A new monte carlo algorithm for growing compact self avoiding walks

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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) algorithm, does not suffer from attrition on a square lattice at zero temperature, in contrast to the existing algorithms. More importantly, the IGW algorithm 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 algorithm correctly describes the collapse transition of a homopolymer in two dimensions.

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The configurational properties of linear polymers undergoing a collapse transition at a tricritical temperature $T_\theta$, called the $\theta$-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) behaviour characterized by the exponents $\nu$ and $\gamma$ 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 neighbour (nbNN) interactions have been proposed [4].

Let $S_N$ denote an ensemble of equally weighted $N$-step SAW configurations, generated on a lattice by a standard algorithm[5]. If $\epsilon_0$ 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 can 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 $I_N(\beta)$. By this definition, $I_N(\beta = 0)$ is the same as $S_N$ 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, $S_N$ can be thought of as representing a polymer at ‘infinite’ temperature. The statistical accuracy of any physical quantity averaged over $I_N(\beta)$ 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 as large an ensemble, $S_N$, as possible; 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, $G_N$, identically equivalent to $I_N(\beta > 0)$. For example, the Kinetic Growth Walk (KGW) [7] or the SMART Kinetic Walk (SKW) [8] on a hexagonal lattice straightforward generates an ensemble of configurations equivalent to the ISAW ensemble, $I_N(\beta = \ln 2)$. Having generated the athermal ensemble, $G_N$, by such a geometric algorithm, ensemble averages corresponding to a lower temperature could be obtained by Botzmann weighting these configurations appropriately. This would ensure better statistical accuracy as compared to what could be obtained directly from $S_N$. 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 $T \geq 0$. This algorithm, called the Interacting Growth Walk (IGW) algorithm, 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 algorithm is capable of describing the universal behaviour of a SAW above, at and below the $\theta$-point in two dimensions. We also present a speculative Flory thory for the IGW.

We start the growth process by ‘occupying’ an arbitrarily chosen site, $r_0$, of a regular $d$-dimensional lattice of coordination number $z$ whose sites are initially ‘unoccupied’ (by monomers). The first step of the walk can be made in one of the $z$ available directions, by choosing an ‘unoccupied’ NN of $r_0$, say $r_1$, at random. Let the walk be non-reversing so that it has a maximum of $z - 1$
directions to choose from for any further step made. Let \( \{ \mathbf{r}_j^m \mid m = 1, 2, \ldots, z_j \} \) be the 'unoccupied' NNs available for the \( j \)th step of the walk. If \( z_j = 0 \), the walk can not 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 \( n_{NN}^m(j) \) be the number of nbNN sites of \( \mathbf{r}_j^m \). Then, the probability that this site is chosen for the \( j \)th step is given by,

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

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 or less nbNN contacts depending on whether \( \epsilon \) is negative or positive. The probability of kinetically generating a walk configuration, \( C \equiv \{ \mathbf{r}_0, \mathbf{r}_1, \ldots, \mathbf{r}_j, \ldots \} \), is then given by \( P_C = \prod_j p(\mathbf{r}_j) \). We set \( \epsilon_0 \) equal to \(-1\) without loss of generality so that \( \beta \) 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 upto 2500 steps for various values of \( \beta \), and obtained the mean square end-to-end distance, \( \langle r^2(N) \rangle \), as a simple unweighted average (i.e., \( \langle r^2(N) \rangle = \sum_{C} r^2/N \)), where the summation is over all the \( N \) configurations generated. We have presented \( \langle r^2(N) \rangle \) as a function of \( N \) in Fig.2.

![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).](image-url)
class as the $\theta$-point, and then check if our data support this assumption.

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

![FIG. 4. $<r^2(N)>/N^{8/7}$ as a function of $\beta$ for $N = 800$ to 2000 in steps of 200 from bottom to top.](image)

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

Further evidence that it is indeed close to the $\theta$-point is presented in Fig.6, where we have plotted the crossover 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 ($0.419 \pm 0.003$) for $\phi$ is close to the expected exact value $3/7$.

![FIG. 5. The exponent $\gamma$ as a function of $\beta$. Corresponding to the $\theta$-point, $\gamma$ has a value $\sim 1.13$.](image)

![FIG. 6. The crossover exponent, $\phi$, 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 $\sim 0.419 \pm 0.003$.](image)

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, $C$, having a total of $n_{NN}(C) = \sum_{j=1}^{N} n_{NN}(j)$ non-bonded NN contacts, is grown with the probability,

$$P_C = \frac{\exp[-n_{NN}(C)/\beta_0]}{\prod_{j=1}^{N} \left( \sum_{m=1}^{\beta} \exp[-n_{NN}(j)/\beta_0] \right)}$$

(2)

It is possible to write the denominator, $W(C)$, of the above equation as $e^{-n_{NN}(C)/\beta_0}$, where $\beta''$ is an effective inverse temperature. The value of $\beta''$ will be less (greater) than that of $\beta$ if $\epsilon_0$ is positive (negative or zero). Nevertheless, ISAW algorithm can not sample the walk at an effective temperature given by $\beta'' = (\beta'' - \beta)$ because $\beta''$ 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 which 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 generalisation of the KGW, just as PERM is the finite temperature generalisation 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 $\beta \rightarrow 0$, it is of interest to see if survival probability argue-
ments a la Pietronero [14] could be devised for describing its asymptotic behaviour even if only tentatively. Let \( T_N \) be an ensemble of \( N \)-step True Self Avoiding Walk (TSAW) [15] configurations whose end-to-end distances are known to be Gaussian distributed in a space of dimension \( d \geq 2 \). 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 \( \rho_N \) is the chain density and \( \alpha \) 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, \( q_E[\rho_N] \), of the encounter probability per step, \( p_E \). We expect \( q_E[\rho_N] \) to increase implicitly as a function of \( \beta \) subject to the condition that \( q_E[\rho_N] \to 1 \) as \( \beta \to 0 \). On the other hand, since the mean trapping length of IGW has been found to increase exponentially with \( \beta \) (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, \( q_E[\rho_N] \sim \rho_N^\beta \), 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 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, \( \beta_0 = 5 \), corresponding to the exact \( \theta \)-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 \( \nu \), we should have a term proportional to the ratio \( \beta/\beta_0 \) (say, \( \beta \equiv K/\beta_0 \)) rather than \( \beta \) itself in the formula. The proportionality constant \( K \) may then be fixed by the \( \theta \)-point value of \( \nu \): \( K \equiv 2(1 - \nu)/(|d\nu - 1|) \), \( d \equiv 1 \) being a pathological case. The fact that the first-order encounter does not trap the walk at \( T = 0 \) implies that \( \alpha \) also has some temperature dependence. Moreover, the continuous dependence of \( \nu \) on \( \beta \) which the above formula suggests is at variance with the fact that there are only three universal regimes corresponding to \( \beta <, = \) and \( > \beta_0 \) respectively. This needs further study.

We thus have a powerful growth algorithm for generating SAW configurations at any given temperature, \( T > 0 \). 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) \( \theta \)-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.

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[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 Univ. Press, UK, 1998); T. Prellberg, *Lattice models of interacting polymers and vesicles* (Habilitation Thesis, Technische Universität Clausthal, April 2001).

[2] P.G. de Gennes, *Scaling concepts in polymer physics* (Cornell Univ. Press, 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, preprint hep-lat/9405016.

[6] P.H. Poole, A. Coniglio, N. Jan and H.E. Stanley, Phys. Rev. B39, 495 (1989); A. Coniglio, N. Jan, I. Majid and H.E. Stanley, Phys. Rev. B35, 3617 (1987).

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

[8] A. Weinrib and S.A. Trugman, Phys. Rev. B31, 2993 (1985).

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

[10] P. Grassberger, Phys. Rev. E56, 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. (Paris)15, 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, Phys. Rev. Lett. 56, 2430 (1986); L. Pietronero, Phys. Rev. Lett. 56, 2431 (1986).

[15] D.J. Amit, G. Parisi and L. Peliti, Phys. Rev. B27, 1635 (1983); L. Pietronero, Phys. Rev. B27, 5887 (1983); J. Bernasconi and L. Pietronero, Phys. Rev. B29, 5196 (1984).