

Analogy between a rigid-chain polymer and a magnetic material

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A field-theory description is offered for polymer chains of arbitrary rigidity subjected to an arbitrary extension.

The modern theory of strongly fluctuating polymer systems is based on an analogy between a flexible-chain polymer and an n -component magnetic material in the limit $n \rightarrow 0$.^{1,2} This analogy does not, on the other hand, make it possible to describe numerous effects associated with the rigidity of polymer chains. Among these effects are the behavior of polymers subjected to large deformations and the liquid-crystal and "glassy" ordering of the chains at low temperatures.

In this letter we propose a generalization of the polymer-(magnetic material) analogy to describe a system of rigid polymer chains. The microscopic state of such chains is described by the set of quantities $\mathbf{x}(s) = [\mathbf{r}(s), \mathbf{u}(s)]$, where $\mathbf{r}(s)$ is the coordinate of the s th monomer unit, and $\mathbf{u}(s)$ is a unit vector directed along the chain. The rigidity of a polymer chain is characterized by a persistence length l , over which the memory of the direction of the chain is lost.^{3,4}

We first consider the case of a single, noninteracting chain consisting of N units of size a . This chain is characterized⁵ by a distribution function $G(\mathbf{x}, \mathbf{x}'; N0)$ of the quantities $\mathbf{x} = \mathbf{x}(N)$ and $\mathbf{x}' = \mathbf{x}(0)$ for the end units. As in the case of flexible chains,⁵ it is convenient to introduce a generating function

$$G(\mathbf{x}, \mathbf{x}'; \tau) = \int_0^\infty dN e^{-\tau N} G(\mathbf{x}, \mathbf{x}'; N0), \quad (1)$$

which can be written as a correlation function of random Gaussian fields $\bar{\psi}(\mathbf{x})$ and $\bar{\psi}(\mathbf{x})$:

$$G(\mathbf{x}, \mathbf{x}'; \tau) = Z^{-1} \int D\bar{\psi} D\psi \bar{\psi}(\mathbf{x}) \psi(\mathbf{x}') \exp[-S_0\{\bar{\psi}, \psi\}], \quad (2)$$

$$Z = \int D\bar{\psi} D\psi \exp[-S_0\{\bar{\psi}, \psi\}].$$

The effective action S_0 is

$$S_0\{\bar{\psi}, \psi\} = \int d\mathbf{x} \left[\alpha \bar{\psi}(\mathbf{x}) \left(\mathbf{u} \frac{\partial}{\partial \mathbf{r}} \right) \psi(\mathbf{x}) + \tau \bar{\psi}(\mathbf{x}) \psi(\mathbf{x}) \right] - \int d\mathbf{r} d\mathbf{u} d\mathbf{u}' t \bar{\psi}(\mathbf{r}, \mathbf{u}) \psi(\mathbf{r}, \mathbf{u}'). \quad (3)$$

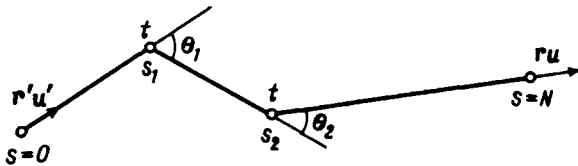


FIG. 1. Trajectory of motion corresponding to the multiple-scattering processes described by effective action (3). Shown here is the second order of a perturbation theory in the parameter t . The total time of the motion, N , which is equal to the sum of the times $s_{i+1} - s_i$, of the motion along the rectilinear parts of the trajectory, does not depend on the shape of the trajectory. In other words, it does not depend on the order of the perturbation theory, on the choice of times s_i , or on the choice of scattering angles θ_i . The corresponding polymer chain is strongly non-Gaussian. Its length along the chain, $L = aN$, is fixed and does not depend on the conformations assumed by the chain. In the case of an isotropic scattering amplitude, $t(\mathbf{u} \cdot \mathbf{u}') = \text{const}$, such a chain is equivalent to a wormlike model with an isotropic flexibility.^{4,5}

The integration over \mathbf{x} means an integration over the coordinates \mathbf{r} and the direction of the unit vector \mathbf{u} . The field $\tilde{\psi}$ is related to the field ψ by a change in the direction of the "motion" of $\mathbf{r}(s)$ in "time" along the chain: $\tilde{\psi}(\mathbf{r}, \mathbf{u}) = \psi(\mathbf{r}, -\mathbf{u})$. The basic distinction between (3) and the effective action of flexible-chain polymers is the presence of a term which is linear (rather than quadratic¹) in the gradients. This term describes a rectilinear motion $d\mathbf{r}(s) = a\mathbf{u}ds$ over distances small in comparison with \tilde{l} . The matrix element t describes scattering through angles $\theta = \arccos(\mathbf{u} \cdot \mathbf{u}')$, which form a diffusion regime of motion at length scales large in comparison with l (Fig. 1).

Evaluating Gaussian integrals (2), and taking inverse Laplace transforms of (1), we easily find the distribution function G for a chain of a given length $L = aN$. We use this function to find the average value of the cosine of the angle between the end sections of the chain:

$$\langle \mathbf{u}\mathbf{u}' \rangle \equiv \int d\mathbf{x}d\mathbf{x}' \mathbf{u}\mathbf{u}' G(\mathbf{x}, \mathbf{x}'; N0) / \int d\mathbf{x}d\mathbf{x}' G(\mathbf{x}, \mathbf{x}'; N0) = e^{-L/\tilde{l}}. \quad (4)$$

According to (4), the quantity $l \equiv a/t$ is the persistence length of the chain. For the rms distance between the ends of the chain, R , we find the simple expression

$$R^2 \equiv \langle (\mathbf{r} - \mathbf{r}')^2 \rangle = 2\tilde{l}^2 (L/\tilde{l} - 1 + e^{-L/\tilde{l}}). \quad (5)$$

The length $l \equiv R^2/L$ (under the condition $L \gg \tilde{l}$) of a Kunovski segment⁴ is equal in order of magnitude to the persistence length ($l = 2\tilde{l}$). The formalism which we have suggested, (2), (3), thus eliminates a disadvantage of the $\{\mathbf{r}(s)\}$ path-integration method,^{5,6} in which the relation $l = a$ holds even when the rigidity of the polymer chain is taken into account. This distinction arises from the non-Gaussian statistics of our chain. In particular, the distribution function G vanishes at length scales R large in comparison with the size ($L = aN$) of a completely extended chain.

The correlations in the relative orientation of neighboring links in real polymers can be taken into account by specifying the functional dependence $t = t(\mathbf{u} \cdot \mathbf{u}')$. In the case of a slow variation of the function $\psi(\mathbf{r}, \mathbf{u})$, we can easily reproduce known ex-

pressions⁴ for both the conformational and orientational entropies of the chain by expanding this function in the gradients of the variables \mathbf{r} and \mathbf{u} .

In rigid-chain polymers, the interaction of chain segments depends on their relative orientation and is described by the function $w(\mathbf{u} \cdot \mathbf{u}') = w_0 + w_1 |\sin \theta|$. To take this interaction into account, we introduce random Gaussian fields $\varphi(\mathbf{x})$ with the correlation functions

$$\langle \varphi(\mathbf{x}) \rangle = 0, \quad \langle \varphi(\mathbf{x}) \varphi(\mathbf{x}') \rangle = w(\mathbf{u} \cdot \mathbf{u}') \delta(\mathbf{r} - \mathbf{r}'). \quad (6)$$

The generating function of a noninteracting chain, $G_0\{\varphi\}$, in an external field $i\varphi$ is given by expressions (2) and (3) with the replacement $\tau \rightarrow \tau + i\varphi$. The exact function G is found by averaging $G_0\{\varphi\}$ over the fluctuating φ field in (6). Writing the denominator in (2) in the form Z^{n-1} , and letting $n \rightarrow 0$, we find, by averaging, the effective action of the interacting chain:

$$S\{\bar{\psi}, \psi\} = \sum_{\alpha=1}^n S_0\{\bar{\psi}_\alpha, \psi_\alpha\} + S_{int}\{\bar{\psi}, \psi\},$$

$$S_{int} = \frac{1}{2} \int d\mathbf{r} d\mathbf{u} d\mathbf{u}' w(\mathbf{u} \cdot \mathbf{u}') \sum_{\alpha, \beta=1}^n \bar{\psi}_\alpha(\mathbf{r}, \mathbf{u}) \bar{\psi}_\beta(\mathbf{r}, \mathbf{u}') \psi_\alpha(\mathbf{r}, \mathbf{u}) \psi_\beta(\mathbf{r}, \mathbf{u}'). \quad (7)$$

For a finite concentration of chains, this action also contains terms which are linear in the fields $\bar{\psi}_1$ and $\bar{\psi}_1$.^{2,3}

In summary, we have proposed a simple field-theory formalism for describing polymer chains of arbitrary rigidity. This formalism yields a rigorous microscopic description of the orientational order in polymers. In this formalism, equilibrium block copolymers consisting of units of different types can be described in the standard way.⁷ Cross-linking, which leads to structures of the polymer-network type, has been taken into account. Finally, the existence of a field-theory formulation makes it possible to take a general approach⁸ to describe rigid-chain polymers with a fixed and otherwise arbitrary chemical structure.

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