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Phase diagrams of liquid crystal polymers

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Abstract. A general formula for the free energy of a polymeric mixture is given. Four terms are shown to be present: the entropy of mixing, the entropy of conformation, an isotropic interaction and an anisotropic interaction. The interaction parameters can be related to microscopic characteristics such as degree of polymerisation (\overline{DP}) and flexibility or persistence length. The \overline{DP} dependence of the order-disorder transition of liquid crystal polymers is discussed.

1. Introduction

Certain polymeric substances can form liquid crystalline phases and have been the object of numerous recent experimental and theoretical studies (Blumstein 1985, Chapoy 1985). Many different types of molecular structure are possible: helical or ribbon-like, rigid mesogen alternating with flexible spacer, side-chain mesogens, semi-rigid or rigid chains. Experiments on phase transitions in the pure melt and in solution have been made by various methods (optical microscopy, viscosity, latent heat of transition) and the rigid-rod lattice model (Flory 1982) has been extensively used to interpret the experimental data. Theories including chain flexibility (Pincus and de Gennes 1978, Khoklov and Semenov 1981, Ten Bosch *et al* 1983, Corradini and Vacatello 1983) have demonstrated the effect of chain characteristics on the transition. The strong isotropic repulsion present in the polymer systems leads to a wide variety of phase diagrams (Brochard *et al* 1984) but quantitative comparison is still difficult.

In comparison, the statistical theory of classical fluids is well developed. Molecular models for the structure and laws of interaction between molecules have been refined and powerful methods based on correlation functions have been given to specify thermodynamic properties from these models. Recently, a density functional approach has also been applied to nematics (Sluckin and Schukla 1983) and to isotropic polymer systems (Hong and Noolandi 1981).

In the following we extend the density functional expansion to nematic polymers. This method proves to be very general and to encompass previous mean-field theories of these systems. It also has the advantage of being applicable to all types of liquid crystal chains simply by appropriate definition of the correlation functions.

2. Calculation of free energy

We consider a mixture of a homopolymer in a solvent. Three different types of solvent are possible: a simple monomolecular liquid, a flexible, non-mesomorphic polymer or a second mesomorphic polymer. In particular, the first case will be pursued in detail.

We denote the number of polymer chains A by $\tilde{N}_A = N_A/L_A$ where N_A is the number of monomer units and L_A the degree of polymerisation. For the solvent, \tilde{N}_B will denote the number of solvent units (molecules or chains), L_B the degree of polymerisation ($L_B = 1$ for the monomolecular solvent) and N_B the number of monomer units $N_B = L_B \tilde{N}_B$.

In the following the index i will be used to label either polymer ($i = A$) or solvent molecules ($i = B$).

The partition function for the mixture is given by

$$Z = \left(\prod_i \frac{Z_i^{\tilde{N}_i}}{\tilde{N}_i!} \right) \int \prod_i \delta\{r_i\} P_i(\{r_i\}) e^{-\beta W} \quad (1)$$

where Z_i is the partition function due to the kinetic energy, W is the intermolecular potential and $P_i(\{r_i\})$ denotes the configurational probability for an individual chain or solvent molecule. Using the integral representation of the δ function, we can introduce the microscopic particle density $\rho_i(r, w)$ at position r with orientation w . Then (η being a normalisation constant) (Hong and Noolandi 1918)

$$Z = \left(\prod_i \frac{Z_i^{\tilde{N}_i}}{\tilde{N}_i!} \right) \eta \int \prod_i \delta\rho_i \delta u_i \prod_i Q_i^{\tilde{N}_i} \exp\left(\sum_i \int dr dw u_i(r, w) \rho_i(r, w) - \frac{1}{2} \sum_{ii'} \int dr dw dr' dw' \rho_i(r, w) V_{ii'}(r, w, r', w') \rho_{i'}(r', w') \right). \quad (2)$$

The major terms are given here by $V_{ii'}(r, w, r', w')$, the intermolecular potential between components ii' with positions rr' and orientations ww' , and the quantities Q_i which describe the molecular model for the component i in the mean field u_i . For example (Freed 1972), if i is a flexible polymer described by the space curve $r_i(t)$ and the statistical Kuhn monomer length b_i

$$P_i(\{r_i\}) = \exp\left[-\frac{3}{2b_i^2} \int_0^{L_i} dt \left(\frac{\partial r_i(t)}{\partial t} \right)^2 \right] \quad (3)$$

t being the segment length from the origin to the point $r_i(t)$ and $w_i(t) = \partial r_i / \partial t$. In the model of semirigid polymers of bend elastic coefficient α and persistence length $B = \beta\alpha$

$$P_i(\{r_i\}) = \exp\left[-\frac{1}{2} B \int_0^{L_i} dt \left(\frac{\partial^2 r_i(t)}{\partial t^2} \right)^2 \right]. \quad (4)$$

Then

$$Q_i = \int \delta r_i(t) P_i(\{r_i\}) \exp\left(-\int_0^{L_i} dt u_i(r_i(t)) \right)$$

where $P_i(\{r_i\})$ is taken from (3) or (4).

If i is a simple liquid

$$Q_i = \int dr \exp(-u_i(r)).$$

The partition function can be written in terms of a free energy functional

$$Z = \eta \int \prod_i \delta\rho_i \delta u_i \exp \mathcal{F}(\rho_i u_i). \quad (5)$$

In the saddle function method the functional $\mathcal{F}(\rho_i, u_i)$ is minimised with respect to ρ_i and u_i . Coupled equations are obtained for the equilibrium densities and mean fields. The equilibrium free energy is then

$$\mathcal{F}(\rho_i, u_i) = \sum_i \frac{N_i}{L_i} \left(\ln \frac{N_i}{L_i} - 1 \right) - \sum_i \frac{N_i}{L_i} \ln Q_i - \sum_i \int \mathbf{d}\mathbf{r} \mathbf{d}\mathbf{w} \rho_i(r, \mathbf{w}) u_i(r, \mathbf{w}) \\ + \frac{1}{2} \sum_{ii'} \int \mathbf{d}\mathbf{r} \mathbf{d}\mathbf{w} \mathbf{d}\mathbf{r}' \mathbf{d}\mathbf{w}' \rho_i(r, \mathbf{w}) V_{ii'}(r, \mathbf{w}, r', \mathbf{w}') \rho_{i'}(r', \mathbf{w}').$$

The first term gives the entropy of mixing, the second term leads to a conformational entropy, the third term takes the mean-field interactions into account and the final term accounts for the average two-particle interactions.

Correspondingly, in the pure materials (the number of monomer units is N_i^0 , the density distribution is ρ_i^0 and the mean field is u_i^0):

$$\mathcal{F}_i(\rho_i^0, u_i^0) = \frac{N_i^0}{L_i} \ln \left(\frac{N_i^0}{L_i} - 1 \right) - \frac{N_i^0}{L_i} \ln Q_i^0 - \int \mathbf{d}\mathbf{r} \mathbf{d}\mathbf{w} \rho_i^0(r, \mathbf{w}) u_i^0(r, \mathbf{w}) \\ + \frac{1}{2} \int \mathbf{d}\mathbf{r} \mathbf{d}\mathbf{w} \mathbf{d}\mathbf{r}' \mathbf{d}\mathbf{w}' \rho_i^0(r, \mathbf{w}) V_{ii'}(r, \mathbf{w}, r', \mathbf{w}') \rho_{i'}^0(r', \mathbf{w}')$$

where Q_i^0 (the equivalent of Q_i in the mixture) describes the molecules in the pure-material mean fields.

In the mixture, the free energy of mixing can be defined

$$\Delta \mathcal{F} = \mathcal{F} - \sum_i \frac{N_i}{N_i^0} \mathcal{F}_i.$$

3. Liquid crystalline polymer in a simple solvent

3.1. Model free energy

We will study in more detail the case of a semirigid polymer in solution in a simple solvent. The sample density is uniform in the pure materials and in the mixture and the density distribution depends on the orientation alone. The number density is $n_i = N_i/V$.

The number density of the pure materials, $n_i^0 = N_i^0/V$, can be used to define the partial volumes $v_i = 1/n_i^0$. We assume no volume change on mixing and $V = \sum_i N_i v_i$ is the total sample volume. We introduce the volume concentration of polymer A, $x = n_A/n_A^0$, and of solvent B, $1 - x = n_B/n_B^0$. These quantities correspond closest to the weight concentrations given by experiment. We use $v_A = v_B = v$.

The two-particle interaction is expanded in spherical harmonics as (Nakagawa and Akahane 1982)

$$V_{ii'}(r\mathbf{w}\mathbf{w}') = \sum_{\substack{l_1 l_2 \\ m_1 m_2}} C(l_1 l_2 m m_1 m_2) Y_{lm}(\mathbf{r}/r) Y_{l_1 m_1}(\mathbf{w}) Y_{l_2 m_2}^*(\mathbf{w}') V_{ii'}(r, l_1 l_2) \quad (6)$$

where $C(l_1 l_2 m m_1 m_2)$ are the Clebsch-Gordan coefficients.

Inserting expansion (6) into (5), introducing the volume concentration x and neglecting as usual linear terms in x which do not contribute in the calculation of

phase diagrams, we find for the free energy of mixing per site, limiting the expansion to $l=0, 2$,

$$\begin{aligned} \Delta F = \frac{\Delta \mathcal{F}v}{V} = \frac{x}{L_A} \ln x + (1-x) \ln(1-x) - \frac{x}{L_A} \ln \varrho_A \\ - \frac{1}{2} x^2 V_{AA}(022) S^2 + \frac{1}{2} x^2 V_{AA}(000) \\ + \frac{1}{2} (1-x)^2 V_{BB}(000) + x(1-x) V_{AB}(000) \end{aligned} \quad (7)$$

where

$$\varrho_A = Q_A \exp(x L_A V_{AA}(000)) = \int d\mathbf{w} d\mathbf{w}' g_A(\mathbf{w}\mathbf{w}' L_A)$$

and $g_A(\mathbf{w}\mathbf{w}' L_A)$ given by

$$g_A(\mathbf{w}\mathbf{w}' L_A) = \int_{\mathbf{w}(0)=\mathbf{w}}^{\mathbf{w}(L_A)=\mathbf{w}'} d\mathbf{w} \exp \left\{ - \int_0^{L_A} dt \left[\frac{B}{2} \left(\frac{\partial \mathbf{w}}{\partial t} \right)^2 + u_A(\mathbf{w}) \right] \right\}$$

solves the equation for a chain in the presence of the orientational (liquid crystal type) mean field alone:

$$\left(\frac{\partial}{\partial t} - \frac{1}{2B} \Delta_{\mathbf{w}} + u_A(\mathbf{w}) \right) g_A(\mathbf{w}\mathbf{w}' t) = \delta(t) \delta(\mathbf{w} - \mathbf{w}'). \quad (8)$$

The orientational distribution function of monomers $f(\mathbf{w})$ is calculated from $f(\mathbf{w}) = \rho_A(\mathbf{w})/n_A$:

$$f(\mathbf{w}) = \frac{1}{L_A \varrho_A} \int_0^{L_A} dt \int d\mathbf{w}' d\mathbf{w}'' g_A(\mathbf{w}', \mathbf{w}, t) g_A(\mathbf{w}, \mathbf{w}'', L_A - t).$$

The average order parameter S is given by the average Legendre polynomial

$$S = \int d\mathbf{w} P_2(\mathbf{w}) f(\mathbf{w}).$$

The space averages

$$V_{ii'}(0ll) = \frac{1}{v} \int d\mathbf{r} r^2 V_{ii'}(r, 0ll) \left(\frac{2l+1}{4\pi} \right)^{1/2}$$

play the role of effective interaction parameters and $u_A(\mathbf{w}) = x V_{AA}(022) S P_2(\mathbf{w})$.

Note that a similar form for the free energy has been proposed by Brochard *et al* (1984) and, neglecting the isotropic interactions, also by Khoklov and Semenov (1981). The limit, $V_{AA}(022) = 0$, corresponds to the well known Flory-Huggins model (flexible polymers) and $\{L_A = 1, L_A/B \rightarrow 0, V_{AA}(000) = 0\}$ corresponds to the Maier-Saupe rigid-rod liquid crystal (Humphries and Luckhurst 1976). In most cases, the interaction parameters have been determined empirically and considered to be constant in temperature, monomer concentration, etc. These parameters can also be related to the microscopic properties of the polymer.

3.2. Effective interaction

Because of the interaction between monomers and the coupling of individual monomers along a chain, the monomers tend to positions which effectively reduce their potential energy. The resulting screening, well known in electrolytes and flexible polymers, has

recently been studied in semirigid liquid crystalline polymers (Ten Bosch and Sixou 1985) and the effective isotropic ($l=0$) and liquid crystal potential ($l=2$) were calculated to give

$$V_{AA}(000) = v_{AA}(000)/(kT + xL_A v_{AA}(000))$$

$$V_{AA}(022) = v_{AA}(022)/(kT + xL_A^* v_{AA}(022)).$$

The average bare potential in an expansion in spherical harmonics as in (6) is $v_{AA}(0l)$.

L_A^* is a function of the persistence length B :

$$L_A^* = \frac{2}{15} B \{1 + (B/3L_A)[\exp(-3L_A/B) - 1]\}.$$

In most cases $v_{AA}(000) > 0$ and in liquid crystal polymers $v_{AA}(022) < 0$.

We define $kT_0 = L_A v_{AA}(000)$, $kT_* = L_A^* v_{AA}(022)$. Neglecting correlation with the solvent, the effective interactions are then

$$V_{AA}(000) = \frac{v_{AA}(000)}{k(T + xT_0)} \quad (9)$$

$$V_{AA}(022) = \frac{v_{AA}(022)}{k(T - xT_*)}.$$

In the absence of screening, the Flory isotropic interaction parameter, inversely proportional to the temperature, appears. The screening term in $V_{AA}(000)$ may explain temperature discrepancies found in some polymer-solvent systems (Patterson and Robard 1978). The total screening of the isotropic interactions at infinite chain length is achieved ($V_{AA}(000) \rightarrow 0$, $L_A \rightarrow \infty$). The anisotropic interactions behave quite differently with L_A . This will affect molecular weight dependence of phase diagrams which will be discussed next.

3.3. Nematic transition temperature

In the pure mesomorphic polymer, the temperature T_c^0 for the transition to an ordered phase ($S \neq 0$) is calculated from the condition of equality of the free energy (7) in the isotropic and anisotropic phases. This also defines the 'pseudotransition' temperature in mixtures, i.e. the limit for stability of the nematic phase (Brochard *et al* 1984). The results can be fitted to a simple function in L_A/B .

If the effective interaction is taken to be constant,

$$\frac{kT_c^0}{Bv_{AA}(022)} = 0.15 \{1 + \frac{1}{3}(B/L_A)[\exp(-3L_A/B) - 1]\}.$$

If screening effects as given by (9) are included, then

$$\frac{kT_c^0}{Bv_{AA}(022)} = \frac{kT_*}{Bv_{AA}(022)} + 0.15 \{1 + \frac{1}{3}(B/L_A)[\exp(-3L_A/B) - 1]\}.$$

In both cases, we find that T_c^0 shows an initial sharp increase in L_A for low degrees of polymerisation. This flattens at high L_A . This is indeed observed in many liquid crystalline polymer melts (Seurin *et al* 1983).

Screening effects tend to stabilise the nematic phase by increasing the transition temperature. Although qualitative agreement is found, the approximations introduced

in the screening theory do not permit a quantitative fit. Uncertainties also exist as to the value of the persistence length B in these materials. A dependence of the persistence length on degree of polymerisation due to screening could account for the slow increase of T_c^0 at high L found in some liquid crystalline polymers.

The order parameter at the transition is found to vary between $0.43(L_A/B \rightarrow 0)$ and $0.35(L_A/B \rightarrow \infty)$.

3.4. Phase diagrams

As discussed in Brochard *et al* (1984), the phase diagrams in the polymer solvent system can be calculated from the equilibrium conditions, as follows:

- (i) the equation for the order parameter, $\partial\Delta F/\partial S = 0$,
- (ii) the equation for equality of the chemical potential, $\mu = (\partial\Delta F/\partial x)_T$, and
- (iii) the equation for equality of the pressure, $\pi = \Delta F - x\mu$.

Equilibrium between a nematic phase (N) of concentration x_N and isotropic phase (I) of concentration x_I is defined by solutions of the equations

$$\begin{aligned}\mu_N(x_N, T) &= \mu_I(x_I, T) \\ \pi_N(x_N, T) &= \pi_I(x_I, T).\end{aligned}\tag{10}$$

This combination of equations requires a numerical solution and will be presented in a future paper. At high polymer concentration ($x \rightarrow 1$) an analytical solution is possible in the vicinity of the pure polymer transition temperature T_c^0 .

For $x_N \rightarrow x_I \rightarrow 1$

$$\begin{aligned}x_N - x_I &= V_{AA}(022) \frac{1}{2} S^2 \left(\frac{T_c^0 - T}{T_c^0} \right) \\ \frac{1 - x_N}{1 - x_I} &= \exp\left(-\frac{1}{2} V_{AA}(022) S^2\right)\end{aligned}\tag{11}$$

where $V_{AA}(022)$ and S are given here by the values in the pure polymer. We obtain for the transition temperature $T_1(x)$ to the isotropic liquid, usually plotted in experiments,

$$T_1(x) = T_c^0 - (1-x) \frac{[1 - \exp(-V_{AA}(022)S^2/2)]}{V_{AA}(022)S^2/2}.$$

We can relate $V_{AA}(022)$ to the pure melt transition temperature T_c^0 by either $V_{AA}(022) = v_{AA}(022)/kT_c^0$ or, including screening effects, $V_{AA}(022) = v_{AA}(022)/k(T_c^0 - T_c^*)$.

In both cases we find that the slope, $(-\partial T_1(x)/\partial x)$, of $T_1(x)$, decreases with increasing L_A to flatten at high L_A . This is in agreement with experimental phase diagrams on hydroxypropylcellulose in a simple solvent and in a non-mesomorphic polymer (Seurin *et al* 1984). We also find that the separation $x_N - x_I$ at constant T increases with increasing L_A .

4. Discussion

The theory presented here for polymeric liquid crystals introduces isotropic interactions, flexibility of the macromolecule and resultant screening of the molecular interactions.

In the pure polymer, the critical value of the order parameter at the transition is found to be $S_c \leq 0.44$ as in Maier-Saupe theory. This result is not in agreement with experiments which generally lead to high values of S_c (Volino and Blumstein 1984). The discrepancy may be due to difficulties in the experiments, especially polydispersity of the samples and resultant biphasic separation. It has also been suggested that the simple mean-field picture used here may not be valid in these systems.

The semirigidity of the chain has important consequences on the ordered liquid crystalline phase. The orientational entropy is not given simply by the rigid-rod limit ($L_A/B \rightarrow 0$) used in the papers of Khoklov and Semenov (1981) and Brochard *et al* (1984). This affects the phase diagrams, especially the dependence on the degree of polymerisation.

The screening or self-consistent renormalisation of the interaction between segments has also been considered. Although the qualitative trends seem to be correct, the question deserves further investigation and is related to a better knowledge of correlation functions in polymer systems (Lipson *et al* 1985). This question, as well as further studies on correlation functions, should be pursued. In side-chain liquid crystal polymers, the mesomorphic units are weakly correlated by the flexible main chain and the interaction parameters are then simply constants referring to a certain mixture (Brochard *et al* 1984).

Finally, it should be emphasised that in comparing calculated and experimental phase diagrams, it is often found that the slow dynamics of phase separation in high molecular weight polymers often masks or alters the observation of biphasic zones which may also differ depending on the experimental method used. This makes quantitative comparison difficult in these systems.

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