Semiflexible Polymer in a Strip

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We study the thermodynamic properties of a semiflexible polymer confined inside strips of widths $L \leq 9$ defined on a square lattice. The polymer is modeled as a self-avoiding walk and a short-range interaction between the monomers and the walls is included through an energy ϵ associated with each monomer placed on one of the walls. Also, an energy ϵ_b is associated with each elementary bend of the walk. The free energy of the model is obtained exactly through a transfer matrix formalism. The profile of monomer density and the force on the walls are obtained. We notice that as ϵ_b is decreased, the range of values of ϵ which the density profile is neither convex nor concave increases, and for sufficiently attracting walls ($\epsilon < 0$) we find that in general the attractive force is maximum for $\epsilon_b < 0$, that is, for situations where the bends are favored.

I Introduction

Polymers are often modeled as self- and mutually avoiding walks placed on a lattice, and much has been learned about their thermodynamic properties through such models [1, 2]. Grand-canonical models of this kind, where the number of monomers incorporated into the chain is allowed to fluctuate controlled by an activity $z = \exp(\mu/k_B T)$, display a phase transition at some value of the activity (for infinite chains, that is, in the polymer limit). This transition is discontinuous in the one dimensional case $d = 1$ [3], and continuous for $d > 2$. Rather precise estimates of the critical value of z were found in two dimensions through transfer matrix calculations [4] and series expansions [5]. Also, exact values for the critical exponents are available in this case [6].

More recently, properties of such models on lattices limited by walls have attracted much interest [7], following studies of magnetic models in the same situation [8]. The short range interaction between the wall and the polymer may be introduced by associating a Boltzmann factor $\omega = \exp(-\epsilon/k_B T)$ with each monomer placed on the wall, so that $\epsilon < 0$ corresponds to attracting walls while repulsive walls are described by $\epsilon > 0$. The grand-canonical partition function for a model of a single chain is

$$Y(x, \omega) = \sum z^N \omega^{N_w}, \qquad (1)$$

where N is the number of monomers in the chain, the sum is over all configurations of the chain with the ini-

tial monomer placed on the wall, and $N_w \leq N$ stands for the number of monomers located on the wall. Such a model shows interesting features, and even in the limit where the self avoidance constraint is neglected (the so-called *ideal* chains) one finds that for sufficiently large values of $\omega > \omega_0$ the surface polymerization transition will occur at a lower value of the activity z than the one in the bulk [9]. The point (z_0, ω_0) in the phase diagram where the bulk (also called ordinary) transition line meets the surface transition line is called the adsorption transition point. In two dimensions, such models have been studied through transfer matrix calculations [10] and series expansions [11]. Additional walls may be added, confining the polymer inside a strip, slab or pore [7], and the force applied on the walls in such situations is of interest even from the point of view of applications of polymers as adhesives [12]. The model of ideal chains confined in a slab has been studied in the past [12, 13], and it was found that the force on the walls is attractive if ω exceeds the adsorption value ω_0. In the case of self-avoiding chains confined in a strip on the square lattice, transfer matrix calculations show that attractive forces appear for ω below ω_0 [13]. Also, the profile of the monomer density inside the strip was obtained [14], and, unlike what happens for ideal chains, for a self-avoiding chain profiles which are neither convex nor concave are found for a range of values of ω. Finally, similar techniques have also been applied to shed light on the scaling behavior of such models for strips with periodic boundary conditions (cylinders) as

the width of the strips becomes large [15].

Another generalization of the original polymer model is to introduce an energy associated with the operation of bending the chain. On hypercubic lattices, the elementary bends will always be at right angles, and an energy ϵ_b may be associated with each of them. This semiflexible polymer problem (also called persistent or biased walks), has been studied some time ago [16, 17, 18]. Recently, this model has attracted renewed interest , since it may describe some relevant aspects in the protein folding problem [19]. The thermodynamic properties of the model have been studied on the Bethe lattice [20] and, equivalently, in the Bethe approximation [21]. The end-to-end distance of semi-flexible chains on Bethe and Husimi lattices was obtained [22]. In this paper we study the thermodynamic behavior of a semiflexible polymer confined inside a strip. The partition function of the model may be written as

$$Y(x, \omega) = \sum z^N \omega^{N_w} \omega_b^{N_b}, \qquad (2)$$

where N_b is the number of elementary bends in the configuration and $\omega_b = \exp(-\epsilon_b/k_B T)$ is the Boltzmann factor associated with each elementary bend and the sum is over all configurations of the chain. We define a transfer matrix for the model and obtain the grand-canonical partition function in the thermodynamic limit, determined by the largest eigenvalue of this matrix. In order to be able to obtain the distribution of monomers in the transverse section of the strip, we define a position dependent activity for the monomers. Also, the force applied by the polymer on the walls is calculated, as a function of the width of the strip, ω and ω_b. All thermodynamic properties are calculated at the polymerization transition, that is, at the value of the activity of a monomer for which the number of monomers incorporated into the polymer diverges.

In section II the model is defined in detail and its solution is presented. The results we find for the thermodynamic behavior of the model are shown in section III as well as final conclusions and discussions.

II   Definition of the model and its solution

The self avoiding chain is constrained inside a strip of width m defined on the square lattice in the (x, y) plane, so that $0 \leq x \leq m$. The chain runs through the whole strip, from $y \to -\infty$ to $y \to +\infty$. We may define a transfer matrix for the problem following a prescription proposed by Derrida, in a way to take into account the self-avoidance constraint exactly [4]. The connectivity

properties of all vertical bonds of the chain arriving at a line y_0 from below are specified through the indication of

1. The (unique) bond connected to the initial monomer of the chain (placed in $y \to -\infty$) through a path lying entirely below the line y_0 (passing though sites with $y < y_0$);

2. The pairs of bonds connected to each other through a path lying entirely below the line y_0.

In Fig. 1 the five configurations for the case $m = 2$ are depicted, and a portion of the chain placed inside the strip is shown with each configuration indicated. Configurations 1 and 3, as well as 4 and 5, are related to each other by reflection symmetry. We define column dependent activities z_i, $i = 1, 2, ...n_a(m)$ according to this reflection symmetry, as indicated also in Fig. 1. The number of activities $n_a(m)$ is equal to $m/2 + 1$ for even values of m and $(m + 1)/2$ for odd values of m.
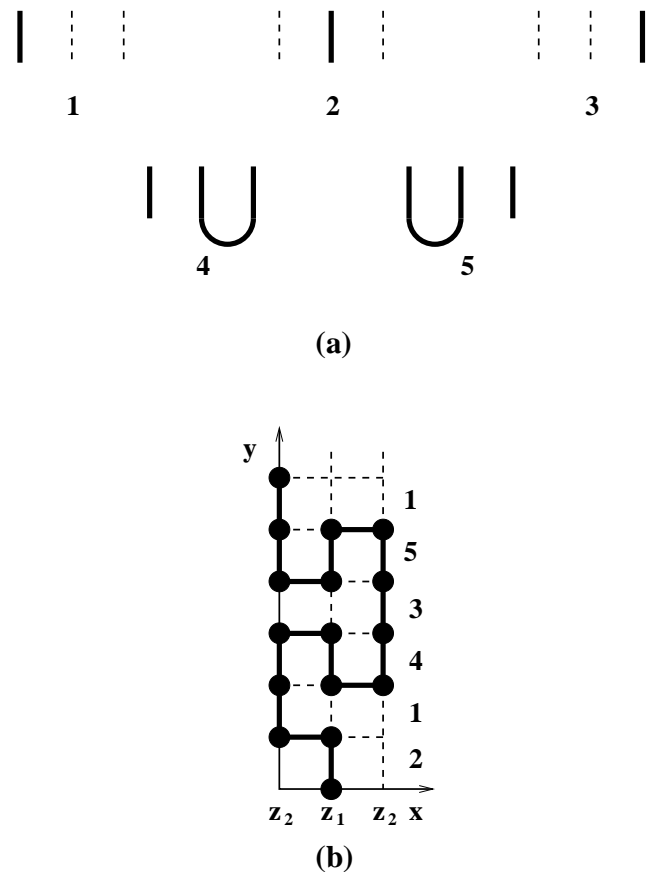

Figure 1. a) The five connectivity configurations for $m = 2$. b) Portion of the chain, with the number of each connectivity configuration indicated.

For a fixed connectivity configuration of a set of $m + 1$ vertical bonds arriving at the line y_0, the possible configurations of the set of vertical bonds arriving

at $y_0 + 1$ may be obtained, as well as the contribution to the partition function from the sites comprised between both sets of vertical bonds. This contribution will be given by

$$\omega_b^{N_{b,y_0}} \prod_{i=1}^{n_a(m)} z_i^{N_{i,y_0}}$$

where N_{i,y_0} is the number of monomers with activity z_i in line y_0 and N_{b,y_0} is the number of elementary bends in this line. These contributions, shown for a particular example in Fig. 2, define a line of the transfer matrix. For $m = 2$ the transfer matrix will be given by

$$\mathbf{T} = \begin{pmatrix} z_2 & z_1 z_2 \omega_b^2 & z_1 z_2^2 \omega_b^2 & z_1 z_2^2 \omega_b^2 & 0 \\ z_1 z_2 \omega_b^2 & z_1 & z_1 z_2 \omega_b^2 & 0 & 0 \\ z_1 z_2^2 \omega_b^2 & z_1 z_2 \omega_b^2 & z_2 & 0 & z_1 z_2^2 \omega_b^2 \\ 0 & 0 & z_1 z_2^2 \omega_b^2 & z_1 z_2^2 & 0 \\ z_1 z_2^2 \omega_b^2 & 0 & 0 & 0 & z_1 z_2^2 \end{pmatrix}. \tag{3}$$
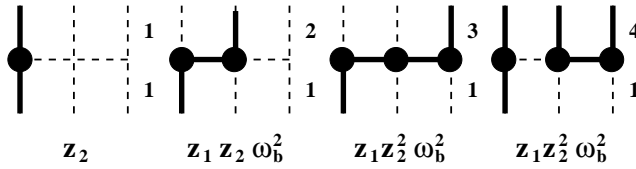

Figure 2. Contributions to the first line of the transfer matrix for the case $m = 2$. The connectivity configurations are indicated following the enumeration adopted in Fig. 1.

The grand canonical partition function of the model, considering periodic boundary conditions in the y direction, will be given by

$$\Xi = (\mathrm{Tr}) \mathbf{T}^{N_y}, \tag{4}$$

where N_y is the total length of the strip in the y direction, so that the total number of sites is given by $N_s = N_y(m + 1)$. The number of monomers with activity z_i is

$$N_i = \frac{z_i}{\Xi} \frac{\partial \Xi}{\partial z_i}, \tag{5}$$

and the total number of monomers in the chain will be

$$N = \sum_{i=1}^{n_a(m)} N_i. \tag{6}$$

The fraction of monomers placed at column x is

$$\rho(x) = \frac{N_{x+1}}{(2 - \delta_{x,m/2})N}, \tag{7}$$

where $x = 0, 1, \ldots, n_a(m) - 1$ and $\rho(x) = \rho(m - x)$. The Kronecker delta in the denominator contributes only for even values of m.

In the thermodynamic limit $N_y \to \infty$ the partition function 4 is dominated by the largest eigenvalue of the transfer matrix λ_1, so that $\Xi \sim \lambda_1^{N_y}$ and in this limit

$$N_i = N_y \frac{z_i}{\lambda_1} \frac{\partial \lambda_1}{\partial z_i}. \tag{8}$$

The first order polymerization transition in the finite strip will take place when the thermodynamic potential

$$\psi = -k_B T \ln(\Xi) \tag{9}$$

is equal to the one for the empty lattice $\psi_0 = 0$. Thus, since in the thermodynamic limit we have

$$\psi/N_s = -k_B T(m + 1) \ln(\lambda_1) \tag{10}$$

the polymerized phase will coexist with the non-polymerized phase for $\lambda_1 = 1$. Therefore, all thermodynamic quantities below will be calculated for $z_i = z, i = 1, \ldots, n_a(m) - 1$ and $z(n_a(m)) = \omega z$, where the activity z is then fixed at the coexistence value z_c so that, for a given value of ω_b, we have $\lambda_1 = 1$.

Finally, the force applied on the walls is given by

$$F = \frac{1}{a} \left(\frac{\partial \Xi}{\partial m} \right)_{z, \omega, \omega_b}, \tag{11}$$

where a is the lattice parameter and positive values correspond to attractive forces. An adimensional force per monomer at the coexistence may be then defined as

$$f = \frac{Fa}{k_B T N} = \frac{-\left(\frac{\partial \Xi}{\partial m}\right)_{z,\omega,\omega_b}}{z \left(\frac{\partial \Xi}{\partial z}\right)_{m,\omega,\omega_b}} = \frac{1}{z_c} \left(\frac{\partial z_c}{\partial m} \right)_{\omega,\omega_b}. \tag{12}$$

Since our results correspond to integer values of m, the force f was estimated making the discrete approximation

$$f(m + 1/2, \omega, \omega_b) \approx \frac{2}{z_c(m + 1, \omega, \omega_b) + z_c(m, \omega, \omega_b)} \times [z_c(m + 1, \omega, \omega_b) - z_c(m, \omega, \omega_b)]. \tag{13}$$

A simple calculation may be performed in the limit of rigid rods $\omega_b = 0$, where bends are not allowed. In this limit the transfer matrix is diagonal of size $(m + 1) \times (m + 1)$. For $\omega > 1$ all monomers are on the walls, for $\omega = 1$ they are uniformly distributed, whereas for $\omega < 1$ an uniform distribution in the sites away from the walls is found. As expected, in this limit the force on the walls vanishes. In the numerical results below we consider $\omega_b \geq 1$.

III Numerical results and conclusion

The transfer matrices for the model were obtained exactly for strips of widths ranging from 3 to 9. After using the reflection symmetry, the sizes of the matrices are, respectively, equal to 6, 16, 38, 100, 256, 681, and 1805. We obtained the density profile at the coexistence condition for values of ω and ω_b mostly between 1 and 3.
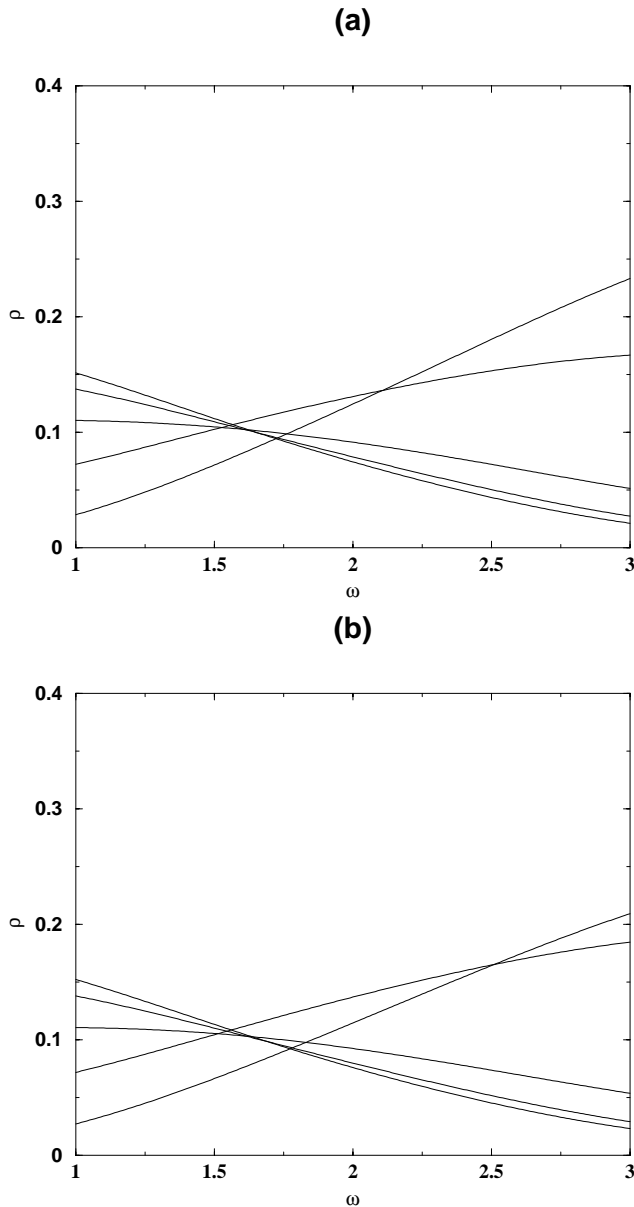
(a)

(b)

Figure 3. Density of monomers as function of ω for a strip with $m = 9$. (a) corresponds to $\omega_b = 2$ and (b) to $\omega_b = 3$. Curves are for different values of x and $\rho(x) = \rho(m - x)$. At $\omega = 1$ the highest density corresponds to the center of the strip ($x = 4$ and $x = 5$) and the density decreases monotonically outwards, being lowest at the wall ($x = 0$ and $x = 9$). At $\omega = 3$ the density profile is convex in both cases, with the maximum density located on the walls.

For neutral walls ($\omega = 1$) the density profile is always concave, with a higher density in the center. This may be understood since the region away from the walls is favored entropically. As ω becomes larger, monomers on the walls are energetically favored, so for sufficiently large values of ω a convex density profile is expected. For ideal flexible chains ($\omega_b = 1$), at the adsorption value $\omega = 4/3$ the density profile is flat for all sites which are not on the walls [12, 14]. Such a flat transition profile is not observed for self-avoiding chains, where convex profiles are separated from concave ones by an interval of values of ω, located well below the adsorption transition value, where the profile is neither convex nor concave. This interval is quite narrow for flexible chains [14]. In Fig. 3 the densities are plotted as functions of ω for two values of ω_b. It is clear that as ω_b is increased, favoring bends, the interval of values of ω with a profile without well defined convexity grows.

The values of ω below which the density profile is concave (ω_1)and those above which the profile is convex (ω_2) are plotted in Fig. 4 as functions of ω_b for two values of m. As is apparent the range with no defined convexity grows with ω_b in a nearly linear way. As a general rule, we found that as ω_b is increased from 1, the first pair of densities to cross, destroying concavity, is always correspondent to the columns which are first and second neighbors to the walls. Also, the last crossing, which turns the profile convex, is between densities corresponding to the columns at the wall and the neighbor columns. In the limit $\omega_b \to \infty$ we found that $\omega_2 \to \infty$.
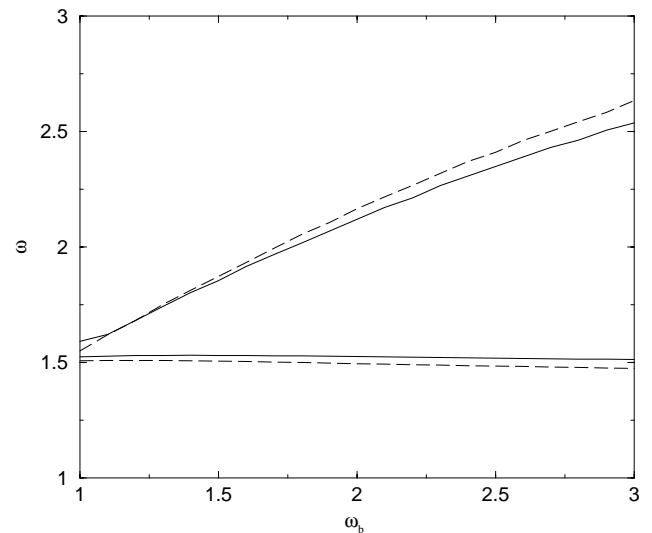

Figure 4. Boltzmann weights below which the density is concave (lower curves) and above which it is convex (upper curves) for $m = 6$ (dashed curves) and $m = 9$ (full curves).

Finally, we calculated the force per monomer on the walls for pair of widths m, $m + 1$, using expression 13.

As already found for flexible self-avoiding chains [13], attractive forces appear for sufficiently large values of ω. Fig. 5 shows results for the force as a function of ω for some values of ω_b. The origin of attractive forces in the system are portions of the chain limited by monomers adsorbed on opposite walls. Thus, as expected, the curves $f \times \omega$ display a maximum, because the force vanishes as $\omega \to \infty$, since in this limit such "bridge" segments are absent.
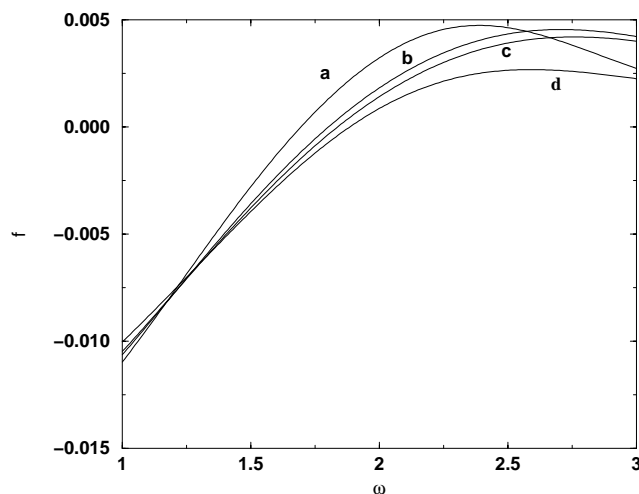

Figure 5. Force per monomer on the walls as function of ω for (a) $\omega_b = 1$, (b) $\omega_b = 2$, (c) $\omega_b = 3$, and (d) $\omega_b \to \infty$. Results shown are for $m = 8.5$.

In Fig. 6 the maximum force per monomer (with respect to ω) is plotted as a function of ω_b. It is apparent that the maximum of these curves is located at $\omega_b > 1$, and thus we conclude that polymers for which bends are somewhat favored give rise, in general, to larger attractive forces than flexible ones. As ω_b is increased, the maximum attractive force occurs at higher values of ω

The force per monomer as a function of the width of the strip m, for ω above a threshold, shows a stable equilibrium point at very low separation m_1 and an unstable equilibrium point at a larger separation m_2 [13]. The force is attractive in the interval $m_1 < x < m_2$.
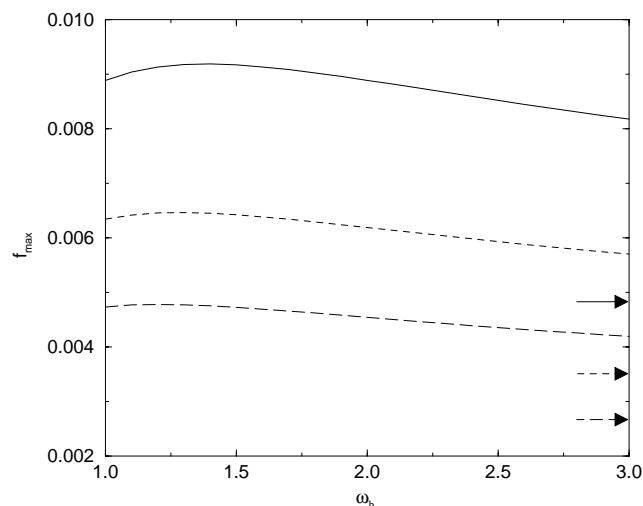

Figure 6. Maximum force per monomer on the walls for $m = 6.5$ (full line), $m = 7.5$ (dotted line), and $m = 8.5$ (dashed line) as functions of ω_b. Arrows indicate the maximum force for $\omega_b \to \infty$.

The stable equilibrium point $m_1(\omega, \omega_b)$ is found in the range $0.5 \le m_1 \le 1.5$, showing little variation as a function of the Boltzmann factors, as long as ω is larger than the threshold value. The unstable equilibrium point $m_2(\omega, \omega_b)$ shows a rather strong monotonic dependence on both variables, being an increasing function of ω and a decreasing function of ω_b.

In conclusion, we may summarize the behavior of semiflexible chains confined inside strips observing that as the presence of elementary bends in the chains is favored, the range of values of ω for which the density profile has no defined convexity grows. Also, the largest attractive forces are found for $\omega_b > 1$, that is, when the bending of the chains is favored. It should be noticed that the nonmonotonic behavior observed for the tension as a function of the width of the strip, with two equilibrium points, happens in a regime where the finite size scaling behavior has not yet been reached [13].

Acknowledgements

References

[1] P.J.Flory, *Principles of Polymer Chemistry*, Cornell University Press, Ithaca, New York (1953).

[2] P.G. de Gennes, *Scaling Concepts in Polymer Physics*, Cornell University Press, Ithaca, New York (1979).

[3] P. M. Pfeuty and J. C. Wheeler, Phys. Rev. A **27**, 2178 (1983).

[4] B. Derrida, J. Phys. A **14**, L5 (1981).

[5] A. R. Conway and A. J. Guttmann, Phys. Rev. Lett. **26**, 5284 (1996).

[6] B. Nienhuis, Phys. Rev. Lett. **49**, 1062 (1982); see also B. Nienhuis in *Phase Transitions and Critical Phenomena*, vol 11, ed. by C. Domb and J. L. Lebowitz, Academic Press (1987).

[7] K. De'Bell and T. Lookman, Rev. Mod. Phys. **65**, 87 (1993).

[8] K. Binder in *Phase Transitions and Critical Phenomena*, vol. 8, ed. by C. Domb and J. L. Lebowitz, Academic Press (1983).

[9] R. J. Rubin, J. Chem. Phys. **43**, 2392 (1965).

[10] I. Guim and T. Burkhardt, J. Phys. A**22**, 1131 (1989); Phys. Rev. E **49**, 1495 (1994).

[11] D. Zhao, T. Lookman and K. De'Bell, Phys. Rev. A **42**, 4591 (1990).

[12] E. A. DiMarzio and R. J. Rubin, J. Chem. Phys. **55**, 4318 (1971).

[13] J. F. Stilck and K. D. Machado, Eur. Phys. J. B **5**, 899 (1998); J. F. Stilck, Braz. J. of Phys. **28**, 369 (1998).

[14] J. F. Stilck, Europhys. Lett. **40**, 19 (1997); Physica A **257**, 233 (1998).

[15] T. W. Burkhardt and I. Guim, Phys. Rev. E **59**, 5833 (1999).

[16] M.F. Thorpe and W.K.Scholl, J. Chem. Phys. **75**, 5143 (1981); W.Scholl and A.B. Thorpe, J. Chem. Phys. **76**, 6386 (1982); J.W.Halley, H. Nakanishi, and R. Sundarajan, Phys.Rev. B **31**, 293 (1985); S. B. Lee and H. Nakanishi, Phys.Rev. B**33**, 1953 (1986); M.L. Glasser, V. Privman, and A. M. Szpilka, J. Phys. A **19**, L1185 (1986); V. Privman and S. Redner, Z. Phys. B**67**,129 (1987); V. Privman and H.L.Frish, J. Chem. Phys. **88**, 469 (1988); J.W.Halley, D. Atkatz, and H. Nakanishi, J. Phys. A**23**, 3297 (1990).

[17] J. Moon and H. Nakanishi, Phys. Rev. A **44**, 6427 (1991).

[18] C.J.Camacho, M. E. Fisher, and J. P. Straley, Phys.Rev. A **46**, 6300 (1992).

[19] S. Doniach, T. Garel, and H. Orland, J. Chem. Phys. **105**, 1601 (1996); U. Bastolla and P. Grassberger, J. Stat. Phys. **89**, 1061 (1997).

[20] E. Botelho and J. F. Stilck, Phys. Rev. E **48**, 723 (1993).

[21] S. Lise, A. Maritan, and A. Pelizzola, Phys. Rev. E **58**, R5241 (1998).

[22] J. F. Stilck, C. E. Cordeiro, and R. L. P. G. do Amaral, Phys. Rev. E **61**, 5520 (2000).