

Phase Transition of Polymers on Surfaces

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Introduction

Polymers are long-chain molecules, created by the large number of repetitions of basic units called monomers. The monomers are typically connected via strong covalent bonds to produce long-chain molecules, which in turn interact with each other mostly via weaker Van der Waal forces (at least for non-cross link polymers). While chemists spend much of their time synthesizing polymers and characterizing their chemical or physical properties, physicists are more interested in the universal properties which emerge out of the 'bare-bone' fact that a polymer is simply a long linear molecule and how the properties are affected by 'large scale quantities' such as the quality of the solvent in which the polymer is immersed, the temperature, the presence of surface and e.t.c [1]. In addition, we note that in a polymer chain, we can assume that the bond directions are no longer correlated beyond a certain persistent length, l_p .

With the above in mind, the simplest reasonable model of a polymer is that of a random walk [2] on a lattice, with each lattice site representing a chain of monomers of length l_p . In this scheme, considering a d-dimensional cube, a random walker currently at site i has equal probability, $1/2d$, of going to each of its nearest neighbor. The number of distinct paths, C_N , after N steps is thus given as

$$C_N = (2d)^N \quad (1)$$

This allows us to calculate the entropy S_N of this one-polymer system is thus given by

$$S_N = k_B \ln(C_N) = k_B N \ln(2d) \quad (2)$$

Another property, the end-to-end distance of the chain length, R_N , which is a measure of the spread of the polymer can also be obtained easily. Suppose that \mathbf{R}_N is the end-to-end vector of a given walk, it can be written as the sum of the (unit) vectors \mathbf{u}_i which forms the walk

$$\mathbf{R}_N = \sum_{i \in \text{Walk}} \mathbf{u}_i \quad (3)$$

Thus,

$$R_N^2 \equiv \langle \mathbf{R}_N \cdot \mathbf{R}_N \rangle = \sum_{i,j \in \text{Walk}} \langle \mathbf{u}_i \cdot \mathbf{u}_j \rangle = \sum_{i,j \in \text{Walk}} \delta_{ij} = N \quad (4)$$

The Kronecker Delta terms are obtained due to the fact that in a random walk, different steps are uncorrelated, giving rise to $\langle \mathbf{u}_i \mathbf{u}_j \rangle = 0$ if $i \neq j$. Although the random walk model may seem crude and does not take into account important factors such as the excluded volume of the monomer, this model can be solved exactly and the results give us an intuition of what to expect in more accurate models, such as the self-avoiding walks model (SAWs).

Self-Avoiding Walks

SAWs takes into account of the fact that each monomer has an associated volume (the excluded volume) which may not be occupied by another monomer. Polymers are almost always immersed in a solvent [3]. In a good solvent, it is energetically favorable for a monomer to be surrounded by solvent molecules and hence, the probability of finding another monomer within a certain associated volume is very small. The idea of self avoidance can easily be incorporated in the random walk model discussed in the previous section. Considering a d -dimensional cubic lattice, each lattice site is the excluded volume. The walker at site i no longer have an equal chance of moving to each of the $2d$ (nearest neighbor) directions. If the walker steps into an occupied site, the step has to be rejected. This simple additional constraint generates a sufficiently difficult mathematical problem that few exact results are available [4]. The trajectories of a random walk (30,000 steps) and a SAW (2,500 steps) are shown in figure 1. As expected, the SAW results in a larger spread. Exact results for SAW have also been sought, albeit essentially at small and large values of N . The asymptotic values (at large N) for C_N and R_N are shown in (5) and (6) respectively. The reader is referred to [1] for more detailed discussion.

$$C_N \sim \mu^N N^{\gamma-1} \quad (5)$$

$$R_N \sim N^{\nu} \quad (6)$$

Here both γ and ν are critical exponents which depends on dimensionality while μ is often called the connective coefficient. As can be seen, the random walk is a special case of these asymptotics with μ , γ and ν being $2d$ (twice the number of nearest neighbors), 1 and $\frac{1}{2}$ respectively.

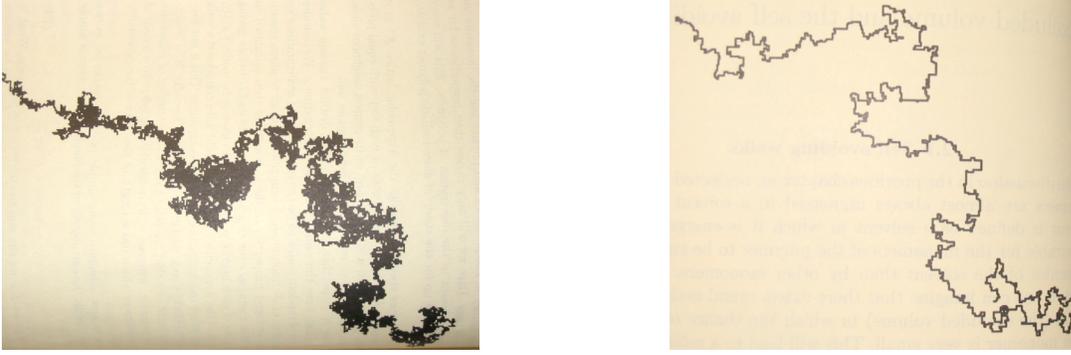


Figure 1: (Left) A random walk of 30,000 steps. (Right) An SAW of 2,500 steps [1].

Connection with Critical Phenomena

The existence of the critical exponents in (5) and (6) is derived from the fact that the SAW is equivalent to the magnetic $O(n)$ model with $n \rightarrow 0$. This relation, due to P.G. de Gennes [5-7] allows the application of all techniques from the theory of critical phenomena to polymer models. A brief outline is shown here (based on [1]) and the reader is referred to [1,4] for a more detailed explanation. The relation involves the high temperature expansion of the Ising model [8] and it starts off from the familiar partition function of the Ising model

$$Z_1 = Tr \prod_{\langle i, j \rangle} \exp(K s_i s_j) \quad (7)$$

where $\langle i, j \rangle$ denotes nearest neighbor sites on a lattice and K is the reduced coupling constant, and the spin s_i can take on either a value of 1 or -1. And if the lattice contains N_B edges

$$\begin{aligned} Z_1 &= Tr \prod_{\langle i, j \rangle} (\cosh K + s_i s_j \sinh K) \\ &= (\cosh K)^{N_B} Tr \prod_{\langle i, j \rangle} \exp(1 + s_i s_j \tanh K) \end{aligned} \quad (8)$$

By dropping the trivial $\cosh K$ factor and introducing $v = \tanh K$, we can define the partition function of the $O(n)$ model as

$$Z_n = Tr \prod_{\langle i, j \rangle} (1 + v \mathbf{s}_i \cdot \mathbf{s}_j) \quad (9)$$

where \mathbf{s} is a n -dimensional spin vector with fixed length of $n^{1/2}$, i.e $\mathbf{s} \cdot \mathbf{s} = n$. In addition, the following regarding the spin components hold

$$Tr s^\alpha s^\beta = \delta_{\alpha\beta} \quad (10)$$

where s^α , s^β are components of the spin vectors. The correlation function is considered next

$$G_n(k, l) \equiv \langle s_k s_l \rangle = \frac{Tr(s_k s_l) \prod_{\langle i, j \rangle} (1 + v s_i s_j)}{Z_N} \quad (11)$$

The terms are then expanded in terms of v . And each term of the expansion is evaluated in the limit $n \rightarrow 0$ by applying the result for the trace in (10). It can be verified that only products graphically represented by a self avoiding path of bonds from k to l have non zero contribution to the correlation function. We then obtain the result

$$G_0(k, l) \equiv \lim_{n \rightarrow 0} G_n(k, l) / n = \sum_{\substack{SAW \\ k \rightarrow l}} v^N \quad (12)$$

The grand partition function for SAWs can be obtained by summing over l . The resulting quantity is the susceptibility χ_0 of the $O(n)$ model.

$$\chi_0 \equiv \sum_l G_0(k, l) = \sum_{all SAW} v^N = \sum_N C_N v^N \quad (13)$$

The last term in (13) is the grand partition of the SAW, thus showing the equivalence between the susceptibility of the $O(n=0)$ model and the grand partition function of SAW.

Phase Transitions near Surfaces

As discussed previously, polymers modeled with SAW exhibits critical phenomena which correspond to the $O(n=0)$ system. The problem can be made more interesting if an impenetrable surface is added to the system, which gives rise to more critical phenomena. In addition, it allows us to model adhesion of polymers on surfaces which has always been an area of interest: polymers at surfaces may have important applications as glues or lubricants, plus the fact that solvent quality is often an issue (e.g. when the original solvent has evaporated, the polymer is now exposed to air, which is a bad solvent).

The surface adhesion problem is modeled by considering SAW on a semi-infinite lattice, bounded by a surface of $d-1$ dimension. Figure 2 shows a schematic of an SAW attached to a surface, which is often assumed to be attractive. As such an energy contribution of ϵ_s (< 0) is made for each step on the surface. This leads to an increased probability characterized by the Boltzmann factor $\omega = \exp(-\beta \epsilon_s)$ where $\beta = 1/(k_B T)$. In a good solvent, monomer-monomer interaction can be considered as repulsive and hence, need

not be modeled. At low temperatures, the polymer will be adsorbed to the surface, while at high temperature it desorbs and stays as a bulk phase. It is thus clear that there exists a phase transition between a high temperature phase described by a d-dimension SAW behavior and a low temperature phase exhibiting a (d-1)-dimension behavior. This system has been widely studied [4] and a phase diagram (obtained from [9]) is shown in figure 3, which is obtained from Monte Carlo simulations on a simple cubic lattice. The parameters p and q are the fugacity (which is assumed to be temperature independent) and the Boltzmann factor arising from an attractive surface ($q \equiv \omega$). The ensemble which the simulation is performed on is defined by the following partition function

$$Z^{(1)}(p, q) = \sum_{N, m} q^m p^N C_{N, m} \quad (14)$$

where $C_{N, m}$ denotes the number of configurations with N self avoiding steps, having m sites on the surface. The notation 1 indicates that one end of the chain is attached to the surface. Figure 3 shows 3 different phases. The upper part is the bulk phase where the single polymer chain fills the bulk volume with finite density. The lower right part is the surface phase containing a long adsorbed polymer and the lower left phase is the sub-critical phase composed of short chains. For small p and q , long chains are suppressed and the ensemble is largely composed of short chains. At small p , a phase transition (termed the surface transition) is observed when q is increased to a point $q_0(p)$, where the polymer chain adsorbs onto the surface with diverging average chain length. Likewise, desorbed short chains can grow indefinitely when p goes beyond p_c . It is noted that p_c is independent of q . This is because p_c is just the critical value of p for SAWs in the bulk (i.e. without considering the effect of surface) and the value of p_c is simply $1/\mu$. The tricritical point $S=(p_c, q_c)$ is where the 2 curves $q = q_0(p)$ and $p = p_c$ meets. The line to its left corresponds to the ordinary transition (where the polymer length simply diverges without any adsorption involved). The line to right of S denotes the extraordinary transition (polymer length is kept infinite, polymers simply desorbs).

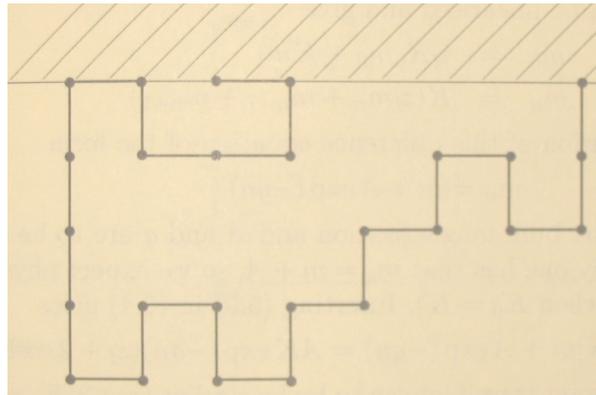


Figure 2: A SAW attached to a surface [1].

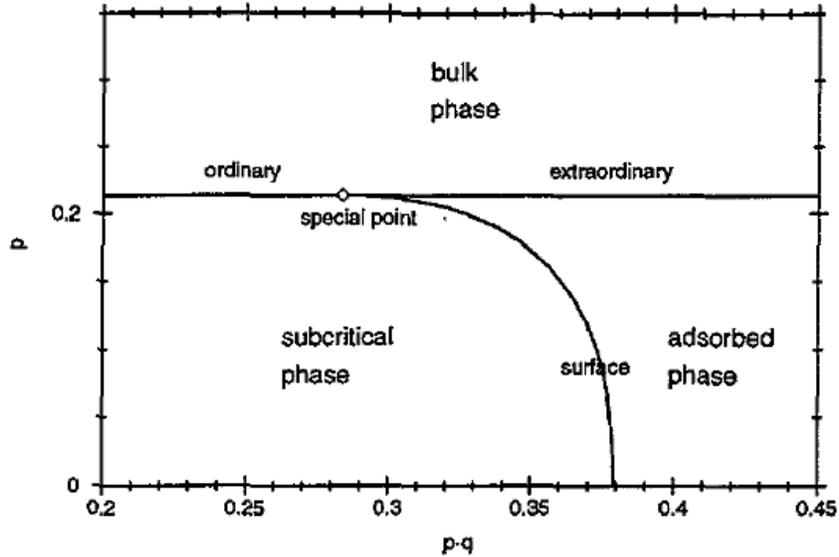


Figure 3: The phase diagram of a polymer in good solvent modeled with SAW with one end attached to an impenetrable surface [9].

Self Attracting SAW

The situation described above is however different for the case of a polymer chain immersed in a poor solvent. In this case, on top of the energy related to surface adsorption, ϵ_s , one needs to introduce $\epsilon_p (< 0)$ which is the monomer-monomer (nearest neighbor) interaction. Again, we define a Boltzmann factor related to this interaction: $u = \exp(-\beta\epsilon_p)$. The self attracting SAW was performed in [10] on a semi-infinite square lattice and the obtained phase diagram is shown in figure 4. The results are obtained via direct enumeration of walks with $N < 29$.

As observed in figure 4, there are 4 different phases. For better comparison to figure 3, it is noted that a low value of ω or u corresponds to a high temperature state (given that the interactions ϵ_s and ϵ_p are fixed). The DE (desorbed expanded) state occurs at small values of ω and u and it corresponds to the bulk state (see figure 3) described in the previous section. And keeping the value of ω low and increasing u , a phase transition to the DC (desorbed collapsed) states occurs at u_c . This state is not present in a good solvent and is a result of the attractive interaction of the monomers in a poor solvent. In the DC state, the polymer exists as a compact globule of finite density. The radius of gyration R_N

varies with $N^{1/d}$ in d -dimension instead of N^{ν} (6) in the bulk (or DE) case. Keeping u constant ($u < u_c$) and increasing ω (decreasing temperature), we obtain the familiar extraordinary transition (see figure 3) at $\omega = \omega_c$. The AE (adsorbed expanded) phase is equivalent to the adsorbed phase in figure 3. This transition occurs at a small value of u , i.e the monomer-monomer interaction is small. From the AE phase, one can expect a phase transition to the SAG (surface-adsorbed globule) phase when u is large, i.e a compact globule with small surface wetting area is preferred. The size of the polymer in the directions transverse and perpendicular to the surface varies as $N^{1/d}$ in the SAG phase as opposed to the usual relation in (6) for the AE case [11]. Note that ν_{AE} takes on the self-avoiding walk exponent in $d-1$ dimension.

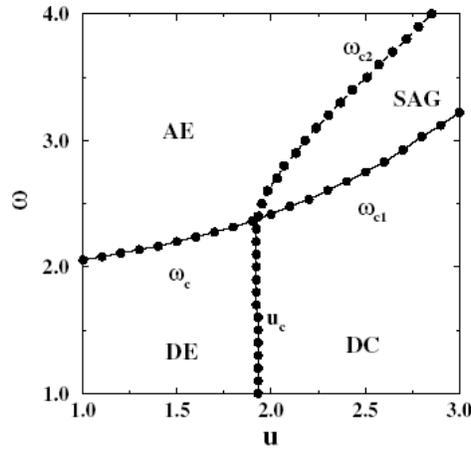


Figure 4: The phase diagram of a surface interacting linear polymer in 2-d space using self attracting SAW [10].

Conclusion

In this paper, we have discussed how polymers can be modeled by self avoiding walks (SAWs) on a lattice. In particular, a parallel can be drawn between a SAW and the $O(n)$ model of magnetic systems with $n \rightarrow 0$. This allows us to import the techniques and ideas from the critical phenomena into the SAW model. The model has been used to study polymer systems under various conditions and situations such as its interaction with a surface. The existence of an attractive surface results in addition critical phenomena. The problem of surface adhesion under different solvent conditions can also be explored with this model. In a good solvent, the monomer-monomer interaction is repulsive and can be neglected. Whereas in a bad solvent, this interaction is attractive and it competes with the surface attraction when the polymer chain is close to the surface. The phase diagrams obtained under these 2 conditions has been compared and contrasted in this paper.

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