Energy of the Interacting Self-Avoiding Walk at the $\theta$–point

Simone Franchini and Riccardo Balzan

*Dipartimento di Fisica, Sapienza Università di Roma, P.le Aldo Moro 1, 00185, Roma, Italy*

We perform a numerical study of a new microcanonical polymer model on the three dimensional cubic lattice, consisting of ideal chains whose range and number of nearest-neighbor contacts are fixed to given values. Our simulations suggest an interesting exact relation concerning the internal energy per monomer of the Interacting Self-Avoiding Walk at the $\theta$–point.
It is well known that a polymer chain can collapse from an extended to a compact configuration if the temperature or the solvent quality is lowered below some critical value. This phenomenon, known as Coiltoglobule transition (CG, [1–3]), arises when the attractive interaction between the monomers overwhelm the excluded volume effect. At the transition temperature (commonly called \( \theta \) point) these contributions compensate, resulting in a phase where the chains behave approximately as random walks [1, 4–6].

Let \( \omega_N \) be an \( N \)-steps Simple Random Walk (SRW) on the cubic lattice \( \mathbb{Z}^d \),

\[
\omega_N = \left\{ x_t (\omega_N) \in \mathbb{Z}^d : 0 \leq t \leq N \right\},
\]

by convention we fix the seed monomer at \( x_0 (\omega_N) = 0 \). The chain can be represented through the locations of its monomers \( x_t (\omega_N) \) or equivalently by the orientations of its steps

\[
x_t (\omega_N) - x_{t-1} (\omega_N) \in \Omega_1,
\]

where \( \Omega_1 \) is the set of possible orientations on \( \mathbb{Z}^d \) (for the cubic lattice the number is \(|\Omega_1| = 2^d |\). Then, we indicate with

\[
\Omega_N = \Omega_1^N \ni \omega_N
\]

the set of all possible chain configurations.

Here we present a micro-canonical model where the number of distinct lattice site visited by the walk \( R (\omega_N) \) (range) and the number of nearest-neighbors monomer pairs \( L (\omega_N) \) (links) are constrained to scale with the number of steps \( N \), formally

\[
R (\omega_N) = \lfloor (1 - m) N \rfloor, \quad L (\omega_N) = \lfloor \lambda N \rfloor,
\]

where we denoted by \( \lfloor z \rfloor \) the lower integer truncation of \( z \in \mathbb{R} \), (see Figure 1). The model is controlled by the pair of parameters \( m \) and \( \lambda \), and the Interacting Self-Avoiding Walk (ISA\W, [7–12, 16, 17]) is recovered by taking \( m = 0 \).

We numerically investigated the micro-canonical phase diagram on the plane \( (m, \lambda) \), formulating a conjecture on the location of the transition line \( \lambda = \ell_c (m) \) that is expected to separate the SAW like-phase (where the scaling of the average chain displacement is that of the SAW) from the clustered phase (in which the chains configure into compact clusters).

Based on these computer simulations and some additional theoretical arguments, our analysis suggests that at least in the Thermodynamic Limit (TL) \( N \to \infty \) the critical link density is a linear function of \( m \)

\[
\ell_c (m) = \lambda_c + \delta_c m
\]
and the constant $\lambda_c$ is expected to match the density of contacts per monomer of the ISAW at the $\theta$–point in the TL.

Before going further we need to introduce the model and state some basic properties. For what follows it will be convenient to define a symbol for the two-point matrix associated to $\omega_N$

$$A_{x,y}(\omega_N) = I(x \in \omega_N)I(y \in \omega_N),$$

(6)

where $I(X)$ is the indicator function of the event $X$, and its value is one when $X$ is verified and zero otherwise.

We can now introduce the range $R(\omega_N)$ of the chain $\omega_N$, that is the number of distinct points of $\mathbb{Z}^d$ visited at least once by $\omega_N$. This can be expressed in term of the adjacency matrix as follows

$$R(\omega_N) = N + 1 - M(\omega_N) = \sum_{x,y \in \mathbb{Z}^d} A_{x,y}(\omega_N) I(|x - y| = 0),$$

(7)

without loss of generality we will work with the related quantity $M(\omega_N)$, which represent the number of intersections present in the chain $\omega_N$.

Then, we introduce $L(\omega_N)$, that counts the number of nearest-neighbor pairs of $\omega_N$, which we call links. The number of links contained in $\omega_N$ is given by

$$L(\omega_N) = \frac{1}{2} \sum_{x,y \in \mathbb{Z}^d} A_{x,y}(\omega_N) I(|x - y| = 1),$$

(8)

where the factor $1/2$ corrects for multiple counting of the same link.

Our model is defined by a partition of $\Omega_N$ into subsets $\Omega_N(M,L)$ such that each walk has exactly $M$ intersections and $L$ links

$$\Omega_N(M,L) = \{ \omega_N \in \Omega_N : M(\omega_N) = M, L(\omega_N) = L \},$$

(9)

we indicate with brakets notation $\langle \cdot \rangle_{M,L}$ the average at fixed $N$, $M$ and $L$

$$\langle \cdot \rangle_{M,L} = \frac{1}{|\Omega_N(M,L)|} \sum_{\omega_N \in \Omega_N(M,L)} (\cdot),$$

(10)

while the dependence on $N$ is kept implicit. Also, we can define the probability of uniformly extracting a chain with $M$ intersections and $L$ links

$$p_0(M,L) = \frac{|\Omega_N(M,L)|}{(2d)^N}$$

(11)

that by definition sums to one

$$\sum_{M,L} p_0(M,L) = 1.$$

(12)
Figure 1. Range and link count for a chain $\omega_8 = \{x_0, x_1, ..., x_8\}$ of $N = 8$ steps on $\mathbb{Z}^2$, shown on top. A shows the actual walk, while B highlights the range points (black circles) and the links (dotted segments) of $\omega_8$. The total range is $R(\omega_8) = 7$, the number of self-intersections is then $M(\omega_8) = 8 + 1 - R(\omega_8) = 2$, occurring at the 6–th and 7–th steps. The total number of links is $L(\omega_8) = 8$, as it counts also the links imposed by the chain condition (in A the only non-trivial link is that between monomers $x_0$ and $x_3$).

We remark that the link counter $L(\omega_N)$ also includes the links between consecutive monomers, hence is always bounded by the range $R$ from below and by $dR$ from above, for $d = 3$

$$1 \leq \frac{L(\omega_N)}{N + 1 - M(\omega_N)} < 3,$$

also, notice that $L(\omega_N)$ can increase only if $M(\omega_N)$ does not (the variables are anti-correlated).

I. RELATIONS WITH CANONICAL MODELS

In the simplest case, the CG transition can be modeled by incorporating attractive nearest-neighbors interactions in the Self-Avoiding Walk (SAW) $[13, 15, 17, 27, 34]$. Let introduce the local times (the number of visits to a given site $x$) associated to $\omega_N$

$$\phi_x(\omega_N) = \sum_t I(|x - x_t(\omega_N)| = 0),$$

and the non-centered local field correlation function

$$C_{x,y}(\omega_N) = \phi_x(\omega_N) \phi_y(\omega_N).$$

Now define the topological constraint

$$Y_{x,y}(\varepsilon, \gamma) = \varepsilon I(|x - y| = 0) + \gamma I(|x - y| = 1)$$
where the ratio $\varepsilon / \gamma$ controls the balance between terms, then we can construct the Hamiltonian

$$H_s (\omega_N) = \sum_{x,y} C_{x,y} (\omega_N)^s Y_{x,y} (\varepsilon, \gamma)$$  \hspace{1cm} (17)$$

with $s$ real valued parameter. Independently from the choice of $s$, for $\varepsilon \to \infty$ this Hamiltonian always converges to the ISAW because the SAW condition $M (\omega_N) = 0$ always implies $\phi_x (\omega_N)$ can be only 0 or 1.

Many models can be represented from this Hamiltonian, for example when $s = 1$, $\varepsilon_0 = \varepsilon + \gamma$ we get the Interacting Domb-Joyce model (IDJ)

$$H_1 (\omega_N) = \sum_{x,y} C_{x,y} (\omega_N) Y_{x,y} (\varepsilon, \gamma) = \varepsilon_0 \sum_x \phi_x^2 (\omega_N) + \gamma \sum_{x,y} \phi_x (\omega_N) \phi_y (\omega_N)$$  \hspace{1cm} (18)$$

while if also $\gamma \to 0$ we obtain the classical Domb-Joyce model (or Weakly Self-Avoiding Walk, see [13, 14, 17, 27]).

The canonical version of our model is instead obtained in the limit $s \to 0$. In this case we have

$$\lim_{s \to 0} C_{x,y} (\omega_N)^s = A_{x,y} (\omega_N) \in \{0, 1\}$$  \hspace{1cm} (19)$$

for any $\omega_N \in \Omega_N$ (not only the Self-Avoiding Walks). The Hamiltonian is

$$H_0 (\omega_N) = \varepsilon M (\omega_N) + \gamma L (\omega_N).$$  \hspace{1cm} (20)$$

The competition between the repulsive range term $\varepsilon M (\omega_N)$ versus the attractive nearest-neighbor interaction $\gamma L (\omega_N)$ allows for the CG transition.

Given the parameters $\beta_1 / \beta = \varepsilon$ and $\beta_2 / \beta = \gamma$ the associated Gibbs measure is

$$\mu_{\beta} (\omega_N) = \frac{e^{-\beta_1 M (\omega_N) - \beta_2 L (\omega_N)}}{Z_{\beta}}$$  \hspace{1cm} (21)$$

Notice that the partition function can be expressed as a sum over $M$ and $L$ using the formula

$$Z_{\beta} = \sum_{\omega_N \in \Omega_N} e^{-\beta_1 M (\omega_N) - \beta_2 L (\omega_N)} = \sum_{M,L} |\Omega_N (M, L)| e^{-\beta_1 M - \beta_2 L},$$  \hspace{1cm} (22)$$

and we can also define a pseudo-Gibbs measure

$$p_{\beta} (M, L) = \frac{|\Omega_N (M, L)| e^{-\beta_1 M - \beta_2 L}}{Z_{\beta}}$$  \hspace{1cm} (23)$$

that allows to express the thermal averages

$$\langle \cdot \rangle_{\beta} = \sum_{\omega_N \in \Omega_N} \mu_{\beta} (\omega_N) (\cdot) = \sum_{M,L} p_{\beta} (M, L) \langle \cdot \rangle_{M,L}$$  \hspace{1cm} (24)$$

in terms of the microcanonical averages $\langle \cdot \rangle_{M,L}$. 
Based on the existing literature on the IDJ model \cite{17-19}, the limit $N \to \infty$ of our model should exist for any choice of the parameters, and then we expect that for any $\beta$ and any ratio $\beta_1/\beta_2$ the probability measure $p_\beta([mN],[\lambda N])$ concentrates on some point of the $(m,\lambda)$ plane.

We indicate with $M_N$ the average number of intersections for a SRW of $N$ steps

$$M_N = \sum_{M,L} p_0(M,L) \cdot M,$$

while $L_N$ is the average number of links

$$L_N = \sum_{M,L} p_0(M,L) \cdot L,$$

By standard SRW theory \cite{16, 26-28}, the average densities of intersections and links are given by the formulas

$$M_N = m_0N + u_0\sqrt{N} + o\left(\sqrt{N}\right),$$

$$L_N = \lambda_0N + w_0\sqrt{N} + o\left(\sqrt{N}\right),$$

the constants can be exactly computed (for example one has $m_0 = C_3$ Polya constant \cite{16}). Also, the fluctuations

$$\Delta M(\omega_N) = M(\omega_N) - M_N,$$

$$\Delta L(\omega_N) = L(\omega_N) - L_N,$$

are expected to satisfy a joint Central Limit Theorem (CLT) centered at zero, and then $p_0(M,L)$ should concentrate in a $O(\sqrt{N})$ neighborhood of the point $(m_0N,\lambda_0N)$ on the $(M,L)$ space. As we shall see in short, this assumption is of central importance to locate the critical line in three dimensions. We will discuss its grounds when dealing the conjectured phase diagram.

\section{Locating the Transition Line}

It is easy to verify that the proposed Hamiltonian converges to the ISAW in the limit $\epsilon \to \infty$ (if also $\beta_2 = 0$ corresponds to the SAW). Under the assumption that $\log p_0(0,[\lambda N])$ is convex in $\lambda$ at least in the SAW phase, we can expect that

$$\lim_{N \to \infty} \lim_{\beta_1 \to \infty} \lim_{\beta_2 \to \beta_c} \frac{\langle L(\omega_N) \rangle_\beta}{N} = \lim_{N \to \infty} \frac{\langle L(\omega_N) \rangle_{0,[\lambda N]}}{N} = \lambda_c,$$
Figure 2. Surface $\rho_N(m, \lambda)$ for a ISAW of $N = 50$. In the top figure A $\rho_N(m, \lambda)$ is computed for a large part of the parameter space using a PERM algorithm, which is the gray area in B. The bottom figure B shows some level lines $\rho_N(m, \lambda) = r$ as scatter points, the line $\rho_N(m, \lambda) = 1$ and the boundaries of the allowed parameter space are highlighted by solid lines. Although the considered chains are very small, the linear behavior of the level lines in the image B is still surprising. A simulation of a larger chain of $N = 100$ steps (not shown) gave the same picture.

ie, that in the TL the critical energy densities should be the same in both the canonical and microcanonical version.

To present the essential features of the phase diagram we will first discuss the quantity

$$v(m, \lambda) = \lim_{N \to \infty} \frac{\log \langle \chi_N^2 (\omega_N) \rangle }{2 \log N},$$

(32)
which represents the critical exponent of the squared end-to-end distance when \( M \) and \( L \) are constrained to grow proportionally to \( N \).

For \( \gamma \to 0 \) one obtains the so called Stanley model for \( \varepsilon_0 > 0 \), of Hamiltonian \( H_0(\omega_N) = \varepsilon M(\omega_N) \) (for \( \varepsilon_0 < 0 \) is the Rosenstock Trapping model). The corresponding microcanonical model is

\[
\Omega_N(M) = \bigcup_L \Omega_N(M,L)
\]

and has been studied in \([20,21]\) where numerical simulations and additional theoretical arguments supports that the displacement exponent of the set \( \Omega_N(\lfloor mN \rfloor) \)

\[
\nu(m) = \lim_{N \to \infty} \log \left( \frac{\langle x^2_N(\omega_N) \rangle_{\lfloor mN \rfloor}}{\lfloor \lambda N \rfloor} \right)
\]

has a drop around \( \lambda_c = C_3 \), with a drop band slowly narrowing as \( O(1/N^\alpha) \) and \( \alpha = 0.29 \pm 0.1 \) (\([20]\), an independent scaling analysis, not shown, gave \( 0.31 \pm 0.1 \)).

Based on these preliminary studies we conjecture that for any value of \( m \) there is some critical link density \( \ell_c(m) \) such that if \( \lambda < \ell_c(m) \) the exponent \( v(m,\lambda) \) matches the critical exponent \( \nu_3 \) of the SAW. The conjectured phase diagram is then

\[
v(m,\lambda) = \begin{cases} 
\nu_3 & \lambda < \ell_c(m) \\
1/2 & \lambda = \ell_c(m) \\
1/3 & \lambda > \ell_c(m) 
\end{cases}
\]

where \( \nu_3 \) is the critical exponent of the SAW governing the end-to-end distance \([17-19]\). If the link density is exactly \( \lambda = \ell_c(m) \) the energy contributions from range and links should balance, giving a SRW-like critical behavior with exponent \( v(m,\ell_c(m)) = 1/2 \), while for \( \lambda > \ell_c(m) \) we expect to be in the cluster phase, then \( v(m,\lambda) = 1/3 \). Notice that for \( m \to 0 \) we must have \( \ell_c(0) = \lambda_c \) energy density of the ISAW at the theta point.

Although an investigation of the parameter \( v(m,\lambda) \) should be carried on to verify the phase exponents (as is done in \([20]\) for the Range Problem), we believe that the existing literature on IDJ-like models \([4-9,11-13,15-17]\) already support the existence of a non-trivial transition line, and we decided to locate \( \ell_c(m) \) by computing the level lines of the estimator

\[
\rho_N(m,\lambda) = \frac{\langle x^2_N(\omega_N) \rangle_{\lfloor mN \rfloor,\lfloor \lambda N \rfloor}}{N},
\]

that by previous considerations satisfy

\[
\rho_N(m,\lambda) = \begin{cases} 
O(N^{2\nu_3-1}) & \lambda < \ell_c(m) \\
O(1) & \lambda = \ell_c(m) \\
O(N^{-2/3}) & \lambda > \ell_c(m) 
\end{cases}
\]
We computed the set \( \ell_N(m,r) \) that satisfy
\[
\rho_N(m,\ell_N(m,r)) = r
\]
by numerical simulations using a PERM algorithm \cite{22-25}. For very short chains \((N \leq 100)\) we were able to explore a large portion of the space \((m, \lambda)\), finding that for very short chains
\[
N\ell_N(m,r) = [\lambda_N(r)N + \delta_N(r)\cdot mN]
\]
is verified with extremely high accuracy at any observed \(r\). For small chains we observe that the level curves of \(\rho_N(m,\lambda)\) appears to be straight lines (see Figure 3).

Given the small size of the chains we cannot conclude much from this observation, but driven by this preliminary experiment we decided to perform an intensive investigation of the curve \(\ell_N(m,1)\),
\[
\rho_N(m,\ell_N(m,1)) = 1,
\]
which from previous considerations is expected to converge to the critical line
\[
\lim_{N \to \infty} \ell_N(m,1) = \ell_c(m).
\]

The PERM algorithm, which is very efficient in simulating \(\theta-\)point chains, allowed to evaluate \(\ell_N(m,1)\) up to chains with \(N = 500\) in a macroscopic portion of the \((M,L)\) space. We found stronger evidences that at least the curve \(\ell_N(m,1)\) is still a line up to integer truncation,
\[
N\ell_N(m,1) = [\lambda_N(1)N + \delta_N(1)\cdot mN],
\]
suggesting the conjecture that the critical line may remain a line in the thermodynamic limit, with critical coefficients eventually satisfying
\[
\lim_{N \to \infty} \lambda_N(1) = \lambda_c, \lim_{N \to \infty} \delta_N(1) = \delta_c.
\]

This linearity property can be explained roughly as follows. Following \cite{21}, let slice the chain \(\omega_N\) into a number \(n\) of sub-chains
\[
\omega_N = \{\omega^0_T, \omega^1_T, \ldots, \omega^n_T\}
\]
each of size \(T = N/n\). The sub-chains are indicated with
\[
\omega^i_T = \{x^i_0, x^i_1, \ldots, x^i_T\} \subset \omega_N
\]
Figure 3. Transition line \( \rho_N (m, \lambda) = 1 \) for chains up to \( N = 500 \) for a large portion of the parameter space using a PERM algorithm. The line from different \( N \) are shown on the same graph to allow comparison. The length of the chains varies from \( N = 25 \) to 500. The linear behavior of the critical level line seems present also for longer chains. The intercepts at \( M = 0 \), extrapolated from linear fits, are shown as white squares in the next Figure 4 A.

and satisfy the chain constraint \( x_T^i = x_T^{i+1} \). If we neglect the self-intersections between the blocks, as is expected in a SRW-like chain [17], we can approximate the probability measure conditioned on the transition line with a product measure.

Now, as in [21] we assume that each sub-chain can be either a critical ISAW, with local densities \((0, \lambda_0)\), or a SRW, with average local densities \((m_0, \lambda_0)\). Then we could write

\[
p_0 ([mN], [\ell_c (m) N]) \simeq \prod_{i=1}^{n} p_0 (0, [\lambda_c N]^T) p_0 ([m_0 N], [\lambda_0 N])^{(1-\phi)^T} \tag{46}
\]

with \( \phi^i \in \{0, 1\} \) keeping record of the subchain type. One in the end finds that under the above product measure condition the averages of \( M (\omega_T) \) and \( L (\omega_T) \) satisfy the relation

\[
\langle L (\omega_N) \rangle_{[mN], [\ell_c (m)]} \simeq \lambda_c N - \left( \frac{\lambda_c - \lambda_0}{m_0} \right) \langle M (\omega_N) \rangle_{[mN], [\ell_c (m)]}. \tag{47}
\]

Notice that unlike in the \( \Omega_N (M) \) model of [21], where the product measure condition is expected to be only approximate due to the strong excluded volume effects for \( m < m_0 \), here the constraint to stay on the transition line forces the chains to behave like SRWs and then the product measure condition should hold exactly.
III. A CONSEQUENCE FROM SRW THEORY

An important consequence of the previous conjecture is that the critical energy density of the ISAW $\lambda_c$ would be computable in terms of SRW measurable quantities.

In fact, we remark that the $p_0([mN],[\lambda N])$ is expected to concentrate on $(m_0,\lambda_0)$. Since the average squared end-to-end distance in the SRW is exactly $N$ we can conclude that also this point must lie on the transition line

$$\ell_c (m_0) = \lambda_0$$

(48)

Then, by the previous linearity conjecture we should be able to conclude that the ratio

$$\delta_N^* = \frac{\langle L(\omega_N) \rangle_{\beta} - \langle L(\omega_N) \rangle_0}{\langle M(\omega_N) \rangle_{\beta} - \langle M(\omega_N) \rangle_0}$$

(49)

converges to the actual $\delta_N$ (and then to the angular coefficient of the critical line in the TL) under the constraint of constant end-to-end distance

$$\langle x_2^2 (\omega_N) \rangle_{\beta} = \langle x_2^2 (\omega_N) \rangle_0.$$  

(50)

To compute this estimator we expand the Boltzmann factor in the limit of infinite temperature, i.e., for small $\beta$

$$e^{-\beta_1 M - \beta_2 L} = 1 - \beta_1 M - \beta_2 L + O(\beta^2)$$

(51)

and then compute the averages. It can be shown after some algebra that in the limit of infinite temperature the differences are then approximated by the expressions

$$\langle L(\omega_N) \rangle_{\beta} - \langle L(\omega_N) \rangle_0 = -\beta_2 \Delta L_N^2 - \beta_1 \Delta Q_N$$

(52)

$$\langle M(\omega_N) \rangle_{\beta} - \langle M(\omega_N) \rangle_0 = -\beta_2 \Delta Q_N - \beta_1 \Delta M_N^2$$

where in order to simplify the formulas we introduced a notation for the variances of links and intersections,

$$\Delta L_N^2 = \langle \Delta L^2 (\omega_N) \rangle_0, \Delta M_N^2 = \langle \Delta M^2 (\omega_N) \rangle_0,$$

(53)

and one for the correlation between $M(\omega_N)$ and $L(\omega_N)$ under the SRW measure

$$\Delta Q_N = \langle \Delta M(\omega_N) \Delta L(\omega_N) \rangle_0.$$

(54)

The ratio $\beta_1/\beta_2$ is obtained from the constraint of having a constant average end-to-end distance applied to the first order expansion in $\beta$, 

$$\langle x_2^2 (\omega_N) \rangle_{\beta} - \langle x_2^2 (\omega_N) \rangle_0 \simeq -\beta_1 \Delta P_N - \beta_2 \Delta T_N = 0$$

(55)
where we again simplified the notation by introducing a symbol for the correlations between $M(\omega_N)$ and $x^2_N(\omega_N)$,

$$\Delta P_N = \langle \Delta M(\omega_N) \Delta x^2_N(\omega_N) \rangle_0$$  \hspace{1cm} (56)$$
and that between $L(\omega_N)$ and $x^2_N(\omega_N)$, which is

$$\Delta T_N = \langle \Delta L(\omega_N) \Delta x^2_N(\omega_N) \rangle_0.$$  \hspace{1cm} (57)$$
Finally, substituting the ratio $\beta_2/\beta_1$ obtained from the last formula into the approximate expression for $\delta^*_N$ we obtain the relation

$$\delta^*_N = \frac{\Delta Q_N + \left( \frac{\Delta P_N}{\Delta M_N^2} \right) \Delta L_N^2}{\Delta M_N^2 + \left( \frac{\Delta P_N}{\Delta M_N^2} \right) \Delta Q_N}$$  \hspace{1cm} (58)$$
that, assuming true our conjecture, would allow to compute the critical energy density of the ISAW in the TL from the formula

$$\lambda^*_N = L_N + \delta^*_N M_N.$$  \hspace{1cm} (59)$$

IV. CONCLUSIONS AND OUTLOOKS

Concerning the form of the transition line, it is important to remark that the conjecture in Eq. (59) would open to interesting analytical prospects. In fact, the quantity $\delta^*_N$ does not depend on $\beta$ and all the averages are respect to the SRW measure. We expect that, apart from messy algebra, the asymptotics of the necessary correlation functions can be computed using the very same techniques developed by Jain and Pruitt to compute the variance of the SRW range [27, 29–31, 33]. This would be a nice result, since to the best of our knowledge no exact expression is known or even conjectured for the ISAW critical energy.

Another interesting fact is that the model can be described by a seven color urn model. Since $L(\omega_N)$ can increase only if $M(\omega_N)$ does not, it holds

$$L(\omega_{N+1}) - L(\omega_N) = \left\{ 1 - [M(\omega_{N+1}) - M(\omega_N)] \right\} \frac{\pi(\omega_{N+1})}{2d}$$  \hspace{1cm} (60)$$
Figure 4. Comparison between the critical ISAW energy from independent PERM simulations with the estimator of Eq. (59) up to $N = 1000$ computed with an unbiased algorithm. In the top figure A, semi-log scale, the black line is the estimator $\lambda_N^*$ with its error (standard deviation), obtained from an unbiased simulation, while the black dots are values obtained with an independent PERM simulation. Finally, the white squares are the intercepts at $M = 0$ from linear fits of the previous Figure [5]. The bottom image B shows the difference $\lambda_N^* - \lambda_N$ between ISAW critical energy and Eq. (59) in log-log scale. The difference is fitted with a power law $K_0 x^{-c}$, with $K_0 = 0.1124 \pm 0.0005$ and exponent $c = -0.38 \pm 0.01$. Notice that the error bars in B mostly comes from the unbiased SRW simulation, as PERM algorithms are much more efficient in computing theta-polymers than random walks.

where we used the symbol

$$\pi (\omega_N) = \langle M(\omega_{N+1}) - M(\omega_N) | \omega_N \rangle_0 = \frac{1}{2d} \sum_{x \in \mathbb{Z}^d} I(x \in \omega_N) I(|x - x_N(\omega_N)| = 1)$$  \hspace{1cm} (61)
to indicate the atmosphere of the chain (see \[21\]). Given the urn kernels

\[
\pi^{(k)}_N(M,L) = \langle I(L(\omega_N) - L(\omega_{N-1}) = k) \rangle_{M,L}
\]  

(62)

for \(0 \leq k \leq 2d\) we conjecture that

\[
\pi^{(k)}(m,\lambda) = \lim_{N \to \infty} \pi^{(k)}_N(\lfloor mN \rfloor, \lfloor \lambda N \rfloor)
\]  

(63)

exists for all considered \(k\), and that it would be possible to extend the urn techniques presented in \[21\,32\] to deal with the urn model controlled by the kernels \(\pi^{(k)}(m,\lambda)\). Notice that for \(k = 0\) one would have

\[
\pi^{(0)}_N(M,L) = \langle I(L(\omega_N) - L(\omega_{N-1}) = 0) \rangle_{M,L} = \langle I(M(\omega_N) - M(\omega_{N-1}) = 1) \rangle_{M,L}
\]  

(64)

and that by definition must hold

\[
1 - \pi^{(0)}_N(M,L) = \sum_{k=1}^{2d} \pi^{(k)}_N(M,L).
\]  

(65)

We conclude with one last remark. Due to difficulties in simulating long chains when \(m\) is close to 1 we where unable to directly check the behavior in this region. At first we where tempted to further push the conjecture and guess that in the TL the critical line hits the value \(\lambda = 0\) at \(m = 1\), but our PERM estimates seem to exclude this simple ansatz because the observed \(\lambda_N(1)\) is always below the value \(\lambda_c = \lambda_0 / (1 - C_3) \approx 1.5238\) for which a “linear” critical line can pass trough the point \((m_0, \lambda_0)\), that must lie on the critical line in any case (from SRW theory \(\lambda_0 = 6 \cdot C_3 / (1 + C_3) \approx 1.005\) and \(m_0 = C_3 \approx 0.3405\) [16]),

and then hit the boundary 3 \((1 - m)\) of the allowed parameter space at \(m = 1\) exactly.

Then, if the linear behavior of \(\ell_N(m)\) can be really extended in the whole \(m\) range and \(\lambda_c < \lambda_0 / (1 - C_3)\) this would imply the existence of a second critical value for the intersection density, ie the \(m^* = C_3 \cdot (\lambda_c - 3) / (\lambda_c - \lambda_0 - 3 \cdot C_3)\) at which the crossing between the critical line \(\ell_c(m)\) and the boundary 3 \((1 - m)\) actually happens, and after this value the clustered phase would not be possible anymore except for values of \(\lambda\) concentrating on the boundary of the parameter range. For or example, the conjecture would imply that no CG transition can occur for \(m < 1\) in the \(\Omega_N(0, \lfloor mN \rfloor)\) model, where the nearest neighbor pairs are forbidden. This is likely because in a clustered phase we necessarily have a partial saturation of the nearest neighbor sites of each monomer, and such phase would be extremely unfavored by a small link density.

V. ACKNOWLEDGMENTS

We would like to thank Giorgio Parisi (Sapienza Univeristà di Roma) and Valerio Paladino (Amadeus IT) for interesting discussions and suggestions. This project has received funding from the European Re-
search Council (ERC) under the European Union’s Horizon 2020 research and innovation programme (grant agreement No [694925]).

[1] P. J. Flory, Principles of Polymer Chemistry (Cornell University Press, 1971).
[2] I. Nishio, S.-T. Sun, G. Swislow and T. Tanaka, Nature 281, 208–209 (1979).
[3] K. Minagawa Y. Matsuzawa K. Yoshikawa A. R. Khokhlov and M. Doi, Biopolymers 34, 555-558 (1994).
[4] P. G. de Gennes, Scaling Concepts in Polymer Physics, Cornell University Press (1979).
[5] J. des Cloizeaux and G. Jannink, Polymers in solutions: Their Modelling and Structure, Clarendon Press, Oxford (1990).
[6] A. Y. Grosberg and D. V. Kuznetsov, Macromolecules 25, 1970 (1992).
[7] P. P. Nidras, J. Phys. A: Math. Gen. 29, 7929 (1996).
[8] M. C. Tesi, E. J. J. van Rensburg, E. Orlandini and S. G. Whittington, J. Phys. A: Math. Gen. 29 2451 (1996).
[9] M. C. Tesi, E. J. J. van Rensburg, E. Orlandini and S. G. Whittington, J. Stat. Phys. 82, 155–181 (1996).
[10] S. Caracciolo, M. Gherardi, M. Papinutto and A. Pelissetto, J. Phys. A 44, 115004 (2011).
[11] C.-N. Chen, Y.-H. Hsieh and C.-K. Hu, EPL 104, 20005 (2013).
[12] N. R. Beaton, A. J. Guttmann and I. Jensen, J. Phys. A: Math. Theo. 53, 165002 (2020).
[13] C. Domb and G. S. Joyce, J. Phys. C: Solid State Phys. 5, 956 (1972).
[14] N. Clisby, J. Phys.: Conf. Ser. 921 012012 (2017).
[15] G. Slade, Proc. R. Soc. A, 475, 20181549 (2019).
[16] J. F. Douglas and T. Ishinabe, Phys. Rev. E 51, 1791 (1995).
[17] N. Madras and G. Slade, The Self-Avoiding Walk (Birkhauser, Boston, 1996).
[18] N. Clisby, Phys. Rev. Lett. 104, 055702 (2010).
[19] N. Clisby, J. Phys. A: Math. Theor. 34, 5773 (2013).
[20] S. Franchini, Phys. Rev. E 84, 051104 (2011).
[21] S. Franchini and R. Balzan, Phys. Rev. E 98, 042502 (2018).
[22] The Pruned-Enriched Rosenbluth Method (PERM) is a classic stochastic growth algorithm which combines the Rosenbluth-Rosenbluth method with recursive enrichment. One starts by building instances according to a biased distribution, then corrects for this by cloning desired and killing undesired configurations to contain the weights fluctuations, see [23–25] for reviews and [23] for a pseudocode.
[23] P. Grassberger, Phys. Rev. E 56, 3682 (1997).
[24] T. Prellberg and J. Krawczyk, Phys. Rev. Lett. 92, 120602 (2004).
[25] H.-P. Hsu and P. Grassberger, J. Stat. Phys. 144, 597 (2011).
[26] F. Spitzer, Principles of Random Walk (Springer, New York, 2001).
[27] B. D. Hughes, Random Walks and Random Environments, Vol.1 (Clarendon Press, Oxford, 1995).
[28] W. Feller, An introduction to Probability Theory and Its Applications, Vol. 1 (Wiley, New York, 1950).
[29] N. C. Jain and W. E. Pruitt, J. Analyse Math. 24, 369 (1971).
[30] N. C. Jain, S. Orey, Isr. J. Math. 6, 373 (1968).
[31] A. Dvoretzky and P. Erdos, Proc. 2nd Berkley Symp. on Prob. and Stat., 353 (1951).
[32] S. Franchini, Stoc. Proc. Appl. 127 (2017).
[33] F. Den Hollander, J. Stat. Phys. 37 (1984) 331-367.
[34] D.C. Brydges and G. Slade, J. Stat. Phys. 159 (2015) 421-667.