Isotropic-Nematic Phase Transition and Angular Correlations in Isotropic Suspensions of Tobacco Mosaic Virus

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The specific magnetic-field–induced birefringence is measured in isotropic suspensions of the rodlike particle tobacco mosaic virus as a function of concentration and added salt. This quantity is proportional to the angular correlations between particles at zero field. In addition, the isotropic-nematic coexistence concentrations are measured as a function of ionic strength. The data compare well with a scaled functional theory assuming decoupling between the angular and spatial degrees of freedom.

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Liquid crystals composed of particles interacting with only repulsive potentials are important for fundamental, practical, and biological reasons. First, the study of simple liquids has shown that repulsive forces largely determine the structure of liquids and that attractive potentials can be successfully treated perturbatively. Thus hard-rod liquid crystals may serve as a reference state to study thermotropics. Indeed, recent Monte Carlo simulations have demonstrated that hard-core liquid crystals exhibit a smectic phase similar to thermotropics. Second, hard-core liquid crystals of large length-to-diameter (aspect) ratio approximate main chain polymer liquid crystals which have found applications, for example, in the production of high-strength fibers. Third, aligned charged filaments with liquid-crystalline properties such as muscle fibers and retinal cells play important roles in the biological milieu.

The first microscopic theory for the isotropic-to-nematic (I-N) phase transition in a hard-rod system was developed by Onsager. It predicts that a dilute suspension of very anisotropic, hard, rigid rods forms an orientationally ordered (nematic) phase at a critical volume fraction which depends only on the aspect ratio of the rods. Onsager considered two-body interactions which limits the theory to particles with an aspect ratio greater than about 100. However, it is expected that shorter hard rods also form nematic phases since three-body interactions act to stabilize the nematic phase.

While suspensions of hard, rigid rods are interesting theoretically they do not occur in nature and such rods are difficult to synthesize. On the other hand, charged rods are abundant in nature and similarly to hard particles, interact with a pair potential dominated by repulsion. The effect of charge is twofold. First, at a given ionic strength it has been argued that the free energy of the electrostatic repulsion between particles is equivalent to increasing the diameter of the particle by the distance at which the interparticle repulsive potential falls to a value of about $kT$. Second, the angular-dependent electrostatic potential between two like charged cylinders acts to misalign the particles and its magnitude is characterized by the “twist” parameter $g$. Tobacco mosaic virus (TMV) is in many ways a model rigid charged rod. TMV suspensions in water can be made monodisperse through careful preparation. Viewed at low resolution in an electron microscope, TMV appears as a rigid rod of length $L = 3000 \text{Å}$ and diameter $D = 180 \text{Å}$ (Ref. 6) and light-scattering studies have failed to detect any flexibility. In addition, in the pH range of 7–8 TMV has a high negative charge density distributed uniformly along its length. It was first recognized in 1936 that suspensions of TMV formed a nematic phase at a sufficient particle concentration. TMV has also been observed to form more highly ordered phases, although the identification of the phases remains to be determined.

At number concentrations, $c$, below the nematic transition, the particle axes point in all directions with equal probability when averaged over the entire sample and the suspension is optically isotropic. However, locally there are angular correlations between neighboring rods. Application of a magnetic field induces partial alignment of the particles and the sample becomes birefringent. Straley calculated, using the Onsager model, that due to correlations, the specific magnetic birefringence ($\Delta n/c$) of a suspension should increase by a factor of 5.7 from the limit of infinite dilution to the concentration of the I-N transition. Photinos and Saupe pointed out that $\Delta n/c$ is proportional to the magnitude of the angular correlations between particles at zero field, a result consistent with linear-response theory and similar to the case of thermotropics. Magnetic-birefringence measurements investigating pretransitional correlations in suspensions have been performed on two types of rodlike particles. Nakamura and Okano examined suspensions of the virus $fd$ for a wide range of concentrations and one ionic strength and found that $\Delta n/c$ only doubled from the dilute limit to the I-N transition. The $fd$ sample has an effective aspect ratio of about 100, long enough for the Onsager approximation to be valid, but $fd$ is also some-
what flexible\textsuperscript{7} which is expected to strongly affect the \textit{I-} \textit{N} transition.\textsuperscript{4,14} In a second study, \( \Delta n \) of suspensions of TMV was measured as a function of temperature for one ionic strength and at low TMV concentrations.\textsuperscript{15} It was found that the magnetically induced birefringence had a temperature dependence inconsistent with hard, rigid particles and a concentration dependence consistent with the Onsager model.\textsuperscript{11,12}

In this Letter we present measurements of the magnetic birefringence of the isotropic phase of TMV from the \textit{I-N} coexistence point down to the low-concentration limit where interparticle correlations are small. We also present the first measurements of the \textit{I-N} coexistence region for monodisperse suspensions of TMV as a function of ionic strength. Incidentally, we know of no other similar measurements in any other liquid crystal composed of polyelectrolytes. Measurements of the effect of temperature and sample polydispersity on both the magnetic birefringence and coexistence concentrations will be presented in a future paper.

To interpret our results we apply a simple functional scaling argument that was first applied to suspensions of hard spherocylinders by Lee.\textsuperscript{16} The theory has the limits of the accurate Carnahan-Starling equation of state of hard spheres when the length of the spherocylinder core is zero and reduces to the Onsager theory when the spherocylinder length is infinite. We extended the theory of Lee to include the effects of charge\textsuperscript{2,5} and magnetic field\textsuperscript{1,11,12} in the isotropic phase. We find that the degree of alignment of the particles along the field as measured by the nematic order parameter \( S \) (defined as usual as the second-Legendre-polynomial-weighted average of the angular distribution of rod axes) is

\[
S = \frac{\Delta \chi H^2}{15kT} \left[ 1 - \frac{c}{c^*} \frac{1 - \frac{1}{4} \phi}{(1 - \frac{1}{2} h)} \right]^{-1},
\]

where \( \Delta \chi \) is the anisotropy of the diamagnetic susceptibility of TMV, \( H \) the magnetic field, \( kT \) the thermal energy, \( c \) the number density, \( \phi = cV \) the volume fraction, \( V = \pi D_{\text{eff}}^2 (1 + 3L/2D_{\text{eff}})/6 \) the volume of a spherocylinder, \( L \) the length of a spherocylinder, \( D_{\text{eff}} \) the effective diameter of a charged spherocylinder, \( c^* = 16/\pi L^2 D_{\text{eff}} \) the critical concentration at which the isotropic phase is thermodynamically unstable,\textsuperscript{4,5} and \( h = \kappa^{-1}/D_{\text{eff}} \) the twist parameter,\textsuperscript{5} with \( \kappa \) the Debye screening length. We calculated the effective diameter \( D_{\text{eff}} \) and twist parameter \( h \) using an analytic approximation for the Poisson-Boltzmann equation\textsuperscript{17} as outlined by Stroobant, Lekkerkerker, and Odijk.\textsuperscript{5} If \( h \) is greater than \( \frac{1}{4} \), the nematic phase will never form\textsuperscript{4} and the particles will be anticorrelated at zero field. However, \( h \) is small for TMV (Ref. 5) and the dominant factor governing the angular correlations is \( D_{\text{eff}} \). The TMV was modeled as a charged spherocylinder of bare dimensions \( L = 2820 \text{ Å}, D = 180 \text{ Å} \), and with a linear charge density of 0.5 \( e/\text{Å} \). However, this latter value is not too important since at these high charge densities \( D_{\text{eff}} \) is only weakly dependent on charge.\textsuperscript{5}

The field-induced birefringence \( (\Delta n) \) is simply the product of the order parameter \( (S) \) and the birefringence of a perfectly aligned suspension \( (\Delta n_{\text{sat}}) \) of mass concentration \( \rho \):

\[
\Delta n = \Delta n_{\text{sat}} S, \quad (2)
\]

with \( \Delta n_{\text{sat}} = 2.1 \times 10^{-5} \rho \),\textsuperscript{18} where the mass concentration \( \rho \) (mg/ml) is related to the number concentration \( (\text{ml}^{-1}) \) by \( \rho = c (4 \times 10^{10} \text{mg})/6 \times 10^{22} \).

The TMV was prepared following the basic procedure of Boedtker and Simmons.\textsuperscript{19} The ionic strength of the three samples used in the magnetic-birefringence measurements was obtained by dialyzing against potassium phosphate buffer at pH 7.2. Additional samples used in determining the coexistence concentrations were dialyzed in TRIS-HCl buffer at pH 8.0. TMV concentrations were determined spectrophotometrically using an extinction coefficient of 3.05 cm\(^2\)mg\(^{-1}\) at a wavelength of 265 nm.\textsuperscript{19}

The magnetic-birefringence measurements were made with quartz or Teflon cells with quartz windows of path lengths varying between 0.2 and 3.0 cm. These were placed in a temperature-stabilized sample holder in a Bitter magnet which had a small radial optical bore. The field-induced birefringence was measured using a combined photoelastic modulation and compensation technique.\textsuperscript{20} The magnetic field was calibrated by measuring the current passing through the magnet and separately determining the field-current relationship. The birefringence and magnetic field were registered on a personal computer from which the Cotton-Mouton \( (K_{\text{CM}}) \) constant was calculated,

\[
K_{\text{CM}} = \Delta n/\lambda H^2, \quad (3)
\]

with \( \lambda \) (6328 Å) the wavelength of light. The maximum attainable field in this magnet was 12.5 T and the smallest measurable \( K_{\text{CM}} \) value was about 1 \times 10^{-15} \text{ G}^{-2} \text{ cm}^{-1}.\textsuperscript{20} In this study all measurements were made at 20°C.

For all isotropic samples studied the induced birefringence \( \Delta n \) was found exactly proportional to \( H^2 \), indicating the small degree of magnetic alignment. The concentration-dependent terms of the order parameter of Eq. (1) can be isolated by measuring the inverse of the specific Cotton-Mouton constant divided by its value in the limit of \( c \rightarrow 0 \), or

\[
\frac{c/K_{\text{CM}}}{c/K_{\text{CM}}|_{c=0}} = 1 - \frac{c}{c^*} \frac{(1 - \frac{1}{4} \phi)(1 - \frac{1}{2} h)}{(1 - \phi)^2}. \quad (4)
\]

In Fig. 1 the results for three TMV samples of different ionic strengths at the same pH are plotted in this way for the entire isotropic phase. The right-hand side of Eq. (4), shown in Fig. (1) as solid lines, was calculated by modeling TMV as a spherocylinder as before and \( D_{\text{eff}} \).
and \( h \) were calculated for the three samples as indicated above. Data and theory agree well. Each data point in Fig. 1 was the result of two independent measurements: the concentration \( c \) and the Cotton-Mouton constant \( K_{CM} \). At high concentrations, near the \( I-N \) transition, only 0.025 ml of solution were used in the concentration measurement because of the necessity to conserve as much material as possible for the remaining \( K_{CM} \) measurements. The resulting error in concentration was about 10% while the error in \( K_{CM} \) was much less than 1%. Greater volumes of sample were used in determining \( c \) as the sample was diluted and the error in \( c \) decreased while the error in \( K_{CM} \) increased. At the lowest concentrations measured (about 1 mg/ml TMV) the error in both \( c \) and \( K_{CM} \) was approximately 1%. The quantity \( (c/K_{CM})|_{c=0}=\lambda_c 15kT/\Delta\chi\Delta n_{sat} \) varied slightly for the three samples (most probably due to polydispersity) and was measured to be \((1.22 \pm 0.12) \times 10^{13} \text{G}^2 \text{mg cm}^{-2} \) at 20°C. This gives \( \Delta\chi=1.5 \times 10^{-25} \text{erg/G}^2 \) which is about 30% smaller than the previously reported value. After the magnetic-birefringence measurements all TMV samples were examined for polydispersity using an analytical centrifuge. Only samples with less than 10% aggregates by mass were included in this study. In Fig. 1 we also include Monte Carlo data for hard spherocylinders with the aspect ratio of \( L/D=5 \). The highest concentration of all four data sets is the concentration of the isotropic phase in coexistence with the nematic. Likewise the termia of the theoretical lines are the coexistence concentrations of the \( I-N \) transition given in Ref. 16 for spherocylinders with an aspect ratio \( L/D_{eff} \). Note that at the \( I-N \) transition the magnetic birefringence is between 2 and 3 times larger than at the limit of zero concentration.

The coexistence concentrations for TMV suspensions as a function of ionic strength are presented in Fig. 2. The ratio of the volumes of the isotropic and nematic phases was measured to be independent of temperature from 5 to 30°C. Above this temperature irreversible aggregation of TMV occurred in 25-mM phosphate buffer. The theoretical results for the Onsager theory including charge and the hard spherocylinder theory of Lee are also shown. \( D_{eff} \) and \( h \) were calculated as before and both of these quantities were used in comparison with the Onsager theory. However, for the theory of Lee we set \( h=0 \) to use the previously calculated coexistence concentrations for hard spherocylinders with aspect ratio \( L/D_{eff} \). The critical concentration \( c^* \) is the same in the two theories. As expected, the Onsager theory predicts higher transition concentrations than are measured for TMV. The hard spherocylinder theory of Lee, which attempts to take into account the higher virial coefficients, predicts transition concentrations close to the measurements. However, Lee’s theory also predicts that the ratio of concentrations of the nematic and isotropic phases varies from 1.24 in the Onsager limit of long rods to 1 when \( L/D=1.75 \) and the nematic phase disappears. Experimentally the coexistence region is much wider. This could be due to a small amount of polydispersity or the twisting effect of charge, which are not included in the coexistence calculations.

We have measured the increase in angular correlations...
between TMV particles in the isotropic phase as a function of ionic strength and particle concentration and determined the coexistence concentrations of the I-N boundary for monodisperse samples as a function of ionic strength. The field-induced-birefringence data compare well with a theory of the I-N transition that assumes decoupling between the translational and rotational degrees of freedom when extended to include the effects of magnetic field and charge of the spherocylinders. The ratio of the nematic and isotropic concentrations in coexistence is higher than predicted by the hard spherocylinder model. It would be interesting to extend the hard-rod theories, and the theory of Lee, to include the effect of charge and compare the results with our data.

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