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Dynamics of polymers in dilute solutions: an explanation of anomalous indices by cross-over effects

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Résumé. — On montre que les propriétés dynamiques de longs polymères de N maillons en solution convergent beaucoup plus lentement vers leur limite asymptotique (N → ∞) que les propriétés statiques. Cet effet dont la raison est simple explique pourquoi les mesures dynamiques des indices critiques conduisent à des résultats qui semblent en désaccord avec les mesures statiques et les théories récentes.

Abstract. — It is shown that the dynamical properties of long polymers made of N links, in solutions, converge much more slowly to the asymptotic limit (N → ∞) than the static properties. This effect, which has a simple origin, explains why dynamical measurements of critical indices lead to results which seem to disagree with static measurements and recent theories.

1. Introduction. — The mean size of a polymer in a dilute solution can be measured by static or dynamic experiments.

A static measurement may be a diffraction experiment which gives directly the size of the polymer. Static measurements are rather reliable and give answers which agree with the theoretical predictions.

A dynamic experiment such as the determination of a diffusion coefficient or of an intrinsic viscosity consists, in fact, in measuring directly or indirectly a relaxation time. As the relaxation times of a polymer are, for macroscopic deformations, increasing functions of the volume of the polymer, the size of a polymer can be measured by a dynamic experiment.

However, the dynamic results do not agree with the static results. Indeed, for large values of the number N of segments, our expectations are the following. The radius of gyration of a polymer in a good solvent varies as

$$R_g^2 \propto N^{2v}$$

(1)

where v is the excluded volume index, and in the asymptotic limit, it is the only length which characterizes the polymer.

Therefore, homogeneity arguments show that in the asymptotic non free draining limit, the intrinsic viscosity scales as

$$[\eta] \propto \frac{R_g^2}{M} \propto N^{3v-1}$$

(2)

(where M is the molecular weight), the translational diffusion constant as

$$D = \frac{1}{R_g} \propto N^{-v}$$

(3)

and the sedimentation coefficient as

$$S = \frac{M}{R_g} \propto N^{1-v}.$$

(4)

The value of v originally proposed by Flory (v = 0.60) has been recently recalculated using more sophisticated and exact arguments relying on renormalization theory with the result [1] v = 0.588.

Indeed, measurements of R_g as a function of N by light and neutron scattering techniques [2] give v = 0.595 ± 0.020 for polymers of high molecular weights in good solvents. However, the molecular weight dependences of [\eta], D and S, measured in the same range of molecular weights, are characterized by indices which are different from those predicted by relations (2), (3) and (4).

For polystyrene in benzene for example, D has been found proportional [4] to N^{-0.55±0.02} (instead of N^{-0.59}) and [\eta] proportional [4] to N^{0.725} (instead...
of $N^{0.77}$). More generally, the indices of $[\eta]$ found in the literature for various polymer-good solvent systems are scattered between 0.7 and 0.8.

Several attempts have been made to trace the origin of these discrepancies [5]. Thus, the Kirkwood Riseman approximation has been used to show that the expression (2) of the intrinsic viscosity of a Gaussian chain should be replaced by the more exact equality

$$[\eta] \propto \frac{R_G^2}{M(1/R_D)}$$

where

$$R_G^2 = \frac{1}{2(N+1)^2} \sum_{ij} \langle r_{ij}^2 \rangle$$

and

$$\frac{1}{R_D} = \frac{1}{2(N+1)^2} \sum_{ij} \langle \frac{1}{r_{ij}} \rangle.$$  \hfill (6)

$$\frac{1}{R_D} = \frac{1}{2(N+1)^2} \sum_{ij} \langle \frac{1}{r_{ij}} \rangle.$$  \hfill (7)

In the case of a chain with excluded volume, the evaluation of these two quantities by a perturbation expansion can explain at least qualitatively the observed differences in the molecular weight dependence. Several attempts of the same type using other perturbation expansions or more consistent calculations of the static averages (6) and (7) are reviewed in the book by Yamakawa [7]. They cannot however predict properly the asymptotic behaviour.

On the other hand, dynamic properties can always be related to relaxation times. As will be shown, the relaxation time $\tau$ associated with a large scale motion of a polymer is always proportional to $\beta \eta_0$ where $\eta_0$ is the solvent viscosity and $\beta = 1/kT$. Homogeneity considerations show then that $\tau/\beta \eta_0$ has the dimension of a volume. A normal behaviour implies $\tau/\beta \eta_0 \propto R_G^3 \propto N^{3v}$. However, the theory does not exclude $a priori$ the possibility of an anomalous behaviour [8] for $\tau$, of the form $\tau/\beta \eta_0 \propto N^{3v-\zeta}$ where $\zeta$ is an anomalous dynamic index. This would imply the introduction of a dynamical length which would not scale like $R_G$ and it has been thought that this could provide another possible explanation of the discrepancy between the results of static and dynamic measurements.

In this paper, we propose an explanation of the discrepancies, which is consistent with the following rules :

a) Most dynamical properties can be approximately expressed in terms of the lengths $R_G$ and $R_D$ defined by eqs. (6) and (7).

For instance, we may write

$$[\eta] \propto \frac{R_G^2 R_D}{M}.$$  \hfill (8)

$$D \propto \frac{1}{R_D}.$$  \hfill (9)

$$S \propto \frac{M}{R_D}.$$  \hfill (10)

b) $R_G$ and $R_D$ are proportional in the asymptotic limit ($N \to \infty$) and therefore their index is the same $R_D \propto R_G \propto N^v$.

c) The distance between two monomers $i$ and $j$ along an isolated chain scales according to two different laws for small and large values of $|i-j|$. The cross-over occurs for $|i-j| > n_c$ where $n_c$ is independent of the molecular weight.

For $|i-j| < n_c$, the subchain limited by the monomers $i$ and $j$ has a Gaussian behaviour ; for $|i-j| > n_c$, it has an excluded volume behaviour.

As a consequence, $R_D$ reaches the asymptotic limit at much larger values of $N$ than $R_G$ and the dynamical quantities which depend on $R_D$ show an apparently anomalous molecular weight dependence.

Points a), b), c) will be discussed in more detail in sections 2, 3, 4. A specific model enabling a quantitative calculation of $R_G$ and $R_D$ as a function of $N/n_c$ is presented in section 5. In section 6, this model is applied to derive a relation between the classical expansion factor $\xi = R_G/R_G^0$ and the ratio $\xi^0 = [\eta]/[\eta]_0$.

2. Mean relaxation time and relaxation lengths. — Let us recall that all the dynamical properties of a polymer are contained in the relaxation operator which can be defined as follows.

Let us denote by $X$ the set of all the components $r_i$ of the vectors $r_i$ defining the positions of the monomers (or points of the chain). With each configuration, we associate the energy $U(X)$. At a given time $t$, the probability corresponding to a configuration will be $P(X, t)$. At equilibrium, the probability is given by Boltzmann's law

$$P(X, t) = P_0(X) \exp[-\beta U(X)].$$  \hfill (11)

More generally, $P(X, t)$ obeys a Fokker-Planck equation of the form

$$\frac{\partial}{\partial t} P(X, t) = KP(X, t)$$  \hfill (12)

where $K$ is a linear operator which has been studied by Kirkwood [9].

This operator is not Hermitian but it can be transformed into an Hermitian operator $L$

$$L = -e^{\theta U(X)} K e^{-\theta U(X)}$$  \hfill (13)

which we shall call the relaxation operator.

Then eq. (12) can be written

$$\frac{\partial}{\partial t} \varphi(X, t) = -L \varphi(X, t).$$  \hfill (14)

where

$$\varphi(X, t) = e^{\theta U(X)} P(X, t).$$  \hfill (15)
The eigenfunctions of $L$ define the relaxation modes

$$\frac{1}{\tau_n} \varphi_n(x) = L \varphi_n(x). \quad (16)$$

By definition, the eigenvalue $\tau_n$ is the relaxation time corresponding to this mode.

The ground state is given by

$$\varphi_0(x) \propto \exp[-\beta U(x)/2]$$

and the corresponding relaxation time is infinite

$$L \varphi_0(x) = 0. \quad (17)$$

Thus the general solution of eq. (12) can be written

$$P(x, t) = \left[ a_0 \varphi_0(x) + \sum_{n \neq 0} e^{-\beta \tau_n} a_n \varphi_n(x) \right] e^{-\beta U(x)/2}$$

and this equality defines completely the dynamical properties of the system.

The order of magnitude of the relaxation times associated with large scale motions will now be determined in the frame of Kirkwood's theory [9].

In this case, we have (here $\partial_i \rightarrow \partial_i / \partial r_i^2$)

$$\beta L = - \left[ \partial_i - \frac{\beta}{2} \partial_i U(X) \right] \times$$

$$\times D^{\text{is},ij} \left[ \partial_j + \frac{\beta}{2} \partial_j U(X) \right] \quad (19)$$

where $D^{\text{is},ij}(X)$ is given by

$$D^{\text{is},ij}(X) = \frac{1}{6 \pi \eta_0} \left[ \delta_{ij} \delta_{is} - \frac{3(1 - \delta_{ij})}{4 r_{ij}} \times \right.$$

$$\left. \left( \delta_{ij} \delta_{is} + \frac{\delta_{ij} r_{ij}^2}{r_{ij}^2} \right) \right]$$

where $b$ is the radius of a monomer.

The second term is the well known Oseen's tensor; it is the only important term in the asymptotic limit and the first one will be dropped.

A straightforward calculation shows that

$$[[L, r_{ij}], r_{ij}] = - \frac{1}{2 \pi \beta \eta_0} \frac{1}{r_{ij}} \quad i \neq j. \quad (20)$$

Then, using the notation $\varphi_n(x) = \langle X \mid n \rangle$, we obtain

$$\langle 0 \mid \frac{1}{r_{ij}} \mid 0 \rangle = 4 \pi \beta \eta_0 \sum_n \frac{1}{r_n} \langle 0 \mid r_{ij} \mid n \rangle \langle n \mid r_{ij} \mid 0 \rangle. \quad (21)$$

We may now assume that the modes $n$ which are coupled to the ground state (or equilibrium states) correspond to large scale motions and therefore that the corresponding relaxation times $\tau_n$ are all of the same order of magnitude. Thus, one may define a mean relaxation time $\tau$ by setting

$$\frac{1}{\tau} = \sum \frac{1}{\tau_n} \left[ \sum \langle 0 \mid r_{ij} \mid n \rangle \langle n \mid r_{ij} \mid 0 \rangle \right] / \sum \langle n \mid r_{ij} \mid 0 \rangle \langle 0 \mid r_{ij} \mid n \rangle. \quad (22)$$

Using this definition, we deduce from (21) the equality

$$\sum \langle 0 \mid \frac{1}{r_{ij}} \mid 0 \rangle = \frac{4 \pi \beta \eta_0}{\tau} \sum \langle 0 \mid r_{ij} \mid 0 \rangle. \quad (23)$$

Let us now recall the definition of $R_G$ and $R_D$ (eqs. (6) and (7)) and also the definition of $\varphi_0(x) = \langle X \mid 0 \rangle$ (eq. (17)). We have

$$R_G^2 = \frac{1}{2 N^2} \sum \langle 0 \mid r_{ij}^2 \mid 0 \rangle \quad (24)$$

Thus eq. (23) can be written

$$\tau = 4 \pi \beta \eta_0 \frac{R_G^2}{R_D}. \quad (25)$$

Thus the mean relaxation time $\tau$ can be expressed in terms of two lengths $R_G$ and $R_D$.

We can now use this fundamental relation to determine the properties of dynamic quantities in the cross-over region where $R_G$ or $R_D$ do not behave in the same way. This can be done by applying the following prescription.

**Practical rule**: The approximate dependence of a dynamical constant with respect to $N$ can be found by expressing this constant in terms of lengths and times in the most logical way; a length is then replaced by $R_G$ and a time by $\tau$.

Thus the diffusion constant is obtained by dividing the square of a length by a time

$$D \propto \frac{L^2}{\tau} \propto \frac{R_G^2}{\tau} = \frac{1}{\beta \eta_0 R_D}. \quad (26)$$

Incidentally, it might seem strange that the behaviour of a diffusion constant should depend on a relaxation time. However, consider the eigenfunctions of $L$ with momentum $k$. The relaxation time $\tau(k)$ of the eigenfunction with the largest relaxation time is given by

$$\tau(k) \propto (D k^2)^{-1} \quad (k R_G \ll 1). \quad (27)$$

We see that at the limit $k = 1/R_G$,

$$\tau(1/R_G) = \frac{R_G^2}{D} = \tau \quad (28)$$

according to eq. (26).

This result shows that the characteristic time
which is relevant for a diffusion process is the time which is needed by the polymer for moving over a distance of the order of its own size.

The mobility $\mu$ is directly related to the diffusion constant by Einstein’s law

$$\mu = \beta D \propto \frac{1}{\eta_0 R_D^2}. \tag{29}$$

On the other hand, the sedimentation velocity is proportional to $\mu$ and, thus, we get

$$S \propto M\mu \propto \frac{M}{\eta_0 R_D}. \tag{30}$$

The variation of the viscosity of a solvent in which a small amount of polymer is added is obtained by measuring a variation of time of flow.

Thus we may write

$$\frac{\eta - \eta_0}{\eta_0 C_p} \propto \beta^{-1} \tau \tag{31}$$

where $C_p$ is the number of polymer molecules per unit volume (note that $\beta$ has to be introduced for homogeneity).

Therefore, from eq. (25), we deduce

$$[\eta] = \frac{\eta - \eta_0}{\eta_0 M C_p} \propto \frac{R_G^2 R_D}{M}. \tag{32}$$

3. Asymptotic behaviour of the dynamical properties. — From the definitions of $R_G$ and $R_D$, it is clear that these quantities must scale in the same way.

Therefore, we have

$$\lim_{N \to \infty} \frac{\delta(\ln R_G)}{\delta(\ln N)} \left|_{N \to \infty} \frac{\delta(\ln R_D)}{\delta(\ln N)} = v \right. \tag{33}$$

This result shows that for large $N$, $\tau \propto N^{3v}$, in agreement with de Gennes’ predictions [11] and precludes the existence of anomalous dynamical indices.

This is fully consistent with the conclusions of a preceding article by des Cloizeaux [10]. In this article, the mobility $\mu$ has been written in the form

$$\mu = \frac{1}{6 \pi \eta_0 R_H} \tag{34}$$

and the validity of an inequality of the form

$$R_H > CR_G \quad (C = \text{constant}) \tag{35}$$

has been proved in the asymptotic limit, in order to show that the observed anomalous dynamic properties cannot result from the existence of anomalous dynamical indices.

By comparing eqs. (29) and (34), we see that $R_H \propto R_D$.

Therefore $R_H$ and $R_G$ should be proportional in the asymptotic limit and this result is quite compatible with the strong inequality (35).

However, in the cross-over region, we can define for $R_G$ and $R_D$ different effective indices which depend slowly on $N$

$$v_G = \frac{\delta(\ln R_G)}{\delta(\ln N)}$$

$$v_D = \frac{\delta(\ln R_D)}{\delta(\ln N)}. \tag{36}$$

The difference may explain the apparent dynamic anomalies as will be shown in section 4.

4. Scaling laws for an isolated chain and the critical chemical distance $n_c$. — It is now well established that the excluded volume interaction $v$ swells the coil only if $v/b^3 > N^{-1/2}$, where $b$ is the step length of the chain (i.e. in the absence of excluded volume $R_G^2 = Nb^2/[6]$). Since $v$ is a linear function of the reduced temperature $T_R = (T - \theta)/\theta$, in the neighbourhood of the $\theta$ temperature, the chain becomes swollen if $N^{-1/2} \ll T_R$.

An important step toward the understanding of the cross-over phenomenon has been introduced [12, 13] with the extension of this condition to any chemical distance $n \leq N$. At a given $T_R$ there exists a characteristic value $n_c \approx T_R^{-2}$ : for $|i - j| > n_c$, all distances $r_{ij}$ are swollen ; for $|i - j| < n_c$, all distances $r_{ij}$ remain practically unperturbed.

The existence of such a spatial cross-over at $n = n_c$ is reflected in the single chain scattering factor $S(q)$ which has two different behaviours on both sides of a critical value $q^* \sim (n_c b^2)^{-1/2}$ of the momentum transfer $q$.

For $q > q^*$, $S(q)$ reflects the Gaussian statistics and is therefore proportional to $q^{-2}$. For $q < q^*$, $S(q)$ reflects the excluded volume statistics and is therefore proportional to $q^{-5/3}$. Such a spatial cross-over has indeed been observed in neutron scattering experiments [13].

Considering the influence of small distances on $R_D$, one can predict the inequality $v_D < v_G$ in the cross-over region as will be explicitly shown on the following simple model.

5. An explicit calculation of the effective indices $v_G$ and $v_D$ for a simple model. — We shall study a crude model in which all fluctuations are neglected. Here, $R_G$ and $R_D$ are defined by

$$R_G^2 = \frac{1}{2 N^2} \sum_{i < j} r_{ij}^2 \quad \frac{1}{R_D^2} = \frac{1}{2 N^2} \sum_{i < j} \frac{1}{r_{ij}} \tag{37}$$

where $r_{ij}$ will be considered as a function of $|i - j|$. This function has different behaviours for different values of $|i - j|$. Again we may define an effective index $v_{ij}$

$$v_{ij} = \frac{\delta(\ln r_{ij})}{\delta(\ln |i - j|)} \tag{38}$$

which is schematically depicted on figure 1.
Fig. 1. — Schematic representation of the effective index $v_{ij}$ as a function of $|i - j|$. Its value at small $|i - j|$ reflects the local rigidity of the chain. We can replace the exact dependence of $v_{ij}$ (shown on Fig. 1) by a very simple dependence with three values for $v_{ij}$

\[ v_{ij} = \begin{cases} 
1 & |i - j| < n_0 \\
0.5 & n_0 < |i - j| < n_c \\
v & |i - j| > n_c 
\end{cases} \]

Here, $n_0$ can be taken as the number of monomers in a statistical segment. We may now consider the length of a statistical segment as the unit length and label the statistical segments by indices $i$ and $j$. The number of statistical segments will be $N$, the characteristic number will be $N_c = n_c/n_0$ and the distance $r_{ij}$ between two such segments will be given by the scaling laws

\[ r_{ij} = |i - j|^{1/2} \quad N \leq N_c \]
\[ r_{ij} = N_c^{1/2} \left| \frac{i - j}{N_c} \right|^v \quad N \geq N_c \]

We can now perform the double summation involved in relations (37). Assuming that $N$ and $N_c$ are large ($N \geq 1, N_c \geq 1$), we may replace the sums by integrals and we obtain

\[ R_G = \left( \frac{N}{6} \right)^{1/2}, \quad R_D = \frac{3}{4} N^{1/2} \]

\[\begin{align*}
\frac{R_G}{N_c^{1/2}} &= \left[ \frac{2 v - 1}{2(2 v + 1)} \left( \frac{N}{N_c} \right)^{1-v} + \frac{2 v - 1}{3(2 v + 2)} \left( \frac{N}{N_c} \right)^{-v} \right. \\
&\quad \left. + \frac{1}{(2 v + 1)(2 v + 2)} \left( \frac{N}{N_c} \right)^{2v+1/2} \right]^{1/2} \\
\frac{R_D}{N_c^{1/2}} &= \left[ -\frac{2 v - 1}{2 v + 1} \left( \frac{N}{N_c} \right)^{-1} + \frac{2 v - 1}{3(2 v - 2)} \left( \frac{N}{N_c} \right)^{-v} \right. \\
&\quad \left. + \frac{1}{(2 v - 1)(2 v)} \left( \frac{N}{N_c} \right)^{-v} \right]^{-1} .
\end{align*}\n
The result is plotted on figure 2 for $v = 0.59$, as a function of $x = N/N_c$. We define effective indices

\[ v_G(x) = \frac{\partial \ln R_G}{\partial \ln (N)} \]
\[ v_D(x) = \frac{\partial \ln R_D}{\partial \ln (N)} \]

which are represented on figure 3 and this graph shows that $v_G(x)$ reaches the asymptotic limit $v = 0.59$ much faster than $v_D(x)$.

Considering figures 2 and 3, it is very easy to understand that it will be very difficult to detect experimentally a small curvature in the $\ln R_D$ versus $\ln N$ plot in the range $10 < x < 10^3$ but the best fit slope will give a value of $v_D$ intermediate between 0.5 and 0.59.

In that respect, it is interesting to consider the case of polystyrene in benzene already mentioned. Choosing

\[ v_G = 0.59 \]
\[ v_D = 0.55 \]
we get
\[ v_G \propto M^{0.59} \]
\[ D \propto M^{0.55} \]
\[ [\eta] \propto M^{0.73} \]

in excellent agreement with the following experimental results [2, 3, 4]

\[ R_G \propto M^{0.67 \pm 0.02} \]
\[ D \propto M^{0.55 \pm 0.02} \]
\[ [\eta] \propto M^{0.72 \pm 0.02} \]

These values \( v_G \) and \( v_D \) correspond on figure 3 to the range \( 10 < x < 10^3 \).

In principle the cross-over value can be obtained from \( S(q) \). The experiment has not been performed for polystyrene in benzene but it has been made for polystyrene in cyclohexane at various temperatures [13]. It is possible to obtain an approximate value of \( n_c \) by comparing experiments, in which the thermodynamic interactions are the same in both solvents and by extrapolating. This gives an estimated \( n_c \sim 200 \) monomers (i.e. \( M \sim 2 \times 10^4 \)) and shows that the measurements of dynamic quantities for polystyrene in benzene have indeed been made for values of \( x \) belonging to the range \( 10 < x < 10^3 \).

6. Relation between the expansion factors for \( R_G \) and \( [\eta] \). — The preceding model can also be tested with respect to the relation between the expansion factors

\[ x_G = \frac{R_G}{[R_G]_0} \]
\[ x^3 = \frac{[\eta]}{[\eta]_0} \]

where \( R_G \) and \( [\eta] \) are the radius of gyration and intrinsic viscosity in \( \theta \) conditions. From eq. (32), we see that

\[ x^3 = x_G^2, x_D. \quad (43) \]

Analytical expressions for \( x_G \) and \( x_D \) are readily obtained from eqs. (43) and (41)
A plot of \( \ln x^2_G \ln D \) versus \( \ln \theta' \) (for \( v = 0.59 \)) is shown on figure 4 and compared with the data collected by Yamakawa [7] to test his semi-empirical relation

\[
x_G = \left[ \frac{3(2v - 1)}{2v + 1} x^{-2} - \frac{2(2v - 1)}{2v + 2} x^{-3} + \frac{6}{(2v + 1)(2v + 2)} x^{2v-1} \right]^{1/2}
\]

\[
x_D = \left[ -\frac{3}{4(1-v)} x^{-1/2} + \frac{2v - 1}{4(2-v)} x^{-3/2} + \frac{3}{4(2-v)(1-v)} x^{(1/2-v)} \right]^{-1}.
\]

(44)

A plot of \( \ln x_G^2, \ln x_G \) versus \( \ln x_D^2 \) (for \( v = 0.59 \)) is shown on figure 4 and compared with the data collected by Yamakawa [7] to test his semi-empirical relation

\[
x_d^3 = x_G^{2.43}.
\]

These data are of various kinds:

a) data obtained with polymer solvent systems for which the \( \theta \) temperature can be experimentally reached and for which the expansion factor has been measured as a function of temperature; they are represented by circles of various kinds,

b) data obtained with polymer-solvent systems for which the \( \theta \) temperature cannot be experimentally reached. The data belonging to this class have been retained when \( n_0 \) and \( R^2 \) have been measured for identical samples in another solvent at temperature \( \theta \) and only in this case. These data are represented by triangles and squares. In order to avoid polydispersity effects, we rejected the data when the \( \theta \) values have to be interpolated by using a molecular weight dependence established with a different sample. Moreover, the viscosity results obtained with high molecular weight fractions have been carefully examined because non Newtonian effects might systematically lower \( x_G \). However, for large values of \( x_G \) (high molecular weights and very good solvent) the dispersion of points is large.

In spite of this fact, figure 4 shows that the agreement between experiments and our theoretical expectations is very satisfactory and our theory describes reality better than the perturbation expansion of \( x_G \) and \( x_D \). In particular, we note that the slope of our curve varies from the value 2/3 (for \( x = 1 \)) to the value 1 (when \( x \to \infty \)).

7. Conclusions. — It appears that the discrepancy between the exponents defining the molecular weight dependence of static and dynamic properties does not result from a difference in the static and dynamic scaling laws, but from the bigger influence of the spatial cross-over on hydrodynamic properties. In most cases, the polymer is not sufficiently flexible (large \( n_0 \)) and the solvent not sufficiently good (large \( n_C \)) for \( v_D \) to reach its asymptotical value in the experimental range of molecular weights where \( v_G \) is already equal to \( v \).

Static measurements of the critical indices are possible but it seems very difficult to measure these indices by dynamic methods because very high molecular weights would be needed. Similar considerations might also help to interpret the apparent dynamic scaling laws observed for semi-dilute solutions [3]. In that case, the hydrodynamic properties of the system are related to the behaviour of subchains of size equal to the screening length. It is then clear that the hydrodynamic properties of these subchains are generally sensitive to the same cross-over effects as an isolated chain.

References

[10] DES CLOIZEAUX, J., J. Physique Lett. 39 (1978) L-151. Note that the quantity \( \langle u \rangle/L^2 \) defined in this article (see Eq. (33)) is related to \( R_D \).