A Monte Carlo Study of Living Polymers in 2D: Effect of Small Chains on Static Properties

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Abstract. — A slithering snake algorithm is combined with a binding and breaking chain algorithm to simulate the static behavior of living polymers according to Cates' description. It is shown that this simple two-dimensional simulation on a square lattice gives good agreement with the mean field theory. However, the large amount of small contour length chains for small values of the mean average length $\langle L \rangle$ appears to be one of the reasons for the discrepancies observed between the simulated results and the mean field theory. This finding could explain disagreements between experimental observation and theory. Also, the results are not in favor of a swelling of the greater chains by the smaller one.

Introduction

The so-called "living polymers" are systems in which polymerization is believed to take place under condition of chemical equilibrium between the polymers and their respective monomers. These long (one-dimensional) aggregates break and recombine reversibly. Therefore, they are seen as linear macromolecules in equilibrium with respect to their molecular weight distribution.

A number of examples have been studied, including liquid sulfur [1–3] and selenium [4], poly (α-methylstyrene) [5], polymer-like micelles [6, 7] and protein filaments [8].

A lot of theoretical works within the mean field approximation describe the dependence of the length and distribution with temperature and concentration.

Due to experimental difficulties [7] the properties of living polymers still pose a number of questions. Controversial results about the extent of the growth in micelles with decreasing temperature or rising density are reported [9–12]. However, no direct measurements of the molecular weight distribution have been published yet.

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 which influence experiments, might help much in understanding the thermodynamic behavior and the properties of living polymers. However, up to now only a small number of simulational

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studies [13–18] 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.

Until now, most of the computational research was focused on the transition between an oriented ordered phase and a disordered state [1, 13–18]. In parallel, theoretical works show that reversible aggregation of monomers into linear polymers exhibits critical phenomena which can be described by the $n \longrightarrow 0$ limit of the n-vector model of magnetism for linear chains [3,19].

Since Cates and co-workers [7,20–24] have developed a mean-field description of living polymers both for dynamic and static properties, discrepancies were found between the mean field results and the simulation on a simple square lattice in two dimensions. The origin of those differences comes from the inclusion of interactions in the system studied by computational methods (van der Waals interactions without binding of the monomers). In fact, the computational models were not suited to study the "simplest" case described by Cates and co-workers.

In the following, it will be shown that a simple two-dimensional simulation on a square lattice also gives good agreement with the mean field theory (at least for the static properties) for a canonical ensemble.

1. The Model

Various two-dimensional models have been used (F-model, q-state Potts model) [13,15,17,18] directly inspired by magnetic models. These "grand canonical" simulations define a system with three parameters: σ, the stiffness, w, the energy of the van der Waals interchain interaction, and V, the energetical value of a covalent bond (or their equivalent magnetic counter parts). In the Monte Carlo (MC) simulations so far [17,18] the polydisperse system of polymer chains was mapped on a Potts model whereby different spin values were taken to represent bonded and non-bonded monomers as well as vacancies on a lattice. Among all possible models presented by Cates and co-workers to describe the dynamics of combination of monomers, only two deals with relaxation of the chain distribution: the one presented here and its variant, the end evaporation [20]. This last one has shown a very slow kinetic [27] of relaxation and is then of no use for the study of static properties.

In previous works, the study of the living polymer system using Bond Fluctuation Model (BFM) [28,29] in three dimension has shown excellent agreement with the mean field theory [25,26] when the van der Waals interaction is set to zero (*i.e* $w = 0$), so that no phase separation into dense and dilute components could take place.

The 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 non-bonded interactions between monomers may be neglected as compared to the bond energy along the backbone of the macromolecules. However, memory restriction reduces the largest lattice size which can be currently studied with the BFM to a $30 \times 30 \times 30$ cubic lattice. Moreover, it is not clear if the dynamics of the bond fluctuation model in two dimensions for living polymers, applied directly in the same way as for the three dimensional system, is correct, entanglement effects arising in this case [29] due to the binding algorithm.

Hence, for the present work, dealing only with static properties, a slithering snake based algorithm has been developed. The slithering snake algorithm is very efficient in dense systems and allows fast relaxation, both of the chain conformation and system configuration. The same algorithm as in the BFM based program is used for the scission recombination processes of the monomers. The effect on the program structure and speed when changing from the

slithering snake move to the BFM move is the same as the one extensively described in reference [30] between Madden's and Mansfield's version of their pseudokinetic mechanism for the rearrangement of chain segments.

Only one monomer at a time may be present on a lattice site (excluded volume interaction between monomers). Those sites of the lattice which are not occupied by monomers are considered empty (vacancies) and contribute to the free volume of the system.

An energy $-V$ ($V > 0$) is set 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. This last condition avoids the formation of rings [13,14] which gives a different length distribution for even and odd chain length (in monomer units) with temperature.

This is not really a constraint if we consider micellar systems in which rings are not likely to occur [7].

The present investigation was focused 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.

A MCS (Monte Carlo Step) is organized as follows:

(i) The chains are allowed to perform a reptation move.

(ii) A monomer is chosen at random. If the monomer happens to be at the end of a chain, an attempt is made to create a bond with another monomer which might be present on any one of the four neighboring sites also chosen at random. If the end of another polymer is present on the chosen neighboring site, the Metropolis algorithm [28] is applied, that is, a new bond is created if the value of a random number between 0 and 1 is smaller than $\mathrm{Min}\left(1, \exp\left(\dfrac{-V}{k_\mathrm{B}T}\right)\right)$

(iii) Finally, a monomer is chosen at random. If a bond on the right of the current monomer exists, it attempts to break, also according to the Metropolis rule.

During one MCS one carries out (ii) - (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.

The move sequence is based on the number of polymers, but the scission and recombination process must strictly depend on a random choice of the monomers.

Such a remark was not necessary for the BFM based programme, because move and the scission and recombination process were both built on the random choice of a monomer. If the scission and recombination process depends on the (fluctuating) number of chains, the probability of a binding or breaking trial is no longer the same with the awaited consequences.

A number of structural properties are sampled during the simulation: mean average values like the mean average contour length $\langle L \rangle$ and the mean average square end-to-end distance $\langle R_\mathrm{e}^2 \rangle$ (an average over all the chains) which can be estimated experimentally, and more precise data, like the distribution of chain lengths or the mean square end-to-end distance R_e^2 of chains of given length L which has not been yet given experimentally. The mean square end-to-end distance is the mean value of the square end-to-end distance taking into account the chains only *i.e.* a monomer is a chain without any bond and has an end-to-end distance radius of zero. The distribution of chain lengths (in monomer unit) was also recorded in order to check if the system was sensitive to the finite number of monomer in the system [27]. The system takes usually about 2500 MCS in order to be equilibrated. After equilibration, measurements of data were performed in intervals of 2500 MCS and about 500 independent data sets have been sampled. The simulations have been carried out on a 100×100 square lattice with periodic boundary conditions. The absence of finite size effects was checked (for lattice size 50×50 and 200×200) but it has already been proved that such effects are absent, at least for boxes greater then 14 side length, for both simulation in two dimensions [18] and with bond fluctuation model in three dimensions [25]. The start configuration consists of non-bonded monomers.

Because the Boltzmann factor is a function of $\left(\dfrac{-V}{k_{\mathrm{B}}T}\right)$ only ($\sigma = w = 0$), all the simulations with the same $\left(\dfrac{-V}{k_{\mathrm{B}}T}\right)$ ratio give the same results [25]. The slithering snake algorithm [28] moves the chains independently of their contour length and is therefore dynamically incorrect but gives rather quick equilibration of the coils. On the other hand, the breaking of the chain reduces the non-ergodicity of the algorithm [28,29]. In fact, it should suppress it completely: it has been proved [31] that the slithering snake algorithm with a non-N conserving algorithm is ergodic. This algorithm, allowing the chain to reduce or grow from one unit at one end is similar to the end evaporation model [20].

The results obtained with this simulation are then only correct for static properties. In contrast to Pott's model-like simulation [18], the one-dimensional aggregates are treated as polymer chains in the sense that during a move the connectivity of the monomer in the chain is conserved. This simulation could be seen as a development of the algorithm of references [16,32] for living polymers.

In general, a high concentration system of polymers is non-trivial to simulate [23,32] and some authors have artificially introduced a chain breaking and recombination process to study them [30,33,34]. The study at high concentration is easier with living polymers and is carried out in this article to some extent.

2. Brief Summary of the Mean Field Approximation Treatment of Living Polymers

At the level of mean-field approximation in the absence of closed rings, one can write the free energy for a system of linear chain as:

$$\frac{F}{k_{\mathrm{B}}T} = \sum_{L} c\,(L,T) \left[\ln\,c\,(L,T) - (L-1)\frac{V}{k_{\mathrm{B}}T} \right] \tag{1}$$

where $c\,(L,T)$ is the molecular weight distribution for chain length L. Minimization of equation (1) with respect to $c\,(L,T)$, subject to the condition:

$$\phi = \sum_{l} L\,c\,(L,T) \tag{2}$$

with ϕ the density of the system yields:

$$c\,(L,T) = \exp\left(-\left(\frac{V}{k_{\mathrm{B}}T}+1\right)\right)\exp\left(-\frac{l}{\langle L\rangle}\right)$$

$$\langle L\rangle = \sqrt{\frac{\phi}{e}}\,\exp\left(\frac{V}{2k_{\mathrm{B}}T}\right) \tag{3}$$

This result should be valid when correlations, brought about by the mutual avoidance of the chain, are negligible.

3. Results

The $1/T$ curve *versus* log $\langle L\rangle$ is plotted in Figure 1. It presents a slope of $0.96 \cong V/2$ for $V = 2$ in agreement with [7]. In another publication, the curve was not a straight line [18] and this was only due to a non-zero value of w.

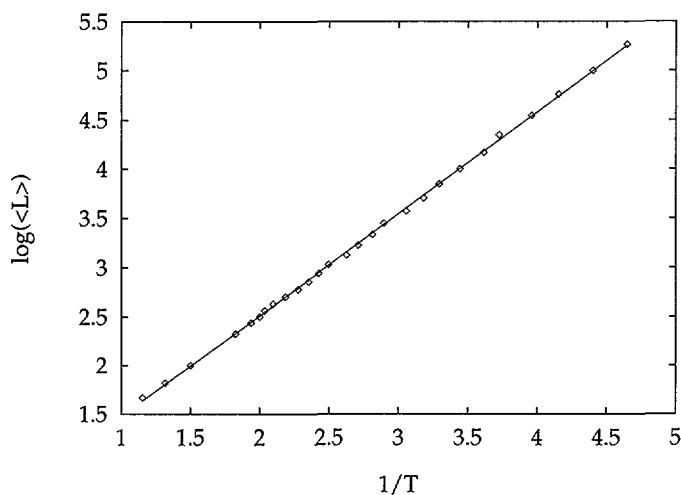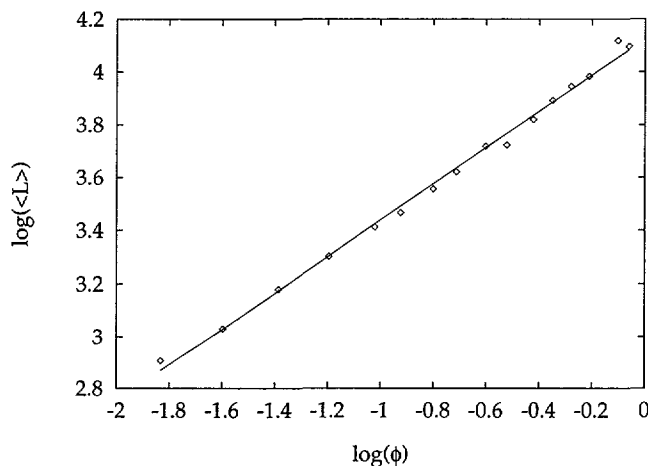Fig. 1. — Variation of $\langle L \rangle$ with inverse temperature, $\phi = 0.25$.

Fig. 2. — Variation of $\langle L \rangle$ with total density $\phi, T = 0.27$.

The log-log plot of $\langle L \rangle$ *versus* the concentration ϕ of monomers in the system (Fig. 2) at fixed temperature displays a slope of $\alpha = 0.69 \approx 2/3$, a value between the one given by mean field approximation, namely $1/2$, and the one given by scaling consideration [21] in a semi-dilute regime (~ 0.84 in two dimensions). Such an intermediate value has also been seen in three dimensions [25].

At constant concentration $\phi = 0.25$, the log-log plot (Fig. 3) of the square end-to-end distance *versus* $\langle L \rangle$ has a slope of $2v \approx 1.36$ which is less than the theoretical value of 1.5 because the system is semi-dilute. Both with Pott's model-like simulation [14] and BFM model [25], the gyration radius follows a scaling law with $\langle L \rangle$ for large enough values of $\langle L \rangle$.

Generally, these finding agree with the prediction of Cates and co-workers [7].

It is also possible to plot the same picture, but changing now the mean length $\langle L \rangle$ with concentration (Fig. 4) instead of temperature. The curve is qualitatively the same (Fig. 5) as
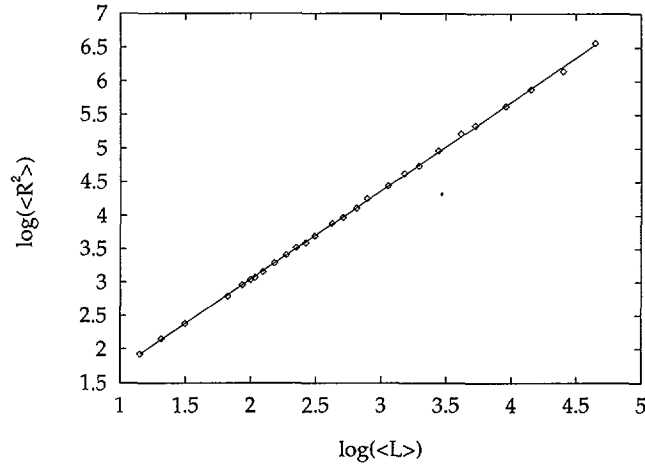
Fig. 3. — Scaling plot of $\langle R_e^2 \rangle$ with the mean chain length $\langle L \rangle$. $\langle L \rangle$ is changed through a change in temperature, $\phi = 0.25$.
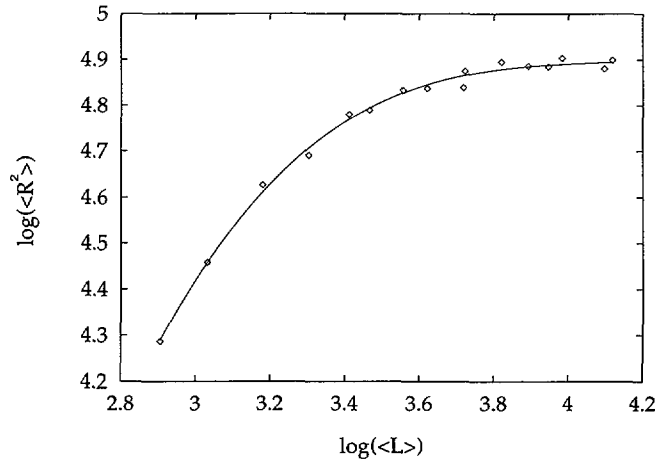

Fig. 4. — Scaling plot of $\langle R_e^2 \rangle$ with the mean chain length $\langle L \rangle$. $\langle L \rangle$ is changed through a change in density. The line is only a guide for the eye, $T = 0.27$.

the log-log plot of the mean end-to-end square distance with concentration. In fact, this shows the power dependence of $\langle L \rangle$ on ϕ, as stated above.

The result is however very different for a monodisperse system of chains of equivalent chain length $\langle L \rangle$: computer simulations have shown a decrease in the radius with increasing concentration [29, 35, 36]. This fact was already predicted by scaling laws [37]:

$$R^2 \sim N\phi^{-1/4} \qquad (4)$$

in three dimensions. R^2 represents either the square end-to-end distance or the square gyration radius. In our polydisperse case, we see an increase followed by a leveling of the chain radius with increasing concentration, instead of a decrease, over a large range of $\langle L \rangle$.
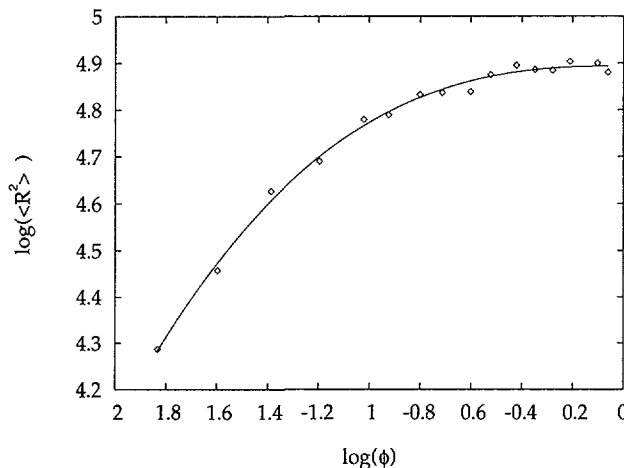
Fig. 5. — Scaling plot of $\langle R_e^2 \rangle$ with concentration. The line is only a guide for the eye.

Following reference [37], a similar calculation as the one giving equation (4) yields for a two dimensional system of monodisperse chains:

$$R^2 \approx N\phi^{-3/4} \tag{5}$$

i.e. the decrease of the chain radius with increasing concentration should be even stronger than in three dimensions. At first sight, because there is an increase in the mean chain length with concentration, we could expect that the curve $\langle R^2 \rangle = f(\phi)$ shows in fact short chains behavior for low ϕ values and long chains behavior for higher ϕ values. It means that two chain populations could coexist with different static properties like a different scaling dependence of R with the contour length L. There are two possibilities for the existence of two populations: (i) the shorter chains swell the greater one. For a system containing long enough chains, at a given concentration, we should see a log-log plot of $R^2 = f(L)$ displaying two slopes, $2\nu_{\text{short}}$ for short chains and $2\nu_{\text{long}}$ for long chains with $\nu_{\text{short}} < \nu_{\text{long}}$. This is the classical "Russian dolls" pictures;

(ii) due to the exponential distribution, the shorter chains, too short to obey a scaling behavior, give a major contribution to the mean value $\langle R^2 \rangle$ and a log-log plot of $R^2 = f(L)$ would display $\nu_{\text{short}} > \nu_{\text{long}}$.

The snapshot (Fig. 6) does not show any evidence of a swelling of the greater chains by the smaller one and the plot $R^2 = f(L)$ (Fig. 7) shows that $\nu_{\text{short}} > \nu_{\text{long}}$, confirming the hypothesis (ii). The value of ν_{long} goes as awaited from a value close to that of a dilute system ($\nu = 3/4$) to a value near that of a melt i.e. chains at the θ point ($\nu = 4/7$) [38] with increasing ϕ.

In reference [13], the value of ν given by a plot $R^2 = f(L)$ was measured only for chain contour length lower than $\langle L \rangle$. With decreasing value of $\langle L \rangle$, the author found an increasing value of ν, which is clearly due to measuring a "scaling exponent" where the scaling hypothesis is no longer valid.

Going back to equation (5), valid for long enough chains obeying the scaling, and inserting for N our measurement $\langle L \rangle \propto \phi^{0.69}$ we find
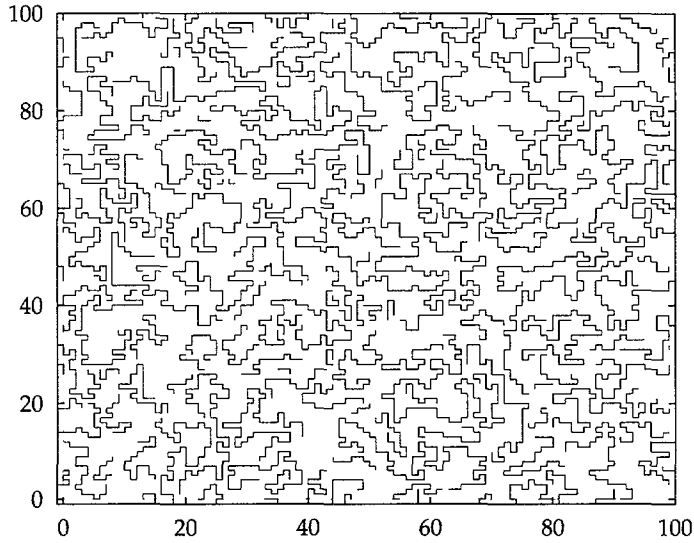
$$\langle R^2 \rangle \propto \phi^{-0.06}$$

Fig. 6. — A snapshot of a typical system configuration at $T = 0.27$ and $\phi = 0.49$. Monomers are not shown for sake of clarity.
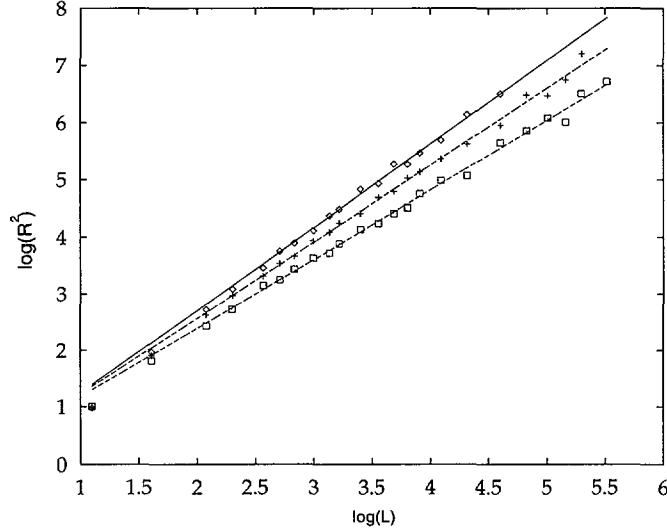

Fig. 7. — Scaling plot of R_e^2 with the chain length L. The lines show the asymptotic behavior for long enough chains. The small chains display an apparent exponent $\nu_{short} > \nu_{long}$. $\phi = 0.16$ (diamonds) $\nu_{long} = 0.74$, $\phi = 0.49$ (cross) $\nu_{long} = 0.68$, $\phi = 0.81$ (square) $\nu_{long} = 0.62$, $T = 0.27$.

which is a very weakly decreasing function and is consistent with the apparent leveling of the curve Figure 5. The confusion between a polydisperse system of living polymers and a monodisperse system of chains of length $\langle L \rangle$ is only valid for systems with a sufficiently great value of $\langle L \rangle$ i.e. systems for which the influence of small non-scaling chains become negligible. It means that $\langle L \rangle$ should be several and not only a few time greater than the persistence length in order for the wormlike description to be valid.
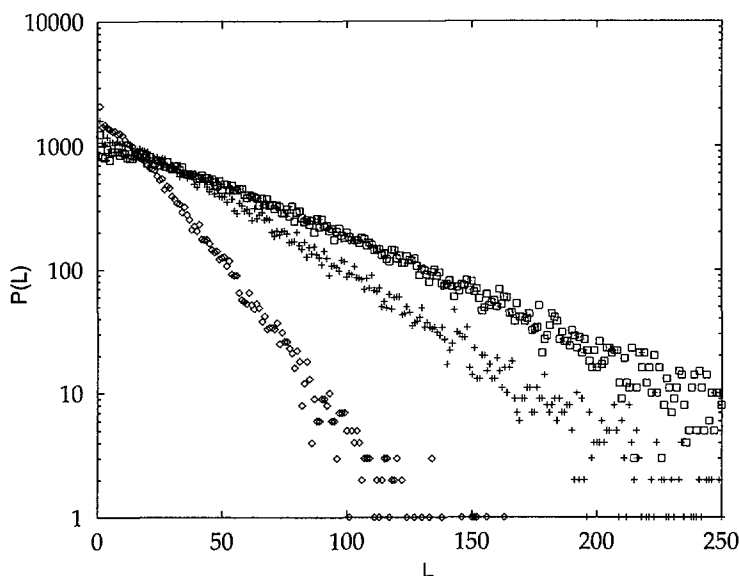
Fig. 8. — Probability distribution of chains at various concentrations for $L < 250$. $\phi = 0.16$ (square), $\phi = 0.49$ (cross), $\phi = 0.81$ (diamonds). $T = 0.27$.

Figure 5 is qualitatively the same as Figure 3 in [39]. Indeed, the authors used the geometrical size of a living polymer to extract the contour length, taking as hypothesis that the micelles are wormlike scaling object in the range studied. They draw the conclusion that at higher density the dependence of $\langle L \rangle$ on ϕ deviates from the expected behavior $\sqrt{\phi}$ and tend to saturation. It cannot be ruled out, however, that the finding of [39] is due to the same effect as observed in the present work.

Apart from effects due to the presence of rings [15,17], no perceptible disagreement between mean field prediction an simulations have been shown in the probability distribution of chain lengths [18,25]. It is also the case here. The distribution of chain length in monomer units follows the exponential law theoretically expected for long enough chains (Fig. 8).

An interesting point is the jump between the monomer and the chains concentration in the distribution. This is also seen in references [14,25], which use different kind of algorithm. The monomers seem to have a different probability to find a polymer end or another single monomer in the neighborhood as other species.

Conclusion

The results of the present computer simulation demonstrate that the agreement between mean-field predictions and numerical experiment depends strongly on whether the system behavior is dominated by short (non-scaling) chains, or by chains long enough to display a polymer-like behavior (scaling).

While in the case of changing temperature, the average mean end-to-end distance scales with the average length, in agreement with theoretical predictions, in the case of changing density, the scaling behavior ($\langle R^2 \rangle \propto \phi^{-0.06}$) is only observed for long average mean chain length.

This could be a possible cause for misinterpretation of experimental data, in case when measurement of $\langle R^2 \rangle$ are used for the determination of $\langle L \rangle$.

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