Shape of the isotropic-(para)nematic coexistence curve in sheared nanotube suspensions

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A geometrical argument is used to account for the exponent of 1/3 describing the isotropic-(para)nematic phase boundary of sheared carbon nanotube dispersions [E. K. Hobbie and D. J. Fry, Phys. Rev. Lett. **97**, 036101 (2006)]. Through simplifying assumptions motivated by the effects of concentration and attractive interactions, the behavior is explained by relating the mean strain-induced alignment to the average distance between nanotubes for the scenario of limited anisotropy in non-Brownian suspensions.

A quantitative description of the development of (para)nematic order in sheared suspensions of rigid-rod polymers and colloids is a nontrivial problem of practical and pedagogical interest and importance. It generally involves a solution of the Smoluchowski equation describing the evolution of an orientational distribution function (ODF) that gives the probability of finding a rod aligned at a specified angle with respect to the direction of flow [1–4]. From this distribution, the order parameter tensor can then be computed. Solutions of this type are nontrivial, requiring either numerical treatment or an approximation scheme that highlights the physics of interest. In two recent papers [5,6] we offer experimental evidence that the degree of shear-induced alignment in semidilute rigid-rod nanotube suspensions with attractive interactions scales with nanotube volume fraction ϕ as $\phi^{1/3}$. In one of these papers [6], we allude to a simple physical argument as to why this might be the case. As presented this argument is quite terse and it is the purpose of the present communication to clarify the details and underlying assumptions.

For the sake of simplicity we assume uniaxial symmetry in the ODF, which is an approximation dictated by the measurements of interest here [7]. The tensor characterizing the degree of alignment is

$$\mathbf{S} = \tfrac{1}{2}[3\langle \hat{\mathbf{n}}\hat{\mathbf{n}} \rangle - \mathbf{1}], \qquad (1)$$

where $\hat{\mathbf{n}}$ denotes the orientation of a nanotube and $\mathbf{1}$ is the identity tensor. The brackets in Eq. (1) denote an average in solid angle over the ODF, $p(\theta)$, where θ is the angle a nanotube makes with the axis of mean alignment, x. The scalar order parameter is the projection of Eq. (1) along the direction of mean alignment,

$$S = \hat{\mathbf{x}} \cdot \mathbf{S} \cdot \hat{\mathbf{x}} = \langle P_2(\cos\theta) \rangle. \qquad (2)$$

Previously reported experimental results [6] suggest that there is a discontinuity in S at a critical shear stress σ_c that marks—equivalently—the limit of full nanotube dispersion and the isotropic-(para)nematic phase boundary in semidilute "sticky" non-Brownian nanotube suspensions. We denote this discontinuity $S_0(\phi)$, with the data further suggesting $S_0(\phi) \propto \phi^{1/3}$ [6]. Another previous study of completely analogous non-Brownian nanotube suspensions suggests an iden-

tical power law for S in the limit of very large rotational Peclet number [5], defined here as the ratio of shear rate $\dot{\gamma}$ to the thermal rotational diffusion coefficient D_r.

To explain this power law, we expand Eq. (2) around the isotropic state by introducing the deviation

$$\delta\hat{\mathbf{n}} = \hat{\mathbf{n}} - \hat{\mathbf{n}}_i, \qquad (3)$$

where the subscript i refers to the initial isotropic configuration. To leading order, Eq. (2) then becomes

$$S \simeq 3\langle (\hat{\mathbf{x}} \cdot \hat{\mathbf{n}}_i)(\hat{\mathbf{x}} \cdot \delta\hat{\mathbf{n}}) \rangle = 3\langle (\hat{\mathbf{x}} \cdot \delta\hat{\mathbf{n}}) \cos\theta_i \rangle. \qquad (4)$$

By appealing to geometry we model the anisotropy of the suspension as shown in Fig. 1, where the effect of the shear flow is to introduce a degree of uniaxial orientation along x. What are drawn as movable contacts in Fig. 1 should be viewed as points of the strongest interaction. The anisotropy can be characterized by

$$\varepsilon = R\cos\theta - R_i\cos\theta_i, \qquad (5)$$

where θ_i and R_i represent the flow angle and distance between points of the interaction, respectively, in the isotropic state, with θ and R being the analogous quantities after the deformation. If the mean distance between points of interaction is identical to the mean separation between nanotubes, R_0 (which to leading order is assumed to be unaltered by the anisotropy), then
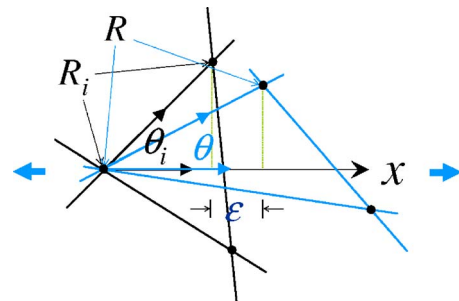

FIG. 1. (Color online) A drawing showing an idealized geometry of a strained semidilute nanotube suspension, where the labeled variables are identified in the text.

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$$\frac{\varepsilon}{R_0} \simeq \cos\theta - \cos\theta_i = \hat{\mathbf{x}} \cdot \delta\hat{\mathbf{n}}, \qquad (6)$$

and Eq. (4) becomes

$$S \simeq 3\frac{\langle \varepsilon \cos\theta_i \rangle}{R_0}. \qquad (7)$$

Note that $\varepsilon \cos\theta_i$ is positive in the interval $0 \le \theta_i \le \pi$, being symmetric around $\theta_i = \pi/2$, and we thus need only consider the more convenient interval $0 \le \theta_i \le \pi/2$. Replacing $\cos\theta_i$ in Eq. (7) with the isotropic root-mean-square value of $1/\sqrt{3}$, we get

$$S \simeq \sqrt{3}\frac{\langle \varepsilon \rangle}{R_0}. \qquad (8)$$

This relation is completely general and will apply to limited anisotropy in any rigid-rod network. As suggested by the data in Ref. [6], the mean deformation $\langle \varepsilon \rangle$ is a function of the reduced shear stress, σ/σ_c, and Eq. (8) gives the correct behavior in the isotropic limit. Since $R_0 \propto \phi^{-1/3}$, our argument is complete.

The suspensions of interest are unique in that they are extremely non-Brownian due to the viscosity of the suspending fluids [5,6]. They are also inherently "sticky" with an isotropic state characterized by macroscopic aggregation [8]. It is well established that caging effects greatly slow rotational diffusion in semidilute rigid-rod suspensions [1] and this effect has been quantitatively confirmed for the suspensions of interest here [5]. Attractive interactions will also have the effect of extending the lifetime of transient contacts in the (para)nematic state, further slowing rotational diffusion. The drawing in Fig. 1, which relies on a local configuration of nanotubes that is in some sense static, is a gross oversimplification, but it captures the qualitative features of the measured projection of the ODF [5]. Whether or not the argument retains a degree of validity in light of a more rigorous and quantitative treatment remains to be seen.

It should be emphasized that a key aspect of the argument is shear-induced anisotropy that is in some sense weak, since this will be consistent with a deviation from an isotropic state that can be viewed as being in some sense small. Values of S measured with video microscopy support this requirement [9] as they never exceed $S_{max} \approx 0.5$. The limited anisotropy that develops in these suspensions under shear also explains why the anisotropic dispersions show light-scattering profiles more characteristic of isotropic rigid-rod suspensions [5,6]. Rigorously speaking, the "fractal" chain dimension $d_f \approx 1$ will only apply to a random *isotropic* collection of rigid rods. As such an ensemble becomes uniaxially aligned, the exponent describing the shape of the scattering profile projected along the axis of alignment will cross over from 1 to 2, where the latter value reflects the large argument envelope of the square of the zeroth-order spherical Bessel function corresponding to the form factor of an infinitely thin straight rod. Specifically, for a monodisperse collection of uniformly straight rods of length L and negligible diameter the relevant projection is

$$I(q_x) \propto \int_{-1}^{1} d(\cos\theta)p(\theta)\frac{\sin^2(Lq_x\cos\theta/2)}{(Lq_x\cos\theta/2)^2}, \qquad (9)$$

where q_x is the component of the scattered wave vector along the axis of mean alignment. For constant $p(\theta)$, the right-hand side of Eq. (9) scales as $(q_x)^{-1}$ for $Lq_x \gg 1$, which for large L is easily satisfied in the regime of wave vector relevant to light scattering. In the other limit $p(\theta) \propto \delta(\cos\theta - 1)$, the scattering projection scales as $(q_x)^{-2}$. In between these two extremes, Eq. (9) is evaluated numerically for a Gaussian ODF of varying width, which gives a high-q power-law exponent of $d_f = 1.04$ for $S = 0.1$, $d_f = 1.12$ for $S = 0.2$, and $d_f = 1.21$ for $S = 0.3$. Physically, this reflects the characteristic width of $\sin^2(x)/x^2 \simeq \exp(-x^2/3)$ dominating the integrand in Eq. (9) until the ODF becomes sufficiently sharp. Weak tube deformation will move this crossover to higher S, since in the formalism we adopt the order parameter is set by the body director of the nanotube while the scattering will be sensitive to the internal structure [10]. For even modest anisotropy, a power law with an exponent of -1 will thus give a reasonably good accounting for the measured scattering profile, consistent with what has been reported experimentally [5,6].

It is also important to reconcile the varied descriptions offered previously for the dependence of S on shear rate [5,6,11]. In terms of rotational Peclet number (Pe), flow birefringence and dichroism data for the nanotubes in question have been interpreted in terms of a power law with a rather small exponent [5,11]: $S \propto \mathrm{Pe}^{0.16}$. More recently, however, we have suggested that the dependence of S on shear rate is in fact logarithmic and we have offered a very simple physical explanation as to why this might be the case [6]. In light of the magnitude of Pe in these non-Brownian suspensions, it indeed seems more attractive to adopt the approach used in Ref. [6], which defines the appropriate dimensionless group as the ratio of the shear stress to the critical stress required for nanotube dispersion. The two different interpretations may in fact be reconciled by noting that a logarithmic dependence is quite difficult to distinguish from a power law with a small critical exponent and the previously reported $\mathrm{Pe}^{0.16}$ behavior would in fact be quite difficult to discern from an underlying logarithmic growth law.

Finally, we note that the value of S measured rheo-optically is highly dependent on the value of the intrinsic differential optical anisotropy that one adopts as characteristic of the nanotubes. The order parameter can be determined from the relations

$$S(\phi,\dot{\gamma}) \simeq \frac{2n_s\Delta n'(\phi,\dot{\gamma})}{\phi\Delta\alpha'} = \frac{2n_s\Delta n''(\phi,\dot{\gamma})}{\phi\Delta\alpha''}, \qquad (10)$$

where $\Delta n = \Delta n' + i\Delta n''$ is the measured anisotropy in the complex index of the refraction tensor, $\Delta\alpha = \Delta\alpha' + i\Delta\alpha''$ is the complex intrinsic differential optical anisotropy of the nanotubes at the wavelength employed, and n_s is the index of refraction of the suspending fluid [10–12]. For a given system one thus needs an independent measure of S that can be used to "calibrate" $\Delta\alpha$ before Eq. (10) can be employed as a

precise and efficient means of quantitatively measuring the shear-induced alignment. In a previous study we used video microscopy to do this by obtaining a direct—if approximate—measure of the ODF [5,9]. For the multi-walled carbon nanotubes in question, this approach correctly gives $\Delta\alpha' \approx 3.5$ and $\Delta\alpha'' \approx 2.7$ at a wavelength of 670 nm. These values are larger than previously reported [9] and are actually larger than comparable values measured for single-wall carbon nanotubes [5,11]. To explain this difference, we suggest that despite the presence of more structural defects, the multiwalled tubes may in fact have optical coefficients that are more characteristic of bulk semiconductors [13], giving them an intrinsic optical anisotropy that is larger than that previously measured rheo-optically for single-walled tubes.

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