Bond percolation of polymers

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(April 12, 2004)

We study bond percolation of N non-interacting Gaussian polymers of ℓ segments on a $2D$ square lattice of size L with reflecting boundaries. Through simulations, we find the fraction of configurations displaying *no* connected cluster which span from one edge to the opposite edge. From this fraction, we define a critical segment density $\rho_c^L(\ell)$ and the associated critical fraction of occupied bonds $p_c^L(\ell)$, so that they can be identified as the percolation threshold in the $L \to \infty$ limit. Whereas $p_c^L(\ell)$ is found to decrease monotonically with ℓ for a wide range of polymer lengths, $\rho_c^L(\ell)$ is non-monotonic. We give physical arguments for this intriguing behavior in terms of the competing effects of multiple bond occupancies and polymerization.

Studied for many decades, the percolation problem is rich and venerable [1]. To this day, interesting new issues continue to surface, for example, in the context of percolation of circles [2], ellipses [3], random surfaces [4] and polymers [5]. Motivated by recent experiments on transport of small gas molecules across a polymer membrane [6], we investigate a novel aspect, namely, bond percolation with a specific correlation between the bonds. In particular, we consider a standard model for polymers: a chain of ℓ segments linked to form a random walk (RW) in space. If, instead of continuous space, we use discrete lattices, it is natural to place the segments on the bonds. With certain considerations for our physical system in mind, we study ordinary (i.e., non self-avoiding) RW's. Clearly, the locations of the bonds occupied by one polymer are strongly correlated, except for the $\ell = 1$ case. If we place N such polymers randomly on a finite lattice and ask when the occupied bonds percolate, we face a "correlated-bond" percolation problem.

Before defining our problem in detail, let us devote a paragraph to a typical experiment. First, a thin polymer membrane is formed by quenching a polymer melt to a temperature far below its glass transition. To study permeation by small gas molecules, a pressure gradient is set up across the membrane and the gas current, in an effective steady state, is measured. The focus of the experiments in [6], namely, how aging the membrane affects such transport properties, serves only as a motivation for our model and investigation here. Detailed studies of gas transport will be published elsewhere.

For simplicity, we introduce a two-dimensional ($2D$) version of this system. As the polymers originated from a rubbery state, we feel justified to neglect the complications due to self-avoidance; further, the polymer matrix is essentially static on the time scales associated with gas transport. Therefore, we represent each polymer as a simple RW, on a square lattice of size L^2 (cf. Fig. 1). To model a finite system with real boundaries, we im-

pose brick wall boundary conditions on these walks. To be specific, we start a "walker" at a randomly chosen site, with each step to a nearest-neighbor site (a bond) modeling a segment of the polymer. When a walker arrives at a boundary site, the probability for reversing direction is $1/2$ (instead of $1/4$ in the bulk). In this way, a bond represents a "segment" of the polymer of the persistence length, rather than a physical monomer. Note that, since the RW's are not self-avoiding, each bond may be multiply occupied and we will use the term "m-occupied" to signify a bond carrying m segments. Meanwhile, the gas molecules are located on the cells of our lattice and diffusion is modeled by hopping to a nearest-neighbor cell, *across* a bond. The rate for a hop across an m-occupied bond will be controlled by an activation barrier: $\exp\left(-m\epsilon/k_B T\right)$, where T is the temperature and ϵ is an energy associated with jumping over a single segment.

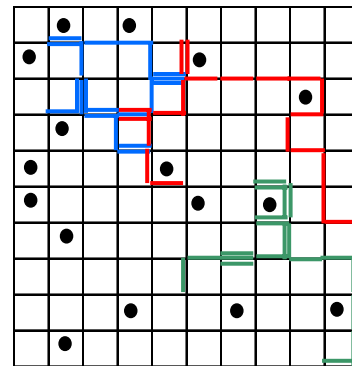
FIG. 1. Gas molecules diffusing from left to right across a 10×10 lattice, carrying $N = 3$ polymers of length $\ell = 20$.

As the polymers are static in this model, we are dealing with driven diffusion in a *quenched* random medium. Transport through static disordered media with random, energy barriers has been extensively studied in the past few decades. Unlike many previous studies [7] of this

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type, the energy barriers in our medium possess strong *spatial correlations* since the segments of a single RW are highly correlated. In this letter, we focus on a much simpler question: In the low-T, high-ϵ limit, what is the probability that there will be *any* current through the membrane? In this limit, crossing any occupied bond is forbidden. Thus, for a $2D$ system, the quantity of interest is precisely the probability for the occupied bonds to form a connected cluster that spans the system in the direction *transverse* to the pressure gradient, i.e., the percolation probability in one of the directions. Of course, the picture is more complex for a $3D$ system, on which we will comment at the end.
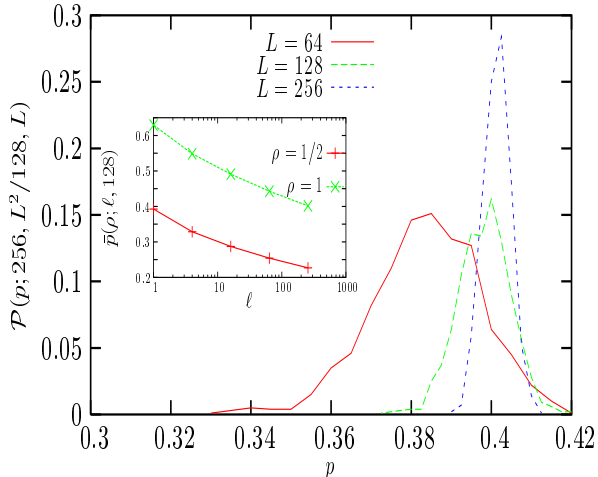

FIG. 2. The probability distribution $\mathcal{P}(p;\ell,N,L)$ for the fraction of occupied bonds p for $\rho = 1$, $\ell = 256$, and different system sizes. Inset: The mean value $\bar{p}$ vs. polymer length ℓ for $\rho = 1/2$ and $\rho = 1$. The RMS deviation for all data points is of the order of 10^{-3}.

Let us briefly comment on the differences between our focus and earlier studies which addressed this problem [5,8]. Previously, all polymers were modeled as self-avoiding walks (SAW). Clearly, these pose more challenging combinatorial questions than our RW's, so that analytic progress is essentially impossible. In another respect, however, SAW's are simpler: Since bonds are at most singly occupied, a given density of polymers maps directly into a delta distribution for the probability of bond occupation. Further, only relatively short polymers ($\ell \leq 16$ in [5]) were considered, focusing on singular properties near the percolation threshold. Thus, finite size scaling techniques were invoked to draw conclusions in the thermodynamic limit. By contrast, the samples in permeation experiments are quite thin so that ℓ and L can become comparable. As a result, we will need to pay attention to finite system sizes here. To the best of our knowledge, ours is the first attempt to study percolation of polymers on a lattice with multiple bond occupancies, in this particular scaling limit.

Turning to the specifics of our problem, we place the pressure gradient in the x-direction, so that the presence

of a particle current translates into the absence of a connected cluster of occupied bonds spanning the boundaries $y = 1, L$. Our question is now well posed: Of all systems with N random walks (polymers) of ℓ steps (segments), placed randomly on a L^2 lattice, what is f, the fraction which contains *no* cluster of connected segments spanning the system in one of the directions?

Clearly, in a gas permeation experiment, f is just the fraction of 'open' configurations, allowing nonzero current. Let us emphasize that, due to multiple occupancies, there is no simple, 1-1 relation between p, the fraction of occupied bonds, and the segment density, $\rho \equiv N\ell/(2L^2)$ (proportional to the mass density of the sample). In contrast, for the SAW's in [5], p is exactly ρ. Here, we have a *distribution* of p's, a quantity to be denoted by $\mathcal{P}(p;\ell,N,L)$. Even in the $\ell = 1$ case – for which single segments are randomly placed and we can easily find the probability for a bond to be *unoccupied*: $[1 - 1/(2L^2)]^N$ – the entire distribution is nontrivial [9]. For arbitrary ℓ, we are not aware of an analytic expression for $\mathcal{P}$. However, for large N and L, with fixed ℓ, we may expect $\mathcal{P}$ to be sharply peaked, as illustrated in Fig. 2. In all cases, we may define the average $\bar{p} \equiv \sum p\mathcal{P}$ and use it as a control parameter instead of ρ. Of course, their relationship is of interest. In general, we have no analytic expression for $\bar{p}(\rho;\ell,L)$ though we are able to find good estimates in some regimes [10]. To demonstrate this nontrivial dependence, we show in the inset of Fig. 2 simulation results for $\bar{p}(\rho;\ell,L)$ vs ℓ at two different densities and $L = 128$. We find that increasing ℓ at fixed ρ decreases the fraction of occupied bonds, since longer polymers tend to overlap more. Note that neither the details of $\mathcal{P}$ nor its average $\bar{p}$ are needed for determining the main quantity of interest: $f(\ell,N,L)$. We raise these issues related to p purely for those familiar with the standard question of ordinary bond percolation: If a fraction p of the bonds is occupied, what is the probability for the system to percolate?
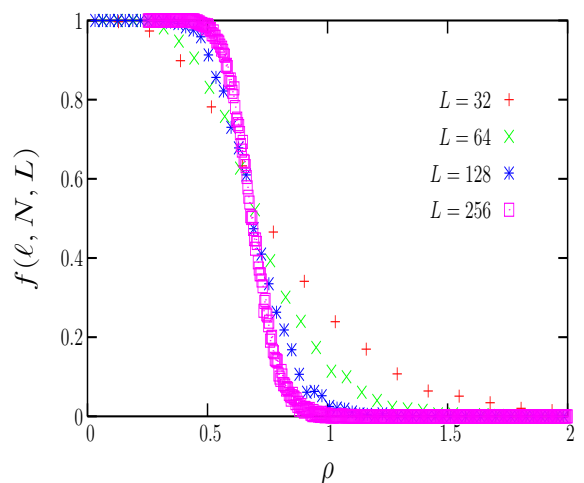

FIG. 3. The percolation probability $f(\ell,N,L)$ vs. the segment density ρ for fixed $\ell = 256$ and several L.

To study f, we perform simulations for various $\rho \in [0.25, 2.0]$ and $L \in [32, 256]$. With a full range of ℓ's and N's, we find not only the typical percolation transition, but also seemingly contradictory effects due to the correlations. Focusing on the first aspect, we consider the data for *fixed* ℓ but increasing L. For example, in Fig. 3, we plot f against ρ, with $\ell = 256$ and $L = 32, 64, 128, 256$. Not surprisingly, f is essentially unity for small ρ and zero for large ρ. In the $L \to \infty$ limit, we expect f to become a step function, vanishing for $\rho > \rho_c$, i.e., the "percolation threshold." For our finite systems, we see the approach to this behavior, namely, $f(\rho)$ falling off more steeply as L increases. As an estimate for ρ_c, we construct the (average) local gradients, $-\partial_\rho f(\rho)$, which we expect to approach $\delta(\rho - \rho_c)$ with increasing L. Exploiting $-\partial_\rho f$ as a "distribution" over $\rho \in [0, \infty]$, we compute the average $-\int_0^\infty \rho \partial_\rho f$ and define it as the "critical" $\rho_c^L(\ell)$ for each L. For the above L's, these are respectively, 0.849, 0.754, 0.711, and 0.688. A naive extrapolation (linear in $1/L$) leads to $\rho_c^\infty(\ell = 256) \simeq 0.67$. To express this result in the usual language of percolation, we find $\bar{p}(\ell, \rho; L)$ from the numerical data and define the "critical" p via $p_c^L(\ell) = \bar{p}(\ell, \rho = \rho_c^L(\ell); L)$. Extrapolating to $L \to \infty$ as before yields the percolation threshold $p_c^\infty(\ell = 256) \simeq 0$.295 (data for $L = 32, 64$ and 128 shown in Fig. 4). This value is consistent with the $\ell \to \infty$ projected value for the SAW's [5]: 0.349 ± 0.001 (based on extrapolation from $\ell \leq 16$). A more quantitative comparison must wait for better statistics and more sophisticated analyses (e.g., finite size scaling) and will be reported at a later time.
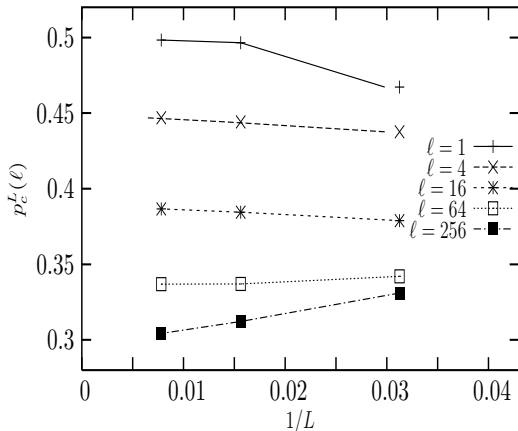

FIG. 4. The effective percolation threshold $p_c^L(\ell)$ vs. $1/L$ for various polymer lengths ℓ.

Next, we turn to a second, very natural question: If we fix the *density* of segments in a system, how will *polymerizing* them, into chains of increasing length ℓ, affect $f(\ell, N, L)$? Here, we discover a rather intriguing aspect of this problem, illustrated in Fig. 5: For small densities, $f(\ell, N, L)$ *decreases* with ℓ, but displays the opposite trend for high densities – *increasing* with ℓ. For insight into these seemingly contradictory findings, we provide some intuitive arguments. At low densities, linking

isolated segments together into longer chains clearly enhances the chances of spanning. As an extreme example, consider L segments so that only one configuration can span the lattice. For $\ell = 1$, at the least, all of them must have the same orientation and lie in the same column, so that the probability of spanning is $o((2L)^{-L})$. Yet, if they are linked to form a single polymer, this probability rises to $O(4^{-L})$. In contrast, at high densities correlations have the opposite effect: if randomly distributed segments percolate, linking them together into chains tends to localize them and enhances overlaps. As a result, percolating paths can be broken, and $f(\ell, N, L)$ increases.
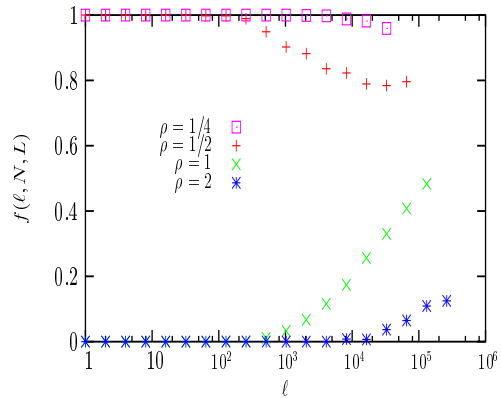

FIG. 5. The percolation probability $f(\ell, N, L)$ for fixed density $\rho = N\ell/(2L^2)$ is plotted against ℓ for system size $L = 128$.
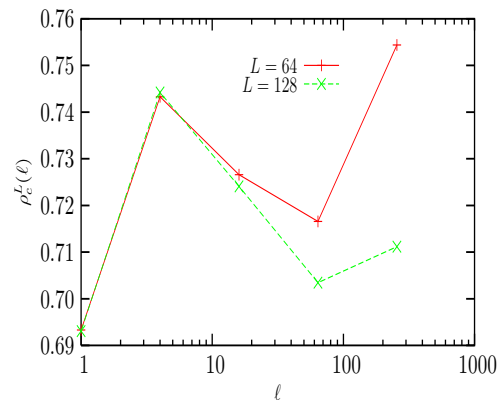

FIG. 6. The critical segment density $\rho_c^L(\ell)$ vs. ℓ at the percolation threshold for two system sizes. For $L \to \infty$, this plot may be viewed as a phase diagram: above the line, the polymers form a percolating path, while none exists below. The data points correspond to $\ell = 4^n$ where $n = (0, 1, 2, 3, 4)$.

These competing effects of polymerization induce a dramatic ℓ-dependence in the critical density ρ_c^L. As illustrated in Fig. 6, there appear to be three distinct regimes, with two extremal points for $\rho_c^L(\ell)$. Let us provide some intuitive arguments for these properties. Focusing on the first regime ($\ell \lesssim 4$), consider $\ell = 1$, where our data suggest a critical density of $\rho_c^\infty(1) \simeq 0.69$ (in ex-

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cellent agreement with the theoretical $\ln 2 \simeq 0.693$). If we now generate the same segment density (0.69) with polymers of length 2, the second segment has a probability of 1/4 to overlap with the first one, so that this density will *not suffice* for percolation. Thus, $\rho_c^L(2)$ must be higher than $\rho_c^L(1)$, in agreement with our observations($\rho_c^L(2) \approx 0.74$ in simulations). This effect continues to dominate up to a certain value ℓ^*; from the data shown in Fig. 6, we may conclude $4 \leq \ell^* < 16$. Our data indicate only a very weak L-dependence in this regime, so that we are confident that the $L \to \infty$ limit is essentially reached. Next, we consider the third regime: polymers with $\ell \gtrsim L$ (the last two data points in Fig. 6). Here, each polymer already occupies a significant fraction of the system. Thus, adding another increases ρ noticeably, but changes bond occupations only marginally. In this sense, a disproportionately larger number of polymers is required to span the system, leading again to increasing ρ_c^L with ℓ. Since this regime is dominated by the finite size of the system, we expect it to shift to larger ℓ for bigger L's. Sandwiched between these two regimes, we observe the *opposite* effect, due to polymerization: After reaching a maximum at ℓ^*, the critical density *decreases*. In this regime, for reasons yet to be understood, the argument we presented above applies again: tieing segments together generates "longer" objects that percolate more easily. We conjecture that this second regime extends to infinity in the thermodynamic limit, so that $\rho_c^\infty(\ell)$ exhibits only a single extremal point at ℓ^*, with $4 \leq \ell^* < 16$.

In contrast, when expressed in terms of the bond occupancy, we observe no surprises: $p_c^L(\ell)$ is monotonically decreasing. Since we also expect a monotonic dependence of p on ρ (for fixed ℓ), it is all the more remarkable that the effects of correlations built into the segments by polymerization are so subtle to produce non-monotonic behavior in $\rho_c^L(\ell)$.

In summary, we have investigated $f(\ell, N, L)$, the probability that N Gaussian polymers of ℓ segments, randomly distributed on the bonds of a square lattice, do not span an $L \times L$ system. Since the polymers are simple random walks, the bonds are frequently occupied by more than one segment, leading to a nontrivial correspondence between segment density, $\rho = N\ell/(2L^2)$, and bond-occupation probability, p. For a given ℓ, a sharp percolation threshold emerges as $L \to \infty$. For finite L, we define "critical" values $\rho_c^L(\ell)$ and $p_c^L(\ell)$. Measuring them by simulations, we study their behavior for various ℓ. We find that the subtle interplay of polymerization and multiple occupancies leads to dramatic effects, especially for $\rho_c^L(\ell)$. Several limits, e.g., the extreme case of $f(\ell = 2\rho L^2, 1, L)$, are analytically accessible and will be reported elsewhere [10].

It is worthwhile to devote a few lines to comment on the experimental implications of our work. Although our simulations were restricted to two dimensions, we believe that our principal result, i.e., the two opposite effects of polymerization on percolation probability (lowering p_c on one hand, while making more free bonds available via multiple bond occupancies on the other) should be present in higher dimensions also. Percolation-related transitions in permeation properties have been observed experimentally, eg. in [11] where a jump in the gas current is seen when the volume fraction of the flexible component of the polymer is increased beyond a threshold value. It would be interesting if the non-monotonic variation of the critical density with polymer length could be tested experimentally.

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[9] H.J. Hilhorst, private communication. $\mathcal{P}(p; 1, N, L) \propto S(N, M) (2L^2)! / (2L^2 - M)!$, where S is Stirling number of the second kind and $M \equiv 2pL^2$ is the total number of occupied bonds. See also [10].

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