Competing Interactions among Supramolecular Structures on Surfaces

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The design of noncentrosymmetric structures using copolymers has been a subject of great recent interest.[1,2] Noncentrosymmetric bulk copolymer structures have been analyzed using mean field continuous models.[3,4] In this communication we determine the conditions for obtaining noncentrosymmetric structures, and how to tune the net macroscopic polarizibility by solving a lattice model exactly. The model describes the self-organization of nanoaggregates of rodcoil molecules into polar films.[1,5,6] An important property of these nanoaggregates is their organization into macroscopic polar materials when cast from solution and annealed without the involvement of an external electric field. Transmission electron micrographs of film cross sections and X-ray scattering experiments reveal the formation of layered domains with a head-to-tail polar arrangement.[5] Interestingly, the measured macroscopic polarization of these films is much less than one would expect for a monodomain of oriented nanoaggregates.[6] One possible explanation for the relatively small macroscopic polarity is cancellation among domains in the bulk of the film. In this communication we explore the possibility of a nonrandomly oriented microstructure by finding the ground state of a simple model. The model is constructed to account for the competing interactions among nanoaggregates. The noncentrosymmetric structure of the nanoaggregates suggests they have a net dipole moment, and this leads to dipolar interactions among them. On the other hand, the enthalpic and entropic factors associated with contacts between coil and rod portions of neighboring aggregates suggests Ising-like nearest neighbor interactions.

In our model the nanoaggregates are represented by dipoles of constant strength D on a cubic lattice of size a. While it is possible to consider very general models in which dipoles are free to orient in any direction, based on experiments the system we are interested in modeling contains dipoles than can be aligned either parallel or antiparallel to the z axis, perpendicular to the $x-y$ substrate plane. Also, even though we included a penalty for reversing the orientation of a dipole with respect to its neighbors by means of an Ising coupling of strength J, there should be other steric forces associated with the shape and size of the nanoaggregates which are not considered here explicitly. These forces could maintain the dipoles oriented along a given axis. The ground states of the dipole ($J = 0$) and of the Ising ($D = 0$) interactions along the $z-x$ plane are shown in Figure 1, parts a and b, respectively. The ground state when $J = 0$ is antiferromagnetic along x and y (columns along z), and when $D = 0$ is a homogeneous state with all dipoles pointing in the same direction (monodomain). With nonzero values of D and J, an intermediate stripe state of periodicity λ is possible in which dipoles have the same orientation within equal size domains ($\lambda_\uparrow = \lambda_\downarrow = \lambda/2$) along the x or y axis and contiguous domains have antiparallel orientations (see Figure 1c). This stripe structure has been obtained previously in 2d magnetic systems[7] and in lipid monolayers.[8,9] We extended the model to finite thickness films.[10] In infinite thickness films, we found a first-order transition from a monodomain ($\lambda/a = \infty$) to antiparallel domains with extremely small domain sizes ($\lambda/a \leq 4$) as D/J increases. However, in films of finite thickness, the domain periodicity λ was found to decrease continuously as D/J increases. We add here a short-range interaction between the dipoles and the surface and show that in this case the dipole up ($\lambda_\uparrow$) and dipole down ($\lambda_\downarrow$) domains no longer have equal widths as shown in Figure 1c, leading to net macroscopic polarization. We find that λ and the macroscopic polarization can be modulated by varying the film thickness.

Consider a 3d lattice, with dimensions L_x, L_y, and L_z, composed of dipoles $\mathbf{s_m}$ with orientations up $\mathbf{s_m} = (0,0,1)$ or down $\mathbf{s_m} = (0,0, -1)$. The energy from the Ising interactions is given by

$$E_\mathrm{I} = -\frac{J}{2}\sum_{\langle \mathbf{m},\mathbf{m}'\rangle} \mathbf{s_m}\cdot\mathbf{s_{m'}} \qquad (1)$$

where $\langle \mathbf{m},\mathbf{m}'\rangle$ are the nearest neighbors. The energy due to dipolar interactions is

$$E_\mathrm{D} = \frac{D}{2}\sum_{\mathbf{m}}\sum_{\mathbf{m}\neq\mathbf{m}'} \frac{\mathbf{s_m}\cdot\mathbf{s_{m'}} - 3(\mathbf{s_m}\cdot\hat{r})(\mathbf{s_{m'}}\cdot\hat{r})}{|\mathbf{m}-\mathbf{m}'|^3} \qquad (2)$$

where $\hat{r}$ is the unit vector in the direction of $\boldsymbol{m} - \boldsymbol{m}'$.

The monolayer ($L_z = 1$) case can be analyzed readily given that the second term in E_D vanishes. The existence of antiparallel domains (stripes) in this 2d case has been justified by expanding the free energy in powers of the Fourier components $\phi(\mathbf{k})$ of a continuous field $\phi(\mathbf{r})$ proportional to the local polarizability as,[9] $F = \sum_\mathbf{k} \phi(\mathbf{k})(G_0^I + G_0^D)\phi(-\mathbf{k})$ + *quartic local terms*. Here, the Ising contribution G_0^I is equal to $G_0^I = 4\gamma J(-1 + 2a^2k^2) + k_\mathrm{B}T$, where γ is the number of nearest neighbors, T is the temperature, and k_B is the Boltzmann constant. The dipolar contribution is given by the 2d Fourier transform of the potential in eq 2, $G_0^D(k) = (2\pi D/a)({}_1F_2(-1/2;\ {}^1/_2,\ 1;\ -a^2k^2/4) - |k|a)$, where ${}_1F_2$ is the generalized hypergeometric function. When D/J is small the $-|k|$ term in $G_0^D(ka \ll 1) = (2\pi D/a)(1 - |k|a + k^2a^2/2)$ added to the $+k^2$ terms in G_0 gives a minimum F at a k^* mode that changes continuously from $k^* = 0$ (a monodomain) at $D/J = 0$ to $k^* \neq 0$ (a periodic structure) as soon as $D/J \neq 0$. The lowest energy structure is a stripe[11,12] along x or y with periodicity $\lambda/a = 2\pi/k^*a = 4\pi + 16a/(D/J)$. This continuous analysis, however, is not accurate for neither $D/J > 0.1$ nor low T.[8] The stripe

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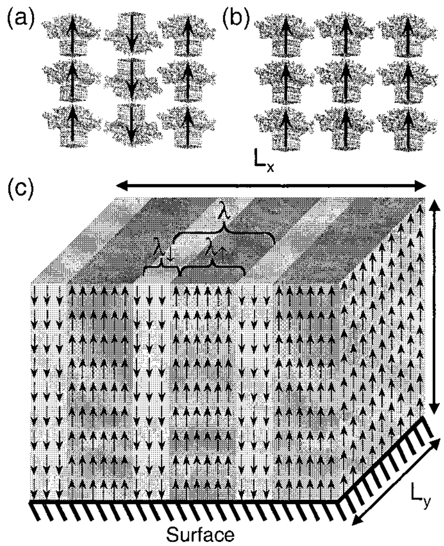

Figure 1. Ground-state configurations for a system of supramolecular aggregates with dipole−dipole interactions only (a) and with Ising interactions only (b). The stripe structure under the surface influence is also shown (c).

structure melts via defects,[8] with a local λ given by the exact $T = 0$ value,[7] $\lambda = A \exp(2aJ/D)$. The exponential decay of λ/a from ∞ to 2 as D/J increases (followed by an antiferromagnetic state), agrees well with the exact numerical $T = 0$ results given below.

To analyze the stripe structure in films of arbitrary thickness we consider the system as a set of $y-z$ planes of one lattice thickness, stacked along x. Since within each plane all the dipoles have the same orientation, one can assign a new parameter s_i^p to represent the configuration of all the dipoles within the plane. The Ising and dipolar energies per dipole between two planes for a repeat unit of width λ is given by

$$E_{\mathrm{I}} = -J\,\frac{\lambda - 4}{\lambda} \tag{3}$$

and

$$E_{\mathrm{D}} = \frac{D}{\lambda}\sum_{i=1}^{\lambda}\sum_{i'=i+1}^{\infty} V_D^p(|i' - i|)s_i^p\, s_{i'}^p \tag{4}$$

respectively, where $V_D^p(|i' - i|)$ is the dipolar potential between planes i and i'. We compute $V_D^p(|i' - i|)$ by summing over all the individual dipole−dipole interactions that form the planes

$$V_D^p(|i' - i|) = \sum_{\mathbf{m_i}}\sum_{\mathbf{m_{i'}}} \frac{\mathbf{s_{m_i}}\cdot\mathbf{s_{m_i}}' - 3(\mathbf{s_{m_i}}\cdot\hat{r})(\mathbf{s_{m_i}}'\cdot\hat{r})}{|\mathbf{m_i} - \mathbf{m_{i'}}|^3} \tag{5}$$

where $\boldsymbol{m}_{\mathbf{i}}$ and $\mathbf{m_{i'}}$ are the spins in planes $\mathbf{i}$ and $\mathbf{i'}$ respectively. V_D^p has a strong dependence on L_z, such that as L_z increases V_D^p decreases at short distances and increases at long distances. Therefore, the range of interaction is longer in thicker films.

The interaction with the substrate can be easily included into this model. Let us assume the presence of a substrate in the $x-y$ plane which favors the up configuration for the first layer of dipoles. The energy per dipole due to the interaction with this substrate can be written as

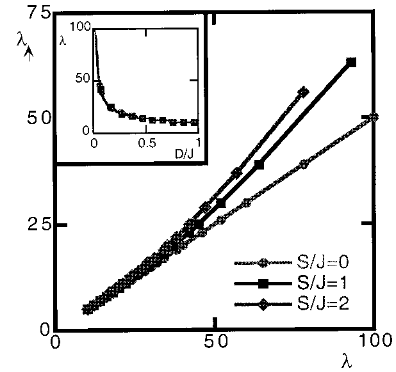

Figure 2. Results for $\lambda_\uparrow$ vs λ for different surface interaction strengths for a film of 21 layers, $S/J = 0$ (●), $S/J = 1$(■), and $S/J = 2$(◆). The inset shows λ vs D/J for the same S/J values.

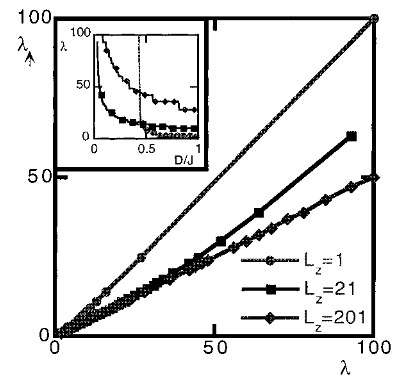

Figure 3. Effect of film thickness L_z on the ratio $\lambda_\uparrow/\lambda$ for a monolayer (●), 21 layers (■), and 201 layers (◆). The inset shows λ vs D/J for the same film thicknesses.

$$E_S = -\frac{S}{\lambda L_z}\sum_{i=1}^{\lambda}(s_i^p) \tag{6}$$

This potential distorts the relative width of domains of dipoles up and down, such that $\lambda_\uparrow/\lambda \neq 0.5$.

Figure 2 shows the effect of surface interaction on the ground state configuration, obtained by numerically minimizing the total energy of the system. The calculations are carried out for a film of 21 layers of dipoles and infinite dimensions in the $\hat{x}$ and $\hat{y}$ directions. Surfaces with $S/J = 0$,1 and 2 give similar λ variations as D/J increases. The domain size decreases continuously from infinite to finite values over a very narrow D/J range as shown in the inset in Figure 2. The effect of the surface interaction is revealed in the $\lambda_\uparrow$ vs λ plot. The $S/J = 0$ case yields $\lambda_\uparrow/\lambda = 0.5$. As the surface interaction is turned on, the relative width of up and down domains changes such that $\lambda_\uparrow/\lambda \geq 0.5$ (Figure 1c), and an increase of the surface potential raises this difference further.

The thickness of the film has a drastic effect on the ground-state configuration, such that in the extreme limit of a bulk system the domain structure is destroyed. We analyzed three systems with film thickness, $L_z = 1$ (a monolayer), $L_z = 21$, and $L_z = 201$, all with $S/J = 1$. As shown in Figure 3, these three systems show a remarkably different parameter dependence. For large values of D/J the monolayer has a periodicity of $\lambda/a = 2$, and the domain size grows rapidly at about $D/J \cong 0.45$, as shown in the inset in Figure 3. This sharp onset disappears for films with 21 and 201 layers. When we compare the ratio $\lambda_\uparrow/\lambda$, it is clear that the monolayer acquires a monodomain configuration with full macroscopic polarization and the amount of polarization decreases as the film thickness increases. Since the model assumes that the surface interacts only with the first layer of dipoles, it is clear that the overall effect of the surface becomes less dominant as L_z increases.

In our model, we assume an Ising interaction which favors parallel configuration both along the z axis and within the $x-y$ plane. On the basis of short-range energetic considerations, one might conclude that the configuration along z would be antiparallel, since this would enable to some degree the phase separation of coil and rod blocks. However this simplification in our model alters the ground state of the system only when D/J is very small. That is, if we include an Ising interaction favoring an antiparallel configuration along the z axis, the ground state is a monodomain of bilayers when $D/J \ll 1$. When D/J increases, however, the parallel configuration along z, favored by the dipolar interaction, dominates even when the Ising interaction favors an antiparallel configuration along z.

We conclude that the ground state of a system composed of dipolar supramolecular aggregates that interact with a surface is a periodic domain structure with a net macroscopic polarization. Furthermore, one can control the magnitude of this polarization through variations in the dimension of the system and the strength of the surface force constant. Monte Carlo simulations for some hexagonal lattices and smectic-A structures with directional order also give stripe structures with a similiar λ dependence on film thickness.

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