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Effect of persistent flexibility on the isotropic, nematic and columnar ordering in a self-assembling system

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Concentrated solutions of reversibly assembling amphiphilic molecules often exhibit a variety of liquid-crystalline mesophases due to the asymmetry of their aggregates. For strongly elongated rod-like micelles flexibility may significantly influence the relative stability of these phases. This question is addressed for a simple model for a self-assembling system of monodisperse linear rod-like aggregates which are considered to be persistent flexible. Analogously to a recent calculation for a self-assembling system in which the rod-like aggregates are assumed to be perfectly rigid, persistent flexible aggregates may exhibit the same isotropic–nematic–columnar progression of phases. However, increasing the flexibility reduces the concentration range over which the nematic phase is stable. For sufficiently flexible aggregates the nematic phase is abandoned altogether and a direct isotropic–columnar transition occurs.

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1. Introduction

Many amphiphiles in aqueous solution exhibit lyotropic liquid-crystalline mesophases, characterized by various types of orientational (e.g. nematic) and translational (e.g. smectic or columnar) order. The observed ordering can often be understood in terms of the steric interactions within a particle population consisting of monomers and polydisperse asymmetric aggregates of variable size. The main difference with ordinary lyotropic liquid crystals is the inherent coupling of reversible aggregate assembly and long range order.

Here we are interested in a sub-class of these systems, where rod-like aggregates are reversibly assembled via linear aggregation, i.e. the aggregate cross section contains only one monomer. Recently, Taylor and Herzfeld [1] have carried out a theoretical study for this case, taking into account orientational and positional ordering as well as polydispersity. For weak aggregation, i.e. when the average aggregate size is small, they obtain a direct isotropic–columnar transition (or an isotropic–crystalline for very weak aggregation) with increasing amphiphile concentration. However, if the aggregation is sufficiently strong, i.e. when the aggregates are on average sufficiently elongated, they always find a stable nematic phase intervening between the isotropic and the columnar phase. Because their theory assumes completely rigid aggregates, it is interesting to study effects due to flexibility which are expected to become important for strong aggregation, when the aggregates are sufficiently elongated.

Recently, we have extended the Khokhlov–Semenov approach to long range orientational order in solutions of inert monodisperse persistent flexible main chain polymers [2] by including hexagonal columnar ordering [3]. The present calculation is a further extension to include reversible assembly of monodisperse linear aggregates.

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The isotropic–nematic transition of the monodisperse self-assembling system has previously been studied for rigid aggregates by Briehl and Herzfeld [4, 5] and Gelbart *et al.* [6, 7], and for persistent-flexible aggregates by Odijk [8]. The main result of the present inclusion of the columnar phase for the monodisperse reversibly assembling system, as for the inert monodisperse system [3], is that the nematic phase is squeezed out between the isotropic low concentration phase and the columnar high concentration phase with increasing flexibility, until, finally, a direct isotropic–columnar transition occurs. In the case of rigid rod-like aggregates studied by Taylor and Herzfeld [1], the nematic phase disappears when the aggregates are short, i.e. when aggregation is weak and the aggregates are essentially spheroidal. The present calculations suggest that the nematic phase may also become unstable due to the micellar flexibility of long aggregates, i.e. when aggregation is strong. In addition to the phase diagram, this work reports results for the aggregate size, the deflection length, the orientational order parameter and the columnar inter axial separation between aggregates at the different transitions.

2. Coexistence equations for the isotropic, nematic, and hexagonal columnar phases

The self-assembling system studied here consists of monodisperse labile aggregates modelled as long slender continuously bend-elastic (i.e. persistent flexible) cylindrical rods of unit diameter, which interact via hard core steric repulsions. It is well known that hard core interactions alone can induce orientational [9] and translational [10] order in systems of highly asymmetric particles. In the following, the focus is on the relative stability of the isotropic, the nematic and the columnar phase as function of the aggregate flexibility. It is reasonable to concentrate on these types of phases for rod-like aggregates because other types of transitional order (e.g. smectic order) are disfavoured due to the polydispersity of the aggregates in realistic self-assembling systems. The free energy (per unit volume and $k_B T$) describing the present simplified system can be written as

$$f = f^* + f_{\text{ex-vol}} + f_{\text{int}}. \tag{1}$$

The first term is given by

$$f^* = c(-q + \ln c - 5 \ln L + \sigma), \tag{2}$$

where c is the particle concentration, q is a constant, L is the variable aggregate length in units of the aggregate diameter, and σ denotes the orientational free energy which depends on the aggregate flexibility. The term $-5 \ln L$ arises from the inclusion of rotational ($-7\frac{1}{2}$) and translational ($-3\frac{1}{2}$) degrees of freedom, in addition to mixing, in analogy with the work of Gelbert *et al.* [6, 7]. Here and in the following, contributions due to the particular shape of the rod ends (e.g. flat ends or hemispherical ends) are omitted.

Previously, it was shown that σ is well described by the function

$$\sigma(\alpha, L) = \begin{cases} 0 & \text{isotropic case} \\ \ln \alpha - 1 + z(3z + 2r)/(z + r) + O(\exp(-\alpha/2)) & \text{nematic and columnar case} \end{cases} \tag{3}$$

with

$$z = \frac{L}{P} \frac{\alpha - 1}{12} \quad \text{and} \quad r = \ln 4 - 1,$$

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where P is the persistent length divided by the rod diameter [11]. The variational parameter $1/\alpha$ is a measure for the width of the angular distribution of tangential unit vectors along the contour of the rod. Usually, in the nematic and columnar phase this distribution, which is approximated using the Onsager trial function [9], is sufficiently narrow to justify the omission of additional terms containing exponentials in $-\alpha$. In the limit of stiff rods, $L/P \to 0$, σ reduces to the usual Onsager form $\ln \alpha - 1$ [9], whereas in the limit of worm-like rods, $L/P \to \infty$ and σ goes like $(1/4)L\alpha/P$. The quantity P/α is termed the deflection length, because it is the characteristic length scale on which the contour of the persistent flexible aggregate is deflected in the direction of the director (cf. [12]). If P/α is of the order of or smaller than L, the rods can no longer be considered rigid. It is important to realize that the deflection length is significantly smaller than the persistence length, because usually α is already quite large at the nematic transition ($\alpha \gtrsim 10$) and quickly increases with increasing concentration. Expression (3) for σ in the nematic and columnar case is an interpolation between the limits including the leading terms and the corresponding first correction terms [11].

The second term in equation (1) denotes the hard core excluded volume interactions. Unfortunately, translationally ordered phases usually occur at concentrations beyond the validity of a second virial approach. The following calculation therefore utilizes an approximate expression for $f_{\text{ex-vol}}$ which is sufficiently accurate at high volume fractions. The expressions for $f_{\text{ex-vol}}$ used here were derived previously for rigid rods, but they are approximately valid for persistent flexible polymers as well, because hard core steric repulsion governing the excluded volume manifests itself on a scale of the order of the aggregate diameter, on which the aggregates are considered to be rigid cylinders [3].

For the isotropic and nematic case, Lee [13] has shown for rigid rods that $f_{\text{ex-vol}}$ can be approximated over a wide range of concentrations by combining the Carnahan–Starling description of the hard sphere fluid with a functional scaling that decouples orientational and translational degrees of freedom for elongated particles. The accuracy of this approximation is comparable to the accuracy of scaled particle theory. Lee's expression for $f_{\text{ex-vol}}$, which is the one used here, can be shown to perform well for persistent flexible rod-like particles [11].

For the case of columnar ordering, on the other hand, we have shown previously [14, 15] that $f_{\text{ex-vol}}$ in a columnar phase of aligned rigid rods can, to a good approximation, be written in terms of two contributions, $f^{1\text{D}}_{\text{fluid}}$ and $f^{2\text{D}}_{\text{crystal}}$, where the former represents the non-ideal contribution to the free energy of a one dimensional fluid of hard lines and the latter represents the non-ideal contribution to the free energy of a two dimensional crystal of discs. The physical picture is that of cylindrical rods confined to move inside hexagonal tubes of diameter Δ, which form a hexagonal array. It is important to note that Δ, which is also the mean perpendicular separation of the long particle axes in the columnar phase, is not an independent model parameter but is determined by optimizing the free energy. Thus, in order to obtain consistency with the underlying physical picture, this optimization has to yield values for $\Delta \lesssim 2$ in a stable columnar phase to prevent the doubling-up of rods inside the tube. A detailed discussion of this model for positional ordering is given in [14, 15].

The explicit expressions for $f_{\text{ex-vol}}$ for the three different types of ordering are given by

$$f_{\text{ex-vol}} = c \begin{cases} v(1-3v/4)/(1-v)^2\,[4+L\rho(\alpha)] & \text{isotropic and nematic case} \\ -\ln\,[1-(v/v_{cp})\,\Delta^2] - \ln\,[1-1/\Delta]^2 & \text{columnar case.} \end{cases} \tag{4}$$

Here v is the aggregate volume fraction (note that $v \propto cL$), and

$$\rho(\alpha)=\begin{cases}1 & \text{isotropic case } (\alpha=0)\\ 2I_2(2\alpha)/\sinh^2\alpha & \text{nematic case,}\end{cases} \tag{5}$$

where I_2 is a Bessel function. In the limit $v \to 0$ and for $L\rho(\alpha) \gg 1$, the expression for $f_{\text{ex-vol}}$ describing the isotropic and nematic case reduces to the well-known Onsager result for rigid, slender rods [9]. In the columnar case, the first term of $f_{\text{ex-vol}}$ is the exact non-ideal contribution to the free energy of a one dimensional hard particle fluid. The quantity $v\Delta^2/v_{cp}$, where $v_{cp}=\pi/(2\sqrt{3})$, is the corresponding one dimensional volume fraction. The second term represents a cell model description of the non-ideal contribution to the free energy of a two dimensional hexagonal crystal of hard discs. Note that the argument of the logarithm is the ratio of the free volume to the cell volume. Note also that the two contributions to the columnar $f_{\text{ex-vol}}$ are coupled via Δ.

In the nematic case, σ as well as $f_{\text{ex-vol}}$ depend on α, where, as mentioned previously, $1/\alpha$ is a measure for the nematic confinement of the thermal contour undulations. On the other hand, in the columnar case σ depends on α whereas $f_{\text{ex-vol}}$ depends on the width Δ of the columnar tube. However, here the nematic confinement is merely replaced by the hard walls of the tube. Therefore, there ought to be an approximate relation $\Delta=\Delta(\alpha)$, which allows us to express Δ in terms of α in the above columnar expression for $f_{\text{ex-vol}}$. This relation was derived previously using a simple scaling argument which yields

$$\Delta=1+P(\kappa/\alpha)^{3/2}, \tag{6}$$

where $\kappa=O(1)$ is an undetermined constant [3]. As pointed out in [3], equation (6) is derived under the assumption that L is significantly larger than the deflection length P/α in the columnar phase to avoid end-effects.

Finally, the third term in equation (1) is the internal free energy, which, in analogy to [1], is given by a phenomenological one parameter expression of the form

$$f_{\text{internal}}=-c(b_{\text{agg}}/b_{\text{mon}}-1)\Phi, \tag{7}$$

where b_{agg} and b_{mon} denote the volume of the single aggregate and the volume of the monomer, respectively (note that $cb_{\text{agg}}=v$ and that $b_{\text{agg}}/b_{\text{mon}}$ equals the number of monomers in an aggregate). Thus, the bracketed quantity is the number of contacts in the linear aggregate, which is multiplied by the decrease in free energy per contact $-\Phi$ (in units of k_BT). In [1], it is assumed that Φ varies inversely with temperature, however, the exact dependence of Φ on temperature is unknown, and in the following Φ simply assumes the role of a model parameter.

The globally stable free energy is calculated by minimizing the free energy with respect to L and α. Note that c and L are related via $c=\text{constant } v/L$. For the isotropic case ($\alpha=0$ and $\sigma=0$) we obtain the simple result

$$\ln L=\frac{1}{6}\left(6+\Phi'+\ln v+4v\frac{1-3v/4}{(1-v)^2}\right), \tag{8}$$

where $\Phi'=\Phi-q$. Otherwise L and α are determined via the two coupled equations given by

$$0=-6\ln L+5+\Phi'+\ln\alpha-\frac{rz^2}{(z+r)^2}+\ln v+4v\frac{1-3v/4}{(1-v)^2}, \tag{9}$$

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$$0=1+\frac{\alpha}{12}\frac{L}{P}\frac{2r^2+3z^2+6rz}{(z+r)^2}+\alpha Lv\frac{1-3v/4}{(1-v)^2}\frac{\partial\rho}{\partial\alpha}, \tag{10}$$

in the nematic case or by

$$0=-6\ln L+5+\Phi'+\ln\alpha-\frac{rz^2}{(z+r)^2}+\ln v-\ln\left(1-\frac{v}{v_{cp}}\Delta^2\right)-2\ln\left(1-\frac{1}{\Delta}\right), \tag{11}$$

$$0=\frac{1}{3}\Delta\left(1-\frac{v}{v_{cp}}\Delta^2\right)\left(1+\frac{\alpha}{12}\frac{L}{P}\frac{2r^2+3z^2+6rz}{(z+r)^2}\right)+1-\frac{v}{v_{cp}}\Delta^3, \tag{12}$$

in the columnar case. (Numerical solutions are easily found using, for instance, the AMOEBA algorithm described in [16] or the FindRoot routine of [17].)

The solutions of equations (9)–(12) determine the globally stable free energy. It is important to realize that the idealized description of columnar ordering in terms of a one dimensional fluid confined to impenetrable tubes imposes constraints which force the isotropic–columnar transition as well as the nematic–columnar transition to be first order [14]. However, here the focus is on the relative stability of the phases as a function of the model parameters rather than on the details of the transitions themselves. The equilibrium phase diagram can then be calculated in the usual fashion employing the equality of the osmotic pressure and the chemical potential across the transition. The osmotic pressure is calculated using the relation

$$\pi=-\frac{\partial Vf}{\partial V}=-f+v\frac{\partial f}{\partial v}, \tag{13}$$

where V is the total volume (cf. [18]). Using equation (13), π can be written as

$$\pi=\pi^*+\pi_{\text{ex-vol}}, \tag{14}$$

where

$$\pi^*=c \tag{15}$$

and

$$\pi_{\text{ex-vol}}=c\begin{cases}\frac{1}{2}(4+L\rho(\alpha))v(2-v)/(1-v)^3 & \text{isotropic and nematic case}\\ -(1-(v_{cp}/v)(1/\Delta^2))^{-1} & \text{columnar case.}\end{cases} \tag{16}$$

The solute chemical potential follows from

$$\mu=\frac{\partial Vf}{\partial V_{\text{agg}}}=f+(1-v)\frac{\partial f}{\partial v}=\frac{1}{v}((1-v)\pi+f), \tag{17}$$

where $V_{\text{agg}}(=Vv)$ is the total aggregate volume (cf. [18]).

3. Results and discussion

Figure 1 shows the phase diagram in the Φ'-v plane for three different persistence lengths P and for two different values of the parameter κ. The main feature is that the nematic phase, which decreases in width with decreasing persistent length for the two larger values of P, becomes unstable for the smallest value of P, and a direct isotropic–nematic transition occurs. The vanishing of the nematic phase with increasing flexibility is not too surprising in light of our previous investigation of the phase

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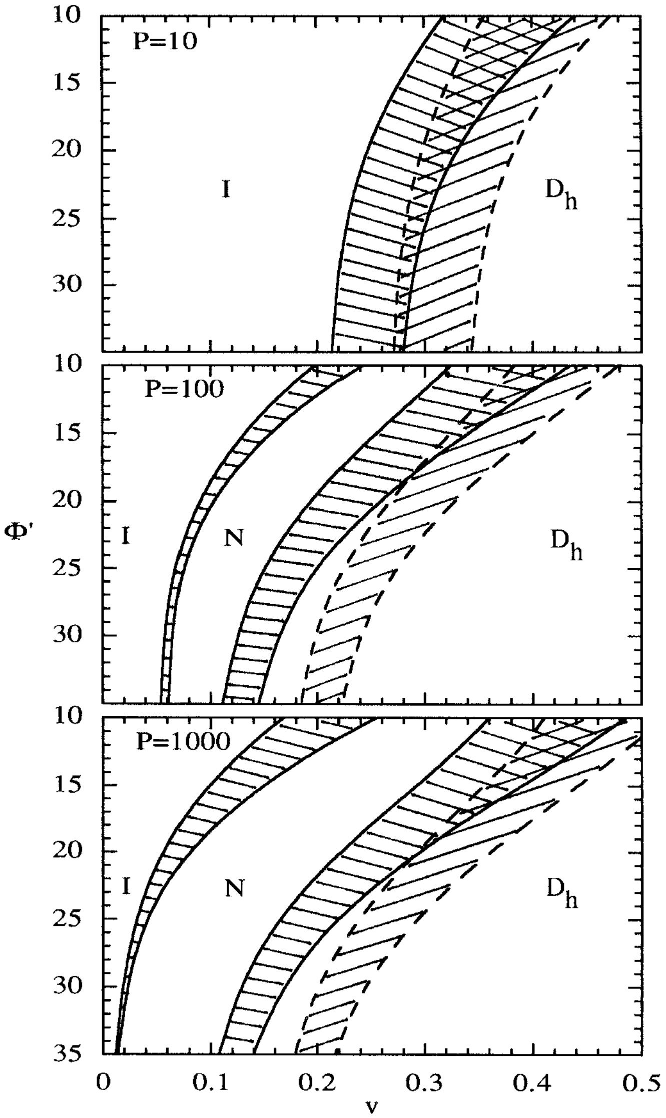

Figure 1. The phase diagram as a function of the growth parameter Φ' and the volume fraction v for three different persistence lengths P. Capital letters denote the isotropic phase (I), the nematic phase (N), and the hexagonal columnar phase (D_h). Shaded areas indicate phase coexistence. Solid lines correspond to $\kappa = 3{\cdot}0$ and dashed lines to $\kappa = 3{\cdot}5$. Note that the isotropic–nematic transition does not depend on κ.

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behaviour of inert monodisperse persistent flexible rods. In [3], we find independent of L that if P is small enough (the exact value depends on κ) there is no stable nematic phase in the range of validity of the model. For fixed P, the phase boundaries in the self-assembling system recede to smaller volume fractions as Φ' increases. The isotropic–nematic transition occurs because increasing Φ' also increases the length of the aggregates L. For the nematic–columnar transition, however, Taylor and Herzfeld [1], using the same cell model description for the columnar phase of rigid rod-like aggregates, find that the concentration at which the nematic–columnar transition occurs is virtually independent of Φ. Inclusion of flexibility, on the other hand, obviously imposes a strong Φ' dependence (and, therefore, also a strong Φ dependence) on the location of the nematic–columnar transition for $\Phi' \lesssim 25$. Finally, increasing the parameter κ, which is not determined *a priori* by this theory, shifts the nematic–columnar transition to higher volume fractions. This is because according to equation (6) increasing κ for fixed tube width Δ implies stronger orientational constraints, which in turn reduce the stability of the columnar phase. The two different values of κ used in figure 1 roughly represent the range of reasonable κ values. This range is based on fitting the osmotic pressure data obtained for poly(γ-benzyl-L-glutamate) with a theoretical osmotic pressure calculated according to this model for inert rod-like particles [3]. Note that κ should be independent of the particular system as long as the inter particle interactions are well-described in terms of hard core repulsions.

In the present work, no attempt has been made to find the exact location of the isotropic–nematic–columnar triple point in terms of the persistence length. In a realistic system, P and especially Φ' will have strong and different dependencies on temperature (e.g. [19]). In addition, polydispersity, which is omitted here, will also affect the quantitative aspects of the qualitative effects discussed in this work. Thus, a detailed investigation of the triple point cannot yield much useful information on this level. However, for the corresponding inert monodisperse system, the dependence of the triple point on L and P is discussed in some detail in [3].

Figure 2 shows the aggregate length L plotted along the phase boundaries in figure 1. Note that in the present work, the range of Φ' is bound from below by the condition that L should be sufficiently large ($L \gtrsim 10$) to avoid end-effects. Generally, the dependence of $\ln L$ on Φ' is almost linear. In addition, comparing equivalent curves for $P = 100$ and 1000 shows that there is only a weak dependence of L on P along the phase boundaries. It is worth noting, however, that this dependence is significantly stronger for L as a function of v keeping Φ' constant. In this case, increasing flexibility significantly diminishes the growth of the aggregates, which is discussed in detail for the nematic phase in [8] (as in [8], we find for the present model that L increases monotonically with v). It is also worth noting that besides flexibility, the translational and rotational terms in the free energy (cf. equation (2)) [6] (and soft repulsive interactions between the aggregates [20] reduce aggregate growth. This is important in order to avoid exaggerated and unphysical aggregate growth in the orientationally ordered phases (e.g. [6]).

As we have mentioned, the quantity P/α is the deflection length and the ratio $L/(P/\alpha)$ rather than L/P is the relevant measure for the importance of the aggregate's flexibility. Only if $\alpha L/P \ll 1$ can the rods be considered as rigid [12]. In figure 3, $\alpha L/P$ is plotted along the nematic and columnar phase boundaries in figure 1. Apparently, $\alpha L/P$ is never small so that flexibility is always important. Interestingly, this is the case even for the small values of Φ', where the smallness of L/P (cf. figure 2) may lead us to believe otherwise.

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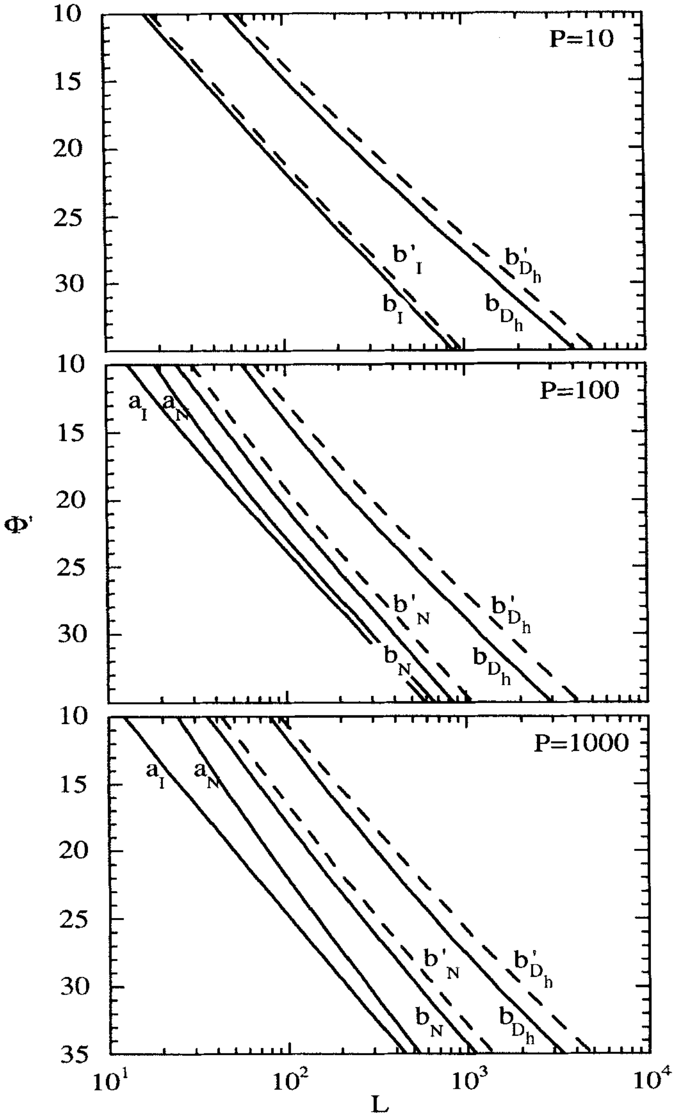

Figure 2. The aggregate length L (in units of the aggregate diameter) along the phase boundaries in the three panels of figure 1. Solid lines correspond to $\kappa = 3{\cdot}0$ and dashed lines to $\kappa = 3{\cdot}5$. The letter coding is chosen so that a indicates the isotropic–nematic transition and b the isotropic–columnar and nematic–columnar transitions. The phase boundaries are indicated by the indices: I, isotropic; N, nematic; and D_h, hexagonal columnar. Letters with a prime label the dashed lines.

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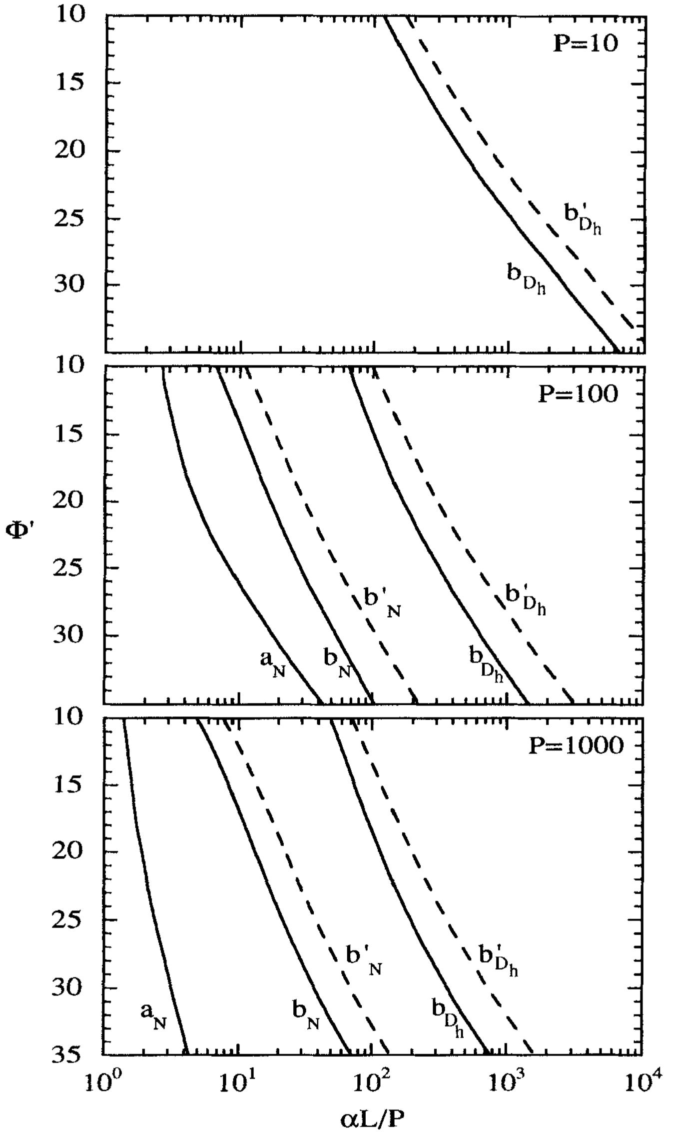

Figure 3. The aggregate length L divided by the deflection length P/α along the nematic and columnar phase boundaries in figure 1. Solid lines correspond to $\kappa = 3{\cdot}0$ and dashed lines to $\kappa = 3{\cdot}5$. The letter coding is chosen so that *a* indicates the isotropic–nematic transition and *b* the isotropic–columnar and nematic–columnar transitions. The phase boundaries are indicated by the indices: N, nematic; D_h, hexagonal colmnar. Letters with a prime label the dashed lines.

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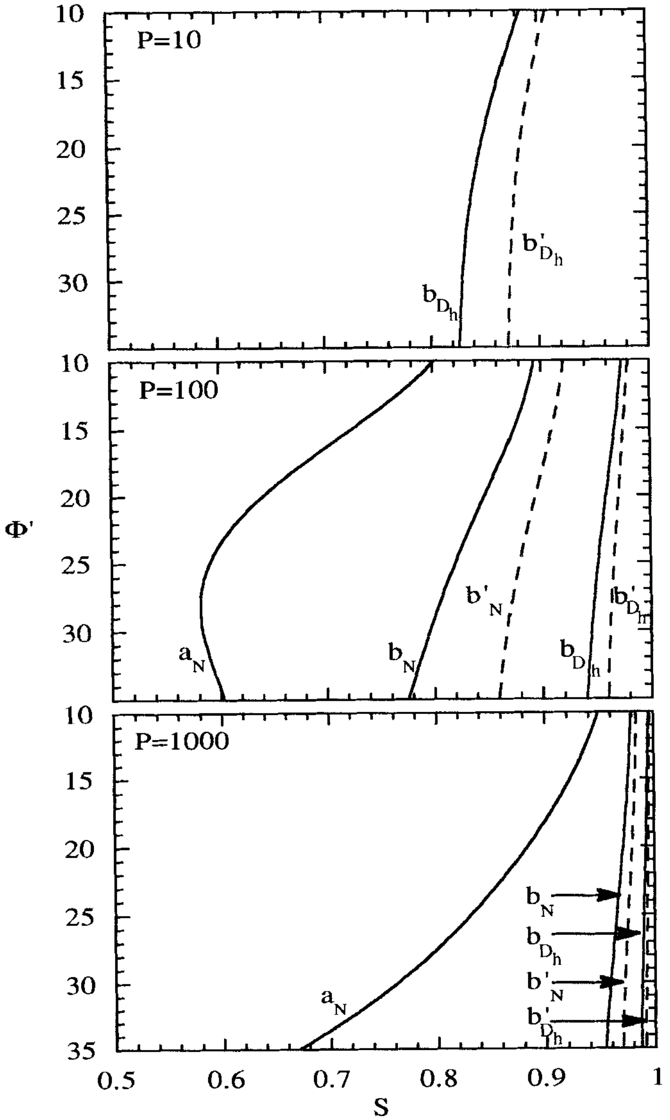

Figure 4. The orientational order parameter S along the nematic and columnar phase boundaries in figure 1. Solid lines correspond to $\kappa = 3{\cdot}0$ and dashed lines to $\kappa = 3{\cdot}5$. The letter coding is chosen so that a indicates the isotropic–nematic transition and b the isotropic–columnar and nematic–columnar transitions. The phase boundaries are indicated by the indices: N, nematic; D_h, hexagonal columnar. Letters with a prime label the dashed lines.

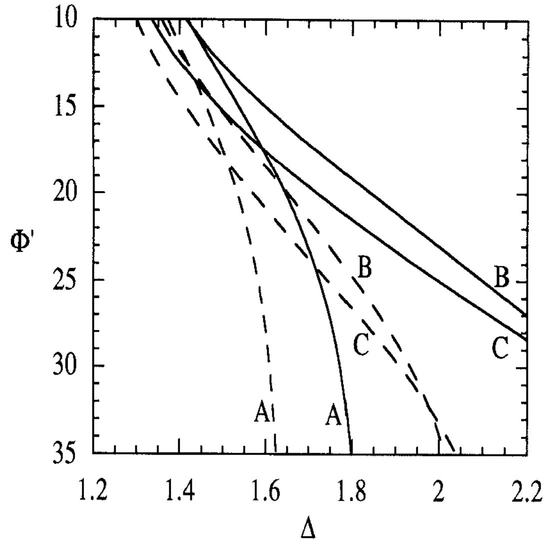

Figure 5. The width Δ of the columnar tube (in units of the aggregate diameter) along the columnar phase boundaries in figure 1. Solid and dashed lines correspond to $\kappa = 3{\cdot}0$ and $\kappa = 3{\cdot}5$, respectively. The letter coding distinguishes curves obtained for the three different persistence lengths: A, P = 10; B, P = 100; and C, P = 1000.

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Figure 4 shows the orientational order parameter $S = 1/2\ \langle 3\cos^2\theta - 1\rangle$, where θ is the angular contour deviation from the director, along the nematic and columnar phase boundaries in figure 1. Comparing the plots of S for $P = 100$ with the plots of S for $P = 1000$ it is apparent that near the transition the stiffer rods are orientationally more ordered, as we might expect. Note that the orientational order along the phase boundaries decreases somewhat with increasing Φ'. An exception to this behaviour is the minimum of the nematic order parameter for $P = 100$. Regardless of the value of P, however, we find pronounced orientational ordering along the columnar phase boundaries.

Finally, figure 5 shows the tube width Δ as a function of Φ' along the columnar phase boundary of the isotropic–columnar and the nematic–columnar transitions in figure 1. Δ increases with increasing Φ' corresponding to the shift of these transitions to lower volume fractions with increasing Φ'. As we have mentioned, the physical picture of the columnar phase in terms of hard tubes is a good description only if $\Delta \lesssim 2$. Figure 5 shows that this is indeed the case except for the small value of κ (i.e. $\kappa = 3{\cdot}0$) for $P = 100$ and 1000 when $\Phi' \gtrsim 23$. However, since Δ decreases rapidly with increasing volume fraction, the condition $\Delta \lesssim 2$ is generally fulfilled for $v \gtrsim 0{\cdot}23$. This number can be understood in terms of the quantity $v_c\Delta^2/v_{cp}$ (cf. equation (4)), which is the one dimensional volume fraction along the tube at the columnar phase boundary v_c. $v_c\Delta^2/\phi_{cp}$ is found to be close to unity ($> 0{\cdot}95$ for the results shown here), which indicates that in the columnar phase the end-to-end distance between aggregates is always small.

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