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Equilibrium statistics of irregularly branched and dendrimeric polymeric liquid crystals

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In this paper we develop a self-consistent model for the equilibrium statistics of nematic branched polymeric liquid crystals in the mean-field approximation. We have solved the resulting system of equations numerically and find a nematic–isotropic phase transition. We find that the order–disorder transition temperature scales as a function of the bond continuation probability, or equivalently the molecular weight, with an exponent that depends on the interaction potential. These results are compared with the experimentally observed behaviour.

1. Introduction

Polymeric liquid crystals are polymers that on average orient themselves along some spatial axis. Polymeric liquid crystals are generally synthesized by polymerizing monomers that have a long rigid segment attached to a relatively flexible tail. The rigid segments tend to orient the polymer as if it were a traditional liquid crystal due to their steric repulsion and intermolecular interactions, while the flexible tails connecting the monomers to each other introduce correlations between adjacent monomers and limit the motion of individual monomers. Depending on the chemistry, the rigid segments will either be part of the polymer backbone itself (main-chain polymeric liquid crystals) or will hang off it like pendants (side-chain polymeric liquid crystals).

In linear polymers every interior monomer has exactly two neighbours. If the monomers are able to connect to more than two other monomers, the polymer will form a branched structure. A perfectly reacted, or regular branched, polymer has each interior monomer connected to the maximum number of possible neighbours, while an imperfectly reacted polymer has a non-zero probability that any given interior bond is unreacted. Recently, Percec *et al.* synthesized imperfectly [1, 2] and regularly [3] branched polymeric liquid crystals, and experimentally examined their physical properties. In this paper we construct a statistical model for both imperfectly and perfectly reacted main-chain polymers with nematic ordering.

2. The model

We will use a model for branched polymeric liquid crystals that is an extension in two ways of previous models for linear main-chain polymeric liquid crystals. First, this model allows for multiple connections to a given monomer and thus a branched polymer can be constructed. Second, a more detailed interaction potential between the mesogens is used. We believe that this is the first work that has used such realistic potentials in a calculation of this kind. In the context of this model, we then calculate the model partition function and free energy for a branched polymer by use of a mean-field technique.

Our model consists of bonding and non-bonding interactions. The bonding interactions are those interactions between monomers mediated by the strong polymer linkages between the monomers on a single polymer chain. The inter-polymeric interactions are the non-bonding interactions (hard core repulsion and van der Waals interactions) between monomers, whether or not they are on the same chain. These interactions and the symbols we will use to describe them are illustrated in figure 1. Each monomer in the branched polymers considered may be bonded to up to three other monomers. The statistical weight of any given monomer configuration is controlled, in part, by the bonding interactions between these monomers. The three different chemical bonds will, in principle, each have a different set of statistical weights. We will assume that two bonds can be attached to one end, the 'tail', of each monomer and one bond can be attached to the other end, the 'head', of a monomer. We will assume that bonds can only be formed 'head' to 'tail'. The statistical weight associated with the linkages between monomers can then be described as functions of the orientations $\hat{\mathbf{u}}$ of the monomers that are bonded to each other.

Since there is some stiffness to the backbone, if the monomer $k-1$ has an orientation given by the unit

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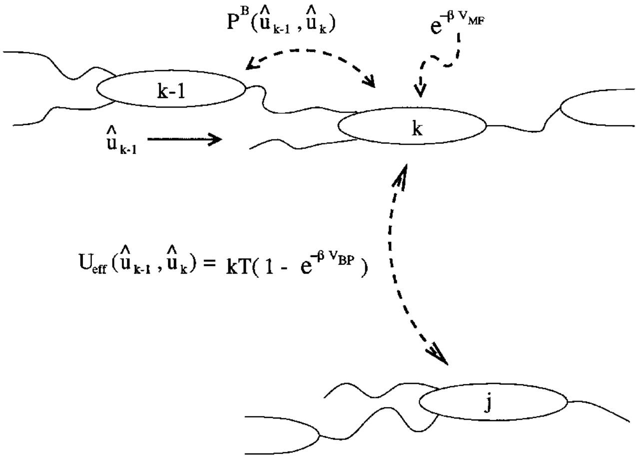

Figure 1. Illustration of the various interactions in the model.

vector $\hat{\mathbf{u}}_{k-1}$, then there is some probability distribution for the connected monomer k to have an orientation $\hat{\mathbf{u}}_k$. This joint probability distribution, in the absence of other interactions between the monomers, is $P^{\mathrm{B}}(\hat{\mathbf{u}}_{k-1}, \hat{\mathbf{u}}_k)$. In principle there are two such functions since the two 'tail' linkages will have different statistical weights. In this paper, however, we ignore this distinction.

Similarly, if the heads of two monomers with orientations $\hat{\mathbf{u}}_1$ and $\hat{\mathbf{u}}_2$ are attached the tails of a monomer with orientation $\hat{\mathbf{u}}$, then there is an associated probability distribution $P_2^{\mathrm{B}}(\hat{\mathbf{u}}, \hat{\mathbf{u}}_1, \hat{\mathbf{u}}_2)$. This again reflects the stiffness of the polymer. These functions, $P^{\mathrm{B}}(\hat{\mathbf{u}}, \hat{\mathbf{u}}_1)$ and $P_2^{\mathrm{B}}(\hat{\mathbf{u}}, \hat{\mathbf{u}}_1, \hat{\mathbf{u}}_2)$, will be discussed in more detail below.

Next, there are interactions between monomers located on different polymer backbones. We will use an effective potential $U^{\mathrm{eff}}(\hat{\mathbf{u}}, \hat{\mathbf{u}}'; \vec{r}, \vec{r}\,')$ to represent these interactions. The effective potential U^{eff} is based on the Mayer function of the anisotropic potential of Berne and Pechukas [4]. This potential was developed for simulations of liquid crystals and will be discussed in more detail later on. In our calculation we also include a mean field potential $V_{\mathrm{mf}}(\hat{\mathbf{u}}_k)$, which will be solved for self-consistency.

Given the partition function for a reference system, an upper bound on the free energy of an interacting system can be determined using the Gibbs–Bogoliubov identity

$$F \leqslant F_0 + \langle H - H_0 \rangle_0 \tag{1}$$

where F is the Helmholtz free energy, H is the Hamiltonian of the system, and the subscript '0' indicates that these terms are evaluated using the known reference states. F, in terms of the canaonical partition function Z_0, is given by

$$F_0 = -NT \log(Z_0)$$

where N is the number of particles in the system.

As in previous work [5], we will solve for the partition function approximately by including the bonding interactions and the mean-field in the reference hamiltonian H_0. It follows that $H - H_0$ is $U^{\mathrm{eff}} - V_{\mathrm{mf}}$. If we then consider the inequality in (1) to be an equality we now find

$$F \simeq F_0 + \langle U^{\mathrm{eff}} - V_{\mathrm{mf}} \rangle_0 . \tag{2}$$

Assuming $U^{\mathrm{eff}} - V_{\mathrm{mf}}$ contains only pairwise monomer–monomer interactions operating via the effective interaction potential in the presence of the mean field [5], as described above, we find

$$\begin{aligned} \langle U^{\mathrm{eff}} - V_{\mathrm{mf}} \rangle_0 = {} & \frac{1}{2V^2} \sum_{j,k} \int P_j(\hat{\mathbf{u}}_j) \int P_k(\hat{\mathbf{u}}_k) \\ & \times \iint U^{\mathrm{eff}}(\hat{\mathbf{u}}_j, \hat{\mathbf{u}}_k; \vec{\mathbf{r}}_j, \vec{\mathbf{r}}_k)\, \mathrm{d}\hat{\mathbf{u}}_j\, \mathrm{d}\hat{\mathbf{u}}_k\, \mathrm{d}\vec{r}_j\, \mathrm{d}\vec{r}_k \\ & - \sum_l \int P_l(\hat{\mathbf{u}}_l) V_{\mathrm{mf}}(\hat{\mathbf{u}}_l)\, \mathrm{d}\hat{\mathbf{u}}_l \end{aligned} \tag{3}$$

where $P_j(\hat{\mathbf{u}}_j)$ is the probability distribution for a monomer j to have an orientation $\hat{\mathbf{u}}_j$. The sums in (3) run over all monomers in the system. $P(\hat{\mathbf{u}})$ is defined to be the average probability distribution that any given monomer will have an orientation $\hat{\mathbf{u}}$,

$$P(\hat{\mathbf{u}}) \equiv \frac{1}{N} \sum_j P_j(\hat{\mathbf{u}}) \tag{4}$$

where N is the total number of monomers in the polymer. The average probability distribution (4) can equivalently be written as a functional derivative [5]

$$P(\hat{\mathbf{u}}) = \frac{-1}{\beta \langle N \rangle} \frac{\delta \log(Z_0)}{\delta V_{\mathrm{mf}}(\hat{\mathbf{u}})} \tag{5}$$

where $\langle N \rangle$ is the average number of monomers per polymer and β is the inverse temperature. If N_{p} is the total number of polymers, then $N = \langle N \rangle N_{\mathrm{p}}$.

For the model-effective potential, we used a Mayer f-function [6]

$$\begin{aligned} U^{\mathrm{eff}}(\hat{\mathbf{u}}_1, \hat{\mathbf{u}}_2; \vec{r}_{12}) &= f_{12}(\hat{\mathbf{u}}_1, \hat{\mathbf{u}}_2; \vec{r}_{12}) \\ &= \beta^{-1}\{1 - \exp[-\beta V_{\mathrm{BP}}(\hat{\mathbf{u}}_1, \hat{\mathbf{u}}_2; \vec{r}_{12})\} \end{aligned} \tag{6}$$

with interactions given by the Berne and Pechukas overlap potential [4, 7] (a modified Lennard–Jones potential)

$$\begin{aligned} & V_{\mathrm{BP}}(\hat{\mathbf{u}}_1, \hat{\mathbf{u}}_2; \vec{r}_{12}) \\ & = 4\varepsilon(\hat{\mathbf{u}}_1, \hat{\mathbf{u}}_2) \left\{ \left[\frac{\sigma(\hat{\mathbf{u}}_1, \hat{\mathbf{u}}_2, \hat{\mathbf{r}})}{|\vec{r}\,|} \right]^{12} - \left[\frac{\sigma(\hat{\mathbf{u}}_1, \hat{\mathbf{u}}_2, \hat{\mathbf{r}})}{|\vec{r}\,|} \right]^{6} \right\} \end{aligned} \tag{7}$$

with the definitions

$$\varepsilon(\hat{\mathbf{u}}_1, \hat{\mathbf{u}}_2) = \varepsilon_0 [1 - \chi^2 (\hat{\mathbf{u}}_1 \;\; \hat{\mathbf{u}}_2)^2]^{-1/2} \tag{8}$$

and

$$\sigma(\hat{\mathbf{u}}_1, \hat{\mathbf{u}}_2, \hat{\mathbf{r}}) = \sigma_0 \left[1 - \frac{\chi}{2} \left(\frac{[\hat{\mathbf{r}} \;\; \hat{\mathbf{u}}_1 + \hat{\mathbf{r}} \;\; \hat{\mathbf{u}}_2]^2}{1 + \chi[\hat{\mathbf{u}}_1 \;\; \hat{\mathbf{u}}_2]} + \frac{[\hat{\mathbf{r}} \;\; \hat{\mathbf{u}}_1 - \hat{\mathbf{r}} \;\; \hat{\mathbf{u}}_2]^2}{1 - \chi[\hat{\mathbf{u}}_1 \;\; \hat{\mathbf{u}}_2]} \right) \right]^{-1/2}. \tag{9}$$

In the above equations (7–9), $\chi \equiv (r_\parallel^2 - r_\perp^2)/(r_\parallel^2 + r_\perp^2)$ is the anisotropy parameter (for typical liquid crystal dimensions, $\chi \approx 0.885$) and ε_0 and σ_0 are parameters describing the potential well depth and interaction range respectively. We will assume that these parameters are all independent of temperature.

In a self-consistent theory, the functional variation of the free energy (2) with respect to the mean-field potential, $V_{\mathrm{mf}}(\hat{\mathbf{u}})$, must be zero. Since the variation of the log of the partition function with respect to the mean-field potential is given by equation (5), we find a self-consistent expression for the mean-field potential

$$V_{\mathrm{mf}}(\hat{\mathbf{u}}) = \rho_{\mathrm{m}} \int P(\hat{\mathbf{u}}') \tilde{U}(\hat{\mathbf{u}}, \hat{\mathbf{u}}') \,\mathrm{d}\hat{\mathbf{u}}' \tag{10}$$

where $\rho_{\mathrm{m}} = N/V$ is the monomer number density and $\tilde{U}(\hat{\mathbf{u}}, \hat{\mathbf{u}}')$ is given by substituting equation (6) into (3) and integrating out the radial variables. Evaluating the integrals in equation (3) gives

$$\begin{aligned} \tilde{U}(\hat{\mathbf{u}}_1, \hat{\mathbf{u}}_2) &= \frac{4}{3} \beta \varepsilon(\hat{\mathbf{u}}_1, \hat{\mathbf{u}}_2) \int \sigma(\hat{\mathbf{u}}_1, \hat{\mathbf{u}}_2, \hat{\mathbf{r}}_{12})^3 \,\mathrm{d}\hat{\mathbf{r}}_{12} \\ &\quad \times \int_0^\infty (2x^{1/2} - x^{-1/2}) \exp[-4\beta\varepsilon(\hat{\mathbf{u}}_1, \hat{\mathbf{u}}_2)(x^2 - x)] \,\mathrm{d}x. \end{aligned} \tag{11}$$

The radial (dx) integral in equation (11) has an exact solution in terms of parabolic cylindrical functions [8].

Next, we need to determine the partition function for a single branched polymer in a mean-field potential. Following Petschek and Terentjev [5], we begin with the recursion relation for the partial partition function of a *linear* chain polymer in a mean-field potential

$$\begin{aligned} m_k(\hat{\mathbf{u}}_k) = \int & P^{\mathrm{B}}(\hat{\mathbf{u}}_k, \hat{\mathbf{u}}_{k-1}) m_{k-1}(\hat{\mathbf{u}}_{k-1}) \\ & \times \exp[-\beta V_{\mathrm{mf}}(\hat{\mathbf{u}}_{k-1})] \,\mathrm{d}\hat{\mathbf{u}}_{k-1} \end{aligned} \tag{12}$$

where $m_k(\hat{\mathbf{u}}_k)$ is the partial partition function for the kth monomer (the sum over all states to the 'tail' of the kth monomer) and $P_{\mathrm{B}}(\hat{\mathbf{u}}_k, \hat{\mathbf{u}}_{k-1})$ is the conditional bond orientational probability of finding the kth monomer with an orientation $\hat{\mathbf{u}}_k$ given that the $(k-1)$th monomer has an orientation $\hat{\mathbf{u}}_{k-1}$ on a chain with stiffness Ω. For $P^{\mathrm{B}}(\hat{\mathbf{u}}_k, \hat{\mathbf{u}}_{k-1})$, Petschek and Terentjev [5] used a simple potential

$$P^{\mathrm{B}}(\hat{\mathbf{u}}_1, \hat{\mathbf{u}}_2) = \frac{\Omega}{4\pi \sinh(\Omega)} \exp[\Omega(\hat{\mathbf{u}}_1 \;\; \hat{\mathbf{u}}_2)]. \tag{13}$$

This correctly reflects the fact that the bonds in the polymer chain are flexible with a flexibility parameter Ω which corresponds approximately to a ten carbon alkyl chain at room temperature. Alkyl chains can also have sharp bends (*gauche* bonds). This is not, however, included in our model of the statistical weight for the monomer–monomer bond.

Generalizing equation (12) to the case of branched polymers, it is important to make two distinctions between this work and the previous work of others on linear polymers [5]. First, the monomers in a branched polymer have a uniquely identifiable direction, having one connecting chain at their 'head' and two at their 'tail'. Second, the presence of an unreacted tail in a branched polymer no longer implies an end to the chain as it does for linear chains. In general, three possible configurations occur: monomers with no further connections, monomers with a single connecting chain, and monomers connected to two new monomers (we ignore the possibility of ring formations). As mentioned earlier, the statistical weights of these three configurations are, in principle, independent quantities.

Let $m_k(\hat{\mathbf{u}}_k)$ be the partial partition function or state for all monomers connected to the tail of the kth monomer (see figure 2)

$$\begin{aligned} m_k(\hat{\mathbf{u}}_1) &= P_0 + P_1 \int m^{(1)}_{k-1}(\hat{\mathbf{u}}_2) \exp[-\beta V_{\mathrm{mf}}(\hat{\mathbf{u}}_2)] P^{\mathrm{B}}(\hat{\mathbf{u}}_1, \hat{\mathbf{u}}_2) \,\mathrm{d}\hat{\mathbf{u}}_2 \\ &\quad + P_2 \int m^{(1)}_{k-1}(\hat{\mathbf{u}}_2) \exp[-\beta V_{\mathrm{mf}}(\hat{\mathbf{u}}_2)] \\ &\quad \times \int m^{(2)}_{k-1}{}'(\hat{\mathbf{u}}_3) \exp[-\beta V_{\mathrm{mf}}(\hat{\mathbf{u}}_3)] \\ &\quad \times P^{\mathrm{B}}_2(\hat{\mathbf{u}}_1, \hat{\mathbf{u}}_2, \hat{\mathbf{u}}_3) \,\mathrm{d}\hat{\mathbf{u}}_2 \,\mathrm{d}\hat{\mathbf{u}}_3 \end{aligned} \tag{14}$$

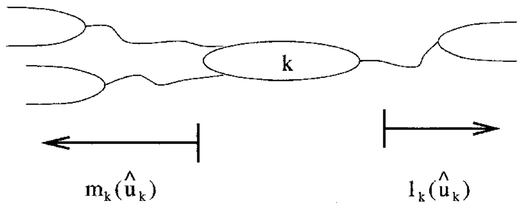

Figure 2. Recursion directions for $m_k(\hat{\mathbf{u}})$ and $l_k(\hat{\mathbf{u}})$.

where P^{B} is the joint probability distribution for a monomer with one connected tail, P_n are the statistical weights for monomers with n connected tails

$$P_n = \exp(\beta\mu_n), \quad n = 0, 1, 2 \tag{15}$$

and $P_2^{\mathrm{B}}(\hat{\mathbf{u}}_1, \hat{\mathbf{u}}_2, \hat{\mathbf{u}}_3)$ is the joint conditional bond orientational probability.

Inverting equation (15), the chemical potentials of the three possible configurations are just

$$\mu_n = \beta^{-1} \log(P_n). \tag{16}$$

While $m_k(\hat{\mathbf{u}}_k)$ represents the influence of all prior monomers in the polymer, we still need to account for the influence of all subsequent monomers. Let $l_k(\hat{\mathbf{u}}_k)$ be the partial partition function of all monomers connected to the head of the kth monomer (again, see figure 2),

$$\begin{aligned} l_k(\hat{\mathbf{u}}_1) &= Q_0 + Q_1 \int l_{k+1}(\hat{\mathbf{u}}_2) \exp[-\beta V_{\mathrm{mf}}(\hat{\mathbf{u}}_2)] P^{\mathrm{B}}(\hat{\mathbf{u}}_1, \hat{\mathbf{u}}_2)\, \mathrm{d}\hat{\mathbf{u}}_2 \\ &\quad + Q_2 \int l_{k+1}(\hat{\mathbf{u}}_2) \exp[-\beta V_{\mathrm{mf}}(\hat{\mathbf{u}}_2)] \\ &\quad \times \int m_{k'}(\hat{\mathbf{u}}_3) \exp[-\beta V_{\mathrm{mf}}(\hat{\mathbf{u}}_3)] P_2^{\mathrm{B}}(\mathbf{uf}_1, \hat{\mathbf{u}}_2, \hat{\mathbf{u}}_3)\, \mathrm{d}\hat{\mathbf{u}}_3\, \mathrm{d}\hat{\mathbf{u}}_2 \end{aligned} \tag{17}$$

where the Q_n are again the statistical weights of configurations that depend on n subsequent monomers; that is, Q_0 represents a monomer with an unconnected head chain, Q_1 represents a monomer with a connected head chain connected to a monomer with only one reacted tail, and Q_2 represents a monomer connected to a monomer with two connected tails. Note that since they represent different views of the same polymer, the statistical weights Q_n can always be specified in terms of the statistical weights P_n.

Given these definitions, the total probability that the kth monomer will have an orientation $\hat{\mathbf{u}}_k$ in the presence of a mean-field potential $V_{\mathrm{mf}}(\hat{\mathbf{u}}_k)$ is

$$P_k(\hat{\mathbf{u}}_k) = \frac{m_k(\hat{\mathbf{u}}_k) \exp[-\beta V_{\mathrm{mf}}(\hat{\mathbf{u}}_k)] l_k(\hat{\mathbf{u}}_k)}{\int m_k(\hat{\mathbf{w}}) \exp[-\beta V_{\mathrm{mf}}(\hat{\mathbf{w}})] l_k(\hat{\mathbf{w}})\, \mathrm{d}\hat{\mathbf{w}}}. \tag{18}$$

This is easily seen since $m(\hat{\mathbf{u}}_k)$ has the interpretation as a sum over all possible orientations of monomers to the tail of the kth one given that the kth monomer has orientation $\hat{\mathbf{u}}_k$, $l(\hat{\mathbf{u}}_k)$ has the same interpretation with regards the head of the monomer, and $\exp[-\beta V_{\mathrm{mf}}(\hat{\mathbf{u}}_k)]$ is the statistical weight of an isolated monomer with orientation $\hat{\mathbf{u}}_k$ in a mean-field potential $V_{\mathrm{mf}}(\hat{\mathbf{u}})$.

For the remainder of the paper, we will assume that in the mean-field limit each of the two tail chains contribute independently to the bond orientational probability $P_2^{\mathrm{B}}(\hat{\mathbf{u}}, \hat{\mathbf{u}}_2, \hat{\mathbf{u}}_3)$, and therefore it factors into the product of the bond probabilities of the individual chains

$$P_2^{\mathrm{B}}(\hat{\mathbf{u}}, \hat{\mathbf{u}}_2, \hat{\mathbf{u}}_3) = P^{\mathrm{B}}(\hat{\mathbf{u}}, \hat{\mathbf{u}}_2) P^{\mathrm{B}}(\hat{\mathbf{u}}, \hat{\mathbf{u}}_3). \tag{19}$$

This will simplify the computation significantly.

3. Randomly branched polymers

For randomly branched polymers we will assume that all monomers are statistically equivalent and therefore the subscripts on individual monomers can be dropped. This assumption can only be used with randomly branched polymers because regularly branched polymers have uniquely defined 'interior' and 'exterior' monomers (see figure 3) which are clearly not statistically equivalent.

The recursion relations (14) and (17) now take the form

$$\begin{aligned} m(\hat{\mathbf{u}}) &= P_0 + P_1 \int P^{\mathrm{B}}(\hat{\mathbf{u}}, \hat{\mathbf{u}}') m(\hat{\mathbf{u}}') \exp[-\beta V_{\mathrm{mf}}(\hat{\mathbf{u}}')]\, \mathrm{d}\hat{\mathbf{u}}' \\ &\quad + P_2 \left[\int P^{\mathrm{B}}(\hat{\mathbf{u}}, \hat{\mathbf{u}}') m(\hat{\mathbf{u}}') \exp[-\beta V_{\mathrm{mf}}(\hat{\mathbf{u}}')]\, \mathrm{d}\hat{\mathbf{u}}' \right]^2 \end{aligned} \tag{20}$$

and

$$\begin{aligned} l(\hat{\mathbf{u}}_1) &= Q_0 + Q_1 \int P^{\mathrm{B}}(\hat{\mathbf{u}}, \hat{\mathbf{u}}') l(\hat{\mathbf{u}}') \exp[-\beta V_{\mathrm{mf}}(\hat{\mathbf{u}}')]\, \mathrm{d}\hat{\mathbf{u}}' \\ &\quad + Q_2 \int P^{\mathrm{B}}(\hat{\mathbf{u}}, \hat{\mathbf{u}}') l(\hat{\mathbf{u}}') \exp[-\beta V_{\mathrm{mf}}(\hat{\mathbf{u}}')] \\ &\quad \times \int P^{\mathrm{B}}(\hat{\mathbf{u}}', \hat{\mathbf{u}}'') m(\hat{\mathbf{u}}'') \exp[-\beta V_{\mathrm{mf}}(\hat{\mathbf{u}}'')]\, \mathrm{d}\hat{\mathbf{u}}''\mathrm{d}\hat{\mathbf{u}}'. \end{aligned} \tag{21}$$

Similarly, the probability (18) becomes

$$P(\hat{\mathbf{u}}) = m(\hat{\mathbf{u}}) \exp[-\beta V_{\mathrm{mf}}(\hat{\mathbf{u}})] l(\hat{\mathbf{u}}) \Big/ \int m(\hat{\mathbf{w}}) \exp[-\beta V_{\mathrm{mf}}(\hat{\mathbf{w}})] l(\hat{\mathbf{w}})\, \mathrm{d}\hat{\mathbf{w}}. \tag{22}$$

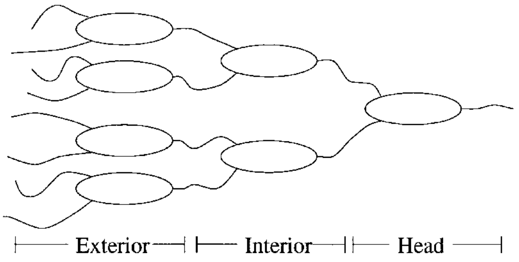

Figure 3. Sketch of a regularly branched polymer, showing the 'head' monomer.

Since we wish to model the physically realistic situation in which chemical reactions do not occur, we will fix the mean molecular weight at some constant value. To simplify the analysis, we also assume that the probability of bond formation is a constant and this probability is always equal to $(1 - P_{\mathrm{I}})$. Strictly speaking, this, together with our assumption that all monomers are statistically equivalent, is not the same as saying that no further chemical reactions occur. Rather, it is the same as the assumption that chemical reactions can occur provided the number average molecular weight remains constant. We do not believe, however, that this seriously changes the physics of our model.

From experiments, it is well known that real randomly branched polymers are a mixture of molecular weights. Thus, according to the Gibbs phase rule the isotropic–nematic transition occurs over a range of temperatures. Our previous assumptions, however, will cause a sharp isotropic–nematic transition, again by the Gibbs phase rule. Thus we cannot predict the (small) width of these transitions. We do not believe, however, that this seriously affects the predicted qualitative trends we will see in the transition temperatures.

If N_j is the number of monomers with j connected tails and there are $\langle N \rangle$ monomers in the polymer, then P'_j, the probability that a monomer has j unreacted tails, is just

$$P'_j = N_j / \langle N \rangle . \tag{23}$$

For any branched network, there are exactly $(\langle N \rangle + 1)$ unreacted tails and exactly *one* unreacted head. Therefore, the probability, Q'_0, that a monomer has an unconnected head is just $1/\langle N \rangle$. The head monomer has on average $(P'_1 + 2P'_2)$ neighbours. These monomers have in turn $(P'_1 + 2P'_2) \times (P'_1 + 2P'_2)$ neighbours, etc. For an entire chain, then,

$$\langle N \rangle = (P'_0 - P'_2)^{-1} \tag{24}$$

and thus $Q'_0 = 1/(P'_0 - P'_2)$ where P_{I} is defined as

$$P_{\mathrm{I}} \equiv (2P'_0 - P'_1)/2 \tag{25}$$

which is equivalent to our previous definition of $1 - P_{\mathrm{I}}$ as the probability that any given bond is connected to another monomer. Thus, the probabilities P'_j in equation (23) are

$$P'_0 = P_{\mathrm{I}}^2$$

$$P'_1 = 2P_{\mathrm{I}}(1 - P_{\mathrm{I}})$$

and

$$P'_2 = (1 - P_{\mathrm{I}})^2 .$$

and the number average molecular weight $\langle N \rangle$ is [9]

$$\langle N \rangle = (2P_{\mathrm{I}} - 1)^{-1} .$$

Both Q'_1 (the probability that the head chain is connected and it forms the only connected tail on the next monomer) and Q'_2 (the probability that the head chain is connected as one of two connected tails on the next monomer) can be completely specified in terms of in terms of P'_j. Since P_{I} is defined as the probability that any given tail chain in a randomly branched polymer is unconnected, it is easy to show that

$$Q'_1 = (1 - Q'_0) P_{\mathrm{I}}$$

and

$$Q'_2 = (1 - Q'_0)(1 - P_{\mathrm{I}}). \tag{26}$$

Substituting for P_{I} and rearranging terms yields

$$\begin{aligned} Q'_0 &= (P'_0 - P'_2)^{-1} \\ Q'_1 &= (1 - Q'_0)(2P'_0 + P'_1)/2 \\ Q'_2 &= (1 - Q'_0)(2P'_2 + P'_1)/2. \end{aligned} \tag{27}$$

Now, knowing that $\int P(\hat{\mathbf{u}}) \mathrm{d}\hat{\mathbf{u}} \equiv 1$ with $P(\hat{\mathbf{u}})$ given by equation (22), we can compute term by term the statistical weights P_j and Q_j in equations (20, 21) in terms of the probabilities P'_j and Q'_j:

$$\begin{aligned} P_0 &= P'_0 \Lambda \left\{ \int l(\hat{\mathbf{u}}) \exp[-\beta V_{\mathrm{mf}}(\hat{\mathbf{u}})] \, \mathrm{d}\hat{\mathbf{u}} \right\}^{-1} \\ P_1 &= P'_1 \Lambda \left\{ \int l(\hat{\mathbf{u}}) \exp[-\beta V_{\mathrm{mf}}(\hat{\mathbf{u}})] \right. \\ &\quad \left. \times \int P^{\mathrm{B}}(\hat{\mathbf{u}}, \hat{\mathbf{u}}') m(\hat{\mathbf{u}}') \exp[-\beta V_{\mathrm{mf}}(\hat{\mathbf{u}}')] \, \mathrm{d}\hat{\mathbf{u}}' \mathrm{d}\hat{\mathbf{u}}' \right\}^{-1} \\ P_2 &= P'_2 \Lambda \left\{ \int l(\hat{\mathbf{u}}) \exp[-\beta V_{\mathrm{mf}}(\hat{\mathbf{u}})] \right. \\ &\quad \left. \times \left[\int P^{\mathrm{B}}(\hat{\mathbf{u}}, \hat{\mathbf{u}}') m(\hat{\mathbf{u}}') \exp[-\beta V_{\mathrm{mf}}(\hat{\mathbf{u}}')] \, \mathrm{d}\hat{\mathbf{u}}' \right]^2 \mathrm{d}\hat{\mathbf{u}} \right\}^{-1} \\ Q_0 &= Q'_0 \Lambda \left\{ \int m(\hat{\mathbf{u}}) \exp[-\beta V_{\mathrm{mf}}(\hat{\mathbf{u}})] \, \mathrm{d}\hat{\mathbf{u}} \right\}^{-1} \\ Q_1 &= Q'_1 \Lambda \left\{ \int m(\hat{\mathbf{u}}) \exp[-\beta V_{\mathrm{mf}}(\hat{\mathbf{u}})] \right. \\ &\quad \left. \times \int P^{\mathrm{B}}(\hat{\mathbf{u}}, \hat{\mathbf{u}}') l(\hat{\mathbf{u}}') \exp[-\beta V_{\mathrm{mf}}(\hat{\mathbf{u}}')] \, \mathrm{d}\hat{\mathbf{u}}' \mathrm{d}\hat{\mathbf{u}}' \right\}^{-1} \\ Q_2 &= Q'_2 \Lambda \left\{ \int m(\hat{\mathbf{u}}) \exp[-\beta V_{\mathrm{mf}}(\hat{\mathbf{u}})] \right. \\ &\quad \times \int P^{\mathrm{B}}(\hat{\mathbf{u}}, \hat{\mathbf{u}}') l(\hat{\mathbf{u}}') \exp[-\beta V_{\mathrm{mf}}(\hat{\mathbf{u}}')] \\ &\quad \left. \times \int P^{\mathrm{B}}(\hat{\mathbf{u}}, \hat{\mathbf{u}}'') m(\hat{\mathbf{u}}'') \exp[-\beta V_{\mathrm{mf}}(\hat{\mathbf{u}}'')] \, \mathrm{d}\hat{\mathbf{u}}'' \mathrm{d}\hat{\mathbf{u}}' \mathrm{d}\hat{\mathbf{u}} \right\}^{-1} \end{aligned} \tag{28}$$

with normalization term Λ given by

$$\Lambda = \int m(\hat{\mathbf{u}}) \exp[-\beta V_{\mathrm{mf}}(\hat{\mathbf{u}})] l(\hat{\mathbf{u}}) \, \mathrm{d}\hat{\mathbf{u}}. \tag{29}$$

From equations (20, 21, 28), it is apparent that the mean-field potential is specified only to within a constant V'. We define V', then, to be such that Λ is always equal to unity. We would like to note in passing that the above transformation (28) from statistical weights to probabilities can also be performed as a Legendre transformation of the partial partition function from fixed chemical potentials, μ_n, to fixed mean numbers, $\langle N_n \rangle$, which results in an identical system of equations. This is physically reasonable since once the reactions end, the molecular weight of the polymer remains constant.

To turn the partial partition function into a partition function, it is now necessary to integrate over all possible orientations of the final monomer. In randomly branched networks, unlike the linear chains first considered in reference [5], the determination of the final monomer is somewhat ambiguous. Branched networks have, however, only one monomer that does not have a reacted head chain and as a consequence $l_N(\hat{\mathbf{u}}_1) \equiv 1$, which greatly simplifies the integration. Taking this monomer to be the 'end' of our polymer, the partition function of a single polymer is

$$Z_0 = \int m(\hat{\mathbf{u}}) \exp[-\beta V_{\mathrm{mf}}(\hat{\mathbf{u}})] \, \mathrm{d}\hat{\mathbf{u}}. \tag{30}$$

For a canonical partition function with mean-field interactions and a fixed total number of monomers N, the free energy F_0 of a collection of N_{p} polymers is

$$F_0 = -N_{\mathrm{p}} \beta^{-1} \log(Z_0) + N \sum_j \mu_j P'_j \tag{31}$$

where the summation is over all chemical species present. Substituting equations (31) and (16) into (2) we find the final expression for the free energy per monomer

$$\begin{aligned} F/N = {} & (-\beta \langle N \rangle)^{-1} \log \left\{ \int m(\hat{\mathbf{u}}) \exp[-\beta V_{\mathrm{mf}}(\hat{\mathbf{u}}) \, \mathrm{d}\hat{\mathbf{u}}] \right\} \\ & - \frac{1}{2} \int P(\hat{\mathbf{u}}) V_{\mathrm{mf}}(\hat{\mathbf{u}}) \, \mathrm{d}\hat{\mathbf{u}} \\ & + \beta^{-1} [P'_0 \log(P_0) + P'_1 \log(P_1) + P'_2 \log(P_2)]. \end{aligned} \tag{32}$$

4. Regularly branched polymers

The monomers in a regularly branched polymer, unlike those in a randomly branched polymer, are *not* statistically equivalent—the probabilities P'_i are functions of the monomer index. In addition to a sequential index k, we will assign to each monomer in the regularly branched polymer a generation number G. The generation of the 'head' monomer we define to be 1. The two monomers connected to it have a generation number of 2. The four monomers connected to the second generation have a generation number of 3, and so on. The number of monomers per polymer $\langle N \rangle$ in terms of the generation number is

$$\langle N \rangle = 2^G - 1.$$

Because we now have an explicit index, the simplified form of the recursion relations (20, 21) cannot be used, but instead we must use the more general relations (14, 17), subject to the approximation (19) for the joint conditional probability. From figure 3, however, we see that the dependence of the probabilities P'_i and Q'_i on the monomer index can be expressed in terms of the generation number alone. This allows us to simplify the computation of the statistical weights P_i and Q_i significantly. Interior monomers will always be connected to two additional monomers, so $P_1 = 0$ for these monomers. The head monomer ($G = 1$) is unique since $Q'_0 = 1$ for this monomer while $Q'_0 = 0$ everywhere else. Finally, the tail monomers are never reacted, so only P'_0 and Q'_2 are non-zero for these monomers. These simplifications are easily exploited when solving equations (14) and (17) numerically. The conversion from probabilities to statistical weights and the remainder of the analysis are the same as that of §3.

5. Numerical results

Equations (14, 17) and (20, 21) are both systems of nonlinear integral equations that must be solved before the free energy, and hence the transition temperature, can be determined. We solved the system of simultaneous equations for the regularly branched (10, 14, 17) and randomly branched (10, 20, 21) polymers numerically using an iterative fixed-point algorithm until the root mean square difference between iterations converged to within some precision ($\Delta\varepsilon < 10^{-9}$). The radial integral in equation (11) was expressed as the Taylor series expansion in $\beta\varepsilon(\hat{\mathbf{u}}, \hat{\mathbf{u}}')$ of its analytic solution in parabolic cylindrical functions [8]. We evaluated the various angular integrals using Gaussian quadrature [10] over a grid of 512 nodes. The following parameters were used throughout the calculations: $\rho_{\mathrm{m}} = 1.0$, $\Omega = 3.0$, $\sigma_0 = 0.5$, and $\varepsilon_0 = 0.5$. The dimensions of ε_0 are inverse temperature, σ_0 is a length, ρ_{m} is a number density and Ω is dimensionless. Note that when the statistical weights are expressed in terms of the probabilities P'_n as given in equation (28) and substituted into either (14–17) or (20–21), the resulting equations and the resulting free energy are independent of the absolute magnitude of both $m(\hat{\mathbf{u}})$ and $l(\hat{\mathbf{u}})$. There is no reason, then, to assume that a recursive technique will converge to a meaningful solution unless the magnitudes of l and m are somehow constrained. We thus impose the constraints

$$\int m(\hat{\mathbf{u}})\,\mathrm{d}\hat{\mathbf{u}} = 1$$

$$\int l(\hat{\mathbf{u}})\,\mathrm{d}\hat{\mathbf{u}} = 1 \tag{33}$$

which improves the convergence of the algorithm and reduces the available degrees of freedom.

The resulting system of equations were solved over a range of temperatures T and for a range of polymer sizes $\langle N \rangle$. After finding the average orientation distribution, we computed the scalar nematic order parameter, S, of the system; S, is computed as an integration over the orientational distribution $P(\hat{\mathbf{u}})$ [11],

$$S \equiv \int P(\hat{\mathbf{u}})\left[\frac{3}{2}(\hat{\mathbf{u}}\;\hat{\mathbf{z}})^2 - \frac{1}{2}\right]\mathrm{d}\hat{\mathbf{u}} \tag{34}$$

where $P(\hat{\mathbf{u}})$ is the probability given in equation (22). At the isotropic–nematic phase transition, the order parameter changes discontinuously from zero to $S \approx 0.4$ which corresponds to a first order transition from a disordered to an ordered state (see figures 4 and 5 for the case of randomly and regularly branched polymers, respectively). The exact range of transition order parameters can be altered by changing the strength of the effective interaction (by changing ε_0 and σ_0). In principle then, it is possible to model almost any reasonable change in the order parameter, ΔS, by carefully choosing the physical parameters of the system.

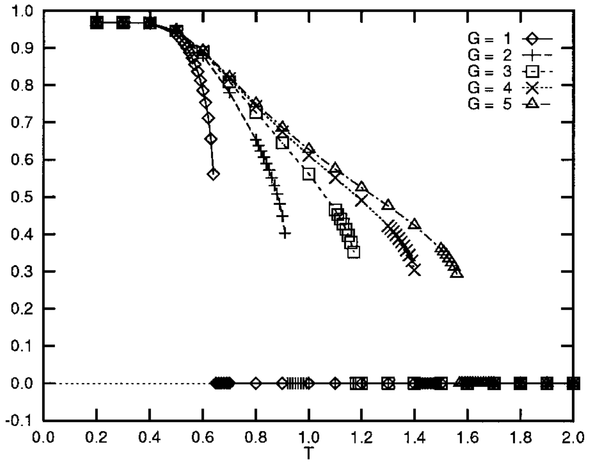

Figure 5. Calculated order parameter (S) vs. temperature (T) for a regularly branched polymer. The molecular weight in terms of the generation number G is $\langle N \rangle = 2^G - 1$.

Having evaluated the free energy over a range of temperatures and chemical potentials, we next fitted the transition temperatures T_c determined from the order parameter calculations to the probability P_1. Doing so reveals a non-universal scaling relation between the polymer transition temperature $T_c(P_1)$ and the monomer transition temperature $T_0 = T_c(P_1 = 1)$,

$$T_c(P_1) = \frac{(1 - aP_1^{\nu})}{(1 - a)}T_0 \tag{35}$$

or, in terms of the molecular weight $M_n = \langle N \rangle M_1$

$$T_c(M_n) = \left\{\frac{1 - a[(M_n + M_1)/2M_n]^{\nu}}{1 - a}\right\}T_0 \tag{36}$$

where M_1 is the monomer mass. The fitting parameters a and ν depend on the interaction parameters (σ_0, ε_0, etc.). For our choice of interaction parameters ($\Omega = 3$, $\varepsilon_0 = 0.5$, $\sigma_0 = 0.5$, and $\chi = 0.885$) we find for randomly branched polymers that $a = 0.35$ and $\nu = -2.5$. As shown in figure 6, the agreement between the fit and the data is excellent. The regularly branched data follow the same

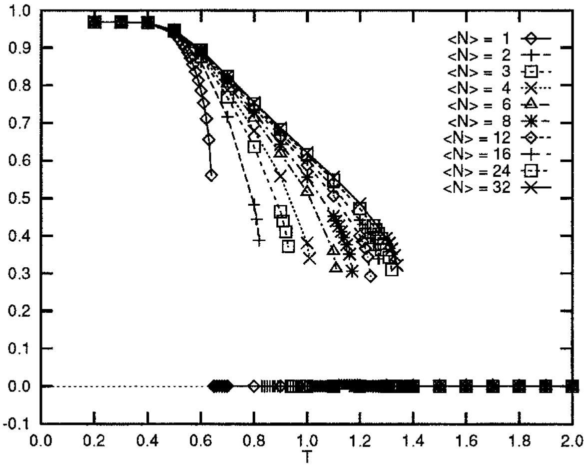

Figure 4. Calculated order parameter (S) vs. temperature (T) for a randomly branched polymer.

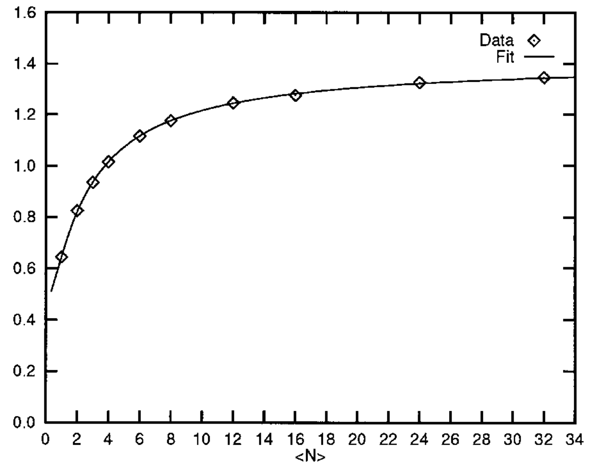

Figure 6. Isotropic–nematic transition temperature (T) vs. reduced molecular mass ($M_n/M_1 = \langle N \rangle$).

empiric scaling relation, although the fit is not as good due to the relatively small number of data points (only integer generation numbers have physical meaning).

6. Extensions to mean-field theory

Mean-field theories are valid up to a point, but ultimately many-body interactions become important and the theory breaks down. In order to determine the limits of this model, we calculated an estimate of the first correction to the mean-field theory, due to polymer self-interactions as sketched in figure 7. We will only derive the case for randomly branched polymers although the derivation for regularly branched polymers is completely analogous.

When intra-polymer interactions are included, the expression for the mean-field potential takes the form

$$\begin{aligned} V_{\mathrm{mf}}(\hat{\mathbf{u}}) = {} & \rho \int P(\hat{\mathbf{u}})\tilde{U}(\hat{\mathbf{u}}, \hat{\mathbf{u}}')\,\mathrm{d}\hat{\mathbf{u}}' \\ & + \rho \iint P^{(2)}(\hat{\mathbf{u}}, \hat{\mathbf{u}}', \vec{q})U^{\mathrm{eff}}(\hat{\mathbf{u}}, \hat{\mathbf{u}}', \vec{q})\,\mathrm{d}\hat{\mathbf{u}}'\mathrm{d}\vec{q} \end{aligned} \tag{37}$$

where $U_{\mathrm{eff}}(\hat{\mathbf{u}}, \hat{\mathbf{u}}', \vec{q})$ is the Fourier transform of equation (6) and $P^{(2)}(\hat{\mathbf{u}}, \hat{\mathbf{u}}', \vec{q})$ is the two particle conditional probability (the probability that given a monomer with orientation $\hat{\mathbf{u}}$ there is another monomer on the same polymer with orientation $\hat{\mathbf{u}}'$ with a separation given by wave vector $\vec{q}$).

Let $G(\hat{\mathbf{u}}, \hat{\mathbf{u}}', \vec{q})$ be the transfer operator that connects two monomers on the same chain with orientations $\hat{\mathbf{u}}, \hat{\mathbf{u}}'$ and separation $\vec{q}$. If $\tilde{m}(\hat{\mathbf{u}})$ is the partition function of a monomer which has at least one leg connected

$$\begin{aligned} \tilde{m}(\hat{\mathbf{u}}) \equiv {} & \left\{ \iint m(\hat{\mathbf{w}}) \exp[-\beta V_{\mathrm{mf}}(\hat{\mathbf{w}})] P^{\mathrm{B}}(\hat{\mathbf{w}}, \hat{\mathbf{u}})\,\mathrm{d}\hat{\mathbf{w}} \right\}^{-1} \\ & \times [m(\hat{\mathbf{u}}) - P_0] \end{aligned} \tag{38}$$

then $G(\hat{\mathbf{u}}, \hat{\mathbf{u}}', \vec{q})$ is given by the integral equation

$$\begin{aligned} G(\hat{\mathbf{u}}, \hat{\mathbf{u}}', \vec{q}) = P^{\mathrm{B}}(\hat{\mathbf{u}}, \hat{\mathbf{u}}', \vec{q}) + & \int P^{\mathrm{B}}(\hat{\mathbf{u}}, \hat{\mathbf{w}}, \vec{q})\tilde{m}(\hat{\mathbf{w}}) \\ & \times \exp[-\beta V_{\mathrm{mf}}(\hat{\mathbf{w}})] G(\hat{\mathbf{w}}, \hat{\mathbf{u}}', \vec{q})\,\mathrm{d}\hat{\mathbf{w}} \end{aligned} \tag{39}$$

where $P^{\mathrm{B}}(\hat{\mathbf{u}}, \hat{\mathbf{u}}', \vec{q})$ is the conditional bond orientational probability for chemically bonded monomers.

In terms of $G(\hat{\mathbf{u}}, \hat{\mathbf{u}}', \vec{q})$, the probability $P^{(2)}(\hat{\mathbf{u}}, \hat{\mathbf{u}}', \vec{q})$ becomes

$$\begin{aligned} P^{(2)}(\hat{\mathbf{u}}, \hat{\mathbf{u}}', \vec{q}) = {} & (P_1 + P_2)m(\hat{\mathbf{u}}) \exp[-\beta V_{\mathrm{mf}}(\hat{\mathbf{u}})] \\ & \times G(\hat{\mathbf{u}}, \hat{\mathbf{u}}', \vec{q})\tilde{m}(\hat{\mathbf{u}}') \exp[-\beta V_{\mathrm{mf}}(\hat{\mathbf{u}}')] l(\hat{\mathbf{u}}') \\ & + P_2 \int \mathrm{d}\hat{\mathbf{w}} m(\hat{\mathbf{u}}) \exp[-\beta V_{\mathrm{mf}}(\hat{\mathbf{u}})] \\ & \times G(\hat{\mathbf{u}}, \hat{\mathbf{w}}, \vec{q}) \exp[-\beta V_{\mathrm{mf}}(\hat{\mathbf{w}})] l(\hat{\mathbf{w}}) \\ & \times G(\hat{\mathbf{w}}, \hat{\mathbf{u}}', -\vec{q}) \exp[-\beta V_{\mathrm{mf}}(\hat{\mathbf{u}}')] m(\hat{\mathbf{u}}'). \end{aligned} \tag{40}$$

The coefficients P_1 and P_2 are the statistical weights given in equations (28). The two terms in (40) reflect that if each monomer in the network has only one head group then any two monomers in the polymer must be connected by either a single linear segment (the first term) or by two separate segments joined together at a single point (the second term).

Since we are only interested in an order of magnitude estimate, we assume that the $\vec{q}$ dependence of all functions can be factored out and handled separately. Specifically, we assume that

$$U^{\mathrm{eff}}(\hat{\mathbf{u}}, \hat{\mathbf{u}}', \vec{q}) \approx \tilde{U}(\hat{\mathbf{u}}, \hat{\mathbf{u}}')U^{\mathrm{HS}}(\vec{q}) \tag{41}$$

$$P^{\mathrm{B}}(\hat{\mathbf{u}}, \hat{\mathbf{u}}', \vec{q}) = P^{\mathrm{B}}(\hat{\mathbf{u}}, \hat{\mathbf{u}}')P(\vec{q}) \tag{42}$$

$$G(\hat{\mathbf{u}}, \hat{\mathbf{u}}', \vec{q}) = G(\hat{\mathbf{u}}, \hat{\mathbf{u}}')G(\vec{q}) \tag{43}$$

where $U^{\mathrm{HS}}(\vec{q})$ is a Fourier transformed hard sphere potential and $P(\vec{q})$ is the Fourier transform of the Gaussian distribution

$$P(\vec{R}_{12}) = (a\sqrt{\pi})^3 \exp[(\vec{R}_{12} - \vec{L})^2/a^2]. \tag{44}$$

Hence,

$$U^{\mathrm{HS}}(\vec{q}) = 4\pi R_0 q^{-2}[q^{-1}R_0^{-1}\sin(qR_0) - \cos(qR_0)] \tag{45}$$

and

$$P(\vec{q}) = \exp(\mathrm{i}\vec{q}\ \ \vec{L}) \exp(-q^2a^2/4). \tag{46}$$

For the remainder of this paper, we will take the ratio $|\vec{L}|/a$ to be 10.0 (a typical value for the small polymers we will be discussing). To obtain $G(\vec{q})$, we invert equation (39) and solve for $G(\vec{q})$. This yields

$$G(\vec{q}) = \frac{P(\vec{q})P^{\mathrm{B}}(\hat{\mathbf{u}}, \hat{\mathbf{u}}')}{G(\hat{\mathbf{u}}, \hat{\mathbf{u}}') - P(\vec{q}) \displaystyle\int P^{\mathrm{B}}(\hat{\mathbf{u}}, \hat{\mathbf{w}})\tilde{m}(\hat{\mathbf{w}}) \times \exp[-\beta V_{\mathrm{mf}}(\hat{\mathbf{w}})] G(\hat{\mathbf{w}}, \hat{\mathbf{u}}')\,\mathrm{d}\hat{\mathbf{w}}} \tag{47}$$

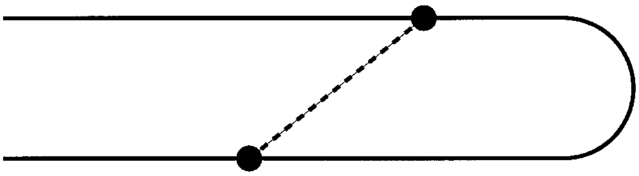

Figure 7. First order corrections to mean-field theory. The solid line represents the polymer, the dashed line represents interactions.

from which the two particle probability (40) can be computed.

In terms of the two particle probability, the first correction to mean-field theory is given by

$$\frac{1}{2(2\pi)^3}\int d^3\vec{q}\,\mathrm{Tr}_{1=2} \times \log\left[1+\int d\hat{\mathbf{w}}P(\hat{\mathbf{u}}_1,\hat{\mathbf{w}},\vec{q})U(\hat{\mathbf{w}},\hat{\mathbf{u}}_2,\vec{q})\right]. \qquad (48)$$

where this is much smaller than the free energy (31) given by mean-field theory, we expect our results to be valid. As seen in figure 8, corrections are expected to be important only at low temperatures, well away from the isotropic–nematic phase transition. The explicit temperature dependence was factored out of figure 8 simply to be dimensionally consistent with equation (48).

7. Discussion

Several approximations were made in deriving this model. First, we assumed that the ordering influence of one monomer on its adjacent neighbour(s) could be factored into two independent contributions and each could be considered separately. This is clearly not the case since the two monomers cannot occupy the same volume of space. More subtly, the angular distribution used in equation (13) does not distinguish between chains with even or odd numbers of atoms even though the chemical properties of the two are known to be, in general, quite different.

Comparison of these theoretical results with the experimental data [1–3] nevertheless shows a reasonable qualitative agreement. To predict the actual transition temperatures of different polymers is not a simple task; even if the model is faithful to the original, it is still necessary to know the correct values for ε_0, σ_0, and Ω. The interaction range σ_0 is defined in [4] as

$$\sigma_0 \equiv \sqrt{2}\sigma_\perp$$

where $\sigma_\perp$ is the semi-minor axis of the ellipse of revolution used to model the monomers, which can be deduced from the chemistry. Molecular modelling techniques may permit a first principles calculation for Ω for a given polymer although the effort involved might easily become overwhelming, especially if multiple candidate monomers need to be examined. Finally, the interaction strength ε_0 can be estimated from an experimentally measured Hamaker coefficient [12], although the calculations involved are fairly tedious. To the best of our knowledge, however, the Hamaker coefficient of these materials has not been measured.

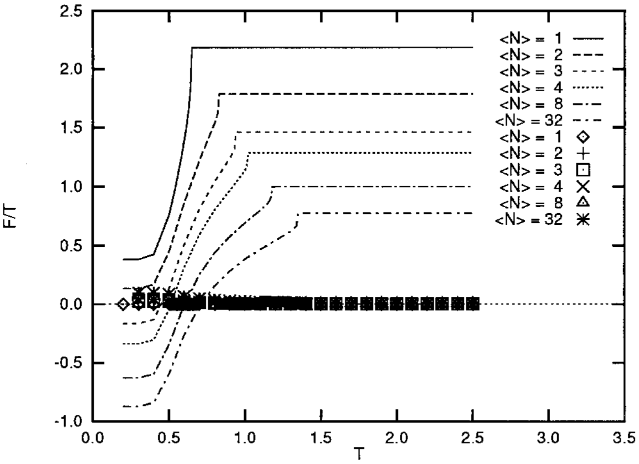

Figure 8. $-\beta F$ in the mean-field approximation (lines) and first correction (points) at a variety of molecular weights vs. temperature (T). Note that $-\beta F$ is much greater than the first correction near the phase transition for each value of $\langle N \rangle$.

8. Conclusions

In this paper, we have derived a self-consistent model for branched polymeric liquid crystals. This model shows a first order isotropic–nematic transition, in agreement with experiments. The parameters ε_0 and σ_0 can be adjusted to match the predicted scalar order parameter at the phase transition to an experimentally measured order parameter. Order of magnitude estimates of the first order, polymeric self-interaction, corrections to the mean-field theory show that our model is likely valid down to temperatures much smaller than the transition temperatures, at least for the polymers considered in this paper. Finally, we found an empirical scaling relation between the observed transition temperature and the average molecular weight.

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