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V. Yamakov
University of Southern Mississippi

D. Stauffer
University of Southern Mississippi

A. Milchev
University of Southern Mississippi

G.M. Foo
University of Southern Mississippi

R.B. Pandey
University of Southern Mississippi

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Crossover Dynamics for Polymer Simulation in Porous Media

V. Yamakov,^{1,*} D. Stauffer,^{1,2} A. Milchev,^{1,*} G. M. Foo,^{1,3} and R. B. Pandey¹

¹*Department of Physics and Astronomy, University of Southern Mississippi, Hattiesburg, Mississippi 39406-5046*

²*Institute for Theoretical Physics, Cologne University, 50923 Köln, Germany*

³*Supercomputing and Visualization Unit, National University of Singapore, Singapore, 119620*

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Off-lattice Monte Carlo simulations show anomalous diffusion at intermediate times without a clear Rouse regime, for the motion of chains through a random porous medium. [S0031-9007(97)04063-5]

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The static properties of polymer chains are described, e.g., by their fractal dimension, relating their mass to their radius of gyration via an asymptotic power law. The dynamics can be described by an exponent ν such that the mean square distance $\langle R^2 \rangle$ traveled in time t varies asymptotically as

$$\langle R^2 \rangle \propto t^\nu.$$

If $\nu = 1$ we have normal diffusion, otherwise we have anomalous diffusion.

The Rouse theory [1,2] deals with the motion of a bead connected to its neighboring beads by a spring-like potential in a viscous background and heat bath of the surrounding chains. It gives for short, intermediate, and long times the exponents $\nu_m = 1, \approx 0.5$, and 1 again, if R refers to the motion of a single monomer in the chain, while for the motion of the center of mass, the corresponding exponent $\nu_{c.m.}$ equals one for all times. In the presence of many polymer chains the motion of each chain in the melt is hindered by the presence of the other chains: "entanglement." Now, after the Rouse regime, a reptation regime with an exponent $\frac{1}{4}$ is predicted, and thus the sequence of theoretically expected values is $\nu_m = 1, \frac{1}{2}, \frac{1}{4}, \frac{1}{2}$, and 1 for the motion of a single monomer; the center of mass has the exponents $\nu_{c.m.} = 1, \frac{1}{2}$, and 1. The asymptotic behavior for very long times is difficult to reach in computer simulations, but indications for reptation behavior, $\nu_m = \frac{1}{4}$, were found some time ago [3] and substantiated recently by Ebert *et al.* [4].

In the reptation theory [2], one assumes that the polymer chain moves mainly within a fixed tube formed by the other polymers. In reality, of course, this tube can also move and be deformed. In contrast, in a porous medium such as a static gel matrix, the polymer chains can move only through the fluid pores and do not change the solid part. Thus, if a tube is formed by the porous gel, it is fixed (quenched disorder). Therefore one might hope to also get good, and perhaps even better, reptation behavior for a single polymer chain moving through a porous medium with the help of a solvent, as this has been observed for chains moving in a straight tube with smooth impenetrable walls [5]. Such a simulation is presented here, similar in spirit to Ref. [6].

To allow for both short and intermediate times, $1 \leq t \leq 10^7$, we avoided the numerically more efficient lattice models and worked instead on a continuum. Our model was described before [7,8], and consists of atoms interacting via a Morse potential $\propto \exp(-48r) - 2\exp(-24r)$, which defines our length scale for the distance r . In addition, the atoms (monomers) on the same chain are permanently bound through a potential $\propto -\ln(1 - (r - 0.7)^2/0.09)$ for $|r - 0.7| < 0.3$; for larger elongations this potential is infinite, so as to guarantee that chains do not intersect with themselves or other chains.

The porous medium is generated by distributing the barrier particles randomly in space, similar to continuum percolation. Each particle interacts with a Morse potential as the nonbonding interaction with the neighboring chain beads mentioned above with a well-defined hard-core radius as in discrete lattice simulations (Ref. [9]). We start with many chains of N monomers each. (The proportionality factors are chosen as in Ref. [8], so that the polymer chains stay in the "good solvent" regime.) In this way we define a bead-spring chain model.

We used C atoms per cell in a linked-cell algorithm [7]; this corresponds to a volume fraction of about $C/4$ for the atoms, if the monomer radius is defined through the minimum of the Morse potential. The concentration C can be larger than one, but simulations are already difficult near $C = 1$. For larger $C \approx 1.1$, some sort of percolation threshold would be reached, where the pore space ceases to offer an infinite channel through which the chains can move with reasonable probability; the fraction of pore space then is about $1 - C/4 \approx 0.7$, as found by observing the diffusivity of chains of length $N = 1$.

Now we let the chains move via Monte Carlo simulations using the Metropolis technique: An energy increase ΔE is accepted only with probability $\exp(-\Delta E/k_B T)$ if a randomly selected monomer tries to move a random distance in a random direction. (For numerical efficiency we let about seven chains move simultaneously through this porous medium and allow them to interpenetrate without interacting with each other.) One time step corresponds to one attempt to move, on average, every chain monomer once. For short times we increase our statistics by regarding the motion from time τ to time $\tau + t$ as

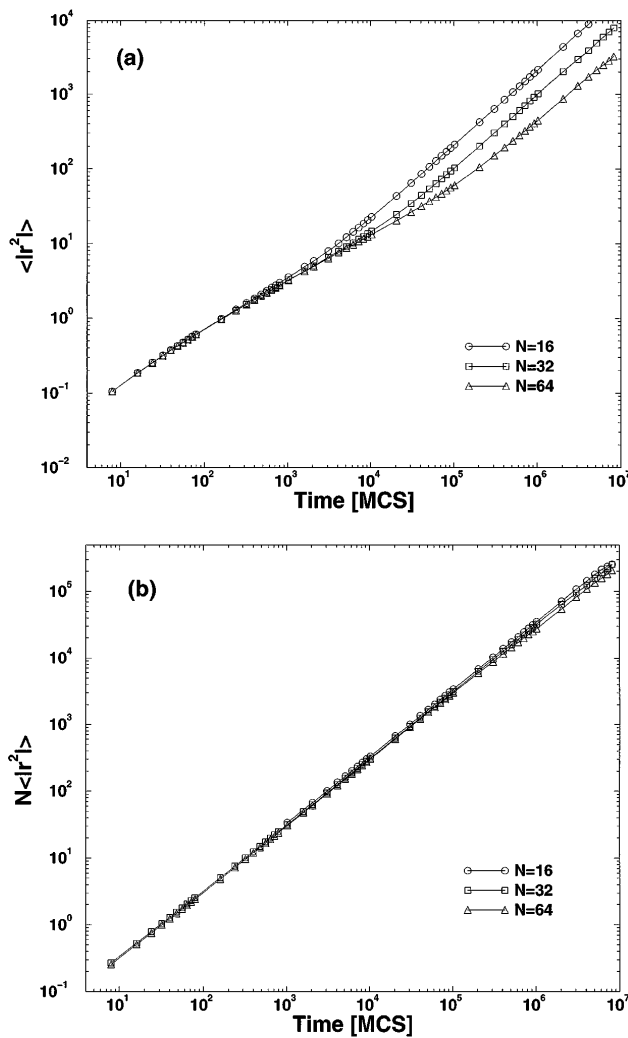


FIG. 1. (a) Mean square distance traveled by the monomer in the center of the chain, versus time, at zero concentration (no solid obstacles) and for chain lengths 16, 32, and 64. (b) The corresponding quantity for the center-of-mass motion, except that now the mean square distance is multiplied by the chain length N .

motion over t steps; thus from 10^7 iterations we obtain 1000 data for $t = 10^4$, and the fluctuations are smaller for short times. (We averaged over 20–500 realizations of the porous medium.)

Figure 1 for motion without a porous medium and Fig. 2 for $C = 0.5$ show a behavior similar to Refs. [2,3]: The motion of the center of mass is simpler than that of the single monomer in the center of the chain. Note that for the center of mass we multiplied the mean square distance by the chain length N to account for the theoretically predicted [1] diffusivity proportional to $1/N$. But the accuracy of our data allows for closer inspection by determining, from two consecutive times of Figs. 1 and 2, the slope, i.e., the effective exponent $\nu(t)$. Now we see in Figs. 3 and 4 that there is no clear Rouse region with $\nu_m = 1$ for short times.

Figure 5 shows how the plateau value ν_{eff} for the monomer motion in the center of the chain decreases

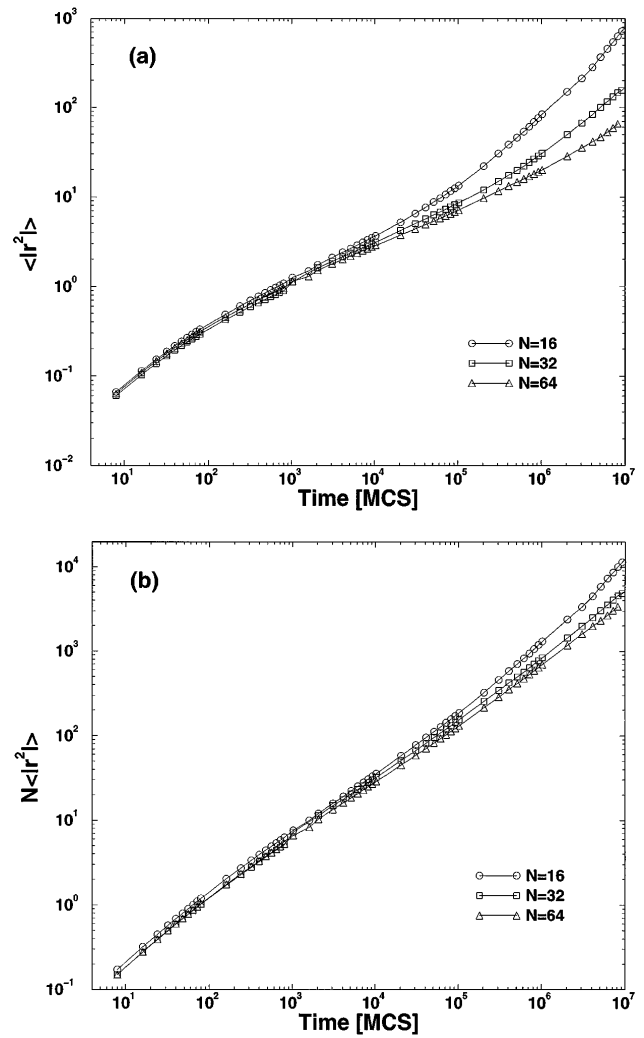


FIG. 2. Same as Fig. 1 but at a concentration $C = 0.5$ of solid material in the porous medium.

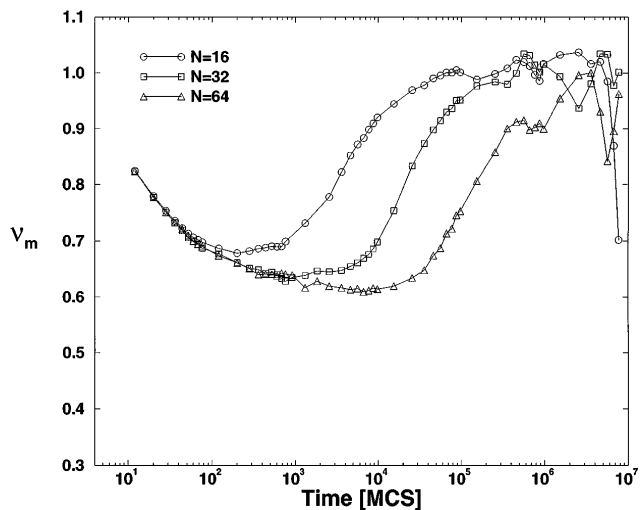


FIG. 3. Effective exponents ν_m versus time from Fig. 1(a) ($C = 0$).

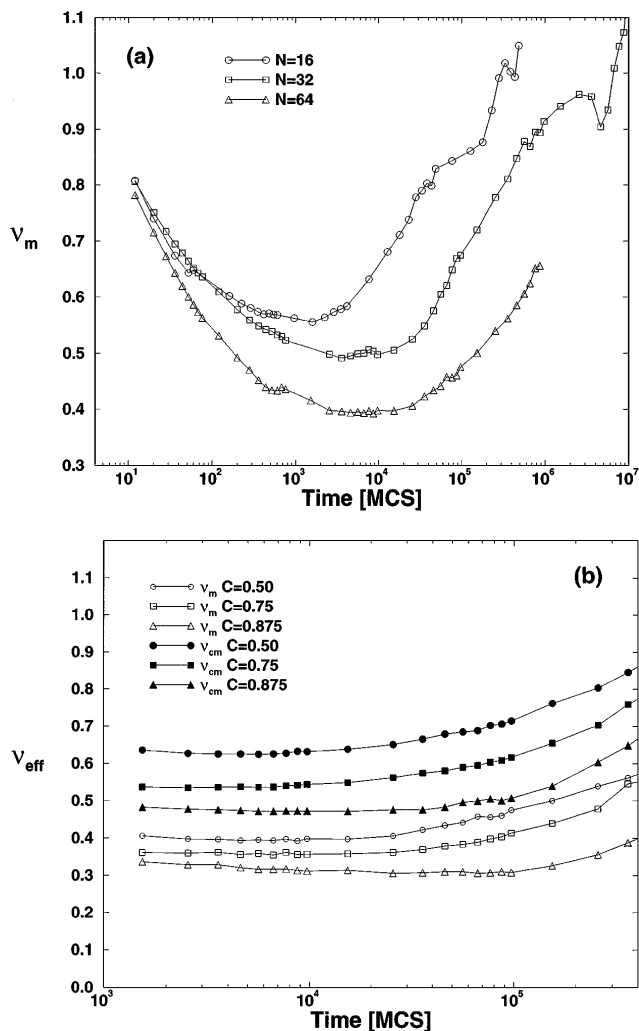


FIG. 4. (a) Effective exponents ν_m versus time from Fig. 2(a) ($C = 0.5$; about 20 samples). (b) Effective ν_m and $\nu_{\text{c.m.}}$ for $N = 64$, various concentrations, and 512 samples.

with increasing concentration C and with increasing chain length N towards about $\frac{1}{4}$, the value predicted by reptation theory, but no clear convergence was seen. We are not aware of a reptation theory with a concentration dependent exponent, as observed here. Thus the Rouse theory ($\nu_m \approx \frac{1}{2}$), and perhaps also the reptation theory ($\nu_m \approx \frac{1}{4}$), is questioned by our data. For long times [2,3] below the percolation threshold, we again expect normal diffusion as if the whole chain would be a pointlike particle; our data for low concentrations C are compatible with this expectation.

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*Permanent address: Institute for Physical Chemistry, Bulgarian Academy of Sciences, G. Bonchev Street,

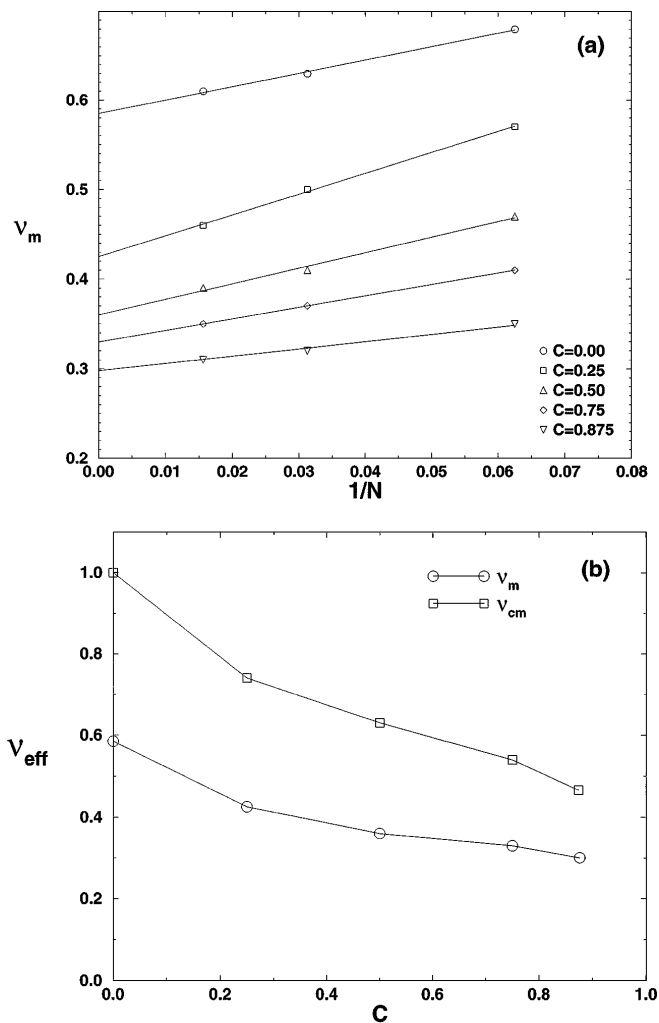


FIG. 5. Minimum exponent value versus reciprocal chain length (a), and extrapolated intercepts for infinite lengths versus concentration (b).

Block 11, 1113 Sofia, Bulgaria.

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