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One long chain among shorter chains : the Flory approach revisited

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Abstract. — We consider the mean square end-to-end distance of a long chain immersed in a monodisperse, concentrated solution of shorter, chemically identical chains. In contrast with the earlier work of Flory, no simplifying assumption on the wave vector dependence of the effective potential between segments is made. In order to obtain a closed form expression for the dimension of the long chain, we first derive a general expression for the mean square end-to-end distance of a flexible chain with arbitrary two-body interactions using the Edwards-Singh method.

1. Introduction.

In dilute solutions with a good solvent, (nonoverlapping) polymer chains are swollen to a size $R \sim N^{3/5}$ (N being the number of segments per chain) [1]. What happens if we increase the concentration and reach a concentrated regime ? It was argued by Flory [2] a long time ago that in (monodisperse) concentrated solutions or melts the coils must be Gaussian ($R \sim N^{1/2}$) : each chain is no more repelled by itself than by all the others around it and so has no preference to swell. This conjecture has been confirmed theoretically by Edwards [3] who established the *screening* of the excluded volume interaction as the polymer concentration is increased. Consider a dense solution (monomer concentration c) of chains with a bare excluded volume interaction between any two segments (intra and intermolecular interaction) of the type

$$u_{\text{bare}}(\mathbf{r})/k_{\text{B}}\,T = v\,\delta\,(\mathbf{r})\,. \tag{1}$$

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Using the Gaussian approximation for concentration fluctuations, Edwards showed [3] that the effective potential $u(\mathbf{r})$ between two monomers on a single polymer chain is given by

$$u(\mathbf{r})/k_B T = v[\delta(\mathbf{r}) - (4\pi\xi^2 r)^{-1}\exp(-r/\xi)] \tag{2}$$

where ξ is the Edwards screening length

$$\xi^{-2} = 12\, cv\ell^{-2} \tag{3}$$

and ℓ is the step length. In addition to the strong repulsive part ($v\delta(\mathbf{r})$) of very short interaction range, the effective potential (2) contains a weak attractive part ($-v(4\pi\xi^2 r)^{-1}\exp(-r/\xi)$) of interaction range ξ [4].

As a consequence of the screening of the excluded volume interaction, the conformation of an individual chain becomes Gaussian [3] :

$$\langle \mathbf{R}^2 \rangle = N\ell^2\left(1 + \frac{12\, v\xi}{\pi\ell^4}\right). \tag{4}$$

For a reason that will become apparent below, it is important to notice that the expression (2) for the effective potential is an approximation valid only at length scales smaller than the radius of gyration $R_g = \ell N^{1/2}/\sqrt{6}$. This is more easily seen in terms of $\tilde{u}(\mathbf{k})$, the Fourier transform of $u(\mathbf{r})$. Within the framework of the Gaussian, or random phase approximation [4] one has (see Fig. 1, curve (a))

$$\tilde{u}(\mathbf{k})/k_B T = \frac{v}{1 + vcg_0(\mathbf{k}\,;N)} \tag{5}$$

where the Debye function $g_0(\mathbf{k}\,;N)$ is the structure factor for the Gaussian chain [4] :

$$g_0(\mathbf{k}\,;N) = \frac{2N}{(k^2R_g^2)^2}[\exp(-k^2R_g^2) - 1 + k^2R_g^2]. \tag{6}$$

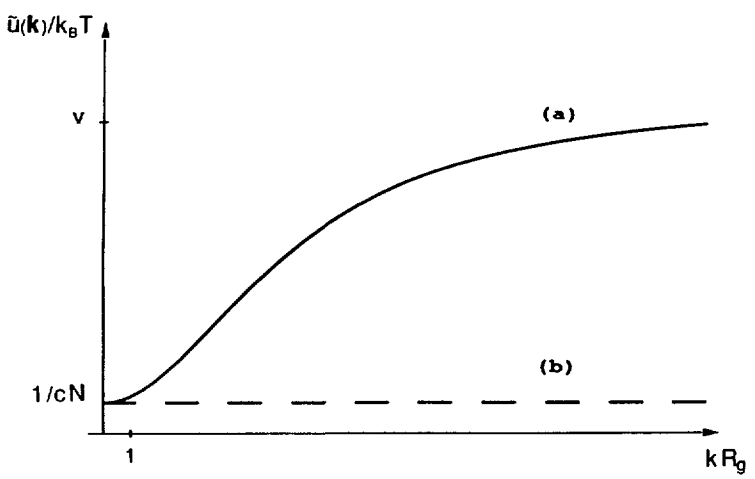

Fig. 1. — a) Schematic representation of the Fourier transform $\tilde{u}(\mathbf{k})/k_B T$ of the effective potential between segments in a concentrated solution (Eq. (5)). b) The approximate potential used in the classical approach of Flory.

Equation (2) corresponds to the use of the asymptotic form $g_0(\mathbf{k}\,;N) \approx 2\,N/(k^2\,R_g^2)$ $(kR_g \gg 1)$:

$$\tilde{u}(\mathbf{k})/k_B\,T \approx v\left[1 - \frac{1}{1 + k^2\,\xi^2}\right]. \tag{7}$$

Thus the behavior of equation (7) departs from that of the more accurate answer (5) for $k < R_g^{-1}$. In particular, while equation (7) goes to zero with vanishing k, the correct answer (5) does not :

$$\lim_{k \to 0} \tilde{u}(\mathbf{k})/k_B\,T = \frac{1}{cN} \tag{8}$$

(where we have neglected 1 compared with vcN). The distinction between equations (5) and (7) is irrelevant as long as one considers a monodisperse solution (since in that case the only length scales of interest are smaller than R_g). However, the difference becomes important in polydisperse situations (see below).

In this paper we consider the statistical properties of a long chain (degree of polymerization N_1) immersed in a monodisperse melt of shorter, chemically identical chains (degree of polymerization N) (1) [5]. If $N_1 = N$, we know that the chain is Gaussian. On the other hand, if N_1 is much greater than N, the chain sees the matrix of short chains as a good solvent and is swollen. Our purpose is to describe the crossover between these two limits.

The classical approach to this problem is due to Flory [2]. More recently de Gennes has considered the case of a long chain immersed in a semi-dilute solution of shorter, chemically identical chains [6]. In the Flory approach, the free energy of the long chain is written as (ignoring numerical factors of order unity)

$$\frac{F}{kT} \cong \frac{\ell^3}{N}\frac{N_1^2}{R^3} + \frac{R^2}{\ell^2\,N_1} \tag{9}$$

The first term of equation (9) is a repulsive term due to the screened excluded volume interaction. The second term is an elastic deformation energy ($\ell^2\,N_1$ being the ideal chain mean squared end-to-end distance, R_0^2). From equation (9) we can define a dimensionless parameter ζ which tells us whether the chain is ideal or not :

$$\zeta \cong \frac{\ell^3}{N}\frac{N_1^2}{R_0^3} \cong \frac{N_1^{1/2}}{N} \tag{10}$$

(i) if $N_1 \ll N^2$, the perturbation parameter ζ is small and the chain is ideal $(R \cong R_0)$;
(ii) if $N_1 \gg N^2$, the chain is swollen.

The criterion $N_1 \lesseqgtr N^2$ is usually refereed to as the *Flory criterion*. For intermediate ζ values the behavior of the chain may be described by the interpolation formula [2]

$$\alpha^5 - \alpha^3 = \text{Const.}\quad \zeta \tag{11}$$

where α is the expansion factor : $\alpha^2 \equiv \langle \mathbf{R}^2 \rangle\,(\ell^2\,N_1)^{-1}$

(1) We will in fact consider a slightly more general problem, where instead of a melt, we have a dense solution with a concentration c greater than the critical concentration $c^{**} \approx v/\ell^6$ [4]. The case of a melt corresponds to the limit $c \approx 1/\ell^3$.

The expressions (9) and (11) deserve some comments. They implicitly assume that the interaction can be approximated by a delta function of strength ℓ^3/N. In other words, the function $\tilde{u}(\mathbf{k})$ (Eq. (5)) is replaced by a constant equals to its value at the origin (Eq. (8)) [6] ; see figure 1. One may wonder how good this approximation is to describe the statistical properties of the chain and in particular the crossover regime between the ideal and the swollen state. Our aim in this paper is to investigate these questions in detail. In order to do so, we will need first to derive a closed form (analogous to (11)) for the general case of a nondelta function potential. The paper is organized as follows : the conventional two-parameter model for a chain with excluded volume interaction is reviewed in section 2.1. In section 2.2 we consider the case of a nondelta potential. The configuration of a long chain immersed in a (monodisperse) dense solution of shorter, chemically identical chains is then studied in section 3. The paper ends with a discussion.

2. Chain with excluded volume interaction.

The influence of the excluded volume interaction on the statistical properties of macromolecules has been one of the central problems in the field of polymer solution theory since the original studies of Kuhn [7] and Flory [2]. In section 2.1 we briefly summarize the conventional two-parameter model. In this model, the interaction between segments is represented by a delta function pseudopotential. In addition to the familiar perturbation approach, we also present the Edward-Singh method to obtain a closed form for the chain dimension. We then generalize these methods to the case of an arbitrary potential, keeping in mind the nondelta potential (2).

2.1 THE TWO-PARAMETER MODEL. — One of the simplest model used to describe a linear flexible chain (of contour length L) with excluded volume interaction is the *two-parameter model* [8, 9]. The chain is considered to be a space curve $\mathbf{r}(s)$, where s is an arc length variable ($0 \leq s \leq L$). The random walk constraint is represented by a Wiener measure

$$\exp\left\{-\frac{3}{2\ell}\int_0^L \mathrm{d}s\left[\frac{\partial \mathbf{r}(s)}{\partial s}\right]^2\right\}. \tag{12}$$

In expression (12), ℓ is the step length, so that $L/\ell = N$ is the number of segments in the chain.

The excluded volume interaction between two polymer segments at a distance $\mathbf{r}$ apart is modeled by a delta function pseudopotential $k_B\, Tv\, \delta(\mathbf{r})$; the total potential energy of the chain is thus given by

$$\frac{w}{2}\int_0^L \mathrm{d}s \int_0^L \mathrm{d}s'\, \delta[\mathbf{r}(s) - \mathbf{r}(s')] \tag{13}$$

where $w \equiv v\ell^{-2}$. In what follows we shall assume $w > 0$ (repulsive interaction).

The probability distribution $\Psi[\mathbf{R}, L]$ for the end-to-end vector $\mathbf{R}$ is thus given by

$$\Psi[\mathbf{R}, L] \propto \int_{\mathbf{r}(0)=\mathbf{0}}^{\mathbf{r}(L)=\mathbf{R}} D[\mathbf{r}] \exp\left\{-\frac{3}{2\ell}\int_0^L \mathrm{d}s\left[\frac{\partial \mathbf{r}(s)}{\partial s}\right]^2 - \frac{w}{2}\int_0^L \mathrm{d}s \int_0^L \mathrm{d}s'\, \delta[\mathbf{r}(s) - \mathbf{r}(s')]\right\}. \tag{14}$$

The expression $\int D[\mathbf{r}]$ denotes the summation over all possible paths between the end of the chain $\mathbf{r}(0)$ which is taken to be the origin and $\mathbf{r}(L) = \mathbf{R}$. This model is called the two parameter model since it includes only two parameters ; ℓ, which represents the short range interaction,

and w, which represents the long range interaction (the terms « short » and « long » representing the distance along the chain) [4].

The mean square end-to-end distance of the chain is given by

$$\langle \mathbf{R}^2 \rangle = \int \mathrm{d}\mathbf{R}\, R^2\, \Psi[\mathbf{R}, L] / \int \mathrm{d}\mathbf{R}\, \Psi[\mathbf{R}, L]\,. \tag{15}$$

We now review two theoretical approaches for the properties of the chain described by equation (14).

2.1.1 *Perturbation calculation.* — Perturbation theory is made by expanding the distribution function (14) in terms of w. Hence $\langle \mathbf{R}^2 \rangle$ can be calculated as a power series of w. This method — initiated by Fixman [10] — has been recently taken to as many as six terms by Muthukumar and Nickel [11]. The third order perturbation result is

$$\langle \mathbf{R}^2 \rangle = L\ell \left\{ 1 + \frac{4}{3} z - 2.075\, z^2 + 6.297\, z^3 - \cdot \right\} \tag{16}$$

where the dimensionless interaction parameter z is defined by

$$z = (3/2\pi)^{3/2}\, w L^{1/2}\, \ell^{-3/2} \tag{17}$$

Since z is proportional to $\sqrt{L}$, equation (16) has a very limited range of validity. It has been shown that the series (16) is asymptotic, and suffers from an explosive increase in its coefficients [12].

2.1.2 *Uniform expansion model.* — In order to improve the difficulty of the perturbation calculation, Edwards and Singh [13] have derived a simple scheme of calculation. In this scheme, it is assumed that the expansion of the chain is represented by the expansion of the step length, i.e., that the distribution of $\mathbf{R}$ can be approximated by

$$\Psi'[\mathbf{R}, L] \propto \int_{\mathbf{r}(0)=\mathbf{0}}^{\mathbf{r}(L)=\mathbf{R}} D[\mathbf{r}] \exp\left\{ -\frac{3}{2\ell'} \int_0^L \mathrm{d}s \left[\frac{\partial \mathbf{r}(s)}{\partial s} \right]^2 \right\} \tag{18}$$

where ℓ' is an expanded bond length still to be determined. We briefly summarize the method. The perturbation theory provides

$$\langle \mathbf{R}^2 \rangle = L\ell \left\{ 1 + \kappa \frac{w L^{1/2}}{\ell^{3/2}} - \cdot \right\} \tag{19}$$

with $\kappa \equiv (4/3)\,(3/2\pi)^{3/2}$ Introducing the effective step length ℓ' such that

$$\langle \mathbf{R}^2 \rangle \equiv L\ell' \tag{20}$$

and expanding $1/\ell$ around $1/\ell'$ so that

$$\begin{aligned} \frac{1}{\ell} &= \frac{1}{\ell'} + \frac{1}{\ell} - \frac{1}{\ell'} = \frac{1}{\ell'} \left[1 + \ell' \left(\frac{1}{\ell} - \frac{1}{\ell'} \right) \right] \\ \ell &= \ell' \left[1 - \ell' \left(\frac{1}{\ell} - \frac{1}{\ell'} \right) + \ell'^2 \left(\frac{1}{\ell} - \frac{1}{\ell'} \right)^2 \quad \right], \end{aligned} \tag{21}$$

equation (19) becomes

$$\langle \mathbf{R}^2 \rangle = L\ell' \left\{ 1 + \left[\frac{\kappa w L^{1/2}}{\ell'^{3/2}} - \ell' \left(\frac{1}{\ell} - \frac{1}{\ell'} \right) \right] + \cdot \right\}. \tag{22}$$

Since ℓ' is defined by equation (20), the first order correction (the square bracket) must vanish. This condition gives

$$\frac{\kappa w L^{1/2}}{\ell'^{3/2}} = \ell' \left(\frac{1}{\ell} - \frac{1}{\ell'} \right) . \tag{23}$$

Next, we define an expansion factor α in the usual way :

$$\alpha^2 \equiv \frac{\langle \mathbf{R}^2 \rangle}{L\ell} \tag{24}$$

Equation (20) gives $\alpha^2 = \ell'/\ell$, so that equation (23) is written as :

$$\alpha^5 - \alpha^3 = \frac{4}{3} z . \tag{25}$$

For small z, this theory agrees with the first order perturbation result (Eq. (19)). On the other hand, for large z the theory gives $\langle \mathbf{R}^2 \rangle \sim L^{6/5}$ in agreement with the original Flory theory [14]. Thus the theory gives an interpolation between the two cases. The closed form (25) is called the modified Flory formula.

It can be shown that the structure of the equation (25) is stable to all order in perturbation about ℓ' [12]. For the limitations of the uniform expansion model, see reference [4].

2.2 A MORE GENERAL MODEL. — In the two-parameter model (see preceding section) the interaction between two segments is modeled by a delta function of appropriate strength. In this section we generalize the model for arbitrary pair interactions. The probability distribution $\Psi[\mathbf{R}, L]$ for the end-to-end vector $\mathbf{R}$ is then given by

$$\Psi[\mathbf{R}, L] \propto \int_{\mathbf{r}(0)=\mathbf{0}}^{\mathbf{r}(L)=\mathbf{R}} D[\mathbf{r}] \exp\left\{ -\frac{3}{2\ell} \int_0^L \mathrm{d}s \left[\frac{\partial \mathbf{r}(s)}{\partial s} \right]^2 - \right.$$
$$\left. - \frac{1}{2} \int_0^L \mathrm{d}s \int_0^L \mathrm{d}s' \, W[\mathbf{r}(s) - \mathbf{r}(s')] \right\} \tag{26}$$

where $k_B T \ell^2 W(\mathbf{r})$ is the interaction energy between two segments at a distance $\mathbf{r}$ apart (in what follows we shall assume that $W(\mathbf{r})$ depends only on the magnitude of the vector $\mathbf{r}$).

2.2.1 *Perturbation calculation.* — The first order perturbation calculation of $\langle \mathbf{R}^2 \rangle$ (Eq. (15)) is rather straightforward and gives

$$\langle \mathbf{R}^2 \rangle = L\ell \left[1 + \frac{\kappa L^{1/2}}{\ell^{3/2}} \int_0^{+\infty} \mathrm{d}u \, h(u) \, \tilde{W}\left(\sqrt{\frac{6}{\ell L}} u \right) - \cdot \quad \right] \tag{27}$$

where $\tilde{W}(k)$ is the 3d Fourier transform of $W(r)$

$$\tilde{W}(k) = \int \mathrm{d}\mathbf{r} \, W(r) \exp(-i\mathbf{k} \cdot \mathbf{r}) \tag{28}$$

and $\kappa \equiv (4/3)\,(3/2\pi)^{3/2}$ The function $h(u)$ is defined by

$$h(u) = \frac{12 + 8\,u^2 + 2\,u^4 - 12 \exp(u^2) + 4\,u^2 \exp(u^2)}{\pi^{1/2} u^4 \exp(u^2)} \tag{29}$$

and satisfies

$$\int_0^{+\infty} \mathrm{d}u\, h(u) = 1\,. \tag{30}$$

Figure 2 shows the dependence of $h(u)$ *vs.* u.

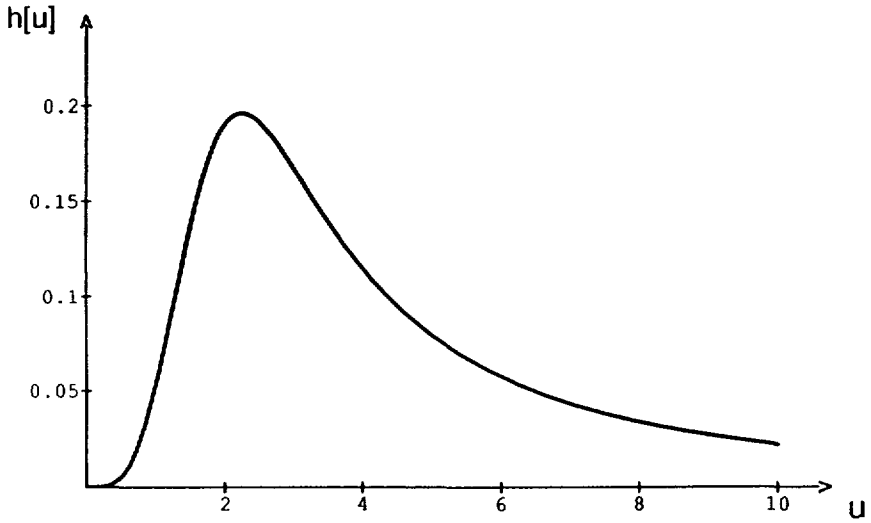

Fig. 2. — The function $h[u]$ defined by equation (29).

We shall now examine some consequences of the expression (27). If the interaction between two segments is modeled by a delta function (i.e. $W(\mathbf{r}) = w\delta(\mathbf{r})$) then $\tilde{W}(\mathbf{k}) = w$, and equation (27) becomes (see Eq. (30))

$$\langle \mathbf{R}^2 \rangle = L\ell \left[1 + \kappa \frac{wL^{1/2}}{\ell^{3/2}} - \cdot \quad \right] \tag{31}$$

in agreement with the familiar result of the two parameter model (Eq. (19)). In the general case of a non-delta interaction, the first order correction depends on the shape of the potential (see Eq. (27)). However, in the particular limit of very long chains ($L \to +\infty$), and provided that $\tilde{W}(k = 0)$ exists [15], the first order correction can be approximated as

$$\frac{4}{3} \left(\frac{3}{2\pi} \right)^{3/2} \frac{L^{1/2}}{\ell^{3/2}} \tilde{W}(k = 0) \tag{32}$$

and one recovers an equation similar to equation (31) with w simply replaced by $\tilde{W}(k = 0)$.

2.2.2 *Uniform expansion model.* — We now use the Edwards-Singh method to obtained a closed form expression for the chain dimension. Starting from the perturbation result (31) and expanding $1/\ell$ around $1/\ell'$ (Eq. (21)) we obtain

$$\langle \mathbf{R}^2 \rangle = L\ell' \left\{ 1 + \left[\frac{\kappa L^{1/2}}{(\ell')^{3/2}} \int_0^{+\infty} \mathrm{d}u\, h(u)\, \tilde{W}\left(\sqrt{\frac{6}{\ell' L}}\, u \right) - \ell' \left(\frac{1}{\ell} - \frac{1}{\ell'} \right) \right] + \cdot \quad \right\}. \tag{33}$$

Since ℓ' is defined by equation (20) the first order correction must vanish. This condition gives

$$\frac{\kappa L^{1/2}}{(\ell')^{3/2}} \int_0^{+\infty} \mathrm{d}u\, h(u)\, \tilde{W}\left(\sqrt{\frac{6}{\ell' L}}\, u\right) = \ell' \left(\frac{1}{\ell} - \frac{1}{\ell'}\right) . \tag{34}$$

Introducing the expansion factor α (Eq. (24)) we obtain

$$\alpha^5 - \alpha^3 = \frac{4}{3}\left(\frac{3}{2\pi}\right)^{3/2} \frac{L^{1/2}}{\ell^{3/2}} \int_0^{+\infty} \mathrm{d}u\, h(u)\, \tilde{W}\left(\frac{1}{\alpha}\sqrt{\frac{6}{\ell L}}\, u\right) . \tag{35}$$

The closed form (35) is a generalization of the modified Flory formula (Eq. (25)) to the case of an arbitrary two-body interaction. For a given form of the potential $\tilde{W}(k)$, equation (35) gives the value of the expansion factor α as a function of the chain length L. We shall now examine some consequences of this expression :

(i) If the interaction between two segments is modeled by a delta function (i.e. $W(\mathbf{r}) = w\, \delta(\mathbf{r})$) then the right hand side of equation (35) is independent of α and we have

$$\alpha^5 - \alpha^3 = \frac{4}{3}\left(\frac{3}{2\pi}\right)^{3/2} \frac{L^{1/2}}{\ell^{3/2}}\, w \tag{36}$$

(i.e. we recover the usual modified Flory formula, Eq. (25)).

(ii) In the general case of a non-delta interaction, the right hand side of equation (35) depends on α.

If the effect of the excluded volume interaction is weak, α is close to 1 and the expression (35) agrees with the result of the first order perturbation expansion (27).

On the other hand, in the limit of large α values, one can evaluate the right hand side of equation (35) as

$$\frac{4}{3}\left(\frac{3}{2\pi}\right)^{3/2} \frac{L^{1/2}}{\ell^{3/2}}\, \tilde{W}(k=0) , \tag{37}$$

provided that $\tilde{W}(k=0)$ [15] exists (for a counterexample see Sect. 4.1). In this limit the mean square end-to-end distance is given by

$$\langle \mathbf{R}^2 \rangle \cong L^{6/5}\, \ell^{2/5} \left\{\tilde{W}(k=0)\right\}^{2/5} \tag{38}$$

in agreement with the classical result $\langle \mathbf{R}^2 \rangle \sim L^{6/5}$ [14].

The intermediate regime is described by the full expression (35).

3. Size of a single chain.

Having derived a closed form for the expansion factor in the general case of a non-delta potential, we can now return to a deeper discussion of the conformation of a long chain (contour length L_1) immersed in a (monodisperse) dense solution of shorter, chemically identical chains (contour length L).

The effective interaction between any two segments is given by (see Sect. 1)

$$\tilde{u}(\mathbf{k})/k_\mathrm{B}\, T = \frac{w\ell^2}{1 + w\ell^2\, c g_0(\mathbf{k}\,;L)} \tag{39}$$

where the function $g_0(\mathbf{k}\,;L)$ is the structure factor for the Gaussian chain (Eq. (6)). For

convenience of calculation, we approximate $g_0(\mathbf{k}\,;L)$ by [4]

$$g_0(\mathbf{k}\,;L) \approx \frac{L/\ell}{1 + k^2 \dfrac{L\ell}{12}}\,. \tag{40}$$

The error of this equation is less than 15 % for the entire region of k [4]. Inserting equations (39) and (40) into equation (35) we obtain the closed form

$$\alpha^5 - \alpha^3 = \frac{4}{3}\left(\frac{3}{2\pi}\right)^{3/2} (L_1/\ell)^{1/2}\,(w/\ell)\,F\,[\sqrt{2\,\alpha^2(L_1/L)}\,;\,\sqrt{2\,\alpha^2 X(L_1/L)}] \tag{41}$$

where the function $F\,(x\,;y)$ is defined by

$$F\,(x\,;y) \equiv \int_0^{+\infty} \mathrm{d}u\; h(u)\,\frac{u^2 + x^2}{u^2 + y^2}\,. \tag{42}$$

An explicit expression of $F\,(x\,;y)$ is given in the Appendix. The parameter X is defined by :

$$X \equiv 1 + (w/\ell)\,(c\ell^3)\,(L/\ell) \approx (w/\ell)\,(c\ell^3)\,(L/\ell) \tag{43}$$

(for convenience of calculation, we assume that the size of the matrix chains is large enough for the above indicated approximation to be valid ; when this is not case, one has simply to use the full definition of X).

In the limit $\alpha \to +\infty$, the function $F\,[\sqrt{2\,\alpha^2(L_1/L)}\,;\,\sqrt{2\,\alpha^2(w/\ell)\,(c\ell^3)\,(L_1/\ell)}]$ becomes independent of α and tends to

$$\lim_{\alpha \to +\infty} F\,[\sqrt{2\,\alpha^2(L_1/L)}\,;\,\sqrt{2\,\alpha^2(w/\ell)\,(c\ell^3)\,(L_1/\ell)}] = (w/\ell)\,(c\ell^3)\,(\ell/L)\,. \tag{44}$$

Thus, if one replaces the r.h.s. of equation (41) by its asymptotic value *while keeping the l.h.s. unchanged,* one obtains

$$\alpha^5 - \alpha^3 = \frac{4}{3}\left(\frac{3}{2\pi}\right)^{3/2} \frac{(L_1/\ell)^{1/2}}{(L/\ell)\,(c\ell^3)} \tag{45}$$

which corresponds to the Flory results (Eq. (11)). We can therefore anticipate that the Flory theory will describe correctly the high swelling regime (large values of α), but will not necessary give a good description of the crossover regime.

3.1 NUMERICAL RESULTS. — In what follows we shall solve numerically equations (41) and (45) and compare the results obtained.

Figure 3 shows the dependence of α^2 *vs.* L_1 for a given length L of the matrix chains. The figure compares the result obtained by solving equation (41) to the corresponding result obtained from the Flory theory (Eq. (45)). The main modification is an increase in the expansion factor of the large chain. The reason for this increase can be traced back to the α dependence of the r.h.s. of equation (41) ; the r.h.s. is a decreasing function of α, so that the crossover with the l.h.s. (an increasing function of α) occurs for a larger value of α. Figure 3 indicates that the two curves (a) and (b) converge for large values of α, as expected.

3.2 DISCUSSION. — In the previous section the closed form (41) has been solved numerically,

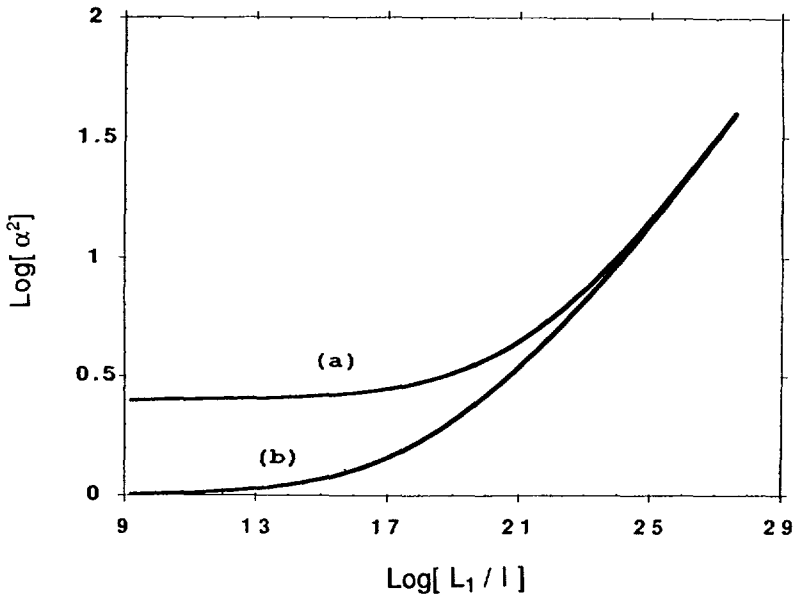

Fig. 3. — The Log-Log plot of α^2 *vs.* L_1/ℓ for $L = 10^4\,\ell$, $w\ell^{-1} = 1$ and $c\ell^3 = 1$; a) plot of equation (41), b) plot of the Flory prediction equation (45).

using the full definition of the function $F(x\,;y)$ (see Appendix). In order to obtain a more tractable closed expression for α, one can approximate the function $F[\sqrt{2\,\alpha^2(L_1/L)}\,;\sqrt{2\,\alpha^2(w/\ell)\,(c\ell^3)\,(L_1/\ell)}]$ by

$$F[\sqrt{2\,\alpha^2(L_1/L)}\,;\sqrt{2\,\alpha^2(w/\ell)\,(c\ell^3)\,(L_1/\ell)}] \approx \frac{1}{(w/\ell)\,(c\ell^3)\,(\ell/L)} + \frac{1}{\alpha}\sqrt{\frac{2\pi\,(\ell/L_1)}{(w/\ell)\,(c\ell^3)}} \tag{46}$$

Equation (40) then becomes

$$\alpha^5 - \alpha^3 \approx \frac{4}{3}\left(\frac{3}{2\pi}\right)^{3/2}\left[\frac{(L_1/\ell)^{1/2}}{(L/\ell)\,(c\ell^3)} + \frac{1}{\alpha}\sqrt{\frac{2\pi\,(w/\ell)}{(c\ell^3)}}\right]. \tag{47}$$

This (approximate) expression indicates that the expansion factor α depends on L and L_1 only through the ratio $L_1^{1/2}/L$.

Equation (47) should be compared to the Flory result equation (45). For large values of α, the second term in the square bracket of the r.h.s. of equation (47) can safely be neglected. However, in the crossover regime (α of order unity), both terms in the square bracket are important and equation (47) gives rise to an expansion factor larger than the one predicted by equation (45).

Figure 4 represents the variations of the square of the expansion factor α^2 as a function of the ratio $(L_1/\ell)^{1/2}/(L/\ell)$ for $L = 10^4\,\ell$, $v\ell^{-3} = 1$ and $c\ell^3 = 1$. The curve (a) corresponds to equation (47) while the curve (b) corresponds to the Flory result equation (45). For large values of $(L_1/\ell)^{1/2}/(L/\ell)$, the two curves (a) and (b) are both asymptotic to the curve $\alpha^2 = [6/\pi^3]^{1/5}[(L_1/\ell)^{1/2}/(L/\ell)]^{2/5}$ At the other end, for $L_1 = L$, equation (47) gives $\alpha^2 = 1.495$ while equation (45) gives a lower value $\alpha^2 = 1.004$. For both curves (a) and (b) the crossover regime is rather broad. If one tries to define a crossover criterion as the intersection of the

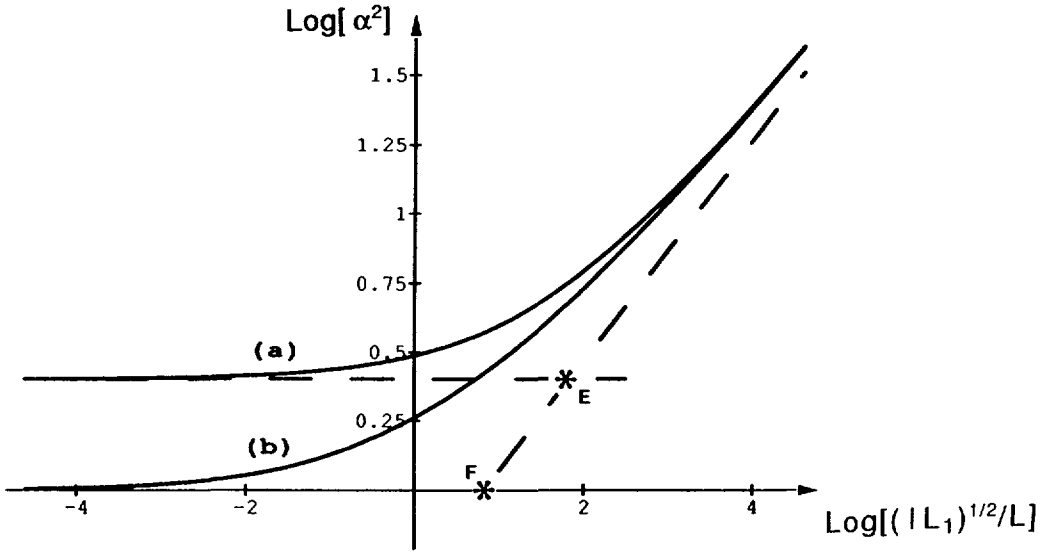

Fig. 4. — The Log-Log plot of α^2 *vs.* $(L_1/\ell)^{1/2}/(L/\ell)$ for $L = 10^4\,\ell$, $w\ell^{-1} = 1$ and $c\ell^3 = 1$; a) plot of equation (45), b) plot of the Flory prediction equation (44). The points E and F correspond to the crossover between the asymptotic behaviors (see text).

asymptotic behaviors (see points E and F in Fig. 4), one obtains $(L_1/\ell) \lesseqgtr 38.652\ (L/\ell)^2$ for curve (a), and $(L_1/\ell) \lesseqgtr 5.176\ (L/\ell)^2$ for curve (b). Therefore the usual Flory criterion $(L_1/\ell) \lesseqgtr (L/\ell)^2$ retains it significance as far as the scaling laws are concerned, but the actual numerical factor could be quite large.

4. Discussion.

1. One aspect of this paper is the derivation of a closed form expression for the mean square end-to-end distance of a flexible chain with arbitrary two-body interactions (Eq. (35)). This expression has been obtained by using the uniform expansion model introduced by Edwards and Singh in the case of a delta function pseudopotential. These authors have shown that the structure of equation (45) is stable to all orders of perturbation about ℓ' (Eq. (21)) : if one goes to higher orders, only the numerical coefficient of the r.h.s. of equation (25) is modified. It would be interesting to investigate whether this remarkable feature is still retained in the case of an arbitrary interaction.

Note that in addition to the modified Flory formula (Eq. (25)), many approximate closed expressions for α exist in the literature [16]. However, like equation (25), they generally assume a delta function pseudopotential.

One might consider using the closed expression equation (35) in the case of long-range forces. Consider for example the case of a Coulomb potential. For a single linear flexible chain of contour length L, with a charge density fe (e is the electronic charge) and immersed in a salt free θ-solvent, the interaction energy between two monomers is given by $k_B\,T\,\ell^2\,W(\mathbf{r})$ with

$$W(\mathbf{r}) = \frac{\ell_B\,f^2}{\ell^2\,r} \tag{48}$$

(ℓ_B is the Bjerrum length $\ell_B = e^2/(4\,\pi\,\varepsilon k_B\,T)$ and ε the solvent dielectric constant). The r.h.s.

of equation (41) can be easily calculated and we obtain :

$$\alpha^5 - \alpha^3 = \frac{2}{15}\left(\frac{8}{3\pi}\right)^{1/2} \frac{L^{3/2}\,\ell_B\,f^2}{\ell^{5/2}}\,\alpha^2 \tag{49}$$

or, equivalently,

$$\alpha^3 - \alpha = \frac{2}{15}\left(\frac{8}{3\pi}\right)^{1/2} \frac{L^{3/2}\,\ell_B\,f^2}{\ell^{5/2}} \tag{50}$$

If the r.h.s. of equation (50) is small, the electrostatic interactions are weak and the chain has statistics which are nearly Gaussian

$$\alpha^2 = 1 + \frac{2}{15}\left(\frac{8}{3\pi}\right)^{1/2} \frac{L^{3/2}\,\ell_B\,f^2}{\ell^{5/2}} + \cdot \tag{51}$$

One the other hand, if the r.h.s. of equation (50) is large, the electrostatic interaction dominates and

$$\alpha^3 \cong \frac{2}{15}\left(\frac{8}{3\pi}\right)^{1/2} \frac{L^{3/2}\,\ell_B\,f^2}{\ell^{5/2}} \tag{52}$$

Neglecting all numerical prefactors, the mean square end-to-end distance is then given by

$$\langle \mathbf{R}^2 \rangle \approx (\ell_B\,f^2/\ell)^{2/3}\,L^2 \tag{53}$$

The overall size of the chain is thus proportional to L. Equation (53) is in agreement with the early work of de Gennes *et al.* [17].

This agreement in the case of a Coulomb interaction might however be rather fortuitous and the ability of equation (35) to describe properly the behavior of a self-interacting polymers with long-range repulsive forces might be questioned. Consider for example the case of a $1/r^2$ repulsion. According to the variational approach of Bouchaud *et al.* [18], one expects in the limit of very long chains : $R \sim L$ (with some logarithmic corrections) while equation (35) predicts $R \sim L^{3/4}$

2. Another aspect of this work concerns the size of a long chain immersed in a monodisperse, concentrated solution of shorter, chemically identical chains. Using our general formula (Eq. (35)) as well as the effective potential calculated by Edwards (Eq. (5)) we have shown that the classical approach of Flory underestimate the swelling of the long chain. This effect could provide a qualitative explanation for some of the discrepancies between the experimental results obtained by Kirste and Lehnen using neutron scattering [19] and the Flory theory (Eq. (45)). We hope to return to this point in a later paper.

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Appendix.

The function $F(x\,;y)$ defined by

$$F(x\,;y) \equiv \int_0^{+\infty} \mathrm{d}u\; h(u)\,\frac{u^2 + x^2}{u^2 + y^2} \tag{A1}$$

with

$$h(u) = \frac{12 + 8\,u^2 + 2\,u^4 - 12\exp(u^2) + 4\,u^2\exp(u^2)}{\pi^{1/2}\,u^4\exp(u^2)} \tag{A2}$$

can be calculated explicitly. One obtains :

$$F(x\,;y) = x^2\left[-\frac{2\pi^{1/2}}{y^3} + \frac{12}{y^4} - \frac{6\pi^{1/2}}{y^5}\right] + \left[1 + \frac{2\pi^{1/2}}{y} - \frac{12}{y^2} + \frac{6\pi^{1/2}}{y^3}\right] + \\ + \frac{6 - 4\,y^2 + y^4}{y^3}\,\pi^{1/2}\left(\frac{x^2}{y^2} - 1\right)\,[1 - \mathrm{Erf}\,(y)]\exp(y^2) \tag{A3}$$

where Erf denotes the error function :

$$\mathrm{Erf}\,(y) \equiv \frac{2}{\pi^{1/2}}\int_0^y \mathrm{d}u\,\exp(-\,u^2)\,. \tag{A4}$$

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[15] One may recognize in $\ell^2\,\tilde{W}(k=0) = \ell^2\int \mathrm{d}\mathbf{r}W(r)$ the virial coefficient in the soft potential approximation. For hard potentials one should replace this by the excluded volume $\int \mathrm{d}\mathbf{r}\,[1 - \exp(-\,\ell^2\,W(r))]$ (see [8]).

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