

The Influence of Temperature on the Percolation Threshold in Two-Dimensional Polymer Systems

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Received: 11 December 2020; revised: 23 December 2020; accepted: 24 December 2020; published online: 29 December 2020

Abstract: The structure of a two-dimensional film formed by strongly adsorbed polymer chains was studied by means of Monte Carlo simulations. We investigated the percolation in systems consisting of flexible polymer chains. A coarse-grained polymer chains representation was assumed and polymer chains were represented by linear sequences of lattice beads. The positions of these beads were restricted to vertices of a two-dimensional square lattice. Properties of the model system were determined by means of Monte Carlo simulations with a refined Verdier-Stockmayer sampling algorithm. Percolation thresholds macromolecules were determined. The methodology concerning the determination of the percolation thresholds for an infinite chain system was discussed. The influence of the chain length and the temperature on the percolation was discussed. It was shown that the introduction of long-range interactions changes the behavior of the percolation threshold dramatically. The percolation threshold initially decreases with the chain length while for longer ones it is stable.

Key words: lattice models, Monte Carlo method, percolation, polymer films

I. INTRODUCTION

Percolation is a phenomenon in which a cluster formed by given objects becomes infinite, which means that in real systems it spans from one border of the system to another [1]. One of theoretical procedures is to determine the percolation threshold in a given system, i.e., the minimum concentration of objects at which the percolation takes place. The percolation theory has a lot of applications, especially in disordered systems and porous media. Computer simulation of this process can usually be realized by Random Sequential Adsorption (RSA) [2–4] and Monte Carlo simulations [5, 6]. The lattice approximation is commonly used for the consideration of the RSA percolation in many systems in order to suppress the degree of freedom and for computational purposes. The most popular objects studied using the RSA method up to date were stiff rods (needles) [7–9]. The per-

colation and jamming (the maximum coverage of surface) thresholds were determined for such systems. Systems containing other elongated objects (ellipsoids, rectangles) were also studied and shown that the aspect ratio was a crucial parameter that determined the percolation threshold [10–12]. The behavior of polymer chains which can change their conformation size and shape instantaneously was found quite different from stiff objects. The process of the adsorption of stiff and flexible macromolecules on surfaces was also realized using the RSA procedure [6, 13–21]. Studies of mixtures of short extended objects (oligomers) on a triangular lattice by means of the RSA method were also recently performed by the RSA method [15, 16]. A different category of models of adsorption, i.e., three-dimensional polymer chains was the subject of many studies [22] employing computer simulations [23, 24] and theoretical considerations [25–27]. Detailed studies on the universality of the percola-

tion process and the influence of the lattice representation on it has been performed recently [5, 16, 19]. Mixtures of small objects (oligomers) of a different shape were also studied by means of the RSA method [15] while mixtures of stiff rods and flexible chains appeared to be tractable by a theory (a connectedness Ornstein-Zernike formalism) [28].

An alternative method for studying the percolation in macromolecular systems was recently proposed using the cooperative motion algorithm [29, 30]. The influence of the presence of explicit solvent molecules, analysis of the clusters formed by macromolecules and confirmation of the universal critical behavior of these systems were the main results discussed in these works [5]. These studies concerned athermal systems and up to date the influence of the temperature on the percolation was the subject of a single publication [13]. In this paper we present some initial results of studies of the percolation in two-dimensional systems consisting of flexible linear polymers. Chains were represented as sequences of identical beads and positions of these beads were restricted to vertices of a square lattice. A simple square-well polymer-polymer potential was introduced into this model. The main question addressed was the influence of the temperature on the percolation in such systems.

II. THE MODEL AND THE METHOD

Due to limitations of the RSA method applied to systems of flexible chains we decided to study the percolation of macromolecules by means of the dynamic Monte Carlo simulations [6]. We used a coarse-grained representation of polymer chains (with all atomic details suppressed and with beads representing several chemical mers) and a lattice approximation. The presented results concern simulations on a two-dimensional square lattice with the coordination number equal to 4 and with the bond length equal to 1. Each chain in the system consisted of N beads (monodisperse system) and the number of chains n was also constant during the simulation.

Each lattice site is allowed to be occupied by one chain bead, which corresponds to short-range repulsions and it means that the chains could not cross each other. Long-distance interactions were assumed in a form of a contact square-well potential of a pair of polymer beads:

$$V(r_{ij}) = \begin{cases} \infty & \text{for } r_{ij} < 1, \\ \varepsilon & \text{for } r_{ij} = 1, \\ 0 & \text{for } r_{ij} > 1, \end{cases} \quad (1)$$

where r_{ij} is a distance between i^{th} and j^{th} beads. The reduced temperature T is proportional to $1/\varepsilon$. No local potential was introduced and therefore chains were fully flexible. Periodic boundary conditions were imposed in both directions. The problem concerning the finite size of the Monte Carlo box in our studies will be discussed below in the next Section.

In order to generate a series of independent configurations of the system we used Monte Carlo simulations with an algorithm based on local and non-local changes of chain's conformation. The set of these local moves consisted of 1-bead motion, 2-bead motion, 1-bead end modification and 2-bead end modifications [31]. Additionally the algorithm was enriched with pivot motions, where fragments of chain having random length are randomly rotated, and the reptation motion. These two last micromodifications are essential for the ergodicity of the process and make the relaxation of the system considerably faster [32]. A polymer bead attempted move and was accepted/rejected due to geometrical constraints and the Metropolis criterion. A Monte Carlo cycle was defined as one attempt of each motion applied in average to one bead. An initial polymer's conformation was constructed in a process of the simultaneous growing and the equilibration procedure: a system containing n chains, each consisting of N beads, was eventually built. For each system under consideration 20–25 independent Monte Carlo simulation runs were performed. Each simulation run consisted of 10^8 – 10^{10} cycles and at the start of the each simulation run the equilibration run was performed, which lasted 10^6 – 10^9 cycles. The criterion of the equilibration of the system was the stability of some time-mean parameters of the system, such as the end-to-end distance and the radius of gyration. When neighboring chains form a continuous path from one system edge to the opposite one, this is called percolation. In order to recognize the moment of percolation a Newman-Ziff algorithm based on the union-find procedure was applied [33].

III. RESULTS AND DISCUSSION

Simulations were performed for a chain length N varied between 3, 5, 10, 25, 50, 75 and 100. In order to determine the influence of the size of the system on the values of the percolation threshold simulations were performed in the Monte Carlo box with various edges: $L = 50, 100, 200, 1000$ and 2000 for each set of parameters N , n and T . The polymer concentration was defined as a fraction of lattice sites occupied by chains, i.e., the ratio of the number of polymer beads to the total number of sites in the system: $\varphi = nN/L^2$. The structure of a strongly adsorbed polymer layer was frequently the subject of theoretical and simulation studies [22] and is well-known, which is why we focus on the percolation problem only.

Percolation probability was determined as the ratio of the number of configurations where the percolation occurred to the total number of generated configurations. Fig. 1 presents the percolation probability P as a function of the polymer density φ for chain $N = 10$ at some different temperatures. All $P(\varphi)$ curves are typical, i.e., S-shaped, and the decrease of the temperature shifts the curve towards lower polymer concentrations. The size of short chains weakly depends on

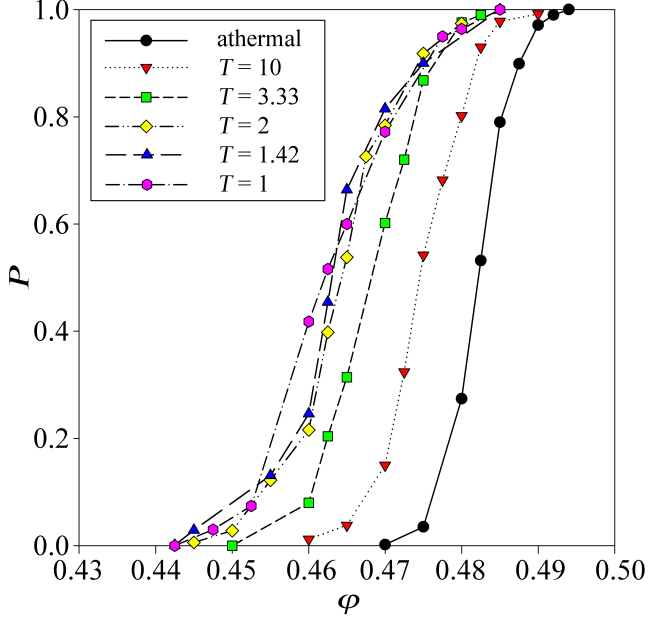


Fig. 1. The percolation probability P as a function of the polymer concentration φ . The case of the Monte Carlo box $L = 1000$ and chain length $N = 10$. The temperatures are given in the inset

the temperature and thus all curves exhibit similar slope contrary to the similar curves for athermal chains where lengths were varied [5]. Qualitatively the same behavior of the percolation probabilities was found for other athermal two-dimensional polymer chains: short chains on a square lattice [16, 17, 34], long linear chains with explicit solvent molecules on a triangular lattice [5] and for off-lattice hard ellipsoids [10]. This behavior of the percolation probability is similar to that found for stiff elongated objects (needles) in the RSA process [8, 9, 14].

The percolation threshold can be determined from an S-shaped probability curve as its inflection point. In order to calculate the value of the thresholds for an infinitely large system the following procedure is proposed. The inflection point on a $P(\varphi)$ curve is determined using the following fitting [16, 34]:

$$P(\varphi) = 1 - \left[1 + \exp\left(\frac{\varphi - c_p}{a}\right) \right]^{-1}, \quad (2)$$

where a is a constant that determines the slope of the curve; when $a \rightarrow 0$ the curve reduces to the step function (which should be observed for an infinitely long chains). In the next step the finite-size scaling analysis was made. The calculated percolation threshold was extrapolated to the thermodynamic limit was done by fitting to the scaling relation:

$$|c_p(L) - c_p(\infty)| \sim L^{-1/\nu}, \quad (3)$$

where $c_p(L)$ and $c_p(\infty)$ are percolation thresholds for the Monte Carlo box $L \times L$ and for an infinite system, respectively. The critical exponent ν was assumed to be equal to

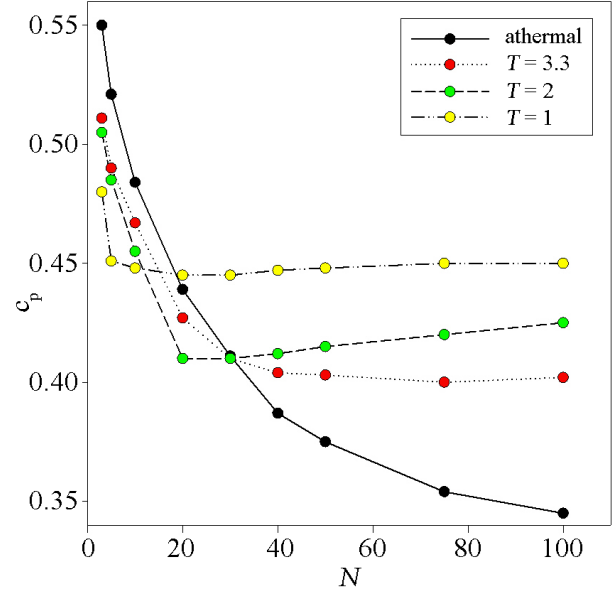


Fig. 2. The percolation threshold c_p as a function of the chain length N . The temperatures are given in the inset

4/3 as elucidated from theoretical considerations [1] and conformed in simulations of polymer systems [5].

The changes of the percolation threshold with chain length are presented in Fig. 2. One can observe that the threshold of athermal chains (no attractive interactions) decreases with the increase of the length of the macromolecule. A formula describing the influence of the chain length on the percolation threshold was recently proposed [19]

$$c_p = c_p^* + \Omega \exp\left(-\frac{\kappa}{N}\right), \quad (4)$$

where c_p^* , Ω and κ are fitting parameters and c_p^* corresponds to the percolation threshold for an infinitely long chain. The calculations based on their data gave $c_p^* = 0.461 \pm 0.001$ but it must be remembered that they studied very short chains only ($N \leq 15$). Fitting of our athermal data gives a similar result for short chains ($c_p^* = 0.447$) while quite a different result for chains in the entire range of the chain lengths under consideration ($c_p^* = 0.261$). Thus, the parameters of the above equation depend on the chain length and the formula is not valid and should be rejected. It must be noticed that c_p^* for athermal chains does not scale as N^{-a} but this relation is apparently stronger. The same results were recently obtained by means of the RSA method [16] while percolation thresholds of short self-avoiding walks scales as $N^{-0.1}$ [16].

The behavior of chains with the attractive potential presented in Fig. 2 is quite different. For short chains the percolation threshold decreases with the chain length in a similar way as athermal chains do. The decreases of the temperature (or the increases of the strength of attraction) shifts this part of the $c_p(N)$ curve lower. This behavior can be explained by

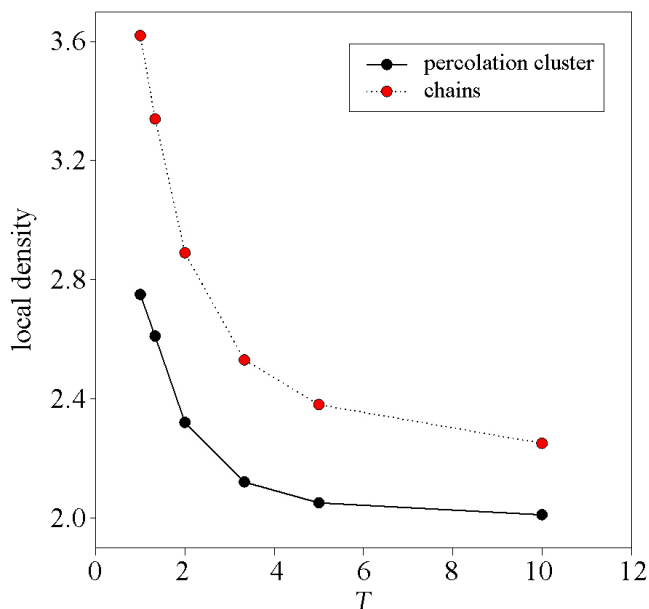


Fig. 3. The local density in a polymer chain and in the percolation cluster as functions of the temperature. The case of chain $N = 50$. The values of local density a polymer chain and in the percolation cluster are marked in red and black, respectively

the fact that the size of chains decreases during the annealing and the number smaller (more compact and more dense) chains required to form a large cluster spanning the space has to be higher. For longer chains the percolation threshold becomes almost constant. The crossover to this regime depends strongly on the temperature: the lower the temperature is, the shorter an initial regime is where the threshold decreases with N . The plateau visible for longer chains means that the formation of clusters is rather governed by the temperature than by the polymer concentration: at lower temperature there are again more compact objects. The influence of the temperature on the percolation threshold showed by Kondrat [13] and concerned systems of semi-flexible chains was even more complicated: thresholds exhibit a minimum for certain temperatures. This study suggests that a certain shape of a flexible chain exists where the percolation threshold achieves its minimum.

Fig. 3 presents the changes of the local polymer density in both chains and percolation clusters. The local densities were determined near the percolation thresholds. They were calculated as $N/\langle S^2 \rangle$ for chains and $N_{\text{per}}/\langle S^2 \rangle_{\text{per}}$ for clusters, respectively. N_{per} is the number of polymer beads in the percolation cluster, $\langle S^2 \rangle$ is the mean squared radius of gyration of a polymer chain and $\langle S^2 \rangle_{\text{per}}$ is the mean squared radius of gyration calculated for the percolation cluster. One can observe that in spite of the fact that for attractive chains the percolation thresholds exhibit two distinguishable regimes but the dependencies of the chain length on local both densities do not. Both densities increase during the annealing although density inside a chain

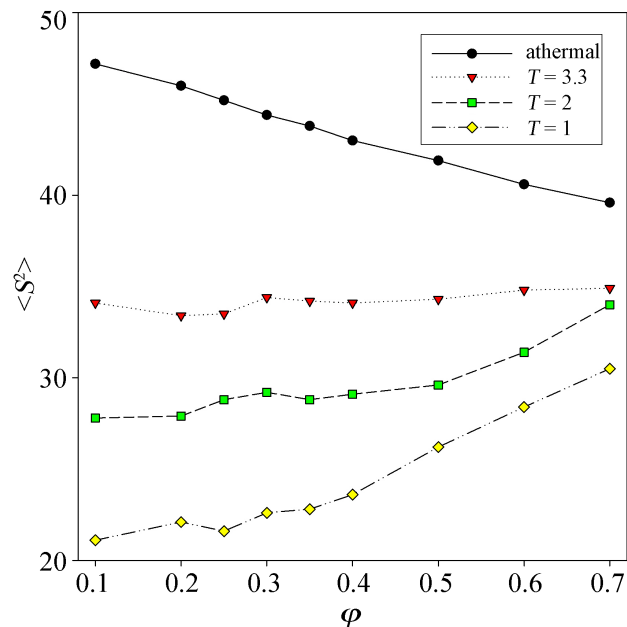


Fig. 4. The mean-squared radius of gyration $\langle S^2 \rangle$ as a function of the polymer density φ . The temperatures are given in the inset

increases slightly faster. The sampling algorithm used in our simulations is not efficient at temperatures $T < 1$ and thus we cannot see the stabilization of the density. Additional information can be obtained by the referencing changes of the percolation threshold to changes in size of macromolecules. In Fig. 4 we show changes of an average chain size (represented as usual by the mean-squared radius of gyration) as a function of polymer concentration for some temperatures. In the athermal system the size of chains decreases with the polymer concentration as φ^{-1} , which is expected based on theoretical considerations [35]. One can observe that systems with polymer-polymer attractive interaction behave differently than the athermal system as the size of chains increases here with the polymer concentration. The stronger the polymer-polymer attraction, the smaller the size of chains and the size of chains increases with the polymer density. No rapid changes of size at densities corresponding to dramatic changes of the percolation thresholds were found. The sequence of the chain sizes is found to be inversely proportional to the percolation threshold. Fluctuations of $\langle S^2 \rangle$ near $\varphi \approx 0.3$ can be attributed to a crossover where intrachain interactions prevails inter-chain interactions but they require further studies.

Figs. 5(a)–7(a) show examples of configurations of the systems studied. These snapshots concern polymer chains of an intermediate length ($N = 50$) near the percolation threshold for three different temperatures: for athermal system (an infinite temperature), high temperature and low temperature. Comparing the configurations of the polymer systems one must remember that the snapshots were taken at different densities, which is clearly visible as the percolation thresh-

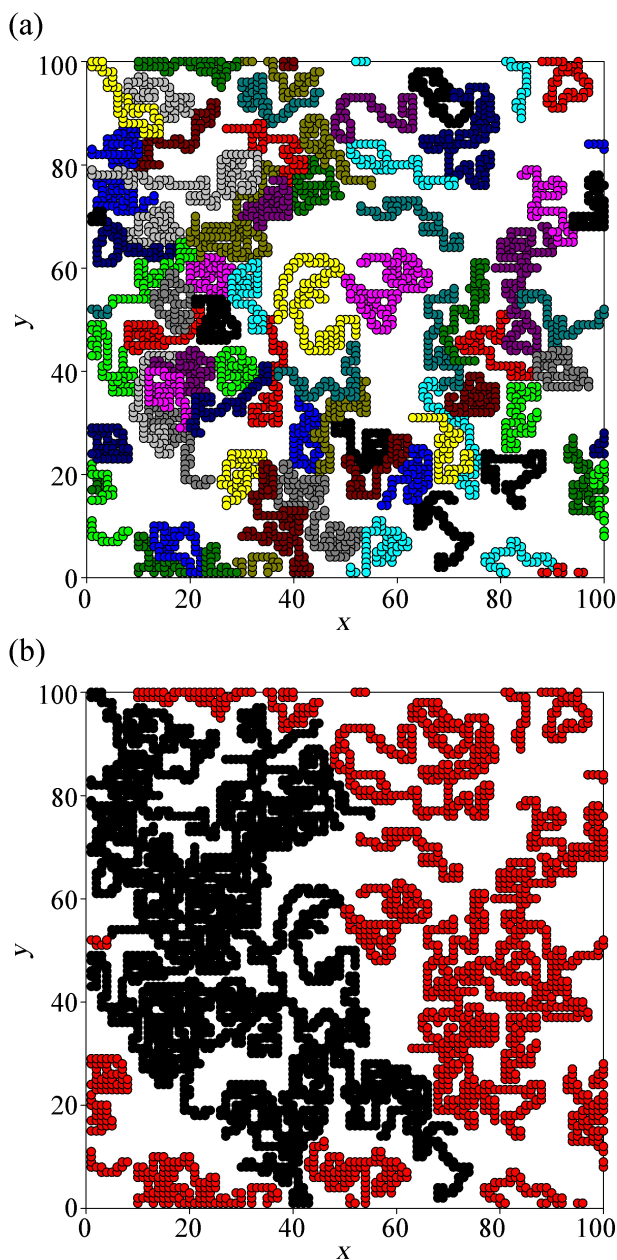


Fig. 5. Snapshots of the athermal system at the percolation threshold for chains $N = 50$: chains (a) and clusters (b). The percolation cluster is marked in black while all remaining clusters are in red

old changes here from 0.375 (the athermal case) to 0.348 ($T = 1$). The differences in polymer concentrations are visible but one can see in Figs. 5(a)–7(a) chains collapsed and partially collapsed at lower temperature and full collapsed ones at low temperature (although even collapsed chains can interpenetrate). The size of chains decreases with strength of the polymer-polymer attraction (or increases with the temperature), which confirms changes presented in Fig. 4. Figs. 5(b)–7(b) present percolation clusters for the same configurations as presented in Figs. 5(a)–7(a). Percolation clus-

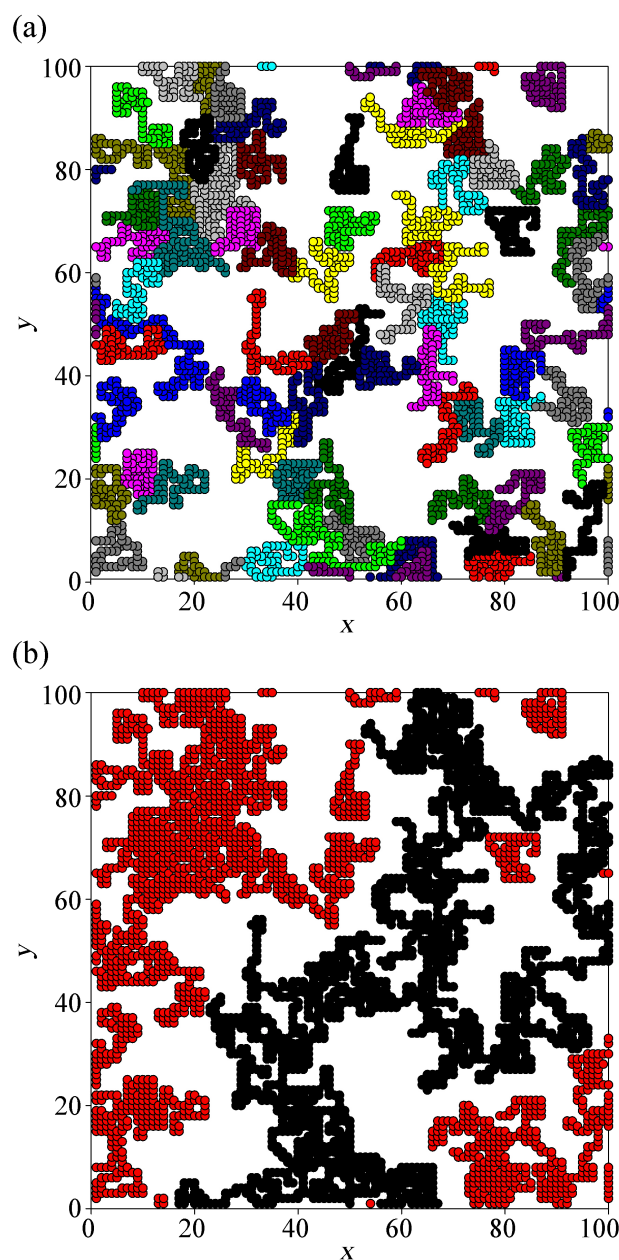


Fig. 6. Snapshots of the system at the percolation threshold for chains $N = 50$ at $T = 3.33$: chains (a) and clusters (b). The percolation cluster is marked in black while all remaining clusters are in red

ters are the largest among other clusters and their size increases considerably with the chain length and decreases during the annealing. One can also observe the presence of non-percolated islands inside the percolation cluster and the decreasing number of these non-percolating islands while going towards lower temperature. It should be noted that in lattice models the mobility of collapsed structures is limited and therefore further studies should also be employed to other models and simulation tools.

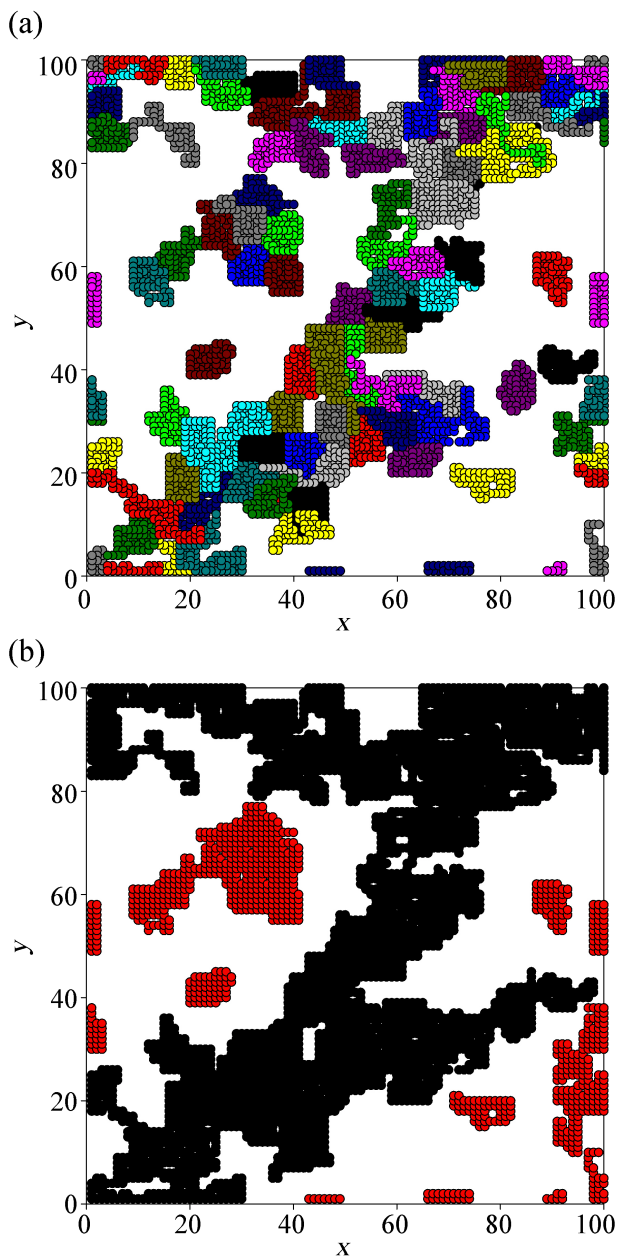


Fig. 7. Snapshots of the system at the percolation threshold for chains $N = 50$ at $T = 1$: chains (a) and clusters (b). The percolation cluster is marked in black while all remaining clusters are in red

IV. CONCLUSIONS

A simple polymer model was developed in order to study the influence of the temperature on the percolation in systems containing linear flexible macromolecules. In this model the polymer chains were represented by sequences of identical beads and the positions of these beads were restricted to vertices of a square lattice. One-parameter simple potential of interaction between polymer beads was assumed

in order to introduce the temperature into the system. Dynamic Monte Carlo simulations with a Metropolis-like algorithm were performed in order to determine the properties of the model.

The application of a dynamic Monte Carlo simulation method allowed efficient studies of the percolation in the system of flexible chains, which was almost impossible using the RSA method. Our results indicate that the percolation threshold for polymers with attractive potential behave in a different way comparing to the athermal case. The percolation threshold decreases for shorter chains only and this decrease is rather rapid. It appeared that for longer chains the percolation threshold almost does not depend on the chain length. The thresholds decrease during the annealing due to compact and more spherical chains at these conditions. Percolation clusters are more dense and smaller at lower temperatures although their densities are considerably lower comparing to those of single chains.

Acknowledgment

The computational part of this work was done using the computer cluster at the Computing Center of the Department of Chemistry at the University of Warsaw.

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