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Temperature dependence of hydrodynamic lengths in the polystyrene-cyclohexane system

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Résumé. — Nous présentons des résultats expérimentaux sur le comportement dynamique du système polystyrène-cyclohexane en fonction de la température au voisinage du point θ (0 ≤ T - θ < 30 °C). Il est trouvé que la dépendance en température des rayons hydrodynamiques, RH et ξH, d'une chaîne en régime dilué et d'un blob en régime semi-dilué sont respectivement :

\[ RH \sim (T - \theta)^{0.034 \pm 0.005} \]
\[ \xi_H \sim (T - \theta)^{-0.33 \pm 0.04} . \]

Nous montrons que ces variations sont dues à la relative insensibilité des longueurs hydrodynamiques aux effets de volume exclu. Les comportements observés semblent compatibles avec l'interprétation sur l'exposant dynamique apparent par Weill et des Cloizeaux.

Abstract. — We present experimental data on the dynamic temperature behaviour of the polystyrene-cyclohexane system in the neighbourhood of the θ point (0 ≤ T - θ < 30 °C). It is found that the temperature dependence of the hydrodynamic radii RH and ξH of a chain in dilute regime and a blob in semi-dilute regime are respectively :

\[ RH \sim (T - \theta)^{0.034 \pm 0.005} \]
\[ \xi_H \sim (T - \theta)^{-0.33 \pm 0.04} . \]

We show that these variations are due to the relative insensitivity of the hydrodynamic lengths to excluded volume effects. The behaviours observed seem compatible with the Weill-des Cloizeaux explanation on the apparent dynamic exponent.

1. Introduction. — It has been shown, in the past few years, that the dynamic properties of dilute and semi-dilute polystyrene solutions can be deduced from the static properties if an effective dynamical exponent v_H, smaller than the static exponent v, is introduced [1]. The aim of this study is to compare static and dynamic temperature scaling laws. The static laws, deduced from an analogy, between critical phenomena and polymer systems, have been verified by elastic neutron scattering [2]. Here we report the dynamic temperature scaling laws obtained from Rayleigh light scattering experiments on polystyrene-cyclohexane system.

In the first part we recall the static scaling laws and their extension to dynamic temperature laws obtained with the help of phenomenological arguments. Then, we report experimental results obtained in well defined temperature concentration domains. The specifications of these domains have been done using theory and static experimental results [2]. The data are fitted to power laws [23], in order to compare those results with :

— previous static [2] and dynamic results [1],
— scaling laws theory [2, 17],
— the different explanations on the dynamic exponent v_H (effective or real exponent [3, 4]).

Finally we discuss the comparison of our results with the recent Weill-des Cloizeaux explanation [3] of an effective exponent v_H.

2. Theoretical considerations. — A polymer solution is considered [5] as :

— dilute, if intermolecular interactions can be neglected. In this case the characteristic length is R the radius of gyration of the chain ;
— semi-dilute, if intermolecular interactions are dominant. In a semi-dilute solution the chains inter-penetrate each other and the monomer concentra-
tion [6] is bigger than the overlap concentration \( c^* \) defined by: \( c^* \approx N/R_3 \), where \( N \) is the number of statistical elements in a chain;

— **concentrated**, if the monomer concentration is of the order of magnitude of the solvent concentration. We will not consider them, here.

### 2.1 Dilute Regime.

We consider an isolated chain of \( N \) statistical elements at a temperature \( T \), above the \( \theta \) point. The \( \theta \) point corresponds to the temperature where intramolecular interactions vanish. The mean distance between two monomers, separated by \( n \) statistical elements, has a Gaussian behaviour if \( n < n_c \) and an *excluded volume* behaviour if \( n > n_c \).

The \( n_c \) value can be derived from an extension of the well known Flory equation of the expansion factor [8]:

\[
\alpha^5 - \alpha^3 \approx (v/l^3) n^{1/2}
\]

where \( l \) is the length of a statistical element and \( v \) the excluded volume parameter. The excluded volume interactions are dominant when \( \alpha \gg 1 \) or

\[
n_c \approx (v/l^3)^{-2} \approx \tau^{-2},
\]

which leads to:

\[
n_c \approx (v/l^3)^{-2} \approx \tau^{-2},
\]

using a linear approximation in the neighbourhood of the \( \theta \) point, \( v \) is proportional to the reduced temperature \( \tau = (T - \theta)/\theta [7] \).

At a temperature \( T > \theta \), one can visualize [9, 10] the chain as being formed by a succession of \( N/n_c \) Gaussian subchains of size:

\[
r_c \approx n_c^{1/2}/l.
\]

Since excluded volume effects exist only between subchains, the radius of gyration \( R \) of one isolated chain is equal to:

\[
R \approx (N/n_c) r_c.
\]

From expressions (1) and (2) we obtain [2]:

\[
R \approx N^{\nu} r_c l; \quad a = 2 \nu - 1 = 0.2 \text{ if } \nu = 0.6.
\]

In the temperature domain \( \tau \gg N^{-1/2} \), this law is valid because the number of subchains is very high \( (N/n_c) \gg 1 \). In the \( \theta \) domain \( \tau \ll N^{-1/2} \), the conformation of the chain is essentially Gaussian. The limit between these two behaviours is \( \tau^* \approx N^{-1/2} \) which will be called the cross-over temperature (see Fig. 1).

Now, we extend these results to the hydrodynamic radius \( R_H \) defined as:

\[
R_H = k_B T/6 \pi \eta_0 D_0
\]

where \( D_0 \) is the translational diffusion coefficient of the isolated chain and \( \eta_0 \) the viscosity of the solvent.

From an experimental point of view, it is known that:

\[
D(c) \propto c^a, \quad a = 2 \nu - 1 \ll 0.2.
\]

For the dynamic behaviour, we have by analogy with (3):

\[
R_H \approx (N/n_c)^{\nu_H} r_c.
\]

The hydrodynamic radius, \( r_{ch} \) of a subchain (Gaussian conformation) is proportional to \( r_c \). Taking the expressions (6), (2) and (1), we have in the temperature domain [13] \( \tau \gg \tau^* \):

\[
R_H \approx N^{\nu_H} \tau^{\nu_H}, \quad a_H = 2 \nu_H - 1 < 0.2.
\]

The value of the dynamic exponent \( \nu_H \), smaller than \( \nu \), implies that the hydrodynamic radius must increase with the temperature more slowly than the radius of gyration. The thermal behaviour of \( R_H \) can be determined by quasi-elastic light scattering experiments on a solution of finite monomer concentration \( c \ll c^* \), at a momentum transfer \( K \) such that \( KR \ll 1 \). The characteristic coherent time of the scattered light is [12, 14]:

\[
\tau_c = 1/D(c) K^2.
\]

\( D(c) \) is the diffusion coefficient of the coil at finite concentration. The experimental hydrodynamical radius, \( R_H(c) \), is deduced from the \( D(c) \) measurements from:

\[
\tilde{R}_H^{-1} = 6 \pi \eta_0 D(c)/k_B T.
\]

In the dilute regime, concentration dependence of the diffusion coefficient, can be written as:

\[
D(c) = \frac{k_B T}{6 \pi \eta_0 R_H} (1 + \varphi c).
\]
By extrapolation to infinite dilution \((c \to 0)\) we obtain the hydrodynamic radius of an isolated chain.

The interaction parameter \(\phi\) is given by [15, 6]:

\[
\phi = 2 m^2 N A_2 - \varphi T - \bar{v} m \tag{11}
\]

where \(m\) is the mass of monomer and \(\bar{v}\) the specific volume of the polymer which is a constant in the temperature range investigated [16]. \(A_2\) is the second virial coefficient and \(\varphi\), the hydrodynamic interaction parameter of the friction coefficient (see appendix). We demonstrate in the appendix that the variation of \(\phi\) with the temperature is:

\[
\varphi + \bar{v} m = - B_1 (1 + \tau) \quad \text{for} \quad \tau < \tau^* \tag{12}
\]

\[
\varphi + \bar{v} m = B_2 \left( 1 - B_3 \frac{1}{\tau^*} \right) \quad \text{for} \quad \tau > \tau^*
\]

where \(B_1, B_2, B_3\) are temperature independent positive factors (see appendix). Difference between hydrodynamic and geometric exponent implies that the sign of \(\varphi + \bar{v} m\) must change at a finite, positive temperature \(\tau_0\).

2.2 SEMI-DILUTE REGIME. - At a monomer concentration, \(c\), higher than the overlap concentration \(c^*\), contact points exist between interpenetrated chains. The average distance between adjacent contact points, \(\xi\), is independent of the polymerization index of the chains and decreases with concentration [5].

The semi-dilute solution at a temperature \(T > 0\) can be considered as a non-interacting assembly of small chains of size \(\xi\), called blobs, having \(N(\xi)\) statistical elements. One can visualize one blob as a succession of \(N(\xi)/n_c\) Gaussian subchains with excluded volume effects between them. Using an argument similar to the argument developed in section 2.1, we deduce:

\[
\xi \simeq \frac{(N(\xi)/n_c)^{\gamma}}{r_c} \tag{13}
\]

with the expressions of \(r_c\) and \(n_c\) as a function of the reduced temperature (1, 2) and the value of \(N(\xi)\):

\[
N(\xi) \simeq c \xi^3 \tag{14}
\]

we obtain [2]:

\[
\xi \simeq (c \xi^3)^{\frac{1}{1-3\gamma}} (1 - \nu/(3 \nu - 1) = 0.25 \tag{15}
\]

The size of the blob decreases with increasing temperature as it has been verified by elastic neutron scattering experiments [2]. The expression (15) is meaningful only if \(N(\xi)/n_c \gg 1\), this leads (using (1), (14) and (15)) to the condition \(\tau \gg \tau^{**}\) where \(\tau^{**} = c \xi^3\).

In the \(\theta\) domain \(\tau \ll \tau^{**}\), the blob is essentially Gaussian (see Fig. 1).

Let us consider now the temperature behaviour of the hydrodynamic length \(\xi_H\) [17] defined as:

\[
\xi_H = k_B T/6 \pi \eta_0 D(\xi) \tag{16}
\]

where \(D(\xi)\) is the diffusion coefficient of the blob and \(\eta_0\) the viscosity of the solvent. From light scattering experiments [1, 18] it has been found that \(\xi_H\) is not proportional to \(\xi\) and scales with \(N(\xi)\) as:

\[
\xi_H \sim N(\xi)^{\gamma_H}.
\]

Using an argument analogous to the one developed in the dilute regime we found that:

\[
\xi_H \simeq (N(\xi)/n_c)^{\gamma_H} r_c \quad \tau > \tau^{**}. \tag{17}
\]

Using expressions (1), (2), (14) and (15) we obtain:

\[
\xi_H \simeq (c \xi^3)^{\frac{1}{1-3\gamma}} (1 - \nu/(3 \nu - 1) > 0.25 \tag{18}
\]

Since \(\nu_H\) is smaller than \(\nu\), the hydrodynamic length \(\xi_H\) must vary with temperature more rapidly than the static length.

The behaviour of \(\xi_H\) can be determined from quasi-elastic light scattering on a semi-dilute solution at \(c > c^*\) and at a momentum transfer \(K\) such that \(K \xi \ll 1\). The coherent characteristic time of the scattered light is:

\[
\tau_c = 1/D(\xi) K^2 \tag{19}
\]

from which we deduce the length \(\xi_H\) by:

\[
\xi_H = k_B T/6 \pi \eta_0 D(\xi) \tag{20}
\]

In the following section, we describe the experiments which allow us to deduce the exponent values of the temperature laws.

3. Experimental procedure. — The dynamic lengths are determined from spectral measurements of the Rayleigh light scattered by cyclohexane-polystyrene system, in the 35 to 65 °C range temperature, by light beating spectrometry.

Here we give the experimental conditions and the data processing used in order to determine \(\xi_H\) and \(R_H\), we do not enter into the details of the light beating spectrometer which have been widely described in ref. [1].

3.1 EXPERIMENTAL CONDITIONS. — The temperature regulation is achieved by a copper jacket regulated by a thermoresistance and ATNE monitor, within ± 0.01 °C. The copper jacket, in which the optical cell containing the solution takes place, is thermalized by a second chamber. The temperature is measured by mean of a thermocouple, in contact with the cell, within an accuracy of ± 0.04 °C.

To investigate the thermal behaviour of \(R_H\) and \(\xi_H\), it is necessary to carry out the experiments in well defined regions. To this goal, it is useful to locate the boundaries between the different regions, \(c^*, \tau^*\) and \(\tau^{**}\), given in the diagram (Fig. 1). The cross-over temperature, \(\tau^*\) and \(\tau^{**}\), are determined from

\[
\tau_c = 1/D(\xi) K^2
\]

\[
\xi_H = k_B T/6 \pi \eta_0 D(\xi)
\]
the temperature concentration diagram drawn with results obtained by neutron scattering experiments in P.S. cyclohexane system [2]. It is found that:
\[ \theta t^* \approx 3 \times 10^3 M^{-1/2} \text{ in the dilute regime, } \]
\[ \theta t^{**} \approx 35 c \text{ in the semi-dilute regime. } \] (21)

\( M \) is the molecular weight of the macromolecule, and \( c \) the monomer concentration [6] in g/cm³. The \( \theta \) temperature in the polymer-solvent system studied is equal to 35 °C [19]. To define the dilute regime, it is important to know the order of magnitude of the overlap concentration \( c^*(\theta) \). We estimate that:
\[ c^*_\theta < c^*(\theta) \leq c^*_G \] (22)

where \( c^*_\theta \) and \( c^*_G \) are the overlap concentrations at the \( \theta \) temperature and in a good solvent, respectively. They are obtained using the following expression:
\[ c^*_\theta = M/AR^2_\theta, \] (23)
where \( A \) is the Avogadro number, \( R^2_\theta \) is the radius of gyration found by intensity light scattering experiments [20]. The characteristics of the samples used are reported in Table I. In order to observe macroscopic properties we have performed the experiments at:
\[ K R^2_\theta < 0.5 \text{ in the dilute regime, } \]
and
\[ K \xi \approx K R^2_\theta \left( \frac{c}{c^*_\theta} \right)^{-1} < 0.1 \text{ in the semi-dilute regime. } \] (24)

We use an homodyne spectrometer in the dilute regime, and an heterodyne spectrometer with separated beams in the semi-dilute regime [1].

3.2 DATA PROCESSING. — As we deal with diffusing macroscopic process, the autocorrelation function of the scattered light intensity has an exponential profile with a characteristic time \( \tau_c \) inversely proportional to \( K^2 \). This allows to determine a diffusion coefficient \( D = \tau^{-1}_c / K^2 \).

The momentum transfer \( K \) is related to the scattering angle \( \psi \), in the solution, by the relation:
\[ K = (4 \pi / \lambda) \sin \psi / 2, \] (25)

\( \lambda (4.880 \text{ Å}) \) is the wavelength of the incident beam and \( n \) is the refractive index of the solution. \( K \) has been determined from measurements in air of the scattering angle, taking for the cyclohexane refractive index [21]:
\[ n = 1.4428 - 56 \times 10^{-5} T (\text{°C}) \] (26)

under these conditions, we have obtained diffusion coefficients with an experimental accuracy of 0.5 % in the dilute regime and 1 % in the semi-dilute regime.

We have deduced \( R_\theta \) and \( \xi_\theta \) from \( D \) using expressions (9), (16) respectively and a temperature dependence of the cyclohexane viscosity \( \eta_0(T) \) established from a compilation of experimental results [22]:
\[ \eta_0(T) = 6.1739 \times 10^{-5} \exp[1.4816 \times 10^3/(273 + T (\text{°C})] \] (27)

the accuracy on \( \eta_0(T) \) is better than 1 %. This process gives \( R_\theta(c \rightarrow 0) \) and \( \xi_\theta \) within an accuracy of 1.5 % and 2 %, respectively.

4. Results and discussions. — 4.1 Dilute regime — The study of \( \bar{R}^{-1}_\theta \) as a function of the concentration, at a given temperature, shows that \( \bar{R}^{-1}_\theta \) varies linearly with concentration (Fig. 2). From the experimental results and the expression [6]:
\[ \bar{R}^{-1}_\theta (t, c) = R^{-1}_\theta (t) \left( 1 + \frac{\varphi(t)}{m} c \right) \] (28)
we can deduce \( R^{-1}_\theta (t) \) and \( \varphi(t) \) defined in (5) and (9).

4.1.1 Hydrodynamic radius \( R_\theta \) at finite dilution. — The expansion factor \( R_\theta/R_{100} \) varies by less than 8 % (see Table II) in the temperature range investigated:
\[ 0 \text{°C} < \theta T < 27 \text{°C} \]

Assuming a power law [23], in the domain \( \tau/\tau^* \geq 1.4 \), the best fit gives [24]:
\[ R_{100}/R_{100} = (9.53 \times 10^{-1} \pm 0.1 \times 10^{-1}) \theta T^{-n}, \] (29)
\[ a_{100} = 0.034 \pm 0.005. \]

The variation of \( R_{100}/R_{100} \), in the domain \( \tau/\tau^* > 1.4 \) (domain 1 in figure 1) as a function of \( \theta T \) is repre-

Table I. — Characteristics of the samples used where the symbols have their usual meaning. \( c^*_G \) is calculated using of the expression (23) where \( R_\theta \) is the radius of polystyrene-dissolved in benzene [20].

<table>
<thead>
<tr>
<th>Sample</th>
<th>( M_W )</th>
<th>( M_W/M_n )</th>
<th>( c ) (g/cm³)</th>
<th>( c/c^*_G )</th>
<th>( c/c^*_\theta )</th>
<th>( \theta T^* ) or ( \theta T^{**} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.43 \times 10^{-4}</td>
<td>3.4 \times 10^{-3}</td>
<td>1.5 \times 10^{-3}</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>5.1 \times 10^{-4}</td>
<td>1.2 \times 10^{-2}</td>
<td>5.3 \times 10^{-3}</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>1.66 \times 10^{-3}</td>
<td>3.9 \times 10^{-2}</td>
<td>1.7 \times 10^{-2}</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>8.2 \times 10^{-3}</td>
<td>1.9 \times 10^{-1}</td>
<td>8.6 \times 10^{-2}</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>8.4 \times 10^{-2}</td>
<td>—</td>
<td>4 \text{°C}</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

| 3.8 \times 10^{6}  | < 1.2 | 3 \text{°C}                  |
Fig. 2. — Variation of the inverse of the apparent hydrodynamic radius as a function of the monomer concentration, in the dilute regime, at \( T = 38.5 \, ^\circ\text{C} \). Representative error bar is shown.

### Table II. \( R_H \) and \( \xi_H \) experimental values obtained at various temperature.

<table>
<thead>
<tr>
<th>( \theta ) ((^\circ\text{C}))</th>
<th>( R_H \times 10^7 ) (cm)</th>
<th>( \theta ) ((^\circ\text{C}))</th>
<th>( \xi_H \times 10^6 ) (cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>9.12</td>
<td>0</td>
<td>3.02</td>
</tr>
<tr>
<td>2</td>
<td>9.21</td>
<td>1.9</td>
<td>2.63</td>
</tr>
<tr>
<td>3.5</td>
<td>9.26</td>
<td>8.8</td>
<td>1.62</td>
</tr>
<tr>
<td>4.5</td>
<td>9.36</td>
<td>11.8</td>
<td>1.53</td>
</tr>
<tr>
<td>5</td>
<td>9.36</td>
<td>14.3</td>
<td>1.42</td>
</tr>
<tr>
<td>6.5</td>
<td>9.35</td>
<td>16.9</td>
<td>1.36</td>
</tr>
<tr>
<td>8</td>
<td>9.35</td>
<td>18.4</td>
<td>1.31</td>
</tr>
<tr>
<td>9.5</td>
<td>9.39</td>
<td>20.5</td>
<td>1.27</td>
</tr>
<tr>
<td>10</td>
<td>9.42</td>
<td>22.3</td>
<td>1.27</td>
</tr>
<tr>
<td>12</td>
<td>9.47</td>
<td>24.4</td>
<td>1.21</td>
</tr>
<tr>
<td>19</td>
<td>9.59</td>
<td>24.5</td>
<td>1.20</td>
</tr>
<tr>
<td>23</td>
<td>9.63</td>
<td>26.7</td>
<td>1.15</td>
</tr>
<tr>
<td>27</td>
<td>9.77</td>
<td>27.6</td>
<td>1.16</td>
</tr>
</tbody>
</table>

The \( R_H \) and \( \xi_H \) values presented on a log-log scale in figure 3. The \( a_H \) exponent value is confirmed by the representation used in figure 4:

\[
\frac{R_H}{R_{H_0}} \propto \theta^{-0.34}
\]

has a constant value for \( \tau/\tau^* \geq 1.1 \), but a decreasing value for \( \tau/\tau^* < 1 \), which means that in the \( 0 \) domain the results cannot be described by a power law. We can note that the cross-over temperature \( \tau^* \) coincides with the value determined from eq. (21). The exponent \( a_H \) found is much smaller than the exponent \( a = 0.2 \) predicted for the geometric expansion; hydrodynamic and geometric length are not proportional. This result is in agreement with ref. [25] where the ratio \( R_H/R \) is measured as a function of temperature in polystyrene-cyclohexane solution. \( R_H/R \) is found to decrease as the temperature increases. From the expression (7) and the experimental value \( a_H \), we deduce an effective dynamic exponent \( v_H = 0.52 \). The exponent value obtained is smaller than \( v(0.6) \) and \( v_H(0.55) \) obtained in very good solvent [1, 12].

The very low relative variation of \( R_H \) compared to the experimental accuracy does not allow us to rely on the exponent value obtained from this experiment. The important point is that the hydrodynamic radius is relatively insensitive to the excluded volume effects compared to the geometric length.

#### 4.1.2 Concentration dependence of the hydrodynamic radius

In the temperature range investigated (0 \(^\circ\text{C} < \theta < 27 \, ^\circ\text{C}\)), the parameter

\[
\phi(\tau) = m^{-1} \tau
\]

is negative and increases as the reduced temperature increases. The variation of \( \phi(\tau) \) with temperature is given in figure 5.

In the \( \theta \) domain \( \tau < \tau^* \), the \( \phi \) variation with the reduced temperature can be considered as being linear. In the domain \( \tau > \tau^* \), experimental data are compared with calculated values obtained using eq. (12) with:

- the exponent value found previously \( v_H = 0.52 \),
- and \( \bar{v} = 0.92 \, \text{cm}^3/\text{g} \) found by densitometry [16].

The constant factor \( B_2 \) and \( B_3 \) are adjusted by means of least square fit.
The interaction parameter $\phi$ and the excluded volume effects increase as the temperature increases. $\phi$ is negative in the neighbourhood of the $T$ point and positive for a good solvent [1, 12, 26] and it becomes equal to zero at a temperature $T_g \approx 35^\circ C$ much higher than the $T$ temperature [2]. This change of sign of the parameter indicates that the thermodynamic factor $NA_2$ is not proportional to the hydrodynamic parameter $Q_f$. This fact confirms that $R$ and $R_H$ do not have the same temperature dependence (see appendix).

4.2 SEMI-DILUTE REGIME. — The measurement of $\xi_H$ at a given concentration ($c \approx 4 C_p^*$), as a function of the temperature, shows that $\xi_H$ decreases as the temperature increases (see Table II). The results obtained in the region $\tau/\tau^{**} > 5.5$ are plotted on a log-log scale as a function of the reduced temperature (Fig. 6). It is found that [24] :

$\xi_{Hj}/\xi_H = (1.12 \pm 0.14) \theta \tau^{-b_{H}}$; \hspace{1cm} $b_{H} = 0.33 \pm 0.04$ .

(30)

This exponent value is bigger than the value $b = 0.25 \pm 0.01$ determined by neutron scattering in the same temperature domain [2]. The hydrodynamic length $\xi_H$ is not proportional to the geometric length $\xi$.

In figure 7 we present the experimental results over the whole temperature range investigated. We see that $\xi_{Hj}/\xi_H$ has two different behaviours, the quantity $\frac{\xi_{Hj}}{\xi_H} \times \theta \tau^{0.33}$ is :

- a constant value for $\tau/\tau^{**} > 4$ ,
- a decreasing value for $\tau/\tau^{**} < 4$ ,

the temperature $\tau^{**} = 4 \tau^{***}$, where $\xi_H$ reaches an asymptotic behaviour, is in agreement with the corresponding value obtained for $\xi$ by elastic neutron scattering experiments [2], but is much bigger than the temperature $\tau^{***}$ determined from eq. (21). Now, using expression (18) and the experimental value $b_{H}$, we found that the effective dynamic exponent $\eta_{H}$ is equal to 0.54. The discrepancy between the exponent values found for the geometric length $\xi$ and the hydrodynamic length $\xi_{Hj}$ is due to the insensitivity of $\xi_{Hj}$ to the excluded volume effects.

Fig. 6. — Variation of the relative hydrodynamic length $\xi_{Hj}/\xi_H$ in semi-dilute regime as a function of the temperature, $\theta \tau \geq 18.4^\circ C$ (log-log scale). — Full line is the best fit of the experimental points; ----- Dotted line is the variation of geometric length which has been calculated using arbitrary $\xi/\xi_{a} = \xi_{Hj}/\xi_H$ at $\theta \tau = 18.4^\circ C$.

4.3 DISCUSSION ON THE DYNAMIC EXPONENT. — The existence of an effective dynamic exponent $\eta_{H}$ smaller than the static exponent $\eta$ allows us to explain the temperature behaviour of the dynamic quantities. Let us relate our results with the Weill-des Cloizeaux [3a] (W.D.C.) interpretation of the apparent exponent $\eta_{H}$.

They (W.D.C.) calculate the radius of gyration ($R \sim N^\eta$) and the hydrodynamic radius ($R_H \sim N^\eta$) of a chain taking as for hypothesis the Gaussian conformation of the chain at shorter distances, they
determine the effective exponents \( v(N/n_c) \) and \( v_H(N/n_c) \). At a low \( N/n_c \) value, \( v_H \) is found to be smaller than \( v \). As \( N/n_c \) increases \( v \) reaches its asymptotic value \([27][0.6]\) more rapidly than \( v_H \).

This treatment can be extended to the calculation of the effective temperature exponents if one notes:

- \( n_c \) is proportional to \( \tau^{-2} \) in the neighbourhood of the \( \theta \) point,
- the blob is analogous to an isolated chain of size \( \xi \) with \( N(\xi) \sim c^3 \) statistical elements.

In figure 8 we give the variation of the effective temperature exponents \( a, a_H \), \( b \) and \( b_H \) as a function of \( \sqrt{N/n_c} \). In the dilute regime, for the temperature range \( 1 < \tau/\tau^* < 4 \) (or \( 1 < \sqrt{N/n_c} < 4 \)) where the experiments have been performed, the effective temperature exponent varies between 0 and 0.1; the mean value correspond roughly to the exponent determined experimentally \((a_H = 0.034)\). From figure 8, \([28]\) we observe that the exponent \( -b_H \) decreases very rapidly and reaches a minimum value \((-b_H = -0.3)\) at \( \sqrt{N(\xi)/n_c} \approx 2.5 \) and then increases very slowly with \( N(\xi)/n_c \) \((- b_H = -0.29 \) for \( \sqrt{N(\xi)/n_c} = 5 \)). Experiments, in semi-dilute regime, have been performed in the temperature range \( 1 < \tau/\tau^* < 3 \) which correspond, making an over estimation, to \( 1 < \sqrt{N(\xi)/n_c} < 3 \). In this temperature domain \( b_H \) is approximately a constant \( b_H \approx 0.3 \) which must be compared to the value determined experimentally \( b_H = 0.33 \) \([29]\). We can note that, in order to determine \( v_H \) from \( b_H \) we must know the \( v \) corresponding value, because using the asymptotic value \( v = 0.6 \) one over estimates the exponent value \( v_H \).

This discussion leads to the conclusion that the explanation given by Weill and des Cloizeaux is in qualitative agreement with our experimental results.

The main problem aroused by W.D.C calculation lies in its basic assumption: does the local Gaussian conformation exist?

This assumption is verified in a \( \theta \) solvent; but there is no experimental evidence of its validity in a good solvent.

By elastic neutron scattering the size \( r_\xi \) of the Gaussian conformation, in polystyrene-cyclohexane solution near \( \theta \) temperature, has been measured \([30]\). \( r_\xi \) decreases as the temperature increases and becomes equal to the statistical length \( (l \approx 10 \text{ Å}) \) when

\[ t \approx 57^\circ \text{C} \quad (\tau \approx 6 \times 10^{-2}) \]

Since benzene, at room temperature is a better solvent than cyclohexane at 57 \( ^\circ \text{C} \) for polystyrene \((R_{\text{benzene}} > R_{\text{cyclohexane}} 57^\circ \)) the local Gaussian conformation does not exist in the system polystyrene-benzene. This observation casts some doubt on the validity of W.D.C. calculation and we believe that direct experimental confirmations are indispensable.

One of these, could be, to find some polymer solvent systems where this cross-over effect is negligible, in order to verify that \( v_H \) could indeed reach the asymptotic value \((0.6)\).

5. Conclusion. — From these experiments, done in the neighbourhood of the \( \theta \) temperature on PS-cyclohexane system, we conclude: that the hydrodynamic radius \( R_H \) of a chain is relatively insensitive to changes in the segment distribution arising from excluded volume effects \([31]\). This conclusion can be extended, in the semi-dilute regime, to the hydrodynamic length of a blob \( \xi_H \).

The concentration and molecular weight dependence of \( \xi_H \) and \( R_H \) at the \( \theta \) temperature, have not been verified but the temperature exponents found, suggest that, \( \xi_H \sim c^{-1} \) and \( R_H \sim M^{0.5} \). This last point is in agreement with experiments done at the \( \theta \) point \([11]\). Our results are in qualitative agreement with an explanation of anomalous dynamic exponents by cross-over effects. But those experimental results \((\text{Table II})\) allow any theoretical approach on the problem of dynamic exponents, to be verified.

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Appendix. — Let us recall the expression of the interaction parameter \( \varphi \) \([6, 15]\):

\[ \varphi = 2 m^2 NA_2 - \varphi_t - \bar{\varpi}m. \]  

(A.1)

Here we relate, the second virial coefficient \( A_2 \) and the hydrodynamic interactions parameter \( \varphi_t \), to the
macromolecular parameters in order to calculate the thermal behaviour of $\varphi$.

In the domain $\tau > \tau^*$, $A_2$ is proportional to the volume occupied by one chain [8, 5], with eq. (4), we have:

$$A_2 \sim \frac{R^2(\tau)}{N^2} \sim \tau^{2a}.$$  \hspace{1cm} (A.2)

In the $\theta$ domain $\tau < \tau^*$, $A_2$ is proportional to the excluded volume parameter [8] which is a linear function of the reduced temperature $A_2 \sim \tau$ \hspace{1cm} (A.3)

$\varphi_\tau$ is defined [6, 15] by:

$$f(c) = f_0(1 + \varphi_\tau c)$$ \hspace{1cm} (A.4)

where $f_0$ and $f(c)$ are the frictional coefficients of a chain at infinite and finite dilution, respectively. To evaluate $\varphi_\tau$ let us select a chain amongst the other and determine its effective friction coefficient $f(c)$:

$$f(c) = 6 \pi \eta_0 R_H + \delta f(c)$$ \hspace{1cm} (A.5)

the additional friction coefficient $\delta f(c)$ is due to the macroscopic increment of the viscosity $\delta \eta$ due to the presence of the other chains:

$$\delta f = \beta \delta \eta R_H.$$ \hspace{1cm} (A.6)

$\beta$ is a numerical factor which is no longer equal to $6 \pi$ since the size of the selected chain is equal the size of the other chains [32]. $\delta \eta$ is related by definition [6, 8] to the intrinsic viscosity $[\eta]$ by:

$$\delta \eta = \eta_0 [\eta] mc.$$ \hspace{1cm} (A.7)

Using the expressions (A.4)-(A.7) we obtain:

$$\varphi_\tau \sim [\eta].$$ \hspace{1cm} (A.8)

It has been shown [33] that:

$$[\eta] \sim \tau_1/N$$ \hspace{1cm} (A.9)

where $\tau_1$ (characteristic time of the first mode of the chain) is the time required by a chain to diffuse on a distance equal to its size [34] $R$:

$$\tau_1 \approx R^2/D_0 \sim R^2 R_H.$$ \hspace{1cm} (A.10)

Using (A.8), (A.9) and (A.10) we find that:

$$\varphi_\tau \approx R^2 R_H/N.$$ \hspace{1cm} (A.11)

In the domain $\tau \gg \tau^*$ using the thermal behaviour proposed for $R_H$, $R$, $A_2$ and the expression of $\varphi$ (eqs. (4), (7), (A.2) and (A.1)), we have:

$$\varphi + \bar{\eta}m = B_2 \tau^{2(\nu_2+1)}[1 - B_3 \tau^{2(\nu_2-\nu)}].$$ \hspace{1cm} (A.12)

In the $\theta$ domain, $\tau \ll \tau^*$, a temperature expansion can be made:

$$\varphi + \bar{\eta}m = -B_1(1 + \varepsilon \tau).$$

Factors $B_1$, $B_2$, $B_3$ and $\bar{\nu}$ are independent of the reduced temperature. The specific volume $\bar{\nu}$ can be considered as a constant in the temperature range experimentally investigated [16]. $B_1$ is proportional to the intrinsic viscosity (positive factor), thus at the point $\varphi + \bar{\eta}m$ is negative. $B_2$ and $B_3$ are positive and respectively proportional to $N^{3\nu_2-1}$ and to $N^{\nu_2-\nu}$.

The reduced temperature $\tau_0$ at which $\varphi + \bar{\eta}m$ vanishes is molecular weight dependent ($\tau_0 \sim N^{-1/2}$).

References and notes


[7] See for instance:


TEMPERATURE DEPENDENCE OF HYDRODYNAMIC LENGTHS


[23] Since the analytical expression proposed in ref. [3b] does not allow the authors to obtain a quantitative agreement. We fit our data by power laws.

[24] A variation of 1 °C in the $\theta$ value give no appreciable change in the exponent value (6 %).


King, T. A., Knox, A., McAdam, J. D. G., *Polymer* 14 (1973) 293.

[27] A more accurate value for $\nu$ is 0.588 (see ref. [4]).

[28] After this paper was written, we received a preprint by M. Daoud giving similar theoretical results on the thermal behaviour in semi-dilute range.

[29] One can remark that the maximum theoretical value of $b_\eta$ (using $\nu = 0.6$) is smaller than the experimental value.


