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The theta-point and critical point of self-avoiding walks : a phenomenological approach

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Résumé. — Partant de l'idée que l'état de référence d'une chaîne polymérique est un chemin sans recouplement et non un chemin brownien, nous proposons une version modifiée des modèles de Flory et de Flory-Huggins. Nous obtenons toutes les caractéristiques du point θ d'une chaîne et du point critique d'une suspension de chaînes à partir du dénombrement des configurations et des contacts d'une chaîne en bon solvant. Les résultats expérimentaux sont parfaitement reproduits pour $d = 3$ (en particulier nous trouvons une concentration critique $\phi_c \sim N^{-0.382}$). Pour $d = 2$ la description des phénomènes critiques semble correcte, mais le point θ n'est pas situé tout à fait à l'endroit trouvé par Duplantier et Saleur.

Abstract. — Considering that the reference state of a polymer chain is the self-avoiding walk and not the Brownian walk, we propose modified forms of the Flory and Flory-Huggins models. All our results for the θ -point of a chain and for the critical point of a suspension are based on the number of contacts and the number of configurations of a chain in a good solvent. Results for $d = 3$ fit remarkably well with experiment (in particular we find a critical volume fraction $\phi_c \sim N^{-0.382}$). For $d = 2$, the results concerning the critical point seem to be correct but the θ -point does not coincide with the Duplantier-Saleur result.

1. Introduction.

The Flory description of a single polymer chain [1] gives amazingly good results in spite of well-known shortcomings [2, 3]. The Flory-Huggins description of a suspension [4, 5] shares the same status of a successful, widely used and severely criticized model. Most of the criticisms are centered on the impossibility for those mean-field models to account for the spatial correlations between distant parts of the chain. An attempt to include the proper correlations in the Flory-Huggins model was developed by Muthukumar [6]. He obtained

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results for the critical point markedly different from the mean-field ones, but the fit with experiment was not perfect. The reasons for this half-success are not clear and a satisfactory description of the correlations is still to be found.

We propose here a new approach based on the idea that the reference state of the polymer chain is the self-avoiding walk (SAW) and not the Brownian walk. To deduce the size of a single polymer chain we will use the same energy minimum principle as in the Flory model, but the Gaussian statistics and the mean-field estimate of the repulsive energy will be replaced by non mean-field quantities relevant to a SAW with short-range attractions. Stated differently, while Flory deduced the excluded volume exponent ν as a result of repulsive forces acting on a Brownian walk with $\nu_\theta = 1/2$, we want here to recover the exponent ν_θ from attractive forces acting on a SAW with given $\nu(d)$. We will also modify the Flory-Huggins model for it to describe a *dilute* suspension of porous particles with a mutual interaction depending on the temperature and degree of polymerisation. In short, we closely follow the phenomenological level of the two famous models, but we feed them with results concerning SAW. Due to the phenomenological character of the approach, we insist on exponents and not on numerical prefactors. All our results for the θ -point of a single chain and for the critical point of a suspension will be expressed in terms of two basic exponents : the so-called excluded volume exponent $\nu(d)$ and the des Cloizeaux exponent $\theta_2(d)$ related to the probability of contact between two points of a SAW [7].

Some general features of demixion are presented in section 2. The size of a chain is considered in section 3 and the chain-chain interaction energy in section 4. Section 5 deals with the upper critical dimension in a suspension while the last section will be devoted to a discussion of the results.

2. Demixion in a suspension of porous particles.

We assume that the whole demixion domain, and in particular the whole coexistence curve, occurs at low enough volume fractions ϕ for the polymer chains to behave like porous particles of size R . The average concentration of monomers in such a particle is noted ϕ^* , i.e. $\phi^* \sim Na^d/R^d$ where N is the number of monomers per chain and a^d is a measure of their volume in a d -dimensional space. The apparent concentration of chains in the suspension is $\varphi = \phi/\phi^*$ and we limit our description to $\varphi < 1$. We assume that the free energy of mixing is similar to that of a simple mixture [8]

$$\frac{R^d F}{k_B T} = \varphi \text{Log } \varphi + (1 - \varphi) \text{Log } (1 - \varphi) + \chi^* \varphi (1 - \varphi).$$

The positive parameter χ^* is a measure of the effective interaction energy between two chains. It is proportional to the average number of mutual contacts when two chains collide. As a consequence, χ^* is likely to depend on the porosity $1 - \phi^*$, while ϕ^* is itself a function of N and the temperature T . We now make a second assumption and suppose that neither χ^* nor ϕ^* depend on the apparent concentration of chains as long as they are not closely packed, i.e. when $\varphi < 1$. Then, we eliminate all terms linear in ϕ since their only role is to modify the energies by a constant amount. For the free-energy in a volume a^d of the suspension, we finally get

$$\frac{a^d F}{k_B T} = \frac{\phi}{N} \text{Log } \phi + \frac{1}{N} (\phi^* - \phi) \text{Log} \left(1 - \frac{\phi}{\phi^*} \right) - \frac{\chi^*}{N \phi^*} \phi^2 \quad (1)$$

This is the modified Flory-Huggins free-energy in the dilute concentration range $\phi < \phi^*$. It is

straightforward to obtain the coexistence curve from that expression. The result appears as

$$\text{Log} \left(\frac{\phi^*}{\phi_D} - 1 \right) = \chi^* \left(1 - \frac{2\phi_D}{\phi^*} \right)$$

and

$$\phi_{SD} = \phi^* - \phi_D$$

where the indices D and SD are adopted only to follow the widely used notation of a dilute and a semi-dilute branch of the coexistence curve. This curve is *symmetric* in the representation $(\chi^*, \phi/\phi^*)$ and the critical point is located at

$$\chi_c^* = 2 \quad \text{and} \quad \phi_c = \phi^*/2. \quad (3)$$

The osmotic pressure associated with (1) has a very simple expression

$$\frac{\alpha^d \Pi}{k_B T} = - \frac{\phi^*}{N} [\text{Log} (1 - \phi) + \chi^* \phi^2]$$

and the second virial coefficient of a very dilute suspension of chains ($\phi \ll \phi^*$) appears as

$$A_2 = \frac{1 - 2\chi^*}{N\phi^*} \quad (4)$$

Three consequences are noteworthy. The first concerns good solvents for which χ^* vanishes and $R \sim N^\nu$ so that $A_2 \sim N^{-(2-\nu d)}$, in agreement with [2]. The second concerns the vanishing of A_2 which occurs when $\chi^* = 1/2$. And the third consequence concerns the critical point where the second virial coefficient is negative and satisfies to

$$A_{2c} N \phi_c = -3/2$$

in agreement with the experimental result of Perzinski, Delsanti and Adam [9].

All the results concerning the coexistence curve, the critical point and the second virial coefficient were obtained without any particular assumption concerning χ^* and ϕ^* (except their independence on ϕ). If we want to make any further progress, we need explicit expressions for $\chi^*(T, N)$ and $\phi^*(T, N)$. This is the purpose of the next two sections.

3. The chain size and the θ -point.

To get the chain size as a function of the temperature and monomer number, we use a Flory-like method [1] based on a minimization of free energy. Two important points should be clarified at the outset: our reference state is a chain in good solvent i.e. a self-avoiding walk and not a random walk, and we consider the gyration radius instead of the end-to-end distance. Suppose we know both the number $C_N(r)$ of different configurations of a N -monomer chain with gyration radius r , and the number $M_N(r)$ of contacts between non-consecutive monomers. If each contact lowers the energy by $k_B T \chi$, the free energy of the chain is

$$\frac{F(N, \chi, r)}{k_B T} = -\text{Log} C_N(r) - \chi M_N(r).$$

The minimum will happen for a certain size $r = R(N, \chi)$, which is all we need to calculate

$\phi^*(N, T)$ provided we know the temperature dependence of χ . We insist that the two statistical distributions $C_N(r)$ and $M_N(r)$ refer to a polymer chain in a good solvent, the only interaction between distant parts of the chain being a pure hard-core repulsion. Hence, the minimization procedure gives the equilibrium state in a poor solvent from the knowledge of two statistical quantities relative to good solvent conditions. When χ vanishes, the equilibrium state is the one with a maximum number of configurations. When χ is some positive number, the equilibrium is displaced towards more compact configurations, the loss in entropy being compensated by a gain in contact energy.

The two statistical distributions can be deduced from numerical experiments on self-avoiding walks generated on a lattice [11-13]. The results seem to confirm the simple scaling laws that were proposed recently for $C_N(r)$ [10] and for $M_N(r)$ [13]. For completeness we repeat here the arguments, and we begin with the number of configurations of a self-avoiding walk. The total number of configurations scales like $N^{\gamma-1} \mu^N$ [2]. We divide this total number into « slices » corresponding to a given gyration radius $r = ax$ (a is the monomer size) with $N^{1/d} < x < N$. For a fully stretched chain, the number of configurations rapidly tends to zero and for a compact globule the number of Hamiltonian walks is far less than μ^N . We conclude that the μ^N factor should be completely compensated when x is in the neighbourhood of $N^{1/d}$ and N . The only possibility for $C_N(x)$ is an exponential decrease for both limiting cases, i.e.

$$\text{Log } C_N(x) \sim N [1 - (N/x^d)^{1/(1-\alpha)} - (x/N)^\delta]$$

where all numerical coefficients were set equal to one for a better display of the main features. The two exponents $(1-\alpha)^{-1}$ and δ should be positive and the reason for their strange writing will appear soon; α and δ can be completely determined if the SAW is supposed to be a self-similar object whose properties depend on x/N^ν only, where aN^ν is the equilibrium chain size in a good solvent. In this case, the one and only solution is

$$\alpha = 2 - \nu d \quad \text{and} \quad \delta = (1 - \nu)^{-1} \quad (5)$$

and consequently

$$\text{Log } C_N(x) \sim N - (N^\nu/x)^{1/(\nu-1/d)} - (x/N^\nu)^{1/(1-\nu)}$$

That scaling law is most simply expressed if we define the relative expansion X as

$$X = (x/N^\nu)^{1/(\nu-1/d)} \quad (6)$$

This variable will play a role somewhat analogous to $x/N^{1/2}$ in the Flory model. With it, the number of configurations simply scales like

$$\text{Log } C_N(X) \sim N - \frac{1}{X} - X^\eta \quad (7)$$

where

$$\eta = \frac{\nu - 1/d}{1 - \nu} \quad (8)$$

Note that the possible values for X are in the range $N^{-1} < X < N^{1/\eta}$ and that the maximum number of configurations occurs for $X = 1$, while the θ -point and the critical point are expected to occur for $X \ll 1$.

A rather similar approach leads to the scaling law for the number of contacts in a self-

avoiding chain. The distribution $M_N(X)$ is a decreasing function of the gyration radius which must satisfy three requirements : the first one concerns the compact limit where the number of contacts is expected to be of order N (more exactly $(z - 2) N/2$, where z is the number of nearest neighbours). The second one concerns the fully stretched limit with no contact at all. The third one (certainly the less intuitive requirement) concerns the SAW with a gyration radius of order N^ν i.e. $X \cong 1$; according to des Cloizeaux [7], its number of internal contacts is *still of order N* (with a coefficient smaller than in the compact case) and more precisely [13]

$$M_N(1) \sim N + 1 + N^{-\beta_2} + \dots \tag{9}$$

The exponent β_2 is simply related to the contact exponent θ_2 of des Cloizeaux

$$\beta_2 = \nu(d + \theta_2) - 2. \tag{10}$$

In so far as $\beta_2 \geq 0$, the terms in (9) are written in decreasing order from left to right. Let us neglect the β_2 contribution for a while. The simplest scaling which satisfies the above three requirements is

$$M_N(X) \sim N + \frac{1}{X} - X^\eta$$

The gross features of $C_N(X)$ and $M_N(X)$ are represented in figure 1. With these two scaling laws, the free energy minimum occurs when

$$2\chi = \frac{1 - X^{1+\eta}}{1 + X^{1+\eta}}$$

We have written 2χ just to enhance the similarity with Flory's special value $\chi_F = 1/2$. The true coefficient is not exactly 2 according to [13], but this has no importance since we want to stress the scaling behaviour only. The above result describes the variation of the SAW size with the monomer interaction parameter χ . Much like the Flory model, it predicts a sudden

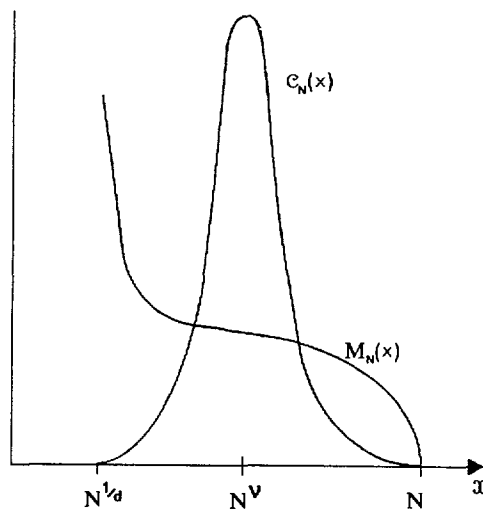


Fig. 1. — Sketchy representation of the number of configurations $C_N(x)$ and the number of contacts $M_N(x)$ of a self-avoiding walk of N steps with adimensional gyration radius x .

collapse for $\chi = 1/2$. This non-physical behaviour was corrected by the introduction of three-body interactions into Flory's free energy [14]. Here we will not invoke any many-body force but we will say that the number of contacts includes an « anomalous » part M^* besides the « regular » one that was written above. It is fair to say that the numerical experiments [13] could not conclude about the existence or non-existence of M^* . So, all that will be said below concerning M^* is largely speculative. Let us write

$$M_N(X) \sim N + \frac{1}{X} - X^\eta + M^*(X, N) \quad (11)$$

and suppose that the number of configurations is still given by (7) (i.e. there is no anomalous contribution to $C_N(X)$). The free energy is then minimum for

$$2\chi = \frac{1 - X^{1+\eta}}{1 + X^{1+\eta} - X^2(\partial M^*/\partial X)} \quad (12)$$

which means that the θ -point occurs when

$$\chi = 1/2 \Leftrightarrow \partial M^*/\partial X = X^{\eta-1} \quad (13)$$

We must now propose some explicit expression for M^* . First we can think of a contribution involving a $N^{-\beta^2}$ term to fulfil the requirement (9). Since this contribution, stemming from the statistics of loops inside the chain, is likely to play a larger role when the chain is stretched ($X \geq 1$) we propose

$$M_1^* \sim - (X/N)^{\beta^2}$$

The minus sign is needed to have a continuous decrease of the chain size with increasing values of χ .

We now need a contribution which operates mainly for a shranked chain and which must decrease the number of contact points so as to soften the collapse. The physical mechanism is not clear in the author's mind. It can be due to some local stiffness of the chain as suggested in [15, 16]. A possible form for this contribution is

$$M_2^* \sim - 1/N^{4-d} X^2$$

Our proposal for M^* is the sum of the two contributions from the loop statistics and the short-range rigidity

$$M^* \sim - (X/N)^{\beta^2} - 1/N^{4-d} X^2 \quad (14)$$

Note that M^* is always negative, that the M_1^* contribution is dominant for a chain in good solvent ($X \cong 1$) while the role of M_2^* increases as the chain size decreases.

With the statistical distributions (7), (11) and (14), it is an easy play to obtain the free-energy of the chain. For $d = 3$, and if we delete the terms merely proportional to N , the result is

$$F/k_B T \sim (1 + 2\chi) X^\eta + 2\chi (X/N)^{\beta^2} + N [(1 - 2\chi)(NX)^{-1} + 2\chi (NX)^{-2}].$$

This free-energy for a SAW has a structure rather similar to the Flory free-energy for a Gaussian chain. If one notices that $(NX)^{-1} \sim (\phi^*)^{1/(3\nu-1)}$, the terms in brackets are reminiscent of the development in powers of the monomer concentration in the extended Flory model [14] but the powers of ϕ^* in this development are different from the mean-field ones.

Since M^* includes two contributions, the size at the θ -point depends on their relative importance. When solving (13) one can prove that the short-range rigidity M_2^* has the leading role near the θ -point if

$$\eta/(3 + \eta) < \beta_2 < \eta . \tag{15}$$

This inequality is satisfied for $d = 2$ since $\beta_2 = 11/16$ [17], and $\eta = 1$ [18]. It is also satisfied for $d = 3$ ($\beta_2 \cong 0.18$ [7] and $\eta \cong 0.618$ [19]) but notice that the value of $\eta/(3 + \eta)$ is 0.171 which is quite close to the assumed value for β_2 . We return to this point in section 5 and here we take the above inequality for granted. In that case the θ -point occurs when $X \sim N^{-(4-d)/(2+\eta)}$ or equivalently when $x \sim N^{\nu_\theta}$ where

$$\nu_\theta = \nu - (\nu - 1/d) \frac{4-d}{2+\eta} \tag{16}$$

According to (8), the exponent η is a function of d and $\nu(d)$ so that (16) ultimately gives $\nu_\theta(d)$ as a function of $\nu(d)$.

4. The chain-chain interaction and the critical point.

The energy of mixing for the chain suspension was depicted by χ^* . One can think of this parameter as a measure of the energy difference between two separated and two interpenetrating chains. χ^* is proportional to the monomer-solvent interaction parameter χ with a proportionality coefficient depending on the average number of contacts between two colliding chains. Moreover, $\chi^* > \chi$ because even in the extreme case of two fully stretched chains, one can have one contact point. We will write

$$\chi^* = \chi (1 + P_N(X)) . \tag{17}$$

One can suspect some link between $P_N(X)$ and the number of contacts inside a chain. More precisely, since $P_N(X)$ is bound to the structure of the outer part of the chain (the chain « surface ») while $M_N(X)$ is related to both the inner and outer parts, we expect P_N to be connected with $\partial M_N/\partial X$. We propose here to analyse the consequences of the assumption

$$P_N(X) \sim X (\partial M^*/\partial X) . \tag{18}$$

We have no general proof for this conjectured relation between P_N and what we called the anomalous number of contacts. In fact, such a relation was suggested to us by considering the special case of a particle filled with a gas of monomers : in that special case, each monomer interacts with the monomers present in a sphere of volume a^d and the number of contacts per particle is $N\phi^*$. This expression slightly exceeds the correct value because we overestimated the true number of contacts of the monomers belonging to the outer shell of the particle. The proportion of monomers belonging to that outer shell is of order $1/x$ and each monomer sees a concentration ϕ^* on the one side and zero on the other side. The correct number of contacts is obtained when ϕ^* is replaced by $\phi^*(1 - 1/x)$. Now, if the particle is surrounded with other particles occupying an apparent volume fraction $\varphi = \phi/\phi^*$, a proportion $1 - \varphi$ of its surface is occupied by neighbours and the number of contacts per particle amounts finally to $N\phi^*(1 - (1 - \varphi)/x)$. Hence, a chain of size x filled with N uncorrelated monomers is depicted by

$$M_N(x) = N\phi^* - N\phi^*/x$$

and

$$P_N(x) = N\phi^*/x.$$

In this special case the anomalous number of contacts is $(-N\phi^*/x)$ and P_N actually satisfies (18). Needless to say that this example of free monomers is far from the SAW reality, but our aim here was just to give some feeling of how M^* and P_N were linked to each other in a particularly simple case.

Taking (18) for granted and combining (17) with (12), one deduces the conditions of vanishing of the second virial coefficient

$$\chi^* = 1/2 \Leftrightarrow \partial M^*/\partial X = 0 \quad (19)$$

together with the location of the critical point

$$\chi^* = 2 \Leftrightarrow X(\partial M^*/\partial X) \cong 1. \quad (20)$$

With our proposal (14) for M^* we can make these general results a little more precise. The second virial coefficient vanishes when $x \sim N^{\nu_2}$ where

$$\nu_2 = \nu - (\nu - 1/d) \frac{4 - d - \beta_2}{2 + \beta_2} \quad (21)$$

and the critical point is reached when $x \sim N^{\nu_c}$ where

$$\nu_c = \nu - (\nu - 1/d) \frac{4 - d}{2} \quad (22)$$

Note that the critical volume fraction and the value χ_c at the critical point (deduced from (12)) are

$$\phi_c \sim N^{-(\nu_c d - 1)} = N^{-(\nu d - 1)(d - 2)/2} \quad (23)$$

and

$$2\chi_c - 1 \sim N^{-(d - 2)/2} \quad (24)$$

5. The link between θ_2 and ν for $d = 3$.

One knows from the renormalization group approach (see e.g. [22]) that $d = 3$ is the upper critical dimension for the suspension, while our results seem to give no special role to any dimension but $d = 4$. What is proved by renormalization is the ultimate transformation of any n -body interactions ($n \geq 3$) into an effective two-body interaction. When this effective interaction balances the true one, the second virial coefficient vanishes. This implies that the second virial vanishes while the monomer-solvent interaction is in the range $\chi < 1/2$. Transposed into our model, the renormalizability of the n -body interactions implies

$$\nu_2 \geq \nu_\theta. \quad (25)$$

This condition is clearly satisfied for $d = 2$ if we introduce in (16) and (21) the values $\nu = 3/4$ [18] and $\theta_2 = 19/12$ [3, 17]. This is less obvious for $d = 3$ where the theoretical result $\theta_2 \cong 0.71$ [3, 7] gives for ν_2 a value which is quite close to ν_θ . It is then tempting to *assume* that

$$\nu_2 = \nu_\theta \quad \text{for} \quad d = 3 \quad (26)$$

and to guess that $\nu_2 < \nu_\theta$ for $d > 3$, thus violating the necessary condition (25) and fixing the upper critical dimension at the expected value. It should be clear that the above equality imposes a relation between β_2 and η

$$\beta_2 = \frac{\eta}{3 + \eta} \quad \text{for} \quad d = 3 \tag{27}$$

or equivalently between θ_2 and ν

$$\theta_2 = \frac{3(1 - \nu)(5 - 6\nu)}{2\nu(4 - 3\nu)} \quad \text{for} \quad d = 3. \tag{28}$$

We have two possibilities for ν : the field theory value $\nu = 0.588$ [19] which leads to $\theta_2 = 0.692$, or the Flory value $\nu = 3/5$ which leads to $\theta_2 = 7/11 \cong 0.636$. These two possible values for θ_2 are smaller than the 0.71 proposed by des Cloizeaux [3, 7] but they are compatible with one of the enumeration results obtained by Redner [23].

6. Discussion of results.

In table I we give all the numerical values predicted by our results (16) and (21) to (24).

For $d = 3$ we have considered the two different possibilities for ν and we used relation (28). It is noticeable that we get the expected result for the θ -point with the Flory value for ν , while if we adopt the field theory value, we find a θ -chain more compact than the Brownian walk, a rather unexpected result which suggests that (14) is for the true M^* what the Flory value is for the true ν . Concerning the critical point, a synthesis of experimental results obtained by six different teams was presented by Perzinski [21, 9]. The conclusion was $\phi_c \sim N^{-0.38 \pm 0.01}$ and $2\chi_c - 1 \sim N^{-0.50 \pm 0.01}$. A similar analysis of published data led Muthukumar [6] to the conclusion that $\phi_c \sim N^{-0.39 \pm 0.01}$. Our predictions are thus pretty close to the experimental results whatever is the choice for ν .

Let us now analyse the results obtained for $d = 2$. We do not obtain the expected result for the θ -point, i.e. the Duplantier-Saleur exponent $\nu_\theta = 4/7$ [20]. The value we find, $\nu_\theta = 7/12$, is slightly larger but it is remarkable that it was recently obtained by a quite different route. De Queiroz [16] found this value when combining the Gaussian elastic energy

Table I. — Results deduced from assumed values for $\nu(d)$ [18, 19] and $\theta_2(d = 2)$ [17]. The value of $\theta_2(d = 3)$ is deduced from equation (28).

Quantity and definition		Space dimension		
		$d = 3$	$d = 3$	$d = 2$
	ν	0.588	3/5	3/4
	θ_2	0.692	7/11	19/12
Eq. (8)	η	0.618	2/3	1
Eq. (10)	β_2	0.171	2/11	11/16
Eq. (21)	ν_2	0.491	1/2	27/43
Eq. (16)	ν_θ	0.491	1/2	7/12
Eq. (22)	ν_c	0.461	7/15	1/2
Eq. (23)	ϕ_c	$N^{-0.382}$	$N^{-2/5}$	1/2
Eq. (24)	$2\chi_c^{-1}$	$N^{-1/2}$	$N^{-1/2}$	$\cong 1$

with a screened three-body interaction energy. This coincidence suggests that there should be some link between screened three-body interactions and our anomalous number of contacts, in particular its contribution M_2^* . Concerning the critical point, demixion is predicted for $\nu_c = 1/2$ (compact chains) and a surface fraction $\phi_c = 1/2$, independent of the chain length. The recent experiments of Mann *et al.* [24] on PDMS spread on a water-air interface have concluded to the existence of domains with different surface densities. No experimental value of ν_c could be determined and ϕ_c seems to be somewhat less than 1/2, possibly due to the presence of long-range dipolar forces. Surface-pressure measurements were performed on PMMA by Vilanove *et al.* [25]. They observed a negative second virial coefficient and a particle size corresponding to $\nu = 0.53$. No phase separation was observed which means that $\nu_c < 0.53 < \nu_2$.

Concerning the coexistence curve, many efforts were made to present it in a symmetric form [26, 27]. We showed in section 2 that the coexistence curve of SAWs is symmetric when represented with the variables ϕ/ϕ^* and χ^* . The expressions we proposed for ϕ^* and χ^* display a severe variation with N and $\chi(T)$ in the demixion region. This is certainly one of the sources of the dissymetry of the coexistence curve when represented with the variables ϕ and T . But this is not the whole story. We strived to handle the spatial correlations between monomers as precisely as possible, but we discarded any correlations between solvent molecules. Hence we cannot expect the coexistence curve of SAW to display the critical exponents of simple binary mixtures that were found in experimental curves by Sanchez [26]. However, we are now in a better position to distinguish the role of the monomer correlations from the role of solvent correlations. For instance, the good results we obtained for ϕ_c and $\chi_c - 1/2$ suggest that the location of the critical point depend on the monomer correlations only. Obviously, such a conclusion can not be extended to the whole coexistence curve.

To sum up, our results for $d = 3$ fit rather well with experiment, while those for $d = 2$ are somewhat open to criticism. It is possible that our proposal (14) is not suitable for a two-dimensional space. In fact, our main objective here was to show that a model with *no a priori reference to the random walk or Gaussian statistics* could compete advantageously with the classical models to explain what happens in the neighbourhood of both the θ -point and the critical point. The cornerstone of the approach is M^* , the anomalous number of contacts, and there is certainly some progress to be done in the modelisation of that quantity.

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