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BOSON REPRESENTATION OF RAYLEIGH SCATTERING BY CHAIN POLYMERS*

A. HORTA

Institute of Physical Chemistry "Rocasolano" (CSIC), Serrano 119, Madrid 6, Spain

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Abstract—The effect of excluded volume on the particle scattering factor (P) of a linear polymer chain in solution is described in terms of the boson formalism introduced by Fixman. P is calculated with the lowest order boson approximation to the equilibrium distribution, which gives a modified Gaussian function. The results obtained show the variation of P with the excluded volume parameter (z). They are compared with those from other theories.

1. INTRODUCTION

A BOSON formalism has been introduced by Fixman to treat systematically excluded volume forces on flexible polymer chains.[1] The lowest order approximation of such boson formalism is especially useful in the theory of polymer dynamics. It has been used in the calculation of viscosity[2] and translational diffusion[3] and also of geometric properties of the chain in equilibrium, such as the end-to-end distance[1] and the radius of gyration.[4] This same approximation is used in the present work to calculate another equilibrium property: the particle scattering factor (P) which expresses the angular distribution of light scattered by an isolated polymer coil. For a chain with average orientation, P can be written as

$$P(\omega) = \frac{1}{(N+1)^2} \sum_{i=1}^{N+1} \sum_{j=1}^{N+1} \left\langle \frac{\sin \omega r_{ij}}{\omega r_{ij}} \right\rangle. \tag{1}$$

Here ω is related to the difference between incident and scattered wavevectors and depends on the conditions of experiment through

$$\omega = \frac{4\pi}{\lambda} \sin \frac{\theta}{2}, \tag{2}$$

θ being the angle of observation and λ the wavelength of the scattering medium. In Eqn. (1), r_{ij} is the distance between segments i and j of the chain which is assumed to have $(N + 1)$ segments in all. P is directly related to the statistics of the coil because the average in Eqn. (1) is the characteristic function of the distribution $W(\mathbf{r}_{ij})$ of intrachain vector distances:

$$\left\langle \frac{\sin \omega r_{ij}}{\omega r_{ij}} \right\rangle = \int d\mathbf{r}_{ij} \exp (i\boldsymbol{\omega} \cdot \mathbf{r}_{ij})\, W(\mathbf{r}_{ij}). \tag{3}$$

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2. PARTICLE SCATTERING FACTOR

To calculate $<\sin \omega r_{ij}/\omega r_{ij}>$ in the boson theory, r_{ij} has to be translated into boson language and the average formed with the boson operator distribution. Instead of following such direct calculation, this paper will stay within co-ordinate language, avoiding reference to boson operators, by use of the equilibrium distribution function previously calculated with the lowest order boson approximation [Eqn. (26) in Ref. 3]. Such distribution has a Gaussian form and can be written as

$$W(\mathbf{r}_{ij}) = \left(\frac{2}{3}\pi < r_{ij}^2 >\right)^{-3/2} \exp\left(-\frac{r_{ij}^2}{\frac{2}{3} < r_{ij}^2 >}\right) \tag{4}$$

with $< r_{ij}^2 >$ given by

$$< r_{ij}^2 > = \frac{3}{2} \sum_{l=1}^{N} \left(\frac{Q_{il} - Q_{jl}}{a_l}\right)^2 (1 + G_l)^{-1}. \tag{5}$$

All the symbols used in Eqn. (5) have the same meaning as in previous boson papers.[1–4] Q_{il} and a_l are related to the normal co-ordinate transformation which diagonalizes the chain backbone potential. Their values are

$$Q_{il} = \left(\frac{2}{N}\right)^{1/2} \cos l\pi \frac{i}{N} \tag{6}$$

$$a_l = \frac{6^{1/2}}{b_0 \alpha} \sin \frac{l\pi}{2N} \simeq \left(\frac{3}{2}\right)^{1/2} \frac{l\pi}{N b_0 \alpha} \tag{7}$$

where b_0 is the mean length between neighbouring segments in the unperturbed backbone, and α is an expansion factor which defines a uniformly expanded chain as zeroth-order approximation to the excluded volume effect. The real chain is distorted with respect to such uniform expansion and the amount of the distortion is gauged by the G_l's, which are excluded volume force constants. They are given by

$$G_l = \alpha^2 - 1 - \frac{z}{\alpha^3} g_l \tag{8}$$

where the g_l's are just numbers [defined in Eqn. (75) of Ref. 1], and z is the usual dimensionless parameter of excluded volume defined in terms of the binary cluster integral X as

$$z = \left(\frac{2}{3}\pi\right)^{-3/2} \frac{X}{b_0^3} N^{1/2}. \tag{9}$$

The distribution $W(\mathbf{r}_{ij})$, given by Eqns. (4) and (5), depends on excluded volume only through the parameter z because, in the boson theory, α is forced to follow the relation

$$\alpha^5 - \alpha^3 = g_1 z \tag{10}$$

in order that certain boson operator expansions have convenient convergence properties.

The dependence of the particle factor P on scattering angle and coil size will be represented in terms of the variable χ, defined as*

$$\chi = \omega^2 < R^2 > = (Nb_0^2\,\omega^2/6)\,\alpha_R^2. \tag{11}$$

Here $< R^2 >$ is the chain mean square radius of gyration and α_R^2 its expansion factor over the random flight value $Nb_0^2/6$. In the boson theory, α_R^2 is given by [4]

$$\alpha_R^2 = \frac{6a^2}{\pi^2}\sum_{l=1}^{N}(1+G_l)^{-1}\,l^{-2} \tag{12}$$

which is obtained by substitution of Eqn. (5) into

$$< R^2 > = (N+1)^{-2}\sum_{i>j} < r_{ij}^2 >.$$

The form of P, corresponding to the distribution in Eqn. (4), reads

$$P(\omega) = \frac{1}{(N+1)^2}\sum_{i=1}^{N+1}\sum_{j=1}^{N+1}\exp\,(-\,\omega^2 < r_{ij}^2 >/6) \tag{13}$$

with $< r_{ij}^2 >$ given by Eqn. (5).

In the calculation of P, the sums over chain segments in Eqn. (13) have been approximated by integrals according to the transformation $i = Nx$, $j = Ny$, which gives

$$P(\omega) \simeq 2\int_0^1 \mathrm{d}x\int_0^x \mathrm{d}y\,\exp\left(-\,\frac{Nb_0^2\,\omega^2}{6}\,\beta_{xy}(z)\right). \tag{14}$$

The dependence on excluded volume for each pair x, y, is contained in the function $\beta_{xy}(z)$, defined by

$$\beta_{xy}(z) = \sum_{l=1}^{N}\frac{2a^2}{1+G_l}\left(\frac{\cos l\pi x - \cos l\pi y}{l\pi}\right)^2. \tag{15}$$

P has been calculated as a function of χ for different values of the excluded volume parameter z. For each z, χ was calculated according to Eqns. (11) and (12), and P according to Eqns. (14) and (15). The results for the reciprocal scattering factor are shown on Table 1 and Fig. 1. They have been obtained by Gauss quadrature of the integrals in Eqn. (14). The convergence of the sums over l in Eqn. (15) was poor, but could be improved by subtraction of a Fourier series (of a known function) having an asymptotic behaviour (for large l) similar to the one of $\beta_{xy}(z)$. Quadrature with 20 points for each variable and summation over l up to $l = 35$, produced the results shown on Table 1. They are insensitive to an increase in the number of Gauss points or/and in the number of l-terms summed. The values of χ were obtained by extrapolation of the sums in Eqn. (12) after correct summation of the first 1000 terms. Table 2 shows the corresponding values of α_R.

*The use of this variable as argument for P, is discussed in Ref. 6 (where it is called v instead of χ).

TABLE 1. RECIPROCAL PARTICLE SCATTERING FACTOR $P^{-1}(\chi)$ CALCULATED BY THE BOSON THEORY FOR SEVERAL VALUES OF THE EXCLUDED VOLUME PARAMETER z

	P^{-1}							
z =	0	0·0747	0·2432	0·6574	1·7644	4·947	14·658	45·646
χ = 0·5	1·1734	1·1732	1·1728	1·1724	1·1717	1·1707	1·1697	1·1684
1	1·3591	1·3583	1·3567	1·3549	1·3520	1·3481	1·3435	1·3382
2	1·7616	1·7577	1·7511	1·7426	1·7301	1·7135	1·6941	1·6723
3	2·195	2·186	2·170	2·150	2·121	2·083	2·039	1·9913
4	2·650	2·633	2·605	2·567	2·515	2·448	2·373	2·293
5	3·120	3·091	3·047	2·988	2·908	2·808	2·695	2·579
7·5	4·327	4·264	4·169	4·042	3·875	3·674	3·457	3·239
10	5·556	5·450	5·293	5·085	4·818	4·503	4·171	3·845
12·5	6·793	6·639	6·414	6·116	5·739	5·304	4·851	4·414
15	8·036	7·829	7·529	7·136	6·644	6·084	5·507	4·957
20	10·526	10·206	9·747	9·150	8·416	7·595	6·765	5·988
25	13·02	12·58	11·95	11·14	10·151	9·061	7·972	6·964
30	15·52	14·95	14·14	13·11	11·86	10·492	9·142	7·903
40	20·51	19·67	18·50	17·00	15·21	13·28	11·40	9·697
50	25·51	24·39	22·83	20·84	18·51	16·00	13·58	11·41
60	30·51	29·10	27·14	24·66	21·76	18·67	15·71	13·07
70	35·51	33·80	31·43	28·45	24·98	21·31	17·80	14·69
90	45·51	43·19	39·99	35·99	31·34	26·48	21·88	17·83

TABLE 2. EXPANSION COEFFICIENT OF THE RADIUS OF GYRATION CALCULATED BY THE BOSON THEORY AS A FUNCTION OF THE EXCLUDED VOLUME PARAMETER z

z	α_R
0	1
0·0747	1·040
0·2432	1·102
0·6574	1·194
1·7644	1·327
4·947	1·512
14·658	1·764
45·646	2·100

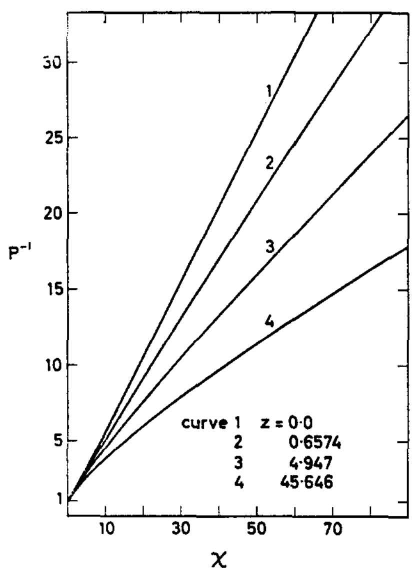

FIG. 1. Influence of excluded volume on the reciprocal scattering factor calculated by the boson theory.

3. DISCUSSION

Existing data on the variation of $P(\chi)$ with excluded volume make it very difficult to compare the present theory with experiment. It is possible to discuss, however, what role it plays among other theoretical approaches. The distribution of chain segments here is a non-uniform Gaussian. Most other theories of the scattering factor P for non-random flight chains, *postulate* the Gaussian nature of the distribution as a simplification. The excluded volume effect (or chain stiffness[5]) is then introduced by assuming a convenient form for the second moment $<r_{ij}^2>$. If we write $<r_{ij}^2>$ proportional to its random coil value

$$< r_{ij}^2 > = b_0^2 \, \alpha_{ij}^2 \, | i - j | \qquad (16)$$

TABLE 3. VALUES OF THE EXCLUDED VOLUME PARAMETER z FOR WHICH THE BOSON THEORY CALCULATES THE SAME $P^{-1}(\chi)$ AS OTHER THEORIES (AT EQUAL χ)

	χ =	z								
		1	3	5	10	20	30	50	70	100
PL,	ϵ = 0·1	1·0	0·8	0·8	0·8	—	0·8	0·9	1·0	—
	0·2	4·1	3·8	3·7	3·7	—	3·9	4·6	4·9	—
	0·3	14·3	12·5	11·3	11·7	—	12·7	15·2	16·2	—
CAC,	σ = 0·6	3·5	2·8	2·4	1·6	—	1·0	0·9	0·8	—
	1·2	16·4	12·1	9·7	6·2	—	3·8	3·2	2·8	—
	1·8	46·4	31·2	23·2	16·0	—	9·0	7·3	6·4	—
Mazur *et al.*[9]		—	—	0·2	0·5	1·0	—	1·9	—	2·7

then the various Gaussian theories differ only in the form attributed to α_{ij}. Two very widely used representations of α_{ij} are the power law (PL)[6–8] and the constant average correlation $<\cos(ij)>$ (CAC)[6] models. The influence of excluded volume on α_{ij} for each of these models is given by

$$\alpha_{ij}^2 = \begin{cases} | i - j |^{\epsilon} & \text{PL} \\ 1 + \delta \, | i - j | & \text{CAC} \end{cases} \tag{17}$$

ϵ and δ being parameters that vanish for random flight chains. In contrast to Eqn. (17), the α_{ij} from the boson theory is not simply related to the difference $| i - j |$, since it depends on i and j in the more complicated way [see Eqn. (5)]:

$$\alpha_{ij}^2 = \left| \frac{i}{N} - \frac{j}{N} \right|^{-1} \sum_{l=1}^{N} \frac{2a^2}{1 + G_l} \left(\frac{\cos l\pi \dfrac{i}{N} - \cos l\pi \dfrac{j}{N}}{l\pi} \right)^2. \tag{18}$$

The boson results for P can be compared with those from the PL and the CAC models in the following way. The P^{-1} values obtained with each one of these two models (for several values of χ and of their excluded volume parameters) are interpolated among those on Table 1. This interpolation, performed at fixed χ, gives the values of z for which the boson theory calculates the same P^{-1} as the model considered. Table 3 shows the z values thus obtained as a function of χ and of the excluded volume parameters ϵ (for PL) and $\sigma = N\delta$ (for CAC). The numbers on Table 3 indicate that the inverse scattering envelopes are very similar in the PL model and in the boson theory. Small differences between the results of both calculations arise in the regions $3 > \chi > 30$, where the deviations from random flight values are larger for the PL curves. The differences between the results of the boson theory and of the CAC model, however, are seen to be considerable. The slopes of the inverse scattering envelopes are smaller (in the whole range of χ shown) for the boson theory than for the CAC model, which means that the form factor with this model has a lower sensitivity to excluded volume effects.

The last row of Table 3 compares the boson results with those reported by Mazur *et al.*[9]* for a non-Gaussian P (calculated with a distribution function obtained from computer experiments of self-avoiding random walks on a lattice). The difference between P^{-1} and its random flight value is seen to increase with growing χ *faster* in Mazur's non-Gaussian results than in the boson ones.

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*The values taken from Ref. 9 for this comparison are for monodisperse systems.

Résumé—On décrit l'effet de volume exclu sur le facteur de diffusion (*P*) d'une particule d'une chaîne polymérique linéaire en solution en utilisant le formalisme de boson introduit par Fixman. *P* est calculé en prenant l'approximation du plus petit ordre du boson comme distribution à l'équilibre, ce qui conduit à une fonction Gaussienne modifiée. Les résultats obtenus présentent la variation de *P* avec le paramètre de volume exclu (z). Ils sont comparés avec les résultats obtenus par d'autres théories.

Sommario—L'effetto del volume escluso sul fattore di scattering di particelle (*P*) di una catena polimerica lineare in soluzione é descritto nei termini del formalismo dei bosoni introdotto da Fixman. *P* é calcolato con l'approssimazione dei bosoni dell'ordine più basso alla distribuzione d'equilibrio, che dà una funzione Gaussiana modificata. I risultati ottenuti mostrano la variazione di *P* con il parametro (z) del volume escluso. Questi sono raffrontati con quelli ottenuti con altre teorie.

Zusammenfassung—Der Einfluß des ausgeschlossenen Volumens auf den Streuformfaktor (*P*) einer linearen Polymerkette in Lösung wird nach dem von Fixman eingeführten "Boson" Formalismus beschrieben. *P* wird mit der niedrigsten Ordnung der "Bosonen" Näherung für die Gleichgewichtsverteilung berechnet, was eine modifizierte Gauss Funktion ergibt. Die Ergebnisse zeigen die Änderung von *P* mit dem Parameter des ausgeschlossenen Volumens (z). Sie werden mit den aus anderen Theorien abgeleiteten Ergebnisse verglichen.