

Liquid-state theory of anisotropic flexible polymer fluids

Galen T. Pickett and Kenneth S. Schweizer

Departments of Materials Science and Engineering and Chemistry, and Materials Research Laboratory, University of Illinois, 1304 W. Green Street, Urbana, Illinois 61801

(Received 15 December 1998; accepted 3 February 1999)

We extend the liquid-state theory of polymer fluids to include anisotropy as a key feature. The formalism is quite general. In determining the structure of anisotropic polymer fluids, it yields thermodynamic information as well. Our first application is to describe the nematic phases of flexible polymers, and to demonstrate a novel lyotropic transition. © 1999 American Institute of Physics. [S0021-9606(99)52414-8]

In polymer fluids, it is natural that *structure* at the single-chain level together with microscopic monomer–monomer interactions determine the intermolecular packing over many length scales. Polymer liquid structure is of fundamental interest in its own right, and also leads to an understanding of thermodynamics. Since the late 1980's, much progress has been made in understanding polymer solutions, melts, block copolymers, and blends within the Polymer Reference Interaction Site Model (PRISM).¹ The model generalizes the RISM theory of Chandler and Andersen² to macromolecules. Although the model is restricted to homogeneous, isotropic fluids, PRISM provides useful input to inhomogeneous problems like crystallization, confinement, and surface structure.¹

In this communication, we extend PRISM to describe *anisotropic* liquids. Through external means or through thermodynamics, anisotropy is a key feature in many important polymer applications. For example, shear flows align polymers so that the single-chain statistics are markedly anisotropic, thus affecting the intermolecular packing, and dynamics.³ Also, lubricating films exhibit anisotropy and significant inhomogeneities. If the film thickness is much larger than the surface-induced inhomogeneity, yet much smaller than the bulk polymers, then confinement defines the anisotropy of the chains, and naturally affects both the thermodynamic and dynamic response of the layer.⁴ Anisotropy also arises in liquid crystalline polymers (LCPs). As a concrete example, we discuss nematic liquid crystallinity in flexible polymers. In contrast to most prior theoretical work,^{5–8} our approach is not limited to low-order virial expansions nor tied to phenomenology, but rather is capable of sensibly accounting for realistic microscopic interactions.

We employ the simplest athermal “thread chain” model of the PRISM integral equation theory¹ in order to clarify our approach. The simplifying assumptions are: (1) Flory ideality;^{9,10} (2) molecular lengths are irrelevant;¹¹ (3) equivalency of “sites”; and, (4) the monomer–monomer interaction is a hard-core repulsion. Polymers are modeled as chains of “sites” of diameter d , and the overall conformation is a random walk of N steps of length σ_o . The “thread” limit^{1,11} corresponds to $d \rightarrow 0$, maintaining a finite monomer, or site, number density, ρ . The system is well described by a single site–site intermolecular pair correlation function $g(r)$, and a

single total correlation $h(r) = g(r) - 1$.¹ For threads, hard-core exclusion requires $g(r \rightarrow 0) \equiv 0$. Significantly, the Percus–Yevick (PY)¹² inspired thread model correctly predicts thermodynamic (e.g., osmotic pressure, virial coefficients) and structural [e.g., $g(r)$, correlation hole, mesh size] properties of dilute and semi-dilute good and theta solutions.^{1,11,13} The thread model is rigorously justified up to semi-dilute densities in the PRISM framework by the solution of Fuchs for the PY closure.¹⁴ In that work, d is an “irrelevant” length scale in semi-dilute solution, recovering the results of the $d=0$ thread model, consistent with scaling and universality.⁹

Polymer structure enters via the single-chain scattering function, $\omega(\mathbf{q})$, which for flexible, isotropic chains is the Debye function, approximately:¹

$$\omega(\mathbf{q}) = \frac{N}{1 + \frac{N\sigma_o^2 \mathbf{q} \cdot \mathbf{q}}{12}}, \quad (1)$$

where σ_o and N are related through $R_g^2 = N\sigma_o^2/6$, with R_g the coil radius of gyration. This expression describes the *isotropic* phase [Fig. 1(A)]. A natural anisotropic extension is:

$$\omega(\mathbf{q}) = \frac{N}{1 + \frac{N\sigma_z^2 q_z^2}{12} + \frac{N\sigma_\perp^2 q_\perp^2}{12}}. \quad (2)$$

Thus the chains are anisotropic random walks with *different* step lengths in the $\hat{z}(\sigma_z)$ and the perpendicular (σ_\perp) directions. When $\sigma_z \gg \sigma_\perp$, the chains are compressed in the perpendicular direction, and expanded along \hat{z} [Fig. 1(B)]: the *nematic* phase. In the opposite limit, the chains resemble disks perpendicular to \hat{z} : a *discotic*like phase [Fig. 1(C)], but chains are not allowed to collect into the columns characteristic of true discotics.¹⁵

We define the nematic order parameter, τ . Consider an entropic spring of mean-squared end-to-end length $\sqrt{3}\sigma_o$. Let θ be the angle between the spring end-to-end vector and \hat{z} . A chain made of many such springs has isotropic step lengths, σ_o . Let

$$\tau = \frac{3}{2} (\langle \cos^2 \theta \rangle - 1/3). \quad (3)$$

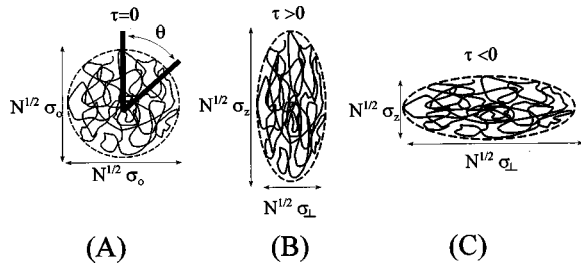


FIG. 1. Schematic of (A) typical isotropic, (B) nematic, and (C) discotic phase chain conformations. θ measures (in real space) an azimuthal angle relative to the nematic director, \hat{z} .

The isotropic phase has $\tau=0$, the nematic phase has $\tau>0$, and the discotic phase has $\tau<0$. The rms projection of the oriented spring along \hat{z} is σ_z :

$$\sigma_z(\tau) = \sqrt{3} \langle \cos^2 \theta \rangle^{1/2} \sigma_o = \sigma_o \sqrt{1+2\tau}. \quad (4)$$

Similarly, the step length in the perpendicular direction, σ_\perp is:

$$\sigma_\perp(\tau) = \sigma_x = \sigma_y = \sigma_o \sqrt{1-\tau}. \quad (5)$$

With anisotropy entering at the level of a single chain, the closure approximation determines the fixed τ structure of the oriented fluid. For threads, the interchain site-site direct correlation function is a contact or delta-function form:¹¹ $c(\mathbf{r}) = c_o \delta(\mathbf{r})$, in the spirit of the site-site PY approximation for hard-core liquids.^{1,2,12} Thus the PRISM, or Chandler-Andersen, integral equation reads in wave vector space

$$h(\mathbf{q}) = \frac{c_o \omega^2(\mathbf{q})}{1 - \rho c_o \omega(\mathbf{q})} \equiv c_o \omega(\mathbf{q}) \hat{S}(\mathbf{q}), \quad (6)$$

where $\hat{S}(\mathbf{q})$ is the collective liquid structure factor. The parameter c_o is chosen self-consistently to enforce the thread hard-core condition [$g(r=0)=0$], and thus is a functional of $\omega(\mathbf{q})$. This is the key physical feature of the RISM approach and our anisotropic generalization of it. Thus we find:

$$c_o = - \frac{\pi \sigma_\perp(\tau)^2 \sigma_z(\tau)}{3\sqrt{3}\sqrt{N}} - \frac{\pi^2 \rho \sigma_\perp(\tau)^4 \sigma_z(\tau)^2}{108}. \quad (7)$$

As the chains become aligned (that is, $\sigma_\perp \rightarrow 0$ for nematics, or $\sigma_z \rightarrow 0$ for ‘‘discotics’’) the repulsive force strength parameter, $|c_o|$, decreases. A long-ranged orientation evidently reduces the overlap of neighboring chains, suppressing the influence of the hard-core interactions.

With c_o as above, the anisotropic scattering function is:

$$\hat{S}(q_\perp, q_z) = \frac{N}{1 - c_o(\tau)N\rho + \frac{N\sigma_\perp^2(\tau)q_\perp^2}{12} + \frac{N\sigma_z^2(\tau)q_z^2}{12}}. \quad (8)$$

Thus the theory predicts the collective structure (e.g., physical mesh or blob size) of the aligned fluid to be anisotropic as well. Anisotropic pair correlations follow from Eqs. (2), (6), and (8). Note that *interchain* orientational correlations are not explicitly taken into account, as spatial fluctuations of τ are not considered.

Let us now consider a spontaneous equilibrium through which $\tau \neq 0$ arises, and construct a τ -dependent free energy in the ‘‘compressibility’’ route. The result is a toy model of liquid crystallinity, but a nontrivial one that can be analytically solved. The isothermal compressibility, κ_T , is determined via $\hat{S}(0) = \rho k_B T \kappa_T$. For convenience, $k_B T$ (Boltzmann’s constant multiplied by temperature) is the basic energy scale. Using standard thermodynamics [$P = \int \hat{S}^{-1}(0) d\rho$, $F = \int P/\rho^2 d\rho$]:

$$\hat{S}^{-1}(0) = \frac{1}{N} - \rho c_o(\tau), \quad (9)$$

$$P = \frac{\rho}{N} + \frac{\pi \rho^2 \sigma_o^3 (1-\tau) \sqrt{1+2\tau}}{6\sqrt{3}\sqrt{N}} + \frac{\pi^2 \rho^3 \sigma_o^6 (1-\tau)^2 (1+2\tau)}{324}, \quad (10)$$

$$F = a(\tau) + \frac{\ln \rho}{N} + \frac{\pi \rho \sigma_o^3 (1-\tau) \sqrt{1+2\tau}}{6\sqrt{3}\sqrt{N}} + \frac{\pi^2 \rho^2 \sigma_o^6 (1-\tau)^2 (1+2\tau)}{648}. \quad (11)$$

Notice that the pressure, P , naturally includes up to the third virial, in contrast to other theories⁵⁻⁸ that are intrinsically limited to the estimate of only the second virial. Also note that as $N \rightarrow \infty$, the only term in the equation of state is $\sim \rho^3$, just as for isotropic semidilute solutions.⁹ Thus our theory describes *anisotropic* dilute and semidilute solutions.

We specify $a(\tau)$, the single-chain free energy needed per segment to maintain the anisotropy τ , in the Gaussian bead-spring model:⁹

$$a(\tau) = -\ln[\sigma_\perp^2(\tau)\sigma_z(\tau)] = \text{const} - \ln[(1-\tau)\sqrt{1+2\tau}]. \quad (12)$$

F takes a simple form through defining:

$$\rho^*(\tau) = \frac{N}{R_z R_y R_x} = \frac{N}{N^{3/2} \sigma_\perp^2(\tau) \sigma_z(\tau)} = \frac{1}{N^{1/2} \sigma_o^3 (1-\tau) \sqrt{1+2\tau}}. \quad (13)$$

$\rho^*(\tau)$ is the semi-dilute overlap threshold of τ chains. Because ρ^* has its *minimum* at $\tau=0$, the system becomes more ‘‘dilute’’ at fixed ρ for $\tau \neq 0$. This stabilizes the liquid crystalline phase by reducing the repulsive interchain interactions. In terms of $\rho^*(\tau)$, the free energy/site is:

$$F = \text{const.} + \ln \rho^*(\tau) + \frac{\ln \rho}{N} + \frac{\pi}{6\sqrt{3}N} \left[\frac{\rho}{\rho^*(\tau)} \right] + \frac{\pi^2}{648N} \left[\frac{\rho}{\rho^*(\tau)} \right]^2. \quad (14)$$

The excess contribution to F is a function of ρ/ρ^* , consistent with semi-dilute scaling. In fact, Eq. (14) can be derived from a physically motivated ‘‘scaling’’ theory where ρ/ρ^* is the scaling variable. From this perspective, PRISM theory

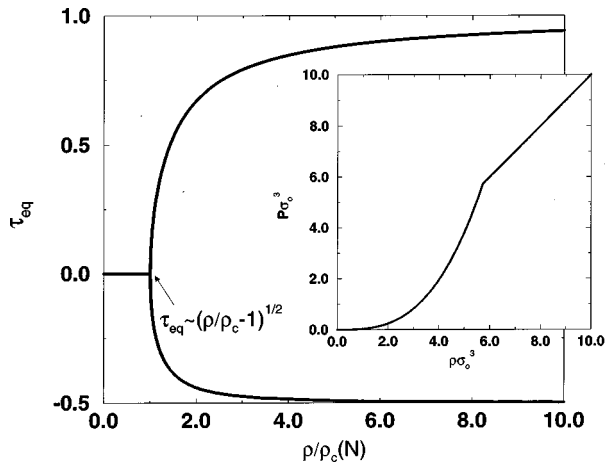


FIG. 2. $\tau_{eq}(\rho/\rho_c)$: For $\rho/\rho_c(N) < 1$, $\tau_{eq} = 0$ (isotropic phase). When $\rho > \rho_c(N)$, τ_{eq} takes both positive (nematic) and negative (discotic) values. Near the transition, $\tau_{eq} \sim \pm(\rho/\rho_c - 1)^{1/2}$. Inset is the equation of state in the limit $N \rightarrow \infty$. The pressure increases as ρ^3 up to the transition, at which point it becomes linear.

determines the numerical prefactors quantifying the two- and three-body contributions in Eq. (14).

The equilibrium value of τ is determined by: $\partial F / \partial \tau = 0$. When $\rho < \rho_c(N)$ with

$$\rho_c = \frac{9\sqrt{3+4N} - \sqrt{3}}{\sqrt{N}\pi\sigma_o^3} \quad (15)$$

the equilibrium rests at $\tau = 0$: the isotropic phase. When $\rho > \rho_c(N)$, the isotropic solution is unstable, and two equivalent minima emerge from $\tau = 0$: the nematic and discotic phases. The equilibrium value of the order parameter satisfies:

$$(1 - \tau_{eq})\sqrt{1 + 2\tau_{eq}} = \frac{\rho_c(N)}{\rho}, \quad (16)$$

as shown in Fig. 2. The critical density decreases as the chains become shorter, and hence more easily oriented, consistent with intuition and simulation.¹⁶ Thus “thread” polymers undergo a novel second-order phase transition, in our admittedly *mean field* analysis which ignores fluctuations of the order parameter and molecular-scale features such as d and local chain stiffness. Whether this transition is observable for physical polymers either in the laboratory or via simulation is a delicate issue we address below.

The equation of state in the ordered phases is $P = (1 + (1/N))\rho$, when $\rho \geq \rho_c(N)$. The ordered-phase equation of state is, apart from an $O(N^{-1})$ correction, simply the ideal gas law of the *disconnected* segments. This law cannot hold under dense conditions, as the finite volume occupied by a single polymer coil becomes important near close packing. Interestingly, computer simulations find a linear law between P and ρ in the nematic phases of long thin hard rods up to rather high packing fractions.¹⁷ The ordered phase is far from an ideal gas of segments, for which $g(r) = 1$. The intermolecular liquid structure is anisotropic on all length scales:

$$g(z, r_\perp) = g_o(r'\sigma_o), \quad \text{with } r' = \sqrt{z^2/\sigma_z^2 + r_\perp^2/\sigma_\perp^2}, \quad (17)$$

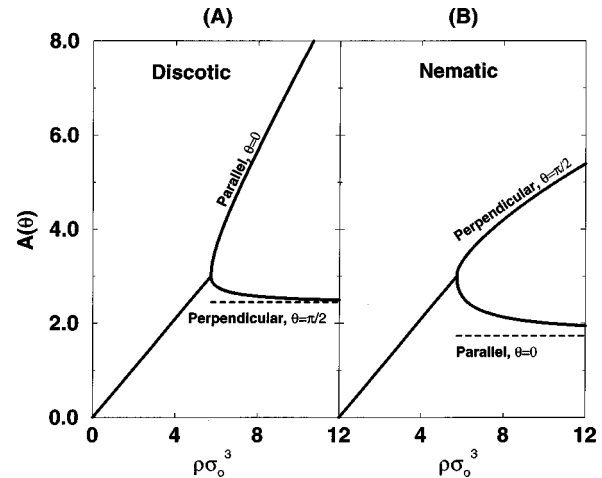


FIG. 3. “Contact” value of $g(r)$: $A(\theta) \equiv \sigma_o \partial_r g(r, \theta)|_{r=0}$ for infinitely long chains. By construction, thread chains have $g(r=0, \theta) = 0$ (core condition). Therefore, a useful measure of the “contact” value of the pair correlation is the contact partial derivative. $A(\theta)$ is the rate at which interchain contacts increase along the direction specified by θ (Fig. 1). (A) Discotic phase. $A(\pi/2) \approx \sqrt{6}$ as $\rho\sigma_o^3 \rightarrow \infty$. (B) Nematic phase. $A(0) \approx \sqrt{3}$ as $\rho\sigma_o^3 \rightarrow \infty$.

where $g_o(r)$ is the isotropic-phase site-site pair correlation:¹¹

$$g_o(r) = 1 + \frac{3}{\pi\rho\sigma_o^2 r} [e^{-r/\xi} - e^{-r\sqrt{2}/R_g}], \quad (18)$$

and $\xi^{-1} = \pi\rho\sigma_o^2/3 + 2^{1/2}/R_g$ is the density screening (or “mesh”) length. The *local* correlation hole becomes shallower with increasing density in the isotropic phase [$A(\theta)$ in Fig. 3 increases], while in the nematic phase, the hole weakly deepens along \hat{z} with increasing orientational order. The direction-dependent reduction of local contacts has significant dynamical implications, as the local collision rate is proportional to the anisotropic “contact value” of the pair correlation.^{3,12} The physical mesh and long-range correlation hole are also anisotropic in the liquid crystalline phase, and this has important consequences for transport in entangled LCP fluids.^{3,18}

The nematic and discotic phases are degenerate because the free energy depends on τ only through $\rho/\rho^*(\tau)$. The crucial connection between the nematic and discotic phases is that the free energy depends less on the *shape* of the chain configuration than on its *invaded volume*. For each nematic state, there is a discotic state with the same spanned volume $\sim R_\perp^2 R_z$, and hence $\rho^*(\tau)$. Thus the model (even at the scaling hypothesis level) exhibits a novel symmetry between the nematic and discotic phases, resulting in a continuous transition.

The molecular “thickness” of the chains ($d \neq 0$) can be captured in the “string” closure.^{11,13} The PY style approximation, $c(\mathbf{r}) = c_o \delta(\mathbf{r})$, is retained, but finite site volume is crudely enforced in an average manner through $\int_0^d d\mathbf{r} g(\mathbf{r}) \equiv 0$. In semi-dilute solution, d is irrelevant, but for concentrated solutions the string model introduces realistic corrections, and captures a finite close-packed density.¹³ With $d \neq 0$, our nematic-discotic symmetry is broken, because both ρ/ρ^* and $\rho\sigma_o^2 d$ appear as scaled densities. In fact, the intro-

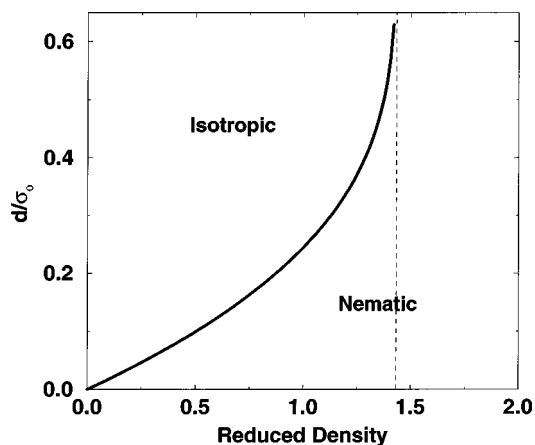


FIG. 4. String model phase diagram in terms of reduced density $= \rho \sigma_o^2 d$ and the hard-core diameter d , or equivalently the "aspect ratio" σ_o/d . The vertical dashed line is the maximum reduced density for the isotropic string model fluid. The isotropic and nematic phases are separated by a line of first-order transitions.

duction of *any* other length scale (e.g., the persistence length for semi-flexible polymers) must destroy this symmetry, and result in a discontinuous transition. The properties of this more realistic string model¹⁸ are that: (1) the pressure contains contributions through all orders in density; (2) the isotropic-nematic transition is weakly first order; and, (3) the nematic phase is the only equilibrium ordered phase. The reduced transition density decreases monotonically with increasing σ_o/d , in accord with physical intuition (Fig. 4). A rough connection to experiment can be made by recalling that denser than $\approx 70\%$ close packing, most liquids either crystallize or vitrify. Thus a thermotropic nematic transition in a dense melt must occur for density < 1 in Fig. 4. This corresponds to the criterion that a *minimum* aspect ratio of $\sigma_o/d \geq 5$ is required for thermotropic nematics, in accord with prior theories.^{6,7,19} As σ_o/d increases, the transition is eventually pushed into the semi-dilute regime, becoming very nearly the lyotropic transition of *thread* polymers.

We conclude by discussing extensions and limitations of anisotropic PRISM. Explicit attractive interchain interactions can be numerically appended to the theory. Backbone semi-flexibility or complete rigidity can be introduced through the appropriate $\omega(\mathbf{q})$.¹⁸ The exploration of system-specific effects on anisotropic fluid structure and thermodynamics is therefore possible. In fact, PRISM predictions for a rigid rod

model²⁰ are in qualitative agreement with all features of the classic Onsager theory.⁵ The theory also provides crucial static input to microscopic theories of dynamics,³ and a framework for treating other anisotropic systems such as confined fluids/thin films, stretched rubbers, and microphase separated block copolymers. One major limitation is our assumption of conformational ideality, although tools within the PRISM framework exist for including self-consistently the *intrachain* excluded volume.¹⁰ Chemically realistic models will require appropriate numerical modeling of the microscopic single-chain structure factor, $\omega(\mathbf{q})$, and the numerical determination of an anisotropic $c(\mathbf{r})$. The fundamental ideas proposed here should, however, remain valid.

ACKNOWLEDGMENT

This work was supported by the U.S. DOE Division of Materials Science Grant No. DEFG02-96 ER45539 through the University of Illinois Materials Research Laboratory.

- ¹For reviews, see: K. S. Schweizer and J. G. Curro, *Adv. Chem. Phys.* **98**, 1 (1997); *Adv. Polym. Sci.* **116**, 319 (1994).
- ²D. Chandler, in *Studies in Statistical Mechanics*, edited by E. W. Montroll and J. L. Lebowitz (North-Holland, Amsterdam, 1982), Vol. VIII, p. 274.
- ³K. S. Schweizer, M. Fuchs, G. Szamel, M. Guenza, and H. Tang, *Macromol. Theory Simul.* **6**, 1037 (1997).
- ⁴A. R. C. Baljon and M. O. Robbins, *MRS Bull.* **22**, 22 (1997).
- ⁵L. Onsager, *Proc. NY Acad. Sci.* **51**, 627 (1949).
- ⁶A. R. Khokhlov and A. N. Semenov, *Physica A* **108**, 546 (1981); **112**, 605 (1981).
- ⁷A. M. Gupta and S. F. Edwards, *J. Chem. Phys.* **98**, 1588 (1993).
- ⁸A. Tkachenko, *Physica A* **249**, 380 (1998).
- ⁹P. G. deGennes, *Scaling Concepts in Polymer Physics* (Cornell University Press, Ithaca, 1979).
- ¹⁰J. Melenkevitz, J. G. Curro, and K. S. Schweizer, *J. Chem. Phys.* **99**, 5571 (1993); C. J. Grayce, A. Yethiraj, and K. S. Schweizer, *ibid.*, **100**, 6857 (1994).
- ¹¹K. S. Schweizer and J. G. Curro, *Macromolecules* **21**, 3070 (1988); **21**, 3082 (1988); *Chem. Phys.* **149**, 105 (1990).
- ¹²J. P. Hansen and I. R. McDonald, *Theory of Simple Liquids* (Academic, London, 1986).
- ¹³A. P. Chatterjee and K. S. Schweizer, *Macromolecules* **31**, 2353 (1998).
- ¹⁴M. Fuchs, *Z. Phys. B* **103**, 521 (1997).
- ¹⁵D. Frenkel, Les Houches, Session L1, 1989, *Liquids, Freezing, and Glass Transition*, edited by J. P. Hansen, D. Levesque, and J. Zinn-Justin (Elsevier, B. V., 1991); G. J. Vroege and H. N. W. Lekkerkerker, *Rep. Prog. Phys.* **55**, 1241 (1992); P. G. deGennes, *Physics of Liquid Crystals* (Oxford University Press, Oxford, 1974).
- ¹⁶A. Yethiraj and H. Fynewever, *Mol. Phys.* **93**, 693 (1998).
- ¹⁷R. Eppenga and D. Frenkel, *Mol. Phys.* **52**, 1303 (1984).
- ¹⁸G. T. Pickett and K. S. Schweizer (unpublished).
- ¹⁹P. J. Flory, *Adv. Polym. Sci.* **59**, 1 (1984).
- ²⁰G. T. Pickett, A. P. Chatterjee, and K. S. Schweizer (unpublished).