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Notes

Dynamic Mean-Field Model for the Mesoscale Morphologies of Liquid Crystalline Polymers

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More than half of all polymers employed are semicrystalline or liquid crystalline. The properties and thus the applicability of these materials depend not only on their chemistry but also on internal mesoscale structures.[1,2] Mesoscale time-dependent Landau models for liquid crystalline polymers are either based on well-chosen phenomenological free energy functionals[3,4] or by expansion of a suitable polymer path integral similar to RPA.[5] A few years ago, we have introduced a mean-field dynamic density functional method for modeling mesoscale structures in mixtures of flexible block copolymers.[6,7] The method combines a microscopic description of the molecules as Gaussian chains in a mean field with a dynamical evolution equation, and thereby avoids the lack of chemistry inherent in phenomenological models, and also by construction does not suffer from truncation problems in expansion methods. While the Gaussian chain model is suitable to describe block copolymers characterized by a flexible backbone, it is insufficient for modeling liquid crystalline polymers molecules, which are more suitably described by a stiff wormlike chain. In this note we present the first self-consistent dynamical mean-field simulation of morphology formation in liquid crystalline polymers.[8] The details of the new calculation method will be presented elsewhere.

Making use of the summation convention to sum over repeated subscripts, the mean-field free energy functional derived for the homopolymer melt reads as

$$F[\rho,S_{ij}] = -kT\ln\frac{\phi^n}{n!} - \int_V U\rho\,\mathrm{d}\mathbf{r} - \int_V T_{ij}S_{ij}\,\mathrm{d}\mathbf{r} + \frac{w}{2}\int_V S_{ij}S_{ij}\,\mathrm{d}\mathbf{r} + \frac{\kappa_\mathrm{H}}{2}\int_V(\rho-\rho_0)^2\,\mathrm{d}\mathbf{r} \quad (1)$$

where n is the number of polymers, ρ is the scalar order parameter (density of beads), and S_{ij} is component ij of the tensorial order parameter (ordering of segments); U and T_{ij} are the external potentials conjugated to ρ and S_{ij}, w is a Maier−Saupe coefficient, ρ_0 is the average bead concentration (fixed), κ_H is a compressibility coefficient, and ϕ is the single-chain partition function for a chain embedded in the external fields U and T_{ij}, i.e.

$$\phi \propto \int \mathrm{d}\mathbf{R_1}...\mathrm{d}\mathbf{R}^\mathrm{N} \prod_{s\in\mathrm{seg}} \delta\left(\frac{1}{a}\left\|\mathbf{r_s}\right\| - 1\right) \times \exp\left[-\frac{1}{kT}\left(\sum_{s\in\mathrm{beads}} U(\mathbf{R}_s) + \sum_{s\in\mathrm{seg}} T_{ij}(\mathbf{R}_{\mathrm{seg},\boldsymbol{s}})\,Q_{ij}(\mathbf{r}_s) - \kappa\sum_{s\in\mathrm{joints}}\cos(\varphi_s)\right)\right] \quad (2)$$

The product of delta functions in eq 2 defines the length of the chain segment vectors $\mathbf{r}_s = \mathbf{R}_{s+1} - \mathbf{R}_s$, $||\mathbf{r}_s|| = a$ linking the chain beads $\mathbf{R}_{i=1...N}$. In the exponent of the Boltzmann weight the energy of the chain conformation is scaled by the thermal energy kT. The conformational energy consists of three contribution, which are in order of the sums (i) the positional energy of the chain beads, (ii) the orientational energy of the chain segments, and (iii) the bending energy of the chain joints, which is proportional to the bending modulus κ. The orientation of the chain segments is represented by the tensor $Q_{ij}(\mathbf{r}_s) = (r_i)_s(r_j)_s/\mathbf{r}_s^2 - {}^1\!/_2\delta_{ij}$, which interacts with the potential T_{ij} at the midpoint of the segment $\mathbf{R}_{\mathrm{seg},s} = {}^1\!/_2(\mathbf{R}_s + \mathbf{R}_{s+1})$, and the angle between consecutive segment vectors is denoted by $\varphi_s = \angle(\mathbf{r}_s,\mathbf{r}_{s+1})$. The equation for the free energy (1) is closed by the self-consistent-field equations for the density and the tensorial order

$$\rho = -nkT\,\frac{\delta\ln\phi}{\delta U} \quad (3)$$

$$S_{ij} = -nkT\,\frac{\delta\ln\phi}{\delta T_{ij}} \quad (4)$$

The evolution equations are

$$\frac{\partial\rho}{\partial t} = M\nabla^2(-U + \kappa_\mathrm{H}\rho) + \eta_\rho \quad (5)$$

$$\frac{\partial S_{ij}}{\partial t} = -\gamma(-T_{ij} + wS_{ij}) + \eta_{S_{ij}} \quad (6)$$

where M and γ are mobility coefficients (assumed constant); η_ρ and $\eta_{S_{ij}}$ are noise fields.

In Figure 1, we present results of a numerical calculation of the morphology evolution in a 2D system, where we have used a Crank−Nicholson integration scheme for the evolution equations and a second-order propagator scheme for the path integral calculations.

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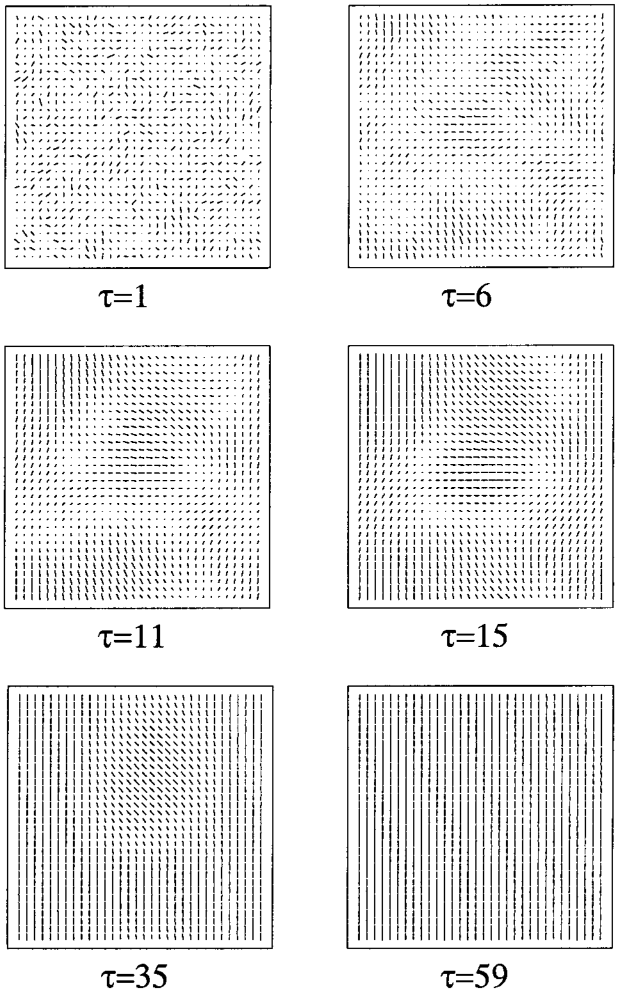

Figure 1. Snapshots of the evolution of order in the system, where dashes indicate the most probable chain segment orientation. The angle $\alpha(\mathbf{r})$ of the dashes with the horizontal is calculated as $\alpha(\mathbf{r}) = {}^1/_2 \arccos[S_{11}(\mathbf{r})/({}^1/_2 S(\mathbf{r})_{ij}S(\mathbf{r})_{ij})^{1/2}]$ and the relative length of the dashes $\propto (S(\mathbf{r})_{ij}S(\mathbf{r})_{ij})^{1/2}$ represents the degree of ordering at each time step.

The system contains 32^2 cells, each cell of size h^2; the dimensionless time steps for the two evolution equations are the same, $\Delta\tau_M \equiv kTM\Delta t/\rho_0 h^2 = \Delta\tau_\gamma = kT\gamma\Delta t/\rho_0 = 0.1$. The chain with bending stiffness $\kappa/kT = 3$ consists of $N = 7$ beads, connected by six segments of constant length $a = h$. The critical Maier−Saupe parameter for the system is $\rho_0 w_c/kT = -2.1$; the parameter value used in the calculation is $\rho_0 w/kT = -2.5$. At each time step, uniformly distributed white noise is added with spread $0.01\rho_0^2$. The compressibility parameter $\rho_0\kappa_H/kT = 40$, which is so high that the average deviation form homogeneity is less than $||\rho/\rho_0 - 1|| \leq 2\%$.

The changing morphology of the system can be related to the evolution of the free energy (Figure 2). In the beginning the simulation demonstrates fluctuating growth patterns, in which first small oriented patches appear and disappear, and then the fluctuating patches are replaced by a few larger domains, $0 < \tau < 6$. The free energy of the system decreases steeply as the domains grow, and the degree of orientation approaches its saturation level within the different domains, $6 < \tau < 15$. As the differently oriented domains compete for space, defects are formed, which are annealing as the system evolves, $15 < \tau < 35$. After the annealing of the defects we still observe an oriented droplet immersed in a differently oriented monodomain. In the last phase of the transformation, $35 < \tau < 59$, the droplet is shrinking until the whole system consists of a single oriented monodomain. The reorientation dynamics is nonlocal, since the Boltzmann weight in the path integral links regions in space on the length scale of the polymer molecule. In real experiments phase separation dynamics are seldom completed to equilibrium, but rather halted at an intermediate stage.[1,2] The proposed simulation method is thus excellently suited to study the early and intermediate stages. It is now straightforward to extend the simulations to a whole new class of polymer systems, having in mind semiflexible copolymers, with different boundary conditions under the influence of external fields. We will address these systems in the near future.

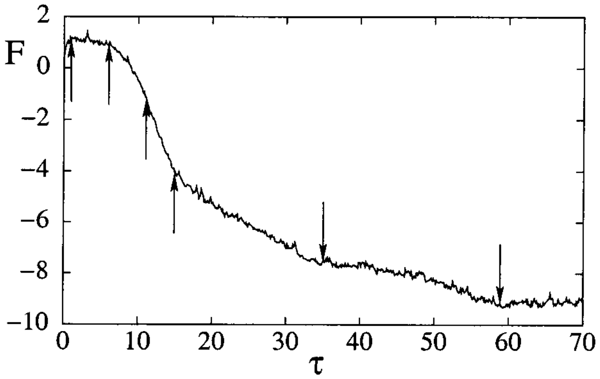

Figure 2. Free energy in arbitrary units vs dimensionless time $\tau = tMkT$. The arrows indicate the times of the snapshots in Figure 1.

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