

θ -point temperature and exponents for the bond fluctuation model

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We calculate the θ -temperature and the associated critical exponents for the bond fluctuation polymer model of Carmesin and Kremer in two dimensions. The critical exponent values are in agreement with the theoretical predictions. We find that the extra mobility introduced by the flexible bond serves to shift the crossover to the ideal tricritical behavior to a shorter polymer length, compared with previously studied lattice models. In particular, bond-flexible simulations with polymer lengths of the order of 50 already successfully reproduce the properties of infinite chains.

Computer simulations have played an important role in the development of the theory of polymers, ranging from the understanding of the universal behavior of isolated polymers to the complexities of interacting polymers. Many models have been proposed in the past, and successfully implemented using computer simulations to study the static and dynamic properties of polymer systems. However, the computational times required for the description of fairly large systems of long polymers have often restricted the class of tractable models to those of the lattice type. These models, which represent the polymer as a walk on a lattice, can be very efficiently programmed and even allow Monte Carlo studies of “slow processes” such as phase separation, development of interfaces and polymer diffusion [1–5].

Recently a new lattice model for polymers has been proposed [1]. This model does not constrain the bond length to any predetermined value, but allows it to fluctuate between two fixed limits. Carmesin and Kremer [1] have shown that this bond fluctuation (BF) method produces the correct Rouse dynamics in the diluted limit for all spatial dimensions, and is very efficient from a computational point of view. The BF method also offers an ergodic algorithm [1, 5] for simulating two-dimensional systems and, more importantly, for simulating branched polymers and connected clusters of polymers (polyfunctional condensation).

As a preliminary step towards the application of this model to phase separation and gelation, it is worth studying whether the BF algorithm gives results consistent with the scaling theory for polymers and estimate for which polymer length N the lattice effects become negligible. With this aim we have calculated the θ -temperature [6–8] for the BF model as well as the critical exponents associated with this transition point in $d = 2$. We have studied the scaling properties of the mean-square radius of gyration $\langle R_g^2 \rangle$ and of the mean-square end-to-end distance $\langle R^2 \rangle$ as a function of N , for different temperatures. N is defined as the number of bonds between monomers. We find that the extra mobility introduced by the fluctuating bonds shifts the crossover to the ideal tricritical behavior to a much lower value of N compared with previously studied models [9–12].

The tricritical exponents ν_t and φ_t associated with the θ -point are defined by the scaling relation [8]

$$\langle R_g^2 \rangle \sim N^{2\nu_t} f(N^{\varphi_t} \tau). \quad (1)$$

Here τ is the reduced temperature, $\tau = (T - \theta)/\theta$, ν_t is the tricritical exponent, φ_t is a crossover exponent, and $f(x)$ is a scaling function with different power law asymptotic behavior above and below the θ -point [8, 9]:

$$f(x) \sim \begin{cases} x^{(3/2 - 2\nu_t)/\varphi_t}, & x \gg 0, \\ 1, & x = 0, \\ |x|^{(1 - 2\nu_t)/\varphi_t}, & x \ll 0. \end{cases} \quad (2)$$

According to the theory of Duplantier and Saleur [13] $\nu_t = \frac{4}{7}$ and $\varphi_t = \frac{3}{7}$. A relation analogous to (1) holds for $\langle R^2 \rangle$.

The ideal tricritical type of behavior described by eqs. (1) and (2) can be observed only for sufficiently large values of N . For lattice models, the behavior predicted by eqs. (1) and (2) is usually found for $N > 100$ [9–12]. For smaller values of N the lattice effects and corrections to scaling are significant.

At the θ -temperature, the chain assumes a well defined conformation intermediate between the conformations for $T > \theta$ and $T < \theta$. At $T = \theta$, the slope on a log–log plot of $\langle R_g^2 \rangle$ plotted against N gives the exponent ν_t . For $T < \theta$ and $T > \theta$ one generally finds that the slopes change with N [9]. In particular, the successive slopes of the curves $\ln \langle R_g^2 \rangle$ against $\ln N$ increase for $T > \theta$ and decrease for $T < \theta$. For $T > \theta$ they tend to $3/2$ (the self-avoiding walk exponent [14]) and for $T < \theta$ to 1 (the exponent for the dense globular state [8]). At $T = \theta$, since $f(0) = 1$, the successive slopes are constant and equal to $2\nu_t$. Then eqs. (1) and (2) predict that the second derivative of $\ln \langle R_g^2 \rangle$ against $\ln N$ goes through zero at $T = \theta$.

The dependence of $\ln \langle R_g^2 \rangle$ on T and $\ln N$ for the BF model is shown in fig. 1. Each point represents the average over 10^8 – 10^9 Monte Carlo steps^{*1}, following the equilibration process (10^5 – 10^6 Monte Carlo steps). The lines in fig. 1 are the least-squares fit with a second-order polynomial functions^{*2}. The inset in fig. 1 shows the temperature dependence of the coefficient of the quadratic term, $c(T)$. We observe that $c(T)$ goes through zero close to $T \approx 2.2$, in units of the monomer–monomer interaction energy. Thus we estimate that the θ -temperature for the BF model is $\theta = 2.2 \pm 0.1$. Also, we estimate ν_l from the coefficient of the linear term for $T = 2.2$ to be $\nu_l = 0.56 \pm 0.02$. Surprisingly, we find that the ideal behavior predicted by eqs. (1) and (2) is already seen

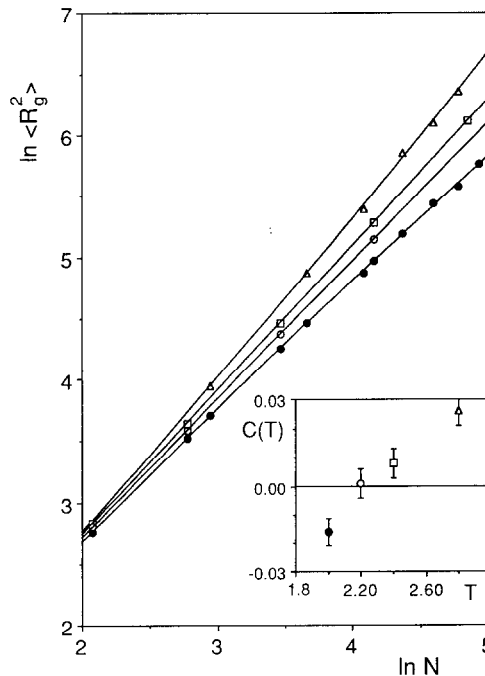


Fig. 1. Log-log plot of mean-square radius of gyration $\langle R_g^2 \rangle$ plotted against number of bonds N for different temperatures (Δ , $T = 2.8$), (\square , $T = 2.4$), (\circ , $T = 2.2$), and (\bullet , $T = 2.0$). Lines show the quadratic least-squares fits to the data for each temperature. The inset shows the temperature dependence of the coefficient of the quadratic term of the fit. The coefficient of the linear term for $T = 2.2$ ($\equiv 2\nu_l$) is 1.12 (cf. discussion in text).

^{*1} One Monte Carlo step is defined as N attempts to move a monomer of the chain.

^{*2} We check the validity of the quadratic fit by measuring the successive slopes of the graphs in fig. 1. We observe an increase of the successive slopes of the curves $\ln R_g^2$ against $\ln N$ for $T = 2.4$ and $T = 2.8$, and a decrease for $T = 2.0$. At $T = 2.2$ the successive slopes are independent of N , within the quoted error bar.

for $N = 16$. Our results for ν_l are consistent with the theoretical predictions [13] and with previous numerical studies for models of on-lattice polymers (with rigid bonds) [9–12]. It is important to observe that in those studies (see, e.g., figs. 5 and 6 in ref. [10]) the ideal behavior was observed only for $N > 100$. We also find that the dependence of $\langle R^2 \rangle$ on N yields the same values of ν_l and θ .

To find φ_l , we used the method of Poole et al. [10]. From eq. (1) we define

$$Q_N \equiv \frac{1}{\langle R_g^2 \rangle} \left(\frac{\partial \langle R_g^2 \rangle}{\partial \tau} \right)_{\tau=0} \sim N^{\varphi_l}. \quad (3)$$

Now

$$\langle R_g^2 \rangle \equiv \frac{\sum_{\mathbf{c}} R_g^2(\mathbf{c}) \exp(-N_{\mathbf{c}}/T)}{Z_N}, \quad (4)$$

where

$$Z_N \equiv \sum_{\mathbf{c}} \exp(-N_{\mathbf{c}}/T), \quad (5)$$

and $N_{\mathbf{c}}$ is the number of interacting monomers in a configuration \mathbf{c} . Hence we can express the derivative in (3) in terms of quantities that may be calculated. Eq. (3) takes the form

$$Q_N \propto \frac{\langle N_{\mathbf{c}} \rangle \langle R_g^2 \rangle - \langle N_{\mathbf{c}} R_g^2 \rangle}{\langle R_g^2 \rangle}. \quad (6)$$

From (3) the slope in a log–log plot of Q_N against N gives the exponent φ_l .

We measured Q_N at $T = 2.2$ for $N = 8, 16, 32, 64$, and found the successive ratios

$$\mathcal{R}_N \equiv \frac{\ln \langle Q_{2N}/Q_N \rangle}{\ln 2}, \quad (7)$$

which gave us successive approximations to φ_l . In agreement with previous studies [9–12], we found that \mathcal{R}_N decreases with increasing N from 0.85 for $N = 8$ to 0.5 for $N = 32$. The results for $\langle R^2 \rangle$ and $\langle R_g^2 \rangle$ are very close to each other. Thus we can conclude that the asymptotic value of φ for infinite chains is smaller than 0.5, which does not contradict the theoretical value of $\varphi_l = 3/7 = 0.42$ [13]. Note that the value of $\mathcal{R}_N \approx 0.5$ is obtained for the BF model for much shorter chains than for traditional lattice models for which N is about 100–300.

To measure the third critical exponent γ [7] at the θ -point we have studied $F(x)$, the probability of finding in one realization an R^2 value smaller than $x\langle R^2 \rangle$.

For the case of a good solvent, $F(x)$ is known to be independent of N and has the following asymptotic behavior [7]:

$$F(x) \sim \begin{cases} 1 - \exp(-Cx^{\delta/2}), & x \rightarrow \infty, \\ x^{g/2+1}, & x \rightarrow 0, \end{cases} \quad (8)$$

where

$$\delta = \frac{1}{1-\nu}, \quad g = \frac{\gamma-1}{\nu}, \quad (9)$$

and γ and ν are the analogs of γ_t and ν_t for a good solvent. According to the scaling hypothesis at the θ -point, eqs. (8) and (9) are still valid if the exponents ν and γ are replaced by their tricritical values ν_t and γ_t , respectively. Indeed, fig. 2a shows $F(x)$ for BF polymers of different lengths N . The quality of data collapse shown in fig. 2a supports the validity of eq. (8) for $T = \theta$ and allows us to calculate the exponents δ and g by estimating the slopes of the plot of $\ln[-\ln(1-F)]$ against $\ln x$ and of $\ln F$ against $\ln x$ respectively (see figs. 2b and 2c, respectively). We find $\delta/2 = 1.16 \pm 0.04$ and $g/2 = 0.10 \pm 0.05$.

Then, from eq. (9), we obtain $\nu_t = 0.57 \pm 0.02$ and $\gamma_t = 1.12 \pm 0.06$. Again, comparing with the estimate of γ_t for other lattice models [11, 12] at the same value of N we observe a substantial reduction of the correction to scaling.

The agreement between the two independently calculated values for ν_t further supports the validity of our calculation and of the extension of eq. (9) to the θ -point.

In summary, we have

(i) calculated the θ -temperature for the BF model of Carmesin and Kremer [1];

(ii) calculated the critical exponents ν_t and γ_t for an isolated polymer at $T = \theta$ and given an upper boundary for φ_t consistent with theoretical predictions [13];

(iii) confirmed that the functional form (8–9), derived for polymers in a good solvent, can be extended to the θ -temperature by substituting ν_t and γ_t for ν and γ .

For all the calculated quantities, the introduction of a large number of orientational degrees of freedom due to bond flexibility substantially decreases the lattice effects and the corrections to scaling. BF simulations with N of order 50 already successfully reproduce the properties of the infinite chain. We

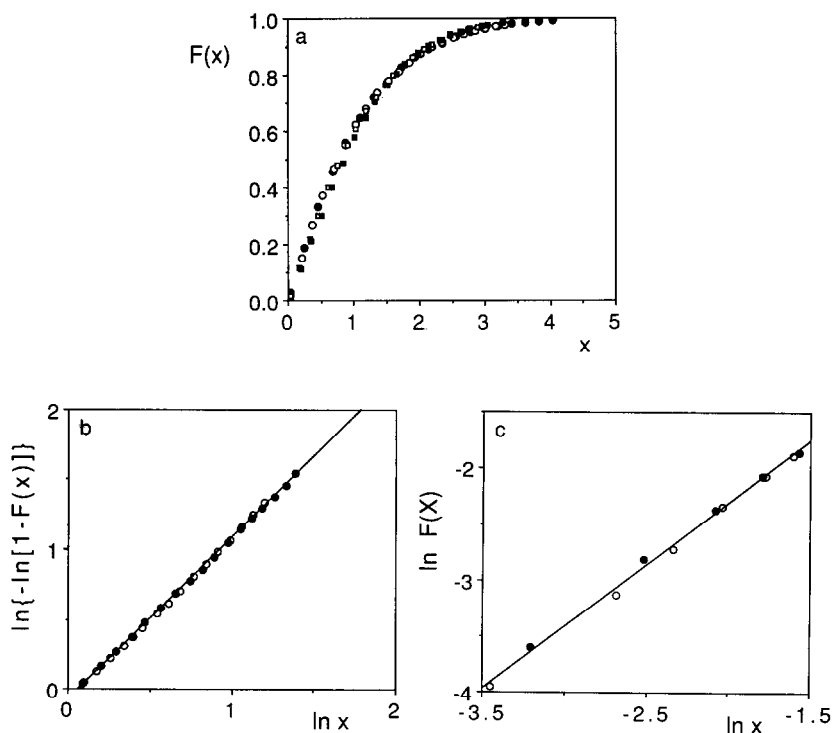


Fig. 2. (a) The probability distribution function $F(x)$ for BF polymers of different chain lengths N at $T = \theta$ ($x = R^2/\langle R^2 \rangle$). Here (\blacksquare , $N = 8$), (\square , $N = 16$), (\circ , $N = 32$), and (\bullet , $N = 64$). (b) The double-log plot of $1 - F(x)$ against x at $T = \theta$, for large values of x . The slope of this curve is equal to $\delta/2$ (eq. (8)). (c) The log-log plot of $F(x)$ against x at $T = \theta$ for small values of x . The slope of this curve is equal to $g/2 + 1$ (eq. (8)).

propose that the BF model has the potential to be applied to the simulation of critical phenomena in polymer melts and solutions; work along these lines is underway [15].

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