Scaling of polymers in aligned rods

J. M. Deutsch and M. Warkentin

Department of Physics, University of California, Santa Cruz, CA 95064.
(Dated: March 23, 2022)

We study the behavior of self avoiding polymers in a background of vertically aligned rods that are either frozen into 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.

PACS numbers:

The statistics of a flexible polymer molecule in a background of randomly placed vertical rods has been considered previously [1, 2]. The problem was first investigated [2] in a dynamical context in order to better understand the effects of entanglements. Later, [1] the equilibrium statistics were examined, and an elongation of the chain in the vertical direction was predicted. As we will show using both scaling and simulations, elongation does take place, but is actually much larger than was first thought.

We also analyze how this problem is very closely related to a polymer in a background of mobile vertical rods. We argue that this would be an interesting system to investigate experimentally, perhaps being related to liquid crystal polymer mixtures.

This work has overlap with many other problems of interest. For example, vortices in superconductors with columnar disorder has been extensively studied [3, 4] and is related to the current polymer problem, a major difference being that the polymer (or vortex) was stretched and threaded the entire vertical dimension having a line tension, meaning that it is appropriate to use directed polymers in this situation [3]. This apparently leads to completely different scaling behavior [4].

Our findings are also relevant to the study of mixtures of rods and polymers. It is possible to solubilize many rod-shaped particles—for example nanotubes [5], or more commonly, 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 [6, 7]. Furthermore, it is now possible to possible to fabricate arrays of vertical nanotubes on a substrate [8] which allows for the possibility of observing the scaling behavior predicted here (the case of quenched disorder).

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 self avoiding chain (SAW) that also is excluded from point defects. In that case, an elegant argument of Cates and Ball [9, 10] cleared up a decade of controversy 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.

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 will analyze how finite size lattices alter the above conclusion. But first we analyze the annealed (mobile rod) problem.

Denote the probability distribution of the SAW with coordinates \( r_1, r_2, \ldots, r_N \), as \( P_{SAW}(r_i) \). When it is placed in a random potential \( V(r) \) at temperature \( T \), the annealed average probability distribution becomes

\[
P_{SAW}(r_i) \left[ e^{-\frac{1}{k_B T} \sum_j V(r_j)} \right]^V
\]

The average depends on the statistics of \( V \). First we review the case of a completely uncorrelated \( V \) [11, 12], 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 [13].

Now we turn to the case of columnar disorder. Here the average in eqn 1 now leads to an attractive interaction of all monomers that have the same x and y coordinates, regardless of their separation in the z direction. 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 \( \rho \) 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 \( R_{xy} \sim N/N_{xy} \) where \( N_{xy} \) is the number of monomers corresponding to an SAW of dimension \( R_{xy} \sim N_{xy}^{1/\nu} \), where \( \nu \approx .59 \) is the excluded volume exponent in three dimensions. Minimizing the pressure term and tube confinement terms gives:

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

Note that the exponent 0.27 is much less than in the pure SAW case—the pure SAW problem is isotropic and so \( \nu \) 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

\[
R_z \sim R_{xy}N/N_{xy} \sim N^{3(1/2+1/\nu)} \sim (R_{xy})^3 \approx N^{0.81}.
\]

This exponent is thrice the \( x-y \) exponent, and is larger than \( \nu \) for the pure SAW. Therefore for long chains the system becomes highly elongated. The overall radius of gyration therefore scales the same way as \( R_z \).

Note that for long chains, the chain density projected on to the \( x-y \) plane grows algebraically for large \( N \). 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 only differ from each other 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. However the case of frozen finite size systems is harder to analyze through analytical means as the above argument does not apply. In general for a finite size system, one does expect a difference between the quenched and annealed cases. Therefore we performed extensive simulations of this system to verify the above predictions and better understand the effects of finite sizes.

Chains of length 32 to 4096 were simulated on a cubic lattice with different densities of vertical rods. First we allowed both rods and chains to move according to rules that satisfied detailed balance. The polymers were moved according to reptation dynamics [20] 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 positions also satisfying detailed balance. We checked that our program did indeed give a reasonable excluded positions also satisfying detailed balance. We checked that our program did indeed give a reasonable excluded positions also satisfying detailed balance. We checked that our program did indeed give a reasonable excluded positions also satisfying detailed balance. We checked that our program did indeed give a reasonable excluded positions also satisfying detailed balance. We checked that our program did indeed give a reasonable excluded positions also satisfying detailed balance. We checked that our program did indeed give a reasonable excluded positions also satisfying detailed balance. We checked that our program did indeed give a reasonable excluded positions also satisfying detailed balance. We checked that our program did indeed give a reasonable excluded positions also satisfying detailed balance. We checked that our program did indeed give a reasonable excluded positions also satisfying detailed balance. We checked that our program did indeed give a reasonable excluded positions also satisfying detailed balance. We checked that our program did indeed give a reasonable excluded positions also satisfying detailed balance. We checked that our program did indeed give a reasonable excluded positions also satisfying detailed balance. We checked that our program did indeed give a reasonable excluded positions also satisfying detailed balance. We checked that our program did indeed give a reasonable excluded positions also satisfying detailed balance. We checked that our program did indeed give a reasonable excluded positions also satisfying detailed balance. We checked that our program did indeed give a reasonable excluded positions also satisfying detailed balance.

![FIG. 1: Mean monomer separation squared as a function of arclength defined in eqn 1 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 best fit to the upper graph is line is \( 2 \times .974 \).](image-url)
gyration becomes independent of 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 data, which predicts this cross-over chain length \( N_c \) scales as \( N_c \sim \rho^{-2\nu} \).

The “+” symbols with the straight line fit going through them is the radius of gyration in the x-y plane. It is not clear if this has reached an asymptotic power law regime even at the larger chain lengths because the slope of this line is quite small and therefore crossover effects from short chains should be much larger than for \( R_g \). The slope of the fit shown is \( .23 \) which is nonetheless not too far from the predicted value of \( .27 \).

Now we turn to the results found when the rods are frozen to random positions. In this case we did not go higher than a rod filling fraction .16 because we wanted to stay far away from the percolation transition and the break down of ergodicity associated with it. The lattice size was \( 128 \times 128 \) in the x-y direction. The chains were averaged over a large number of steps. The most time consuming case were the longest chains, \( N = 4096 \). Before averaging, a chain was equilibrated for \( 1.6 \times 10^8 \) steps and averaged over \( 1.28 \times 10^8 \) 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 .16 and .08 respectively. The slope of the line going through the .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—figure 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 eqn. 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 figure 3. A polymer chain in a fixed tube has a overall radius of gyration \( R_g \propto N^{1.01} \) in good agreement with our findings.

To confirm this explanation, we ran the simulation for chains of length 4096 for different horizontal system sizes, \( 16 \times 16 \) up to \( 128 \times 128 \). The horizontal radius of gyration for different lattice sizes is plotted in figure 4 as a function of inverse system size. The point at zero represents the annealed cases 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, they will stack on top of each other but should not interpenetrate as this strongly raises the free energy. From the above scaling argument, eqn[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 ex-

---

**FIG. 2:** Radius of gyration squared versus chain length on a log-log plot for annealed SAW’s and vertical rods. The best fit line is \( 2 \times .82 \) for the points at the highest rod filling fractions (.32). The +’s show the radius of gyration in the x-y plane for the same conditions. The other points show the radius of gyration at lower rod filling fractions.

**FIG. 3:** Radius of gyration squared versus chain length on a log-log plot for quenched SAW’s and vertical rods. The \( \times \) and square symbols denote a rod filling fraction of .16 and .08 respectively. The best fit line is \( 2 \times 1.01 \) for the points at filling fractions of .16. The +’s and *’s show the radius of gyration in the x-y plane for the same conditions.
In the pillar regime, two chains that finally managed to coalesce. However, it was observed that the center of mass diffusion of polymers is very slow on a monte-carlo time scale. This 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 eqn. 11, 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 \( N >> N_{c} \), \( R_{xy} \sim L^{1/3}(N/N_{c})^{1/2} \sim L^{1/3}L^{-1(1/(2\nu))/3}N^{1/2} \sim L^{-1(6\nu)/3}N^{1/2} \). Therefore we expect a slow drift of the SAW in the vertical direction that decreases with increasing \( L \).

In conclusion, we have shown that a polymer in the presence of either mobile or frozen vertical rods forms tube-like vertical conformations where the tube diameter and tube length scale as in eqns 4 and 8. 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 suitably coated to make them repulsive to polymer chains. 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.

[1] E.A. Di Marzio, Phys. Rev. Lett. 64 2791 (1990).
[2] A. Baumgartner and M. Moon, Europhys. Lett. 9 203 (1989).
[3] D.R. Nelson, Phys. Rev. Lett. 60, 1973 (1988).
[4] T. Nattermann and R. Lipowsky, Phys. Rev. Lett. 61 2508 (1988).
[5] M. Kardar and Y.-C. Zhang, Phys. Rev. Lett. 58, 2087 (1987).
[6] I. Arsenin, T. Halpin-Healy, and J. Krug, Phys. Rev. E 49 R3562 (1994).
[7] M.F. Islam MF, E. Rojas, D.M. Bergey, A.T. Johnson and A.G. Yodh, Nano Lett. 3 269 (2003).
[8] Z. Dogic, K. R. Purdy, E. Grelet, M. Adams and S. Fraden, Phys Rev E 69 051702 (2004).
[9] R.P. Sear, J. Phys. II France 7 877 (1997).
[10] J. Buitenhuis, L. N. Donselaar, P. A. Buining, A. Stroobants, and H. N. Lekkerkerker, J. Colloid Interface Sci. 175, 46 (1995).
[11] M. P. B. van Bruggen and H. N. W. Lekkerkerker, Macromolecules 33, 5532 (2000).
[12] C. D. Edgar and D. G. Gray, Macromolecules 35, 7400 (2002).
[13] J. X. Tang, S. Wong, P. T. Tran, and P. A. Janmey, Ber. Bunsenges. Phys. Chem. 100, 796 (1996).
[14] R. de Vries, Biophys. J. 80, 1186 (2001).
[15] V. Semet, Vu Thien Binh, P. Vincent, D. Guillot, M. Chhowalla, G. A. J. Amarasinghe, W. I. Milne, P. Legagneux and D. Pribat, Appl. Phys. Lett. 81 343 (2002)
[16] M. E. Cates and C. Ball, J. Phys. (France) 49, 2009 (2008).
[17] J. Machta and R.A. Gayer, J. Phys. A 22 2539 (1989).
[18] S.B. Lee and H. Nakanishi, Phys. Rev. Lett. 61, 2022 (1988).
[19] P.G. de Gennes ‘‘Scaling Concepts in Polymer Physics’’ Cornell University Press (1985).
[20] F.T. Wall and F Mandell, J. Chem. Phys. 63 4592 (1975).
[21] F.Brochard and P.G. de Gennes, J. Phys. Lett. (France) 40 399 (1979).
[22] J.H. van Vliet, M.C. Luyten and G. ten Brinke, J. Phys. II (France) 603 (1993).