

Percolation of a collection of finite random walks - a model for gas permeation through thin polymeric membranes.

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Abstract. Motivated by recent studies of gas permeation through polymer networks, we consider a collection of ordinary random walks of fixed length ℓ , placed randomly on the bonds of a square lattice. These walks model polymers, each with ℓ segments. Using computer simulations, we find the critical concentration of occupied bonds (i.e., the critical occupation probability) for such a network to percolate the system. Though this threshold decreases monotonically with ℓ , the critical “mass” density, defined as the total number of segments divided by total number of bonds in the system, displays a more complex behavior. In particular, for *fixed mass densities*, the percolation characteristics of the network can change several times, as shorter polymers are linked to form longer ones.

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1. Introduction

Offering wide-ranging applications and considerable theoretical challenges, the percolation problem is a venerable one in statistical mechanics [1]. Here, we revisit the *bond* percolation problem on a square lattice, motivated by recent studies of gas permeation through polymer networks [2, 3]. When the bonds are distributed randomly, many analytically exact results are available. When the bonds are correlated, much less is known. Here, we focus on correlations induced by joining the bonds together, into chains of Gaussian walks. We begin with a brief description of the experiments and of our model for thin films. In the next section, we provide simulation data for percolation of such a collection of (finite) random walks. The last section is devoted to generalizations of the model to the physical dimension and the wider context of currents through the network of Gaussian chains.

Thin films are common in daily usage and generally, the more impermeable (or selective) the material is, the more desirable. As an example, if a ‘good’ film is used to wrap garlic stored in the refrigerator, the odor will be contained so that the flavors of other foods remain unaffected. Obviously, there are less mundane examples in industrial and research settings. Such films are often prepared by quenching a polymer melt and

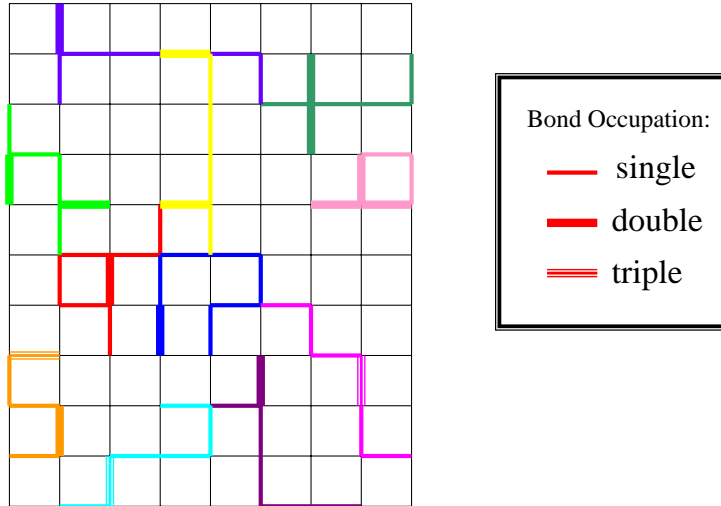


Figure 1. An example of $M = 11$ “octa-mers” (Gaussian chains of $\ell = 8$ bonds) on a 8×10 lattice. Colors (on-line) are for convenience of distinguishing one polymer from another. Though the absolute limit for multiple occupancy is 88 for this illustration, no bond is more than triply occupied. This specific network does not percolate (in the vertical direction).

stretching the resultant, so that the end product is a random network of polymers. Permeation experiments consist of mounting a film across a vacuum chamber, injecting various gases into one part of the chamber and maintaining constant pressure, and then measuring the pressure in the other part as a function of time. Apart from a short transient period, the pressure increases linearly, indicating that the molecules within the film have settled into a steady state, with a constant concentration gradient across the film and a steady current through it. The goal is to characterize the dependence of these currents on how the film is prepared, how long it has aged, and under what conditions the aging process has taken place [2, 4].

Our model and goal, especially in this article, is much more modest. To begin, let us consider a two-dimensional version of this problem, so that the film is just a strip of finite width (modeling the film thickness) and infinite length (modeling the macroscopic dimension of the film). In practice, however, we only use $L \times L$ samples in simulations (with $L \leq 8192$). On such a square lattice, we randomly place M ordinary random walks on the bonds. Each walk is a chain of ℓ bonds, modeling a polymer with ℓ segments. In Fig. 1, we illustrate a realisation with $M = 11$ and $\ell = 8$ on a 8×10 lattice. Note that the polymers are *not* self-avoiding, so that a bond can be occupied by any number (m) of segments. The particles which model the gas molecules (not shown in Fig. 1) occupy the cells and diffuse by hopping to nearest-neighbor cells. The polymer segments act as barriers for the hopping and, with finite temperature T , control the hop through an activation probability: $\exp\{-m\epsilon/kT\}$, where ϵ represents the energy barrier associated with just one segment. In the $T = 0$ limit, only unoccupied bonds

can be traversed and so, diffusion across the film ceases when the occupied bonds span the transverse direction. To be specific, we can fill/empty the left/right boundary of our lattice with particles to model the pressure gradient in the experiment, and impose either periodic or brickwall boundary conditions on the top/bottom rows. Then, if the polymers “percolate” in the vertical direction, no current can flow in the $T = 0$ limit. Our goal here is simple: For a given “mass density” of the polymers ρ (i.e., a fixed density of *segments*), how does the percolation threshold depend on ℓ ? For $\ell = 1$, the problem is easy. First, compute the relationship between ρ and p , the probability that a bond is occupied. Then the critical density, ρ_c , is just given, via this relationship, by the critical occupation probability: $p_c = 1/2$. Now, imagine joining the segments together to form ℓ -mers (but keeping ρ , i.e., the total number of segments, fixed), so that the number of *randomly placed* polymers is now reduced by a factor of ℓ . How does ρ_c or p_c change? This linking process obviously induces non-trivial correlations amongst the occupied bonds. In this sense, we are exploring the effects of a very special type of correlation [5] on the percolation process.

2. Simulation results

We are not aware of existing, nor are we able to develop, analytic solutions to our problem. Yet it is relatively simple to simulate the system. The main challenge is computational power, since many realisations of each ρ and ℓ must be tested on lattices of various L 's so that finite-size scaling techniques can be applied. Simple minded simulations with finite systems will always produce a smooth function $P(\rho)$ - the probability of having a spanning cluster as a function of ρ (or p). Thus, only crude estimates of the percolation threshold can be obtained [6, 3]. Only in the thermodynamic limit will P be a step function, being zero and unity, respectively, for ρ below and above ρ_c .

The setup of our study is straightforward. Consider M ordinary random walks of ℓ segments, randomly placed on the bonds of a square lattice. Defining N ($\sim 2L^2$ for this study) to be the number of all bonds in a system, our control parameter is the density of segments

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

In experimental setups, a convenient control parameter is the mass density, which is just ρ times the mass of a segment. On the other hand, the conventional control parameter in the theory of bond percolation is p , the probability that a bond is present. For our model, a “present” bond is one occupied by one or more segments. Thus, defining N_o as the total number of occupied bonds, we have the “occupation probability”:

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

Due to multiple occupancies, $p \neq \rho$ in general. In fact, there is a whole *distribution* for p associated with a given ρ , since not every realisation of the network will have the

same N_0 . Let us just focus on the *average* occupation probability, which we will simply denote as p . The relationship between ρ and p depends on ℓ and is tractable (even for finite lattices) albeit somewhat tedious. Starting with B_ℓ , the average number of *distinct* bonds covered by the walk, we have $1 - p = (1 - B_\ell/N)^M$, so that for $N \rightarrow \infty$,

$$1 - p \cong e^{-\rho A_\ell} \quad (3)$$

where $A_\ell = B_\ell/\ell$. Now, B_ℓ can be found through its generating function [7]

$$\hat{B}(z) \equiv \sum_{\ell=1}^{\infty} B_\ell z^\ell \\ = \frac{4z}{(1-z)^2 [3 + (1+z)G(z)]},$$

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). Here, it suffices to state that A_ℓ is a rather dull, monotonically decreasing function: 1, 7/8, 5/6, It merely reflects the intuitive notion: There are more chances for longer walks to traverse bonds repeatedly (especially in low-dimensional systems such as ours). The large ℓ behavior is non-trivial and more interesting, but that is outside the scope of this article.

For our studies, we generate up to 10^7 realisations of such ℓ -mer configurations with various ρ and L . Histograms of those that “percolate”, i.e., contain at least a spanning cluster, are compiled. For large N , the spread in p is small and there is little difference between this ensemble and the one with a single p fixed through (3). To access system sizes much larger than previously investigated, we exploit the Hoshen-Kopelman cluster counting algorithm [8], so that our maximum L is 8192 here. Finally, finite-size scaling methods are used to determine accurate values for the percolation thresholds $p_c(\ell)$ (or $\rho_c(\ell)$), as well as critical exponents. Due to space limitations, we will present only the results here, deferring the details of this analysis to elsewhere [9].

Fig. 2 shows the percolation threshold as a function of ℓ . While p_c is a monotonically decreasing function of ℓ , we note that, remarkably, ρ_c is not monotonic. As a result, “re-entrant” behavior can be manifested by choosing ρ appropriately and tuning ℓ . For example, if we randomly fill 72% of the bonds with single segments, there will be a spanning cluster. But, if we “tie every other segment together” to form dimers, we would break enough connections in the macroscopic cluster so that the network no longer percolates. This demonstrates how strong the effects of correlations can be. Yet, if we continue to tie more segments together, a percolation cluster reemerges (for $\ell > 20$, in this case). An intuitive argument for these unexpected properties is as follows. First, the behavior of p_c can be understood in terms of the typical shapes of random walks. Contrary to naive belief, they are *not* isotropic: For large ℓ , rotational invariance dictates that the *average* shape is isotropic. However, if we first compute, say, the eigenvalues of the moment tensor of each walk, and then perform the ensemble average, the distribution peaks at unequal values[10]. Since moment tensors with two different eigenvalues can be represented as ellipses. Further, there is a long tail in the distribution of eccentricities [11]. In a nutshell, random walks are “long and thin.” Now, (mono-dispersed) ellipses

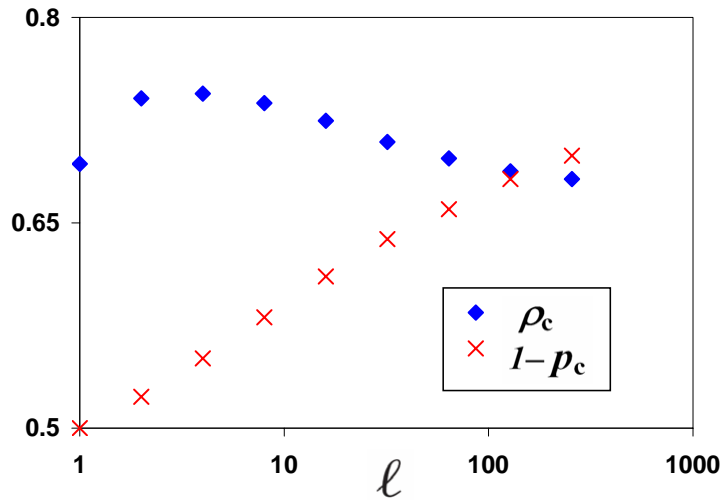


Figure 2. Percolation thresholds for a collection of random walks of length $\ell = 1, 2, 4, \dots, 256$. ρ_c is the critical density of segments, beyond which the polymer network spans our system. Here, $1 - p_c$ is the (threshold) probability that a bond is *unoccupied* by segments. Its rise with ℓ implies that longer chains are “more efficient” at forming a spanning cluster.

with higher eccentricity are known [12, 13] to be “more efficient” at spanning the system. In other words, longer random walks are “more efficient” at forming bridges and require fewer (occupied) bonds to span the system. By contrast, this picture is more complex when viewed in terms of the mass density, ρ . Longer chains are “less efficient” at occupying bonds (due to more repeated bond traversals) and the two competing effects lead to the observed non-monotonicity in $\rho_c(\ell)$. To predict which effects dominate at which ℓ is clearly non-trivial and remains a serious challenge. Beyond this issue, we see from Fig. 2 that $1 - p_c$ is practically linear in $\ln \ell$. On closer examination, we find peculiar, though small, deviations which fail to fit well to polynomials (in $\ln \ell$) as high as a cubic. Systematic errors in the numerics, though conceivable, are unlikely, leading us to suspect that these small “oscillations” may be an inherent and intriguing property. It would be very interesting to investigate the asymptotics for large ℓ .

3. Summary and Outlook

In this article, we considered a well posed problem: How does the percolation threshold change if the bonds on a square lattice are correlated through “being tied together” into random chains of length ℓ ? Using computer simulations, we find that p_c , the critical bond occupation probability, decreases monotonically with ℓ . By contrast, ρ , the threshold in terms of the mass density, displays a more interesting structure, leading to a curious “re-reentrant” phenomenon. At present, we only have an intuitive argument for these complex behaviors. When an analytic result of $p_c(\ell)$ becomes available, we may be able to develop better insights into these remarkable properties.

From a purely theoretical viewpoint, there are obvious generalizations of interest. The most urgent, so that comparisons with physical experiments can be made, is an extension to three dimensions. Of the many possibilities, one is to use a cubic lattice, with the particles again occupying the cells. Since the “barriers” between the cells are the *faces*, we should model the polymers by random walks on these faces. For example, we can let an ℓ -mer be a sequence of ℓ random steps across the *diagonals* on the *faces* of the cubes and, at a vertex, the next step can take one of twelve directions. Furthermore, there are two percolation-like problems: Of course, we can look for a cluster of segments that span the system. The other is a “dual” problem, suitable for considering particle currents: Labeling a face as “occupied” if there are one or more segments on either diagonal, we may ask for a critical density of segments so that the occupied faces block all pathways for a particle to traverse the system. Unlike in two dimensions, these two percolation thresholds are clearly distinct.

Another interesting theoretical question is crossover. Above, we have considered the thermodynamic limit ($L, M \rightarrow \infty$, finite ρ) with fixed ℓ . The other extreme is to let ℓ diverge with N while keeping M fixed at unity (just one polymer). In this limit, $P(\rho)$ is simply related to the span of random walk; it smooth and analytically known [10]. How does the system cross over from the percolation problem posed above to this other extreme? These issues are particularly interesting in two dimensions, since $\ell \propto N \propto L^2$ means that the radius of gyration is precisely proportional to L . Thus, naive considerations alone do not offer an immediate answer to percolation as the system size becomes macroscopic.

Finally, let us briefly mention some of the many aspects of the experiment which remain to be investigated. (a) Self-avoidance may be important. Certainly, our theoretical percolation problem will be quite different [5]. (b) When the film is created from quenching and stretching a melt, there may be correlations frozen in from this process. How can these be incorporated into a model? Stretching induces anisotropy, so that one simple generalization of the problem studied above is to have *biased* random walks instead. (c) The experiments are performed with non-vanishing T , of course. The presence of a spanning cluster (percolation) alone will not make the current vanish. The distribution of multiple occupancies will play a role. Thus, we should also take into account $p^{(m)}$, the probability that a bond is occupied by m segments. How this depends on ρ is clearly more complex than $p(\rho)$ above and it can be computed also from the results in [7]. To fully understand this phenomenon at a satisfying theoretical depth will be highly nontrivial. On the other hand, it is straightforward, though computationally intensive, to perform simulations so as to find how the average current depends on the various properties of the network and T [14] and to provide meaningful comparisons with experimental data. (d) Finally, since the experiments probe the effects of aging, we will need to go beyond randomly generated polymer networks and introduce a model for the dynamics of the polymers. To explore these dynamical issues will be challenging, even if we rely only on simulations. In this sense, our work here should be considered as a very small, initial step towards the goal of understanding all the intricate facets of

gas permeation through thin polymeric membranes.

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