

# Nematic ordering problem as the polymer problem of the excluded volume

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**Abstract:** Based on a solution of the polymer excluded volume problem, a technique is proposed to estimate some parameters at the isotropic-nematic liquid crystal phase transition (the product of the volume fraction of hard sticks and the ratio of the stick length,  $L$ , to its diameter,  $D$ ; the maximum value of this ratio at which one cannot regard the stick as hard). The critical exponents are estimated. The transition of a swelling polymer coil to ideal is revealed as the polymerization degree of a macromolecule increases. The entanglement concentration obtained agrees with experimental data for polymers with flexible chains. The number of monomers between neighbor entanglements is assumed to be the ratio  $L/D$ . A comparison of the theory with other ones and recent experimental data is made.

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## 1 Introduction

In 1966, while deciding the so-called excluded volume problem, M. Fisher obtained an expression for the probability density of self-avoiding walks, that is, for the distribution function of polymer chain ends [1]. He assumed that the generating function  $P(\mu, \mathbf{r})$  of polymer statistics was roughly analogous to the pair correlation function  $G(\mathbf{r}, 1/T)$  of the two-dimensional Ising model in zero field, as it followed from Onsager's exact solution. There  $\mu$  was the ratio of the chemical potential of a chain monomer to temperature,  $T$ , which was expressed in energy units;  $\mathbf{r}$  was the distance between correlated points.

The subsequent extending of the theory was connected with P.-G. de Gennes [2]. Using the Wilson renormalization method [3], he showed that the polymer excluded volume

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problem could be decided in frameworks of the fluctuation theory of phase transitions and critical phenomena. The Hamiltonian of the task was chosen in the form suggested by Ginzburg and Landau for the phenomenological theory of superconductivity.

The main assumption made in the present study is to regard the Fisher distribution as only one factor in the expression of a full probability for polymer statistics. The second factor can be taken into account by the way we will demonstrate below. As a result we are going to estimate some parameters of the isotropic-nematic liquid crystal (LC) phase transition such as i) the product of the volume fraction of hard sticks and the ratio of the stick length,  $L$ , to its diameter,  $D$ ; ii) the maximum value of this ratio at which one cannot regard the stick as hard. The suggested method will lead to better understanding of both polymer and LC problems.

## 2 Results and discussion

### 2.1 Pair correlation function of the space-density correlation

We are going to consider the pair-correlation function of the space-density correlation for a polymer chain with the excluded volume. The study is based on the following assumption: all probability (density) distribution functions have a very sharp maximum. In that case, we can replace variables by their mean values. The shape of the function for the excluded volume problem has been discussed by Fisher [1]. He has shown that in this case the generating function must decay exponentially as the end-to-end distance tends to infinity.

Let us define the pair correlation function  $g(R) = \langle n(\mathbf{0})n(\mathbf{R}) - \langle n \rangle^2 \rangle / \langle n \rangle$  for short wave lengths

$$kR > 1 \quad (1)$$

as follows [4]:

$$g(R) = \langle n \rangle^{-1} \left| \int (2\pi)^{-d} \exp(i\mathbf{k}\mathbf{R}) \langle n_{\mathbf{k}} \rangle d^d k \right|^2. \quad (2)$$

Here and below we suppose that  $\mathbf{R}$  is the radius vector between two monomers located far from each other along the chain;  $|\mathbf{R}| = aN^\nu$ , that is, a correlation radius  $\xi \sim R$  is the single scale distance for the system involved;  $\nu$  is the critical exponent [1-3];  $a$  is the monomer diameter (the lattice constant);  $\mathbf{k}$  is the wave vector;

$$\langle n \rangle = N/R^d \quad (3)$$

is the mean concentration of the chain monomers inside the polymer coil;  $d$  is the space dimension.

In order to find  $g(R)$ , it is necessary to define  $\langle n_{\mathbf{k}} \rangle$ . We choose the Debye structural factor,  $4d/(ka)^2$ , for wave vectors

$$N(ka)^2 \gg 1 \quad (4)$$

as a probe function for  $\langle n_k \rangle$ . In order to estimate the integral (2) in a simple way, we write the equation (6), which is true if

$$ka \ll 1 \tag{5}$$

$$\langle n_{\mathbf{k}} \rangle \sim 1/(\exp(\theta) - 1) = \sum_{N=1}^{\infty} \exp(-\theta N) \tag{6}$$

where

$$\theta = (ka)^2/(2d). \tag{7}$$

In that case, we can obtain the following equation for  $g(R)$  by integrating (2) over angles:

$$g(R) \sim a^{-4}R^{-2}\langle n \rangle^{-1} \left| \int_0^{\infty} \sum_{N=1}^{\infty} \sin(kR)k^{d-2} \exp(-N(ka)^2/(2d))dk \right|^2. \tag{8}$$

We do not write a constant in (8) since the estimation (6) of  $\langle n_{\mathbf{k}} \rangle$  is not correct when  $k \rightarrow 0$  (see (4) and (1)). We will calculate the constant below.

In (2) we change the order of the integration and the summation, integrate over  $dk$ , then replace the summation over  $N$  by the integration over  $dN$  between the limits of 0 to  $\infty$ , since the integrand converges. As a result, we find the well-known (if  $d = 3, \nu = 0.5$ ) expression for the Debye correlation function in the coordinate space:

$$g(R) \sim a^{-4}R^{-2}\langle n \rangle^{-1} = a^{-4}R^{d-2}/N = 1/a^2r \tag{9}$$

where  $r \sim aN^{1-\nu}$  and we used (3). However, if  $\nu > 0.5$ , then  $r \ll R$ , since  $N \gg 1$ . That means that there exists a fluctuation attraction between the chain ends, owing to screening the volume interactions, since the end monomers seem to repulse approximately two times weaker than other monomers. The mechanism of the interaction in polymer solutions was described elsewhere [5]. The attraction compresses the coil in one direction. Consequently, its shape looks like an oblate, spherical ellipsoid. Let us estimate the maximum gyration radius  $r_g$  from the third invariant of the deformation tensor as  $R^3 \sim rr^2$  and find that

$$r_g \sim aN^{2\nu-0.5}. \tag{10}$$

We emphasize that real polymer chains can be broken by thermal fluctuations if (10) is not satisfied. Otherwise, the formula (10) is a condition for the invariant theory.

Let us continue to study properties of the probability density [1]:

$$p_N(r) \cong B/R^d (r/R)^\varphi \exp(-(r/R)^{1/(1-\nu)}) \tag{11}$$

where  $B^{-1} = (2\pi\nu)^{1/2}(1-\nu)^{1/\nu}\Gamma(1/\nu)S_d$ ;  $S_d = 2\pi^{d/2}/\Gamma(d/2)$  is the surface area of the  $d$ -dimensional sphere of unit radius; and

$$\varphi = 0.5/(1-\nu) + 1/\nu - d. \tag{12}$$

We will use the ‘‘symmetrical’’ function (11), although we have found that the coil shape is asymmetric, for the following reason. *A priori* the function  $P(0, \mathbf{r})$  is not known.

One may suppose that the function is “symmetrical,” since the space is isotropic at large scales. If we introduce the two mean scale lengths  $r$  and  $r_g$  (respectively, parallel and perpendicular to the field compressing the coil), then one can obtain probability density distribution functions, as well as the function (11) [1]. However, in that case  $r$  becomes a function of  $R$ , and the exponent  $\varphi$  depends on the details of defining  $r$  and  $r_g$ . We will use the simplest function (11). The rest parameters of the model can be found from the invariants of the deformation tensor. If  $\lambda = r_g/R \gg 1$ , then the first invariant  $I_1$  is proportional to  $2\lambda$  and the second invariant  $I_2 \sim \lambda^2 = R/r$  (see (10)).

In (11) one should substitute  $r_g$  for  $r$  because this formula is asymptotically true by definition [1], if the ratio of the radii

$$r/R > 1. \quad (13)$$

Only  $r_g$  can satisfy the condition, however; the rest parameters such as  $r$  and  $R$  do not. Thus, we can draw an important conclusion: the Fisher distribution does not correspond to the probability density of the end-to-end distance. The mean end-to-end distance is  $r \sim aN^{1-\nu}$ .

## 2.2 Calculation of the critical exponent of the correlation radius; a thermodynamic consideration

The logarithm of the function (11) is proportional to  $\mu N$ , in accordance with the origin of the function [1]. However, in practice we study the system with  $N = const$ , but not with  $\mu = const$ . This thermodynamic condition results in the “renormalization” of the chemical potential (see, for example [6])

$$\mu \sim N^{\alpha-1} \quad (14)$$

where the critical exponent  $\alpha$  may be expressed as [3]

$$\alpha = 2 - \nu d. \quad (15)$$

Substituting (10) for  $r$  in (11) and using (14), one can find that

$$\alpha = (\nu - 1/2)/(1 - \nu). \quad (16)$$

We determine  $\nu$  from (15) and (16). If  $d = 3$  it is equal to  $1 - 6^{-1/2} \approx 0.5918$ , and is in a good agreement with the value of  $\nu \approx 0.5918$  received by the second order  $\varepsilon$  - expansion [3], if the number of components of an ordering field  $n = 0$ . (The value of  $\nu < 1$  should be chosen, since the polymer chain can not be longer than its length  $\sim aN$ .) Using other considerations, the author [7] has obtained a similar estimation. Note that the recent methods [8-10] have given values of the critical exponents not much different from the ones calculated here and below. However, the discussion of the special question is outside the scope of this paper.

### 2.3 Estimation of the critical exponent evaluating the total number of self-avoiding walks

If we define the square of the ordering parameter about the critical point as ( $\mu_{cr} = 0$ , where one can take  $R \sim \xi \rightarrow \infty$ )

$$W^2 = \int p_N(r)\delta(r - r_g)dr / (\langle n \rangle g(R)a^d) \sim N^{-\nu+\varphi(\nu-0.5)} \sim N^{-2\beta} \tag{17}$$

then one may obtain the critical exponent  $\beta$ :

$$2\beta = \nu - \varphi(\nu - 0.5). \tag{18}$$

Comparing the definition with the conventional expression [3]

$$2\beta = \nu(d - 2 + \eta)$$

we see that

$$\eta = -\varphi(\nu - 0.5)/\nu. \tag{19}$$

Finally, one can find the exponent,  $\gamma$ , since [3]

$$\gamma = \nu(2 - \eta). \tag{20}$$

Substituting (19) for  $\eta$  in (20) we obtain

$$\gamma - 1 = 2(\nu - 0.5) - \nu\eta = (\nu - 0.5)(2 + \varphi). \tag{21}$$

Using (12) and the estimation of  $\nu = 1.6^{-1/2}$ ,  $\gamma \approx 1.1757$  and agrees with the value of 1.1758 obtained by the second order  $\varepsilon$  - expansion [3], if  $n = 0$ .

It should be noted that we define the ordering parameter (17) as the ratio of the two probabilities,  $p_N(r_g)R^d/N$  and  $g(R)a^d$ , that is,  $W^2$  is the probability to find the gyration radius  $r_g$  for the swelling coil if the end-to-end distance is  $r$ .

We have just modified the Fisher method. Note that  $g(R)$ , by its definition [4], satisfies the condition to locate the different monomers in different sites of the lattice. Let us write the value of  $\eta \approx 0.0132$  using (19). The  $\varepsilon$ -expansion results in  $\eta \approx 1/64 \approx 0.0156$ [2].

### 2.4 Another definition of $g(R)$

We may substitute (7) for  $\theta$  in (6) and, using  $\langle n_{\mathbf{k}} \rangle \sim 1/\theta$  when  $\theta \rightarrow 0$ , obtain  $g_N(R) = g(R)/N$  for  $2 < d < 4$  by fulfilling the procedures used above:

$$g_N(R) = (2Ct)a^{-4}R^{-2}\langle n \rangle^{-1} \left| \int_q^\infty dk \sin(kR)k^{d-4} \right|^2$$

where  $qR > 1$ . Integrating by parts and neglecting the term with the greatest degree of  $R^{-1}$  one may find

$$g_N(R) = Ct a^{-4} R^{-4} \langle n \rangle^{-1} q^{2(d-4)} \tag{22}$$

where

$$C' = S_d^2(2d)^2/2(2\pi)^{2d}. \quad (23)$$

If the maximum of  $r_g$  is expressed as the reciprocal value of the minimum of the wave vector  $1/(aq) \sim r_g/R$ , then  $aq \sim N^{0.5-\nu}$ , and  $g_N(R)$  in (22) is proportional to  $g(R)/N$ . The value of  $q$  satisfies the conditions (1), (4), and (5). Consequently, only now can we try to estimate the constant in (8).

Note that the factor  $(2\pi)^{-2d}$  in (23) comes from the density of states in the momentum space. This contradicts the definition  $W^2$  as a condition probability. In that case, one should get the probability from the probability density. Therefore, we sum over all states of a wave vector. The following equation for the adjusting constant  $C$  (see below) of the functions,  $g(R)$  and  $g_N(R)$ , can then be written:

$$C = S_d^2(2d)^2/2. \quad (24)$$

### 3 Conclusions: estimations of the entanglement concentration and parameters of transition to the LC state

Since we defined  $g(R)a^3 = g_N(R)Na^3$  above as a probability, it cannot be  $> 1$ . Let us regard  $g(R)a^3/N$  as a probability of the binary collision of the chain monomers. We may determine  $N_e$  from the expression with the help of (9), (22), and (24) and obtain

$$N_e = C^{1/(2-\nu)} \approx 283. \quad (25)$$

This means that, in general, for low enough values of the polymerization degree, the probability that two different end monomers of the chain interact is equal to 1, if two-particle collisions take place.

We regard  $N_e$  as a value that can correspond to the number of the monomer between (self-)entanglements of the chain. The reason for this follows. We know that the parameter  $N_e$  is used in studying both the high frequency elastic responses of polymer melt and the low frequency viscous properties. The behavior is possible if  $N_e$  is a thermodynamic parameter, such as temperature or pressure. Therefore, it must certainly be defined in our theory.

Experimental data show [6, 11] that  $N_e = 50-300$ . This is the first argument for the use of the constant (24).

The second argument can be obtained from the following considerations. For high enough  $N$ , we suppose that the system shall become unstable. Then the transition to an ideal coil will occur, and  $W^2$  will not depend on  $N$ . If  $W_{cr}^2 = (B/C)^2$ , then  $W = W_{cr}$  at  $N_{cr} = (C/B)^{1/(2\beta)} \approx 8 \times 10^6$ . On the other hand,  $g(R)a^3$  cannot be  $> 1$ . Consequently, the formula  $\ln C = (1 - \nu) \ln N$  gives the value of  $N_{cr}$  for an ideal coil if  $\nu = 0.5$ :  $N_{cr} = C^2 \approx 8 \times 10^6$ . Thus the chain screens its volume interactions and transforms from the swelling state to the ideal coil at  $N_{cr}$ .

At last, let us obtain the parameters of the transition to the LC state. The value  $N_e$  is calculated from the determination of the probability of the binary collision of the chain

monomers, if the two monomers do not occupy the same site of the lattice. At  $N < N_e$  the probability is one by its definition. We suppose that sticks with the length-diameter ratio  $L/D$  proportional to  $N_e$  can form the nematic ordering phase, since the viscosity of polymer melt is proportional to  $N$  in this case. The volume fraction of the sticks may be found from (3) as  $\Phi_{nematic} = \langle n \rangle a^3 = N_e^{1-\nu d}$ . The product of the volume fraction and  $N_e$  is

$$\Phi = N_e^\alpha = 3.6$$

and must be compared with the value  $\Phi_{nematic} L/D = 4.5$  from Onsager theory [12] or with other models [5].

According to our consideration,  $N_e$  is a parameter of flexibility and the value  $L/D = N_e = 283$  is the maximum, above which one cannot regard the stick as hard.

Thus, the estimations for the LC task may be obtained from other fields of statistical physics. This is the important result of the present work, since the suggested method enables the solution of different problems from varied fields of statistical physics.

The recent SANS experimental data [13] confirm the result obtained above. At low temperatures, the exponents of the scaling laws of the dependence of gyration radii on polymer molecular weight, in the directions parallel and perpendicular to the director of the studied nematic phase, are measured as follows:  $\nu_{\parallel} \approx 0.66 \pm 0.02$  and  $\nu_{\perp} \approx 0.46 \pm 0.02$ . These values are close to the polymeric exponents:  $2\nu - 0.5$  and  $1 - \nu$ . As the temperature increases,  $\nu_{\parallel}$  and  $\nu_{\perp}$  tend to 0.5 when the nematic–isotropic phase transition occurs. A similar effect has been described above for the polymer system: the polymerization degree increase is the prime cause for the transition to the isotropic state.

In conclusion, let us turn briefly to the question of using the suggested technique for any probability (density) distribution function. Following Fisher’s method [1], one can see that the generating function must decay exponentially as the end-to-end distance tends to infinity. As an example, a Gaussian distribution satisfies the condition. However, the consideration of three-particle collisions of monomers results in some logarithmic factors [6]. Even if they can be neglected, the conditions (1), (4), and (5) can restrict the possible use of the distribution. Thus, in a general case, the question needs a separate investigation.

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## References

- [1] M.E. Fisher: “Shape of a Self-Avoiding Walk or Polymer Chain”, *J. Chem. Phys.*, Vol. 44, (1966), pp. 616–622.

- [2] P.-G. de Gennes: “Exponents for the Excluded Volume Problem as Derived by the Wilson Method”, *Phys. Lett.*, Vol. 38A, (1972), pp. 339.
- [3] K.G. Wilson and J. Kogut: “The renormalization group and the  $\varepsilon$ -expansion”, *Phys. Rep.*, Vol. 12C, (1974), pp. 75–199.
- [4] L.D. Landau and E.M. Lifshitz: *Statistical Physics*, 3rd ed., Pergamon, Oxford, 1980.
- [5] A.Yu. Grosberg and A.R. Khokhlov: *Statistical Physics of Macromolecules*, American Institute of Physics Press, New York, 1994.
- [6] P.-G. de Gennes: *Scaling Concepts in Polymer Physics*, Cornell University Press, New York, Ithaca and London, 1979.
- [7] A.N. Yakunin: “A Globule in a Stretching Field. The Role of Partial Melting During Drawing of Crystalline Polymers”, *Intern. J. Polymeric Mater.*, Vol. 22, (1993), pp. 57–64.
- [8] S. Caracciolo, M.S. Causo, A. Pelissetto: “High-precision determination of the critical exponent  $\gamma$  for self-avoiding walks”, *Phys. Rev. E*, Vol. 57, (1998), pp. R1215-R1218.
- [9] G. Besold, H. Guo, M.J. Zuckermann: “Off-Lattice Monte Carlo Simulation of the Discrete Edwards Model”, *J. Polym. Sci.: Part B: Polym. Phys.*, Vol. 38, (2000), pp. 1053–1068.
- [10] J. Zinn-Justin: “Precise determination of critical exponents and equation of state by field theory methods”, *Phys. Rep.*, Vol. 344, (2001), pp. 159–178.
- [11] R.P. Wool: “Polymer Entanglements”, *Macromolecules*, Vol. 26, (1993), pp. 1564–1569.
- [12] P.-G. de Gennes: *The physics of liquid crystals*, Clarendon Press, Oxford, 1974.
- [13] A. Brûlet, V. Fourmaux-Demange, J.P. Cotton: “Temperature Dependence of the Conformation of a Comblike Liquid Crystalline Polymer in a  $N_I$  Nematic Phase”, *Macromolecules*, Vol. 34, (2001), pp. 3077–3080.