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Monte Carlo study of living polymers with the bond-fluctuation method

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The highly efficient bond-fluctuation method for Monte Carlo simulations of both static and dynamic properties of polymers is applied to a system of living polymers. Parallel to stochastic movements of monomers, which result in Rouse dynamics of the macromolecules, the polymer chains break, or associate at chain ends with other chains and single monomers, in the process of equilibrium polymerization. We study the changes in equilibrium properties, such as molecular-weight distribution, average chain length, radius of gyration, and specific heat with varying density and temperature of the system. The results of our numeric experiments indicate a very good agreement with the recently suggested description in terms of the mean-field approximation. The coincidence of the specific heat maximum position at $k_BT = V/4$ in both theory and simulation suggests the use of calorimetric measurements for the determination of the scission-recombination energy V in real experiments.

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I. INTRODUCTION

Systems in which polymerization is believed to take place under condition of chemical equilibrium between the polymers and their respective monomers are termed "living polymers." These polymers are long linear-chain macromolecules that can break and recombine reversibly and so are in equilibrium with respect to their molecular-weight distribution (MWD). A number of examples have been studied in recent years, including liquid sulfur [1–3] and selenium [4], poly(α-methylstyrene) [5], polymerlike micelles [6,7], and protein filaments [8].

The irreversible aggregation of monomers into linear polymers exhibits critical phenomena which can be described by the $n \to 0$ limit of the n-vector model of magnetism [9,10]. Unlike mean-field models, the n-vector model allows for fluctuations of the order parameter, the dimension n of which depends on the nature of the polymer system. (For linear chains $n \to 0$, whereas for ring polymers $n = 1$.) In order to study living polymers in solutions, one should model the system using the *dilute* $n \to 0$ magnet model [10]; however, a theoretical solution presently exists only within the mean-field approximation (MFA) where it corresponds to the Flory theory of polymer solutions [11].

Due to experimental difficulties [7] the properties of living polymers still pose a number of questions. While phase diagrams can be reasonably described by the MFA [5], the experimental evidence concerning microscopic properties, such as, e.g., the extent of growth in micelles, is controversial [12]. Some light scattering, NMR, and sedimentation experiments [13] suggest that micelles in solutions grow considerably with decreasing temperature and rising density; other neutron scattering measurements [14] and transient fluorescent experiments [15] have been interpreted in terms of much smaller growth with temperature and density. So far we are not aware of any direct measurements of the MWD in such systems.

Given the shortcomings of an approximate analytical treatment (MFA) and the difficulties with the laboratory measurements, it is conceivable that numeric experiments, being exact within the framework of the respective model and able to account explicitly for various factors that influence experiments, might help much in understanding the thermodynamic behavior and the properties, both static and dynamic, of living polymers. However, up to now only a small number of simulational studies [16–18] have been carried out. Indeed, while the connectivity of polymer chains and the resulting slow dynamics render computer simulations a demanding task in its own terms, the scission-recombination processes, which are constantly under way in living polymers, impose additional problems on computational algorithms. In the Monte Carlo (MC) simulations so far [16,17] the polydisperse system of polymer chains was mapped on a Potts model whereby different spin values were taken to represent bonded and nonbonded monomers as well as vacancies on a lattice. Such models are very efficient for studying static properties of living polymers since at each update of the lattice all sites are assigned new spin values subject to a Boltzmann probability whereby the restrictive topological connectivity of the chains is violated. Since the way in which equilibrium properties of the system are attained is not essential, it is clear that static features may thus be faithfully reproduced. However, the kinetics of such models is fictitious and they cannot be employed for studies that include dynamic features as yet.

In the present work we use a new Monte Carlo algorithm, based on the highly efficient bond fluctuation model [19,20] (BFM) which is known to be very accurate in faithfully reproducing both static and dynamic properties of polymer chains in melts and solutions. The BFM is modified so as to allow for the association-dissociation events in the process of equilibrium polymerization and provides a basis for a thorough investigation of various properties of living polymers. In the current investigation we focus on the static properties of such systems and examine the dependencies of thermodynamic—e.g., internal energy, specific heat as well as of structural properties—weight average association number (average chain length), MWD, radius of gyration, on density and temperature of the system. Our first results indicate that the MFA description provides an amazingly good semiquantitative picture of the properties of living polymers at least for the case when nonbonded interactions between monomers may be neglected as compared to the bond energy along the backbone of the macromolecules. The specific heat of the system, which we introduce in this paper, turns out to be an interesting alternative to other measurable properties of solutions of living polymers. With varying temperature the specific heat exhibits a maximum whose position measures directly the energy of association in such systems.The present paper is organized as follows: In Sec. II we give a brief description of the BFM and of the MC procedure, in Sec. III we present our results, and in Sec. IV we summarize our finding.

II. MODEL

The bond fluctuation model is a coarse-grained model of polymer chains, in which an "effective monomer" consists of an elementary cube whose eight sites on the hypothetical cubic lattice are blocked for further occupation—see Fig. 1. This defines the largest possible density of the polymer which, in terms of the ratio of occupied to total volume, is 0.5. A polymer chain is made of effective monomers joined by bonds. A bond corresponds to the end-to-end distance of a group of 3–5 successive chemical bonds and can *fluctuate* in some range. It is represented by vectors $\mathbf{l}$ of the set $P(2,0,0)$, $P(2,1,0)$, $P(2,1,1)$, $P(3,0,0)$, and $P(3,1,0)$ which guarantee that intersections of the polymer chain with other chains, or with itself, are virtually impossible. All lengths are here measured in units of the lattice spacing and the symbol P stands for all permutations and sign combinations of the cartesian coordinates (l_x, l_y, l_z). The algorithm displays Rouse behavior for all spatial dimensions and combines typical advantages of the lattice MC methods with those from the continuous Brownian dynamics algorithm. The adequacy of the BFM algorithm to describe static and dynamic behavior of polymers has been proven in sensitive investigations [20].

In our model, we set an energy $-V$ $(V > 0)$ for the creation of a bond between monomers. In the present study the ends of a given polymer chain are not allowed to bind together so that the formation of rings is impossible. Those sites of the lattice that are not occupied by monomers are considered empty (vacancies) and contribute to the free volume of the system. In principle we assign an energy $-w$ $(w > 0)$ for the nonbonded interaction between monomers in the system, and another energy σ governs the flexibility of the chains, $\sigma > 0$ being the cost for converting a single bond from *trans*- into *gauche*-configuration. In the present investigation, however, we focus exclusively on the process of equilibrium polymerization of entirely flexible chains, setting $w = 0$ and $\sigma = 0$, so that no phase separation into dense and dilute components should take place.

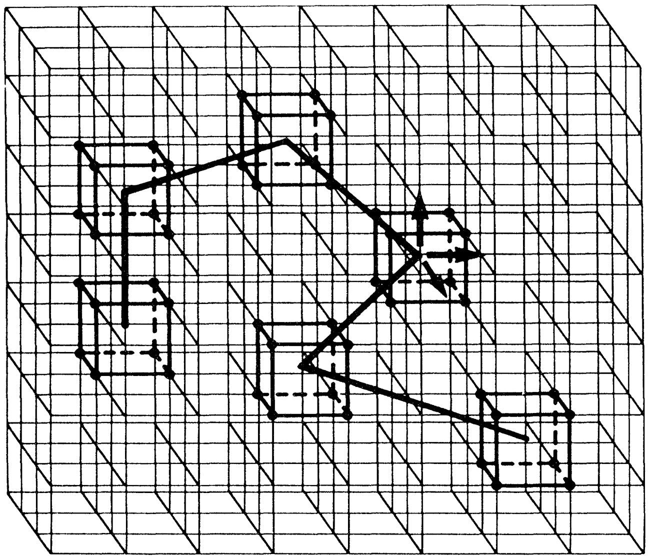

FIG. 1. Sketch of the BFM of polymer chains on the three-dimensional simple cubic lattice. Each repeat unit or "effective monomer" occupies eight lattice points. Elementary motions consist of random moves of the repeat unit by one lattice spacing in one lattice direction. These moves are accepted only if they satisfy the constraints that no lattice site is occupied more than once (excluded volume interaction) and that the bonds belong to a prescribed set of bonds. This set is chosen such that the model cannot lead to any moves where bonds should intersect, and thus it automatically satisfies entanglement constraints. Reprinted with permission from W. Paul, K. Binder, D. W. Heermann, and K. Kremer, J. Phys. (France) II **1**, 37 (1991).

Time is measured, as usually, in Monte Carlo steps (MCS) *per monomer* of the systems and a MCS is organized as follows:

(i) A monomer is chosen at random and allowed to perform a move according to the BFM algorithm.

(ii) If the monomer happens to be at the end of a chain, an attempt is made to create a bond with another monomer that might be present on any one of the 108 neighboring sites that is also chosen also at random. If the end of another polymer is present on the chosen neighboring site, the Metropolis algorithm [21] is applied, that is, a new bond is created if the value of a random number between 0 and 1 is smaller than $\min(1, \exp[-V/k_BT])$.

(iii) Finally, if a bond on the right of the current monomer exists, it is attempted to break, also according to the Metropolis rule. During one MCS one carries out (i)–(iii) as many times as there are monomers in the system. The order in which these sequences are carried out does not play any role. A number of structural properties are sampled during the simulation. Thus the mean-square gyration radius $\langle R_g^2\rangle$, the mean-square end-to-end distance $\langle R_e^2\rangle$, the mean-square bond length $\langle l^2\rangle$, and the average chain length $\langle L\rangle$, are measured for chains, starting from a dimer and larger, i.e., for those which are defined by the presence of bonds. Single monomers do not contribute thus to the gyration radius or to the end-to-end distance. The density ϕ was usually varied between 0.16 and 0.4. One should bear in mind that densities around 0.5 correspond to extremely dense systems in the BFM since the blocking of neighboring sites by existing monomers leaves no room for movement and the system goes effectively into a glassy state [19,20]. Therefore, at density 0.4 and for large enough chains, the so-called "dense" regime of polymer solutions, characterized by effective screening of the excluded volume interaction, is observed—Fig. 2.

The simulations have been carried out mostly on a $30 \times 30 \times 30$ cubic lattice with periodic boundary conditions but finite-size effects were also tested with smaller lattices of size $10\times10\times10$, $16\times16\times16$, and $20\times20\times20$. The system takes usually about 10 000 MCS in order to be equilibrated. The start configuration consists of randomly distributed and nonbonded monomers. After equilibration, measurements of data were performed in intervals of 100 to 160 MCS so that the sampled configurations should be possibly uncorrelated. Depending on temperature, usually about 600 independent data sets have been sampled. It turns out that, in order to get a reasonable statistics, a great number of monomers is needed at small temperatures. Indeed, since no chain can be larger than the total number of monomers present in the system, the presence of free monomers during the simulation guarantees that with the given set of energy and thermodynamic parameters one is still in the equilibrium regime. Thus, to ensure good average values, the mean chain length was kept equal or smaller than 10% of the total number of monomers in the system. For the smaller lattices, however, this condition severely restricts the choice of the lowest temperature.

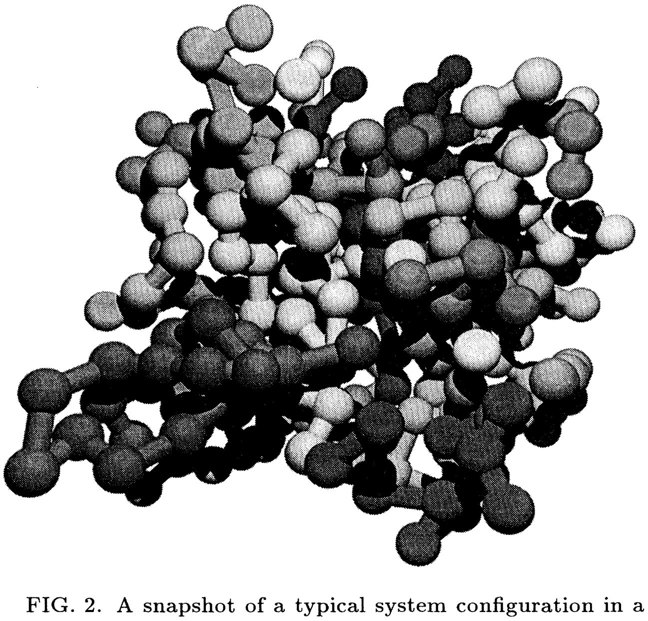

FIG. 2. A snapshot of a typical system configuration in a $20 \times 20 \times 20$ lattice with a total of 400 monomers present. Polymer chains of increasing chain length appear increasingly darker. The longest chain here consists of 99 monomers. The average chain length $\langle L\rangle = 7.76$. The thermodynamic parameters are $T = 0.5$ and $\phi = 0.4$, and $V = 2.0$.

III. RESULTS

Before turning to the results of the present investigation we recall briefly some essential points in the MFA treatment of living polymers [7]. As pointed out by Flory [11], the principle of equal reactivity, according to which the opportunity for reaction (fusion or scission) is independent of the size of the participating polymers, implies an exponential decay of the number of polymers of size l as a function of l. Indeed, at the level of mean-field approximation in the absence of closed rings, one can write the free energy for a system of linear chains [7] as

$$\frac{F}{k_BT} = \sum_l C(l,T)\left[\ln C(l,T) + \frac{V}{k_BT}\right], \qquad (1)$$

where the MWD for chain length l is denoted by $C(l,T)$ and k_B stands for the Boltzmann constant. The density of the system ϕ is then

$$\phi = \sum_l lC(l,T). \qquad (2)$$

Minimization of Eq. (1) with respect to $C(l,T)$, subject to the condition Eq. (2), yields

$$C(l,T) = \exp-\left(\frac{V}{k_BT} - 1\right)\exp\left(-\frac{l}{\langle L\rangle}\right), \qquad (3)$$

$$\langle L\rangle = \sqrt{\frac{\phi}{e}}\exp\left(\frac{V}{2k_BT}\right). \qquad (4)$$

This result should be valid for sufficiently high density ϕ where correlations, brought about by the mutual avoidance of the chains, are negligible. Due to the recombination-scission process a polydisperse solution of living polymers should absorb or release energy as the temperature is varied. This is reflected by the specific heat c_v, which can be readily obtained from Eq. (1) as a derivative of the internal energy U,

$$U = V\sum_l C(l,T) = \langle L\rangle\exp-\left(\frac{V}{k_BT} - 1\right). \qquad (5)$$

For c_v one has

$$c_v = \sqrt{\phi e}\frac{\exp -(\frac{V}{2k_BT})}{2k_BT^2}V, \qquad (6)$$

which has a maximum at $k_BT_c = V/4$.

In Fig. 3 we show the measured variation of the mean chain length $\langle L\rangle$ with temperature for different strength of the bonds between monomers. The specific heat c_v, reflecting the process of equilibrium polymerization, is also indicated. Evidently, in a comparatively narrow temperature interval, marked by a maximum in the specific heat, a sharp increase of $\langle L\rangle$ with decreasing temperature is observed in agreement with theory [1–3]. As mentioned in Sec. II, it is the finite size of the systems that does not allow us to go down to even lower temperature since the largest chain would then consume all available monomers in the lattice. This is clearly visible for the smallest size of the $10 \times 10 \times 10$ system by the sharp drop in c_v at $T = 0.45, 0.4$ where the equilibrium size of the longest chain exceeds the total number of monomers in the box. As compared to the MFA result, Eq. (6), the maxima of c_v occur at $k_BT \approx V/4$ for sufficiently large system sizes. This appears to be a remarkably good agreement with the prediction of Eq. (6), given the known shortcomings of the MFA in general. However, while the positions of the c_v maximum do not differ appreciably in theory and simulation, the overall shape of the simulational c_v is much sharper than that of Eq. (6). In order to check for finite-size effects, which might affect our results, we studied several system sizes: 10^3, 16^3, 20^3, and 30^3—the latter being able to accommodate about 1350 monomers. Despite considerable fluctuations in our data, it is seen from Fig. 4 that for all lattice sizes studied, no appreciable finite-size effects can be detected. This result is in agreement with an earlier investigation of finite-size effects in computer simulations of living polymers [17] with $w \neq 0$ which found that finite-size effects can be observed below lattice sizes of 14^3 only. All data in Fig. 4 refer to $V = 2.0$ and it is seen that c_v maximum occurs at $\approx V/4$ indeed.

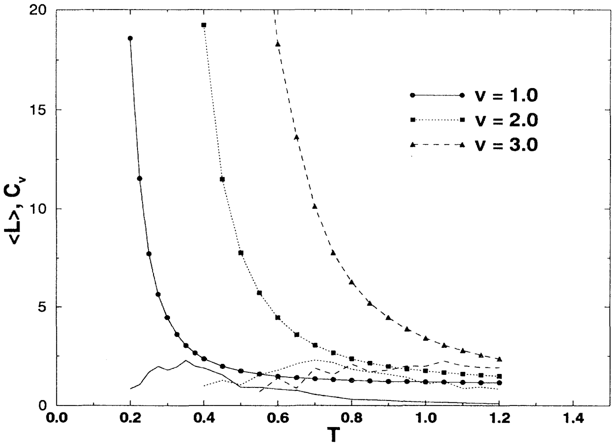

FIG. 3. Variation of $\langle L\rangle$ with temperature for three different values of the bond energy V (full symbols) and $\phi = 0.4$. The specific heats of the respective systems are also shown by lines.

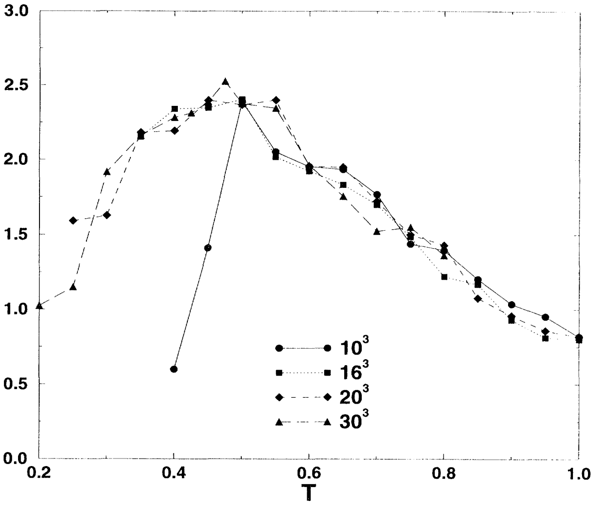

FIG. 4. Variation of specific heat c_v with temperature for system size: $10^3, 16^3, 20^3$, and 30^3.

The distribution of chain lengths at equilibrium, $C(L,T)$, is represented in Fig. 5 in semilog coordinates. The fluctuations in the sampled lengths increase considerably for very long chains where correlations between successive configurations deteriorate the statistics. Nevertheless, qualitatively the distributions agree very well with the MFA result, Eq. (3). An attempt to get all distributions collapsed on a single master curve by rescaling the chain lengths with the mean chain length $\langle L\rangle$ as Eq. (4) suggests, is less successful. It appears that the average chain length is somewhat larger at low temperature, and, respectively, smaller at higher temperature, than a perfect scaling plot according to Eq. (3) would require. Here we should also like to point out that this

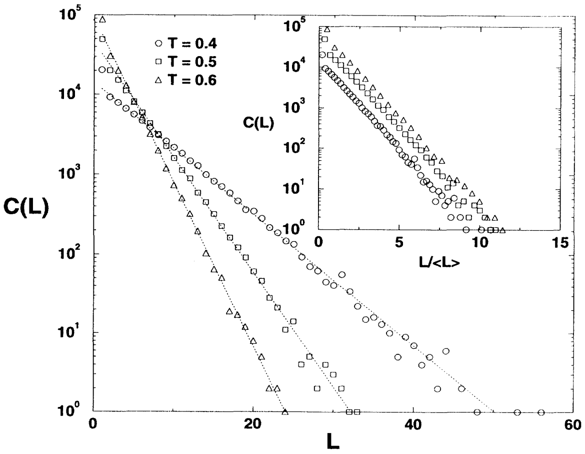

FIG. 5. Probability distribution $C(L)$ of chains with length L at various temperatures (given as a parameter) and $\phi = 0.4$. In the inset an attempted scaling of $C(L)$ in the form of $e^{-\frac{L}{\langle L\rangle}}$ is also shown.

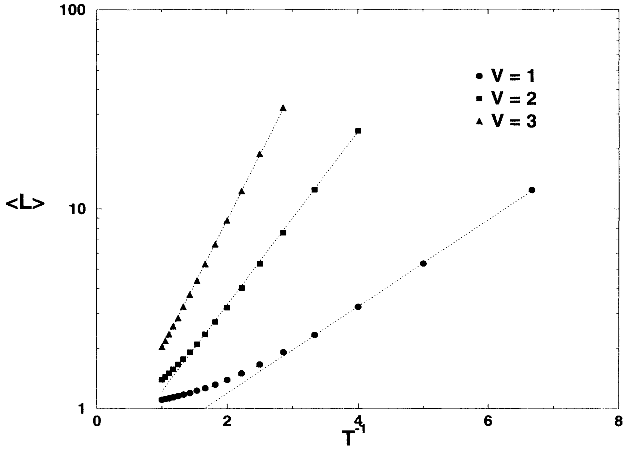

FIG. 6. Variation of $\langle L\rangle$ with inverse temperature for three values of the bond energy V (given as a parameter) and $\phi = 0.4$. The measured slopes are equal to $V/2$.

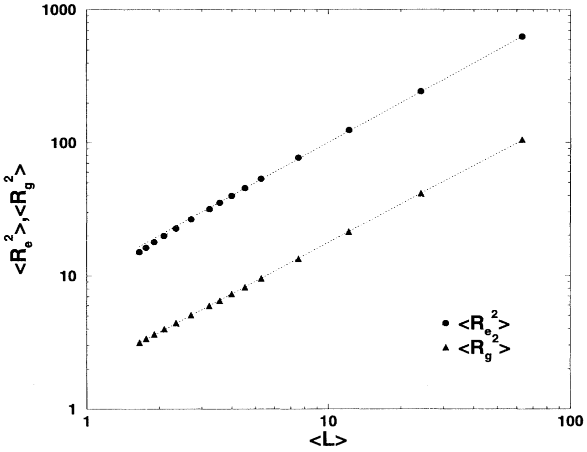

FIG. 8. Scaling plot of $\langle R_g^2\rangle$ and $\langle R_e^2\rangle$ with the mean chain length $\langle L\rangle$ for $V = 2.0$ and $\phi = 0.4$. The slope is $\approx 1.00{\pm}0.01$.

form of the distribution, which reveals a typical curvature for small chain lengths (monomers), has been observed in a MC simulation of a three-dimesional system of living polymers employing a qualitatively different model [17] so it is by no means an artefact of the present algorithm.

Another comparison between numeric experiment and analytic predictions is presented in Fig. 6 where we show a semilog plot of $\langle L\rangle$ vs inverse temperature for three different values of the bond energy V. Evidently our data fit straight lines well for $\langle L\rangle \geq 2$. All slopes of the curves are indeed given by $V/2$, cf. Eq. (4). Also, the dependence of $\langle L\rangle$ on density ϕ shows good agreement with the MFA prediction, Eq. (4). In Fig. 7 the variation of $\langle L\rangle$ with density ϕ is plotted for two temperatures, above, $T = 0.6$, and below, $T = 0.4$, the respective T_c for $V = 2.0$ in log-log coordinates. For $T = 0.4$, i.e., for long enough chains, we measure an exponent of 0.567 which exceeds slightly the expected $\sqrt{\phi}$ law and tends to the value of ≈ 0.6 [7] which has been derived on the basis of scaling theory considerations [22]. As the density of our polymer system is considerable, excluded volume is screened at rather short distances and one deals effectively with an assembly of Gaussian chains with $\nu = 0.5$. That is why we interpret the value of 0.567 as marking the crossover between a semidilute and a dense regime for our system. At $T = 0.6$ the system is apparently dominated by very short chains $\langle L\rangle \leq 2$, which explains the rather low value of the measured exponent ≈ 0.44.

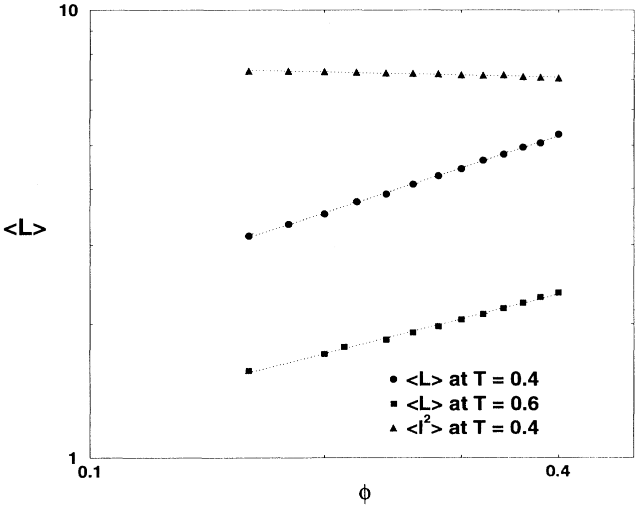

FIG. 7. Variation of $\langle L\rangle$ with total density ϕ at two different temperatures $T = 0.4$ and $T = 0.6$. The slope of the data is 0.567 ± 0.005 at $T = 0.4$ and 0.44 ± 0.01 at $T = 0.6$. Filled triangles denote the change in the mean-squared bond length $\langle l^2\rangle$ with ϕ which goes with a slope of -0.039.

Finally, in Fig. 8 we demonstrate the scaling behavior of the mean-square end-to-end distance $\langle R^2\rangle$ and of the mean-square gyration radius $\langle R_g^2\rangle$ with the average chain length $\langle L\rangle$ for a system with $V = 2.0$. Not surprisingly, deviations from the scaling behavior are observed for very short chain lengths, $\langle L\rangle \leq 2$. While $\langle R^2\rangle/\langle R_g^2\rangle \approx 6$, the measured slope of $\approx 1.01 \pm 0.01$ reveals that both $\langle R^2\rangle$ and $\langle R_g^2\rangle$ scale with $\langle L\rangle$ with an effective exponent $\nu \approx 0.5$ as for Gaussian polymer chains. This, as a matter of fact, is what one should expect since the density $\phi = 0.4$ of the system corresponds to the high-density regime in which excluded-volume interactions are almost completely screened. Simulations of the system with other values of V (not shown here) produce the same value of ν.

IV. CONCLUSIONS

In the present investigation of equilibrium properties of living polymers we apply the bond fluctuation model of a MC simulation, which is known to reproduce the correct Rouse dynamics of macromolecules in the absence of solvent molecules. The algorithm allows for the stochastic movements of the monomers and for the processes of scission and recombination of energy bonds (in this study no formation of ring polymers is allowed). Structure and thermodynamic properties of polydisperse systems (wormlike micelles) undergoing equilibrium polymerization are studied for the "pure" case when nonbonded monomer interactions are set to zero so that the overall picture is not complicated by phase separation at low temperature. For the sake of clarity the chains are considered as absolutely flexible, too. Our simulational results reveal very good semiquantitative agreement with the mean-field predictions for the properties of living polymers:

(i) The probability distribution of chain lengths in the polydisperse system closely follows the expected exponential form Eq. (5). The failure to get all distributions collapsed on a single scaling function e^{-x} with $x = L/\langle L\rangle$, however, suggests that the measured values of $\langle L\rangle$ slightly differ from those, required for a perfect collapse, probably due to the particular temperature interval (*at* the polymerization transition) where the measurements have been carried out.

(ii) The maximum of the specific heat c_v which marks the onset of rapid growth of $\langle L\rangle$ occurs at a critical temperature $k_BT_c \approx \frac{V}{4}$ where V denotes the energy of a single bond in the polymer chain in good agreement with the MFA prediction, Eq. (6).

(iii) The mean chain length $\langle L\rangle$ is found to grow exponentially with decreasing temperature, and the measured "activation" energy for the growth is $\frac{V}{2}$, as expected from MFA considerations.

(iv) Concerning the density dependence of $\langle L\rangle$, we find that $\langle L\rangle \propto \phi^{0.567\pm0.005}$, marking a crossover between the predicted $\sqrt{\phi}$ dependence by MFA, and the exponent of ≈ 0.6, following from scaling considerations.

(v) At the comparatively high density $\phi = 0.4$, where most of our simulations have been performed, the excluded volume interactions appear to be entirely screened and we observe a scaling relationship $\langle R_g^2\rangle \propto \langle R^2\rangle \propto \langle L\rangle^{2\nu}$ with $\nu \approx 0.5$ as for Gaussian polymer chains [22].

We believe that the present work unambiguously confirms the main results of the MFA treatment of living polymers in most aspects concerning their static properties at equilibrium. It may be concluded that the principal MFA results provide a qualitatively correct description of such systems and in most aspects these results turn out to be even quantitively correct, at least within the framework of the underlying model. An interesting check for the theory would be the simulation of the observed dynamics and relaxation kinetics of living polymers where our studies are currently under way.

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[1] R. L. Scott, J. Phys. Chem. **69**, 261 (1965).

[2] J. C. Wheeler, S. J. Kennedy, and P. Pfeuty, Phys. Rev. Lett. **45**, 1748 (1980).

[3] S. J. Kennedy and J. C. Wheeler, J. Phys. Chem. **78**, 953 (1984).

[4] G. Faivre and J. L. Gardissat, Macromolecules **19**, 1988 (1986).

[5] K. M. Zheng and S. C. Greer, Macromolecules **25**, 6128 (1992).

[6] J. Appel and G. Porte, Europhys. Lett. **12**, 185 (1990).

[7] M. E. Cates and S. J. Candau, J. Phys. Condens. Matter **2**, 6869 (1990).

[8] F. Oozawa and S. Asakura, *Thermodynamics in the Polymerization of Proteins* (Academic Press, New York, 1975).

[9] P. G. de Gennes, Phys. Lett. **38A**, 339 (1972); J. des Cloiseaux, J. Phys. **36**, 281 (1975).

[10] J. C. Wheeler and P. Pfeuty, Phys. Rev. A **24**, 1050 (1981).

[11] P. J. Flory, *Principles of Polymer Chemistry* (Cornell University Press, Ithaca, NY, 1953).

[12] D. Blankschtein, G. Thurston, and G. Benedek, J. Chem. Phys. **85**, 7268 (1986).

[13] W. Brown, R. Johnsen, P. Stilbs, and B. Lindman, J. Phys. Chem. **87**, 4548 (1983).

[14] M. Zulauf *et al.*, J. Phys. Chem. **89**, 3411 (1985).

[15] R. Zana and C. Weill, J. Phys. Lett. **46**, L-953 (1985).

[16] A. Milchev, Polymer **34**, 362 (1993).

[17] A. Milchev and D. P. Landau (unpublished).

[18] G. I. Menon, R. Pandit, and M. Barma, Europhys. Lett. **24**, 253 (1993).

[19] I. Carmesin and K. Kremer, Macromolecules **21**, 2819 (1988).

[20] W. Paul, K. Binder, D. Heermann, and K. Kremer, J. Chem. Phys. **95**, 7726 (1991).

[21] See e.g., *Monte Carlo Methods in Statistical Physics*, edited by K. Binder (Springer Verlag, Berlin, 1979).

[22] P. G. de Gennes, in *Scaling Concepts in Polymer Physics* (Cornell University Press, Ithaca, NY, 1979), Chap. 1.

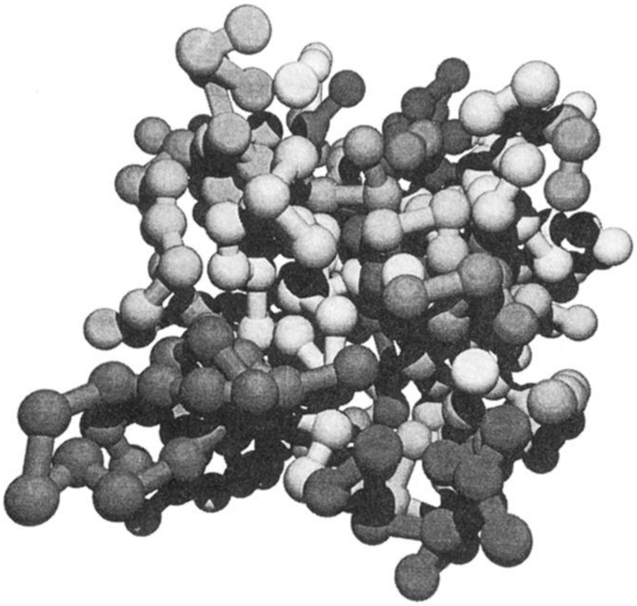

FIG. 2. A snapshot of a typical system configuration in a $20 \times 20 \times 20$ lattice with a total of 400 monomers present. Polymer chains of increasing chain length appear increasingly darker. The longest chain here consists of 99 monomers. The average chain length $\langle L \rangle = 7.76$. The thermodynamic parameters are $T = 0.5$ and $\phi = 0.4$, and $V = 2.0$.