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Binary and ternary cluster integrals of polymer segments as determined by small angle neutron scattering

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Résumé. — On analyse à l'aide de la théorie de Moore les résultats expérimentaux de diffusion de neutrons aux petits angles par des solutions semi-diluées de polystyrène dans le cyclohexane deutéré au voisinage de la température θ obtenus par Cotton *et al.* et on détermine les valeurs des intégrales de vertex à deux et trois corps.

Abstract. — The results of small angle neutron scattering by semi-dilute polystyrene solutions in deuterated cyclohexane near the θ temperature (Cotton *et al.* [3]) are analysed using the theory of Moore [2] and the values of binary and ternary cluster integrals are determined.

In a previous paper [1] we have reported the measurement of small angle X-ray scattering (SAXS) by semi-dilute solutions of polystyrene in poor solvents such as methyl ethyl ketone and cyclohexane, and showed that the results were successfully analysed by the recent theory of Moore [2]. Using this theory we were able to obtain the values of ternary cluster integrals in addition to the binary cluster integrals of polymer segments in these semi-dilute, poor solvent, solutions.

In the present note we show that the results of the small angle neutron scattering (SANS) by semi-dilute solutions of polystyrene in deuterated cyclohexane, reported by Cotton *et al.* [3] also conform to the above mentioned theory and the temperature dependency of binary and ternary cluster integrals of polystyrene in the neighbourhood of the θ temperature (38 °C in this case) can be determined.

We are concerned with the semi-dilute, poor solvent, solutions defined by the following inequalities :

$$\begin{aligned} \frac{4\pi}{3} \left(\frac{1}{6} N b^2 \right)^{3/2} &\gtrsim \frac{N}{\rho} \\ Z_1 \equiv \frac{\beta_1}{b^3} N^{1/2} &< 1 \\ Z_2 \equiv \frac{\beta_2}{b^6} &< 1. \end{aligned} \quad (1)$$

Here b^2 is the mean square length of a polymer segment, N the number of segments in a polymer chain, ρ the overall number density of segments in solution, and β_1 and β_2 are respectively the binary and ternary

cluster integrals of polymer segments in solution. Then the density-density correlation function of polymer segments in semi-dilute poor solvent solutions as calculated by Moore leads to the angular dependence of the intensity of SANS (or SAXS) in the intermediate momentum range

$$\left(\left(\frac{1}{6} N b^2 \right)^{-1/2} < q < b^{-1} \right) :$$

$$I(q) = I(0) \frac{1}{1 + \xi^2 q^2} \quad (2)$$

$$\frac{1}{\xi^2} = 12 \frac{\beta_1}{b^2} \rho + 36 \frac{\beta_2}{b^2} \rho^2. \quad (3)$$

The momentum transfer, q , is given by

$$q = \frac{4\pi}{\lambda} \sin \frac{\theta}{2} \quad (4)$$

where λ is the incident wave length and θ is the scattering angle. As in the previous paper [1], we use, instead of the quantities N , b^2 , β_1 , β_2 and ρ , the observable quantities M , A^2 , B_1 , B_2 and C defined respectively by the following relations,

$$\begin{aligned} M A^2 &= N b^2, \\ M^2 B_1 &= N^2 \beta_1, \\ M^3 B_2 &= N^3 \beta_2, \\ C &= \rho \frac{M}{N_A}, \end{aligned} \quad (5)$$

Fig. 1. — Plots of $1/(\xi^2 C)$ vs. C for a solution of hydrogenous polystyrene in deuterated cyclohexane at various temperatures.

where M is the molecular weight of a polymer molecule and N_A is the Avogadro number. Then eq. (3) reduces to

$$\frac{1}{\xi^2 C} = 12 N_A \frac{B_1}{A^2} + 36 N_A^2 \frac{B_2}{A^2} C. \quad (6)$$

We proceed to analyse the SANS data by Cotton *et al.* [3] for semi-dilute solutions of polystyrene (molecular weight 1 400 000) in deuterated cyclohexane near the θ temperature (38 °C). We have used the values of the screening length ξ as given by table IV in the paper cited and plotted $1/(\xi^2 C)$ against C . As shown in figure 1, $1/(\xi^2 C)$ depends almost linearly on C in accordance with the theoretical prediction (5).

Fig. 2. — Temperature dependences of B_1 and B_2 .

From the figure we were able to determine the values of B_1 and B_2 for various temperatures near the θ temperature. Here, we have used the value of $A = 0.7 \text{ \AA}$ as given in the literature [4]. The temperature dependency of B_1 and B_2 is shown in figure 2. It is remarkable that the behaviours of the cluster integrals B_1 and B_2 bear a strong resemblance to those of second and third virial coefficients of an imperfect gas near its Boyle temperature. We see that the prediction of the scaling theory by Daoud and Jannink [5]

$$\xi^{-2} \sim C^2 \quad (7)$$

is valid in the immediate neighbourhood of the θ temperature. In the close vicinity of the θ temperature, B_1 is expected to behave as

$$B_1 = B_0 \left(1 - \frac{\theta}{T}\right). \quad (8)$$

As shown in figure 3, B_1 as a function of $1 - \theta/T$ is not linear over a wide temperature range. The initial slope of figure 3 gives the value $B_0 = 8 \times 10^{-27} \text{ cm}^3$. Finally, we note that the value of Z_2 is about 0.01 and is almost independent of temperature, whereas the value of Z_1 is less than unity up to about 60 °C. The smallness of Z_2 indicates that the contribution of B_2 to the chain dimensions of polystyrene in cyclohexane is very small and the conformation of polystyrene chains in dilute solutions of cyclohexane is essentially unperturbed at the θ temperature.

Fig. 3. — Variation of B_1 with $\left(1 - \frac{\theta}{T}\right)$. The full straight line shows the initial tangent and has a slope of $8 \times 10^{-27} \text{ cm}^3$.

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