Random polymers and generalized urn processes

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We describe a microcanonical approach for polymer models that combines atmospheric methods with urn theory. We show that large deviation properties of urn models can provide quite deep mathematical insight by analyzing the random walk range problem in $\mathbb{Z}^d$. We also provide a new mean-field theory for the range problem that is exactly solvable by analogy with the Bagchi-Pal urn model.

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I. INTRODUCTION

In this paper we present an alternative approach to deal with microcanonical polymer models derived in analogy with urn process theory. The main point in this method is that it is possible to relate the density of states of an interacting chain with the problem of computing the large deviation behavior of an associated Markov urn process [1–3] once the urn function of the problem is identified (see below). Here we deal with models that can be related to a two-color urn, first introduced by Hill, Lane and Sudderth (HLS) [4,5] for which a detailed large deviations theory has been recently developed [6,7]. In particular, we will provide an explicit example by studying the classic random walk (RW) range problem {(RP), [8–12]}, that is, computing the number of different lattice sites visited by a random walk of given length (see Fig. 1).

The HLS urn is a Markov process first introduced in Ref. [4]. Consider an infinite capacity urn with a finite number of black and white balls, and let y_t be the fraction of black balls inside the urn at a certain time t of the evolution, then in a HLS process of *urn function* $\pi(y)$ at each step a black ball is added with probability $\pi(y_t)$, and a white one is added otherwise. The process is then parametrized by the function $\pi(y)$ that represents the probability of adding a black ball at the considered step on the condition that the urn has reached a certain fraction of black balls.

The second ingredient is the *end-point atmosphere*, introduced some years ago within the study of the self-avoiding walk as the number of ways in which a chain of N steps can be continued by adding one monomer to the end point [13]. As we will see, it is possible to combine these two ideas together and define HLS processes that converge to a given polymer model in the thermodynamic limit by interpreting the probability that adding a step to a given chain produces an increase in an energy analog to adding a black ball in the associated urn process, i.e., the number of black balls will represent the total energy of our polymer.

Before starting let introduce some notation. Let $\mathbb{L}$ be some regular lattice, and let L_1 be the possible orientations on $\mathbb{L}$. Then we call a chain $\omega_N \in L_1^N$ of N steps on $\mathbb{L}$ the ordered sequence of steps $\delta x_t \in L_1$ for $1 \leqslant t \leqslant N$ with L_1^N as the set of distinct random walks of N steps on $\mathbb{L}$, thus $\omega_N = \{\delta x_1, \ldots, \delta x_N\}$. If we fix the starting point x_0 we can also represent ω_N by the positions $x_t \in \mathbb{L}$, related to the steps δx_t by $\delta x_t = x_t - x_{t-1}$. Hereafter we will assume that $x_0 \equiv 0$ and

$$\omega_N = \{x_0, x_1, \ldots, x_N\}, \tag{1}$$

with steps $x_t - x_{t-1} \in L_1$ for all times $1 \leqslant t \leqslant N$.

Now consider the interaction energy $H(\omega_N)$, that is, the energy associated with the chain configuration ω_N. We assume that the interaction energy H can be defined for arbitrary size N of the walks. In general, we can define the free energy density per monomer of the interaction H supported by L_1^N in the thermodynamic limit,

$$f(\beta) = -\lim_{N\to\infty} \frac{1}{\beta N} \ln \sum_{\omega_N \in L_1^N} e^{-\beta H(\omega_N)}. \tag{2}$$

After rescaling by the number of possible walks we can write $-\beta f(\beta = \ln|L_1| + \zeta(\beta)$ where $\zeta(\beta)$ is the cumulant generating function (CGF) of the variable $H(\omega_N)$,

$$\zeta(\beta) = \lim_{N\to\infty} \frac{1}{N} \ln\langle e^{-\beta H(\omega_N)}\rangle_{L_1^N}, \tag{3}$$

with the average over ω_N taken uniform on L_1^N.

Then, let ω_N be a random chain of N steps and define the sequence $\omega_t \subset \omega_N$ subwalks of ω_N according to the monomer ordering t, i.e., $\omega_t = \{x_0, \ldots, x_t\}$. In this paper we will deal with energy functions that satisfy

$$H(\omega_{t+1}) - H(\omega_t) \in \{0, 1\} \tag{4}$$

for all $\omega_N \in L_1^N$ and all t. This condition ensures that the energy can either increase by one unit or not increase at all when a monomer is added to the end point of ω_N and is an important technical point to connect with the HLS urns as it allows to directly identify an increase in energy followed by one step that grows with adding a black ball to the associated urn. It is possible to generalize to include more general transition spectra (multicolor urns), but here we consider the binary cases as the large deviation principle for such urns has been already developed in detail [7].

II. HLS URNS

Before going further we need to introduce the HLS process [4–7] and sketch some of its main properties we will use in the

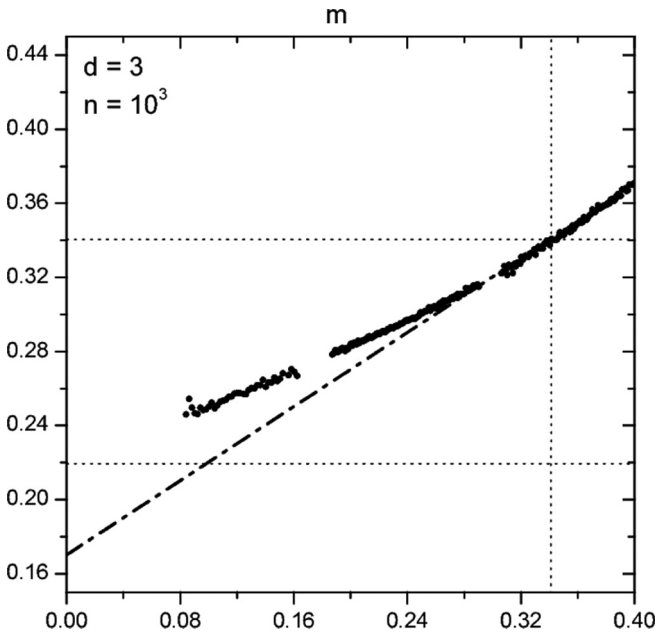

FIG. 1. Numerical estimate of $\pi_N(\lfloor Nm \rfloor)$ from Eq. (17) for dimensions $d = 3$ and $0 \leqslant m \leqslant 0.4$. The lengths of the chains were $N = 1000$. The vertical dotted line and the upper horizontal dotted line show the Pólya RW constant C_3 [16] and crosses at the RW point. The lower horizontal dotted line is the limit $\pi_\infty(0) = \eta_3$ [17,18] according to Ref. [19]. The dashed dotted line is the MF approximation $\pi_{\rm MF}(m) = (C_3 + m)/2$, computed according to Eqs. (28) and (29).

following. A HLS urn is a two-color urn process that is governed by a functional parameter $\pi(y)$ called the *urn function* [7]. Let us consider an infinite capacity urn containing two kinds of elements, say black and white balls, and denote by

$$Y = \{Y_{t_0}, Y_{t_0+1}, \ldots, Y_N\}, \tag{5}$$

the process describing the number of black balls inside the urn during its evolution from $t = t_0$ to N. The process Y evolves as follows: let $y_t = Y_t/t$ be the fraction of black balls at time t, then at step $t + 1$, a new ball is added, whose color is black with probability $\pi(y_t)$ and white with probability $1 - \pi(y_t)$.

Then, let Y be an HLS urn process stopped at N with initial condition $Y_{t_0} = M_0$, describing the number of black balls in the evolution of a HLS urn of urn function π. By simple arguments on conditional expectations it is not hard to prove that the process satisfies the following master equation:

$$P(Y_{N+1} = M + 1) = \pi\left(\frac{M}{N}\right) P(Y_N = M) + \left[1 - \pi\left(\frac{M+1}{N}\right)\right] P(Y_N = M + 1), \tag{6}$$

that can be iterated backward to the initial condition,

$$P(Y_{t_0} = M_0) = I(Y_{t_0} = M_0), \tag{7}$$

where π is the urn function and $I(Y_{t_0} = M_0)$ is the indicator function, valued as one if $Y_{t_0} = M_0$ and zero otherwise.

In Ref. [7] the cumulant generating function of the process,

$$\zeta(\beta) = \lim_{N\to\infty} \frac{1}{N} \ln \sum_{k\leqslant N} e^{-\beta k} P(Y_N = k) \tag{8}$$

is studied in detail, and it is proven that it must satisfy the following nonlinear differential equation:

$$\partial_\beta \zeta(\beta) = \pi^{-1}\left(\frac{e^{\zeta(\beta)} - 1}{e^\beta - 1}\right), \tag{9}$$

with π^{-1} as the inverse urn function. Of special interest for our scope will be the case of linear urn functions,

$$\pi(y) = a + by, \tag{10}$$

that in Ref. [7] are shown to be equivalent to the Baghi-Pal model [3,6], a widely investigated model due to its relevance in studying branching phenomena and random trees (see Refs. [1–3] for some reviews). Linear urn functions satisfy the differential equation,

$$\partial_\beta \zeta(\beta) = -\frac{a}{b} + \frac{1}{b}\left(\frac{e^{\zeta(\beta)} - 1}{e^\beta - 1}\right). \tag{11}$$

The above equation can be integrated exactly. Although the solution depends on the considered parameter region, for our analysis it will suffice to take $a > 0$, $a + b < 1$ and $b > 0$, $\beta > 0$. From Corollary 10 of Ref. [7] we have that

$$1 - e^{-\zeta(\beta)} = \frac{a}{b} e^{-(a/b)\beta} (1 - e^{-\beta})^{1/b} B\left(\frac{a}{b}, \frac{b-1}{b}; 1 - e^{-\beta}, 1\right), \tag{12}$$

where $B(q, p; u, v)$ is a generalized hypergeometric function of the second kind,

$$B(q, p; u, v) = \int_u^v dt (1 - t)^{q-1} t^{p-1}. \tag{13}$$

As we will see in short our mean-field (MF) theory will be described by the linear urn theory above.

III. URN ANALOGY

Although the limitations are imposed by Eq. (4), simple two-color HLS urns still allow for describing interesting models (that are not limited to polymer physics). The problem we investigate here is the the random walk RP on the cubic lattice $\mathbb{Z}^d$ [9,10,12], a model showing [12] a full crossover from self-avoiding walks (SAWs) [17] to a collapsed globular configuration in the range density per monomer and is shown to have an interesting geometric *coil-to-globule* (CG) transition (the chain collapses from an extended random coil to a liquidlike cluster [14,15]) at a critical range density for any $d \geqslant 3$.

Take a walk $\omega_N \in L_1^N$, and define the number of different sites of $\mathbb{L}$ visited by ω_N. We will approach the RP by studying interaction energy,

$$H(\omega_N) = N - R(\omega_N) = N - \sum_{x\in\mathbb{Z}^d} I(x \in \omega_N), \tag{14}$$

a Hamiltonian first introduced by Stanley *et al.* [11] (see also Ref. [22]) and Ref. [23]. To show the urn process analogy we first need to introduce some microcanonical estimators. Let

$$L_N(M) = \left\{\omega_N \in L_1^N : H(\omega_N) = M\right\} \tag{15}$$

be the fraction of walks of length N with an energy of exactly M, then call $P[H(\omega_N) = M]$ the probability that a chain

ω_N uniformly picked from L_N has energy M. Note that the constraint of binary energy increase guarantees that, for all these functions, m is a real parameter between zero and one. Then, let us consider a walk of N steps $\omega_N \in L_1^N$ and define the average of the energy after a random continuation $\omega_1^* \in L_1$ from the end point of ω_N,

$$\delta H_1(\omega_N) = \langle H(\omega_N \cup \omega_1^*) - H(\omega_N)\rangle_{L_1} = \frac{1}{|L_1|}\sum_{x\in\mathbb{Z}^d} I(x \in \omega_N) I\,(x \in L_1). \quad (16)$$

Since energy can increase only by zero or one, then the average increase $\delta H_1(\omega_N)$ equals the probability that a random continuation of the walk ω_N from its end point x_N produces a self-interaction according to H. We then define the atmosphere,

$$\pi_N(M) = \langle \delta H_1(\omega_N)\rangle_{L_N(M)}, \quad (17)$$

that is, the probability of self-intersection after a random continuation of ω_N, conditioned to the event that the range is $R(\omega_N) = N - M$.

It can be proven that $P[H(\omega_N) = M]$ satisfies the following master equation:

$$P[H(\omega_{N+1}) = M] = \pi_N(M)P[H(\omega_N) = M] + [1 - \pi_N(M+1)]P[H(\omega_N) = M+1], \quad (18)$$

with initial condition,

$$P[H(\omega_1) = M] = I(M = 0). \quad (19)$$

If we take $H(\omega_N) = Y_N$ it is clear that the master equation for the measure of the event is the same as the event $Y_N = M$ of a HLS urn of nonhomogeneous urn function $\pi_N(M)$. In Ref. [7] it is shown that if

$$\lim_{N\to\infty} |\pi_N(\lfloor Nm\rfloor) - \pi(m)| = 0, \quad (20)$$

then the cumulant generating function of the process is the same of a HLS urn of urn function $\pi(m)$. The existence of $\pi(m)$ for the RP can be inferred by subadditivity, but we do not give a proof here because the convergence of $\pi_N(\lfloor Nm\rfloor)$ toward some smooth $\pi(m)$ is already clear from our numerical analysis (see Fig. 3).

IV. NUMERICAL RESULTS

In Figs. 1–3 we present our numerical results concerning the urn function $\pi_N(M)$ associated with the RP on $\mathbb{Z}^d$, $3 \leqslant d \leqslant 6$ for which some properties can be deduced also from known results in random and self-avoiding walks theory [9,17,18].

The numerical simulations were performed by a standard implementation of the pruned-enriched Rosenbluth method (PERM), see Refs. [24–27]. For $3 \leqslant d \leqslant 6$ we restricted our attention to the region $M/N < m_c$ where the typical configuration of ω_N is supposed to be in the universality class of the self-avoiding walk.

In a previous paper [12] we numerically studied the event $H(\omega_N) = \lfloor mN\rfloor$ and found a CG transition for some critical

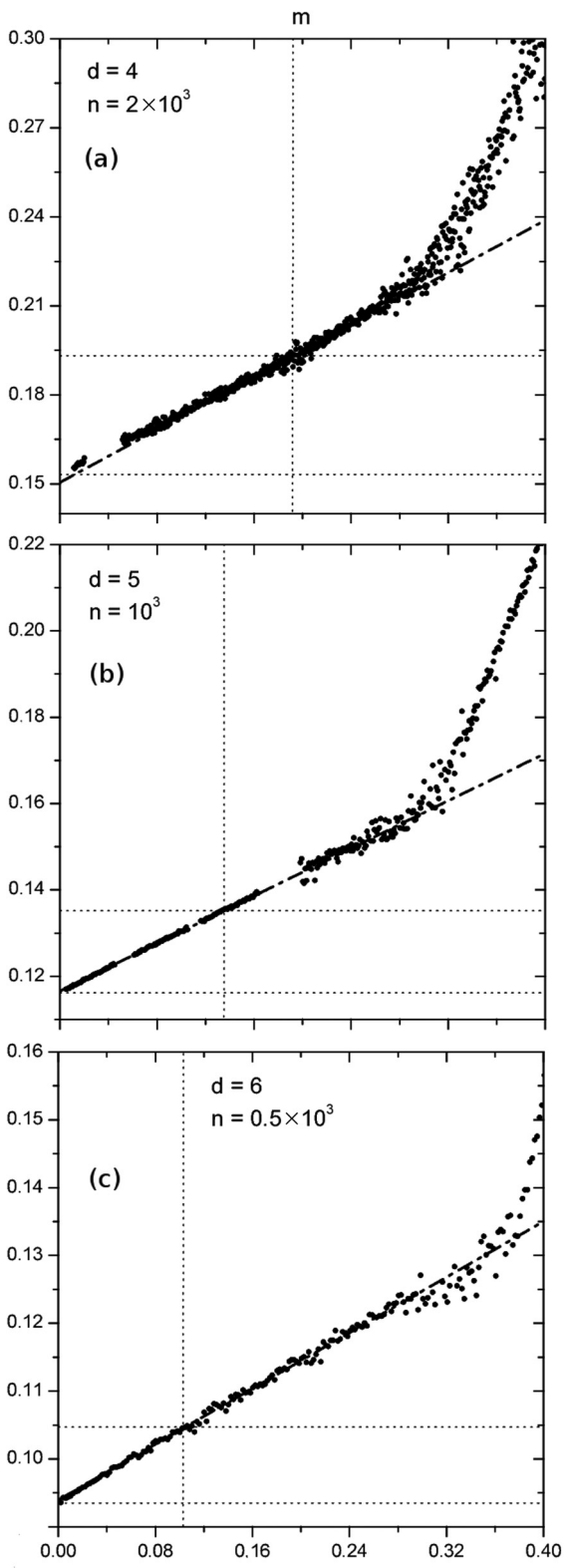

FIG. 2. Numerical estimation of $\pi_N(\lfloor Nm\rfloor)$ from Eq. (17) for $d = 4$–6 and $0 \leqslant m \leqslant 0.4$. As for $d = 3$, the lengths of the chains were $N = 2000$ for $d = 4$, $N = 1000$ for $d = 5$, and $N = 500$ for $d = 6$. For each plot, the vertical and the upper horizontal dotted lines are Pólya constants C_d [9,16], whereas the lower horizontal dotted lines are $\pi_\infty(0) = \eta_d$ from Refs. [17,18]. The dashed dotted lines are $\pi_{\rm MF}(m) = C_d(1 - B_d) + B_d m$ of Eqs. (28) and (29) (not linear fits).

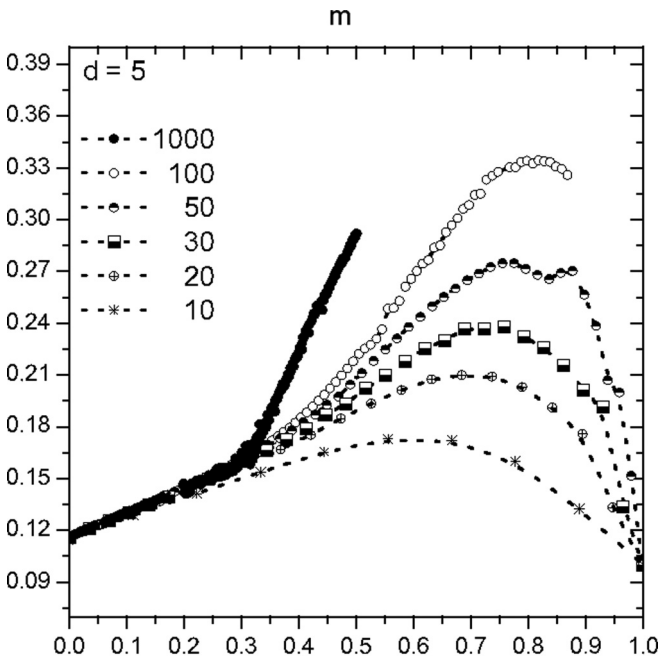

FIG. 3. Numerical estimation of $\pi_N(\lfloor Nm \rfloor)$ from Eq. (17) for $d = 5$, $0 \leqslant m \leqslant 1$ and from $N = 10$ to $N = 1000$. The convergence to some limit urn function $\pi(m)$ is observed in the SAW region $m < m_c$.

value of $m = m_c \in (0, 1)$. We studied the critical exponent governing the mean square displacement,

$$\nu_d(m) = \lim_{N\to\infty} \frac{\ln \langle x_N^2 \rangle_{C_N(\lfloor Nm \rfloor)}}{2 \ln N}, \tag{21}$$

concluding the above limit exists and $\nu_d(m < m_c) = \nu_d$, $\nu_d(m = m_c) = \nu_c$, $\nu_d(m > m_c) = 1/d$, where ν_d is the critical exponent governing the end-to-end distance of the self-avoiding walk [17]. Also, for the $\nu_c = 1/2$, $m_c = C_d$ Pólya constants [16] for $d = 3, 4$ and that for $d \geqslant 5$, it is expected that $m_c > C_d$ (see Ref. [12] for further details about this topic).

Here we observe that $\pi_N(M)$ approaches some continuous $\pi(M/N)$ uniformly on the considered range. Quite surprisingly, we also observe that for $d \geqslant 4$ the function π suddenly approaches some linear function (see Figs. 2 and 3),

$$\pi_{\mathrm{MF}}(m) = a_{\mathrm{RP}} + b_{\mathrm{RP}} m, \tag{22}$$

in the region $0 \leqslant m \leqslant m_c$. Assuming a linear urn function, the coefficients can be computed exactly from RW theory by relating them to the variance of the energy σ_d^2.

The constant σ_d can be computed from Jain-Pruitt theorem on the variance of the RP ([9,28–31], see also Ref. [32] for an explicit computation). For $d = 3$, Hughes [9], Jain and Pruitt [28], and Jain and Orey [29] have shown that the leading order of the variance of $R(\omega_N)$ for a random walk is $\sigma_3^2 N \ln(N)$ with σ_3 exactly computable, whereas for $d \geqslant 4$ the same authors show that the variance is $\sigma_d^2 N$ with σ_d expressed by the relation,

$$\sigma_d^2 = C_d(1 - C_d) + 2a. \tag{23}$$

Accurate estimates for C_d are in Ref. [16]. To determine a, we follow Refs. [9,18,28,29,32]. Let us first introduce the propagator,

$$G(x) = \int_{[-\pi,\pi]^d} \frac{dq}{(2\pi)^d} e^{iqx} [1 - \tilde{\lambda}_d(q)]^{-1}, \tag{24}$$

where $\tilde{\lambda}_d(q)$, $q \in [-\pi, \pi]^d$ is the *structure factor* of the hypercubic lattice $\mathbb{Z}^d$,

$$\tilde{\lambda}_d(q) = \frac{1}{d} \sum_{i=1}^{d} \cos(q_i), \tag{25}$$

and where q_i's are the components of the dual vector q. The quantity $G(x)$ represents the expected number of visits to a given site $x \in \mathbb{Z}^d$ for an infinite length random walk. From standard random walk theory follows [9]:

$$\frac{C_d}{1 - C_d} = \sum_{x \in \mathbb{Z}^d \setminus \{0\}} G(x) \tag{26}$$

for the Pólya constants. For $d \geqslant 3$, by the Jain-Pruitt theorem it is also possible to write a in terms of the $G(x)$ function as well [32]

$$a = \sum_{x \in \mathbb{Z}^d \setminus \{0\}} \frac{(1 - C_d)^4 G(x)^3}{1 + (1 - C_d) G(x)}. \tag{27}$$

Then, from the convergence condition of a generic HLS urn $C_d = \pi(C_d)$ (see Ref. [7]), it follows that:

$$a_{\mathrm{RP}} = C_d(1 - b_{\mathrm{RP}}). \tag{28}$$

By computing the variance of the linear urn from the CGF of Eq. (11) and confronting with the expression of the RP variance from the Jain-Pruitt theorem above we get

$$b_{\mathrm{RP}} = \frac{1}{2}\left(1 - \frac{C_d(1 - C_d)}{\sigma_d^2}\right). \tag{29}$$

Linear urns with the above values are shown as dotted lines in Figs. 1 and 2. A detailed computation will be presented elsewhere.

V. TWO-COLOR MEAN-FIELD THEORY

Besides the computational advantages in numerically studying the atmosphere instead of counting the number of walks, that has been already exploited in Ref. [13], the urn theory allows for different interesting analytic approaches. For example, here we give a simple model that matches the linear urn theory suggested by our numerical simulations. In the spirit of the classic Pincus–De Gennes blob picture [14] let us slice the chain ω_N into a number n of subchains,

$$\omega_N = \{\omega_T^0, \omega_T^1, \ldots, \omega_T^n\}, \tag{30}$$

each of size $T = N/n$. The subchains are indicated with

$$\omega_T^i = \{x_0^i, x_1^i, \ldots, x_T^i\} \subset \omega_N, \tag{31}$$

and satisfy the chain constraint,

$$x_T^i = x_0^{i+1}. \tag{32}$$

If we neglect the mutual self-intersections between different blocks we can approximate the energy with

$$H(\omega_N) \simeq \sum_{i=1}^{n} H\left(\omega_T^i\right), \tag{33}$$

and the energy increment,

$$\delta H_1(\omega_N) \simeq \delta H_1\left(\omega_T^1\right). \tag{34}$$

The probability measure conditioned to $H(\omega_N) = \lfloor Nm \rfloor$ is then approximated by a product measure,

$$\mu_m(\omega_N) \simeq \prod_{i=1}^{n} \mu_{m_i}\left(\omega_N^i\right). \tag{35}$$

Note that the approximation of Eqs. (33) and (34) is expected to hold at least if both $N, T \to \infty$ and $d \geqslant 4$ because above the critical dimension the interaction between different subwalks is negligible in the thermodynamic limit [8–10,17]. If instead we take T to be finite, then the mutual intersections between the segments are no longer negligible, nonetheless, since the typical length between two self-intersection is on the order of $O(1/2d)$, we expect that the above linear approximation will be asymptotically exact also for $T < \infty$ in the limit $d \to \infty$.

Now, we approximate by assuming that the subchain distributions can be of two kinds only, say A and B,

$$\mu_i\left(\omega_N^i\right) = \varphi^i \mu_A\left(\omega_N^i\right) + (1 - \varphi^i)\mu_B\left(\omega_N^i\right). \tag{36}$$

This recalls again the two-color approximation and seems a crucial technical point to obtain linear urns. We can give a simple physical understanding of this by taking A to be, for example, a self-avoiding walk $m_A = 0$, T equal to the average number of steps a SRW can perform without self-intersecting and B to contain a self-intersection such that the local range density is $1 - m_B$ with $m_B = C_d > 0$. Forcing a self-intersection in one block will certainly bring a decrease in the total range density; on the other side this will affect the atmosphere only if the self-intersection happens near the end point where we are supposed to grow the chains.

In the previous formula Eq. (36) we introduced a binary sequence,

$$\varphi = \{\varphi^1, \ldots, \varphi^n\}, \tag{37}$$

with $\varphi^i \in \{0, 1\}$, that kept a record of whether a subchain is either of one kind or the other, and can be interpreted as the color of the ball we add. For a walk in a given state we assume that the range density is peaked around some value,

$$H\left(\omega_T^i\right) \simeq m_A T \varphi^i + m_B T(1 - \varphi^i), \tag{38}$$

concerning the energy and

$$\delta H_1(\omega_N) \simeq \pi_B + (\pi_A - \pi_B)\varphi^1 \tag{39}$$

for the energy increment. Given this we find

$$H(\omega_N)/N \simeq m_B + (m_A - m_B)\frac{1}{n}\sum_{i=1}^{n} \varphi^i, \tag{40}$$

TABLE I. In this table is shown $\eta_d^{(u)} = C_d(1 - b_{\mathrm{RP}})$ from MF theory and numerically determined η_d from literature [17,19–21]: Although $d = 3$, there is a heavy underestimation (more that 20%), yet, for $d = 4$, there is an error of 2%, and $d \geqslant 5$ under the percentage. An exhaustive analysis of our results about the range problem will be published in a dedicated paper.

d	b_{RP}	$\eta_d^{(u)}$	η_d	$\eta_p^{(u)}/\eta_d - 1$
3	1/2	0.17026(9)	0.2193(5)	−22.38%
4	0.22080(9)	0.15054(1)	0.1532445(6)	−1.76%
5	0.13767(2)	0.11656(8)	0.1161456(3)	0.36%
6	0.10266(0)	0.09396(5)	0.0934921(3)	0.51%
7	0.08291(2)	0.078727(3)	0.07837021(4)	0.46%
8	0.07030(6)	0.067786(5)	0.0675464(2)	0.36%

then, taking the average over $C_N(M)$ with

$$\langle \varphi^1 \rangle_{C_N(M)} = \frac{1}{n}\sum_{i=1}^{n} \langle \varphi^i \rangle_{C_N(M)}, \tag{41}$$

we arrive at a linear expression for the urn function,

$$\pi_N(M) \simeq a_{\mathrm{RP}} + b_{\mathrm{RP}} M/N, \tag{42}$$

with coefficients $a_{\mathrm{RP}} = \pi_B - m_B b_{\mathrm{RP}}$ and

$$b_{\mathrm{RP}} = \frac{\pi_A - \pi_B}{m_A - m_B}. \tag{43}$$

There are various ways to obtain these coefficients from random walks theory. If we take A to be the RW and B to be the SAW, we arrive to the linear urn described before, where a_{RP} equals the SAW normalized connective constant η_d [17,18] and $b_{\mathrm{RP}} = 1 - \eta_d/C_d$. By comparing to a mean-field value we obtain an expression for the rescaled connective constant of the self-avoiding walk [17,18],

$$\eta_d \simeq \frac{C_d}{2}\left(1 + \frac{C_d(1 - C_d)}{\sigma_d^2}\right) = \eta_d^{(u)}. \tag{44}$$

A computation of $\eta_d^{(u)}$ via numerical integration (see Table I) suggests excluding that this is the correct value for η_d, at least, for $d \leqslant 8$, although our numerical analysis shows narrow discrepancies as d increases.

We conclude by remarking that in the above mean-field theory a critical ingredient is to assume that we can obtain the urn function via interpolation between any two fixed energy states, for example, subchains that are either self-avoiding or critically collapsed or between self-avoiding chains and random chains as well. The reason for this to hold so well in high dimensions is not clear.

The numerical estimates $\eta_d^{(u)}$ in Table I, based on the linear urn analogy and the Jain-Puitt theorem, seem to indicate that Eq. (38) is slightly deviating from the accurate numerical values available in literature, at least, for $d \leqslant 8$. Unfortunately, we expect this simple linear urn analogy to be only asymptotic for $d \to \infty$, but we also expect that a more refined estimate of the urn function can be obtained by a proper accounting of mutual self-intersections between the blocks. Further investigations on this aspect would be of certain interest, also, it would be interesting to understand the meaning of higher order polynomial urn functions. We expect that some light on this may be obtained, at least, in $d = 4$ by confronting with a recently developed exact renormalization scheme based on lace expansion [33].

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