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Phase diagram and critical behaviour of homopolymers with steric frustration

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Abstract. The effect of steric frustration on the collapse of a linear homopolymer is investigated. Depending on the temperature and the strength of the frustration, we find that three different phases exist: swollen, compact and branched. We study the phase diagram and the critical behaviour of the system through exact enumerations and Monte Carlo simulations. In addition we present an analytical argument which determines qualitatively the phase boundaries. Despite the similarity between our model and one previously introduced in the literature, there is a discrepancy on the value of a critical exponent.

A polymer in a good solvent is usually modelled by a self-avoiding walk (SAW). The self-avoiding constraint takes into account the repulsive forces acting between monomers in a real polymer. In this regime the polymer radius of gyration grows as $\langle R \rangle \sim N^{\nu_{\text{SAW}}}$, where N is the molecular weight and $\nu_{\text{SAW}} = \frac{3}{4}$ [1] in $d = 2$ and $\nu_{\text{SAW}} \sim 0.59$ [2] in $d = 3$.

If, however, the polymer is immersed in a poor solvent, attractive van der Waals interactions between the monomers will also come into play. They will cause, at sufficiently low temperatures, a collapse of the polymer from a self-avoiding into a compact, globular configuration where the exponent ν takes on the value $\frac{1}{d}$, where d is the dimension of space. The transition point is called θ point [2, 3] and it is characterized by an exponent $\nu_{\theta} = \frac{4}{7}$ in $d = 2$ [4] ($d = 3$ turns out to be the upper critical dimensionality, so that $\nu_{\theta} = \frac{1}{2}$).

The θ transition has in recent years attracted much theoretical interest, mostly in connection with universality issues [4, 5]. In all these studies the short-range interactions were modelled in the simplest ways and no particular attention has been paid to verify whether their form can influence the nature of the collapsed phase. Recently, however, several authors [6–8] have outlined the possibility that peculiar interaction mechanisms can induce a collapse in different stages and towards different compact phases. This possibility would imply a richer scenario and a wider degree of nonuniversality than those contemplated in the usual θ point physics. In this respect we find of particular interest a model introduced in [8], since it exhibits a rich phase diagram with a swollen ($\nu_s = \frac{3}{4}$ [1]), a compact ($\nu_c = \frac{1}{2}$) and a branched polymer phase ($\nu_b = 0.64075 \pm 0.00015$ [9]).

In this work we consider a two-dimensional homopolymer that differs from the model in [8] only in microscopic details. These differences turn out to be irrelevant, so that the two models present the same scaling behaviour. It is interesting to note that both formulations

can be directly related to a model recently introduced [10] to mimic protein behaviour and in particular to take into account that different amino acids have different sizes and therefore a different capability of admitting surrounding molecules. We believe this provides a nice physical interpretation, not underlined in [8].

For the sake of simplicity we consider the model on a square lattice, but generalization to different lattices and/or higher dimensions is also possible. Let $i = 0 \dots N$ be the coordinate of the vertices along the walk. A pair of nonconsecutive vertices in the chain ($|i - j| \neq 1$) interact through an attractive nearest-neighbour potential ω . This would be the standard lattice model studied for the collapse transition of linear polymers [5]. In addition, we have included an effect of steric frustration by assigning an energy penalty ϵ to each monomer i with four nearest-neighbour sites occupied (including possibly monomers $i + 1$ and $i - 1$). The partition function of the model can be written as

$$Z_N = \sum_{m,l} C_N(m, l) e^{\omega m - \epsilon l} \quad (1)$$

where $C_N(m, l)$ denotes the number of distinct N -step SAWs with m contacts and l ‘frustrated’ monomers. For $\epsilon = 0$ the model reduces to a standard attractive SAW: it undergoes a θ collapse at a critical $\omega_c \approx 0.65$. In the limit $\epsilon \rightarrow \infty$, instead, each monomer is forced to have at most three nearest-neighbour sites occupied. The polymer therefore optimizes its energy by arranging itself in two parallel straight segments at a distance of one (in lattice units). This consideration suggests that for small enough temperatures (and $\epsilon = \infty$) the polymer could prefer a branched structure (on a coarsed-grained level). The difference from the model considered in [8] is restricted to the form of the interaction favouring ramification: in [8] a fugacity y was given to every step of the walk having two parallel steps at unit distance.

We first studied the phase diagram of the system as a function of ϵ and ω by performing exact enumerations of SAWs up to $N = 28$ steps, extending the $N = 26$ steps analysis of [8]. We have determined the series of $C_N(m, l)$ and $S_N(m, l)$, where $S_N(m, l)$ is the sum of the radius of gyration of all N -step SAWs having m contacts and l frustrated monomers. From these quantities the average radius of gyration of the polymer can be easily computed as

$$R_N^2 = \frac{\sum_{m,l} S_N(m, l) e^{\omega m - \epsilon l}}{\sum_{m,l} C_N(m, l) e^{\omega m - \epsilon l}} \quad (2)$$

To avoid parity effects we have grouped separately even and odd lengths and then formed effective exponents ν_N through the relation

$$2\nu_N = \frac{\ln \frac{R_N^2}{R_{N-2}^2}}{\ln \frac{N}{N-2}} \quad (3)$$

In figure 1 we have plotted ν_N as a function of ω for (a) $\epsilon = 0.2$ and (b) $\epsilon = \infty$. In both cases the curves intersect at a common point, signalling the presence of a transition from a high- to a low-temperature phase [11]. From scaling theory we have taken the coordinates of this intersection to be the critical ω and the value of the exponent ν at the collapse transition. In figure 2 we have reported the behaviour of ν along the transition line as a function of ϵ . We have identified the transition point to be where the dispersion of the ν_N curves is at a minimum. For small values of ϵ the critical exponent is $\nu = 0.58 \pm 0.01$, whereas by increasing ϵ further it seems to move to a different value. This is an indication that a transition from a swollen to a branched phase takes place. Universality class considerations suggest that the curve of figure 2 ideally should be a step function and the rounded shape is

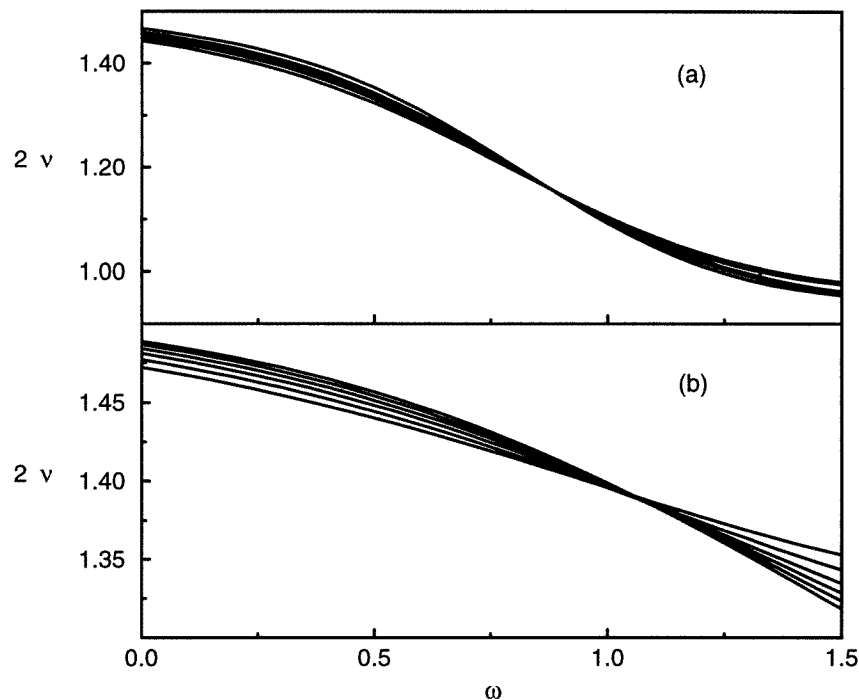


Figure 1. Exact enumeration results for the effective exponent ν_N as a function of ω for (a) $\epsilon = 0.2$ and (b) $\epsilon = \infty$. The lengths are $N = 18, 20, 22, 24, 26, 28$. Similar plots result from considering odd lengths.

just a crossover effect. All the points in the transition line from the swollen to the compact phase presumably belong to the universality class of the θ -collapse of a linear polymer, so that the correlation length exponent is $\nu_{s-c} \approx 0.57$. Similarly one can predict that the transition from swollen to branched polymer is dominated by a different unique fixed point, which determines the critical exponents ν_{s-b} ($0.64 \leq \nu_{s-b} \leq 0.75$).

The complete phase diagram obtained from series analysis is shown in figure 3 as isolated points. This is in good agreement with the phase diagram reported in [8]. The relatively large error bars on the points determining the compact–branched transition reflect the intrinsic difficulty of using series to describe such a transition [12]. Indeed most of the ν_N curves do not intersect, although a region where their distance has a pronounced minimum is visible. For this reason we have complemented the analysis by looking at a thermal quantity such as the specific heat. The corresponding curves show a peak which grows and sharpens with increasing N , possibly indicating the presence of a phase transition.

The phase behaviour of the system could also be conjectured from the following heuristic argument, based on energy–entropy balance. We assume the polymer can be in three different phases (swollen, compact and branched) and we estimate the corresponding free energies by the competition between energy and entropy.

(i) *Swollen phase.* The average number of contacts $\langle m \rangle$ in a noninteracting SAW is $\langle m \rangle \sim aN$, with $a \approx 0.16$ [13], whereas the total number of SAWs scales as $N_{\text{SAW}} \sim \mu_{\text{SAW}}^N$, where $\mu_{\text{SAW}} \approx 2.64$ [14] is the connectivity constant of the SAWs. For sufficiently high temperatures, the free energy of the swollen phase is therefore reasonably approximated by

$$\beta F_s \simeq -aN\omega - N \ln \mu_{\text{SAW}} \quad (4)$$

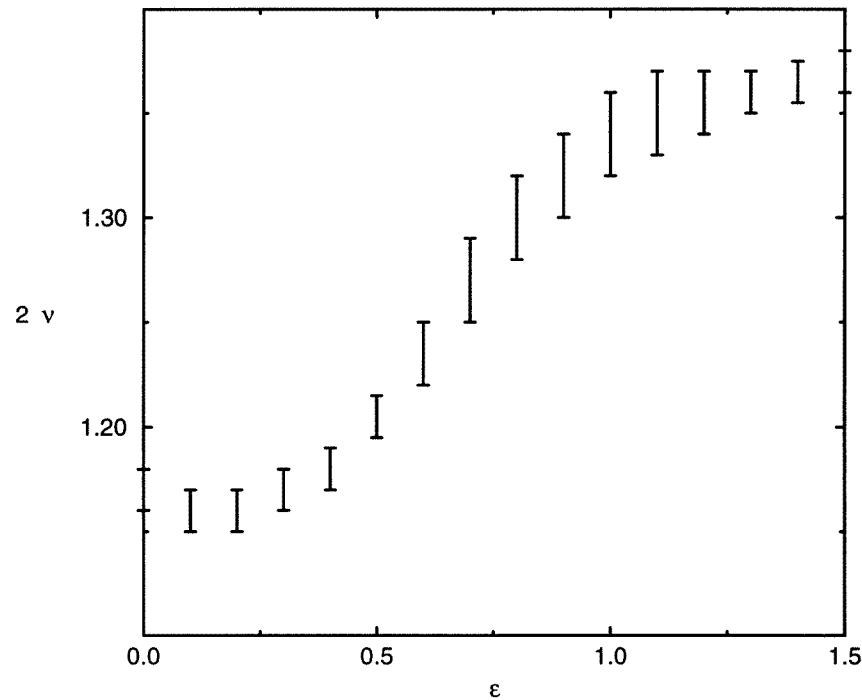


Figure 2. Behaviour of the correlation length exponent ν along the compact–swollen and branched–swollen transition line, as obtained from series.

where $\beta = 1/\kappa_B T$. In principle one should also include in (4) a contribution proportional to ϵ . We have determined from series the average number of vertices with four nearest neighbour sites occupied $\langle l \rangle$. It scales like $\langle l \rangle \sim bN$, with $b \simeq 0.03$ and it is therefore negligible.

(ii) *Compact phase.* The compact phase of a polymer can be suitably modelled by a Hamiltonian walk, which is a space filling SAW visiting all sites of a lattice of linear size $N^{1/2}$. In this limit

$$\beta F_c \simeq -N(\omega - \epsilon) - N \ln \mu_{HW} \quad (5)$$

since each monomer has four nearest-neighbour sites occupied and the number of nonbonded contacts is exactly N . The connectivity constant could be taken to be $\mu_{HW} = \frac{4}{e}$, which is a mean-field approximation in very good agreement with the exact value [15].

(iii) *Branched phase.* In the limit $\epsilon \rightarrow \infty$, the free energy of the branched phase is roughly

$$\beta F_b \simeq -\frac{N}{\alpha} \omega - \frac{N}{\alpha} \ln \mu_{BP} \quad (6)$$

with $\mu_{BP} \sim 5.21$ [16]. The factor α in equation (6) arises from the peculiar structure of the branched polymer, which makes the effective length of the chain shorter and, at the same time, forces a certain number of contacts between monomers. Although α can be easily inferred to be between 2 and 3, a precise determination of its value eludes us. For this reason we have set $\alpha \simeq 2.35$, in order to fit the branched–swollen transition asymptotically, as determined from series analysis.

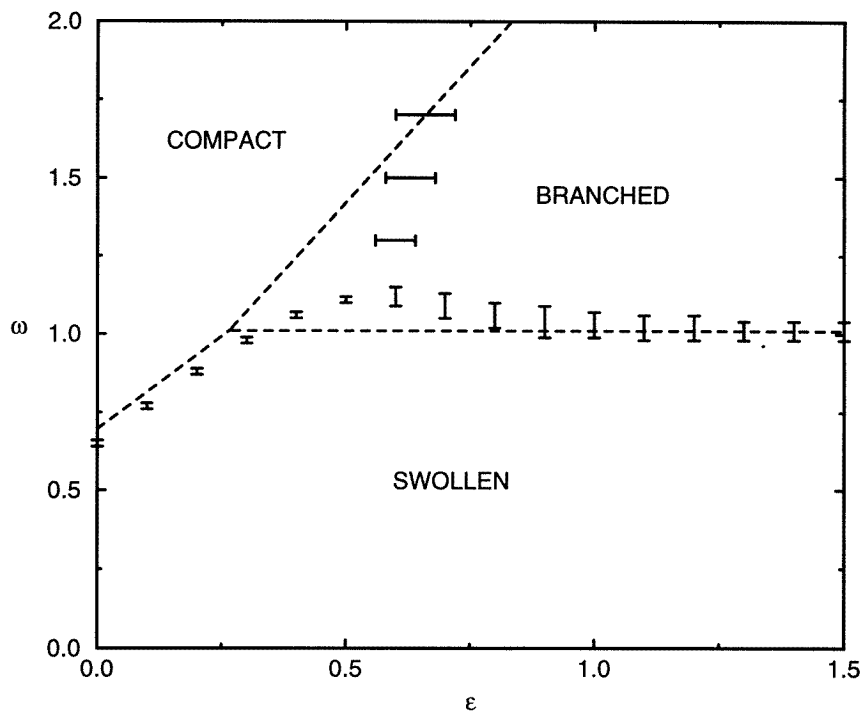


Figure 3. Phase diagram of the system as a function of ω and ϵ . The isolated points are obtained from series analysis. The broken lines show the conjecture from heuristic calculations.

The broken lines in the phase diagram of figure 3 result from comparing expressions (4)–(6) as a function of ω and ϵ . The stable phase is determined by the lowest value of the free energy.

To estimate the value of the critical exponent ν_{s-b} accurately we have considered the case $\epsilon = \infty$ separately. In this limiting case, all sites of the walk are prevented from having more than three occupied neighbouring sites (including bonding neighbours). From series analysis we quote $\nu = 0.70 \pm 0.01$. This value seems to be higher than that obtained in [8], i.e. $\nu \simeq 0.65$. For this reason we have complemented the analysis by carrying out two distinct Monte Carlo procedures based on ‘dynamical growth’ [17] and pivot [18] algorithms. The two approaches turned out to be statistically equivalent and in excellent agreement with the series results obtained for N up to 28.

The stochastic techniques allowed an accurate calculation of the square gyration radii for walks up to 45 sites with an estimated error of at most 1% for $0 < \beta < 1.2$. The values of ν were obtained by first performing a smoothing procedure as described in [19] (which involves a sum over an increasing number of R_N^2). Then, by identifying the crossing of the curves pertaining to length N and $N+8$ we identified the values of ν_{N+4} . Plotting ν_N against $1/N$ shows a marked linear behaviour, the correlation coefficient being $r \approx -0.85$. By linear regression we extrapolated the asymptotic value $\nu_{N \rightarrow \infty}$ obtaining $\nu_{s-b} = 0.695 \pm 0.006$ and thus confirming the discrepancy with $\nu \simeq 0.65$.

In summary we have determined the phase diagram of model (1) by performing exact enumerations of SAWs up to 28 steps and through a heuristic argument. Such a phase diagram presents a swollen, a compact and a branched phase, in agreement with that obtained

by Dekeyser *et al* [8]. The tricritical line separating the compact and the swollen phase is in the θ point universality class. There is, instead, some uncertainty on the exponent ν_{s-b} for the transition between the linear and branched polymer. Our value, deduced from series analysis and Monte Carlo simulations, seems to be higher than those obtained in both [8] and [6] (with a different model). The compact–branched phase transition, finally, needs more investigations owing to a common limitation of series expansion for a similar problem [12]. It is important to stress the importance of the square lattice in obtaining a branched polymer phase. In the continuum, or on some other lattices the model (1) (if not suitably modified) might replace this phase with a somewhat loosely packed compact phase[†].

The model we have investigated can be thought of as an annealed version of an attractive SAW. There are two types of beads: small beads which are allowed to have as many nearest neighbours as possible and large beads which allow only one, nonbonded, nearest neighbour. The parameter ϵ plays the role of a fugacity for large beads. An interesting perspective would be to analyse the model in its quenched version where a bead is small with probability p and large with probability $1 - p$. In this case it is believed to capture the size effect of different amino acids in the protein folding problem.

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References

- [1] Nienhuis B 1982 *Phys. Rev. Lett.* **49** 1062
- [2] Flory P J 1953 *Principle of Polymers Chemistry* (Ithaca, NY: Cornell University Press)
- [3] de Gennes P G 1953 *Scaling Concepts in Polymer Physics* (Ithaca, NY: Cornell University Press)
- [4] Duplantier B and Saleur H 1987 *Phys. Rev. Lett.* **59** 539
- [5] See for example: Coniglio A, Jan N, Maij I and Stanley H E 1987 *Phys. Rev. B* **35** 3617
Seno F and Stella A L 1988 *J. Physique* **49** 739
Chang I S, Shapir Y and Meirovitch H 1990 *J. Phys. A: Math. Gen.* **23** L537
Vanderzande C, Stella A L and Seno F 1991 *Phys. Rev. Lett.* **67** 2757
- [6] Orlandini E, Seno F, Tesi M C and Stella A L 1992 *Phys. Rev. Lett.* **68** 488
- [7] Bradley R M 1993 *Phys. Rev. E* **48** R4195
- [8] Dekeyser R, Orlandini E, Stella A L and Tesi M C 1995 *Phys. Rev. E* **52** 5214
- [9] Derrida B and Stauffer D 1985 *J. Physique* **46** 1623
- [10] Micheletti C, Banavar J R, Maritan A and Seno F 1998 *Phys. Rev. Lett.* **80** 5683
- [11] Privman V 1986 *J. Phys. A: Math. Gen.* **19** 3287
- [12] See the discussion in Seno F and Vanderzande C 1994 *J. Phys. A: Math. Gen.* **27** 5813
- [13] Douglas J F and Ishinabe T 1995 *Phys. Rev. E* **51** 1791
- [14] Guttmann A J 1987 *J. Phys. A: Math. Gen.* **20** 1839
- [15] Orland H, Itzykson C and de Dominicis C 1985 *J. Physique Lett.* **46** 353
- [16] Gaunt D S and Ruskin H 1978 *J. Phys. A: Math. Gen.* **11** 1369
- [17] Seno F and Stella A L 1988 *Europhys. Lett.* **7** 605
- [18] Lal M 1969 *Mol. Phys.* **17** 57
Madras N and Sokal A D 1988 *J. Stat. Phys.* **56** 109
- [19] Igloi F 1986 *J. Phys. A: Math. Gen.* **19** 3077

[†] We thank an anonymous referee for pointing this out.