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THE LAGRANGIAN THEORY OF POLYMER SOLUTIONS AT INTERMEDIATE CONCENTRATIONS

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Résumé. — De Gennes a montré que les propriétés d'un polymère isolé en solution pouvaient être déduites de l'étude d'une théorie Lagrangienne pour un champ à zéro composante sans champ extérieur. Ce résultat est généralisé au cas de solutions de polymères à des concentrations intermédiaires. On montre qu'un grand ensemble de polymères peut être décrit en utilisant une théorie Lagrangienne pour un champ à zéro composante, couplé à un champ extérieur. Les concentrations C_p de polymères (chaînes) et C_m de monomères (maillons de chaînes) sont fixées par deux potentiels chimiques. On montre que la pression osmotique obéit à une loi d'échelle de la forme

$$(P/KTC_p) = F(C_p N^{\nu})$$

où N est le nombre moyen de monomères par polymère ($N = C_m/C_p$) et ν l'indice critique définissant la taille d'un long polymère isolé. La fonction $F(\lambda)$ peut être développée en puissances de λ ; elle est donnée implicitement par la fonction génératrice des fonctions de vertex à moments nuls, tirée de la théorie Lagrangienne. Les résultats semblent en bon accord avec l'expérience.

Abstract. — De Gennes has shown that the properties of an isolated polymer in a solution (a chain with excluded volume) can be deduced within the framework of a Lagrangian theory for a zero component field in the absence of an external field. This result is generalized to the case of polymer solutions at intermediate concentrations. It is shown that a grand ensemble of polymers can be described by using a Lagrangian theory for a zero component field coupled to an external field. The concentrations C_p of polymers (chains) and C_m of monomers (links) are fixed by two chemical potentials.

It is shown that the osmotic pressure obeys a scaling law of the form

$$(P/KFC_p) = F(C_p N^{\nu})$$

where N is the mean number of monomers per polymer ($N = C_p/C_m$) and ν the critical index defining the size of a long isolated polymer. The function $F(\lambda)$ can be expanded in powers of λ and it is given implicitly by the generating functional of the zero-momentum vertex functions derived from the Lagrangian theory. The results seem to be in good agreement with experiments.

1. Introduction. — A few years ago, P. G. de Gennes [1] showed that the theory of a self-avoiding chain (polymer) is equivalent to a Lagrangian field theory of the *Wilson* type. For a field with n components, the Green's functions can be expanded in terms of the interaction, it is possible to pass to the limit $n = 0$ and, in this way, to build a theory determining the statistical properties of a single chain made of a large number of links (monomers).

More recently, this approach has been used by the author [2] to investigate the asymptotic behaviour of the correlation function between the extremities of a single chain.

The purpose of this article is to generalize this method and apply it to the case of polymer solutions. We will show that the properties of such solutions can be studied by using a Lagrangian theory with a source. In other terms, a linear term is added to

the original Lagrangian and this term couples the fluctuating field to an external constant field.

The equivalence is obtained by considering the polymer solution as a grand canonical ensemble : the total number of polymers and the total number of monomers are not fixed but their averages are determined by two chemical potentials. We note that magnetic systems are described by the same kind of Lagrangian [3, 4] but with $n \geq 1$; thus extending the language adapted to these systems to the case of polymer solutions (i. e. for $n = 0$), we may say that the chemical potentials which we introduce correspond respectively to the magnetic field and the temperature. As an application, we express the osmotic pressure and the concentrations C_m of monomers (links) and C_p of polymers (chains) in terms of two parameters. The results depend only on a universal function which, unfortunately, is only partially known. In this way, we obtain a scaling law which has non-trivial consequences.

Thus the main purpose of this article is to demonstrate that the Lagrangian theory with external field can be directly applied to study the properties of polymer solutions and that it leads to useful results.

However, we must note that the equivalence has been established only in the case where the length of the chains is large compared to the length of a link. Thus, the continuous limit popularized by S. F. Edwards is used for describing the chains. In the absence of any interaction, the chains would be Brownian and the mean square distance would be written $\langle r^2(L) \rangle = 2lL$ where L is the length of the chain and l an elementary length. Thus even for continuous chains we can define a quantity $\mathcal{N} = L/l$ which will be called the number of links.

For reasons of simplicity, we assume that the chain interactions are given by a δ -function of amplitude g_0 . Thus the strength of the interaction can be determined by a dimensionless constant (see section 6)

$$a = g_0 l^\varepsilon \quad (d = 4 - \varepsilon = \text{space dimension}). \quad (1.1)$$

Consequently, the free energy is a function of three dimensionless parameters a , $C_p l^d$ and $C_m l^d$, and the average number of links per chain can be defined as

$$\mathcal{N} = C_m / C_p. \quad (1.2)$$

However for practical applications and in particular for the calculation of the osmotic pressure, we shall consider only polymer solutions belonging to a critical domain characterized as follows. The excluded volume effects are supposed to be strong. For an isolated chain, it is not difficult to show from dimensionality arguments that in this case

$$\langle r^2(L) \rangle = Ll(g_0^{1/\varepsilon} L)^{2\nu-1} = l^2 a^{(2\nu-1)/\varepsilon} \mathcal{N}^{2\nu} \quad (1.3)$$

where ν is the critical index associated with the swelling of the chain.

Thus, we have to assume the condition $g_0^{1/\varepsilon} L \gg 1$ which can be written

$$a^{1/\varepsilon} \gg L/l = 1/\mathcal{N}. \quad (1.4)$$

On the other hand, it is clear that the concentration of monomers must remain small. When the chains overlap strongly, they have a tendency to become Brownian and this fact is consistent with our results but a close examination of our equations seems to indicate that the method is valid only, if, on a small scale, the chains retain their excluded volume behaviour.

More precisely, we note that the chains begin to overlap for $\mathcal{N} > \mathcal{N}_c$ where

$$C_p (la^{(2\nu-1)/2\varepsilon} \mathcal{N}^{\nu})^d = 1 \quad (1.5)$$

and in agreement with eq. (1.3) and (1.4), we assume that $a^{1/\varepsilon} \gg 1/\mathcal{N}_c$.

Thus we obtain a second condition

$$C_p l^d \ll a^{d/2\varepsilon},$$

which can be more conveniently written

$$C_m l^d \ll \mathcal{N} a^{d/2\varepsilon}. \quad (1.6)$$

It is clear that conditions (1.4) and (1.6) are always satisfied if \mathcal{N} is large and if we deal with a good solvent (we must be reasonably far from the Θ point since $a = 0$ at the Θ point).

We note also that the situations for which $C_m l^d > 1$ seem rather unrealistic from a physical point of view and need not be considered.

Thus the theory presented here has a large domain of validity. Moreover, if the chains do not exactly satisfy our conditions, it is possible to calculate corrections to scaling in the frame of the Lagrangian theory but this question is beyond the scope of the present article.

In section 2, we recall the formalism of Lagrangian theory without external field. In section 3, we show how the concept of Green's function and vertex function can be used in polymer theory. These two sections, therefore, describe in a systematic way the concepts introduced by De Gennes. In section 4, we indicate how the Lagrangian theory formalism is modified by the introduction of an external field. In section 5, we introduce grand ensembles of polymers and the formalism described in section 4 is applied to the study of polymer solutions. A grand partition function is defined. The osmotic pressure and the concentrations of chains and links are expressed in terms of this partition function and, after some transformations, in terms of the generating functional of the vertex functions. In section 6, the theory is renormalized, the expressions obtained for the osmotic pressure and the concentrations are

simplified and a scaling law is derived. This law is studied in section 7 and compared in section 8 with the results of older theories. In section 9, it is shown that it agrees with experiments. Finally, a few remarks concerning the correlation functions are made in section 10.

2. Lagrangian formalism in the absence of an external field. — The action is defined by

$$A \{ \varphi \} = A_0 \{ \varphi \} + A_1 \{ \varphi \} \quad (2.1)$$

$$A_0 \{ \varphi \} = \frac{1}{2} \int d^d x \left\{ \sum_{i,j} [\partial_i \varphi^j(\mathbf{x})]^2 + m_0^2 \sum_j [\varphi^j(\mathbf{x})]^2 \right\} \quad (2.2)$$

$$A_1 \{ \varphi \} = \frac{1}{8} \int d^d x \int d^d y \times \sum_{j,l} [\varphi^j(\mathbf{x})]^2 [\varphi^l(\mathbf{y})]^2 V(\mathbf{x} - \mathbf{y}) \quad (2.3)$$

where $j = 1, \dots, n, d = \text{space dimension}$.

The mean value of a functional $\mathcal{O} \{ \varphi \}$ of the field is defined by

$$\langle \mathcal{O} \{ \varphi \} \rangle = \frac{\int d\omega \{ \varphi \} \mathcal{O} \{ \varphi \} \exp[-A \{ \varphi \}]}{\int d\omega \{ \varphi \} \exp[-A \{ \varphi \}]} \quad (2.4)$$

where $d\omega \{ \varphi \}$ is the element of integration for the functional integral.

Fourier transforms are defined by setting

$$\varphi^j(\mathbf{k}) = \int d^d x e^{i\mathbf{k}\cdot\mathbf{x}} \varphi^j(\mathbf{x}) \quad (2.5)$$

$$\tilde{V}(\mathbf{q}) = (2\pi)^{-d} \int d^d x e^{i\mathbf{q}\cdot\mathbf{x}} V(\mathbf{x}). \quad (2.6)$$

We deal only with short range potentials and therefore for $d < 4$, after renormalizing the mass m_0 , it will be convenient to set :

$$\tilde{V}(\mathbf{q}) = g_0. \quad (2.7)$$

In this case, there really exists a Lagrangian

$$\mathcal{L}(\mathbf{x}) = \sum_{i,j} [\partial_i \varphi^j(\mathbf{x})]^2 + m_0^2 \sum [\varphi^j(\mathbf{x})]^2 + (2\pi)^d g_0 \left[\sum_j [\varphi^j(\mathbf{x})]^2 \right]^2. \quad (2.8)$$

In the general case, the Green's functions are defined by

$$\begin{aligned} \mathcal{G}_{j_1 \dots j_d}^{(g)}(\mathbf{x}_1, \dots, \mathbf{x}) &= \langle \varphi^{j_1}(\mathbf{x}_1) \dots \varphi^{j_d}(\mathbf{x}_d) \rangle \\ G_{j_1 \dots j_d}^{(g)}(\mathbf{k}_1, \dots, \mathbf{k}_d) &= \langle \tilde{\varphi}^{j_1}(\mathbf{k}_1) \dots \tilde{\varphi}^{j_d}(\mathbf{k}_d) \rangle. \end{aligned} \quad (2.9)$$

The Green's functions $\tilde{G}_{j_1, \dots, j_d}(\mathbf{k}_1, \dots, \mathbf{k}_d)$ can be expanded with respect to the interaction.

Using Wick's theorem and the trivial result

$${}^0 G_{jj'}(\mathbf{k}, \mathbf{k}') = \langle \varphi^j(\mathbf{k}) \varphi^{j'}(\mathbf{k}') \rangle_0 = \delta_{jj'} \frac{\delta(\mathbf{k} + \mathbf{k}')}{k^2 + m_0^2} \quad (2.10)$$

(free propagator) we can represent the Green's functions $G_{j_1, \dots, j_d}^{(g)}(\mathbf{k}_1, \dots, \mathbf{k}_d)$ by diagrams in the usual manner (see Fig. 1).

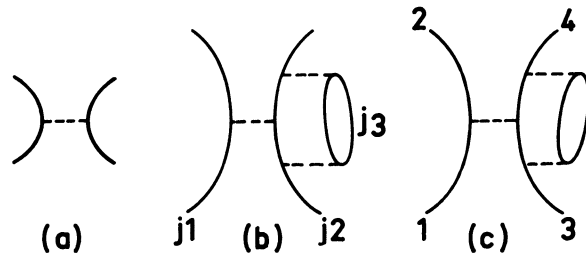


FIG. 1. — a) The interaction vertex. b) A general diagram for $n \neq 0$, the line indices have been indicated but not the momenta. c) The same diagram for an ordered Green function. The corresponding contribution is proportional to n because the diagram contains one loop.

The rules for calculating a diagram are the following (see Fig. 1).

- 1) A factor $(k^2 + m_0^2)^{-1}$ is associated with each part of a solid line.
- 2) A factor $V(\mathbf{q})$ is associated with each dashed line.
- 3) A factor of the form $\delta(\mathbf{k} + \mathbf{k}' + \mathbf{q})$ is associated with each vertex (momentum conservation).
- 4) Proper symmetry numbers are introduced and all the free momenta are integrated in dimension d .
- 5) Each solid line corresponds to a well defined component j of the field. However, for closed loops, we may sum over j and this gives a factor n .

It is convenient to introduce *ordered Green's functions* $G^{(2, \mathcal{M})}(\mathbf{k}_1 \dots \mathbf{k}_{2, \mathcal{M}})$ as the sum of the contributions of diagrams defined as follows.

A diagram of rank \mathcal{F} is made of \mathcal{F} open lines and any number of closed loops (each closed loop is connected at least with one open line).

Each line is labelled by an index M (where $M = 1, \dots, \mathcal{M}$) and by definition the corresponding ingoing momenta are \mathbf{k}_{2M-1} and \mathbf{k}_{2M} . Thus, the indices j do not appear in the definition of

$$G^{2, \mathcal{M}}(\mathbf{k}_1 \dots \mathbf{k}_{2, \mathcal{M}})$$

but this expression is a function of n (a series of powers of n : see Fig. 1). Consequently, it has meaning for any values of n and, in particular, for $n = 0$.

Conversely, when n is a positive integer, we may express all the Green's functions in terms of ordered

Green's functions

$$G_{j_1 \dots j_{2\mathcal{M}}}^{(2\mathcal{M})}(\mathbf{k}_1, \dots, \mathbf{k}_{2\mathcal{M}}) = \frac{1}{2^{\mathcal{M}} \mathcal{M}!} \times \sum_{\mathfrak{P}} [\delta(j_{\mathfrak{P}1} - j_{\mathfrak{P}2}) \dots \delta(j_{\mathfrak{P}(2\mathcal{M}-1)} - j_{\mathfrak{P}(2\mathcal{M})})] \times G^{(2\mathcal{M})}(\mathbf{k}_{\mathfrak{P}1} \dots \mathbf{k}_{\mathfrak{P}(2\mathcal{M})}) \quad (2.11)$$

where $\mathfrak{P}1, \dots, \mathfrak{P}(2\mathcal{M})$ are the numbers obtained by any permutation \mathfrak{P} of $1, \dots, 2\mathcal{M}$.

Thus

$$\frac{1}{(2\mathcal{M})!} G_{1 \dots 1}^{(2\mathcal{M})}(0, \dots, 0) = \frac{1}{2^{\mathcal{M}} \mathcal{M}!} G^{(2\mathcal{M})}(0, \dots, 0).$$

The generating functional

$$Z\{\mathbf{H}\} = 1 + \sum_{N=1}^{\infty} \frac{1}{N!} \int d^d k_1 \dots d^d k_N \times H_{j_1}(-\mathbf{k}_1) \dots H_{j_N}(-\mathbf{k}_N) G_{j_1 \dots j_N}^{(N)}(\mathbf{k}_1 \dots \mathbf{k}_N) = 1 + \sum_{\mathcal{M}=1}^{\infty} \frac{1}{2^{\mathcal{M}} \mathcal{M}!} \int d^d k_1 \dots d^d k_{2\mathcal{M}} \times [\mathbf{H}(-\mathbf{k}_1) \cdot \mathbf{H}(-\mathbf{k}_2)] \dots [\mathbf{H}(-\mathbf{k}_{2\mathcal{M}-1}) \cdot \mathbf{H}(-\mathbf{k}_{2\mathcal{M}})] G^{(2\mathcal{M})}(\mathbf{k}_1 \dots \mathbf{k}_{2\mathcal{M}}) \quad (2.12)$$

can also be expressed in terms of the connected Green's functions

$$Z\{\mathbf{H}\} = \exp[W\{\mathbf{H}\}] \quad (2.13)$$

where $W\{H\}$ is obtained by replacing in eq. (2.12)

$$G_{j_1 \dots j_N}^{(N)}(\mathbf{k}_1, \dots, \mathbf{k}_N) \text{ by } G_{C, j_1 \dots j_N}^{(N)}(\mathbf{k}_1, \dots, \mathbf{k}_N)$$

and

$$G^{(2\mathcal{M})}(\mathbf{k}_1, \dots, \mathbf{k}_{2\mathcal{M}}) \text{ by } G_C^{(2\mathcal{M})}(\mathbf{k}_1, \dots, \mathbf{k}_{2\mathcal{M}}).$$

The connected Green's functions are simpler than the ordinary Green's functions but the most important quantities are the vertex functions. The vertex functions $\Gamma_{j_1, \dots, j_N}^{(N)}(\mathbf{k}_1, \dots, \mathbf{k}_N)$ and $\Gamma^{(2\mathcal{M})}(\mathbf{k}_1, \dots, \mathbf{k}_{2\mathcal{M}})$ are obtained for $N > 2$ and $\mathcal{M} > 1$ by amputating (of their external lines) the corresponding one particle irreducible Green's functions and by changing the sign.

On the other hand, for $\mathcal{M} = 1$ we have, by definition :

$$G^{(2)}(\mathbf{k}_1, \mathbf{k}_2) = \delta(\mathbf{k}_1 + \mathbf{k}_2) [\Gamma^{(2)}(\mathbf{k}_1, \mathbf{k}_2)]^{-1}. \quad (2.14)$$

The generating functional

$$\Gamma(\mathbf{M}) = \sum_{N=1}^{\infty} \frac{1}{N!} \int d^d k_1 \dots d^d k_N M^{j_1}(-\mathbf{k}_1) \dots M^{j_N}(-\mathbf{k}_N) \delta(\mathbf{k}_1 + \dots + \mathbf{k}_N) \times \Gamma_{j_1, \dots, j_N}^{(N)}(\mathbf{k}_1, \dots, \mathbf{k}_N) = \sum_{\mathcal{M}=1}^{\infty} \frac{1}{2^{\mathcal{M}} \mathcal{M}!} \int d^d k_1 \dots d^d k_{2\mathcal{M}} \times$$

$$\times [\mathbf{M}(-\mathbf{k}_1) \cdot \mathbf{M}(-\mathbf{k}_2)] \dots \dots [\mathbf{M}(-\mathbf{k}_{2\mathcal{M}-1}) \cdot \mathbf{M}(-\mathbf{k}_{2\mathcal{M}})] \times \delta(\mathbf{k}_1 + \dots + \mathbf{k}_{2\mathcal{M}}) \Gamma^{(2\mathcal{M})}(\mathbf{k}_1, \dots, \mathbf{k}_{2\mathcal{M}}) \quad (2.15)$$

can also be defined as the Legendre transformation of $W\{\mathbf{H}\}$

$$W\{\mathbf{H}\} + \Gamma\{\mathbf{M}\} - \int d^d x \mathbf{M}(\mathbf{x}) \cdot \mathbf{H}(\mathbf{x}) = 0$$

$$M^j(\mathbf{x}) = \frac{\partial W\{\mathbf{H}\}}{\partial H^j(\mathbf{x})}$$

$$H^j(\mathbf{x}) = \frac{\partial \Gamma\{\mathbf{M}\}}{\partial M^j(\mathbf{x})}. \quad (2.16)$$

3. Polymer theory. — Let us consider \mathcal{M} chains in a box.

Each chain is labelled by an index m ; the corresponding length of a chain is L_m . We associate with each point of a chain a vector $\mathbf{r}_m(\lambda_m)$ where λ_m is the length, measured along the chain between the point defined by \mathbf{r}_m and one end of the chain

$$(0 < \lambda_m < L_m).$$

Following S. F. Edwards [5], we may express the energy of a configuration \mathcal{C} of this classical system by writing

$$\mathcal{H}(L_1, \dots, L_{\mathcal{M}}; \mathcal{C}) = \mathcal{H}_0(L_1, \dots, L_{\mathcal{M}}; \mathcal{C}) + \mathcal{H}_1(L_1, \dots, L_{\mathcal{M}}; \mathcal{C})$$

$$\mathcal{H}_0(L_1, \dots, L_{\mathcal{M}}; \mathcal{C}) = \sum_{m=1}^{\mathcal{M}} \frac{1}{4l} \int_0^{L_m} d\lambda_m \left[\frac{\partial \mathbf{r}_m(\lambda_m)}{\partial \lambda_m} \right]^2 \quad (3.1)$$

$$\mathcal{H}_1(L_1, \dots, L_{\mathcal{M}}; \mathcal{C}) = \frac{l^2}{2} \sum_{m=1}^{\mathcal{M}} \sum_{m'=1}^{\mathcal{M}} \times \int_0^{L_m} d\lambda_m \int_0^{L_{m'}} d\lambda_{m'} V[\mathbf{r}_m(\lambda_m) - \mathbf{r}_{m'}(\lambda_{m'})].$$

These Hamiltonians are dimensionless, and the length l can be considered, in some way, as the length of one link (though we have proceeded to the continuous limit).

According to Boltzmann's law, the mean value of a functional $\mathcal{O}\{\mathcal{C}\}$ of a configuration is given by

$$\langle \mathcal{O}\{\mathcal{C}\} \rangle = \frac{\int d\Omega_{\mathcal{M}} \exp[-\mathcal{H}(L_1, \dots, L_{\mathcal{M}}; \mathcal{C})] \mathcal{O}\{\mathcal{C}\}}{\int d\Omega_{\mathcal{M}} \exp[-\mathcal{H}_0(L_1, \dots, L_{\mathcal{M}}; \mathcal{C})]} \quad (3.2)$$

(the temperature is included in the definition of the Hamiltonians).

The element of integration can be formally defined by

$$d\Omega_{\mathcal{M}} = \prod_1^{\mathcal{M}} d\omega_m$$

$$d\omega_m = \prod_{\lambda=0}^{\lambda=L_m} d^d r_m(\lambda) \quad (3.3)$$

From a theoretical point of view, the most interesting quantities are the probabilities associated with given configurations of the extremities of the chains. They may not be very easily measurable but at least they correctly describe the main correlation effects and they have a very simple interpretation.

For this reason, we consider the probabilities :

$$\mathcal{S}(\mathbf{r}_1, \dots, \mathbf{r}_{2\mathcal{M}}; L_1, \dots, L_{2\mathcal{M}}) =$$

$$= [Vl^{-d}]^{\mathcal{M}} \left\langle \prod_{m=1}^{m=\mathcal{M}} \delta(r_m(0) - r_{2m-1}) \delta[r_m(L_m) - r_{2m}] \right\rangle \quad (3.4)$$

and their Fourier transform

$$\tilde{\mathcal{S}}(\mathbf{k}_1, \dots, \mathbf{k}_{2\mathcal{M}}; L_1, \dots, L_{2\mathcal{M}}) = [V(2\pi l)^{-d}]^{\mathcal{M}} \times$$

$$\times \left\langle \exp \left\{ -i \sum_{m=1}^{m=\mathcal{M}} \left[\mathbf{k}_{2m-1} \cdot \mathbf{r}_m(0) + \mathbf{k}_{2m} \cdot \mathbf{r}_m(L_m) \right] \right\} \right\rangle.$$

These quantities can be expanded in terms of the interaction and the functional integrals can be eliminated as follows.

Let us consider one chain ($\mathcal{M} = 1$) of length L , a set of lengths $\lambda_1 \dots \lambda_J$ and a set of momenta $\mathbf{q}_1, \dots, \mathbf{q}_J$.

For a free chain (no interaction), we define the mean value

$$I\{\mathbf{q}, \lambda\} = \left\langle \exp \left\{ -i \left[\mathbf{k}_0 \cdot \mathbf{r}(0) + \mathbf{k}_1 \cdot \mathbf{r}(L) + \sum_{j=1}^{j=J} \mathbf{q}_j \cdot \mathbf{r}(\lambda_j) \right] \right\} \right\rangle_0 \quad (3.5)$$

A simple calculation shows that

$$I\{\mathbf{q}, \lambda\} = (2\pi)^d V^{-1} \delta(\mathbf{k}_0 + \mathbf{k}_1 + \mathbf{q}_1 + \dots + \mathbf{q}_J) \times$$

$$\times \exp \left\{ -l[\lambda_1 \mathbf{k}_0^2 + (\lambda_2 - \lambda_1) (\mathbf{k}_0 + \mathbf{q}_1)^2 + \dots + (\lambda_J - \lambda_{J-1}) (\mathbf{k}_0 + \mathbf{q}_1 + \dots + \mathbf{q}_{J-1})^2 + (L - \lambda_J) (\mathbf{k}_0 + \mathbf{q}_1 + \dots + \mathbf{q}_J)^2] \right\}. \quad (3.6)$$

On the other hand in $\mathcal{H}_l(L_1, \dots, L_{\mathcal{M}})$, we express the potential in terms of its Fourier transform

$$V[\mathbf{r}_m(\lambda_m) - \mathbf{r}_{m'}(\lambda_{m'})] =$$

$$= \int d^d q \tilde{V}(\mathbf{q}) \exp \left\{ -i\mathbf{q}[\mathbf{r}_m(\lambda_m) - \mathbf{r}_{m'}(\lambda_{m'})] \right\} \quad (3.7)$$

and therefore with the help of the preceding identity, we can easily find the successive terms of the expansion.

Now, it is convenient to define the *ordered Green's functions*

$$G^{(2,\mathcal{M})}(\mathbf{k}_1, \dots, \mathbf{k}_{2\mathcal{M}}) = l^{\mathcal{M}(d+2)} \int \frac{dL_1}{l} \dots \frac{dL_{\mathcal{M}}}{l} \times$$

$$\times e^{-sLl^{-1}} \tilde{\mathcal{S}}(\mathbf{k}_1, \dots, \mathbf{k}_{2\mathcal{M}}; L_1, \dots, L_{\mathcal{M}}) \quad (3.8)$$

where $L = L_1 + \dots + L_{\mathcal{M}}$.

These functions depend on s but the same notation is used as in section 2, for reasons which will appear obvious below.

These Green's functions will once again be defined by diagrams. Each solid line in the diagram corresponds to one polymer (but this polymer has not any more a definite length).

In order to determine exactly how $G(\mathbf{k}_1, \dots, \mathbf{k}_{2\mathcal{M}})$ must be calculated, we introduce the intermediate expression

$$I(\mathbf{k}_0, \mathbf{k}_1, \mathbf{q}_1, \dots, \mathbf{q}_J) = l^2 \int_0^{\infty} \frac{dL}{l} e^{-sLl^{-1}} \times$$

$$\times \int d\lambda_1, \dots, d\lambda_J I\{\mathbf{q}, \lambda\} \quad (3.9)$$

$$0 < \lambda_1 < \dots < \lambda_J < L.$$

We obtain immediately

$$I(\mathbf{k}_0, \mathbf{k}_1, \mathbf{q}_1, \dots, \mathbf{q}_J) =$$

$$= (2\pi)^d V^{-1} l^{-J} \delta(\mathbf{k}_0 + \mathbf{k}_1 + \mathbf{q}_1 + \dots + \mathbf{q}_J)$$

$$\frac{1}{sl^{-2} + \mathbf{k}_0^2} \frac{1}{sl^{-2} + (\mathbf{k}_0 + \mathbf{q}_1)^2} \dots$$

$$\dots \frac{1}{sl^{-2} + (\mathbf{k}_0 + \mathbf{q}_1 + \dots + \mathbf{q}_J)^2}.$$

Now, we introduce the notation

$$s = m_0^2 l^2 \quad (3.11)$$

and we see by direct inspection of eq. (3.1) and of eq. (3.4) to (3.11) that the rules for calculating the expansion of $G^{(2,\mathcal{M})}(\mathbf{k}_1, \dots, \mathbf{k}_{2\mathcal{M}})$ are exactly those which have been given in section 2. The only difference comes from the fact that, now, we have never any loop in any diagram (see Fig. 2) and this remark shows that for polymers $n = 0$. Thus, we generalize to \mathcal{M} polymers the result of de Gennes [1].

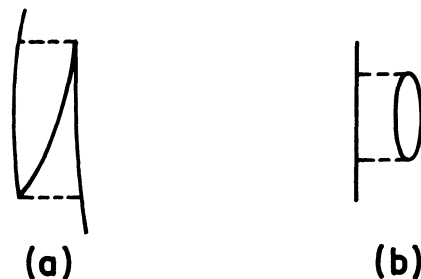


FIG. 2. — a) This diagram appears in polymer theory. b) This diagram does not appear in polymer theory (since $n = 0$).

4. **Lagrangian formalism with external field.** — Let us introduce a constant external field \mathbf{H}_0 . We start with a new action ($\mathbf{H}_0(x) = \mathbf{H}_0$)

$${}^H A \{ \varphi \} = A \{ \varphi \} - \sum_j H_0^j \int d^d x \varphi^j(\mathbf{x}). \quad (4.1)$$

The corresponding generating function for the Green's functions is

$${}^H Z \{ \mathbf{H} \} = \frac{Z \{ \mathbf{H} + \mathbf{H}_0 \}}{Z \{ \mathbf{H}_0 \}}. \quad (4.2)$$

In order to define ${}^H W \{ \mathbf{H} \}$ and its Legendre transform ${}^H \Gamma \{ M \}$, we may rewrite eq. (2.15) as follows

$$M^j(\mathbf{x}) + M_0^j = \frac{\partial W \{ \mathbf{H} + \mathbf{H}_0 \}}{\partial H^j(\mathbf{x})}$$

$$H^j(\mathbf{x}) + H_0^j = \frac{\partial \Gamma \{ \mathbf{M} + \mathbf{M}_0 \}}{\partial M^j(\mathbf{x})}$$

$$W \{ \mathbf{H} + \mathbf{H}_0 \} + \Gamma \{ \mathbf{M} + \mathbf{M}_0 \} - \int d^d x [\mathbf{M}(\mathbf{x}) + \mathbf{M}_0] [\mathbf{H}(\mathbf{x}) + \mathbf{H}_0] = 0. \quad (4.3)$$

The magnetic moment M_0 is related to H_0 in the following way.

We may set

$$\begin{aligned} W \{ \mathbf{H}_0 \} &= V W(H_0) \\ \Gamma \{ \mathbf{M}_0 \} &= V \Gamma(M_0) \end{aligned} \quad (4.4)$$

where $W(H_0)$ and $\Gamma(M_0)$ have finite limits when the volume V becomes infinite. Thus, from (4.3), we deduce the relations

$$M_0 = \frac{\partial W(H_0)}{\partial H_0}$$

$$H_0 = \frac{\partial \Gamma(M_0)}{\partial M_0}$$

$$W(H_0) + \Gamma(M_0) - M_0 H_0 = 0. \quad (4.5)$$

This functional $\Gamma(M_0)$ can be easily expressed in terms of the ordered vertex functions and since

$$M_0(\mathbf{k}) = (2\pi)^{d/2} M_0 \delta(\mathbf{k}) \quad (4.6)$$

we find (see eq. (2.13) and (2.14))

$$\Gamma(M_0) = \sum_{\mathcal{M}=1}^{\infty} \frac{1}{2^{\mathcal{M}} \mathcal{M}!} [M_0 (2\pi)^{d/2}]^{2\mathcal{M}} \Gamma^{(2,\mathcal{M})}(0, \dots, 0). \quad (4.7)$$

Now, we may give the following definitions of ${}^H W \{ H \}$ and ${}^H \Gamma \{ M \}$ which are suggested by the

structure of eq. (4.3)

$$\begin{aligned} {}^H W \{ \mathbf{H} \} &= W \{ \mathbf{H} + \mathbf{H}_0 \} - \\ &\quad - W \{ \mathbf{H}_0 \} - \int d^d x \mathbf{M}_0 \cdot \mathbf{H}(\mathbf{x}) \\ {}^H \Gamma \{ \mathbf{M} \} &= \Gamma \{ \mathbf{M} + \mathbf{M}_0 \} - \\ &\quad - \Gamma \{ \mathbf{M}_0 \} - \int d^d x \mathbf{H}_0 \cdot \mathbf{M}(\mathbf{x}). \end{aligned} \quad (4.8)$$

Thus, by construction, these quantities appear as Legendre transforms of each other (i. e. they satisfy equations similar to eq. (2.15)).

Using these generating functions, we may define *modified Green's functions* or *modified vertex functions* (which again correspond to 1-irreducible diagrams).

Thus, we may set

$$H_0^j = \delta_{1j} H_0 \quad M_0^j = \delta_{1j} M_0 \quad (4.9)$$

and in this case, we find

$$\begin{aligned} {}^H G_{C, j_1 \dots j_N}(\mathbf{k}_1 \dots \mathbf{k}_N) &= \sum_{N'=0}^{\infty} \frac{1}{N'!} [H_0 (2\pi)^{d/2}]^N \times \\ &\quad \times G_{C, j_1 \dots j_N, 1 \dots 1}^{(N+N')}(\mathbf{k}_1 \dots \mathbf{k}_N, 0 \dots 0) \end{aligned} \quad (4.10)$$

$$\begin{aligned} {}^H \Gamma_{j_1 \dots j_N}(\mathbf{k}_1 \dots \mathbf{k}_N) &= \sum_{N'=0}^{\infty} \frac{(-)^{N'}}{N'!} [M_0 (2\pi)^{d/2}]^N \times \\ &\quad \times \Gamma_{j_1 \dots j_N, 1 \dots 1}^{(N+N')}(\mathbf{k}_1 \dots \mathbf{k}_N, 0, \dots, 0). \end{aligned} \quad (4.11)$$

Again, we may define ordered Green's functions and ordered vertex functions but there are several kinds of such functions.

For instance let us consider the vertex function of rank two. When n is an integer, we may define longitudinal and transversal Green's functions by setting

$$\begin{aligned} {}^H \Gamma_{jj}^{(2)}(\mathbf{k}, -\mathbf{k}) &= \delta_{j1} \Gamma_L^{(2)}(\mathbf{k}, -\mathbf{k}) + \\ &\quad + (1 - \delta_{j1}) \Gamma_T^{(2)}(\mathbf{k}, -\mathbf{k}). \end{aligned} \quad (4.12)$$

Using eq. (4.11) and, for vertex functions, an equation exactly similar to eq. (2.11), we obtain

$$\begin{aligned} {}^H \Gamma_T^{(2)}(\mathbf{k}, -\mathbf{k}) &= \sum_{\mathcal{M}=0}^{\infty} \frac{[M_0 (2\pi)^{d/2}]^{\mathcal{M}}}{2^{\mathcal{M}} \mathcal{M}!} \times \\ &\quad \times \Gamma^{(2,\mathcal{M}+2)}(\mathbf{k}, -\mathbf{k}, 0 \dots 0) \end{aligned} \quad (4.13)$$

$$\begin{aligned} {}^H \Gamma_L^{(2)}(\mathbf{k}, -\mathbf{k}) - {}^H \Gamma_T^{(2)}(\mathbf{k}, -\mathbf{k}) &= \sum_{\mathcal{M}=0}^{\infty} \frac{[M_0 (2\pi)^{d/2}]^{\mathcal{M}}}{2^{\mathcal{M}} \mathcal{M}!} \times \\ &\quad \times 2 \mathcal{M} \Gamma^{(2,\mathcal{M}+2)}(\mathbf{k}, 0, -\mathbf{k}, 0 \dots 0). \end{aligned}$$

These functions have also a meaning when n is not an integer and a limit when $n \rightarrow 0$.

5. Representation of polymer solutions by grand ensembles. — Let us consider a large box of volume V containing polymers.

In an infinite space, a quantity such as

$$\tilde{S}(0 \dots 0; L_1 \dots L_{\mathcal{M}})$$

is infinite and meaningless. But, in a large box, we may give a reasonable meaning to such quantities by writing

$$\delta(0) = V(2\pi)^{-d}. \quad (5.1)$$

Using this consistent notation, we see immediately from eq. (3.2) and (3.4) that the number of configurations $Z(L_1, \dots, L_{\mathcal{M}})$ of the polymers in the box is given by :

$$Z(L_1, \dots, L_{\mathcal{M}}) = \tilde{S}(0 \dots 0; L_1 \dots L_{\mathcal{M}}). \quad (5.2)$$

We introduce a grand partition function $Z(H_0)$ depending on two chemical potentials H_0 and $s = m_0^2 l^2$

$$Z(H_0) = 1 + \sum_{\mathcal{M}=1}^{\infty} \frac{1}{2^{\mathcal{M}} \mathcal{M}!} [H_0 l^{(d/2)+1} (2\pi)^{d/2}]^{2\mathcal{M}} \times \int_0^{\infty} \frac{dL_1}{l} \dots \int \frac{dL_{\mathcal{M}}}{l} e^{-sL_1} Z(L_1 \dots L_{\mathcal{M}}) \quad (5.3)$$

with $L = L_1 + \dots + L_{\mathcal{M}}$.

Here $H_0 l^{(d/2)+1}$ must be considered as a dimensionless parameter, and therefore H_0 can be interpreted as a *magnetic field*. The integral $\int l^{-1} dL_p$ amounts to a summation over the links of the chain of order p since the number of links is by definition $N_p = l^{-1} L_p$. Using eq. (3.8) and (5.2), we see immediately that

$$Z(H_0) = 1 + \sum_{\mathcal{M}=0}^{\infty} \frac{1}{2^{\mathcal{M}} \mathcal{M}!} [H_0 (2\pi)^{d/2}]^{2\mathcal{M}} \times G^{(2\mathcal{M})}(0, \dots, 0). \quad (5.4)$$

If, in eq. (2.12), we set

$$H^i(x) = H_0 \delta_{1j} \quad \mathbf{H}(k) = (2\pi)^{d/2} H_0 \delta_{1j} \delta(\mathbf{k}) \quad (5.5)$$

we find that, by proceeding to the limit $n = 0$, we may write

$$Z(H_0) = Z\{\mathbf{H}_0\}_{n=0}. \quad (5.6)$$

Using eq. (2.13) and (4.4), we find

$$Z(H_0) = \exp[VW(H_0)]. \quad (5.7)$$

It is not difficult to show that $W(H_0)$ is directly related to the osmotic pressure P

$$P/KT = W(H_0). \quad (5.8)$$

The concentration C_p of polymers (chains) and the concentration C_m of monomers (links) are given by (see eq. (5.3) and (5.7)).

$$C_p = \frac{\langle \mathcal{M} \rangle}{V} = \frac{H_0}{2} \frac{\partial W(H_0)}{\partial H_0},$$

and

$$C_m = \frac{\langle Ll^{-1} \rangle}{V} = -\frac{\partial}{\partial s} W(H_0). \quad (5.9)$$

In particular, when there is no interaction

$$G^{(2)}(0, 0) = \frac{V(2\pi)^{-d}}{sl^{-2}} \quad (5.10)$$

therefore

$$W(H_0) = \frac{l^2 H_0^2}{2s}. \quad (5.11)$$

Thus, we obtain the classical relation

$$P = KTC_p \quad (5.12)$$

and for the average number of links per chain

$$\mathcal{N} = \frac{C_m}{C_p} = \frac{1}{2s}. \quad (5.13)$$

When there are interactions, the vertex functions are more elementary objects than the connected Green's functions, and therefore it is convenient to express P , C_p and C_m in terms of $\Gamma(M_0)$.

Using eq. (4.5), we find immediately

$$P/KT = M_0 \frac{\partial \Gamma(M_0)}{\partial M_0} - \Gamma(M_0)$$

$$C_p = \frac{M_0}{2} \frac{\partial \Gamma(M_0)}{\partial M_0}$$

$$C_m = \frac{\partial \Gamma(M_0)}{\partial s}. \quad (5.14)$$

Here the quantity s plays the same role as the temperature T for magnetic systems. In the plane (M_0, s) , the half axis ($s > s_c$, $M_0 = 0$) represents infinitely diluted chains. We, then, have $\Gamma(M_0) = 0$ and therefore $C_p = 0$ and $C_m = 0$. On the other hand, the number of links is given approximately by $\mathcal{N} = 1/(s - s_c)$.

On the coexistence curve $\partial \Gamma / \partial M_0 = 0$, $M_0 \neq 0$ and therefore the concentration C_m of monomers remains finite. Thus, the length of the polymers becomes infinite and it is not difficult to see that in this case, the polymers overlap very strongly.

6. Renormalization and scaling law for the osmotic pressure. — Until now all the quantities which have been introduced are unrenormalized and they have a meaning only when the potential has a finite range.

We shall now consider the case, where the short range potential is replaced by a delta function interaction (see eq. (2.7)). Thus

$$V(\mathbf{q}) = g_0 \delta(\mathbf{q}). \quad (6.1)$$

The coupling constant g_0 is not a pure number but it can be written as

$$g_0 = al^{-\varepsilon} \quad (6.2)$$

where $\varepsilon = 4 - d$. Now, a is a pure number which can be chosen as we wish.

In order to obtain finite results within this limit we must first of all renormalize the theory [6]. If $\varepsilon = 4 - d$ is finite, a simple mass subtraction is needed as can be shown by power counting, but if $d = 4$, a field renormalization and a vertex renormalization are also needed. These field and vertex renormalization are useful in both cases for the investigation of the critical behaviours near the critical point, and they are singular at this point. For polymer solutions, this critical domain which we wish to study here corresponds to dilute solutions of long polymers. In other words the concentration of monomers remains small but the polymers are so long that they can overlap with one another.

In the absence of an external field, we may define a renormalized field φ_R and a renormalized mass m by means of two constants $z_1(s)$ and $z_2(s)$. By definition

$$\begin{aligned} \varphi &= z_1(s) \varphi_R \\ m^2 &= z_2(s) [m_0^2 - m_{0c}^2]. \end{aligned} \quad (6.3)$$

As above we assume that $s = m_0^2 l^2$. The mass m_{0c} is the critical mass; it is infinite when there is no cut off but in this case $(m_0^2 - m_{0c}^2)$ remains finite. The coefficients $z_1(s)$ and $z_2(s)$ can be considered as the renormalization constants of the fields φ and φ^2 , respectively.

The relations between the renormalized and unrenormalized Green's functions or vertex function are the following

$$\begin{aligned} G^{(N)}(\mathbf{k}_1 \dots \mathbf{k}_N) &= [z_1(s)]^N G_R^{(N)}(\mathbf{k}_1 \dots \mathbf{k}_N) \\ \Gamma^{(N)}(\mathbf{k}_1 \dots \mathbf{k}_N) &= [z_1(s)]^{-N} \Gamma_R^{(N)}(\mathbf{k}_1 \dots \mathbf{k}_N). \end{aligned} \quad (6.4)$$

The renormalization constants $z_1(s)$ and $z_2(s)$ are determined by the renormalization condition

$$\Gamma_R^{(2)}(\mathbf{k}, -\mathbf{k}) \simeq m^2 + k^2 + \dots \quad (6.5)$$

for small values of k .

Near the critical point ($s \rightarrow s_c$), it can be shown that they may be written as

$$\begin{aligned} z_1(s) &= b(s) (s - s_c)^{(2\nu - \gamma)/2} \\ z_2(s) &= c^2(s) (s - s_c)^{2\nu - 1} \end{aligned} \quad (6.6)$$

where $b = b(s_c)$ and $c = c(s_c)$ are finite.

Eq. (4.2) shows that

$$\Gamma(M_0) = \Gamma_R(M_0/z_1(s)). \quad (6.7)$$

One the other hand, from dimensionality arguments, we find that

$$\Gamma_R^{(2, \mathcal{M})}(0 \dots 0) = f_{\mathcal{M}} m^{d + \mathcal{M}(2-d)}. \quad (6.8)$$

Thus, setting

$$\Psi(X) = (2\pi)^{d/2} \sum_{\mathcal{M}=1}^{\infty} \frac{1}{2^{\mathcal{M}} \mathcal{M}!} f_{\mathcal{M}} X^{2\mathcal{M}} \quad (6.9)$$

we obtain from eq. (4.7) and (6.7) that

$$\Gamma(M_0) = m^d \Psi[M_0 m^{1-(d/2)}/z_1(s)]. \quad (6.10)$$

However, according to eq. (6.3) and (6.6) for small values of $s - s_c$

$$\begin{aligned} ml &= c(s - s_c)^\nu \\ z_1(s) &\simeq b(s - s_c)^{(2\nu - \gamma)/2}. \end{aligned} \quad (6.11)$$

Thus

$$\begin{aligned} \Gamma(M_0) &= l^{-d} c^{d/2} (s - s_c)^{\nu d} \times \\ &\times \Psi(M_0 l^{(d/2)-1} (s - s_c)^{-\beta} c^{1/2} b^{-1}) \end{aligned} \quad (6.12)$$

where β is defined as usual by

$$\beta = \frac{1}{2}(\nu d - \gamma). \quad (6.13)$$

It seems that this function has a singularity when $s \rightarrow s_c$, but this is an illusion. Here s_c plays the role of the critical temperature for magnetic systems. Thus, it is clear that in this case, when an external field is applied, nothing special appears at the critical temperature. Consequently, $\Gamma(M_0)$ must be regular with respect to $(s - s_c)$. This property has been explicitly proved by E. Brezin and J. Zinn-Justin [4], who have shown that for large values of X

$$\Psi(X) \propto X^{\nu d/\beta}. \quad (6.14)$$

Thus, it is convenient to set

$$\begin{aligned} y &= X^{-1/\beta} \\ \Psi(X) &= c^{d/2} y^{-\nu d} \varphi(y) \end{aligned} \quad (6.15)$$

since $\varphi(y)$ is a regular function of y around the value $y = 0$.

Defining two new variables y and z

$$\begin{aligned} z^{-\beta} &= M_0 l^{(d/2)-1} c^{1/2} b^{-1} \\ y &= (s - s_c) z \end{aligned} \quad (6.16)$$

we may write

$$\Gamma(M_0) = z^{-\nu d} \varphi(y). \quad (6.17)$$

On the other hand

$$M_0 \frac{\partial}{\partial M_0} = -\beta^{-1} \left[z \frac{\partial}{\partial z} + y \frac{\partial}{\partial y} \right] \quad (6.18)$$

$$\frac{\partial}{\partial s} = z \frac{\partial}{\partial y}.$$

Thus, eq. (5.14) can be written more explicitly

$$(P/KT) l^d = \beta^{-1} z^{-vd} [(vd - \beta) \varphi(y) - y\varphi'(y)]$$

$$C_p l^d = \frac{1}{2} \beta^{-1} z^{-vd} [vd\varphi(y) - y\varphi'(y)] \quad (6.19)$$

$$C_m l^d = z^{1-vd} \varphi'(y).$$

A measure of the average length per chain is given by

$$\mathcal{N} = \frac{C_m}{C_p} = 2\beta z \frac{\varphi'(y)}{vd\varphi(y) - y\varphi'(y)}. \quad (6.20)$$

These expressions give a parametric representation of the scaling law

$$(P/KTC_c) = F(C_p l^d \mathcal{N}^{vd}) = F\left(\frac{l^d C_m^{vd}}{C_p^{vd-1}}\right). \quad (6.21)$$

They are valid for $y_0 < y < +\infty$ where y_0 is a solution of the equation

$$vd\varphi(y_0) - y_0 \varphi'(y_0) = 0. \quad (6.22)$$

For the corresponding value X_0 of X (i. e. $y_0 = y_0^{-\beta}$) we have (see eq. (6.15))

$$\Psi'(X_0) = 0 \quad (6.23)$$

or according to eq. (6.8)

$$\frac{\partial \Gamma(M_0)}{\partial M_0} = 0. \quad (6.24)$$

Thus, for this value the field H_0 vanishes and this equation defines the spontaneous magnetization curve.

The behaviour of $\varphi(y)$ and $\varphi'(y)$ in the vicinity of y_0 , i. e. the behaviour of $\psi'(x)$ and $\psi(x)$ near the value $x = x_0$ are not exactly known; this point has been only partially studied for $n > 1$ and anomalies appear for $n < 1$.

However, it seems reasonable to assume that $\psi(x_0)$ is finite: thus $\varphi(y_0)$ is also finite and we have

$$\varphi'(y_0) = vd \frac{\varphi(y_0)}{y_0}. \quad (6.25)$$

Accordingly, for high concentrations of monomers eq. (6.19) can be reduced to the simple form

$$(P/KT) l^d = A [C_m l^d]^{vd/vd-1} \quad (6.26)$$

where

$$A = [y_0/vd]^{vd/vd-1} [-\varphi(y_0)]^{1/(vd-1)}. \quad (6.27)$$

This means that, for large values of λ , the asymptotic expression of $F(\lambda)$ (see eq. (6.21)) must be

$$F(\lambda) \simeq A \lambda^{1/(vd-1)}. \quad (6.28)$$

One may wonder whether, in this limit, the chains can be considered as Brownian. To give a precise answer to this question, it is necessary to study correlation functions. However, we may remark that even in the case of strong overlap, the chains cannot be considered as purely Brownian. We must remember that, according to our assumptions each chain is continuous and can always be divided into smaller parts. Then, it appears that a small part of a chain cannot behave in a Brownian way; probably it looks more like a small part of an isolated chain. Thus even in the case of strong overlap, the excluded volume effects cannot be forgotten and this fact appears clearly in eq. (6.28).

7. The scaling law for low concentrations. — For dilute solutions, y is large and X is small and it is therefore convenient to express our results in terms of $\Psi(X)$.

Thus, according to eq. (6.15) and (6.19) we may write

$$P/KTC_p = 2 \frac{[X\Psi'(X) - \Psi(X)]}{X\Psi'(X)}$$

$$C_p l^d \mathcal{N}^{vd} = \frac{l^d C_m^{vd}}{C_p^{vd-1}} = c^{-d/2} \frac{[vd\Psi(X) - \beta X\Psi'(X)]^{vd}}{[X\Psi'(X)]^{vd-1}}. \quad (7.1)$$

We may now use the fact that $\Psi(X)$ can be expanded as a series with respect to X^2 as follows

$$(2\pi)^{-d/2} \Psi(X) = \frac{X^2}{2} + f_2 \frac{X^4}{8} + f_3 \frac{X^6}{48} + \dots \quad (7.2)$$

Consequently, the function $F(\lambda)$ (see eq. (6.21)) can be expanded as a series with respect to λ

$$F(\lambda) = 1 + F_1 \lambda + F_2 \lambda^2 + \dots \quad (7.3)$$

where

$$F_1 = \frac{f_2}{4} \left(\frac{vd-2\beta}{2} \right)^{-vd} c^{d/2}$$

and

$$F_2 = \left[\frac{f_3}{12} + \frac{(f_2)^2}{16} \left(\frac{v^2 d^2}{vd-2\beta} - 4 \right) \right] \left(\frac{vd-2\beta}{2} \right)^{-2vd} c^d. \quad (7.4)$$

The critical indices have been expanded with respect to $\varepsilon = d - 4$, up to third order by Brezin, Le Guillou, Zinn-Justin and Nickel [8]. Unfortunately the series does not converge at all for $\varepsilon = 1$ and it seems reasonable to keep only the first two terms.

Thus for $n = 0$ (and $\varepsilon = 1$), we have

$$\begin{aligned} \nu &\simeq \frac{1}{2} \left[1 + \frac{\varepsilon}{8} + \frac{15 \varepsilon^2}{256} \right] = 0.592 \\ \gamma &= \nu d - 2\beta \simeq 1 + \frac{\varepsilon}{8} + \frac{13 \varepsilon^2}{256} = 1.175. \end{aligned} \quad (7.5)$$

Using the results of Brezin, Le Guillou and Zinn-Justin [9] we find for small values of ε

$$\begin{aligned} c &= (24 \pi^2 \varepsilon^{-1} g_0 l^{-\varepsilon})^{1/8} \\ \frac{\pi^{d/2}}{\Gamma(d/2)} f_2 &\simeq \frac{\varepsilon}{8} \left[1 + \frac{37 \varepsilon}{32} \right] \end{aligned}$$

which gives for $d = 3$, $f_2 \simeq 0.343$.

A second order calculation of $f_3/(f_2)^2$ has been made (see Fig. 3) and we find

$$f_3/(f_2)^2 \simeq \frac{13}{8} \varepsilon + \varepsilon^2 \left(\frac{I}{8} - \frac{147}{256} \right)$$

where

$$I = \int_0^\infty \frac{dt}{1-t+t^2} \ln t \simeq -1.172.$$

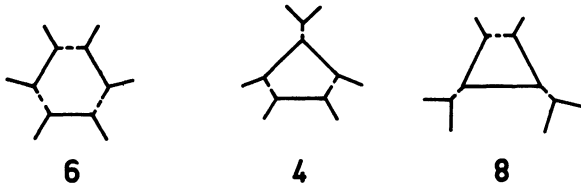


FIG. 3. — Diagrams contributing to f_3 , with their symmetry numbers.

From an experimental point of view, the most interesting quantity is

$$F_2/F_1^2 = \frac{4}{3} f_3/(f_2)^2 + \frac{\nu^2 d^2}{\nu d - 2\beta} - 4.$$

For small ε

$$F_2/F_1^2 \simeq \frac{2\varepsilon}{3} + \left(\frac{I}{6} - \frac{1}{2} \right) \varepsilon^2.$$

For $\varepsilon = 1$, we obtain the approximate result

$$F_2/F_1^2 = 0.362.$$

8. Comparison with previous theories. — Let us now compare our results with those obtained by Edwards [5] and Flory [10].

Using our notation, we may write Edwards' result as follows

$$\begin{aligned} (P/KTC_p) &= 1 + 18(2\pi)^3 a \frac{(l^3 C_m)^2}{l^3 C_p} - \\ &\quad - \sqrt{3}(2\pi)^4 a^{3/2} \frac{(l^3 C_m)^{3/2}}{l^3 C_p} \end{aligned} \quad (8.1)$$

where a is given by eq. (6.2).

Comparing this result with our eq. (6.21) and (7.3), we see immediately that the expression given by Edwards cannot be considered as an expansion for dilute solutions. This is not surprising since Edwards' expression should apply in a domain of concentrations where the chains are supposed to overlap sufficiently to insure strong interactions between neighbouring chains ($\lambda > 1$). We note also that Edwards' result is incompatible with the scaling law given by eq. (6.21). It would become compatible if the last term was dropped, but this would give for ν , the Stockmaier results ($\nu_{St} = \frac{2}{3}$) and we know that this value is not very good. However for large values of λ , our eq. (6.21) and (6.28) give

$$P/KTC_p \simeq A l^{d/(\nu d - 1)} \frac{C_m^{\nu d / \nu d - 1}}{C_p} \quad (8.2)$$

and this result is not very different of the first term given by Edwards since for $d = 3$, $\nu d/(\nu d - 1) \simeq 2.25$.

We may also compare our result with an expression given by Flory [10]

$$P/KTC_p = 1 + \frac{1}{2} UC_p \quad (8.3)$$

where U is the excluded volume associated with two polymer molecules.

However, keeping the first non-trivial term in the expansion of $F(\lambda)$, we find

$$P/KTC_p = 1 + F_1 N^{\nu d} (l^d C_p). \quad (8.4)$$

This formula is in agreement with the expression given by Flory. The polymer molecules can be replaced by hard spheres of radius proportional to N^ν as suggested by Flory. The corresponding excluded volume is therefore proportional to $N^{\nu d}$ and this expectation is consistent with eq. (8.2) and (8.3).

9. Comparison with experimental data (dilute solutions). — In general, the experimental data are expressed in terms of C_m and, therefore, for small values of λ , it is convenient to write our result as follows

$$P/KTC_m = \frac{1}{N} + F_1 N^{\nu d - 2} C_m. \quad (9.1)$$

Thus, by plotting the logarithm of $A_2 = F_1 N^{\nu d - 2}$ versus the logarithm of N (i. e. of M the molecular mass of one polymer), we may calculate ν . The experimental data quoted by Flory [11] in his book give $\nu = 0.62$ for polyisobutylene fractions in cyclohexane and $\nu = 0.61$ for polystyrene fractions in toluene.

Thus, since we know that the exact value of ν is probably not far from the Flory value ($\nu_{Fl} = 0.6$), we see that the present theory agrees rather well with the experimental values.

On the other hand, the crude estimate $F_2/F_1^2 = 0.362$ is quite compatible with the experimental values [12] i. e. $0.1 < F_2/F_1^2 < 0.4$.

10. **Correlation functions for polymers.** — The same kind of discussion can be used to study the properties of the correlation functions by using the formalism given in Sections 4 and 5.

The correlations between the extremities of one polymer are determined by a transverse Green's function which can be expressed in terms of a momentum k and of the parameters y and z . However, for values of y which are not very near to y_0 , we do not expect a very drastic change in the behaviour of this Green function.

On the other hand, if we study the correlations of one end of a polymer with one end of another polymer, we have to deal with the longitudinal Green's functions.

Unfortunately, these functions are not very well known at the present time and much work remain to be done in the future in order to determine precisely their properties.

Conclusion. — In this article, we have shown that the Lagrangian theory can be used to study polymer solutions as well as individual polymer (i. e. chains with excluded volume). However the theory applies only for small concentration of monomers.

We have used a grand ensemble with two chemical potentials and we have shown that in some way a polymer solution is similar to a magnetic system. Thus the chemical potential which is associated with the concentration of monomers corresponds to the temperature of the magnetic system and the chemical potential which is associated with the concentration of polymers corresponds to the magnetic field.

As an application of this formalism, we have derived a scaling law for the osmotic pressure. This law agrees very well with the experimental data and using this result, we find a new method for measuring ν . A calculation of the first terms of the virial expansion has also been made.

Thus, all the results which have been obtained recently illustrate the power of this Lagrangian theory and we anticipate new and interesting applications of this method for investigating the properties of polymers in solutions. The aim of the present article was to show that this is possible, but more work is needed in order to clarify some details and to study the correlation functions.

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 [6] See for instance BREZIN, E., LE GUILLOU, J. C. and ZINN-JUSTIN, J., *Phys. Rev.* **D 8** (1973) 434.
 [7] BREZIN, E. and WALLACE, D. J., *Phys. Rev.* **B 7** (1973) 1967.
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 [9] BREZIN, E., LE GUILLOU, J. C. and ZINN-JUSTIN, J., *Phys. Rev.* **D** (1973) 434. The notation in this article differs from ours. The correspondence is :

$$[g_0]_{\text{BGZ}} = 3(2\pi)^d g_0$$

$$[\Gamma_{(0\dots 0)}^{(2n)} / (2n)!]_{\text{BGZ}} = (2\pi)^{d(n-1)} [\Gamma_{(0\dots 0)}^{(2n)} / 2^n n!]$$

 [10] FLORY, P. J., *Principles of polymer chemistry* (Cornell University Press-Ithaca and London) 1969, ch. XII, eq. (70), p. 531.
 [11] FLORY, P. J., *loc. cit.*, figure 117, p. 536 and figure 118, p. 537.
 [12] YAMAKAWA, H., *Modern theory of polymer solutions* (Harper and Row New York, Evanston, San Francisco, London) ch. 7, p. 360 (in this book our F_3/F_1^2 is called g).