Random Walks in Polymer Physics

Erich Eisenriegler

Institut für Festkörperforschung, Forschungszentrum Jülich,
D–52425 Jülich, Germany

Abstract. Long flexible polymer chains can be modelled as self-avoiding random walks and their properties analyzed by exploiting the polymer-magnet analogy and using field theoretical tools. We discuss the behavior of chains in an infinite unbounded space and the interaction of chains with impenetrable boundaries, such as those of mesoscopic spheres and cylinders. This is relevant for colloidal particles immersed in a solution of free nonadsorbing polymers, and the understanding of polymer–depletion effects is advanced considerably if we use properties of the field theory such as the local character of renormalization, various operator expansions for short distances, and conformal invariance.

1 Introduction

Dilute solutions of long flexible polymer chains in good solvent show a behavior that is independent of most of the details of the chemical microstructure of the chains and of the (low molecular weight) solvent. As an example consider the mean square end-to-end distance or the radius of gyration \( R^2 \) of a single isolated chain. It follows a power law [1, 2, 3]

\[
R^2 \sim N^{2\nu}
\]

as the number \( N \) of repeat units (monomers) along the chain becomes large. Although the chemical structure of repeat units is quite different for different types of polymer chains [4], the exponent \( \nu \) is the same. In three dimensions \( d = 3 \) and in the case of a good solvent (effective repulsion between monomers)

\[
\nu = 0.588
\]

Another example is the osmotic pressure \( \Pi \) of polymer chains. It obeys a scaling law [1, 2, 3]

\[
\Pi = k_BT c_p X(c_p R^d)
\]

where \( c_p \) is the number density of polymer chains and \( c_p R^d \) characterizes the degree of overlap between chains. Although it is assumed that \( N \) is large and that the monomer density \( c_p N \) is much smaller than in a dense polymer melt, the overlap may be either large (semidilute solution) or small (dilute solution). Eq. (1.2) contains two nontrivial statements. First, for a given substance, e.g. PMM in acetone, the dependence of \( \Pi/(k_BTc_p) \) upon the two
variables \( c_p \) and \( \mathcal{R} \) is only via the product \( c_p \mathcal{R}^d \). Second, the same (universal) scaling function \( X \) appears for different substances [5].

This poses two questions: How does the universal scaling behavior come about, and how can one calculate the universal quantities (such as \( \nu \) or \( X \))? A first hint comes from an oversimplified treatment that treats the polymer chain configurations as random walks where each of the \( N \) steps is statistically independent. For such an 'ideal' polymer chain, scaling and universality follow from the central limit theorem that tells us that the scaling function of the end-to-end distance distribution is a Gaussian and that \( \nu_{id} = 1/2 \), independent of the detailed form of the probability distribution for one step. For a chain at the \( \theta \) point [1, 2, 3] in \( d = 3 \) this is indeed essentially realized. However, for a chain in good solvent the repulsive (excluded volume) interaction between monomers is important. For such a 'self avoiding random walk' (SAW) \( \nu \) is larger, and the end-to-end distribution is non-Gaussian. A sufficiently general framework to explain the universality in this case is provided by the renormalization group. This is known from other critical systems, such as lattice spin models or field theories. Here we use the result that the SAW can be mapped onto a special type of near-critical field theory in order to calculate physical properties of SAW's.

First polymers are considered in an infinite unbounded space and then the interaction of polymers with boundaries. With applications to mesoscopic colloidal particles in mind, we consider not only planar but also curved boundaries, such as surfaces of spheres and cylinders.

2 Modelling a Polymer Chain in a Good Solvent and Relation to Field Theory

Since many details are irrelevant, there is much freedom in choosing a model. One of the most convenient models for analytical calculations is the 'bead and spring'-model with the single chain partition function

\[
Z_N(r_B, r_A) = \int dr_{N-1} \cdots \int dr_1 P(r_B, r_{N-1}) \cdots P(r_1, r_A) \cdot \prod_{i,i'} [1 - bl^d \delta(r_i - r_{i'})]
\] (2.1)

Here the product of \( N \) normalized Gaussians

\[
P(r, r') = (4\pi l^2)^{-d/2} e^{-r(r-r')^2/(4l^2)}
\] (2.2)

defines the chain structure with fixed end points at \( r_A, r_B \) and \( N - 1 \) internal beads at \( r_1, \ldots, r_{N-1} \), and it introduces a characteristic size \( l \) per monomer. The product \( \prod \) is over the \( \binom{N-1}{2} \) pairs \((i,i')\) of internal beads. Since \( b > 0 \), it decreases the probability weight for those configurations where the beads overlap. The hat on \( \prod \) means that only those products of \( \delta \)-functions are