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1982 J. Phys. A: Math. Gen. 15 1361

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Susceptibility of liquid-crystalline solutions of semiflexible macromolecules in an external orientational field

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Received 12 August 1981

Abstract. The susceptibility of solutions of semiflexible macromolecules in an external orientational field of the dipole type is considered both for the isotropic and the liquid-crystalline phases. It is shown that the concentration dependence of the zero-field susceptibility in the anisotropic phase depends essentially on the character of the flexibility distribution along the chain contour. For a localised flexibility mechanism (freely jointed chain) the susceptibility in the anisotropic phase is practically independent of concentration, whereas for a persistent flexibility mechanism it increases exponentially with concentration. Similar differences exist in the concentration dependence of the mean-square end-to-end distance for freely jointed and persistent macromolecules in the anisotropic phase. In an Appendix it is shown that the problem under consideration is analogous to the well known quantum mechanical problem of the energetic spectrum of a particle in two identical wells separated by a high potential barrier.

1. Introduction

Considerable attention has been paid recently to studies of liquid-crystalline ordering in solutions of stiff-chain polymers (Papkov and Kulichikhin 1977, Flory 1978, Grosberg and Khokhlov 1981). In particular, in recent papers (Khokhlov 1978, Khokhlov and Semenov 1981) we have proposed a theory of the liquid-crystalline transition in solutions of semiflexible macromolecules (i.e. of macromolecules whose persistent length, \bar{l} , is much larger than the characteristic width of the chain, d , but much smaller than the total contour chain length, L).

It was shown that the properties of this transition in a good solvent are not universal for all types of semiflexible macromolecules—they differ essentially depending on the character of the flexibility distribution along the chain contour. Two of the most frequently used models of semiflexible macromolecules were considered in detail: a chain of freely jointed rigid cylindrical rods of length $l = 2\bar{l}$ and of diameter d ($l \gg d$), and a persistent chain, which can be represented as an elastic filament, homogeneous along the chain, of diameter d and of persistent length \bar{l} (effective Kuhn segment $l = 2\bar{l}$, $l \gg d$). In the first case all the chain flexibility is localised at the junction points, while in the second case flexibility is homogeneously distributed along the chain contour. It was shown (Khokhlov and Semenov 1981) that in the case of the persistent model the liquid-crystalline ordering occurs at significantly higher polymer concentrations and the order parameter at the transition point is much smaller than for the freely jointed model with the same parameters l and d .

Although the differences mentioned in the properties of the liquid-crystalline transition are rather significant, they are, nevertheless, purely quantitative in the sense that the functional dependences on the parameters of the system (such as l and d) are the same for both models, since only numerical coefficients in these dependences depend on the model adopted. From the experimental point of view for reliable discrimination between the cases of localised and homogeneously distributed chain flexibility mechanisms it is advisable to find some characteristic of the liquid-crystalline phase which would depend on the parameters of the system in a qualitatively different way for the two models described above.

In this paper we shall show that the susceptibility, χ_0 , of the liquid-crystalline solution in zero external orientational field of the dipole type† (i.e. in the field in which the potential energy of a straight chain segment forming the angle θ with the orientational axis is proportional to $-\cos \theta$) has the properties of such a characteristic. We shall show that for the freely jointed model the value of χ_0 depends only slightly on the concentration, while in the case of the persistent model the concentration dependence of χ_0 in the anisotropic phase is very pronounced (exponential). Thus, measurements of the susceptibility in an external orientational field of the dipole type, which can easily be performed experimentally, can give useful information concerning flexibility mechanisms of stiff-chain polymers.

It is worthwhile also to note from the very beginning that the value of χ_0 is directly connected with the mean-square size of a polymeric coil along the anisotropy axis (see equation (6) below).

2. Free energy of the solution of semiflexible macromolecules

For the calculation of the susceptibility χ_0 it is necessary, first of all, to write down the expression for the free energy of the solution of freely jointed and persistent semiflexible macromolecules. Let L be the contour length of macromolecules, $N = L/l$ the number of effective segments per macromolecule, T the temperature, c the average concentration of effective segments, and $\vartheta = \pi d^2 lc/4$ the volume fraction occupied by macromolecules in the solution. Let us introduce also the orientational distribution function, $f(\mathbf{n})$, for the unit vectors \mathbf{n} tangential to the chain (defined in the usual way—see Onsager (1949)). As was shown by Khokhlov (1978) and Khokhlov and Semenov (1981), in the absence of external fields the free energy of the solution *per macromolecule*, F , can be written as a sum of two terms, $F = F_1 + F_2$, where F_1 is the contribution due to the orientational entropy and F_2 is the free energy of the interaction of segments. For the freely jointed model (Khokhlov 1978)

$$F_1 = NT \int f(\mathbf{n}) \ln[f(\mathbf{n})] \frac{d\Omega_{\mathbf{n}}}{4\pi}, \quad (1)$$

whereas for the persistent model (Khokhlov and Semenov 1981)

$$F_1 = NT \int \frac{[\nabla f(\mathbf{n})]^2 d\Omega_{\mathbf{n}}}{4f(\mathbf{n}) 4\pi} \quad (2)$$

(in equations (1)–(2) we have chosen the following normalisation for the function

† The external magnetic (electric) field in the case when polymer chain segments have a constant magnetic (electric) moment directed along the chain is an example of the field of the dipole type.

$f(\mathbf{n})$: $\int f(\mathbf{n}) d\Omega_{\mathbf{n}}/4\pi = 1$). As for the free energy of the interaction of segments, F_2 , at small polymer volume fractions in the solution ($\vartheta \ll 1$) it can be written using the second virial approximation,

$$F_2 = \frac{1}{2}NTc \int f(\mathbf{n})f(\mathbf{n}')B(\mathbf{n}, \mathbf{n}') \frac{d\Omega_{\mathbf{n}}}{4\pi} \frac{d\Omega_{\mathbf{n}'}}{4\pi}, \quad (3)$$

where $B(\mathbf{n}, \mathbf{n}') = 2l^2 d |\sin \gamma|$ is the second virial coefficient of the interaction of straight segments of length l , whose orientations (specified by the unit vectors \mathbf{n} and \mathbf{n}') form the angle γ with each other. In the paper by Khokhlov and Semenov (1981) it was shown that equation (3) is valid for the persistent model, as well as for the freely jointed model. If $l \gg d$ the use of the second virial approximation in equation (3) leads at $\vartheta \ll 1$ only to negligible error (Straley 1973).

In the presence of an external orientational field of the dipole type we must add a third term to the free energy of the solution: $F = F_1 + F_2 + F_3$. For both models

$$F_3 = -NTu \int \cos \theta f(\mathbf{n}) \frac{d\Omega_{\mathbf{n}}}{4\pi}, \quad (4)$$

where θ is the angle between the vector \mathbf{n} and the orientation axis, and u is the dimensionless parameter of the field, which has the meaning of the potential energy (in temperature units) of the effective segment completely stretched along the orientation axis.

The order parameter corresponding to this field can be introduced as follows: $Q = \langle \cos \theta \rangle$ (averaging is performed using the equilibrium function $f(\mathbf{n})$). Susceptibility is defined as $\chi = \partial Q / \partial u$. Our aim is the determination of the concentration dependence of the susceptibility in the zero field, $\chi_0 = \partial Q / \partial u|_{u=0}$, for freely jointed and persistent models.

3. Concentration dependence of the susceptibility

Equations (1), (3)–(4) (for the freely jointed model) or equations (2)–(4) (for the persistent model) give the free energy of the solution of semiflexible macromolecules as a function of $f(\mathbf{n})$. To determine the equilibrium free energy the value of F should be minimised with respect to all possible distribution functions $f(\mathbf{n})$. For the minimisation we shall use the approximate variational method (a more exact consideration, which is, however, valid only in the concentration range $d/l \ll \vartheta \ll 1$, is presented in the Appendix). Let us choose the trial function in the form†

$$f(\mathbf{n}) = \text{constant} \times \cosh(\alpha \cos \theta + s), \quad (5)$$

where α and s are the variational parameters and ‘constant’ is the normalising constant. Substituting function (5) in the expression for the free energy and minimising $F = F_1 + F_2 + F_3$ with respect to α and s , we find the equilibrium function $f(\mathbf{n})$, the equilibrium free energy and the values of Q and χ_0 (calculations are analogous to those described by Grosberg and Khokhlov (1981) and Khokhlov and Semenov (1981)).

† Onsager (1949) used the trial function $f(\mathbf{n}) \sim \cosh(\alpha \cos \theta)$. In the presence of the external field of the dipole type, because of the non-equivalence of the direction \mathbf{n} and $-\mathbf{n}$ for this field, the introduction of the second variational parameter s is necessary.

The calculated dependence of the susceptibility χ_0 on $x = \vartheta l/d$ (the value of x is proportional to the polymer concentration in the solution) is shown in figure 1(a) (freely jointed model) and in figure 1(b) (persistent model). In both cases $x_0^{(i)}$ and $x_0^{(a)}$ are the boundaries of the phase separation region: at $x < x_0^{(i)}$ the solution is isotropic and at $x > x_0^{(a)}$ it is anisotropic. For the freely jointed model $x_0^{(i)} = 3.25$, $x_0^{(a)} = 4.86$ (Khokhlov 1978), whereas for the persistent model $x_0^{(i)} = 10.48$, $x_0^{(a)} = 11.39$ (Khokhlov and Semenov 1981).

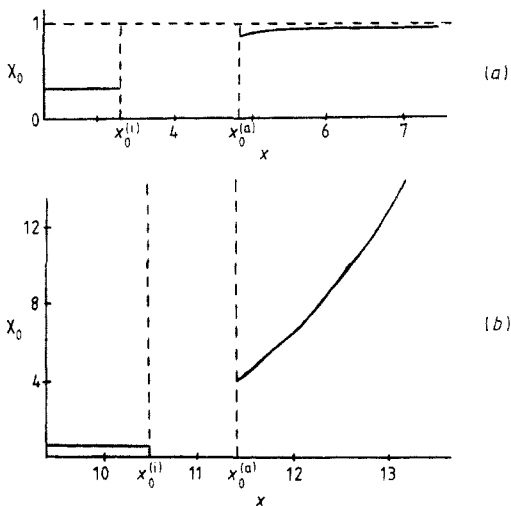


Figure 1. Dependence $\chi_0(x)$ for freely jointed (a) and persistent (b) models.

From figure 1 it can be seen, first of all, that when the liquid-crystalline phase appears the susceptibility in the zero field, χ_0 , in both cases undergoes a leap from the constant isotropic-phase value $\frac{1}{3}$ to the value close to unity (for the freely jointed model) or to the value $\chi_0 \sim 4$ (for the persistent model). Further, it is important that when the polymer concentration in the anisotropic phase ($x > x_0^{(a)}$) increases, the value of χ_0 for the freely jointed model remains practically unchanged, tending to unity in the limit $x \gg 1$, while for the persistent model at $x > x_0^{(a)}$ the susceptibility χ_0 increases rapidly with the increase in x . It is easy to show that at $x \gg 1$ the increase of χ_0 for the persistent model is exponential: $\chi_0(x) \sim \exp(1.72x^{2/3})$ (at the values of x shown in figure 1(b) this asymptotic relation is not yet achieved).

Further, it is noteworthy that from general thermodynamics it follows that

$$\chi_0 = \langle R_z^2 \rangle / Nl^2, \quad (6)$$

where $\langle R_z^2 \rangle$ is the mean square of the projection of the end-to-end distance vector on the orientation axis. Hence, it is clear that the value of the susceptibility in the zero field, χ_0 , is closely connected with the mean-square end-to-end distance, $\langle R^2 \rangle$. In particular, approximate invariance of χ_0 in the anisotropic phase for the freely jointed model means that in this case the value of $\langle R^2 \rangle$ also changes very insignificantly as the concentration increases; exponential increase of the function $\chi_0(x)$ in the anisotropic phase for the persistent model leads to a similar exponential increase of the function $\langle R^2 \rangle(x)$ (see figure 2).

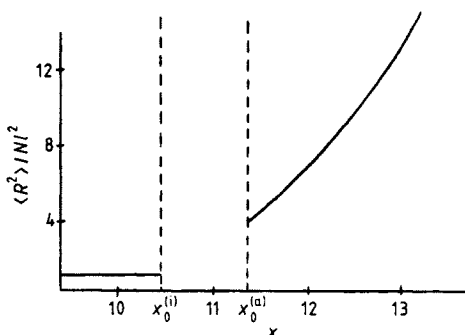


Figure 2. The value of $\langle R^2 \rangle / Nl^2$ as a function of x for the persistent model, calculated using the variational method.

Physical meanings of the differences obtained in the behaviour of the solutions of freely jointed and persistent macromolecules can be interpreted as follows. For both models the function $f(\mathbf{n})$ in the anisotropic phase has two sharp maxima along the anisotropy axis (i.e. at $\theta = 0$ and $\theta = \pi$); with an increase of the degree of orientational order the 'amplitude' of these maxima increases, while their width decreases. Due to the localised flexibility mechanism in the freely jointed chain, in the absence of field each segment can belong to either minimum with probability $\frac{1}{2}$ independently of the orientation of the adjacent segments; this means that $\langle R_z^2 \rangle \sim Nl^2$, i.e., according to equation (6), $\chi_0 \sim 1$. For a persistent macromolecule with homogeneously distributed flexibility the situation is different: in this case, as the order parameter in the anisotropic phase increases (i.e. as the concentration increases), the 'switching' of the chain orientation from one maximum to another requires more and more free energy to be expended, i.e. the average chain length between two such 'switchings' exponentially increases. It is easy to understand that the value of $\langle R_z^2 \rangle$ (and, consequently, of χ_0) is proportional to this average length, which is the reason for the exponential increase of the functions $\chi_0(x)$ and $\langle R^2 \rangle(x)$ obtained.

Using similar considerations, let us estimate the limits of the increase of χ_0 . As the concentration increases, the degree of orientation in the anisotropic phase can increase to such an extent that the average chain length between two 'switchings' can become comparable to the total chain length. In this case the whole chain will behave approximately as one segment of length $L = Nl$, so that $\chi_0 \approx N$. It is clear that as soon as the values $\chi_0 \sim N$ are reached, further increase of the function $\chi_0(x)$ ceases (dependence $\chi_0(x)$ undergoes saturation at $\chi_0 \sim N$).

The effect described above can be called (somewhat approximately) the 'stiffening' of the persistent macromolecule induced by the increase in the degree of anisotropy. It takes place because of the specific structure of the function $f(\mathbf{n})$ at high degrees of anisotropy (with two identical sharp maxima). In other words, this effect is due to the fact that the segments of the persistent macromolecule in the anisotropic solution feel the action of the self-consistent field, which has the form of two deep potential minima (along the directions $\theta = 0$ and $\theta = \pi$) separated by a high potential barrier. In the Appendix we shall establish the exact analogy between the problem under consideration and the well known quantum mechanical problem of the energetic spectrum of a particle situated in two identical potential wells separated by a high potential barrier, and we shall calculate with higher accuracy (without the use of the variational method) the dependence $\chi_0(x)$ for a persistent macromolecule at $1 \ll x \ll l/d$.

Appendix. Susceptibility of the solution of persistent macromolecules and the behaviour of a quantum mechanical particle in two potential wells separated by a barrier

Let us consider a solution of persistent semiflexible macromolecules for which the free energy is given by equations (2)–(4). Minimisation of the free energy (taking into account the additional normalising condition $\int f(\mathbf{n}) d\Omega_n/4\pi = 1$) leads to the integro-differential equation

$$-T\nabla^2\psi + U_{\text{eff}}\psi = E\psi, \quad (\text{A1})$$

where

$$\begin{aligned} \psi(\mathbf{n}) &= [f(\mathbf{n})]^{1/2}, & E &= \lambda T, \\ U_{\text{eff}}(\mathbf{n}) &= U_{\text{ext}} + U_{\text{self}} = -uT \cos \theta + cT \int f(\mathbf{n}') B(\mathbf{n}, \mathbf{n}') \frac{d\Omega_{\mathbf{n}'}}{4\pi}, \end{aligned} \quad (\text{A2})$$

and λ is the indefinite Legendre multiplier. Equation (A1) is equivalent to the Schrödinger equation for a quantum mechanical particle in the potential field $U_{\text{eff}}(\mathbf{n})$. Solution of the polymer problem corresponds to the ground state solution ($E = E_0$) of the quantum mechanical problem, the value of E_0 having the sense of the chemical potential of the segment, μ , in polymer solution: $E_0 = \mu$.

Since our aim is the calculation of the susceptibility χ_0 in a *zero* external field, it is natural to consider the field U_{ext} as a perturbation and to use perturbation theory. If ψ_n and E_n are the normalised eigenfunctions and the corresponding eigenvalues of equation (A1) in the absence of perturbation (external field), the correction to the wavefunction of the ground state, $\delta\psi_0$, due to the external field can be calculated using the formula (Landau and Lifshitz 1974)

$$\delta\psi_0 = \sum_{m=1}^{\infty} \frac{\langle m | \hat{U}_{\text{ext}} | 0 \rangle}{E_0 - E_m} \psi_m, \quad (\text{A3})$$

where

$$\langle m | \hat{U}_{\text{ext}} | n \rangle = \int \psi_m^* U_{\text{ext}} \psi_n d\Omega_n/4\pi.$$

Let us consider a highly anisotropic polymer solution, which appears at the concentrations $x \gg 1$ (let us assume, however, that $x \ll l/d$, i.e. that the polymer volume fraction in the solution is much smaller than unity). In this case the unperturbed potential $U_{\text{ext}}(\mathbf{n})$ consists of two deep potential wells, localised around the directions $\theta = 0$ and $\theta = \pi$, separated by a high potential barrier. It is well known (Landau and Lifshitz 1974) that the spectrum of such a system has a doublet structure with exponentially small splitting. Hence, we can take into account in the sum (A3) only the first term. If $\psi(\mathbf{n})$ is the normalised wavefunction of the ground state of one isolated well, we have (Landau and Lifshitz 1974)

$$\begin{aligned} \psi_0(\mathbf{n}) &= \frac{1}{\sqrt{2}}(\psi(\mathbf{n}) + \psi(-\mathbf{n})), & \psi_1(\mathbf{n}) &= \frac{1}{\sqrt{2}}(\psi(\mathbf{n}) - \psi(-\mathbf{n})), \\ \frac{E_1 - E_0}{T} &= 2\psi(\theta) \frac{\partial\psi}{\partial\theta} \Big|_{\theta=\pi/2} = \frac{\partial\psi^2}{\partial\theta} \Big|_{\theta=\pi/2}. \end{aligned} \quad (\text{A4})$$

Taking into account the equality $\psi = f^{1/2}$, the definition of χ and equation (A3), it is easy to show that

$$\chi_0 = 2T/(E_1 - E_0). \quad (\text{A5})$$

Thus to find χ_0 it is necessary to determine the function $\psi(\mathbf{n})$ near the equator ($\theta = \pi/2$). In this region we can use the WKB method:

$$\psi \cong \frac{A}{(q \sin \theta)^{1/2}} \exp\left(-\int q \, d\theta\right), \quad (\text{A6})$$

where $q = [(U_{\text{self}}(\theta) - \mu)/T]^{1/2}$ and A is the normalising constant. The value of the chemical potential, μ , can be found using the variational method with the trial function $f(\mathbf{n}) = \text{constant} \exp(-\beta \sin^2 \theta)$ —in this case the inaccuracy of the variational method will influence only the numerical factors in the final result, but not the functional dependences. As a result we obtain $\mu = 5T(2/\pi)^{1/3} x^{2/3}$. From the normalisation requirement we have $A = 2x^{1/3}$. In the case of high anisotropy, if the angle θ is not too small $U_{\text{self}}(\theta) = (8/\pi)xT \sin \theta$. Substituting all these expressions in equations (A4)–(A6), we obtain finally

$$\chi_0 \cong 0.25x^{-2/3} \exp(-7.07x^{1/6} + 3.82x^{1/2}). \quad (\text{A7})$$

Functional dependences in equation (A7) in the case $1 \ll x \ll l/d$ ($d/l \ll \vartheta \ll 1$) are exact, but all the numerical coefficients are written down approximately.

At very large x equation (A7) gives $\chi_0 \sim \exp(3.82x^{1/2})$. At the same time, using the variational method we have obtained above the asymptotic form $\chi_0 \sim \exp(1.72x^{2/3})$. We can conclude that although the variational method expresses correctly the fact of the exponential increase of the susceptibility in the anisotropic phase, it gives, nevertheless, qualitatively inaccurate results for the function $\chi_0(x)$ at $x \gg 1$. For more exact calculation of the dependence $\chi_0(x)$ equation (A7) should be used.

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