Pis'ma v ZhETF, vol.60, N4, pp.277 - 284

NEMATIC PHASE TRANSITION IN ENTANGLED DIRECTED POLYMERS

S.Nechaev

L.D.Landau Institute for Theoretical Physics
117940 Moscow, Russia

Submitted 12 July 1994

A Flory-type mean field theory of a nematic phase transition in the system of nonphantom entangled directed polymers has been elaborated. According to the conjectures expressed in [8], the "link complexity" of the chains is characterized by the highest power of the Jones invariant for the corresponding closed braid. The phase diagram is presented in the coordinates "the link complexity" versus the ordering ineraction constant. The order of the phase transition is shown to be different for "weakly" and "strongly" entangled chains.

A considerable number of works is devoted to the investigation of the liquid-crystalline-type phase transitions in the systems of long chain molecules (for review see for instance [1, 2]). Apparently, at present the scope of problems dealing with the nematic-type ordering in polymers is one of the most examined branches of statistical physics of macromolecules. However, as far as we know, all the existing theories do not take into account the effects caused by entanglements between the chains in such systems.

The purpose of the present note consists in developing of the simple mean-field theory of the ordering phase transition in the system of entangled "directed polymers" with fixed topology.

Let us stress from very beginning that we do not claim to find the new kind of phase transitions or to describe the new class of real physical systems. We pursue two main goals only:

– To utilize the knowledges acquired in the knot theory, namely in construction of the algebraic knot invariants, to extract the simplified nonabelian topological invariant which will serve as a "link complexity" and could be convenient tool for the investigation of systems of entangled chain molecules;

– To show in the framework of Flory-type theory on the example of known models how the presence of topological constraints modifies the usual disorder-nematic phase transition.

1. The model. Consider the ensemble of directed random walks embedded in 2+1 dimensions. It is possible to represent each trajectory by a world line of a particle randomly moving on the plane. Imagine that at the first time slice, $j = 0$, there is a given initial distribution of M such particles. Then let them allow to move randomly on the plane (x, y) under two conditions: a) the trajectories of the particles being projected to the plane do not escape some circle of the diameter D; b) at the time slice $j = N$ all particles return to their starting points. Supposing the phase trajectories of the particles in the space-time to be nonphantom, we obtain a system of directed entangled random walks confined in a cylinder with the dimensions of order $D \times D \times N$ – see Fig.1. If we make now a closure

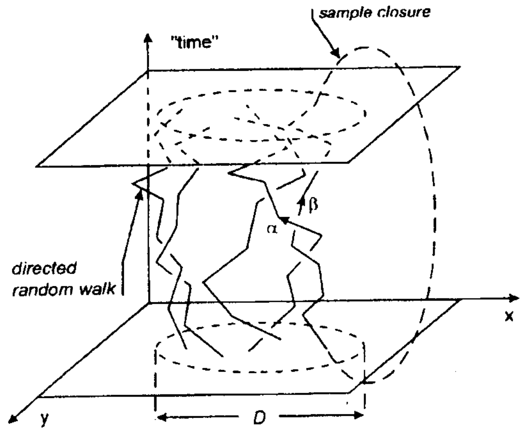

Рис.1

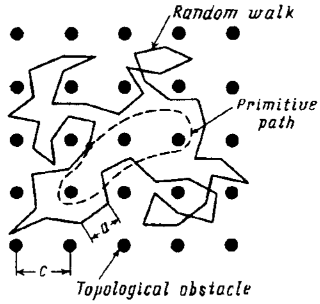

Рис.2

Fig.1. Braided system of entangled directed random walks
Fig.2. Closed trajectory of the random walk in the lattice of obstacles (solid line) and its topological invariant – the primitive path (dashed line)

identifying the ends of each phase trajectory, the system of M directed lines will represent itself as a set of linked loops i.e., *the closed braid* embedded in $2+1$ dimensions.

The interactions we introduce in the following way. Take two subsequent time sections, j and $j+1$, and consider the segments of the world lines in the "time slit" between these sections. Let us require that two segments α and β ($\{\alpha,\beta\} \in [1,M]$) with the coordinates of the centers $\mathbf{r}_\alpha$ and $\mathbf{r}_\beta$ interact with each other with an energy

$$U(\mathbf{n}_\alpha, \mathbf{r}_\alpha; \mathbf{n}_\beta, \mathbf{r}_\beta) = g \cos(\mathbf{n}_\alpha \mathbf{n}_\beta)\, \varphi(|\mathbf{r}_\alpha - \mathbf{r}_\beta|), \tag{1a}$$

where g is the interaction constant, $\mathbf{n}_{\alpha,\beta}$ are the unit vectors directed along the segments α, β in the given time slit and the function $\varphi(|\ldots|)$ depends only on the distance between the centers of these segments.

For the function $\varphi(|\mathbf{r}_\alpha - \mathbf{r}_\beta|)$ $(\alpha \neq \beta)$ we assume the hard core behavior

$$\varphi(|\mathbf{r}_\alpha - \mathbf{r}_\beta|) = \begin{cases} 1 & \text{if } |\mathbf{r}_\alpha - \mathbf{r}_\beta| \le a \\ 0 & \text{if } |\mathbf{r}_\alpha - \mathbf{r}_\beta| > a \end{cases}, \tag{1b}$$

where a is the length of the world line segment in the given time slit.

Suppose now the topology of a braid of M directed polymers to be quenched in an arbitrary given state which does not change in course of thermal fluctuations of the chains.

The nature of an expected phase transition from the disordered state to the ordered one can be easily understood from the following conjectures. Let us start with the situation when the chains in the braid are strongly entangled. In this case one can see that some chains wind around other ones making therefore impossible in average the parallel displacement of neighboring segments. On the other hand, the attraction energy (Eqs.(1a,b)) is maximal when the neighboring segments are parallel. The competition between the entropic disordering for the fixed topological state of the chains and the direct attraction of the chain segments could lead to a partial ordering in the system under consideration. The less entangled are the chains the more favorable is the ordering transition. In details the corresponding phase diagram in the coordinates "link complexity" versus g (strength of interaction in Eq.(1a)) is analysed in section 3.

2. "Link complexity" and entropy of entangled paths. The problem of describing the entangements in the system of nonphantom directed random walks has a long history with the roots in polymer's [3] and anyon's businesses [4]. The substential progress in this field is connected with recent works [4, 5] where the Chern – Simons path-integral formalism has been applied for investigating the superconductivity and the quantum Hall effect. Nevertheless the following problem remains: how to introduce the rough quantitative characteristics of the complexity of entanglements in the system, which will correctly reproduce the nonabelian properties of the linked chains. We describe here the evident way of construction of such characteristics, which we call *the link (knot) complexity*, η, for the system defined in the preceding section.

Consider the ensemble, Ω, of all allowed closed conformations of our chains in the space-time. Due to the presence of topological constraints the entire phase volume, Ω, splits into disconnected domains, $\omega\{\Gamma\}$, $(\omega \in \Omega)$ of homotopically equivalent paths characterized by the topolofical invariant, Γ. The entropy of the given topological state of the system we can formally write as follows

$$S\{\Gamma\} \equiv \ln \omega\{\Gamma\} = \ln \sum_{\{\Omega\}} \delta\left(\Gamma\{\mathbf{n}_1, \mathbf{r}_1; \ldots; \mathbf{n}_M, \mathbf{r}_M; j=0|\ldots|\mathbf{n}_1, \mathbf{r}_1; \ldots; \mathbf{n}_M, \mathbf{r}_M; j=N\} - \Gamma\right). \quad (2)$$

To be more definite, we use for Γ the polynomial invariant introduced by V.F.R.Jones, $V(t)$, where t is the usual "spectral parameter" [6]. Let us remind that Jones invariant is a Lourent polynomial in t and is constructed according to the 2D knot diagram turned to some general position (i.e., the crossing points on the projection are produced by pair intersections of chain segments only). The main condition on $V(t)$ is that this function should be invariant under Reidemeister moves (see for details [7]).

According to the ideas expressed in [8] let us use for the quantitative characteristics of the knot complexity, η, the highest power of Jones invariant, $V(t)$, i.e.,

$$\eta = \lim_{t\to\infty} \frac{\ln|V(t)|}{\ln t}. \quad (3)$$

It is noteworthy that instead of Jones polynomial we could take Alexander invariant, $\nabla(t)$, and define η as a highest power of $\nabla(t)$ for a given braid.

Of course, the choice of the link complexity is completely arbitrary and depends mostly on the author's taste. However we guess that our selection is rather general and bring in its support the following arguments:

- The fact that the knot complexity, η, is more rough characteristic than the complete algebraic polynomial is not a lack, but an advantage if we are dealing with the statistical models. Actually, one and the same value of η characterizes a narrow class of "topologically similar" knots which is at the same time much broader than the class represented by the complete invariant. This allows one to introduce the smoothed measures and distribution functions for η (as it will be explained below);

- The value of η describes correctly, from the physical point of view, the limit cases: $\eta = 0$ corresponds to "weakly entangled" trajectories whereas $\eta \sim N$ matches the system of "strongly entangled" paths. The later case has been discussed in details in [8];
- There is a direct relation between the knot complexity, η, and the length of the "primitive path", μ, of an test chain in the 2D lattice of obstacles, (for a more simplified model this relation has been explained in [9]). The "primitive path" of a closed trajectory on a plane entangled with an array of removed points (obstacles) is defined as a shortest uncontractible path (shown in Fig.2 by the dashed line) which remains after deleting of all "double folded" parts of the trajectory. The primitive path is a well known topological invariant widely used for describing of entanglements in statics and dynamics of a polymer systems (see for review [10]).

The last argument is specified in the following assertion:

Statement.

1. Take the system of M nonphantom directed random walks of length $L = Na$ with the fixed ends and without ordering interactions, confined in the circle of diameter D on the projection (see Section 2 and Fig.1 for details). Define the averaged value of the "knot complexity", $<\eta>$

$$<\eta(N, M, D, a)> = \frac{1}{\Omega} \sum_{\Omega} \eta\, \omega(\eta), \tag{4}$$

where Ω (see above) is the total number of the microstates in an ensemble of directed random walks with the fixed ends and $\omega(\eta)$ is the subset of Ω of paths with the fixed value of the highest power of the Jones invariant, η.

2. Consider the closed random walk (with selfintersections) of the length L on the plane in the lattice of topological obstacles with the average spacing $c \simeq D/\sqrt{M}$ and define the averaged value of the primitive path, $<\mu>$

$$<\mu(N, M, D, a)> = \frac{1}{\tilde{\Omega}} \sum_{\tilde{\Omega}} \mu\, \tilde{\omega}(\mu), \tag{5}$$

where $\tilde{\Omega}$ is the total number of the microstates in an ensemble of closed nonphantom random walks on the plane and $\tilde{\omega}(\mu)$ is the subset of $\tilde{\Omega}$ of walks with the fixed value of the primitrive path, μ, in the lattice of obstacles[1)].

There exists the nonrandom "time-independent" limit

$$\lim_{N \to \infty} \frac{<\eta(N, M, D, a)>}{<\mu(N, M, D, a)>} = \mathrm{const}(M, D, a). \tag{6}$$

We should say that the complete mathematically rigorous proof of this statement is still not known for us, but the mentioned relation is very clear phyiscally following from the Fürstenberg theorem [11]. This theorem establishes the limit behavior of the highest Lyapunov exponent, $\lambda(N)$, for the product of N independent identically distributed random matrices. For our system the Jones invariant can be written as follows ([12])

$$V(t|N, M, D, a) = \mathrm{Tr} \prod_{j=1}^{N} \hat{W}_j \left\{t|\mathbf{n}_1, \mathbf{r}_1; \ldots; \mathbf{n}_M, \mathbf{r}_M\right\} \tag{7}$$

1) The nonphantomness of the random walk implies the existence of topological constraints caused by the lattice of obstacles only. The volume interactions are not taken into account.

where $\hat{W}_j(\ldots)$ are the "braiding" opreators; they are random on each time slice, j, and obey the Yang–Baxter algebra. So, the quantity $\ln|V(t|\ldots)|$ is proportional both to the highest exponent of Jones polynomial and to the Lyapunov exponent of the operator product in (7). From the other hand, the fact that the highest Lyapunov exponent is directly proportional to the "primitive path" of the random walk in the lattice of obstacles is known from the consideration of the random walks on the so-called free group–the covering space for the plane with the lattice of removed points–as it has been explained in [9, 13].

The partition function, $Z(\mu, N, c, a_\perp)$, of the random walk of length $L = Na_\perp$ in the $2D$ lattice of obstacles with the spacing, c, and the primitive path of length μ is given by the following equation ([14, 13])

$$Z(\mu, N, a_\perp, c) = \text{const}\left(\frac{c^2}{Na_\perp^2}\right)^{3/2}\frac{\mu}{c}\exp\left(\frac{Na_\perp^2}{c^2}\ln(2\sqrt{3}) + \frac{\mu}{2c}\ln 3 - \frac{\mu^2}{2Na_\perp^2}\right), \tag{8}$$

where the numerical coefficients correspond to the square lattice of obstacles and $a_\perp$ is the length of the segment projection to the plane (x, y) (see Fig.2).

Finally, the entropic (elastic) contribution to the free energy, F_{el}, as a function of the link complexity, η, for the system of M entangled directed random walks, reads

$$F_{el}(\eta, N, M, D, a_\perp) = -M\ln Z\left(\mu \equiv \eta, N, a_\perp, c = \frac{D}{\sqrt{M}}\right) \simeq$$

$$\simeq -\frac{Na_\perp^2 M^2}{D^2}\ln(2\sqrt{3}) - \frac{\eta M^{3/2}}{2D}\ln 3 + \frac{M\eta^2}{2Na_\perp^2} - M\ln\left(\frac{\eta D^2}{(Na_\perp^2)^{3/2}M}\right) + \text{const}, \tag{9}$$

where we have $T \equiv 1$ for the temperature and $c = D/\sqrt{M}$ for the average distance between the effective topological obstacles.

3. Mean-field theory of phase transition in system of entangled directed chains. In the mean-field approximation the total free energy of the system, F, is a sum of "elastic", F_{el}, and "ordering", F_{int}, terms. Suppose also that in average all segments form one and the same angle θ with respect to z-axis, i.e.

$$< \cos(\mathbf{n}_\alpha \mathbf{n}_\beta) > = \frac{1}{2}\cos^2\theta \qquad \{\alpha, \beta\} \in [1, M], \tag{10}$$

thus, we have $a_\perp = a\sin\theta$.

Collecting (1a,b), (9), (10) and taking into account that $F_{int} = - < U(\mathbf{n}_\alpha, \mathbf{r}_\alpha; \mathbf{n}_\beta, \mathbf{r}_\beta) >$ we obtain the following expression for the non-equilibrium free energy of the system of entangled directed random walks

$$F(\theta) = -\frac{Na^2M^2\ln(2\sqrt{3})}{D^2}\sin^2\theta - \frac{\eta M^{3/2}\ln 3}{2D} + \frac{M\eta^2}{2Na^2}\sin^{-2}\theta - M\ln\left(\frac{\eta D^2}{(Na^2)^{3/2}M}\sin^{-3}\theta\right) -$$

$$-\frac{gNa^2M^2}{2D^2}\cos^2\theta + \text{const}, \tag{11}$$

where $\sin^2\theta = w$ is the variational parameter changing in the region $w \in [\eta^2/(Na)^2, 1]$ and the interaction term is written in the second virial approximation. In principle the free energy (11) should be minimized with respect to D (as well as to w) to reach the equilibrium density but we start with the simplified case supposing density to be constant.

Let us define the dimensionless density, ρ, and the relative length of the averaged primitive path (called further "relative link complexity"), τ, as follows

$$\rho = \frac{Ma^2}{D^2}; \qquad \tau = \frac{\eta}{Na} \quad (0 \le \tau \le 1). \tag{12}$$

The normalized free energy, $f(w)$, reads now

$$f(w) \equiv \frac{2}{NM} F(\sin^2\theta = w) = \rho(g - \ln 12)w + \frac{\tau^2}{w} + \frac{3}{N}\ln w + C(\rho, \tau, N), \tag{13}$$

where

$$\tau^2 \le w \le 1$$

and the function $C(\rho, \tau, N) = -\rho^{1/2}\tau \ln 3 + \frac{2}{N}\ln\rho$ does not depend on w.

The variable $w = \sin^2\theta$ plays a role of the "order parameter" in our model. In the isotropic phase we have for the distribution function $\psi(\theta) = \frac{1}{2\pi}$. Thus, $w_{iso} = \int w(\theta)\,\psi(\theta)\,d\theta = \frac{1}{2}$. Let us assume that

- for $w < \frac{1}{2}$ the chains are in the ordered (nematic-like) phase;
- for $w \ge \frac{1}{2}$ the chains are in the disordered[2] phase.

The phase transition curve we determine comparing the minimal value of the free energy $f(\bar{w})$ on the intrval $\tau^2 \le \bar{w} < w_{iso}$ to the value $f(w_{iso} = \frac{1}{2})$. It can be easily seen that the *first-order* phase transition is possible only if $g < \ln 12$. Thus the condition on the transition is as follows

$$\left\{ \begin{array}{l} f(w = \bar{w}) = f(w = w_{iso}) \\ 0 < \bar{w} < \frac{1}{2} \end{array} \right. \tag{14}$$

where

$$\bar{w} = \max\left\{\tau^2;\ w_{min} = \frac{-3 + \sqrt{9 + 4(N\tau)^2\rho(g - \ln 12)}}{2N\rho(g - \ln 12)}\right\}. \tag{15}$$

The *second-order* transition appears for $g > \ln 12$ as well as for $g < \ln 12$ when the point of the free energy minimum reaches the upper boundary of the interval $\left[\tau^2, \frac{1}{2}\right]$. The transition point in this case is determined by the equation

$$w_{min} = \frac{1}{2} \tag{16}$$

which has the obvious solution

$$\tau = \frac{1}{2}\sqrt{\frac{6}{N} + \rho(g - \ln 12)}. \tag{17}$$

The complete phase diagram in the coordinates (τ, g) is presented in Fig.3, where the border of the transition from the disordered phase to the ordered one is drawn for the particular choice of the the parameres: $\{\rho = 0.03;\ N = 1000\}$. It can be seen that this border consists of two curves corresponding to the first-order transition ($g < \ln 12$) and the second-order one shown by solid and brocken lines respectively. In between of the first-order and second-order transition curves there is an instability ("hysteresis") region. The shape of the transition curves in not very sensitive to the changing of the parameters ρ and N exept the fact that the hysteresis region is extended to the value $\tau_0 = \sqrt{\frac{3}{2N}}$ and is very small for large N.

[2] Actually the values of the order parameter w greater than $1/2$ correspond to the ordering in the layers normal to z-axis, but in the framework of the model we discuss the transition between two phases only-ordered (nematic-like) and disordred ones.

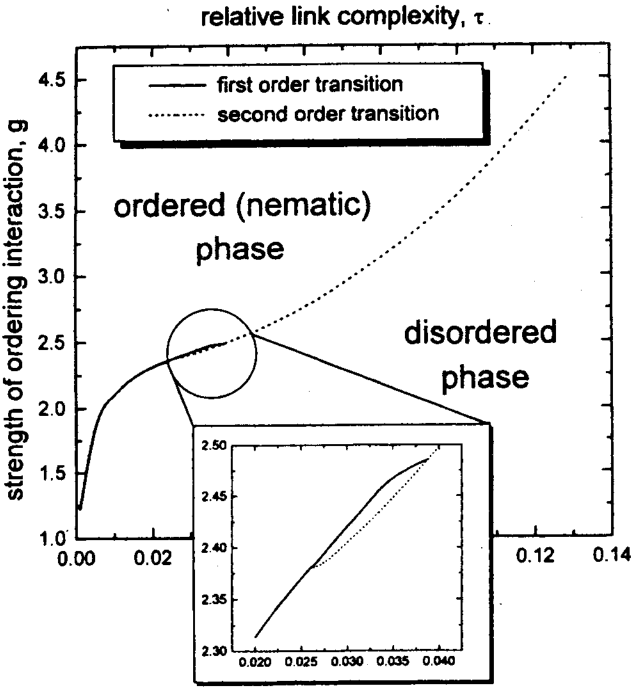

Fig.3. The phase separation diagram

Let us summarize briefly the main findings of the present work.

- We develop the ideas expressedim [8] and use the highest power of the Jones invariant as a quantitative characteristic of the "link complexity", η, for the system of entangled directed N-step random walks (braid). On the basis of conjectured relation between η and the length of the primitive path, μ, for the N-step random walk in the effective lattice of obstacles we estimate the entropy of the braid for the given topological state.
- We construct the simple mean-field theory of the ordering transition in the system of entangled directed random walks in the broad interval of the values of the "link complexity" and show that the order of the phase transition is different for "weakly" and "strongly" entangled chains.

The ideas expressed here could be developed in the following directions.

– To prove rigorously the fact that the distribution function $\mathcal{P}(\eta, N)$ of the highest power, η, of the Jones invariant for the randomly generated braid of length N has the limit behavior

$$\mathcal{P}(\eta, N) \propto \frac{1}{N^{3/2}} \exp\left\{-\frac{(\eta-\gamma_1 N)^2}{\gamma_2 N}\right\},$$

where γ_1 and γ_2 are the numerical constants depending on the details of the model. (The paper [15] devoted to related problem is in prepartion now).

– To take into account in the framework of the theory proposed above the possibility to reach the equilibrium density of the chain segments considering ρ (Eq.(12)) as an additional variational parameter of the free energy.

– To investigate the influence of topological constraints on the smectic-type ordering in the layers parallel to the (x, y)-plane.

– To extend the proposed theory beyond the mean-field approximation for investigating the influence of the global topological constraints on the local correlation functions of the chain segments.

I am very grateful to Y. Rabin for his kind hospitality and creating of a nice atmosphere during my staying at Bar-Ilan University in May 1994, when this work was started; also I highly appreciate helpful critical comments of A. Grosberg. I would like to thank the International Science Foundation for the financial support (Grant No. M5R000).

---

1. A.R.Khokhlov and A.N.Semenov, Physica, **108-A** 546 (1981); **112-A** 605 (1982).
2. J.V.Seilinger and R.F.Bruinsma, Phys. Rev. (A)**43**, 2910, 2922 (1991).
3. M. Doi and S.F.Edwards, *Theory of Polymer Dynamics*, Academic Press, N.Y., 1986.
4. R.MacKenzie and F.Wilczek, Int. J. Mod. Phys. (A)**3**, 2827 (1988); C.Lai and C.Ting, Nucl. Phys. (B)**396**, 429 (1993).
5. E.Fradkin, *Field Theory of Condenced Matter Systems*, World. Sci., Singapore, 1990.
6. V.F.R.Jones, Bull. Am. Math. Soc. **12** 103 (1985).
7. L.Kauffman, *Braid Group, Knot Theory and Statistical Mechanics*, World Sci., Singapore, 1989.
8. A.Grosberg and S.Nechaev, Europhys. Lett. **20**, 613 (1992).
9. S.Nechaev and A.Vershik, J. Phys.(A): Math. Gen. **27** 2289 (1994).
10. P. de Gennes, *Scaling Concepts in Polymer Physics*, Cornell Univ. Press, Ithaka, N.Y., 1979.
11. H.Fürstenberg, Trans. Am. Math. Soc., **198** 377 (1963); V.N.Tutubalin, Prob. Theory and Appl. **10**, 15 (1965) (in Russian).
12. W.B.R.Lickorish, Bull. London Math. Soc., **20**, 558 (1988).
13. L.Koralov, S.Nechaev, and Ya.Sinai, Prob. Theor. and Appl. **38** (1993) (in Russian); Chaos **1**, 131 (1991).
14. E.Helfand and D.S.Pearson, J. Chem. Phys. **79**, 2054 (1983); M.Rubinstein and E.Helfand, J. Chem. Phys. **82**, (1985); A.Khokhlov and S.Nechaev, Phys. Lett. (A)**112**, 156 (1985).
15. S.Nechaev, A.Vershik, and A.Grosberg, Comm. Math. Phys., to be submitted.