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Simulation of polymers with rebound selection

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A crossover from dilute to semidilute regimes of lattice chains has been simulated with the help of a novel method. A Monte Carlo step tries to replace an existing chain by a new chain constructed in biased, excluded volume avoiding steps. Reserve bifurcations are allocated at small intervals of steps and after each interval a selective lottery restores an effectively nonbiased probability distribution. If a construction fails the selection at an nth step, it falls back to $n-1$, $n-2$, until it ''rebounds'' from an unutilized bifurcation. Selection on the go combined with a freedom to rebound, make the construction self-corrective; the principle may have a broad applicability. © *1998 American Institute of Physics.* [S0021-9606(98)50537-5]

I. INTRODUCTION

The simulation of multichain systems at equilibrium, like polymer melts or semidilute solutions requires an introduction of a new method. The principal problem is that the large scale rearrangements associated with bringing a system to equilibrium are hindered by mutual entanglement of chains. Consequently dynamic algorithms which apply local bond moves suffer from relaxation times which increase enormously with the chains' length and density. The much faster ''slithering snake'' appears to get entrapped in cages.[1–3] More promising seems to be the CBMC method[4] which at a Monte Carlo step tries to substitute an entire existing chain by a new one. The new chain is constructed with the help of a biased random walk proposed by Rosenbluth and Rosenbluth (RR).[5] The present article proposes a new simulation method, nicknamed *rebound selection*. Rebound selection is tested here on a hard core problem, notably a crossover from dilute to semidilute regime, as polymer length increases at a fixed density.

The system is modeled by M lattice chains with excluded volume (EV), contained in a cube L^3. Each chain consists of $N \gg 1$ bonds. Polymer density therefore is $\rho = MN/L^3$. Our point of departure is the RR biased random walk. At time t a trial new chain is constructed in $n = 1,...,N$ random steps. A direction of an nth bond is chosen only from among the subset of w_n bonds that avoid EV. On the cubic lattice $5 \geqslant w_n \geqslant 0$. If $w_n = 0$ occurs the construction terminates. (The new chain tries to replace a particular old chain picked at random, therefore EV encounters with the latter are ignored.) Since w_n is microscopically variable, an nth step is sampled with a bias probability $1/w_n$, and an entire trial new chain is sampled with a total bias probability $p_{\mathrm{bias},w}(N) = \Pi_{n=1}^{N}(1/w_n)$. This bias has to be compensated in order to restore correct unbiased sampling. Consequently a trial new chain which has attained N is accepted with a probability $p_{\mathrm{accep}}(N)$ which is proportional to inverse total bias probability. Let the latter be called RR bias-weight $W_w(N) \equiv 1/p_{\mathrm{bias},w}(N)$. Thus

$$p_{\mathrm{accep}}(N) \propto W_w(N) = \prod_{n=1}^{N} w_n . \tag{1}$$

The replacement of an old chain by a new one at t is carried out if and only if the latter passes such a global posterior selection. Up to this point, the procedure is equivalent to RR's biased random walk. Its application to many-chain systems within the CBMC scheme, particularly to dense and long chains is beset by a twofold difficulty. First, the termination of a construction whenever $w_n = 0$, makes the fraction of trial chains that succeed to attain N exponentially decreasing with N. Second, the fluctuation of $W_w(N)$ also increases exponentially; consequently only a minute fraction of the (few) chains that reach N, manages to pass the posterior selection of Eq. (1).

In order to overcome this dual problem, the present simulation introduces a dual strategy. The termination is overcomed by reserve bifurcations spaced at fixed intervals. If a construction fails in the middle it falls back to a nearest available reserve bifurcation and restarts from there. The construction becomes biased on two accounts. Due to the choice of EV avoiding bond-directions, and also due to an employment or nonemployment, of reserve bifurcations. The bias is eliminated with the help of a selective lottery at the end of each interval. Such an ongoing stepwise elimination of the bias obviates the need for a crippling global selection among the trial new chains that succeed to attain N. True the ongoing selective lottery augments termination, hence augments the need for using bifurcation, which in turn *increases* the bias. However in practice this instability is contained and fast resolved by a tuning of adjustable parameters.

II. METHOD

A growing new chain is subdivided into a sequence of segments $s = 1,...,S$ consisting of a bonds each. Thus $Sa = N$, and segments $s = 1,2,...,S$ originate from chain's sites $n = 0, a, \ldots, (S-1)a$. In what follows we shall denote by n and s, respectively, sites in general and sites at the origin of a segment (i.e., whose n is a multiple of a). In the first place, after completion of a segment extending from a site s to $s+1$, bias compensation is carried out with the help of a lottery with acceptance probability $p_{\mathrm{accep}}(s)$. Such on the go selection strives to ensure that all the chains that succeed to

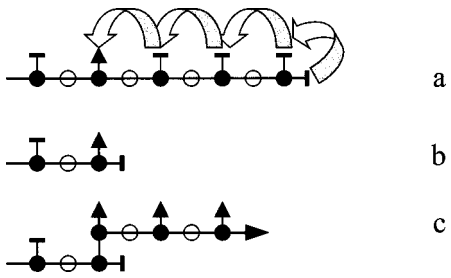

FIG. 1. A schematic drawing of a rebound random walk, with one reserve bifurcation at every second step, viz., initial bifurcation is $b_s^0=2$, and segment length is $a=2$. Circles denote sites, solid ones denote a segment's origin. (a) A walk fails and falls back (cf. shadowed arrows), skipping over 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 reducing b_s from two to one, and rebound starts; (c) the construction grows once more creating on the way new reserve bifurcations.

attain N are accepted, without a need for a posterior selection. Yet a selection on the go enhances termination in midgrowth; applied alone it would merely shift the problem from a crippling global posterior selection, to an equally crippling cumulative termination. In the second place therefore, the termination is compensated. Each of the sites $s=1,...,S-1$ is initially allotted $b_s^0=2$ bifurcations, one regular and one reserve. After a new chain grows beyond the sth site for the first time, it utilizes the regular bifurcation. A reserve bifurcation is utilized as follows. If a chain's construction fails to attain an nth site, either because of $w_{n-1}=0$ or because of the selection, the construction falls back erasing one after bonds $n'=n-1$, $n-2$,..., until it encounters a site $n'=s'a$ that still possesses an unutilized reserve bifurcation [see Fig. 1(a)]. The construction then ''rebounds'' from that site. Its reserve bifurcation is utilized, $b_{s'}$ reduces to one, and chain growth from s' towards N restarts in precisely the same manner it did after the first visit of the that site [see Figs. 1(b) and 1(c)]. In this manner a construction shuffles back and forth; ultimately it either attains N whereupon the new chain replaces an old one or else, it falls all the way back to $n'=0$ and terminates. However the employment of bifurcations brings with it another problem. Clearly a construction that in order to attain N had to mobilize a large part of its reserve bifurcations (leaving mostly $b_s=1$ at $s=1,2,...,S-1$, is more biased and has a smaller bias-weight, than a construction that attained N without having to do so. The utilization of bifurcation gives therefore rise to a secondary bias, that comes on top of the primary bias due to employment of EV avoiding bond directions [represented by the RR bias-weight $W_w(s)$ of Eq. (1)]. Without yet undertaking an evaluation, let us merely denote the combined primary and secondary bias-weight by subscript ''w,b.'' Let also the combined bias-weight before and after a lottery be denoted as $W_{w,b}^0(s)$ and $W_{w,b}(s)$, respectively. After completion of a segment that starts from an sth site the lottery's procedure is the following. First we multiply the bias-weight $W_{w,b}^0(s)$ by a suitably chosen constant C. Thereafter the sth segment is accepted with a transition probability,

$$t_{\mathrm{accep}}(s)=\begin{cases} CW_{w,b}^0(s) & \text{if } CW_{w,b}^0(s)\leqslant 1; \\ 1 & \text{if } CW_{w,b}^0(s)>1. \end{cases} \tag{2}$$

After a lottery with $t_{\mathrm{accep}}(s)$ we get

$$CW_{w,b}(s)=[CW_{w,b}^0(s)]/t_{\mathrm{accep}}(s). \tag{3}$$

Equations (2) and (3) give the bias-weight after a lottery

$$CW_{w,b}(s)=\begin{cases} 1 \ \text{(unbiased)} & \text{if } CW_{w,b}^0(s)\leqslant 1 \\ CW_{w,b}^0(s) & \text{if } CW_{w,b}^0(s)>1. \end{cases} \tag{4}$$

The constant C (for given ρ and N) is chosen small enough so that the unbiased case $CW_{w,b}(s)=1$ predominates. It is impractical to set C such that the case occurs *always*, this would drastically reduce the yield of successful chains. A reasonable compromise value of C is such that the average deviation of $CW_{w,b}(s)$ from unity does not exceed a few hundreths (as it turns out sometimes even a couple of tenths may be tolerated). Further decrease of C merely reduces the yield of successful chains, but has no effect on results of physical importance. In connection to the present study of the dilute–semidilute crossover, the quantity of primary importance is the chains' shape, represented by a mean radius. In what follows we assume that such effectively unbiased behavior is obeyed.

A particular construction of a new chain at an sth site is associated with a distinct local state $\alpha(s)$, specifying the location of $M-1$ chains of length N each, and of all bonds of the new chain up to $n=sa-1$. A local state $\alpha(s)$ determines to some extent the chain's future evolution, notably the probability $p_{\mathrm{succ}}[N;\alpha(n)]$ for a construction to successfully attain N, without first falling all the way back to s. The number of still available bifurcations is $b_s=2$, or 1, respectively, for a first or repeated (after a fallback) visit of the site. The case $b_s=2$ implies that, conditional on a success with $p_{\mathrm{succ}}[N;\alpha(s)]$, we are allowed to attain N in two alternative ways; if $b_s=1$ we are allowed one alternative only.[6] If a successful attainment of N is chosen as one out of b_s available alternatives, the associated contribution to bias-weight $W_{w,b}^0(s)$ at an sth site is a factor equal to b_s. Concurrently the sequence of a bond directions in the sth segment contributes a factor like in Eq. (1) but extending from $n=sa$ to $(s+1)a-1$. The combined factor contributed to $W_{w,b}^0(s-1)$ after completion of the sth segment is therefore

$$f_{w,b}(s)=W_{w,b}^0(s)/W_{w,b}(s-1)=b_s\times\prod_{n=sa}^{(s+1)a-1} w_n. \tag{5}$$

After a first passage through the sth site we still do not know whether the subsequent construction will attain N (if at all), after this or only after a second passage. Therefore we still do not know the value of b_s in Eq. (5). Yet if we wish to apply a selection on the go, we cannot leave this question open until the construction ends. Therefore after a first passage through the sth site we provisionally set $b_s=2$, whence $f_{w,b}(s)=2\times\Pi w_n$, with $W_{w,b}^0(s)$ and $t_{\mathrm{accep}}(s)$ calculated accordingly. If the subsequent construction attains N without first falling back to s, our provisional choice of $b_s=2$ becomes justified. In the opposite case however, we have to set $b_s=1$ and divide out the previous provisional factor $b_s=2$. Consequently for the second passage through s we put $f_{w,b}(s)=(1/2)\times\Pi w_n$, and calculate $W_{w,b}^0(s)$ and $t_{\mathrm{accep}}(s)$ accordingly. (The fact that in the first passage we have over-

estimated these values by factor two need not worry us, because even so the subsequent construction had flunked the selection.)

Equations (2), (4), and (5) combined with a choice of adjustable parameters a and C, determine the algorithm for the present rebound selection. Still the following remarks should be added.

(a) The discussion leading to Eq. (5) does not dwell on an important distinction between a bias due to using one out of w_n alternative bond directions on one hand and on the other, due to using one out of b_s alternative trial constructions from s to N. In the former case the alternative directions constitute precisely equivalent objects, allowing us to proceed from an nth site to $n+1$, without encountering EV. In the latter case however, the b_s alternative trial constructions have only a same *a priori probability* $p_{\mathrm{succ}}[N,\alpha(s)]$ to successfully attain N from an sth site in a local state $\alpha(s)$. This probability determines how often a successful attainment of N occurs after one, or after two visits of an sth site, corresponding to $b_s=2$ or 1, respectively. Thus the distribution of $b_s=2$ or 1 helps us to accord a correct bias weight to different local states $\alpha(s)$. However actual constructions from s towards N exhibit a stochastic variation independent of $\alpha(s)$, which of course affects the actually measured values of b_s. This stochastic variation makes our assignment of a correct bias weight to different states $\alpha(s)$ statistically noisy. The consequent evaluation of $f_{w,b}(s)$ and $W^0_{w,b}(s)$ in Eq. (5) is therefore approximate. True a stochastic noise independent of $\alpha(s)$ should ultimately average itself out as a constant factor in a ''sufficiently'' large sample of new chains but the convergence is difficult to assess. Ways of minimizing the effect of employing such a noisy bias weight $W^0_{w,b}(s)$ have been investigated in actual simulations.

(b) Another criterion of a satisfactory sampling is provided by an average value of of the RR bias-weight of the M chains due to bonds' direction alone, $W_w(N)$ [cf. Eq. (1)]. In an athermal system this RR bias weight is related to a chemical potential as[7] $\mu=\mathrm{const}-\log W_w(N)$. Hence the larger a value of $W_w(N)$ is, the closer to equilibrium is a system generated by a simulation. This objective criterion is of course more appealing than a mere reliance on an independence of simulations' results of a further reduction of parameter C. Unfortunately this objective criterion turns out to be not very practical. The accuracy available with $W_w(N)$ is relatively low, while the effect of long range behavior which is of primary interest here, makes only a minor contribution to it. For that reason values of $W_w(N)$ served only as an auxiliary criterion of satisfactory sampling, the main criterion being an independence of a measured chain's radius of C.

(c) Since a construction with the help of our simulation is effectively nonbiased, a new chain is selected according to its true ensemble weight. Consequently a new chain which succeeds to attain N automatically replaces one of M old chains picked at random. Or, the acceptance of a new chain only depends of its own bias weight. It does not depend on the bias-weight of the replaced old chain. The tacit assumption behind such *one-sided* selection is that an old chain too has been accepted according to its true ensemble weight at some previous time, and that subsequent rearrangements of the entire system did not affect this weight. This is obviously correct at equilibrium but constitutes only a plausible assumption in what concerns a relaxation towards equilibrium. In contrast, with CBMC a posterior *two-sided* selection is determined by bias-weights of both new and old chains (jointly as a ratio at constant ρ, or of each in turn at constant μ). Such a two-sided posterior selection requires a reconstruction of the bias-weight of the old and new chains. It is also possible to incorporate the rebound construction proposed here, in a two-sided posterior selection like in CBMC. A future publication will describe such an alternative utilization of the rebound construction (variously nicknamed ''recoil growth'').[8] The alternative avoids the assumption associated with a one-sided selection, but at a price of a greatly reduced efficiency. This because a selection on the go, which restores nonbiased sampling becomes impossible. The need to reconstruct the bias-weight also sets a practical limit on the maximum allowable number of consecutive fallbacks (the remark concerning statistically noisy evaluation of the bias-weight seems to apply but to a lesser degree).

III. RESULTS AND DISCUSSION

Simulations have been carried out at density $\rho=0.2$ and 0.6. The system size was kept at $M\approx 16$. Sample size of new chains vary from tens of thousands with short N, to several thousands with the longest. Two average quantities of the M chains have been measured at fixed intervals of Monte Carlo steps, the RR bias-weight $W_w(N)$ [Eq. (1)] and the radius of gyration R_g. In order to avoid huge values of $W_w(N)$, factors w_n have been divided by an approximate $\langle w_n\rangle$. In this way values of parameter C that ensure effective nonbiased sampling, are on the order of one-half. Thus using $b^0_s=2$ and segment length $a=2$, and $1/\langle w_n\rangle=0.216$ *and* 0.298 for $\rho=0.2$ *and* 0.6, respectively, values of C in the range 0.39–0.44 (significant to ± 0.005), ensure a nonbiased sampling, giving $CW_{w,b}(N)\approx 1$. The corresponding tolerated fluctuation of bias weight is $\Delta CW_{w,b}(N)\leqslant 0.03$; $\leqslant 0.15$ *and* $\leqslant 0.25$ for $\rho=0.2$ *and* 0.6, respectively.

In principle rebound selection involves three adjustable parameters; initial bi(multi)furcation b^0_s, segment length a, and the selection parameter C. This may appear forbidding but actually the choice of their values is quite simple, at least in the system studied. The optimal value of b^0_s is two. It minimizes the aforementioned perturbing effect of noisy values of b_s. Given $b^0_s=2$, segment-length a has to be such that under nonbiased regime a bifurcation is critical; notably the number of successful new chains neither increases nor decreases exponentially with N. It turns out that in all cases the optimal a is 2, at most 3. Consequently values of the selection parameter C alone require tuning; a somewhat surprising result is that they too turn out to depend on ρ and N quite slightly. The efficiency of the method in unit computer time

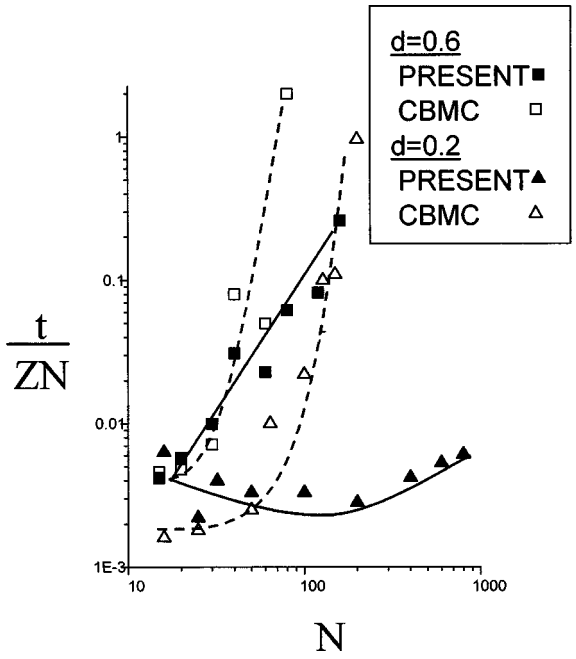

FIG. 2. The dependence of execution time (in minutes×1000 of a PENTIUM 200), per one bond of a successful new chain (viz., total time divided by total number Z of successful chains, and by chain length N), as a function of N. Solid triangles and squares correspond, respectively, to rebound selection results at density $\rho=0.2$ *and* 0.6; corresponding open symbols describe results of the CBMC method (Ref. 4).

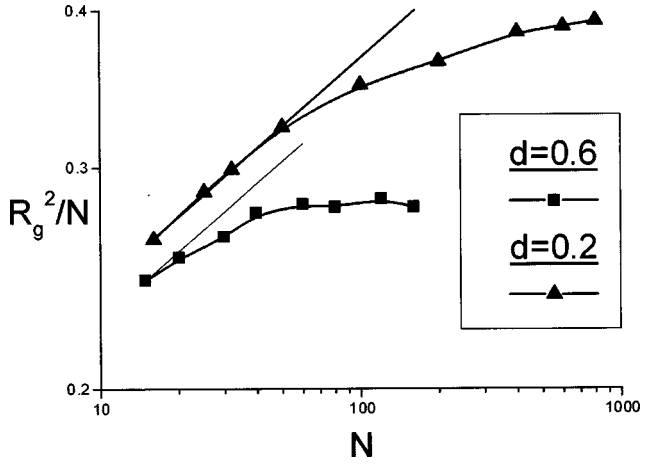

FIG. 3. Reduced square radius of gyration R_g^2/N, as a function of N. Solid symbols correspond to those of Fig. 2. Thin lines are fitted to a dilute regime dependence obeying $R_g^2/N=AN^{0.18}$.

depends of two factors. The number Z of successful new chains and the number of back and forth steps spent on one chain. Figure 2 displays a total execution time divided by Z and by N. For purpose of comparison values are also given for chains generated with the help of CBMC. The reproducibility of results for very long chains at high ρ is low, because simulations tend to become entrapped for prolonged periods of time, failing to generate a single successful new chain. Despite such problems encountered under extreme conditions, general trends are clear. The advantage of rebound selection over CBMC at $\rho=0.2$ is striking; at $\rho=0.6$ the advantage persists but becomes less pronounced. Most important, with the present method the time seems to increase as a powerlaw of N, whereas with CBMC the increase is exponential.

Figure 3 displays a reduced square radius of gyration R_g^2/N as a function of N at given ρ. At low N, a dilute behavior clearly holds true, $R_g^2/N \propto N_{2\nu-1}$ with $2\nu-1\approx 0.18$. At higher N a crossover to semidilute behavior sets in and approaches the ideal value $2\nu-1=0$. Once more, the crossover is particularly well displayed at $\rho=0.2$, but subject to a scatter it is also well displayed at other ρ. Clearly the crossover value N_{cross} decreases with increasing ρ, but the accuracy does not suffice to test the theoretical prediction $N_{\text{cross}} \propto \rho^{-5/4}$. In conclusion the results lend significant support to a blob theory of semidilute behavior,[9] investigated previously with the help of a ''fluctuating bond'' simulation.[10] Results for R_g^2/N in a dilute regime obtained with the help of CBMC, agree with those of rebound selection to within experimental error. The comparison however cannot be extended to semidilute regime due to a total breakdown of CBMC. Incidentally in the region attainable by CBMC, its results for RR bias-weight $W_w(N)$ are slightly higher (just exceeding an experimental error of especially massive simulations), than those of rebound selection. According to remark (b) after Eq. (5), the implication is that rebound selection results are less accurate than CBMC. This presumably reflects a less satisfactory simulation of EV avoidance on the short length scale, due to noisy values of b_s.

IV. SUMMARY

A new method is proposed for a simulation of many chain systems. One tries to replace an old chain by a new chain constructed with the help of a biased EV avoiding walk, which at intervals of a bonds is alloted a reserve bifurcation. A construction of a new chain proceeds therefore in segments of length a. After completion of a trial new segment, a selective lottery restores nonbiased sampling. If a segment survives the lottery, the construction towards N continues. If however the trial segment fails the selection, the construction falls back until it encounters an unutilized reserve bifurcation. The construction then rebounds (Fig. 1), it utilizes the reserve bifurcation, and moves forward once more. A construction thus moves back and forth until it successfully completes the chain's length N, or fails. In the former case the new chain is accepted at once because it is effectively sampled with its correct ensemble weight. The method is orders of magnitude better than conventional CBMC,[4] especially in a medium range of polymer density (Fig. 2).

Rebound selection has been applied to a study of a crossover from dilute to a semidilute regime[9] in a model system of athermal three-dimensional lattice chains. The results demonstrate neatly the crossover of a square radius dependence $R_g^2 \propto N^{2\nu}$, from $2\nu\approx 1.18$ to $2\nu=1$, for the dilute and semidilute regime respectively (Fig. 3). With the help of a trivial modification, rebound selection may be extended to an open system, and to tethered and branched lattice chains. An extension to off-lattice and to thermal chains though trivial too, may be less successful because of numerous and diversely

weighted degrees of freedom at each step. Extension of the principle of rebound selection to simulation of the nonpolymer semiordered system may perhaps be feasible too, with due adaptation to the problem at hand.

Beyond an application to simulations, it is interesting to observe that a selection on the go, combined with the possibility to renew on rebound a process that fails at one of its steps, makes our construction self-corrective. If it evolves into an inhibitory region, it falls back and rebounds in a better direction. Moreover, since it may fall back any number of steps, regions on any length scale may be dealt with in this manner. Such attributes may perhaps serve as a model of ''foresighted'' evolution. A related remark is that the rebound construction constitutes an intriguing random object which is *quasi* linear, with a potential to form branches but only one at a time.

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[1] E. Leontidis, B. M. Forrest, A. H. Widmann, and U. W. Suter, J. Chem. Soc., Faraday Trans. **91**, 2355 (1995).

[2] A. D. Sokal, in *Monte Carlo and Molecular Dynamics Simulations in Polymer Science*, edited by K. Binder (Oxford University Press, Oxford, 1995).

[3] Tests which measure a square displacement in unit time, averaged over all chains may miss an entrapment of some of them; more helpful would be a measurement of the time per a large scale displacement.

[4] J. I. Siepmann, Mol. Phys. **70**, 1145 (1990); J. I. Siepmann and D. Frenkel, *ibid.* **75**, 59 (1990).

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

[6] Let us calculate the average number k of alternative ways to attain N in $b_n=2$ trials starting at n. Let $p=p_{\mathrm{succ}}[N;\alpha(n)]$ be the probability to attain N. Then $k=p^2\times 2+p(1-p)\times 1+(1-p)p\times 1=2p$. Since we are interested only in an average k conditional on an attainment of N with probability p (events with probability $1-p$ are taken care of by failures of the construction), the number of alternatives is $k_{\mathrm{cond}}=b_s=2$.

[7] D. Frenkel, G. C. A. M. Mooij, and B. Smit, J. Phys.: Condens. Matter **4**, 3053 (1992).

[8] S. Consta, N. B. Wilding, D. Frenkel, and Z. Alexandrowicz (in preparation).

[9] P. G. De Gennes, *Scaling Concepts in Polymer Physics* (Cornell University Press, Ithaca, 1979).

[10] W. Paul, K. Binder, D. W. Heermann, and K. Kremer, J. Phys. (Paris) II **1**, 37 (1991).