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Flory theory revisited

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Résumé. — La théorie de Flory pour une chaîne polymérique est obtenue comme l'ordre dominant d'un développement en cumulants. Dans cette approche, l'énergie libre originale de Flory (y compris le terme logarithmique) est obtenue. L'exposant α est donné par $\alpha = (\nu - \frac{1}{2})d$ et ne satisfait pas la relation entre exposants $\alpha = 2 - \nu d$. Les préfacteurs des énergies libres élastique et répulsive sont dérivés à partir des paramètres microscopiques. La méthode peut être appliquée à d'autres types d'interactions entre monomères, et on discute le cas d'une chaîne en mauvais solvant. La méthode peut être généralisée au cas de plusieurs chaînes (solutions de polymères), et on en déduit les changements de comportement en fonction de la concentration en chaînes. Finalement, la méthode permet un développement systématique autour de la théorie de Flory. Les corrections à la théorie de Flory comportent des termes extensifs (proportionnels au nombre N de monomères) et des puissances de $N^{2-\nu d}$. Ces termes divergent à la limite thermodynamique, mais moins vite que le développement de Fixman, en puissances de $N^{2-d/2}$.

Abstract. — The Flory theory for a single polymer chain is derived as the lowest order of a cumulant expansion. In this approach, the full original Flory free energy (including the logarithmic term), is recovered. The critical exponent α comes out naturally as $\alpha = (\nu - \frac{1}{2})d$, and is not related to ν by the hyperscaling relation $\alpha = 2 - \nu d$. The prefactors of the elastic and repulsive energy are calculated from the microscopic parameters. The method can be applied to other types of monomer-monomer interactions, and the case of a single chain in a bad solvent is discussed. The method is easily generalized to many chain systems (polymers in solutions), yielding the usual crossovers with chain concentration. Finally, this method is suitable for a systematic expansion around the Flory theory. The corrections to Flory theory consist of extensive terms (proportional to the number N of monomers) and powers of $N^{2-\nu d}$. These last terms diverge in the thermodynamic limit, but less rapidly than the usual Fixman expansion in $N^{2-d/2}$.

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1. Introduction.

The size of a polymer in a solvent is characterized by an exponent ν , which relates the radius of gyration R of the chain to the degree of polymerization N (number of monomers) through the formula [1-3]

$$R \sim N^\nu \quad (1)$$

In an ideal Θ solvent, chains are Brownian with $\nu = 1/2$. In a good solvent, chains are swollen, and the index ν is larger than $1/2$.

Flory [1] has devised a simple argument to compute the exponent ν of a chain in a good solvent, which gives amazingly good agreement for all dimensions d . The argument, as presented in reference [2] goes as follows: consider a chain of N monomers of length a , with local repulsive interaction characterized by an excluded volume parameter v . The swollen chain will acquire a radius of gyration R ; the monomer concentration is $c = N/R^d$, and the repulsive energy is thus

$$\begin{aligned} E_{\text{rep}} &= \frac{1}{2} v c^2 R^d \\ &= \frac{1}{2} v \frac{N^2}{R^d} \end{aligned} \quad (2a)$$

The elastic energy of the chain is given by

$$E_{\text{el}} = T \frac{R^2}{N a^2} \quad (2b)$$

up to a multiplicative constant (T is the temperature).

The total free energy is

$$F = T \frac{R^2}{N a^2} + \frac{v N^2}{2 R^d} \quad (3)$$

and minimization with respect to R yields the celebrated Flory exponent

$$\nu_{\text{F}} = \frac{3}{d+2} \quad (4)$$

which is exact for $d = 1, 2, 4$, and almost exact for $d = 3$ (see reference [3]; $\nu_{\text{F}} = 0.6$ whereas the best numerical estimates give $\nu = 0.588$).

Note that this simplified derivation of the Flory theory misses a logarithmic term in the free energy, which is present in the original derivation of Flory [1]. In any case, the derivations of the Flory exponent are quite empirical, and any attempt to go beyond it, by improving on any of the two terms of (2a) or (2b) turns out to ruin the argument (see Ref. [2] for a discussion of that point). Moreover, the free energy increases like $N^{\frac{4-d}{d+2}}$ instead of increasing like N as it should in the asymptotic limit of large N (the free energy is not extensive).

Des Cloizeaux has proposed a Gaussian variational procedure to tackle this problem [4], but the outcome was $\nu_c = \frac{2}{d}$, by far too large a result. Also, Edwards has proposed a self-consistent method [5] which yielded the Flory formula, but, as noted by des Cloizeaux [3], this approximation yields unrealistic chain configurations.

More recently, Edwards and Singh [6] have proposed the uniform expansion model, which yields exactly the Flory equation. This method amounts to expanding the end to end radius to first order around a Gaussian chain with expanded monomer length, adjusting this length so as to cancel the first order correction.

To be complete, let us also mention the approach of Bouchaud and Georges [7], which interpret the Flory formula in terms of sums of correlated random variables, and that of Kamien [8], who gets it from a self-consistent renormalization group method.

In this paper, we propose a cumulant expansion, which to lowest order generates a Flory type free energy from the microscopic model, and which can be easily generalized to the study of more complex systems (polyelectrolytes, chains in bad solvents, membranes and interfaces, solutions of polymers, etc...). This method allows for a systematic expansion around Flory theory.

2. One chain system.

We start from the Edwards continuous representation of a chain

$$Z = \int_{\mathbf{r}(N)=\mathbf{r}(0)} \mathcal{D}\mathbf{r}(s) \delta \left(\frac{1}{N} \int_0^N ds \mathbf{r}(s) \right) \exp \left(-\frac{1}{2} \int_0^N ds \dot{\mathbf{r}}^2 - \frac{1}{2} \int_0^N ds ds' v(\mathbf{r}(s) - \mathbf{r}(s')) \right) \quad (5)$$

where $v(\mathbf{r} - \mathbf{r}')$ is the interaction between a monomer at point \mathbf{r} and a monomer at \mathbf{r}' and units have been chosen so that the persistence length a is equal to 1.

The first δ -function is used to constrain the center of mass of the chain at the origin. Furthermore, to simplify calculations, we have assumed that the chain is closed, i.e. $\mathbf{r}(N) = \mathbf{r}(0)$. As will be seen later, this constraint is unessential, as far as the method is concerned.

Performing a Gaussian transform on (5), and denoting by $v^{-1}(\mathbf{r})$ the inverse of the kernel $v(\mathbf{r})$, we have [9]

$$Z = \int \mathcal{D}\phi(\mathbf{r}) \exp \left(-\frac{1}{2} \int d\mathbf{r} d\mathbf{r}' \phi(\mathbf{r}) v^{-1}(\mathbf{r} - \mathbf{r}') \phi(\mathbf{r}') \right) Z_\phi \quad (6a)$$

where

$$Z_\phi = \int_{\mathbf{r}(N)=\mathbf{r}(0)} \mathcal{D}\mathbf{r}(s) \delta \left(\frac{1}{N} \int_0^N ds \mathbf{r}(s) \right) \exp \left(-\frac{1}{2} \int_0^N ds \dot{\mathbf{r}}^2 - i \int_0^N ds \phi(\mathbf{r}(s)) \right) \quad (6b)$$

Using the identity

$$1 = \int_0^\infty dQ \delta \left(Q - \frac{1}{N} \int_0^N ds \mathbf{r}^2(s) \right) \quad (7a)$$

where Q is the square of the radius of gyration, we can rewrite (6b) as

$$Z_\phi = \int_0^\infty dQ Z_\phi(Q) \quad (7b)$$

where

$$Z_\phi(Q) = \int_{\mathbf{r}(N)=\mathbf{r}(0)} \mathcal{D}\mathbf{r}(s) \delta \left(\frac{1}{N} \int_0^N ds \mathbf{r}(s) \right) \delta \left(Q - \frac{1}{N} \int_0^N ds \mathbf{r}^2(s) \right) \times \exp \left(-\frac{1}{2} \int_0^N ds \dot{\mathbf{r}}^2 - i \int_0^N ds \phi(\mathbf{r}(s)) \right) \quad (7c)$$

Defining $\langle \ \rangle$ as the average with respect to the partition function $Z_0(Q) = Z_{\phi=0}(Q)$, we can write

$$\begin{aligned} \frac{Z_\phi(Q)}{Z_0(Q)} &= \left\langle \exp \left(-i \int_0^N ds \phi(\mathbf{r}(s)) \right) \right\rangle \\ &= \left\langle \exp \left(-i \int d\mathbf{r} \phi(\mathbf{r}) \rho(\mathbf{r}) \right) \right\rangle \end{aligned} \quad (8)$$

where $\rho(\mathbf{r}) = \int_0^N ds \delta(\mathbf{r} - \mathbf{r}(s))$.

We use the cumulant expansion

$$\langle e^{-A} \rangle = \exp \left(-\langle A \rangle + \frac{1}{2} (\langle A^2 \rangle - \langle A \rangle^2) - \frac{1}{6} (\langle A^3 \rangle - 3 \langle A^2 \rangle \langle A \rangle + 2 \langle A \rangle^3) + \dots \right) \quad (9)$$

To lowest order, we have

$$Z_\phi(Q) \simeq Z_0(Q) \exp \left(-i \int d\mathbf{r} \phi(\mathbf{r}) \rho_Q(\mathbf{r}) \right) \quad (10a)$$

where

$$\begin{aligned} Z_0(Q) &= \int_{\mathbf{r}(N)=\mathbf{r}(0)} D\mathbf{r}(s) \delta \left(\frac{1}{N} \int_0^N ds \mathbf{r}(s) \right) \delta \left(Q - \frac{1}{N} \int_0^N ds \mathbf{r}^2(s) \right) \\ &\quad \times \exp \left(-\frac{1}{2} \int_0^N ds \dot{\mathbf{r}}^2(s) \right) \end{aligned} \quad (10b)$$

and

$$\begin{aligned} \rho_Q(\mathbf{r}) &= \langle \rho(\mathbf{r}) \rangle \\ &= \frac{1}{Z_0(Q)} \int_0^N ds \int_{\mathbf{r}(N)=\mathbf{r}(0)} D\mathbf{r}(s) \delta \left(\frac{1}{N} \int_0^N ds \mathbf{r}(s) \right) \delta \left(Q - \frac{1}{N} \int_0^N ds \mathbf{r}^2(s) \right) \\ &\quad \times \exp \left(-\frac{1}{2} \int_0^N ds \mathbf{r}^2(s) \right) \delta(\mathbf{r} - \mathbf{r}(s)) \end{aligned} \quad (10c)$$

$Z_0(Q)$ and $\rho_Q(\mathbf{r})$ are respectively the partition function and monomer concentration for a Brownian chain with center of mass constrained at the origin and radius of gyration square constrained to Q .

Finally, performing the $\{\phi\}$ Gaussian integral of (6a), we obtain

$$Z \simeq Z_F = \int_0^\infty \frac{dQ}{N} Z_0(Q) \exp \left(-\frac{1}{2} \int d\mathbf{r} d\mathbf{r}' \rho_Q(\mathbf{r}) v(\mathbf{r} - \mathbf{r}') \rho_Q(\mathbf{r}') \right) \quad (11)$$

The F index in (11) stands for Flory, since, as we shall see, Z_F is just the Flory partition function.

A straightforward calculation of (10b) and (10c) yields (see the appendix), for $Q/N \rightarrow \infty$ (swollen chain)

$$Z_0(Q) \simeq \frac{(2\pi)^{2d}}{(d-1)!} \left(\frac{Q}{N} \right)^{(d-1)} \exp \left(-\frac{2\pi^2 Q}{N} \right) \quad (12a)$$

and

$$\rho_Q(\mathbf{r}) \simeq N \left(\frac{d}{2\pi Q} \right)^{d/2} \exp \left(-\frac{d}{2Q} \mathbf{r}^2 \right) \quad (12b)$$

In the thermodynamic limit, $N \rightarrow +\infty$, and (11) can be evaluated by applying the saddle-point method on Q . Assuming a standard contact interaction

$$v(\mathbf{r}) = v \delta(\mathbf{r}) \quad (13)$$

where v is the excluded volume parameter, the function to minimize is

$$\beta F_F = -(d-1) \ln \left(\frac{Q}{N} \right) + 2\pi^2 \frac{Q}{N} + \frac{v}{2} \left(\frac{d}{4\pi} \right)^{d/2} \frac{N^2}{Q^{d/2}} \quad (14a)$$

where β is the inverse temperature, and the radius of gyration $R_G = \sqrt{Q}$ satisfies the minimization equation

$$-\frac{2(d-1)}{R_G} + 4\pi^2 \frac{R_G}{N} - \frac{vd}{2} \left(\frac{d}{4\pi} \right)^{d/2} \frac{N^2}{R_G^{d+1}} = 0 \quad (14b)$$

We recognize in equations (14) the Flory free energy, with calculated prefactors, including the logarithmic term, present in the original Flory theory. The role of this term is just to ensure a crossover from a Brownian regime in $d > 4$ to a swollen regime in $d \leq 4$. Indeed, to solve (14b), we must balance two terms of opposite signs, and check that the third one is negligible with respect to them.

Balancing the 2nd and 3rd terms in (14b) yields the Flory result, $\nu_F = \frac{3}{d+2}$. The consistency requirement: $\frac{1}{R_G} \ll \frac{R_G}{N}$ is satisfied provided that $d \leq 4$.

Balancing the 1st and 2nd terms in (14b) yields the Brownian exponent $\nu = 1/2$, and the consistency check $\frac{N^2}{R_G^{d+1}} \ll \frac{R_G}{N}$ is satisfied for $d \geq 4$.

Thus the logarithmic term indeed, enforces the crossover between the 2 regimes.

To conclude this part, let us note that this method yields naturally a value of the critical exponent α for polymers. It is the exponent α which comes out, because we have considered closed polymer chains. Using (11) together with (12) and (14), and calculating the quadratic fluctuations around the Flory radius of gyration, we find that the partition function (11) takes the form

$$Z_F = N^{\alpha-2} \exp(-N^{\frac{4-d}{d+2}} f) \quad (14c)$$

where f is a constant independent of N , and the exponent α is given by

$$\alpha = (\nu_F - \frac{1}{2})d \quad (14d)$$

Note that this value of α does not satisfy the hyperscaling relation $\alpha = 2 - \nu d$ predicted by the renormalization group theory. Equation (14d) gives $\alpha = 1/2$ in $d = 2$ and $\alpha = 0$ in $d = 4$, which are the exact values, and 0.3 in $d = 3$ compared to the best numerical value $\alpha = 0.25$ (for a review of numerical values of exponents, see Ref. [3]).

The method can be applied to any type of two-body interaction $v(\mathbf{r})$ and denoting by $v(\mathbf{k})$ its Fourier transform, the Flory free energy becomes

$$\beta F_F = -(d-1) \ln \left(\frac{Q}{N} \right) + 2\pi^2 \frac{Q}{N} - \frac{\beta}{2} \int d\mathbf{k} v(\mathbf{k}) \exp \left(-Q \frac{\mathbf{k}^2}{d} \right). \quad (14)$$

Application of this method to the case of polyelectrolytes, where the two-body interaction is the Coulomb potential $v(\mathbf{r}) = \frac{1}{r^{(d-2)}}$, yields the well-known Flory exponent [10] $\nu = \frac{3}{d}$. This is known to be incorrect for dimensions larger than 3, where the exact exponent is $\nu = \frac{2}{d-2}$ (see Ref. [10]).

Finally, let us show how this method works for a chain in a poor solvent. In this case, in addition to the second virial coefficient v which is attractive, one has to introduce the third virial coefficient w which is repulsive. The partition function of the chain reads

$$Z = \int_{\mathbf{r}(N)=\mathbf{r}(0)} \mathcal{D}\mathbf{r}(s) \delta\left(\frac{1}{N} \int_0^N ds \mathbf{r}(s)\right) \exp\left(-\frac{1}{2} \int_0^N ds \dot{\mathbf{r}}^2 + \frac{v}{2} \int_0^N ds ds' \delta(\mathbf{r}(s) - \mathbf{r}(s')) - \frac{w}{6} \int_0^N ds ds' ds'' \delta(\mathbf{r}(s) - \mathbf{r}(s')) \delta(\mathbf{r}(s) - \mathbf{r}(s''))\right). \quad (15a)$$

In the present case, the alternative to the Gaussian transform is to constrain the monomer density $\rho(\mathbf{r})$ as a new integration variable through the identity

$$1 = \int \mathcal{D}\phi(\mathbf{r}) \mathcal{D}\rho(\mathbf{r}) \exp\left(i \int d\mathbf{r} \phi(\mathbf{r}) \rho(\mathbf{r}) - i \int_0^N ds \phi(\mathbf{r}(s))\right). \quad (15b)$$

Inserting identity (15b) in equation (15a) yields

$$Z = \int \mathcal{D}\phi(\mathbf{r}) \mathcal{D}\rho(\mathbf{r}) \exp\left(i \int d\mathbf{r} \phi(\mathbf{r}) \rho(\mathbf{r}) + \frac{v}{2} \int d\mathbf{r} \rho^2(\mathbf{r}) - \frac{w}{6} \int d\mathbf{r} \rho^3(\mathbf{r})\right) Z_\phi \quad (15c)$$

where Z_ϕ is defined by equation (6b). Using identity (7a) in the above equation together with the lowest order cumulant (see Eq. (10a)) and integrating over the fields ϕ and ρ yields the expression

$$Z \simeq \int_0^\infty dQ Z_0(Q) \exp\left(+\frac{v}{2} \int d\mathbf{r} \rho_Q^2(\mathbf{r}) - \frac{w}{6} \int d\mathbf{r} \rho_Q^3(\mathbf{r})\right) \quad (16)$$

where $Z_0(Q)$ and $\rho_Q(\mathbf{r})$ are defined in equations (10b, c).

In the case $v < 0$, we are back to the previous situation, and the chain is swollen. The free energy reads

$$\beta F_F = -(d-1) \ln\left(\frac{Q}{N}\right) + 2\pi^2 \frac{Q}{N} - \frac{v}{2} \left(\frac{d}{4\pi}\right)^{d/2} \frac{N^2}{Q^{d/2}} + \frac{w}{6} \left(\frac{d}{18\pi}\right)^d \frac{N^3}{Q^d}. \quad (17a)$$

At the Θ point, $v = 0$, and the free energy is still given by the above expression with $v = 0$. This regime corresponds to an exponent $\nu = \frac{2}{d+1}$. In $d = 3$, as is well known, this yields a Brownian exponent $\nu = 1/2$. Note that, in this case, since the free energy of equation (17a) is finite, one cannot evaluate the integral (16) by the saddle-point method. Quadratic corrections must then be included to compute the free energy.

In the collapsed regime, $Q/N \rightarrow 0$ and $Z_0(Q)$ is no more given by (12a), although the asymptotic form of $\rho_Q(\mathbf{r})$ is given by (12b). We show in the appendix that the correct form for $Z_0(Q)$ in dimension $d = 3$ is

$$Z_0(Q) = \frac{3}{16\sqrt{(2\pi)}} \left(\frac{N}{Q}\right)^{5/2} \exp\left(-\frac{N}{8Q}\right) \quad (17b)$$

yielding a different Flory free energy

$$\beta F_{\text{F}} = -\ln \left(\frac{3}{16\sqrt{(2\pi)}} \left(\frac{N}{Q} \right)^{5/2} \right) + \frac{N}{8Q} - \frac{v}{2} \left(\frac{3}{4\pi} \right)^{3/2} \frac{N^2}{Q^{3/2}} + \frac{w}{6} \left(\frac{1}{6\pi} \right)^3 \frac{N^3}{Q^3}. \quad (17c)$$

In this regime, we recover the usual exponent $\nu = \frac{1}{3}$.

The method described above can be applied to any type of interaction $v(\mathbf{r})$, and can easily be generalized to the case of membranes or interfaces [11].

3. Pair correlation function.

At this level of approximation, it is easy to compute the corresponding pair correlation function $g(\mathbf{r})$. Using the following definition

$$g(\mathbf{r}) = \frac{1}{N} \int_0^N ds \int_0^N ds' \langle \delta(\mathbf{r}(s)) \delta(\mathbf{r} - \mathbf{r}(s')) \rangle \quad (18a)$$

or

$$g(\mathbf{q}) = \frac{1}{N} \int_0^N ds \int_0^N ds' \langle \exp(i\mathbf{q}(\mathbf{r}(s) - \mathbf{r}(s'))) \rangle \quad (18b)$$

in Fourier space and the lowest order cumulant expansion (10a), we show in the appendix that the pair correlation function is given by

$$g(\mathbf{q}) = N(d-1)! \int_0^\pi \frac{d\theta}{\pi} \left(\frac{1}{Q(1 - \cos\theta)\mathbf{q}^2} \right)^{\frac{d-1}{2}} J_{d-1} \left(2\sqrt{Q(1 - \cos\theta)}\mathbf{q} \right) \\ \times \exp \left(-\frac{N\mathbf{q}^2}{4\pi^2} \left(1 + \frac{\cos\theta}{2} - (\pi - \theta) \sin\theta \right) \right) \quad (19a)$$

where the square radius of gyration Q is given by its saddle-point value as computed in the previous section, and J_{d-1} denotes the Bessel function of integer order $(d-1)$.

At small \mathbf{q} , i.e. large distances $\mathbf{q}^2 Q \ll 1$, the function reduces to

$$g(\mathbf{q}) = N \int_0^\pi \frac{d\theta}{\pi} \exp(-Q(1 - \cos\theta)\mathbf{q}^2/d) \quad (19b)$$

whereas at smaller distances $\mathbf{q}^2 Q > 1$, a simple scaling argument shows that

$$g(\mathbf{q}) \simeq \frac{1}{q^{1/\nu}} \simeq \frac{1}{q^{5/3}} \quad (19c)$$

in three dimensions. This result agrees with the prediction of Edwards [5].

4. Many chains systems.

Consider now a system of \mathcal{N} polymer chains of length N (polydispersity effects can be trivially included). The partition function of the system reads

$$Z = \int_{\mathbf{r}_i(N)=\mathbf{r}_i(0)} \prod_{i=1}^{\mathcal{N}} \mathcal{D}\mathbf{r}_i(s) \exp \left(-\frac{1}{2} \sum_{i=1}^{\mathcal{N}} \int_0^N ds \dot{\mathbf{r}}_i^2 - \frac{v}{2} \sum_{i,j=1}^{\mathcal{N}} \int_0^N ds ds' \delta(\mathbf{r}_i(s) - \mathbf{r}_j(s')) \right). \quad (20)$$

Introducing a center of mass coordinate \mathbf{R}_i and a square radius of gyration Q_i for each chain, the same procedure as in Sect. 2) yields the following expression

$$Z \simeq Z_F = \int \prod_{i=1}^{\mathcal{N}} d\mathbf{R}_i dQ_i \exp \left(\sum_{i=1}^{\mathcal{N}} \left((d-1) \ln \left(\frac{Q_i}{N} \right) - 2\pi^2 \frac{Q_i}{N} \right) - v \frac{N^2}{2} \sum_{i,j} \left(\frac{d}{2\pi(Q_i + Q_j)} \right)^{d/2} \exp \left(-\frac{d}{2} \frac{(\mathbf{R}_i - \mathbf{R}_j)^2}{Q_i + Q_j} \right) \right) \quad (21a)$$

Each polymer chain is represented by a coordinate \mathbf{R}_i (center of mass) and a radius of gyration square Q_i . The determination of the size Q_i will be done by a saddle-point method, and it is natural (for monodisperse systems) to assume that all sizes are equal: $Q_i = Q$. We obtain:

$$Z_F = \exp \left(\mathcal{N} \left[(d-1) \ln \left(\frac{Q}{N} \right) - 2\pi^2 \frac{Q}{N} \right] \right) \times \int \prod_{i=1}^{\mathcal{N}} d\mathbf{R}_i \exp \left(-\frac{vN^2}{2} \left(\frac{d}{4\pi Q} \right)^{d/2} \sum_{i,j=1}^{\mathcal{N}} \exp \left(-\frac{d}{4Q} (\mathbf{R}_i - \mathbf{R}_j)^2 \right) \right) \quad (21b)$$

Thus, the partition function contains a Flory-like term, which is characteristic of the properties of each individual chain, and a partition function which represents a liquid of interacting chains with a smoothed interaction:

$$V(\mathbf{R}) = vN^2 T \left(\frac{d}{4\pi Q} \right)^{d/2} \exp \left(-\frac{d}{4Q} \mathbf{R}^2 \right) \quad (22)$$

The range of the interaction is the size of the chains $\sqrt{2Q}$. Once Z_F is calculated, the radius of gyration R_G is to be determined by minimizing the total free energy of the system with respect to Q .

Defining the monomer concentration $c = N\mathcal{N}/\Omega$ (where Ω is the volume) , and the overlap threshold concentration $c^* = \frac{N}{R_G^d} \simeq N^{(1-\nu d)}$ (where $R_G = \sqrt{Q}$ is the radius of gyration of a chain, and ν is the Flory exponent $\nu = \frac{3}{(d+2)}$), the various regimes of chain concentration can easily be recovered.

i) *Dilute regime* $c \ll c^*$: it is the gas type regime, where the density of chains is such that the typical interchain distance is much larger than the chain size R_G . In this case, we have a gas of weakly interacting single chains. The partition function can be evaluated by using the virial expansion [12], and the osmotic pressure reads:

$$\Pi = T \frac{c}{N} (1 + A_2 \frac{c}{N} + \dots) \quad (23a)$$

where $c/N = \mathcal{N}/\Omega$ is the polymer concentration, and A_2 is the second virial coefficient calculated with (22)

$$A_2 = -\frac{1}{2} \int d\mathbf{R} (\exp(-\beta V(\mathbf{R})) - 1). \quad (23b)$$

A simple evaluation of this integral yields

$$A_2 \simeq R_G^d (\ln N)^{d/2} \quad (23c)$$

Note the logarithmic term in the virial coefficient A_2 , absent from standard calculations. The total free energy per polymer reads

$$F/\mathcal{N} = F_F + c/N A_2 T \quad (23d)$$

where F_F is the single chain Flory free energy as given by (14a). Minimization of (23d) with respect to Q yields the usual Flory exponent.

ii) *Melt* $c^* \ll c \simeq 1/a^d$ (where a is the monomer size) : when interchain distances become smaller than the radius R_G , the chains overlap strongly, and the monomer concentration is constant, with small fluctuations. Using a Gaussian transform, equation (21b) can be written as

$$\begin{aligned} Z_F = & \exp \left(\mathcal{N} \left[(d-1) \ln \left(\frac{Q}{N} \right) - 2\pi^2 \frac{Q}{N} \right] \right) \\ & \times \int \mathcal{D}\phi(\mathbf{R}) \exp \left(-\frac{\beta}{2} \int d\mathbf{R} \int d\mathbf{R}' \phi(\mathbf{R}) V^{-1}(\mathbf{R} - \mathbf{R}') \phi(\mathbf{R}') + \mathcal{N} \ln \left(\int d\mathbf{R} \exp(i\beta\phi(\mathbf{R})) \right) \right) \end{aligned} \quad (24a)$$

where $V^{-1}(\mathbf{R} - \mathbf{R}')$ is the inverse kernel of $V(\mathbf{R} - \mathbf{R}')$.

This functional integral can be evaluated by the saddle-point method. Assuming a uniform monomer concentration is equivalent to assume a constant field $\phi(\mathbf{R}) = \phi_0$. A simple calculation shows that the saddle-point is given by

$$\beta\phi_0 = iNc\nu^2 \quad (24b)$$

so that the free energy becomes

$$\beta F_F \simeq -\mathcal{N} \left((d-1) \ln \frac{Q}{N} - 2\pi^2 \frac{Q}{N} + \ln \Omega \right) + \frac{\nu(N\mathcal{N})^2}{2\Omega} \quad (24c)$$

Minimization of (19c) with respect to Q yields the standard Brownian exponent $\nu = 1/2$, and the osmotic pressure is given by: $\Pi\beta = \frac{\nu}{2}c^2$

The interchain interactions screen out completely, and the chains become Brownian, as is well known [13]. A systematic expansion around the mean-field ϕ_0 can easily be done, and the lowest order turns out to be identical to the usual RPA [9].

iii) *Semi-dilute regime* $c^* \ll c \ll 1/a^d$: it is the liquid type regime, which requires more involved calculations of the liquid-like partition function [12]. A careful analysis of the generic term of the virial expansion of (16b) leads to the scaling form proposed by Des Cloizeaux [14]

$$\beta\Pi = c/N f \left(\frac{c}{N} R_G^d \right) \quad (25a)$$

which under a scaling hypothesis leads to the well-known behaviour

$$\beta\Pi = c^{\frac{9}{4}} \quad (25b)$$

in dimension $d = 3$.

5. Corrections to the Flory theory.

One great advantage of this method is that it allows to compute corrections to the Flory theory. Indeed, using equation (9) to second order, we have

$$Z_\phi(Q) \simeq Z_0(Q) \exp \left(-i \int d\mathbf{r} \phi(\mathbf{r}) \rho_Q(\mathbf{r}) - \frac{\lambda}{2} \int d\mathbf{r} d\mathbf{r}' \phi(\mathbf{r}) G_Q(\mathbf{r}, \mathbf{r}') \phi(\mathbf{r}') \right) \quad (26a)$$

where $G_Q(\mathbf{r}, \mathbf{r}')$ is the connected Debye function [15] of a Brownian chain with constrained square radius of gyration Q

$$G_Q(r, r') = \int_0^N ds ds' (\langle \delta(\mathbf{r} - \mathbf{r}(s)) \delta(\mathbf{r}' - \mathbf{r}(s')) \rangle - \langle \delta(\mathbf{r} - \mathbf{r}(s)) \rangle \langle \delta(\mathbf{r}' - \mathbf{r}(s')) \rangle) \quad (26b)$$

and is given in momentum space by (see appendix)

$$G_Q(\mathbf{k}, \mathbf{k}') = \frac{N^2}{2\pi} \int_0^{2\pi} du \exp \left(-\frac{Q}{2d} (\mathbf{k}^2 + \mathbf{k}'^2) \right) \left(\exp \left(-\left(\frac{Q}{d} \cos u - \frac{N}{4\pi} \sin u \right) \mathbf{k} \mathbf{k}' \right) - 1 \right). \quad (26c)$$

The parameter λ in (26a) is just a remainder to keep trace of the orders of the expansion. Integration over the ϕ variables yields

$$Z = \int_0^\infty dQ \exp \left(- \left(-(d-1) \ln \left(\frac{Q}{N} \right) + 2\pi^2 \frac{Q}{N} \right) - \frac{1}{2} \text{Tr} \ln (\delta(\mathbf{r} - \mathbf{r}') + \lambda v G_Q(\mathbf{r}, \mathbf{r}')) - \frac{v}{2} \int d\mathbf{r} d\mathbf{r}' \rho_Q(\mathbf{r}) (\delta(\mathbf{r} - \mathbf{r}') + \lambda v G_Q(\mathbf{r}, \mathbf{r}'))^{-1} \rho_Q(\mathbf{r}') \right). \quad (27a)$$

Expanding to lowest order in λ , we obtain:

$$\beta F_1 = \beta F_F + \lambda \left(\frac{v}{2} \int d\mathbf{r} G_Q(\mathbf{r}, \mathbf{r}) - \frac{v^2}{2} \int d\mathbf{r} d\mathbf{r}' \rho_Q(\mathbf{r}) G_Q(\mathbf{r}, \mathbf{r}') \rho_Q(\mathbf{r}') \right). \quad (27b)$$

The first correction term is thus of the form:

$$\begin{aligned} \int d\mathbf{r} G_Q(\mathbf{r}, \mathbf{r}) &= \int \frac{d\mathbf{k}}{(2\pi)^d} G_Q(\mathbf{k}, -\mathbf{k}) \\ &= \frac{N^2}{\pi} \int \frac{d\mathbf{k}}{(2\pi)^d} \int_{\frac{2\pi a}{N}}^\pi du \exp(-\frac{Q}{d} \mathbf{k}^2) \left(\exp \left(\left(\frac{Q}{d} \cos u - \frac{N}{4\pi} \sin u \right) \mathbf{k}^2 \right) - 1 \right) \\ &= AN + B \frac{N^2}{Q^{d/2}} \end{aligned} \quad (28a)$$

where A and B are finite numerical constants depending on the monomer size a and space dimension d , and the natural cut-off $\frac{2\pi a}{N}$ has been introduced to avoid ultra-violet divergences. The term linear in N is the expected extensive part of the free energy, which in the Flory expansion appears thus as a correction term, and the second term is a correction to the standard Flory term in the repulsive energy.

The second correction term is given by

$$\int d\mathbf{r} d\mathbf{r}' \rho_Q(\mathbf{r}) G_Q(\mathbf{r}, \mathbf{r}') \rho_Q(\mathbf{r}') = C \left(\frac{N^2}{Q^{d/2}} \right)^2 \quad (28b)$$

where C is a finite constant, depending only on the monomer size a and the dimension d . This term scales like the square of the Flory repulsive energy.

More generally, it can be proven that the expansion of the free energy around the Flory theory will generate extensive terms, as well as powers of $\frac{N^2}{Q^{d/2}}$. This is in contrast with the usual Fixman expansion [16], which also contains extensive terms, but which is done in powers of $N^{2-d/2}$. The Flory expansion is in terms of $N^{2-\nu d} = N^{\frac{4-d}{2}}$.

As is often the case when calculating corrections to mean field theories, correction terms are much larger than the mean field contribution, in the critical region ($N \rightarrow +\infty$).

This allows the definition of a Ginzburg region [17], i.e. a typical size N_{\max} such that for $N < N_{\max}$, the correction terms are small compared to the Flory free energy. The precise value of N_{\max} depends on all the parameters of the problem, and we have not computed it explicitly, since it is in fact a crossover size, and its precise value is not very illuminating.

However, it is clear that the Flory expansion will have a much larger domain of validity than the Fixman expansion, since for any dimension smaller than 4, we have $N^{\frac{4-d}{2}} \ll N^{\frac{4-d}{2}}$, and therefore, this slower divergence of the Flory expansion might be the clue to its success.

6. Conclusion.

We have shown how the original Flory theory of polymers can be derived rigorously from a cumulant expansion. We obtain a Flory-like free energy, with the correct original logarithmic term. This method can be generalized to other types of monomer interactions (e.g. bad solvent, polyelectrolytes, etc.) and can be applied to solutions of polymers in a straightforward manner. It can also certainly be useful to other classes of problems (membranes, interfaces, etc...). Finally, we show how this method can generate a systematic expansion around the Flory theory. The calculations are somewhat cumbersome, but they show that the leading corrections diverge when $N \rightarrow +\infty$, but much less rapidly than the usual Fixman expansion.

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Appendix.

In this section, we show how to compute partition and correlation functions for a Brownian chain with constrained center of mass, and constrained radius of gyration. Consider the partition function:

$$Z_0(Q) = \int_{\mathbf{r}(N)=\mathbf{r}(0)} \mathcal{D}\mathbf{r}(s) \delta\left(\frac{1}{N} \int_0^N ds \mathbf{r}(s)\right) \delta\left(Q - \frac{1}{N} \int_0^N ds \mathbf{r}^2(s)\right) \\ \times \exp\left(-\frac{1}{2} \int_0^N ds \dot{\mathbf{r}}^2(s)\right). \quad (\text{A1})$$

In order to compute it, we expand the trajectories $\mathbf{r}(s)$ as Fourier series:

$$\begin{aligned} \mathbf{r}(s) &= \sum_{n=-\infty}^{+\infty} e^{i\frac{2\pi}{N}s} \mathbf{r}_n \\ \mathbf{r}_n &= \frac{1}{N} \int_0^N ds e^{-i\frac{2\pi}{N}s} \mathbf{r}(s). \end{aligned} \quad (\text{A2})$$

The center of mass constraint implies that the Fourier component \mathbf{r}_0 vanishes. The δ -function constraining the radius of gyration can be represented by its Fourier integral, and then the remaining Gaussian integral on \mathbf{r}_n can be performed. After some simple algebra, we obtain

$$Z_0(Q) = \int_{-\infty}^{+\infty} \frac{dz}{2\pi} e^{izQ} \prod_{n=1}^{+\infty} \left(\frac{1}{1 + \frac{izN}{2\pi^2 n^2}} \right)^d \quad (\text{A3})$$

This integral can be computed by the method of residues. The poles of the function are given by

$$z_n = \frac{2i\pi^2 n^2}{N} \quad (\text{A4})$$

and they are of order d .

Using the analytic expression for the infinite product [18]

$$\prod_{n=1}^{+\infty} \left(1 + \frac{x^2}{n^2 \pi^2} \right) = \frac{\sinh x}{x}, \quad (\text{A5})$$

we can write

$$Z_0(Q) = \int_{-\infty}^{+\infty} \frac{dz}{2N\pi} f(z) \quad (\text{A6})$$

with

$$f(z) = e^{izq} \left(\frac{\sqrt{\frac{iz}{2}}}{\sinh \sqrt{\frac{iz}{2}}} \right)^d \quad (\text{A7})$$

where we have defined $q = \frac{Q}{N}$. In the following, we will forget the N factor which appears in the denominator of (A6), since it is just a normalization constant. We have thus

$$Z_0(Q) = i \sum_{n=1}^{+\infty} \text{res}(f, z_n) \quad (\text{A8})$$

where res denotes the residue of the function.

The exponential factor in the function f implies terms of the form $\exp(-2n^2\pi^2q)$ in the sum (A8).

In the case of a swollen chain, the exponent ν is larger than $1/2$, and thus, $q \rightarrow +\infty$ when $N \rightarrow +\infty$. Therefore, in the sum (A8), only the pole $n = 1$ will contribute, all other poles being exponentially subdominant. The sum (A8) reduces to

$$Z_0(Q) \simeq \frac{(2\pi)^{2d}}{(d-1)!} \left(\frac{Q}{N} \right)^{(d-1)} \exp\left(-\frac{2\pi^2 Q}{N}\right). \quad (\text{A9})$$

In the case of a collapsed chain, the exponent ν is smaller than $1/2$, and thus, $q \rightarrow 0$ when $N \rightarrow +\infty$. Therefore, in the sum (A8), all poles contribute equally, but the calculation of the residue is simplified by the fact that q is small. Since the calculation of the residue of a pole of order d involves the calculation of a derivative of order d , we will specialize to dimension $d = 3$. A simple calculation of the residues yield the asymptotic formula

$$Z_0(Q) = - \sum_{n=1}^{+\infty} (-1)^n 6n^2 \pi^2 e^{-2n^2 \pi^2 q} \quad (\text{A10})$$

for $\frac{Q}{N} \rightarrow 0$. Equation (A10) can be recast in a form which emphasizes its resemblance to the Jacobi elliptic Theta functions [18]

$$Z_0(Q) = 3 \frac{d}{dq} \sum_{n=1}^{+\infty} \exp(-2n^2 \pi^2 q + in\pi). \quad (\text{A11})$$

Using the Poisson summation formula, we obtain

$$Z_0(Q) = \frac{3}{2} \frac{d}{dq} \sum_{n=-\infty}^{+\infty} e^{-\frac{(2n+1)^2}{8q}} \quad (\text{A12})$$

In the limit $\frac{Q}{N} \rightarrow 0$, this reduces to:

$$Z_0(Q) = \frac{3}{16\sqrt{2\pi}} \frac{1}{q^{\frac{5}{2}}} e^{-\frac{1}{8q}}. \quad (\text{A13})$$

We now turn to the calculation of correlation functions.

Consider the generating function for correlation functions, defined by

$$\begin{aligned} G(\mathbf{k}(s)) = & \frac{1}{Z_0(Q)} \int_{\mathbf{r}(N)=\mathbf{r}(0)} \mathcal{D}\mathbf{r}(s) \delta \left(\frac{1}{N} \int_0^N ds \mathbf{r}(s) \right) \delta \left(Q - \frac{1}{N} \int_0^N ds \mathbf{r}^2(s) \right) \\ & \times \exp \left(-\frac{1}{2} \int_0^N ds \dot{\mathbf{r}}^2(s) \right) + \frac{i}{N} \int_0^N ds \mathbf{k}(s) \cdot \mathbf{r}(s). \end{aligned} \quad (\text{A14})$$

The various usual correlation functions can be obtained from (A14), by taking the proper sum of δ -functions for the function $\mathbf{k}(s)$ (see below, Eqs. (A19), (A20)). Defining the Fourier component of $\mathbf{k}(s)$ by

$$\mathbf{k}_n = \int_0^N ds e^{i\frac{2\pi}{N}s} \mathbf{k}(s), \quad (\text{A15})$$

the generating function can be rewritten as

$$G(\mathbf{k}_n^*, \mathbf{k}_n) = \frac{1}{Z_0(Q)} \int_{-\infty}^{+\infty} \frac{dz}{2\pi} f(z) \exp \left(-\frac{N}{2} \sum_{n=1}^{+\infty} \frac{|\mathbf{k}_n|^2}{iz + 2n^2 \pi^2} \right) \quad (\text{A16})$$

where $f(z)$ is given by (A7). This integral can again be evaluated by the method of residues. The poles are the same as before, given by (A4), but now, due to the new exponential term, they are of infinite order.

In the swollen case, $q \rightarrow +\infty$, again only the pole $n = 1$ contributes. The calculation of the residue can be done and yields

$$G(\mathbf{k}_n^*, \mathbf{k}_n) = e^{-\frac{N}{4\pi^2} \sum_{n=2}^{+\infty} \frac{|\mathbf{k}_n|^2}{n^2-1}} \sum_{p=0}^{+\infty} \frac{(d-1)!}{p!(p+d-1)!} (-1)^p \left(\frac{Q |\mathbf{k}_1|^2}{2} \right)^p \quad (\text{A17})$$

which can be written in terms of Bessel functions [18] as

$$G(\mathbf{k}_n^*, \mathbf{k}_n) = (d-1)! \left(\frac{2}{Q |\mathbf{k}_1|^2} \right)^{\frac{d-1}{2}} J_{d-1} \left(\sqrt{2Q} |\mathbf{k}_1|^2 \right) e^{-\frac{N}{4\pi^2} \sum_{n=2}^{+\infty} \frac{|\mathbf{k}_n|^2}{n^2-1}} \quad (\text{A18})$$

The monomer density $\rho(\mathbf{k})$ is obtained by taking

$$\mathbf{k}(s) = N \delta(s - s_0) \mathbf{k} \quad (\text{A19})$$

and the pair correlation functions used in equations (19) and (26) are obtained by taking

$$\mathbf{k}(s) = N (\delta(s - s_0) \mathbf{k} + \delta(s - s'_0) \mathbf{k}'). \quad (\text{A20})$$

In the large distance limit, $Q |\mathbf{k}_1|^2 \rightarrow 0$, we obtain :

$$\rho(\mathbf{k}) = N e^{-\frac{Q}{2a} \mathbf{k}^2} \quad (\text{A21})$$

and

$$G(\mathbf{k}_n^*, \mathbf{k}_n) = e^{-\frac{Q}{2a} |\mathbf{k}_1|^2 - \frac{N}{4\pi^2} \sum_{n=2}^{+\infty} \frac{|\mathbf{k}_n|^2}{n^2-1}} \quad (\text{A22})$$

which is the form used in (19) and (26).

In the collapsed case, $q \rightarrow 0$, all poles contribute, but in the large distance limit, the calculations simplify, and yield, for the density, exactly the same result as above.

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