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Coarse-grained Flory approximation for a polymer chain at the Θ point in two dimensions

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An interpretation of the Flory approximation as a course graining of the free energy of a polymer chain, recently introduced by R. Dekeyser, A. Maritan, and A. L. Stella [Phys. Rev. A **36**, 2338 (1987)] is used for the discussion of the conformational properties of a polymer chain at the Θ point in two dimensions. With the inclusion of a short-range nonintersection condition together with long-range three-body repulsion, and the use of scaling invariance arguments, the estimate $\nu_\Theta=\frac{7}{12}=0.583\ldots$ is obtained for the scaling of the average end-to-end distance with the number of monomers. This is in very good agreement with experimental and numerical work, and just 2% off the conjectured exact value $\nu_\Theta=\frac{4}{7}=0.571\ldots$.

The conformational properties of a flexible polymer chain in a poor solvent result from the competition between excluded-volume effects (which tend to swell the chain) and net van der Waals attraction between monomers.[1] At high temperatures, excluded volume dominates and the self-avoiding random walk (SAW) model is a good description for the problem. As temperature is lowered, the relative importance of van der Waals forces grows, until the chain collapses at a critical temperature $T_c=\Theta$. Below T_c, attraction wins over excluded volume, and the chain is compact. At the Θ point, repulsion and attraction somehow balance each other, giving rise to a third (intermediate) behavior between SAW and that of the collapsed state. Considering the average end-to-end distance $\langle R_N^2\rangle^{1/2}$ for an N-monomer chain in space dimensionality d, one then has

$$\langle R_N^2\rangle^{1/2}\sim\begin{cases}N^{\nu_{\mathrm{SAW}}}, & T>\Theta\\ N^{\nu_\Theta}, & T=\Theta\\ N^{1/d}, & T<\Theta\end{cases}\tag{1}$$

where $\nu_{\mathrm{SAW}}\cong 3/(d+2)$, as given by the Flory formula,[2] for $1\leq d\leq 4$.

The details of the mechanism responsible for the intermediate behavior at the Θ point are not entirely clear as yet. It is usually accepted that the two-body attraction cancels the excluded volume condition at the Θ temperature and that a three-body net repulsion then becomes the leading term in the free energy. However, in $d=3$ the three-body interaction becomes irrelevant and a three-dimensional chain at the Θ point behaves ideally (that is, $\nu_\Theta=\frac{1}{2}$).[3] Actually, since $d=3$ is the upper critical dimensionality for the three-body interactions in this case, logarithmic corrections are expected,[4] but these are extremely difficult to observe. Experiments and numerical work support $\nu=\frac{1}{2}$ in this case.[5] In the only other physically realizable dimension, $d=2$, three-body repulsion is relevant, and one must have $\frac{1}{2}<\nu_\Theta<\nu_{\mathrm{SAW}}=\frac{3}{4}$. Experiments[6] and numerical work[7-12] indeed give ν_Θ in the range 0.55–0.58. It has been proposed that a polymer chain in two dimensions at the Θ point has the same statistics as the hull of a two-dimensional percolation cluster,[13] for which the (conjectured) exact value of the exponent ν is $\frac{4}{7}$.[14] (Actually, the equivalence is between the hull of the percolation cluster and a SAW with annealed obstacles, which in turn is believed to be in the same universality class as a polymer at the Θ point[13,15].) Thus one predicts $\nu_\Theta=\frac{4}{7}=0.5714\ldots$, in agreement with the above-mentioned estimates.

In spite of the general belief in the three-body mechanism, it is important to note that this is not explicitly included in numerical work, either in three[5] or two[7-12] dimensions. What researchers do, is insert only the following two elements: (i) the SAW condition and (ii) two-body attraction between nearest-neighbor visited sites which are not adjacent along the chain. From this, they find SAW behavior at high temperatures, collapse at low temperatures, and an intermediate state in between, which is then identified with the Θ-point regime. To the present author's knowledge, a three-body interaction term has been explicitly taken into account only in the early work of de Gennes;[4,5] through an ε expansion in the context of a field-theoretical study of the tricritical point of the zero-component vector model, the estimate $\nu_\Theta\cong 0.5055$ in $d=2$ was obtained there. Very recently, it has been shown[16] that SAW's with annealed obstacles in $2<d<4$ are identical to the standard model of the Θ point in the sense that the annealed disorder induces two-body attractive plus three-body repulsive forces. At $d=2$, however, all orders of interactions are relevant in the annealed disorder model, and one cannot draw a conclusion about the Θ point behavior. On the other hand, a simple Flory approximation (to be discussed in detail below) which includes three-body repulsion correctly predicts ideal behavior in $d=3$, but gives $\nu_\Theta=\frac{2}{3}\cong 0.67$ in $d=2$. Thus one may well ask whether modeling a chain at the Θ point explicitly through a three-body repulsion or through the SAW condition plus two-body attraction are physically compatible descriptions. The above-mentioned results seem to indicate that the answer is no, and that experimental results tend to favor the latter picture. However, for the following reasons it is not easy to discard the three-body repulsion scenario completely. First, it correctly predicts that the chains at the Θ point are ideal in $d=3$ and slightly swollen (but not as much as pure SAW's) in $d=2$ (this is obtained only *a posteriori* from calculations performed on SAW's with two-body attractions). Second, since the Θ transition always takes place in the limit of very low monomer concentration ρ,[5] properties such as the osmotic pressure must be properly described by the nonzero term of lowest order in a virial expansion in powers of ρ; as the Θ transition is usually associated to the vanishing of the second virial coefficient (although this is not rigorous, see below), the physical picture at the Θ point must be dominated by the third virial coefficient, related to a three-body interaction. Third, it can be argued that the numerical result of de Gennes is poor because its obtainment involves the stretching, up to $\varepsilon=1$, of an expansion to second order in the (supposedly small) parameter $\varepsilon\equiv 3-d$.

In what follows, we show that a Flory-like approach to the conformational properties of a polymer chain at the Θ point in $d=2$ gives results entirely in agreement with experiment and numerical work (although there is a slight discrepancy relative to the conjectured exact $\nu_\Theta=\frac{4}{7}$). To the standard arguments (which give $\nu_\Theta=\frac{2}{3}$) we add (i) the assumption that, on small scales for $d=2$, the excluded volume condition prevails, as has been noticed in extensive Monte Carlo work in $d=3$;[5] and (ii) scaling-invariance ideas derived from an interpretation of the Flory approximation as a coarse graining of the free energy, which in turn has been introduced by Dekeyser, Maritan, and Stella.[18,19] The physical picture emerging from this indicates that, while the long-range SAW condition is balanced by the two-body attraction, the short-range SAW condition actually *screens* the three-body repulsion to some extent; by lowering the number of contacts between monomers on short scales, the SAW condition acts as a centrifugal force between parts (each composed by several monomers) of the chain (blobs). This lowers the repulsive energy originated from three-blob contacts.

The standard Flory approach for a chain with N monomers and end-to-end distance R, with three-body repulsion, goes as follows: the energy is approximated as the integral over the volume ($\sim R^d$) of the cube of the average density $[\sim(N/R^d)^3]$; the entropy is that of a random walk ($\sim R^2/N$). The free energy is then

$$F\sim aN^3R^{-2d}+bR^2N^{-1}\;. \tag{2}$$

Assuming $R\sim N^{\nu_\Theta}$ and minimizing F relatively to R, one obtains

$$\nu_\Theta=2/(d+1) \tag{3}$$

for $d\leq 3$. For $d>3$, the Flory approximation correctly predicts the energy to be irrelevant, thus $\nu=\frac{1}{2}$. The logarithmic corrections at the borderline dimension $d=3$ cannot be obtained from this approach. The result for $d=2$, however, overshoots the conjectured exact value $\frac{4}{7}$ by $\simeq 17\%$. This means that the repulsive energy has been greatly overestimated, and screening effects must be present in the actual physical problem. Below, we first reobtain the unscreened energy in the coarse-graining interpretation, then proceed to include screening within the same context.

Following Dekeyser, Maritan, and Stella,[19] we divide the chain into segments with l monomers each ($1\ll l\ll N$). In the spirit of the Flory approach, each segment is considered as a noninteracting random walk, with linear dimension $\sim\sqrt{l}$. In space dimension d, the average number of three-segment encounters (self-intersections) will be $\sim(N/l)^3(R/\sqrt{l})^{-2d}$, again in the mean-field context.[20] In order to give the energy, that is, the total number of *three-monomer* interactions, this must be multiplied by the number of intersections between independent replicas of segments (mutual intersections). This is the average segment elongation ($\sim\sqrt{l}$) raised to the fractal dimension of the set of mutual intersections. Now, for the energy to be properly l independent one must consider the fractal dimensionality of the set of *triple* intersections of random walks[19,21] [which for general k-multiple intersections in dimension d is given by $kd_w-(k-1)d$, where $d_w=2$ is the fractal dimension of a random walk]. Thus we have the number of mutual intersections $\sim(\sqrt{l})^{6-2d}$. Although in the special case $d=2$ this set has dimension 2 for any k (see above), thus our argument below is insensitive to this, we note that this is the *only* way for the coarse-grained energy to be l independent for generic k and d in this approach. This implies that the fractal dimension of k-multiple points (instead of, e.g., double points) must be considered when counting mutual segment-segment intersections. This point has not been made previously. The unscreened three-body interaction is then given by $(N/l)^3(R/\sqrt{l})^{-2d}(\sqrt{l})^{6d-2d}=N^3R^{-2d}$, as before. The entropy in this picture is $\sim(R/\sqrt{l})^2/(N/l)=R^2/N$, remaining unchanged as well. We now specialize to $d=2$.

Screening effects are included by recalling that, in $d=3$, short-range chain stiffness has been noticed to persist even at the Θ point.[5] As the authors of Ref. 5 point out, at the Θ-point two-body attractions and long-range SAW condition cancel, but the short-range SAW condition remains. This is the only remaining interaction, since in $d=3$ the three-body term is already irrelevant, and does not have any long-range effect. On the other hand, if we assume that in $d=2$ the short-range SAW condition persists as in $d=3$, its effects on the three-body (long-range) term can be calculated as follows.

It has been found by Dekeyser, Maritan, and Stella[19] that the number of mutual intersections of N-step 5-tolerant walks in $d=2$ is lowered by a factor $N^{-\alpha}$ relative to self-intersections of the same walk (which is $\sim N$). This screening is due to the existence of self-repulsion effects which eventually induce SAW behavior (if it were otherwise, the number of mutual intersections between two pure random walks would differ from that of self-intersections of a single walk). It is found numerically that $\alpha=\frac{1}{2}$, and a simple fractal argument[19] shows that in general $d,\alpha=d\nu_{\mathrm{SAW}}-1$ (in $d=2$, with $\nu_{\mathrm{SAW}}=\frac{3}{4}$, $\alpha=\frac{1}{2}$ follows immediately). As the energy term has been calculated with the three-body interaction alone, we now include the additional short-range SAW condition via the screening of mutual intersections on the segment scale [number of steps $=l$, thus screening $\sim(l)^{-1/2}$ in $d=2$]. That is, instead of being $\sim(\sqrt{l})^{6-2d}=(\sqrt{l})^2$, the number of mutual intersections will be $\sim(\sqrt{l})$. The identification of the (immaterial) segment length l with the range of the SAW condition must not be taken literally: all that matters is that short-range effects be properly taken into account under coarse graining. Now, for the energy term to remain l independent (which is a necessary requisite in this interpretation of the Flory approach[19]), the self-intersection term $(N/l)^3(R/\sqrt{l})^{-2d}$ must be multiplied by $l^{1/2}$. As it is the number of intersections (and not, e.g., a distance) which is being renormalized, the proper combination is $(N/l)^{-1/2}$. Thus the energy becomes

$$\left[\frac{N}{l}\right]^{-1/2}\left[\frac{N}{l}\right]^{3}\left[\frac{R}{\sqrt{l}}\right]^{-2d}(\sqrt{l})^{6-2d}(l)^{-1/2} \sim N^{5/2}R^{-2d} \qquad (4)$$

in $d=2$. Assuming $R\sim N^{\nu_\Theta}$, and with the entropy written as R^2N^{-1}, the usual minimization gives

$$\nu_\Theta=\tfrac{7}{12}=0.583\ldots\ (d=2)\ . \qquad (5)$$

This is in very good agreement with experiment [which gives $\nu_\Theta=0.56\pm0.01$ (Ref. 6)], and numerical work (e.g., Ref. 12 gives $\nu_\Theta=0.570\pm0.015$), although slightly overestimated. The situation is similar to that of pure SAW's in $d=3$, where the Flory approach gives $\nu=\frac{3}{5}$, while experiment and numerical work point to $\nu\sim0.59$.[22] Assuming $\nu_\Theta=\frac{4}{7}$ to be exact in the present case, the discrepancy is $\sim2\%$, of the same order as that for $3d$ SAW's.

It will not be surprising if the value $\nu_\Theta=\frac{7}{12}$ turns out not to be exact; at the moment, however, numerical accuracy does not seem enough to allow a clear decision between it and the conjectured $\frac{4}{7}$ (or to show that neither is true). On the other hand, the main point of this work has been to show that the picture of a polymer at the Θ point as a SAW with two-body attractive interactions is compatible with that of a random walk with three-body repulsion, provided that a short-range SAW condition is included in the latter. This is consistent with the idea that the Θ temperature is *not* coincident with the Boyle temperature, at which the second virial coefficient vanishes[1,23] (see also Fig. 13 of Ref. 5). One could speculate that the value of $\nu_\Theta=\frac{2}{3}$ for the unscreened three-body interaction in $d=2$ would relate to a second transition, at the Boyle temperature. There is, however, no evidence that such a transition occurs; on the contrary, theoretical work[24] points to the existence of a unique Θ transition in $d=2$.

In summary, it has been shown that, for polymers at the Θ point in $d=2$ the following physical picture is consistent with experimental and numerical work. Although long-range SAW condition and two-body attraction cancel each other, a short-range SAW condition persists, which actually *screens* the (longer-range) three-body repulsion, thus causing in $d=2$ a decrease in the linear dimensions of the chain, relative to what these would be with the bare three-body term. In $d=3$, this mechanism is irrelevant. From a Flory approach incorporating the basic remaining interactions, and with the help of a coarse-graining interpretation, together with scaling-invariance concepts, the value of $\nu_\Theta=\frac{7}{12}$ has been obtained. This is in very good agreement with experimental and numerical results (which are in the range 0.55–0.58) and only $\sim2\%$ off the conjectured exact $\nu_\Theta=\frac{4}{7}$.

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