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Self-assembly of globular particles in a nematic dispersion of colloidal rods

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Small spherical guest particles added to a nematic liquid-crystalline dispersion of colloidal rods self-assemble linearly into chain-like aggregates. We argue that the formation of these chains is induced by the excluded-volume coupling of the globules to the nematic matrix, and that pretransitional fluctuations in the mixture give rise to the structural reorganization of the linear aggregates observed in experiment. Ultimately, the repulsive interactions between the globules and the rods either promote large-scale demixing or a transition to a microphase-separated lamellar state, depending on the concentration of rods in the host dispersion. © 2002 American Institute of Physics. [DOI: 10.1063/1.1501476]

Notwithstanding that attractive interactions play a subtle and only partially understood role in the stability of colloidal dispersions, an important driving force of phase transitions in this sort of system is not given by attractive but by repulsive interactions between the particles.¹ Steric or hard-core (excluded-volume) repulsion alone can cause phenomena as diverse as the crystallization of globular particles,² the liquid-crystalline ordering of anisometric ones,³ and the demixing of colloids of different size and/or shape.⁴ The reason for this is that dispersions not only optimize an (ideal) entropy of mixing favoring homogeneous phases, but also a packing entropy that promotes exactly the opposite, namely the demixing and ordering of particles.¹ Packing effects predominate when the concentration of dispersed material is high, i.e., when free volume becomes a limiting factor.

Remarkably, in addition to promoting large-scale demixing, repulsive interactions also give rise to microphase-separated states in dispersions containing differently shaped particles.⁵ Evidence for this comes from the host of mesoscopically textured phases recently discovered by Fraden and collaborators in aqueous mixtures of long, rodlike virus particles and globular polymeric colloids.⁶ In the so-called lamellar phase, the rods were found to arrange themselves in a smectic A-type layered structure, expelling the (much smaller) globules to the space separating the rod layers. Also observed were widely spaced columnar and cubic arrangements of globules in liquid-crystalline phases of virus particles, and a nematic phase containing self-assembled chains of globules ordered along the preferred direction of the nematic (the director).⁶ Qualitatively, the emergence of the lamellar phase and that of the strings of globules in the nematic can be explained in terms of steric interactions between the globular and rodlike particles.^{5–8}

The focus of this Communication is the intriguing structure of the chainlike aggregates of globular colloids that were

observed in the nematic phase of rodlike virus particles.^{6,9} At low rod densities, the chains appear mainly to be of a “dense” type, with each of the globules touching their immediate neighbors along the chain as shown in Fig. 1(b). At higher rod densities the assemblies attain a more “open” configuration, in which the spacing of the globules is typically a rod length or more; see Fig. 1(a), and Fig. 4 in Ref. 6. Relying on density functional theory calculations, we put forward that the structural transformation of the self-assembled chains of globules with increasing rod density is connected with the underlying tendency of the mixture to cross over to the lamellar, microphase-separated state. Our calculations confirm that steric repulsion can indeed cause the self-assembly of spherical particles in a nematic host dispersion of rodlike colloids, with the provision that the guest particles are much smaller than the rods. In the opposite limit of large spheres, the self-assembly may be induced by a deformation of the director field.¹⁰

In the following, we first briefly discuss the basic principle of how so-called depletion interactions can cause the spheres to self-assemble linearly.⁸ Next we calculate the partial structure factor of the globules in the mixture, and show that the coupling to prelamellar density fluctuations in the background nematic drives the structural reorganization of the assemblies.

We consider a nematic dispersion of perfectly rigid, cylindrical particles of length L and width $D \ll L$. In the nematic state the rods are uniaxially ordered along a director. According to the classical Onsager theory,¹¹ the mean-square angular deviation from the director obeys $\langle \theta^2 \rangle \sim \pi D^2/L^2 \phi_r^2 \ll 1$ assuming that the rods interact via a hard-core potential, where ϕ_r denotes the volume fraction of rods. Associated with the angular dispersion is a length $\delta_\perp \equiv L \langle \theta^2 \rangle^{1/2} \ll L$ that is a measure of the average lateral excursion of the tips of the rods away from the perfectly aligned configuration.⁸ The hard-rod nematic is stable against dilution all the way down to $\phi_r \approx 4.2D/L \ll 1$, below which the isotropic phase appears.^{11,12} In the high density regime a transition to a

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FIG. 1. Calculated diagram of states of hard globules dispersed in a hard-rod nematic for the aspect ratio $L/D=100$ and the rod-sphere size ratio $L/\sigma=10$, with ϕ_s the volume fraction of spheres and ϕ_r that of the rods. The solid line marks the spinodal instability to the lamellar phase, and the dash-dotted line that to macroscopically demixed phases. The dotted line separates the region where self-assembled chains are of the "open" type (a) from that where they are of the "dense" type (b).

smectic A phase takes place at a density $\phi_r \approx 0.42$ if $L/D \gg 1$.^{13,14}

To the nematic we add low concentrations of globular colloids with a diameter σ much smaller than the length of the rods, but much larger than their width $D \ll \sigma \ll L$. The interactions between the globules are of the hard-core type, as are those between the globules and the rods. This means that each colloid must be at the center of a zone that is significantly depleted of rods.¹⁵ For colloids of size $\sigma \gg \delta_\perp$, the depletion zone will have the approximate shape of a cylinder of length L and diameter $\sigma + \delta_\perp$, oriented parallel to the nematic director.⁸ If the depletion zones of two approaching colloids overlap, an imbalance in osmotic pressure builds up that acts to push them together.¹⁵ The effect of this may be translated in terms of an effective, nematic medium-induced pair potential between the spheres. This depletion potential is attractive and approximately equal to the negative of the product of the osmotic pressure of the medium and the volume of overlap of the two depletion zones.¹⁵ For the former we use the known result from the Onsager theory,¹¹ while the latter may be obtained from geometry, which results in our estimate of the depletion potential to be

$$\frac{V(R, \omega)}{k_B T} \approx -\frac{3}{\pi} \phi_r \frac{\sigma^2}{D^2} \left(1 - \frac{R}{L} \cos \omega \right) (1 - \alpha - \sin \alpha) \quad (1)$$

with $\alpha \equiv 2 \arcsin(\sin \omega / \sin \omega_0)$ and $\sin \omega \leq \sin \omega_0 \equiv (\sigma + \delta_\perp)/R$; $V(R, \omega) \approx 0$ for $\omega \geq \omega_0$. Here, ω denotes the (smaller) angle between the director and the vector connecting the centers of two test spheres, R their distance, and $k_B T$ the thermal energy, where k_B is Boltzmann's constant and T the absolute temperature. Superimposed on Eq. (1) is the bare, hard-core potential which takes a positive infinite value within the range of one particle diameter.

From Eq. (1) we conclude that the depletion interaction is highly anisotropic in both its range and strength. Parallel

to the director, the range of the attraction is a rod length $L \gg \sigma$, while perpendicular to that it is a lateral length $\delta_\perp \ll L$. For conditions which are not too close to where the isotropic-to-nematic phase transition takes place the interaction is very much weaker perpendicular than parallel to the director. Indeed, setting $\omega = \pi/2$ and $\omega = 0$ gives for the ratio of the contact potentials $V(\sigma, \pi/2)/V(\sigma, 0) \approx (\delta_\perp/\sigma)^{3/2} \approx (D/\sigma)^{3/2} \phi_r^{-3/2} \ll 1$. Presumably, the attraction becomes strong enough to destabilize the homogeneous mixture for spheres of large enough radius $\sigma \gg \sqrt{LD}$, because then $|V(\sigma, 0)| \approx 3 \phi_r (\sigma/D)^2 k_B T \gg k_B T$. If not strong enough to induce macroscopic demixing, the highly directional nature of the potential plausibly causes quasi linear aggregates to form along the director. The mean length of the aggregates may be predicted by standard theory of self-assembly.⁸ If $\langle N \rangle$ denotes their mean aggregation number, ϕ_s the volume fraction of spheres, and we assume pair-wise additivity of the depletion potential, we find that $\langle N \rangle \sim \sqrt{\phi_s} \exp \frac{1}{2} \phi_r (\sigma/D)^2 \gg 1$ if $\phi_s \gg \exp -\sigma^2/LD$.

Although our approximate depletion theory rationalizes the linear aggregation of globules in the nematic of rods, the actual induced interaction must be much more complex due to long-range correlations between the rods. Unfortunately, the coupling between translational and rotational degrees of freedom prohibits the straightforward application of more advanced treatments of depletion interactions to mixtures containing non-spherical particles.¹⁶ Therefore, instead of calculating corrections to an effective potential in a one-component description, we proceed by studying the fluid structure of the mixture directly in a procedure amenable to systematic approximation.

Our starting point is the free energy functional

$$\frac{\mathcal{F}}{k_B T} = \sum_i \left\langle \ln \rho_i v_i + \frac{\psi_i}{k_B T} - \frac{1}{2} \sum_j \langle f_{ij} \rangle_j' \right\rangle_i, \quad (2)$$

where the summation is implied for both the rods ($i=r$) and the spheres ($i=s$), and where in the averages $\langle \cdots \rangle_i \equiv \int d\mathbf{r} \int d\mathbf{u} \rho_i(\mathbf{r}, \mathbf{u}) \langle \cdots \rangle$ the integrations are performed over the positional and the angular coordinates $\mathbf{r}$ and $\mathbf{u}$ of the particles, with a similar prescription for $\langle \cdots \rangle_i'$ in terms of the primed variables $\mathbf{r}'$ and $\mathbf{u}'$. The local number density $\rho_i = \rho_i(\mathbf{r}, \mathbf{u})$ normalizes to $\langle 1 \rangle_i = \phi_i V v_i^{-1}$, where v_i and ϕ_i denote the particle volume and volume fraction of species i , and V the volume of the system. The first term of Eq. (2) represents an ideal entropy, while the second accounts for the coupling to an external field $\psi_i = \psi_i(\mathbf{r}, \mathbf{u})$. The third term describes the hard-core interactions between the particles. The Mayer function $f_{ij} = f_{ij}(\mathbf{r} - \mathbf{r}', \mathbf{u}, \mathbf{u}')$ equals -1 if the hard cores of two particles overlap, and 0 in all other instances.¹¹

The second virial approximation implicit in Eq. (2) is accurate only for $\phi_s, \phi_r \ll 1$, implying a low volume fraction of added spheres and a host nematic that is near the transition to the isotropic phase.¹¹ Equation (2) can, therefore, only be expected to provide a qualitative description of the transition to the lamellar phase, which occurs at relatively high volume fractions of rods. A significant improvement of the description of the lamellar transition should be possible by including

three-body virials,¹³ but for reasons of tractability we choose not to do that. For our purposes a second virial theory has sufficient precision as it contains all the physics we are interested in, including long-range correlations between particles, which build up through chains of binary collisions.¹⁷

To obtain information on the fluid structure from Eq. (2), we evaluate the linear responses of the local density fields to suitably chosen external potentials, and subsequently extract the partial structure factors from these. Under conditions of thermal equilibrium, the densities $\rho_i(\mathbf{r}, \mathbf{u})$ functionally minimize the free energy Eq. (2) subject to the condition of the conservation of mass, and are found to obey a set of coupled non-linear integral equations. For the purpose of obtaining response functions, we linearize these equations by inserting $\rho_i(\mathbf{r}, \mathbf{u}) = \bar{\rho}_i(\mathbf{u}) + \delta\rho_i(\mathbf{r}, \mathbf{u})$ and expanding them to first order in the external field, where $\bar{\rho}_i$ is the mean density in zero field and $\delta\rho_i$ a perturbation linear in the external field. Clearly, $\bar{\rho}_s(\mathbf{u}) = \phi_s/4\pi v_s$. An explicit expression for $\bar{\rho}_r(\mathbf{u})$ is not known, so we use the Gaussian angular distribution advanced by Odijk.¹²

We now describe the external fields applied in this study. In Fourier space, the external field conjugate to a density fluctuation $\delta\hat{c}_s(\mathbf{q}) \equiv \int d\mathbf{u} \delta\hat{\rho}_s(\mathbf{q}, \mathbf{u})$ of the spheres is given by $\hat{\psi}_s(\mathbf{q}, \mathbf{u}) = -\varepsilon_s k_B T$ with $\mathbf{q}$ the wave vector and ε_s a dimensionless field strength, and where the hats indicate Fourier transformed quantities. The external field conjugate to the mass density fluctuations $\delta\hat{c}_r(\mathbf{q}) \equiv \int d\mathbf{u} j_0(\mathbf{q} \cdot \mathbf{u} L/2) \delta\hat{\rho}_r(\mathbf{q}, \mathbf{u})$ of the rods is $\hat{\psi}_r(\mathbf{q}, \mathbf{u}) = -\varepsilon_r j_0(\mathbf{q} \cdot \mathbf{u} L/2) k_B T$,¹⁷ where ε_r is again a field strength and $j_0(x) = \sin x/x$ a spherical Bessel function. Switching off the external field acting on the rods (i.e., setting $\varepsilon_r = 0$) we obtain the partial structure factor of the spheres $S_{ss}(\mathbf{q})$ from the density response $\delta\hat{c}_s(\mathbf{q})$ through the well-known Yvon equation $\delta\hat{c}_s(\mathbf{q}) = -\varepsilon_s S_{ss}(\mathbf{q}) \phi_s / v_s$.¹⁸ On the other hand, if we put $\varepsilon_s = 0$ the partial structure factor of the rods $S_{rr}(\mathbf{q})$ follows similarly from $\delta\hat{c}_r(\mathbf{q})$.

Our results for $S_{ss}(\mathbf{q})$ and $S_{rr}(\mathbf{q})$ depend on the solution of a linear integral equation, which we solve approximately by means of a variational principle described elsewhere.¹⁸ For the sphere-sphere structure factor we find

$$\frac{1}{S_{ss}(\mathbf{q})} = \frac{1}{S_{ss}^0(\mathbf{q})} - \Gamma(\mathbf{q}) S_{rr}^0(\mathbf{q}) \quad (3)$$

with $\mathbf{q} \equiv (q_{\parallel}, q_{\perp})$ the momentum transfer in terms of its components parallel and perpendicular to the director, $S_{ii}^0(\mathbf{q})$ the structure factor of component i in the absence of component $j \neq i$, and a coupling term

$$\Gamma(\mathbf{q}) = 6L\phi_r\phi_s J_1^2\left(\frac{1}{2}q_{\parallel}\sigma\right) / D^2 q_{\parallel}^2 \sigma \quad (4)$$

with J_1 a Bessel function of the first kind. The structure factor of a dispersion containing only the spheres is found to obey $1/S_{ss}^0(\mathbf{q}) = 1 - \phi_s v_s^{-1} \hat{f}_{ss}(q)$, where $q \equiv \sqrt{q_{\parallel}^2 + q_{\perp}^2}$ and $\hat{f}_{ss}(q)$ the Fourier transform of the sphere-sphere Mayer function. The structure factor of the pure nematic obeys $F(\mathbf{q})/S_{rr}^0(\mathbf{q}) = 1 + 4F(\mathbf{q}) + 8\phi_r G(\mathbf{q})$, with $F(\mathbf{q}) \equiv \langle j_0^2(\mathbf{q} \cdot \mathbf{u} L/2) \rangle_r / \langle 1 \rangle_r$ the form function of the rods, and $G(\mathbf{q}) \equiv \langle j_0(\mathbf{q} \cdot \mathbf{u} L) \rangle_r / \langle 1 \rangle_r$, a function driving the smectic instability. (The averages are taken at zero external field.) $S_{rr}^0(\mathbf{q})$ has

FIG. 2. Partial structure factor of the globules in the nematic $S_{ss}(q_{\parallel}, 0)$ vs the scaled momentum transfer $q_{\parallel} L$ along the director, for $L/D = 100$, $L/\sigma = 10$ and $\phi_s = 0.02$. From top to bottom: $\phi_r = 0.08, 0.07, 0.06$, and 0.05 . For comparison we have also inserted the structure factor of the globules in the absence of the rods (the lowermost curve). Inset: $S_{ss}(q_{\parallel}, 0)$ for $\phi_r = 0.22, 0.20, 0.15, 0.1$ and 0.08 (from top to bottom).

a highly nontrivial dependence on $(q_{\parallel}, q_{\perp})$ due to translation-rotation coupling. For the length scales $qD \lesssim 1$ relevant to our problem we find that $S_{rr}^0(\mathbf{q}) = S_{rr}^0(q_{\parallel} L, q_{\perp} \delta_{\perp})$, i.e., perpendicular to the director the correlation length is set by the lateral length $\delta_{\perp}$, while parallel to that by the rod length L .

The correlations between the spherical colloids are completely enslaved by the fluctuating background of rods according to Eqs. (3) and (4), for $\Gamma(q\sigma \lesssim 1)/\phi_s \approx 3/2L\sigma\phi_r/D^2 > \sigma/D \gg 1$. The reduced structure factor describing these fluctuations, S_{rr}^0/F , has a number of interesting properties. First, parallel to the nematic director we find presmectic correlation peaks, where the primary peak diverges at the spinodal instability to the smectic A phase. According to our second virial theory, the pure nematic becomes unstable to density fluctuations parallel to the director at a critical wave vector $q_{\parallel} L \approx 4.85$ and a volume fraction $\phi_r \approx 0.79$. This agrees qualitatively with the best estimates currently available of $q_{\parallel} L \approx 5.07$ and $\phi_r \approx 0.42$ for $L/D \rightarrow \infty$.^{13,14} Second, perpendicular to the director the liquidlike correlation peaks do not present themselves on the scale of L , nor $\delta_{\perp}$. Positional correlations do appear at much smaller lengths corresponding to $q_{\perp} D \approx 6$, but they remain insignificant due to the finite dispersion of the rod orientations that acts to diminish any lateral order in the fluid.

Now that we have ascertained that the correlations along the director are the most important, we set $q_{\perp} \delta_{\perp} = 0$. Figure 2 gives our prediction for the partial structure factor $S_{ss}(q_{\parallel}, 0)$ as a function of $q_{\parallel} L$ for variable ϕ_r , and fixed $\phi_s = 0.02$, $L/D = 100$ and $\sigma/D = 10$. For small wave vectors the structure factor has a value considerably greater than what it would have had if no rods were present (as shown by

the lowermost curve), confirming that the rods induce an effective attraction between the spheres. The quasilinear increase of $S_{ss}(0,0)$ with the rod density is consistent with the prediction of Eq. (1). However, Eq. (1) does not explain the shift of maximum in the structure factor to a non-zero $q_{\parallel}L$ at higher rod concentrations, shown in the inset to Fig. 2. This peak diverges at the spinodal to the lamellar phase, and points at the presence of pretransitional fluctuations in the mixture.

Due to the correlations between the colloids being enslaved by the structure of the host dispersion, we conclude that the shift in the position of the primary maximum of $S_{ss}(q_{\parallel},0)$ from zero to nonzero momentum transfer signals the crossover from the dense to the open aggregates as observed in experiments.^{6,9} Within our treatment, this occurs at an almost universal density of $\phi_r^* \approx 0.13 + O(\sigma^2/L^2)$. The structural transition of the aggregates is limited to globule concentrations below a critical value of $\phi_s^* \approx 32/(L\sigma D^{-2} - 256) \ll 1$ that rapidly approaches zero with increasing colloid size. For $\phi_s > \phi_s^*$ the structure factor diverges at $q_{\parallel}L = 0$, thus marking a fluid–fluid type of demixing instability. It takes place when $\phi_r \approx 10(1 + 8\phi_s)/(3L\sigma D^{-2}\phi_s - 128\phi_s - 16) \leq \phi_r^*$. If both $\phi_s < \phi_s^*$ and $\phi_r \geq \phi_r^*$, the structure factor does not diverge at $q_{\parallel}L = 0$ but, instead, at the aforementioned nonzero value associated with a spinodal instability to the lamellar phase. The critical wave vector of the lamellar instability decreases with increasing volume fraction globules, and becomes 0 when reaching ϕ_s^* . Figure 1 shows the diagram of states calculated for $L/D = 100$ and $\sigma/D = 10$. Note the very small amount of spheres needed to destabilize the nematic, which is in qualitative agreement with experimental observation.⁶

In conclusion, excluded volume interactions at the two body level are sufficient to explain the emergence of several of the mesoscopically textured phases observed by Fraden and collaborators in aqueous mixtures of colloidal spheres

and rodlike virus particles.⁶ These include the lamellar phase as well as a nematic phase containing ordered, string-like assemblies of globules. It appears that pretransitional fluctuations associated with the vicinity of the lamellar spinodal give rise to a restructuring of the string-like assemblies from the dense to the open type. We speculate that including three-body virials may prove sufficient not only to come to a quantitative description of the lamellar and stringy nematic phases, but also to shed light on the other types of phases found in mixtures of rods and spheres.⁶

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