Capillary Condensation in Liquid-Crystal Colloids

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We study capillary condensation between two spherical particles dispersed in the isotropic phase of a nematic liquid crystal. Within the Landau–de Gennes theory, we calculate interaction energies due to the formation of capillary bridges that reproduce experimental observations. Close to the critical point of the transition line separating the no-bridge from the bridge configuration, fluctuations in the particle cluster might be described by an effective two-state system. We show that the transition line vanishes for small particles and that the shape of the interaction potential depends on particle size.

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Liquid crystal colloid dispersions, i.e., the suspension of particles in an anisotropic fluid such as a nematic phase, constitute an attractive new type of soft matter [1]. They give rise to interesting dynamic behavior and to novel interactions, mediated by topological defects and elastic distortions in the orientational order. As a result, prominent structure formation involving chaining [2], ''soft solids'' [3], and even ordered structures [4] are observed. A ''transparent nematic phase'' of suspended nanoparticles is under debate [5,6], and a numerical method to simulate several particles in a nematic host was developed [7]. In other anisotropic host fluids, such as cholesteric liquid crystals, particle-stabilized defect gels [8] or long-range ordering of nanoparticles [9] are found.

This Letter is motivated by experiments of Kočevar and Muševič, where the interaction between a flat substrate and a microsphere immersed in a nematic liquid crystal above the nematic-isotropic phase transition is measured using an atomic force microscope [10]. By carefully preparing the bounding surfaces, the authors could vary the strength of the anchoring of the mesogenic molecules. For weak anchoring, a Yukawa-type interaction due to nematic wetting layers is observed [11] and well understood within a harmonic approximation of the Landau–de Gennes free energy [12]. For strong anchoring, the authors obtain a much stronger and long-ranged force, which they attribute to capillary condensation, i.e., the formation of a bridge of condensed nematic phase between the substrate and the particle [13]. A first approximate theoretical approach to the experiments is given in [13,14]. This Letter presents a full description of this novel colloidal interaction by investigating the interaction potential of two spherical particles. Since the potential is easily tunable by temperature and, as we show, its strength and shape depend on the particle size, it provides a means to control colloidal ordering both in the bulk and at structured surfaces [15,16].

Capillary condensation means a surface-induced shift of a first-order transition whenever the system under investigation is restricted to a confining geometry, such as porous media [17]. Therefore, it is important for phenomena like adhesion and friction. The formation of capillary bridges between close surfaces has been observed in a variety of systems [18]. Calculations for two spheres immersed in a simple binary fluid exist [19], and the observation of flocculation of colloids in simple liquid mixtures was attributed to capillary condensation [20]. In liquid crystals, the anchoring of the mesogenic molecules to the surfaces is not only of technological importance; it also leads to a variety of wetting and/or surface transitions [21]. Capillary condensation in a slab geometry was first studied by Sheng [22], and then extended by others [23]. Here we investigate the formation of capillary bridges between two spherical particles on the basis of the Landau–de Gennes theory. We demonstrate how temperature and the size of the particles influence the continuous or discontinuous formation of the capillary bridges. Furthermore, we are able to compare directly to the experiments reported in Refs. [10,13].

To quantify the surface-induced orientational order, we use a traceless and symmetric second-rank tensor Q_{ij}, also called an alignment tensor. We perform our analysis with the help of the Landau–Ginzburg–de Gennes free energy density [24]: $f(Q_{ij}) = \frac{1}{2}a_0(T - T^*)Q_{ij}Q_{ij} - \frac{1}{3}bQ_{ij}Q_{jk}Q_{ki} + \frac{1}{4}c(Q_{ij}Q_{ij})^2 + \frac{1}{2}L_1(Q_{ij,k})^2$, where summation over repeated indices is implied and the symbol $,k$ means spatial derivative with respect to x_k. The first three terms describe the nematic-isotropic phase transition; a_0 and c are positive constants, and T^* denotes the supercooling temperature of the isotropic phase. In the fourth term we adopt, for simplicity, the one-constant approximation of the elastic energy, which penalizes any nonuniform orientational order. The number of parameters is reduced by using a rescaled order parameter $\mu_{ij} = Q_{ij}/s$ [$s = b/(3\sqrt{3}c)$] and temperature $\tau = 27ca_0(T - T^*)/b^2$ so that the free energy of the orientational order

in the volume around the two spheres becomes

$$\frac{F[Q_{ij}(\mathbf{r})]}{\Delta f a^2 \xi_r} = \frac{a}{\xi_r}\int d^3\bar{r}\Big(\frac{1}{2}\tau\mu_{ij}\mu_{ij} - \sqrt{3}\mu_{ij}\mu_{jk}\mu_{kl} + \frac{1}{4}(\mu_{ij}\mu_{ij})^2 + \frac{1}{2}\frac{\xi_r^2}{a^2}(\mu_{ij,k})^2\Big).$$

The lengths are given in terms of the particle radius a ($\bar{\mathbf{r}} = \mathbf{r}/a$), the unit of the free energy density is $\Delta f = b^4/(729c^3)$, and $\xi_r = (27cL_1/b^2)^{1/2}$ is the nematic coherence length at the nematic-isotropic phase transition. Typical values for the nematic compound 5CB are $\Delta f = 0.5 \times 10^5$ erg/cm^3 and $\xi_r = 10$ nm, and the temperature interval $\Delta\tau = 1$ corresponds to 1.12 K. A uniaxial order parameter, $\mu_{ij} = S(n_i n_j - \delta_{ij}/3)$, where $\mathbf{n}$ is the nematic director and δ_{ij} the Kronecker symbol, minimizes the first three terms of the free energy $F[Q_{ij}(\mathbf{r})]$. The bulk nematic-isotropic phase transition from $S = 0$ to $S_b = \sqrt{3}$ occurs at $\tau_c = 1$, and $\tau^\dagger = 9/8$ is the superheating temperature of the nematic phase. To evaluate the main features of capillary condensation between two spheres, we choose rigid boundary conditions; i.e., at the particle surfaces we assume a constant uniaxial order parameter $\mu_{ij} = S_0(\hat{\nu}_i\hat{\nu}_j - \delta_{ij}/3)$, where $\hat{\boldsymbol{\nu}}$ is a unit vector parallel to the local surface normal and $S_0 = 2$ is close to S_b. Our choice of rigid boundary conditions is justified by the experiments of Kočevar *et al.* [10,13], where a strong anchoring of the liquid-crystal molecules was prepared. We will demonstrate below that we obtain quantitative agreement with these experiments. However, by using rigid anchoring, we will not observe possible prewetting transitions, which we have studied recently [25].

The capillary condensation between two spherical particles is investigated by numerically minimizing the free energy $F[Q_{ij}(\mathbf{r})]$ for various distances to contact d/a, temperatures τ, and particle radii a. Details of our numerical approach are reported in Ref. [26]; here we just summarize them. We employ bispherical coordinates that have several advantages. First, they provide a grid where the infinite space around the two spheres is mapped on finite coordinate intervals. Second, between the particles, where a capillary bridge forms and therefore high resolution is required, the grid lines are denser. Third, the surfaces of the spheres correspond to coordinate lines so that the implementation of the boundary conditions becomes trivial. Under the reasonable assumption of rotational symmetry around the particle-particle axis, we evaluate the Euler-Lagrange equations from the variation of the free energy $F[Q_{ij}(\mathbf{r})]$, discretize them, and use the relaxational dynamics of model A in the Hohenberg-Halperin notation to solve them. The discretized free energy is evaluated numerically with the help of the trapezoidal rule. To calculate the interaction energy of the particles with sufficient accuracy, we had to take 256×128 grid points in the (ζ, θ) space (see Ref. [26]). Therefore, extensive numerical calculations were required. Furthermore, since the density of the bispherical grid lines diverges in the space between the particles when the distance of contact d approaches zero, we could not calculate the interaction energy for $d \to 0$.

Two orientational configurations are identified. For large distances to contact d, each particle is surrounded by a surface-induced nematic wetting layer. We call this the no-bridge configuration. At sufficiently small d, a bridge of condensed nematic phase develops, as illustrated, e.g., in the insets of Fig. 2, where we identify the orientational order by plotting a grey-scale picture of $\mu_{ij}\mu_{ij}$. In the uniaxial case, $\mu_{ij}\mu_{ij}$ is proportional to the square of the Maier-Saupe parameter S, which measures how well the molecules are aligned. Investigations of the biaxiality show that the order parameter stays essentially uniaxial in regions of noticeable orientational order. In Fig. 1, we plot the interaction energy $F(d) - F(d \to \infty)$ as a function of the reduced distance d/a for a reduced particle radius $a/\xi_r = 35$. At the bulk phase transition temperature $\tau_c = 1$, we notice a clear hysteresis. Reducing the distance d/a from large values, the two-particle system stays in the no-bridge configuration with an interaction-energy close to zero. At $d/a \approx 0.6$ the bridge configuration becomes metastable, and at $d/a \approx 0.53$ there should be a first-order transition to the bridge configuration. However, due to activation barriers much larger than the thermal energy, we expect the system to stay in the no-bridge configuration until $d/a \approx 0.4$, where it loses its metastability. On the other hand, pulling two spheres apart, the bridge should stay until $d/a \approx 0.6$. In the bridge configuration, the interaction energy is approximately linear in d/a, which is in good agreement with measurements of a nearly constant interaction force in Ref. [10]. Note that such a force profile, although with a larger hysteresis, is used to model the viscoelastic behavior of wet granular media, where a liquid bridge forms when the grains come close to each other [27]. For $\xi_r = 10$ nm, i.e., a particle radius of 350 nm, the extrapolated interaction energy at zero distance amounts to $600k_BT$. The value agrees quantitatively with Fig. 8 in Ref. [10], when in the evaluation of the force per particle radius we

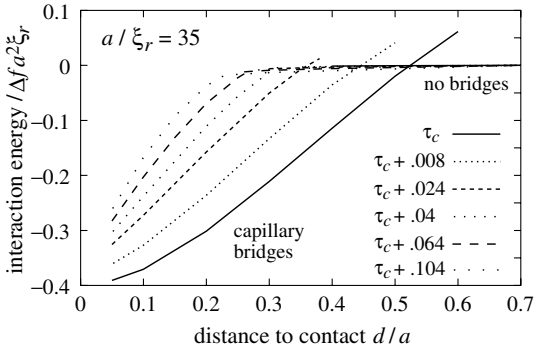

FIG. 1. Interaction energy in units of $\Delta f a^2 \xi_r$ as a function of the reduced distance to contact d/a. The reduced particle radius is $a/\xi_r = 35$ and temperature serves as parameter.

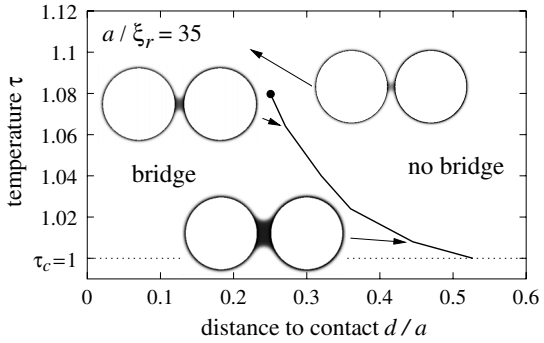

FIG. 2. In a τ, d diagram for a reduced particle radius $a/\xi_r = 35$, the first-order transition line between the no-bridge and the bridge configuration ends in a critical point. The insets depict the capillary bridges at different locations on and beyond the transition line.

take $a = 350$ nm. This suggests that our assumption of rigid anchoring is reasonable.

With increasing temperature, the interaction-energy profiles in Fig. 1 become steeper, which means larger force in accordance with experiments (see Ref. [13]). In addition, the width of the hysteresis decreases until the interaction profile becomes smooth. Figure 2 presents the first-order transition line between the no-bridge and the bridge configuration in a temperature-distance diagram [28]. It ends in a critical point, which we determined by extrapolating the width of the hysteresis to zero. This diagram is in full analogy to Sheng's study [22]. However, due to the curvature of the particles, which reduces the transition temperature and prevents the growth of an infinitely thick wetting film [25], the transition line intersects $\tau_c = 1$ at a finite distance of $d/a = 0.53$. The insets show capillary bridges at different locations along the transition line. Clearly, the bridge itself becomes smaller and smaller. We observe that even beyond the critical point, the smooth creation of the capillary bridge takes place in a very narrow interval for the distance of contact d. If, in a Gedanken experiment, one were able to move the colloids close to the appropriate distance where the smooth or continuous bridge–no-bridge transition occurs, then small fluctuations in the colloids' positions would induce stochastic transitions between both configurations. This might be considered as an effective two-state system, which also occurs, e. g., in the complex unfolding transition of RNA under a load force [29].

We observe that for decreasing particle radius the transition line in Fig. 2 shrinks until the critical point reaches the bulk transition temperature $\tau_c = 1$ at around $a/\xi_r = 11$. We attribute this to the strong director deformations close to smaller particles, which prevent the discontinuous formation of the capillary bridges. Figure 3 gives a qualitative account of the location of the critical points as a function of τ and a/ξ_r. Below the line, a first-order transition between the no-bridge and the bridge configuration occurs when the distance to contact d is decreased. Whereas above the line, the configurations evolve continuously into each other. For $a/\xi_r \to \infty$, i.e., for the slab geometry, the line approaches $\tau = 1.244$ [22]. The inset shows interaction potentials as a function of d/a for different particle radii at $\tau = 1$. Clearly, the strength of the interaction potential scales with $a^2\xi_r$. For $a/\xi_r = 11$ the potential just becomes smooth at the critical distance $d \approx 0.75\,a$. The capillary bridge is already well established. Note that, as mentioned before, the transition from the no-bridge to the bridge configuration occurs in a very narrow interval of d. At $a/\xi_r = 3.5$, the potential is completely smooth. The capillary bridge at the minimum (see inset) possesses weaker orientational order compared to the previous cases. The repulsion at small d/a is due to strong elastic distortions in the director field when the particles come close to each other. The dotted line corresponds to our numerical calculation, whereas the full line is a fit to the Morse potential $U(d) = D[(1 - e^{-c(d-d_0)}]^2 - 1]$, with $D = 0.21$ and $d_0 = 0.63$ being, respectively, the dissociation or binding energy of the two-particle cluster and the equilibrium distance. The constant $c = 2.25$ is connected to the frequency with which the particles oscillate around d_0 when treated as a harmonic oscillator [30]. Morse potentials are used to describe nonlinear effects in the vibration spectrum of diatomic molecules [31]. Considering the fact that colloids are often viewed as models for atomic systems [32], our results concerning the Morse potential might suggest that capillary bridges mediate the formation of *colloidal molecules* [33] which could be used to model aspects of molecular systems [34]. Experimental techniques to test our predictions are confocal microscopy or light scattering [32].

In conclusion, we have presented a detailed study of two-particle interactions due to the formation of capillary bridges close to a nematic-isotropic phase transition. We have demonstrated that the first-order transition line, which separates the bridge from the no-bridge transition and ends in a critical point, vanishes below a particle

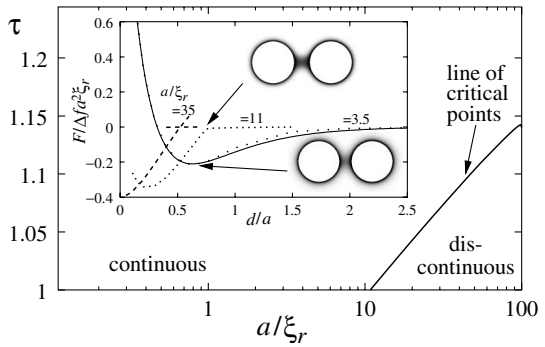

FIG. 3. In a τ, a diagram, the line of critical points separates regions where the transition between the no-bridge and the bridge transition is either discontinuous or smooth. The inset shows interaction profiles for different particle radii at $\tau = 1$. The solid line is a fit to a Morse potential.

radius of $a/\xi_r \approx 11$. Furthermore, we have speculated about an effective two-state system close to the critical points. Since the interaction energy scales with $a^2\xi_r$, varying the particle radius provides a means to create two-particle potentials with an attraction whose strength ranges from very strong (which explains the sticking of particles [35]) to weak. For sufficiently small particles, the interaction potential can be approximated by a Morse potential, which suggests the formation and study of colloidal molecules [33] including, e.g., their vibrational spectrum. In addition, the binding energy or the energy gain due to the creation of a capillary bridge approaches the thermal energy so that fluctuations and therefore probably Casimir forces, also discussed within liquid crystals [36], become important. Introducing a finite anchoring strength of the mesogenic molecules gives a further control parameter for the two-particle interaction. This all shows that two- and also many-particle interactions due to the formation of capillary bridges in liquid-crystal colloids present an attractive means to study the self-assembly of colloidal structures both in the bulk and on structured surfaces. Finally, such capillary bridges might also contribute to protein-protein interactions in binary biomembranes [37].

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