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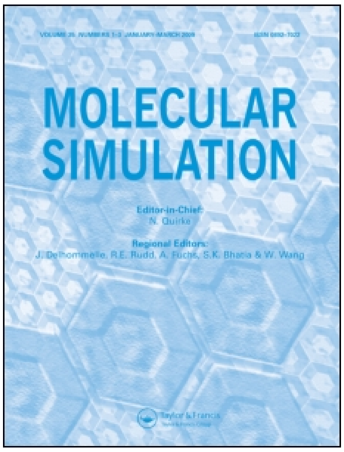

Molecular Simulation
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713644482

Beyond Flory's Theory: A Computer Aided Phenomenology for Polymers

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To cite this Article Imbert, J. B. and Victor, J. M.(1996) 'Beyond Flory's Theory: A Computer Aided Phenomenology for Polymers', Molecular Simulation, 16: 4, 399 — 419

To link to this Article: DOI: 10.1080/08927029608024088

URL: http://dx.doi.org/10.1080/08927029608024088

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Molecular Simulation, 1996, Vol. 16, pp. 399–419
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BEYOND FLORY'S THEORY: A COMPUTER AIDED PHENOMENOLOGY FOR POLYMERS

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(Received June 1995, accepted July 1995)

Extending the histogram method of Ferrenberg and Swendsen to the problem of a SAW in a bad solvent, we obtain a new expression for the free energy of such a system, which fits very properly the numerical results of our Monte Carlo simulations. The basic difference with Flory's theory lies in the reference system: instead of considering random walks (RW) we start with self-avoiding walks (SAW) for which we already proposed a model expression for the distribution of the radius of gyration. This distribution is universal for any class of homo- or heteropolymers and contains all the information concerning the excluded volume problem. For homopolymers we consider the standard case where attractive nearest neighbours interactions simulate a bad solvent. At a given radius of gyration r we compute the density of states $P(r, m)$ for an interacting self avoiding walk (ISAW) as a function of its number of contacts m. We build a microscopic phenomenology for $P(r, m)$ based on a factorisation procedure: $P(r, m)$ is split into an *a priori* probability $P(r)$ of finding a SAW with a given r, and a *conditional* probability $P(m/r)$ of finding such a conformation with m contacts. A complete scaling is given for $P(r)$ whereas $P(m/r)$ is found to be well approximated by a gaussian distribution. Scaling laws for the first two cumulants of $P(m/r)$ are exhibited from a finite-size scaling analysis. The theta-point temperature is recovered along with its dependence on the polymer length and the free energy of the globule phase is well reproduced. This approach is shown to be generalizable to heteropolymers by merely replacing m by u, the energy per monomer, and computing the density of states $P(r, u)$ at a given r. The case of sequenced and random copolymers is examined with special attention to polyampholytes.

KEY WORDS: Polymer, Flory's theory, Monte Carlo, Histogram method, Hamiltonian walks, theta point.

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1 INTRODUCTION

The statistical mechanics of an isolated polymer chain in solution has been given much attention since the pioneering work of Flory [1]. Scaling laws have been proposed [2] and observed by numerical simulations [3]. Exact results, mainly concerning critical exponents, have been obtained for a few models, especially in 2 dimensions [4, 5]. However the free energy of a realistic macromolecule is still generally evaluated by means of a Flory type calculation. Also the behaviour of the globule density under the theta-point as a function of temperature is treated at the same level of approximation. Hence Flory's theory remains a widely used reference, largely because of its simplicity but also because it is very hard improving it.

Let us remember that Flory's theory relies on two strong assumptions:

(F1) The chain is supposed to be ideal and perturbed by the interactions, namely excluded volume and monomer-monomer attraction.
(F2) The potential energy resulting from these interactions is computed as in a simple fluid.

It comes out from F1 and F2 that the topology (*i.e.* the excluded volume constraint) is entirely contained in the entropic term S of Flory's free energy and totally ignored in the energetic term U, and reversely that the attractive interactions are entirely put in U and ignored in S. Energetics and topology are completely decoupled.

The most striking feature of Flory's theory is the incredibly good estimation of the so-called Flory exponent ν relating the equilibrium radius of gyration Rg to the chain length (equivalently molecular weight) N through $\mathrm{Rg} \propto N^{\nu}$. According to Flory, $\nu = 3/(d+2)$ for a d-dimensional chain, which is exact in 1, 2 and 4 dimensions, and very near to the well known result 0.588 in 3 dimensions. The counterpart is that neither U nor S are extensive: they go both as $N^{(4-d)/(d+2)}$ in d dimensions, so that Flory's free energy $\mathrm{F}_0(r, \mathrm{T})$, where T is the temperature, is largely incorrect. However its variation with r is nevertheless satisfying. The success of the theory relies on an extremely subtle compensation between both errors made on U and S. The origin and mechanism of such a compensation is still puzzling. Hence improving separately the energetic or entropic contribution is bound to fail.

We therefore attempt here to compute directly the partition function $Z_{\mathrm{N}}(r, T)$ of one macromolecule of length N as a function of its radius of gyration r and at temperature T. We chose the simplest model of interactions, however canonical for the coil-globule transition, which is the Interacting Self-Avoiding Walk (ISAW) model [6]. This is a lattice model where a SAW interacts with itself through nearest neighbours interactions called contacts. The contribution of each contact to the potential energy is $-J$. The self-avoiding condition takes into account the short range repulsion between monomers and the contact interaction acts as a balance between monomer-monomer, monomer-solvent and solvent-solvent interactions as usual. An exact calculation of the partition function $Z_N(r, \mathrm{T})$ is a priori out of question. However, thanks to the improvement of computers and algorithms, it happens to be possible to get reliable values over a large domain of r and T. Such values are nothing but tables of numbers or graphics which are meaningless in themselves. As a matter of fact, computing numerical estimates of $Z_N(r, \mathrm{t})$ is useless while we have no way to analyse them. We therefore need to build a phenomenological approach which could enlighten these tables of numbers and be a guide throughout the results.

Our phenomenological approach relies on a natural factorisation of the density of states $P_N(r, m)$ which constitute the raw data. In the case of an ISAW, m is a geometrical quantity which also accounts for the energy of the chain: $\mathrm{U} = -J\ m$. The files $P_N(r, m)$ are obtained thanks to a Monte Carlo simulation [3] (see details in Table 1). An importance sampling algorithm has been used in relation with a histogram method similar in principle with the standard Ferrenberg and Swendsen's method [7], but different in the way of using it. Details are given in the appendix. A finite-size scaling analysis has been applied which allows to extrapolate to the thermodynamic limit.

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Table 1 Details of Monte Carlo runs. Five chain lengths have been simulated by the standard 'Slithering snake method' of Wall & Mandel [23]: $N = 20, 50, 80, 100$ and 150. One step corresponds to moving one monomer from the tail onto the head of the chain. The number of independent conformations (Nb. of Ind. Conf.) is equal to the total number of steps divided by the so called decorrelation time (equal to the mean number of steps needed for moving every monomer of one given conformation).

N	*Nb. of steps (in millions)*	*Nb. of Ind. Conf.*
20	25	200 735
50	710	205 777
80	710	73 065
100	1220	47 617
150	3210	106 485

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The model and related technicalities which allow to compute the density of states $P_N(r, m)$ are described in Section 2. Section 3 is devoted to the factorisation of $P_N(r, m)$ into an a *priori* probability P_N (r) and a *conditional* probability P_N $(m|r)$. Flory's theory is revisited throughout: thanks to numerical simulations it becomes possible to obtain $P_N(r)$ very accurately with no more need in using the statistics of Random Walks (RW). The results concerning $P_N(r)$ are exposed in Section 4. Section 5 deals with P_N $(m|r)$: different approximation levels are presented for P_N $(m|r)$ and consequently for the resulting free energy in Section 6. Section 7 treats of the coil-globule transition and of the globule phase. Finally Section 8 aims at extending our results to the more general case of heteropolymers such as polyampholytes.

2 COMPUTING THE DENSITY OF STATES FOR AN ISAW

The ISAW is the canonical model for studying the coil-globule transition of homopolymers[6]: a SAW is embedded in a square or cubic lattice depending on the dimensionality of space. Two monomers are said to be in contact when they are nearest neighbours (except of course when they are bound along the chain). An effective contact interaction $-J$ is then assumed between them, which takes into account the monomer-monomer J_{m-m}, monomer-solvent J_{m-s} and solvent-solvent J_{s-s} interactions: $J = J_{m-m} - 2J_{m-s} + J_{s-s}$.

Following Flory's spirit we spread all configurations among classes depending on their radius of gyration r. We also divide them into subclasses according to their number of contacts m. The variable m is discrete going from 0 (no contact) to $(d\text{-}1)N$ (compact state where every monomer has its maximum number of neighbours); r is also discrete but has a much larger number of values, so that we divided the interval of r-values into sub-intervals with an arbitrary length $\delta r = 0.1$. $P_N(r, m)$ then accounts for the fraction of conformations that have m contacts and a radius of gyration between r and $r + \delta r$.

In order to get data all over the space of conformations, it was necessary to use a bias of selection in our Monte Carlo simulation, usually called importance sampling. Large values of m are obtained thanks to a weighting factor $e^{\chi m}$, whereas large values of r are reached with a weighting factor $\exp(\chi r^2)$. It turns out that $e^{\chi m}$ is also the actual Boltzmann factor because the energy is $U = -Jm$ and $e^{-\beta U} = e^{\chi m}$ where $\chi = \beta J$. However, it is just by happening and if another energy were taken, $e^{\chi m}$ would differ from the actual Boltzmann factor and nevertheless favour great numbers of contacts. It is sufficient to run the simulation for a few values of χ to cover the entire space of conformations. However it is also necessary to collapse the data obtained at different values of χ into a single histogram. We did so in a manner reminiscent to Ferrenberg and Swendsen's, however substantially different, which is described in the appendix.

3 A NATURAL FACTORIZATION OF $P_N(r,m)$

The complete histogram of the density of states $P_N(r,m)$ is a raw datafile for which a phenomenological approach is needed. We propose to factorize $P_N(r,m)$ into a product of an *a priori* probability $P_N(r)$ and a conditional probability $P_N(m|r)$:

(i) $P_N(r)$ is the probability of finding a SAW conformation with a radius of gyration r, irrespective to its energy or any other weighting but the constraint of excluded volume ($P_N(r)$ is a geometrical distribution),

(ii) $P_N(m|r)$ is the conditional probability of finding a conformation with m contacts among all conformations with a given radius of gyration r.

This factorization is very natural for an ISAW and may be extended to any other model of interactions by simply changing the number of contacts m into the potential energy U.

It may be of interest to realize that this factorization naturally leads to Flory's theory. The probability distribution $P_N^{\mathrm{RW}}(r)$ of finding a RW conformation with a radius of gyration r, thus corresponding to $P_N(r)$ for RWs, has been calculated exactly by Orland [8]. The 3-dimensional result is:

$$P_N^{\mathrm{RW}}(r) \propto (r^2/N)^2\, e^{-2\pi^2 r^2/N} \qquad \text{if} \quad r \propto N^{\nu} \tag{1a}$$

and

$$P_{\mathrm{N}}^{\mathrm{RW}}(r) \propto (N/r^2)^{5/2}\, e^{-N/8r^2} \qquad \text{if} \quad r \propto N^{1/d} \tag{1b}$$

Now if $P_N(m|r)$ is approximated by a delta-function peaked on the mean number of contacts in a solution of monomers with the same density N/r^d, namely $\delta(m - N^2/r^d)$, the partition function $Z_N(r,\mathrm{T})$ writes

$$Z_N^{\mathrm{Flory}}(r,\mathrm{T}) = \aleph_N P_N(r) e^{\chi N^2/r^d} \tag{2}$$

where $\aleph_{\mathrm{N}}$ is the total number of SAWs with a length N.

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Hence the resulting free energy is simply

$$\beta F_N^{\text{Flory}}(r, \mathrm{T}) = 2\pi^2 \frac{r^2}{N} - \chi \frac{N^2}{r^d} - 2\ln\left(\frac{r^2}{N}\right) \tag{3}$$

which is nothing but Flory's result, including the logarithmic correction $-2\ln(r^2/N)$.

The factorization of $P_N(r, m)$ takes into account the mean field nature of Flory's theory by merely approximating the conditional probability $P_N(m|r)$ by a delta-function. And both main assumptions F1 and F2 of Flory's theory correspond respectively to using $P_N^{\text{RW}}(r)$ for the *a priori* distribution and using $\delta(m - N^2/r^d)$ for the *conditional* one. Hence the factorization achieves the decoupling between topology and energy in agreement with Flory's assumptions. We stress on the fact that $P_N(r)$ is universal, *i.e.* independent of the interactions between monomers and is characteristic of the excluded volume. Obviously $P_N(r)$ depends quantitatively (but not qualitatively) on the lattice.

4 THE PROBABILITY DISTRIBUTION $P_N(r)$

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We chose the radius of gyration r instead of the end-to-end distance r_{1N} because r is directly related to the intrinsic density $\rho = N/r^d$ whereas r_{1N} is not, and $\rho^{1/2}$ is the conventional order parameter Ψ of the coil-globule transition [2].

For SAWs, Lhuillier [9] proposed a scaling law of the form

$$P_N(r) = P_N(r_0)\, e^{-A\,[(r/r_0)^{-1/(\nu-1/d)} + ((1-\nu)/(\nu-1/d))(r/r_0)^{1/(1-\nu)} - (1-1/d)/(\nu-1/d)]} \tag{4}$$

where $r_0 = \lambda_0 N^\nu$ is the location of the maximum of $P_N(r)$. Equation (4) was numerically reproduced very well in 2 dimensions by Victor & Lhuillier [10] and later on in 3 dimensions by Bishop & Saltiel [11]. However, the scaling was verified for a rather narrow interval of r values: $r_0/2 \leqslant r \leqslant 2r_0$.

Now a paradox arises from the numerical values A fitted in [10] and [11]. Indeed, when extrapolating to compact conformations, *i.e.* for the minimum value $r_{\min}$ of r, equation (4) gives

$$\frac{P_N(r_{\min})}{P_N(r_0)} \cong e^{-A\,(r_{\min}/r_0)^{-1/(\nu-1/d)}} \tag{5}$$

Now $r_{\min} = \lambda_{\min} N^{1/d}$ because $r_{\min}$ corresponds to a spherical compact conformation and therefore $\lambda_{\min} = \sqrt{3/5}\,(3/4\pi)^{1/3}$ in 3 dimensions.

Hence equation (5) writes as well

$$\frac{P_N(r_{\min})}{P_N(r_0)} \cong e^{-AN\,(\lambda_{\min}/\lambda_0)^{-1/(\nu-1/d)}} \tag{6}$$

But $P_N(r_{\min})/P_N(r_0)$ is also the ratio of the number of hamiltonian walks (HWs) to the total number of SAWs. It is well accepted [12] that the number of HWs goes like $N^{\gamma_H - 1}\mu_H^N$ whereas the total number of SAWs $\aleph_N$ goes like $N^{\gamma-1}\mu^N$. μ and μ_H are respectively the connectivity constant of SAWs and HWs on a cubic lattice. Hence

$P_N(r_{\min})/P_N(r_0)$ should be equal to $(\mu_H/\mu)^N$ up to some power of N and subsequently, in the thermodynamic limit ($N \to \infty$)

$$\ln\frac{\mu}{\mu_H} = A\left(\frac{\lambda_{\min}}{\lambda_0}\right)^{-1/(\nu-1/d)} \tag{7}$$

which is far from being true as can be seen from Table 2. We therefore suspected that some deviation from Lhuillier's prediction should happen for dense conformations.

Whereas $P(r)$ is a function of $s = r/N^\nu$ in the coil phase ($r \propto N^\nu$), it becomes a function of ρ in the globule phase ($r \propto N^{1/d}$):

$$P_N(r) \propto e^{-NG(\rho)} \tag{8}$$

Both equations (4) and (8) must be equivalent as $\rho \to 0$ (continuous transition from a globule to a coil) so that

$$NG(\rho) \approx A\left(\frac{r}{r_0}\right)^{-1/(\nu-1/d)} \quad \text{as}\ \rho \to 0 \tag{9}$$

We may define a new variable t as

$$t = \frac{1}{N}\left(\frac{r}{N^\nu}\right)^{-1/(\nu-1/d)} = \rho^{1/(d\nu-1)} \tag{10}$$

with which equation (9) writes

$$G(\rho) \cong \tilde{A}\,t \quad as\ t \to 0 \tag{11}$$

and $\tilde{A} = A\,\lambda_0^{1/(\nu-1/d)}$. Note that t is related to the order parameter $\psi = \rho^{1/2}$ of the coil-globule transition through:

$$t = \psi^{2/(d\nu-1)} \tag{12}$$

Equation (8) may be written as well

$$P_N(r) \propto e^{-Ng(t)} \tag{13}$$

with $g(t) = G(\rho)$.

According to (11) $g(t)$ is linear for vanishing t. Now (7) is obtained when assuming that $g(t)$ remains linear up to the maximum value t_m of t. From (10) we get $t_m = \rho_m^{1/(d\nu-1)}$ where $\rho_m = N/r_{\min}^d = \lambda_{\min}^{-d}$ is the maximum density, so that $t_m = \lambda_{\min}^{-1/(\nu-1/d)}$

Table 2 3-dimensional values relative to the distribution $P_N(r)$ introduced in Section 4. $\lambda_{\min} = \sqrt{3/5}\,(3/4\pi)^{1/3}$. μ and μ_H are respectively the connectivity constant of SAWs and HWs on a cubic lattice. A theoretical prediction due to Orland *et al.* [13] gives $\mu_H = 6/e \cong 2.21$. $A(\lambda_{\min}/\lambda_0)^{-1/(\nu-1/d)}$ is about half the value of $\ln \mu/\mu_H$ in strong opposition with equation (7). However taking into account that $g(t)$ is not linear leads to the corrected value $g(t_m)$ which is now very close to $\ln \mu/\mu_H$.

$\lambda_{\min}$	λ_0	$A\left(\frac{\lambda_{\min}}{\lambda_0}\right)^{-1/(\nu-1/d)}$	t_m	$g(t_m)$	μ	μ_H	$\ln\frac{\mu}{\mu_H}$
0.4805	0.39 ± 0.01	0.359	15.63	0.770 ± 0.015	4.683	2.21	0.751

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(see Table 2 for numerical values of λ_0, $\lambda_{\min}$ and t_m in 3 dimensions). Thanks to the histogram method we found numerically that $g(t)$ more and more deviates from its linear behaviour as t is growing up to t_m (see Fig. 1).

Looking further for the expansion of $g(t) - \tilde{A}t$ we found:

$$g(t) - \tilde{A}t \cong \tilde{B}t^n \tag{14}$$

with $n \cong 2.5$ as comes out from the log-log plot on Figure 2. Hence we get the following scaling function for $g(t)$:

$$g(t) = \tilde{A}t + \tilde{B}t^n \tag{15}$$

which fits accurately the numerical data up to $t \approx 10$ as shown on Figure 1. It can also be noted that $g(t_m)$ is now very close to the predicted value of Orland *et al.* [13] shown in Table 2.

5 MODELING $P_N(m|r)$

The conditional probability $P_N(m|r)$ which happens to be a geometrical property of SAW conformations contains the overall information on energy. This function

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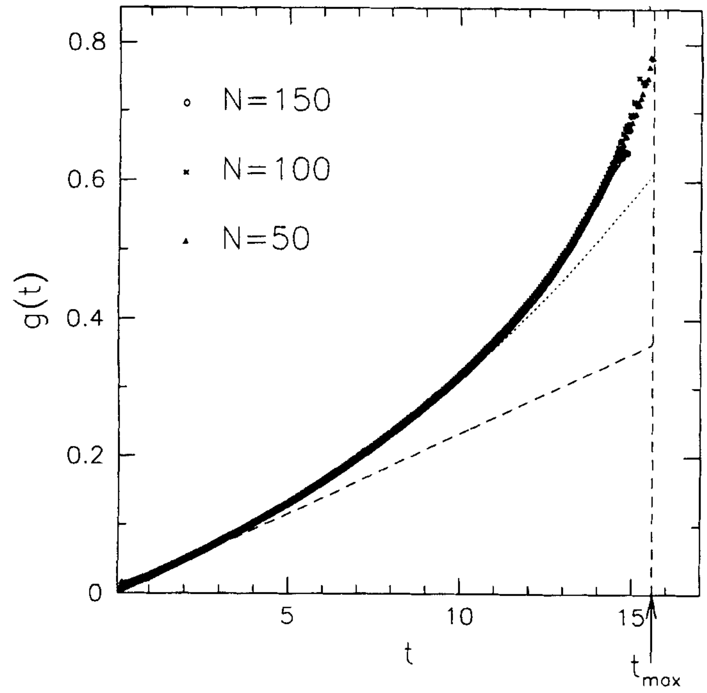

Figure 1 Scaling of the function $g(t)$. The maximum $g(t\max)$ leads to a rather good value of the connectivity constant for hamiltonian self-avoiding walks.

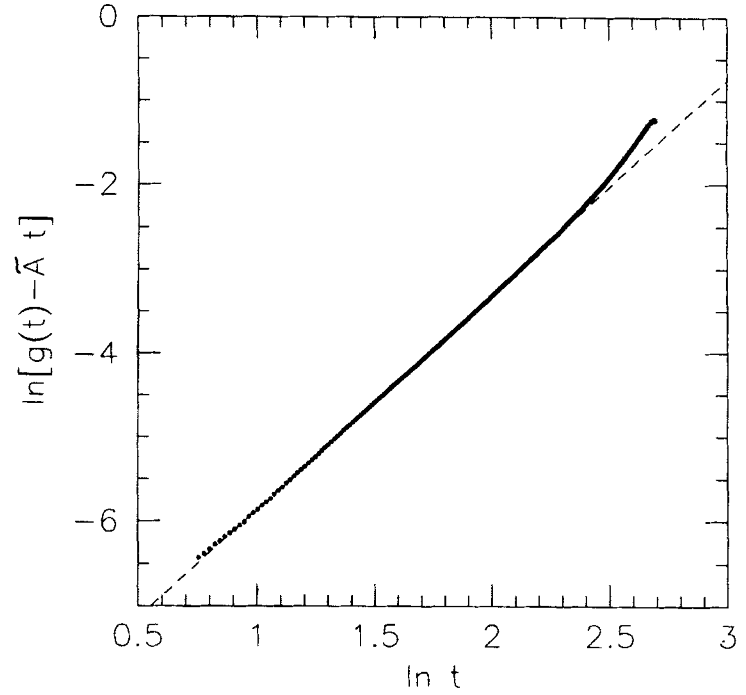

Figure 2 log-log plot of $g(t)-\tilde{A}t$ vs t, showing a power low correction to $g(t)$ according to (14): $g(t)-\tilde{A}t \cong \tilde{B}t^n$ with $n \cong 2.5$ and $\tilde{B} \cong 2.2\,10^{-4}$.

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is characteristic of the nature of the interactions between monomers (apart from the excluded volume) as well as $P_N(r)$ is characteristic of the excluded volume (irrespective to the other interactions between monomers). The scaling properties of $P_N(m|r)$ may be summed up as follows:

–In the coil state, *i.e.* when $r \propto N^\nu$, $P_N(m|r)$ is a function of $s = r/N^\nu$ and m.

–In the globule state, *i.e.* when $r \propto N^{1/d}$, that is to say when t remains finite as $N \rightarrow \infty$, $P_N(m|r)$ becomes a function of t and m/N:

$$P_N(m|r) \approx e^{-Nf((m/N),t)} \tag{16}$$

where the function f does not depend on N any longer. Due to this simplification we will focus on the globule phase, where the functional dependence of f can be modelled thanks to a cumulant expansion.

We first note that

$$P_N(m|r) \approx \left\{p_t\left(\frac{m}{N}\right)\right\}^N \tag{17}$$

where $p_t\left(\frac{m}{N}\right)=e^{-f((m/N),t)}$.

We write the characteristic function of $p_t\left(\frac{m}{N}\right)$ as

$$\hat{p}_t(\chi)=\sum_m p_t\left(\frac{m}{N}\right)e^{\chi^{m/N}} \tag{18}$$

Now its comulant expansion is the expansion of $\ln[\hat{p}_t(\chi)]$ with respect to χ:

$$\ln[\hat{p}_t(\chi)]=\sum_l \frac{\kappa_l(t)}{l!}(\chi)^l \tag{19}$$

$\kappa_1(t)$ is the mean number of contacts per monomer of all SAWs with a given density t:

$$\kappa_1(t)=\langle\frac{m}{N}\rangle(t) \tag{20}$$

whereas $\kappa_2(t)$ is the variance of the distribution $p_t\left(\frac{m}{N}\right)$

$$\kappa_2(t)=\langle\left(\frac{m}{N}\right)^2\rangle(t)-\langle\frac{m}{N}\rangle^2(t) \tag{21}$$

Scaling laws have been found for the first two cumulants $\kappa_1(t)$ and $\kappa_2(t)$. Higher cumulants may be neglected up to the error bars all over the globular phase (see Fig. 3). Hence $p_t(\frac{m}{N})$ may be well approximated by a gaussian distribution (see Fig. 4):

$$p_t\left(\frac{m}{N}\right)=\frac{1}{\sqrt{2\pi\kappa_2(t)}}e^{-[(m/N)-\kappa_1(t)]^2/2\kappa_2(t)} \tag{22}$$

5.1 *Scaling of the Mean Number of Contacts per Monomer: $\kappa_1(t)$*

We first note that there is no Boltzmann weighting in defining $\kappa_1(t)=\langle m/N\rangle(t)$, so that $\kappa_1(t)$ is also the usual mean number of contacts of an ISAW at infinite temperature and density t. A scaling law was previously given [14] for $m(r)=\langle m\rangle(r)$, the mean number of contacts of SAWs with a given r, which is formally very close to the scaling of $P(r)$: again $m(r)$ is a function of $s=r/N^{\nu}$ in the coil phase

$$m(r)=aN+bs^{-1/(\nu-1/d)}-Ds^{1/(1-\nu)} \tag{23}$$

whereas in the globule phase $\langle m/N\rangle$ becomes a function of t. Now a correction to scaling arises in the globule phase due to surface effects: because the number of contacts per monomer on the surface of the globule is less than inside, a correcting term proportional to $N^{(1-1/d)}$ has to be subtracted. This term is also proportional to the mean number of contacts per monomer (actually proportional to t because the surface correction disappears at vanishing density) so that the scaling becomes:

$$\kappa_1(t)=a+bt-cN^{-1/d}t \tag{24}$$

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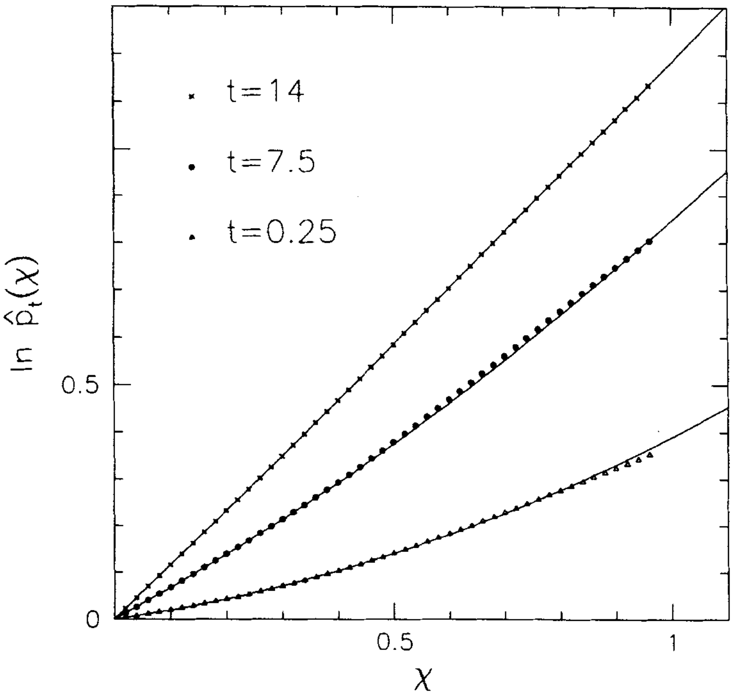

Figure 3 Comparison between the logarithm of the characteristic function $\hat{p}_t(\chi)$ and the second order cumulant expansion $\kappa_1(t)\chi + \kappa_2(t)\chi^2/2$. $t = 0.25$ corresponds to a swollen conformation (coil) and $t = 14$ to a nearly compact globule.

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Moreover, here again a deviation from this linear scaling occurs for growing densities. A complete scaling is proposed as follows:

$$\kappa_1(t) = a + (b - cN^{-1/d})t + \beta t^\alpha \ln t \tag{25}$$

with $\alpha \cong 0.5$. Eq. (25) is well obeyed all over the globule phase for $50 < \mathrm{N} < 150$ (see Fig. 5).

5.2 Scaling of the Variance of the Distribution $p_t(\frac{m}{N})$: $\kappa_2(t)$

We found that the variance $\kappa_2(t)$ of the distribution $p_t(\frac{m}{N})$ also goes like:

$$\kappa_2(t) = \Sigma_0 + \Sigma_1 t + \Sigma_2 t^\alpha \ln t \tag{26}$$

as can be seen from Figure 6, so that the mean $\kappa_1(t)$ and the variance $\kappa_2(t)$ of $p_t(\frac{m}{N})$ happen to have the same behaviour with respect to t. Such a behaviour, including the funny t^α ln t term, is observed in 2, 3 and 4 dimensions as well (with α depending on the dimension) [15].

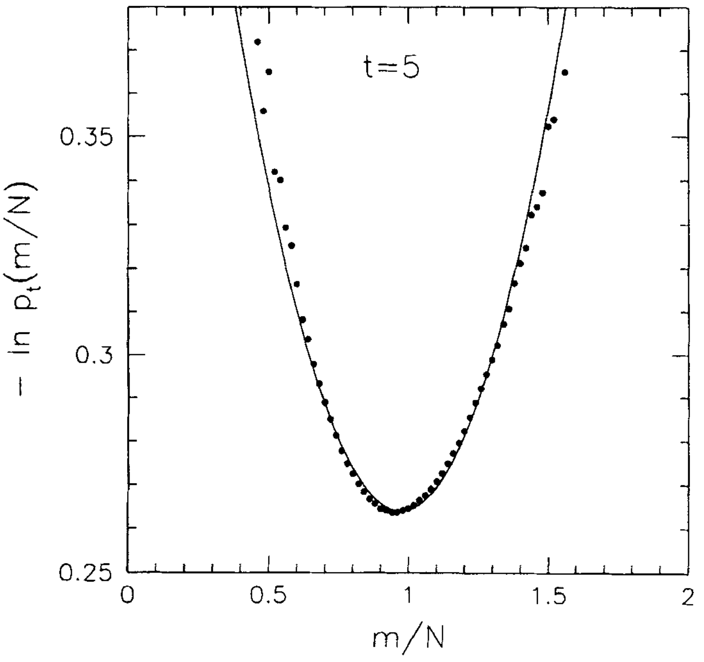

Figure 4 Validity of the gaussian approximation (22) for $p_t(\frac{m}{N})$ in the globular phase.

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6 MODELING THE FREE ENERGY

The partition function of an ISAW at a temperature T, that is to say for a coupling $\chi = J/k_B\mathrm{T}$ where k_B is the Boltzmann constant, writes

$$Z_N(\mathrm{T}) = \sum_r Z_N(r, \mathrm{T}) \tag{27}$$

with

$$Z_N(r, \mathrm{T}) = \aleph_N \sum_m P_N(r, m) e^{\chi m} \tag{28}$$

The factorization of $P_N(r, m)$ then leads to

$$Z_N(r, T) = \aleph_N P_N(r) \sum_m P_N(m|r) e^{\chi m} \tag{29}$$

where the functions $P_N(r)$ and $P_N(m|r)$ are known from sections 4 and 5. We remind that $Z_N(r, \mathrm{T})$ is the basic function of Flory's theory. Two levels of approximation for $Z_N(r, \mathrm{T})$ can be deduced from the corresponding approximations of $P_N(m|r)$ introduced in the preceding section:

(i) A mean-field approximation is derived by replacing $P_N(m|r)$ by a delta function centred on the true mean value $m(r)$ introduced in section V: $P_N(m|r) \cong$

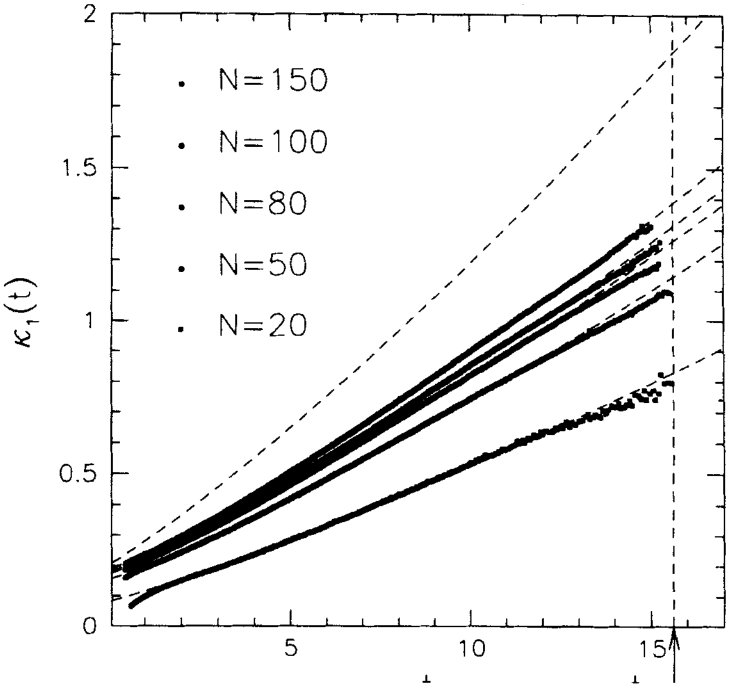

Figure 5 Validity of the scaling function (25) for the mean number of contacts per monomer $\kappa_1(t)$: $a \cong 0.20$, $b \cong 0.08$, $c \cong 0.12$, $\beta \cong 0.0029$ and $\alpha \cong 0.5$. The upper dashed line accounts for the thermodynamic limit.

$\delta[m - m(r)]$ where $m(r)$ is the mean number of contacts of SAWs with a radius of gyration r. This approximation differs from Flory's one because $P_N(r)$ is no longer relative to random walks and $m(r)$ is neither given by a simple fluid calculation. We stress on the fact that $m(r)$ is still of order N at vanishing densities, whereas N^2/r^d is clearly not.

Hence the mean-field approximation writes:

$$P_N^{\mathrm{MF}}(m|r) = \delta(m - m(r)) \tag{30}$$

and accordingly

$$Z_N^{\mathrm{MF}}(r,\mathrm{T}) = \aleph_N P_N(r) e^{\chi m(r)} \tag{31a}$$

$$\frac{\beta \mathrm{F}^{\mathrm{MF}}}{N}(r,\mathrm{T}) = -\ln \mu - \frac{1}{N} \ln P_N(r) - \chi \frac{m(r)}{N} \tag{31b}$$

where μ is the connectivity constant of SAWs on a cubic lattice.

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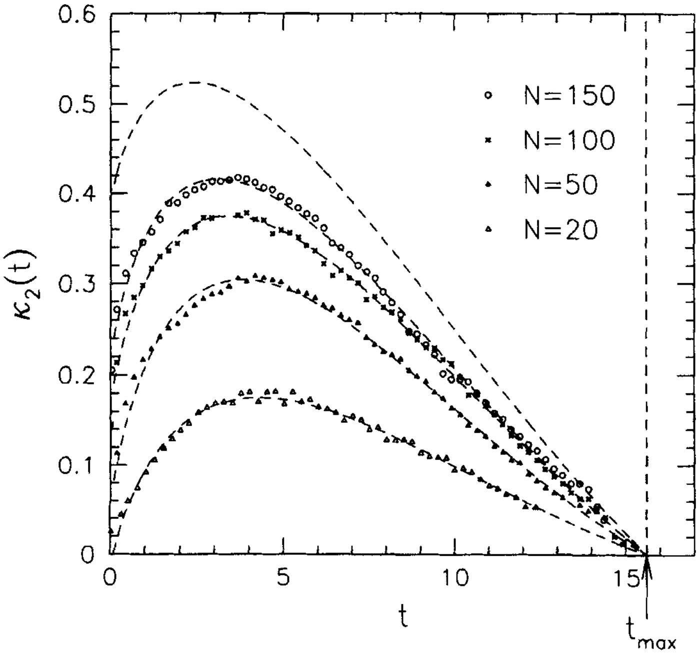

Figure 6 Validity of the scaling function (26) for the variance $\kappa_2(t)$ of the distribution $p_t(\frac{m}{N})$. The upper dashed line accounts for the thermodynamic limit: $\sum_0 \cong 0.39$, $\sum_1 \cong -0.30$ and $\sum_2 \cong 0.04$.

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(ii) Equations (17) and (22) give the following gaussian expression for $P_N(m|r)$:

$$P_N^{\mathrm{G}}(m|r) = \frac{1}{\sqrt{2\pi\sigma_N^2(r)}} e^{-[m-m(r)]^2/2\sigma_N^2(r)} \tag{32}$$

where

$$\sigma_N^2(r) = N\kappa_2(t) \tag{33}$$

Note that $\sigma_N(r)$ is the standard deviation of the distribution $P_N(m|r)$.

The partition function and free energy then write

$$Z_N^{\mathrm{G}}(r,\mathrm{T}) = \aleph_N P_N(r)\, e^{\chi m(r) + \frac{\chi^2}{2}\sigma_N^2(r)} \tag{34a}$$

$$\frac{\beta \mathrm{F}^{\mathrm{G}}}{N}(r,\mathrm{T}) = -\ln\mu - \frac{1}{N}\ln P_N(r) - \chi\frac{m(r)}{N} - \frac{\chi^2}{2}\frac{\sigma_N^2(r)}{N} \tag{34b}$$

In the globule phase, a simple expression arises

$$\frac{\beta \mathrm{F}^{\mathrm{G}}}{N}(t,\mathrm{T}) = -\ln\mu + g(t) - \chi\kappa_1(t) - \frac{\chi^2}{2}\kappa_2(t) \tag{35}$$

where $g(t)$ has been defined in (13) and expressed in (15).

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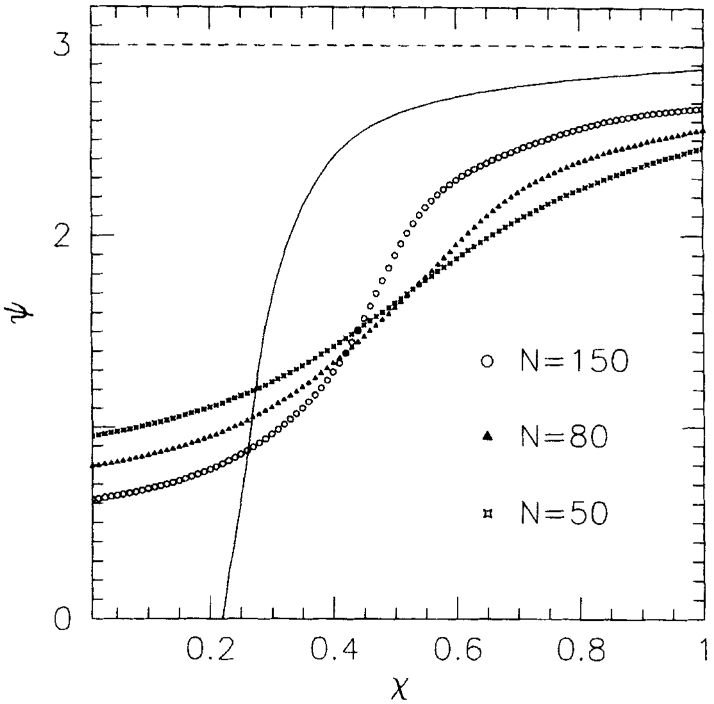

Figure 7 Variation of the order parameter $\psi = \rho^{1/2} = [t(\chi)]^{(d\nu-1)/2}$ as observed for $N = 50, 80$ and 150. The solid line is the thermodynamic limit as results from equation (36).

With help of (15), (25) and (26) it comes (for $N \rightarrow \infty$)

$$\frac{\beta \mathrm{F}^{\mathrm{G}}}{N}(t, \mathrm{T}) = -\ln\mu - \chi a - \frac{\chi^2}{2}\Sigma_0 + P(\chi)t - Q(\chi)t^{\alpha}\ln t + \tilde{B}t^{n} \tag{36}$$

with

$$P(\chi) = \tilde{A} - \chi b - \frac{\chi^2}{2}\Sigma_1 \tag{37a}$$

and

$$Q(\chi) = \chi\beta + \frac{\chi^2}{2}\Sigma_2 \tag{37b}$$

Remembering that $t = \rho^{1/(d\nu-1)}$ we get the equivalent expression

$$\frac{\beta \mathrm{F}^{\mathrm{G}}}{N}(\rho, \mathrm{T}) = -\ln\mu - \chi a - \frac{\chi^2}{2}\Sigma_0 + P(\chi)\rho^{1/(d\nu-1)}$$
$$-\frac{1}{d\nu-1}Q(\chi)\rho^{\alpha/(d\nu-1)}\ln\rho + \tilde{B}\rho^{n/(d\nu-1)} \tag{38}$$

The equilibrium radius of gyration Rg is the value of r which minimizes $F(r, T)$. In the globule phase $t(\chi) = (N/\mathrm{Rg}^d)^{1/(d\nu - 1)}$ denotes as well the equilibrium density for the coupling χ (note that χ is also proportional to the usual Flory's parameter). The order parameter $\psi = [t(\chi)]^{(d\nu - 1)/2}$ introduced in (12) has been drawn on Figure 7 for different values of N along with an extrapolation into the thermodynamic limit ($N \to \infty$).

Deriving the entropy and the energy of an ISAW at temperature T is straightforward. We get

$$\frac{\mathrm{U}}{NJ} = -\kappa_1[t(\chi)] - \chi\kappa_2[t(\chi)] \tag{39a}$$

$$\frac{\mathrm{S}}{Nk_B} = \ln\mu - g[t(\chi)] - \frac{\chi^2}{2}\kappa_2[t(\chi)] \tag{39b}$$

where $t(\chi)$ is the equilibrium density. Note that U and S are now extensive in opposition to Flory's result.

7 THE COIL-GLOBULE TRANSITION

The order parameter ψ drawn on Figure 7 vanishes at a critical value χ_θ. This critical point is usually called the θ-point and corresponds to a tricritical phase transition [16, 17] between a coil ($\psi = 0$ when $\chi < \chi_\theta$) and a globule ($\psi > 0$ when $\chi > \chi_\theta$). Because ψ is just a power of t, we may use t as well instead of ψ for studying the transition. The critical coupling χ_θ may be evaluated either from the mean field expression (31b) or from the gaussian one (36). In both cases χ_θ is obtained by first minimizing the free energy with respect to t, thus giving $t(\chi)$, and then solving $t(\chi) = 0$.

(i) In the mean-field approximation, we simply get

$$t = 0 \quad \text{if } \tilde{A} - \chi b > 0 \tag{40a}$$

$$t = t_m \quad \text{if } \tilde{A} - \chi b < 0 \tag{40b}$$

which means a first order transition at $\chi_\theta^{\mathrm{MF}} = \tilde{A}/b$.

(ii) In the gaussian approximation, we get

$$P(\chi) - \alpha Q(\chi) t^{\alpha - 1} + n\tilde{B}t^{n-1} = 0 \tag{41}$$

As the equilibrium value $t(\chi)$ vanishes, $P(\chi)$ goes to 0. Hence, we obtain a continuous transition at a value χ_θ^{G} which is a solution of

$$\frac{\Sigma_1}{2}\chi^2 + b\chi - \tilde{A} = 0 \tag{42}$$

leading to

$$\chi_\theta^{\mathrm{G}} = \frac{b}{\Sigma_1}\left[\sqrt{1 + \frac{2\Sigma_1\tilde{A}}{b^2}} - 1\right] \tag{43}$$

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Table 3 Numercial values of $\tilde{A}, b$ and $\sum_1$ as deduced respectively from $g(t), \kappa_1(t)$ and $\kappa_2(t)$. They lead to the mean field theta-temperature (actually theta-coupling) $\chi_\theta^{\mathrm{MF}} = \tilde{A}/b$ and to the gaussian approximation χ_θ^{G} according to (43). $\chi_\theta^{\mathrm{ML}}$ is the best known numerical result for the ISAW on a cubic lattice [18]. Note that $\chi_\theta^{\mathrm{G}} < \chi_\theta^{\mathrm{ML}} < \chi_\theta^{\mathrm{MF}}$.

$\tilde{A}$	b	$\sum_1$	$\chi_\theta^{\mathrm{MF}}$	χ_θ^{G}	$\chi_\theta^{\mathrm{ML}}$
0.023 ± 0.001	0.07 ± 0.01	0.3 ± 0.1	0.33	0.22	0.275

Note that $\chi_\theta^{\mathrm{G}} < \chi_\theta^{\mathrm{MF}}$. Values of $\chi_\theta^{\mathrm{MF}}$ and χ_θ^{G} are shown in Table 3 along with the best known value of χ_θ obtained by Meirovitch & Lim [18]. Evaluating the critical exponents from equation (41) is an open problem which will be examined elsewhere.

8 EXTENSION TO HETEROPOLYMERS

The phenomenological approach so far developed for an ISAW can be extended formally to any macromolecule, either composed of one kind of monomers (homopolymers) or of different kinds of monomers (heteropolymers, also called copolymers by chemists). The nature and the number of components are not sufficient to characterize heteropolymers: their specificity also lies in the sequence of their components. Regular sequences, corresponding to a regular alternance of given patterns give rise to sequenced copolymers, whereas statistic copolymers correspond to random sequences. The nature of the monomers also involves their electrical charge: a chain where + and − charges coexist is called a polyampholyte [19] (PA). Random and alternate PAs exist and are believed to have radically different behaviours [19, 20, 21]. Note that biopolymers are generally PAs with a special mention for proteins.

We first note that the density of states $P_N(r, m)$ of the ISAW may well be generalized to any model of interactions by simply changing m into U, the potential energy. The factorization of $P_N(r, m)$ between $P_N(r)$ and $P_N(m|r)$ still works for $P_N(r, \mathrm{U})$, because $P_N(r)$ does not depend on the interactions (universality of $P_N(r)$). We also conjecture that $P(\mathrm{U}|r)$ is still normally distributed as is $P(m|r)$. The microscopic phenomenology built for $P_N(r, m)$ is therefore assumed to be general. The corresponding methodology may be summed up as follows:

(i) Compute $P_N(r, \mathrm{U})$ thanks to a histogram method or any equivalent numerical method (including exact enumeration for short chain lengths).

(ii) Extract the conditional probability $P_N(\mathrm{U}|r)$ from $P_N(r, U)$:

$$P_N(U|r) = P_N(r, \mathrm{U})/P_N(r) \tag{44}$$

where $P_N(r) \propto e^{-Ng(t)}$ is known from Section 4 (distribution of SAWs).

(iii) Introduce the distribution $p_t(\frac{\mathrm{U}}{\mathrm{N}})$ according to

$$P_N(\mathrm{U}|r) = \left\{p_t\left(\frac{\mathrm{U}}{N}\right)\right\}^N \tag{45}$$

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(iv) Compute the first two cumulants $\kappa_1(t)$ and $\kappa_2(t)$ of $p_t(\frac{U}{N})$. Note that $\kappa_1(t)$ is the mean energy $u(t)$ per monomer and $\kappa_2(t)$ is the variance $\sum^2(t)$ of $p_t(\frac{U}{N})$.

(v) Compute the free energy at a given density t and temperature T according to the gaussian approximation:

$$\frac{\beta F^G}{N}(t, T) = -\ln\mu + g(t) + \beta u(t) - \frac{\beta^2}{2}\sum^2(t) \tag{46}$$

As an example we present the results obtained for an alternate as well as for a random PA. The aforementioned model used for the ISAW has been extended by merely assigning a + or − charge to each monomer. In the alternate case there is a regular alternance of + and − monomers along the chain (... + − + − + − ...), whereas in the random case the charges have been distributed at random with the constraint of global neutrality (Kantor & Kardar [22] have shown indeed that a PA with a global charge larger than about $N^{1/2}$, where N is the number of monomers which compose the PA, has the same behaviour as a polyelectrolyte and is therefore rodlike at low temperatures).

The mean energy $u(t)$ and the variance $\sum^2(t)$ have been computed for both systems and are drawn on Figure 8 for comparison. The alternate PA is very similar to

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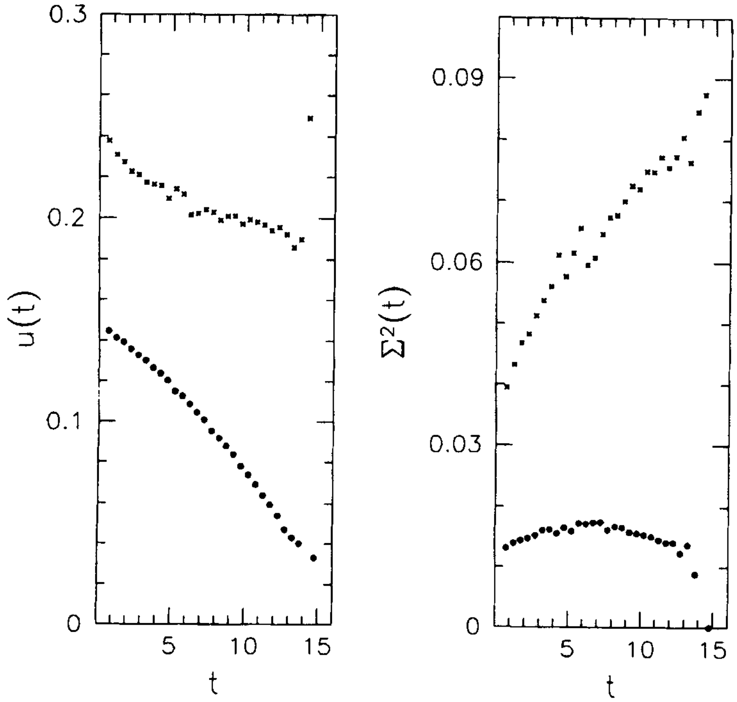

Figure 8 Mean energy per monomer $u(t)$ and variance of the distribution $p_t(\frac{U}{N})$ for an alternating polyampholyte (•) and a random polyampholyte (*).

the ISAW: $u(t)$ and $\sum^2(t)$ are respectively very close to $-\kappa_1(t)$ and $\kappa_2(t)$ of the ISAW as can be seen from Figures 5 and 6. We consider this similarity as a further indication for the existence of a regular theta-point in the phase space of an alternate PA, as was observed numerically by Victor & Imbert [20] and argued theoretically by Wittmer *et al.* [21].

On the contrary, in the random case, $\sum^2(t)$ is found to grow steadily with t whereas the ISAW's variance $\kappa_2(t)$ has a well defined maximum and vanishes at the maximum density. Also $u(t)$ decreases much more slowly than in the alternate case. Therefore the equilibrium density $t(\beta)$ of a random PA is quite different from the alternate situation. However the lack of scaling functions for $u(t)$ and $\sum^2(t)$ prevents from studying any further the phase diagram of random PAs and discussing their possible coil-globule transition, which remains an open problem.

9 CONCLUSION

We tried in this paper to tackle the thermodynamics and conformational analysis of any macromolecule by means of a new phenomenological approach. This approach is based on a factorization of the density of states, leading to a simple and reliable expression of the free energy. Such an expression overcomes the main backgrounds of Flory's theory, especially the non-extensivity of the free energy. We call this approach a 'Computer Aided Phenomenology' inasmuch as the basic ingredients required for building the free energy are obtained by means of a numerical simulation. We showed how to get these ingredients for the ISAW model and proved that the resulting free energy is actually quite good. We expect this phenomenological theory to be helpful in studying heteropolymers: polyampholytes and hopefully proteins. Finally an extension to solutions would be quite desirable.

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APPENDIX

In the following, we focus on a standard Monte Carlo simulation using the Boltzmann factor $\exp(-\beta \mathrm{U})$ with U the potential energy and $\beta = 1/k\mathrm{T}$ as usual. Moreover we suppose that we have run the simulation at different temperatures T_i and stored the numbers of independent configurations (actually chain conformations) with the energy U into histograms $\mathrm{H}_{\mathrm{T}_i}(\mathrm{U})$. The corresponding probabilities $P_{\mathrm{T}_i}(\mathrm{U})$ can be written as

$$P_{\mathrm{T}_i}(\mathrm{U}) = W_i(\mathrm{U})\, e^{\beta_i(\mathrm{F}_i - \mathrm{U})} \tag{A1}$$

where $W_1(\mathrm{U})$ is the density of states and F_i is the (still unknown) free energy of the system at T_i. Equation (A1) leads to

$$W_i(\mathrm{U}) = e^{-f_i} P_{\mathrm{T}_i}(\mathrm{U})\, e^{\beta_i \mathrm{U}} \tag{A2}$$

where $f_i = \beta_i \mathrm{F}_i$ remains to be determined. The central problem of the histogram method lies in determining this parameter, in order to collapse the different histograms $W_i(\mathrm{U})$ into a single one $W(\mathrm{U})$. Reminding that two histograms $W_i(\mathrm{U})$ and $W_j(\mathrm{U})$ are actually two estimates of the same theoretical histogram $W(\mathrm{U})$ (see Figure 9) and taking the logarithm of equation (A2) leads to

$$\ln(P_{\mathrm{T}_i}(\mathrm{U})e^{\beta_i \mathrm{U}}) - \ln(P_{\mathrm{T}_j}(\mathrm{U})e^{\beta_j \mathrm{U}}) = f_i - f_j = \delta f_{ij} \tag{A3}$$

δf_{ij} doesn't depend on U any longer and is easily determined using a least square fit calculation, *i.e.* minimizing the quantity (A4)

$$\sum_{\mathrm{U}}\left[\lambda_{ij}(\mathrm{U})\ln\left(\frac{P_{\mathrm{T}i}(\mathrm{U})e^{\beta_i \mathrm{U}}}{P_{\mathrm{T}j}(\mathrm{U})e^{\beta_j \mathrm{U}}}\right) - \delta f_{ij}\right]^2 \tag{A4}$$

where λ_{ij} takes into account the statistical errors associated with $P_{\mathrm{T}_i}(\mathrm{U})$ and $P_{\mathrm{T}_j}(\mathrm{U})$. As the variance (squared standard deviation) of the value $\ln P_{\mathrm{T}_i}(\mathrm{U})$ is $\mathrm{H}_{\mathrm{T}_i}^{-1}(\mathrm{U})$, one gets

$$\lambda_{ij}(\mathrm{U}) = \frac{1}{\mathrm{H}_{\mathrm{T}i}(\mathrm{U}) + \mathrm{H}_{\mathrm{T}j}(\mathrm{U})} \tag{A5}$$

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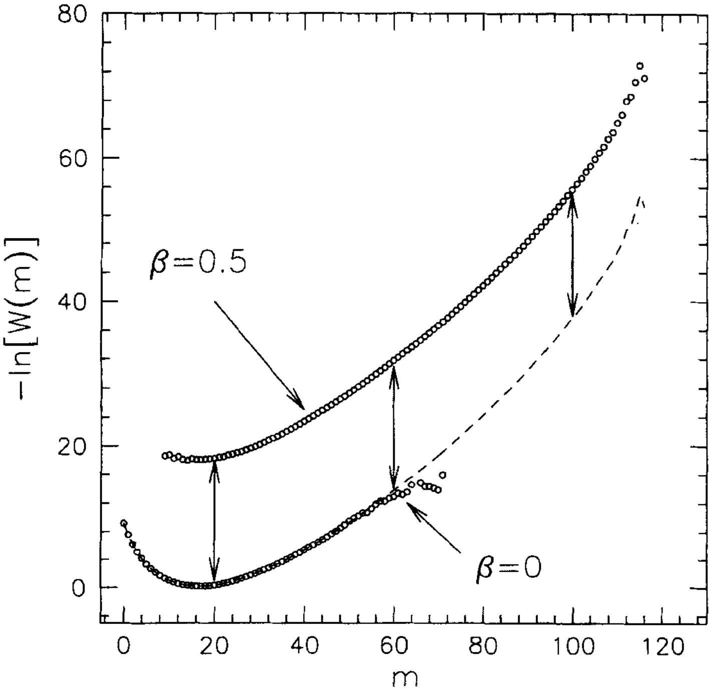

Figure 9 Logarithmic histograms of the density of states $W_i(m)$ computed at two different temperatures for the ISAW. The energy U is related to the number of contacts m through $\mathrm{U} = -Jm$. Both histograms are merely translated from each other by a shift which is exactly δf_{ij} according to (A1 – A3). The dashed line shows schematically the resulting complete histogram as obtained from (A6).

The last step leading to $W(\mathrm{U})$ is

$$\ln W(\mathrm{U}) = \frac{1}{\sum_j H_{\mathrm{T}_j}(\mathrm{U})} \sum_i H_{\mathrm{T}_i}(\mathrm{U}) \ln W_i(\mathrm{U}) \tag{A6}$$

In other words, ln $W(\mathrm{U})$ is the barycentric average of the logarithms of the histograms, *i.e.* ln $W_i(\mathrm{U})$, weighted with $H_{\mathrm{T}_i}(\mathrm{U})$. The variance of the value ln $W(\mathrm{U})$ then writes

$$Var[\ln W(U)] = \frac{1}{\sum_j H_{T_j}(U)} \tag{A7}$$

As equation (A7) points it out, the error on ln $W(\mathrm{U})$ decreases as the number of histograms $W_i(\mathrm{U})$ increases.

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