Polymers simulated with an improved "rebound selection"

Z. Alexandrowicz

Citation: The Journal of Chemical Physics **110**, 12202 (1999); doi: 10.1063/1.479157
View online: http://dx.doi.org/10.1063/1.479157
View Table of Contents: http://scitation.aip.org/content/aip/journal/jcp/110/24?ver=pdfcov
Published by the AIP Publishing

Polymers simulated with an improved ''rebound selection''

Z. Alexandrowicz
Materials and Interfaces, Weizmann Institute of Science, Rehovot 76100, Israel

(Received 16 February 1999; accepted 29 March 1999)

An improved ''rebound selection'' simulation constructs a polymer chain in biased excluded volume avoiding steps. A construction that in midcourse accumulates a low bias weight tends to be arrested by a selection. Conversely a high weight construction sprouts reserve bifurcation and if subsequently it is arrested, it falls back and rebounds from such bifurcations. The simulation is applied to a condensation transition of thermal $2d$ lattice chains, and to a dilute–semidilute transition of athermal chains. Semidilute $2d$ chains do not mix, $3d$ ones mix as blobs. © *1999 American Institute of Physics.* [S0021-9606(99)50324-3]

I. INTRODUCTION

Recently a new method called Rebound Selection[1] has been proposed for the simulation of multichain systems at equilibrium (like thermal and athermal polymers, in melt or in solution). The present article describes a significant improvement of this new method. New methods are needed because bringing a multichain system to equilibrium requires a large scale rearrangement of mutually entangled chains. Consequently dynamic algorithms which apply local bond moves suffer from relaxation times that increase enormously with chains' length. Very possibly chains become entrapped in cages,[2–4] creating an illusory appearance of being at equilibrium. It seems therefore that what is needed is a simulation that achieves a large scale variation at one go, something akin to the cluster dynamics[5] devised for spin systems.

Thus a Configuration Bias Monte Carlo (CBMC) method[6] tries to replace an existing ''old'' chain by a new one, utilizing detailed balance of entire chains. The new chain is constructed with the help of a biased random walk proposed by Rosenbluth and Rosenbluth (RR).[7] However a RR construction is beset by a dual difficulty. The majority of constructions sooner or later run into a trap and fail before N is attained (sample attrition). Those that do manage to attain N almost always have a very low bias weight and fail to pass a detailed balance lottery (null acceptance). The present Rebound Selection (RS) method tries to provide a joint answer to sample attrition and to null acceptance. A construction of a new chain is allotted a reserve bifurcation every few steps. If a construction fails it does not terminate entirely; instead it falls back to a nearest unutilized bifurcation and rebounds from there. Sufficient bifurcation prevents sample attrition but the problem of a low weight of almost new chains has to be dealt with as well. Hence a sequence of selections is performed on the go throughout the stepwise construction. The selections filter out low weight constructions and bring up the weight of (almost all) surviving constructions to a uniform value. This overcomes the problem of null acceptance. Indeed in that case about one half of new chains pass the detailed balance lottery. However before proceeding in more detail, let us introduce the notation and explain further the twin problems of sample attrition and of null acceptance.

Our model system consists of M lattice chains with excluded volume (EV), of length N each and contained in volume $V=L^d$, d being the dimensionality. Polymer density is $\rho=MN/V$. A (trivial) extension to chains with thermal interaction is deferred to later on, to make the introductory notation simple. A RR biased construction of a trial new chain proceeds in $n=1,..,N$ random steps. A direction of an nth bond is chosen from among a subset of w_n directions that avoid EV. (A new chain tries to replace a designated old chain, EV encounters with the latter are therefore ignored.) Clearly $z-1\geqslant w_n\geqslant 0$, where z is the coordination (if a trap $w_n=0$ occurs the construction terminates). Thus an nth step is sampled with a bias probability $p_n=1/w_n$. Unbiased sampling requires that the step be accorded a statistical weight proportional to $1/p_n$. Or, w_n represents a microscopically variable bias-weight of an nth step. An entire new chain is sampled with a total bias-weight,

$$W_w^{\text{new}}=\prod_{n=1}^{N} w_n^{\text{new}}. \tag{1}$$

A similar *re*construction is carried out with respect to an old chain and gives W_w^{old}. The only difference is that the direction of an nth step must follow that of the actual nth bond. Hence a reconstruction cannot run into $w_n=0$ and fail. (This is correct because old chains belong to a subset of RR constructions that do attain N.) Detailed balance is fulfilled if a new chain be accepted with a transition probability

$$t_{\text{accep}}=\begin{cases} W_w^{\text{new}}/W_w^{\text{old}} & \text{if } \leqslant 1 \\ 1 & \text{else.} \end{cases} \tag{2}$$

The RR construction is myopic. At an nth step it picks w_n directions out of z, which are EV avoiding. It does not however discriminate against w_n' out of w_n directions, which at an $n+1$th step will bring the construction into a trap $w_{n+1}(w_n')=0$ (the same goes for a subset w_n'' out of w_n which will bring the construction into a trap at a subsequent $n+2$th step, etc.). Furthermore at an nth step, the w_n EV avoiding directions $d_1,d_2,\ldots$ are accorded a uniform probability. This ignores the fact that at an $n+1$th step, $w_{n+1}(d_1)$ is not necessarily equal to $w_{n+1}(d_2)$. Evidently such myopic indiscriminate choice of directions at an nth

step deviates from the true equilibrium one, and leads to a smaller bias weight at the $n+1$th step $\langle w_{n+1}\rangle_{\mathrm{RR}} < \langle w_{n+1}\rangle_{\mathrm{equil}}$ (and the same for the $n+2$th step, etc.). Both effects of myopic choice accumulate over N steps. The former causes sample attrition, since the probability of a trial chain to avoid termination decreases exponentially with N. The latter causes null acceptance, since $\langle W_w^{\mathrm{new}}\rangle/\langle W_w\rangle_{\mathrm{equil}}$ also decreases exponentially with N.

In order to overcome these twin problems the present RS simulation combines an enriching bifurcation with a stepwise selection.

A. Enriching bifurcation

If the bias weight $W_w(n)$ at an nth step exceeds a certain threshold [for example, if $W_w(n)\geqslant 2$] it is divided by two, $W_w(n)\rightarrow W_w(n)/2$. On account of this division the construction is allowed to continue in two alternative ways instead of one, viz., the nth site is allotted a reserve bifurcation. If the construction fails in the middle, it falls back to a nearest available reserve bifurcation and rebounds from there. Termination occurs only if all bifurcations have been exhausted. Adequate bifurcation overcomes sample attrition.

B. Stepwise selection and detailed balance

Low values of $W_w(n)$ at an nth step are eliminated by performing a selection lottery with a probability proportional to $W_w(n)$. Adequate stepwise selection ensures that new chains that manage to attain N are associated with an almost uniform bias weight W_w^{new}. Strictly uniform ensemble weight implies that new chains are sampled with their ensemble probability distribution and their acceptance with a detailed balance lottery becomes superfluous. Yet with RS the attainment of a uniform weight can never be complete, and detailed balance cannot be relinquished entirely. Such corrective employment of detailed balance could not be applied within the framework of the original version of RS, which did not allow one to evaluate the bias weight W_w^{old} of an old chain. That made the method inherently approximate. The present improved version of RS removes this shortcoming. It estimates W_w^{old} and applies detailed balance, correcting an imperfect stepwise selection. The balancing of bifurcation with selection becomes less demanding and is performed with the help of a single adjustable parameter. The improved method is applied to a study of a condensation transition of thermal chains with near neighbor attraction, and to a more extensive study of a dilute to semidilute transition of athermal chains.

II. METHOD

A new chain is grown in EV avoiding steps associated with the bias weight $W_w(n)$, just like in the RR construction. However at preset intervals of a steps the chain undergoes our selection/bifurcation procedure. In practice the value adopted was $a=2$ but $a=1$ and $a=3$ were almost equally satisfactory.

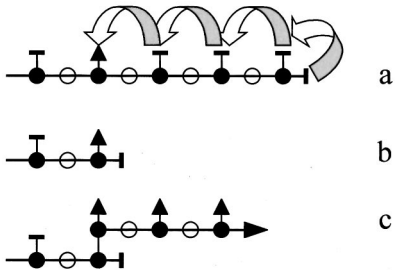

FIG. 1. A schematic drawing of a rebound walk. Circles denote sites, solid ones denote those with a bifurcation. (a) A walk fails and falls back (cf. shadowed arrows), skipping over already utilized bifurcations (pointers blocked by a bar), until it encounters an unutilized bifurcation (pointer ending in a solid arrow); (b) the bifurcation is utilized and rebound starts; (c) the construction grows once more creating on the way new reserve bifurcations.

A. Selection

Selection at an nth step (such that $\mathrm{MOD}(n,a)=0$), proceeds as follows. The bias weight prior to the selection $W_w^0(n)$, is multiplied by a selection parameter C and the construction is accepted with a transition probability

$$t_{\mathrm{accep}}(n)=\begin{cases} CW_w^0(n) & \text{if } \leqslant 1 \\ 1 & \text{else.} \end{cases} \tag{3}$$

The new bias weight (times C), of a construction accepted a probability $t_{\mathrm{accep}}(n)$ is

$$W_w(n)=CW_w^0(n)/t_{\mathrm{accep}}(n). \tag{4}$$

Equations (3) and (4) give

$$W_w(n)=\begin{cases} 1 \ \text{(unbiased)} & \text{if } CW_w^0(n)\leqslant 1 \\ CW_w^0(n) & \text{else.} \end{cases} \tag{5}$$

B. Bifurcation

Like in the Evolution of Species a selection on the go would achieve nothing unless it is accompanied by a parallel production of alternatives. For that purpose rebound selection introduces bifurcation. If after a selection we have a weight $W_w(n)\geqslant 2$, we divide its value equally between two alternative branches. The new bias weight at an nth site becomes $W_w(n)=CW_w^0(n)/2$, while the number of branches sprouting from the site becomes $b_n^0=2$, instead of the linear chain value $b_n^0=1$. One branch is utilized at once for growth towards the $n+1$th site, while the other one is kept in reserve. (The cutoff value $\geqslant 2$ is arbitrary, any value somewhat larger than one would do.) A record is kept of available reserve bifurcations. If a construction fails at an nth site, either because of $w_{n'}=0$ or because of the selection, the construction falls back erasing bonds $n'-1,n'-2,...$, until it encounters a site n that still possesses an unutilized reserve bifurcation [see Figs. 1(a) and 1(b)]. The construction then ''rebounds'' from that site. Its bifurcation is utilized, b_n reduces to one, and the chain growth from n towards N is renewed in precisely the same manner as before, undergoing selections when $CW_w^0(n)\leqslant 1$, and creating new bifurcations whenever $W_w(n)\geqslant 2$ [see Fig. 1(c)]. In this manner a con-

struction shuffles back and forth; ultimately it either attains N or else falls all the way back to $n=0$ and terminates.

C. Unutilized bifurcations

A new chain that attains N is associated with a RR bias weight W_w, and a set of u unutilized bifurcations, at sites $n_1<\cdots<n_u$. Each such bifurcation has a potential for attaining N over again. In order to find how many do realize that potential, we work our way backwards. Thus first we fall back from the end of the actual chain to the n_uth site, and try to grow a virtual branch from with the usual RS procedure of selections and bifurcations, attaining some site $n' \leqslant N$. We repeat the attempt with the n_{u-1}th site, etc., ultimately finding a number v of virtual branches that attain N successfully. A virtual branch from n to N implies that a new chain's actual pathway has been chosen with a bias probability of one half, doubling the chain's bias weight by factor 2. Total weight doubling associated with v virtual branches sprouting from unutilized bifurcations is,

$$W_{\text{bifur}}=2^v. \tag{6}$$

The argument leading to Eq. (6) paraphrases the one presented for the RR bias weight W_w of Eq. (1). However there are two important differences. The first is that actually there exists an *ensemble* of RS pathways that originate from our chain's nth site (in a microstate defined by its previous $n-1$ steps and by the other chains of the system). Some of these pathways attain N and some do not. Our determination whether a single trial branch sprouting from n does or does not attain N, constitutes only a *sampling* of that ensemble (viz. W_{bifur} is an estimator). The second difference is that our biased construction does not discriminate between the $1+v$ pathways (the actual and the virtual respectively), in accordance to their RS bias weight. The first to attain N is adopted as an actual one. However since such random choice is reproduced in a reconstruction of an old chain, detailed balance is not impaired. (An algorithm discriminating between the $1+v$ pathways might be more efficient but does not appear to be feasible.[8] Therefore a total bias weight of a new chain constructed with the help of RS is

$$W_{\text{RS}}^{\text{new}}=W_w\times W_{\text{bifur}}, \tag{7}$$

with W_w and W_{bifur} given, respectively, by Eq. (1) (modified by the stepwise selection), and by Eq. (6).

D. Detailed balance acceptance

In order to evaluate $W_{\text{RS}}^{\text{old}}$ we reconstruct an old chain with the help of the RS procedure: We follow the old chain's pathway; evaluate $W_w(n)$; perform stepwise selections and create and utilize reserve bifurcations. However an old chain belongs to a subset of RS constructions that successfully attain N [see a similar provision in connection to the CBMC, Eq. (2)]. Consequently we take for granted that it wins all the encountered selections, bringing up the bias weight to unity [Eq. (5)]. At a reconstruction's end we obtain W_w and a set of u unutilized bifurcations. The latter enable us to evaluate W_{bifur} and $W_{\text{RS}}^{\text{old}}$ in the manner of Eqs. (6)–(7). A new chain is then accepted with a transition probability analogous to the CBMC, Eq. (2),

$$t_{\text{accep}}=\begin{cases} W_{\text{RS}}^{\text{new}}/W_{\text{RS}}^{\text{old}} & \text{if } \leqslant 1 \\ 1 \quad \text{else}. \end{cases} \tag{8}$$

In order to check the evaluation of $W_{\text{RS}}^{\text{old}}$, the reconstruction procedure has been also applied to new chains, giving an oldlike $(W_{\text{RS}}^{\text{new}})_{\text{reconst}}$, and a control ratio $q=W_{\text{RS}}^{\text{new}}/(W_{\text{RS}}^{\text{new}})_{\text{reconst}}$. In the systems studied $q=1$ was confirmed to within experimental error.

E. Choice of *C*

Our choice of the selection parameter C is dictated by a balance of two opposing requirements. On one hand C should be small enough in order to ensure an effective stepwise selection with the help of Eq. (3). In long chains a too large C leads to an explosively increasing number of bifurcations u, which consumes time; more importantly however, $W_{\text{bifur}} \gg 1$ nullifies the efficacy of our stepwise selection. On the other hand a too small C prevents the creation of bifurcations and brings back sample attrition. A similar balance is encountered in a stepwise construction of critical clusters[9] and suggests the following. Bifurcation at an nth step b_n may be 0, 1, *or* 2 corresponding respectively to a termination, linear growth or bifurcation. An average b_n which is smaller or larger than one implies, respectively, an exponential sample attrition, or an exponential growth of u. Hence the right choice of C is such that an average b_n (evaluated over constructions that do or do not attain N), is precisely one. Thus

$$C_{\text{optimal}}=C(\text{giving } \langle b_n\rangle_{n\to N}=1). \tag{9}$$

In practice a quite approximate fulfillment of Eq. (9) is sufficient.

F. Maximal partition function estimator

The problem with a simulation employing an inefficient biased sampling lies not only in the expense of computing time. Such simulations often bring a system to a stable state which in reality only reflects an inability to approach equilibrium in any reasonable time. It is then very difficult to judge the relative merit of various methods. Examples are provided by a Monte Carlo simulation of spin systems close to a transition, or by a bond-displacement simulation of long polymers. However some simulations enable one to evaluate an estimator for the partition function. In that case (barring exceptional behavior), an objective comparison becomes possible; a simulation which yields a higher estimator is better.[10] With polymers we are in the lucky situation that methods based on a stepwise growth of a polymer chain, like the simple unbiased, the scanning,[11] the RR and our RS constructions, enable one to evaluate an estimator for an ensemble bias weight $\Omega^{-1}\Sigma_\Omega W_{\text{bias}}$. The sum is taken over all Ω trial constructions of a new chain, successful and failed alike; for a failed one $W_{\text{bias}}=0$. The ensemble bias weight

constitutes a partition function per an athermal polymer molecule (minus logarithm of which gives an excess chemical potential[12]). With sufficient sampling all methods should yield the same estimator for $\Omega^{-1}\Sigma_\Omega W_{\rm bias}$. However, a finding that one method yields a smaller estimator than another, signals that it provides a less satisfactory sampling of true equilibrium. (Admittedly such comparisons are not easy since estimates of a partition function are notoriously difficult to carry out.) With CBMC (employing the RR construction) that estimator is $\langle W_{\text{CBMC-bias}}\rangle=\langle W_w^{\rm trial}\rangle V$ (the origin of a chain is chosen with a probability V^{-1}). With RS, W_w is multiplied by C [cf. Eq. (3)] $i=N/a$ times over, and finally by $W_{\rm bifur}$; hence the estimator is $\langle W_{\text{RS-bias}}\rangle=\langle W_w^{\rm trial}W_{\rm bifur}\rangle VC^{-i}$. Thus

$$\Omega^{-1}\sum_\Omega W_{\rm bias}\geqslant\begin{cases}\langle W_{\text{RS-bias}}\rangle=\langle W_w^{\rm trial}W_{\rm bifur}\rangle VC^{-i} & \text{for RS}\\ \langle W_{\text{CBMC-bias}}\rangle=\langle W_w^{\rm trial}\rangle V & \text{for CBMC}.\end{cases}\tag{10}$$

Equation (10) has been tested under conditions when both CBMC and RS performed with great ease; in that case the respective estimators $\langle W_{\text{CBMC-bias}}\rangle$ and $\langle W_{\text{RS-bias}}\rangle$ agreed quite well with one another. However under more difficult conditions described in the following section, values of $\langle W_{\text{CBMC-bias}}\rangle$ become become order(s) of magnitude smaller than $\langle W_{\text{RS-bias}}\rangle$. Cross tests have been carried out as well: For a system simulated with the help of CBMC, an attempt is made to introduce a trial new chain constructed with the help of RS giving $\langle W_{\text{RS-bias}}\rangle_{\text{CBMC-equil}}$, and vice versa giving $\langle W_{\text{CBMC-bias}}\rangle_{\text{RS-equil}}$. Under easy conditions the cross and the direct results converge on the same value. Under difficult conditions however the cross results lie (mostly) below $\langle W_{\text{RS-bias}}\rangle$, and above $\langle W_{\text{CBMC-bias}}\rangle$, as expected.

G. Original and improved RS

The original version of Rebound Selection[1] did not apply detailed balance and relied instead on an almost perfect attainment of a Boltzmann distribution on the go, with the help of stepwise selections. The present version introduces the following improvement. (a) The bias weight is evaluated with the help of Eqs. (6)–(7). It thus becomes possible to reconstruct the bias weight of an old chain $W_{\rm RS}^{\rm old}$ and to apply a detailed balance lottery of Eq. (8). (b) Consequently an imperfect attainment of the Boltzmann distribution on the go is easily corrected by the ultimate detailed balance lottery. Because of that, a tuning of the selection parameter C becomes more a matter of the method's efficiency than of accuracy. The most efficient value of C makes the bifurcation critical, that is just large enough to prevent sample attrition [Eq. (9)]. In contrast, in the original version one had to seek a C sufficiently small to attain a desired accuracy (of chains' radius for example). (c) Finally the present version utilizes the fact that an average bias weight provides an estimator for a partition function which is maximal at equilibrium [Eq. (10)]. On that basis it judges the relative accuracy of the CBMC and RS simulations.

The article describing the original version of RS was followed by another one describing a different implementation of the rebound idea, variously called ''recoil growth.''[13] That article does apply detailed balance; however it does not perform a selection on the go. Instead it applies an effective coordination number, $z_{\rm eff}\leqslant z$, which also filters low weight constructions, but less efficiently. Another difference is that a fallback is restricted to a maximum of l steps which for $N/l\gg 1$ brings back a sample attrition. Recoil growth resembles a ''double scanning'' variant of the classic Meirovitch's scanning method,[11] the latter's ''future continuations'' are equivalent to the former's ''fallbacks,'' both restricted to a maximal length l.

H. Thermal interactions

An extension of RS to chains with a near neighbor attraction is trivial, just like for CBMC. An EV avoiding dth direction of an nth step ($d=1,\ldots,w_n$), is allotted a Boltzmann factor $f_{d;n}=\exp(\nu_{d;n}K)$, where K is the reciprocal temperature while $0\leqslant\nu_{d;n}\leqslant z-1$ is the number of near neighbor attractive contacts. A particular d is chosen with a probability $p_{d;n}=f_{d;n}/w_n^K$, where $w_n^K=\Sigma_{d'=1}^{w_n}f_{d';n}$. The thermal weight of an nth step is given by a product of a bias weight p_n^{-1}, times the Boltzmann factor of attractions $f_{d;n}$. Therefore $f_{d;n}$ cancels out in the product and the weight of an nth step of a thermal chain is $w_n^K=\Sigma_{d'=1}^{w_n}\exp(\nu_{d';n}K)$. All previous equations describing the CBMC and the RS methods apply to thermal chains, with w_n^K replacing the athermal weight w_n. Except for a weighted lottery among w_n directions, the simulation procedure, the difficulties encountered by CBMC and the solutions offered by RS remain precisely the same.

III. RESULTS

A. Thermal chains in 2d

Simulations of $2d$ chains with near neighbor attraction have been carried out at a reciprocal temperature $K=1$ [well above a collapse transition at circa $K_t=0.66$ (Ref. 14)], for $M=10$ chains of length $N=64$. A dimension $2d$ and a small number of chains have been chosen in order to facilitate a visual inspection. Density ranged as $\rho=0.00025-0.5$. Average quantities of old chains measured at fixed intervals of Monte Carlo steps are, the radius of gyration R_g^2 and the number of contacts that a bond makes internally with preceding bonds or externally with other chains, $\nu_{\rm int}$ and $\nu_{\rm ext}$, respectively. Like in an evaluation of thermal weight w_n^K, the contacts are made by all the w_n potential directions of an nth bond (i.e., a shell thicker than the one around an actual nth bond). An average time $t_{\rm exch}$, required for one exchange of an old chain by a new one has has been measured for RS and CBMC alike. Another quantity measured with both methods is an estimator of the ensemble bias weight [giving a polymer partition function, cf. Eq. (10)]. Statistical accuracy of the results displayed in figures is by and large indicated by the points size. However substantially lower accuracy attaches to the estimators of bias weight, as indicated by their noisy functional dependence. Thus Fig. 2 displays results for $\langle W_{\text{RS-bias}}\rangle$, and $\langle W_{\text{CBMC-bias}}\rangle$ for comparison, together with those for interchain contacts $\nu_{\rm ext}$, as a function of density ρ, for $N=64$. Despite low accuracy the results show that a

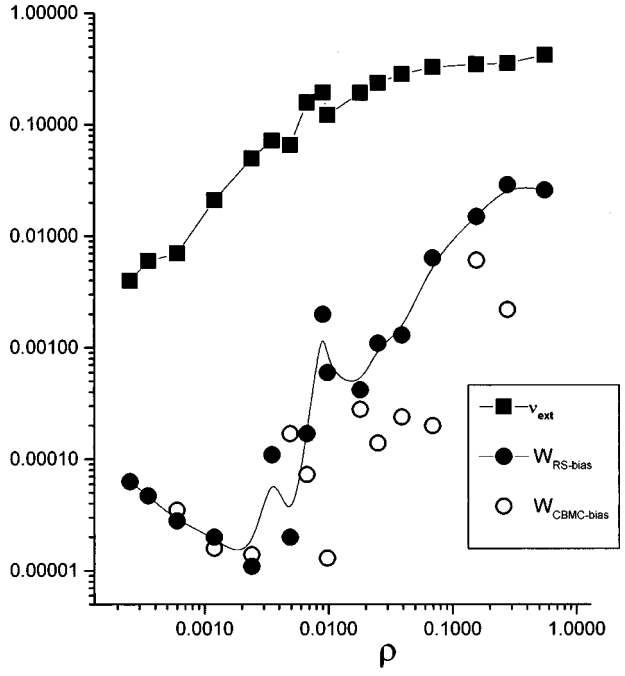

FIG. 2. The dependence of bias weight on ρ for $2d$ thermal chains of $N=64$. Estimators $\langle W_{\text{CBMC-bias}}\rangle$ and $\langle W_{\text{RS-bias}}\rangle$ (divided by $2.2VE54$), refer to values obtained with the help of CBMC and present RS, respectively. Solid line is drawn through the latter. On top is a corresponding ρ dependence of ν_{ext}.

condensation transition associated with a reversal of the variation with ρ of the bias weight [with trivial factor V of Eq. (10) included], and with a substantial increase of intermolecular contacts, occurs in the approximate range $\rho=0.001-0.01$. Visual displays of the $2d$ lattices show that at low ρ the collapsed chains are isolated one from another, with an occasional formation of dimer clusters. At high ρ they condense into a single blob consisting of unmixed collapsed chains packed together, as exemplified by Fig. 3(a). Throughout the condensation internal contacts remain constant at $\nu_{\text{int}}\simeq 0.4$ while R_g^2/N increases slightly, from $R_g^2/N=0.28$ to 0.38, indicating a slight dilatation in the condensate. The following observation concerns a comparison of the CBMC and RS methods. Up to the onset of a condensation values of $\langle W_{\text{CBMC-bias}}\rangle$ are comparable to $\langle W_{\text{RS-bias}}\rangle$. Beyond it by and large the former become about ten times smaller than the latter, showing that the CBMC simulation does not succeed to bring the system to equilibrium. Results for longer chains $N=128$ at $\rho=0.017$ demonstrate that point even more forcefully. Our RS simulation gives $\nu_{\text{ext}}\simeq 0.27$ and $\langle W_{\text{RS-bias}}\rangle\simeq 2\times VE89$, while CBMC gives $\nu_{\text{ext}}\simeq 0.14$ and an average bias weight three thousand times smaller, $\langle W_{\text{CBMC-bias}}\rangle\simeq 6\times VE85$. The results show that CBMC just fails to simulate the condensation of clusters into a single blob. A visual support of that is given in Fig. 3(b) vis-à-vis Fig. 3(a). Yet for both $N=64$ and $N=128$ the exchange times t_{exch} of the CBMC and RS simulations are comparable, creating a false impression that the two perform equally well!

B. Athermal chains in $2d$ and $3d$

Athermal $2d$ chains of variable N have been measured at $\rho=0.125$, 0.25, and 0.5, with the help of the CBMC and RS methods. System size varied around $M=60$. Results for exchange time as a function of N at $\rho=0.125$, are shown in Fig. 4. For CBMC the exchange time appears to increase exponentially with N and convergence could not be attained beyond $N=128$. With RS the exchange time of long chains is one or more orders of magnitude smaller, and appears to increase as a power law. The results for R_g^2/N in Fig. 5 display a broad region of crossover from a dilute to a semidilute regime, corresponding, respectively to $R_g^2/N\approx N^{0.5}$ (taking $2\nu-1=0.5$) and to $R_g^2/N\approx$const. Placing an arbitrary midpoint of the transition at $\approx N^{0.25}$, leads to $N_{\text{tr}}=730$, 180, and 45, for $\rho=0.125$, 0.25, and 0.5, respectively. This agrees very well with a theoretical prediction[15] $N_{\text{tr}}\approx\rho^{1/(1-2\nu)}=\rho^2$. The bottom part of Fig. 6 displays ν_{int} and ν_{ext} as a function of N. An initial increase of ν_{int} (shown for $\rho=0.125$ but very similar at $\rho=0.25$ and 0.5), saturates under the semidilute regime. This relatively slight increase of ν_{int} with N is accompanied by a strong *decrease* of ν_{ext}, which scales as $\nu_{\text{ext}}\approx N^{-0.75}$ and $\nu_{\text{ext}}\approx N^{-0.5}$ for $\rho=0.125$ and 0.5, respectively, with $\rho=0.25$ exhibiting an intermediate behavior. We note that in the range of the decrease, the dilute scaling $R_g^2\approx N^{1.5}$ and the semidilute scaling $R_g^2\approx N^1$, predominate for $\rho=0.125$ and 0.5, respectively, with $\rho=0.25$ lying in between (Fig. 5). A reasonable explanation seems to be that the $2d$ chains may be represented by coils of an average density $\rho_{\text{int}}\approx N/R_g^2$ that do not penetrate one another, not only in a dilute *but in a semidilute regime as well*.[15] The external contacts of a chain-coil are therefore restricted to its perimeter, that is to a fraction that scales as R_g/R_g^2. For dilute and semidilute chains, respectively, this implies $\nu_{\text{ext}}\approx N^{-0.75}$ and $\nu_{\text{ext}}\approx N^{-0.5}$, just as in Fig. 6. Visual support of the picture is given in Fig. 7 which shows that $2d$ semidilute chains exhibit no interchain mixing. Results for exchange time and for R_g^2/N of $3d$ chains resemble those obtained elsewhere with the help of the original version of RS. Results obtained here for ν_{int} and ν_{ext} as a function of N at $\rho=0.2$, are given on top of Fig. 6. The two respectively increase and decrease upon the dilute to semidilute transition (with $N_{\text{tr}}\simeq 150$), until saturation. The behavior is consistent with the blob theory.[15] Semidilute chains consist of blobs, with $\rho_{\text{blob}}\simeq\rho$. Chains mix mutually and are screened on scales larger than blob size, but blobs themselves are impermeable one to another. Accordingly ν_{int} increases with N, until dilute coiled chains attain blob size at N_{tr}; simultaneously the dilute coils' surface/bulk ratio and consequently ν_{ext} too decreases until N_{tr}.

IV. SUMMARY AND DISCUSSION

Recently a new method called Rebound Selection (RS) (Ref. 1) has been proposed for a simulation of multi-chain systems. The present article describes a significant improvement of RS. Like the classic CBMC method,[6] the improved RS tries to replace an existing ''old'' chain of length N by a new one, with an acceptance probability determined by a detailed balance of their respective bias weights. In the

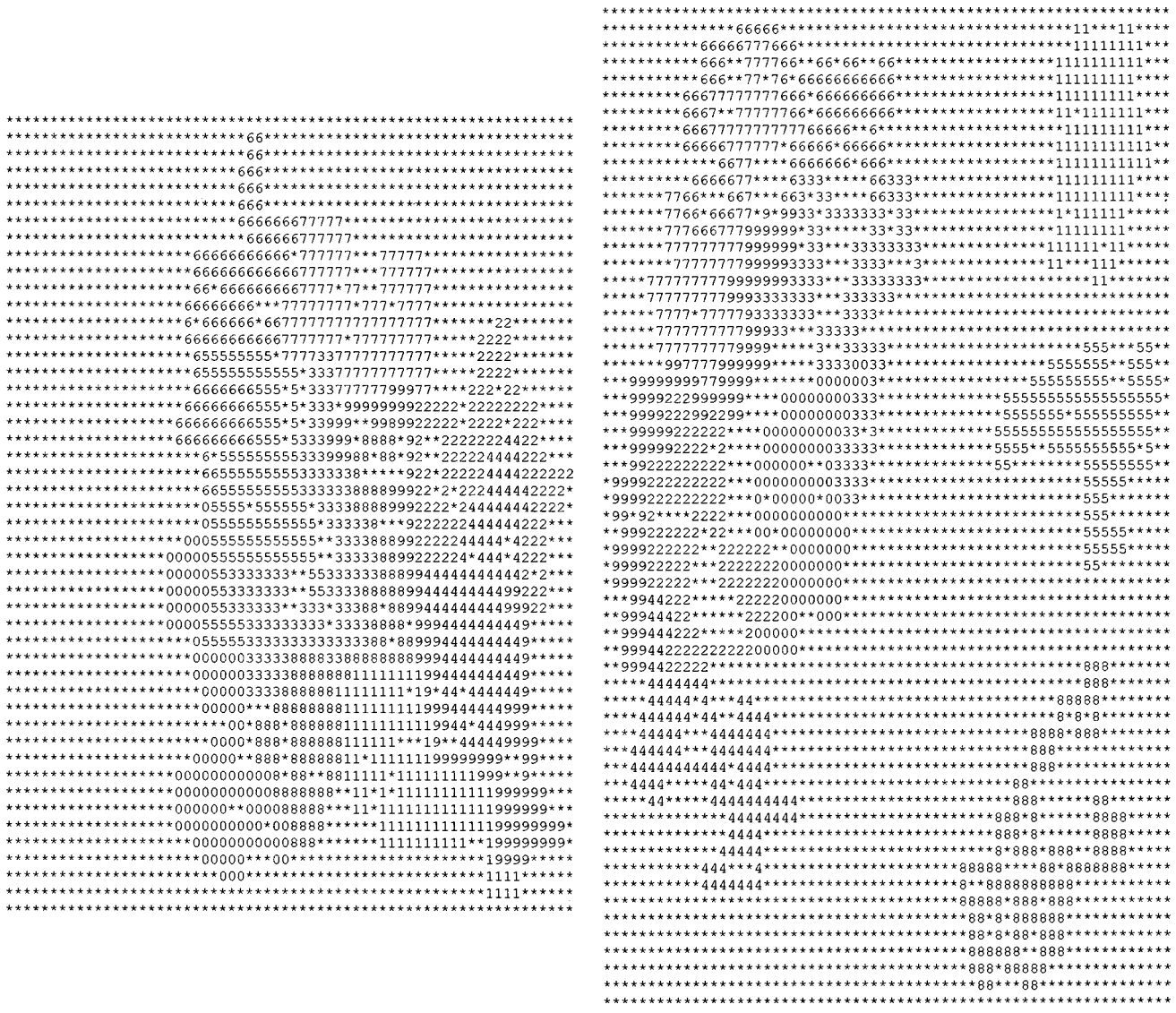

FIG. 3. a. A typical $2d$ lattice containing ten thermal chains (numbered 0,1,...,9 respectively), of length $N=128$ density $\rho=0.017$ and at reciprocal temperature $K=1$, simulated with the help of the present RS method. (Empty space is partially pruned away.) (b) Same as (a) but simulated with the help of CBMC.

CBMC scheme a new chain is constructed (or an old one is reconstructed), with the help of a RR algorithm[7] proposed long ago. The latter constructs a chain in a sequence of biased EV avoiding steps, associated with a corresponding bias weight W_w^{new} [Eq. (1)]. However, the RR construction and hence the CBMC method suffer from two problems, both related to that the EV avoiding steps are myopic and fail to ''foresee what lies ahead.'' Consequently constructions run into a trap and terminate (sample attrition). The few constructions that manage to attain N almost always have a very low bias weight because myopic steps fail to discover advantageous high weight pathways. Consequently new chains fail to pass the detailed balance lottery (null acceptance). Both difficulties accumulate exponentially with the number of steps.

In a sense these twin difficulties exemplify a very general problem in the simulation of semiordered systems. We wish to construct a (typical) object consisting of $N\gg 1$ mutually connected particles (such as a polymer, critical cluster or even a long diffusion pathway), with the help of random steps that assign N particles' coordinates in a sequence. Since typical objects constitute a vanishingly small minority in an ensemble of all possible assignments of N coordinates, a sequence of purely random steps will fail to generate this minority in any reasonable number of trials. One therefore may turn to biased steps that favor certain assignments over others on the basis of a *local* information; the EV avoiding steps of the RR construction provide a case in point. The employment of biased steps is perfectly legal: Each sequence of steps becomes associated with a corresponding bias weight and the object it produces is weighted accordingly in an ensemble. The problem is that such biased steps fail to take into account nonlocal consequences of a local assignment. Sooner or later a myopic step takes a wrong turn, and then another etc., and a long enough sequence almost inevitably produces a totally atypical object. What comes to mind is to endow a myopic construction with an ability to retract a relatively small accumulation of wrong turns on the go, and

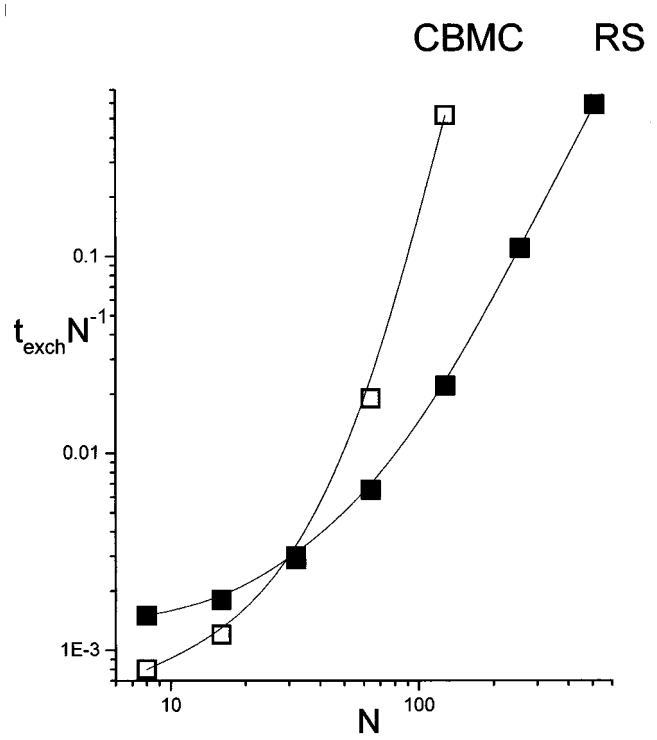

FIG. 4. Reduced exchange time t_{exch}/N (in minutes$\times$1000 of a PENTIUM 200) as a function of N, for athermal $2d$ chains at $\rho=0.125$. Solid and open squares correspond to present RS and to CBMC, respectively.

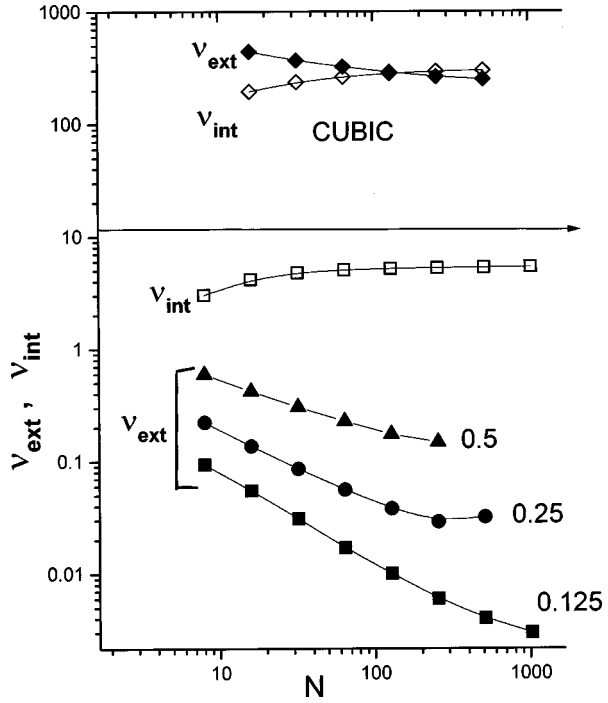

FIG. 6. At the bottom, near-neighbor external contacts ν_{ext} as a function of N, for athermal $2d$ chains at $\rho=0.125$, 0.25, and 0.5. Above it, *ditto* for internal contacts ν_{int} (multiplied be 20), at $\rho=0.125$. At the top, external and internal contacts for athermal $3d$ chains ν_{ext} and ν_{int}, respectively (both multiplied by 1000), as a function of N at $\rho=0.2$.

to restart in another direction. (Thinking of Evolution of Species, selection and mutation, is irresistible!)

The present RS method indeed introduces a joint strategy of a selection on the go combined with a parallel allotment of bifurcations. The selections filter out preferentially constructions whose current bias weight $W_w^0(n)$ is relatively low, and establish an almost uniform weight of all constructions. Details of a selection with the help of an acceptance probability $t_{\text{accep}}(n)$ that is proportional to $W_w^0(n)$ multiplied by a selection parameter C, are given in Eqs. (3)–(5). A construction is accepted with $t_{\text{accep}}(n)=CW_w^0(n)$ and acquires a uniform bias weight $W_w(n)=1$, else it fails. In the opposite case, if $CW_w^0(n)$ is relatively high, the nth site is allotted a reserve bifurcation and at correspondence the bias weight is halved, $CW_w=CW_w^0(n)/2$. Reserve bifurcations allow a construction that fails in midcourse (due to a selection or a trap), to fall back to a nearest available bifurcation and to rebound from there. A construction thus shuffles back and forth seeking a typical pathway. If it fails and no bifurcations remain, it terminates. If it attains N successfully its bias weight is not very different from the uniform value $W_w^{\text{new}}=1$. It is however associated with a variable number u of unutilized bifurcations. An evaluation of the latters' contribution to a total bias weight of a new chain $W_{\text{RS-bias}}^{\text{new}}$ is described in Eqs. (6)–(7). A similar reconstruction yields $W_{\text{RS-bias}}^{\text{old}}$, and finally a new chain is accepted with the help of detailed balance Eq. (8). The choice between selection and bifurcation is achieved with the help of a single parameter C. A too low value leads to insufficient bifurcation and brings back the problem of sample attrition. A too high value brings about an explosive time consuming bifurcation and worse than that, neutralizes the selection and brings back the problem of null acceptance. Previous experience concerning stepwise construction of critical clusters and branched polymers,[9] indicates that a correct choice of C just margin-

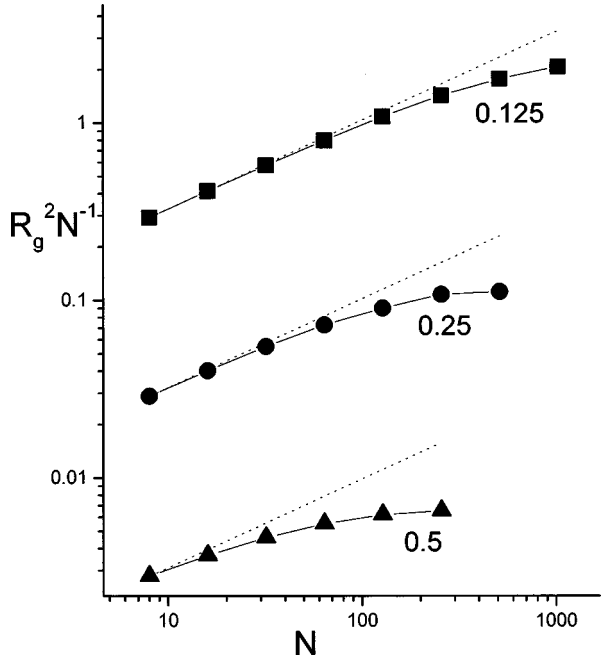

FIG. 5. Reduced square radius of gyration R_g^2/N as a function of N, for athermal $2d$ chains at $\rho=0.125$, 0.25 and 0.5. Dotted lines are fitted to a dilute regime $R_g^2/N\approx N^{0.5}$.

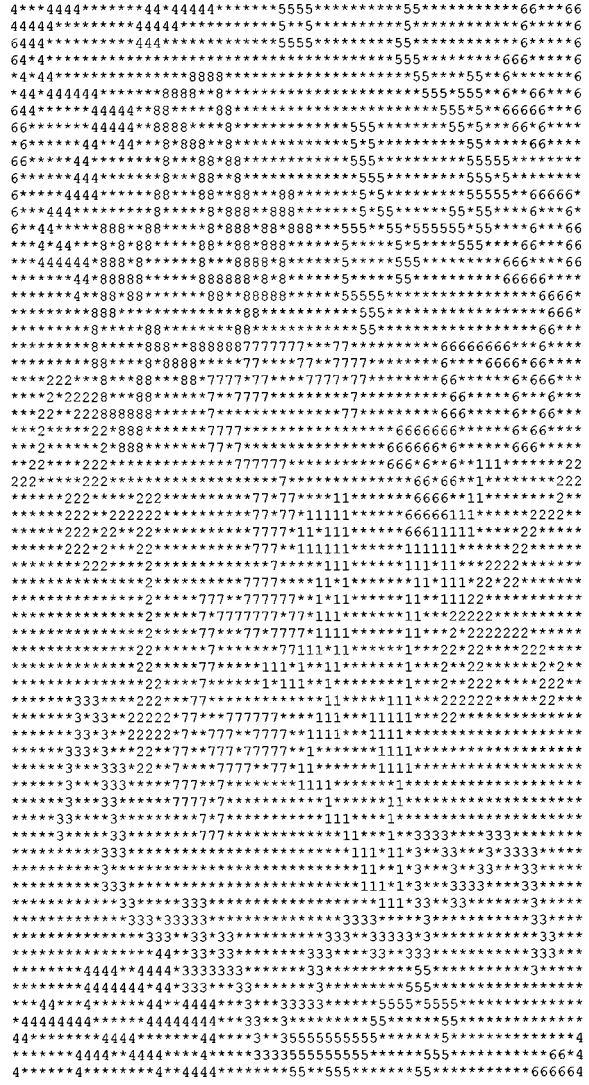

FIG. 7. A typical $2d$ lattice containing eight semidilute athermal chains of length $N=154$ at density $\rho=0.3$, simulated with the help of the present RS.

ally offsets termination, ensuring that an average number of continuations of an nth step $\langle b_n \rangle$ equals precisely one [Eq. (9)].

The relative merit of RS vis-à-vis CBMC is tested in a study of a dilute to semidilute transition as a function of N, for athermal chains in $2d$ and $3d$. Results for an average time t_{exch} per one old→new exchange in $2d$ show that the increase of t_{exch} with N seems to be exponential with CBMC, whereas with RS it is much slower and seems to constitute a power law (Fig. 4). Similar behavior has been observed before[1] with $3d$ chains. An added feature of these simulations is a measurement of neighbor contacts of a chain, ν_{int} and ν_{ext}, that a bond makes with preceeding bonds and with other chains, respectively (Fig. 6). The results show that in $2d$, ν_{ext} decreases as N increases under dilute and semidilute regime alike, but with a different power law. The results strongly suggest that semidilute $2d$ chains do not mix mutually, and that the screening of EV repulsions is internal. (Incidentally concentrations at midpoint of the transition obey very well a predicted theoretical dependence.) In contrast results in $3d$ are consistent with that on a scale of blobs semidilute chains do mix mutually and screen out EV repulsions externally. Returning however to our comparison of RS and CBMC: The superiority of RS is even more striking in the case of collapsed $2d$ thermal chains undergoing a condensation transition as concentration increases. Superficially CBMC and RS seem comparable, because their respective t_{exch} are not very different. The actual situation however is very different: A simulation that gives a larger average bias weight of trial chains [which constitutes an estimator of a polymer partition function, Eq. (10)], is closer to true equilibrium state.[10] The results for $N=64$ chains in Fig. 2 show that the values of RS are larger than those of CBMC by 10 and more. Much more dramatic is the disparity found with $N=128$ chains; the values of RS are larger than those of CBMC by more than one thousand(!). Figure 5 shows graphically that chains simulated with the help of RS fold nicely into a single blob, but those simulated with CBMC fail to do so.

In conclusion it may be said that rebound selection appears to offer a promising approach to the difficult problem of a simulation of multichain systems. An extension to branched or tethered, etc. chains on a lattice should be trivial. Extension to off-lattice chains though trivial too, may be less successful because of numerous differently weighted degrees of freedom at each step. Extension of the principle of rebound selection to simulation of nonpolymer semiordered systems (such as critical clusters), may perhaps be feasible too. Finally, repeating an observation made before,[1] a rebound construction constitutes an intriguing random object which is *quasi*linear, with a potential to form branches but only one at a time. Intriguing too is the possibility to ''teach'' through trial and error a blind random process to proceed in an intelligent way.

ACKNOWLEDGMENT

I wish to thank Dr. Marcus Muller for a very helpful discussion.

[1] Z. Alexandrowicz, J. Chem. Phys. **109**, 5622 (1998).
[2] E. Leontidis, B. M. Forrest, A. H. Widmann, and U. W. Suter, J. Chem. Soc., Faraday Trans. **91**, 2355 (1995).
[3] A. D. Sokal, in *Monte Carlo and Molecular Dynamics Simulations in Polymer Science*, edited by K. Binder (Oxford University Press, Oxford, 1995).
[4] Tests which measure a square displacement in unit time, averaged over all chains may miss an entrapment of some chains; more helpful would be a measurement of the time per a large scale displacement.
[5] R. H. Swendsen and J. S. Wang, Phys. Rev. Lett. **58**, 86 (1987).
[6] J. I. Siepmann, Mol. Phys. **70**, 1145 (1990); J. I. Siepmann and D. Frenkel, *ibid.* **75**, 59 (1990).
[7] M. N. Rosenbluth and A. W. Rosenbluth, J. Chem. Phys. **23**, 356 (1955).
[8] It would require a construction of an entire virtual tree sprouting from the actual chain. The tree would consist of branches sprouting from each of the v virtual branches, branches from branches,..., etc. The actual path of a new chain would then have to be redetermined with the help of a lottery that takes into account the relative weight of all pathways through that tree. Presumably however such a redetermination of a pathway cannot be applied with respect to W_{bifur} of an old chain.
[9] Z. Alexandrowicz, Phys. Lett. **80A**, 284 (1980); Phys. Rev. Lett. **76**, 2101 (1996).

[10] Z. Alexandrowicz, J. Chem. Phys. **55**, 2765 (1971); K. Huang, *Statistical Mechanics* (Wiley, New York, 1963).
[11] H. Meirovitch, J. Chem. Phys. **89**, 2514 (1988).
[12] H. Meirovitch, J. Chem. Phys. **97**, 5803 (1992); D. Frenkel, G. C. A. M. Mooij, and B. Smit, J. Phys.: Condens. Matter **4**, 3053 (1992).
[13] S. Consta, N. B. Wilding, D. Frenkel, and Z. Alexandrowicz, J. Chem. Phys. **110**, 3220 (1999).
[14] H. Meirovitch and H. A. Lim, J. Chem. Phys. **91**, 2544 (1989).
[15] P. G. De Gennes, *Scaling Concepts in Polymer Physics* (Cornell University Press, Ithaca, 1979).