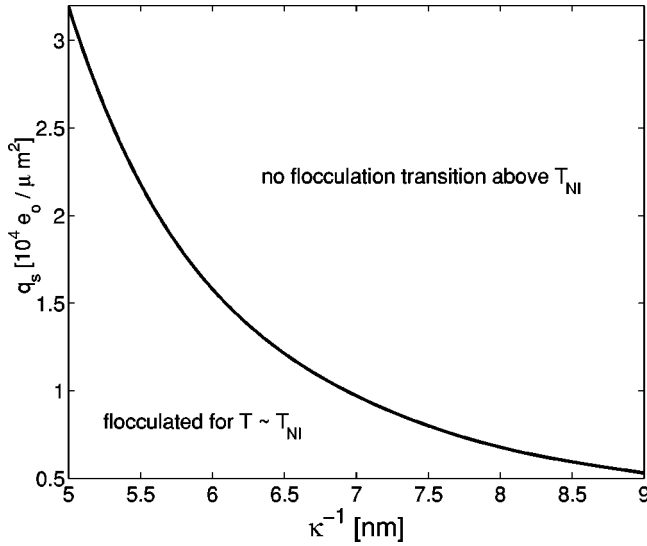


FIG. 9. Flocculation end line, i.e., the smallest surface charge density for which particles are dispersed even at T_{NI} , as a function of the Debye length.

tures above T_{NI} . The flocculation end line decreases very strongly with increasing Debye length. This can be easily understood from the following. When the Debye length is increased as a result of a smaller ionic concentration, the screening of the surface charge q_s is reduced. Therefore, a smaller value of q_s is sufficient to prevent particles from flocculating.

B. Steric stabilization

In Fig. 10 we show the interaction U as a function of particle separation d for some values of temperature above T_{NI} . To achieve the conditions which result in a flocculation transition the radius of the particles is reduced to 70 nm. The interaction exhibits a hard core repulsion at $d = 4$ nm, resulting from the coating of particles by organic molecules. A minimum in the potential occurs at $d \approx 4$ nm. It is relatively

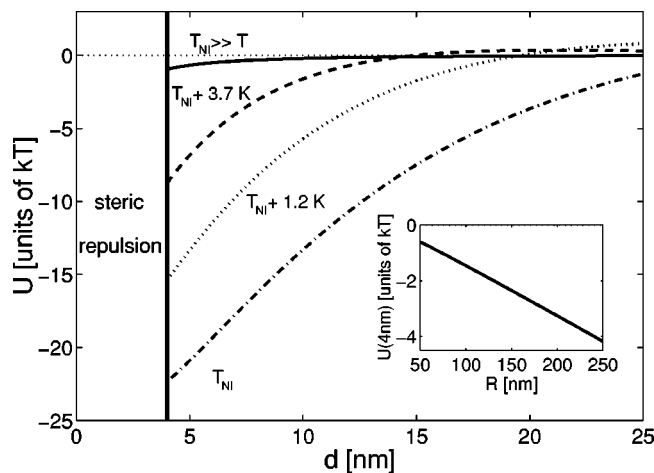


FIG. 10. Interaction U as a function of particle separation for different values of temperature. The radius of particles equals 70 nm. U at a particle separation just beyond hard core repulsion as a function of particle radius is shown as an inset. Temperature is more than 10 K above T_{NI} .

deep for temperatures close to T_{NI} due to the strong liquid crystal mediated attraction. The attraction is reduced when the temperature is increased. However, even at temperatures of 10 K or more above T_{NI} , where the liquid crystal mediated interaction has basically vanished, the depth of the minimum is still of the order of a few kT due to the van der Waals attraction. We can therefore conclude that particles are flocculated at temperatures close to T_{NI} while at $T \gg T_{NI}$ there should be an equilibrium of a dispersed and flocculated phase as discussed in Sec. II. Although the flocculation transition will not be as dramatic as in the case of electrostatic stabilization, a conversion to the fully aggregated state, when lowering the temperature, should be visible.

A complete dispersion of particles can either be achieved by increasing the length of the organic molecules grafted on the particle surface or by reducing the particle radius R . In the inset of Fig. 10, we plot $U \approx U_{VW}$ as a function of R . The separation is $d \approx 4$ nm, where the potential minimum is located, and the temperature is more than 10 K above T_{NI} , i.e., U_{LC} is negligible. The depth of the minimum is increasing linearly with the particle radius, as can be verified explicitly by expression (3) for the van der Waals interaction in the case of $d \ll R$. For small particles ($R \sim 50$ nm), it is of the order of 0.6 kT , i.e., the majority of particles will be dispersed, and a flocculation transition is observed when lowering the temperature. However, compared to the electrostatic stabilization, where the transition takes place within a few tenth of a K, it will occur more gradually within a temperature range of several K. For 250 nm particles, the depth of the minimum is increased to 5 kT , and all particles are basically aggregated.

IV. CONCLUSIONS

Particles dispersed in a liquid crystal above the nematic-isotropic phase transition are surrounded by a surface-induced nematic layer whose thickness is of the order of the nematic coherence length. The particles experience a strong liquid crystal mediated attraction when their nematic layers start to overlap since then the effective volume of liquid crystalline ordering and therefore the free energy is reduced. A repulsive correction results from the distortion of the director field lines connecting two particles. The new colloidal interaction is easily controlled by temperature. In this article we have presented how it can be probed with the help of electrostatically or sterically stabilized dispersions.

In the first case, for sufficiently weak and short-ranged electrostatic repulsion, we observe a sudden flocculation within a few tenth of a Kelvin close to T_{NI} . It is reminiscent to the critical flocculation transition in polymer stabilized colloidal dispersions [1,36]. The flocculation is due to a deep potential minimum in the total two-particle interaction followed by a weak repulsive barrier. We have thoroughly studied the two-particle potential as a function of the relevant parameters. To map out its effects on the stability of the colloidal dispersion, we have presented two phase diagrams. The first diagram illustrates the flocculation temperature as a function of surface charge density and Debye length, the

second one shows for which parameters of the screened electrostatic interaction the flocculation occurs at all. Although thermotropic liquid crystals represent organic solvents, we have given some first examples which demonstrate that electrostatic stabilization should be achievable in such systems. This should initiate further experimental studies. Our work directly applies to lyotropic liquid crystals, i.e., aqueous solutions of non-spherical micelles, when the nematic-isotropic phase transition is controlled by temperature. They are appealing systems since electrostatic stabilization is more easily achieved. When the phase transition is controlled by the micelle concentration ρ_m , as it is usually done, then our diagrams are still valid but with temperature replaced by ρ_m .

Polymeric stabilization is more often applied since it stabilizes colloidal dispersion for a longer time and allows for higher particle concentrations in comparison to electrostatic repulsion [36]. Instead of long polymer chains grafted onto the particle surface, we have considered organic molecules whose length is comparable to the liquid crystalline molecules. They provide well-defined homeotropic boundary conditions on which we have concentrated in this article. We find that large particles ($R \sim 250$ nm) are flocculated at all temperatures above T_{NI} due to van der Waals forces. Small particles ($R \sim 50$ nm), however, are basically dispersed well above T_{NI} . Cooling the dispersion down towards T_{NI} should induce a gradual onset of aggregation, in contrast to electrostatic stabilization where flocculation occurs in a very narrow temperature interval. For intermediate particle radii and at temperatures well above T_{NI} , a phase equilibrium of a dispersed and flocculated state should be observable. It is transformed into a completely aggregated state when temperature is decreased. Our findings are in agreement with experiments by Böttger *et al.* who reported that 90 nm silica particles aggregated above T_{NI} as soon as their volume fraction was 10^{-4} or larger. When long flexible polymer chains are grafted onto the particle surface, the boundary conditions for the liquid crystal molecules are not as well defined as for short organic molecules. Further research, both experimental and theoretical, is needed to address this situation.

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APPENDIX

In the appendix we present a brief summary of the liquid crystal mediated interaction between two spherical particles [20]. In order to obtain an analytical expression for the interaction the model structure is simplified by modelling the two spherical particles with a sequence of conical surfaces.

The liquid crystal which fills the area between the two particles is divided into several regions where each region is bounded by two conical surfaces and by its neighboring regions, and region i encircles region $i-1$. In order to determine the interaction $U(d)$, which is defined as a free energy of the liquid crystal at particle separation d subtracted by the free energy at large particle separation, free energy of liquid crystal in regions where surface elements are close together has to be calculated. The free energy is obtained following Landau–de Gennes phenomenological approach. In order to make the expression more transparent we divide it into two parts, one corresponding to the contribution of scalar order parameter Q which turns out to be attractive U_a and the second one corresponding to the contribution of the distorted director field which yields repulsion U_r . The attractive contribution is the following:

$$U_a = \sum_{i=1}^n 3\pi \frac{L_1}{\xi_N} Q_s^2 (l_{i+1}^2 - l_i^2) \left[\frac{\tanh(\bar{d}_i/2\xi_N)}{1 + \gamma_Q \tanh(\bar{d}_i/2\xi_N)} - \frac{1}{1 + \gamma_Q} \right]. \quad (\text{A1})$$

Here $\xi_N = \sqrt{3L_1/a\Delta T}$ is the nematic coherence length, $\Delta T = T - T^*$, L_1, a, Q_s, T^* are material dependent constants, \bar{d}_i represents the average distance between surface elements bounding region i , β_i is the tilt angle of surface element in region i with respect to that symmetry plane of the system, which halves the particle separation, γ_Q and γ_n are parameters which are proportional to $1/\xi_N$ and describe the strength of the surface coupling, and l_i represents the closest distance of the surface elements in region i from the symmetry axes. The repulsive contribution equals

$$U_r = \sum_{i=1}^n \frac{9}{2} \pi L_1 Q_s^2 \frac{l_{i+1}^2 - l_i^2}{\cosh^2(\bar{d}_i/2\xi_N) [1 + \gamma_Q \tanh(\bar{d}_i/2\xi_N)]^2} \times \left[(1 - \epsilon_i)^2 \frac{4 \sin^2 \beta_i}{R_o^2} \Phi(R_o) + 2\epsilon_i(1 - \epsilon_i) \times \frac{4 \sin \beta_i}{R_o \kappa_i(\bar{d}_i)} \Phi(R_o) + \epsilon_i^2 \left(\frac{4}{\kappa_i^2(\bar{d}_i)} \Phi(\bar{d}_i) + \frac{4 \gamma_n \xi_N}{\kappa_i^2(\bar{d}_i)} \frac{\cosh^2(\bar{d}_i/2\xi_N)}{1 + \gamma_Q \tanh(\bar{d}_i/2\xi_N)} \right) \right]. \quad (\text{A2})$$

Here in addition R_o is a parameter which is fixed to 2 nm, $\Phi(x) = \xi_N \sinh(x/2\xi_N) \cosh(x/2\xi_N) + x/2$, $\kappa_i(\bar{d}_i) = \eta_i + 2\Delta R_i$, and $\eta_i = l_{i+1} - l_i + (\bar{d}_i/\tan \beta_i)$, while ϵ_i equals $\epsilon_i = (1 - R_o/\eta_i \sin \beta_i) \{1 - 2(R_o/\eta_i \sin \beta_i) + [\Phi(\bar{d}_i)/\Phi(R_o)] [R_o^2/(\eta_i \sin \beta_i)^2]\}^{-1}$ and parameter ΔR_i stands for $\gamma_n \xi_N [1 + \gamma_Q \tanh(\bar{d}_i/2\xi_N)]^{-1} (\sin \beta_i)^{-1}$.

In our study the following parameters of a typical liquid crystal material are taken into account [37–39]: $a = 0.18 \times 10^6$ J/m³ K, $L_1 = 9 \times 10^{-12}$ J/m, and $T^* = 313.5$ K. Then,

according to the Landau–de Gennes approach, the temperature T_{NI} of the nematic-isotropic phase transition is equal to $T_{\text{NI}} = T^* + 2b^2/9ac \approx T^* + 1.3$ K, and the corresponding coherence length $\xi_N = \sqrt{3L_1/(a\Delta T)}$, at $\Delta T = 1.3$ K is ξ_N

≈ 10 nm. Parameters Q_s , γ_s , and γ_n which depend on the nature of the surface coupling are taken to be $Q_s = 0.3$, and $\gamma_Q = 1/\xi_N \times 13.5$ nm, $\gamma_n = \gamma_Q/5$. We have taken into account regions 1 to 9, i.e., $n = 9$.

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