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On the second virial coefficients of two different polymer chains

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Résumé. — Les exposants critiques des seconds coefficients du viriel de deux chaînes différentes sont déterminés au premier ordre en $\varepsilon = 4 - d$ (d = dimension de l'espace), en utilisant la théorie simple des perturbations. Les deux chaînes peuvent exister indépendamment l'une de l'autre aussi bien dans l'état dilaté que dans l'état idéal et, par conséquent, on trouve trois comportements différents décrits par des exposants différents.

Abstract. — The critical exponents of the second virial coefficients of two different chains are determined to order $\varepsilon = 4 - d$ (d = dimensionality of the space), by means of simple perturbation theory. The two chains may exist independently in expanded or ideal states so that three different behaviours are found, described by different critical exponents.

The osmotic pressure Π of a solution of two different polymers in the limit of large dilutions can be written as [1, 2] :

$$\Pi/(RT) = \rho_1 + \rho_2 + A_{11} \rho_1^2 + 2 A_{12} \rho_1 \rho_2 + A_{22} \rho_2^2 + \dots, \quad (1)$$

where ρ_1 and ρ_2 stand for the concentrations of the two species in numbers of macromolecules per volume and A_{ij} [$i, j = 1, 2$] are the second virial coefficients. These three different coefficients describe the interactions between two chains of the first kind, two different chains and two chains of the second kind respectively. They are correlated with the macroscopic behaviour of two interacting chains and they can be written in terms of the partition function of the two chains C_{ij} and the partition functions of the single chains C_i as [3] :

$$A_{ij} = - \frac{V}{2} \left[\frac{C_{ij} - C_i C_j}{C_i C_j} \right], \quad (2)$$

where V is the volume of the system.

Recently the second virial coefficient between two identical chains have been studied by means of renormalization group methods [4, 5]. It was found to be proportional to the volume $\sim N^{vd}$ of the coil written as :

$$A \sim u' N^{vd}, \quad u' = \int dr [1 - \exp(-V(r)/KT)]. \quad (3)$$

In equation (3), N represents the number of units of the chain, ν is the critical exponent of the linear dimensions of the coil, d is the dimensionality of the space and u' , in units of volume, is the excluded volume parameter written in terms of the mean potential $V(\mathbf{r})$ between two polymeric units. In the good solvent region u' is positive and at the dimensionality $d = 4 - \varepsilon$, ν to first order in ε is equal to $\nu = (1/2) + (\varepsilon/16)$ so that

$$A \sim u' N^\delta \quad \text{with} \quad \delta = 2 - (\varepsilon/4). \quad (4)$$

When two different chains are present in the solution three different interaction parameters u'_1 , u'_2 and u'_{12} are possible written in terms of the mean potentials between two similar units from the first and second chains and between two different units from the two chains respectively. The study of properties of two different chains like A_{12} corresponds to the solution of problems with these three interaction parameters. Recently we have studied problems of more than one interaction parameters at $d = 4 - \varepsilon$ [6]. By means of second order perturbation theory the structure of the macroscopic properties was determined by finding the fixed points and the critical exponents [7]. In this work we extend the technique to the study of problems of different chains. The second virial coefficients A_{ij} as given by relation (2) are found.

Two different chains of the same molecular weight and unit length l are considered to occupy the volume V . The probability for their units to be found at the points $\mathbf{R}_i \{ i = 1, 2, \dots, N \}$, $\mathbf{R}'_i \{ i = 1, 2, \dots, N \}$ is given by :

$$P_{12}(\{\mathbf{R}_i\}, \{\mathbf{R}'_i\}) = (d/2\pi l^2)^{Nd} \exp \left\{ - (d/2 l^2) \sum_{i=1}^{N-1} (\mathbf{R}_i - \mathbf{R}_{i+1})^2 - (d/2 l^2) \sum_{i=1}^{N-1} (\mathbf{R}'_i - \mathbf{R}'_{i+1})^2 - \right. \\ \left. - u'_1 \sum_{i=1}^N \sum_{j=1}^N \delta^d(\mathbf{R}_i - \mathbf{R}_j) - u'_2 \sum_{i=1}^N \sum_{j=1}^N \delta^d(\mathbf{R}'_i - \mathbf{R}'_j) - 2 u'_{12} \sum_{i=1}^N \sum_{j=1}^N \delta^d(\mathbf{R}_i - \mathbf{R}'_j) \right\}. \quad (5)$$

The present discrete model [1] in which the positions of the polymeric units are denoted by the N position vectors $\mathbf{R}_i$ is equivalent to the continuous model in which the chain is represented by the continuous line $\mathbf{R}(s)$, where s is the contour length along the chain [8]. We can go from one model to the other by replacing the difference $\mathbf{R}_i - \mathbf{R}_{i+1}$ with the derivative $\frac{d\mathbf{R}(s)}{ds}$ and the summations

with integrations. There are several diagrams in perturbation theory which are equal to multiple summations in the discrete model, while in the continuous model these summations are equivalent to multiple integrations. In the limit of large N 's, the summations can be approximated with integrations so that the two models, beyond some divergences in the limit of small lengths which characterize the continuous model, are interchangeable. The partition function C_{12} of the two chains can be written as $C_{12} = \int \prod_{i=1}^N \prod_{j=1}^N d^d \mathbf{R}_i d^d \mathbf{R}'_j P_{12}(\{\mathbf{R}_i\}, \{\mathbf{R}'_j\})$, so that the second virial coefficient A_{12} up to third order in u 's is given in a diagrammatic language by [7] :

$$A_{12} = u'_{12} \left[\left(\text{---} \right) - u_{12} (4 \text{---} \text{---}) + (2/3) u'^2_{12} (12 \text{---} \text{---} + 24 \text{---} \text{---}) + \right. \\ \left. + u_{12} (u_1 + u_2) (16 \text{---} \text{---} + 8 \text{---} \text{---} + 16 \text{---} \text{---} + 8 \text{---} \text{---} - 4 \text{---} \text{---} 2 \text{---} \text{---}) \right], \quad (6)$$

where the u 's without prime are equal to $u = u'(d/2\pi l^2)^{d/2}$. Notice that the u'_{12} outside the brackets are in units of volume while the u 's without prime inside the brackets are dimensionless. The multiplicities of the topologically different diagrams are written in front of them. The diagrams represent two interacting chains and are produced from the action of the delta functions of equation (5) which bring in contact two different units. For each u_{12} two units from different chains come into contact while for each u_1 or u_2 two units from the same chain come into

contact. In order to find the values of these diagrams the performance of multiple well-behaved summations have to be done. For large molecular weights the summations are approximated with integrations which can also be taken from the continuous model. The finite $\ln N$ parts of

Table I. — *The forms and the values of the diagrams for the second virial coefficients.*

Form of the diagram	Value for $d = 4$
$\text{+} = \int_0^N di \int_0^N dj$	N^2
$\text{8} = \int_0^N di \int_i^N dj \, 1/(j-i)^{d/2}$	$-\ln N$
$\text{X} = \int_0^N di \int_i^N dj \int_0^N dk \int_k^N dl \, 1/(j-i+l-k)^{d/2}$	$N^2 [\ln N + (\varepsilon/4) \ln^2 N]$
$\text{O} = \int_0^N di_1 \int_{i_1}^N dj_1 \int_{j_1}^N dk_1 \int_0^N di_2 \int_{i_2}^N dj_2 \int_{j_2}^N dk_2 \times$ $\times 1/(j_1-i_1+j_2-i_2)^{d/2} (k_1-j_1+k_2-j_2)^{d/2}$	$N^2 \ln^2 N$
$\text{Z} = \int_0^N di_1 \int_{i_1}^N dj_1 \int_{j_1}^N dk_1 \int_0^N di_2 \int_{i_2}^N dj_2 \int_{i_2}^{j_2} dk_2 \times$ $\times 1/(l_1 \, l_2 + l_1 \, l_3 + l_2 \, l_3)^{d/2}, \, l_1=j_1-i_1+k_2-i_2, \, l_2=j_2-k_2, \, l_3=k_1-j_1$	$(1/2) N^2 \ln^2 N$
$\text{Y} = \int_0^N di \int_i^N dj \int_0^i di_1 \int_{i_1}^i dj_1 \int_0^N di_2 \int_{i_2}^N dj_2 \times$ $\times 1/(j-i)^{d/2} (j_1-i_1+j_2-i_2)^{d/2}$	$-N^2 \ln^2 N$
$\text{8} = \int_0^N di \int_i^N dj \int_0^i di_1 \int_j^N dj_1 \int_0^N di_2 \int_{i_2}^N dj_2 \times$ $\times 1/(j-i)^{d/2} (j_1-i_1-j+i+j_2-i_2)^{d/2}$	$\mathcal{O}(N^2 \ln^2 N)$
$\text{X} = \int_0^N di \int_i^N dj \int_i^j di_1 \int_{i_1}^j dj_1 \int_0^N di_2 \int_{i_2}^N dj_2 \times$ $\times 1/(l_1 \, l_2 + l_1 \, l_3 + l_2 \, l_3)^{d/2}, \, l_1=j_2-i_2, \, l_2=j_1-i_1, \, l_3=j-i-j_1+i_1$	$(1/2) N^2 \ln^2 N$
$\text{O} = \int_0^N di \int_i^N dj \int_0^i di_1 \int_j^j dj_1 \int_0^N di_2 \int_{i_2}^N dj_2 \times$ $\times 1/(l_1 \, l_2 + l_1 \, l_3 + l_2 \, l_3)^{d/2}, \, l_1=j_1-i, \, l_2=j-i_1, \, l_3=j_2-i_2+i-i_1$	$(1/2) N^2 \ln^2 N$

these integrations together with their forms are written in table I. By means of the values of the diagrams, A_{12} takes the form :

$$A_{12} = u'_{12} N^2 [1 - 4 u_{12} \ln N - u_{12} \varepsilon \ln^2 N + 16 u_{12}^2 \ln^2 N + 4 u_{12} (u_1 + u_2) \ln^2 N + \dots]. \quad (7)$$

In the cases of problems of a single interaction parameter u like A_{11} and A_{22} which refer to the same species of polymers, or the excluded volume problem of a polymer chain [7], the n th order perturbation term yields a $\ln^n N$ term. For the specific value u^* of the interaction parameter at the fixed point all these terms sum up to an exponential form $e^{a \ln N} = N^a$ giving rise to power laws. The critical exponent a can be determined by means of u^* . In the cases of problems of more than one interaction parameter [6], like A_{12} , the existence of $\ln N$ terms again presages power laws which are characterized by certain critical exponents. These exponents depend on the values of all interaction parameters at the fixed points. An analysis similar to that of single parameter problems can also be followed for the case of problems of more interaction parameters. The exponentiation for example of the series (Eq. (7)) at the fixed points where the interaction parameters take the specific values (u_1^* , u_2^* , u_{12}^*) gives for the second virial coefficients the form :

$$A_{12} \sim u'_{12} N^\delta, \quad \delta = 2 - 4 u_{12}^*, \quad \text{to first order in } \varepsilon. \quad (8)$$

For the series (Eq. (7)) to fit into an exponential function the second order term must be equal with the half of the square of the first order term, so that the following characteristic equation is taken [7] :

$$(1/2) (4 u_{12}^*)^2 = - u_{12}^* \varepsilon + 16 u_{12}^{*2} + 4 u_{12}^* (u_1^* + u_2^*) \Rightarrow 8 u_{12}^* + 4(u_1^* + u_2^*) = \varepsilon. \quad (9)$$

Something to notice is that although equation (9) is a result of the acceptance of the power law (Eq. (8)), for the specific values u_1^* , u_2^* and u_{12}^* , this power law and the meaning of the exponent are valid up to second order regardless of any assumption. The values u_1^* and u_2^* representing excluded volume interactions in the two chains are 0 when the chains are in the ideal state and $\varepsilon/16$ when the chains are in the expanded state [7]. The states of the two chains determine through equation (9) the value u_{12}^* of the interaction parameter between the chains and consequently all properties which depend on u_{12}^* like the second virial coefficients A_{12} . Three different cases are possible for the system of the two chains and these are written in table II together with the values of the critical exponent δ .

Table II. — *The values of the interaction parameters at the fixed points and the critical exponents to order ε .*

States of the chains	u_1^*	u_2^*	u_{12}^*	δ
Two ideal chains	0	0	$\varepsilon/8$	$2 - (\varepsilon/2)$
Two expanded chains	$\varepsilon/16$	$\varepsilon/16$	$\varepsilon/16$	$2 - (\varepsilon/4)$
One ideal + one expanded	$\varepsilon/16$	0	$3 \varepsilon/32$	$2 - (3 \varepsilon/8)$

Under changes of the temperature, the quality of the solvent or the polymers, the interaction parameters u_1 , u_2 and u_{12} vary, falling in this way in the neighbourhoods of the fixed points of

table II where the corresponding macroscopic behaviour occurs. Regarding the exponent δ , for the cases of two ideal or two expanded chains the general formula $\delta = \nu d$ is obeyed [9] while for the case of one ideal and one expanded chain a new exponent emerges lying between these two cases.

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