PHYSICAL REVIEW E, VOLUME 65, 010801(R)

Interacting growth walk: A model for generating compact self-avoiding walks

S. L. Narasimhan,[1,*] P. S. R. Krishna,[1,*] K. P. N. Murthy,[2,†] and M. Ramanadham[1,‡]
[1]*Solid State Physics Division, Bhabha Atomic Research Centre, Mumbai - 400 085, India*
[2]*Materials Science Division, Indira Gandhi Centre for Atomic Research, Kalpakkam - 603 102, Tamilnadu, India*
(Received 29 August 2001; published 14 December 2001)

We propose an algorithm based on local growth rules for kinetically generating self-avoiding walk configurations at any given temperature. This algorithm, called the interacting growth walk (IGW) model, does not suffer from attrition on a square lattice at zero temperature, in contrast to the existing algorithms. More importantly, the IGW model facilitates growing compact configurations at lower temperatures—a feature that makes it attractive for studying a variety of processes such as the folding of proteins. We demonstrate that our model correctly describes the collapse transition of a homopolymer in two dimensions.

DOI: 10.1103/PhysRevE.65.010801 PACS number(s): 36.20.Ey, 05.10.Ln, 87.10.+e

The configurational properties of linear polymers undergoing a collapse transition at a tricritical temperature T_θ, called the θ point, have been studied extensively because of their relevance to a wide variety of applications such as, for example, the protein folding problem [1]. The average radius of gyration (or equivalently, the average end-to-end distance) and the configurational entropy of a long polymer chain have a *universal* (i.e., system-independent) behavior characterized by the exponents ν and γ, respectively [2]. These exponents have distinct sets of values for the three temperature regimes, $T>T_\theta$, $T=T_\theta$, and $T<T_\theta$ [2,3]. In order to understand the statistical nature of polymer conformations in these three universal regimes, interacting self-avoiding walk (ISAW) models with appropriate non-bonded nearest neighbor (nbNN) interactions have been proposed [4].

Let $\mathcal{S}_N$ denote an ensemble of equally weighted N-step SAW configurations, generated on a lattice by a standard algorithm [5]. If ϵ_0 is the energy associated with any nbNN contact, a SAW configuration with a total of n_{NN} such contacts will have an energy $E=n_{NN}\epsilon_0$. Hence, one may assign to it a Boltzmann weight proportional to $e^{-\beta E}$, where $\beta=1/k_BT$, k_B is the Boltzmann constant and T the temperature. Such Boltzmann-weighted SAW configurations constitute an ISAW ensemble, denoted by $\mathcal{I}_N(\beta)$. By this definition, $\mathcal{I}_N(\beta=0)$ is the same as $\mathcal{S}_N$ because all the configurations of the former have the same probability of occurrence irrespective of their energies. Therefore, in the context of the ISAW ensemble, $\mathcal{S}_N$ may be thought of as representing a polymer at ''infinite'' temperature. The statistical accuracy of any physical quantity averaged over $\mathcal{I}_N(\beta)$ becomes poorer at lower temperatures because significant contribution comes from a smaller number of configurations [6]. In order to improve the statistics, especially at low temperatures, it is necessary to generate a very large ensemble, $\mathcal{S}_N$; this process could become prohibitively slow due to severe attrition for large N.

A better solution is to devise an algorithm based on suitable geometrical (*athermal*, or ''infinite'' temperature) rules for generating an ensemble, $\mathcal{G}_N$, identically equivalent to $\mathcal{I}_N(\beta>0)$. For example, the kinetic growth walk (KGW) [7] or the smart kinetic walk [8] on a honeycomb lattice straightaway generates an ensemble of configurations equivalent to the ISAW ensemble $\mathcal{I}_N(\beta=\ln 2)$. Having generated the *athermal* ensemble $\mathcal{G}_N$ by such a geometric algorithm, ensemble averages corresponding to a lower temperature could be obtained by Boltzmann weighting these configurations appropriately. This would ensure better statistical accuracy as compared to what could be obtained directly from $\mathcal{S}_N$. Yet, whether it is possible at all to sample a statistically significant number of maximally compact configurations is a moot point to consider because it involves a ''zero''-temperature sampling.

In this paper, we present an algorithm for kinetically growing a SAW configuration at any given temperature $T\geqslant 0$. This algorithm, called the interacting growth-walk (IGW) model, is able to generate more accurate data for longer walks at lower temperatures because sample attrition is less severe at lower temperatures. In fact, on a square lattice, the walk grows indefinitely into maximally compact configurations at $T=0$, in contrast to the conventional sampling algorithms [9,10]. We demonstrate that our model is capable of describing the universal behavior of a SAW above, at, and below the θ point in two dimensions.We also present a speculative Flory-like argument for the IGW.

We start the growth process by ''occupying'' an arbitrarily chosen site $\mathbf{r}_0$ of a regular d-dimensional lattice of coordination number z whose sites are initially ''unoccupied'' (by monomers). The first step of the walk may be made in one of the z available directions, by choosing an ''unoccupied'' NN of $\mathbf{r}_0$, say $\mathbf{r}_1$, at random and with equal probability. Let the walk be nonreversing so that it has a maximum of $z-1$ directions to choose from for the next step. Let $\{\mathbf{r}_j^m|m=1,2,\ldots,z_j\}$ be the ''unoccupied'' NN's available for the jth step of the walk. If $z_j=0$, the walk cannot grow further because it is geometrically ''trapped.'' It is, therefore, discarded and a fresh walk is started from $\mathbf{r}_0$. If $z_j\neq 0$, the walk proceeds by choosing one of the available sites with a probability defined as follows:

Let $n_{\mathrm{NN}}^m(j)$ be the number of nbNN sites of $\mathbf{r}_j^m$. Then, the probability that this site is chosen for the jth step is given by

*Email address: glass@apsara.barc.ernet.in
†Email address: kpn@igcar.ernet.in
‡Email address: ramu@magnum.barc.ernet.in

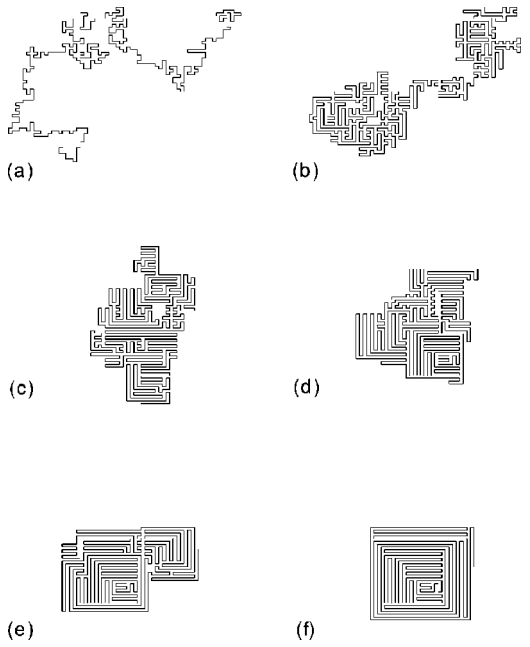

FIG. 1. Typical configurations of a 1000-step walk on a square lattice for $\beta=0(a)$, $2.0(b)$, $3.0(c)$, $4.0(d)$, $5.0(e)$, and $300(f)$.

$$p_m(\mathbf{r}_j) \equiv \frac{\exp[-\beta n_{\mathrm{NN}}^m(j)\epsilon_0]}{\sum_{m=1}^{z_j} \exp[-\beta n_{\mathrm{NN}}^m(j)\epsilon_0]}, \tag{1}$$

where the summation is over all the z_j available sites. At ''infinite'' temperature ($\beta=0$), the local growth probability $p_m(\mathbf{r}_j)$ is equal to $1/z_j$ and thus, the walk generated will be the same as the KGW. However, at finite temperatures, the walk will prefer to step into a site with more (less) nbNN contacts depending on whether ϵ is negative (positive). The probability of kinetically generating a walk configuration $\mathcal{C} \equiv\{\mathbf{r}_0,\mathbf{r}_1,\ldots,\mathbf{r}_j,\ldots,\}$ is then given by $P_{\mathcal{C}}=\Pi_j p(\mathbf{r}_j)$. We set ϵ_0 equal to -1 without loss of generality so that β could correspond to the dimensionless temperature.

In Fig. 1, we have shown the typical configurations of a 1000-step walk on a square lattice for $\beta=0$, 2.0, 3.0, 4.0, 5.0, and 300. Evidently, the walk grows into a more compact configuration at lower temperatures, made up of a chain of square blobs having ''helical'' and ''sheetlike'' structures.

We have generated ten million configurations of walks up to 2500 steps for various values of β, and obtained the mean square end-to-end distance, $\langle r^2(N)\rangle$, as a simple unweighted average (i.e., $\langle r^2(N)\rangle=\Sigma_{\mathcal{C}} r^2/\mathcal{N}$, where the summation is over all the $\mathcal{N}$ configurations generated). We have presented $\langle r^2(N)\rangle$ as a function of N in Fig. 2.

Sample attrition is the most severe problem for $\beta=0$ and it becomes less and less severe as the value of β increases. Consequently, we have presented the data up to a maximum of $N=350$ for $\beta=0$ and $N=2500$ for $\beta=300$. It is clear that the dotted lines with slopes 1.5 and 1.0 indicate the asymptotic behavior of the data for $\beta=0$ and $\beta\rightarrow\infty$, corresponding to the SAW and the collapsed walk limits, respectively. We do not know *a priori* whether a collapse transition

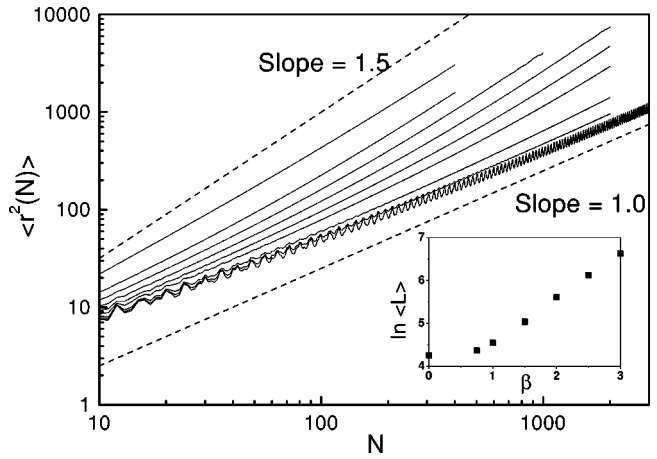

FIG. 2. Log-log plot of the mean square end-to-end distance as a function of N for $\beta=0$, 1.0, 1.5, 2.0, 2.5, 3.0, 4.0, 5.0, and 300, from top to bottom. Inset: Logarithm of the mean trapping length, $\ln\langle L\rangle$ as a function of β.

exists for our walk. We assume that it exists and is in the same universality class as the θ point, and then check if our data support this assumption.

Since it is known that the exponents ν and γ have the exact values 4/7 and 8/7 at θ point in two dimensions [4], we have plotted $\langle r^2(N)\rangle^{1/2}/N^{4/7}$ as a function of $\log(N)$ in Fig. 3. The data tend to flatten out for $\beta\sim 4$ implying thereby that the θ point is located near this value of β. We have also plotted $\langle r^2(N)\rangle/N^{8/7}$ as a function of β in Fig. 4 for $N=800$, 1000, 1200, 1400, 1600, 1800, and 2000. The crossover value of β (~ 4 in our case) is expected [11] to correspond to the θ-point value.

Independently, we have obtained the exponent γ from the fraction of successful walks, $S(N)\sim N^{\gamma-1}e^{-\lambda N}$, where λ is the attrition constant and plotted them for six different values of β in Fig. 5. We find that γ has a value (~ 1.13) close to the expected theoretical value 8/7 for $\beta=4$.

Further evidence that it is indeed close to the θ point is presented in Fig. 6, where we have plotted the crossover

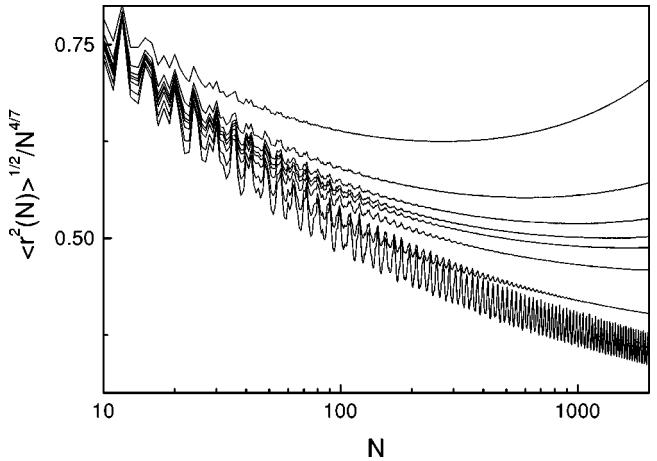

FIG. 3. Semi-log plot of $\langle r^2(N)\rangle^{1/2}/N^{4/7}$ as a function of $\log(N)$ for $\beta=3.0$, 3.5, 3.75, 3.9, 4.0, 4.25, 5.0, and 300, from top to bottom.

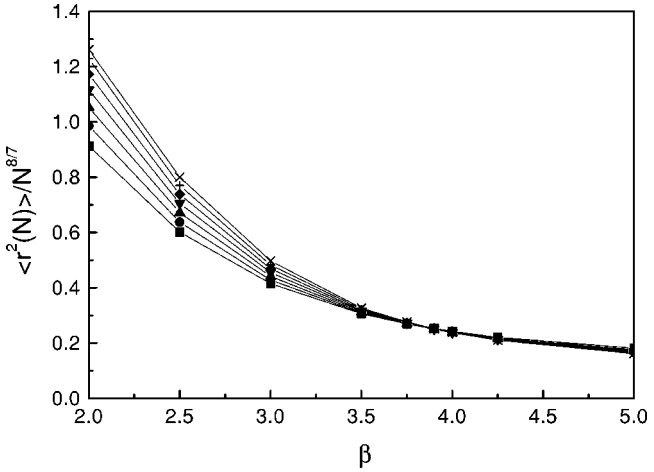

FIG. 4. $\langle r^2(N)\rangle/N^{8/7}$ as a function of β for $N=800$ to 2000 in steps of 200 from bottom to top.

exponent $\phi(N)$ as a function of $1/N$ at $\beta=4$ using the prescription of Grassberger and Hegger [12]. The solid line is a quartic polynomial fit to the data drawn so as to guide the eye. The extrapolated value (0.419 ± 0.003) for ϕ is close to the expected exact value 3/7.

All these figures put together suggest that a collapse transition for this walk exists and the corresponding dimensionless nbNN contact energy is close to -4.

The walk configuration $\mathcal{C}$ having a total of $n_{\rm NN}(\mathcal{C})=\Sigma_{j=1}^{N} n_{\rm NN}(j)$ nonbonded NN contacts, is grown with the probability

$$P_{\mathcal{C}}=\frac{\exp[-n_{\rm NN}(\mathcal{C})\beta\epsilon_0]}{\prod_{j=1}^{N}\left(\sum_{m=1}^{z_j}\exp[-n_{\rm NN}^{m}(j)\beta\epsilon_0]\right)}. \tag{2}$$

It is possible to write the denominator of the above equation as $e^{-n_{\rm NN}(\mathcal{C})\beta''\epsilon_0}$, where β'' is an effective inverse temperature. The value of β'' will be less (greater) than that of β if ϵ_0 is

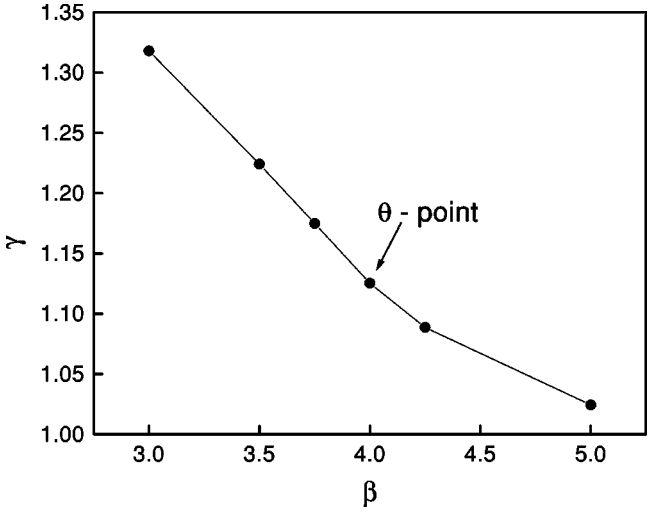

FIG. 5. The exponent γ as a function of β. Corresponding to the θ point, γ has a value ~1.13.

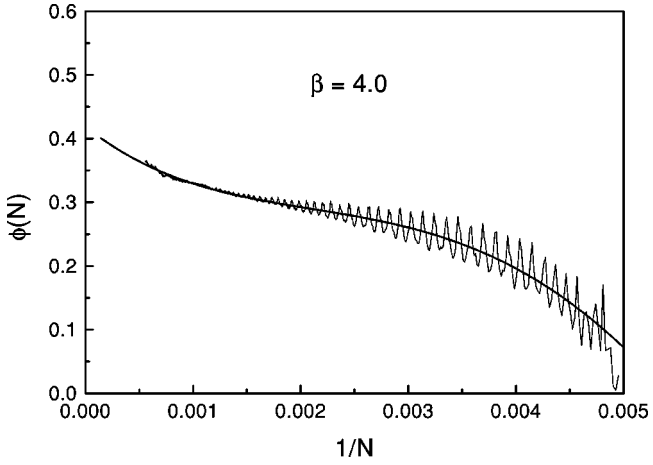

FIG. 6. The crossover exponent ϕ as a function of $1/N$. The solid line is a quartic polynomial fit and is drawn to guide the eye. The extrapolated value is $\sim0.419\pm0.003$.

positive (negative or zero). Nevertheless, ISAW algorithm cannot sample the walk at an effective temperature given by $\beta'\equiv|(\beta''-\beta)|$ because β'' can only be estimated *a posteriori* on the basis of the configuration generated. An alternative is to have a kinetic algorithm, such as what we have proposed in this paper, which grows a walk by sampling the available growth sites as per their *local* energies. This is in contrast with the ISAW algorithm that samples fully grown and equally weighted SAW configurations (i.e., *chains*) according to their *total* energies. To underline this basic difference, we refer to our walk as the interacting growth walk (IGW).

It is appropriate at this juncture to note that the difference between our algorithm and the PERM algorithm (method B) of Grassberger [10] is analogous to that between the Rosenbluth-Rosenbluth algorithm (RR) [13] and the KGW [7]. Ours is the finite-temperature generalization of the KGW, just as PERM is the finite-temperature generalization of the RR method. There is no *a priori* reason therefore to expect that IGW will belong to the same universality class as ISAW, they both being different models altogether. Yet, our data seem to suggest that it may well be so.

Since the IGW is equivalent to the KGW in the limit $\beta\rightarrow0$, it is of interest to see if survival probability arguements such as Pietronero [14] could be devised for describing its asymptotic behavior even if only tentatively. Let $\mathcal{T}_N$ be an ensemble of N-step true self-avoiding walk [15] configurations whose end-to-end distances are known to be Gaussian distributed in a space of dimension $d\geqslant2$. As we move along an arbitrarily chosen configuration, we try to estimate the probability of surviving self intersections and geometrical trappings. This involves accounting for the probability per step of encounter p_E and the probability of trapping, p_T, which together determine the survival of the walk. Assuming that the trapping probability per step is a constant and also that the encounter probability per step $p_E\sim\rho_N^{\alpha}$, where ρ_N is the chain density and α is the order of encounter (i.e., the number of nbNN contacts), it has been shown that $\nu=(\alpha+2)/(d\alpha+2)$ for the KGW.

The observed fact that the IGW becomes more compact at lower temperatures (Fig. 1) implies, within the framework of the above Flory-like arguments, that there should be an enhancement q_E of the encounter probability per step, p_E. We expect q_E to increase implicitly as a function of β subject to the condition that $q_E \to 1$ as $\beta \to 0$. On the other hand, since the mean trapping length of IGW has been found to increase exponentially with β (inset of Fig. 2), the trapping probability per step may be expected to be attenuated by a factor proportional to $\exp(-\beta)$. So, if we assume an implicit temperature dependence $q_E \sim \rho_N^{\beta}$, we can show that $\nu=(\alpha+\beta+2)/[d(\alpha+\beta)+2]$. While it obviously reduces to the Pietronero's formula in the limit $\beta \to 0$, it reduces to the form $\nu=1/d$ for the collapsed state in the limit $\beta \to \infty$. Since the first-order encounter ($\alpha=1$) is sufficient to trap the walk, we have $\nu=(\beta+3)/2(\beta+2)$ in two dimensions. This yields the value $\beta_\theta=5$ corresponding to the exact θ-point exponent $\nu=4/7$. It may be noted that this value is fortuitously close to our numerically estimated value. However, in order to ensure universality of ν, we should have a term proportional to the ratio β/β_θ (say, $\tilde{\beta} \equiv K\beta/\beta_\theta$) rather than β itself in the formula. The proportionality constant K may then be fixed by the θ-point value of ν: $K+\alpha=2(1-\nu_\theta)/(d\nu_\theta-1)$, $d=1$ being a pathological case. The fact that the first-order encounter does not trap the walk at $T=0$ implies that α also has some temperature dependence. Moreover, the continuous dependence of ν on β that the above formula suggests is at variance with the fact that there are only three universal regimes corresponding to $\beta <, =$ and $> \beta_\theta$, respectively. This needs further study.

We thus have a powerful growth algorithm for generating SAW configurations at any given temperature $T \geqslant 0$. Its strength lies in the fact that it suffers less attrition and is able to selectively grow compact configurations at lower temperatures. Because it is capable of generating maximally compact configurations at zero temperature, it may prove to be a very useful algorithm for studying protein folding processes. We have also demonstrated explicitly in two dimensions that it correctly describes the collapse transition of a homopolymer. Whether it is exactly the same as the (ISAW) θ point is an interesting open question, especially because the minimum walk length required to be in the asymptotic regime increases exponentially with the inverse of temperature even in two dimensions.

We are thankful to T. Prellberg and S. Bhattacharjee for helpful comments on this work.

[1] D. Napper, *Polymeric Stabilization of Colloidal Dispersions* (Academic, NY, 1983); H.S. Chan and K. Dill, Annu. Rev. Biophys. Biophys. Chem. **20**, 447 (1991); C. Vanderzande, *Lattice Models of Polymers* (Cambridge University Press, Cambridge, 1998); T. Prellberg, Habilitation thesis, Technische Universität Clausthel, 2001.

[2] P.G. de Gennes, *Scaling Concepts in Polymer Physics* (Cornell University Press, New York, 1979).

[3] K. Barat and B.K. Chakrabarti, Phys. Rep. **258**, 377 (1995).

[4] H. Saleur, J. Stat. Phys. **45**, 419 (1986); B. Duplantier and H. Saleur, Phys. Rev. Lett. **59**, 539 (1987).

[5] A.D. Sokal, e-print hep-lat/9405016.

[6] P.H. Poole, A. Coniglio, N. Jan, and H.E. Stanley, Phys. Rev. B **39**, 495 (1989); A. Coniglio, N. Jan, I. Majid, and H.E. Stanley, *ibid.* **35**, 3617 (1987).

[7] I. Majid, N. Jan, A. Coniglio, and H.E. Stanley, Phys. Rev. Lett. **52**, 1257 (1984); K. Kremer and J.W. Lyklema, *ibid.* **55**, 2091 (1985); I. Majid, N. Jan, A. Coniglio, and H.E. Stanley, *ibid.* **55**, 2092 (1985).

[8] A. Weinrib and S.A. Trugman, Phys. Rev. B **31**, 2993 (1985).

[9] F. Seno and A.L. Stella, J. Phys. (Paris) **49**, 739 (1988).

[10] P. Grassberger, Phys. Rev. E **56**, 3682 (1997).

[11] M.P. Taylor and J.E.G. Lipson, J. Chem. Phys. **109**, 7583 (1998).

[12] P. Grassberger and R. Hegger, J. Phys. I **5**, 597 (1995).

[13] M.N. Rosenbluth and A.W. Rosenbluth, J. Chem. Phys. **23**, 356 (1955).

[14] L. Pietronero, Phys. Rev. Lett. **55**, 2025 (1985); A.L. Stella, *ibid.* **56**, 2430 (1986); L. Pietronero, *ibid.* **56**, 2431 (1986).

[15] D.J. Amit, G. Parisi, and L. Peliti, Phys. Rev. B **27**, 1635 (1983); L. Pietronero, *ibid.* **27**, 5887 (1983); J. Bernasconi and L. Pietronero, *ibid.* **29**, 5196 (1984).