PHYSICAL REVIEW E VOLUME 55, NUMBER 2 FEBRUARY 1997

Monte Carlo study of the molecular-weight distribution of living polymers

Yannick Rouault[1] and Andrey Milchev[2]
[1]INRA Versailles Station de Science du Sol, Route de Saint-Cyr F-78026, France
[2]Institute for Physical Chemistry, Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria

(Received 10 September 1996)

A Monte Carlo simulation in two dimensions shows that the distribution of chain lengths in a system of living polymers is well described by a Schultz molecular-weight distribution $C(l,T)\propto(l/L)^{\gamma_{\mathrm{eff}}-1}\exp(-l/L)$, with an effective exponent γ_{eff}, reflecting the crossover from dilute to semidilute regime. Beyond the crossover density ϕ^* the distribution function gradually reduces to a purely exponential form $C(l,T)=\phi/L^2\exp(-l/L)$ known from mean-field approximation treatments. In the case of numerical simulation the determination of ϕ^* can be done by seeking the maximum of γ_{eff}. [S1063-651X(97)11702-0]

PACS number(s): 61.25.Hq, 64.60.Cn, 05.50.+q

In this brief communication we report some recent computer studies of the molecular-weight distribution (MWD) of living polymers by means of a Monte Carlo simulation of a polydisperse system of flexible linear chains on a two-domensional square lattice.

It is well known that living polymers, that is, systems in which linear chain polymers can break and recombine reversibly in the process of equilibrium polymerization, are characterized by a polydisperse molecular-weight distribution which changes when temperature T and/or density ϕ of the system are varied. However, the precise form of the MWD is still a matter of debate and controversy [1,2] due to approximations in the analytical treatment of such systems and difficulties in the relevant laboratory experimentation. In this sense a computer experiment, which is ''exact'' in terms of the particular model, and free from the undesirable side effects of the real experiment, is believed to be a useful means in gaining more insight into the nature of this interesting class of soft condensed matter systems, which include different substances, such as sulfur, selenium, various detergents (wormlike micelles), and polymers like poly(α-methylstyrene) [3,4].

In the mean-field approximation (MFA), the MWD of the wormlike polymer species in thermal equilibrium is given by [3]

$$C(l,T)=\frac{\phi}{L^2}\exp\left(-\frac{l}{L}\right), \tag{1}$$

where ϕ denotes the total concentration of monomers in the system and L is the average chain length,

$$L=\sqrt{\phi/e}\exp\left(\frac{V}{2k_BT}\right), \tag{2}$$

with V the energy of a bond along the backbone of the chain, and k_B the Boltzmann factor.

The distribution [Eq. (1)] is normalized such that a summation of mass over all chains lengths of the system should yield the total monomer density ϕ, that is, $\int_0^\infty lC(l,T)dl=\phi$. In a series of computer experiments, we have observed recently a very good agreement [5–8] between simulational results and MFA predictions, Eq. (1), at least for the case of dense solutions and sufficiently large L in three dimensions.

However, this distribution is not valid in a dilute regime for chains which are short enough to be smaller than the blob size [9]. It is known that chains, which are fully swollen and may slip through the network made up of the chains of average size L without being seriously perturbed by the interchain interaction, are subject to a power-law distribution,

$$C(l,T)\propto l^{\gamma-1}, \tag{3}$$

where $\gamma>1$ is a standard critical exponent. These small chains behave essentially as isolated chains.

A ''Schultz distribution'' form of the MWD has been proposed [2] to unify the two limiting cases

$$C(l,T)\propto\left(\frac{l}{L}\right)^{\gamma-1}\exp\left(-\frac{l}{L}\right). \tag{4}$$

This form follows from the partition function of self-avoiding walks of length l and reflects an important isomorphism between the standard Landau-Ginzburg spin model in the formal limit of vanishing spin dimensionality and the model of long flexible macromolecules. A similar distribution with a negative power has been also proposed [10] in order to explain experimental results of *enhanced* anomalous diffusion in living polymers

$$C(l,T)\propto\left(\frac{l}{L}\right)^{-2\sigma}\exp\left(-\frac{l}{L}\right), \tag{5}$$

with $\sigma>0$. In this latter case the observed chain distribution would even decay faster with l than the MFA result, Eq. (1).

This is, at first sight, completely the opposite to what is expected theoretically [1–3] and observed numerically [5–8].

Unfortunately, we do not dispose, at present, with MWD's obtained directly from a real experiment and there has been hardly any numerical evidence for a distribution in the form of Eq. (4), either in three dimensions or in two dimensions. This seems, at first sight, rather surprising, at least in the latter case, since the value of γ is greater in two dimensions (2D) than in three dimensions (3D): $\gamma_{2\mathrm{D}}=\frac{43}{32}$

1063-651X/97/55(2)/2020(3)/$10.00

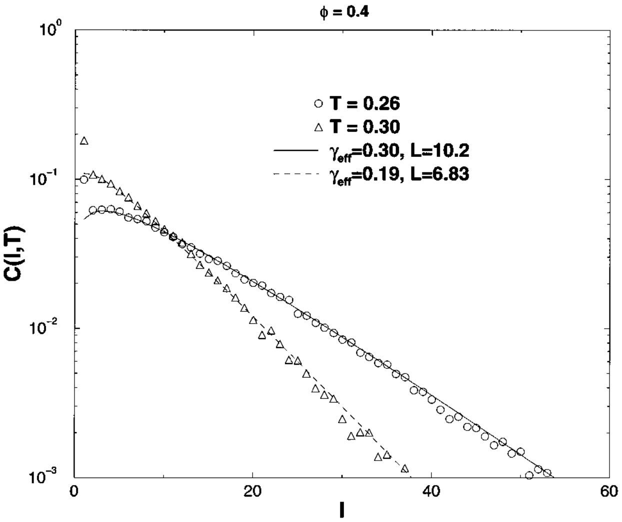

FIG. 1. Semilog plot of the MWD at $T=0.26$ and $T=0.30$. Full lines represent a fit with Eq. (4) and parameters, given in the legend. The total monomer density in the system is $\phi=0.4$.

$\simeq 1.34$, $\gamma_{3D} \simeq 1.15$. One could assume that this has been mainly due to the simulation of too short chains.

Recently, a new model for the study of living polymers in two dimensions was developed to study the static properties of wormlike micelles without the formation of rings [11]. It uses basically the same binding-breaking algorithm as in an earlier work [6], but the chains are moved by means of an efficient *slithering snake* algorithm in order to get faster equilibration of the system.

In the present investigation we use this model at fixed density $\phi=0.25$, and the dimensionless energy V/k_BT is varied in order to achieve a change in the degree of interpenetration (''overlap'') of the chains. In this way the crossover from a dilute to a semidilute regime at density ϕ^* and its impact on the MWD can be examined. Thus, although the number of chains decreases in the system, by increasing V/k_BT, due to the strong excluded volume effect in two dimensions, the chains gyration radius increases rapidly with the contour length L. Another possibility would be to increase systematically ϕ, but then nontrivial effects arise, as shown in [11]. After equilibration of the system, measurements of the MWD were performed in intervals of 200 Monte Carlo steps (MCS) per monomer. Depending on temperature, usually about 60 independent data sets have been sampled.

Two typical MWD are shown in Fig. 1 for $T=0.26$ and $T=0.30$. Some interesting features are immediately seen in Fig. 1. As has also been seen in other simulations, albeit less pronounced, the number of single monomers appears to be much greater than expected from analytical predictions.

If the monomers are omitted, all MWD curves are in the form of Eq. (4). The data for the curves without the monomers has been fitted with three parameters a, b, L: $C(l,T)=a(l/L)^b \exp(-l/L)$ so that an effective exponent $\gamma_{eff}=1+b$ and a ''mean chain length'' L have been determined.

The results for γ_{eff} and L, as well as for the true average chain length, $\langle L\rangle$, end-to-end distance of the chains, R_e^2, and the percentage of single monomers with respect to all other chains, N_1, and to the total number of monomers in the system, C_1, are reported in Table I.

TABLE I. Parameters for the MWD curves.

T	L	$\langle L\rangle$	b	R_e^2	$N_1[\%]$	$C_1[\%]$
0.22	18.53	23.81	0.26	113.2	0.0391	0.001 65
0.23	14.60	19.57	0.27	84.29	0.0529	0.002 71
0.24	13.66	17.01	0.273	70.16	0.0649	0.003 83
0.25	11.60	14.78	0.275	56.90	0.0727	0.004 93
0.255	10.65	13.65	0.28	50.75	0.0815	0.005 98
0.26	10.17	12.91	0.295	47.05	0.0889	0.0069
0.265	9.60	12.05	0.285	42.92	0.0958	0.007 98
0.27	9.165	11.17	0.250	38.40	0.1	0.009 28
0.28	8.388	9.88	0.221	32.32	0.12	0.0124
0.29	7.475	8.80	0.200	27.77	0.14	0.0159
0.30	6.833	7.87	0.190	23.48	0.15	0.0196

$\langle L\rangle$ is the true average chain length of the system whereby also the single monomers are taken into account. R_e^2 is 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 end-to-end distance of the chains.

The values, given in Table I, appear quite reasonable. A plot of C_1 vs inverse temperature T^{-1} in semilog coordinates yields a perfect straight line with slope 2, as the energy needed to detach a monomer from the chain, $V=2$, is. The average end-to-end distance of the chains, R_e^2, scales with average chain length, $\langle L\rangle$, with a power of ≈ 1.41. This value for the exponent $2\nu_{2d}$ is expected since some screening in the semidilute regime takes effect for lower T and larger $\langle L\rangle$, and the exact exponent $\nu_{2d}=3/4$ is effectively diminished. If the fitting parameter, L, instead of $\langle L\rangle$, is used for these plots, however, some unrealistic values of the scaling exponents result, suggesting that L does not represent the true mean chain length of the system once the single monomers have been exempted from consideration.

As pointed out by Schäfer [1], Eq. (4), which is known to be rigorously correct in the limit of isolated chains, is expected to reduce to the MFA result, Eq. (1), in the limit of large chain overlap. Indeed, from Table I it is evident that the effective (measured) value of γ, γ_{eff}, increases toward the value of γ_{2D} as one approaches the critical density ϕ^* at $T\approx 0.26$ of the transition from a dilute to a semidilute regime.

The initial increase of γ_{eff} reflects the buildup of correlations in the system as the average chain length $\langle L\rangle$ grows, but the density still remains below ϕ^*. For a dilute solution of polymers the correlation length, ξ, is a measure of the radius of gyration R_g of the individual, independent polymer coils.

Above ϕ^*, γ_{eff} slowly decreases towards unity and the distribution, Eq. (1), becomes relevant. This is reasonable too, since strong overlapping drives the system of chains into the θ regime. This respective value of γ for ''collapsed'' chains, γ_θ may differ from the mean-field value of 1. Indeed, for monodisperse chains in two dimensions, the θ chains are not Gaussian [12] and display a value for the critical exponent $\nu_\theta=\frac{43}{76}$ instead of $\nu_{\mathrm{Gaussian}}=\frac{1}{2}$, which corresponds to globular chains. In another work [2], the same value ($\nu_\theta = \frac{43}{76}$) has been found for a system of polydisperse chains. Thus it cannot be ruled out that γ_θ also has a particular value in two dimensions [12,13]. The transition from a dilute to a semidilute system is seen experimentally by a maximum of scattered intensity or a minimum of diffusion coefficient [3]. In the case of numerical simulation the determination of ϕ^* can be done by seeking the maximum of γ_{eff}.

Summarizing, we believe that our Monte Carlo simulations in two dimensions show that the distribution of chain lengths in a system of living polymers is well described by a Schultz MWD, Eq. (4), with an effective exponent γ_{eff}, reflecting the crossover from a dilute to a semidilute regime. Beyond the crossover density ϕ^* the distribution function gradually reduces to purely exponential form, Eq. (1), known from MFA treatments [3]. In three dimensions this effect would be much less pronounced due to the proximity of γ to unity.

We are indebted to L. Schäfer for stimulating discussion of the problem. This research has been sponsored by the Bulgarian Foundation for Scientific Research, Grant No. $X-300/96$.

---

[1] L. Schäfer, Phys. Rev. B **46**, 6061 (1992).
[2] P.D. Gujrati, Phys. Rev. B **40**, 5140 (1989).
[3] M.E. Cates and S. J. Candau, J. Phys. **2**, 6869 (1990).
[4] S. C. Greer, in *Advances in Chemical Physics*, edited by Prigogine and S. A. Rice (Wiley, New York, 1996), Vol. XCIV, p. 261.
[5] A. Milchev, Polymer **34**, 362 (1993).
[6] Y. Rouault and A. Milchev, Phys. Rev. E **51**, 5905 (1995).
[7] A. Milchev and D. P. Landau, Phys. Rev. E **52**, 6431 (1995).
[8] A. Milchev and D. P. Landau, J. Chem. Phys. **104**, 9161 (1996).
[9] M.E. Cates, J. Phys. (France) **49**, 1593 (1988); L. Schäfer and T. A. Witten, J. Chem. Phys. **66**, 2121 (1977); A. Knoll, L. Schaefer, and T. A. Witten, J. Phys. (France) **42**, 767 (1981).
[10] A. Ott, J. P. Bouchaud, D. Langevin, and W. Urbach, Phys. Rev. Lett. **65**, 2201 (1990).
[11] Y. Rouault, J. Phys. (France) II **6**, 1301 (1996).
[12] T. M. Birshtein and S. V. Buldyrev, Polymer **32**, 3387 (1991).
[13] B. Duplantier and H. Saleur, Phys. Rev. Lett. **59**, 539 (1987).