Coupling between Thermodynamics and Conformations in Wormlike Polymer Nematics

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Received May 25, 1995; Revised Manuscript Received August 21, 1995[⊗]

ABSTRACT: We adapt the Gupta–Edwards theory of wormlike main-chain nematics to the case of finite-length polymers. The thermodynamic parameters of lyotropic and thermotropic phase transitions are obtained for arbitrary polymer lengths and we find that the crossover between long- and short-chain regimes takes place for polymers of relatively low chain length (shorter than the persistence length). We show that this is related to the fact that in the nematic phase there are two qualitatively different length scales, which are analogous to the persistence length in the isotropic phase. One scale, $\xi_\perp$, defines the contour length associated with independent fluctuations of chain segments about the nematic director and decreases with the nematic field. Another scale, $\xi_\parallel$, determines the correlation length of the longitudinal component of the tangent vector. This size is larger than $\xi_\perp$ and increases exponentially with the strength of the nematic interaction. This allows one to identify an intermediate range of chain length $\xi_\perp \ll L \ll \xi_\parallel$, in which the isotropic–nematic phase transition is determined by the long-chain limit but the single-molecule conformation is practically a straight line. The implications of our results for the crystallization of short polymers, such as normal alkanes, are discussed.

1. Introduction

Molecules which form orientationally ordered mesophases (liquid crystals) can be broadly classified into two categories, depending on the chemical structure of their microscopic costituents: rigid anisotropic molecules[1] and high molecular weight semiflexible polymers[2] (here we will be concerned only with main-chain nematics). On the theoretical side, there exists a rigorous theory due to Onsager[3] of the isotropic–nematic transition in dilute solutions of long rigid-rod polymers (lyotropic nematics). More recently, the Onsager approach has been adapted to semiflexible polymers by Semenov and Khokhlov.[2] A phenomenological mean-field description of small-molecule thermotropic nematics has been developed by Maier and Saupe[4] and later generalized to the case of semiflexible polymers by Ronca and Yoon[5] and by Gupta and Edwards.[7] Lattice models of nematic polymers were studied extensively by Flory and co-workers.[6]

While theories of short- and long-chain liquid crystals predict different thermodynamic parameters of the isotropic–nematic transition, it is usually found that, at least as far as thermotropic systems are concerned, the qualitative features of the transition are quite similar in the two cases and that essentially no new physics is introduced by connecting small anisotropic molecules into long polymer chains. However, when microscopic information about the structure of the mesophases became available through high-intensity X-ray scattering experiments, some new and exciting features were revealed. For example, it was found that chain molecules of intermediate molecular weight (e.g., normal alkanes with $10 < n < 100$, where n is the number of monomers) have a large variety of *rotator* mesophases that lie between the liquid and the crystalline phases, in which long-range positional and orientational ordering coexists with some degree of conformational disorder of the chain molecules.[8] It was also found that normal alkanes (and some other chain molecules in the above molecular weight range) exhibit *surface freezing* and form a hexagonally ordered surface monolayer in which chains are stretched normal to the interface, and which coexists with a disordered bulk liquid phase over a temperature range that depends on the molecular weight of the constituents.[9]

It became clear that in order to make progress toward the understanding of the above phenomena, one has to develop a tractable statistical mechanical model of the thermotropic orientational ordering of finite length chain molecules which are long enough to be flexible in the isotropic state, but not sufficiently long to be described by the Gaussian chain model of high molecular weight polymers. The theory should be able to predict how chain length and flexibility affect the thermodynamic parameters (e.g., temperature) of the ordering transtion and how the conformation of the chain is affected by the thermodynamic state of the system. The construction of such a model is the goal of the present work.

In section 2 we present the wormlike chain Hamiltonian, introduce the Maier–Saupe-type interaction Hamiltonian which incorporates both athermal (excluded-volume) and thermotropic contributions, define the nematic order parameter, and express the interaction free energy as a functional of a tensor field which contains information about the partial density of labeled monomers. In section 3 we derive a general expression for the total thermodynamic free energy of a system of interacting persistent chains of arbitrary length and show how it can be calculated self-consistently by evaluating the functional integrals in the steepest descent approximation. In section 4 we express the total thermodynamic free energy of the spatially homogeneous (i.e., isotropic and nematic) phases as the sum of interaction, translational entropy, and conformational contributions and calculate the latter by the steepest descent method (i.e., obtain the conformational free energy of a chain in a self-consistent potential field). We derive the mean-field equations from which the thermodynamic parameters of the isotropic–nematic transition (nematic order parameter, critical density, and transition temperature) are calculated numerically for chains of arbitrary length and flexibility. We show

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[⊗] Abstract published in *Advance ACS Abstracts*, November 1, 1995.

that while the order parameter and the critical density decrease rapidly with chain length and tend to the long chain limit for chains of order of the persistence length, the critical temperature increases with molecular weight and approaches the asymptotic limit at much larger chain length ratios. Finally, in section 6 we present the analysis of the conformation of a long persistent chain in a quadrupolar field (e.g., in a nematic environment). We show that the presence of the external field produces two different correlation lengths, transverse and longitudinal. The transverse correlation length characterizes the linear size of chain segments that behave effectively as rigid rods which fluctuate in a small angular interval about the field direction. This length defines the number of independent rotational modes per chain and decreases with the strength of the applied field (the number of such modes increases with the field!). We discuss the geometry and the probability of abrupt reversals in the direction of the chain (hairpins) and find that the characteristic size of a hairpin is of the order of the transverse persistence length. The average distance between hairpins introduces a new length scale into the problem—the longitudinal correlation length. This length increases rapidly with the external field and leads to complete stretching of the chain in the strong field limit.

2. Hamiltonian of Interacting Wormlike Chains

Consider a system of semiflexible polymers of length L and diameter d. The single-chain Hamiltonian which governs the conformation of a wormlike chain $\mathbf{r}(s)$ ($0 < s < L$), is given by the expression:[10]

$$H^{(0)} = \int_0^L \frac{\tilde{\epsilon}_s}{2}\left(\frac{\partial \mathbf{t}_s}{\partial s}\right)^2 \mathrm{d}s \qquad (1)$$

Here $\mathbf{t}_s = (\partial\mathbf{r}/\partial s)$ is a unit tangent vector. The parameter $\tilde{\epsilon}_s$ represents the effective rigidity of the chain, i.e. the energy penalty for bending. The rigidity parameter is directly related to the statistical segment length (persistence length): $l_s = 2\tilde{\epsilon}_s/T$. In the general case, l_s is not assumed to be uniform along the chain and can be different for different segments as, for example, in the case of a heteropolymer.

We will not restrict ourselves to the temperature dependence of the persistence length $l = \mathrm{const}/T$ given by the Kratky–Porod model. In general, it is some arbitrary function of temperature which can be extracted from experimental measurements of the gyration radius of the polymer in the isotropic phase. For example, if the flexibility of the chain is due to gauche–trans rotations of molecular bonds, the length of the statistical segment is proportional to the corresponding Boltzmann factor: $l = l_0 \exp(\Delta/T)$, where Δ is the energy difference between gauche and trans states.

Consider the case of strong nematic interaction between the molecules that corresponds to the limit in which the persistence length considerably exceeds the typical hard core diameter of the chains: $d \ll l$. At *low concentrations* this leads to the Onsager form of the excluded-volume interaction between two semiflexible chains α and β:

$$v_{\alpha\beta} = d\int_0^L \int_0^L \mathrm{d}s\, \mathrm{d}s'\, \delta\,(\mathbf{r}_\alpha(s) - \mathbf{r}_\beta(s'))|\sin\theta_{\alpha\beta}^{ss'}| \qquad (2)$$

Here $\sin\theta_{\alpha\beta}^{ss'} = [\mathbf{t}_{\alpha s} \times \mathbf{t}_{\beta s'}]$ is the sine of the angle between monomers s and s' on chains α and β, respectively.

Taking into account the attractive interactions between nonbonded monomers, we arrive at the following interaction Hamiltonian:

$$\frac{H^{(\mathrm{int})}}{T} = \frac{1}{2}\sum_{\alpha\beta} \int_0^L \int_0^L \mathrm{d}s\, \mathrm{d}s'\, V_{ss'}(|\sin\theta_{\alpha\beta}^{ss'}|)\delta(\mathbf{r}_\alpha(s) - \mathbf{r}_\beta(s')) \qquad (3)$$

where the angle-dependent interaction potential between the monomers is

$$V_{ss'}(|\sin\theta_{\alpha\beta}^{ss'}|) = d\left(\left|\sin\theta_{\alpha\beta}^{ss'}\right| - \frac{\chi_{ss'}(|\sin\theta_{\alpha\beta}^{ss'}|)}{T}\right) \qquad (4)$$

Let us first consider the case of isotropic attractions. Within the assumption that the attractive interaction between the monomers is of the van der Waals type, $\chi_{ss'}^{\mathrm{iso}} \sim (\alpha_s - \tilde{\alpha})\,(\alpha_{s'} - \tilde{\alpha})$, where α_s and $\tilde{\alpha}$ represent the polarizabilities of the sth chain monomer and of the solvent, respectively, and therefore, $\chi_{ss'}^{\mathrm{iso}} = \sqrt{\chi_{ss}\chi_{s's'}}$. The condition that the average second virial coefficient for infinitely long homopolymers must vanish at the Θ-temperature leads to the following expression for $\chi_{ss'}$:

$$\chi_{ss'}(|\sin\theta_{\alpha\beta}^{ss'}|) = \frac{1}{2}\sqrt{\Theta_s\Theta_{s'}}\,\kappa\,(|\sin\theta_{\alpha\beta}^{ss'}|) \qquad (5)$$

Here κ is some function of the relative angle between the two monomers, that satisfies $\langle\kappa\rangle = 1$, and Θ_s is the Θ-temperature of a reference homopolymer which is composed of monomers identical to the sth one.

The anisotropic potential (4) can be expanded in terms of the spherical functions:

$$V_{ss'}(|\sin\theta^{ss'}|) = V_{ss'}^{(0)} + V_{ss'}^{(2)}P_2(\cos\theta^{ss'}) + V_{ss'}^{(4)}P_4(\cos\theta^{ss'}) + \ldots \qquad (6)$$

We will keep only the first two terms in the Legendre expansion of the interaction potential. This corresponds to the Maier–Saupe approach, which is essentially a Landau-type expansion valid for moderate values of the nematic order parameter η.

The resulting interaction Hamiltonian is identical to that of Gupta and Edwards[7]

$$\frac{H^{(\mathrm{int})}}{T} = \frac{1}{2}\sum_{\alpha\beta} \int_0^L \int_0^L \mathrm{d}s\, \mathrm{d}s'\, (w_{ss'} + u_{ss'}[\mathbf{t}_{\alpha s} \times \mathbf{t}_{\beta s'}]^2)\delta(\mathbf{r}_\alpha(s) - \mathbf{r}_\beta(s')) \qquad (7)$$

where $u_{ss'}$ and $w_{ss'}$ are interaction parameters which contain both athermal and thermotropic contributions. Using (4) they can be expressed in terms of the typical hard-core diameter d and the Θ-temperatures for the corresponding reference polymers:

$$w_{ss'} \simeq \frac{d}{2}\left(1 - \frac{(3 + \varpi)}{2}\frac{\sqrt{\Theta_s\Theta_{s'}}}{T}\right) \qquad (8)$$

$$u_{ss'} \simeq \frac{3d}{8}\left(1 + \varpi\frac{\sqrt{\Theta_s\Theta_{s'}}}{T}\right) \qquad (9)$$

The parameter $\varpi \sim 1$ determines the strength of the thermotropic contribution to the anisotropic interaction.

It is convenient to introduce a tensor field $\hat{\sigma}_s(\mathbf{r})$, which describes both nematic order in the system and its possible spatially nonuniform properties, with components:

$$\sigma_s^{ij}(\mathbf{r}) \equiv \sum_\alpha t_{\alpha s}^i t_{\alpha s}^j \delta\,(\mathbf{r}_\alpha(s) - \mathbf{r}) \tag{10}$$

Recall that in the Gaussian model of polymer chains, $\hat{\sigma}_s(\mathbf{r})$ can be interpreted as the stress tensor which describes the contribution of the sth monomers to the local stress at point $\mathbf{r}$ (this interpretation is not valid in general and can not be applied to the present case). The trace of this tensor, $\rho_s(\mathbf{r}) = \sigma_s^{ii}(\mathbf{r})$, represents the density of the sth monomers at a given point $\mathbf{r}$. The total monomer density is given by the integral of ρ_s over all s:

$$\rho(\mathbf{r}) = \int_0^L \mathrm{d}s\; \sigma_s^{ii}(\mathbf{r}) \tag{11}$$

The tensor $\hat{\sigma}_s(\mathbf{r})$ contains information both about the spatial distribution of total density and about the local composition, i.e., the partial density of the sth monomers. Note that the monomer density introduced in (11) has the dimension of length^{-2} and is the measure of the total length of the chains in some region of space per its volume.

In the cylindrically-symmetric case, the eigenvalues of $\hat{\sigma}_s(\mathbf{r})$ are $\sigma_{s\|}(\mathbf{r})$ and $\sigma_{s\perp}(\mathbf{r})$ (the latter are doubly-degenerate). This allows one to express the local nematic order parameter in terms of $\hat{\sigma}_s(\mathbf{r})$:

$$\eta(\mathbf{r}) \equiv \frac{\int_0^L \mathrm{d}s\; (\sigma_{s\|}(\mathbf{r}) - \sigma_{s\perp}(\mathbf{r}))}{\rho(\mathbf{r})} \tag{12}$$

Moreover, $\hat{\sigma}_s(\mathbf{r})$ contains also the information about the nematic ordering of the sth monomer units:

$$\eta_s(\mathbf{r}) \equiv \frac{\sigma_{s\|}(\mathbf{r}) - \sigma_{s\perp}(\mathbf{r})}{\rho_s(\mathbf{r})} \tag{13}$$

We can represent the interaction Hamiltonian (7) as a local functional of the field $\hat{\sigma}_s(\mathbf{r})$:

$$\frac{H^{(\mathrm{int})}}{T} = \frac{1}{2}\int \mathrm{d}\mathbf{r} \int_0^L \mathrm{d}s \int_0^L \mathrm{d}s'\; \hat{\sigma}_s(\mathbf{r})\hat{\mathbf{U}}_{ss'}\hat{\sigma}_{s'}(\mathbf{r}) \tag{14}$$

where

$$\hat{\sigma}_s(\mathbf{r})\, \hat{\mathbf{U}}_{ss'}\hat{\sigma}_{s'}(\mathbf{r}) \equiv \sigma_s^{ij}(\mathbf{r}) U_{ss'}^{iji'j'} \sigma_{s'}^{i'j'}(\mathbf{r}) \tag{15}$$

and

$$U_{ss'}^{iji'j'} \equiv (w_{ss'} + u_{ss'})\, \delta^{ij}\, \delta^{i'j'} - u_{ss'}\delta^{ii'}\, \delta^{jj'} \tag{16}$$

Since the Maier–Saupe approach gives the correct qualitative features of the isotropic to nematic transition in dense thermotropic systems, we proceed to generalize the Gupta–Edwards interaction Hamiltonian (7) and (14) to the dense case. Assuming that the correlation length associated with all excluded-volume and soft potential interactions is considerably smaller than the persistence length, the interaction part of the free energy of the system can be written as an integral over the space of the system, of a local free energy density functional $f[\hat{\sigma}_s(\mathbf{r})]$:

$$\frac{F^{(\mathrm{int})}}{T} = \frac{1}{2}\int \mathrm{d}\mathbf{r}\, f[\hat{\sigma}_s(\mathbf{r})] \tag{17}$$

This functional can be expanded in the vicinity of the uniform (we consider the case of a uniform density of sth monomers) isotropic state in which $\sigma_s^{ij}(\mathbf{r}) = \mathrm{const} = c\delta^{ij}/3$ (here $c = \langle\sigma_s^{ii}\rangle = \langle\rho\rangle/L$ is the average concentration of polymers):

$$\frac{F^{(\mathrm{int})}}{T} = \mathrm{const} + \int \mathrm{d}\mathbf{r} \left[\int_0^L \mathrm{d}s\; \delta\hat{\sigma}_s(\mathbf{r})\hat{\Pi}_s + \frac{1}{2}\int_0^L \mathrm{d}s \int_0^L \mathrm{d}s'\; \delta\hat{\sigma}_s(\mathbf{r})\hat{\mathbf{U}}_{ss'}\delta\hat{\sigma}_{s'}(\mathbf{r})\right] \tag{18}$$

where

$$\delta\hat{\sigma}_s(\mathbf{r})\hat{\Pi}_s \equiv \delta\sigma_s^{ij}(\mathbf{r})\Pi_s^{ij} \tag{18a}$$

and where the tensors $\hat{\Pi}_s$ and $\hat{\mathbf{U}}_{ss'}$ are expansion coefficients and $\delta\sigma_s^{ij}(\mathbf{r}) = \sigma_s^{ij}(\mathbf{r}) - c\delta_{ij}/3$. Since the reference state is uniform and isotropic, the most general forms of the coefficients are $\Pi_s^{ij} = \Pi_s\delta_{ij}$ and that given by (16) for $\hat{\mathbf{U}}_{ss'}$. Inserting the above expression for Π_s^{ij} into (18a) and making use of the fact that $\int \mathrm{d}\mathbf{r}\; \delta\hat{\sigma}_s(\mathbf{r}) = 0$, the first term in the integral in (18) vanishes. Since we can replace $\delta\hat{\sigma}_s$ by $\hat{\sigma}_s$ in (18) (up to an irrelevant constant), we conclude that the expansion of the interaction free energy about the uniform isotropic state of a dense system, formally coincides with the two-particle interaction Hamiltonian, (14). Although the form of the above expansion is identical to that of a virial expansion, its derivation did not assume that the polymer solution is dilute and, therefore, the results can be applied to dense systems (as long as one does not approach the limit of an incompressible close-packed liquid, in which the expansion cannot be terminated at second order). Note also that the quadrupolar term in the angle-dependent potential, (6), gives rise to spinodal decomposition of the isotropic phase. Therefore, even in the low-density (Onsager) case one can use the Maier–Saupe form of interaction for the calculation of the stability limit of the isotropic phase. Although the Maier–Saupe model cannot be rigorously applied to the description of the nematic phase in which the nematic order parameter is not necessarily small, we will follow Gupta and Edwards and use it in the following.

3. Free Energy

The total free energy of the system is defined as a functional integral over all possible configurations of interacting wormlike chains:

$$F = -T \ln\left\{\frac{1}{N!}\int D[\mathbf{r}_\alpha(s)] \exp\left[-\frac{1}{T}\left(\sum_\alpha H_\alpha^{(0)} + H^{(\mathrm{int})}\right)\right]\right\} \tag{19}$$

Here N is the total number of chains. Using the results of the previous section, this free energy can be expressed in terms of $\hat{\sigma}_s$:

$$F = -T \ln\left\{\frac{1}{N!} \int D[\mathbf{r}_\alpha(s)] D[\hat{\sigma}_s(\mathbf{r})] \delta(\mathbf{t}_{\alpha s}{}^2 - 1) \times \delta\Big(\sigma_s^{ij}(\mathbf{r}) - \sum_\alpha t^i_{\alpha s} t^j_{\alpha s} \delta(\mathbf{r}_\alpha(s) - \mathbf{r})\Big) \times \exp\left[-\left(\frac{1}{2}\int \mathrm{d}\mathbf{r} \int_0^L \mathrm{d}s \int_0^L \mathrm{d}s'\, \hat{\sigma}_s(\mathbf{r}) \hat{\mathbf{U}}_{ss'}(\mathbf{r}) \hat{\sigma}_{s'}(\mathbf{r}) + \sum_\alpha \int_0^L \frac{l_s}{4} \dot{\mathbf{t}}_{\alpha s}{}^2\, \mathrm{d}s\right)\right]\right\} \tag{20}$$

Using the Fourier representation of the δ-function, one can introduce the field $\hat{\psi}_s$ (with components ψ_s^{ij}) conjugate to $\hat{\sigma}_s$, in order to recast the above free energy into the form:

$$F = -T \ln\left\{\frac{1}{N!} \int D[\mathbf{r}_\alpha(s)] D[\hat{\sigma}_s(\mathbf{r})] D[\hat{\psi}_s(\mathbf{r})] \delta(\mathbf{t}_{\alpha s}{}^2 - 1) \times \exp\left[-\int \mathrm{d}\mathbf{r}\left(\frac{1}{2}\int_0^L \mathrm{d}s \int_0^L \mathrm{d}s'\, \hat{\sigma}_s(\mathbf{r}) \hat{\mathbf{U}}_{ss'} \hat{\sigma}_{s'}(\mathbf{r}) - \mathrm{i} \int_0^L \mathrm{d}s\, \hat{\sigma}_s(\mathbf{r}) \hat{\psi}_s(\mathbf{r})\right)\right] \exp\left[-\sum_\alpha \int_0^L \mathrm{d}s \left(\frac{l_s}{4} \dot{\mathbf{t}}_{\alpha s}{}^2 + \mathrm{i} t^i_{\alpha s} t^j_{\alpha s}\, \psi_s^{ij}(\mathbf{r}_\alpha(s))\right)\right]\right\} \tag{21}$$

In the thermodynamic limit, the free energy is determined by the steepest descent estimates of the functional integrals over the fields $\hat{\psi}_s$ and $\hat{\sigma}_s$. It can be represented as a sum of translational entropy, interaction, and conformational contributions:

$$F[\hat{\sigma}_s(\mathbf{r}), \hat{\psi}_s(\mathbf{r})] = TN \ln N + NF^{(\mathrm{con})}[\hat{\psi}_s(\mathbf{r})] + T\int \mathrm{d}\mathbf{r}\left(\frac{1}{2}\int_0^L \mathrm{d}s \int_0^L \mathrm{d}s'\, \hat{\sigma}_s(\mathbf{r}) \hat{\mathbf{U}}_{ss'}(\mathbf{r}) \hat{\sigma}_{s'}(\mathbf{r}) - \mathrm{i}\int_0^L \mathrm{d}s\, \hat{\sigma}_s(\mathbf{r}) \hat{\psi}_s(\mathbf{r})\right) \tag{22}$$

Here $F^{(\mathrm{con})}$ is the conformational free energy of a single chain in the presence of an external tensor field $\mathrm{i}\psi_s$ which represents the interaction of a probe chain with its neighbors:

$$F^{(\mathrm{con})} = -T \ln\left\{\int D[\mathbf{r}_s] \delta(\mathbf{t}_s{}^2 - 1) \exp\left(-\int_0^L \left(\frac{l_s}{4}\dot{\mathbf{t}}_s{}^2 + \mathrm{i}\psi_s^{ij}(\mathbf{r}_s) t_s^i t_s^j\right) \mathrm{d}s\right)\right\} \tag{23}$$

The free energy $F[\hat{\sigma}_s(\mathbf{r}),\hat{\psi}_s(\mathbf{r})]$ should be minimized with respect to both fields. The conditions $(\delta F/\delta\hat{\sigma}) = 0$ and $(\delta F/\delta\hat{\psi}) = 0$ result in the following expressions for $\hat{\psi}$ and $\hat{\sigma}$:

$$\hat{\psi}_s(\mathbf{r}) = -\mathrm{i}\int_0^L \hat{\mathbf{U}}_{ss'} \hat{\sigma}_{s'}(\mathbf{r})\, \mathrm{d}s' \tag{24}$$

$$\hat{\sigma}_s(\mathbf{r}) = -\mathrm{i}N \frac{\delta F^{(\mathrm{con})}}{\delta \hat{\psi}_s(\mathbf{r})} \tag{25}$$

The physical meaning of both relationships is as follows. (24) shows how the orientational field $\hat{\psi}$ is related to the presence and ordering of different monomer units at a given point $\mathbf{r}$. The field $\hat{\sigma}$ parameterizes the monomer composition and orientation and must satisfy the condition of self-consistency (25). Note that (24) holds only in equilibrium while (25) is a more general relationship. In the Gaussian approach (keeping only quadratic contributions in the deviations from the steepest descent value of $\hat{\psi}$, in the free energy, (22)), the minimization of the free energy with respect to $\hat{\psi}$ corresponds to the integration over this fictitious field in (21).

For further developments it is convenient to subtract the spatially nonuniform contribution $(\hat{\sigma}_s^{(1)}(\mathbf{r}))$ from $\hat{\sigma}_s(\mathbf{r})$:

$$\hat{\sigma}_s(\mathbf{r}) = \hat{\sigma}_s^{(0)} + \hat{\sigma}_s^{(1)}(\mathbf{r}) \tag{26}$$

Here $\int \hat{\sigma}_s^{(1)}(\mathbf{r})\, \mathrm{d}\mathbf{r} = 0$. One can expand the total free energy in terms of $\hat{\sigma}_s^{(1)}(\mathbf{r})$:

$$F = F^{(0)}[\hat{\sigma}_s^{(0)}] + \delta F[\hat{\sigma}_s^{(1)}(\mathbf{r});\hat{\sigma}_s^{(0)}] \tag{27}$$

$F^{(0)}$ determines the thermodynamics of spatially homogeneous phases and provides an adequate description of the isotropic–nematic transition (since the distribution of the *s*th monomers is spatially homogeneous in both phases). If one is interested in spatially modulated phases (such as the smectic or the crystalline phases), one has to include the contribution of δF. In the case of stiff molecules, one can obtain an alternative molecular theory for both smectic and nematic behavior of thermotropic liquid crystals. Note that while the McMillan theory of smectics[11] introduces an ad hoc nonlocal effective potential, our modification of Gupta–Edwards theory is sensitive to the internal structure of the molecules and the effective interaction between the chain molecules arises in a natural way from the local interaction between their segments.

4. Isotropic–Nematic Transition

Using the results of the preceding section, one can show that the free energy of a system of interacting wormlike chains of length L is given by

$$\frac{F^{(0)}(\hat{\sigma}_s^{(0)})}{V} = -\frac{1}{2}T\int_0^L \mathrm{d}s \int_0^L \mathrm{d}s'\, \hat{\sigma}_s^{(0)} \hat{\mathbf{U}}_{ss'} \hat{\sigma}_{s'}^{(0)} + Tc \ln c + cF^{(\mathrm{con})}(\hat{\psi}_s^{(0)}) \tag{28}$$

Here $\hat{\psi}_s^{(0)}$ is related to $\hat{\sigma}_s^{(0)}$ by (24) and $c = N/V = \langle\rho\rangle/L$ is the average concentration of chains.

4.1. Conformational Free Energy. We proceed to simplify the expression for the conformational free energy, (23). The δ-function is eliminated by the introduction of a new scalar field λ_s:

$$F^{(\mathrm{con})} = -T \ln\left\{\int D[\mathbf{t}_s] D[\lambda_s] \exp\left(-H[\mathbf{t}_s,\hat{\psi}_s^{(0)}] - \int_0^L \mathrm{i}\lambda_s(\mathbf{t}_s{}^2 - 1)\, \mathrm{d}s\right)\right\} \tag{29}$$

where

$$\mathrm{H}[\mathbf{t}_s,\hat{\psi}_s^{(0)}] \equiv \int_0^L \left(\frac{l_s}{4}\dot{\mathbf{t}}_s{}^2 + \mathrm{i}\psi_s^{(0)ij} t_s^i t_s^j\right) \mathrm{d}s$$

In order to carry out the functional integration over $\mathbf{t}_s$ $(0 < s < L)$, we introduce the Fourier transform of its symmetric extension into the range $-L < s < L$:

$$\mathbf{t}_s = \sum_{n=0}^{\infty} \mathbf{t}_{(n)} \cos\frac{\pi n s}{L} = \frac{1}{2}\sum_{n=-\infty}^{+\infty} \mathbf{t}_{(n)} \exp\left(\mathrm{i}\frac{\pi n s}{L}\right) \qquad (30)$$

$$\mathbf{t}_{(n)} = \mathbf{t}_{(-n)}$$

In this way we avoid the unphysical restriction $\mathbf{t}_0 = \mathbf{t}_L$ which follows from the condition of periodicity of a direct Fourier expansion of the function $\mathbf{t}_s$ in the interval $0 < s < L$.

The conformational free energy in the Fourier representation is given by

$$F^{(\mathrm{con})} = -T \ln\left\{\int \prod_{n=-\infty}^{\infty} \mathrm{d}\mathbf{t}_{(n)}\, \mathrm{d}\lambda_{(n)}\, \delta\,(\mathbf{t}_{(n)} - \mathbf{t}_{(-n)}) \times \delta(\lambda_{(n)} - \lambda_{(-n)}) \exp(\mathrm{i}L\lambda_{(0)}) \exp\left(-\sum_{\nu}\sum_{n',n=-\infty}^{+\infty} \frac{t^{\nu}_{(n)}t^{\nu}_{(-n')}}{4} \left[\frac{\pi^2 n n'}{4L} l_{(n-n')} + L\psi^{(0)\nu}_{(n-n')} + \mathrm{i}L\lambda_{(n-n')}\right]\right)\right\} \qquad (31)$$

Here

$$l_{(n)} = \frac{1}{L}\int_0^L l_s \cos\frac{\pi n s}{L}\,\mathrm{d}s \qquad (32)$$

$$\hat{\psi}^{(0)}_{(n)} = \frac{1}{L}\int_0^L \hat{\psi}^{(0)}_s \cos\frac{\pi n s}{L}\,\mathrm{d}s \qquad (33)$$

and

$$\lambda_{(n)} = \frac{1}{L}\int_0^L \lambda_s \cos\frac{\pi n s}{L}\,\mathrm{d}s \qquad (34)$$

The index ν parameterizes the eigenvalues of $\hat{\psi}^{(0)}_s$. We assume that the directions of its eigenvectors are independent of s, consistent with the cylindrical symmetry of the final solution.

In what follows we keep only uniform (along the contour s) contributions to the fields l_s, $\hat{\psi}^{(0)}_s$, and λ_s (higher modes can be introduced as perturbations). The condition $l_s = l_{(0)} =$ const corresponds to the case of a uniform persistent chain. When the interactions between the segments are also uniform along the chains, the interaction parameters $w_{ss'}$ and $u_{ss'}$ are constant (i.e., independent of s and s') and we obtain

$$\hat{\psi}^{(0)}_s = \hat{\psi}^{(0)}_{(0)} = -\mathrm{i}\hat{\mathbf{U}} \int_0^L \hat{\sigma}^{(0)}_s\,\mathrm{d}s = \mathrm{const} \qquad (35)$$

In principle, the higher modes of the field λ are important for the analysis of the nematic ordering of definite parts of the chains or of the orientational correlations between them. As long as one is interested only in the thermodynamic analysis of the phase transition, it is sufficient to keep only $\lambda_{(0)}$ (this is equivalent to replacing $\mathbf{t}^2 = 1$ with the mean spherical approximation $\langle\mathbf{t}^2\rangle_s = 1$, where $\langle\,\rangle_s$ denotes averaging over the chain contour):

$$F^{(\mathrm{con})} = -T \ln\left\{\int \mathrm{d}\lambda_{(0)} \prod_{n=0}^{\infty} \mathrm{d}\mathbf{t}_{(n)} \times \exp(\mathrm{i}L\lambda_{(0)}) \exp\left(-\sum_{\nu}\sum_{n=-\infty}^{+\infty} \frac{t^{\nu}_{(n)}t^{\nu}_{(-n)}}{4}\left[\frac{\pi^2 n^2}{4L} l_{(0)} + \mathrm{i}L\psi^{\nu}_{(0)} + \mathrm{i}L\lambda_{(0)}\right]\right)\right\} = -\ln\left[\int f(z)\mathrm{e}^{\mathrm{i}z}\,\mathrm{d}z\right] + \mathrm{const} \qquad (36)$$

where we define $\zeta \equiv 4L/l$, $\phi^{\nu} \equiv \mathrm{i}L\psi^{\nu}_{(0)}$, $z \equiv \lambda_{(0)}L$, and

$$f(z) \equiv \exp\left\{\sum_{\nu} -\frac{1}{2}\left[\ln(\phi^{\nu} + \mathrm{i}z) + \sum_{n=1}^{\infty} \ln\left(1 + \frac{\zeta(\phi^{\nu} + \mathrm{i}z)}{\pi^2 n^2}\right)\right]\right\} \qquad (37)$$

Note that the Gaussian integration in (36) is well-defined only for Re $(\phi^{\nu} + \mathrm{i}z) > 0$, i.e., Im $z < \min \phi^{\nu}$.

In order to perform the summation in (37) we introduce the following transformations:

$$\sum_{n=1}^{\infty} \ln\left(1 + \frac{a}{n^2}\right) = \frac{1}{2}\int_0^a \left(-\frac{1}{x} + \sum_{n=-\infty}^{+\infty} \frac{1}{x + n^2}\right)\mathrm{d}x = \ln\frac{\sinh \pi\sqrt{a}}{\pi\sqrt{a}} + \mathrm{const} \qquad (38)$$

A straightforward calculation yields

$$F^{(\mathrm{con})} = -T\ln\left\{\int_{-\infty+\mathrm{i}\vartheta}^{+\infty+\mathrm{i}\vartheta} \prod_{\nu} \frac{1}{\sqrt{\mathrm{i}z + \phi^{\nu}}} \sqrt{\frac{\sqrt{\zeta(\mathrm{i}z + \phi^{\nu})}}{\sinh\sqrt{\zeta(\mathrm{i}z + \phi^{\nu})}}}\,\mathrm{e}^{\mathrm{i}z}\,\mathrm{d}z\right\} + \mathrm{const} \qquad (39)$$

where

$$\vartheta < \min \phi^{\nu}$$

Both the single-chain and the interaction parts of the initial Hamiltonian possess cylindrical symmetry. As there is no physical reason to break this symmetry in the final solution, one can introduce the average nematic order parameter $\eta \equiv (1/\langle\rho\rangle)\int_0^L(\sigma^{(0)}_{s\parallel} - \sigma^{(0)}_{s\perp})\,\mathrm{d}s$ and the conjugate parameter $\gamma \equiv \phi_{\perp} - \phi_{\parallel}$. After the transformation $\mathrm{i}z + \phi_{\parallel} = \mathrm{i}z'$, the conformational free energy (39) can be expressed as

$$F^{(\mathrm{con})} = \phi_{\parallel} + \tilde{F}(\gamma) \qquad (40)$$

where

$$\tilde{F}(\gamma) \equiv -T\ln\left\{\int_{-\infty-\mathrm{i}\delta}^{+\infty-\mathrm{i}\delta} \frac{\mathrm{e}^{\mathrm{i}z'}\,\mathrm{d}z'}{(\gamma + \mathrm{i}z')\sqrt{\mathrm{i}z'}} \times \left(\sqrt{\frac{\sqrt{\mathrm{i}\zeta z'}}{\sinh\sqrt{\mathrm{i}\zeta z'}}\,\frac{\sqrt{\zeta(\gamma + \mathrm{i}z')}}{\sinh\sqrt{\zeta(\gamma + \mathrm{i}z')}}}\right)\right\} \qquad (41)$$

4.2. Isotropic–Nematic Transition. The total free energy, (28), can be written as the following function of γ:

$$\frac{F(\gamma)}{V} = c\left[T\left(\frac{\gamma}{uL\,\langle\rho\rangle} - 2\right)\frac{\gamma}{3} + \tilde{F}\,(\gamma)\right] + \text{const} \qquad (42)$$

In deriving the above expression, we used the relationship between the parameters γ and η which follows from (35)

$$\gamma = uL\langle\rho\rangle\eta \qquad (43)$$

The minimization of the free energy with respect to γ yields the self-consistency relation which corresponds to (25):

$$\eta = \frac{\gamma}{uL\,\langle\rho\rangle} = 1 - \frac{3}{2T}\frac{\partial\tilde{F}}{\partial\gamma} \qquad (44)$$

In the limit of stiff (or short) rods when $\zeta \ll 1$, (41) becomes

$$\frac{\tilde{F}\,(\gamma)}{T} = -\ln\left(\int_{-\infty-\mathrm{i}\delta}^{+\infty-\mathrm{i}\delta} \frac{\mathrm{e}^{\mathrm{i}z'}\,\mathrm{d}z'}{(\gamma + \mathrm{i}z')\sqrt{\mathrm{i}z'}}\right) = -\ln\left(\int_{-\infty+\mathrm{i}\epsilon}^{+\infty+\mathrm{i}\epsilon} \frac{\mathrm{e}^{-x^2}\,\mathrm{d}x}{(\gamma - x^2)}\right) = \gamma - \ln(2\int_0^{+1} t\,\mathrm{d}t \int_{-\infty+\mathrm{i}\epsilon}^{+\infty+\mathrm{i}\epsilon} \mathrm{d}x\,\mathrm{e}^{t^2(\gamma - x^2)}) = \gamma - \ln(\int_{-1}^{+1} \mathrm{e}^{\gamma t^2}\,\mathrm{d}t) \qquad (45)$$

In this limit, (44) gives the well-known self-consistency relation of the Maier–Saupe theory:

$$\eta = \frac{\gamma}{uL^2c} = \frac{3}{2}\left(\frac{\int \cos^2\theta \exp(\gamma\cos^2\theta)\,\mathrm{d}\Omega}{\int \exp(\gamma\cos^2\theta)\,\mathrm{d}\Omega} - \frac{1}{3}\right) \qquad (46)$$

This theory predicts an isotropic–nematic phase transition with parameters $uL^2c \simeq 7$ and $\eta \simeq 0.42$.

In the opposite case of chains much longer than the persistence length, $\zeta \gg 1$, one can perform the steepest descent calculation in (41) and obtain

$$\frac{\tilde{F}(\gamma,z)}{T} = -\mathrm{i}z - \gamma + \sqrt{\zeta(\gamma + \mathrm{i}z)} + \frac{\zeta\sqrt{\mathrm{i}z}}{2} \qquad (47)$$

where z is defined by the steepest descent condition

$$\frac{\partial\tilde{F}(\gamma,z)}{\partial z} = 0 \qquad (48)$$

(44) and (48) give the following system of equations

$$2 = \sqrt{\frac{\zeta}{(\gamma + \mathrm{i}z)}} + \frac{1}{2}\sqrt{\frac{\zeta}{\mathrm{i}z}} \qquad (49)$$

$$\eta = \frac{\gamma}{uL\,\langle\rho\rangle} = 1 - \frac{3}{4}\sqrt{\frac{\zeta}{(\gamma + \mathrm{i}z)}} \qquad (50)$$

This yields the Gupta–Edwards self-consistent equation:

$$\frac{(1-\eta)^2(1+2\eta)^2}{27(2+\eta)} = \frac{1}{4lu\langle\rho\rangle} \qquad (51)$$

according to which the transition takes place at $lu\langle\rho\rangle \simeq 12$. The order parameter at the point of the phase transition, $\eta = 0.25$, is considerably lower than the corresponding parameter for a system of stiff rods. A similar trend for the chain-length dependence of the nematic order parameter at the transition point was found for polymeric liquid crystals with Onsager interactions.[2] The physical reason for the above difference will be discussed in a subsequent section.

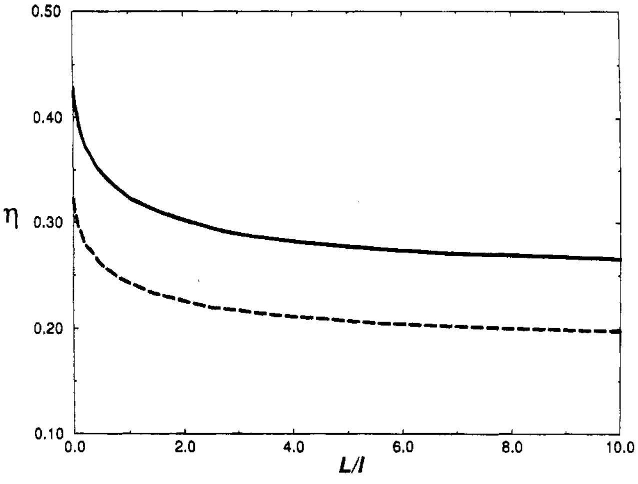


Figure 1. Nematic order parameter at the point of isotropic–nematic phase transition plotted as a function of molecular weight. The dashed line shows the order parameter at the spinodal of the nematic phase.

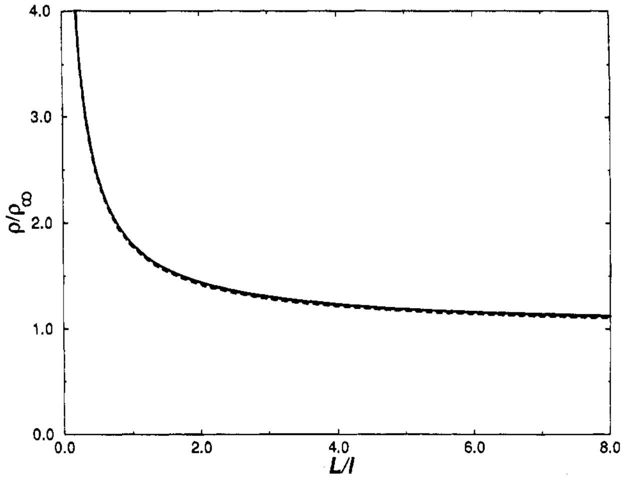


Figure 2. Dependence of the reduced critical density ρ/ρ_∞ on the molecular weight. The dashed line corresponds to the spinodal of the nematic phase.

Analysis of (41) shows that the crossover between the above limiting regimes is determined by the parameter $\sqrt{\zeta\gamma} = (2L/l)\sqrt{lu\langle\rho\rangle\eta}$. It can be shown that the chain can be considered as a stiff rod if it is shorter than some characteristic length

$$\xi = \frac{l}{2\sqrt{lu\,\langle\rho\rangle\,\eta}} \qquad (52)$$

which decreases with increasing η. This scale is smaller than the bare persistence length l and its physical meaning will be discussed in the next section.

The numerical evaluation of the free energy (42) allows one to obtain the thermodynamic parameters of the phase transition for any chain length L. The dependence of the order parameter η and of the reduced critical density ρ/ρ_∞ on the molecular weight L/l is shown in Figures 1 and 2 (the solid and the dashed line correspond to the coexistence curve and to the spinodal, respectively). Note that the crossover between the two

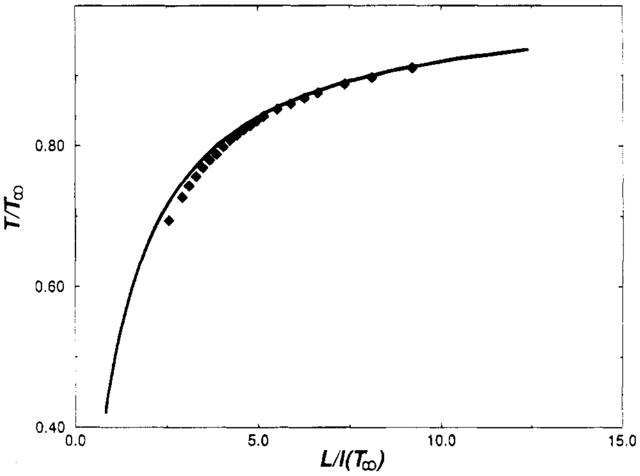


Figure 3. Reduced transition temperature T/T_∞ as a function of reduced molecular weight $L/l(T_\infty)$. The solid line corresponds the rotational isomer state model of chain rigidity with $\Delta/T_\infty = 1$. The experimental points show the observed dependence of the crystallization temperature of normal alkanes on the molecular weight.

limiting values of the order parameter takes place at small values of this parameter ($L/l \leq 1$), i.e., for chain lengths smaller than the persistence length. While the Gupta–Edwards approach gives a better quantitative fit to the exact curve for the order parameter than the Landau–de Gennes expansion,[13] it misses an interesting universal feature of such curves which was found both analytically[13,14] and numerically,[15] in different liquid crystalline polymeric systems. The above authors observed that the critical order parameter depends nonmonotonically on the molecular weight, reaching its minimum at a finite chain length. For longer chains there is a slight increase of the order parameter to the infinite chain value $\eta \simeq 0.35$, instead of the Gupta–Edwards result $\eta \simeq 0.25$. We will show in the next section that the slight increase of the order parameter with molecular weight is a chain-end effect, which cannot be accounted for by the mean spherical approximation used in our derivation.

The phase behavior of thermotropic polymeric liquid crystals is determined by the temperature dependence of the persistence length and by the anisotropic part of the attractive potential. The dependence of the reduced transition temperature T/T_∞ (T_∞ is the transition temperature for an infinite chain) on the molecular weight (represented by the temperature-independent dimensionless combination $L/l(T_\infty)$) is shown in Figure 3, for the rotational isomer state mechanism of chain rigidity, with the typical energy parameter for hydrocarbon chains, Δ = 400 K. The anisotropic potential u is assumed to be purely athermal, i.e., caused by steric interactions. The resulting phase diagram in the (T, L) plane closely resembles the experimental temperature versus molecular weight curve for *crystallization* of normal alkanes (see, for example, ref 12). This observation suggests that the freezing of semiflexible polymers may be initiated by their nematic ordering.

5. Wormlike Chain in a Quadrupolar Field

In order to get physical intuition about the results obtained in the previous section, we consider the behavior of an individual chain in a quadrupolar field and calculate the correlation length of the tangent vector in the nematic state.

The free energy of the chain in a constant (cylindrically-symmetric) quadrupolar field with strength characterized by the parameter Q, is given by

$$F_Q = -T\ln\left\{\int D[\mathbf{t}_s]\delta(\mathbf{t}^2 - 1)\exp\left[-\int_0^L ds\left(\frac{l}{4}\left(\frac{\partial\mathbf{t}}{\partial s}\right)^2 + \frac{Q\mathbf{t}_\perp^{\,2}}{2}\right)\right]\right\} \quad (53)$$

In the limit of a sufficiently strong orienting field, fluctuations in the directions normal to the field are suppressed ($\mathbf{t}_\perp^2 \ll 1$) and, using the geometrical constraint $\mathbf{t}_\perp^2 + \mathbf{t}_\parallel^2 = 1$, the free energy can be rewritten as

$$F_Q = -T\ln\left\{\int\frac{D[\mathbf{t}_{s\perp}]}{\cos|\mathbf{t}_{s\perp}|}\exp\left[-\int_0^L ds\left(\frac{l}{4\cos^2|\mathbf{t}_\perp|}\times\left(\frac{\partial\mathbf{t}_\perp}{\partial s}\right)^2 + \frac{Q\boldsymbol{t}_\perp^{\,2}}{2}\right)\right]\right\} \simeq -T\ln\left\{\int D[\mathbf{t}_{s\perp}]\times \exp\left[-\int_0^L ds\left(\frac{l}{4}\left(\frac{\partial\mathbf{t}_\perp}{\partial s}\right)^2\left(1 + \frac{\langle\mathbf{t}_\perp^{\,2}\rangle}{2}\right) + \frac{Q\boldsymbol{t}_\perp^{\,2}}{2}\right)\right]\right\} \quad (54)$$

where, in the second line, we expanded the chain Hamiltonian to second order in $\mathbf{t}_\perp$.

5.1. Transverse Correlation Length. In the case when the quadrupolar field is a self-consistent field due to the nematic environment, we must impose the self-consistency condition, $Q = 2u\langle\rho\rangle\eta$. Using the quadratic approximation to the Hamiltonian, (54), we can calculate the order parameter in the nematic range, down to the transition to the isotropic state. In this range, we obtain an expression for the second moment $\langle\mathbf{t}_\perp^2\rangle$ (for the *infinite chain* case):

$$\langle\mathbf{t}_\perp^{\,2}\rangle = \frac{2}{3}(1 - \eta) = \sqrt{\frac{2}{l(1 + \langle\mathbf{t}_\perp^{\,2}\rangle/2)Q}} \quad (55)$$

This yields the self-consistency relation:

$$\frac{\eta(1 - \eta)^2(4 - \eta)}{27} = \frac{1}{4lu\langle\rho\rangle} \quad (56)$$

The above result is in good numerical agreement with the Gupta–Edwards equation (51), for order parameters in the range from 1.0 to 0.25. Plots of η vs $lu\langle\rho\rangle$ predicted by the two models are presented in Figure 4.

In order to use the above model for a more detailed analysis of the behavior of a chain in a quadrupolar field, we introduce a Fourier transform of the function $\mathbf{t}_{s\perp}$ by analogy with (30):

$$\mathbf{t}_{s\perp} = \sum_{n=0}^{\infty}\mathbf{t}_{\perp(n)}\cos\frac{\pi ns}{L} = \frac{1}{2}\sum_{n=-\infty}^{+\infty}\mathbf{t}_{\perp(n)}\exp\left(i\frac{\pi ns}{L}\right) \quad (57)$$

with

$$\mathbf{t}_{\perp(n)} = \mathbf{t}_{\perp(-n)}$$

It follows from (54) that

$$\langle t^{\nu}_{\perp(n)}t^{\iota}_{\perp(n')}\rangle = \frac{(2\delta_{nn'} - \delta_{n0}\delta_{n'0})\,\delta_{\nu\iota}}{(\pi^2n^2l/2L)(1 + \langle\mathbf{t}_\perp^{\,2}\rangle/2) + QL} \quad (58)$$

Here ι, $\nu = x, y$ are indices which label the components

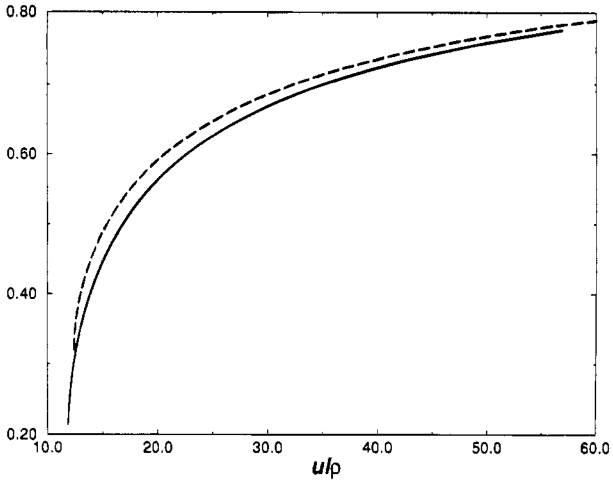


Figure 4. Dependence of the order parameter in the nematic phase on the control parameter u/ρ predicted by the Gupta–Edwards theory (solid line) and by the quadratic approximation to the Hamiltonian introduced in the text (dashed line).

of the 2-dimensional vector $\mathbf{t}_{\perp(n)}$. Away from the ends of the chain we get the following expression for the above correlator in the s-representation:

$$\langle t^{\nu}_{\perp s} t^{\iota}_{\perp s'}\rangle = \langle \mathbf{t}_{\perp}^{2}\rangle \frac{\delta^{\nu\iota}}{2}\exp\left(-\frac{|s-s'|}{\xi_{\perp}}\right) \qquad (59)$$

where

$$\xi_{\perp} = \frac{l}{2}\sqrt{\frac{2}{l\,(1+\langle \mathbf{t}_{\perp}^{2}\rangle/2)\,Q}} \qquad (60)$$

Since $Q = 2u\langle\rho\rangle\eta$, the correlation length $\xi_\perp$ practically coincides with the length ξ (eq 52), which determines the crossover between the short and the long chain regimes discussed in the previous section. It is considerably smaller than the persistence length in the isotropic phase, l. Using (55), the expression for $\xi_\perp$ can be recast into the form

$$\xi_{\perp} = \frac{l}{3}(1-\eta) \qquad (61)$$

Thus, $\xi_\perp$ is the characteristic length over which the chain changes its orientation by an angle of $\sqrt{2(1-\eta)/3}$, which characterizes the typical range of angular fluctuations of rods about the nematic director. It is also the contour length associated with the appearance of a twist in a bent chain (a change in the direction of $\mathbf{t}_\perp$). We therefore conclude that it is $\xi_\perp$ rather than the larger bare persistence length l which determines whether a chain of length L behaves as a rigid rod or as a semiflexible polymer. Further support for this interpretation comes from the Khokhlov–Semenov theory[14] which predicts a crossover between the classical Onsager and the long-chain regimes at $L \sim 0.1l$. Indeed, at $\eta = 0.5$ typical for lyotropic liquid crystalline polymers, (61) gives $\xi_\perp \sim 0.1l$.

The above discussion leads to a simple physical interpretation of the observation made in the previous section, that the order parameter at the point of isotropic–nematic transition is considerably higher for rodlike molecules than for long persistent chains. In the case of stiff rods, the dependence of the orientational entropy on the order parameter can be estimated as (for η sufficiently close to unity)

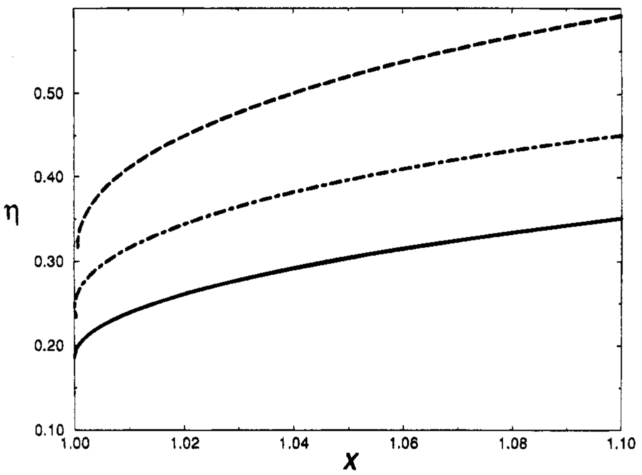


Figure 5. Nematic order parameter vs the reduced control parameter $X \sim u/\rho$ ($X = 1$ at the spinodal of the nematic phase) for rigid rods (dashed line), infinite polymers (solid line), and finite polymers with $L/l = 0.7$ (dot-dashed line).

$$S_{\mathrm{or}} \sim \ln \delta\Omega \sim \ln(1-\eta) \qquad (62)$$

where $\delta\Omega$ is a typical solid angle defined by the orientational confinement in the nematic state.

In the case of long wormlike chains, the effective correlation length decreases with the order parameter as $1-\eta$ (see (61)) and, therefore, *the number of independently rotating segments (rotational degrees of freedom) increases with nematic ordering as* $(1-\eta)^{-1}$. The orientational entropy of independently rotating segments can be used to estimate the *conformational* entropy of a chain in a nematic environment:

$$S_{\mathrm{con}} \sim \frac{S_{\mathrm{or}}}{1-\eta} \sim \frac{\ln(1-\eta)}{1-\eta} \qquad (63)$$

Inspection of (63) shows that the conformational entropy of long polymers decreases with the order parameter much faster than the orientational entropy of short molecules. This results in the observed decrease of the critical order parameter with the increase of molecular weight. Another corollary of the above effect is depicted in Figure 5 which shows that, in the nematic phase, the variation of the order parameter η with the change of the control parameter u/ρ is stronger for short molecules than for long ones.

The correlation length $\xi_\perp$ determines the size of the chain region where chain-end effects are significant. To analyze the influence of these ends on the nematic ordering, we calculate the position-dependent parameter $\langle t^{\nu}_{\perp s} t^{\iota}_{\perp s}\rangle$ in the vicinity of the chain ends ($s = 0$):

$$\langle t^{\nu}_{\perp s} t^{\iota}_{\perp s}\rangle = \sum_{n=0}^{\infty} \langle t^{\nu}_{\perp(n)} t^{\iota}_{\perp(n)}\rangle \cos^{2}(\pi n s) = \langle \mathbf{t}_{\perp}^{2}\rangle \frac{\delta^{\nu\iota}}{2}\left(e^{-s/\xi_{\perp}} + 1\right) \qquad (64)$$

This prediction is in good agreement with the numerical results obtained by Chen[15] for polymers with Onsager interactions. The fact that the typical length of the end regions is $\xi_\perp$ allows one to understand qualitatively the dependence of the critical parameters on the chain length (Figures 1 and 2). For $L \gg \xi_\perp$, the two end segments are practically independent of each other and the corrections to the transition parameters are proportional to the fraction of the end segments in the system: $\rho - \rho_\infty \sim \eta - \eta_\infty \sim \xi_\perp/L$. In this regime the system is equivalent to a mixture of chain-end and internal segments and, since the ends possess higher orientational entropy, the transition to the nematic state is determined only by the internal parts of the chain molecules. At the point of the phase transition both the partial density and the order parameter of the internal segments must coincide with those of the infinite chains. The presence of the ends gives rise to a positive correction to the total critical density and diminishes the average order parameter. This explains the observation that the exact curve for the order parameter versus molecular weight exhibits a slight increase at sufficiently high molecular weight. When $L \sim \xi_\perp$, the strong correlation between the two ends of a chain induces the crossover to the stiff-rod limit.

5.2. Hairpins and Longitudinal Correlation Length. Up to now we discussed the correlations of the transverse component of the tangent vector $\mathbf{t}_s$. The correlations of the longitudinal component have been studied by other investigators in the context of "hairpins".[16-18] In order to complete the physical picture of chain conformations in the nematic phase, we present a brief discussion of this subject and consider the variation of the longitudinal component $t_{\|s}$ across a "hairpin", i.e., between two points at which it changes its direction. If the contour distance between these points considerably exceeds $\xi_\perp$, we can average $t_{\|s}$ over fluctuations on the scale of the correlation length $\xi_\perp$:

$$\bar{t}_{\|s} = \pm\langle\sqrt{1 - \mathbf{t}_\perp^{\,2}}\rangle \simeq \pm\sqrt{\langle t_\|^{\,2}\rangle}$$

Here $\bar{t}_{\|s}$ denotes the average over small-scale ($\sim\xi_\perp$) fluctuations and $\langle\ \rangle$ is the usual thermodynamic average. The above averaging does not affect the given configuration of a hairpin. Let $N_{\rm hp}$ be the number of hairpins between two contour points s and s' for some conformation of the polymer. Then

$$\overline{t_{\|s}t_{\|s'}} = (-1)^{N_{\rm hp}}\langle t_\|^{\,2}\rangle \tag{65}$$

Suppose that $t_{\|s}$ changes its sign in some interval between points s_1 and s_2. The Hamiltonian of the chain

$$h_{12}[\mathbf{t}_s] = \int_{s_1}^{s_2} {\rm d}s\left(\frac{l}{4}\left(\frac{\partial \mathbf{t}_s}{\partial s}\right)^2 + \frac{Q\mathbf{t}_{s\perp}^{\,2}}{2}\right) \tag{66}$$

gives the energy cost of the given realization $\mathbf{t}_s$ of the hairpin. When this energy is sufficiently high (in units of temperature), one can neglect the fluctuations of the trajectories near the "classical" path which minimizes the Hamiltonian, (66). In this case, the integrand in the above equation can be viewed as the Lagrangian of a classical particle on a sphere of unit radius, in the presence of the potential $W(\theta) = -(Q/2)\sin^2\theta$, provided that one interprets the variable s as "time", and ϵ as the "mass" of the particle. The conserved "energy" of the particle is given by the sum of the "kinetic energy" $(l/4)(\partial\mathbf{t}_s/\partial s)^2$ associated with the bending of the chain and the "potential energy" $W(\theta)$ due to its interaction with the external field. Note that an energy barrier turns into a potential well in this picture and, therefore, the Hamiltonian h_{12} can be interpreted as an effective "action" of a particle in a potential well.

We proceed to minimize this action with respect to the trajectory $\mathbf{t}_s$ and the length of the "time" interval $|s_1 - s_2|$, with the boundary conditions $\theta(s_1) = 0$ and $\theta(s_2) = \pi$. Physically, this corresponds to finding the minimal energy cost of creating a hairpin, provided that we are allowed to vary the length of the chain between its ends. Note that if the chain segment between the points s_1 and s_2 is too short, this implies the existence of a sharp bend and results in a large bending energy. On the other hand, a long segment can have a very gradual turn, thus minimizing the bending energy, but as a result, a longer portion of the chain will be oriented normal to the external field and the interaction energy will increase.

The minimal action is realized for zero initial "momentum", i.e., $\partial\mathbf{t}/\partial s = 0$ at $s = s_1$ and s_2. Due to "energy" conservation this results in the following relationship:

$$\frac{l}{4}\left(\frac{\partial\theta\,(s)}{\partial s}\right)^2 - \frac{Q}{2}\sin^2\theta = {\rm const} = 0 \tag{67}$$

Thus

$${\rm d}s = \left|\sqrt{\frac{l}{2Q}}\,\frac{{\rm d}\theta}{\sin\theta}\right| \tag{68}$$

Substituting (67) and (68) into (66) and taking into account (55), we can calculate both the minimal value of the action and the optimal length of the "time" interval:

$$h_{12}^{(\rm min)} = \int_0^\pi \left|Q\sin\theta\,\sqrt{\frac{l}{2Q}}\,{\rm d}\theta\right| = 2\sqrt{\frac{Ql}{2}} \simeq \frac{3}{1-\eta} \tag{69}$$

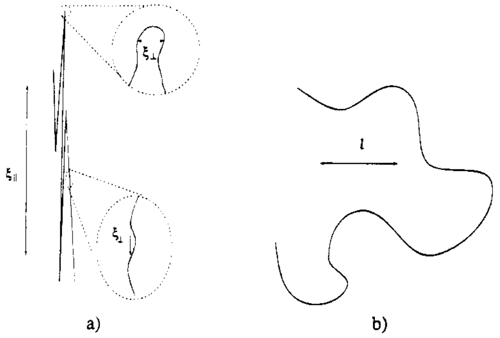
and

$$\Delta s = |s_1 - s_2| = \int_\delta^{\pi-\delta}\left|\sqrt{\frac{l}{2Q}}\,\frac{{\rm d}\theta}{\sin\theta}\right| = -2\sqrt{\frac{l}{2Q}}\,\ln(\tan\delta) \simeq \xi_\perp \ln\!\left(\frac{1}{1-\eta}\right) \tag{70}$$

Here we introduced a cutoff at small θ, $\delta \simeq \sqrt{1-\eta}$, which corresponds to the range of the angular fluctuations of the persistent segments about the nematic director. We conclude that, up to a logarithmic correction of order unity, the radius of curvature associated with a typical hairpin is of order $\xi_\perp$.

In order to estimate the density of hairpins in a long polymer chain, we note that an interval between two points on the chain, s and s', contains $N_{ss'} = |s - s'|/\Delta s$ segments of length Δs. Within the above quasi-classical approach (noninteracting hairpins), the probability to create a hairpin is $P_{\rm hp} = \exp(-h^{(\rm min)})$, for every such segment of the chain. Hence, for $|s - s'| \gg \max\{\xi_\perp,\Delta s\}$, the correlator of the longitudinal components of the tangent vector is given by (using (65))

$$\langle t_{\|s}t_{\|s'}\rangle = \langle\overline{t_{\|s}t_{\|s'}}\rangle = \langle\mathbf{t}_\|^{\,2}\rangle \sum_{N_{\rm hp}=0}^{N_{ss'}} (-1)^{N_{\rm hp}}\frac{N_{ss'}!}{N_{\rm hp}!(N_{ss'} - N_{\rm hp})!}\exp(-N_{\rm hp}h^{(\rm min)}) \simeq \langle\mathbf{t}_\|^{\,2}\rangle \sum_{N_{\rm hp}=0}^{\infty}\frac{(-N_{ss'}e^{-h^{(\rm min)}})^{N_{\rm hp}}}{N_{\rm hp}!} = \langle\mathbf{t}_\|^{\,2}\rangle\exp\!\left(-\frac{|s-s'|}{\xi_\|}\right) \tag{71}$$



a) b)

Figure 6. Typical conformations of a chain in the nematic (a) and isotropic (b) phases.

where

$$\xi_\parallel = \Delta s \exp h^{(\min)} \tag{72}$$

Within logarithmic accuracy this size is given by

$$\xi_\parallel \simeq \xi_\perp \exp\left(\frac{3}{1-\eta}\right) \tag{73}$$

We conclude that in the presence of a strong external field, $\xi_\parallel$ which describes the average contour distance between neighboring hairpins, is much larger than the characteristic size of a hairpin. Note that while the result for $\xi_\perp$, (61), is model-independent, the expression for $\xi_\parallel$, (73), holds only for a quadrupolar orientational field. In a different model, the hairpin energy $h^{(\min)}$, (69), will be given by some other function which increases with the field and, correspondingly, with the order parameter.

Summarizing the preceding results, we can identify three different behaviors, depending on the length scale one is concerned with. On length scales smaller than $\xi_\perp$, the chain behaves as a rigid rod. On length scales larger than $\xi_\perp$ but smaller than $\xi_\parallel$ the chain fluctuates about the nematic director but does not reverse its direction (i.e., the transverse component of the tangent vector is everywhere much smaller than the longitudinal component). Finally, on length scales much larger than $\xi_\parallel$, one observes abrupt reversals of the chain direction, separated on the average by a contour distance $\xi_\parallel$. This should be contrasted with the isotropic situation (in the absence of an external field), where there is a single persistent length l (see Figure 6).

Note that the transverse (59) and the longitudinal (71) correlators can be represented in the following unified form (**e** is a unit vector along the nematic director):

$$\langle t^i_s t^j_{s'}\rangle = \frac{(\delta_{ij} - e^i e^j)}{3}(1-\eta)\exp\left(-\frac{|s-s'|}{\xi_\perp}\right) + \frac{e^i e^j}{3}(1+2\eta)\exp\left(-\frac{|s-s'|}{\xi_\parallel}\right) \tag{74}$$

We now calculate the mean square spatial distance between points separated by contour length $L \gg \xi_\perp$:

$$\langle \Delta R^i \Delta R^j\rangle_L = \frac{4(\delta^{ij} - e^i e^j)}{3}(1-\eta)\,\xi_\perp L + \frac{2e^i e^j}{3}(1 + 2\eta)\xi_\parallel L\left(1 - \frac{\xi_\parallel}{L}\left(1 - \exp\left(-\frac{L}{\xi_\parallel}\right)\right)\right) \tag{75}$$

For the intermediate range of chain lengths, $\xi_\perp \ll L \ll \xi_\parallel$, this form leads to a stretched conformation, with a superimposed random walk in the transverse direction:

$$\langle \Delta \mathbf{R}_\perp^{\,2}\rangle_L = \frac{4}{3}(1-\eta)\,\xi_\perp L \tag{76}$$

$$\langle \Delta R_\parallel^{\,2}\rangle_L \simeq \langle \Delta \mathbf{R}^2\rangle_L = \frac{1+2\eta}{3}L^2 \tag{77}$$

In the limit $L \gg \xi_\parallel$ there is an anisotropic random walk, which is equivalent to the conformation of a strongly stretched Gaussian chain:

$$\langle \Delta \mathbf{R}_\perp^{\,2}\rangle_L = \frac{4}{3}(1-\eta)\,\xi_\perp L \tag{78}$$

$$\langle \Delta R_\parallel^{\,2}\rangle_L \simeq \langle \Delta \mathbf{R}^2\rangle_L = \frac{2\,(1+2\eta)}{3}\xi_\parallel L \tag{79}$$

The above results appear to suggest that very long chains, for which the distance between neighboring hairins is smaller than the contour length, should be described by (79) and therefore, cannot be fully stretched ($\langle \Delta \mathbf{R}^2\rangle_L \sim L^2$) by the application of an external field of arbitrary strength! Note, however, that since $\xi_\parallel$ diverges when $\eta \to 1$ (eq 73), for any chain of arbitrarily large (but fixed) molecular weight, there is always a critical value of the external field for which $\xi_\parallel = L$ and, for stronger external fields, one should use (77) which predicts full stretching (this problem was discussed in ref 19).

The ratio $\langle \Delta R_\parallel^{\,2}\rangle_L / \langle \Delta \mathbf{R}_\perp^{\,2}\rangle_L$ characterizes the anisotropy of the chain's conformation. Our calculation predicts the following behavior of this parameter in different regimes:

$$\frac{\langle \Delta R_\parallel^{\,2}\rangle}{\langle \Delta \mathbf{R}_\perp^{\,2}\rangle} = \frac{1+2\eta}{2\,(1-\eta)} \times \begin{cases} 1, & L \ll \xi_\perp \\ L/\xi_\perp & \xi_\perp \ll L \ll \xi_\parallel \\ \xi_\parallel/\xi_\perp & \xi_\parallel \ll L \end{cases} \tag{80}$$

This dependence is in good agreement with numerical results of Chen.[20]

6. Conclusion

We have extended the Gupta–Edwards theory of infinite main-chain nematics to the case of finite-length polymers. Our calculations show that the crossover between long- and short-chain regimes takes place for polymers of relatively low molecular weight, the length of which is smaller than the bare persistence length (note, however, that the chain length dependence of the transition temperature persists for much larger values of L/l). A more detailed analysis of the single chain behavior in the nematic phase allows one to identify this characteristic chain length with the correlation length of the transverse component of the tangent vector, $\xi_\perp$.

Upon the transition to the nematic phase, the bare persistence length of a wormlike chain splits into two qualitatively different length scales. One scale, $\xi_\perp$, defines the contour length associated with independent fluctuations of chain segments about the nematic director. It also controls the size of the regions where chain end effects are relevant and determines the crossover between the long-chain and short-chain regimes of the isotropic–nematic phase transition.

Another scale, $\xi_\parallel$, is related to the typical contour distance between neighborng "hairpins"; i.e., it determines the correlation length of the longitudinal component of the tangent vector. This size is exponentially larger than $\xi_\perp$. This allows one to identify an intermediate range of chain lengths $\xi_\perp \ll L \ll \xi_\parallel$, in which the isotropic–nematic phase transition is determined by the long-chain limit but the single-molecule conformation is practically a straight line. This should be contrasted with the true infinite chain limit, in which the chain can be modeled as a uniaxial random walk.

While $\xi_\parallel$ increases monotonically with the order parameter, $\xi_\perp$ decreases with it. As a consequence of the latter effect, the number of independent rotational modes (conformational degrees of freedom) increases with η. Thus, the entropy loss associated with the transition to the nematic state is larger for long persistent chains than for rigid rods of identical length. This observation explains why the order parameter at the isotropic–nematic transition is generally smaller for liquid crystalline polymers than for rodlike molecules. Note that the existence of two distinct correlation lengths in a wormlike polymer in an anisotropic environment reflects a fundamental difference between the wormlike and the freely-jointed chain models of polymers. In the latter model, the persistence length of angular correlations is identical to the length of the rodlike segments between the joints and is not affected by the environment in which the probe chain is embedded. As there is no penalty for making an abrupt turn (a hairpin) at a joint in a freely-jointed chain, there is no distinct correlation length associated with hairpins in this model.

It is interesting to note that the chain-length dependence of the transition temperature in our model closely resembles the experimental data on the crystallization temperature of normal alkanes as a function of their length. This suggests that the crystallization of alkanes may be initiated by the onset of the nematic instability of the disordered liquid phase (the formation of a nematic state can be preempted by the appearance of translational order, the discussion of which is beyond the scope of this work). If this conjecture is correct, the appearance of rotator phases upon cooling of the liquid can be interpreted as the signature of the predicted increase of the number of conformational degrees of freedom (associated with bending and twist about the nematic director) as the result of the transition to a stretched anisotropic state. In this picture, the subsequent transition from the rotator phase to a crystalline herringbone arrangement of all-trans chains can take place due to steric interactions (not accounted for in our treatment) between neighboring chains which suppress the twist-type motions of the stretched polymers. Such effects will not be present in the case of low molecular weight liquids in which internal degrees of freedom cannot be thermally excited and which undergo a direct liquid to crystal transition due to a density modulation-type instability.

Finally, we would like to mention that although the analysis presented in this work deals with spatially homogeneous phases, the underlying formalism allows one to describe transitions to spatially nonuniform states. Work is in progress on the application of the theory to the nematic–smectic transition in liquid crystalline polymers and to microphase separation in semiflexible copolymers.

Acknowledgment. We thank M. Deutch for valuable discussions and corrections. This work was supported by grants from the Israeli Academy of Science and Humanities and from Bar-Ilan University.

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MA950728D