

# Simulation of phase separation of polymer–liquid-crystal mixtures and the effect of confining external surfaces

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A Monte Carlo simulation is performed on a lattice model of a binary mixture of nematogenic liquids and polymers to study the main aspects of phase separation including the influence of external surfaces. The system was investigated at various temperatures, concentrations, and degrees of polymerization. The results seem to fit well within Flory-Huggins theory predictions. It is also shown that in some cases the anisotropy plays an important role in structure formation. The influence of the external surfaces on the condensation of one of the phases was studied on systems that experience the separation by nucleation and growth. It has been noticed that the surfaces that prefer nematogenic molecules act as better condensation nuclei, especially if they are ordered.

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## I. INTRODUCTION

Polymer-liquid crystal mixtures have reached a considerable scientific and technical importance in recent years mostly due to some novel materials such as polymer dispersed liquid crystals (PDLCs) [1,2]. They have raised some interesting problems mostly connected with phase separation, structure formation, and liquid crystal confinement that are still not well understood. The first comes from the fact that the most used techniques for preparing PDLCs all involve phase separation of an initially homogeneous state. It can be reached through cooling the system below some critical temperature, also known as thermally induced phase separation (TIPS), or by increasing the degree of polymerization, known as polymerization induced phase separation (PIPS). The former is the method of choice for fundamental studies, because it is cheap and easy to handle, while the latter is a better choice when a better control over the local variation of separation process is needed.

The main mechanism leading to the phase separation phenomenon is the competition between the two contributions to the free energy. The separated state is energetically favorable while the homogeneous one has higher entropy. At lower temperatures the energy contribution will prevail over the entropy contribution, and vice versa. At some intermediate temperatures the phase transition occurs. In this way TIPS is driven. The mechanism leading to PIPS is the decrease of entropy while polymerizing the monomers, namely, the bounded monomers have a lower freedom of motion because they can only move in the vicinity of the monomer they are bound to. The decrease of entropy is of course bigger in the homogeneous than in the separated state.

These systems were broadly investigated in recent years. In addition to various phenomenological continuous models [3–8], based mainly on the coupling of the Landau–de Gennes and Flory-Huggins free energy densities, also some microscopic approaches were used. Some of them assumed

in advance the structure and the interface between the phases of the separated system, and then the orientational distribution was analyzed with some simpler models [9,10]. Some models that focused on the structure formation used isotropic instead of anisotropic molecules, assuming that both would give the same result [11]. Our results show that in most cases this holds, but in some particular cases the anisotropy plays an important role. Also some two-dimensional (2D) models were simulated [12,13]. In two dimensions the polymer coils present a topological barrier and as such they cannot be simulated properly. This argument led us to the choice of a 3D model.

Such materials are mostly synthesized as thin films on various substrates; thus the interaction of the binary mixture with the external surface should be taken into account. Although the type of surface seems to play a crucial role in the phase separation mechanism and structure formation, there are just a few investigations done about it. The main three aspects of the external surface influence on polymer–liquid-crystal mixtures are the local variation of concentration of both compounds which can have an impact on condensation nuclei formation, the external nematic anchoring, and finally a possible intrusion of the smecticlike layers.

## II. MODEL DESCRIPTION

Because of computing time limitations we decided to choose a three-dimensional model discrete in space and continuous in orientation. The simulations were performed using the Metropolis Monte Carlo method. The model particles were allowed to move from site to site of a fcc lattice. The latter was chosen because it is close packed and it has a local hexagonal structure as was observed in our previous continuous model simulations of the liquid and solid phases. The main advantage of a discrete model over the continuous one is a well defined neighborhood; the interactions with particles on other sites can be neglected. This simplification substantially reduced the computing time. The typical number of Monte Carlo sweeps was on the average 300 000 per molecule before reaching thermal equilibrium from the ran-

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domly chosen initial state. The trial moves were randomly chosen among translation of molecules, rotation of the nematogenic molecules, and reptation of the entire polymer chains.

The potentials between the particles reflected the nature of the compounds. The interaction between the monomer molecules was isotropic and its energy was  $\epsilon_{mm} = -\epsilon$  (it was chosen as the energy unit) if the particles were closest neighbors and infinite or zero otherwise, depending whether the particles were bound in the same polymer or not. Another restriction was that two particles could not occupy the same place in the lattice. The interaction between nematogenic molecules was Lebwohl-Lasher-like [14],  $\epsilon_{ll} = -\epsilon[a_1 + a_2(\mathbf{n}_1 \cdot \mathbf{n}_2)^2]$ . The constants were chosen in such a way that the effective interactions between the particles of the same kind were comparable in the temperature region where the simulations were performed ( $a_1 = 0.3$  and  $a_2 = 0.9$ ). The potential between the particles of different kinds was isotropic but weaker than the previous two  $\epsilon_{ml} = -\gamma\epsilon$  (in our particular case  $\gamma = 0.75$ ).

To mimic the polymerization of monomers and shorter polymers the following procedure was used. A uniformly randomly chosen lattice site was first checked if it held a monomer that had at least one bond free. If the site passed the test and if at least one of its neighbors was also able to form polymer bonds, then the bond was formed. The polymerization process proceeded slowly enough that the system went only through thermally equilibrated states. This restriction was made due to the nature of the Monte Carlo technique, which can give only statistical averages rather than the time evolution of the system.

The external surface was simulated as a layer of motionless dummy particles with particular interactions adapted to the needs of our investigations. As we focused on the aspect of condensation nuclei formation, these potentials were almost in all cases isotropic but different for both kinds of molecules. The particles were positioned at the surface and had no dynamic—they could not change their position or their orientation.

To simulate better the continuous model also some lattice sites were left empty. Empty sites break the local structure and change the number of neighbor interacting particles. The number of these sites does not affect the simulation results substantially if it is properly chosen. However if it is too big (more than approximately 5–10% depending on the temperature) then eventually a bubble can be formed in the system, acting as an additional condensation nucleus in the phase separation process. For this reason we choose the total number of molecules to be 62 000 in a  $40 \times 40 \times 40$  bulk system and 61 000 in a confined system of the same size (dummy particles on the surface excluded). Nevertheless the system size in all the simulations was in all cases  $40 \times 40 \times 40$ .

For the sake of simplicity all the simulation parameters and results were given in a dimensionless form. The distance between neighbor sites was chosen as the length unit and the potential between adjacent monomers  $\epsilon$  as the energy unit. The temperature unit  $\epsilon/k_B$  was chosen such that the Boltzmann constant was equal to  $k_B = 1$ .

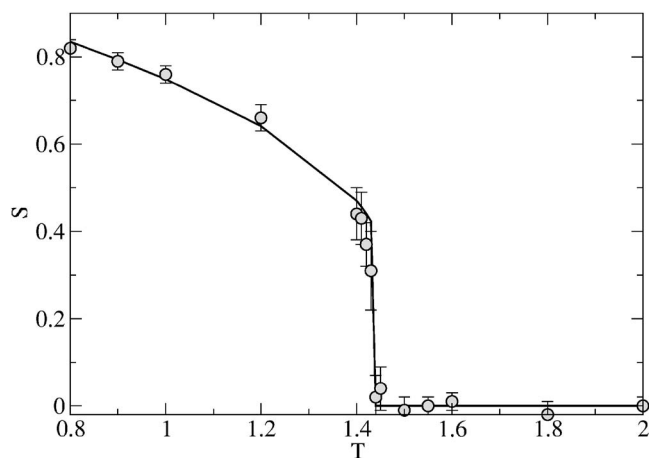


FIG. 1. Temperature dependence of the nematic order parameter  $S$  and the fit to the Landau–de Gennes theory.

### III. SIMULATION RESULTS

At the beginning some simulations of pure compounds were made to compare them with other well known theoretical and simulation models. As can be seen from Fig. 1, the temperature dependence of the scalar order parameter  $S$  in the nematogenic system is in a good accordance with Landau–de Gennes theory (if its phenomenological parameters are chosen properly) and other hexagonal Lebwohl-Lasher simulation models [15]. Also the nematic correlation length  $\xi$  can be calculated (Fig. 2). This was done by imposing an external anchoring surface with different orientational order and observing the decrease of the order parameter with increasing distance from it. Also in this case a good accordance with Landau–de Gennes theory is observed.

In the polymerization simulation of the pure polymer system the investigation was focused on the distribution of monomers within a single polymer. Mainly it was described with two parameters: the mean degree of polymerization  $\langle N \rangle$  (the average number of monomers in a polymer) and the

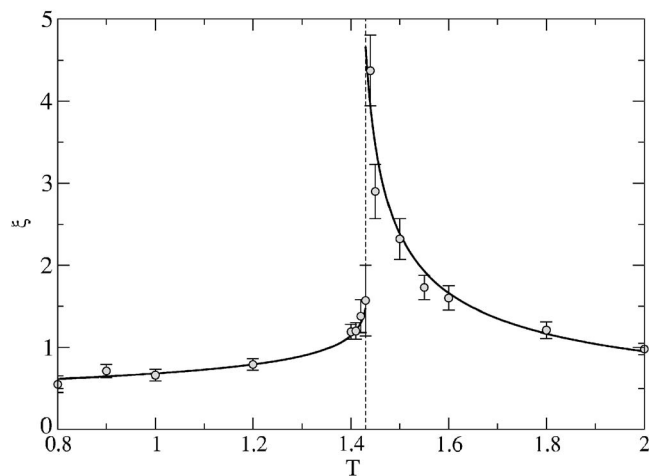


FIG. 2. Temperature dependence of the nematic correlation length  $\xi$  and its comparison with Landau–de Gennes theory predictions.

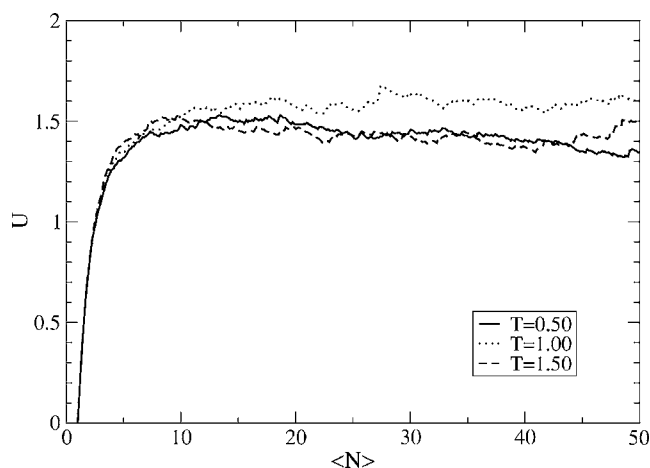


FIG. 3. Polydispersity coefficient  $U$  and its dependence on the average degree of polymerization  $\langle N \rangle$  at various temperatures. It is independent of the temperature within the error region that can be deduced from the fluctuations of the lines, which should be smooth.

polydispersity coefficient  $U$  (the deviation from the mean value). It was found out that the distribution, resulting from above described polymerization procedure, is almost independent of the temperature as we can see from the polydispersity coefficient (Fig. 3) within the error region. This leads us to the conclusion that the number of monomer distributions with the same mean value are independent of the temperature and the course of the polymerization.

In the next step the behavior of the mixture in the bulk was investigated. For the qualification of the degree of separation the *separation correlation lengths*  $\xi_m$  and  $\xi_{lc}$  were used. They were defined as

$$\xi = \frac{1}{1 - g_0} \int_0^\infty [g(r) - g_0] dr, \quad (1)$$

where  $g(r)$  is the probability to find the particle of the same kind at the distance  $r$  and  $g_0$  is its value in the limit when  $r$  goes to infinity. In practice  $g$  was calculated by counting appropriate particles at some fixed distance and in all directions and then calculating the average over the sample origin particles. The quantity is defined in such a way that if  $g$  approaches its limit in an exponential fashion, then  $\xi$  is the relaxation length.

First the temperature induced phase separation of the non-polymerized system was observed. For the system of 20 000 nematogenic and 42 000 monomer particles on a  $40 \times 40 \times 40$  lattice a homogeneous-separated phase transition was observed at the temperature  $T_c = 0.83$  (Fig. 4) in the units where  $k_B = 1$  and  $\epsilon_{mm} = -1$ . This is far below the nematic-isotropic transition ( $T_{NI} = 1.43$ ). In addition to the sudden fall of the separation correlation lengths (Fig. 4), which is the main indicator that the transition has occurred, also the melting of the average nematic order is observed (Fig. 5). We refer to the average nematic order  $\langle S \rangle$  (the mean value over all nematogenic molecules) in the whole system rather than the order  $S$  in the nematic rich phase only, because the latter would not be defined in the homogeneous state.

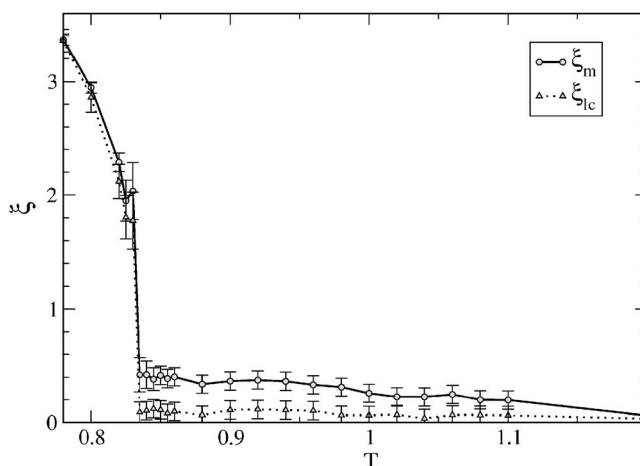


FIG. 4. Separation correlation lengths during the temperature induced phase separation of the system of 20 000 nematogenic and 42 000 monomer molecules. A substantial drop at the temperature  $T_c = 0.83$  indicates a separated-to-homogeneous state phase transition.

This means that the homogeneous phase is always isotropic. The same effect was observed in systems with other proportions of both compounds except for those with very high ratio (above 5:1) of nematogenic molecules, which experienced the nematic-isotropic phase transition above the separation temperature.

On the same system also some investigations about PIPS were done. As can be seen from Fig. 6 the system can be both in separated and homogeneous states depending on the temperature and the average degree of polymerization. Above some temperature the system will be always in the homogeneous state no matter the degree of polymerization. This temperature was marked as  $T_h$  and for this system it was  $T_h = 1.12$ .

The behavior of such a system can be well described by the modified Flory-Huggins theory [16]. It basically consists

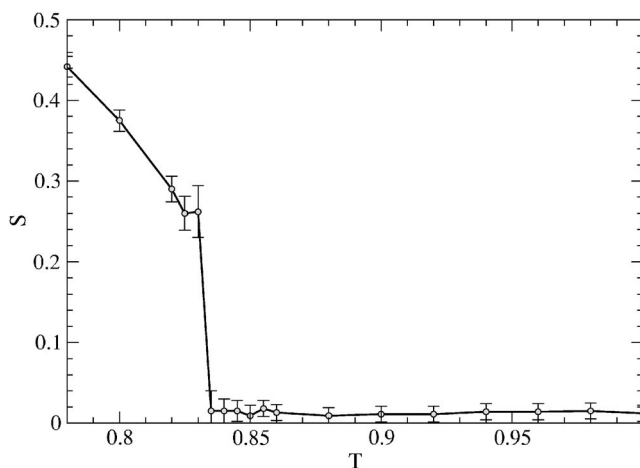


FIG. 5. The melting of the average nematic order at the transition to the homogeneous state for the same system as in Fig. 4. In the homogeneous state the mixture is isotropic also in the temperature region where the pure liquid crystal would be in the nematic phase.

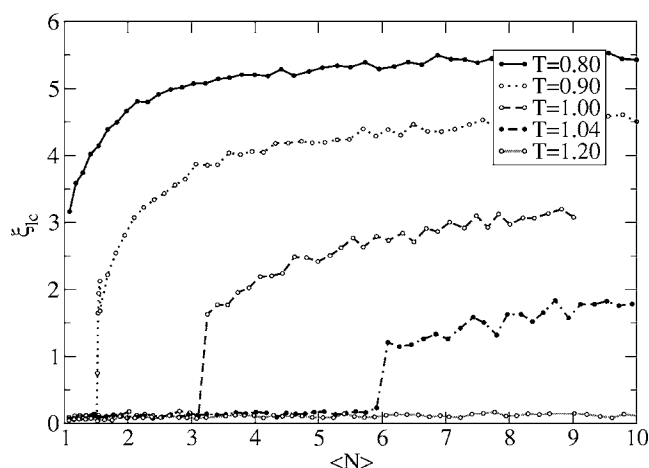


FIG. 6. Separation correlation length for nematic molecules  $\xi_{lc}$  at various temperatures during the polymerization induced phase separation of the system of 20 000 nematogenic and 42 000 monomer molecules. The system exhibits a separation process by nucleation and growth indicated by the sharp increase of the correlation length. It can be noticed that below some temperature the system is always in the separated state (e.g.,  $T=0.80$ ) and above some other temperature always in the homogeneous one (e.g.,  $T=1.20$ ).

in minimizing the mixture free energy  $\Delta F$ . The latter is described as the change in transitional contribution to the entropy while the change in energy is approximated by the probability of overlapping two particles of different kinds:

$$\Delta F = n_c \tilde{R} T \left( \phi_l \ln \phi_l + \frac{\phi_m}{N} \ln \phi_m + \chi \phi_l \phi_m \right). \quad (2)$$

Here  $n_c$  and  $\tilde{R}$  are some constants related to the effective molar density and the gas constant,  $\phi_l$  and  $\phi_m$  are the volume fractions of nematic and monomer particles,  $N$  is the degree of polymerization, and  $\chi$  is the Flory-Huggins parameter and is temperature dependent. An immediate consequence of this simple theory is that the nematic phase would be much cleaner than the polymer one. This is in good agreement with our simulation where the concentration of the nematogenic particles in the nematic phase was close to 1 while in the polymer phase it was approximately 0.2.

Finally the phase diagram for this system was calculated (Fig. 7). If compared to the Flory-Huggins theory predictions using the simplest model for the temperature dependence of the Flory parameter  $\chi$

$$\chi = \chi_s + \frac{T_\chi}{T}, \quad (3)$$

where  $\chi_s = -2.16$  and  $T_\chi = 3.53$  (the values in accordance with  $T_c = 0.83$  and  $T_h = 1.12$ —the temperatures of the homogeneous-separated transition of the nonpolymerized and completely polymerized systems), a good agreement can be seen. The discrepancy can be attributed to the fact that the theory holds for a monodisperse system which is far from our situation. The two terms in Eq. (3) are often referred to as the entropy and energy contributions to  $\chi$ .

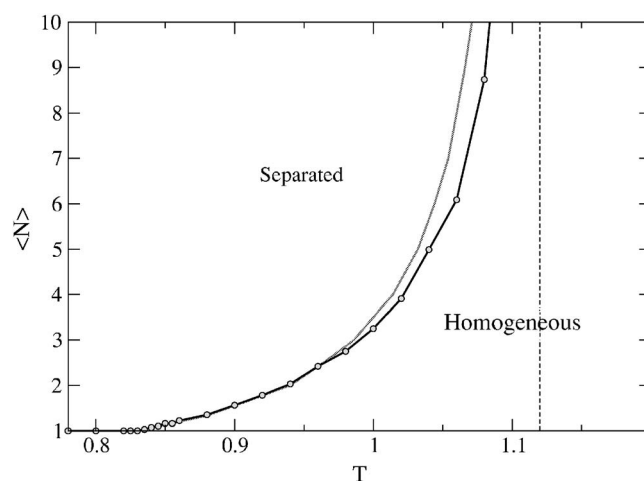


FIG. 7. Phase diagram for the system of 20 000 nematogenic and 42 000 monomer molecules. The bright curve shows the predictions of the Flory-Huggins theory. The discrepancy between the both can be attributed to the fact, that the simulated system was not monodispersed. The vertical line points to the maximal temperature where PIPS can be achieved.

At higher concentrations of nematogenic molecules the separated-homogeneous phase transition loses its sharpness (Fig. 8 and 9). In Fig. 9 it can be seen that the higher the concentration of nematogenic molecules, the more gradual is the change in the correlation length with increasing degree of polymerization. The same gradualness is observed when lowering the temperature in systems with high concentration of nematogenic compound (Fig. 8). This is also in good agreement with the Flory-Huggins theory, which predicts systems rich with the more polymerized compound to separate in a nucleation and growth fashion, while systems rich with the less polymerized compound exhibit spinodal decomposition. The former are locally stable while in the homogeneous state and need some condensation nuclei to actually separate, while the latter are locally unstable and follow continuously the change of external parameters.

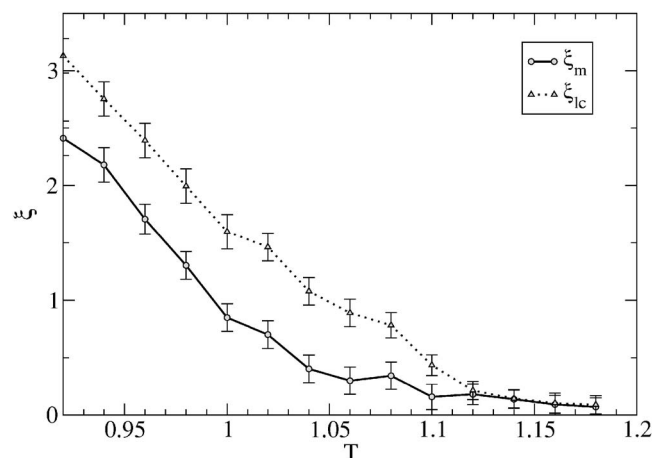


FIG. 8. Separation correlation lengths of the system of 51 000 nematogenic and 10 000 monomer molecules show a spinodal decomposition process indicated by a continuous change of the separation correlation length.

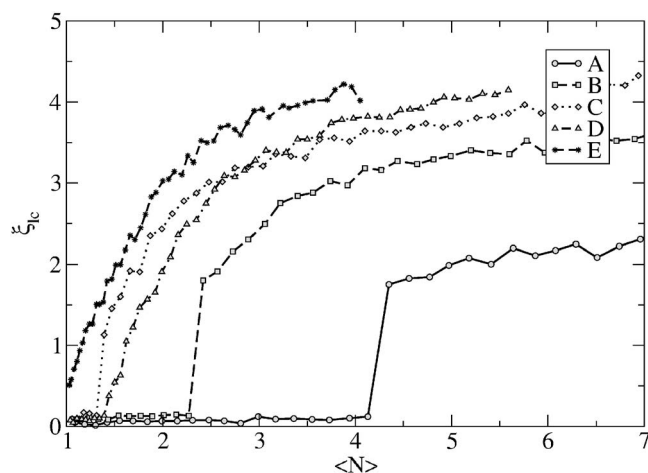


FIG. 9. PIPS for various systems: (A)  $N_{lc}=10\,000$ ,  $N_m=51\,000$ , and  $T=0.85$ ; (B)  $N_{lc}=20\,000$ ,  $N_m=42\,000$ , and  $T=0.96$ ; (C)  $N_{lc}=31\,000$ ,  $N_m=31\,000$ , and  $T=1.00$ ; (D)  $N_{lc}=42\,000$ ,  $N_m=20\,000$ , and  $T=1.10$ ; (E)  $N_{lc}=51\,000$ ,  $N_m=10\,000$ , and  $T=1.10$ .  $N_{lc}$  and  $N_m$  are the numbers of nematogenic and monomer molecules, respectively, and  $T$  is the temperature at which the polymerization is performed.

Besides the course of the phase separation itself also the final structure formation and its morphology is very interesting. At lower concentrations of nematogenic molecules nematic droplets were formed. At higher concentrations (above 0.5) and at certain conditions the nematic phase formed capillarylike channels (Fig. 10). At still higher concentrations also the planar structure of both phases, polymer fibers and finally polymer droplets were observed.

In a first approximation the final structure can be predicted by the minimization of the energy of surface tension; thus by minimizing the surface separating the two phases. In Fig. 11 the dependence of the surface area on the partial volume of the phase is shown for five different structures. At this point it should be stressed that the partial volume is in

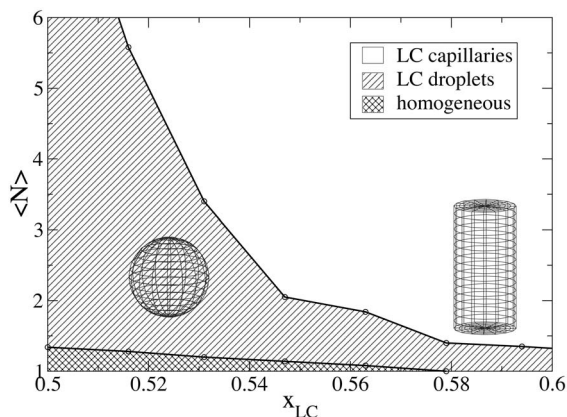


FIG. 10. Phase diagram for the system at various ratios of the nematic molecules ( $x_{LC}$ ) at the temperature  $T=1.00$ . Depending on the concentration of the compounds and the degree of polymerization the system can exhibit a homogeneous state or a separated state. In the latter case the liquid crystal phase can form different morphologies: droplets or capillaries.

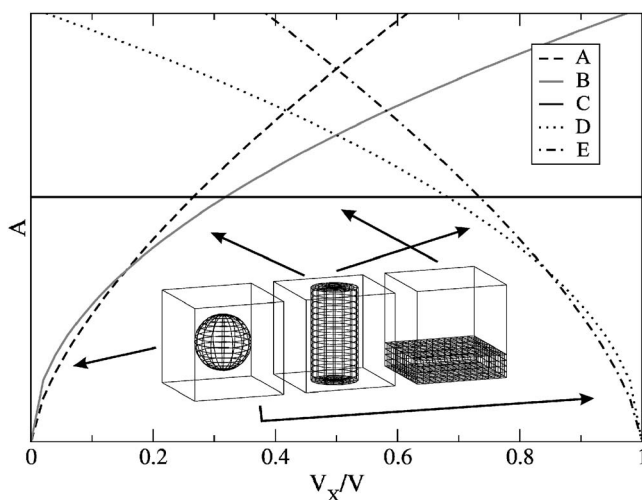


FIG. 11. Minimal surface  $A$  versus the ratio of the volume fraction  $V_X/V$  of the phase  $X$  for various structures: (A) spherical, (B) cylindrical, (C) planar, (D) inverse cylindrical, and (E) inverse spherical. The system will preferably form the structure that has the minimal interface surface.

general different from the concentration. While the nematic phase is almost clean, the mostly polymer phase contains a considerable amount of nematogenic molecules. This is the reason that at a concentration of liquid crystals close to 0.5 the nematic droplet is still formed.

Of course there are also other effects that influence the structure formation; for instance the internal stress in the polymer and the orientational distribution of nematic molecules at the interface. One such interesting result was obtained while simulating the mixture of 52 000 nematogenic and 10 000 monomer molecules in the  $40 \times 40 \times 40$  lattice. The system was first polymerized and after that the temperature was changed. While the system had orientational order, the polymer phase formed a fibril structure. Above the critical temperature (1.3) in the isotropic state, the fiber transformed to a polymer droplet (Fig. 12).

#### IV. INTERACTION WITH CONFINING EXTERNAL SURFACE

In the last phase of our research some investigations of the impact of the confining external surfaces on the process of phase separation were done. Special effort was made in the study of the effect of the local concentration variation and indirectly its impact on condensation nuclei formation. For such investigations the systems that separates via nucleation and growth seemed to be the most appropriate. For this reason a system of 41 000 monomer and 20 000 liquid crystal molecules on a  $40 \times 40 \times 40$  lattice with 1600 dummy particles was chosen. For the sake of clarity it should be stressed once again that the effective size of the layer was  $40 \times 40 \times 39$ , while the reminding layer was filled with fixed surface particles.

These dummy particles were put on a single layer of the lattice and broke its periodicity in the direction perpendicular to the layer. On one side their potential was zero, while on

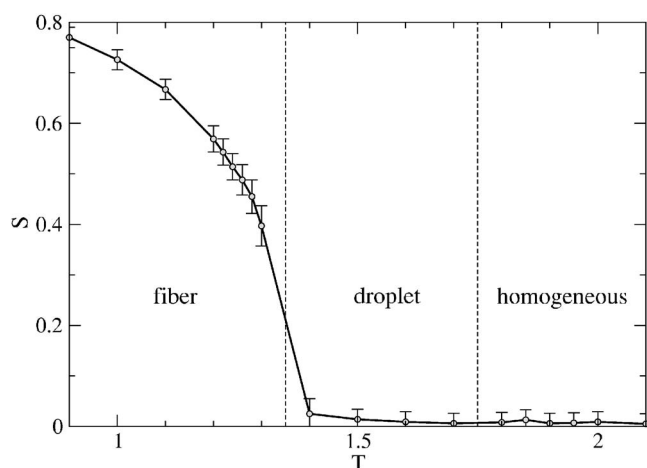


FIG. 12. The correlation between the fiber-to-droplet and nematic-to-isotropic liquid transitions. It can be clearly seen that the temperature of the fiber to droplet transition coincides with the temperature of the nematic-to-isotropic transition.

the opposite the interaction was chosen to satisfy the needs of our investigations. The simulation was started at some temperature where the nonpolymerized system was in the homogeneous state. For our purposes  $T=0.90$  was chosen.

At the beginning the investigation was focused on the concentration profile of the initial state with the noninteracting surface at both sides acting only as a topological barrier (Fig. 13). An increase of the concentration of nematogenic molecules was observed and the decrease of the concentration of monomers as well. We attributed this behavior to the fact that the nematogenic molecules are isotropically distributed in the homogeneous state. This is energetically unfavorable and they prefer to move toward the external surface where they have fewer neighbors to interact with.

These variations of the liquid crystal concentration can favor the formation of condensation nuclei of the phase rich with nematic. Indeed a nematic droplet was formed on one of the surfaces when the initial system was polymerized. The

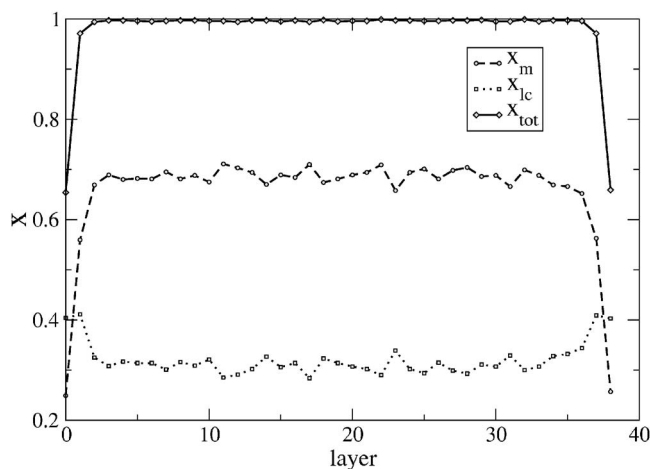


FIG. 13. The profile of the concentrations of both compounds for the system of 20 000 nematogenic and 41 000 monomer molecules at the temperature  $T=0.90$ . The layer is bounded with two noninteracting surfaces.

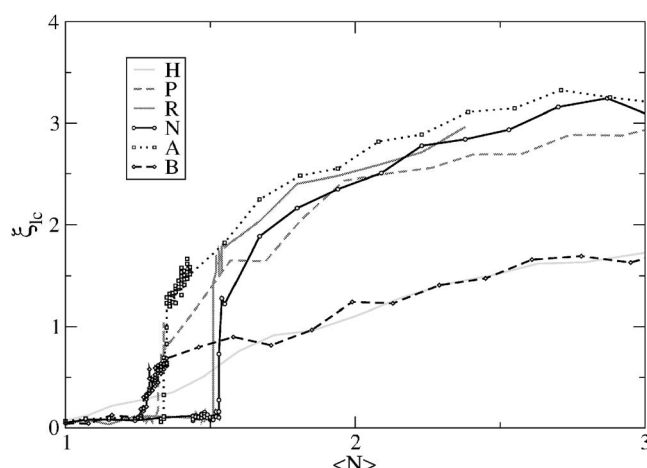


FIG. 14. The course of separation for various external surfaces: (*H*) homeotropically ordered quenched nematic molecules; (*P*) planarly randomly ordered quenched nematic molecules; (*R*) uniformly randomly ordered quenched nematic molecules; (*N*) noninteracting surface; (*A*) preferential monomer surface; (*B*) preferential nematic surface.

same analysis was conducted when instead of a noninteracting surface an interacting one was used on one of both sides. First an isotropic potential of depth  $\pm 1$  was given to the dummy molecules in order to simulate preferable nematogenic and preferable monomer surfaces. As expected, the latter speeded up the separation process (Fig. 14), because the local variation of the concentration of liquid crystals in this case is even more pronounced. On the contrary, also the preferably monomer surface speeded up the condensation nucleus formation, but on the noninteracting surface. This can be attributed to the fact that the interacting layer attracts some monomer molecules from the bulk, thus increasing the concentration of nematogenic particles on the opposite side.

Instead of isotropic also anisotropic confining external surfaces can be used. For this purpose the potential for the dummy particles was the same as the one for the nematogenic molecules. Three different alignments were given to the dummy particles on the surface: homeotropic, isotropically randomly distributed, and planarly randomly distributed (Fig. 14). The isotropically randomly distributed surface did not favor condensation nuclei formation and the condensation nucleus was formed on the noninteracting side. This is why the phase separation course is very similar to the system with the noninteracting surface. In the case of the planarly distributed surface a nematic droplet is formed on it, but its formation is still slower than with the isotropic nematic-favorable surface. As expected, the fastest separation is achieved with aligned surfaces. In this case the nematic molecules append continuously to the surface with increasing degree of polymerization.

At first sight it seems that the values for the separation correlation length converge to two different values. But if a closer look at higher degrees of polymerization is taken, all systems converge to the same value (Fig. 15). Furthermore, the change of behavior is very sharp, indicating some sort of transition. Indeed, from the profile analysis a change of the structure on the surface from half cylindrical to planar was observed.

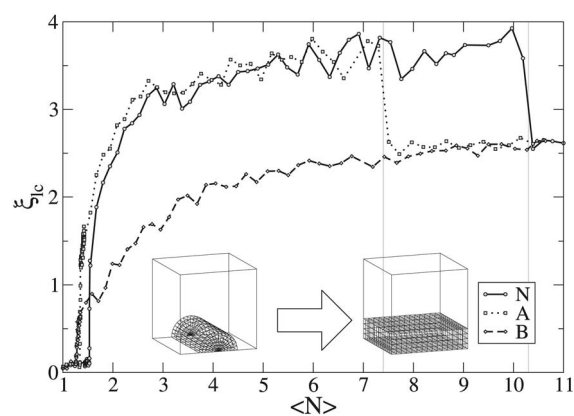


FIG. 15. Transitions of the superficial structures at higher degrees of polymerization for (N) noninteracting, (A) preferential monomer, and (B) preferential nematic surfaces.

As in the previous section also this transition can be explained with minimization of the energy of the surface tension. In this case three different structures are supposed to minimize it: half of a sphere, half of a cylinder, and a planar layer (Fig. 16). The surface of the first two structures depends also on the wetting angle, which is further dependent on the surface tensions between the surface and the nematic phase, between the surface and the polymer phase, and finally between both phases.

## V. CONCLUSION

We have introduced a 3D discrete anisotropic model for the simulation of the binary mixture of nematogenic and polymer molecules and some surface effects connected with it. The results of this simple model are in a good agreement with the predictions of the modified Flory-Huggins theory. In addition, a simple surface tension model was successfully used for the description of the structure formation and its morphology. In the particular case of the polymer fiber to the polymer droplet structure transition it was also shown that in some cases the anisotropy of the nematogenic molecules should be taken into account.

The main achievement of these investigations is a consistent and unified picture of such mixtures. All of the aspects

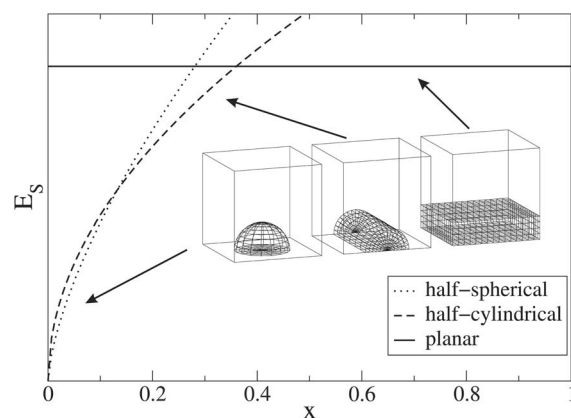


FIG. 16. Energy of the surface tension for three different structures, half spherical, half cylindrical, and planar, and its dependence on the partial volume  $x$  of the superficial structure.

are taken into consideration and no subsystem is assumed to be known in advance. The main consequence is that the structure, concentration, and orientation transitions can be coupled and the relations among them can be investigated. In this sense it is a real microscopic model.

One of the advantages of our model was the possibility of a simple upgrade to the external surface simulations. The impact of the various surface types on the condensation nuclei formation was successfully described. From this point of view we are able to systematize the behavior of the surfaces according to their interactions with other molecules. Also for superficial structure transitions a surface tension model was introduced that gave at least qualitatively good predictions.

Nevertheless, there are still many aspects open and needing to be investigated. Our particular further efforts are focused on the investigations of the possible influence of the direction of the external anchoring layer on the direction of the growth of the polymer fiber and possible competition between the two anchorings.

## ACKNOWLEDGMENTS

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