# Statistical Thermodynamics of Polymer Liquid Crystals: Variation of Concentration of the Mesogenic Component

**Daniel A. Jonah,[†] Witold Brostow,[*,†] and Michael Hess[†,‡]**

*Center for Materials Characterization and Departments of Chemistry and Physics, University of North Texas, Denton, Texas 76203-5308, and Physikalische Chemie, FB6, Universität Duisburg, D-W-4100 Duisburg 1, Federal Republic of Germany*

ABSTRACT: Polymer liquid crystal (PLC) macromolecules consisting of LC and flexible sequences with varying composition $\Theta$ of LC segments are considered using the lattice approach of Flory,[5,6] with the orientational distribution function developed by Flory and Ronca.[8,9] We obtain a partition function dependent on $\Theta$, on the average length of rigid sequence $\bar{\eta}$, on the order parameter $s$, and on temperature $T$. For $\Theta = 1$ the equations reduce to the case of fully rigid rods treated before by Flory and collaborators. A drastic change in the slope of $s$ vs $\bar{\eta}$ curve is observed around $\Theta = 0.2$, indicating a large increase in the chain alignment. A prediction of $T_{LC-i}$ in function of $\Theta$ for a given $\bar{\eta}$ value is shown. LC-rich phases are formed for $\Theta > \Theta_{LC\ limit}$; that limit is discussed in relation to earlier work by Flory and Matheson, experimental evidence, and the present results.

## 1. Introduction and Scope

We need first to sort out liquid-crystalline materials as a function of their relative molecular mass. Following Samulski,[1] we distinguish *monomer liquid crystals* (MLCs)—irrespective of whether these monomers can be polymerized—and *polymer liquid crystals* (PLCs). Since we are in the second century of studies of MLCs, we know much more about them. PLCs constitute a very active area of research.[2-4] However, we know much less than we would like to about their phase structures and phase transformations—the subject of the present paper. We shall now characterize briefly available theoretical approaches and experimental information and, on this basis, define the scope of this paper.

A theoretical approach developed by Flory[5] in 1956 still constitutes the basis for contemporary work. Flory's starting point was an experimental observation that the configurational dimensions of polymer molecules in dilute solutions are often about twice those assuming free rotation about all single bonds (the freely jointed or flexible chain model). Therefore, he argued, we have in such cases semiflexible (or, equivalently, semirigid) chain molecules. Flory developed an ingenious procedure[6] for placing rigid molecules on a lattice, thus taking advantage of the lattice model that he and also Guggenheim[7] used so well. The procedure is based on dividing a rigid chain into submolecules joined together in such a way that the molecule as a whole is oriented at an angle $\neq 0$ with respect to the horizontal (or vertical) lattice orientation; we shall also use this device (see eq 6 below).

When more than 20 years later rigid molecules became a focus of attention, this also because of rigidity exhibited by PLCs, Flory and collaborators applied and extended this approach[8-19] to deal with the statistical mechanics of a number of specific cases: again rods in solution,[8] but now also taking into account orientation-dependent interactions;[9] polydisperse rods and quasi-spherical (solvent) molecules;[10] rods with two different axial ratios and solvent;[11] rods connected by flexible joints plus solvent.[15] For PLCs, which mostly consist of rigid and flexible sequences of segments, one can use the treatment of such macromolecules by Matheson and Flory.[16]

Typically one assumes in the lattice model that a segment has a length equal to its diameter, which makes possible placement at a given lattice site of either a polymer segment or a solvent molecule. Flory has used this device also. However, one can also assume a width of a segment larger than 1; this has been done for rigid sequences by Gallenkamp.[20] However, Gallenkamp considered not only rigid rods but also rigid stars, that is, stiff sequences perpendicular to one another and meeting at a certain segment. He had to introduce a second order parameter but achieved a three-dimensional description of the system. We know that there is a class of star-shaped PLC molecules and that the properties of PLCs are strongly dependent on the class, that is, on the molecular shape.[2,4] Moreover, computer simulations of PLC systems by the method of molecular dynamics show that mechanical properties are defined by the spatial distribution of rigid units in each system.[21,22]

Finally, we need to mention experimental work on the ternary system of the type PLC + flexible polymer + solvent.[23] As expected, an attempt to use the theory of Flory for the rigid rods + flexible chains + solvent system did not produce satisfactory results, since most PLCs including the one studied are only partly rigid (there are a certain number of fully rigid macromolecules, with low solubility and virtually inaccessible melting points, but interesting for other reasons[24]). This situation was the prime motivation for our work. In the present paper we study the PLC systems, that is, copolymers with varying fraction $\Theta$ of rigid sequences.

## 2. Derivation of Equations

Our system consists of $N_p$ copolymer chains, each of which is made up of flexible (coillike) and liquid-crystalline (rodlike) sequences in alternating order. Each copolymer is supposed to consist of $r$ segments, $r_c$ of which belong to flexible sequences, and $r_h$ to rigid sequences. Thus, $r$ is equal to the degree of polymerization. A fixed composition $\Theta$ is defined as the fraction of rigid segments which constitute the rodlike sequences; that is, $\Theta = r_h/r$. The copolymers may differ from each other in three respects: (a) the number of sequences ($n$ of each type) in a copolymer chain; (b) their length distribution (let $\eta_h$ denote the average length of a rodlike sequence); (c) the relative position $l$ of a sequence in the copolymer chain. We shall

* To whom correspondence should be addressed.
† University of North Texas.
‡ Universität Duisburg.

denote these attributes $\{n, \eta, l\}$ simply by $\{\xi\}$, so that $N_{\{\xi\}}$ represents the number of copolymers with identical attributes $\{\xi\}$. Clearly, the parameters just defined are related by $r = r_c + r_h = n(\eta_c + \eta_h)$, where $\eta_c$ is the average length of a flexible sequence in each chain. We shall make the following assumptions: (a) each segment (either in coil- or rodlike sequence) is of the same size as a cell in the cubic lattice—an assumption used often by Flory; (b) interactions between copolymers are through anistropic forces between the rigid segments; only those pairs of segments that are first neighbors are considered; (c) there are no vacancies in the cubic lattice; that is, the number $N$ of lattice sites is the same as the total number $N = rN_p$ of segments in our system.

We can now write the partition function $Z$ of our systems:

$$Z = Z_{comb}Z_{orient} \tag{1}$$

a standard approximation in the literature; here $Z_{comb}$ is the combinatorial or "steric" contribution; $Z_{orient}$ arises from the various orientations of the rigid sequences as well as the anisotropic interactions between their segments. Explicitly, we have

$$Z_{comb} = q_c^{N_p r_c}\prod_{j=1}^{N_p} \nu_j / (\prod_{\{\xi\}} N_{\{\xi\}}!) \tag{2}$$

where $\nu_j$ is the expected number of sites available for the $j$th copolymer molecule after $j - 1$ PLC molecules have been placed on a lattice and $q_c$ is the internal partition function for each of $N_p r_c$ flexible segments relative to $q_h$ for the rodlike segment, which is set to unity. The factorial factors in the denominator ensure that configurations arising from permutations within a set of $N_{\{\xi\}}$ identical copolymers are not counted.

We now derive the expression for $\nu_j$; this may be written as a product of factors as follows:

$$\nu_j = \nu_{c,j}^{(1)}\prod_l \nu_{c,j}^{(\ell)}\prod_m \nu_{h,j}^{(m)} \tag{3}$$

where $\nu_{c,j}^{(l)}$ denotes the expected number of sites available for the $l$th flexible sequence in the $j$th chain, after segments belonging to the preceding sequences have been placed; $\nu_{h,j}^{(m)}$ has analogous significance for the $m$th rodlike sequence in the chain; $l$ ranges over odd integers, and $m$ over even integers. Expression 3 assumes that the initial sequence in the chain to be placed is a flexible one. For the case of a rodlike initial sequence, we would have

$$\nu_j = \nu_{h,j}^{(1)}\prod_l \nu_{h,j}^{(l)}\prod_m \nu_{c,j}^{(m)} \tag{3a}$$

where $l$ and $m$ again range over odd and even integers, respectively. Obviously, (3) and (3a) should yield the same result.

If $z$ is used to denote the coordinate number of the lattice, for $\nu_{c,j}^{(1)}$ we can, to a good approximation, write

$$\nu_{c,j}^{(1)} = (N - r(j - 1)) \times z[N - r(j - 1)]/N \times$$
$$[(z - 1)\{N - r(j - 1)\}/N]^{m_c - 2} \tag{4}$$

assuming that this sequence contains $m_c$ segments. The first factor in (4) gives the number of vacant lattice sites available for the first segment; the second factor is the expected number of neighboring lattice sites available for the second segment; each of the last $m_c - 2$ factors, gives the corresponding expected number of neighboring lattice sites available for the remaining $m_c - 2$ segments.

For the $l$th flexible sequence in the $j$th PLC chain containing $m_c^{(l)}$ segments

$$\nu_{c,j}^{(l)} = [(z - 1)N_{vac}/N]^{m_c^{(l)}} \tag{5}$$

$$N_{vac} = N - r(j - 1) - \sum_i m_h^{(i)} - \sum_k m_c^{(k)} \tag{5a}$$

Each of the $m_c^{(l)}$ factors in (5) gives the expected number of sites available for the first and succeeding segments of the constrained $l$th sequence ($l \neq 1$); $N_{vac}$ gives the number of vacant lattice sites, after all segments belonging to preceding sequences in the $j$th chain have been placed. Obviously, we can to a good degree of approximation write

$$N_{vac} = N - r(j - 1) \tag{5b}$$

To write down an expression for $\nu_{h,j}^{(l)}$, $l \neq 1$, for the $l$th rigid sequence, we follow Flory[6,9] and replace this by $y_j^{(l)}$ contiguous submolecules, each of length $m_h^{(l)}/y_j^{(l)}$ and aligned parallel to the director axis; $y_j^{(l)}$ also serves as a measure of the deviation of the rigid sequence from the director axis. Figure 1, modeled after refs 6, 8, and 10 and in particular after ref 16, shows how this can be accomplished. This procedure of dividing the rigid sequence into submolecules makes the sequence conformable to the lattice. In fact, Figure 1 shows additionally how a flexible sequence (the third from the left) can also be represented by an analogous procedure. Adopting the reasoning of Flory, we have

$$\nu_{h,j}^{(l)} = (z - 1)\frac{N_{vac}}{N}(P_{cond})^{y_j^{(l)}(m_h^{(l)}/y_j^{(l)}-1)}P^{y_j^{(l)}-1} \tag{6}$$

where

$$P_{cond} = N_{vac}/[N_{vac} + \sum_i^{j-1} y_i + (j - 1)r_c] \tag{6a}$$

$$P = N_{vac}/N \tag{6b}$$

$P_{cond}$ denotes the conditional probability that a site following one (in the direction of the director axis) known to be vacant is vacant. Since accessibility of the sites required for a segment, other than the first in each submolecule, is contingent upon the vacancy of the preceding site, $P_{cond}$ gives the probability for the availability of sites for segments following the first in each submolecule; there are $y_j^{(l)}(m_h^{(l)}/y_j^{(l)} - 1)$ such segments; hence the presence of this exponent in the second factor of (6). $P$ simply gives the a priori probability for the availability of a site for the first segment in each submolecule following the first; there are $y_j^{(l)} - 1$ such submolecules; hence the presence of this exponent in the last factor in (6). The first factor in (6) gives the expected number of sites for the first segment in the first submolecule of the rigid sequence. Together, the product of these three factors in (6) gives the expected number of sites which conform to the constrained rigid sequence, characterized by the disorder parameter $y_j^{(l)}$.
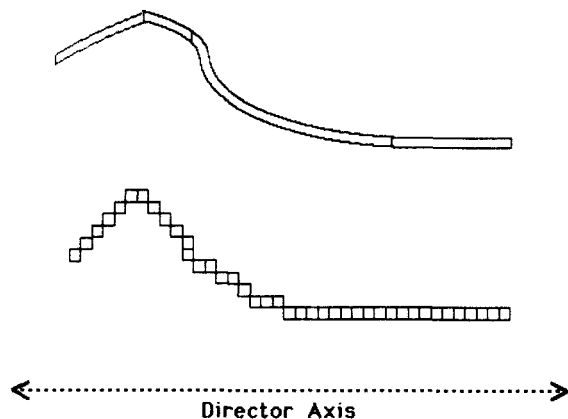
Using (4–6) in (3), we now obtain

$$\nu_j = \frac{z(z - 1)^{r_j - 2}(N - \sum_i^{j-1} r_i)^{r_j}}{N^{r_j c + y_j - 1}\{N - \sum_i^{j-1}(r_i^h - y_i)\}^{r_j h - y_j}} \tag{7}$$

where

$$y_j = \sum_l y_j^{(l)}$$

$l$ ranges over all rigid sequences in the $j$th copolymer molecule.

**Figure 1.** A four-sequence part of the $j$th chain (top) and its lattice representation (bottom). The third sequence from the left is flexible; the remaining ones are liquid crystalline. The first sequence from the left consists of six submolecules, so that $y_j^{(1)} = 6$. As noted in the text, the higher a local $y$ value, the larger the deviation of a given sequence from the LC director axis. Thus, since the fourth sequence from the left is parallel to the axis, and to the horizonal direction of the lattice, $y_j^{(4)} = 1$.

Apart from the factors involving the coordination number $z$ that appear in (7), presumably included in the internal partition function for the coillike segments, the remaining terms are the same as in the Matheson–Flory expression, eq 4 in ref 16.

It can be readily verified that eq 3a, which pertains to placing first a rigid sequence on the lattice, leads to an expression (7) identical to that obtained from (3), except that the leading factor $z$ in (7) is replaced by $z - 1$.

Assuming in our model a monodisperse system gives $r_j$ independent of $j$ and simply equal to $r$; however, we have chosen to use $r_j$ instead of $r$ in (7), in order to make comparison with the Matheson–Flory[16] expression easier. Following their procedure, we shall now introduce certain averages in terms of which the sums in (7) may be expressed:

$$\sum_{i}^{j-1} y_i = (j-1)(\Theta r/\bar{\eta})\bar{y} \qquad (8)$$

$\bar{\eta}$ is the average over all the chains of the length of a rigid sequence; $\bar{y}$ is the average disorientation parameter for all rigid sequences. Since there are $\Theta r$ segments belonging to the rigid sequences in each polymer chain, $\Theta r/\bar{\eta}$ gives the average number of rigid sequences in a chain, and (8) is readily understood. In anticipation of computing $\ln Z_{\text{comb}}$, we consider

$$\sum_{j}^{N_p} \ln \nu_j = r \sum_{j}^{N_p} \ln \{N - (j-1)r\} - \{(1-\Theta)N_p r +$$

$$\Theta N_p r \bar{y}/\bar{\eta} - N_p\} \ln N - \Theta r(1 - \bar{y}/\bar{\eta}) \sum_{j}^{N_p} \ln \{N - (j-1)\Theta r(1 -$$

$$\bar{y}/\bar{\eta})\} + C \qquad (9)$$

where

$$C = N_p \ln z + (r-2)N_p \ln (z-1) \qquad (9a)$$

the sums over $j$ can be approximated by their corresponding integrals; thus

$$\sum_{j}^{N_p} \ln \{1 - (j-1)\beta\} \approx \int_1^{N_p} \ln \{1 - (j-1)\beta\} \, dj + N_p - 1 -$$

$$\{1/\beta - (N_p - 1)\} \ln \{1 - \beta(N_p - 1)\} \qquad (10)$$

Using $\beta = 1/N_p$ for the first sum, and $\beta = Q/N_p$ for the

second sum, where

$$Q = \Theta(1 - \bar{y}/\bar{\eta}) \qquad (11)$$

we have

$$\sum_{j}^{N_p} \ln \nu_j = N_p \ln N + N + r \ln N_p - NQ +$$

$$N(1 - Q) \ln (1 - Q) + C \qquad (12)$$

for $Z_{\text{orient}}$ we use the expression of Flory and Irvine:[17]

$$Z_{\text{orient}} = \prod_{\eta, y} \left[ \left( \omega_{\eta y} \frac{n_y}{n_{\eta y}} \right) \exp(-\eta \epsilon_{\eta y}/2kT) \right]^{n_{\eta y}} \qquad (13)$$

where $n_\eta$ denotes the total number of rigid sequences which are of length $\eta$, $n_{\eta y}$ is the number of these sequences characterized by the disorientation parameter $y$, $\omega_{\eta y}$ is the fractional range of solid angle (or a priori probability) for the interval of orientations corresponding to $y$, and $\epsilon_{\eta y}$ is the mean orientation-dependent energy experienced by one of the segments of the rigid sequence of length $\eta$, in the field of its neighbors.

The equilibrium value of the distribution $n_{\eta y}/n_\eta$ can be obtained by noting that this is proportional to the product $\omega_{y\eta}\nu_{y\eta}$ (the number of configurations available to a rodlike sequence of length $\eta$ and disorientation parameter $y$) and the Boltzmann factor associated with the energy state of the sequence. Thus

$$\frac{n_{\eta y}}{n_\eta} \sim \omega_{\eta y}\nu_{\eta y} \exp\{-\eta \epsilon_{\eta y}(\psi_\eta)/kT\} \qquad (14)$$

where we have displayed the dependence of $\epsilon_{\eta y}$ on the angular deviation $\psi_\eta$ of the sequence from the director axis. To write out $\nu_{\eta y}$ explicitly, we consider the expected number of situations for the last rigid sequence (in the last copolymer) placed on the lattice; this is obtained from (6) by writing $\nu_{hj}^{(1)}$, for $j = N_p$ and 1 for the last sequence. Thus we have

$$\nu_{h,N_p}^{(l)} = (z-1)N_p^{-m_h^{(l)}}(1-Q)^{y_j^{(l)}-m_h^{(l)}} \qquad (15)$$

and we see that $\nu_{h,N_p}^{(l)}$ is proportional to some function of the sequence length, and its disorientation. Obviously, (15) can be taken as applicable to any rigid sequence in our system. Thus, using generic notation $y \equiv y_j^{(l)}$ and $\eta \equiv m_h^{(l)}$, we have for $\nu_{\eta y}$ the relation

$$\nu_{\eta y} \sim \exp(-ay - b\eta) \qquad (16)$$

where

$$a = -\ln (1 - Q) \qquad b = \ln N_p - a$$

Let us assume the length of rigid sequences as the same or sharply distributed around some mean value $\bar{\eta}$. We shall discuss consequences of this assumption in section 5. Now we can simply rewrite (16) in the form

$$\nu_y \sim \exp(-ay) \qquad (16a)$$

and we have for the equilibrium distribution of orientations

$$n_{\eta y}/n_\eta \sim \omega_{\eta y} \exp\{-ay - \bar{\eta}\epsilon_{\eta y}(\psi_\eta)/kT\} \qquad (17)$$

For a more explicit expression, we make use of the following relations:

$$\omega_{\eta y} = \sin \psi \frac{d\psi}{dy}$$

$$\epsilon_{\eta y}(\psi) = -kT^* \phi_h s\left(1 - \frac{3}{2} \sin^2 \psi\right) \qquad (18)$$

where the order parameter $s$ is defined by

$$s = 1 - \frac{3}{2} \langle \sin^2 \psi \rangle \tag{18a}$$

($\langle \ \rangle$ denoting an average over orientations) and $T^*$ is a characteristic temperature defined by

$$kT^* = \text{const} \cdot r^{*-6} (\Delta\beta)^2 \tag{18b}$$

$r^*$ is the distance between neighboring segments in contact and $\Delta\beta$ the difference between the polarizabilities along and normal to the cylindrical axis of a rigid segment.

Use of the fact that

$$\int_0^{\pi/2} \frac{n_{\eta y}}{n_\eta} \frac{d y}{d \psi} \, d\psi = 1$$

yields an expression for $n_{\eta y}/n_\eta$:

$$\frac{n_{\eta y}}{n_\eta} = f_1^{-1} \sin \psi \exp\left(-ay - \frac{3}{2}\phi_h s \tilde{T}^{-1} \sin^2 \psi\right)$$

$$f_1 = \int_0^{\pi/2} \sin \psi \exp\left(-ay - \frac{3}{2}\phi_h s \tilde{T}^{-1} \sin^2 \psi\right) d\psi \tag{19}$$

where $\tilde{T}$ is the reduced temperature defined by $\tilde{T} \equiv T/\eta T^*$. $\phi_h$ is the volume fraction of liquid-crystalline (rigid) sequences in the system. In the present case of pure copolymers, $\phi_h = \Theta$, but we introduce $\phi_h$ in anticipation of dealing with binary and ternary systems in a later paper. In order for (19) to be useful, we need to know $y$ as a function of $\psi$. Flory and Ronca[8] derived the relation

$$\bar{y} = (4/\pi)\bar{\eta} \sin \psi \tag{20}$$

Kloczkowski, Mark, and Erman[25] derived a more accurate but more complex relation that produces somewhat larger values for the ratio $\bar{y}/\bar{\eta}$. For biphasic equilibrium the differences between their values and those from eq 20 are small and stay nearly constant with respect to $\bar{\eta}$, and the conclusion is reached[25] that the use of (20) is "fully justified". Upon adopting (20), we obtain the following equilibrium distribution of orientations:

$$\frac{n_{\eta y}}{n_\eta} = f_1^{-1} \sin \psi \exp\left(-\gamma \sin \psi - \frac{3}{2}\phi_h s \tilde{T}^{-1} \sin^2 \psi\right) \tag{21a}$$

$$f_1 = \int_0^{\pi/2} \sin \psi \exp\left(-\gamma \sin \psi - \frac{3}{2}\phi_h s \tilde{T}^{-1} \sin^2 \psi\right) d\psi \tag{21b}$$

$$\gamma = 4a\bar{\eta}/\pi \tag{22}$$

We now have for the orientational contribution to the partition function:

$$\ln Z_{\text{orient}} = \sum_{\eta, y} n_{\eta y} \left\{ \ln\left(\omega_y \frac{n_\eta}{n_{\eta y}}\right) - \eta \epsilon_{\eta y}/2kT \right\} \tag{23}$$

But

$$n_\eta \sum_{\eta, y} \frac{n_{\eta y}}{n_y} \eta \epsilon_{\eta y}/(2kT) = \eta \frac{n_\eta}{2kT} \langle \epsilon_{\eta y} \rangle$$

where

$$\langle \epsilon_{\eta y} \rangle = -kT^* \phi_h s \left(1 - \frac{3}{2} \langle \sin^2 \psi \rangle\right) \tag{24}$$

Using (21) and (24) in (23), together with the assumption of constant $\eta$, we obtain

$$\ln Z_{\text{orient}} = n_\eta \{ \ln f_1 + \gamma \langle \sin \psi \rangle + \phi_h s \tilde{T}^{-1}(1 - s/2) \} \tag{25}$$

We may now write for the reduced Helmholtz function

per molecule $\tilde{A}$, using (1), (2) with $N_\xi = N_p$, (12), and (25)

$$\tilde{A}(N_p kT)^{-1} = -N_p^{-1}(\ln Z_{\text{comb}} + \ln Z_{\text{orient}}) = \ln\frac{1}{r} +$$
$$r\left\{\left(1 - \frac{1}{r}\right) - (1 - Q) \ln (1 - Q) - Q - (1 - Q) \ln q_c\right\} -$$
$$\frac{n\bar{\eta}}{N_p}\{\ln f_1 + \gamma \langle \sin \psi \rangle + \phi_h s \tilde{T}^{-1}(1 - s/2)\} \tag{26}$$

In writing (26) use has been made of the Stirling approximation in the form $\ln N_p! = N_p \ln N_p - N_p$. For an isotropic phase, $s = 0$, $\bar{y} = \bar{\eta}$, so that $Q = 0$, and $f_1 = 1$. Thus, writing (26) for the isotropic phase, and using the relation

$$A^{\text{anis}} = A^{\text{iso}}$$

which describes equilibrium between an isotropic and an anistropic phase, we arrive at the key equation of this paper:

$$\bar{\eta}(1 - \Theta) \ln (1 - Q) + \bar{\eta}Q + \Theta\{\ln f_1 + \Theta s \tilde{T}^{-1}(1 - s/2)\} = 0 \tag{27}$$

where $Q$ has been defined by (11), while

$$s = 1 - \frac{3}{2}\frac{f_3}{f_1} \tag{27a}$$

$$f_j = \int_0^{\pi/2} \sin^j \psi \exp\left(-\gamma \sin \psi - \frac{3}{2}\Theta s \tilde{T}^{-1} \sin^2 \psi\right) d\psi$$
$$(j = 1, 2, 3) \tag{27b}$$

$$\gamma = -\frac{4\bar{\eta}}{\pi} \ln (1 - Q) \tag{27c}$$

We observe that, in the special case of $\Theta = 1$, when the copolymers reduce to rigid rods of length $\bar{\eta}$, eq 27 reduces (as it should) to the Flory–Ronca equation[8] for biphasic (isotropic-LC) equilibrium for a neat liquid of rodlike polymers.

## 3. Application Range of the Model

A natural question at this stage is, when is the foregoing set of equations applicable? We have assumed partial rigidity of macromolecular chains, but we have not assumed any particular structure of the mesogenic phase. There is a variety of LC-phase structures, including nematic, cholesteric, and several smectic (see, for instance, section 6.10 in ref 26); both MLCs and PLCs can form such phases. Typically, lowering the temperature produces a more complex LC phase, but we also have reentrant nematic phases,[27-29] with a more ordered phase such as a smectic one in the middle of the phase diagram. Our equation for the biphasic equilibrium describes the situation at the clearing temperature. Flory took the same position: we have anisotropic–isotropic equilibrium, but the theory does not deal with details of the anisotropic structure. This fact is important, because one still often assumes, nearly automatically, that the anisotropic phase at the clearing temperature is nematic. Yoon and his colleagues[30,31] studied a LC homopolymer, namely, poly(p-hydroxybenzoic acid) (PHB), by a variety of techniques. They found successive transitions crystal–smectic E–smectic B, but no nematic phase.

We have assumed that the rigid and the flexible segment sequences alternate along the chain. The question here is to what extent real PLC chains fulfill this assumption. Nicely and collaborators[32] studied by nuclear magnetic resonance (NMR) spectroscopy copolymers of poly(ethylene terephthalate) (PET) with PHB. They found that there is a slight preference factor, 1.3, for the two LC

sequences adjacent to each other; no such adjacency results in the factor of 1.0. In our synthesis[33] we could not exceed the preference factor of 1.3 either. However, because of the transesterification reactions in the melt, the small-angle neutron scattering study of Olbrich[34] has shown that the values of $\bar{\eta}$ can be as high as 13.2.

In comparison to fully flexible polymers, the presence of rigid mesogenic units in the chain elevates the melting temperature, $T_m$. Hence PLCs have typically higher $T_m$ values than flexible polymers, and of course the clearing temperatures are still higher, sometimes in the region of thermal decomposition. An advantage of the present theory would be the capability to predict a part of the phase diagram which is hard to determine experimentally.

## 4. Numerical Investigation

Experimentally, one can take a series of PLC copolymers consisting of the same structural units, say flexible A and liquid-crystalline B, and determine the phase transitions in each copolymer. In other words, one then defines the temperature vs composition phase diagram in function of $\Theta$ for a series of $A_{1-\Theta}B_\Theta$ polymer liquid crystals. Similarly, in our computations, with other parameters constant, a PLC chain is fully defined by fixing a value of $\Theta$. The chains we consider are snakes—using the terminology of the graph theory—since they have no branches. We consider longitudinal PLCs[2,4]—a class of PLCs in which the mesogenic units are aligned along the chain backbone. Let us first observe that, for a specified $\Theta$ and known properties of the rodlike segments, each $f_j$ is a function of $\gamma$, $s$, $\bar{\eta}$ and $\tilde{T}$; that is

$$f_j = f_j(\gamma, s, \bar{\eta}, \tilde{T}; \Theta) \tag{28}$$

From (20) and using (21) we can write

$$\frac{\bar{y}}{\bar{\eta}} = \frac{4}{\pi} \langle \sin \psi \rangle = \frac{4}{\pi} \frac{f_2}{f_1} \tag{29}$$

so that $Q$ (see eq 27a) is a function of the same variables as $f_j$. We may now represent the system of equations in (27), whose solutions we seek, as

$$G_j(\gamma, s, \bar{\eta}, \tilde{T}; \Theta) = 0 \qquad (j = 1, 2, 3)$$

where

$$G_1 \equiv \bar{\eta}(1 - \Theta) \ln (1 - Q) + \bar{\eta}Q + \Theta \left\{ \ln f_1 + \Theta s \tilde{T}^{-1} \left(1 - \frac{s}{2}\right) \right\} \tag{30a}$$

$$G_2 \equiv \gamma + \frac{4\bar{\eta}}{\pi} \ln (1 - Q) \tag{30b}$$

$$G_3 \equiv \frac{2}{3}(1 - s) - \frac{f_3}{f_1} \tag{30c}$$

Since eqs 30 constitute a system of three nonlinear equations, one of the four variables $\gamma$, $s$, $\bar{\eta}$, and $T$ needs to be specified. We have employed two algorithms in solving the system of eqs 30: one is the Flory–Ronca iteration scheme, which these authors used to solve the corresponding system for a neat liquid of rodlike polymers; the other makes use of the Newton–Raphson procedure. The Flory–Ronca algorithm chooses to specify $\gamma$ and solve for $s$, $\bar{\eta}$, and $T$ (or $\tilde{T}^{-1}$). The procedure is based on guessing the product $s\tilde{T}^{-1}$, given values of $\Theta$ and $\gamma$; with this information, $f_j$ can be evaluated. Equation 30b is then solved for $\bar{\eta}$, which makes possible the evaluation of $G_1$. If the difference between the absolute value of $G_1$ and zero exceeds a certain tolerance, then $s\tilde{T}^{-1}$ is revised and
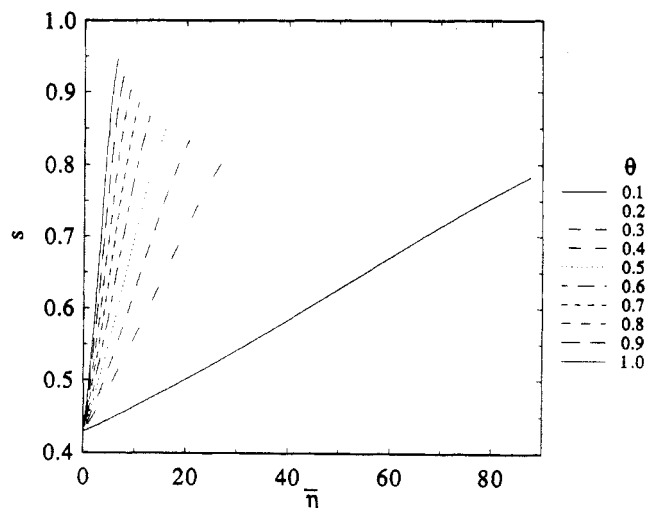


**Figure 2.** Dependence of the order parameter $s$ on the average length $\bar{\eta}$ of rigid sequences in the PLC chain for selected values of the composition $\Theta$ of LC segments.

the iterative process continued until (30a) is satisfied, within a given tolerance. In this way, we obtain values of $\bar{\eta}$, $s$, and $\tilde{T}^{-1}$ corresponding to values of $\gamma$ which had been assumed.

As for using the Newton–Raphson algorithm, values of $\bar{\eta}$ were assumed and the eqs 30 solved for $s$, $\gamma$, and $\tilde{T}^{-1}$. That algorithm requires for its implementation the evaluation of elements of the Jacobian matrix for the system of eqs 30, and these are listed in the Appendix. Use was made of a slightly modified subroutine MNEWT (with its associated subroutines) which is provided by Press, Flannery, Teukolsky, and Vetterling.[35] The use of the Newton–Raphson procedure is in principle quite straightforward, provided the guessed values of the unknown vector are reasonably close to the required roots of the system of equations, within a given tolerance. For given values of two of the four variables $\bar{\eta}$, $s$, $\gamma$, and $\tilde{T}$, it was easy to obtain reasonable starting vectors for use with MNEWT from the points of intersection of contours $G_j = 0$ ($j = 1$, 2, 3); another subroutine was used to generate these contours.

The solutions obtained by both algorithms agree with each other, so that one serves as a check on the other. The use of the two algorithms was also found quite helpful, as it is fairly easy to miss certain solution sets or find incorrect solutions when only one algorithm is applied. The contour plots were crucial in recognition of the real solutions.

## 5. Results and Discussion

In Figure 2 we show the order parameter $s$ (see eq 18a) as a function of the average length $\bar{\eta}$ of rigid sequences for values of $\Theta$ at 0.1 intervals. We find that for $\Theta = 0.1$ the order parameter increases quite slowly with the length of the rigid sequence. We also note that the slope for $\Theta = 0.2$ is much higher. Apparently, since percentagewise we have doubled the concentration of rigid sequences, much more alignment of the chains takes place. The slopes for the values of $\Theta$ between 0.6 and 1 are fairly close. In other words, there is already so much alignment for $\Theta = 0.6$ that a further increase in the concentration of LC sequences hardly affects the situation.

It is instructive to compare Figure 4 of Matheson and Flory[16] with our Figure 2. They had already demonstrated that the concentration of flexible segments "... that can be tolerated increases with $\eta$". Since that concentration is equal to $1 - \Theta$, this is clearly confirmed by our Figure 2: for, say, $\bar{\eta} = 30$ we can have $\Theta = 0.2$ but not $\Theta = 0.8$. Our present treatment is simpler than that of Matheson and
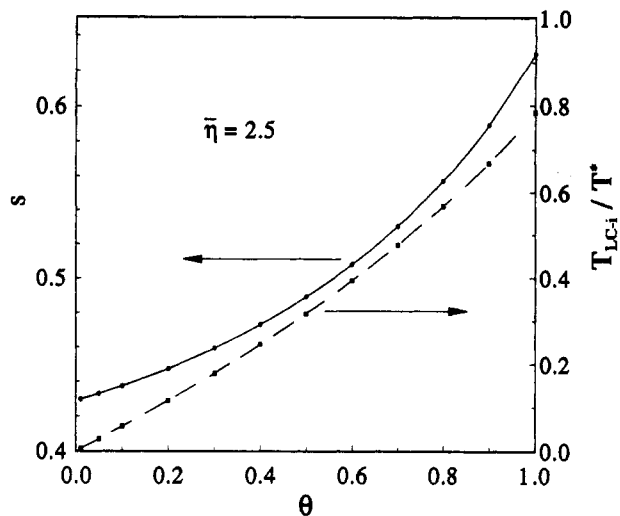
**Figure 3.** Dependence of the order parameter $s$ and the anisotropic–isotropic transition temperature $T_{LC-i}/T^*$ on the LC composition $\Theta$ for $\bar{\eta} = 2.5$.
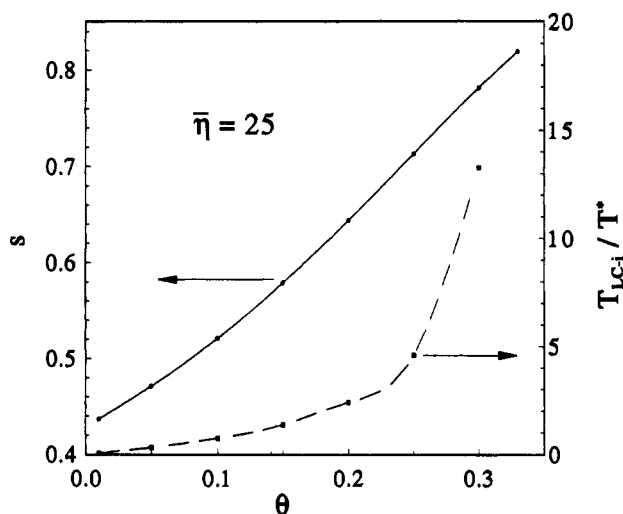


**Figure 4.** The same parameters as in Figure 3 but for $\bar{\eta} = 25.0$.

Flory since we deal with neat liquids only. At the same time, our approach is more complicated since we use a more exact form of Flory and Ronca for the orientational distribution function. Figure 2 provides for the Flory–Ronca model a detailed picture of the effects of varying the concentration of flexible (or rigid) segments.

Our results in Figure 2 include the case of fully rigid rods, $\Theta = 1$, already treated by Flory and Ronca.[9] Their results and our coincide as they should. As can be seen in the figure, the limit of $s$ for $\bar{\eta} = 0$ is common to all values of $\Theta$. As already noted by Flory and Ronca, the limit of the reduced entropy $\Delta S_{LC-i}/k$ for $\bar{\eta} = 0$ had already been predicted by Maier and Saupe[36,37] from their theory. Flory and Ronca derived a relation valid at the anisotropic (LC)–isotropic coexistence, LC-i, namely, $\Delta S_{LC-i}/N_p k = s^2/2T_{LC-i}$. At $\bar{\eta} = 0$ we have $\Delta S_{LC-i}/N_p k = 0.4291$; this gives $s = 0.4347$, a numerically close value.

To better assess changes of the order parameter $s$ with the concentration of rigid sequences $\Theta$, we show in Figures 3 and 4 two curves, for two different values of the rigid rod length $\bar{\eta}$. We have already mentioned an experimental value of $\bar{\eta} = 13.2$ for a longitudinal PLC.[34] We have chosen for our computations two values of $\bar{\eta}$ differing by 1 order of magnitude, so that the value from ref 34 is approximately halfway between them. We see in Figure 3 that for the lower $\bar{\eta}$ the order parameter $s$ changes relatively slowly with the LC concentration. In Figure 4, for the higher $\bar{\eta}$, that change is more rapid. The fact that for larger $\bar{\eta}$ values
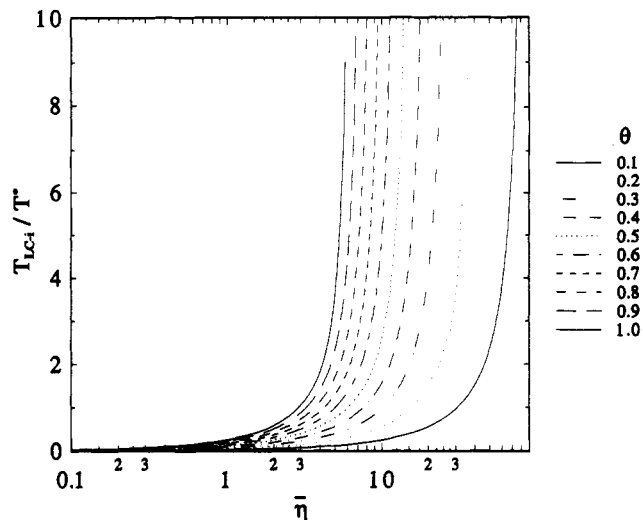


**Figure 5.** Dependence of the anisotropic–isotropic transition temperature $T_{LC-i}/T^*$ on the average length $\bar{\eta}$ of LC sequences for selected values of $\Theta$.

a small absolute increase in chain rigidity $\Theta$ produces large changes in the chain alignment may be helpful for the development of blends in which a PLC provides a significant mechanical reinforcement at relatively low $\Theta$.

In Figure 5 we show a family of curves of $T_{LC-i}/T^*$ as a function of $\bar{\eta}$ for values of $\Theta$ at 0.1 intervals. The characteristic temperatures are approximately between 100 K[9] and several thousands of degrees kelvin,[38] depending of course on the material and also to some extent on the equation of state. A logarithmic scale is used for perspicuous representation. We see in all cases that an increase in the LC concentration $\Theta$ increases the clearing temperature $T_{LC-i}$. While this result is expected, it confirms the physical soundness of the theory. If the melting temperature $T_m$ is less affected by a change in the amount of liquid crystallinity than $T_{LC-i}$ is, then the temperature range within which LC phase or phases exist would go symbatically with $\Theta$. The ascending parts of the curves on the right-hand side of the figure are related to the athermal limit ($T^{-1} \rightarrow 0$) already studied by Flory and Ronca[8,9] for $\Theta = 1$. The $\bar{\eta}$ dependence in Figure 5 might be related to our assumption of having $n$ flexible sequences and also $n$ mesogenic sequences. While longer rigid sequences at fixed $\Theta$ also mean longer flexible sequences, the former thus have a stronger capability to enforce the alignment.

For comparison, in Figure 6 we show a similar family of curves for different $\Theta$ values in function of $\bar{\eta}$, but now the vertical coordinate is $\hat{T}_{LC-i} = T_{LC-i}/\bar{\eta}T^*$, denoted simply by $\hat{T}$. Similarly, as with the preceding figures, Figure 6 shows another consequence of ordering caused by increasing the degree of rigidity.

Our computations pertain to monodisperse systems, so potential effects of polydispersity deserve consideration. Polydispersity is known to blunt otherwise sharp phase transitions. Flory and collaborators have studied polydisperse systems, and also monodisperse ones.[6,8,14,15] Frost and Flory[13] found that concentrations of the coexisting phases and other characteristics of the heterogeneous system formed from a Poisson distribution of solute species conform closely to those for a binary mixture of solvent and monodisperse rods if $\bar{\eta}$ is large.

Another question is whether the relative positions of LC and flexible sequences along the chains affect the properties. This problem was studied by Matheson and Flory,[16] who found that the allocation of the flexible segments between the rods is immaterial; the total number
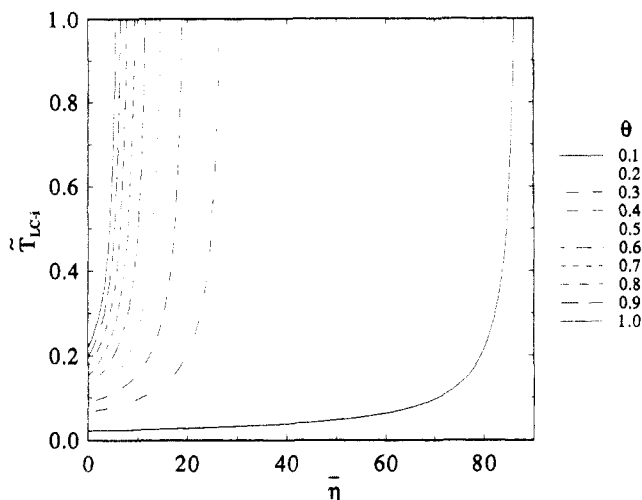
**Figure 6.** Dependence of the reduced anisotropic–isotropic transition temperature $\tilde{T}_{\text{LC-i}}$ on the average length $\bar{\eta}$ of LC sequences for selected values of $\Theta$.
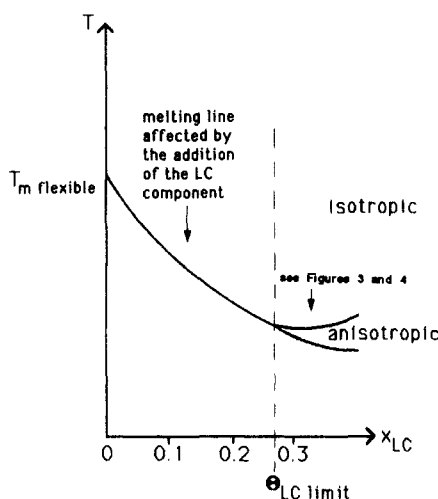


**Figure 7.** Part of a schematic phase diagram starting from the left at the pure flexible polymer with its melting temperature $T_{\text{m flexible}}$. The mole fraction of the liquid-crystalline component $x_{\text{LC}}$ increases toward the right. A LC phase or phases exist to the right of $\Theta_{\text{LC limit}}$.

of rods "suffices to determine the thermodynamic functions".

To consider phase diagrams, return to the $T_{\text{LC-i}}/T^*$ curves as a function of concentration $\Theta$ in Figures 3 and 4, respectively, for fixed values of $\bar{\eta} = 2.5$ and 25.0. As expected, an increase in LC concentration increases the transition temperature. We note that $T_{\text{LC-i}}$ is undefined for $\Theta = 0$, since there is no anisotropic liquid-crystalline phase. For the lowest value of $\Theta = 0.01$ for which our computations were made, that is, when we have very few mesogenic sequences, $T_{\text{LC-i}}/T^* = 0.000\,88$ for $\bar{\eta} = 2.5$.

At $\Theta = 0$ we have the usual melting transition of a fully flexible polymer. Addition of LC sequences at low concentrations *in the same phase* produces the usual lowering of the melting point; LC segments act as an impurity (see Figure 7). This melting line continues inside of the phase diagram until there are enough LC sequences to form a second phase, this at a concentration which we shall call $\Theta_{\text{LC limit}}$. The formation of LC-rich phase regions is known from experiments;[39–43] these regions are approximately spherical in shape and have been called *islands*.[40] The LC-poor matrix surrounding the islands does not exhibit discernible alignment. Therefore, the anisotropic–isotropic phase transformation has to occur in the islands, and equations derived in this paper pertain to that phase. As an example, experiments for PET/PHB copolymers

show that $\Theta_{\text{LC}}$ limit $\approx 0.3$. In other words, since between $\Theta = 0$ and $\Theta_{\text{LC limit}}$ there are not enough LC sequences, the transition which upon heating produces an isotropic phase is melting. At $\Theta_{\text{LC limit}}$, the melting line might continue further right, but it meets at least one more line of the diagram: the LC-isotropic transition branch—also called the clearing temperature line, shown as the upper branch in Figure 7. Except for dividing by $T^*$, that upper branch corresponds to the $T_{\text{LC-i}}/T^*$ vs $\Theta$ curves in Figures 3 and 4. In fact, while for clarity we have included in our computations very low $\Theta$ values, these two figures pertain to the region of $\Theta > \Theta_{\text{LC limit}}$.

The concept of $\Theta_{\text{LC limit}}$ is also supported by the results in Figure 2. At concentrations $\Theta$ around 0.3 (hence, at or near $\Theta_{\text{LC limit}}$), there appears a considerable degree of alignment, affected only little by a further increase in the degree of rigidity $\Theta$.

While we find it convenient to work with $\Theta_{\text{LC limit}}$, Flory[5] attacked essentially the same problem in 1956 using the average degree of chain flexibility $f$, or chain rigidity $1 - f$. In the limit when the Gibbs function of bending per segment becomes zero, he found that the rigidity depends on the coordination number only: $1 - f = 1/(z - 1)$. For the limiting rigidity parameter $f_c$ (corresponding to our LC limit) Flory obtained $\ln (1 - f_c) = -1$. In 1986 Matheson,[44] using results of his and Flory's formalism for chains with interconvertible rodlike and flexible coil sequences,[45] generalized the Flory result. Consider the characteristic ratio $C_\infty = (1 + \Theta)/(1 - \Theta)$. Matheson derived a formula for the limiting ratio $C_\infty^{(c)}$, which accounts also for the chain geometry, involving a measure of the average width of the rigid sequences. If $C_\infty < C_\infty^{(c)}$, an isotropic phase will be formed.[44] Otherwise, a phase which Matheson called an orientationally ordered phase appears. Thus, his treatment is not limited to nematics—a point we discuss in the section 3. Clearly, the problem of $\Theta_{\text{LC limit}}$ (or $f_c$, or $C_\infty^{(c)}$) deserves attention in the future; we hope to deal with it in a later paper.

Finally, we note that computer simulations by molecular dynamics of systems of PLC chains show[21,22] that such systems are ductile at low rigidity while brittle at high $\Theta$; in the latter case, relatively easy crack formation as well as crack propagation takes place. Therefore, there exists an optimum range of chain rigidity in which the material is still ductile while an adequate degree of alignment as characterized by the order parameter $s$ prevails. An LC-containing system with an appropriate composition can be either a PLC copolymer with $\Theta$ in the desired range or a multicomponent system: a PLC with higher $\Theta$ plus one or more flexible polymers, so that $\bar{\Theta}$ averaged over all components (including those with $\Theta = 0$) falls within the range. In the following paper we deal with ternary systems of the type PLC + flexible polymer + a monomeric solvent.[46]

## Appendix

### Elements of Jacobian Matrix.

$$\frac{\partial G_1}{\partial \gamma} = \bar{\eta}\frac{\partial Q}{\partial \gamma}\left\{1 - \frac{(1-\Theta)}{1-Q}\right\} + \frac{\Theta}{f_1}\frac{\partial f_1}{\partial \gamma} \tag{A1}$$

$$\frac{\partial G_1}{\partial s} = \bar{\eta}\frac{\partial Q}{\partial s}\left\{1 - \frac{(1-\Theta)}{1-Q}\right\} + \frac{\Theta}{f_1}\frac{\partial f_1}{\partial s} + \Theta^2\tilde{T}^{-1}(1-s) \tag{A2}$$

$$\frac{\partial G_1}{\partial \tilde{T}^{-1}} = \bar{\eta}\frac{\partial Q}{\partial \tilde{T}^{-1}}\left\{1 - \frac{(1-\Theta)}{1-Q}\right\} + \frac{\Theta}{f_1}\frac{\partial f_1}{\partial \tilde{T}^{-1}} + \Theta^2 s\left(1 - \frac{s}{2}\right) \tag{A3}$$

$$\frac{\partial G_2}{\partial \gamma} = 1 - \frac{4\bar{\eta}}{\pi}\frac{\partial Q/\partial \gamma}{1-Q} \tag{A4}$$

$$\frac{\partial G_2}{\partial s} = -\frac{4\bar{\eta}}{\pi}\frac{\partial Q/\partial s}{1-Q} \tag{A5}$$

$$\frac{\partial G_2}{\partial \tilde{T}^{-1}} = -\frac{4\bar{\eta}}{\pi}\frac{\partial Q/\partial \tilde{T}^{-1}}{1-Q} \tag{A6}$$

$$\frac{\partial G_3}{\partial \gamma} = -\left(f_1^{-1}\frac{\partial f_3}{\partial \gamma} - f_3 f_1^{-2}\frac{\partial f_1}{\partial \gamma}\right) \tag{A7}$$

$$\frac{\partial G_3}{\partial s} = -\frac{2}{3} - \left(f_1^{-1}\frac{\partial f_3}{\partial s} - f_3 f_1^{-2}\frac{\partial f_1}{\partial s}\right) \tag{A8}$$

$$\frac{\partial G_3}{\partial \tilde{T}^{-1}} = -\left(f_1^{-1}\frac{\partial f_3}{\partial \tilde{T}^{-1}} - f_3 f_1^{-2}\frac{\partial f_1}{\partial \tilde{T}^{-1}}\right) \tag{A9}$$

where the partial derivatives of $f_j$ and $Q$ are given by

$$\frac{\partial f_j}{\partial \gamma} = -f_{j+1} \qquad \frac{\partial f_j}{\partial s} = -\frac{3}{2}\Theta\tilde{T}^{-1}f_{j+2} \qquad \frac{\partial f_j}{\partial \tilde{T}^{-1}} = s\tilde{T}\frac{\partial f_j}{\partial s} \tag{A10}$$

and

$$\frac{\partial Q}{\partial \gamma} = -\frac{4\Theta}{\pi}\left(f_1^{-1}\frac{\partial f_2}{\partial \gamma} - f_2 f_1^{-2}\frac{\partial f_1}{\partial \gamma}\right) \tag{A11}$$

$$\frac{\partial Q}{\partial s} = -\frac{4\Theta}{\pi}\left(f_1^{-1}\frac{\partial f_2}{\partial s} - f_2 f_1^{-2}\frac{\partial f_1}{\partial s}\right) \tag{A12}$$

$$\frac{\partial Q}{\partial \tilde{T}^{-1}} = s\tilde{T}\frac{\partial Q}{\partial s} \tag{A13}$$

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