Orientational Ordering of Grafted Nonmobile Rod Polymers

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SYNOPSIS

We studied the orientational ordering of grafted rod polymers on the surface. The rod polymers were nonmobile and allowed to have two configurations: either lying down on the surface or standing up. The only interaction between the rods were hard core interaction. We computed the orientational order parameter using the recently developed random local field theory. We found that the order parameter increased monotonically as a function of the concentration of the rods and, thus, there existed no pancake-brush transition. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

Polymers attached by one end to a substrate are a system of practical interest. However, most researches on this subject have been devoted to flexible polymers that exhibits so-called "pancake-to-brush transition."[1,2] For flexible polymers, due to the so-called equal time constraint, the potential energy under which each polymer moves can be shown to be parabolic,[3-5] which greatly simplifies the problem in studies of the phase transitions of flexible and nonmobile grafted polymers both in low-[6] and high-surface coverage.[7] However, less attention has been paid to rigid grafted rod polymers, while the orientational ordering of such grafted rods is of practical interest due to its relevance to the alignment of liquid crystals on solid–liquid interface. In such case, equal time constrain does not apply, and one might utilize a mean field-type approach. Halperin et al.[8] studied the orientational ordering of grafted but mobile rods using the Onsager theory[9] for isotropic–nematic phase transition in liquid crystal. The main conclusion of ref. 8 was that there are peculiarities in the concentrational dependence of the order parameter, signaling the existence of the orientational phase transition. However, taking into account the symmetry consideration, the authors of refs. 10 and 11 reached a different conclusion, showing that there is no peculiarities in the order parameter.

We recognize that the main restriction of the Onsager theory is that it can be applied only to the case of mobile polymers because it involves the integration of the partition function over space variables.

In this article, we consider an opposite case in which the grafting points are fixed, i.e., the grafted end cannot move on the surface. Such a case might be more relevant than mobile cases in designing commercial screens for TV and watches. In order to calculate the orientational order parameter, we use the random local field theory that has been developed recently by one of us[12,13] for order–disorder phase transitions in random systems. In contrast to the Onsager theory and standard mean field theory, this approach allows one to consider configurational fluctuations in the case of nonmobile quenched particles. The main difference of collective ordering of grafted rods from usual isotropic–nematic phase transition in random systems is that in the case of grafted rods there exist an *anisotropy* of the excluded volume interaction parameter for rods parallel or perpendicular to the surface. As we show below, due to such an anisotropy, the orientational order parameter is not equal to zero at any small concentration of rods. It means that for grafted as well as mobile rods, the isotrophic–hematic phase does not exist.

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We considered a model of two dimensional rods in the x-z reference frame. We considered every rod as a rectangle with long axis "a" and short axis "b." Following Zwanzig,[14] we described the direction of the rod by a unit vector l_i that can be oriented only along x or z direction. In such a model, a real flat surface is represented by a one-dimensional line in the x direction, and

$$l_{ix}^2 = 0, 1; \quad l_{iz}^2 = 0, 1; \quad l_{ix}^2 + l_{iz}^2 = 1. \tag{1}$$

The grafted end of the rod randomly occupies any point on the surface. But due to excluded volume interactions, there exists a strong repulsion between adjacent rods i and j separated by the distance $x_{ij} < a$ if l_i and $l_j \parallel x$, and by $x_{ij} < (a + b)/2$ if $l_i \parallel z$, $l_j \parallel x$ (see Fig. 1).

A model Hamiltonian that represents the above physics picture has a form:

$$H = \sum_{ij} [K_{ij}^x l_{ix}^2 l_{jx}^2 + K_{ij}^z (1 - l_{iz}^2 l_{jz}^2)], \tag{2}$$

It follows from Figure 1 that in a reasonable approximation we can represent the interaction energy constants K_{ij}^x and K_{ij}^z in the form

$$K_{ij}^z = K\xi^z(x_{ij}); \quad K_{ij}^x = K\xi^x x_{ij}, \tag{3}$$

$$\xi^z(x_{ij}) = 1, \quad |x_{ij}| < (a + b)/2, \tag{4a}$$

$$\xi^z(x_{ij}) = 0, \quad |x_{ij}| < (a + b)/2, \tag{4b}$$

$$\xi^x(x_{ij}) = 1, \quad |x_{ij}| < a, \tag{5a}$$

$$\xi^x(x_{ij}) = 0, \quad |x_{ij}| > a, \tag{5b}$$

Due to anisotropy of the interaction potential, the physics of ordering of a grafted rod is quite different from that for isotropic nematic phase transition in liquid crystals without surface interaction. The most important result of the anisotropy is the absence of an orientational phase transition. It means that orientational order parameter S does not equal to zero at any concentration. The physical exploration of this phenomena can be given as follows.

In the two dimensional case considered here, orientational order parameter S is equal to

$$S = \langle \overline{S_i} \rangle = \overline{\langle l_{iz}^2 - l_{ix}^2 \rangle}, \tag{6}$$

where $\langle \cdots \rangle$ denotes thermal average and the overbar denotes average over the random positions of rods on x axis. According to (6), S_i is either $+1$ or -1 and can be considered as a pseudospin variable. Substituting S_i into Hamiltonian (2) and taking into account that $l_{ix}^2 = (1 - S_i)/2$, $l_{iz}^2 = (1 + S_i)/2$, we have:

$$H = \frac{1}{4} \sum_{ij} [S_i S_j (K_{ij}^x - K_{ij}^z) - 2S_i (K_{ij}^z + K_{ij}^x)], \tag{7}$$

where we have neglected a constant term that does not depend on S_{iz}. We also have taken into account the fact that $\sum_{ij} S_j K_{ij} = \sum_{ij} S_i K_{ij}$. Hamiltonian (7) represents a model of Ising spins interacting with additional "static" random field $h_i^s = \frac{1}{4} \sum_j (K_{ij}^z + K_{ij}^x)$, which is independent on spin variables but increases with the rods' concentration.

The mere existence of such a static field gives a nonzero value of orientational order parameter at any concentration of rod particles. This conclusion is the consequence of the symmetry of the system and is in no way affected by the approximations employed here. For usual isotropic nematic phase transitions in the absence of surface interaction we have $K_{ij}^x = -K_{ij}^z$, which gives $h_i^s = 0$ and reduces to eq. (1). In order to calculate the concentration dependence of the order parameter S, we apply the random local field theory that has been developed earlier[12,13] for concentrational phase transition in random systems. The idea of random molecular field theory is the following.

According to (7), we can introduce random local field h_i acting on particle i:

$$H = -\sum_i S_i h_i, \tag{8}$$

where

$$h_i = \frac{1}{4} \sum_j [(K_{ij}^z - K_{ij}^x) S_j + 2(K_{ij}^x + K_{ij}^z)], \tag{9}$$

At given spatial configurations of the particles we can use the identity,[15]

$$\langle S_i \rangle = \langle \tan h(h_i/T) \rangle, \tag{10}$$

Taking from (10) configurational average we have:

$$S = \int dh \tan h(h/T) f(h, S), \tag{11}$$

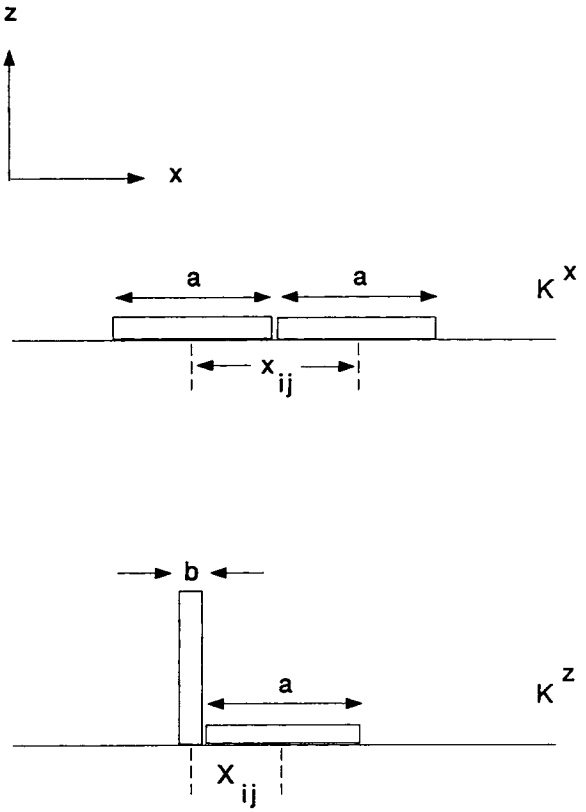

Figure 1 The grafted end of the rod randomly occupies any point on the surface, but due to excluded volume interaction, there exists a strong repulsion between adjacent rods.

where

$$f(h, S) = \overline{\langle \delta(h - h_i) \rangle} \tag{12}$$

is a distribution function of random local field acting on every rod from its neighbors. Equation (11) represents the self-consistent equation for the orientational order parameter S. This equation is exact as long as we don't make approximation to calculate $f(h,S)$. We now make here the simplest approximation neglecting the correlation between values S_i, S_j for different particles, when calculating $f(h, S)$. Using integral representation of the delta function, and neglecting effect of correlations we rewrite (12) in the form:

$$f(h, S) = \frac{1}{2\pi} \int_{-\infty}^{\infty} dh e^{i\rho h} e^{-F(\rho)}, \tag{13}$$

where in the thermodynamic limit $N \to \infty, L \to \infty$, $n = N/L$ = constant (n is the linear rods concentration) $F(\rho)$ is equal to

$$\begin{aligned} F(\rho) &= \ln \overline{\langle e^{i\rho \frac{1}{4}[(K_{ij}^z - K_{ij}^x)S_j + 2(K_{ij}^x + K_{ij}^z)]} \rangle}^N \\ &= \frac{c}{2}[\epsilon(1 + S) + (1 - S)](1 - e^{iK\rho/2}) \\ &= F_1(\rho) + IF_2(\rho), \end{aligned} \tag{14}$$

where

$$c = na, \quad \epsilon = (a + b)/2a, \tag{15}$$

Using the identity

$$\begin{aligned} \int_{\infty}^{\infty} dh e^{i\rho h} \tan h(h/T) \\ = i[(\pi\rho T)/(\sin h(\pi\rho T/2))], \end{aligned} \tag{16}$$

we can rewrite the equation for order parameter in the form:

$$S = T \int_0^{\infty} d\rho \frac{e^{-F_1(\rho)} \sin(F_2(\rho))}{\sin h(\rho\rho T/2)} \tag{17}$$

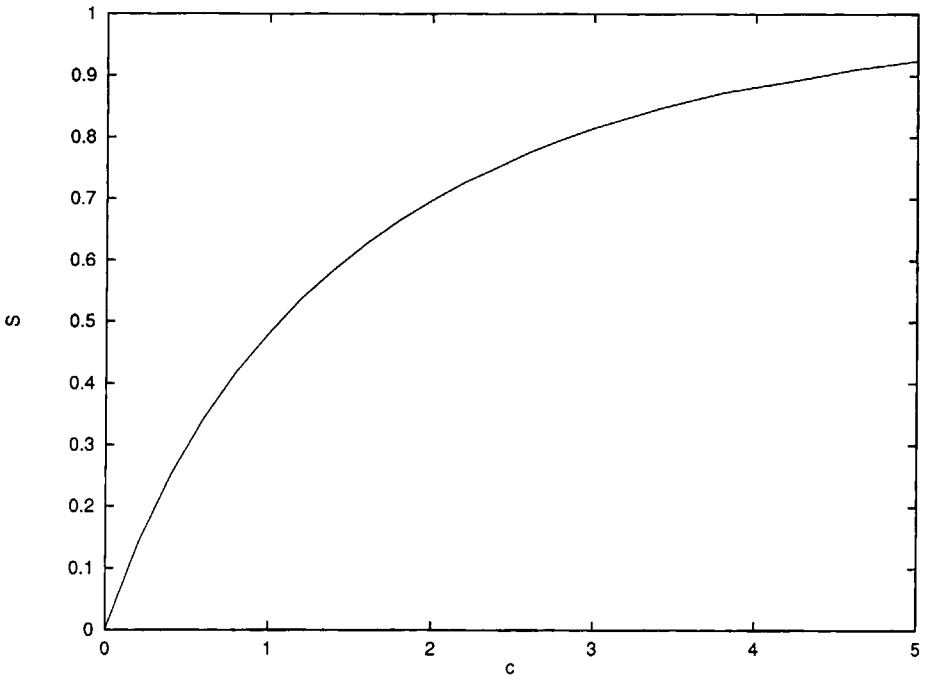

Figure 2 Order parameter S as a function of concentration $c = na$ for $a \gg b$.

In the limit of completely rigid rods that cannot penetrate each others we should take in (17) a limit $K \to \infty$ that makes our system athermal. We obtain the following self-consistent equation:

$$S = \frac{2}{\rho}\int_0^{\infty} \frac{dx}{x} e^{c/2(1-\cos x/2)[\epsilon(1+s)+(1-s)]} \times \sin\frac{c}{2}[\epsilon(1+S)+1-S)]\sin\left(\frac{x}{2}\right), \quad (18)$$

The numerical solution of this equation is displayed in Figure 2, where we assumed $b \ll a$ and put $\epsilon = 1/2$. We see that S is monotonically increasing with increasing the rod concentration without exhibiting any discontinuity. Hence, we conclude there exists no pancake-brush transition, if only one end of the rod interacts with the surface. One might, however, expect a different situation if there is an attractive interaction between a surface and free end of the rod. The detailed investigation of this question will be given elsewhere.

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