

# Theoretical analysis of polydispersity in the nematic phase of self-assembled semiflexible chains\*

Xinjiang Lü and James T. Kindt

*Department of Chemistry and Cherry L. Emerson Center for Scientific Computation,  
Emory University, Atlanta, Georgia 30322 USA*

## Abstract

In recent simulations of semiflexible equilibrium polymers [X. Lü and J. T. Kindt, *J. Chem. Phys.* **120**, 10328 (2004)] a roughly bi-exponential distribution of chain lengths was observed in the nematic phase. In this study, we show that a theory representing the nematic phase as an equilibrium mixture of randomly oriented chains below a critical length  $L_c$  and chains above  $L_c$  obeying a Gaussian orientational distribution reproduces this distribution qualitatively. The agreement between predicted and simulated phase boundaries is improved, with a narrower isotropic-nematic coexistence region, compared with a mono-exponential chain distribution. We find furthermore that the critical length  $L_c$  scales as the inverse of monomer concentration, irrespective of the bond strength of the chains, but that at the phase boundary, the fraction of monomers found in disordered chains peaks at a certain bond strength.

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## I. INTRODUCTION

The nematic ordering transition of hard rigid and semirigid rods is strongly dependent on rod length<sup>1</sup>. In bidisperse and polydisperse mixtures of rods or semiflexible polymers, the length-dependent partitioning of chains between ordered and isotropic phases, and the dependence of order parameter on length, has been studied by theory and simulation<sup>2-4</sup>. In self-assembled systems in which the size distribution of either phase is determined by the forming and breaking of bonds at equilibrium, the length distributions of the two phases are expected to be quite different, as has been verified by simulation<sup>5-7</sup>. In a recent simulation study<sup>5</sup>, we identified the length distribution of the nematic phase in semiflexible equilibrium polymers as being roughly bi-exponential, dropping off quickly for short chains and slowly for longer chains, and found that the division between the two regimes corresponds to a division between low and high order parameters. In this article, we present a simple model for this behavior that gives qualitative agreement with the length distribution seen in simulation with no new adjustable parameters, as well as improved agreement with simulated phase boundaries. The model also predicts an inverse relationship between the crossover length and the total monomer concentration, and that the fraction of monomers found in disordered chains goes through a maximum with increasing bond strength.

## II. THEORY

In simulations of semiflexible hard-sphere chains, the degree of orientational order in the nematic phase increases continuously with chain length, approaching a maximum value for long chains. Taylor and Herzfeld<sup>8</sup> have studied the limiting case of perfectly rigid spherocylinders allowing full optimization of the orientational distribution as a function of rod length. To simplify theoretical calculations, we will instead represent all short chains (those below a variationally determined crossover length  $L_c$  in units of monomer diameter  $\sigma$ ) as isotropically oriented and all long chains (those with contour length greater than  $L_c$ ) as having a Gaussian orientational distribution independent of length. The contributions of each population to the system free energy can then be treated as additive, except for a single cross term describing the excluded volume interactions between short and long chains. The free energy densities of the isotropic and nematic phases can be written<sup>5,9</sup> ( $k_B T \equiv 1$ )

$$f_{\text{iso}} = -E\rho_{\text{tot}} + \sum_{i=1}^{\infty} E\rho(i) + B_2\rho_{\text{tot}}^2 + \sum_{i=1}^{\infty} \rho(i) [\ln \rho(i) - 1]; \quad (1)$$

$$\begin{aligned} f_{\text{nem}} = & -E\rho_{\text{tot}} + \sum_{i=1}^{L_c} E\rho(i) + \sum_{i=L_c+1}^{\infty} \rho(i) \left( E + \ln \frac{\alpha}{4} \right) \\ & + B_2(\rho_s^2 + 2\rho_s\rho_l + \frac{4}{\sqrt{\pi\alpha}}\rho_l^2) + \rho_l \frac{\alpha}{4l_p} \\ & + \sum_{i=1}^{L_c} \rho(i) [\ln \rho(i) - 1] + \sum_{i=L_c+1}^{\infty} \rho(i) [\ln \rho(i) - 1], \end{aligned} \quad (2)$$

where  $E = \ln K_{\text{bond}}$  is the intrachain bond free energy and  $B_2 = 0.85 \sigma^3$  is the second virial coefficient obtained from simulations of isotropic systems in Ref. 5. For simplicity, we ignore the steric end effect<sup>9</sup> here. Assumption of a Gaussian orientational distribution function  $f_G(\theta) = (\alpha/4\pi) \exp(-\alpha\theta^2/2)$  gives the free energy penalty per chain<sup>9-11</sup>  $\ln(\alpha/4)$ , where  $\alpha$  is related to the order parameter  $S = (3\langle \cos^2 \theta \rangle - 1)/2$  through  $\alpha = 3/(1 - S)$ . The configurational entropy contribution is included as  $\alpha/(4l_p)$ , where  $l_p$  is the persistence length<sup>9-11</sup>.

For isotropic chains, the distribution is given by  $\rho(i) = \rho(1)q_1^{i-1}$  with  $q_1 = \rho(1)K_{\text{bond}}$ . The nematic phase is comprised of disordered and ordered components, therefore the total number density  $\rho_{\text{tot}} = \rho_s + \rho_l = \sum_{i=1}^{L_c} i\rho(1)q_1^{i-1} + \sum_{i=L_c+1}^{\infty} i\rho(L_c+1)q_2^{i-(L_c+1)}$ . Equilibrium chain distributions are obtained by equating chemical potentials of monomers within chains to the free monomer monomer chemical potential,  $\mu = \ln \rho(1) + 2B_2\rho_{\text{tot}}$  through

$$\frac{1}{i} \frac{\partial f}{\partial \rho(i)} = \frac{\partial f}{\partial \rho(1)}, \quad (3)$$

yielding

$$q_2 = \rho(1)K_{\text{bond}} \exp \left[ \left( 2 - \frac{8}{\sqrt{\pi\alpha}} \right) B_2\rho_l - \frac{\alpha}{4l_p} \right]. \quad (4)$$

The value of  $\alpha$  is numerically solved from the system of equations:  $\rho_l = \sum_{i=L_c+1}^{\infty} i\rho(i)$  and  $\rho_l = \rho_{\text{tot}} - \rho_s$ .

The free energy is minimized with respect to the unbound monomer density  $\rho(1)$  and the critical length  $L_c$  at any given  $\rho_{\text{tot}}$ ,  $K_{\text{bond}}$ , and  $l_p$ . It is necessary to replace sums by integrals and sample  $L_c$  in a continuum space for the sake of accuracy and precision, especially at high densities. A method to obtain the phase coexistence range is that two equilibrated phases satisfy  $\mu_{\text{iso}}(\rho_{\text{iso}}) = \mu_{\text{nem}}(\rho_{\text{nem}})$  and  $p_{\text{iso}}(\rho_{\text{iso}}) = p_{\text{nem}}(\rho_{\text{nem}})$ , from which we find the phase boundary densities  $\rho_{\text{iso}}$  and  $\rho_{\text{nem}}$ .

### III. RESULTS AND DISCUSSIONS

Figure 1 shows the optimized nematic length distribution near the phase boundary at several values of  $K_{\text{bond}}$  with  $l_p = 1000 \sigma$ . The theory does a good job of capturing the decay of the distribution at low  $L$ , confirming that this short chain length distribution is not an artifact of the simulation method or finite size effects. The slope of the distribution is discontinuous on the semi-log plots, due to the approximation of a discontinuous jump in order parameter at  $L_c$ . It is noteworthy that the free energy-minimized length distributions are continuous at  $L_c$ , even though they are not constrained to be. The physical basis for the difference in growth law between ordered and disordered chain classes is that the long, ordered chains are pre-aligned for end-to-end fusion, and hence have a higher effective bond association constant. Agreement between simulation and theory is best at low density. At high density, due to the omission of steric end effects and three-body effects, the mean chain length of the nematic is significantly underpredicted by the theory.

The phase diagram from the new “bi-exponential” length distribution model is shown in Fig. 2 along with the theory and simulation results from Ref. 5. Allowing the short chains of the nematic phase to be orientationally disordered significantly shifts the nematic phase boundary to a lower density. The driving force for this isotropic-nematic phase transition is the competition between the orientational entropy and the translational (or packing) entropy. The disordering of short chains maximizes the orientational entropy at the cost of increasing the excluded volume interactions between short and long chains. The former stabilizes the system by decreasing the free energy while the latter results in higher packing and ordering of long chains. An optimal fraction of disordering short chains stabilizes the nematic phase, making the phase transition occur at a lower density. The theory continues to give poor agreement with simulations of more flexible ( $l_p = 100 \sigma$ ) chains, suggesting that factors other than the length-dependent ordering are important. These may include the assumption of the Gaussian form for the orientational distribution and, especially at low  $K_{\text{bond}}$  and high  $\rho$ , the truncation of the virial series at the quadratic term.

In Fig. 3 the reciprocal of  $L_c$  is plotted against  $\rho$  and fitted by  $1/L_c = a\rho$ , where  $a \approx 0.388$  is a fit coefficient independent of both the bond constant and the persistence length in a wide range. The universal relationship implies that the crossover length almost solely depends on the density, which determines how long a chain can grow before it is influenced by its

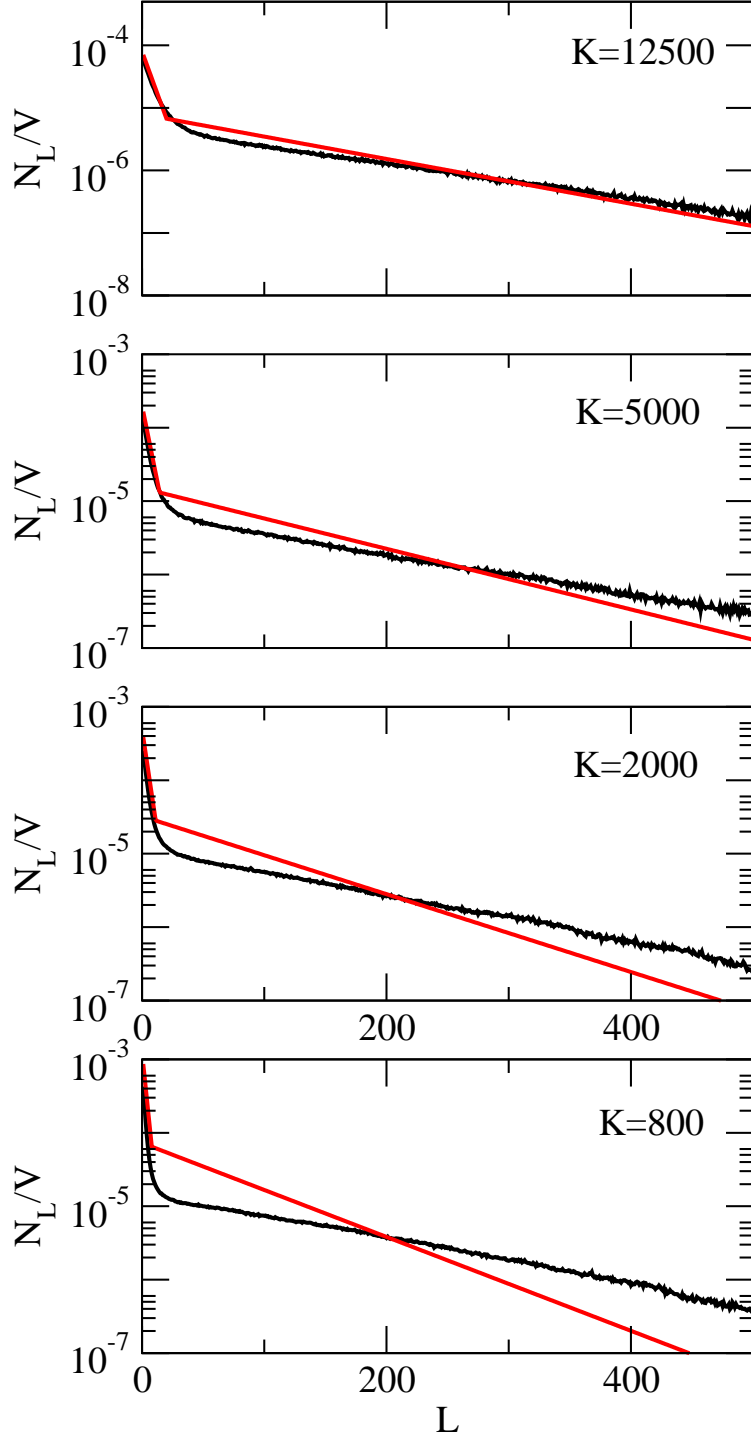


FIG. 1: Semi-log plot of the chain length distributions of simulation (red) and theory (black): average number density of chains of contour length  $L$  versus  $L$  for  $K_{\text{bond}}$  and  $l_p = 1000 \sigma$  for the nematic phase at different constants. The top-to-bottom number densities are 0.118, 0.168, 0.221, and 0.304, respectively.

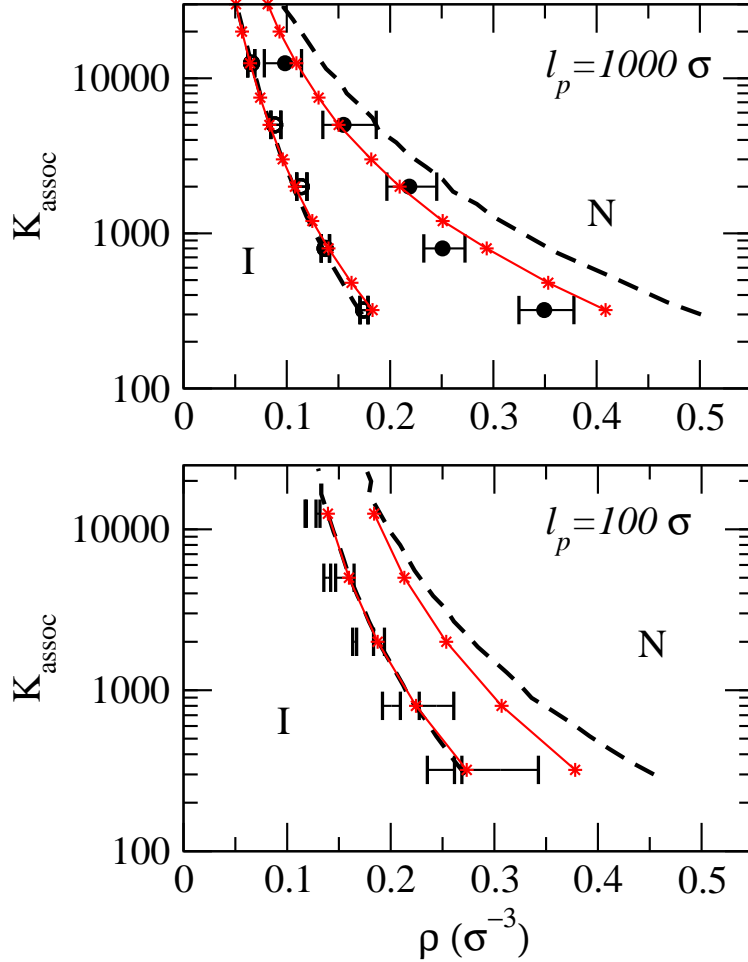


FIG. 2: Comparison of phase boundaries obtained from both simulation and different theoretical models. Dots with error bars from simulation and dashed lines from the old model are as in Ref. 5. Red star-line curves are results of the new “bi-exponential” length distribution model.

neighbors. Not coincidentally, the same inverse relation between length and density is found in the Onsager theory for hard rods. When  $L_c$  approaches  $l_p$  in the extreme low density, the fit underestimate  $L_c$  systematically because the end-to-end distance is no longer linearly proportional to the contour length.

To determine the conditions where the phenomenon of disordered short chains is most important, we plotted the fraction of monomers in disordered short chains over a range of bond association constants and densities in Fig. 4. At constant  $K_{\text{bond}}$ , this fraction drops rapidly with  $\rho$  as  $L_c$  decreases while the mean chain length increases. The highest fraction can therefore be found at the phase boundary. As  $K_{\text{bond}}$  is increased and  $\rho$  decreases, a maximum fraction of approximately 4.6% is reached at  $\rho \approx 0.06$ . A qualitative explanation

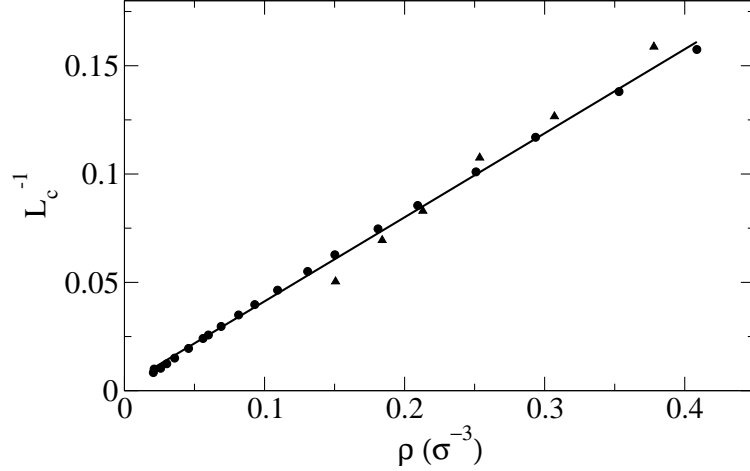


FIG. 3: The reciprocal of  $L_c$  versus the total number density. Dots are at the nematic phase boundary for different association constants at  $l_p = 1000 \sigma$ . The slope of the fit line is 0.388. Triangles are for  $l_p = 100 \sigma$ .

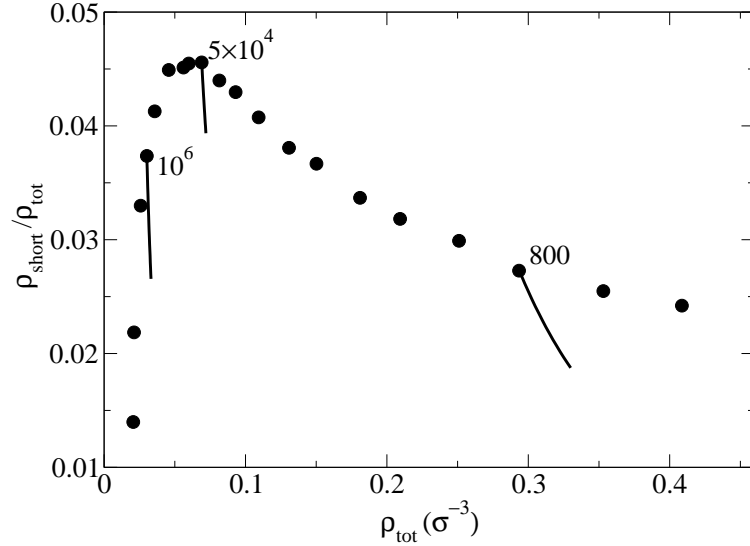


FIG. 4: The fraction of monomers found in disordered short chains at  $l_p = 1000 \sigma$ . Dots are at the nematic phase boundary; three curve segments are in the nematic phase with  $K_{\text{bond}} = 10^6, 5 \times 10^4$ , and 800, respectively.

is that as the density increases, compact ordered long chains “squeeze” many not-that-short chains into the ordered state, i.e.,  $L_c$  decreases as shown in Fig. 3, which results in a smaller fraction of monomers in short chains. At low density, although  $L_c$  is relatively large, high  $K_{\text{bond}}$ ’s result in a great average chain length and a higher fraction of monomers entering

the ordered long chains' component. The composition at the phase boundary is a result of the competition between the average chain length and  $L_c$ .

#### IV. CONCLUSION

This work shows that accounting for the presence of a short-chain disordered component in a mean field model of the nematic phase of a semiflexible equilibrium polymer system leads to a biexponential length distribution similar to that seen in simulations. The revised theory shifts the nematic phase coexistence curve densities, achieving good agreement with simulations of very rigid chains ( $l_p = 1000 \sigma$ ) but not for more flexible chains. The analysis of the critical chain length  $L_c$  and the chain composition helps provide more insight into the isotropic-nematic phase transition of a self-assembled semiflexible polymer system.

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- <sup>1</sup> L. Onsager, Ann. N.Y. Acad. Sci. **57**, 627 (1949).
  - <sup>2</sup> K. Ghosh and M. Muthukumar, Phys. Rev. Lett. **91**, 158303 (2003).
  - <sup>3</sup> A. Speranza and P. Sollich, Phys. Rev. E **67**, 061702 (2003).
  - <sup>4</sup> F. A. Escobedo, J. Chem. Phys. **118**, 10262 (2003).
  - <sup>5</sup> X. Lü and J. T. Kindt, J. Chem. Phys. **120**, 10328 (2004).
  - <sup>6</sup> B. Fodi and R. Hentschke, J. Chem. Phys. **112**, 6917 (2000).
  - <sup>7</sup> A. Chatterji and R. Pandit, Europhys. Lett. **54**, 213 (2001).
  - <sup>8</sup> M. P. Taylor and J. Herzfeld, J. Phys.: Condens. Matter **5**, 2651 (1993).
  - <sup>9</sup> P. van der Schoot and M. E. Cates, Europhys. Lett. **25**, 515 (1994).
  - <sup>10</sup> G. J. Vroege and H. N. W. Lekkerkerker, Rep. Prog. Phys. **55**, 1241 (1992).
  - <sup>11</sup> T. Odijk, Macromolecules **19**, 2313 (1986).