Computer Simulation Studies of Static and Dynamical Scaling in Dilute Solutions of Excluded-Volume Polymers

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ABSTRACT: We have used a novel Monte Carlo method to compute the gyration radius R_G and the hydrodynamic radius R_H of excluded-volume polymer chains. The hydrodynamic radius scales as $N^{\approx 0.55}$ (N is the number of bonds) over at least a decade of chain lengths, whereas the gyration radius exponent is close to the theoretical value of 0.59. The anomalous behavior of R_H is well-known experimentally; it is commonly attributed to the belief that polymers in mediocre solvents are not swollen on short length scales. However, the polymer chains in our simulations are uniformly swollen on all length scales; we suggest that the discreteness of the polymer chain is sufficient to explain the behavior of R_H.

The effective size of a polymer chain scales as a power ν of the molecular weight.[1,2] Static measurements of the radius of gyration of a dilute polymer solution in a good solvent give an exponent $\nu_G = 0.595 \pm 0.005$,[3] close to the renormalization theory result for a self-avoiding random walk, $\nu = 0.588$.[4] Dynamical measurements of diffusion or viscosity coefficients indicate a smaller exponent $\nu_H \approx 0.55$.[5,6] It was suggested initially that the dynamic and static scaling laws are different, but this idea has been generally discarded in favor of arguments based on solvent effects. For a general discussion of the scaling of R_G and R_H, see refs 1 and 2. Weill and des Cloizeaux[7] suggested that in mediocre solvents only large segments of the chain, containing many statistical units (bonds), are swollen; the smaller length segments are ideal; that is, their size scales as the square root of the number of bonds. Thus the observed exponent for a finite length chain will be somewhere between ideal ($\nu = 1/2$) and swollen ($\nu = 0.588$); since the hydrodynamic radius weights the short distances more heavily than the gyration radius, its effective exponent will be smaller. In this work we have used a powerful new Monte Carlo technique, configurational-bias Monte Carlo (CBMC), to examine the connection between the swelling of internal segments of long polymer chains and the hydrodynamic and gyration radii of those chains.

Our polymer model is a freely-jointed chain with a unit bond length between the joints; the excluded volume is introduced by placing rigid spheres of diameter σ ($0 \le \sigma \le 1$) at each joint. Single chains containing between 2 and 1025 spheres were simulated, with 1000 independent chain configurations for each reported result; the statistical errors in the gyration and hydrodynamic radii are then small (0.5%). In order to efficiently generate many statistically independent chain conformations, we employed the recently developed configurational-bias Monte Carlo scheme for fully flexible molecules.[8] The basic Monte Carlo step in this scheme is a partial (or total) regrowth of the chain; the chain is cut at some randomly selected point and regrown from there. Of course, a random regrowth of the polymer would almost certainly result in a self-overlapping (forbidden) conformation. For polymers on a lattice, this problem can be alleviated by regrowing the polymer using a biased procedure due to the Rosenbluths.[9] In this procedure the polymer is not regrown randomly; rather, at every step it only moves in one of the k directions (out of a maximum of b) that are not yet occupied. Due to the bias in the growth process, the conformations are not generated with the correct statistical weight; to compensate for this bias, Rosenbluth and Rosenbluth introduced a weight factor w, defined as

$$w = \prod_{i=1}^{l} (k_i/b) \tag{1}$$

for a trial chain of l segments. In ref 9 it is shown that this factor w should be used as a weighting factor in any statistical average over chain conformations generated using the Rosenbluth prescription. Unfortunately, for long chains this procedure is unreliable because the probability of generating chains with a large "Rosenbluth weight" becomes very small. Recently, it was shown that this drawback of the original Rosenbluth scheme can be overcome by using a Monte Carlo scheme in which the acceptance probability of a trial conformation is proportional to the ratio of the Rosenbluth weights of the new and old conformations $w^{\text{trial}}/w^{\text{old}}$;[10] a less general version of this scheme was presented earlier.[11] We shall refer to this method as the configurational-bias Monte Carlo method. Still, the CBMC method as described in ref 10 is limited to molecules with discrete conformations; recently however, Frenkel et al. showed how the CBMC method can be extended rigorously to fully flexible molecules.[8] In this case, the number of possible trial directions b at any step is, in principle, infinite. However, it is shown in ref 8 that a correct Monte Carlo procedure can be devised by generating a random subset of this infinity of possible trial directions and computing the Rosenbluth weight w for this finite subset. It should be stressed that the validity of this scheme in no way relies on the number of trial directions in this subset; in fact, one could generate only one trial direction per step, in which case the conventional, random-walk sampling would be recovered. The actual number of trial directions is chosen to optimize the computational efficiency of the scheme; typically the number of trial directions varies from 2 to 3 for short chains, to 50 if long chains are regrown. For more details about the CBMC method, the reader is referred to refs 8 and 12.

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