Dynamic measurements on polymer chain dimensions below the $\theta$-temperature

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Résumé. — Des expériences de diffusion de lumière quasi-élastique et de viscosité sont réalisées en dessous de la température $\theta$ pour observer la contraction d'une chaîne flexible. Les échantillons utilisés sont du polystyrène monodisperse dissous dans du cyclohexane ($M_\text{w} = 1.71 \times 10^5$; $M_\text{w} = 4.11 \times 10^5$; $M_\text{w} = 1.26 \times 10^6$). On observe que :

Les facteurs d'expansion hydrodynamique ($\alpha_H$) et de viscosité ($\alpha_s$) s'échelonnent selon la variable réduite

$$\left(\frac{\theta - T}{T}\right)\sqrt{M}.$$ 

$\alpha_H$ et $\alpha_s$ ont un comportement linéaire dans un « domaine $\theta$ » ($0 \leq \left|\frac{\theta - T}{T}\right|\sqrt{M} \leq 10$) qui est symétrique par rapport à $\theta$.

Le « régime asymptotique collapsé » n'est pas observé pour $\left(\frac{\theta - T}{T}\right)\sqrt{M} \leq 35$.

Abstract. — To observe the contraction of a flexible chain, quasi-elastic light scattering and viscosity experiments were performed below the $\theta$-temperature. The systems used were monodisperse polystyrene ($M_\text{w} = 1.71 \times 10^5$, $M_\text{w} = 4.11 \times 10^5$, $M_\text{w} = 1.26 \times 10^6$) dissolved in cyclohexane. It is observed that :

Hydrodynamic and viscosity expansion factors, $\alpha_H$ and $\alpha_s$, scale with the reduced variable $\left(\frac{\theta - T}{T}\right)\sqrt{M}$.

$\alpha_H$ and $\alpha_s$ have a linear behaviour in a « $\theta$ domain » ($0 \leq \left|\frac{\theta - T}{T}\right|\sqrt{M} \leq 10$) which is symmetric with respect to the $\theta$-temperature.

There is no evidence of an asymptotic collapsed regime for $\left(\frac{\theta - T}{T}\right)\sqrt{M} \leq 35$.

Introduction. — For a flexible polymer chain at the theta temperature, the mean interaction between monomers vanishes and the chain has a Gaussian conformation. At temperature below the Flory theta temperature [2] (near the upper critical solution temperature) the attractive interactions between monomers become important. On cooling, the chain contracts and can reach a globular state. More often the contraction below the $\theta$-temperature is called the « coil globule transition ». A large number of theoretical and experimental works have been devoted to this subject [1-12]. The different analyses lead to similar results presented in a simple way by de Gennes [1]. Static and dynamic measurements have been performed on the « coil globule transition » of a polystyrene chain dissolved in cyclohexane [5-10]. Unfortunately the data are sparse. For instance, D. R. Bauer et al. [6] observed a small contraction of the chain and G. Swislow [9] et al. observed a sharp coil globule transition.

Whatever the sharpness of the transition, the main point of the theory is that the expansion factor must scale with the reduced variable $\frac{T - \theta}{T} \sqrt{M}$ as suggested by the experiments of D. R. Bauer et al. [6].

Here our purpose is, to :

- verify whether the expansion factor scales as $\frac{T - \theta}{T} \sqrt{M}$,
— determine the range of $\frac{T - \theta}{T} \sqrt{M}$, where the globular state regime is reached in the case of the well known system polystyrene cyclohexane.

In order to measure the evolution of the size of the chain two complementary experiments are performed: quasi-elastic light scattering and viscosity measurements.

Part 1 of this paper briefly recalls the theory of the coil globule transition, the experimental conditions are described in part 2, and the results obtained by the two techniques are presented and compared in part 3.

1. Theoretical background. — 1.1 SINGLE CHAIN BEHAVIOUR. INFINITE DILUTION. — Let us consider an isolated chain of $N$ statistical units of length $a$. At $\theta$-temperature, its root mean square end to end distance $R$ is $R_0 \approx a \sqrt{N}$. In a mean field description, the chain expansion factor $\alpha = R/a \sqrt{N}$ can be described with a modified Flory equation [1-4]:

$$\frac{\nu}{a^2} \sqrt{N} \approx \alpha^3 - \alpha^3 - \frac{v}{a^2}$$

(1)

$y$ is a steric coefficient and $v$ is the excluded volume between monomers, which is proportional to the reduced temperature $\tau = \frac{\theta - T}{T}$ [13].

In equation (1), the term (a) corresponds to excluded volume interactions. If $T > \theta$, this term favours a swelling of the chain ($v > 0$); if $T < \theta$ these interactions become attractive ($v < 0$) and favour a chain contraction.

The term (b), due to the chain elasticity, prohibits large swelling and is mainly important when $T > \theta$.

The last term (c), a hard core repulsion, slows down the collapse of the chain, it becomes important for $T \ll \theta$.

If $y$ is a constant independent of $T$ and $N$, equation (1) leads to an expansion factor which is a function of only the reduced variable $\tau \sqrt{N}$. Thus, for any temperature and any number of statistical units, the expansion factor can be represented by a single master curve $\alpha = f(\tau \sqrt{N})$.

In the temperature range where attractive interactions dominate ($T < \theta$), $\alpha$ becomes smaller than 1. From formula (1) when $\alpha \ll 1$, that is in the asymptotic regime, $\alpha$ behaves like $(\tau \sqrt{N})^{-1/3}$. Then the chain is collapsed and its volume is proportional to $N$: $R \sim N^{1/3}$.

From a scaling point of view the expansion factor is $\alpha = f(\tau \sqrt{N})$ where the function $f$ is only known in the asymptotic regimes:

- For $\tau \sqrt{N} \ll 1$, $R \sim R_0 \sim N^{1/2}$ the chain is Gaussian.
- For $\tau \sqrt{N} \gg 1$, $R \sim N^{1/3} \tau^{-1/3}$ the chain is a globule.

Thus a mean field [3, 4] as well as a scaling description [1] lead to the same result: the expansion factor $\alpha$ is a function of the single reduced variable $\tau \sqrt{N}$.

1.2 DILUTE SOLUTIONS. — For a given chain length, at finite concentration $c$ and for $T < \theta$, demixing of a polymer solution takes place at a reduced temperature $\tau_D(c)$. The demixing curve, locus of the point $\tau_D(c)$, exhibits a maximum at a critical concentration $c_c \sim \frac{1}{\sqrt{N}}$, the corresponding critical temperature being $\tau_c \sim \frac{1}{\sqrt{N}}$. Using the coordinates $\tau \sqrt{N}$, $\sqrt{N}$, this diagram is universal [11, 14].

The temperature range of interest, where single chain behaviour can be observed, lies between the $\theta$-temperature and the demixing temperature. As $c$ becomes smaller, the reduced temperature range becomes broader and the better are the conditions to observe a chain collapse.

1.3 EXPERIMENTAL EXPANSION FACTORS. — The usual experiments do not measure the end to end expansion factor:

$$\alpha = \frac{R}{R_0}$$

Actually, using intensity light scattering, quasi-elastic light scattering or intrinsic viscosity experiments, one measures different expansion factors defined by:

$$\alpha_d(T) = \frac{R_d(T)}{R_d(\theta)}$$
$$\alpha_H(T) = \frac{R_H(T)}{R_H(\theta)}$$

(2)
average gives high weight at short distances, a static average gives the same weight everywhere. Thus the temperature cross-over for $a_H$ is broader than for $a_g$.

Assuming an abrupt change from Gaussian to excluded volume statistics, it is found [16] that:

$$a_H = 4 \sqrt{\frac{N}{N_t}} \left[ 2 \left( 3 - \frac{N_t}{N} \right) + \frac{3}{(1-\nu)(2-\nu)} \left( \frac{N}{N_t} \right)^{-1} + (1-\nu) \frac{N_t}{N} + \nu - 2 \right]^{-1}$$

(3)

where $N_t$ is the number of statistical units inside each blob and $\nu$ is the excluded volume exponent $\nu = 3/5$.

Also

$$\frac{N}{N_t} = \gamma \tau^2 N,$$

where $\gamma$ is an adjustable parameter. For $T < \theta$, by analogy to $T > \theta$, we can imagine a symmetric description of the chain conformation, i.e. a chain with Gaussian statistics at short distances and globular statistics at long distances.

Equation (3) for the expansion factor $a_H$ with $\nu = \frac{1}{3}$, corresponds to such a description. It implies that the temperature cross-over is broader for $a_H$ than for $a_g$.

Let us now consider the expansion factor $a_g^2$. Qualitatively the intrinsic viscosity is proportional to the volume of the polymer. Thus there exists a relation between $a_g^2$, $a_g$, and $a_H$. Some years ago it was proposed that [15, 17]:

$$a_g^2 = a_g \cdot a_H$$

(4)

If formula (4) is valid, from our two complementary experiments quasi-elastic light scattering and viscosity measurements, we can deduce the expansion factor of the radius of gyration.

2. Experimental conditions. — 2.1 Light scattering measurements. — The incident light is provided by an argon ion laser $\lambda = 4880\ \AA$. Spectral measurements of the Rayleigh light scattered by solutions are made with a light beating spectrometer.

For homodyne detection, it is necessary to have a clean scattering volume: the solutions are prepared one month in advance and their low viscosity allows any dust particles to fall on the bottom of the optic cell.

The auto-correlation $C(t)$ of the output of the photomultiplier is built up by a 24 channels real time Malvern correlator. (For more details see references [18, 19].) In order to observe the Brownian motion of the whole chain the scattering angles $\theta$ are chosen in such a way that $KR_g \leq 0.6$. Where $K$ is the momentum transfer:

$$K = \frac{4 \pi}{\lambda} n(T) \sin \theta/2$$

(5)

$n(T)$ is the refractive index of the solution at the temperature $T$.

In these conditions, we have:

$$C(t) = A + B e^{-t/\tau_c}$$

(6)

$A$ and $B$ are two adjustable parameters, $\tau_c^{-1} = 2DK^2$, where $D$ is the diffusion coefficient of the chain.

The data are fitted to equation (6) by a least squares three parameters procedure. A single characteristic time $\tau_c$ is determined whatever the sample time $\Delta t$: $\tau_c \leq 24 \Delta t \leq 10 \tau_c$. The good quality of the exponential fit and the precision ($5 \times 10^{-3}$) on the decay time measurements confirm the absence of stray light in the scattering volume. By a variation of a factor 10 on $K^2$, we verify that $\tau_c$ is inversely proportional to $K^2$.

The optical cell is set in a copper jacket [20]. The temperature is regulated within ±0.01°C by an ATNE monitor. Lowest temperatures, down to 14°C, are obtained with a cold water circulation. The temperature measurement is made with two thermo-couples in contact with the cell. These procedures allow us to determine the diffusion coefficient $D(T)$ within an accuracy of ±1% against temperature $T$ determined within ±0.04°C.

2.2 Viscosity measurements. — The viscosity $\eta$ of polystyrene solution ($M_w = 4.11 \times 10^5$) is measured with a capillary viscometer: Cannon-Ubbelohde four-bulb shear dilution (type 505384). The viscometer is immersed in a regulated temperature water bath, the temperature being controlled within ±0.025°C.

The flow times (proportional to the viscosity) are measured at five concentrations ($c \leq 5 \times 10^{-3}$ g/cm³) as a function of temperature. The reproducibility of the flow times measurements is better than ±0.5%. The measurements are done at shear rate ranging from 160 s⁻¹ to 500 s⁻¹; within the accuracy of the measurements no shear rate effects are detected.

2.3 Samples. — The polydispersity has a drastic influence on the shape of the demixing curve. For a polydisperse sample, as $T$ is lowered, the highest molecular weight chains demix first. Thus the average molecular weight of the solution and its average concentration evolve as the temperature decreases. So in our experiments we used the best monodisperse polystyrene available ($M_w/M_n < 1.1$). In order to determine the region where the contraction of a polystyrene chain dissolved in cyclohexane can be observed, a preliminary study of the demixing curves was performed. Even with our low polydispersity samples, these curves do not superpose in $\tau_c(\sqrt{N}$, $c\sqrt{N}$ coordinates [21] (in agreement with the observation of Caroline [7]). For a given value of $c\sqrt{M}$, the higher is the molecular weight the larger is $\tau_c \sqrt{M}$ [22]. For instance at $c\sqrt{M} \sim 4 \times 10^{-2}$, we find:

$$\begin{cases}
\tau_c \sqrt{M} \sim 30 \text{ with } M_w = 1.71 \times 10^5 \\
\tau_c \sqrt{M} \sim 37 \text{ with } M_w = 1.26 \times 10^6.
\end{cases}$$
We did not measure the $\theta$-temperature of the polystyrene-cyclohexane system. We choose $\theta = 35^\circ C$, the temperature at which the second virial coefficient becomes equal to zero [23].

Light scattering experiments were performed on samples with the following characteristics:

- $M_w = 1.71 \times 10^5$, $M_w/M_n \approx 1.02$ and $10^{-4}$ g/cm$^3 \leq c \leq 10^{-3}$ g/cm$^3$.
- $M_w = 1.16 \times 10^6$, $M_w/M_n \approx 1.05$ and $5 \times 10^{-5}$ g/cm$^3 \leq c \leq 5 \times 10^{-4}$ g/cm$^3$.

Viscosity measurements were done on:

- $M_w = 4.11 \times 10^5$, $M_w/M_n < 1.1$ and $6 \times 10^{-4}$ g/cm$^3 \leq c \leq 5 \times 10^{-3}$ g/cm$^3$.

3. Experimental results and discussions. — 3.1 Diffusion coefficient. — The diffusion coefficient $D$ was measured by light scattering at different temperatures for each sample. We made a temperature interpolation of the measurements and a linear extrapolation [22] of $D$ to zero concentration. Thus we obtained the diffusion coefficient of a single chain at a given temperature $T : D_0(T)$. The hydrodynamic radius is obtained from:

$$R_0(T) = \frac{k_B T}{6 \pi \eta_s(T) D_0(T)},$$

$\eta_s$ being the solvent viscosity [24].

The experimental measurements at the $\theta$-temperature (see Fig. 1 and appendix II) are in agreement with previous values [6, 7, 20, 25, 26] $R_0(\theta) \approx 0.23 M^{0.5}$ Å and the theoretical predictions. In figure 1 the dynamical expansion factor $a_H = R_0/R_0(\theta)$ is plotted against the reduced variable $\tau \sqrt{M}$. $a_H$ scales on a single curve [6] for our two different molecular weight samples ($M_w = 1.71 \times 10^5$ and $M_w = 1.26 \times 10^6$) and shows various regimes of behaviour:

- $a_H(\tau)$ is a linear function of reduced temperature in the $< \theta$ domain $\{0 \leq \tau \sqrt{M} \leq 10\}$ [27]. Figure 1 shows that this linear behaviour is obeyed in a temperature range symmetric with respect to $\theta$.
- $a_H(\tau)$ departs from its linear behaviour when $\tau \sqrt{M} > 10$. On figure 3, the experimental data obtained for $T < \theta$ are set in a log-log plot. The effective exponent defined as $\frac{d \log a_H}{d \log (\tau \sqrt{M})}$ varies continuously from 0 down to $-0.2$. The hydrodynamic radius is far from its asymptotic regime where the temperature exponent would be equal to a constant value $-1/3$, following section 1.

The similarity in behaviour of $a_H$ on both sides of $\theta$ suggests that, even for $T < \theta$, there is a strong influence of the spatial cross-over on hydrodynamic properties [15]. Thus in figure 2 we have plotted the transposed calculation of blob model (Eq. (2) with $\gamma = 10^{-3}$ and $v = 1/3$). We have normalized the curve at the edge of the $\theta$ domain ($\tau \sqrt{M} \approx 10$ and $R_0 \approx 0.965 R_0(\theta)$). Such an agreement between the calculated and the experimental behaviour is quite surprising. We recall that in this model, the hydrodynamic temperature cross-over must be broader than the static one. This point has to be verified. To our knowledge, the static experiments [5, 8, 10] are in disagreement among themselves. Anyway the main problem of this model is still the symmetrization with respect to $\theta$ (i.e. the existence of a Gaussian blob for lowest temperatures) which is implicitly assumed in the calculation without any strong justification.
From references [9, 10] the collapse of PS in cyclohexane was observed on a sample of $M_w = 2.6 \times 10^7$ and high polydispersity ($M_w/M_n \approx 1.3$). It would be interesting to check whether, in this range of high molecular weights a $\tau \sqrt{M}$ representation is still universal.

3.2 INTRINSIC VISCOSITY. — Interpolations between measurements made at different temperatures, allow us to have at a given temperature, the variation of the viscosity with the monomer concentration. Intrinsic viscosity $[\eta(T)]$ is obtained by extrapolation of $c^{-1}, \eta_{sp}(T)$ where $\eta_{sp}(T)$ is the specific viscosity $\left(\eta_{sp}(T) = \frac{\eta(T)}{\eta_s(T)} - 1\right)$. For the molecular weight $M_w = 4.11 \times 10^5$, the intrinsic viscosity at the temperature $[\eta(\theta)]$ is equal to $53 \pm 3 \text{ cm}^3/\text{g}$, in agreement with values reviewed in reference [28].

$\alpha_\theta(T)$ is obtained in two different ways by using equation (2) and $\alpha_\theta = \lim_{c \to 0} \eta_{sp}(T, c)/\eta_{sp}(\theta, c)$. Within experimental accuracy both treatments lead to the same value.

On figure 3 we give the variation of $\alpha_\theta$ versus the reduced variable $\tau \sqrt{M}$ in a log-log plot. The dotted line represents a linear behaviour and the full line a power law with slope $-1$. $\alpha_\theta = 4.41 \times 10^5$ present work, $\times M_w = 7.56 \times 10^5$ from reference [29] and $\eta M_w = 3.2 \times 10^6$ from reference [30].

On figure 3 we give the variation of $\alpha_\theta$ versus $\tau \sqrt{M}$ in a log-log plot. The dotted line represents a linear behaviour and the full line a power law with slope $-1$. $\alpha_\theta = 4.41 \times 10^5$ present work, $\times M_w = 7.56 \times 10^5$ from reference [29] and $\eta M_w = 3.2 \times 10^6$ from reference [30].

In fact, equation (4) is only an approximation (see appendix I). We have:

$$\alpha_\theta^3 = \beta \alpha_\theta^2 \alpha_H$$

where $\beta$ is a numerical factor depending on temperature and chain statistics. By normalization $\beta = 1$ at the $\theta$ point and $\beta = 1.7$ in the globular state. It seems reasonable to assume that $\beta$ has a monotonic variation between the two asymptotic regimes. So, from the numerical evaluations, $\beta$ increases when the temperature decreases which could explain that experimentally $\alpha_\theta$ is larger than $\alpha_\theta^2$.  

4. Conclusion. — From this set of experiments it appears that hydrodynamic and viscosity expansion factors, $\alpha_H$ and $\alpha_\theta^2$ respectively, scale in a $\left(\frac{\theta - T}{T}\right) \sqrt{M}$ representation which is in agreement with theory [1, 3, 4]. This confirms the hypothesis that the steric viscosity and radius of gyration measured by neutron scattering [5].

We see that for $10 \leq \tau \sqrt{M} \leq 25$ the factor $\alpha_\theta^3$ cannot be described by a simple power law $\alpha_\theta^3 \sim \tau^{-1}$.

Following equation (4) from our two kinds of experiments, we can deduce the expansion factor of the radius of gyration $\tilde{\alpha} = (\alpha_\theta^3/\alpha_H)^{1/2}$. In figure 4, we compare our $\tilde{\alpha}$ with the $\alpha_\theta$ obtained from neutron scattering experiment [5] in the same range of $\tau \sqrt{M}$. We found that : for $\tau \sqrt{M} \leq 10$, $\tilde{\alpha}$ coincides with $\alpha_\theta$ but for $\tau \sqrt{M} \geq 10$, $\tilde{\alpha}$ is larger than $\alpha_\theta$.  

4. Conclusion. — From this set of experiments it appears that hydrodynamic and viscosity expansion factors, $\alpha_H$ and $\alpha_\theta^2$ respectively, scale in a $\left(\frac{\theta - T}{T}\right) \sqrt{M}$ representation which is in agreement with theory [1, 3, 4]. This confirms the hypothesis that the steric

Fig. 3. — Variation of the viscosity expansion factor $\alpha_\theta^2$ versus $\tau \sqrt{M}$ on a log-log scale. The dotted line represents a linear behaviour and the full line a power law with slope $-1$. $\alpha_\theta^2$ present work, $\times M_w = 7.56 \times 10^5$ from reference [29] and $\eta M_w = 3.2 \times 10^6$ from reference [30].

Fig. 4. — Comparison between the expansion factors : $\alpha_H$, $\alpha_\theta$ and $\tilde{\alpha}$ in a log-log plot. The symbols are the same as in figures 1, 2, 3 and 4. $M_w = 2.9 \times 10^4$ from reference [5]. For $\theta - T / \sqrt{M} < 10$ the dotted line represents the linear behaviour of $\alpha_H$. For $\theta - T / \sqrt{M} > 10$ the lines have the same meaning as in figure 2.
coefficient \( y \) in equation (1) is temperature independent.

Hydrodynamic radius data, above and below the \( \theta \)-temperature, show that a « \( \theta \) domain » exists, symmetric with respect to \( \theta \). In this « \( \theta \) domain » the chain is essentially Gaussian and the variation of the expansion factor can be expressed by a linear approximation. Whatever the measurement, the \( \theta \) domain corresponds to \( \frac{\theta - T}{T} \sqrt{M} \leq 10 \) for the polystyrene-cyclohexane system.

In the present dynamic measurements up to \( \left( \frac{\theta - T}{T} \right) \sqrt{M} \sim 35 \) a cross-over regime is observed but no collapsed asymptotic behaviour. It would be interesting to make new experiments to clear two main points:

- For \( T < \theta \), is there a different temperature cross-over for static and dynamic magnitudes?
- Is the scaling in \( T \sqrt{M} \) respected even for high molecular weight monodisperse samples? Or is there a high molecular weight effect related to self entanglements, playing an important role and inducing the sharp collapse of the chain observed by Tanaka?

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Appendix I. — INTRINSIC VISCOSITY AT THE \( \theta \) POINT.

— Following the formula (86, 97b) of Zimm’s paper [31] for the case of large hydrodynamic interactions, we have:

\[
[\eta] = 3.3 \pi N_A \frac{R_H^2}{R_e} \frac{R_H}{M} \quad (A. 1)
\]

\( R_H \) is defined in section 3.1 and \( R_e = R / \sqrt{6} \) if \( R \) is the root mean square end to end distance. \( N_A \) is the Avogadro number and \( M \) is the molecular weight of the polymer.

INTRINSIC VISCOSITY IN THE GLOBULAR STATE AND RELATION BETWEEN THE DIFFERENT EXPANSION FACTORS.

— Following Einstein formula and Stokes law [32]; we have:

\[
[\eta] = \frac{10 \pi N_A}{3} \frac{R_H^3}{M} \quad (A. 2)
\]

For a globule \( R_g = R_H \sqrt{3/5} \) and

\[
[\eta] = 5.5 \pi N_A \frac{R_H}{R_g} \frac{R_H^2}{M} \quad (A. 3)
\]

Equations (A.1), (A.3) lead to:

\[
\alpha_g^3 = 1.7 \alpha_\eta^2 \alpha_H
\]

in the globular state.

**Appendix II.** — Experimental values of \( R_H (\AA) \) deduced from light scattering measurements (accuracy of 1 %) and viscosity expansion factor from intrinsic viscosity measurements, at different temperatures.

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References and notes


[13] For convenience we use a $\tau$ definition of the opposite sign of the usual one.


[21] The number of statistical units $N$ in the chain is proportional to the molecular weight $M_w$ of the polymer. Then\[\tau \sqrt{N} \approx \tau \sqrt{M_w} .\]

[22] Our preliminary results will be published later.


[24] The $\kappa(T)$ temperature dependence is taken into account as in reference [19].


[27] $|\tau \sqrt{M}| \sim 10$ is equivalent to $|\tau| \sim |\tau^*|$ in reference [19].


