Chain self-assembly and phase transitions in semiflexible polymer systems

James T. Kindt and William M. Gelbart
Department of Chemistry and Biochemistry, University of California at Los Angeles, Box 951569,
Los Angeles, California 90095-1569

We present a phenomenological theory of the interplay between linear self-assembly, isotropic attractions, and orientation-dependent repulsions in determining the phase behavior of particles that reversibly polymerize into semiflexible chains. Important examples of such linearly aggregating systems include many proteins, micelles, and dipolar fluids. Four classes of phase diagrams are predicted, featuring coexistence regions between two isotropic phases, an isotropic and a nematic phase, or two nematic phases. We map out the evolution of phase diagrams with changing values of the chain persistence length and of the ratio of intrachain bond energy to isotropic attractive energy, and relate the behavior in equilibrium polymer systems to that of fixed-length polymer systems. In both cases our theory predicts that over a narrow range of persistence lengths, increasing the chain length leads first to the disappearance and then to the recovery of the isotropic–isotropic transition; this behavior is explained by a simple scaling argument. © *2001 American Institute of Physics.* [DOI: 10.1063/1.1332810]

I. INTRODUCTION

The reversible self-assembly of molecules or colloidal particles into one-dimensional aggregates—linear chains—is a characteristic of a variety of systems. These include important biological macromolecules such as actin and tubulin,[1] amphiphiles that form cylindrical (''worm-like'') micelles,[2] dipolar particles in ferrofluids,[3] and electro- or magnetorheological fluids.[4] In all these systems, which can be described generally as equilibrium polymers, particles aggregate reversibly into chains having a polydisperse distribution of chain lengths, with an average length that increases as the system temperature is lowered (except in cases where bonding is entropically driven, when the reverse will hold) and as the total concentration of particles increases. One-dimensional self-assembly, involving only short-range aggregation forces, does not by itself lead to phase separation. Interactions between chains, however, can lead to interesting phase behavior in which coexisting phases may have very different average chain lengths. In the present investigation, our goal is to develop a phenomenological theory of equilibrium polymer systems in which short-ranged anisotropic bonding interactions lead to the formation of chains, isotropic attractive interactions between particles may lead to first-order condensation, and orientation-dependent excluded volume interactions between chains may result in nematic ordering.

Theories for the isotropic–isotropic (I–I′) or gas–liquid transitions in equilibrium polymers have been described in several studies. Blankschtein and co-workers[5] developed a model for self-assembly and condensation in one-dimensional micellar systems, providing a good account of experimental results. Jackson, Chapman, and Gubbins treated the problem as one case in their development of the theory of associating fluids.[6] Recently, Douglas, Dudowicz, and Freed described a model for phase transitions in small-molecule living polymer systems in which chain growth only

occurs at initiator sites.[7,8] All these models share some common features. One such feature is that when phase separation occurs the mean chain length is greater in the dense phase than in the dilute phase. Another is that the critical density for the condensation transition decreases as the ratio of chaining energy to isotropic attractive energy increases.

The phenomenon of nematic ordering in self-assembling systems has also been the focus of several theoretical treatments. Herzfeld and co-workers have considered the subject in the context of the reversible aggregation of biologically important proteins.[9–11] Matsuyama and Kato have considered the self-assembly of rod-like subunits.[12] Orientational ordering in solutions of worm-like micelles has also been addressed by several groups.[13–16] It is generally observed that self-assembly can couple dramatically to the isotropic–nematic (I–N) transition; in fact, when conformational entropy is neglected (that is, when the aggregates are assumed to be perfectly rigid), an ''explosion'' to infinitely long chains is seen in the coexisting nematic phase.

A comprehensive theory of equilibrium polymers requires as its basis a theory for fixed-length polymers capable of describing both monomers and short and long chains in a simple, consistent, and physically reasonable manner. For isotropic phases, the mean-field Flory–Huggins lattice theory satisfies these requirements. For nematic phases of semiflexible chains, no single existing theory is suitable in all respects. The theory of the isotropic–nematic transition in semiflexible polymers was first considered by Flory in 1956,[17] and developed more fully by Khokhlov and Semenov,[18] Ronca and Yoon,[19] and Odijk[20] in the 1980s. More recent progress in this area has included the treatment of blends and inhomogeneous mixtures of semiflexible polymers[21] and the application of microscopic liquid-state theory to anisotropic polymer systems.[22] With few exceptions, however, the interplay between isotropic–isotropic phase transitions and the onset of nematic ordering has not
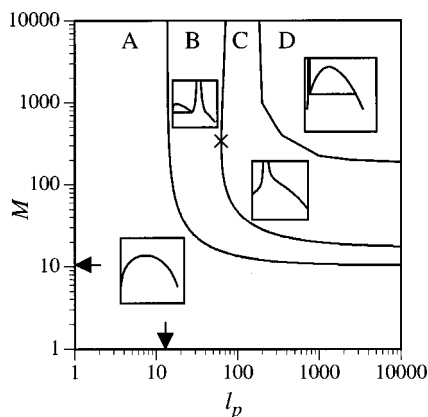
FIG. 1. ''Meta''-phase diagram illustrating evolution of phase behavior of semiflexible fixed-length chains as a function of chain length M and persistence length l_p. Insets show illustrative phase diagrams in the (φ, T) plane. Region (A), only I–I$'$ coexistence; (B), I–I$'$ and I–N; (C), only I–N; (D), I–N and N–N$'$.

been addressed systematically as a function of chain length. Here we present a theory of fixed-length semiflexible polymers, combining the steric free energy as developed from a lattice model by Flory and Ronca,[23] and the conformational free energy derived by Khokhlov and Semenov[24] for worm-like chains. The self-assembly aspect of the problem is then included explicitly and self-consistently for application to equilibrium polymer systems.

In the following section we describe the phenomenological theory used for the free energy of both fixed-length and equilibrium polymers. We then present and discuss our results in the form of traditional phase diagrams, showing examples of coexistence curves in the temperature-concentration plane, as well as ''meta''-phase diagrams that indicate what transitions will appear in the phase diagram for a given set of system properties. The ''meta''-phase diagram representing fixed-length systems (see Fig. 1) shows that for solutions of flexible enough or short enough chains that exert isotropic attractions on each other, the I–I$'$ phase separation is the *only* transition that appears; increasing chain length M or persistence length l_p leads to the appearance of a first-order I–N transition; the I–N transition grows and may eventually supersede the I–I$'$ transition with further increase in M and l_p; and for sufficiently long and rigid chains a nematic–nematic (N–N$'$) coexistence appears. We find a minor but interesting exception to these trends: over a narrow region of persistence lengths, increasing M first takes the system from a two-transition (I–I$'$ and I–N) phase diagram to one in which only the I–N transition appears, and then leads to the recovery of the I–I$'$ coexistence region. Similar trends hold for the evolution of phase diagrams in *equilibrium* semiflexible polymer systems, with the ratio of bond energy to isotropic attractive energy playing the role of M. We show that this analogy breaks down, however, in predicting the existence of the N–N$'$ transition in equilibrium systems, and that this is the result of the l_p dependence of the critical temperature of the N–N$'$ transition. This and other generic coexistence behaviors are rationalized via simple scaling arguments.

II. THEORY

A. Free energy of semiflexible polymers of fixed length

We require an expression for the free energy of a solution of semiflexible chains consisting of M contiguous spherical particles and with persistence length l_p (in units of the particle diameter), as a function of temperature, volume fraction φ, and bond orientational order distribution $n(\theta)$, with θ the angle between the bond vector and the nematic director. We make the standard approximation that the free energy can be partitioned into a steric (packing entropy) term, a rotational entropy term, a conformational entropy term, and an energy of isotropic attraction:

$$f(\varphi, \beta, Q; M, l_p) = f_{st}(\varphi, \beta, Q; M) + f_r(\varphi, \beta, Q; M) + f_c(\varphi, \beta, Q; M, l_p) + f_a(\varphi; \epsilon). \quad (1)$$

Here f represents the Helmholtz free energy per unit volume, and β is $1/k_B T$. Q is defined as

$$Q \equiv 1 - \frac{4}{\pi} \langle \sin \theta \rangle_{n(\theta)}, \quad (2)$$

and ϵ is the attraction energy associated with a pair of neighboring particles.

For the steric packing free energy, which includes the translational entropy of the chains, we use the Flory–Ronca[23] lattice expression as modified by Warner,[25]

$$\beta f_{st} = \frac{\varphi}{M} \ln \frac{\varphi}{M} + (1 - \varphi)\ln(1 - \varphi) - \left[1 - \varphi\left(\frac{M-1}{M}\right)Q \right] \times \ln\left[1 - \varphi\left(\frac{M-1}{M}\right)Q \right] + \varphi\left(\frac{M-1}{M}\right)(1 - Q). \quad (3)$$

Note that in an isotropic phase, $Q = 0$ and the steric term reduces to the standard Flory–Huggins form.[26]

At low densities and large values of M, use of the above expression for βf_{st} leads to qualitative (but not quantitative) agreement with the limiting (second virial coefficient) result of Onsager[27] for the I–N transition of long rods.[18] The benefits of using the lattice-based expression rather than the second virial expression as employed by Khokhlov and Semenov and by Odijk are two-fold. First, finite size effects are incorporated into the lattice expression in a clear and consistent way, so that for $M = 1$ (i.e., free monomers) the packing entropy is simply that of a lattice gas, and the dependence on Q (which is unphysical for spherical monomers) drops out. Similarly, in the limit of perfect alignment ($Q = 1$) the lattice expression gives the appropriate mean-field entropy for packing perfectly aligned rods of length M on a lattice, instead of yielding an M-independent value as in the Khokhlov–Semenov expression. Both of these properties are useful in describing the M-dependent behavior of fixed-length polymers, and will be essential for a consistent theory of equilibrium polymerization. For completeness we mention a third approach to the steric free energy, the lattice model of DiMarzio,[28] which is similar in spirit to the Flory–Ronca–Warner (FRW) model. It has the advantage of being better suited to weakly nematic phases, for which the FRW expression is not designed, and thereby allows treatment of second-

order I–N transitions such as are observed in two-dimensional systems.[29] In moderately to highly aligned nematic phases that result from first-order transitions in three dimensions, however, the FRW expression is based on a more appropriate description of the angle dependence of excluded volume, and is therefore better suited to our purposes.

Next we consider the contributions of rotational and conformational entropy. For rigid rods, the rotational free energy is given by

$$\beta f_r = \frac{\varphi}{M} \int n(\theta)\ln[4\pi n(\theta)]d\Omega, \qquad (4)$$

which reduces to zero for a uniform distribution of bond orientations, $n(\theta) = 1/4\pi$. To obtain tractable expressions for the rotational and conformational entropy of semiflexible chains in nematic phases, we make the simplifying approximation that the bond orientation distribution is the same for all bonds along the chain. (See work by Khokhlov and Semenov[30] for treatments that go beyond this approximation.) With this simplification, we use Eq. (4) to describe the decrease in rotational entropy associated with the ordering of the first bond in the chain. For a chain with nonzero bending rigidity, the second bond orientation is necessarily correlated with the first, so that realizing the distribution function $n(\theta)$ for the second and each subsequent bond in the nematic phase costs less free energy than orienting the first bond. Under the assumption of a single bond orientation distribution to describe all bonds along the chain, this free energy cost will be identical for each of the second and subsequent bonds, of which there are $M-2$. The value per bond will depend not only on $n(\theta)$ but also on $g(\alpha)$, the intrinsic probability distribution of finding the angle α between neighboring bonds on the chain (absent any chain–chain interactions) from which can be calculated a persistence length. A method for calculating the conformational free energy given $n(\theta)$ and $g(\alpha)$ was described by Khokhlov and Semenov[24] based on a result by Lifshitz,[31,32] but we shall simply use the continuum worm-like chain expression featured by Khokhlov and Semenov in which the contribution of $g(\alpha)$ is included only through a persistence length,

$$\beta f_c = \varphi \frac{M-2}{M}(2l_p)^{-1}\int [\nabla n(\theta)]^2/[4n(\theta)]d\Omega. \qquad (5)$$

While in many systems the persistence length will have a temperature dependence, for simplicity we assume here that it is independent of temperature.

In the numerical implementation of the theory we assume that the bond orientational order distribution $n(\theta)$ is Gaussian. For a range of Gaussian functions, we compute Q, and the integrals in Eqs. (4) and (5). The Gaussian function that minimizes the sum of the steric, rotational, and conformational terms in the free energy can then be used to calculate the equilibrium value of the nematic order parameter $\eta = \langle P_2(\cos\theta)\rangle_n$. For fixed M and l_p, each of the first three terms in Eq. (1) is thus obtained as an explicit function of φ and β.

Finally, the energetic contribution to the free energy is given by the standard Bragg–Williams approximation for the isotropic attraction of all monomers,

$$\beta f_a = \frac{1}{2}\beta c\epsilon\varphi(1-\varphi) \equiv 2\beta\epsilon^*\varphi(1-\varphi), \qquad (6)$$

where ϵ is the pairwise energy of isotropic attraction and c is the coordination number in a lattice model. For later convenience we have defined $\epsilon^* \equiv c\epsilon/4$, such that $\beta\epsilon^* = 1$ at the critical temperature of the lattice gas of unconnected monomers.

In the interest of simplicity, we do not include a Maier–Saupe term[33] coupling the attractive potential to orientational order; thus, we neglect the contribution of anisotropic attractions, which can be important to the stability of the nematic phase in real systems. Furthermore, we omit from consideration phases with long-ranged translational order, such as the hexagonal phase, which can narrow or supersede the region of stability of the nematic phase at high volume fraction.[34,35]

B. Equilibrium (linearly self-assembling) polymers

To treat *equilibrium* (self-assembling) polymer solutions, we continue to use the above fixed-length chain theory as a basis. Note that where M enters the free energy in the above section it appears through its reciprocal as a measure of the number of independent chains, or equivalently one-half the number of chain ends. In a polydisperse equilibrium system, therefore, the natural definition of the mean chain length is

$$\bar{M} = \left(\sum_{i=1}^{\infty} i\varphi_i \Big/ \sum_{i=1}^{\infty} \varphi_i\right) = \varphi \Big/ \sum_{i=1}^{\infty} \varphi_i, \qquad (7)$$

where φ_i gives the number density of chains of length i. Each term described in Sec. II A will contribute the same amount to the free energy, within the set of approximations already discussed, for a polydisperse solution of given $\bar{M}$ as for a monodisperse solution of the same M. The exception is that free monomers (i.e., chains of length 1) should not contribute to rotational or conformational entropy terms. This is a minor problem, however, as it will serve only to further destabilize orientationally ordered phases that are rich in free monomers, which will already be unstable with respect to the isotropic phase.

In writing the free energy density of an equilibrium polymer solution we can therefore simply take Eq. (1) for fixed-length polymers, add the free energy of bond formation and the entropy associated with polydispersity, and replace the fixed M with the mean chain length $\bar{M}$, which can now respond to the system conditions to minimize the overall free energy.

We will assume that all bonds have the same dissociation energy U and dissociation entropy S, independent of chain length or position, and that both will be positive. (The theoretical treatment that follows would be identical for the equally important case in which both U and S are negative. The behavior of the resulting phase diagrams can be significantly different, however.)[8–11] The free energy density associated with the bonds then follows simply from multiplying the density of bonds by the free energy per bond,

$$\beta f_b = [\varphi(\bar{M}-1)/\bar{M}](-\beta U + S/k_B). \qquad (8)$$

An identical term could be included in the fixed chain length case, but would only contribute a term linear in φ to the free

energy and would not affect the phase behavior. In the equilibrium system, on the other hand, the mean chain length $\bar{M}$ will adapt to the temperature and volume fraction conditions to minimize the solution free energy, so that the bonding free energy is not linear in φ. The bending rigidity (and therefore the persistence length) is one contribution to the dissociation entropy S, along with stretching rigidity and constraints on internal degrees of freedom of the monomer. For simplicity's sake, however, we will set $S=4k_B$ independent of either l_p or U. This value of S is sufficient to ensure that the system is essentially completely dissociated at all volume fractions if $U=0$.

The final contribution to the free energy of an equilibrium polymer system is the gain in entropy of mixing from having a polydisperse distribution of chain lengths rather than a monodisperse distribution at the same value of $\bar{M}$:

$$\beta f_{\text{poly}}=\sum_{i=1} \varphi_i(\ln \varphi_i-1)-\left[\frac{\varphi}{\bar{M}}\left(\ln \frac{\varphi}{\bar{M}}-1\right)\right], \qquad (9)$$

where φ_i is again the number density of chains of length i. As discussed above, $\bar{M}$ alone, and not any other moment of the length distribution, enters into the steric, conformational, rotational, and bonding terms outlined above. We can therefore choose the distribution that minimizes f_{poly} for any choice of $\bar{M}$. The solution is an exponential distribution, as is the case in all ideal one-dimensional self-assembling systems, such that the number density of a given length chain is

$$\varphi_i=\varphi \bar{M}^{-(i+1)}(\bar{M}-1)^{i-1}. \qquad (10)$$

It can be verified that this distribution satisfies the definition in Eq. (7). Using this optimal distribution in Eq. (9) gives the final term in the free energy density,

$$\beta f_{\text{poly}}=\varphi \frac{\bar{M}-1}{\bar{M}} \ln \frac{\bar{M}-1}{\bar{M}}-\frac{\varphi}{\bar{M}} \ln \bar{M}. \qquad (11)$$

Minimization of the free energy with respect to $\bar{M}$ gives the following exact relation for an isotropic system:

$$\bar{M}=\tfrac{1}{2}+\tfrac{1}{2}\sqrt{1+4\varphi \exp(\beta U-S/k_B)}. \qquad (12)$$

In the limit of large $\bar{M}$, this becomes $\varphi^{1/2} \exp[(\beta U -S/k_B)/2]$, as is familiar from the mean-field treatment of one-dimensional micellization.[36] In an ordered phase, $\bar{M}$ must be optimized numerically,[37] but at large $\bar{M}$ and fixed Q its φ dependence is $[\varphi/(1-Q\varphi)]^{1/2}$.

III. RESULTS AND DISCUSSION

A. Phase behavior of chains of fixed length

Our goal in this section is to understand the phase diagrams of solutions of monodisperse chains of fixed length M and persistence length l_p that experience an isotropic attraction between all pairs of monomers. The ''meta''-phase diagram dividing the (M,l_p) plane into regions that yield a particular topology of phase diagram is shown in Fig. 1. We note that the main features of Fig. 1 could be inferred from the work of Khokhlov and Semenov for the two limiting
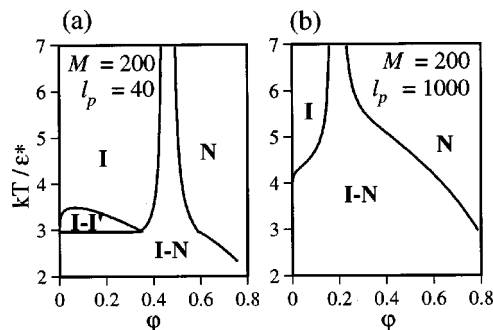

FIG. 2. Phase diagrams of coexistence curves for chains of length 200 and persistence length 40 [panel (a)] and 1000 [panel (b)].

cases where either l_p or M is infinite,[38] but there are important new features that appear when the full ranges of both these physical variables are considered.

For systems of chains with fixed length M, the free energy of an isotropic ($Q=0$) system in the model presented above is simply the Flory–Huggins free energy. At this level of approximation, persistence length does not affect the I–I′ transition. We summarize here the corresponding well-known results: under poor solvent conditions [i.e., positive values of ϵ^* in Eq. (7)] the isotropic phase will develop a critical point for isotropic–isotropic (I–I′) phase separation at $\varphi_c=(1+\sqrt{M})^{-1}$ and $T_c=4\epsilon^*M\varphi_c^2/k_B$. Note that as M is increased, the critical volume fraction φ_c decreases from 0.5 for monomers to $1/\sqrt{M}$ for long chains, while the critical temperature increases from $k_BT_c=\epsilon^*$ for monomers to $k_BT_c\approx 4\epsilon^*$ in the limit of large M.

For sufficiently large M and l_p, the free energy densities of the isotropic and nematic branches will cross at some volume fraction φ_N,

$$f(\varphi_N,\eta=0;M,l_p)=f(\varphi_N,\eta_N>0;M,l_p), \qquad (13)$$

where η_N lies at the local minimum in f with respect to η. (Note that η does not enter the free energy directly, but is derived from the Gaussian bond orientation distribution that is selected to minimize f.) In region (A) of Fig. 1, φ_N does not exist [i.e., there is no $\varphi_N<1$ for which Eq. (13) is satisfied], and the only allowed phase transition is the I–I′ transition described by Flory–Huggins theory. The borders of region (A) in the limits of high M and high l_p indicate that for persistence lengths below 13.5 and for chain lengths below 10.3 (see arrows on axes) our theory does not predict a stable nematic phase.

When φ_N does exist, as it does for systems whose M and l_p values lie in regions (B), (C), and (D) on Fig. 1, the system will phase separate to give coexistence between an isotropic phase less concentrated than φ_N and a nematic phase of higher concentration. As shown in both panels of Fig. 2, the first-order isotropic–nematic (I–N) coexistence region containing φ_N is a narrow ''chimney'' in the high-temperature limit ($T\gg T_c$) but broadens as the temperature is lowered to values where the isotropic attraction becomes significant. If the Flory–Huggins critical volume fraction φ_c falls in the pure isotropic phase at T_c, as it does in the left panel of Fig. 2, then for some range of temperatures there

will be two successive phase transitions as φ is increased: first an isotropic I–I′ phase separation, and then a first-order nematic ordering transition at higher volume fraction. As the temperature is lowered further, both coexistence regions broaden until they intersect and merge at a triple point into a very broad I–N coexistence region. All combinations of chain length and persistence length that fall in region (B) of Fig. 1 will have phase diagrams qualitatively similar to panel Fig. 2(a). If φ_c falls in the coexistence region (or within the pure nematic phase) at T_c, however, the I–I′ transition disappears entirely from the equilibrium phase diagram because one or both of the coexisting isotropic phases will be unstable with respect to I–N phase separation or formation of a uniform nematic phase. (Note that this may be the case even when $\varphi_c < \varphi_N$ if the I–N coexistence region is broad enough.) This leads to a phase diagram of the type shown in the Fig. 2(b), a type that is shared for all systems represented in region (C) of Fig. 1.

A subtle yet curious feature of region (C) in Fig. 1 is that it has an extremum with respect to persistence length at a finite value of chain length, marked on the graph by a "×." The boundary between regions (B) and (C) crosses a narrow range of persistence lengths (between roughly 63 and 76) twice. For any of these persistence lengths, increasing M leads first to the loss of the I–I′ transition and then to its recovery at still higher values of M. This feature can be understood as a result of the scaling behavior of φ_c and φ_N as functions of M. From Flory–Huggins theory, we have $\varphi_c \approx 1/\sqrt{M}$. In the limit where semiflexible chains behave as rigid rods ($l_p \gg M$), the current theory captures Onsager-type behavior, i.e., φ_N scales as M^{-1}. φ_N is therefore a more rapidly decreasing function of M than is φ_c, and may become smaller than φ_c, which is a sufficient (though not a necessary) criterion for the disappearance of the I–I′ transition. If M is increased significantly beyond l_p, however, the stability of the nematic phase becomes independent of M, while the critical density for isotropic phase separation continues to decrease as $1/\sqrt{M}$. Accordingly, for still higher M values we have once again $\varphi_c < \varphi_N$, and the I–I′ transition may reappear. Because of the broadening of the I–N coexistence region by isotropic attraction, simple comparison of φ_c and φ_N is not sufficient to determine whether the I–I′ transition is superseded by the I–N transition; for this reason, the "reentrant" behavior only occurs in marginal cases, and above a persistence length of about 76 the I–N transition is the only one observed even in the limit of infinite chain length.

To describe this reentrance in more physical terms, we consider the origin of the two phase transitions. The I–I′ coexistence depends on a balance between translational entropy and attractive energy, while the I–N coexistence comes from a balance between packing entropy and orientational (including rotational and conformational) entropy. At low M, the gain in packing entropy only overtakes the loss in rotational entropy at large φ, after the I–I′ condensation has been played out; at medium M, both balances come into play at intermediate φ, so that only a single broad I–N transition results; and at high M the translational entropy contribution is small enough that I–I′ condensation occurs at low φ, be-

fore the packing forces that drive the I–N transition come into play.

In region (D) of Fig. 1, corresponding to yet higher values of both M and l_p, two phase transitions once again appear in the phase diagram: a narrow I–N transition at low volume fraction followed by a N–N′ condensation. The N–N′ transition was first predicted by Flory to appear for long rigid rods with isotropic attractions.[39] It also appears in the Khokhlov–Semenov theory of long semiflexible polymers above a critical persistence length,[38] and has been observed in experimental polymer systems.[40,41] To our knowledge, a general discussion of the scaling of the critical point has not appeared in the literature, beyond the observation by Flory[39] that the critical temperature (in units of ϵ^*, the energy of attraction between monomers) should increase with nematic ordering as mixing becomes closer to ideal. Numerical results from the current theory suggest that, in the limit of long chains, the critical volume fraction reaches a constant nonzero value near $\varphi = 0.2$ at sufficiently high persistence length, while the critical temperature scales as $l_p^{1/3}$. This result can be interpreted within the framework laid out by Odijk for the I–N transition in long semiflexible polymers.[20] Assuming a distribution of bond orientational order proportional to $\exp(-\alpha\theta^2/2)$ with α large, the conformational energy density per chain scales as $\varphi\alpha/4l_p$ while the packing entropy scales as $\alpha^{-1/2}f_{st}(\varphi)$, where $f_{st}(\varphi)$ is simply φ^2 in the second virial approximation, but in general will include higher-order terms. Optimizing the sum of these terms with respect to α gives the result that a factor of $l_p^{-1/3}$ factors out of the free energy density

$$\beta f(\varphi; l_p) = \tfrac{1}{2} l_p^{-1/3} \varphi^{1/3} f_{st}^{2/3}(\varphi) = l_p^{-1/3} f_0(\varphi). \tag{14}$$

The entropic contributions to the free energy therefore scale as the inverse cube root of persistence length; the energy required to overcome the steric and conformational barriers to condensation will have the same scaling behavior, so that the critical temperature reduced by this energy of isotropic attraction must scale as $l_p^{1/3}$. The critical volume fraction is determined solely by the position of the inflection point in $f_0(\varphi)$, and is therefore independent of persistence length.

B. Equilibrium (self-assembling) polymer phase behavior

The phase diagram of an equilibrium polymer depends on the behavior of the full range of chain lengths, as the system's composition (assuming positive bond dissociation energy U and entropy S) will evolve from predominantly free monomers at temperatures higher than U/k_B to long chains at low temperature. In systems with isotropic attractions among all solute particles, the ratio $U^* = U/\epsilon^*$ determines the extent of aggregation, and therefore the mean chain length, at the critical temperature and volume fraction for isotropic phase separation. In the limit of high U^* an equilibrium polymer will be essentially completely polymerized near critical conditions. Its behavior under these circumstance will therefore be indistinguishable from that of a fixed-length polymer in the high M limit. Before this limit is reached, however, the phase behavior is influenced by the
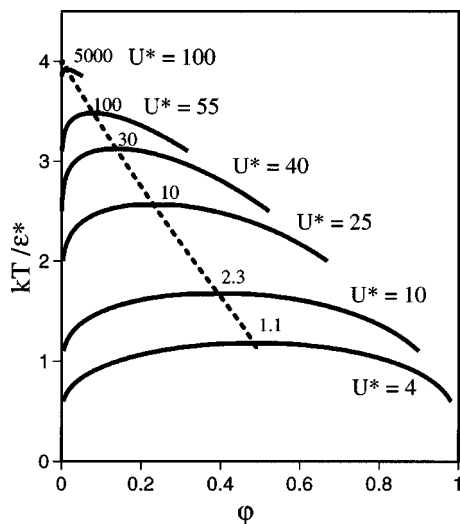
FIG. 3. Critical behavior of flexible equilibrium polymers. Solid lines are coexistence curves at selected values of $U^* = U/\epsilon^*$. Each is labeled with the value of the mean chain length $\bar{M}$ at the critical point. Dashes show curve of critical temperature vs. critical volume fraction.
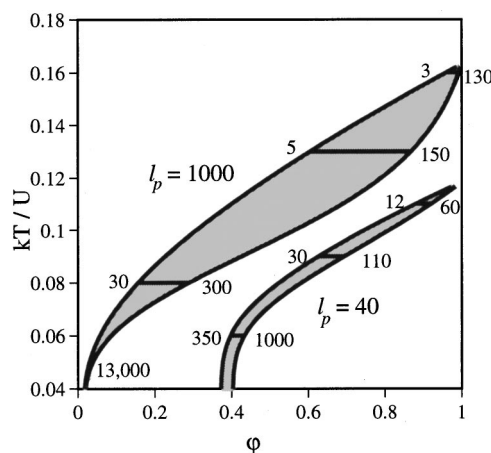

FIG. 4. I–N coexistence curves for equilibrium polymers without isotropic attractions. Upper pair, $l_p = 1000$; lower pair, $l_p = 40$. Labels correspond to mean chain length $\bar{M}$ at coexistence. Gray areas are two-phase regions.

fact that in an equilibrium polymer system coexisting phases need not and will not have the same mean chain length $\bar{M}$. As others have observed using related models,[6,8,42] and as shown for the current model in Fig. 3, as U^* becomes large the critical temperature $k_B T_c$ in units of ϵ^* increases up to a limiting value (here, as in the Flory–Huggins theory, four) and the critical volume fraction decreases. In this model, unlike that in the living-polymer-with-initiator theory of Dudowicz et al.,[8] there is always an I–I' coexistence as long as ϵ^* is positive, even in the limit of high U^*. [It can further be shown that in this limit the critical volume fraction is proportional to $\exp(-U^*/16)$.] This is a necessary consequence of the equivalence of high U^* equilibrium systems and high-M fixed-length systems discussed above, given that phase separation occurs in the Flory–Huggins model even in the limit of infinite chain length. In Fig. 3, coexistence curves are shown for several values of U^* and are labeled by their mean chain length $\bar{M}$ at the critical temperature and density; below the critical temperature, the value of $\bar{M}$ will be lower than the critical value in the dilute phase and higher in the concentrated phase. The result is that near the critical temperature there will be coexistence between phases consisting of chains of only slightly different length, while at very low temperatures the dilute phase will always consist primarily of free monomers in coexistence with a phase of long chains.

The I–N transition in linearly self-assembling systems has been addressed by several groups, in the contexts of self-assembling proteins[9–11] and worm-like micellar solutions.[13–16] Here we review the main features of the transition predicted by our current theory in the absence of attractive interactions (i.e., $\epsilon^* = 0$), which correspond closely to those described by van der Schoot and Cates.[16] Unlike fixed-length semiflexible polymers, equilibrium semiflexible polymers do not have an I–N coexistence "chimney" persisting to infinite temperature. This is because at high temperature

$\bar{M}$ becomes too low to support a stable nematic phase even at high volume fraction. Therefore, the chimney curves over to terminate at $\varphi = 1$; similar "bent chimney" phase diagrams are observed in models of fixed-length polymers in which the persistence length, instead of the chain length, is assumed to decrease with increasing temperature.[43] The I–N transition for equilibrium polymers with $\epsilon^* = 0$ is shown in Fig. 4 for two values of the persistence length. Values of $\bar{M}$ for the two phases at coexistence are labeled at representative points on the graph. The nematic phase has a significantly larger mean chain length than the isotropic phase, even when the density difference is very small; the orientational order-dependent term in Eq. (1), which stabilizes the nematic phase, favors long chains. The coexistence region is broadened, relative to the fixed-chain case for the same l_p without isotropic attractions, due to the difference in $\bar{M}$ in the isotropic and nematic phases. In the case of the stiffer chains ($l_p = 1000$) this gives a rather broad coexistence region at intermediate temperatures. This is a milder manifestation of the extreme result obtained by setting the persistence length to infinity, which (in this as in previous work)[14,15] leads to perfect nematic order, infinite chain length, and $\varphi = 1$ in the coexisting nematic phase. In the low-temperature limit, however, for finite l_p, the I–N transition approaches the same narrow coexistence region as the fixed-chain system of the same persistence length in the limit of infinite M (since $\bar{M} \gg l_p$ for sufficiently low temperature).

Incorporating both isotropic attractions and semiflexibility into the self-assembling polymer model, we can once again construct a "meta"-phase diagram (Fig. 5) akin to Fig. 1, in which U^* replaces M on the ordinate axis. In region (A), there is only an I–I' transition because the chain flexibility is too high to allow for a stable nematic phase. The minimum persistence length for the existence of a stable nematic phase is independent of U^* and is determined by the high-M limit of the fixed-length system, which the equilibrium system will achieve at low temperature.

Region (B) on Fig. 5 represents systems in which both I–I' and I–N coexistences appear in the phase diagram. At
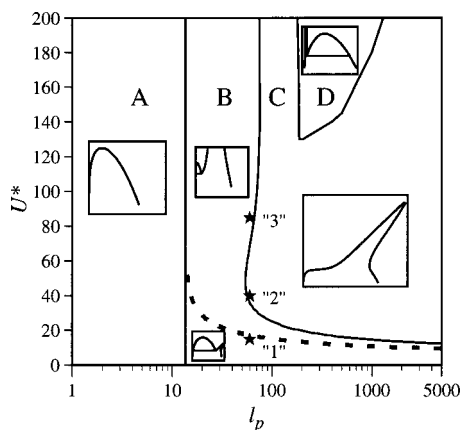
FIG. 5. ''Meta''-phase diagram classifying phase diagrams of semiflexible equilibrium polymer systems as a function of U^* and l_p. Representative phase diagrams are shown in insets. Regions are defined as in Fig. 1, with (B) subdivided by dotted line into regimes based on whether the I–I′ (below) or I–N (above) transition appears at higher temperature. Points 1, 2, and 3 correspond to phase diagrams shown in Fig. 6.

FIG. 6. Phase diagrams showing I–I′ and ''bent chimney'' I–N coexistence curves at a constant persistence length, $l_p=60$, for $U^*=85$ (solid curve ''3''), $U^*=40$ (dotted curve ''2''), and $U^*=15$ (dashed curve ''1''). For the $U^*=40$ curve, the I–I′ curve shown is metastable with respect to I–N phase separation. Curves are labeled with values of $\bar{M}$ in coexisting phases and at critical points.

low values of U^* (where $U \ll \epsilon^*$) there is no significant chain formation at the critical temperature for I–I′ phase separation, so there is no possibility of a nematic phase forming until much lower temperatures are reached. At high values of U^*, the opposite holds, so that polymerization will lead to a ''bent chimney'' I–N coexistence region at temperatures at which isotropic attractions are unimportant, well above the development of an I–I′ coexistence region. The dotted line cutting through region (B) represents the boundary between these two regimes, at which the nematic phase first appears at the critical temperature.

The disappearance of the I–I′ transition [marked by the boundary between regions (B) and (C) on both Fig. 1 and Fig. 5] was interpreted earlier, in Sec. III A, for the fixed-length case in terms of the relative positions of φ_c and φ_N. For equilibrium polymers, as illustrated in Fig. 4, φ_N shifts with temperature as mean chain lengths increase. Increasing U^* leads to increased chain length at T_c (which is of the order ϵ^*/k_B) and so the dependence of the loss of the I–I′ transition on M and l_p, outlined in Sec. III A, is qualitatively reflected in the dependence on U^* and l_p in the equilibrium case. Because both phase transitions are coupled to the mean chain length $\bar{M}$, the details are not identical to the fixed-length case, except in the limit of high U^*. The minimum persistence length (55) at which the I–I′ transition disappears is lower in the equilibrium case than in the fixed-length case (63), leading to a more pronounced protrusion in the boundary between regions (B) and (C). This can be understood by the broadening of the I–N transition through coupling to $\bar{M}$, as discussed earlier.

In illustration of the loss and recovery of the I–I′ transition, Fig. 6 shows phase diagrams representing three points (''1'', ''2'', and ''3'') on Fig. 5 on a line of constant l_p. In case 1, corresponding to a low value of U^*, the I–I′ critical point occurs at a temperature at which only short chains form. A nematic phase does not appear until longer chains are formed at lower temperatures. In case 2, at an intermediate value of U^*, chains of roughly the same length as the
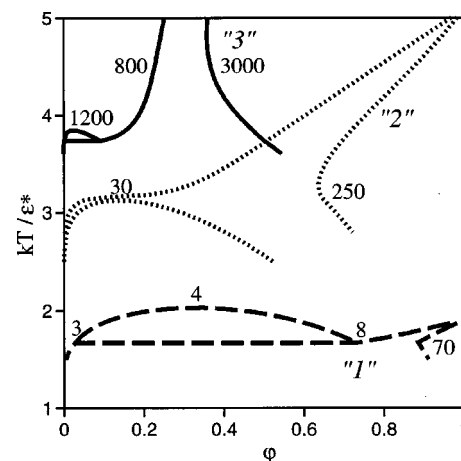
persistence length are present at the critical point of what is now a metastable I–I′ coexistence. In case 3, U^* is sufficiently high that the mean chain length is many times the persistence length at the critical temperature, so that the chains condense at low volume fraction and do not form an ordered phase until higher volume fraction.

Finally, a nematic–nematic coexistence appears in the phase diagram of systems whose properties lie in region (D) of Fig. 5. The striking feature of this region is that the minimum value of U^* required to achieve an N–N′ coexistence region increases with increasing persistence length. As mentioned in the fixed-length case, the critical temperature for the N–N′ transition scales not only with ϵ^* but also with $l_p^{1/3}$. In order to ensure that long chains (whose presence is necessary to stabilize the nematic phase) are in fact present at this critical point, $U^*/l_p^{1/3}$ and not just U^* must therefore be large; accordingly, the region D is limited on the right by a curve which increases without bound, roughly as $l_p^{1/3}$. One implication is that no finite value of U^* can lead to a phase diagram with the N–N′ transition in the rigid-rod limit (l_p infinite). This fits with the previous observation that the stable nematic phase of particles self-assembling into rigid rods is always at $\varphi=1$, which precludes the existence of two coexisting nematic phases in this system.

The present theory was intended to be as idealized as possible in its treatment of self-assembly. One important simplifying assumption is that chains have no junctions or branches. The introduction of junctions between one-dimensional self-assembled structures leads to network-forming systems with rich phase behaviors, analogous to microemulsions.[44] Another assumption made is that there is a well-defined separation between *intra*-chain and *inter*-chain interactions. The dipolar sphere model fluids represent an important class of systems that exhibit a type of equilibrium polymerization in which this assumption does not hold. The electrostatic potential that favors chain formation is long-ranged and therefore also contributes to attractions and repulsions between chains. Whether the electrostatic chain–

J. Chem. Phys., Vol. 114, No. 3, 15 January 2001

Chain self-assembly and phase transitions 1439

chain interactions are strong enough to drive an I–I′ transition is an on-going subject of computational[13,45–48] and theoretical[42,49–51] inquiry and controversy. Furthermore, while long-ranged electrostatic interactions are undoubtedly involved in the formation of a ferroelectric nematic phase of dipolar chains observed in simulations,[52] the contributions of electrostatic and excluded-volume interactions to the stability of this phase are not clear. The simple theory presented here should prove a useful starting point for constructing theories to describe self-assembly and phase behaviors in these more complicated scenarios.

IV. CONCLUSIONS

We have presented a phenomenological statistical thermodynamic theory for fluids of chains consisting of an arbitrary number of spherical monomers with an arbitrary persistence length and magnitude of isotropic attractions, considering both fixed chain-length and equilibrium polymer systems. The simple models have allowed us to merge theories of isotropic phase separation, nematic ordering in semiflexible polymers, and linear self-assembly. The same trends in the phase diagrams are generally observed for increasing the chain length (in fixed-length systems) and increasing the ratio U^* of chaining energy to isotropic attractive energy (in equilibrium systems). This rule does not hold for the appearance of the N–N′ transition, which has a critical temperature that increases not simply with the isotropic attractive energy but also with increasing persistence length. The theory predicts four classes of phase diagram for polymers in poor solvent, in which increasing chain length (or U^*, the ratio of chaining energy to isotropic attractive energy, in the equilibrium polymer case) and persistence length lead first to the addition of an I–N transition to the I–I′ transition, then to the disappearance of the I–I′ transition, and finally to the appearance of an N–N′ condensation. An interesting exception to this trend occurs over a narrow range of persistence lengths for which the I–I′ transition is first lost and then recovered as chain length or U^* is increased. This behavior can be understood through consideration of the scaling with chain length of the critical volume fractions of the I–I′ and I–N transitions. Finally, we anticipate that this theory will provide a useful basis to extend to the study of more complex systems such as branched equilibrium polymers and dipolar model fluids.

Note added in proof: Tlusty and Safran[53] have recently presented a theory describing how phase separation in dipolar fluids may arise from the formation of a network structure containing three-way junctions. A simple means to introduce junctions into the present theory is via a free energy term scaling as $\varphi^2/\bar{M}$, representing a mean-field attraction between chain ends and chain interiors. This leads to phase behavior qualitatively similar to the results of Tlusty and Safran.

[1] J. Herzfeld, Acc. Chem. Res. **29**, 31 (1996).
[2] *Micelles, Membranes, Microemulsions, and Monolayers*, edited by W. M. Gelbart, A. Ben-Shaul, and D. Roux (Springer, Berlin, 1994).
[3] M. J. Stevens and G. S. Grest, Phys. Rev. E **51**, 5976 (1995).
[4] E. M. Furst and A. P. Gast, Phys. Rev. Lett. **82**, 4130 (1999).
[5] D. Blankschtein, G. M. Thurston, and G. B. Benedek, Phys. Rev. Lett. **54**, 955 (1985).
[6] G. Jackson, W. G. Chapman, and K. E. Gubbins, Mol. Phys. **65**, 1 (1988).
[7] J. Dudowicz, K. F. Freed, and J. F. Douglas, J. Chem. Phys. **111**, 7116 (1999).
[8] J. Dudowicz, K. F. Freed, and J. F. Douglas, J. Chem. Phys. **112**, 1002 (2000).
[9] R. W. Briehl and J. Herzfeld, Proc. Natl. Acad. Sci. USA **76**, 2740 (1979).
[10] J. Herzfeld and R. W. Briehl, Macromolecules **14**, 397 (1981).
[11] E. M. Kramer and J. Herzfeld, Phys. Rev. E **58**, 5934 (1998).
[12] A. Matsuyama and T. Kato, J. Phys. Soc. Jpn. **67**, 204 (1998).
[13] W. E. McMullen, W. M. Gelbart, and A. Ben-Shaul, J. Chem. Phys. **82**, 5616 (1985).
[14] T. Odijk, J. Phys. (Paris) **48**, 125 (1987).
[15] P. van der Schoot and M. E. Cates, Langmuir **10**, 670 (1994).
[16] P. van der Schoot and M. E. Cates, Europhys. Lett. **25**, 515 (1994).
[17] P. J. Flory, Proc. R. Soc. London, Ser. A **234**, 60 (1956).
[18] A. N. Semenov and A. R. Khokhlov, Sov. Phys. Usp. **31**, 988 (1988).
[19] G. Ronca and D. Y. Yoon, J. Chem. Phys. **83**, 373 (1985).
[20] T. Odijk, Macromolecules **19**, 2313 (1986).
[21] A. J. Liu and G. H. Fredrickson, Macromolecules **26**, 2817 (1993).
[22] G. T. Pickett and K. S. Schweizer, J. Chem. Phys. **112**, 4881 (2000).
[23] P. J. Flory and G. Ronca, Mol. Cryst. Liq. Cryst. **54**, 289 (1979).
[24] A. R. Khokhlov and A. N. Semenov, Physica A **108**, 546 (1981).
[25] M. Warner, Mol. Cryst. Liq. Cryst. **80**, 67 (1982).
[26] P. J. Flory, J. Chem. Phys. **10**, 51 (1942); M. L. Huggins, Ann. N.Y. Acad. Sci. **43**, 1 (1942).
[27] L. Onsager, Ann. N.Y. Acad. Sci. **51**, 627 (1949).
[28] E. A. DiMarzio, J. Chem. Phys. **35**, 658 (1961).
[29] M. Dijkstra and D. Frenkel, Phys. Rev. E **50**, 349 (1994).
[30] A. R. Khokhlov and A. N. Semenov, Physica A **112**, 605 (1982).
[31] I. M. Lifshitz, Sov. Phys. JETP **28**, 1280 (1969).
[32] I. M. Lifshitz, A. Yu. Grosberg, and A. R. Khokhlov, Rev. Mod. Phys. **50**, 683 (1978).
[33] W. Maier and A. Saupe, Z. Naturforsch. **149**, 882 (1959).
[34] H. Hoffmann, G. Oetter, and B. Schwandner, Prog. Colloid Polym. Sci. **73**, 95 (1987).
[35] P. van der Schoot, J. Chem. Phys. **104**, 1130 (1996).
[36] J. N. Israelachvili, D. J. Mitchell, and B. W. Ninham, J. Chem. Soc., Faraday Trans. 1 **72**, 1525 (1976).
[37] The use of Eq. (5) for the conformational free energy will lead to a clearly unphysical free energy minimum for nematic phases with $\bar{M}<2$ that should be discarded; this is a consequence of the inapplicability of the continuum-derived expressions of Eq. (5) to chains of small numbers of monomers.
[38] A. R. Khokhlov and A. N. Semenov, J. Stat. Phys. **38**, 161 (1985).
[39] P. J. Flory, Proc. R. Soc. London, Ser. A **234**, 73 (1956).
[40] P. S. Russo and W. G. Miller, Macromolecules **16**, 1690 (1983).
[41] J. C. Horton, A. M. Donald, and A. Hill, Nature (London) **346**, 44 (1990).
[42] J. M. Tavares, M. M. Telo da Gama, and M. A. Osipov, Phys. Rev. E **56**, 6252 (1997).
[43] A. Matsuyama, Y. Sumikawa, and T. Kato, J. Chem. Phys. **107**, 4711 (1997).
[44] T. Tlusty, S. A. Safran, and R. Strey, Phys. Rev. Lett. **84**, 1244 (2000).
[45] J.-M. Caillol, J. Chem. Phys. **98**, 9835 (1993).
[46] J. J. Weis and D. Levesque, Phys. Rev. Lett. **71**, 2729 (1993).
[47] M. E. van Leeuwen and B. Smit, Phys. Rev. Lett. **71**, 3991 (1993).
[48] P. J. Camp, J. C. Sheeley, and G. N. Patey, Phys. Rev. Lett. **84**, 115 (2000).
[49] R. P. Sear, Phys. Rev. Lett. **76**, 2310 (1996).
[50] R. van Roij, Phys. Rev. Lett. **76**, 3348 (1996).
[51] Y. Levin, Phys. Rev. Lett. **83**, 1159 (1999).
[52] D. Wei and G. N. Patey, Phys. Rev. A **46**, 7783 (1992).
[53] T. Tlusty and S. Safran, Science **290**, 1328 (2000).