

The structure of percolated polymer systems: a computer simulation study

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Abstract We studied the percolation process in a system consisting of long flexible polymer chains and solvent molecules. The polymer chains were approximated by linear sequences of beads on a two-dimensional triangular lattice. The system was athermal and the excluded volume was the only potential. The properties of the model system across the entire range of polymer concentrations were determined by Monte Carlo simulations employing a cooperative motion algorithm (CMA). The scaling behavior and the structure of the percolation clusters are presented and discussed.

Keywords Lattice model · Monte Carlo method · Percolation · Polymer adsorption

Introduction

Percolation theory is usually applied to critical phenomena, disordered systems, porous media and alloys [1]. In the process of percolation, a portion of space with occupied and unoccupied sites is considered. When a cluster of the occupied sites expands sufficiently to approximately fill the portion of space (i.e., the cluster spans from one side of the portion of space to the opposite side), percolation occurs. Percolation phenomena have been extensively studied

theoretically, but despite this, there are still many issues with percolation that are far from being understood [1].

Theoretical treatments of the percolation process have mostly been performed by applying the random sequential adsorption (RSA) technique [2–8]. In this method, objects (molecules) are randomly deposited onto a substrate. This adsorption is irreversible and the molecules cannot pass through previously deposited molecules (leading to an “excluded volume”). Percolation and jamming thresholds can be determined for systems that are studied in this way. The objects that have been most commonly studied using the RSA method so far have been stiff rods (needles), but some results, especially the scaling properties of the thresholds mentioned above, are still contradictory, and thus require further investigation [4–7, 9]. RSA studies of other large objects (squares, ellipses) show that percolation depends strongly on the shape and size of the objects [10].

The adsorption of polymer chains onto solid surfaces has also been realized using the RSA procedure. The percolation and jamming of short flexible linear chains onto a square lattice were studied by Beckleheimer and Pandey, and these chains were constructed as self-avoiding walks [11, 12]. The adsorption of semi-flexible chains via RSA was recently investigated by Kondrat [13]. His results suggest that there is a certain temperature at which the percolation threshold is minimized (the shape of the chain changes with increased interactions; i.e., with the temperature). Another study was recently carried out by Sikorski et al. where the RSA method was used to investigate the macromolecular architectures of some stiff and flexible chains [7]. In that work, it was shown that the percolation threshold does not depend on the needle length (with the exception of very short needles). The other method that has been used to study polymer adsorption is computer simulation, which utilizes three-dimensional polymer-chain models [14–16]. These studies have mainly focused on the distribution of

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polymer segments and the behavior of structural elements such as trains, loops and tails. Stiff and flexible particles have been studied by means of geometrical excluded volume considerations [17, 18], and using macromolecular integral equation theory combined with the Ornstein–Zernike equation [19, 20].

Our recent study employed the cooperative motion algorithm (CMA) algorithm for two-dimensional lattice polymer systems [21]. It appeared that the percolation threshold did not simply scale with the local chain density as $N/\langle S^2 \rangle$ (where N is the chain length and S is the radius of gyration); rather, it was possible to distinguish different regimes with different scalings. These regimes occur due to rapid changes in polymer structural properties and thus with the changes in the fractal dimension of the chains. This behavior differs from that predicted by De Gennes, in which the percolation threshold always depends linearly on the local density [10] (De Gennes considered the polymer concentration ϕ^* associated with the transition between the dilute and semidilute regimes, when the chains start to come into contact; the concentration ϕ^* corresponds to the percolation threshold).

In this work, we studied systems containing long, flexible homopolymer chains and explicit solvent. These solvent molecules were of the same size as polymer beads. The presence of solvent molecules makes it difficult to investigate such a system with RSA, so, thus far, percolation in systems of polymers with solvent molecules has been studied using a method where the polymers are built up through random walks [22–25]. In order to sample the conformational space efficiently, we applied a Monte Carlo method with a cooperative motion algorithm. The method used in this study is not capable of studying the jamming threshold (i.e., the highest possible concentration of two-dimensional objects on the surface). As the dependence of the percolation threshold on the chain length and critical exponents has already been determined [21], we studied and described the structure of the system near the percolation threshold and across a wide range of polymer concentrations. The properties of percolating clusters were also determined.

The model and the method used

A coarse-grained chain representation was used in order to study the more general properties of macromolecular systems. Therefore, polymer chains were represented as linear sequences of identical beads. Restricting the chain positions to those in a quasicrystalline lattice was the next approximation we used. We used a two-dimensional triangular lattice with a coordination number of 6; i.e., every monomer had six nearest neighbors. Bond lengths

were equal to unity. Each lattice site was occupied by a single molecular element (a chain bead or solvent molecule), and no empty lattice sites were left. It was assumed that the various interactions (polymer–polymer, solvent–solvent and polymer–solvent) that occurred in the system were identical. Thus, the system was considered to be athermal; only the interactions in the excluded volume between solvent molecules and polymer segments were considered. The system under consideration was placed into a two-dimensional Monte Carlo box with periodic boundary conditions in all directions.

We studied the percolation process of long, flexible macromolecules by means of Monte Carlo simulations using a method that can work across the entire range of polymer concentrations. The cooperative motion algorithm (CMA) was employed in order to generate a series of independent configurations of the system. In this method, cooperative movements consisting of rearrangements that satisfy local continuity of the simulated system are used. A fragment of one chain can move only if neighboring segments of the same polymer, a different polymer, or solvent molecules move simultaneously. This can be realized through local motions consisting of displacements of a certain number of molecular elements along closed loops so that each element replaces one of its neighbors in such a way that the sum of displacements of the elements taking part in the rearrangement is zero (the continuity condition). During these rearrangements, the model chains undergo conformational transformations that preserve their lengths. Quantities that characterize the structure of the system were calculated between cooperative rearrangement steps. A time unit corresponded to the number of simulation steps after which one attempt to move each bead was made on average. A detailed description of this algorithm and a discussion on its applicability are provided elsewhere [26–29].

At the beginning of the simulations, the polymer chains were initially fully extended in the x direction and folded if necessary. The system was then equilibrated using the CMA algorithm. The equilibration of the system was monitored by observing several parameters describing structure and autocorrelation functions (radius of gyration and its principal components). The equilibrated systems obtained in this way were used as starting points in production runs where the trajectories of the positions of the chains were collected for the purpose of analysis.

Results and discussion

The simulations were carried out for chains consisting of $N=8, 16, 32, 64, 128$ and 256 beads. The size of the Monte Carlo box was changed and the simulations were performed for $L=32, 64, 128, 512$ and 1024 . The concentration ϕ of the polymer in the system was defined as the ratio of the

number of sites occupied by the polymer beads to the total number of lattice sites in the simulation box:

$$\varphi = \frac{n \cdot N}{L^2}, \tag{1}$$

where n is the number of chains in the system (for a system that only contains chains of equal length). The concentration of solvent in the system is therefore $1 - \varphi$.

Before we give the properties of clusters formed in percolated systems, we will show the structure of the polymer chains. This can be also treated as a test of the model and the method. The size of the polymer chain is usually described via the mean squared radius of gyration $\langle S^2 \rangle$:

$$\langle S^2 \rangle = \frac{1}{N} \sum_i \langle (r_i - r_{cm})^2 \rangle, \tag{2}$$

where r_i is the coordinate of the i th polymer bead, r_{cm} is the coordinate of the chain's center of mass, and the average $\langle \dots \rangle$ was taken over all chain conformations generated. The

statistical error in this parameter was below 3% in all cases. The variations in chain size with the concentration of polymer beads are presented in a semilogarithmic plot in Fig. 1a. The size of the short chains ($N=8$ and 16) does not change significantly, because the number of conformations is rather limited here, and the presence of other chains cannot change this. For longer chains, the chain size decreases when the polymer concentration increases due to the presence of other chains. For polymer concentrations above a certain critical value φ^* , the scaling theory of De Gennes predicts that $\langle S^2 \rangle$ scales as φ^{-1} [10]. Simulation results presented in Fig. 1a show that this law is not obeyed for short chains (mainly because of the lattice approximation), while for longer chains with $\varphi > 0.3$ it works rather well. In two-dimensional systems there is no interpenetration of polymer chains, but quasi-penetration of entire domains is possible with longer macromolecules [30, 31].

The instantaneous shape of a polymer chain can be determined in the following way. One can define a gyration tensor

$$S = \begin{vmatrix} S_{xx} & S_{xy} \\ S_{yx} & S_{yy} \end{vmatrix} \tag{3}$$

that is built from the following elements:

$$\begin{aligned} S_{xx} &= \sum_{i=1}^N (x_{cm} - x_i)^2, \\ S_{xy} = S_{yx} &= \sum_{i=1}^N (x_{cm} - x_i) \cdot (y_{cm} - y_i), \\ S_{yy} &= \sum_{i=1}^N (y_{cm} - y_i)^2 \end{aligned} \tag{4}$$

The diagonalization of the tensor S gives us eigenvalues L_1^2 and L_2^2 , which correspond to the two main axes of the equivalent ellipse [32]. One can describe the instantaneous shape of the chain using the asphericity factor δ , defined as

$$\delta = \frac{\langle (L_1^2 - L_2^2)^2 \rangle}{\langle (L_1^2 + L_2^2)^2 \rangle}. \tag{5}$$

This parameter was designed to take the value 0 for a purely spherical shape and 1 for a one-dimensional rod. The statistical error in this parameter did not exceed 5%. Figure 1b presents the changes in the asphericity factor as a function of the polymer concentration φ . In general, increasing the polymer concentration causes the asphericity to decrease, because elongated conformations are suppressed under such a condition (the decrease in chain size can be seen in Fig. 1a). The longest chains under consideration here ($N=256$) behave differently, because

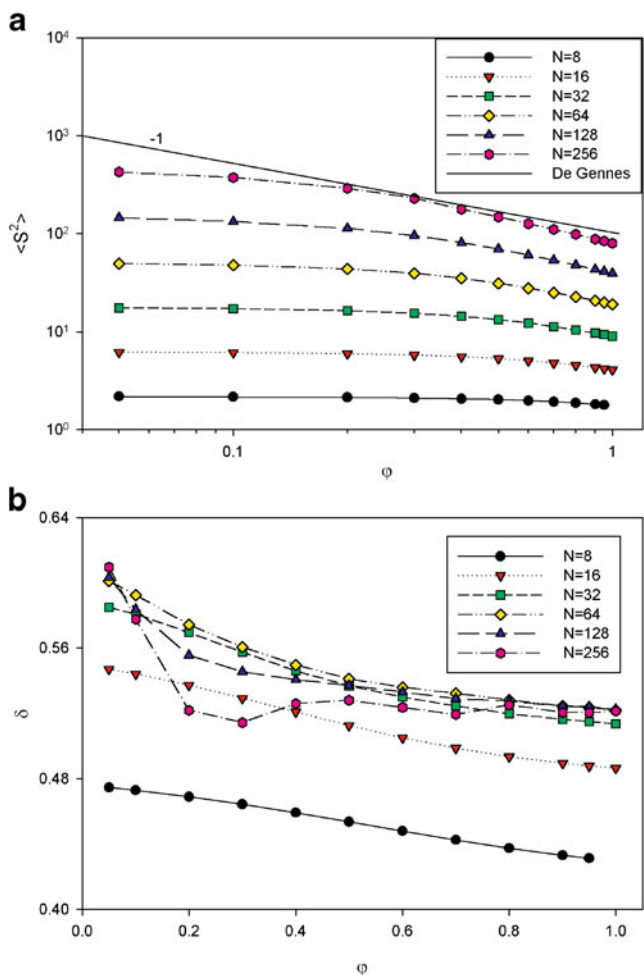


Fig. 1 a–b The mean squared radius of gyration per bead $\langle S^2 \rangle / N$ (a) and the asphericity factor δ (b) as functions of the polymer concentration φ

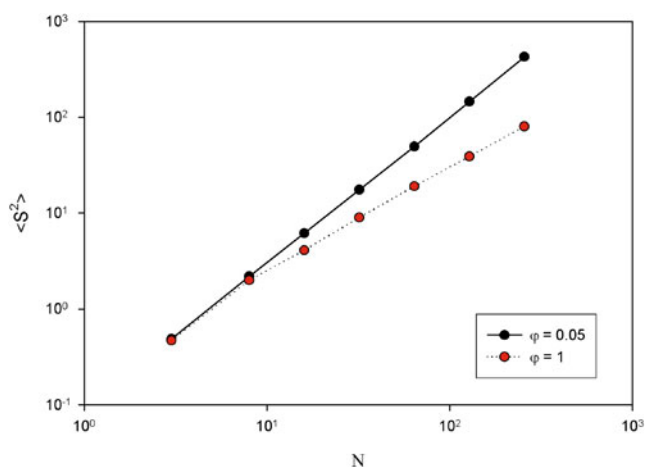


Fig. 2 The mean squared radius of gyration $\langle S^2 \rangle$ as a function of the polymer length N

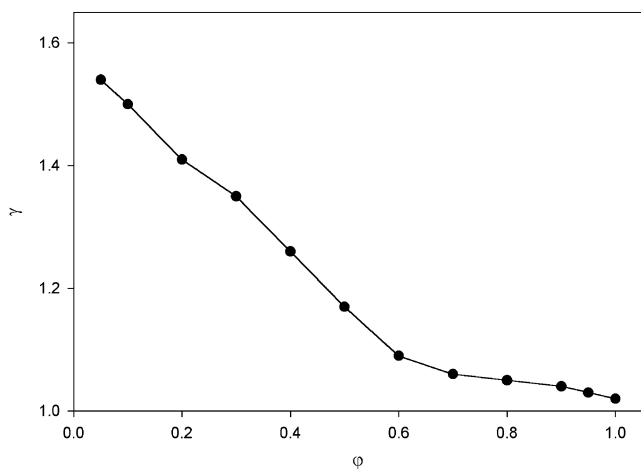


Fig. 3 The exponent γ as a function of the polymer concentration ϕ

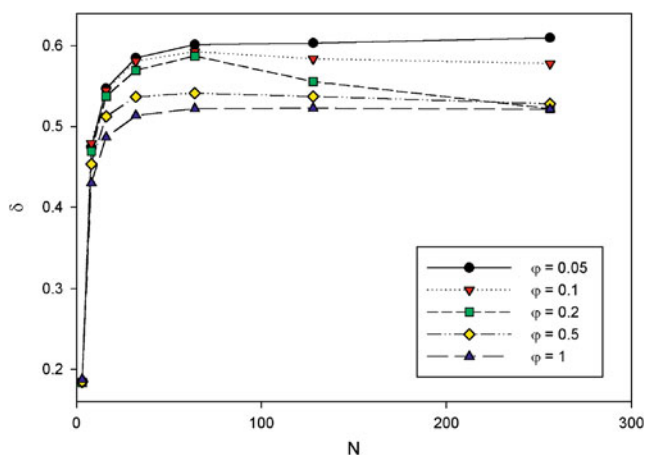


Fig. 4 The asphericity factor δ as a function of the polymer length N

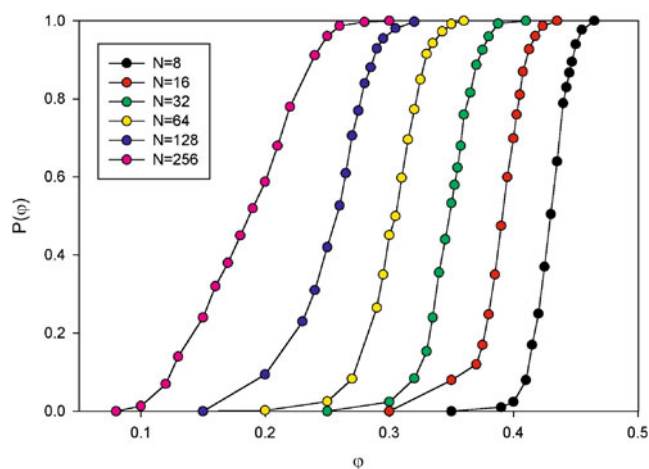


Fig. 5 The percolation probability P as a function of the polymer concentration ϕ . The chain lengths are given in the inset

the curve exhibits a minimum at polymer concentrations between $\phi=0.2$ and 0.4 (for chains with $N=128$ there is a different curve shape in the same concentration range). The presence of such a minimum can be explained by microphase separation in these systems [29]. It is important to note that the percolation thresholds are located within this density range [21].

The changes in polymer size with chain length are presented in Fig. 2 for low ($\phi=0.05$) and high ($\phi=1$) polymer concentrations. The mean size of a single macromolecule scales as N^γ , and the exponent γ changes from 1.54 ± 0.05 to 1.02 ± 0.02 when the concentration of polymer is increased from 0.05 to 1. This behavior is in good agreement with generally accepted values for two-dimensional polymeric systems, where theory predicts $\gamma=3/2$ and 1, respectively [10]. Figure 3 presents the dependence of the exponent γ on ϕ across the entire density range. The changes are monotonous and the influence of the density on the exponent is

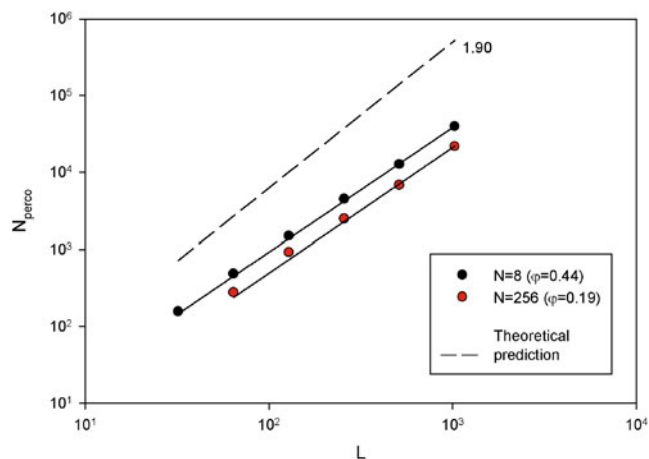


Fig. 6 The number of beads in the percolation cluster as a function of the size of the system. The chain lengths and the polymer densities are given in the inset

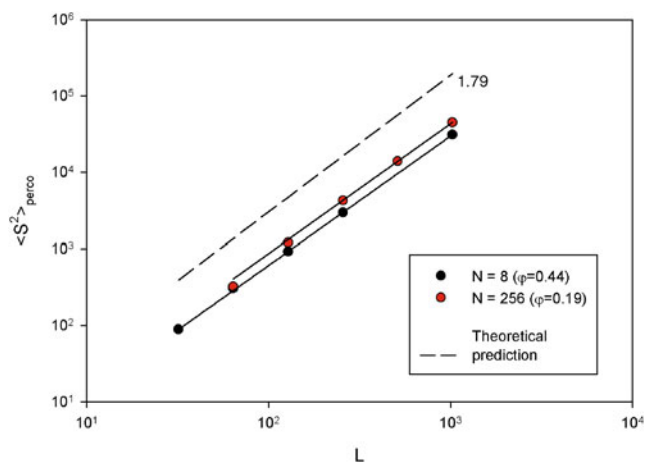


Fig. 7 The size of the percolation cluster as a function of the size of the system. The chain lengths and the polymer densities are given in the inset

considerably stronger for $\varphi < 0.6$. The dependence of chain asphericity on chain length is presented in Fig. 4 for some polymer densities. The chain asymmetry increases with the chain length, and the shape of longer polymers ($N \geq 128$) remains almost constant for densities $\varphi > 0.5$ and δ approaches a constant value of 0.522. The polymer shape only depends on chain length for short polymers, but chain asymmetry grows rapidly in this region. Greatly increasing the polymer concentration (from $\varphi = 0.05$ to $\varphi = 1$) makes the chains more spherical, although these changes in shape are rather small, thus confirming previous findings [31].

The structure of the entire polymer system at the percolation threshold is the next issue under consideration. The percolation threshold was calculated from the behavior of the percolation probability. This probability was simply the ratio of the number of states in which percolation occurred to the total number of generated configurations. Figure 5 presents examples of the percolation probability as a function of the polymer density. The percolation threshold c_p can be determined by fitting the following function [9]:

$$P(\varphi) = 1 - \left(1 + \exp\left(\frac{\varphi - c_p}{a}\right) \right)^{-1}, \tag{6}$$

where P is the percolation probability and a is another constant that determines the slope of $P(\varphi)$. As $a \rightarrow 0$, this function reduces to a step function. Equation 6 was used as $dP/d\varphi$ was expected to behave like the Gaussian distribution [33]. A finite-size scaling analysis was then performed. The extrapolation of the threshold to the thermodynamic limit was achieved by fitting to the scaling relation

$$|c_p(L) - c_p(\infty)| \sim L^{-1/\nu}, \tag{7}$$

where $c_p(L)$ and $c_p(\infty)$ are percolation thresholds for the Monte Carlo box $L \times L$ and for the infinite system, respectively, and ν is a critical exponent (theoretical predictions indicate that $\nu = 4/3$) [1, 21, 33]. There is also an alternative method, where the percolation threshold is estimated as the intersection of the two probability curves for two box sizes [34]. The percolation threshold of the solvent

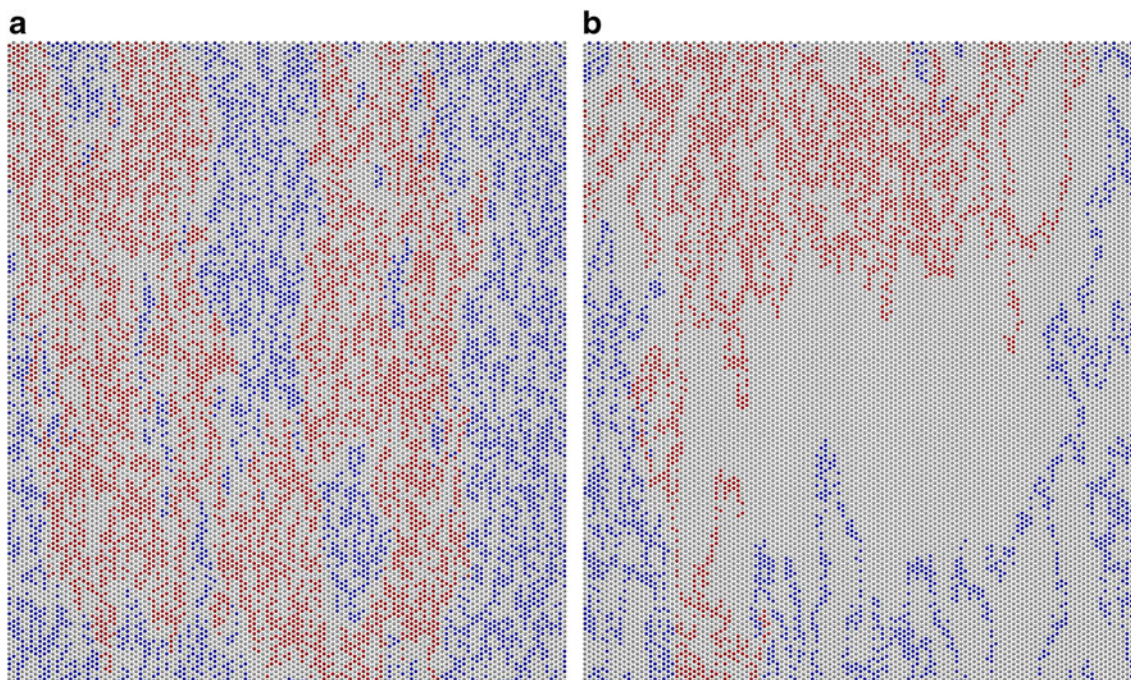


Fig. 8 a–b Snapshots of a percolated system at a concentration just above the percolation threshold. The percolation clusters are shown in red while the remaining chains are shown in blue. a $N=8$, b $N=256$

can be determined in a similar way from the solvent percolation probability P_s as a function of the solvent concentration $1 - \phi$. The percolation threshold decreases sharply with increasing chain length. The percolation threshold appeared to decrease with increasing chain length, from $c_p=0.466$ (for $N=3$) to $c_p=0.188$ (for $N=256$) [21]. However, in general, the percolation threshold was found to depend strongly on the local chain structure. This threshold is a simple function of the polymer local density $N/\langle S^2 \rangle$, and it scales as $(N/\langle S^2 \rangle)^b$. Two scaling regimes were found: $b=0.67$ for longer chains and $b=0.27$ for shorter chains. This result is different from De Gennes' predictions, where $b=1$ [10, 21]. The percolation of polymer chains (and solvent molecules) belongs to the same universality class as the ordinary percolation problem [35].

Figure 6 presents the mean number of polymer beads in the percolation cluster as a function of size of the system at the percolation threshold. The number of beads N_{perco} scales with the size of the box as L^D where the scaling exponent D is close to 1.6 in all cases under consideration: $D=1.62 \pm 0.02$ for $N=8$ and $\phi=0.44$, and $D=1.63 \pm 0.04$ for $N=256$ and $\phi=0.19$. This exponent is a fractal dimension of the percolating cluster and its value is lower than theoretical predictions for single beads (points), where $D=91/48 \approx 1.90$ [1]. Computer simulation of short chains on a square lattice resulted in D values of between 1.836 and 1.922 [33]. The size of the percolation cluster can be expressed via the mean squared radius of gyration $\langle S^2 \rangle_{\text{perco}}$. The dependence of the percolation cluster size on the size of the system is presented in Fig. 7. Scaling also occurs in this case: the size of the percolation cluster depends on the size of the system as L^d where the scaling exponent $d=1.69 \pm 0.01$ for $N=8$ and $\phi=0.44$, and $d=1.70 \pm 0.01$ for $N=256$ and $\phi=0.19$. Simulations of short chains (consisting of up to 10 segments) on a square lattice gave slightly higher values for this exponent—between 1.71 and 1.79 [33]—while theoretical predictions for single beads (points) described this exponent as being the ratio of two critical exponents γ and ν , and thus $d=\gamma/\nu=43/18:4/3 \approx 1.79$ [1].

In Fig. 8, we present examples of a percolated polymer system just above the percolation threshold: at $\phi=0.44$ for short chains ($N=8$) and at $\phi=0.19$ for long chains ($N=256$). One can see that for long chains percolation can be achieved through extended conformations (at low polymer density the chains can be extended, as they only rarely interact), and thus the macromolecules are anisotropic. Large areas consisting of pure solvent are also visible. Short chains are observed at considerably higher densities and thus are rather more compact and isotropic.

This work focused on studying the properties of a two-dimensional macromolecular system across a whole

range of polymer concentrations. It was previously shown that the random sequential adsorption technique is not efficient for long, flexible chains [7, 21]. Therefore, an alternate calculation method was employed. A coarse-grained model of a polymer solution was used, and the mean properties of the system were determined via the cooperative motion algorithm. It was shown that the average polymer size $\langle S^2 \rangle$ obeys De Gennes' prediction that $\langle S^2 \rangle \sim \phi^{-1}$ for longer chains and at moderate and high polymer concentrations ϕ . The scaling of the macromolecular size was exactly as predicted previously by theories and simulations; i.e., between 3/2 and 1. The dependence of the chain asphericity factor on the polymer concentration suggests that microphase separation occurs for longer chains, although all of the systems under consideration were athermal. The values of the critical exponents appeared to be slightly lower than predicted by small-object theory.

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