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2008 J. Phys. A: Math. Theor. 41 025004

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Two-dimensional polymer networks near percolation

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Received 20 September 2007, in final form 14 November 2007

Published 19 December 2007

Online at stacks.iop.org/JPhysA/41/025004

Abstract

We report an extensive finite-size study of polymer networks near the percolation threshold, using numerical techniques. The polymers are modeled by random walks occupying the bonds of a two-dimensional square lattice. We measure the percolation threshold and critical exponents of the networks for various polymer lengths. We find that the critical occupation probability is a decreasing function of the polymer length, and the percolation of polymers with a fixed polymer length belongs to the same universality class as ordinary bond percolation. By adding particles to the lattice cells we can study the diffusion process in polymer networks. Measuring the current near percolation, we observe that its critical exponent is also independent of polymer length.

PACS numbers: 05.40.Fb, 64.60.Ak, 61.41.-e, 75.40.Mg

1. Introduction

Percolation is a well-studied phenomenon that has numerous applications in various fields [1]. In previous studies it was often assumed that the probability of a bond, or site, being occupied is independent of its surroundings. This assumption simplifies the problem, but is not always satisfied in reality. The introduction of correlations into the percolation problem dates back to the 1970s, when Duckers [2, 3] studied site percolation with correlations. These early simulation data seemed to suggest a non-monotonic behavior of the percolation threshold as a function of the correlation strength. Since then, percolation with various types of correlations has been investigated by many authors. In some cases, the emphasis was placed on non-universal properties, such as the percolation threshold, while in others the focus was on universal critical behavior. To mention just a few studies, the ‘environmental percolation’ model was used to describe some diluted magnetic systems [4]. The critical properties of ‘site-bond-correlated’ percolation were studied on two-dimensional lattices, and the associated exponents were found to be the same as those of the usual percolation problem [5]. Research on ‘granular percolation’ was also carried out [6, 7]. In these studies, the grains are grown around seeds up to a specified number of occupied nearest neighbors, and ‘larger’

grains are considered to have ‘stronger’ correlations. It was claimed that the percolation threshold, as a function of the grain size, also followed a non-monotonic relation [6, 7]. Self-avoiding objects, in the form of grains or linear chains, were also considered [8, 9]. Percolation of polymers, modeled by non-interacting random walks, was studied by two of us and collaborators [10, 11].

In the following, we continue this work and focus specifically on the extrapolation to infinite system size. Since our study was motivated by quenching polymer melts into thin films [12], we will model our polymers by Gaussian walks, an approximation which is justifiable on experimental grounds [13, 14]. Specifically, we consider non-interacting random walks on the bonds of a two-dimensional square lattice. For a given system, all polymers have a fixed length ℓ (number of segments in a polymer). Since the walks are non-interacting, any given bond can be occupied by multiple segments, belonging to the same or a different polymer. In experimental setups, a convenient control parameter is the mass density, ρ . In our case, ρ is just the mass of a segment (assumed to be unity here), multiplied by the number of polymer segments and divided by the total number of bonds on the lattice, N (i.e., the ‘volume’ of our system). Defining M as the number of polymers in the system, we have

$$\rho = \frac{M\ell}{N}. \quad (1)$$

In the theory of percolation, the traditional control parameter is the occupation probability p , being the fraction of occupied bonds in the network:

$$p = \frac{N_o}{N}, \quad (2)$$

where N_o is the total number of bonds occupied by *one or more* segments. Due to multiple occupancies, $p \neq \rho$ in general. Similar to the ordinary percolation problem, the system percolates—i.e., there is an infinite cluster of occupied bonds—when p (or ρ) is greater than a characteristic critical value. Critical exponents can also be defined in the same way as in the ordinary bond percolation and measured numerically. One of our goals here is to measure the percolation threshold and the critical exponents accurately.

Our study was motivated by experiments on gas permeation through amorphous polymer films. Such experiments apply constant pressure to one side of the film and measure the gas current in the steady state [12]. In our simulations, gas molecules are modeled as particles occupying the *cells* of the lattice. Particles are allowed to cross unoccupied bonds freely (i.e., with unit probability). In contrast, occupied bonds may only be crossed with a reduced probability, $q < 1$, reflecting the presence of an energy barrier for this process. This simple model provides a baseline against which more complex models for the real experimental situation can be compared.

If the crossing probability q models an energy barrier, then it is also related to the temperature in real experiments. The discussion of polymer percolation is relevant in the zero-temperature limit where the barriers become completely insuperable. Hence, at $q = 0$, a gas current can flow only if the system is not percolated.

A closely related model is the random resistor network which has been intensively studied. The key difference lies in the spatial distribution of the resistors, which is usually assumed to be uncorrelated. Hence, our study introduces a specific type of correlations—namely, those associated with random walks—into the study of resistor networks. Below, we ask whether these correlations lead to any fundamental (i.e., universal) changes in the resistance of the network near the percolation threshold.

The remainder of this paper is organized as follows. In section 2 we present our numerical data. Specifically, we measure the percolation threshold p_c and some of the critical exponents

for several polymer lengths. Section 3 is dedicated to the lattice-gas model. We measure the current (or conductivity) near percolation and discuss its associated critical exponent. In particular, we explore the relevance or irrelevance of the polymer length, ℓ . We conclude with some discussions in section 4.

2. Percolation thresholds and critical exponents

In the previous study [11], numerical simulations indicated that the polymer networks percolate when the density of polymers is high enough, and the percolation thresholds were roughly estimated. However, the estimate was based on systems up to 256^2 . With no attempts at finite-size scaling, it was not possible to come to quantitatively reliable conclusions about the percolation threshold, and so, no extrapolation to infinite systems could be undertaken. In the simulations reported here, we use the famous Hoshen–Kopelman cluster counting algorithm [16] which allows us to boost the system size up to 8192^2 . With the data from these significantly larger system sizes, we can exploit finite-size scaling techniques to arrive at much more accurate estimates for the percolation thresholds for infinite systems.

The results of position-space renormalization group theory for percolation [15] can be readily applied to our polymer system. The theory predicts that

$$p_c - p^*(L) \sim L^{-1/\nu}, \quad (3)$$

where p_c is the critical occupation probability for the infinite system, ν is the correlation length exponent and $p^*(L)$ is the ‘fixed point’ for systems with linear size L , i.e., the occupation probability at which the fraction of percolated configurations $f(p^*)$ equals p^* . One can measure $p^*(L)$ for varying L and then derive p_c and ν by fitting the data to equation (3). An alternate finite-size scaling relation for the fraction of percolated configurations $f(p, L)$ that can be used to roughly locate p_c is

$$f(p, L) = \tilde{f}[(p - p_c)L^{1/\nu}], \quad (4)$$

where $\tilde{f}(x)$ is a scaling function. This equation implies that $f(p_c, L)$ is a fixed value, $\tilde{f}(0)$, independent of the system size. Therefore the curves of $f(p, L)$ as a function of p have a common crossing at p_c , which can be used to locate p_c approximately. Figure 1(a) illustrates this feature for $\ell = 8$ polymer networks.

It is reasonable to assume that the correlation exponent ν does not depend on ℓ , since it is determined by the connectivity of clusters which is a long-range property. In a simulation, ν can be obtained directly, by scaling the maximum of $\partial f(p, L)/\partial p$. In practice, however, the quality of our data is not sufficient to arrive at a good estimate for ν , since the derivative exhibits rather large fluctuations. Hence, we proceed by *assuming* that $\nu = 4/3$ —which is rigorously known for $\ell = 1$ —holds for *any fixed* ℓ , and consider the quality of our finite-size scaling fits as a test for this assumption. Now, the test of equation (3) becomes a one-parameter fit, so that the critical threshold can be determined with much better accuracy which is essential to finding critical exponents. Our results of percolation thresholds for $\ell = 2, 4$ and 8 are listed in table 1. Equation (4) also implies data collapse near p_c , an example being figure 1(b) for the $\ell = 8$ case. Due to limited computer resources, we are only able to generate rough estimates for the percolation thresholds when $\ell > 8$, by locating the common crossing. These estimates, for ℓ up to 256, are shown in figure 2. The critical occupation probability, p_c , clearly decreases monotonically as ℓ increases. By contrast, the *critical mass density*, ρ_c , displays *non-monotonic* behavior. The two quantities are related by

$$p_c = 1 - \exp(-\rho_c b_\ell / \ell). \quad (5)$$

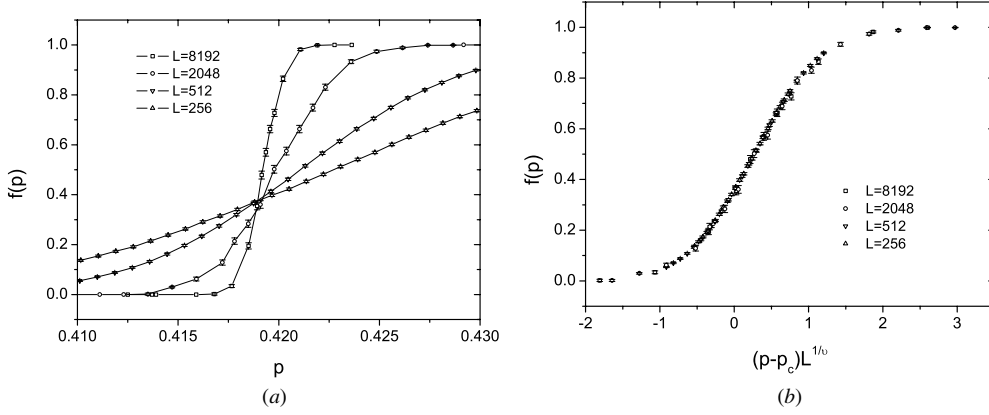


Figure 1. (a) Fraction of percolated configurations $f(p, L)$ as a function of the occupation probability p . The curves for different system sizes L intersect at p_c . (b) Data collapse of $f(p, L)$ for polymers of length $l = 8$.

Table 1. The critical occupation probability p_c and the critical exponents β , γ and τ as functions of the polymer length l .

l	p_c	β/ν	γ/ν	τ/ν
1	0.5(exact)	0.100(1)	1.796(2)	0.932(13)
2	0.47697(4)	0.101(1)	1.796(2)	0.932(12)
4	0.44892(6)	0.103(1)	1.794(2)	0.939(17)
8	0.41880(4)	0.102(1)	1.795(2)	0.955(16)

Here, b_ℓ is the average number of all occupied bonds for a single random walk on an infinite lattice. It can be found analytically via its generating function [17, 18]

$$\sum_{\ell=1}^{\infty} b_\ell z^\ell = \frac{4z}{(1-z)^2 [3 + (1+z)G(z)]}, \quad (6)$$

where $G(z) \equiv \int_k \int_p [1 - z(\cos k + \cos p)/2]^{-1}$ and $\int_k \equiv \int_{-\pi}^{\pi} \frac{dk}{2\pi}$ (for an infinite lattice). The precise expression is somewhat involved and not very illuminating. Instead of presenting it, let us simply remark that b_ℓ/ℓ is a dull, monotonically decreasing quantity: $1, 7/8, 5/6, \dots$ for $\ell = 1, 2, 3, \dots$. Intuitively, this result is not surprising: the longer a random walk, the higher is the probability for any particular bond to be traversed repeatedly. For our square lattice, the large ℓ behavior is more interesting, but beyond our scope here.

It is not obvious why the effect of multiple occupancy is so severe that it overcomes the decrease of p_c from $\ell = 1$ to 4. Nor it is clear why $\rho_c(\ell)$ varies so slowly for large ℓ . Now, it is easy to prove, exploiting the results in [17], that b_ℓ/ℓ in equation (5) vanishes as ℓ goes to infinity. This would lead us to the conclusion that $p_c \rightarrow 0$ at the long polymer limit, unless $\rho_c \rightarrow \infty$ which seems rather unlikely although it cannot be ruled out here. These issues deserve further investigation.

Although we believe that ν is $4/3$ for all fixed ℓ , there is no reason *a priori* that other exponents should also remain independent of the polymer lengths. For example, it is conceivable that the incipient infinite cluster for $\ell > 1$ might have a different fractal

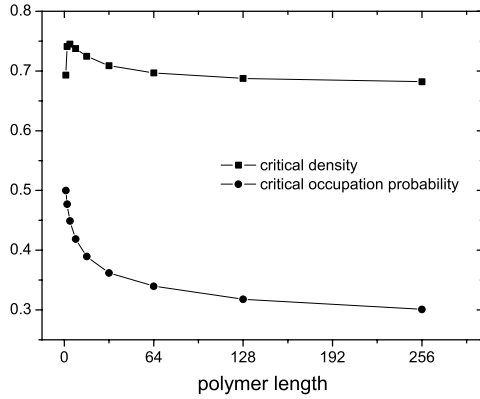


Figure 2. Percolation thresholds in terms of both the occupation probability and the mass density.

dimension $D = d - \beta/\nu$. We now use finite-size scaling relations to estimate the remaining critical exponents.

The percolation probability $\theta(p)$, defined as the probability that a bond belongs to the infinite cluster, is controlled by the critical exponent β near p_c ,

$$\theta(p) \sim (p - p_c)^\beta, \quad p > p_c. \tag{7}$$

Finite-size scaling then gives

$$\tilde{\theta}(p_c, L) \sim L^{-\beta/\nu}, \tag{8}$$

where $\tilde{\theta}$ is the mass of the largest cluster. The ‘mean cluster size’ $\chi(p)$ defines the exponent γ , via

$$\chi(p) \sim |p - p_c|^{-\gamma}. \tag{9}$$

The corresponding finite-size scaling relation is

$$\chi(p_c, L) \sim L^{\gamma/\nu}. \tag{10}$$

Using p_c obtained above, we can fit the simulation data for $\tilde{\theta}(p_c, L)$ and $\chi(p_c, L)$ to equations (8) and (10), respectively. The resultant critical exponents β/ν and γ/ν are also shown in table 1. The error bars are purely statistical.

For the ordinary percolation problem, $\beta/\nu = 5/48 \approx 0.104$ and $\gamma/\nu = 43/24 \approx 1.792$ are known exactly. Compared to our simulation results for $\ell = 1$, these values fall slightly outside the error bars, indicating that there may be small systematic errors. For the other ℓ 's, all exponents are indistinguishable from the $\ell = 1$ case, leading us to conclude that systems with $\ell > 1$ belong to the same universality class as the ordinary bond percolation.

3. Diffusivity near percolation

To study diffusion through polymer networks, we place particles into the lattice cells and let them diffuse. The rule is simple: a randomly chosen particle attempts to move to one of four neighboring cells. If the intervening bond is unoccupied (occupied), the attempt is accepted with probability 1 ($q < 1$). For our two-dimensional system, we keep the leftmost column as the source of particles, in which each cell is always filled with a particle. Similarly, particles at the opposing edge (the rightmost column) are removed immediately. A current J is

maintained by this concentration gradient and can be measured. This system is equivalent to a *correlated* random resistor network on a dual lattice, in which each resistor with conductance q corresponds to an occupied bond. The correlations are, of course, induced by the connectivity of the polymers. In order to study the properties near percolation of occupied bonds, we set $q = 0$. In other words, below p_c , the (infinitely insulating) resistors do not span the system (transverse to the concentration gradient). There is at least one cluster of ‘free paths’ from the left to the right, and a current flows.

Near p_c , the current approaches zero as a power law, governed by another critical exponent τ [19]:

$$J(p) \sim (p_c - p)^\tau. \quad (11)$$

The corresponding finite-size scaling relation is

$$J(p_c, L) \sim L^{-\tau/\nu}, \quad (12)$$

through which the ratio τ/ν can be measured. Following the same method as in [18] in systems with sizes up to 96^2 , our measured values of τ/ν for different polymer lengths are listed in table 1. Again, we find that the correlations considered here are irrelevant. Systems with different polymer lengths have statistically indistinguishable values of the critical exponent τ/ν .

One word of caution is in order. Our results for this exponent are systematically smaller than those found in high-precision Monte Carlo data for the case $\ell = 1$ [20]. This may be due to the much smaller system sizes used here, and to the presence of highly non-trivial corrections to scaling [20] which we did not attempt to take into account. In that regard, it would certainly be worthwhile conducting a more detailed study, to ensure that our conclusion— τ/ν being independent of ℓ —remains valid even after corrections to scaling have been analyzed.

4. Conclusions and discussions

In this paper, we studied the percolation of polymer networks on a two-dimensional square lattice. A polymer is modeled by a simple random chain of ℓ bonds. We measured the percolation threshold and the critical exponents for various ℓ up to 256. We found that the critical occupation probability is a monotonically decreasing function of the polymer length, but the critical mass density shows non-monotonic behavior. Our numerical simulations produced statistically identical critical exponents for $\ell = 1, 2, 4$ and 8. Thus, we confirm an expectation that their properties near the percolation transition belong to the same universality class. We also studied the diffusion of particles through these polymer networks, subjected to a concentration gradient across the lattice. Near the percolation threshold, the current vanishes as a power law in all cases, and again, the associated critical exponent does not appear to depend on ℓ .

In previous studies [2, 3, 6, 7], the relation between the *correlation strength* and the percolation threshold was discussed. In our model, if we deem the polymer length as a measure of the correlation strength, we would conclude that the critical occupation probability decreases as the correlation strength goes up. However, a better point of view is to consider the *shape* of polymers. It is known that the typical shape of Gaussian walks is not isotropic; instead, it is elliptical in two dimensions. If we denote the eigenvalues of the inertia tensor by $\lambda_{1,2}$, the distribution of the ratio λ_1/λ_2 has a long tail, which grows when the polymer length increases [22]. In other words, longer polymers tend to be more eccentric. It is understandable that objects that are more anisotropic percolate more effectively. As an example, ellipses with higher eccentricity percolate more easily [23]. These considerations provide some intuitive

picture for why the critical occupation probability decreases with increasing polymer length. It will be interesting whether $p_c(\ell \rightarrow \infty)$ can indeed be shown to vanish. While we have offered a conjecture, in the discussion of equation (5), further study is required to answer this question fully.

Another intriguing aspect concerns corrections to scaling. These play an important role in the determination of critical exponents in the $\ell = 1$ case [20]. It would be interesting to explore whether these subtleties also emerge for larger ℓ .

Acknowledgments

We thank Olaf Stenull for helpful correspondence and the referees for valuable suggestions. This research is supported in part by the US National Science Foundation through grants DMR-0414122 and DMR-0705152.

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