Nematic phase transition in entangled directed polymers

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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 by Grosberg and Nechaev [Europhys. Lett. **20**, 613 (1992)], 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 interaction constant. The order of the phase transition is shown to be different for "weakly" and "strongly" entangled chains. © *1994 American Institute of Physics.*

The liquid-crystalline-type phase transitions in the systems of long chain molecules have been studied extensively (for review see, for example, Refs. 1 and 2). 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, all the existing theories ignore, to the best of our knowledge, the effects caused by entanglements between the chains in such systems.

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

We stress, at the outset, that we do not claim to find a new kind of phase transitions or to describe a new class of real physical systems. We pursue two main goals only:

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

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

1. The model. Consider an 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. Let us assume that they move randomly in the plane (x,y) under two conditions: a) the trajectories of the particles being projected onto the plane do not escape a circle of diameter D; b) at the time slice $j=N$ all particles return to their starting points. Assuming that this phase trajectories of the particles in the space-time are nonphantom, we obtain a system of directed, entangled, random walks

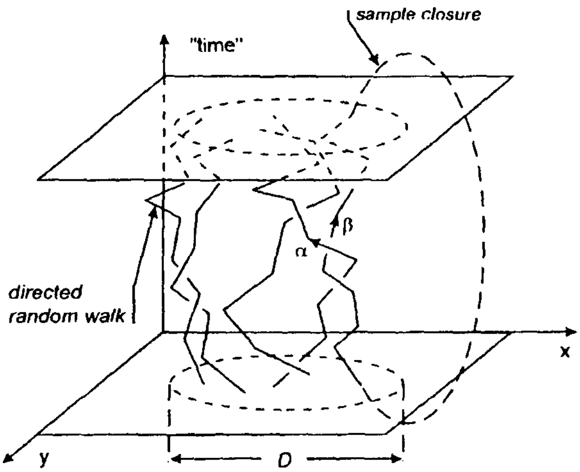

FIG. 1. Braided system of entangled, directed, random walks.

confined in a cylinder with the dimensions of order $D \times D \times N$; see Fig. 1. If we make now a closure 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 can be introduced 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. It is required 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 $\varphi(|...|)$ 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:

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

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

Assume now that the topology of a braid of M directed polymers is quenched in an arbitrary given state, which does not change in the 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 assumptions. Let us start with the case in which the chains in the braid are strongly entangled. In this case one can see that some chains wind around other chains, making it therefore impossible a parallel displacement of the neighboring segments. On the other hand, the attraction energy [Eqs. (1a) and (1b)] 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. The corresponding phase diagram in the coordinates "link complexity" versus g [strength of interaction in Eq. (1a)] is analyzed in Sec. 3.

2. Link complexity and entropy of entangled paths. The problem of describing the entanglements in the system of nonphantom, directed, random walks has a long history traceable to polymers[3] and anions.[4] The substantial progress in this field is connected with the recent studies[4,5] where the Chern–Simons path-integral formalism has been applied in the study of the superconductivity and the quantum Hall effect. Nevertheless, the following problem remains: How does one introduce the rough quantitative characteristics of the complexity of entanglements in the system which correctly reproduces the non-Abelian properties of the linked chains. We describe here the evident way of constructing 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. Because of the presence of topological constraints, the entire phase volume Ω splits into disconnected domains, $\omega\{\Gamma\}$ and $(\omega \in \Omega)$, of homotopically equivalent paths characterized by the topological invariant, Γ. The entropy of the given topological state of the system can formally be written as follows:

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

To be more definite, we use for Γ the polynomial invariant introduced by Jones,[6] $V(t)$, where t is the usual "spectral parameter." We recall that the 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 the chain segments only). The main condition on $V(t)$ is that this function should be invariant under Reidemeister moves (see Ref. 7 for details).

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

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

It is noteworthy that instead of the Jones polynomial we could take the 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 a cruder characteristic than the complete algebraic polynomial is not a disadvantage, but an advantage if we are dealing with the statistical models. Actually, the same value of η characterizes a narrow

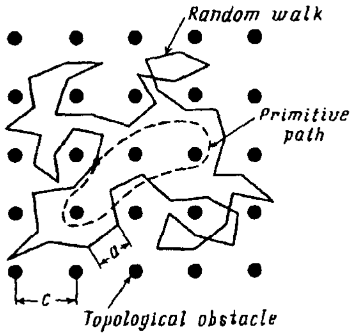

FIG. 2. Closed trajectory of the random walk in the lattice of obstacles (solid line) and its topological invariant—the primitive path (dashed line).

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, and $\eta\sim N$ matches the system of "strongly entangled" paths. The later case has been discussed in detail in Ref. 8;
- There is a direct relation between the knot complexity η and the length of the "primitive path" μ of a test chain in the 2D lattice of obstacles (for a more simplified model this relation was explained in Ref. 9). The "primitive path" of a closed trajectory in a plane entangled with an array of removed points (obstacles) is defined as the shortest, uncontractible path (shown in Fig. 2 by the dashed line) which remains after deleting all "double-folded" parts of the trajectory. The primitive path is a well-known topological invariant which is widely used for describing entanglements in statics and dynamics of polymer systems (see 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 fixed ends and without ordering interactions, confined in a circle of diameter D on the projection (see Sec. 2 and Fig. 1 for details). Define the average value of the knot complexity, $\langle\eta\rangle$

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

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

2. Consider the closed random walk (with self-intersections) of length L in the plane in the lattice of topological obstacles with an average spacing $c\simeq D/\sqrt{M}$ and define the average value of the primitive path, $\langle\mu\rangle$

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

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

There exists a nonrandom "time-independent" limit

$$\lim_{N\to\infty} \frac{\langle \eta(N,M,D,a)\rangle}{\langle \mu(N,M,D,a)\rangle} = \text{const } (M,D,a). \tag{6}$$

The complete, mathematically rigorous proof of this statement is still not known, but the relation shown above clearly physically follows from the Fürstenberg theorem.[11] This theorem establishes the limiting 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]

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

where $\hat{W}_j(\ldots)$ are the "braiding" operators; they are random on each time slice j and obey the Yang–Baxter algebra. The quantity $\ln|V(t|\ldots)|$ is therefore proportional to the highest exponent of the Jones polynomial and to the Lyapunov exponent of the operator product in (7). On 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 Refs. 9 and 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 equation.[13,14]

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

where the numerical coefficients correspond to the square lattice of obstacles, and $a_\parallel$ is the length of the segment projection onto 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 is

$$F_{\text{el}}(\eta,N,M,D,a_\perp) = -M \ln Z\left(\mu\equiv\eta,N,a_\perp,c=\frac{D}{\sqrt{M}}\right) \simeq -\frac{Na_\perp^2 M^2}{D^2}\ln(2\sqrt{3})$$
$$-\frac{\eta M^{3/2}}{2D}\ln 3 + \frac{M\nu^2}{2Na_\perp^2} - M\ln\left(\frac{\eta D^2}{(Na_\perp^2)^{3/2}M}\right) + \text{const}, \tag{9}$$

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 a 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. Assume that, on the average, all segments form the same angle θ with respect to the z axis, i.e.,

$$\langle\cos(\mathbf{n}_\alpha\mathbf{n}_\beta)\rangle=\tfrac{1}{2}\cos^2\theta\{\alpha,\beta\}\in[1,M]. \tag{10}$$

We thus have $a_\perp=a\sin\theta$.

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

$$F(\theta)=-\frac{Na^2M^2\ln(2\sqrt{3})}{D^2}\sin^2\theta-\frac{\eta M^{3/2}\ln 3}{2D}+\frac{M\eta^2}{2Na^2}$$
$$\times\sin^{-2}\theta-M\ln\left(\frac{\eta D^2}{(Na^2)^{3/2}M}\sin^{-3}\theta\right)-\frac{gNa^2M^2}{2D^2}\cos^2\theta+\text{const}, \tag{11}$$

where $\sin^2\theta=w$ is the variational parameter which changes 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 which assumes the density to be constant.

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

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

The normalized free energy $f(\omega)$ can now be written as follows:

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

where

$$\tau^2\leqslant w\leqslant 1,$$

and the function $C(\rho,\tau,N)=-\rho^{1/2}\tau\ln 3+2/N\ln\rho$ 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 $\psi(\theta)=1/2\pi$. Thus, $w_{\text{iso}}=\int w(\theta)\psi(\theta)d\theta=\frac{1}{2}$. Let us assume that

—for $w<\frac{1}{2}$ the chains are in the ordered (nematic-like) phase;

—for $w\geqslant\frac{1}{2}$ the chains are in the disordered[2)] phase.

The phase transition curve is determined by comparing the minimal value of the free energy, $f(\bar{w})$, on the interval $\tau^2 \leqslant \bar{w} < w_{\rm iso}$ to the value $f(w_{\rm iso}=\frac{1}{2})$. It can be easily seen that the *first-order* phase transition is possible only if $g < \ln 12$. Thus the condition for the transition is

$$\begin{cases} f(w=\bar{w}) = f(w=w_{\rm iso}) \\ \quad 0 < \bar{w} < \frac{1}{2} \end{cases}, \tag{14}$$

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 $[\tau^2, \frac{1}{2}]$. 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 shown in Fig. 3, where the border of the transition from the disordered phase to the ordered phase is drawn for the particular choice of the parameters: $\{\rho = 0.03;\ N = 1000\}$. We see that this border consists of two curves corresponding to the first-order transition ($g < \ln 12$) and the second-order transition shown by solid and broken lines, respectively. Between 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, although the hysteresis region is extended to the value $\tau_0 = \sqrt{3/2N}$, and is very small for large N.

Let us summarize briefly the main results of our study.

- We develop the ideas expressed in Ref. 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 the assumed relationship 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 a simple mean-field theory of the ordering transition in a system of entangled, directed, random walks in a broad interval of 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.

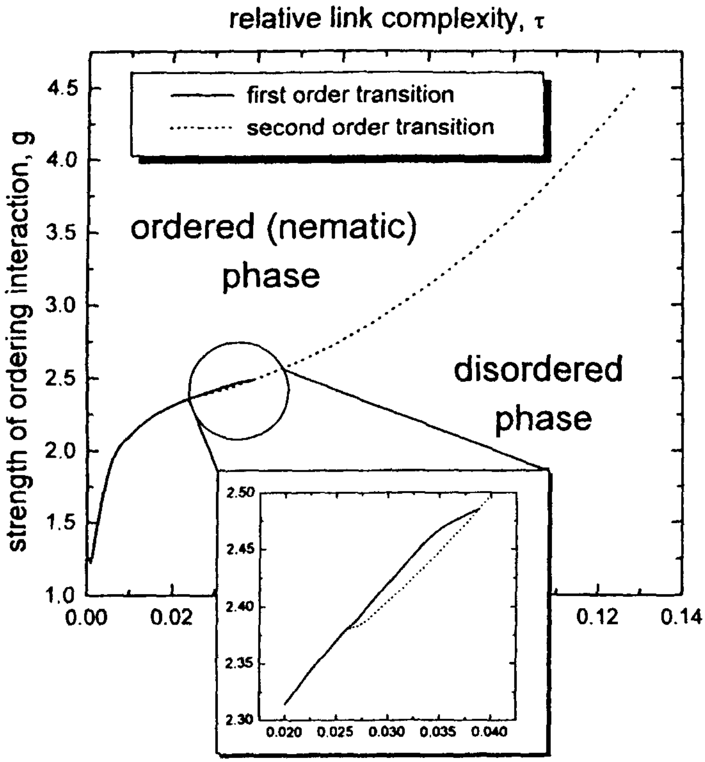

FIG. 3. The phase separation diagram.

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

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

where γ_1 and γ_2 are the numerical constants which depend on the particular features of the model. (The paper[15] devoted to a related problem is in preparation now.)

—To take into account in the framework of the theory proposed above the possibility of reaching 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.

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[1)]The nonphantom nature of the random walk implies the existence of topological constraints caused by the lattice of obstacles only. The volume interactions are ignored.

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

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