

Pivot-coupled grand canonical Monte Carlo method for ring simulations

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A new method is presented for the simulation of an ensemble of polymer rings of variable size at fixed monomer chemical potential. Called pivot-coupled grand canonical Monte Carlo (PC-GCMC), it is based on the directed addition or removal of a monomer to or from a ring, coupled to the pivot of a section of the ring to maintain the ring's continuity. Application of PC-GCMC to single, isolated rings yields the free energy of the ring polymer as a function of number of monomers, information useful in determining equilibrium constants for polymer cyclization. Ring closure probabilities ("J-factors") for flexible and semiflexible polymers, both ideal and self-avoiding, in two and three dimensions are obtained in close agreement with available results from theory and other simulation methods. New results are obtained for two-dimensional semiflexible polygons. Potential applications of the method to simulations of ring-forming equilibrium polymers, disklike micelles, and self-assembling polymer loops are discussed. © 2002 American Institute of Physics.

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I. INTRODUCTION

Theoretical work on the probability of ring formation in self-assembling polymers dates to the mid-twentieth century, when Jacobson and Stockmayer¹ identified the scaling laws describing the decreasing probability of ring formation with ring size for ideal chains within the Gaussian random walk approximation. Motivated to a great extent by interest in the biology and biophysics of cyclization in DNA, a large body of theoretical and simulation work has been undertaken since then to describe the thermodynamics and kinetics of ring closure.² Much work in particular has involved calculating the "J-factor," or nonlocal contribution to the cyclization equilibrium constant, as a function of chain length³ and degree of supercoiling.⁴ Other studies have focused on the equilibrium distribution of ring polymer topological states (with respect to both knottedness and supercoiling^{5,6}), the dimensions and structure of ring polymers,⁷⁻¹⁰ the effects of their topology on inter-ring interactions,^{11,12} and the conditions under which rings are found in equilibrium with chains in self-assembling polymer systems.^{13,14} Rings confined to two dimensions (i.e., polygons) are interesting not only in the context of polymers localized at surfaces or interfaces, but also because two-dimensional mesoscopic domains (for instance, in a Langmuir monolayer) can be efficiently represented by their one-dimensional borders.¹⁵⁻¹⁷

This report describes a novel grand canonical Monte Carlo (GCMC) method for the direct, reversible addition or removal of a single monomer to or from a ring without disrupting ring continuity or bond lengths between neighboring monomers. In general, GCMC methods involve simulations at fixed chemical potential and temperature in which the number of particles in a system is varied by inserting and removing particles. The algorithm proposed here, pivot-

coupled (PC) GCMC, pairs each particle insertion or removal move with a pivot move that either opens the ring to provide space for a new monomer or closes it to fill in the gap left by a removed monomer.

While several methods have been developed specifically to generate ensembles of ring polymer configurations,^{18,19} none is suitable for the reversible addition of monomers to an existing ring. Monte Carlo biasing schemes developed for associating fluid models may accelerate rates of ring formation from free particles, but do not, in general, facilitate changes in size of existing rings.^{20,21} The present method is closely related to fixed-endpoint configuration-bias Monte Carlo methods, which may be used to generate a statistically correct ensemble of rings of fixed size with lattice,²² freely jointed²³ or more sophisticated interaction potentials.^{24,25} A PC-GCMC addition or removal move can be seen as a fixed-endpoint biased regrowth of a section of the ring, in which all bond lengths and most bond angles are unaffected, while the number of monomers changes.

The original motivation for development of the PC-GCMC method was for the efficient simulation of equilibrium polymer systems under conditions where ring formation is favored.¹³ The existence of such conditions has been demonstrated experimentally for a system of wormlike micelles.²⁶ In simulation of such systems without a method like the PC-GCMC algorithm, equilibration of the ring size distribution depends on a slow three-step process of breaking the ring to form a chain, extending or shortening the chain length, and reforming the ring.

Simulation of other classes of systems displaying self-assembly will also be facilitated by the current method. The PC method has the potential to provide a uniquely efficient method to sample area, perimeter, and shape fluctuations for interacting self-assembled disks²⁷ or two-dimensional domains, where the disks or domains are represented by non-overlapping two-dimensional rings. Another potential area of

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application lies in the simulation of systems of fixed-length polymers containing one or more closed loops;^{28,29} in this context, changes of loop size arise from exchange of length with the free ends of the polymer, not from the exchange of monomers with a reservoir of free monomers or other aggregates.

This report is limited to the description of the PC-GCMC method and its validation through the calculation of ring-closure probabilities (J -factors) for isolated chains. The established method for this calculation is to perform a series of simulations, generally with a series of increasingly restrictive biases constraining the ends to move closer and closer together, to derive the probability that the ends of a chain of a given length are close enough and appropriately oriented to form a bond.^{2,30} In the present approach, the PC-GCMC method gives the free energy of the system (to within a constant) as a function of number of monomers (N) over a specified range. J -factors for all values of N within this range may be obtained using this information in conjunction with the chain free energy as a function of number of monomers (trivial for ideal chains, or otherwise obtained by chain-growth GCMC methods), and a single J -factor obtained by another method at a point within this distribution.

The remainder of this report comprises a detailed description of the algorithm for two- and three-dimensional rings, tests of the method against previous results for flexible ideal and self-avoiding rings and for 3D wormlike chain models, and new results for the 2D wormlike chain.

II. METHODS

The generation of monomer addition and removal Monte Carlo moves is described for two- and three-dimensional systems in Secs. II A and II B. A derivation of the weighing factors for acceptance or rejection of these moves is given in Sec. II C, completing the basic description of the method. A method for improving sampling efficiency by angle-biased insertion is described in Sec. II D. The procedure for calculation of J -factors is included in Sec. II E, and notes on other details of the calculations presented here are collected in Sec. II F.

A. Monomer addition and removal in two dimensions

The starting configuration is a ring of N monomers (e.g., the square in Fig. 1) such that the distance between neighboring monomers is a fixed bond-length σ . At random, a pair of connected monomers a and b are chosen between which a new monomer is to be added, and a third monomer p is chosen to define a pivot point. A position on the circle of radius σ around monomer b (circle 1 in Fig. 1) is selected at random to insert a new monomer, n . It is convenient to work with a local polar coordinate system with its origin at point p and with the position of the new monomer defined as $(R_{\text{new}}, 0)$. Monomer a then must be given a new position a' at a distance σ from the new monomer j , and so is rotated from its original position (r_a, θ_a) to a new position (r_a, θ'_a) . Finding this position is a matter of solving for the intersection of two circles, one of radius σ around the inserted

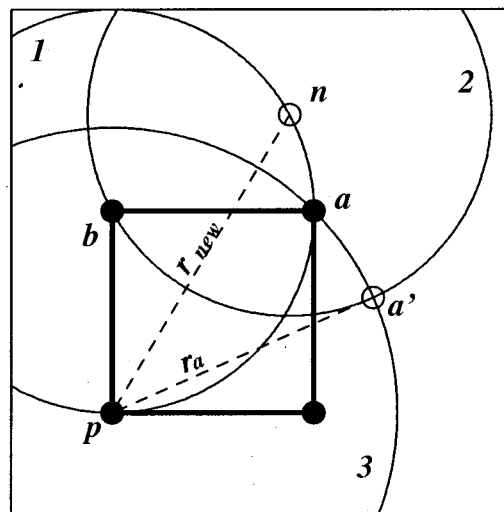


FIG. 1. Illustration of first steps in PC-GCMC particle addition move. Initial ring is shown by filled circles connected by solid segments. Trial positions are shown as small open circles. Points and circles are labeled according to Sec. II A.

monomer's position (circle 2 in Fig. 1), and one of radius r_a centered at the pivot monomer p (circle 3 in Fig. 1). By the law of cosines,

$$\cos \theta'_a = (r_a^2 + r_{\text{new}}^2 - \sigma^2) / 2r_a r_{\text{new}}. \quad (1)$$

If $|r_a - r_{\text{new}}| < \sigma$ and $r_a + r_{\text{new}} > \sigma$, two solutions exist, corresponding to positive or negative values of θ'_a , and one may be selected at random. Otherwise, no solution exists, and the move is rejected. As illustrated in Fig. 2, once position a' is determined, all monomers between a and p (counting around the ring away from b) are rotated around the point p by an angle β equal to $\theta'_a - \theta_a$. The result is a closed ring of $N + 1$ monomers with all bond lengths unaltered.

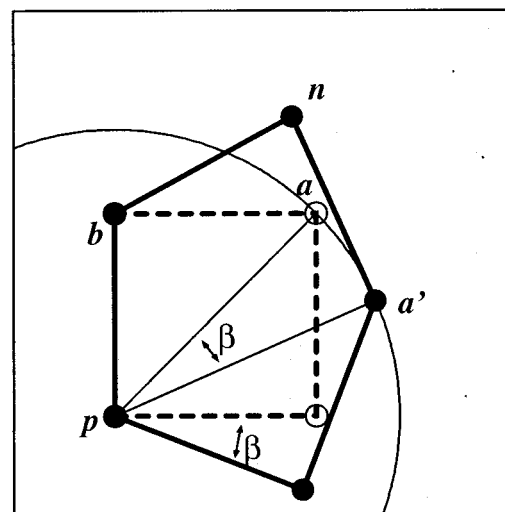


FIG. 2. Illustration of completion of PC-GCMC particle addition move. Initial ring is shown by dashed segments; complete trial ring is represented by solid segments. Angle β is labeled according to Sec. II A.

The reverse step of monomer removal follows the same sequence: selection of a monomer to be removed, selection of a monomer to act as a pivot point, and rotation of a section of the ring about the pivot point to reform the ring. A monomer b (bound to both a and c) to remove and a monomer p (not bound to b) are chosen. Defining a polar coordinate system with origin at p and with the position of monomer c defined as $(r_{\text{new}}, 0)$, the new position of monomer a is again given by (r_a, θ'_a) with $\cos \theta'_a$ defined by Eq. (1). (If $\cos \theta'_a$ is in the allowable range, a sign for θ'_a is again chosen at random; otherwise, the move is rejected.) Lastly, a rotation by $\theta'_a - \theta_a$ about the pivot monomer is performed for monomers in the section of ring connecting a and p .

Although it is easier and more efficient to implement this method with an absolute constraint on the bond length, as described above, any chaining potential with upper and lower bounds σ_{max} and σ_{min} to the bond length can be used. Maximum and minimum values for θ'_a must be determined by solving Eq. (1) twice, once with σ_{max} and once with σ_{min} .³¹ The new trial position for monomer a is then (r_a, θ'_a) , with θ'_a selected from a uniform random distribution with absolute value between these maximum and minimum values.

B. Monomer addition and removal in three dimensions

The steps involved in pivot-coupled monomer addition and deletion for 3D ring polymers are little more difficult than for the two-dimensional case. Again, given an existing ring of monomers with bond-length σ , a new position is chosen on the sphere of radius σ from randomly chosen monomer b , and monomer p (different from b or its neighbor, a) is again selected at random to serve as a pivot point. A spherical polar coordinate system is defined with its origin at p , the new monomer's position at $(r_{\text{new}}, 0, 0)$ and monomer a at $(r_a, \theta_a, \varphi_a)$. Monomer a is to be transferred from the bonding region of monomer b to the bonding region of the new monomer. When $|r_a - r_{\text{new}}| < \sigma$ and $r_a + r_{\text{new}} > \sigma$, Eq. (1) can still be used to solve for θ'_a ; otherwise, the move is rejected. In a three-dimensional system, the locus of possible new positions for monomer a is not a pair of points, but a circle of radius $r_a \sin \theta'_a$ formed by the intersection of the sphere with radius σ centered at $(r_{\text{new}}, 0, 0)$ and the sphere with radius r_a centered at the origin. The position on this circle is determined by φ'_a , which may be chosen from a uniform distribution between 0 and 2π . An axis of rotation is defined containing point p and normal to the plane apa' . The positions of monomers connecting a and p are rotated by an angle β (defined as $\angle apa'$) about this axis in order to reform the ring with the original bond lengths maintained. The procedures for the reverse move of monomer deletion, and for the extension of the method to bond potentials without fixed constraints, follow just as in the two-dimensional case.

C. Acceptance probabilities

The scheme described above for reversibly inserting monomers into rings is most conveniently and efficiently

implemented with exact constraints on the bond-length σ . It is known, however, that systems with exact constraints display different equilibrium properties than systems with arbitrarily stiff bonds.³² In deriving the acceptance probabilities for insertion and deletion moves, it is therefore useful to consider first a system with a small range of possible bond lengths, for instance between σ and $\sigma + \zeta$, and then take the limit $\zeta \rightarrow 0$. For a system of particles with thermal De Broglie wavelength Λ at chemical potential μ and inverse temperature βk_B , the standard grand canonical Monte Carlo ratio of the acceptance probability for the addition of a particle to a system of N particles to the removal of a particle from a system of $N + 1$ particles is given by³³

$$\frac{\text{acc}_{\text{GC}}(N \rightarrow N+1)}{\text{acc}_{\text{GC}}(N+1 \rightarrow N)} = \frac{V}{\Lambda^d(N+1)} \exp\{\beta[\mu - U(N+1) + U(N)]\}. \quad (2)$$

In the present biased addition scheme, the volume V to which monomers are added in the present method is not the total volume of the system, but rather should be replaced by a sum of volumes corresponding to N shells of radius σ and thickness ζ centered at each monomer. With the contribution of the bond energy to the potential energy U given by $(-NU_{\text{bond}})$, and all other contributions (e.g., bending energy, nonbonded interactions) designated U' , Eq. (2) simplifies to

$$\frac{\text{acc}_{\text{GC}}(N \rightarrow N+1)}{\text{acc}_{\text{GC}}(N+1 \rightarrow N)} = \frac{N}{(N+1)} K \exp\{\beta[-U'(N+1) + U'(N)]\}, \quad (3)$$

$$K_{2D} = 2\pi\sigma\zeta\Lambda^{-2} \exp[\beta(\mu + U_{\text{bond}})],$$

$$K_{3D} = 4\pi\sigma^2\zeta\Lambda^{-3} \exp[\beta(\mu + U_{\text{bond}})]. \quad (4)$$

Unlike standard GCMC, the present method requires each insertion or removal step to be coupled to a biased rotation about the pivot monomer, which brings monomer a from a position bound to monomer b to a position bound to the new monomer (after insertion) or to the other neighbor of monomer b (after removal of b). The acceptance ratio for the combined monomer addition (or deletion) and ring pivot is the product of the standard GCMC acceptance ratio and an acceptance ratio γ for the biased rotation. In the 2D case, the probability of this transfer occurring in an *unbiased* rotation move is $(\theta'_{a,\text{max}} - \theta'_{a,\text{min}})/\pi$, and the probability of its being reversed successfully is $(\theta_{a,\text{max}} - \theta_{a,\text{min}})/\pi$, using the notation of Sec. II A. The ratio of these probabilities (in other words, the Jacobian of the transformation) must be maintained in the present *biased* move, so

$$\gamma_{2D} = (\theta'_{a,\text{max}} - \theta'_{a,\text{min}}) / (\theta_{a,\text{max}} - \theta_{a,\text{min}}). \quad (5)$$

If the range of possible angles is set to give bond lengths between σ and $\sigma + \zeta$, then $\theta_{a,\text{min}}$ and $\theta'_{a,\text{min}}$ can be identified with θ_a and θ'_a . To find $\theta_{a,\text{max}}$ in the limit of small ζ , we consider

$$\theta_{a,\max} = \theta_a + \zeta \frac{\partial \theta_a}{\partial r_{ab}} = \theta_a + \frac{\zeta}{r_a \sin \alpha},$$

$$\theta'_{a,\max} = \theta'_a + \zeta \frac{\partial \theta'_a}{\partial r_{a'n}} = \theta'_a + \frac{\zeta}{r_a \sin \alpha'}, \quad (6)$$

with r_{ab} the distance between positions a and b , $r_{a'n}$ the distance between a' and the new monomer, and angles $\alpha = \angle bap$ and $\alpha' = \angle na'p$. Equation (5) becomes

$$\gamma_{2D} = \sin \alpha / \sin \alpha'. \quad (7)$$

By the law of cosines,

$$\cos \alpha = (r_b^2 - r_a^2 - \sigma^2) / 2r_a \sigma,$$

$$\cos \alpha' = (r_{\text{new}}^2 - r_a^2 - \sigma^2) / 2r_a \sigma. \quad (8)$$

Equations (7) and (8) taken together give

$$\gamma_{2D} = \frac{\sqrt{4r_a^2 r_b^2 - (r_a^2 + r_b^2 - \sigma^2)^2}}{\sqrt{4r_a^2 r_{\text{new}}^2 - (r_a^2 + r_{\text{new}}^2 - \sigma^2)^2}}. \quad (9)$$

For three-dimensional systems, the new position for monomer a may be chosen anywhere on a circle of radius $r_a \sin \theta'_a$. With a small range ζ allowable for the bond length, this circle becomes an annulus of width $r_a(\theta'_{a,\max} - \theta'_{a,\min}) = \zeta / \sin \alpha'$ [by Eq. (6)] and area

$$A' = 2\pi r_a \sin \theta'_a (\zeta / \sin \alpha') = 2\pi \zeta r_a r_{\text{new}} / \sigma, \quad (10)$$

where the second equality follows from the law of sines. The corresponding area of possible positions for the reverse move is similarly $2\pi \zeta r_a r_b / \sigma$, yielding the following simple result for the biased rotation acceptance factor in three dimensions:

$$\gamma_{3D} = r_b / r_{\text{new}}. \quad (11)$$

Note that, using the notation of Secs. II A and II B, r_b for a monomer addition step becomes r_{new} for the deletion step that reverses the insertion (i.e., given the same choices of p and a) and vice-versa. Therefore, in both Eqs. (9) and (11), the factor γ is inverted when a step is reversed, as is required by the principle of detailed balance.

The net acceptance probability for a proposed insertion into the ring of N monomers thus becomes

$$\text{acc}_{\text{PC-GC}}(N \rightarrow N+1) = \min \left[1, \frac{N}{(N+1)} \gamma K \right. \\ \left. \times \exp\{\beta[-U'(N+1) + U'(N)]\} \right], \quad (12)$$

and for removal,

$$\text{acc}_{\text{PC-GC}}(N \rightarrow N-1) = \min \left[1, \frac{(N-1)}{N} \gamma K^{-1} \right. \\ \left. \times \exp\{\beta[-U'(N-1) + U'(N)]\} \right]. \quad (13)$$

The factor K defined in Eq. (4) for two- and three-dimensional systems is a constant of the simulation conditions, while the factor γ [defined by Eq. (9) or (11)] depends on the move proposed.

D. Angle-biased insertion

When a monomer is added to a ring through the PC-GCMC method, the bond angles with vertices at points a , b , and p change, and a new bond angle with vertex at point n . For polymer models with stiff bending potentials, the procedure described previously in which monomers are inserted uniformly on the circle or sphere of radius σ around monomer b is very inefficient. Improvement can be made by biasing the choice of the position of the new monomer such that the distribution of angle b within the attempted configurations matches the Boltzmann distribution for the bending potential in question, just as in the generation of trial moves for chain growth in the configuration-bias MC method. Relative to an unbiased addition move, the probability of generating a new monomer position with bond angle Ψ_b changes by a factor $Z^{-1} \exp[-\beta U_{\text{bend}}(\Psi'_b)]$, where Z is the classical configuration integral for a single bond angle:

$$Z_{2D} = (2\pi)^{-1} \int_{-\pi}^{\pi} \exp[-\beta U_{\text{bend}}(\psi)] d\psi,$$

$$Z_{3D} = 1/2 \int_0^{\pi} \exp[-\beta U_{\text{bend}}(\psi)] \sin \psi d\psi. \quad (14)$$

To maintain detailed balance, the ratio of acceptance probabilities for insertion and removal steps [i.e., $\text{acc}(N \rightarrow N+1) / \text{acc}(N+1 \rightarrow N)$] must be reduced by the same factor, giving the following new acceptance probabilities:

$$\text{acc}_{\text{PC-GC,bias}}(N \rightarrow N+1) = \min \left[1, \frac{N}{(N+1)} \gamma Z K \right. \\ \left. \times \exp\{\beta[U_{\text{bend}}(\psi'_b) - U'(N+1) + U'(N)]\} \right], \quad (15)$$

$$\text{acc}_{\text{PC-GC,bias}}(N \rightarrow N-1) = \min \left[1, \frac{(N-1)}{N} \frac{\gamma}{Z K} \right. \\ \left. \times \exp\{\beta[-U_{\text{bend}}(\psi_b) - U'(N-1) + U'(N)]\} \right]. \quad (16)$$

It is convenient to note here that in biased GCMC of self-assembling chain molecules, in which monomers are added and removed only at the end of the chain (to or from position N , using a biased distribution for the position of added particles), the corresponding acceptance probabilities are

$$\text{acc}_{\text{GC-chain,bias}}(N \rightarrow N+1) = \min[1, Z K \exp\{\beta[U_{\text{bend}}(\psi'_N) - U'(N+1) + U'(N)]\}], \quad (17)$$

$$\begin{aligned} \text{acc}_{\text{GC-chain,bias}}(N \rightarrow N-1) &= \min[1, (ZK)^{-1} \\ &\quad \times \exp\{\beta[-U_{\text{bend}}(\psi_{N-1}) - U'(N-1) + U'(N)]\}]. \end{aligned} \quad (18)$$

For systems without nonbonding interactions (i.e., for ideal chains), the energy terms in both expressions cancel exactly to give

$$\text{acc}_{\text{GC-chain,bias}}(N \rightarrow N+1) = ZK, \quad (19)$$

$$\text{acc}_{\text{GC-chain,bias}}(N \rightarrow N-1) = 1. \quad (20)$$

E. Application to calculation of J -factors

Simulations in the grand canonical ensemble allow the calculation of the dependence of system free energy on N . The change in free energy of the system upon changing the number of particles from some reference state N_0 to N is given by

$$\begin{aligned} F(N) - F(N_0) &= -k_B T [\ln(P_N/P_{N_0})] \\ &\quad + (N - N_0)(\mu - d \ln(\Lambda)), \end{aligned} \quad (21)$$

where P_N is the probability of finding N particles in the system. The cyclization probability of a fixed-length polymer with sticky ends depends on the difference in free energies of the chain and ring polymers with the same number of monomers N . This free energy difference is obtained from a thermodynamic cycle:

$$\begin{aligned} \Delta F_{\text{cyc}}(N) &= F_{\text{ring}}(N) - F_{\text{chain}}(N) \\ &= [F_{\text{ring}}(N) - F_{\text{ring}}(N_0)] \\ &\quad - [F_{\text{chain}}(N) - F_{\text{chain}}(N_0)] + \Delta F_{\text{cyc}}(N_0). \end{aligned} \quad (22)$$

The first term on the right-hand side of Eq. (22) is available from the PC-GCMC results by application of Eq. (21). Ring-free energies calculated by the PC-GCMC method correspond to equilibrium polymers, and when applied to rings formed by reversible cyclization of a fixed-length polymer should be corrected by a factor $-k_B T \ln N$ to account for the N -fold degeneracy of a ring with $N-1$ permanent bonds and one unique reversible bond.

The second term may be obtained through a chain growth/shrinking GCMC simulation of the type discussed in Sec. II D. However, for ideal chains without excluded volume or other through-space interactions, Eqs. (19) and (20) apply to the probability of adding or removing monomers to and from the chain ends, and no explicit simulation is required to obtain

$$\begin{aligned} F_{\text{chain}}(N) - F_{\text{chain}}(N_0) &= -(N - N_0)[k_B T \ln(ZK) \\ &\quad - \mu + d \ln(\Lambda)]. \end{aligned} \quad (23)$$

While any method for calculating free-energy differences may be used to obtain $\Delta F_{\text{cyc}}(N_0)$ for any reference size N_0 , the exact free energy of cyclization of a trimer, $\Delta F_{\text{cyc}}(3)$, is readily calculated, making $N_0=3$ a convenient reference state for use in Eq. (22). The trimer has only one internal angle. In the noncyclized trimer, the configuration integral

associated with this angle is $2\pi Z_{2D}$ in two dimensions and $4\pi Z_{3D}$ in three dimensions. In the ring trimer, the angle is restricted to the range $\pm[2\pi/3 - \zeta/\sigma \sin(2\pi/3), 2\pi/3]$, following Eq. (6). The change in energy associated with forming the ring must take into account the extra bond formed and the bending energies of the three angles, giving a Boltzmann factor $\exp[\beta U_{\text{bond}} - 3U_{\text{bend}}(2\pi/3)]$. The free energies of cyclization resulting from the combination of restricted configuration, bond energy, and bending energy are

$$\begin{aligned} \Delta F_{\text{cyc},2D}(3) &= -k_B T \ln \left(\frac{2\zeta}{\pi\sqrt{3}Z_{2D}\sigma} \right) \\ &\quad - U_{\text{bond}} + 3U_{\text{bend}}(2\pi/3), \\ \Delta F_{\text{cyc},3D}(3) &= -k_B T \ln \left(\frac{\zeta}{2Z_{3D}\sigma} \right) \\ &\quad - U_{\text{bond}} + 3U_{\text{bend}}(2\pi/3). \end{aligned} \quad (24)$$

By a combination of an PC-GCMC simulation, a chain-growth simulation or application of Eq. (23) for ideal polymers, and Eqs. (21), (22), and (24), the free energy of cyclization may be obtained at all values of N .

It is useful to separate the cyclization free energy into a term related to the mean free energy of bond formation (ΔF_{bond}) and the free energy of positioning the ends in a manner allowing the bond to be formed ($\Delta F_{\text{position}}$). The former term includes the energy and entropy changes associated with forming a bond and creating two new bond angles:

$$\begin{aligned} \Delta F_{\text{bond},3D} &= -U_{\text{bond}} - k_B T \ln(4\pi\zeta\sigma^2) - 2k_B T \ln(Z_{3D}), \\ \Delta F_{\text{bond},2D} &= -U_{\text{bond}} - k_B T \ln(2\pi\zeta\sigma) - 2k_B T \ln(Z_{2D}). \end{aligned} \quad (25)$$

The latter term,

$$\Delta F_{\text{position}}(N) = \Delta F_{\text{cyc}}(N) - \Delta E_{\text{bond}} \quad (26)$$

contains all of the N -dependence of the cyclization free energy, including the bending energy and conformational restriction of the chain backbone required to form a bond between the chain ends. The contribution of this term to the equilibrium constant for cyclization is known as the J -factor,

$$J(N) = \exp(-\beta \Delta F_{\text{position}}(N)), \quad (27)$$

and can be interpreted as the effective local concentration of one end of the polymer in the vicinity of the other. The definition of Eq. (27) is identical for ideal polymers to the common definition of J -factor as the ratio of the cyclization constant K_{cyc} to the dimerization constant K_{dim} . For nonideal polymers, K_{dim} may have its own N -dependence; to avoid this complication, which is irrelevant to the cyclization equilibrium, Eq. (27) is used in this work to define J -factors for both ideal and nonideal polymers.

F. Practical details

i. Potentials. For persistent chains in two dimensions, a harmonic bending potential was used:

$$U_{\text{bend}} = \frac{1}{2}\kappa\psi^2, \quad (28)$$

with bending constant κ defined in units of $k_B T$ and ψ the deviation from linearity of a bond angle. The corresponding configuration integral [Eq. (14)] evaluates to

$$Z_{2D} = (2\pi\kappa)^{-1/2} \text{erfc}[\pi(\kappa/2)^{1/2}]. \quad (29)$$

In three dimensions, for numerical convenience the harmonic bending potential was approximated by a $\cos(\psi)$ term:

$$U_{\text{bend}} = \frac{1}{2}\kappa(2 - 2\cos\psi), \quad (30)$$

for which Eq. (14) yields

$$Z_{3D} = [1 - \exp(-2\kappa)]/2\kappa. \quad (31)$$

Note that in two dimensions, the definition of persistence length of an ideal chain in terms of the decay in the bond-vector orientation correlation function gives $l_p = 2\kappa\sigma$ and not the more familiar relation $l_p = \kappa\sigma$ valid in three-dimensional wormlike chains. In both cases, the Kuhn length equals $2l_p$.

In studies of three-dimensional self-avoiding rings, a hard-sphere potential of diameter σ was instituted at all vertex points. For two-dimensional self-avoiding polymer models, the self-avoidance criterion was that no bond segments cross.

ii. Additional Monte Carlo moves. It is straightforward to demonstrate that the pivot-coupled addition and removal moves can sample all configuration space of ideal ring polymers. However, it is useful to include a small proportion (10%) of crankshaft (or reflection, in two dimensions) Monte Carlo moves in order to sample more efficiently and to avoid any barriers to ergodicity in nonideal polymers. Inclusion of these moves was found to accelerate convergence to equilibrium distributions but not to affect final results, confirming that the method as implemented gives a canonical distribution *within* a given ring size N .

iii. Umbrella sampling. For simulations with the goal of determining $F(N)$ using Eq. (21), where $P(N)$ may vary over many orders of magnitude, it is useful to implement an adaptive biasing umbrella sampling scheme³⁴ to ensure efficient (i.e., uniform) sampling over the range of N of interest. First, one or more test simulations are performed to calculate a trial weighting function $W(N)$,

$$W(N) = \ln[P(N)]_{\text{test}}. \quad (32)$$

During a longer production run, the function $W(N)$ is added to the potential energy U of all rings of size N in determining acceptance probabilities. The effective free energy determined by Eq. (21) will be the sum of the true free energy and the weighting function. To test for convergence, $W(N)$ was obtained, updated and reused over several successive calculations until fluctuations in $P(N)$ were below 10%. As the sampling of values N takes the form of a one-dimensional random walk, the number of steps required to sample a range $R = (N_{\text{max}} - N_{\text{min}})$ scales as R^2 . Between two and four “windows” or ranges were used to construct the curves presented in the present work.

iv. Efficiency. The efficiency of the method depends on the model of polymer chosen, the range of sizes in of windows calculated, and the number and duration of trial iterations. A procedure for optimizing and automating these

choices has been described by Mezei,³⁴ but was not used in this initial study. As an example to indicate the computational expense of the algorithm, timings were performed for the PC-GCMC simulation of the ideal 3D semiflexible ring with persistence length $l_p = 20\sigma$ over the windows of N between 3–15 and 10–50 monomers. The range in probabilities $P(N)$ associated with these windows spans 28 orders of magnitude; accordingly, multiple iterations were required to achieve a uniform sampling. For each case, ten iterative trial runs were performed, beginning with 1×10^5 MC moves in the first iteration and reaching to 2.56×10^7 in the final trial, with the number of MC moves in each trial increasing by a factor of 2. (Scaling up the duration of trial runs in this manner is a convenient way to balance the benefits of longer trial runs with the benefits of more iterations.) A production run of 3×10^8 moves was then performed. The total CPU time required on a Silicon Graphics Octane2 workstation (360 MHz RS12000 processor) to determine the relative J -factors of polymers in the $N = 3 - 15$ range was 33 min, and 65 min for the $N = 10 - 50$ range. In both cases, the level of accuracy obtained was 10%.

A large number of moves (3×10^8) compared to the square of the size of the range (12^2 or 40^2) was required because the acceptance probability for addition and removal moves in such stiff three-dimensional chains, even using the angle-biased insertion method described in Sec. IID, is of order 0.01. This acceptance probability could potentially be improved through biasing the choice of φ'_a (see Sec. IIB) instead of selecting it from a uniform distribution. The number of Monte Carlo moves required to obtain equivalent statistics for flexible polymer models (as well as for two-dimensional semiflexible polymers) was much lower, due largely to the increased acceptance probability for both addition and removal moves compared to the stiff 3D polymer model.

III. RESULTS

A. Flexible polymer models

To confirm the validity of the PC-GCMC method in determining the free energy of ring polymers as a function of ring size, it was first applied to the determination of the ring closure probabilities for two- and three-dimensional flexible polymers, with and without self-avoidance. These results are shown in Fig. 1, where PC-GCMC results and the procedures of Sec. IIC have been used to calculate the J -factor, which corresponds to the fraction of polymer configurations in which the two ends of the polymer are within a bonding range of each other, normalized to the volume (or area) of a single monomer’s bonding region.

For two- and three-dimensional freely jointed ideal polymers, the results shown in Fig. 3 match the well-known analytic results excellently, both the power law exponent ($-d/2$), where d is the dimensionality of the system, and the prefactors $[(3/2\pi)^{3/2}$ for $d=3$ and π^{-1} for $d=2$].³⁵ Excluded volume effects significantly lower the probability of ring closure for two- and three-dimensional polymers. Martin *et al.* predicted power law exponents of $-11/6$ and $-23/12$ for two- and three-dimensional ring closure prob-

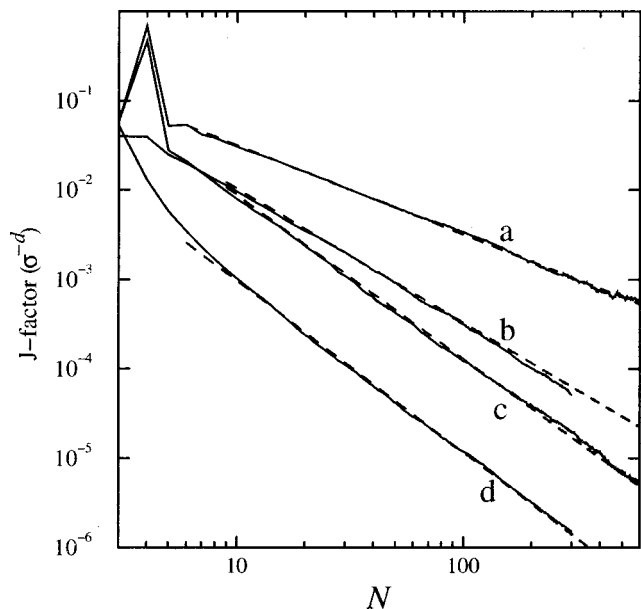


FIG. 3. Scaling of J -factors with number of monomers N for flexible polymer models. PC-GCMC results for ideal 2D (curve a), ideal 3D (curve b), self-avoiding 2D (curve c) and self-avoiding 3D (curve d) polymers are shown with solid lines. Dashed lines show exact high- N limit for ideal polymers [$(3/2\pi)^{3/2}N^{-3/2}$ for 3D rings and $\pi^{-1}N^{-1}$ for 2D rings] and fits to predicted power laws for self-avoiding polymers ($0.6N^{-11/6}$ and $0.08N^{-23/12}$ for 2D and 3D rings, respectively).

abilities, based on extrapolation from exact enumerations of closed self-avoiding lattice walks up to $N=17$ and $N=14$, respectively.³⁶ The current (off-lattice) PC-GCMC results for self-avoiding rings, also shown in Fig. 3, are in excellent agreement with these predicted scaling exponents, for N up to 300 ($d=3$) and 600 ($d=2$), with empirically determined prefactors of 0.08 and 0.6, respectively. In both ideal and self-avoiding two-dimensional systems, there is a strong peak in the J -factor at $N=4$. The legitimacy of this peak (which may be related to even-odd fluctuations observed in lattice ring closures) has been verified by an independent determination of ring closure probability at this value of N .

B. Semiflexible polymer models ($d=3$)

The J -factor as a function of chain length calculated using the PC-GCMC method for a semiflexible ideal polymer in three dimensions (persistence length l_p twenty times the bond-length σ) is shown as the solid curve in Fig. 4. Shimada and Yamakawa⁴ have analytically determined the following function (shown as a long-dashed curve in Fig. 4) for the J -factor of a short three-dimensional wormlike chain of length L and persistence length l_p without excluded volume interactions:

$$J(L) = 32\pi^3 l_p^3 / L^6 \exp\left(-\frac{2\pi^2 l_p}{L} + 0.257 \frac{L}{l_p}\right). \quad (33)$$

Recently, Podtelezhnikov and Vologodskii³⁰ have found quantitative agreement with Eq. (33) using a different simulation method over a broad range of contour lengths. The present PC method likewise gives quantitative agreement, to within 5%, with Eq. (33) near the peak in $J(L)$ at L

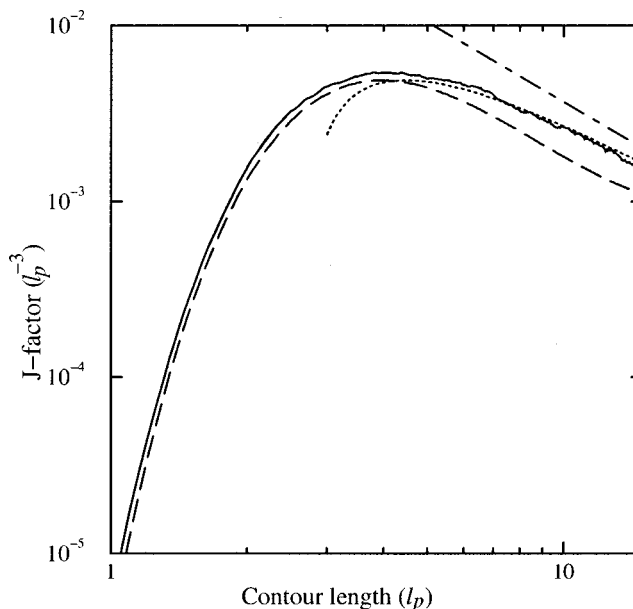


FIG. 4. J -factor for semiflexible ideal 3D polymers as a function of contour length L , in units of persistence length l_p . Solid curve represents PC-GCMC results, dashed curve and dotted curves represent Eqs. 33 and 34, respectively, from theory by Shimada and Yamakawa (Ref. 4), and dotted-dashed curve represents the high- L asymptotic limiting power law [Eq. (35)].

$= 3.96 l_p$. For rings with 10 segments or fewer (i.e., $L < 0.5 l_p$), breakdown of the approximation [Eq. (30)] to the harmonic bending potential of the wormlike chain led to significant discrepancies between the calculated results and Eq. (33). For larger rings ($L > 6 l_p$), the present results show moderate deviation from Eq. (33), which was derived using upon expansions about a minimum energy path and is not expected to hold for large L . Yet another function derived by Shimada and Yamakawa [Ref. 4, Eq. (64)], matches the present data in this region:

$$J(L) = (4\pi l_p L/3)^{-3/2} \left[1 - \frac{11l_p}{4L} + \frac{103l_p^2}{480L^2} \right]. \quad (34)$$

As a reference, the exact scaling result at in the limit of high L is also plotted in Fig. 4 (dotted-dashed line),

$$J(L) = (4\pi l_p L/3)^{-3/2}, \quad (35)$$

demonstrating that the current results approach the high- L regime. The very good agreement between simulation and theory attests both to the accuracy of the PC-GCMC method and to the proficiency of the theorists in performing these difficult calculations. Inclusion of excluded volume interactions as hard spheres of diameter equal to the bond length, or $0.05 l_p$ (similar to the ratio of diameter to persistence length in DNA) made no difference to calculated J -factors in the length range studied to within statistical error of 10% (data not shown).

C. Semiflexible polymer models ($d=2$)

Results for both ideal and self-avoiding (i.e., nonself-intersecting, but without area) semiflexible two-dimensional polygons are shown in Fig. 5. The semiflexible self-avoiding walk in two dimensions has been studied analytically by

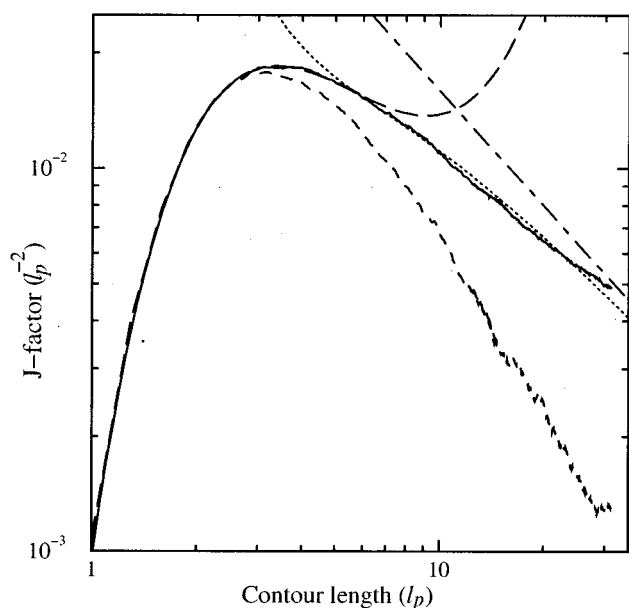


FIG. 5. J -factor for semiflexible 2D polymers as a function of contour length L in units of persistence length l_p . For ideal polymers, solid curve represents PC-GCMC results, dotted-dashed curve represents exact high- L limit, dashed curve and dotted curves represent fits in Eqs. (36) and (37). Short-dashed curve represents PC-GCMC results for self-avoiding polymer.

van Faassen;³⁷ in that study, a spontaneous curvature was incorporated in the bending energy, preventing direct comparison with the present results. To our knowledge, quantitative results on two-dimensional semiflexible ring closure probabilities do not appear in the literature. The J -factor for ideal 2D semiflexible rings has been fit empirically to functions analogous to Eqs. (33) and (34). In the low- L regime ($L < 5l_p$), the data were fit to the following equation:

$$J(L) = 16l_p^2/L^4 \exp\left(-\frac{\pi^2 l_p}{L} + 0.32 \frac{L}{l_p}\right), \quad (36)$$

in which the $\pi^2 l_p/L$ term was fixed (as the bending energy of a circle of circumference L , in two dimensions) and the parameters 16 and 0.32 adjusted to match the data. At lengths above five persistence lengths, a fit was obtained by expanding in powers of L^{-1} about the exact power law result at high L :

$$J(L) = (2\pi l_p L)^{-1} \left[1 - 3.8 \frac{l_p}{L} + 7.5 \frac{l_p^2}{L^2} \right]. \quad (37)$$

Errors in the absolute values of J factors are estimated to be under 10%.

Self-avoidance becomes a measurable factor in cyclization at $L \sim 3l_p$, leading to a decrease in cyclization probability relative to the ideal chain (dashed curve, Fig. 5). The ratio of cyclization probabilities of self-avoiding and ideal chains drops below 50% near $L \sim 10l_p$.

IV. CONCLUSIONS

The PC-GCMC method allows the direct, reversible addition and removal of monomers to and from ring polymers within the grand canonical ensemble. The validity of the

method has been demonstrated through calculations of the J -factor (the contribution of the polymer configuration to the cyclization equilibrium constant) for flexible and semiflexible, ideal and self-avoiding, two- and three-dimensional polymers, in excellent agreement with all available analytical and simulation results. While other methods³⁰ are undoubtedly more efficient for the determination of the absolute value of the J -factor at a predetermined contour length L , the PC-GCMC method is powerful in tasks relying on the relative values of J -factors, such as determining the position and width of a maximum in $J(L)$, and in obtaining averages over an ensemble of rings within a single calculation.

Of yet greater potential usefulness than the generation of an ensemble of isolated ring polymers of varying sizes is the application of the PC-GCMC method to simulations of *interacting* self-assembled ring polymers, loops, or disks (e.g., “bicelles”).^{38–40} Without a mechanism to directly change the size of the aggregate, convergence of aggregate size distribution is limited by a slow intermediate step involving bond-breaking (for equilibrium polymers) or fusion/budding¹⁶ (for domains in two dimensions). In the simulation of disks or domains, changing the number of monomers in the ring will generally change its area as well as the length and curvature of its perimeter; the change in area is readily calculated and incorporated into the acceptance probability for the move, based on the chemical potential and cohesive energy of the interior component of the disk. Additional Monte Carlo moves will be required to create and remove entire rings (for example, through a configuration-bias algorithm) in a manner consistent with the pivot-coupled moves to change the number of particles in existing rings. Efforts in this direction are currently underway.

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