

Scaling of Polymers in Aligned Rods

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We study the behavior of self-avoiding polymers in a background of infinitely long vertically aligned rods that are either frozen in random positions or free to move horizontally. We find that in both cases the polymer chains are highly elongated, with vertical and horizontal size exponents that differ by a factor of 3. Though these results are different than previous predictions, our results are confirmed by detailed computer simulations.

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In this Letter we analyze the statistics of a flexible polymer molecule in a background of vertical rods that are either free to move (annealed), or fixed in location (quenched). We argue that this would be an interesting system to investigate experimentally, perhaps being related to liquid-crystal polymer mixtures. One can solubilize rod-like particles such as nanotubes [1], virus particles, boehmite rods, and cellulose nanocrystals, and rod-polymer mixtures have been studied experimentally and theoretically in the context of demixing and liquid crystalline phase transitions [2–8]. Furthermore, it is now possible to fabricate arrays of vertical nanotubes on a substrate [9] which allows for the possibility of observing the quenched scaling behavior that we have predicted.

This work has overlap with many other problems of interest. For example, vortices in superconductors with columnar disorder have been extensively studied [10] and are related to the current polymer problem, a major difference being that the polymer (or vortex) is stretched and threaded the entire vertical dimension having a line tension, meaning that it is appropriate to use directed polymers in this situation [11]. This apparently leads to completely different scaling behavior [12].

The statistics of a flexible polymer molecule in a background of vertical rods has been considered previously in a dynamical context [13] and for periodic backgrounds [14], but surprisingly, the results for the problem considered here do not appear to have been given.

We use a three-dimensional cubic lattice model to study this problem, where the rods randomly occupy vertical lines, and the chain avoids itself and the rods. This is related to the problem of a self-avoiding walk (SAW) that also is excluded from *point* defects. In that case, an elegant argument of Cates and Ball [15] cleared up a decade of controversy [16] by showing that the quenched version of this problem, where defects are frozen, gives exactly the same statistics for the SAW as the annealed version, where the defects are also mobile. They argued that a frozen background of uncorrelated obstacles on an infinite lattice could be subdivided into very large regions. The statistics of obstacles in each region are independent of

each other. Therefore the statistics of the polymer chain can be obtained by doing an average over all these regions. The statistical weight given to each region gives precisely the same result as an annealed average. Their argument trivially extends to the case we consider here. For a finite volume system, this approach [15] also reconciles the quenched (replica) [17] and annealed predictions. It should be emphasized that if one end of the chain is tethered to a fixed location, then this argument is no longer valid and the conformations of chains will be very different [18].

From the above paragraph, we conclude that for an infinite sized lattice, the problem of frozen rods gives identical polymer statistics to the case where the rods are mobile. Below we analyze how finite size lattices alter the above conclusion. This is important to do, because we find those effects are large and in experimental systems with confined geometries can easily dominate the behavior. But first we analyze the annealed problem.

Denote the probability distribution of the SAW with coordinates $\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N$, as $P_{\text{SAW}}\{\mathbf{r}_i\}$. When it is placed in a random potential $V(\mathbf{r})$ at temperature T , the annealed average probability distribution becomes

$$P_{\text{SAW}}\{\mathbf{r}_i\} \propto \langle e^{-(1/T)\sum_j V(\mathbf{r}_j)} \rangle_V. \quad (1)$$

The average depends on the statistics of V . First we review the case of a completely uncorrelated V [15,19], in which case the average becomes an on-site attractive term between different monomers. However, because the SAW excludes all configurations where two monomers sit on the same site, this cannot alter the probability distribution. Therefore an uncorrelated random potential makes *no difference* to the statistics of an SAW. This result has been confirmed by simulations [20].

Now we turn to the case of columnar disorder. Here the average in Eq. (1) leads to an attractive interaction between all monomers that have the same x - y coordinates, regardless of their vertical separation. In this case, we expect different scaling behavior than we would observe from an SAW. Intuitively, the chain should contract in the x - y plane. We now analyze the annealed statistical mechanics of this problem using a scaling argument.

A dilute gas of rods of density (per unit area) of ρ and at temperature T gives rise to a (two-dimensional) pressure $p = \rho T$. An SAW of N steps placed in a gas of these rods will raise the free energy of the rods by excluding rods from the vicinity of the SAW. This is due to the pressure exerted by the rods, which means that the free energy is raised by pA where A is the cross-sectional area of the rods in the x - y plane. Therefore the SAW has forces acting on it to decrease A . Working in opposition to this is the entropy loss of a polymer chain confined to a cylinder of radius R_{xy} which is $\sim N/N_{xy}$ [21], where N_{xy} is the number of monomers corresponding to an SAW of dimension $R_{xy} \sim N_{xy}^\nu$, where $\nu \approx .59$ is the excluded volume exponent in three dimensions. (This confinement requires fixing the orientation of a monomer, one in every N_{xy} steps lowering the entropy.) Minimizing the pressure and tube confinement terms with respect to R_{xy} gives

$$R_{xy} \sim N^{1/(2+1/\nu)} \approx N^{0.27}. \quad (2)$$

Note that the exponent 0.27 is much less than in the pure SAW case—the pure SAW problem is isotropic and so ν is as well. This shows that the scaling of the polymer chain in this situation differs greatly from a pure SAW. To obtain scaling in the vertical direction R_z , we note that there are “blobs” of size R_{xy} stacked vertically on top of each other. Therefore

$$R_z \sim R_{xy}N/N_{xy} \sim R_{xy}\rho A \sim \rho(R_{xy})^3 \approx N^{0.81}, \quad (3)$$

which is substantially larger than the ν for a pure SAW, and thrice the x - y exponent, leading to highly elongated chains. Note the overall radius of gyration scales as R_z .

The chain density projected onto the x - y plane grows algebraically with N . Therefore for large N we expect complete exclusion of rods in this region, which is consistent with our initial assumption that this was the case. In addition, because monomers in far away blobs are uncorrelated, and the number of blobs grows with N , single configurations all have very close projected x - y densities which will differ from each other only by an inverse power of N . This self-averaging property implies that we are also justified in regarding the polymer as being in an external potential, induced by the rods, and then minimizing the free energy to find the scale of this potential. Therefore we expect our scaling argument to work very well for large N .

As argued above, this is *identical* to the scaling expected in the case of a frozen background for a system of infinite size. But for finite sizes, quenched systems are harder to treat analytically and so we resort to simulations, both to analyze this case and to verify our above predictions.

Single chains of length 32 to 4096 were simulated on a cubic lattice with different densities of vertical rods, all with hard cores. First we allowed both rods and chains to move according to rules that satisfied detailed balance. The polymers were moved according to reptation dynamics [22], and the rods performed long range moves between

randomly selected positions also satisfying detailed balance. We checked that our program did indeed give a reasonable excluded volume exponent in the case of no rods, $\nu \approx 0.59$ and performed a variety of other checks.

We then analyzed the statistics of our longest chain and highest rod density, $N = 4096$ and $\rho = 0.32$. We plot the mean monomer separation squared as a function of arc-length

$$\langle r^2(s) \rangle \equiv \sum_{i < j} \delta_{j-i,s} \frac{1}{N-s} \langle |\mathbf{r}_i - \mathbf{r}_j|^2 \rangle \quad (4)$$

and the analogous quantity projected in the x - y plane, $\langle r_{\perp}^2(s) \rangle$. These two quantities are shown in Fig. 1, the upper and the lower curve being $\langle r^2(s) \rangle$ and $\langle r_{\perp}^2(s) \rangle$, respectively. The best fit slope to $\langle r^2(s) \rangle$ is 2×0.974 . The scaling theory predicts a fractal dimension of 1, which corresponds to a slope of 2 on this plot. $\langle r_{\perp}^2(s) \rangle$ has a large plateau indicating an infinite fractal dimension, consistent with our scaling analysis of chains in a tubelike conformation.

Next we analyzed different chain lengths and rod densities. The results are shown in Fig. 2. The \times 's with the upper fitted line going through them represent a fit of the exponent for chains of length 128 to 4096 when the occupation fraction of rods is $\rho = 0.32$. The fit gives an exponent of 0.82 which compares well with the predicted value 0.81 given in Eq. (3). The $*$'s and \square 's are the same data for filling fractions of 0.16 and 0.08, respectively.

At all filling fractions there is a crossover from small chain lengths, which show the usual self-avoiding behavior, to the elongated regime studied here. From the figure it is clear that for small chain lengths the radius of gyration becomes independent of the rod filling fraction as expected. It is also apparent from the figure that this crossover chain length decreases as rod filling increases, which is in agreement with our theoretical interpretation of the

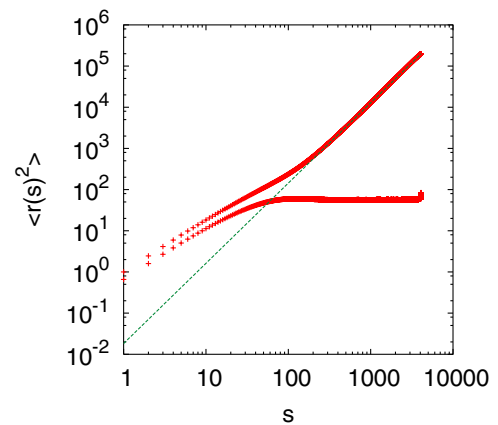


FIG. 1 (color online). Mean monomer separation squared as a function of arclength defined in Eq. (4), both the total (upper curve) and the x - y projection (lower curve) for an SAW of 4096 steps and vertical rods with $\rho = 0.32$ with mobile rods. The slope of the best fit line for the upper graph is 2×0.974 .

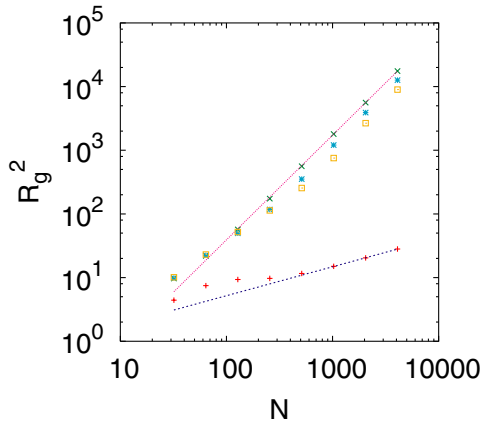


FIG. 2 (color online). Radius of gyration squared versus chain length on a log-log plot for an SAW in annealed vertical rods. The best fit line is 2×0.82 for the points at the highest rod filling fractions (0.32). The +’s show the radius of gyration in the x - y plane for the same conditions. The *’s and \square ’s are the same data for filling fractions of 0.16 and 0.08, respectively.

data, which predicts this crossover chain length N_c scales as $N_c \sim \rho^{-2\nu}$. The radius of gyration in x - y plane (“+” symbols) has a straight line fit of 0.23, but because of its small slope, it is unlikely to have reached asymptotia. Nonetheless, it is not too far from the predicted value of 0.27.

Now we turn to the results found when the rods are frozen to random positions (Fig. 3). In this case we did not go higher than a rod filling fraction 0.16 because we wanted to stay far away from the percolation transition and the breakdown of ergodicity associated with it. The lattice size was 128×128 in the x - y direction. The chains were averaged over a large number of steps. Before averaging, a

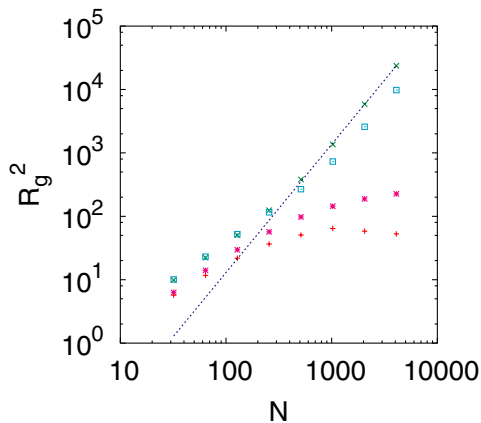


FIG. 3 (color online). Radius of gyration squared versus chain length on a log-log plot for an SAW in quenched vertical rods. The \times and square symbols denote a rod filling fraction of 0.16 and 0.08, respectively. The best fit line is 2×1.01 for the points at filling fractions of 0.16. The +’s and *’s show the radius of gyration in the x - y plane for the same conditions, filling fraction of 0.16 and 0.08, respectively.

chain was equilibrated for 1.6×10^8 steps and averaged over 1.28×10^8 steps. We then averaged the results over 128 realizations of the quenched rods. The radius of gyration squared is plotted as a function of the number of monomers. The \times ’s and the \square ’s denote a rod filling fraction of 0.16 and 0.08, respectively. The slope of the line going through the 0.16 filling fraction data gives $R_g \sim N^{1.01}$, which is *higher* than the annealed case. On the other hand, the radius of gyration in the x - y plane levels off as shown by the two lower curves. The +’s and the *’s are for a rod filling fraction of 0.16 and 0.08, respectively. Here, in contrast to the annealed case—Fig. 2—a leveling off in the curves is apparent.

The higher slope of $R_g(N)$ for quenched as opposed to annealed disorder can be understood as follows. As discussed above, for large enough lattices one expects the quenched average to equal the annealed one. The polymer migrates around the lattice and finds rare locations where it will spend most of its time. In these locations there will be a low rod density, and the radius of the depleted region scales as in Eq. (2). As the chain length grows, this implies that these regions must become successively rarer because the size of these holes must grow in order to accommodate the chain. On the other hand, if the lattice size is finite, then the strength of the most attractive region is now bounded and cannot grow with N , hence the leveling off of the horizontal radius of gyration seen in Fig. 3. A polymer chain in a fixed tube has an overall radius of gyration $R_g \propto N$ [21] in good agreement with our findings.

To confirm this explanation, we ran the simulation for chains of length 4096 for different horizontal system sizes, 16×16 up to 128×128 . The horizontal radius of gyration for different lattice sizes is plotted in Fig. 4 as a function of inverse system size. The point at zero represents the annealed case which should be the same as the infinite lattice. As the system width decreases, the horizontal radius of gyration *increases* indicating that the polymer is less tightly bound to rod-depleted regions.

For many chain systems the rods will induce an attractive interaction between different chains. The annealed case is simplest to understand. When two chains bind,

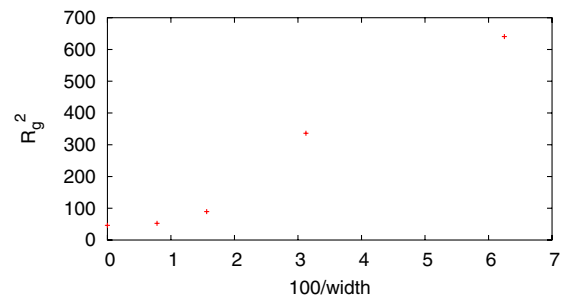


FIG. 4 (color online). Horizontal radius of gyration squared versus horizontal system size. The horizontal axis is 100 times the inverse width.

they will stack on top of each other but should not interpenetrate as this strongly raises the free energy. From the above scaling argument, Eq. (2), the free energy of two chains binding should scale as the horizontal area occupied by a chain $R_{xy}^2 \sim N^{2/(2+1/\nu)} \approx N^{0.54}$. Therefore as polymer concentration is increased from zero, one expects that there will be a transition between a gas phase of isolated chains and a phase of chains stacked on top of each other. Eventually it will reach another regime where one needs to consider the finite extent of rods in the vertical direction. As the concentration is increased, at some point different groups of stacked chains will want to coalesce. At this point the system will demix into rod-rich and polymer-rich regions. The exact nature of the phase diagram is probably quite complex and requires a detailed understanding of the behavior of semidilute polymer solutions in pores [21,23], which itself is quite delicate.

This is also hard to simulate quantitatively (even in the annealed case) because the center of mass diffusion of polymers is very slow. However, it was observed that in the pillar regime, two chains that finally managed to diffuse into the same tube stayed bound to each other.

The results found here differ strongly from those found for a model for an SAW in the presence of a solution of vertically aligned short rods [24] where their SAW's were of order 100 units but the rods were only one or two lattice spacings. In that case, the authors found that the polymers went into disklike configurations instead of the rodlike ones found here. Here it is worthwhile examining the case of rods of length L and chains whose vertical extent is much larger. In this case Eq. (1) implies an attractive potential between monomers with the same x - y coordinates whose vertical separation is less than L . At separations larger than L we expect that chain segments will no longer be stacked in the same tube because of the absence of attraction at this length scale. This, according to Eq. (3), corresponds to a crossover chain length of $N_c \sim L^{(2+1/\nu)/3}$. Beyond this separation, different monomers become unbound and we expect that in the horizontal direction segments execute a random walk. Therefore for large $N \gg N_c$, $R_{xy} \sim L^{1/3}(N/N_c)^{1/2} \sim L^{1/3}L^{-[1+1/(2\nu)]/3}N^{1/2} \sim L^{-1/(6\nu)}N^{1/2}$. Therefore we expect a slow drift of the SAW in the vertical direction that decreases with increasing L . Although the drift in the x - y plane is typically slow, at sufficiently long chain lengths, hairpin configurations will start to appear allowing the chain to double back. But the free energy penalty for such hairpins is large $\rho_3^{1/3}L$, where ρ_3 is the three-dimensional number density of rods [25]. Therefore hairpins are important only for chains that are exponentially long in the rod length.

In conclusion, we have shown that a polymer in the presence of either mobile or frozen vertical rods forms tubelike vertical conformations where the tube diameter and tube length scale as in Eqs. (2) and (3). It should be possible to observe this unusual behavior experimentally.

One possible system for the case of frozen rods would be in forests of vertical nanotubes [9] suitably coated to make them repulsive to polymer chains [1]. These results are also relevant to the more complicated case of polymer-rod mixtures, which are usually analyzed assuming no change in polymer statistics due to the presence of rods.

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