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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 (\( M_w = 1,71 \times 10^5 ; M_w = 4,11 \times 10^5 ; M_w = 1,26 \times 10^6 \)). On observe que :  
— Les facteurs d'expansion hydrodynamique (\( \alpha_H \)) et de viscosité (\( \alpha_3 \)) s'échelonnent selon la variable réduite  
\[
\left( \frac{\theta - T}{T} \right) \sqrt{M}.
\]
— \( \alpha_H \) et \( \alpha_3 \) ont un comportement linéaire dans un « domaine \( \theta \) »  
\[
0 \leq \left| \frac{\theta - T}{T} \right| \sqrt{M} \lesssim 10
\]
qui est symétrique par rapport à \( \theta \).  
— Le « régime asymptotique collasé » n'est pas observé pour  
\[
\left( \frac{\theta - T}{T} \right) \sqrt{M} \lesssim 35.
\]

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 (\( M_w = 1,71 \times 10^5 \), \( M_w = 4,11 \times 10^5 \), \( M_w = 1,26 \times 10^6 \)) dissolved in cyclohexane. It is observed that :  
— Hydrodynamic and viscosity expansion factors, \( \alpha_H \) and \( \alpha_3 \), scale with the reduced variable  
\[
\left( \frac{\theta - T}{T} \right) \sqrt{M}.
\]
— \( \alpha_H \) and \( \alpha_3 \) have a linear behaviour in a « \( \theta \) domain »  
\[
0 \leq \left| \frac{\theta - T}{T} \right| \sqrt{M} \lesssim 10
\]
which is symmetric with respect to the \( \theta \)-temperature.  
— There is no evidence of an asymptotic collapsed regime for  
\[
\left( \frac{\theta - T}{T} \right) \sqrt{M} \lesssim 35.
\]

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 perfo-
med: quasi-elastic light scattering and viscosity
measurements.

Part 1 of this paper briefly recalls the theory of the
coil globule transition, the experimental condi-
tions 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 descrip-
tion, the chain expansion factor $\alpha = R/a \sqrt{N}$ can be
described with a modified Flory equation [1-4]:

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

(a) (b) (c)

$y$ 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 inter-
actions 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
$T < \theta$.

If $y$ is a constant independent of $T$ and $N$, equa-
tion (1) leads to an expansion factor which is a function
of the single 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 inter-
actions 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 $\tau \sqrt{N} \gg 1$, $R \sim N^{1/3} \cdot \tau^{-1/3}$ the chain is a
globule.

Thus a mean field [3, 4] as well as a scaling descrip-
tion [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 tem-
perature $\tauD(c)$. The demixing curve, locus of the
point $\tauD(c)$, exhibits a maximum at a critical concen-
tration $c_c \sim \frac{1}{N}$, the corresponding critical tempe-
rate being $T_c \approx \frac{1}{N}$.

Using the coordinates $T$, $\ln N$, $c$, 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 experi-
ments, one measures different expansion factors
defined by:

$$\alpha_g(T) = \frac{R_g(T)}{R_g(\theta)}, \quad R_g \text{ is the radius of gyration}.$$  

$$\alpha_H(T) = \frac{R_H(T)}{R_H(\theta)}, \quad R_H \text{ is the hydrodynamic radius}.$$  

$$\alpha_\eta(T) = \left[ \frac{\eta(T)}{\eta(\theta)} \right], \quad [\eta] \text{ is the intrinsic viscosity}.$$  

(2)

If the conformation of the chain is the same on all
length scales the different mean values $\alpha_g, \alpha_H, \alpha_\eta$ are
proportional to $\alpha$. This condition is only realized at
the $\theta$ point and in the asymptotic regimes far from the
theta point ($\tau \sqrt{N} \gg 1$).

Above the $\theta$ point and for $\tau \sqrt{N} \gg 1$, refe-
rences [15, 16] consider the chain as a succession
of blobs, the chain has Gaussian statistics inside
the blobs (short distances) and excluded volume
statistics outside the blobs. The expansion factors,
$\alpha_g = \frac{R_g}{R_g(\theta)}$ and $\alpha_H = \frac{R_H}{R_H(\theta)}$ are calculated in refer-
ence [16] using the blob model. A hydrodynamic
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:

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

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

Also

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

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 $\nu = 3/5$, 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 $a_g$. Qualitatively the intrinsic viscosity is proportional to the volume of the polymer. Thus there exists a relation between $a_H^3$, $a_g$ and $a_H$. Some years ago it was proposed that [15, 17]:

$$a_H^3 = a_g^2 a_H.$$  \hspace{1cm} (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 $\lambda = 4880$ Å. 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:

$$K = \frac{4\pi}{\lambda} n(T) \sin \theta/2$$  \hspace{1cm} (5)

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

In these conditions, we have:

$$C(t) = A + B e^{-t/\tau_c}$$  \hspace{1cm} (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 $\pm 0.01 \degree C$ by an ATNE monitor. Lowest temperatures, down to 14 $\degree C$, 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 $\pm 1\%$ against temperature $T$ determined within $\pm 0.04 \degree C$.

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 $\pm 0.025 \degree C$.

The flow times (proportional to the viscosity) are measured at five concentrations ($c \leq 5 \times 10^{-3}$ g/cm$^3$) as a function of temperature. The reproducibility of the flow times measurements is better than $\pm 0.5 \%$.

The measurements are done at shear rates 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 $c\sqrt{N}$, $c\sqrt{N}$ 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 $\tau_p\sqrt{M}$ [22]. For instance at $c\sqrt{M} \sim 4 \times 10^{-2}$, we find:

$$\tau_p/\sqrt{M} \sim 30 \text{ with } M_w = 1.71 \times 10^5$$
$$\tau_p/\sqrt{M} \sim 37 \text{ with } M_w = 1.26 \times 10^6.$$
We did not measure the $\theta$-temperature of the polystyrene-cyclohexane system. We choose $\theta = 35 \, ^\circ\mathrm{C}$, 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 $10^{-4} \, \text{g/cm}^3 \leq c \leq 10^{-3} \, \text{g/cm}^3$.
- $M_w = 1.16 \times 10^6$, $M_w/M_n \approx 1.05$ and $5 \times 10^{-5} \, \text{g/cm}^3 \leq c \leq 5 \times 10^{-4} \, \text{g/cm}^3$.

Viscosity measurements were done on:
- $M_w = 4.11 \times 10^5$, $M_w/M_n < 1.1$ and $6 \times 10^{-4} \, \text{g/cm}^3 \leq c \leq 5 \times 10^{-3} \, \text{g/cm}^3$.

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:

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

with $\eta_s$ 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] $R_h(\theta) \approx 0.23 \, M^{0.5} \, \AA$ and the theoretical predictions. In figure 1 the dynamical expansion factor $\alpha_H = R_H/R_h(\theta)$ is plotted against the reduced variable $\tau \sqrt{M}$. $\alpha_H$ 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:

- $\alpha_H(\tau)$ 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 $\theta$.

- $\alpha_H(\tau)$ 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 $\frac{\partial \log \alpha_H}{\partial \log (\tau \sqrt{M})}$ 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 $\alpha_H$ 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 $\gamma = 10^{-2}$ and $v = 1/3$). We have normalized the curve at the edge of the $\theta$ domain ($\tau \sqrt{M} \approx 10$ and $R_H \approx 0.965, R_h(\theta)$). 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. Intrinsici viscosity $[\eta(T)]$ is obtained by extrapolation of $c^{-1} \eta_{sp}(T)$ where $\eta_{sp}(T)$ is the specific viscosity $\left( \frac{\eta_{sp}(T)}{\eta_s(T)} - 1 \right)$. For the molecular weight $M_w = 4.11 \times 10^5$, the intrinsic viscosity at the $\theta$-temperature $[\eta(\theta)]$ is equal to $53 \pm 3 \text{ cm}^3/\text{g}$, in agreement with values reviewed in reference [28].

$\alpha_3^\phi(T)$ is obtained in two different ways by using equation (2) and $\alpha_3^\phi = \lim_{c \to 0} \eta_{sp}(T, c)/\eta_{sp}(\theta, c)$. Within experimental accuracy both treatments lead to the same value.

On figure 3 we give the variation of $\alpha_3^\phi$ 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 $-1$. $\circ M_w = 4.11 \times 10^5$ present work, $\times M_w = 7.56 \times 10^4$ from reference [29] and $\nabla M_w = 3.2 \times 10^6$ from reference [30].

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

$$\alpha_3^\phi = \beta \alpha_3^\phi,$$

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 $\tilde{\alpha}_3$ is larger than $\alpha_3^\phi$.

4. Conclusion. — From this set of experiments it appears that hydrodynamic and viscosity expansion factors, $\alpha_H$ and $\alpha_3^\phi$ respectively, scale in a $\tau \sqrt{M}$ representation which is in agreement with theory [1, 3, 4]. This confirms the hypothesis that the steric
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 \( \frac{\theta - T}{T} \sqrt{M} \lesssim 10 \) for the polystyrene-cyclohexane system.

In the present dynamic measurements up to \( \frac{\theta - T}{T} \sqrt{M} \sim 35 \) 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 crossover for static and dynamic magnitudes?
- Is the scaling in \( \tau \sqrt{M} \) 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?

Acknowledgments. — The authors thank J. Lebowitz and J. P. Cotton for stimulating discussions. One of us M. D. thanks H. Yu and J. D. Ferry for their hospitality.

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:

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

\( R_H \) is defined in section 3.1 and \( R_H = R_\delta \sqrt{6} \) 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.

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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<th>( M_w = 1.26 \times 10^6 )</th>
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References and notes


[13] For convenience we use a τ 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] \(
\tau \sqrt{M} \approx 10 \) is equivalent to \( \tau \sim \tau^* \) in reference [19].


