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Dynamic correlation length in polymer solutions at the theta temperature

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Résumé. — Des mesures de sédimentation ont été effectuées dans une large gamme de concentration et de poids moléculaire sur des solutions de polystyrène-cyclohexane à 35,4 °C. L'utilisation d'une fraction de très haut poids moléculaire $20,6 \times 10^6$ nous a permis de dilater le régime semi-dilué vers les faibles concentrations. On en déduit que la longueur de corrélation dynamique ξ_H suit une loi d'échelle en concentration $\xi_H \propto c^{-0,96 \pm 0,04}$, en accord avec les prédictions théoriques.

Abstract. — Sedimentation velocity measurements have been performed in polystyrene-cyclohexane solutions at 35.4 °C. The use of extremely high molecular weight fractions, up to 20.6×10^6 , has enabled us to study the concentration dependence of the dynamic correlation length in the semi-dilute regime. ξ_H scales as $c^{-0.96 \pm 0.04}$ in agreement with theoretical predictions.

Coming after the mean-field description of Flory and Huggins [1], the scaling theory introduced by de Gennes [2] and des Cloizeaux [3] has permitted to describe the static and dynamic properties of flexible polymer solutions, especially in the semi-dilute regime where the chains overlap.

However this approach has been plagued by the experimental evidence in good solvents of slight differences between the static and dynamic scaling exponents of the same physical observable [4, 5]. Recently, Weill and des Cloizeaux have suggested [6] that this discrepancy should not be attributed to a fundamental flaw in the theory but rather to the gradual change of statistics from gaussian to excluded-volume for polymer coils dissolved in good solvents [7]. On the contrary, such complications are non-existent in theta solvents where the chain statistics is gaussian at all scales (neglecting local chain rigidity and small logarithmic corrections which are negligible for all practical purposes [2]). This simplification has given us a strong incentive to start careful dynamic studies of the coil radius of gyration and of the correlation

length over a wide range of concentration and/or molecular weight in theta polymer solutions.

In this letter, we report on sedimentation velocity measurements performed with an analytical ultracentrifuge. In the dilute regime, our data are in good agreement with the numerous earlier determinations of the molecular weight dependence of the hydrodynamic radius of gyration. In the semi-dilute regime, our data allow to measure of the concentration dependence of the dynamic correlation length. The cross-over between these two regimes is also clearly observed.

Polystyrene-cyclohexane solutions at 35.4 °C were selected since they represent the most widely studied case of polymer-theta solvent systems. Monodisperse fractions (4.22×10^5 , 1.26×10^6 , 3.84×10^6 , 8.42×10^6 , 20.6×10^6) were obtained from the Toyo Soda Manufacturing Co. Ltd., Japan. Typical M_w/M_n are 1.05-1.1 except for the highest molecular mass. The chains were first lyophilized from the dilute solutions in a good solvent (benzene,

$$c < 10^{-4} \text{ g.cm}^{-3}),$$

then dispersed in hot cyclohexane and finally slowly brought to their theta point. The sedimentation runs were performed with a Spinco model E analytical ultracentrifuge equipped with a schlieren optical system. The sedimentation velocity V of the chains was measured by the moving boundary peak

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method [8] and converted to the sedimentation coefficient $S = V/\omega^2 r$ (ω = rotor angular velocity, r = distance of the sample cell to the rotation axis).

In dilute solutions where the chains act as individual units, S is related to the molecular mass M and to the hydrodynamic size R_H

$$S \sim M/\eta R_H$$

where η is the solvent viscosity.

In semi-dilute solutions where the chains overlap, Brochard and de Gennes [9] have shown that a similar equation still holds, replacing R_H by the dynamic density-density correlation length ξ_H and the total chain mass by smaller subunits, the blobs, each containing g monomers. This apparently simple picture was actually obtained from a Kubo formula involving the static correlation function for the fluctuations of the monomer concentrations [2]. For gaussian chains, $g \sim c\xi_s^3 \sim (\xi_s/a)^2$ where ξ_s is the static correlation length and a the statistical length. The concentration dependence of ξ_s has been calculated by Daoud and Jannink [10] to be $\xi_s \sim (ca^2)^{-1}$. This implies $g \sim (ca^3)^{-2}$. Assuming that the static and dynamic scaling exponents are identical in theta solvents, we obtain $\xi_s \sim \xi_H \sim c^{-1}$ and

$$R_H \sim R_G \sim M^{1/2}.$$

The sedimentation coefficient in the semi-dilute regime is therefore written very simply as

$$S \sim c^{-1}$$

S is inversely proportional to the concentration and does not depend on molecular weight. On the other hand, the cross-over concentration c^* between the dilute and semi-dilute regimes is reached when the monomer density within a single chain is of the order of the macroscopic monomer density. Therefore

$$c^* \sim \frac{M}{[R_G]^3} \sim M^{-1/2}.$$

The results as a function of concentration are shown on logarithmic scales in figure 1. We have used the notation S_q for the experimental values of the sedimentation coefficient S to indicate that the schlieren pictures have been analysed using a quadratic fit for the position of the boundary peak versus elapsed centrifugation time. A linear fit, which neglects hydrostatic pressure and dilution effects within the sample cell, would give slightly different values, $\approx 10\%$ [11].

At low concentrations, the S data vary by a factor of 7 over the range of chain molecular weights investigated but are only little dependent on concentration. It is customary to write S in the dilute regime as $S = S_0(1 + k_s c)^{-1}$ where k_s is a coefficient which describes the hydrodynamic interaction between sedimenting polymer coils [12]. We observe that

$$k_s = (0.052 \pm 0.010) M^{1/2} \text{ cm}^3 \cdot \text{g}^{-1},$$

Fig. 1. — Sedimentation coefficient of different polystyrene chains S_q versus polymer concentration c . The typical error bar on all points is $\pm 2\%$. The continuous lines correspond to $S_q = S_0(1 + k_s c)^{-1}$ at low concentrations (see text) and to $S_q = 1.15 \times 10^{-14} c^{-0.96}$ at high concentrations but they have no precise meaning in the cross-over region between these two extremes. The arrows indicate the estimated position of the cross-over concentration c^* for each molecular weight.

close to a recent result by Mulderije [13]. In figure 2, it is shown that S_0 , the extrapolated value to infinite dilution, varies with molecular weight as

$$S_0 = 1.50 \times 10^{-15} M^{0.50},$$

in excellent agreement with many earlier determinations [13, 14]. All these results in dilute solutions are very classical and we will not elaborate on them.

Fig. 2. — Sedimentation coefficient extrapolated at infinite dilution S_0 versus square root of molecular mass, $M^{1/2}$.

At high concentrations on the contrary, S becomes molecular weight independent but strongly concentration dependent. Typically S decreases by a factor of 50 between 2×10^{-3} and $8 \times 10^{-2} \text{ g} \cdot \text{cm}^{-3}$ when all the data points for the different molecular weights are combined. A best fit yields $S \sim c^{-\alpha}$ with

$$\alpha = 0.96 \pm 0.04.$$

The cross-over concentration c^* which separates these two different concentration regimes can be

estimated for each polymer fraction from the intersection of the straight lines passing through the lowest concentration data points for each molecular weight with the master curve at high concentrations (drawn as a solid straight line on figure 1). As shown in figure 3, c^* varies inversely proportional to the square root of the molecular mass $c^* = 6.75 M^{-0.50}$. This value is in good agreement with the intrinsic viscosity data of Einaga *et al.* [15]

$$[\eta] = 8.8 \times 10^{-2} M^{0.50} \text{ g}^{-1} \cdot \text{cm}^3.$$

Fig. 3. — Cross-over concentration c^* between the dilute and semi-dilute regimes, deduced from figure 1, versus inverse root square of molecular mass, $M^{-1/2}$.

Indeed it is generally admitted that the product $[\eta] c^*$ should be a constant. Values between 0.6 and 3 have been derived from viscosity measurements by various authors [16, 17]. Here we find that $[\eta] c^* = 0.59 \pm 0.02$.

Sedimentation measurements in the semi-dilute regime of theta polymer solutions have already been reported, mainly by the swedish group [18] and also in the pioneering work of Mijnlief and Jaspers [19]. However, they have been performed on relatively low molecular weight chains ($M \lesssim 10^6$). In the present experiments, much higher molecular weight samples have been used. The exponent value

$$\alpha = 0.96 \pm 0.04$$

of the dynamic screening length ξ_H is measured with unprecedented accuracy. Roots and Nyström have also obtained independently, in a higher concentration range, a similar value of 0.95 ± 0.06 for ξ_H through the study of the cooperative diffusion coefficient by the gradient diffusion technique [20].

The close correspondence between these experimental data with the expected 1.0 value supports the scaling arguments. It could also be argued that the same result is derived from a simple extrapolation of the sedimentation formula developed for the dilute regime :

$$S_q = S_0(1 + k_s c)^{-1}.$$

Indeed

$$S_q \rightarrow S_0(k_s c)^{-1} \sim c^{-1} \quad \text{if } k_s c \gg 1.$$

However this approach cannot describe our experiments satisfactorily : i) the prefactor for $S \propto c^{-1}$ calculated using our independent determination of S_0 and k_s is too small by a factor of 2 compared with our experimental value in the semi-dilute regime, ii) more important, such a simple formula has no sound theoretical basis for solution concentrations where $k_s c$ becomes of order unity, iii) last, it must be realized that the physical processes in the semi-dilute regime involve the flow of solvent through a porous plug of mesh size ξ_H [9, 18] rather than the flow of solvent around relatively impenetrable coils as in the dilute regime.

The molecular weight dependence of the cross-over concentration, $c^* \sim M^{-0.50}$, is also in agreement with the predictions. It should be remarked however that the absolute values given here for c^* are somewhat lower (up to a factor of 6 roughly) than the corresponding data obtained by viscometry [16, 17] or by osmotic pressure [18a, 21, 22] measurements. One possible explanation may be that the sharpness of the cross-over concentration region depends on the property studied and considerable rounding-off may occur in the curves, making difficult a precise determination of the c^* position.

If we now compare these hydrodynamic results for R_H and ξ_H with the corresponding static data, we find that the power law exponents take identical values within experimental accuracy. Several determinations of the static radius of gyration R_G showing that $R_G \sim M^{0.50}$ can be found in the literature [23, 24]. On the other hand, there are two reports by small angle neutron scattering [25] and by osmotic pressure techniques [18] showing that the static correlation length ξ_s scales as $\xi_s \sim c^{-1}$. We thus corroborate, at least in theta solvents, one of the assumption of the scaling approach, i.e. the existence of a single power law exponent to describe the spatial properties of polymer solutions in the dilute and also in the semi-dilute regimes. It is necessary however at this stage to point out that the scaling approach makes no prediction on absolute values and that the different parameters, e.g., ξ_H and ξ_s , may simply be proportional to each other.

In conclusion, we have measured the scaling exponents for the hydrodynamic radius of gyration, the cross-over concentration and the dynamic correlation length of quasi-ideal theta solutions. In all cases, data are found to be in good agreement with their static analogs and also with the earlier dynamic determinations.

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