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THE STATISTICS OF LONG CHAINS WITH NON-MARKOVIAN REPULSIVE INTERACTIONS AND THE MINIMAL GAUSSIAN APPROXIMATION

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Résumé. — Dans un espace à s dimensions, nous étudions le comportement de longues chaînes dont tous les points se repoussent (N étant le nombre de maillons) ; la méthode consiste à introduire des probabilités d'essai qui sont déterminées par minimisation de l'énergie libre F_N ; ces probabilités définissent les dimensions moyennes des chaînes. Des théories classiques sont examinées et leurs défauts mis en évidence. L'approximation gaussienne minimale qui semble l'approche self consistante la plus simple, est décrite en détail pour un anneau de N points de vecteurs $\mathbf{r}_j$ ($j = 1, ..., N$ (un maillon joint deux points successifs).

Le calcul montre que la distance moyenne quadratique entre deux tels points $\mathbf{r}_j$ et $\mathbf{r}_{j+n}$ ($n \gg 1$, $n/N \ll 1$) est de la forme $< (\mathbf{r}_{j+n} - \mathbf{r}_j)^2 > = bn^{2\alpha}(\log n)_\beta$ avec les valeurs suivantes : $\alpha = 1$, $\beta = -1$ pour $s = 2$; $\alpha = 2/3$, $\beta = 0$ pour $s = 3$; $\alpha = 1/2$, $\beta = 1/2$ pour $s = 4$; $\alpha = 1/2$, $\beta = 0$ pour $s > 4$.

La structure d'un grand anneau est étudiée et le terme $\Delta F_N = F_N - N \lim_{N' \to \infty} (F_{N'}/N')$ est calculé pour $s = 3$ et $N \gg 1$ ($\Delta F_N \propto \log N$).

On montre également qu'une classe étendue de probabilités d'essai conduit qualitativement aux mêmes résultats que l'approximation gaussienne.

Abstract. — We study long chains (or rings) which occupy a space of s dimensions and which have repulsive interactions between all the points of the chain (N being the number of links) ; the method consists in introducing trial probabilities which are determined by minimization of the free energy F_N ; these probabilities definite the mean size of the chain. Current theories are examined critically and their inconsistencies are revealed. The Minimal Gaussian approximation, which seems the simplest consistent approach, is described in detail for a ring of N links whose end points are assigned coordinates $\mathbf{r}_j$ ($j = 1, ..., N$). The calculation shows that the mean square distance between two such points $\mathbf{r}_j$ and $\mathbf{r}_{j+n}$ ($n \gg 1$, $n/N \ll 1$) is of the form : $< (\mathbf{r}_{j+n} - \mathbf{r}_j)^2 > = bn^{2\alpha}(\log n)_\beta$ with the following values : $\alpha = 1$, $\beta = -1$ for $s = 2$; $\alpha = 2/3$, $\beta = 0$ for $s = 3$; $\alpha = 1/2$, $\beta = 1/2$ for $s = 4$; $\alpha = 1/2$, $\beta = 0$ for $s > 4$.

The structure of a large ring is investigated and the term $\Delta F_N = F_N - N \lim_{N' \to \infty} (F_{N'}/N')$ is calculated for $s = 3$ and $N \gg 1$ ($\Delta F_N \propto \log N$). It is also shown that a large class of trial probabilities leads to the same qualitative results as the Gaussian approximation.

I. **Introduction.** — The statistics of long chains has been studied for three main reasons :

1. — These chains are a good mathematical representation of long molecules and biopolymers.

2. — It is generally recognized that the problem of the behaviour of long chains is closely related to the theory of phase transitions [1].

3. — This study leads to the formulation of well defined and interesting mathematical questions.

The central problem is the determination of the average dimensions of a chain in terms of the number of links. The answer depends very much on the nature of the interactions and especially on their sign. Actually, in long molecules, the interaction often has short range repulsive components and long range attractive ones ; in this case, the behaviour of the chain depends strongly on temperature and phase transitions may occur [2]. Thus, the situation may be very complex. For this reason, we deal here only with the case where the interactions are *short range* and *repulsive*.

A large number of articles, over a period of twenty years have been devoted to this question. Many theoretical papers have been written and numerous machine experiments have given valuable information on the subject. However, very few exact results are available [3, 4] and very little is known with certainty concerning the asymptotic behaviour of these chains. In particular, many theories seem quite inconsistent, and, in the first part of this paper, we study specially important examples.

However, a very interesting Gaussian model has been presented a few years ago by M. Fixman [5]. More recently S. F. Edwards and the author [6] have proposed a new Gaussian approximation which differs from the approach of Fixman but seems more natural and simple. A full account of this method which will be called Minimal Gaussian approximation is given in the second part of this paper. This approximation describes in the simplest mathematical way, the process of swelling of a chain, a notion introduced by Flory [7] many years ago. However, for peculiar reasons, the results of the Minimal Gaussian approximation differ significantly from those of Flory and Fixman, a fact which seems rather strange. They seem also disagree with the results of machine experiments [8] and therefore the Gaussian method may not describe correctly the asymptotic properties of a repulsive chain. However, we think that :

1. — the Minimal Gaussian approximation is both very simple and completely consistent from a mathematical point of view ;
2. — it gives a fairly reasonable description of the physical reality ;
3. — the model has interesting features and its study leads to new and non trivial conclusions which must have a larger range of application than the model itself ;
4. — on the other hand, the machine calculations give very valuable informations but nevertheless there is no complete guarantee that they converge rapidly to the asymptotic limit.

For all these reasons, it seems worthwhile to give here a complete study of this approximation.

In section II, the problem is formulated precisely and notations are introduced. Section III which is independent of the other sections contains a critical review of other approaches. Section IV is devoted to the Gaussian approximation. In section V which is independent of subsections IV F, G, H, I, we examine the properties of more general models.

II. The chains and their thermodynamic properties. — A. DEFINITIONS AND GENERAL ASSUMPTIONS. — We consider a chain of N points, in a space of s dimensions. The position of the point of order j on the chain is denoted by a vector $\mathbf{r}_j$ (with $j = 1, ..., N$). The probability which is associated with a configuration of the chain can be written :

$$P(\mathbf{r}_1, ..., \mathbf{r}_N) = Z^{-1} \exp\{ -\beta U(\mathbf{r}_1, ..., \mathbf{r}_N) \} \tag{II.1}$$

with

$$U(\mathbf{r}_1, ..., \mathbf{r}_N) = U_0(\mathbf{r}_1, ..., \mathbf{r}_N) + U_1(\mathbf{r}_1, ..., \mathbf{r}_N) . \tag{II.2}$$

The function $U_0(\mathbf{r}_1, ..., \mathbf{r}_N)$ defines the chain structure :

$$U_0(\mathbf{r}_1, ..., \mathbf{r}_N) = \sum_{j=1}^{N-1} C(\mathbf{r}_{j+1} - \mathbf{r}_j) . \tag{II.3}$$

We may set for instance :

$$C(\mathbf{r}) = r^2\, s/2\, l^2 \tag{II.4}$$

or if we prefer rigid links :

$$\exp[-\beta C(\mathbf{r})] = \delta(\,|\,\mathbf{r}\,| - l\,) . \tag{II.5}$$

Here, l defines the length of a link :

$$< (\mathbf{r}_{j+1} - \mathbf{r}_j)^2 >_0 = l^2 . \tag{II.6}$$

The interaction is represented by $U_1(\mathbf{r}_1, ..., \mathbf{r}_N)$

$$U_1(\mathbf{r}_1, ..., \mathbf{r}_N) = \sum_{1 \leqslant j < l \leqslant N} V(\mathbf{r}_j - \mathbf{r}_l) , \tag{II.7}$$

where $V(\mathbf{r})$ is a short range repulsive potential.

The probability law is normalized :

$$\int \mathrm{d}^s\mathbf{r}_2 \ldots \mathrm{d}^s\mathbf{r}_N\, P(\mathbf{r}_1, ..., \mathbf{r}_N) = 1 \tag{II.8}$$

and, accordingly, the partition function Z is given by :

$$Z = \int \mathrm{d}^s\mathbf{r}_2 \ldots \mathrm{d}^s\mathbf{r}_N \exp[-\beta U(\mathbf{r}_1, ..., \mathbf{r}_N)] . \tag{II.9}$$

The mean value $< A >$ of a function $A(\mathbf{r}_1, ..., \mathbf{r}_N)$ of the chain configuration is :

$$< A > = \int \mathrm{d}^s\mathbf{r}_2 \ldots \mathrm{d}^s\mathbf{r}_N\, P(\mathbf{r}_1, ..., \mathbf{r}_N)\, A(\mathbf{r}_1, ..., \mathbf{r}_N) . \tag{II.10}$$

In particular, the average size of the chain can be determined by $< (\mathbf{r}_N - \mathbf{r}_1)^2 >$ and for large values of N, we expect an asymptotic behaviour of the following form :

$$< (\mathbf{r}_N - \mathbf{r}_1)^2 > \simeq a N^{2\alpha} \quad \text{with} \quad \tfrac{1}{2} \leqslant \alpha \leqslant 1 , \tag{II.11}$$

(but logarithmic factors cannot be excluded *a priori*). It is generally believed that α depends only on the dimension of space and not on the microstructure of the chain. In particular, the formula must apply to random walks with excluded volume on a lattice, and indeed, the results of machine calculations agree with these views. In the same way, for

$$1 \ll j \ll l \ll N \text{ and } |j - l|/N \ll 1 ,$$

we must obtain :

$$< (\mathbf{r}_j - \mathbf{r}_l)^2 > \simeq b\,|j - l|^{2\alpha} \qquad \text{(II.12)}$$

(but we may have $b \neq a$).

Instead of chains, we may study rings ; in this case, the end effects are eliminated but the formalism does not change ; we have only to replace $U_0(\mathbf{r}_1, ..., \mathbf{r}_N)$ and $U_1(\mathbf{r}_1, ..., \mathbf{r}_N)$ by the following quantities :

$$U'_0(\mathbf{r}_1, ..., \mathbf{r}_N) = U_0(\mathbf{r}_1, ..., \mathbf{r}_N) + C(\mathbf{r}_N - \mathbf{r}_1) \qquad \text{(II.13)}$$

$$U'_1(\mathbf{r}_1, ..., \mathbf{r}_N) = U_1(\mathbf{r}_1, ..., \mathbf{r}_N) - V(\mathbf{r}_N - \mathbf{r}_1) . \qquad \text{(II.14)}$$

(In the following, for the sake of simplicity, the primes are dropped.)

For a ring, when $N \gg |j - l| \gg 1$, eq. (II.12) remains valid. We can also define the correlation function :

$$\mathcal{T}_n(\mathbf{r}) = < \delta(\mathbf{r} - \mathbf{r}_{j+n} + \mathbf{r}_j) > \qquad \text{(II.15)}$$

and, in agreement with Eq. (II.11), we think that in the limit $N \to \infty$, the asymptotic expression of $\mathcal{T}_n(\mathbf{r})$ for $n \gg 1$ should be of the form :

$$\mathcal{T}_n(\mathbf{r}) = n^{-\alpha s}\, q(r/n^\alpha) \qquad \text{(II.16)}$$

with

$$\int d^s\mathbf{r}\; q(r) = 1 . \qquad \text{(II.17)}$$

In particular, when the interaction $U_1(\mathbf{r}_1, ..., \mathbf{r}_N)$ vanishes, the chain is Brownian. In this case, $\alpha = 1/2$ and $q(r)$ is Gaussian

$$q(r) = (2\,\pi b s)^{-s/2}\, \mathrm{e}^{-r^2/2bs} \quad (< r^2 > = b) . \qquad \text{(II.18)}$$

This type of law remains unchanged if $U_0(\mathbf{r}_1, ..., \mathbf{r}_N)$ contains interaction terms between neighbours of order 2, 3 ... p (provided that p is finite) and not only between nearest neighbours as in eq. (II.3).

But, the asymptotic form of $\mathcal{T}_n(r)$ and the value of α change if all the points of the chain interact with one another. This modification in the behaviour of the chain (ring) is related to the appearance of long range correlations between the links of the chain [9]. We may give an example. Let us set

$$\mathbf{a}_j = |\,\mathbf{r}_{j+1} - \mathbf{r}_j\,| . \qquad \text{(II.19)}$$

With this notation, we may write :

$$< (\mathbf{r}_j - \mathbf{r}_l)^2 > = \sum_{\substack{l \leqslant p \leqslant j \\ l \leqslant q \leqslant j}} < \mathbf{a}_p, \mathbf{a}_q > . \qquad \text{(II.20)}$$

We see immediately that the existence of link correlations of the form [10] :

$$< \mathbf{a}_p . \mathbf{a}_q > \simeq f\,|p - q|^{-\gamma} \qquad \text{(II.21)}$$

for $|p - q| > 1$ with $0 < \gamma < 1$ implies immediately that

$$< (\mathbf{r}_j - \mathbf{r}_l)^2 > \simeq b\,|j - l|^{2\alpha} \qquad \text{(II.22)}$$

with

$$\alpha = 1 - \gamma/2 \qquad b = 2f/(1 - \gamma)(2 - \gamma) \qquad \text{(II.23)}$$

and the converse is also true. (Note that in the Brownian case $< \mathbf{a}_p . \mathbf{a}_q >$ would decrease exponentially.)

Machine calculations [10] and simple considerations [6] suggest that α may be given by :

$$\alpha = 3/(s + 2) \qquad 1 \leqslant s \leqslant 4 \qquad \text{(II.24)}$$

and indeed one can show directly that $\alpha = 1$ for $s = 1$ and that $\alpha = \frac{1}{2}$ for $s = 4$ in agreement with eq. (II.24). Several authors tried to derive eq. (II.24) for $s = 2$ and $s = 3$ but objections can be raised to their derivations. Moreover, in section III, we shall see that the Gaussian approximation leads to different results.

B. The minimization of the free energy : trial probability laws. — At a given temperature, the free energy of a chain is given by :

$$F = < U > - \beta^{-1} S \qquad \text{(II.25)}$$

with

$$< U > = \int U(\mathbf{r}_1, ..., \mathbf{r}_N)\, P(\mathbf{r}_1, ..., \mathbf{r}_N) \times \times\, d^s\mathbf{r}_2 \dots d^s\mathbf{r}_N \qquad \text{(II.26)}$$

$$S = - \int P(\mathbf{r}_1, ..., \mathbf{r}_N) \log P(\mathbf{r}_1, ..., \mathbf{r}_N) \times \times\, \mathrm{d}^s\mathbf{r}_2 \dots \mathrm{d}^s\mathbf{r}_N , \qquad \text{(II.27)}$$

where S is the chain entropy [11]. Thus, the free energy can be considered as a functional of the probability $P(\mathbf{r}_1, ..., \mathbf{r}_N)$ which is regarded presently as arbitrary. However, the minimization of F with respect to $P(\mathbf{r}_1, ..., \mathbf{r}_N)$ implies precisely that $P(\mathbf{r}_1, ..., \mathbf{r}_N)$ is given by eq. (II.1). Unfortunately, the exact expression of $P(\mathbf{r}_1, ..., \mathbf{r}_N)$ is very complicated and, in the limit $N \to \infty$, we must try to determine a simpler but asymptotically exact law. More precisely, we would like to determine the following partial probabilities

$$\mathcal{T}(j_1\, \mathbf{r}_{j_1} | \dots | j_p\, \mathbf{r}_{j_p}) = = \lim_{N \to \infty} \int P(\mathbf{r}_1, ..., \mathbf{r}_N) \prod_{l \neq j_1, \dots, j_p} d^s\,\mathbf{r}_l \qquad \text{(II.28)}$$

$$j_1 \ll j_2 \ll \dots \ll j_p \qquad (p \text{ is finite})$$

which define the asymptotic properties of the chain.

For this purpose, we shall use trial probabilities $P_T(\mathbf{r}_1, ..., \mathbf{r}_N)$ depending on unknown parameters. These parameters are to be determined by minimization of the approximate free energy F obtained by replacing $P(\mathbf{r}_1, ..., \mathbf{r}_N)$ by $P_T(\mathbf{r}_1, ..., \mathbf{r}_N)$ in eqs. (II.26) and (II.27). The corresponding partial probabilities will be only approximate but, if $P_T(\mathbf{r}_1, ..., \mathbf{r}_N)$ is realistic enough, they should describe properly the macroscopic properties of the chain ; in particular, the value of α obtained in this way should be exact.

III. **Early approaches.** — A. PERTURBATION TREATMENT. — Let us assume that U_0 is quadratic and given by eqs. (II.3) and (II.4). In this case, as was shown by several authors [12], the free energy F and the mean value $< (\mathbf{r}_N - \mathbf{r}_1)^2 >$ can be expanded in terms of :

$$X = \int \{ 1 - \exp[- \beta V(r)] \} d^s \mathbf{r} . \quad \text{(III.1)}$$

For instance, in three dimensions, the expansion of $< (\mathbf{r}_N - \mathbf{r}_1)^2 >$ obtained by retaining, for each order in X, the leading term in N, has the form :

$$< (\mathbf{r}_N - \mathbf{r}_1)^2 > = $$
$$= Nl^2\left[1 + \left(\frac{4}{3}\right)z - \left(\frac{16}{3} - \frac{28\,\pi}{27}\right)z^2 + \cdots\right], \quad \text{(III.2)}$$

with $z = (3\,\pi l^2/2)^{3/2}\, X N^{1/2}$.

This expansion suggests that the asymptotic value of $< (\mathbf{r}_N - \mathbf{r}_1)^2 >$ is of the form :

$$< (\mathbf{r}_N - \mathbf{r}_1)^2 > = Nl^2 f(z) , \quad \text{(III.3)}$$

though it has not been proved in general that the term of order n in the preceding expansion (III.2) should be proportional to z^n. Unfortunately, the behaviour of $f(z)$ for $z \gg 1$, cannot be found without evaluating the value of the coefficient of z^n in the expression of $< (\mathbf{r}_N - \mathbf{r}_1)^2 >$ for large values of n, and this is a very difficult task because the coefficients of this expression are given by complicated multiple integrals.

The same parameter z also appears in the expression of F. Each term in the expansion of F with respect to N is given by the sum of an infinite series in z, and only the first terms of these series are known. Thus, it is practically impossible to reach any interesting conclusion concerning the variations of F with respect to N.

In summary, the perturbation method does not bring any definite information concerning the size of long repulsive chains.

B. FLORY'S THEORY OF SWELLING. — The theory of Flory [7] is more realistic and can be summarized as follows. For a free chain, the mean density of points ${}^0\rho(\mathbf{r})$, counted from the middle of the chain (which coincides approximately with the center of gravity) is given by :

$${}^0\rho(\mathbf{r}) = N[N\pi l^2/s]^{-s/2} \exp[- r^2\, s/Nl^2] . \quad \text{(III.4)}$$

The presence of a repulsive interaction (excluded volume) produces a swelling of the chain and P. Flory assumes that the general structure of the chain remains unchanged. Accordingly the new densities $f(\mathbf{r})$ can be written :

$$\rho(\mathbf{r}) = \sigma^{-s}\ {}^0\rho(\mathbf{r}/\sigma) , \quad \text{(III.5)}$$

where σ is the swelling coefficient. The aim of the theory is the determination of σ by minimization of the free energy F. For the sake of simplicity, it is assumed that the repulsive potential is smooth and we set :

$$v = \int V(r)\, d^s \mathbf{r} . \quad \text{(III.6)}$$

The energy ΔU is given approximately by :

$$\Delta U = \frac{v}{2} \int \rho^2(\mathbf{r})\, d^s \mathbf{r}$$
$$= vN^{2-s/2}(s/2\,\pi l^2)^{s/2}\, \sigma^{-s} . \quad \text{(III.7)}$$

In the same way, for a free chain, the probability distribution ${}^0\mathcal{T}(\mathbf{r})$ of the distance between the ends is given by :

$${}^0\mathcal{T}(\mathbf{r}) = [2\,\pi N l^2/s]^{-s/2} \exp[- r^2\, s/2\, Nl^2] \quad \text{(III.8)}$$

and it is assumed that for the swollen chain, we have also :

$$\mathcal{T}(\mathbf{r}) = \sigma^{-s}\ {}^0\mathcal{T}(\mathbf{r}/\sigma) . \quad \text{(III.9)}$$

The constraints due to the interaction produce a decrease of the internal free energy F_0 of the system. According to Flory, it can be estimated in the following way :

$$\Delta F_0 = - \int \mathcal{T}(\mathbf{r})[\log \mathcal{T}(\mathbf{r}) - \log {}^0\mathcal{T}(\mathbf{r})]\, d^s \mathbf{r} \quad \text{(III.10)}$$

$$= v\left[\frac{\sigma^2 - 1}{2} - \log \sigma\right]. \quad \text{(III.11)}$$

Consequently :

$$\Delta F = \Delta F_0 + \Delta U = \beta v\left[\frac{\sigma^2 - 1}{2} - \log \sigma\right] +$$
$$+ vN^{2-s/2}(s/2\,\pi l^2)^{s/2}\, \sigma^{-s} \quad \text{(III.12)}$$

and the minimization condition

$$\partial\, \Delta F/\partial \sigma = 0 \quad \text{(III.13)}$$

leads to the well known equation :

$$\sigma^{s+2} - \sigma^s = CN^{2-s/2} . \quad (C = \text{constant}) \quad \text{(III.14)}$$

Finally, in the limit of large N, we find :

$$\sigma \simeq \sigma_0\, N^{\alpha-(1/2)} \quad (\sigma_0 = \text{constant}) \quad \text{(III.15)}$$

with

$$\alpha = 3/(s + 2) \quad (1 \leqslant s \leqslant 4)$$
$$(s = \text{space dimension}) . \quad \text{(III.16)}$$

The agreement with the results of machine calculations seems good, but this theory has two serious defects :

1° The swelling of the chain is not described precisely. In other words, the theory of Flory does not correspond to any specific model. For this reason, several authors have tried to make the theory more consistent by using mean field methods.

2° The theory of Flory is mathematically unsound for the following reason. Let us consider the magnitude of the terms which Flory calculates ; by using eq. (III.15), we find that the order of these « Flory terms » is :

$$\Delta U \propto N^{2-\alpha s} \qquad \text{(III.17)}$$

$$\Delta S \propto N^{2\alpha-1} . \qquad \text{(III.18)}$$

(Eq. (III.8) says also that $2 - \alpha s = 2\alpha - 1$ but presently we may forget this condition).

These terms are small with respect to the main terms which must be proportional to N. Indeed, we should really write

$$\Delta F_0 \simeq A_1 N + B_1 N^{2\alpha-1} \qquad \text{(III.19)}$$

$$\Delta U \simeq A_2 N + B_2 N^{2-\alpha s} . \qquad \text{(III.20)}$$

When minimizing F, one has to minimize the sum $(A_1 + A_2) N$ of the large terms and not the sum of the small Flory terms which for large values of N are completely negligible. Thus, the derivation of Flory which ignores the main terms is incorrect.

One might object that the Flory terms, though they are small, are the most important ones because they characterize the swelling, whereas the main terms which are proportional to N exist also for a Brownian chain and can probably be taken into account independently by using some kind of renormalization. However, we think that such a point of view is not valid ; we think that the really important terms of ΔF are the largest ones, that the swelling can and must be determined by minimizing what we may call the « long range components » [13] of the large terms and that the « Flory terms » are only a by-product of the swelling. The study of the Gaussian approximation illustrates this view, as will be shown in section IV. In fact, the swelling for this Gaussian model is really determined by minimization of the main terms (the swelling is even larger than in Flory's theory) ; in this case, « Flory terms » exist also in ΔF_0 and ΔU and their asymptotic behaviour is given by eqs. (III.17) and (III.18) ; however since the Gaussian approximation does not give the result of eq. (III.8), the two Flory terms are not of the same order of magnitude $(2\alpha - 1 > 2 - \alpha s)$.

3° For $s = 2$ or $s = 3$, the free energy term calculated by using Flory's theory has the wrong sign. In order to establish this fact, let us assume for the moment that Flory's result is right, at least qualitatively. We see immediately that, for $N \gg 1$, the term ΔF given by eqs. (III.12) and (III.13) is positive. Thus, for $s = 2$ or $s = 3$, according to Flory's theory, the asymptotic expression of the free energy must be of the form :

$$F \simeq AN + BN^{\beta} \qquad \text{(III.21)}$$

with $B > 0$, $0 < \beta < 1$ $\left(\text{since } \beta = \dfrac{4-s}{s+2}\right)$.

Consequently, the partition function should be approximately equal to :

$$Z_N \simeq \mu^N \nu^{-N\beta} \quad (\nu = e^B > 1 , \quad KT = 1) . \qquad \text{(III.22)}$$

Since the swelling of a chain is a long range phenomenon, we expect this result to be valid also for a chain with excluded volume on a lattice. For such kind of chain, Z_N is just the number of chains of N links which can be built by starting from a given point of the lattice. But, in this case, we have always :

$$Z_{N+M} < Z_N . Z_M , \qquad \text{(III.23)}$$

since two chains with excluded volume which start from the same point, have a finite probability of overlapping. This inequality is incompatible with eq. (III.22) and therefore, if F has an approximate value of the form (III.21), the sign of B must be negative in contradiction with Flory's theory. Such a result may seem very surprising but it can be understood if one considers that the « Flory terms » are only corrections to the main term and that they are produced by the appearance of a cut off at distances of the order of Nl. Actually, by using the Gaussian approximation for a ring, these Flory terms can be calculated explicitly, but in this case they vanish for very interesting reasons (see section IV.I) and they are replaced by a term proportional to $\log N$, in contradiction with Flory's assumptions.

Finally, for all these reasons, we may conclude that Flory's theory which it does not describe precisely the swelling process, is also unreliable because it is mathematically inconsistent.

C. The self-consistent field method. — In order to determine the macroscopic properties of a repulsive chain in a more detailed way, several author have tried to take the interaction into account by using a self consistent field. Thus, Edwards [14] has assumed that for a chain starting from a point O and going to infinity, the interactions between the points of the chain can be replaced by a self-consistent potential $V(\mathbf{r})$ centered in O. This potential is spherically symmetrical and acts on all the points of the chain. Let $\mathbf{r}_n$ be the vector which defines the position of the n^{th} point on the chain ($\mathbf{r}_0 = 0$). In three dimensions, for large values of n, the calculation of Edwards gives :

$$< | \mathbf{r}_n | > \simeq C n^{3/5} \qquad \text{(III.24)}$$

(in agreement with Flory's equation (III.8)).

Edwards' method amounts to choosing a trial probability $P(\mathbf{r}_1, ..., \mathbf{r}_N)$ of the form :

$$P(\mathbf{r}_1, ..., \mathbf{r}_N) = \prod_{n=1}^{\infty} \delta(|\mathbf{r}_n - \mathbf{r}_{n-1}| - l)\, e^{-V(\mathbf{r}n)} . \tag{III.25}$$

This is precisely the assumption made by Reiss [15] and Yamakawa [16] who determined $V(\mathbf{r})$ by minimizing the free energy F. The calculation gives the same answer (eq. III.24) as the method of Edwards.

However, in spite of this agreement, the method is far from being satisfactory for a reason which, as we shall see now, is related to the behaviour of a chain in a potential $V(\mathbf{r})$. The asymptotic properties of the chain depend on the properties of $V(\mathbf{r})$ for large values of r, at which it varies in a smooth way, and where its influence can be treated by semiclassical methods. More precisely, let us consider an infinite chain interacting with a smooth potential $V(\mathbf{r})$ which need not be spherical. The smoothness conditions are written :

$$l\,|\nabla V(\mathbf{r})| \ll 1 \tag{III.26}$$

(l is defined by eq. (II.6)).

$$l\,|\nabla_j \nabla_l V(\mathbf{r})| \ll 1 \tag{III.27}$$

and the (discontinuous) function $\mathbf{r}(L)$ where L is the length of the chain counted from the origin ($L = nl$) defines the chain. Let $\mathbf{a}(L)$ be the vector associated with the link of order n.

$$\mathbf{a}(L) = \mathbf{r}(L + l) - \mathbf{r}(L) . \tag{III.28}$$

The probability law for $\mathbf{a}$ can be written approximately

$$q(\mathbf{a}) \propto \delta(|\mathbf{a}| - l)\, e^{-\mathbf{a}.\nabla V(\mathbf{r})} \tag{III.29}$$

and we get immediately :

$$< a^2(L) > \simeq l^2 \tag{III.30}$$

$$< \mathbf{a}(L) > \simeq \frac{l^2}{s} \nabla V(\mathbf{r}) . \tag{III.31}$$

Now, we can use an adiabatic approximation. In intervals ΔL which are large with respect to l but small with respect to $|\nabla V(\mathbf{r}(L))|^{-1}$, the function $\mathbf{r}(L)$ can be considered as a random function with independent increments. Thus, by passing to the limit $l \to 0$ (L remaining fixed), we may consider $\mathbf{r}(L)$ as a continuous function of L, which satisfies the following equation :

$$\frac{d\mathbf{r}(L)}{dL} = l[s^{-1} \nabla V(\mathbf{r}) + \varepsilon(L)] , \tag{III.32}$$

where $\varepsilon(L)$ is a Wiener-Levy stochastic vector. The following properties define this function :

1° we have :

$$< \varepsilon_j(L) > = 0$$
$$< \varepsilon_j(L)\, \varepsilon_{j'}(L') > = \delta_{jj'}\, \delta(L - L') ; \tag{III.33}$$

2° the mean value of the product of an odd number of components $\varepsilon_j(L)$ vanishes ; for instance :

$$< \varepsilon_j(L)\, \varepsilon_{j'}(L')\, \varepsilon_{j''}(L'') > = 0 ; \tag{III.34}$$

3° the mean value of the product of an even number of components $\varepsilon_j(L)$ is given by Wick's theorem ; for instance

$$\begin{aligned} < \varepsilon_j(L)\, \varepsilon_{j'}(L')\, \varepsilon_{j''}(L'')\, \varepsilon_{j'''}(L''') > &= \\ = \delta_{jj'}\, \delta_{j''j'''}\, \delta(L - L')\, \delta(L'' - L''') &+ \\ + \delta_{jj''}\, \delta_{j'j'''}\, \delta(L - L'')\, \delta(L' - L''') & \\ + \delta_{jj'''}\, \delta_{j'j''}\, \delta(L - L''')\, \delta(L' - L'') . & \end{aligned} \tag{III.35}$$

These results can be used to study the self-consistent field methods. In particular, we note that passing to the limit $l \to 0$ is legitimate since according to our assumptions, when L increases, the point $\mathbf{r}(L)$ arrives in regions where $V(\mathbf{r})$ becomes smoother and smoother. We see immediately that the first term in the right hand side of eq. (III.32) describes the stretching of the chain whereas the second one is purely Brownian. From this remark, we deduce the behaviour of the chains in regions where $V(\mathbf{r})$ is smooth ; indeed without solving exactly eq. (III.32), we may conclude that in those regions, the chain progresses along a line of force of $V(\mathbf{r})$ (see Fig. 1). If, for instance, $V(\mathbf{r})$ is spherical and for large values of r, decreases in the following way :

$$V(\mathbf{r}) \simeq C r^{1-1/\alpha} \quad \tfrac{1}{2} < \alpha < 1 , \tag{III.36}$$

we find by solving eq. (III.32) (or more precisely the non-Brownian part of it) that :

$$\mathbf{r}(L) \simeq (C\alpha^{-1} L)^{\alpha} \quad (\text{if } \mathbf{r}(0) = 0) . \tag{III.37}$$

In this case, the chain stretches out radially since the influence of $\varepsilon(L)$ is negligible in the mean.

On the other hand, the fluctuations of the chain which are perpendicular to the line of force remain Brownian (they come from $\varepsilon(L)$) and they are of order $L^{1/2}$ (see Fig. 1) as can be seen easily by looking at eq. (III.32).

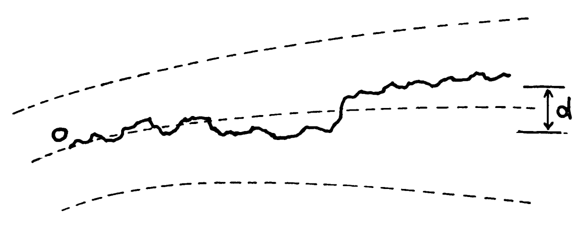

FIG. 1. — Random chain in a smooth potential. The dotted lines represent lines of force. The chain follows L_0. The mean distance of the points of the chain to L_0 gives a measure of the chain width d.

Therefore, for large values of L, the chain takes the shape of a spindle. For instance, if $V(\mathbf{r})$ is given by eq. (III.36) the ratio (width/length) of this spindle is of order $L^{(1/2)-\alpha}$ and goes to zero if $L \to \infty$.

Therefore, when $V(\mathbf{r})$ is spherical and given by eq. (III.36) the concept of mean field becomes meaningless, and the replacement of the interactions between the points of the chain by a smooth field becomes absurd since the influence of the spherical potential $V(\mathbf{r})$, destroys completely the symmetry which should exist between the beginning and the end of the chain [17]. Thus, the self-consistent field method loses all validity and the whole approach (for chains with repulsive interactions) has to be rejected.

IV. **The minimal Gaussian approximation.** — A. RINGS AND THE FUNCTION $g(k)$. — In the following, we study rings instead of chains, for reasons of mathematical convenience : their cyclic invariance enables us to simplify the equations. But, we note that there is no real difference between an infinite chain and an infinite ring, as far as finite parts of them are concerned [18] (i. e. as far as the partial probabilities

$$P(j_1\, \mathbf{r}_{j_1} \mid \dots \mid j_p\, \mathbf{r}_{j_p})$$

defined by eq. (II.28) are concerned).

With a ring of N points ($\mathbf{r}_1, \dots, \mathbf{r}_N$ with $\mathbf{r}_{N+1} \equiv \mathbf{r}_1$), we associate a probability of the form (we set $\beta = 1$) :

$$P(\mathbf{r}_1, \dots, \mathbf{r}_N) = Z^{-1} \exp\left[\frac{s}{2} \sum_{j=1}^{N} (\mathbf{r}_{j+1} - \mathbf{r}_j)^2 - \sum_{1 \leqslant j \leqslant l \leqslant N} V(\mathbf{r}_j - \mathbf{r}_l)\right]. \quad \text{(IV.1)}$$

We assume that the potential $V(\mathbf{r})$ is weak, that it decreases exponentially with $\mathbf{r}$, and that its range l_v is large with respect to the length of the link ($l_v \gg l = 1$).

It is convenient to introduce the cyclic variables $\boldsymbol{\rho}_q$

$$\boldsymbol{\rho}_q = N^{-1/2} \sum_{j=1}^{N} \exp[i\, 2\,\pi jq/N]\, \mathbf{r}_j \quad q = 1, \dots, N \quad \text{(IV.2)}$$

$$\mathbf{r}_j = N^{-1/2} \sum_{q=1}^{N} \exp[-\, i\, 2\,\pi jq/N]\, \boldsymbol{\rho}_q\,. \quad \text{(IV.3)}$$

In particular, the mean value of the products $\boldsymbol{\rho}_q^{(j)}\, \boldsymbol{\rho}_{q'}^{(j')}$ of components of $\boldsymbol{\rho}_q$ and $\boldsymbol{\rho}_{q'}$ are important quantities, and for reasons of cyclic invariance we may write :

$$< \rho_q^{(j)} . \rho_{q'}^{(j')} > = \delta_{jj'}\, \delta_{qq'}\, s^{-1}\, g_N^{-1}(2\,\pi q/N)\,. \quad \text{(IV.4)}$$

Here, $g_N(k)$ is a positive and discontinuous function of k with :

$$k = 2\,\pi q/N\,. \quad \text{(IV.5)}$$

It is even and periodic with period $2\,\pi$.

When N increases the number of points k becomes dense in the interval $2\,\pi$. Accordingly, it is reasonable to assume that the function $g_N(k)$ has a continuous limit $g(k)$ when $N \to \infty$, and the following discussions and calculations justify completely this assertion. The function $g(k)$ satisfies the requirements :

$$g(k) \geqslant 0 \quad g(k) = g(-\,k) \quad g(k + 2\,\pi) = g(k) \quad \text{(IV.6)}$$

$$\lim_{N \to \infty} g_N(k_N) = g(k) \quad (k - \pi/N < k_N \leqslant k + \pi/N)\,. \quad \text{(IV.7)}$$

We want to show that the behaviour of $g(k)$ for small values of k is directly related to the mean size of the chain. In fact, we have :

$$< (\mathbf{r}_j - \mathbf{r}_l)^2 > \equiv b_N(j - l)$$

$$= N^{-1} \sum_{q=1}^{N-1} \{ 1 - \cos\,[2\,\pi(j-l)\, q/N] \} \times g_N^{-1}(2\,\pi q/N) \quad \text{(IV.8)}$$

and by passing to the limit $N \to \infty$, we can define $b(n)$ as follows :

$$b(j - l) = \lim_{N \to \infty} < (\mathbf{r}_j - \mathbf{r}_l)^2 > \quad \text{(IV.9)}$$

and

$$b(n) = \frac{1}{2\,\pi} \int_{-\pi}^{+\pi} \mathrm{d}k (1 - \cos nk)\, g^{-1}(k)\,. \quad \text{(IV.10)}$$

The asymptotic properties of $b(n)$ for $n \gg 1$ depend essentially on the analytic properties of $g^{-1}(k)$. We remark that $b(n)$ must go to infinity if $n \to \infty$ and such a behaviour is a direct consequence of eq. (IV.10) provided that $g(k) \to 0$ when $|\, k\, | \to 0$. More precisely, let us assume that, for small values of k, $g(k)$ has the form :

$$g(k) \simeq g\, |\, k\, |^{1+2\alpha} \qquad \tfrac{1}{2} \leqslant \alpha \leqslant 1\,. \quad \text{(IV.11)}$$

(Incidentally, we remark that this is true if the chain is Brownian : in this case $\alpha = 1/2$.) The singularity of $g^{-1}(k)$ at the origin completely determines the asymptotic behaviour of $b(n)$ and from eq. (IV.10), we deduce (see Appendix A)

$$b(n) \simeq b\, n^{2\alpha}\, (n \gg 1) \quad \text{(IV.12)}$$

if

$$\tfrac{1}{2} \leqslant \alpha < 1 \quad \text{(IV.13)}$$

with

$$b = \frac{1}{2\, g(2\,\alpha)\,!\, \sin \alpha\pi} \quad \text{(IV.14)}$$

which is exactly what we wanted (compare eqs. (II.12) and (IV.9) (IV.12)). Note also that eqs. (IV.12) and (IV.13) are not valid for $\alpha = 1$.

In a similar way, we can estimate the size of large but finite rings containing an even number, N, of points by calculating the mean square distance between opposite points

$$< (\mathbf{r}_{(N/2)+1} - \mathbf{r}_1)^2 > = \\ = 2 N^{-1} \sum_{q=1}^{N-1} g_N^{-1}[2 \pi(2 q - 1)/N] . \quad \text{(IV.15)}$$

If we replace $g_N(k)$ by $g(k)$ in eq. (IV.15), we get :

$$<(\mathbf{r}_{(N/2)+1} - \mathbf{r}_1)^2> \simeq CN^{2\alpha}, \quad \text{(IV.16)}$$

with

$$C = \frac{2}{g(2 \pi)^{2\alpha+1}} \sum_{q=1}^{\infty} \frac{1}{|2 q - 1|^{2\alpha+1}} = \\ = \frac{2 \zeta(2 \alpha + 1)}{g(2 \pi)^{2\alpha+1}[1 + 2^{-(2\alpha+1)}]} \quad \text{(IV.17)}$$

($\zeta(n)$ = Riemann's function)

in agreement with our expectations (compare with eq. (II.11) for a chain). However, the replacement of $g_N(2 \pi q/N)$ by $g(2 \pi q/N)$ in eq. (IV.15) is questionable for small values of q ; as will be seen later in the framework of the Gaussian approximation (section IV.E), this replacement is not completely valid : it gives the right order of magnitude but the value of C has to be corrected. (Eq. (IV.17) is not right : see section IV.-G).

B. The Gaussian trial function. — The Gaussian approximation consists in replacing the true probability $P(\mathbf{r}_1, ..., \mathbf{r}_N)$ by a trial probability $P_T(r_1, ..., r_N)$ which is proportional to the exponential of a quadratic form of the coordinates $\mathbf{r}_j$:

$$P_\text{T}(r_1, ..., r_N) = Z_\text{T}^{-1} \exp[- W(\mathbf{r}_1, ..., \mathbf{r}_N)] \quad \text{(IV.18)}$$

W is given by :

$$W(\mathbf{r}_1, ..., \mathbf{r}_N) = \frac{s}{2} \sum_{j=1}^{N} \sum_{l=1}^{N} G_N(j - l) (\mathbf{r}_j - \mathbf{r}_l)^2 \quad \text{(IV.19)}$$

and Z_T is a normalization constant determined by the condition :

$$\int P_\text{T}(\mathbf{r}_1, ..., \mathbf{r}_N) \, d^s \mathbf{r}_2 \dots d^s \mathbf{r}_N = 1 . \quad \text{(IV.20)}$$

The coefficients $G(n)$ are even and periodic by definition :

$$G(n + N) = G(n) = G(- n) . \quad \text{(IV.21)}$$

They are to be determined by minimization of the free energy F corresponding to the trial probability. The quadratic form W can be diagonalized by using the cyclic variables $\boldsymbol{\rho}_q$. Since we want eq. (IV.4) to be valid, we must have :

$$W(\mathbf{r}_1, ..., \mathbf{r}_N) = \frac{s}{2} \sum_{q=1}^{N-1} g_N(2 \pi q/N) \, \boldsymbol{\rho}_q \cdot \boldsymbol{\rho}_{-q} . \quad \text{(IV.22)}$$

The identification of eq. (IV.19) with eq. (IV.22) gives with the help of definition (IV.2) :

$$g_N(2 \pi q/N) = \sum_{n=1}^{N-1} G_N(n) [1 - \cos (2 \pi qn/N)] \quad \text{(IV.23)}$$

and by setting :

$$G(n) = \lim_{N\to\infty} G_N(n) , \quad \text{(IV.24)}$$

we may write also :

$$g(k) = \sum_{-\infty}^{+\infty} G(n) [1 - \cos kn] . \quad \text{(IV.25)}$$

Two remarks can be made concerning this formula. Firstly, in the Brownian case where $G(n) = 0$ for $|n| \gg p$, we verify that for small values of k, $g(k)$ is of order k^2 in agreement with eq. (IV.11) (with $\alpha = 1/2$). Secondly when all the points of the chain interact with each other, the coefficient α must be larger than 1/2, since owing to the swelling of the chain : therefore the terms of order k^2 which appear in eq. (IV.25) for $|k| \ll 1$ must vanish ; thus : ($\mathbf{a}_j = \mathbf{r}_{j+1} - \mathbf{r}_j$) :

$$\sum_{-\infty}^{+\infty} n^2 \, G(n) = 0 . \quad \text{(IV.26)}$$

This additional condition shows that W can be written in a more restricted form :

$$W(\mathbf{r}_1, ..., \mathbf{r}_N) = \frac{s}{2} \sum D_N(j - l) (\mathbf{a}_j - \mathbf{a}_l)^2 , \quad \text{(IV.27)}$$

which is equivalent to eqs. (IV.17) and (IV.24) as can be easily verified. Incidentally, we note that in this case the non negative form W vanishes when all the links are equal in length and direction

$$(\mathbf{a}_1 = \cdots = \mathbf{a}_n) :$$

the interpretation of this fact remains obscure.

Thus, in this approximation, the second cumulants of products of $\mathbf{a}_j$ are taken into account but the other ones are neglected for reasons of simplicity. But this is the only reason ; the fourth cumulant may actually give contributions of the same order as the second one.

C. Correlation functions. — All the correlation functions of points of the chain are Gaussian since integration on some variables does not change the Gaussian character of the probability law. For instance, for an infinite ring, the correlation function $\mathcal{T}_n(\mathbf{r})$ can be written immediately :

$$\mathcal{T}_n(\mathbf{r}) \equiv < \delta(\mathbf{r}_{j+n} - \mathbf{r}_j - \mathbf{r}) > \\ = [s/2 \pi b(n)]^{s/2} \exp\left[- \frac{sr^2}{2 \, b(n)}\right] \quad \text{(IV.28)}$$

where $b(n)$ is given by eqs. (IV.9) and (IV.10). Moreover, the product of any number of components of $\boldsymbol{\rho}_q$ and consequently of vectors of the form $(\mathbf{r}_j - \mathbf{r}_l)$ can be calculated immediately in terms of the function $g(k)$ by applying Wick's theorem and by using eq. (IV.4).

D. CALCULATION OF THE FREE ENERGY FOR AN INFINITE RING AND MINIMIZATION WITH RESPECT TO $g(k)$. — The function $g(k)$ is the only parameter of the approximation and we want to determine it by minimization of F. For this purpose, we shall express the free energy F, in the limit $N \to \infty$, in terms of $g(k)$ or $b(n)$ which is equivalent.

First, let us calculate the mean energy $< U_0 >$ of the ring :

$$< U_0 >/N = \frac{s}{2N} \sum_{j=1}^{N} < (\mathbf{r}_{j+1} - \mathbf{r}_j)^2 > \simeq \frac{s}{2} b(1) . \tag{IV.29}$$

On the other hand,

$$< U_1 >/N = \frac{1}{N} \sum_{1 \leqslant j \leqslant l \leqslant N} < V(\mathbf{r}_j - \mathbf{r}_l) > \simeq$$

$$\simeq \sum_{n=1}^{\infty} \int d^s \mathbf{r}\, V(\mathbf{r})\, \mathcal{T}_n(\mathbf{r}) , \tag{IV.30}$$

where $\mathcal{T}_n(\mathbf{r})$ is given by eq. (IV.28). As $V(\mathbf{r})$ is small the terms corresponding to small values of n in the right hand side of eq. (IV.30) are also small. The important terms are those which correspond to large values of n, since the asymptotic properties of the chain depend on their existence. On the other hand, the range of $\mathcal{T}_n(\mathbf{r})$ increases with n and for $n \gg 1$, it is much larger than the range of $V(\mathbf{r})$; thus we may write approximately :

$$< U_1 >/N \simeq \sum_{n=1}^{\infty} \mathcal{T}_n(0) \int d^s \mathbf{r}\; V(\mathbf{r}) . \tag{IV.31}$$

In order to simplify the expressions, we set :

$$w = (s/2\,\pi)^{s/2} \int d^s \mathbf{r}\; V(\mathbf{r}) \tag{IV.32}$$

and by using this notation and eq. (IV.28), we may write :

$$<U_1>/N \simeq w \sum_{n=1}^{\infty} \left[b(n)\right]^{-s/2}. \tag{IV.33}$$

We have now to calculate the entropy associated with the probability law. (See eq. (II.27) and (IV.18)) :

$$\begin{aligned} S = - < \log P_{\mathrm{T}}(\mathbf{r}_1, ..., \mathbf{r}_N) > &= \\ = < W(\mathbf{r}_1, ..., \mathbf{r}_N)> &+ \log Z_{\mathrm{T}} . \end{aligned} \tag{IV.34}$$

By using eqs. (IV.22) and (IV.4) we see immediately that :

$$\begin{aligned} < W(\mathbf{r}_1, ..., \mathbf{r}_N) > &= \frac{s}{2} \sum_{q=1}^{N-1} g_N(2\,\pi q/N) < \boldsymbol{\rho}_q . \boldsymbol{\rho}_{-q} > \\ &= \frac{s}{2}(N - 1) . \end{aligned} \tag{IV.35}$$

On the other hand, the value of Z can be deduced immediately from the normalization condition of $P(\mathbf{r}_1, ..., \mathbf{r}_N)$:

$$\begin{aligned} Z_{\mathrm{T}} &= \int d\mathbf{r}_2 \ldots d\mathbf{r}_N\, e^{-W(\mathbf{r}_1, \ldots, \mathbf{r}_N)} \\ &= \int d\mathbf{r}_1 \ldots d\mathbf{r}_N\, \delta(\mathbf{r}_1 + \cdots + \mathbf{r}_n)\, e^{-W(\mathbf{r}_1, \ldots, \mathbf{r}_N)} \\ &= \int d^s \boldsymbol{\rho}_0\, d\Omega(\boldsymbol{\rho})\, \delta(N^{1/2} \rho_0) \times \\ &\times \exp\left[- \frac{s}{2} \sum_{q=1}^{N-1} g_N(2\,\pi q/N)\, \boldsymbol{\rho}_q\, \boldsymbol{\rho}_{-q} \right] . \end{aligned} \tag{IV.36}$$

The volume element $d\Omega(\boldsymbol{\rho})$ which appears in this expression is defined as follows. For $0 < q < N/2$, we get :

$$\begin{aligned} \boldsymbol{\rho}_q &= \frac{1}{\sqrt{2}} (\boldsymbol{\rho}'_q + i\boldsymbol{\rho}''_q) \\ \boldsymbol{\rho}_{-q} &= \frac{1}{\sqrt{2}} (\boldsymbol{\rho}'_q - i\boldsymbol{\rho}''_q) \end{aligned} \tag{IV.37}$$

and we have :

$$d\Omega(\boldsymbol{\rho}) = \prod_{0<q<N/2} d^s \boldsymbol{\rho}'_q\, d^s \boldsymbol{\rho}''_q \qquad N \text{ odd.} \tag{IV.38}$$

$$d\Omega(\boldsymbol{\rho}) = d^s\, \boldsymbol{\rho}_{N/2} \prod_{0<q<N/2} d^s \boldsymbol{\rho}'_q\, d^s \boldsymbol{\rho}''_q \quad N \text{ even.} \tag{IV.39}$$

The transformation (IV.37) diagonalizes completely $W(\mathbf{r}_1, ..., \mathbf{r}_N)$ and from eq. (IV.36) we get immediately :

$$Z_{\mathrm{T}} = N^{-s/2} (2\,\pi/s)^{(N-1)s/2} \prod_{q=1}^{N-1} g_N(2\,\pi q/N)^{-s/2} . \tag{IV.40}$$

The entropy S/N is found by using eqs. (IV.34), (IV.35), (IV.40) and by passing to the limit $N \to \infty$. Thus, we get :

$$S/N = - \frac{s}{4\,\pi} \int_{-\pi}^{+\pi} \log g(k)\, dk + \frac{s}{2}\left[1 + \log(2\,\pi/s)\right] . \tag{IV.41}$$

Finally, from eqs. (IV.29), (IV.33) and (IV.41), we deduce the following expression of F :

$$\begin{aligned} F/N &= < U_0 > + < U_1 > - S \\ &= \frac{s}{2} b(1) + w \sum_{n=1}^{\infty} \left[b(n)\right]^{-s/2} + \\ &+ \frac{s}{4\,\pi} \int_{-\pi}^{+\pi} \log g(k)\, dk + \frac{s}{2}\left[1 + \log(2\,\pi/s)\right] . \end{aligned} \tag{IV.42}$$

The minimization of F gives the equation :

$$\partial F/\partial g(k) = 0 . \tag{IV.43}$$

From eq. (IV.10), we get (when taking the relation $g(k) = g(-k)$ into account)

$$\partial b(n)/\partial g^{-1}(k) = \frac{1}{\pi}(1 - \cos nk) \tag{IV.44}$$

and with the help of this formula eq. (IV.43) can be written :

$$g(k)=(1-\cos k)-w\sum_{n=1}^{\infty}(1-\cos nk)\left[b(n)\right]^{-(s+2)/2}. \tag{IV.45}$$

According to eq. (IV.12) :

$$\left[b(n)\right]^{(s+2)/2} \simeq b^{(s+2)/2}\, n^{\alpha(s+2)} \quad \text{for } n \gg 1 \tag{IV.46}$$

and we see immediately that, for $\alpha \geqslant \frac{1}{2}$ the series

$$\sum_{n=1}^{\infty}\left[b(n)\right]^{-(s+2)/2}$$

converges. Thus eq. (IV.45) gives the Fourier series which determines $g(k)$.

E. Determination of α and general properties of $g(k)$. — The function $g(k)$ and the coefficients $b(n)$ are given by the coupled equations : (eqs. (IV.45) and (IV.10))

$$g(k)=(1-\cos k)-w\sum_{n=1}^{\infty}(1-\cos nk)\left[b(n)\right]^{-(s+2)/2} \tag{IV.47}$$

$$b(n)=\frac{1}{2\pi}\int_{-\pi}^{+\pi}\mathrm{d}k(1-\cos nk)\,g^{-1}(k). \tag{IV.48}$$

Let us discuss the behaviour of $g(k)$ for small values of k. This function is non-negative, since the quadratic form $W(\mathbf{r}_1, \ldots, \mathbf{r}_N)$ is non-negative ; and eq. (IV.47) leads immediately to the inequality :

$$0 \leqslant g(k) \leqslant 1-\cos k. \tag{IV.49}$$

Therefore, $g(k)$ vanishes at the origin and $k^{-2}\,g(k)$ remains bounded $(-\pi < k < +\pi)$ as expected. On the other hand, we find that the series

$$\sigma = \sum_{1}^{\infty} n^2\left[b(n)\right]^{-(s+2)/2}$$

must converge ; otherwise, for small values of k, $g(k)$ would become negative, which is absurd (actually $\sigma \leqslant w-1$). We see also that these requirements are compatible with our assumption (eq. (IV.11)) that, for small values of k, $g(k)$ is of order $|k|^{1+2\alpha}$ $(\alpha \geqslant 1/2)$ with perhaps additional logarithmic factors.

If $s > 4$, we can find a solution for which $\alpha = \frac{1}{2}$ (Brownian ring). In fact, we may write in this case :

$$g(k) \simeq gk^2 = \frac{k^2}{2}\left[1 - w\sum_{1}^{\infty} n^2\left[b(n)\right]^{-(s+2)/2}\right] \tag{IV.50}$$

since the corresponding asymptotic expression of $b(n)$ (see eq. (IV.13))

$$b(n) \simeq n^2/2\,g \qquad (n \gg 1) \tag{IV.51}$$

insures the convergence of the series which appears on the right hand side of eq. (IV.50).

On the contrary, if $s \leqslant 4$, $b(n)$ must increase faster than n^2 ; otherwise, the sum

$$\left[\sum_{1}^{\infty} n^2\left[b(n)\right]^{-(s+2)/2}\right]$$

would diverge. Consequently, the coefficient of k^2 in $g(k)$ must vanish.

$$\sum_{1}^{\infty} n^2\left[b(n)\right]^{-(s+2)/2} = w^{-1}. \tag{IV.52}$$

The convergence of this series implies the condition :

$$\alpha > 3/(s+2), \tag{IV.53}$$

or, if we have additional logarithmic factors, the weaker condition :

$$\alpha \geqslant 3/(s+2). \tag{IV.54}$$

If condition (IV.52) holds, we can write :

$$g(k) \simeq |k|^{\alpha(s+2)-1}\frac{\pi w b^{-(s+2)/2}}{2[\alpha(s+2)-1]\,!\,\cos[\alpha(s+2)\pi/2]} \tag{IV.55}$$

by using the results of Appendix B, after replacing the quantities v, d and d_n which appear in this Appendix by :

$$v = \alpha(s+2) \qquad d_n = \left[b(n)\right]^{-(s+2)/2} \qquad d = b^{-(s+2)/2}. \tag{IV.56}$$

We now identify eq. (IV.11) with (IV.55) and in this way, we can express α, g and b in terms of s and w. Thus, we obtain the important result :

$$\alpha = 2/s \tag{IV.57}$$

which we proceed to discuss.

In three dimensions, we find $\alpha = 2/3$ a value which has already been proposed by Kurata, Stockmaier and Roig [19]. We see that our conditions (IV.13) and (IV.52) are verified. Consequently, we may write :

$$g(k) \simeq g\,|k|^{7/3} \tag{IV.58}$$

$$b(n) \simeq bn^{4/3}. \tag{IV.59}$$

The coefficients g and b are easily determined. The identification of eq. (IV.11) with (IV.55) yields

$$gb^{5/2} = w\pi/(7/3)\,! \tag{IV.60}$$

and, eq. (IV.14) becomes in this case :

$$gb = 1/\sqrt{3}(4/3)\,! \tag{IV.61}$$

The solutions of these equations are :

$$g = w^{-2/3}\,3^{-3/2}(\pi/7)^{-2/3}\left[(4/3)\,!\right]^{-1} \simeq 0.28\,w^{-2/3} \qquad |k| \ll 1 \tag{IV.62}$$

$$b = w^{2/3}\,3(\pi/7)^{2/3} \simeq 1.76\,w^{2/3} \qquad n \gg 1. \tag{IV.63}$$

In two dimensions, we find $\alpha = 1$. Condition (IV.52) is verified but condition (IV.13) is not strictly satisfied, and owing to logarithmic divergences, our approximation breaks down. This indicates that logarithmic factors must occur in the expressions of $g(k)$ and $b(n)$, a fact which is verified in Appendix C. Accordingly, in two dimensions, we have (Appendix C) :

$$g(k) \simeq w^{-1} \frac{12}{\pi^3} k^3 \,|\log k\,|^2 \qquad |\,k\,| \ll 1 \qquad \text{(IV.64)}$$

$$b(n) \simeq w \frac{\pi^2}{12} n^2 (\log n)^{-1} \qquad n \gg 1\,. \qquad \text{(IV.65)}$$

In four dimensions, we find $\alpha = 1/2$. Condition (IV.13) is verified but condition (IV.52) is not strictly satisfied and again owing to logarithmic divergences our approximation breaks down. In this case also, logarithmic factors occur in the expressions of $g(k)$ and $b(n)$ as we show in Appendix D. Accordingly, we have (see Appendix D) :

$$g(k) \simeq \tfrac{1}{2}(2\,w)^{-1/2}\, k^2 \,|\log k\,|^{-3/2} \qquad |\,k\,| \ll 1 \quad \text{(IV.66)}$$

$$b(n) \simeq (2\,w)^{1/2}\, n (\log n)^{1/2} \qquad n \gg 1. \quad \text{(IV.67)}$$

Thus, in four dimensions, the chains are not really Brownian.

F. Comparison with Fixman's Gaussian model. — In an ingenious article, M. Fixman [5] also used a Gaussian approximation and he found the result $\alpha = 3/5$ (Flory's value). Fixman's approach is different from ours and very clever but it seems also more artificial and complicated (at least theoretically). Thus, instead of using the principle of minimization of the free energy which is the only basis of our calculations, he uses more subtle consistency arguments to determine the swelling. We may note also another difference. In our model, in the limit $N \to \infty$, the mean square distance between two points of the chain $\mathbf{r}_{j+n}$ and $\mathbf{r}_j$ increases as $n^{2\alpha}$ ($n \gg 1$) whereas in Fixman's model this distance increases as n which seems rather strange. In particular, this is in contradiction with our interpretation of the swelling in terms of long range correlationsb etween distant links (see the end of section II.A).

G. The continuous ring limit. — When the interaction w is very small ($w \ll 1$) eqs. (IV.47) and (IV.48) which give $g(k)$ and $b(n)$ can be simplified. This is the continuous ring limit (Edwards' limit). The number n is assumed to be large and continuous while $|\,k\,|$ is assumed to be small. In this case, it is legitimate to transform eqs. (IV.47) and (IV.48) into :

$$g(k) = \frac{1}{2} k^2 - w \int_0^\infty (1 - \cos nk) \left[b(n)\right]^{-(s+2)/2} \mathrm{d}n \qquad |\,k\,| \ll 1 \qquad \text{(IV.68)}$$

$$b(n) = \frac{1}{2\,\pi} \int_{-\infty}^{+\infty} \mathrm{d}k\, (1 - \cos nk)\, g^{-1}(k) \qquad n \gg 1\,. \qquad \text{(IV.69)}$$

These equations have nice homogeneity properties which lead to further simplifications. It is not difficult to show that for $s = 2$ and $s = 3$, the solutions of these equations can be written in the form

$$g(k) = \frac{k^2}{2} A(kw^{-\beta}) \qquad \text{(IV.70)}$$

$$b(n) = nB(nw^{\beta})\,, \qquad \text{(IV.71)}$$

where β is given by :

$$\beta = \frac{2}{4-s} \quad (s = \text{space dimensions})\,. \qquad \text{(IV.72)}$$

Here, $A(x)$ and $B(y)$ are universal functions which are given by the following equations :

$$A(x) = 1 - \frac{2}{x^2} \int_0^\infty \frac{1 - \cos xy}{\left[yB(y)\right]^{(s+2)/2}} \qquad \text{(IV.73)}$$

$$B(y) = \frac{2}{\pi y} \int_0^\infty \frac{1 - \cos xy}{x^2\, A(x)} \mathrm{d}x\,, \qquad \text{(IV.74)}$$

and the sum-rule : (eq. (IV.52))

$$\int_0^\infty y^{-1/2} \left[B(y)\right]^{-5/2} \mathrm{d}y = 1\,. \qquad \text{(IV.75)}$$

Since w is small, small sections of the chain must look Brownian. Indeed, the form of $g(k)$ and $b(n)$ in the ranges $w^\beta \ll k \ll 1$ and $1 \ll n \ll w^\beta$ respectively reveal this property. Since $A(+\infty) = 1$ and $B(0) = 1$, we can write approximately

$$g(k) \simeq \frac{k^2}{2} \qquad b(n) \simeq n \qquad \text{(IV.76)}$$

and these equations are characteristic of a Brownian motion.

On the contrary, the ranges $|\,k\,| \ll w^\beta$, $n \gg w^{-\beta}$ correspond to the asymptotic limit. For instance, in three dimensions ($s = 3$, $\beta = 2$), we find without difficulty that :

$$A(x) \simeq 23^{-3/2} (\pi/7)^{-2/3} \left[(4/3)\,!\right]^{-1} x^{1/3} \qquad x \to 0 \qquad \text{(IV.77)}$$

$$B(y) \simeq 3(\pi/7)^{2/3}\, y^{1/3} \qquad y \to \infty \qquad \text{(IV.78)}$$

in agreement with eqs. (IV.62) and (IV.63).

H. Properties of a large but finite ring. — In this section, we try to give a complete picture of the structure of a large but finite ring. For this purpose, we show how to calculate $g_N(2\,\pi q/N)$ for finite values of q, and $b_n(N)$ for finite values of the ratio (n/N). The results of this section will also be used, in the next section to study the dependence of the free energy F_N, with respect to N for $N \gg 1$.

When the number N of links is finite, the minimization of F_N gives the following equations which are very similar to eqs. (IV.47) and (IV.48) :

$$g_N(2\pi q/N) = [1 - \cos(2\pi q/N)] - \\ - \frac{w}{2}\sum_{n=1}^{N-1}[1 - \cos(2\pi nq/N)] \times \\ \times [b_N(n)]^{-(s+2)/2} \qquad \text{(IV.79)}$$

$$b_N(n) = N^{-1}\sum_{q=1}^{N-1}[1 - \cos(2\pi nq/N)] \times \\ \times g_N^{-1}(2\pi q/N). \qquad \text{(IV.80)}$$

The difference $[g_N(2\pi q/N) - g(2\pi q/N)]$ is always small ; however it cannot be treated as a perturbation because it is of the same order as $g(2\pi q/N)$ when q is small. We want to show that in first approximation, we have :

$$g_N(2\pi q/N) \simeq \gamma(q)\, g(2\pi q/N), \qquad \text{(IV.81)}$$

where $\gamma(q)$ is a coefficient which is independent of N.

$$\gamma(q) = \gamma(-q) \quad \gamma(+\infty) = 1. \qquad \text{(IV.82)}$$

In the same way, $b_N(n)$ can be related to $b(n)$. We define $\tilde{b}_N(n)$ by :

$$\tilde{b}_N(n) = N^{-1}\sum_{q=1}^{N-1}[1 - \cos(2\pi nq/N)]\, g^{-1}(2\pi q/N). \qquad \text{(IV.83)}$$

It is a periodic function of n :

$$\tilde{b}_N(n) = \tilde{b}_N(-n) = \tilde{b}(n+N). \qquad \text{(IV.84)}$$

We want to show that, in first approximation, $b_N(n)$ can be written in the form :

$$b_N(n) = \omega(2\pi n/N)\, \tilde{b}_N(n), \qquad \text{(IV.85)}$$

where $\omega(\theta)$ is a periodic function of θ, independent of N ;

$$\omega(\theta) = \omega(-\theta) = \omega(\theta + 2\pi) \qquad \omega(0) = 1. \qquad \text{(IV.86)}$$

In order to justify our assumptions, we shall write equations which determine $\gamma(q)$ and $\omega(\theta)$. The self-consistent equations must be deduced from eqs. (IV.79) and (IV.80). For the sake of simplicity, and in order to avoid the appearance of logarithmic factors, we shall restrict ourselves to the case $s = 3$ and $\alpha = 2/3$. But similar results can be obtained for $s = 2$ and $s = 4$. Thus, in the following, we assume the validity of the equations :

$$g_N(2\pi q/N) = g\gamma(q)\,(2\pi q/N)^{7/3} \qquad |q| < N \quad \text{(IV.87)}$$

$$b(n) \simeq bn^{4/3} \qquad 1 \ll n \ll N. \quad \text{(IV.88)}$$

Accordingly, we write :

$$b_N(n) \simeq b\beta(2\pi n/N)\,(N/2\pi)^{2\alpha} \qquad 1 \ll n \ll N, \quad \text{(IV.89)}$$

where $\beta(\theta)$ is a function related to $\varepsilon(\theta)$ by :

$$\beta(\theta) = \frac{\omega(\theta)}{\pi bg}\sum_{q=1}^{\infty}[1 - \cos\theta q]\, q^{-7/3}. \qquad \text{(IV.90)}$$

This relation is easily derived from eqs. (IV.85), (IV.89) and (IV.83) by remarking that the terms which are important for $1 \ll n \ll N$, in the right hand side of eq. (IV.83) are those for which q is small. By taking eq. (IV.14) into account, eq. (IV.90) can also be written (with $s = 3$, $\alpha = 2/3$) :

$$\beta(\theta) = S(\theta)\,\omega(\theta), \qquad \text{(IV.91)}$$

where $S(\theta)$ is the function :

$$S(\theta) = \frac{\sqrt{3}(4/3)!}{\pi}\sum_{q=1}^{\infty}(1 - \cos\theta q)\, q^{-7/3} \\ = |\theta|^{4/3} + \lim_{n\to\infty}\left\{\sum_{p=1}^{N}\left[|\theta + 2\pi p|^{4/3} + \right.\right. \\ \left. + |\theta - 2\pi p|^{4/3} - 2|2\pi p|^{4/3}\right] - \\ \left. - \frac{2\theta^2}{3\pi}[(2n+1)\pi]^{1/3}\right\}. \qquad \text{(IV.92)}$$

(The derivation of this expansion is given in Appendix E.)

Thus, since $\varepsilon(0) = 1$, we have, for small values of θ :

$$\beta(\theta) \simeq |\theta|^{4/3} \qquad |\theta| \ll 1. \qquad \text{(IV.93)}$$

A relation between $\beta(\theta)$ and $\gamma(q)$ can be obtained from eq. (IV.80) by remarking that the terms which are important for $1 \ll n \ll N$ in the right hand side of this equation are those for which q is small ; therefore, for $1 \ll n \ll N$, we may replace in this equation $b_N(n)$ and $g(2\pi q/N)$ by their approximate expressions (IV.88) and (IV.90)

$$\beta(\theta) = \frac{1}{\pi gb}\sum_{q=1}^{\infty}\gamma^{-1}(q)\,[1 - \cos\theta q]\, q^{-7/3}. \qquad \text{(IV.94)}$$

By taking eq. (IV.14) into account, we obtain :

$$\beta(\theta) = \frac{\sqrt{3}(4/3)!}{\pi}\sum_{q=1}^{\infty}\gamma^{-1}(q)\,(1 - \cos\theta q)\, q^{-7/3}, \qquad \text{(IV.95)}$$

which is the first equation relating $\beta(\theta)$ to $\gamma(q)$. This result is of course compatible with eq. (IV.93) as expected.

Let us now derive another equation relating $\gamma(q)$ to $\beta(\theta)$. Eqs. (IV.79) and (IV.47) give :

$$g_N(2\pi q/N) - g(2\pi q/N) = \\ = \frac{w}{2}\sum_{n=1}^{N-1}[1 - \cos(2\pi nq/N)] \times \\ \times\left\{\sum_{p=-\infty}^{+\infty}[b(n+Np)]^{-5/2} - [b_N(n)]^{-5/2}\right\}. \qquad \text{(IV.96)}$$

The difference is appreciable when q is small and only in this case. When q is small $g_N(2\,\pi q/N)$, $g(2\,\pi q/N)$, $b_N(n)$ and $b(n)$ can be replaced by their asymptotic values (see eqs. (IV.88), (IV.90)) and the sum by an integral.

We set :

$$\xi_\nu(\theta) = \sum_{-\infty}^{+\infty} |\, \theta + 2\,\pi p \,|^{-\nu}\,, \qquad \text{(IV.97)}$$

and with this notation, we may write :

$$\gamma(q) - 1 = \frac{wb^{-5/2}}{2\,g}\, q^{-7/3} \int_0^{2\pi} \mathrm{d}\theta[1 - \cos\theta q] \times \times \{ \xi_{10/3}(\theta) - [\beta(\theta)]^{-5/2} \}\,. \qquad \text{(IV.98)}$$

On the other hand, eq. (IV.60) shows that g and $b^{-5/2}$ are proportional to each other ; by using this property we obtain :

$$1 - \gamma(q) = \frac{1}{2\,\pi}\,(7/3)\,!\, q^{-7/3} \int_0^{2\pi} \mathrm{d}\theta[1 - \cos\theta q] \times \times \{ [\beta(\theta)]^{-5/2} - \xi_{10/3}(\theta) \}\,. \qquad \text{(IV.99)}$$

Thus, for $s = 3$, $\alpha = 2/3$, the existence of the coupled equations (IV.95) and (IV.99) which determine completely $\gamma(q)$ and $\beta(\theta)$ proves implicitly the validity of our assumptions (IV.81) and (IV.85) concerning $g_N(2\,\pi q/N)$ and $b_N(n)$.

The end of this section is devoted to the discussion of these coupled equations, and, in particular to the derivation of an interesting sum-rule. We remark that the behaviour of $[\gamma(q) - 1]$ for large values of q and the behaviour of $\beta(\theta)$ for small values of θ are related to each other. Let us assume for a while that the series

$$\sum_0^\infty [\gamma^{-1}(q) - 1]\, q^{-1/3}$$

converges. If this is true, for small values of θ, we have : see eq. (IV.94)

$$\beta(\theta) \simeq (\theta)^{4/3} + A\theta^2 + \cdots\,. \qquad \text{(IV.100)}$$

The value of A can be calculated easily. For small values of θ, we see that $S(\theta)$ is given by :

$$S(\theta) \simeq |\,\theta\,|^{4/3} + \frac{4}{9}\,(2\,\pi)^{-2/3}\, \zeta(2/3)\, \theta^2\,, \qquad \text{(IV.101)}$$

where $\zeta(\nu)$ is the Riemann function which for $0 < \nu < 1$ can be defined by the equations [13]

$$\zeta(\nu) = \lim_{n\to\infty} \left[\sum_{p=1}^{n} p^{-\nu} - \frac{1}{1-\nu}\, n^{1-\nu} \right] = [1 - 2^{1-\nu}]^{-1} \sum_{p=1}^{\infty} (-)^{\nu+1}\, p^{-\nu}\,. \qquad \text{(IV.102)}$$

By comparing eqs. (IV.95) and (IV.92) and by using eq. (IV.100), we find immediately the value of A :

$$A = \frac{\sqrt{3}\,(4/3)\,!}{2\,\pi} \sum_{q=1}^{\infty} [\gamma^{-1}(q) - 1]\, q^{-1/3} + \frac{4}{9}\,(2\,\pi)^{-2/3}\, \zeta(2/3)\,. \qquad \text{(IV.103)}$$

The behaviour of $[\gamma(q) - 1]$ for large values of q is found by replacing $\beta(\theta)$ in eq. (IV.99) by the expansion (IV.100) (provided that A does not vanish !). For $q \gg 1$, we obtain ($q^{-1} \ll \varepsilon \ll 1$) :

$$\gamma(q) - 1 = \frac{5\,a}{4\,\pi}\,(7/3)\,!\, q^{-7/3} \int_0^{\varepsilon} \mathrm{d}\theta[1 - \cos\theta q]\, \theta^{-8/3} \simeq \tau A q^{-2/3}\,, \qquad \text{(IV.104)}$$

where τ is a well defined positive constant. For $A > 0$, this equation gives the result

$$\sum_1^\infty [\gamma^{-1}(q) - 1]\, q^{-1/3} \to -\infty\,;$$

for $A < 0$ it gives the result

$$\sum_1^\infty [\gamma^{-1}(q) - 1]\, q^{-1/3} \to +\infty\,;$$

both results are inconsistent with the definition of A, but they indicate clearly how the problem must be solved. The series

$$\sum_1^\infty [\gamma^{-1}(q) - 1]\, q^{-1/3}$$

must converge and the constant A must vanish. Thus, we find the following sum-rule :

$$\sum_{q=1}^{\infty} [\gamma^{-1}(q) - 1]\, q^{-1/3} = -\frac{\sqrt{3}\,(2\,\pi)^{1/3}}{3(2/3)\,!}\, \zeta(2/3) = -\zeta(1/3) \simeq 0.97 \qquad \text{(IV.105)}$$

(the relation between $\zeta(n)$ and $\zeta(1 - n)$ is given in Ref. [13]).

Additional informations concerning the behaviour of $\gamma(q)$ for large values of q cannot be obtained easily ; however, we note that the series

$$\sum_{q=1}^{\infty} [\gamma^{-1}(q) - 1]$$

must also converge. Indeed, by using simultaneously eqs. (IV.94), (IV.99) and (IV.107), it is not difficult to establish the identity :

$$\int_0^{2\pi} \mathrm{d}\theta \left\{ 2[\beta(\theta)]^{-3/2} + \xi_{10/3}(\theta) \left[3\,\beta(\theta) - 5\,S(\theta) + \frac{20}{9}\,(2\,\pi)^{-2/3}\, \zeta(2/3)\,(1 - \cos\theta) \right] \right\} = 6\sqrt{3} \left[\frac{2}{7} + \frac{5}{(4/3)\,!} \right] \sum_{q=1}^{\infty} [\gamma^{-1}(q) - 1] + \frac{30\sqrt{3}}{(4/3)\,!}\, \zeta(1/3)\,. \qquad \text{(IV.106)}$$

We remark that from small values of θ, the expansion of $b(\theta)$ is of the form :

$$b(\theta) = |\theta|^{4/3}[1 + \theta^2 \eta(\theta)] \quad \text{with} \quad \eta(0) = 0 . \tag{IV.107}$$

By using this property and the definitions of $\xi_{10/3}(\theta)$ and $S(\theta)$, it is easy to show that, in eq. (IV.108), the integrand vanishes when $|\theta| \to 0$. Consequently, the integral exists and the sum

$$\sum_{q=1}^{\infty} [\gamma^{-1}(q) - 1]$$

must be finite.

I. CALCULATION OF THE FREE ENERGY OF A FINITE RING. — The calculation of the free energy of a large but finite ring gives valuable information concerning the values of the small « Flory terms ». We define the free energy difference $\Delta_N F$ by :

$$\Delta_N F = F_N - N \lim_{N' \to \infty} (F_{N'}/N') , \tag{IV.108}$$

and we want to calculate this expression by using the results of the preceding section. The quantities $\Delta_N < U_0 >$, $\Delta_N < U_1 >$ and $\Delta_N S$ are defined in a similar way and $\Delta_N < U_0 >$ and $\Delta_N < U_1 >$ give the « Flory terms ». However, it will be shown in the following that in three dimensions the contributions of these terms are negligible and that we have $\Delta_N F \simeq \Delta_N S$.

First, we calculate $\Delta_N < U_0 >$:

$$\begin{aligned} \Delta_N < U_0 > &= \\ &= \frac{sN}{2}[b_N(1) - b(1)] \\ &= \frac{sN}{2}\left\{ N^{-1} \sum_{q=1}^{N-1} [1 - \cos(2\pi q/N)]\, g_N^{-1}(2\pi q/N) - \right. \\ &\quad \left. - \frac{1}{2\pi} \int_{-\pi}^{+\pi} (1 - \cos k)\, g^{-1}(k)\, \mathrm{d}k \right\} . \end{aligned} \tag{IV.109}$$

In Appendix F, this difference is calculated in terms of $\gamma(q)$ (defined by eq. (IV.81)) under the assumption that :

$$g(k) \simeq g\,|k|^{1+2\alpha} , \tag{IV.110}$$

and the calculation gives :

$$\Delta_N < U_0 > = C(\alpha)\,(s/2\,g)\,(N/2\,\pi)^{2\alpha - 1} , \tag{IV.111}$$

where $C(\alpha)$ is a constant. In this way, we obtain the first Flory term (see eq. (III.19)). Note however that, in the Gaussian approximation, we have $\alpha s = 2$ and not $\alpha = 3/s + 2$ (Flory's value).

The preceding calculation is strictly valid for $s = 3$, but for $s = 2$ or $s = 4$ the assumption (IV.110) does not hold exactly (there are logarithmic factors) ; therefore for $s = 2$ or $s = 4$, eq. (IV.111) gives only the order of magnitude of the first « Flory term »).

In three dimensions, the coefficient $C(\alpha)$ is given by (see eq. (F.6) with $\alpha = 2/3$) :

$$C(2/3) = \lim_{n \to \infty} \left[\sum_{q=1}^{n} \gamma^{-1}(q)\, q^{-1/3} - \frac{3}{2}\left(n + \frac{1}{2}\right)^{2/3} \right]. \tag{IV.112}$$

By using eq. (IV.102), we may write also :

$$C(2/3) = \sum_{q=1}^{\infty} [\gamma^{-1}(q) - 1]\, q^{-1/3} + \zeta(1/3) . \tag{IV.113}$$

Finally, by applying the sum-rule (IV.105), we find :

$$C(2/3) = 0 . \tag{IV.114}$$

Thus, in three dimensions, the first Flory term disappears completely. On the other hand, the terms of higher order in $\Delta_N < U_0 >$ must be fairly small since

$$\left[\sum_{q=1}^{\infty} \gamma^{-1}(q) - 1 \right]$$

converges as was shown at the end of Section F.

In the same way, we have :

$$\begin{aligned} \Delta_N < U_1 > = \frac{wN}{2} \sum_{n=1}^{N-1} \left\{ [b_N(n)]^{-s/2} - \right. \\ \left. - \sum_{p=-\infty}^{+\infty} [b(n + Np)]^{-s/2} \right\} . \end{aligned} \tag{IV.115}$$

For large values of N, $b_N(n)$ and $b(n)$ may be replaced in this equation by their asymptotic values (eqs. (IV.89) and (IV.12)) and the sum becomes an integral. When the asymptotic form of $b(n)$ is : $b(n) \simeq bn^{2\alpha}$ ($n \gg 1$) the terms which appear in the sum are proportional to $N^{-\alpha s}$. Thus, we obtain the second « Flory term » (see eq. (III.19))

$$\Delta_N < U_1 > = D(\alpha)\, N^{2 - \alpha s} . \tag{IV.116}$$

We see immediately that, in the Gaussian approximation $\Delta_N < U_1 >$ is also a constant and therefore rather uninteresting. For $s = 2$ and $s = 4$ the preceding expression is, of course, only approximate (the logarithmic factors have been omitted) but it is exact for $s = 3$ and in this case $D(2/3)$ is given by :

$$D(2/3) = \pi w b^{-3/2} \int_0^{2\pi} \mathrm{d}\theta \left\{ [\beta(\theta)]^{-3/2} - \xi_2(\theta) \right\} . \tag{IV.117}$$

(See eqs. (IV.115), (IV.89) and (IV.97).)

Let us now calculate $\Delta_N S$. According to eqs. (IV.34), (IV.35), (IV.40) and (IV.41), we have :

$$\begin{aligned} \Delta_N S = - \frac{s}{2} \sum_{q=1}^{N-1} \log [g_N(2\pi q/N)] - \\ - \frac{Ns}{2\pi} \int_{-\pi}^{+\pi} \log [g(k)]\, \mathrm{d}k - \frac{s}{2}[\log(2\pi N/s) + 1] . \end{aligned} \tag{IV.118}$$

It is not difficult to show that :

$$\Delta_N S \simeq -\frac{Ns}{2\pi}\int_0^{\pi/N} \log g(k)\,\mathrm{d}k - \left(\frac{s}{2}\right)\log N \quad \text{(IV.119)}$$

(the terms which are constant with respect to N are dropped).

Thus, by using eq. (IV.11), we obtain :

$$\Delta_N S \simeq \alpha s \log N = 2 \log N . \quad \text{(IV.120)}$$

Therefore, in three dimensions, we find that, in first approximation, $\Delta_N F$ is given by :

$$\Delta_N F \simeq \Delta_N S = 2 \log N . \quad \text{(IV.121)}$$

This kind of dependence agrees with the assumptions of Sykes and his collaborators [6].

V. **More general approximations.** — It is not difficult to improve the Gaussian approximation by choosing more general trial functions. However, a very large class of trial probabilities lead to the same relation $\alpha s = 2$ as the Gaussian approximation. Our aim in this section is to establish this fact and to show its origin. The derivation relies mainly on assumptions concerning the correlation function $\mathcal{T}_n(r)$ (which theoretically can be immediately deduced from the trial probability). We assume that, for large values of n, $\mathcal{T}_n(\mathbf{r})$ is approximately of the form :

$$\mathcal{T}_n(\mathbf{r}) = n^{-\alpha s}\, q(r/n^{\alpha}) \quad \text{(V.1)}$$

and that the corresponding function $q(r)$ is regular at the origin :

$$q(r) \simeq q(0) + \frac{r^2}{2} q''(0) + \cdots \quad | r | \ll 1 \quad \text{(V.2)}$$

with

$$q(0) \neq 0 \quad q''(0) \neq 0 \quad \text{(V.3)}$$

$$\int q(r)\, r^2\, d^3\mathbf{r} < \infty . \quad \text{(V.4)}$$

As previously, we consider a ring of N points. In order to characterize $P(\mathbf{r}_1, \ldots, \mathbf{r}_N)$, we introduce new parameters. We set :

$$\Phi(\boldsymbol{\lambda}_1, \ldots, \boldsymbol{\lambda}_{N-1}) = \left\langle \exp\left[i \sum_{q=1}^{N-1} \boldsymbol{\lambda}_q \cdot \boldsymbol{\rho}_q \right] \right\rangle \quad \text{(V.5)}$$

and we assume that the logarithm of $\Phi(\boldsymbol{\lambda}_1, \ldots, \boldsymbol{\lambda}_{N-1})$ can be expanded in terms of the components $\lambda_q^{(\sigma)}$ of the vectors $\boldsymbol{\lambda}_q$.

$$\log \Phi(\boldsymbol{\lambda}_1, \ldots, \boldsymbol{\lambda}_{N-1}) = \sum_{n=1}^{\infty} \frac{i^n}{n!} \sum_{q,\sigma} \lambda_{q_1}^{(\sigma)} \ldots \lambda_{q_n}^{(\sigma)} < \rho_{q_1}^{(\sigma_1)} \ldots \rho_{q_n}^{(\sigma_n)} >_C . \quad \text{(V.6)}$$

By definition, the coefficients

$$< \rho_{q_1}^{(\sigma_1)} \ldots \rho_{q_n}^{(\sigma_n)} >_C$$

are the cumulants of the mean values

$$< \rho_{q_1}^{(\sigma_1)} \ldots \rho_{q_n}^{(\sigma_n)} > .$$

Of course, these cumulants must satisfy symmetry requirements but otherwise, they are completely independent of each other and they determine $P(\mathbf{r}_1, \ldots, \mathbf{r}_N)$. In particular, the first non vanishing cumulants are of order two :

$$< \rho_q^{(\sigma)} \rho_{q'}^{(\sigma')} >_C = \delta_{qq'}\, \delta_{\sigma\sigma'}\, s^{-1} < \boldsymbol{\rho}_q \cdot \boldsymbol{\rho}_{-q} >_C \quad \text{(V.7)}$$

$$< \boldsymbol{\rho}_q \cdot \boldsymbol{\rho}_{-q} >_C = < \boldsymbol{\rho}_q \cdot \boldsymbol{\rho}_{-q} > . \quad \text{(V.8)}$$

Incidentally, we remark that the Gaussian approximation consists in assuming that all the other cumulants vanish.

In general, we can minimize F by using all these cumulants as independent parameters. In this way, it is in principle possible to determine exactly all the asymptotic properties of the chain. However, for our purpose, it is sufficient to examine the implications of the simplest minimization condition :

$$\partial F / \partial < \boldsymbol{\rho}_q \cdot \boldsymbol{\rho}_{-q} >_C = 0 . \quad \text{(V.9)}$$

Eq. (IV.4) defines $g_N(2\pi q/N)$ and eq. (IV.8) remains valid. We assume the existence of a limiting function $g(k)$ and we admit that the behaviour of this function at the origin is of the form :

$$g(k) \simeq g^{-1}\, | k |^{-(1+2\alpha')} \quad | k | \ll 1 . \quad \text{(V.10)}$$

If the condition (V.4) is valid, we have $\alpha' = \alpha$, and for $| k | \ll 1$, we may write (compare with eq. (IV.11)) :

$$< \boldsymbol{\rho}_q \cdot \boldsymbol{\rho}_q > \simeq g^{-1}\, | 2\pi q/N |^{-(1+2\alpha)} = g^{-1}\, | k |^{-(1+2\alpha)} . \quad \text{(V.11)}$$

With the help of these assumptions, we want to show that, for small values of $| k |$, the derivatives of $< U_1 >$, $< U_2 >$ and S with respect to $< \boldsymbol{\rho}_q \cdot \boldsymbol{\rho}_{-q} >_C$ (i. e. $< \boldsymbol{\rho}_q \cdot \boldsymbol{\rho}_{-q} >$ which is proportional to $g^{-1}(k)$) have the following expansions :

$$\partial < U_0 > / \partial < \boldsymbol{\rho}_q \cdot \boldsymbol{\rho}_{-q} > \simeq s k^2 / 2 \quad \text{(V.12)}$$

$$\partial < U_1 > / \partial < \boldsymbol{\rho}_q \cdot \boldsymbol{\rho}_{-q} > \simeq -\delta_1 k^2 + \delta_2\, | k |^{\alpha(s+2)-1} \quad \text{(V.13)}$$

$$\partial S / \partial < \boldsymbol{\rho}_q \cdot \boldsymbol{\rho}_{-q} > \simeq \delta_3\, | k |^{1+2\alpha} . \quad \text{(V.14)}$$

The discussion of eq. (V.9) is the same as in the Gaussian case. The implications of eqs. (V.12), (V.13) and (V.14) are the following. The k^2 terms coming from the derivatives of $< U_0 >$ and $< U_1 >$ must cancel each other (therefore $\delta_1 = s/2$) ; on the other hand, the term $\delta_2\, | k |^{\alpha(s+2)-1}$ coming from the derivative of $< U_1 >$ and the term $\delta_3\, | k |^{1+2\alpha}$ coming from δ, must be of the same order and must cancel each other. In this way, we get the result :

$$\alpha = 2/s \quad (\text{and } \delta_2 = \delta_3) , \quad \text{(V.15)}$$

which we wanted to derive.

We have now to establish the validity of the expansions (V.12), (V.13), (V.14) (of course this validity is only approximate for $s = 2$ and $s = 4$ since the logarithmic factors which appear in this case have been omitted). First, we calculate $< U_0 >$ (see eqs. (IV.1) and (IV.3)) :

$$< U_0 > = \frac{s}{2} \sum_{j=1}^{N} (\mathbf{r}_{j+1} - \mathbf{r}_j)^2$$
$$= \frac{s}{2} \sum_{q=1}^{N-1} [1 - \cos(2\pi q/N)] < \boldsymbol{\rho}_q \cdot \boldsymbol{\rho}_{-q} >$$
$$\partial < U_0 > / \partial < \boldsymbol{\rho}_q \cdot \boldsymbol{\rho}_{-q} > = = s[1 - \cos(2\pi q/N)] \simeq sk^2/2 \quad (V.17)$$

and therefore eq. (V.12) is proved.

Now, let us calculate $< U_1 >$:

$$< U_1 > = \frac{1}{2} \sum_{j \neq l} V(\mathbf{r}_j - \mathbf{r}_l)$$
$$= \frac{N}{2} \sum_{n=1}^{N-1} \int d^s \mathbf{r} V(\mathbf{r}) \mathfrak{T}_n(\mathbf{r}) \quad (V.18)$$
$$\partial < U_1 > / \partial < \boldsymbol{\rho}_q \cdot \boldsymbol{\rho}_{-q} > =$$
$$= \frac{N}{2} \sum_{n=1}^{N-1} \int d^s \mathbf{r} V(\mathbf{r}) [\partial \mathfrak{T}_n(r) / \partial < \boldsymbol{\rho}_q \cdot \boldsymbol{\rho}_{-q} >] . \quad (V.19)$$

$\partial \mathfrak{T}_n(\mathbf{r}) / \partial < \boldsymbol{\rho}_q \cdot \boldsymbol{\rho}_{-q} >$ is given by the following expression (see Appendix G) :

$$\partial \mathfrak{T}_n(r) / \partial < \boldsymbol{\rho}_q \cdot \boldsymbol{\rho}_{-q} > = 2 N^{-1} [1 - \cos(2\pi q/N)] \Delta \mathfrak{T}_n(\mathbf{r}) . \quad (V.20)$$

Let us bring this value in eq. (V.17). We obtain :

$$\partial < U_1 > / \partial < \boldsymbol{\rho}_q \cdot \boldsymbol{\rho}_{-q} > = \sum_{n=1}^{\infty} [1 - \cos kn] \, d(n) , \quad (V.21)$$

with

$$d(n) = \int d^s \mathbf{r} \, V(\mathbf{r}) \, \Delta \mathfrak{T}(\mathbf{r}, n) . \quad (V.22)$$

For small values of k, the series which appears in the right hand side of eq. (V.20) can be expanded in powers of k. The expansion contains a term of order k^2 and terms of higher order. These other terms depend critically on the behaviour of $d(n)$ for large values of n (see Appendix B). The value of $d(n)$ for $n \gg 1$ can be related to the asymptotic form of $\mathfrak{T}_n(\mathbf{r})$ (see eq. (V.1)). In agreement with our assumptions, we may write :

$$\Delta \mathfrak{T}_n(0) \simeq \frac{s}{2} q''(0) \, n^{-\alpha(s+2)} . \quad (V.23)$$

Therefore, for $n \gg 1$, we have :

$$d(n) \simeq n^{-\alpha(s+2)} [(s/2) \, d^s \mathbf{r} V(\mathbf{r})] . \quad (V.24)$$

Finally, by using the results of Appendix B, ($\alpha > 3/(s + 2)$), we may write :

$$\partial < U_1 > / \partial < \boldsymbol{\rho}_q \cdot \boldsymbol{\rho}_{-q} > =$$
$$= \frac{1}{2} k^2 \sum_{n=1}^{\infty} n^2 \int d^s \mathbf{r} V(\mathbf{r}) \Delta \mathfrak{T}_n(\mathbf{r}) +$$
$$+ k^{\alpha(s+2)-1} q''(0) \frac{(s\pi/4)}{[\alpha(s + 2) - 1] ! \cos[\alpha(s + 2) \pi/2]} . \quad (V.25)$$

Thus, eq. (V.13) is established. Incidentally, we remark that the term proportional to k^2 which appear in eq. (V.25) must be negative in order to compensate the term $sk^2/2$ of eq. (V.12). This observation leads to postulate the validity of the inequalities :

$$q(0) \neq 0 \quad q''(0) < 0 . \quad (V.26)$$

Finally, let us calculate $\partial S / \partial < \boldsymbol{\rho}_q \cdot \boldsymbol{\rho}_{-q} >$. In Appendix H, we show that :

$$\frac{\partial S}{\partial < \boldsymbol{\rho}_q \cdot \boldsymbol{\rho}_{-q} >} = - \frac{1}{2} \sum_{\sigma} \left\langle \frac{\partial^2 \log P(\mathbf{r}_1, ..., \mathbf{r}_N)}{\partial \boldsymbol{\rho}_q^{(\sigma)} \, \partial \boldsymbol{\rho}_{-q}^{(\sigma)}} \right\rangle . \quad (V.27)$$

Let us set :

$$x(k) = | 2 \pi q/N |^{1+2\alpha} \boldsymbol{\rho}_q \cdot \boldsymbol{\rho}_{-q} \quad (V.28)$$
$$F(k, x) = < \delta(x - x(k)) \log P(\mathbf{r}_1, ..., \mathbf{r}_N) > . \quad (V.29)$$

Here $x(k)$ is a random variable which is defined by the index k. Its probability law is obviously a smooth function of k and in particular, we have : (see eqs. (IV.4), (IV.11)) :

$$< x(k) > = g^{-1} . \quad (V.30)$$

Consequently, it is reasonable to admit that $F(x, k)$ is regular with respect to x and k for small values of k. On the other hand, by using the preceding notations, we may write eq. (V.25) in the form :

$$\partial \delta / \partial < \boldsymbol{\rho}_q \cdot \boldsymbol{\rho}_{-q} > =$$
$$= - \frac{1}{2} \sum_{\sigma} < \partial^2 F(x, x(k)) / \partial \rho_q^{(\sigma)} \, \partial \rho_{-q}^{(\sigma)} >$$
$$= - (s/2) \, | k |^{1+2\alpha} < F'_x(k, x(k)) + x(k) \, F''(k, x(k)) > . \quad (V.31)$$

Since $F(k, x)$ is expected to be regular (in k) at the origin the following limit :

$$\delta_3 = - (2/s) \lim_{k \to 0} < F'_x(k, x(k)) + x(k) \, F''(k, x(k)) > \quad (V.32)$$

must exist. Thus, in the limit $k \to 0$, the preceding equations give eq. (V.14).

VI. Summary and conclusions. — The main lines of this study can be summarized as follows. A general method for solving chain problems is presented in Section II ; it consists in minimizing the free energy by means of a trial probability which introduces correlations between the links of the chain (Sections II.A and II.B).

A critical study of current theories is given in Section III. Perturbation theory presents very serious difficulties and gives very few useful results (Section III.A). On the other hand, the approach of Flory is mathematically and physically inconsistent (Section III.B). The free energy terms which are calculated and minimized by Flory appear to be negligible in the limit of large chains. Moreover, general considerations show that the sum of these terms should be non negative and not positive as in Flory's treatment. Finally, it is demonstrated that the mean field methods are also unreliable (Section III.C).

The Minimal Gaussian approximation is studied in Section IV, for a ring containing N links ($N \to \infty$) in a space of dimension s. The trial probability $P(\mathbf{r}_1, ..., \mathbf{r}_N)$ is Gaussian (Sections IV.A and IV.B) and consequently the correlation probability $\mathcal{T}_n(\mathbf{r})$ is also Gaussian (Section IV.C). The minimization of the free energy F_N in the limit $N \to \infty$ (Sections IV.D and IV.E), shows that the mean distance between two points of an infinite chain (ring) is of the form :

$$< (\mathbf{r}_{j+n} - \mathbf{r}_j)^2 > \simeq bn^{2\alpha}(\log n)^{\beta} \quad n \gg 1 \quad n/N \ll 1 , \tag{VI.1}$$

with the following values : $\alpha = 1$, $\beta = -1$ for $s = 2$; $\alpha = 2/3$, $\beta = 0$ for $s = 3$; $\alpha = 1/2$, $\beta = 1/2$ for $s = 4$; $\alpha = 1/2$, $\beta = 0$ for $s > 4$ (Brownian chains). The coefficient b is calculated exactly in our model for $s = 2, 3, 4$. The continuous ring limit is studied (Section IV.F). The properties of large but finite rings are also investigated (Section IV.G).

The free energy difference

$$\Delta_N F = F_N - N \lim_{N' \to \infty} (F_{N'}/N')$$

is calculated for $s = 3$ (Section IV.H). In the Gaussian approximation the contributions to $\Delta_N F$ which are of the same nature as the terms calculated by Flory are proportional to $N^{1/3}$ (i. e. $N^{2\alpha-1}$) and a constant (i. e. $N^{2-\alpha s}$) respectively. But owing to a sum-rule, the term proportional to N vanishes, and in first approximation, we find that $\Delta_N F$ is proportional to $\log N$.

The above results do not depend critically on the nature of the Gaussian approximation and this fact is emphasized in Section V, where we study the properties of more general approximations. We consider trial probabilities for which the correlation function $\mathcal{T}_n(r) = < \delta(\mathbf{r} - \mathbf{r}_{j+n} + \mathbf{r}_j) >$ has the asymptotic form ($n \gg 1$) :

$$\mathcal{T}_n(\mathbf{r}) = n^{-\alpha s}\, q(r/n^{\alpha}) \qquad q(0) \neq 0 \qquad q'(0) = 0 \tag{VI.2}$$

(disregarding possible logarithmic factors).

We assume that $q(r)$ satisfies the conditions :

$$q''(0) < 0 \tag{VI.3}$$

$$\int r^2\, q(r)\, d^3\,\mathbf{r} < \infty , \tag{VI.4}$$

and we show that the swelling of the chain calculated with these trial probabilities is the same ($\alpha s = 2$) as in the Gaussian case. However, this result depends crucially on the validity of conditions (VI.3) and (VI.4). Condition (VI.3) is natural and our discussion shows that the curvature of $\mathcal{T}_n(\mathbf{r})$ must be negative at the origin ; but the case $q''(0) = 0$ cannot be excluded *a priori* since we ignore whether it is possible or not to build effectively a trial function satisfying this condition.

Thus, the Gaussian approximation appears as a very natural and consistent method which leads to plausible conjectures. Whether it is realistic or not remains, however, an open question. *A priori*, the results of our calculations do not seem to agree very well with machine experiments [20], but the interpretation of these machine calculations might be more delicate than it seems *a priori*. More complete and careful investigations are certainly needed in order to get definite answers concerning the behaviour of long chains with repulsive interactions.

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Appendix A. — We consider the coefficient $b(n)$ (where n is an integer) defined by :

$$b(n) = \frac{1}{2\pi} \int_{-\pi}^{+\pi} (1 - \cos kn)\, g^{-1}(k)\, \mathrm{d}k , \tag{A.1}$$

where $g(k)$ is an even, positive (for $k \neq 0$) and periodic function of k of period 2π. For $|k| \ll 1$, we assume that :

$$g(k) \simeq g\,|\,k\,|^{1+2\alpha} \quad \tfrac{1}{2} \leqslant \alpha < 1 \tag{A.2}$$

and we want to show that the asymptotic behaviour of $b(n)$ for $n \gg 1$ is

$$b(n) \simeq bn^{2\alpha} . \tag{A.3}$$

In any domain $\varepsilon \leqslant k \leqslant \pi$ (where ε is an arbitrarily small positive quantity) $g^{-1}(k)$ remains bounded. Consequently, for $n \gg 1$, the main contribution to $b(n)$

comes from values of k belonging to a very small region around the origin ; thus, we may write :

$$b(n) \simeq \frac{1}{2\pi}\int_{-\varepsilon}^{+\varepsilon}(1-\cos kn)\, g^{-1}(k)\,\mathrm{d}k$$

$$\simeq \frac{1}{\pi g}\int_{0}^{\varepsilon}(1-\cos kn)\, k^{-(1+2\alpha)}\,\mathrm{d}k$$

$$= \frac{n^{2\alpha}}{\pi g}\int_{0}^{n\varepsilon}(1-\cos x)\, x^{-(1+2\alpha)}\,\mathrm{d}x$$

$$\simeq \frac{n^{2\alpha}}{\pi g}\int_{0}^{\infty}(1-\cos x)\, x^{-(1+2\alpha)}\,\mathrm{d}x\,. \quad \text{(A.4)}$$

Therefore, the result (A.3) is established and b is given by :

$$b = (\pi g)^{-1}\int_{0}^{\infty}(1-\cos x)\, x^{-(1+2\alpha)}\,\mathrm{d}n$$

$$= \frac{1}{2\, g(2\,\alpha)\,!\,\sin\alpha\pi}\,. \quad \text{(A.5)}$$

Appendix B. — Let $I(k)$ be the sum of the following series :

$$I(k) = \sum_{n=1}^{\infty}\,[1-\cos nk]\, d(n)\,, \quad \text{(B.1)}$$

where $d(n)$ is a coefficient which, for $n \gg 1$, is equal to :

$$d(n) \simeq d(n)^{-\nu} \quad \text{(B.2)}$$

with

$$3 < \nu \leqslant 4 \qquad (\nu = \alpha(s+2))\,. \quad \text{(B.3)}$$

We want to evaluate the first two terms of the expansion of $I(k)$ with respect to $k(\,|\,k\,| \ll 1)$, when the main term is of order two ; this condition implies :

$$\sum n^2\, d(n) < \infty \quad \text{(B.4)}$$

$$\nu > 3 \quad \alpha > 3/(s+2)\,. \quad \text{(B.5)}$$

In this case :

$$I(k) = k^2 \sum_{n=1}^{\infty} n^2\, d(n) + O(k^2)\,. \quad \text{(B.6)}$$

In order to calculate the next term, we differentiate $I(k)$ three times with respect to k :

$$I'''(k) = -\sum_{n=1}^{\infty} n^3 \sin(nk)\, d(n)\,. \quad \text{(B.7)}$$

The series of term $n^4\, d(n) \simeq dn^{4-\nu}$ diverges. Therefore, the important terms are those for which n is large. Accordingly, the sum can replaced by an integral :

$$I'''(k) \simeq -\,d\int_{0}^{\infty} x^{3-\nu}\sin(kx)\,\mathrm{d}x$$

$$= -\,k^{\nu-4}\frac{\pi d}{2(\nu-4)\,!\,\cos(\nu\pi/2)}\,. \quad \text{(B.8)}$$

By integrating this equation and by using the result (B.4), we finally get :

$$I(k) \simeq k^2 \sum_{n=1}^{\infty} n^2\, d(n) -$$

$$-\,k^{\nu-1}\frac{\pi d}{2(\nu-1)\,!\,\cos(\nu\pi/2)} + O(k^{1-\nu}) \quad \text{(B.9)}$$

with $3 < \nu \leqslant 4$.

Appendix C. — In two dimensions, the equations giving $g(k)$ and $b(n)$ are :

$$g(k) = 1 - \cos k - w\sum_{1}^{\infty}(1-\cos nk)\,[b(n)]^{-2} \quad \text{(C.1)}$$

$$b(n) = \frac{1}{2\pi}\int_{-\pi}^{+\pi}(1-\cos nk)\, g^{-1}(k)\,\mathrm{d}k\,. \quad \text{(C.2)}$$

We found in Section IV.D that the corresponding value of α is $\alpha = 1$ and we predicted the presence of logarithmic factors. Accordingly we set :

$$g(k) \simeq g\,|\,k\,|^3\,|\,\log k\,|^{\beta} \qquad |\,k\,| \ll 1\,. \quad \text{(C.3)}$$

The condition $\beta > 1$ insures the convergence of the integral which gives $b(n)$ (eq. (C.2)) and we want to determine β and g.

By using eq. (C.2), we must find the asymptotic behaviour of $b(n)$ when $g(k)$ is given by (C.3) ; we have :

$$b(n) \simeq \frac{1}{g\pi}\int_{0}^{\varepsilon}\frac{1-\cos nk}{k^3\,|\,\log k\,|^{\beta}}\,\mathrm{d}k\,, \quad \text{(C.4)}$$

where ε is a very small positive constant $0 < \varepsilon \ll 1$. We consider values of n such that $\varepsilon\sqrt{n} \gg 1$. In the preceding integral, we divide the interval of integration into three parts which give the contributions I_1, I_2, I_3 (I_1 is the dominant term). We set :

$$I_1 = \int_{0}^{\varepsilon/n}\frac{1-\cos nk}{k^3\,|\,\log k\,|^{\beta}}\,\mathrm{d}k \simeq n^2\int_{0}^{\varepsilon/n}\frac{\mathrm{d}k}{k\,|\,\log k\,|^{\beta}}$$

$$\simeq \frac{n^2}{(\beta-1)\,|\,\log(\varepsilon/n)\,|^{\beta-1}} \simeq \frac{n^2}{(\beta-1)\,(\log n)^{\beta-1}} \quad \text{(C.5)}$$

$$I_2 = \int_{\varepsilon/n}^{\varepsilon/\sqrt{n}}\frac{1-\cos nk}{k^3\,|\,\log k\,|^{\beta}}\,\mathrm{d}k$$

$$< \frac{1}{|\,\log\varepsilon/\sqrt{n}\,|^{\beta}}\int_{\varepsilon/n}^{\varepsilon/\sqrt{n}}\frac{1-\cos nk}{k^3}\,\mathrm{d}k$$

$$< \frac{n^2}{(\log\sqrt{n}/\varepsilon)^{\beta}}\int_{\varepsilon}^{\infty}\frac{1-\cos x}{x^3}\,\mathrm{d}x \quad \text{(C.6)}$$

$$I_3 = \int_{\varepsilon/\sqrt{n}}^{\varepsilon} \frac{1 - \cos nk}{k^3 \mid \log k \mid^\beta} \mathrm{d}k$$
$$< \frac{1}{\mid \log \varepsilon \mid^\beta} \int_{\varepsilon/\sqrt{n}}^{\varepsilon} \frac{1 - \cos nk}{k^3} \mathrm{d}k$$
$$< \frac{2\, n^2}{\mid \log \varepsilon \mid^\beta} \int_{\varepsilon/\sqrt{n}}^{\infty} \frac{\mathrm{d}x}{x^3} = \frac{n}{\mid \log \varepsilon \mid^\beta}. \qquad \text{(C.7)}$$

We see immediately that, $(I_2/I_1) \to 0$ and $(I_3/I_1) \to 0$ when $n \to \infty$. Therefore :

$$b(n) = \frac{1}{g\pi}(I_1 + I_2 + I_3)$$
$$\simeq \frac{I_1}{g\pi} \simeq \frac{n^2}{g\pi(\beta - 1)(\log n)^{\beta - 1}}. \qquad \text{(C.8)}$$

In order to determine $g(k)$ in a self consistent way, we differentiate eq. (C.1), we get for $\mid k \mid \ll 1$:

$$g'''(k) \simeq w \sum_{n=1}^{\infty} \frac{n^3 \sin nk}{[b(n)]^2} \quad \mid k \mid \ll 1. \qquad \text{(C.9)}$$

Since we deal with large values of n, we replace $b(n)$ by ts asymptotic value (C.8) and the sum by an integral :

$$(k) \simeq g^2(\beta - 1)^2 \pi^2 \int_0^\infty \mathrm{d}n \frac{\sin nk}{n} \mid \log n \mid^{2\beta - 2}$$
$$= g^2(\beta - 1)^2 \pi^2 \int_0^\infty \mid \log x - \log k \mid^{2\beta - 2} \frac{\sin x}{x} \mathrm{d}x$$
$$\simeq g^2(\beta - 1)^2 \pi^2 \int_0^\infty \mathrm{d}n \frac{\sin x}{x} \mid \log k \mid^{2\beta - 2}. \qquad \text{(C.10)}$$

Finally we get :

$$g'''(k) \simeq w[g^2(\beta - 1)^2 \pi^3/2] \mid \log k \mid^{2\beta - 2}. \quad \text{(C.11)}$$

On the other hand, eq. (C.3) gives :

$$g'''(k) \simeq 6\, g \mid \log k \mid^\beta. \qquad \text{(C.12)}$$

The identification of eq. (C.11) with eq. (C.12) leads to the value $\beta = 2$ and to the determination of the asymptotic behaviours of $g(k)$ and $b(n)$. Finally, we obtain the results :

$$g(k) \simeq w^{-1} \frac{12}{\pi^3} k^3 \mid \log k \mid^2 \qquad \text{(C.14)}$$

$$b(n) \simeq w \frac{\pi^2}{12} \frac{n^2}{\log n}. \qquad \text{(C.15)}$$

Appendix D. — In four dimensions, the equations giving $g(k)$ and $b(n)$ are :

$$g(k) = 1 - \cos k - w \sum_1^\infty (1 - \cos nk)[b(n)]^{-3} \quad \text{(D.1)}$$

$$b(n) = \frac{1}{2\pi} \int_{-\pi}^{+\pi} (1 - \cos nk)\, g^{-1}(k)\, \mathrm{d}k. \qquad \text{(D.2)}$$

We find in Section IV.D that the corresponding value of α is $\alpha = 1/2$ and we predicted the existence of logarithmic factors. Accordingly, we set :

$$b(n) \simeq bn(\log n)^\gamma. \qquad \text{(D.3)}$$

The logarithmic term insures the convergence of the sum $\sum_1^\infty n^2[b(n)]^{-3}$ for $\gamma > 1/3$ and in this way the condition

$$\sum_1^\infty n^2[b(n)]^{-3} = w^{-1} \qquad \text{(D.4)}$$

can be satisfied as required.

We want to calculate b and γ in a self-consistent way. By using eqs. (D.1) and (D.3), we can determine the behaviour of $g(k)$ for small values of $\mid k \mid$. By differentiation of (C.1), we obtain for $\mid k \mid < 1$

$$g'''(k) \simeq w \sum_1^\infty n^3 \sin nk[b(n)]^{-3}. \qquad \text{(D.5)}$$

Since the important terms are those for which n is large, we may replace the sum by an integral and $b(n)$ by its asymptotic value (D.3) :

$$g'''(k) \simeq wb^{-3} \int_\eta^{+\infty} \frac{\sin nk}{\mid \log n \mid^{3\gamma}} \mathrm{d}n \quad \text{with} \quad \eta > 1 \quad \text{(D.6)}$$

(η is a positive constant which is arbitrary).

The integral

$$I(k) = \int_\eta^{+\infty} \frac{\sin nk}{\mid \log n \mid^{3\gamma}} \mathrm{d}n$$
$$= \frac{1}{2\, i}\left[\int_\eta^{+\infty} \mathrm{d}n \frac{\mathrm{e}^{ink}}{\mid \log n \mid^{3\gamma}} - \int_\eta^{\infty} \mathrm{d}n \frac{\mathrm{e}^{-ink}}{\mid \log n \mid^{3\gamma}}\right] \qquad \text{(D.7)}$$

can be calculated easily. In the right hand side of (D.7), we change the path of integration of each integral in the complex plane of n. It is legitimate to write :

$$I(k) = \frac{1}{2\, i}\left[\int_\eta^{\eta + i\infty} \mathrm{d}n \frac{\mathrm{e}^{ink}}{(\log n)^{3\gamma}} - \int_\eta^{\eta - i\infty} \mathrm{d}n \frac{\mathrm{e}^{-ink}}{(\log n)^{3\gamma}}\right]$$
$$= \frac{1}{2\, k} \int_0^\infty \mathrm{d}x\, \mathrm{e}^{-x}\left[\frac{\mathrm{e}^{ik\eta}}{(\log(\eta + ix/k))^{3\gamma}} + \frac{\mathrm{e}^{-ik\eta}}{(\log(\eta - ix/k))^{3\gamma}}\right]. \qquad \text{(D.8)}$$

For small values of k, we have :

$$I(k) \simeq k^{-1} \mid \log k \mid^{-3\gamma} \qquad \text{(D.9)}$$

and consequently

$$g'''(k) \simeq wb^{-3} \mid k \mid^{-1} (\log k)^{-3\gamma}. \qquad \text{(D.10)}$$

By integration, we obtain :

$$g(k) \simeq [wb^{-3}/2(3\gamma - 1)]\, k^2 \mid \log k \mid^{1 - 3\gamma}. \quad \text{(D.11)}$$

In order to determine $b(n)$ in a self consistent way, we may replace $g(k)$ in eq. (D.2) by its approximate value (D.9). We have :

$$b(n) \simeq \frac{2(3\gamma - 1)}{w\pi} b^3 \int_0^{\varepsilon} \frac{(1 - \cos nk)}{k^2} | \log k |^{3\gamma - 1} \, dk$$

$$0 < \varepsilon < 1 \qquad (D.12)$$

(ε is an arbitrary constant)

$$b(n) \simeq \frac{2(3\gamma - 1)}{w\pi} b^3 \, n \int_0^{\varepsilon} dx \, \frac{1 - \cos x}{x^2} \times$$

$$\times \, | \log n - \log x |^{3\gamma - 1}$$

$$\simeq \frac{2(3\gamma - 1)}{w\pi} b^3 \, n(\log n)^{3\gamma - 1} \int_0^{\infty} \frac{1 - \cos x}{x^2} dx \, . \qquad (D.13)$$

In this way, we obtain for $n \gg 1$

$$b(n) = w^{-1}(3\gamma - 1) \, b^3 \, n(\log n)^{3\gamma - 1} \, . \qquad (D.14)$$

The identification of eq. (D.11) with eq. (D.3) leads to the values $\gamma = 1/2$ and to the determination of the asymptotic behaviour of $b(n)$ and $g(k)$. Finally, we get the results :

$$g(k) \simeq \tfrac{1}{2} (2\,w)^{-1/2} \, k^2 \, | \log k |^{-3/2} \qquad | k | \ll 1 \qquad (D.15)$$

$$b(n) \simeq (2\,w)^{1/2} \, n(\log n)^{1/2} \qquad n \gg 1. \qquad (D.16)$$

Appendix E. — We want to show that in the domain $-2\pi \leqslant \theta \leqslant 2\pi$, we have :

$$S(\theta) \equiv \frac{\sqrt{3}(4/3)\,!}{\pi} \sum_{q=1}^{\infty} (1 - \cos \theta q) \, q^{-7/3}$$

$$= | \theta |^{4/3} + \lim_{n \to \infty} \left\{ \sum_{p=1}^{\infty} [| \theta + 2\pi p |^{4/3} + | \theta - 2\pi p |^{4/3} - 2 | 2\pi p |^{4/3}] - \frac{2\theta^2}{3\pi} [\pi(2n + 1)]^{1/3} \right\} . \qquad (E.1)$$

Let us consider the functions $\varphi_n(\theta)$ ($n > 1$)

$$\varphi_n(\theta) = | \theta |^{-2/3} + \sum_{p=1}^{n} [| 2\pi p + \theta |^{-2/3} + | 2\pi p - \theta |^{-2/3}] - \frac{3}{\pi} [\pi(2n + 1)]^{1/3} . \qquad (E.2)$$

If $n \to \infty$ these functions have a limit :

$$\varphi(\theta) = \lim_{n \to \infty} \varphi_n(\theta) \qquad (E.3)$$

and this limit is a periodic function of θ

$$\varphi(\theta) = \varphi(-\theta) = \varphi(\theta + 2\pi) \, . \qquad (E.4)$$

Let us determine the Fourier series :

$$\varphi(\theta) = \sum_{n=0}^{\infty} a_q \cos q\theta \, . \qquad (E.5)$$

We see immediately that :

$$\int_{-\pi}^{+\pi} \varphi_n(\theta) \, d\theta = 0 \qquad (E.6)$$

$$\int_{-\pi}^{+\pi} \varphi_n(\theta) \cos q\theta \, d\theta = 2 \int_0^{(2n+1)\pi} \theta^{-2/3} \cos q\theta \, d\theta \, . \qquad (E.7)$$

Consequently :

$$a_0 = 0$$

$$a_q = \frac{1}{\pi} \lim_{n \to \infty} \int_{-\pi}^{+\pi} \varphi_n(\theta) \cos q\theta \, d\theta = \frac{2}{\pi} q^{-1/3} \int_0^{\infty} x^{-2/3} \cos x \, dx = q^{-1/3} \frac{\sqrt{3}(-2/3)\,!}{\pi} . \qquad (E.8)$$

Thus :

$$\varphi(\theta) = \frac{\sqrt{3}(-2/3)\,!}{\pi} \sum_{q=1}^{\infty} \cos q\theta q^{-1/3} . \qquad (E.9)$$

Now we may define

$$\psi(\theta) = \frac{1}{3} \int_0^{\theta} \varphi(t) \, dt \, . \qquad (E.10)$$

From eqs. (E.2) and (E.10) we get :

$$\psi(\theta) = \frac{\sqrt{3}(1/3)\,!}{\pi} \sum_{q=1}^{\infty} \sin q\theta q^{-4/3}$$

$$= \varepsilon(\theta) \, | \theta |^{1/3} + \lim_{n \to \infty} \left\{ \sum_{p=1}^{n} [\varepsilon(\theta + 2\pi p) \, | \theta + 2\pi p |^{1/3} + \varepsilon(\theta - 2\pi p) \, | \theta + 2\pi p |^{1/3}] - \frac{\theta}{\pi} [\pi(2n + 1)]^{1/3} \right\} . \qquad (E.11)$$

In the same way, we have :

$$S(\theta) = \frac{4}{3} \int_0^{\theta} \psi(t) \, dt \, , \qquad (E.12)$$

and therefore we finally obtain the expected result :

$$S(\theta) = \frac{\sqrt{3}(4/3)\,!}{\pi} \sum_{q=1}^{\infty} (1 - \cos q\theta) \, q^{-7/3}$$

$$= | \theta |^{4/3} + \lim_{n \to \infty} \left\{ \sum_{p=1}^{n} [| \theta + 2\pi p |^{4/3} + | \theta - 2\pi p |^{4/3} - 2 | 2\pi p |^{4/3}] - \frac{2\theta^2}{3\pi} [\pi(2n + 1)]^{1/3} \right\} . \qquad (E.13)$$

It is easy to verify that the last expression is periodic with the period 2π.

Appendix F. — For $n \gg 1$, we want to calculate :

$$I_N = N^{-1} \sum_{q=1}^{N-1} [1 - \cos(2\pi q/N)] \, g_N^{-1}(2\pi q/N) - \frac{1}{2\pi}\int_{-\pi}^{+\pi} (1 - \cos k) \, g^{-1}(k) \, dk \qquad (F.1)$$

with the assumption that for small values of k

$$g(k) \simeq g \, | k |^{1+2\alpha} \qquad (F.2)$$

$$g_N(2\pi q/N) \simeq \gamma(q) \, g(2\pi q/N) . \qquad (F.3)$$

The behaviour of I_N for large values of N depends only on the singularity of $g(k)$ at the origin. Consequently, we may write :

$$I_N \simeq \frac{1}{g} \lim_{n\to\infty} \left[\frac{1}{N} \sum_{q=1}^{n} \gamma_{(q)}^{-1} \, [2\pi q/N]^{-(2\pi-1)} - \frac{1}{2\pi} \int_0^{\pi(2n+1)/N} k^{-(2\alpha-1)} \, dk \right]. \qquad (F.4)$$

Thus :

$$I_N \simeq \frac{C(\alpha)}{2\pi g} (N/2\pi)^{2\alpha-2} , \qquad (F.5)$$

where $C(\alpha)$ is a constant which is independent of N

$$C(\alpha) = \lim_{n\to\infty} \left[\sum_{q=1}^{n} \gamma_{(q)}^{-1} \, q^{1-2\alpha} - \frac{1}{2 - 2\alpha} (n + \frac{1}{2})^{2-2\alpha} \right]. \qquad (F.6)$$

Appendix G. — We want to prove the relation

$$\partial \mathfrak{T}_n(\mathbf{r}) / \partial < \boldsymbol{\rho}_q \, \boldsymbol{\rho}_{-q} > = \frac{2}{N} [1 - \cos(2\pi n q/N)] \, \Delta \mathfrak{T}_n(\mathbf{r}). \qquad (G.1)$$

The correlation function $\mathfrak{T}_n(\mathbf{r})$ is defined by :

$$\mathfrak{T}_n(\mathbf{r}) = < \delta(\mathbf{r}_{j+n} - \mathbf{r}_j - \mathbf{r}) > = (2\pi)^{-s} \int d^s\mathbf{u} \, e^{-i\mathbf{u}\mathbf{r}} < e^{i\mathbf{u}(\mathbf{r}_{j+n} - \mathbf{r}_j)} > . \qquad (G.2)$$

By using the definition (V.5), we may write :

$$\mathfrak{T}_n(\mathbf{r}) = (2\pi)^{-s} \int e^{-i\mathbf{u}\mathbf{r}} \, \Phi(\mu_1 \mathbf{u}, ..., \mu_{N-1} \mathbf{u}) \, d^s\mathbf{u} , \qquad (G.3)$$

where μ_q is given by :

$$\mu_q = N^{-1/2} [e^{i2\pi(j+n)q/N} - e^{i2\pi jq/N}] . \qquad (G.4)$$

On the other hand, we deduce immediately from eq. (V.7) :

$$\partial \Phi(\boldsymbol{\lambda}_1, ..., \boldsymbol{\lambda}_{N-1}) / \partial < \boldsymbol{\rho}_q \, \boldsymbol{\rho}_{-q} > = - \boldsymbol{\lambda}_q \, \boldsymbol{\lambda}_{-q} \, \Phi(\boldsymbol{\lambda}_1, ..., \boldsymbol{\lambda}_{N-1}) . \qquad (G.5)$$

By differentiating eq. (G.3) with respect to $< \rho_q \rho_{-q} >_C$ and by using (G.5) we obtain :

$$\partial \mathfrak{T}_n(\mathbf{r}) / \partial < \boldsymbol{\rho}_q \cdot \boldsymbol{\rho}_{-q} > = - (2\pi)^{-S} \int e^{-i\mathbf{u}\mathbf{r}} u^2 \, \mu_q \, \mu_{-q} \, \Phi(\mu_1 \mathbf{u}, ..., \mu_{N-1} \mathbf{u}) . \qquad (G.6)$$

The product $\mu_q \, \mu_{-q}$ is calculated easily (see eq. (G.4)) and by direct application of the definition (V.5), we obtain the result (G.1).

Appendix H. — Let us prove the relation

$$\frac{\partial S}{\partial < \boldsymbol{\rho}_q \, \boldsymbol{\rho}_{-q} >_C} = - \frac{1}{2} \sum_{\sigma} \frac{\partial^2 \log P(\mathbf{r}_1, ..., \mathbf{r}_N)}{\partial \rho_q^{(\sigma)} \, \partial \rho_{-q}^{(\sigma)}} . \qquad (H.1)$$

The probability $P(\mathbf{r}_1, ..., \mathbf{r}_N)$ can be considered either as a function of the variables $\boldsymbol{\rho}_q$ or as a functional of ρ_q and of the other cumulants. Before proving (H.1), let us show that :

$$\frac{\partial P(\mathbf{r}_1, ..., \mathbf{r}_N)}{\partial < \boldsymbol{\rho}_q \, \boldsymbol{\rho}_{-q} >} = \frac{1}{2} \sum_{\sigma} \frac{\partial P(\mathbf{r}_1, ..., \mathbf{r}_N)}{\partial \rho_q^{(\sigma)} \partial \rho_{-q}^{(\sigma)}} . \qquad (H.2)$$

The probability $P(\mathbf{r}_1, ..., \mathbf{r}_N)$ is completely determined by the characteristic function $\Phi(\boldsymbol{\lambda}_1, ..., \boldsymbol{\lambda}_{N-1})$ (see eq. (V.5)). Let us now introduce a new characteristic function $\Phi_\varepsilon(\boldsymbol{\lambda}_1, ..., \boldsymbol{\lambda}_{N-1})$ which depends on a set of small parameters ε_q

$$\Phi_\varepsilon(\boldsymbol{\lambda}_1, ..., \boldsymbol{\lambda}_{N-1}) = \exp\left[- \frac{1}{2} \sum_{q=1}^{N-1} \varepsilon_q \, \boldsymbol{\lambda}_q \, \boldsymbol{\lambda}_{-q} \right] \Phi(\boldsymbol{\lambda}_1, ..., \boldsymbol{\lambda}_{N-1}) . \qquad (H.3)$$

By expanding $\Phi_\varepsilon(\boldsymbol{\lambda}_1, ..., \boldsymbol{\lambda}_{N-1})$ in terms of these parameters, we get :

$$\Phi_\varepsilon(\boldsymbol{\lambda}_1, ..., \boldsymbol{\lambda}_{N-1}) = \Phi(\boldsymbol{\lambda}_1, ..., \boldsymbol{\lambda}_{N-1}) + \sum_q \varepsilon_q \frac{\partial \Phi(\boldsymbol{\lambda}_1, ..., \boldsymbol{\lambda}_q)}{\partial < \boldsymbol{\rho}_q \cdot \boldsymbol{\rho}_{-q} >} \qquad (H.4)$$

on the other hand :

$$\Phi(\boldsymbol{\lambda}_1, ..., \boldsymbol{\lambda}_{N-1}) = \int \exp[i \sum \boldsymbol{\lambda}_q \cdot \boldsymbol{\rho}_q] \times P(\mathbf{r}_1, ..., \mathbf{r}_N) \, d\mathbf{r}_2 \ldots d\mathbf{r}_N = N^{-1/2} \int \exp[i \sum \boldsymbol{\lambda}_q \cdot \boldsymbol{\rho}_q] \times P(\mathbf{r}_1, ..., \mathbf{r}_N) \, d\Omega(\rho) \qquad (H.5)$$

where $d\Omega(\rho)$, the element of integration in ρ-space, has been defined by eqs. (IV.38) and (IV.39). Conversely

$$P(\mathbf{r}_1, ..., \mathbf{r}_N) = N^{1/2} \int \exp[- i \boldsymbol{\lambda}_q \cdot \boldsymbol{\rho}_q] \times \Phi(\boldsymbol{\lambda}_1, ..., \boldsymbol{\lambda}_{N-1}) \, d\Omega(\boldsymbol{\lambda}) . \qquad (H.6)$$

In the same way, we can associate with $\Phi_\varepsilon(\boldsymbol{\lambda}_1, ..., \boldsymbol{\lambda}_{N-1})$, a new probability law $P_\varepsilon(\mathbf{r}_1, ..., \mathbf{r}_N)$. As the relation between these two quantities is linear, eq. (H.4) can be transformed into :

$$P_\varepsilon(\mathbf{r}_1, ..., \mathbf{r}_N) = P(\mathbf{r}_1, ..., \mathbf{r}_N) + \sum \varepsilon_q \frac{\partial P(\mathbf{r}_1, ..., \mathbf{r}_N)}{\partial < \boldsymbol{\rho}_q . \boldsymbol{\rho}_{-q} >} . \tag{H.7}$$

On the other hand, $P_\varepsilon(\mathbf{r}_1, ..., \mathbf{r}_N)$ can be written explicitly in terms of $\Phi(\boldsymbol{\lambda}_1, ..., \boldsymbol{\lambda}_N)$

$$P_\varepsilon(\mathbf{r}_1, ..., \mathbf{r}_N) = $$

$$= N^{1/2} \int \exp\left[- \sum_{q=1}^{N-1} \left[i\boldsymbol{\lambda}_q . \boldsymbol{\rho}_q + \frac{1}{2} \varepsilon_q \boldsymbol{\lambda}_q . \boldsymbol{\lambda}_{-q} \right]\right] \times$$

$$\times \Phi(\boldsymbol{\lambda}_1, ..., \boldsymbol{\lambda}_{N-1}) \, d\Omega(\lambda) . \tag{H.8}$$

By differentiation of eq. (H.6) with respect to $\boldsymbol{\rho}_q$ and $\boldsymbol{\rho}_{-q}$, we find

$$\frac{\partial P(\mathbf{r}_1, ..., \mathbf{r}_N)}{\partial < \boldsymbol{\rho}_q . \boldsymbol{\rho}_{-q} >} = - N^{1/2} \int \left[\sum_{p=1}^{N-1} \boldsymbol{\lambda}_p . \boldsymbol{\lambda}_{-q} \right] \times$$

$$\times \exp\left[-i \sum_{q=1}^{N-1} \boldsymbol{\lambda}_q \, \boldsymbol{\rho}_q \right] \Phi(\boldsymbol{\lambda}_1, ..., \boldsymbol{\lambda}_{N-1}) \, d\Omega(\lambda) \tag{H.9}$$

and by comparison with eqs. (H.7) and (H.8), we obtain the expected result (H.2).

The entropy S is given in terms of $P(\mathbf{r}_1, ..., \mathbf{r}_N)$ by :

$$S = - < \log P(\mathbf{r}_1, ..., \mathbf{r}_N) > . \tag{H.10}$$

By differentiating this expression with respect to $< \boldsymbol{\rho}_q \, \boldsymbol{\rho}_{-q} >_C$ and by taking eq. (H.2) into account, we find immediately eq. (H.1).

References and footnotes

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