

Depletion interactions in lyotropic nematics

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(Received 4 January 2000; accepted 1 March 2000)

A theoretical study of depletion interactions between pairs of small, globular colloids dispersed in a lyotropic nematic of hard, rodlike particles is presented. We find that both the strength and range of the interaction crucially depends on the configuration of the spheres relative to the nematic director, and on their size. The interaction is significantly stronger parallel than perpendicular to the director, explaining the emergence of stringlike aggregates observed in experiment. © 2000 American Institute of Physics. [S0021-9606(00)51220-3]

I. INTRODUCTION

Colloidal particles dispersed in uniaxial nematic media exhibit unusual interactions, brought about by the coupling to the surrounding anisotropic fluid. See, e.g., a recent review article by Poulin,¹ and work cited therein. At least three important sources of effective interaction have been identified between colloids in a nematic matrix, provided these are macroscopically large on the scale of the nematogens.² When the anchoring of the nematic to the surfaces of the particles is weak, an initially homogeneous director field will remain largely unaffected by the presence of the foreign particles. What is likely to be perturbed, however, is the ordering of the nematogens in the vicinity of the colloids, as well as the spontaneous fluctuations of the director field between them. A freezing out of director fluctuation modes tends to give rise to a long-range, Casimir-type of attraction between the dispersed colloidal particles.³ Inhomogeneities in the degree of nematic order, including the possible induction of pre-smectic ordering,⁴ also induce an effective interaction, acting when the zones of perturbed nematic order around two approaching particles overlap.^{5,6} A third type of medium-induced interaction arises when the anchoring conditions are so strong that they cause the director field to deform,^{7–9} a situation which seems to predominate. The deformation of the director field allows the surface anchoring energy of the colloids to be minimized, albeit at the cost of a concomitant generation of defects in the surrounding nematic fluid.^{10,11} The stored elastic energy associated with the deformed director field is thought to be the main driving force behind the highly anisotropic effective colloid–colloid interactions observed in this kind of system.¹

It appears that the three medium-induced interactions described conspire to make it generally quite difficult to produce thermodynamically stable colloidal dispersions in nematic liquids at weight fractions in excess of, say, a few percent.¹² It has to be borne in mind, however, that in *lyotropic* nematics one may encounter situations where the dispersed colloidal particles are substantially *smaller* than the particles that make up the nematic matrix. When this hap-

pens to be the case, the foreign colloidal particles cannot distort the director field, nor influence the director fluctuations, or the degree of nematic order. The reason is that these quantities are only defined on a macroscopic scale, i.e., on a length scale large compared to the dimensions of the nematogens.¹³ One would, therefore, perhaps naively expect that adding small colloidal particles to a lyotropic nematic should not be able to perturb this nematic in any significant way. Yet, recent experiments indicate that relatively small amounts of submicron-sized colloidal particles do interfere strongly with a host nematic phase consisting of rodlike viruses in water, leading to all kinds of novel, micro-phase separated phases.^{14,15}

Fraden *et al.* attributed the observed phase behavior in this type of dispersion to so-called *depletion* interactions between the spheres, which come into play when zones around the spherical particles, depleted of rods due to a hard-core exclusion interaction, interpenetrate.¹⁴ The osmotic pressure difference between the overlapping rod-free depletion volumes and the bulk nematic drive the particles together, thereby inducing an attractive interaction between them. As pointed out by Fraden *et al.*¹⁴ and by others,¹⁶ since the overlap volume of two approaching test spheres depends on their relative orientation to the nematic director, the depletion interaction arising in a lyotropic nematic must be highly anisotropic. Although available theoretical work on rod-sphere mixtures rationalizes at least some the observed behavior, many aspects remain poorly understood.^{14,16–19}

In an effort to contribute to the understanding of anisotropic colloidal mixtures, we investigate theoretically the strength, orientation dependence, and range of the depletion interaction between colloidal spheres in a hard-rod nematic. It is shown that even when the spheres are small on the linear scale of rods, the depletion interaction can be very strong indeed. Depending on the size of the globules, the interaction strength at contact can easily reach values of several tens of $k_B T$. This explains the sensitivity of the nematic to small amounts of added colloidal particles, but also suggests that some of the observed behavior may well be kinetically determined. We find that the depletion attraction parallel to the nematic director becomes stronger with increasing concentration of rods, while that perpendicular to the director is not

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only weaker at equal concentrations, but in addition *reduces* in strength the more concentrated the nematic. Perhaps the most important insight obtained is that both the range and the strength of the depletion interaction depend crucially on the size of the spheres relative to the lateral correlation length of the nematic medium.

This paper is organized as follows. In Sec. II, we first briefly review the basics of the hard-rod nematic, guiding us to a simplified physical picture that emerges when the radii of the colloids are large on the scale of the lateral correlation length of the nematic, but small compared to the length of the rods. It allows us to calculate, in Sec. III, the depletion interaction between two spherical test colloids in a (freely rotating) hard-rod nematic, using a straightforward geometric argument. Two configurations in particular are focused on: One where the test spheres are aligned perfectly parallel to the director, and one where the vector connecting their centers-of-mass is perfectly perpendicular to that. Next, the interaction in the parallel configuration is studied more in more detail as a function of the sphere size in Sec. IV, where we make use of an earlier analysis by Auvray of the depletion interaction in an isotropic dispersion of hard needles.²⁰ The calculation confirms our findings for spheres that are much larger than the lateral correlation length, but also shows that when the colloidal particles are smaller than this length scale, both the range and the strength of the depletion potential diminish appreciably. In the discussion of Sec. V, the predictions for depletion interaction in the nematic and isotropic phases are compared with each other, and with experiment. We end this paper with conclusions and a brief summary of the results in Sec. VI.

II. THE NEMATIC PHASE

The starting point is a nematic host dispersion consisting of uniaxially ordered, hard rods, i.e., rods which interact only via their mutually excluded volumes. Provided that these rods are very slender, the second virial treatment advanced by Onsager provides a highly accurate description of the state of affairs.²¹ There are in fact strong indications that the second virial approximation becomes exact in the limit of infinite aspect ratios.²² It is also well-established that the angular distribution of the rods with respect to the preferred direction (the director) may (within reasonable approximation) be represented by a Gaussian.²² Within these approximations, the mean-square angle of the rods, $\langle \theta^2 \rangle$, can be shown to obey the relation $\langle \theta^2 \rangle \sim \pi/2c^2 \ll 1$. Here, c denotes a dimensionless concentration defined as $c \equiv (\pi/4)L^2D\rho$ in terms of the rod length, L , width, $D \ll L$, and number density, ρ . An accurate numerical analysis of the Onsager theory reveals that the hard-rod nematic is more stable than the isotropic phase when $c \gtrsim 4.2$, while for concentrations below $c \approx 3.3$, the isotropic state is the most stable.²³ Note further that at very high concentrations of the order $c \approx O(LD^{-1}) \gg 1$, the nematic becomes unstable with respect to the one-dimensionally crystalline smectic A phase.²⁴ In the following, we shall be assuming the rod density to be far below that where nematic–smectic transition occurs, and ignore the influence of pre-smectic correlations in the nematic fluid.

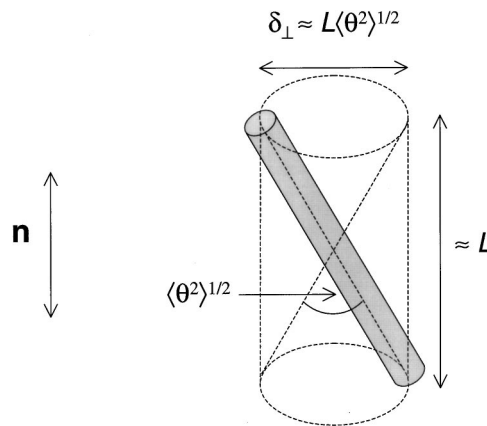


FIG. 1. Average orientational phase volume of a rod of length L in a lyotropic nematic. The double-headed vector \mathbf{n} denotes the preferred direction of the rods (the director), and δ_{\perp} the lateral correlation length of the rods. The lateral correlation length is equal to the rod length multiplied by the root-mean-square angle of the rods with respect to the nematic director, $\langle \theta^2 \rangle^{1/2}$. Since $\langle \theta^2 \rangle^{1/2} \ll 1$ even at coexistence with the isotropic phase, the mean projected length of the rods along the director is, to a reasonable approximation, equal to L .

Despite the fact that the rods in the nematic phase are restricted to relatively small angles of order $\langle \theta^2 \rangle^{1/2}$, the lateral excursions of the rod ends can be quite significant. Let δ_{\perp} denote the length scale associated with these lateral excursions. From geometry, we estimate that $\delta_{\perp} \approx L \langle \theta^2 \rangle^{1/2}$.²⁵ See Fig. 1. Although the lateral length may be small on the scale of the length of the rods, it can be very large compared to their width. Indeed, inserting the concentration dependence of the mean-square angle quoted above, we find that $\delta_{\perp} \approx Lc^{-1} \gg D$ whenever $c \ll LD^{-1}$, i.e., whenever we are not too close to the nematic–smectic transition, which, of course, was one of our presuppositions. It follows, not that L and D are the relevant microscopic length scales of the hard-rod nematic, but rather L and δ_{\perp} . Recent calculations of the structure factor of the nematic phase of hard rods confirm this: L turns out to be the relevant length scale associated with density fluctuations and pre-smectic ordering *along* the director,²⁶ while δ_{\perp} can be associated with the correlation length of density fluctuations *perpendicular* to it.²⁷

An important conclusion that we can now draw is that if colloidal globules of radius $a \ll L$ are added to the nematic, the strength of the depletion interaction crucially depends on whether a is larger or smaller than the lateral length δ_{\perp} . When $a \gg \delta_{\perp}$, the orientationally averaged depletion volume present around each (hard) sphere must have the approximate shape of an end-capped cylinder of approximate length L and radius $a + \delta_{\perp}$, oriented perfectly parallel to the director.²⁸ See Fig. 2. The reason is that (almost) all rod configurations are suppressed by hard-core repulsive interactions when a sphere larger than the lateral length penetrates the volume a test rod sweeps out in the nematic (its “configurational volume,” see Fig. 1). On the other hand, when $\delta_{\perp} \gg a$, a colloidal particle can actually penetrate the configurational volume of a rod, and reduce its angular phase volume only by a relatively small amount. The depletion zone around such a small sphere must, therefore, also be relatively small. Because the depletion interaction is proportional to the overlap

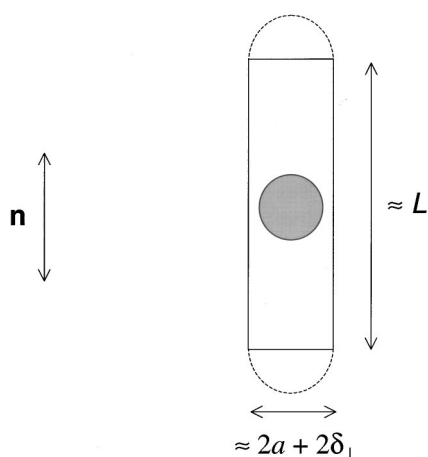


FIG. 2. Zone around a colloidal sphere dispersed in a hard-rod nematic, significantly depleted of rods due to excluded volume interactions. The length of the approximately cylindrically shaped exclusion zone is only slightly larger than the rod length L , in the limit where the sphere radius, a , is small on the linear scale of the rods. Its width is equal to sum of the sphere diameter, $2a$, and two times the lateral correlation length, $2\delta_{\perp}$. We neglect in our calculations the contribution from the end caps, indicated by the dashed hemispheres. The vector \mathbf{n} denotes the director of the nematic.

of the depletion zones of two approaching spheres, we expect the impact of this interaction to be significantly reduced when the radius of the colloids drops below the lateral correlation length. Our analysis of Sec. IV confirms this expectation.

In the next section we first study conditions for which $L \gg a \gg \delta_{\perp}$. This limit should almost always be accessible experimentally, at least in principle, for the length scale δ_{\perp} can be tuned by varying the rod concentration in the nematic. Because the orientationally averaged depletion volume levels off when the sphere radius becomes larger than the lateral correlation length, we shall denote the depletion interactions acting in this limit as *saturated*.

III. SATURATED INTERACTIONS

In the saturated limit, where $L \gg a \gg \delta_{\perp}$, each sphere is surrounded by a zone almost completely devoid of rods. These depletion zones must be rod-shaped, of approximate length L and radius $a + \delta_{\perp}$, and oriented along to the nematic director. See Fig. 2. When the depletion zones of two spheres overlap, this gives rise to a depletion potential.²⁹ The depletion potential, ϕ_{dep} , depends on the osmotic pressure, Π , of the nematic host dispersion, and on the overlap volume of the depletion zones, v , according to²⁹

$$\phi_{\text{dep}}(R, \vartheta) = -\Pi v(R, \vartheta). \quad (1)$$

Although strictly speaking only justifiable in the dilute limit,³⁰ we extrapolate Eq. (1) to higher densities. The limitations of this approximation will be discussed in Sec. V. The overlap volume $v(R, \vartheta)$ depends on the distance between the centers-of-mass of the colloids, R , and on the angle, ϑ , between the vector connecting the centers-of-mass of the two test particles and the nematic director. We first study the case of parallel alignment, with $\vartheta = 0$, and next that of perpendicular alignment, where $\vartheta = \pi/2$.

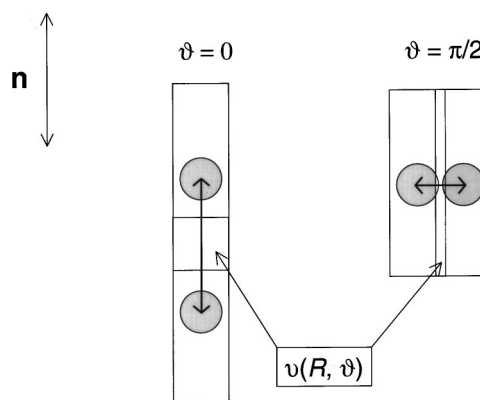


FIG. 3. Overlap of the depletion zones $v(R, \vartheta)$ of two spheres, oriented parallel and perpendicular to the director, indicated by their respective angles $\vartheta = 0$ and $\vartheta = \pi/2$. R denotes the distance between the centers-of-mass of the spheres. See also the main text.

It is easy to convince oneself that the overlap volume of the depletion zones of two spheres in a configuration parallel to the director reads

$$v(R, 0) \approx \pi L a^2 \left(1 - \frac{R}{L}\right), \quad (2)$$

provided $R/L \leq 1$. See Fig. 3. In Eq. (2) we have neglected unimportant terms of order $a/L \ll 1$, and of order $\delta_{\perp}/a \ll 1$. For $R/L \geq 1$ we have, for all practical purposes, $v(R, 0) \approx 0$. (We neglect the small contribution from the end caps of the depletion zones.) Inserting Eq. (2) into Eq. (1), and noting that the osmotic pressure of the nematic is (within the Gaussian approximation) three times that of an ideal solution,²² $\Pi \sim 3\rho k_B T$, we obtain for the depletion potential

$$\phi_{\parallel}(R) \equiv \phi_{\text{dep}}(R, 0) \approx -12ck_B T \frac{a^2}{LD} \left(1 - \frac{R}{L}\right), \quad (3)$$

for $R \leq L$. The depletion potential is negligible or zero when $R > L$, i.e., $\phi_{\parallel}(R > L) \approx 0$. Since $\phi_{\parallel}(2a) \approx -12ck_B T a^2 L^{-1} D^{-1}$ in the limit $a/L \ll 1$, we conclude that the attractive energy of two touching spheres exceeds the thermal energy whenever $a > \sqrt{LD/12c}$. The homogeneous mixture is then highly likely to become unstable at any appreciable concentration of the colloids. The higher the rod density, the smaller the colloidal spheres need to be to be able to destabilize the homogeneous nematic.

The overlap of the cylindrical depletion zones of two spheres in the perpendicular configuration is also fairly straightforward to calculate. (See Fig. 3.) We find, to leading order in $\delta_{\perp}/a \ll 1$

$$v\left(R, \frac{\pi}{2}\right) \approx \frac{4}{3} L a^{1/2} (2\delta_{\perp})^{3/2} \left(1 - \frac{R - 2a}{2\delta_{\perp}}\right)^{3/2}, \quad (4)$$

for $2a \leq R \leq 2a + 2\delta_{\perp}$, and $v(R, \pi/2) \approx 0$ for $R > 2a + 2\delta_{\perp}$. Inserting Eq. (4) into Eq. (1) shows that the depletion interaction for the perpendicular configuration must take the form

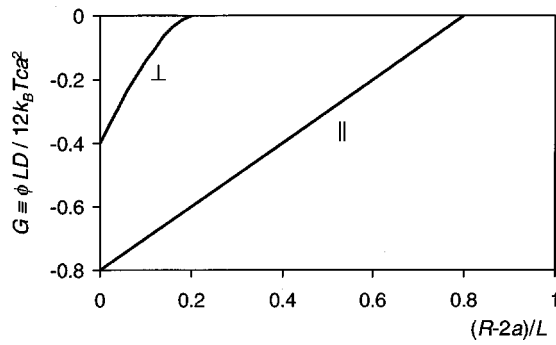


FIG. 4. Normalized depletion potential $G \equiv \phi LD / 12 k_B T c a^2$, parallel (||) and perpendicular (\perp) to the director, as a function of the scaled center-to-center distance, $(R-2a)/L$, according to Eqs. (3) and (5). For reasons of clarity we have extrapolated $a \rightarrow \delta_\perp$. The smaller $\delta_\perp/a < 1$, the shallower and shorter ranged the normalized potential perpendicular to the director is. $\phi_\perp/\phi_\parallel$ vanishes completely in the limit $\delta_\perp/a \rightarrow 0$.

$$\phi_\perp(R) \equiv \phi_{\text{dep}}\left(R, \frac{\pi}{2}\right) \approx -\frac{16}{3\pi} c k_B T \frac{a^2}{LD} \left(\frac{2\delta_\perp}{a}\right)^{3/2} \left(1 - \frac{R-2a}{2\delta_\perp}\right)^{3/2}, \quad (5)$$

provided $R-2a \leq 2\delta_\perp$, and $\delta_\perp \ll a$. For separations $R-2a > 2\delta_\perp$ we have, again for all practical purposes, $\phi_\perp(R) \approx 0$. Comparing Eq. (3) with Eq. (5), it transpires that the depletion potentials ϕ_\perp and ϕ_\parallel differ qualitatively in strength, range, and concentration dependence. Of particular interest is the property of ϕ_\parallel to become *stronger*, and ϕ_\perp to become *weaker* with increasing rod density. The reason is that in the perpendicular configuration the overlap volume decreases with increasing rod density, because $\delta_\perp \propto c^{-1}$. The depletion potential is anyway significantly stronger and longer-ranged in the parallel than in the perpendicular configuration; see Fig. 4. This is not entirely surprising. First, the range of the interaction is determined by the predominant length scale in each direction, that is, by the length of the rods in the parallel configuration, and by the much smaller lateral correlation length in the perpendicular configuration. Second, a significantly larger fraction of the configuration space is suppressed in the parallel than in the perpendicular configuration, exactly because rods inclined at large angles carry very little statistical weight in the nematic phase.

IV. APPROACH TO SATURATION

Although the analysis of the previous section should formally hold in many situations, it seems worthwhile to investigate depletion interactions which are not fully saturated. This applies in particular to mixtures containing very small colloidal particles, such as random-coil polymers or proteins, or when the nematogens are particularly long, as is the case for the rodlike fd virus particles studied by Fraden and collaborators.¹⁴ Fortunately, as will become evident below, the theory of Sec. III remains reasonably accurate all the way down to $a/\delta_\perp \approx 1$. For $a/\delta_\perp \ll 1$, however, significant departure from the predicted behavior in the saturated limit has to be expected, especially with regard to the range of the interaction. We restrict the following analysis to spheres in the

parallel configuration for two reasons. The first is mathematical expedience. The second, perhaps more important reason is that a Gaussian may not very well represent the tail of the angular distribution of the rods in the nematic.³¹ Both ϕ_\perp and ϕ_\parallel will be studied in more detail using density functional techniques in a forthcoming publication.³²

In an elaborate yet elegant paper, Auvray²⁰ studied depletion effects of globular particles mixed with isotropic dispersions of vanishingly thin rods (“needles”). This is a good approximation when the size of the spheres greatly exceeds the diameter of the rods, $a \gg D$, a limit we adhere to in this paper. Let ω denote the angle between the main body axis of a rod, and the vector connecting the centers-of-mass of two test spheres. The overlap of the zones around two test spheres *not* accessible to rods inclined at a *fixed* angle ω obeys²⁰

$$V(R, \theta) \approx (L-R)a^2 \pi \left(1 - \pi \arcsin\left(\frac{\omega}{\omega_0}\right) - 2\left(\frac{\omega}{\omega_0}\right) + \left(\frac{\omega}{\omega_0}\right)^2 \right), \quad (6)$$

for distances $R < L$ and angles $\omega \leq \omega_0$, where $\omega_0 \approx 2a/R$ is a distance dependent cut-off angle. $V(R, \omega) \approx 0$ when $R > L$, and/or $\omega > \omega_0$. As before, we have assumed that $a/L \ll 1$. The overlap volume $v(R, \vartheta)$ can be obtained by averaging $V(R, \omega)$ over all angles ω . Setting $\vartheta = 0$ for the parallel configuration we set out to investigate, ω becomes identical to the angle with the nematic director, θ , defined earlier. Referring to the discussion in Sec. II, we recall that the angular distribution of the rods can be approximated by a Gaussian.²² Hence, we use for the (unnormalized) weight of the distribution $\exp(-\theta^2/\langle\theta^2\rangle)$ when $0 \leq \theta \leq \pi/2$, and $\exp(-(\pi-\theta)^2/\langle\theta^2\rangle)$ when $\pi/2 \leq \theta \leq \pi$, where $\langle\theta^2\rangle \sim \pi/2c^2$ denotes the mean-square angle of the rods in the host nematic. (Note that the nematic has cylindrical as well inversion symmetry.) Performing the averaging over the Gaussian distribution, we get $v(R, 0) \approx 0$ for $R \geq L$, and

$$v(R, 0) \approx \pi L a^2 \left(1 - \frac{R}{L} \right) F\left(\frac{\omega_0^2}{\langle\theta^2\rangle}\right), \quad (7)$$

for $R < L$, where

$$F(x) \equiv 1 - \frac{2}{\pi} \exp(-x) + \frac{2}{\pi} x^{-1} (1 - \exp(-x)) - \frac{2}{\pi} x^{-1/2} \gamma\left(\frac{3}{2}, x\right) - \exp\left(-\frac{1}{2}x\right) I_0\left(\frac{1}{2}x\right), \quad (8)$$

denotes a scaling function, γ an incomplete Gamma function, and I_0 a modified Bessel function.³³ The depletion potential can therefore be written as

$$\phi_\parallel(R) \approx -12 c k_B T \frac{a^2}{LD} \left(1 - \frac{R}{L} \right) F\left(\frac{4a^2 L^2}{\delta_\perp^2 R^2}\right), \quad (9)$$

for $R < L$, and $\phi_\parallel(R) \approx 0$ for $R \geq L$. This more generally applicable result agrees favorably with our previous expression, Eq. (3), because the scaling function $F \sim 1 - \delta_\perp R / \pi^{1/2} a L + \dots$ is very close to unity for all distances $R \geq 2a$, when the limit $a \gg \delta_\perp$ applies. In the opposite limit,

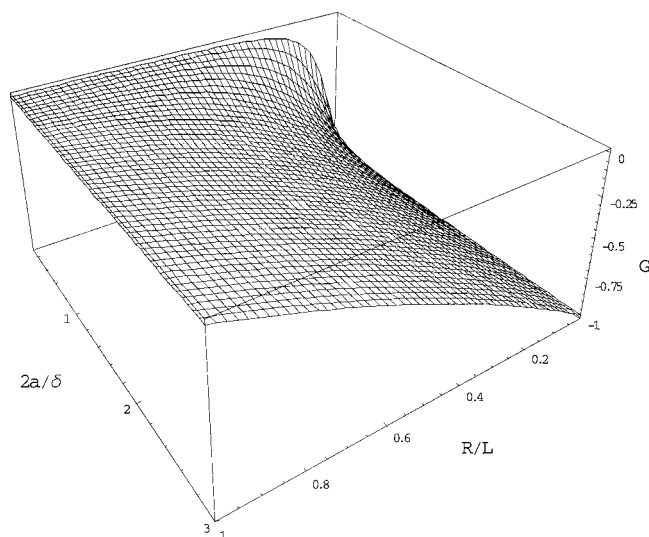


FIG. 5. Normalized depletion potential parallel to the director $G \equiv \phi_{\parallel} LD / 12k_B T c a^2$, according to Eq. (9). Plotted is G as a function of the scaled interparticle distance, R/L , and as a function of the ratio of the particle diameter and the lateral correlation length, $2a/\delta_{\perp}$.

$a \ll \delta_{\perp}$, the scaling function F is again close to unity at short separations $R \ll 2aL/\delta_{\perp} \approx 2ca$, but becomes much smaller than that when $R \gg 2ca$, because then $F \sim (1 - 2/3\pi)4c^2a^2/\pi R^2 \ll 1$. In other words, the range of the interaction is strongly reduced from a rod length L to $\sim 2ca$, when the colloids are smaller than the lateral correlation length δ_{\perp} . Remarkably, provided the interparticle distance is sufficiently small, $2a \leq R \ll 2ca$, Eq. (3) holds for all radii $a \gg D$, irrespective of whether the spheres are large or small compared to the lateral correlation length. We shall use this observation in our comparison with experiment in the next section.

In Fig. 5 we have plotted the scaled depletion potential $G(R) \equiv -(1 - RL^{-1})F \propto \phi_{\parallel}(R)$ as a function of the ratio of the particle size and the lateral correlation length, a/δ_{\perp} . The figure clearly shows that the depletion potential becomes shorter ranged when this ratio drops below unity, in essence because the smaller the colloids are, the more easily they can penetrate the volume swept out by a rod.

V. DISCUSSION

It is instructive to compare our findings with those of Auvray, who studied mixtures of colloidal spheres and isotropic solutions of rods.²⁰ Since we are interested in the strength of the depletion potential all the way up to the concentration regime where the isotropic–nematic transition sets in, we need to extend Auvray's ideal solution theory to higher densities. This can be done in the same spirit as we have done for the nematic, by inserting for the osmotic pressure $\Pi = k_B T \rho(1 + c)$, valid within the second virial approximation.²¹ Here, ρ and c again denote the actual and dimensionless number densities of the rods, although obviously now in the isotropic phase. The mean overlap volume in the isotropic phase, $v(R)$, does not depend on the orientation the spheres, and can be obtained by taking an isotropic angular average over Eq. (6). The (extended) Auvray result

for the depletion potential in the isotropic phase, $\phi_{\text{iso}}(R) \equiv \Pi_V(R)$, becomes in the small sphere limit $a \ll L$,²⁰

$$\phi_{\text{iso}}(R) \approx - \left(1 - \frac{5}{3\pi} \right) c(1+c) k_B T \frac{a^2}{LD} \left(\frac{2a}{R} \right)^2 \left(1 - \frac{R}{L} \right), \quad (10)$$

for $R \leq L$, and $\phi_{\text{dep}}(R) \approx 0$ for $R > L$. [The numerical prefactor in Eq. (10) agrees well with that obtained by a numerical evaluation of the overlap volume by Marques *et al.*³⁴] Both the strength and the distance dependence differ substantially from what we find in the nematic phase, cf. Eqs. (3) and (5). Indeed, the depletion potential is significantly stronger in the nematic than in the isotropic phase, albeit that this is only strictly true for the parallel configuration. Under conditions of isotropic–nematic phase coexistence, we predict that $\phi_{\parallel}(2a)/\phi_{\text{iso}}(2a) \approx 8$ for all $a \ll L$. To obtain this result, we have used the theoretical values for the dimensionless concentrations in the coexisting isotropic and nematic phases earlier quoted, $c_{\text{iso}} \approx 3.3$ and $c_{\text{nem}} \approx 4.2$.²³ On the other hand, we also find that at coexistence $\phi_{\perp}(2a)/\phi_{\text{iso}}(2a) \approx (\delta_{\perp}/a)^{3/2} \ll 1$, at least in the limit $\delta_{\perp} \ll a$. The restriction follows from the limited range of validity of Eq. (5). Referring to the arguments put forward in the Sec. III, we believe $\phi_{\perp}(R)$ always to be substantially weaker than $\phi_{\text{iso}}(R)$, that is, for arbitrary colloid radii $a \leq L$.

We have now arrived at a point, where we can discuss the theoretical predictions in the context of the experimental observations by Fraden and co-workers on aqueous mixtures of polystyrene (PS) spheres and the rodlike fd virus particles.¹⁴ Given the limited scope of the work presented here, we shall not endeavor to explain the full complexity of the experimental phase diagram, not least because we have neglected in our considerations the possible impact of Coulombic interactions, and of a finite bending flexibility of the rods. Some of the observations can nonetheless still be rationalized. For example, up to volume fractions of $\sim 0.5\%$, 50 nm radius PS spheres appear to be fully miscible with the virus particles in isotropic solution, whilst it seems that they cannot be randomly dispersed at all in the nematically ordered phase, where microphase-separated, lamellar and filamentous structures develop. For volume fractions of spheres greater than 0.5%, a lamellar phase appears slightly below the isotropic–nematic transition of the pure virus dispersion. If we insert into Eqs. (3) and (10) for the length and width of the fd virus the known values $L = 880$ nm and $D = 6.6$ nm, and for the spheres a radius $a = 50$ nm, we find that, at coexistence, $\phi_{\text{iso}}(2a) \approx -2.9k_B T$ and $\phi_{\parallel}(2a) \approx -22k_B T$. [A meaningful estimate for $\phi_{\perp}(2a)$ cannot be provided, since we estimate that for the system at hand $\delta_{\perp}/a \approx 4$ under conditions of isotropic–nematic phase coexistence.] The very strong depletion interaction in the nematic phase explains why the spheres cannot be randomly mixed in any appreciable quantity with that phase. At rod concentrations below which the isotropic-to-nematic transition occurs, the depletion potential is, according to Eq. (10), at most $\approx -3k_B T$, making it plausible that the colloids remain largely miscible with the isotropic phase. An effective attractive interaction strength of about $3k_B T$ close to the nematic transition could be sufficient to induce a transition in that phase, but only at

high enough densities of colloidal spheres, which, indeed, seems to be in accordance with observation. One should naturally not over-interpret these estimates, since in reality the particles in the mixture do not interact by purely hard-core interactions alone. One could tentatively deal with the influence of Coulomb interactions by adding to the hard-core dimensions of the particles an estimated Debye screening length of 4 nm. Doing so gives $\phi_{\text{iso}}(2a) \approx -2.4k_B T$ and $\phi_{\parallel}(2a) \approx -15k_B T$, values which do not deviate too much from the previous ones. For this reason we guess our estimates to be quite realistic. Unfortunately, how the slight flexibility of the fd virus particles affects the depletion interaction is difficult to ascertain.

An observation also amenable to interpretation in the context of the present work, is that mixing sufficiently large PS spheres in the fd nematic does *not* lead to the emergence of lamellar phases.¹⁴ It appears that when added in small quantities, PS spheres with a radius of 150 nm very rapidly associate into chainlike aggregates, aligned perfectly along the director. To understand this, we need only to realize that according to Eqs. (3) and (5) the depletion attraction is highly directional. In view of such a strong “stickiness” of the spheres along the nematic director, an emergence of quasi one-dimensional assemblies is not surprising, especially at low concentrations of spheres where a macroscopic phase separation is not likely to intervene. Interestingly, similar types of aggregate are known to form in electro- and magnetorheological fluids. As is well known, the in this type of dispersion externally applied electric or magnetic field induces (mainly) dipolar interactions between the colloidal particles.³⁵ The (lyotropic) nematic matrix discussed in this paper acts, in a sense, also like a symmetry-breaking external field, albeit that the interactions induced are definitely not dipolar. In the *thermotropic* dispersions discussed in the beginning of Sec. I, the coupling between the nematic matrix and the colloidal particles can give rise to interactions that are either dipolar or quadrupolar in nature, depending on the anchoring conditions, the size of the particles, and so forth.¹⁰ In such systems stringlike aggregates have indeed been observed experimentally, but we have to keep in mind that the driving force is completely different from the one studied here.¹

Relying on the standard, mean-field theory of linear self-assembly,³⁶ one would expect the aggregates formed in our nematic rod-sphere mixture to conform to a size distribution proportional to $(1 - \langle N \rangle^{-1})^N$, with N the aggregation number of a linear aggregate, and $\langle N \rangle$ the mean aggregation number of all aggregates in the dispersion. Assuming pair interactions to dominate, the latter obeys within mean-field theory³⁶

$$\langle N \rangle = \frac{1}{2} \left\{ 1 + \left[1 + 4 \eta_c \exp \left(- \frac{\phi_{\parallel}(2a)}{k_B T} \right) \right]^{1/2} \right\}, \quad (11)$$

where η_c is the volume fraction of colloid. Even at very low concentrations of colloid, the aggregates can potentially become very long indeed, since the contact potential $|\phi_{\parallel}(2a)| \gg k_B T$ when $a \gg \sqrt{LD/12c}$. For the 150 nm spheres dispersed in the fd nematic, we estimate from Eq. (3) that $\phi_{\parallel}(2a) \approx -195k_B T$, or $\phi_{\parallel}(2a) \approx -124k_B T$ if we again

crudely account for the effect of screened Coulomb interactions. Clearly, kinetic effects associated with such highly attractive energies must dominate the phase behavior, and possibly block the route to the structured mesophases observed for smaller spheres.¹⁴ Because of its quadratic radius dependence, the depletion potential is very sensitive to the size of the colloids.

An issue we finally address is the adequacy of Eq. (1) beyond the dilute limit. It is now well established that although Eq. (1) is exact when the host dispersion is dilute, spatial correlations between the host particles or *depletants*³⁷ do modify the effective potential they induce between the foreign particles.³⁰ The most important impact the spatial correlations have, is (i) to make the depletion interaction longer ranged, and (ii) to superimpose oscillations on the “bare” depletion potential, which reflect the underlying pair structure of the host dispersion. In our case, the potential will be modified by pre-smectic density correlations along the director, which become an increasingly predominant feature the closer we get to the nematic–smectic transition.²⁶ De Gennes in fact predicted some time ago that correlations in a pre-smectic fluid should be able to give rise to an oscillatory effective interaction between two immersed, macroscopic surfaces.⁴ Experimental evidence for this phenomenon was recently found in a nematic dispersion of discotic micelles.³⁸ From theoretical work on the static structure of a nematic of hard rods,²⁶ we deduce that for the system at hand such oscillations must occur on length scales of the order of a rod length $L \gg a$. This means that the attractive part of the depletion potential studied here, active at interparticle distances below a rod length, should remain largely intact. Therefore, the main conclusions of the theory presented in this paper are probably not affected in any significant way by the subtle influence of rod–rod correlations.

At distances larger than approximately a rod length, one cannot rule out the possibility of repulsive barriers, analogous to what is predicted, e.g., for mixtures of large and small hard spheres,³⁰ and for isotropic mixtures of large spheres and small rods.³⁹ The possibility of pre-smectic barriers in the full depletion potential is conceptually appealing, for it explains why spheres in the chainlike assembly observed by Fraden and co-workers¹⁴ do not all exactly touch their neighbors. Often these spheres are separated by a distance of a rod length, caught in what seems the secondary minimum of the depletion potential. The influence of pre-smectic correlations will be studied in a forthcoming publication.³²

VI. CONCLUSION

Small spherical colloids dispersed in hard-rod nematics experience a highly directional attractive depletion interaction. Both the range and the strength of the depletion interaction is largest for pairs of colloids aligned along the nematic director. Significantly weaker and shorter ranged is the depletion interaction for spheres of which the centers-of-mass are aligned perpendicular to the director. The nematic medium-induced interaction is not only weaker in the perpendicular than in the parallel configuration, it also becomes less strong the more concentrated the nematic. This property

could lead to the emergence of stringlike aggregates when the density of spheres is not sufficiently high to provoke a macroscopic phase transformation.

ACKNOWLEDGMENTS

The work presented in this paper was started while visiting the Van 't Hoff Laboratorium at Universiteit Utrecht. I am grateful to Professor Henk Lekkerkerker for his hospitality, and to Dr. Gerrit Vliegenthart for many illuminating discussions on depletion interactions. I am also grateful to Dr. Zvonimir Dogic and Dr. Valerie Anderson for discussions and a critical reading of the manuscript. This work was partly funded by the Stichting voor Fundamenteel Onderzoek der Materie (Foundation for Fundamental Research on Matter) which is part of the Nederlandse Organisatie voor Wetenschappelijk Onderzoek (Netherlands Foundation for the Advancement of Science).

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