Dynamical scaling exponent $z$ for a single polymer chain by renormalization along the chain

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ÉNONCÉ. — L'exposant dynamique $z$ d'une chaîne polymérique isolée dans des solvants bons et au point thêta est obtenu, à l'ordre $\varepsilon = 4 - d$, pour le modèle de Rouse et Zimm à l'aide d'une transformation de renormalisation le long de la chaîne. Dans la limite où les interactions hydrodynamiques sont absentes, on trouve $z = 4 - \varepsilon/4 + \cdots$ pour un bon solvant ; quand elles sont présentes, $z = 4 - \varepsilon + \cdots$ pour des solvants bons au point thêta. Les résultats sont en accord avec ceux du développement phénoménologique de de Gennes.

Abstract. — The dynamical exponent $z$ for a single polymer chain in good and theta solvents is obtained to order $\varepsilon (= 4 - d)$ for the bead-spring (Rouse-Zimm) model by means of a renormalization transformation along the chain. In the free-draining limit $z = 4 - \varepsilon/4 + \cdots$ for a good solvent. In the non-draining limit $z = 4 - \varepsilon + \cdots$ for both good and theta solvents, all in agreement with the phenomenological predictions of de Gennes.

1. Introduction. — For the dynamics of a dilute solution of polymer chains in a good solvent it is of primary interest to determine the translational diffusion coefficient $D$ and the spectrum of relaxation times $\{\tau_q\}$ for the internal modes $\{q\}$ of a chain [1]. Of particular interest is how they are affected by the presence of excluded volume and hydrodynamic interactions.

Much progress has been made in the understanding of the static (equilibrium) properties of dilute polymer solutions. For an $N$ link chain with excluded volume the mean square end-to-end distance $\langle L^2 \rangle$ behaves as $\langle L^2 \rangle \sim N^{2\nu}$, where $\nu$ is a universal exponent independent, in the good solvent region, of the strength $V$ of the excluded volume interaction between links, but dependent on dimensionality, $d$. By use of the Landau-Ginzburg-Wilson isotropic $n$-vector model in the limit $n \to 0$ [2], $\nu$ can be found by an $\varepsilon$-expansion ($\varepsilon = 4 - d$) to be $\nu = \frac{1}{2}(1 + \varepsilon/8) + O(\varepsilon^2)$. Recently Gabay and Garel [3] have determined $\nu$ to $O(\varepsilon)$ by a direct renormalization group (R.G.) transformation along the chain.

In this letter we extend the use of this transformation to determine to $O(\varepsilon)$ the exponent $z$ associated with the dynamics of a chain; for example, $\tau \sim N^{\nu}$ and $D \sim N^{(2-\nu)/2}$ [4]. In the free-draining limit, when hydrodynamic interactions are neglected, it is found that $z = 4 - \varepsilon/4$, which is consistent with de Gennes' [4] prediction of $z = 2 + 1/\nu$ and with a recent calculation of $z$ to $O(\varepsilon)$ by Jasnow and Moore [5]. If hydrodynamic interactions are included it is found that $z = 4 - \varepsilon$ whether or not excluded volume forces are present, which confirms to $O(\varepsilon)$ de Gennes' conjecture [4] that $z = d$. The result is also consistent with a recent result of de Cloizeaux [6] from which a lower bound for $z$ can be deduced, $z \geq d$. Our value, $z = 4 - \varepsilon$, agrees with the calculation of Jasnow and Moore [5] if there are no excluded volume forces but disagrees with their result $z = 4 - 5 \varepsilon/4$ if excluded volume forces are included. An explanation of this discrepancy is advanced below.

The direct R.G. transformation is a perturbation expansion in $d$-dimensions combined with a blocking procedure. In section 2 we find the perturbation expansion results which allow us to derive recurrence relations to $O(\varepsilon)$, in section 3 where also the R.G. transformation is described, the fixed points are found and $z$ determined to $O(\varepsilon)$.

2. Model used and summary of perturbation theory results. — To describe polymer dynamics we use the Rouse-Zimm [7] bead-spring model with equations of motion

$$\dot{R}_{ij} = \sum_{j\neq i} D_{ij,j} \{ R \} \left[ -\frac{\partial U \{ R \}}{\partial R_{ij}} + f_{ij}(t) \right],$$

(1)
where $R_j(t)$ is the position of the $j$th bead ($j = 1, 2, ..., N$) and $a$ labels the Cartesian component.

$$U\{R\} = U_0\{R\} + U_1\{R\}$$

is the potential energy of a configuration $\{R\}$ given here by

$$(k_B T)^{-1} U\{R\} = (2b^2)^{-1} \sum_{j=1}^{N-1} R_{j-1,j}^2 + \frac{1}{2} V \sum_{k,l} \delta_{k,l} e^{i\theta R_{kj}}, \quad (2)$$

where $R_{kj} = R_k - R_j$ and $b^2 = d<R_{j+1,j}>$. The first term, $U_0$, represents the harmonic forces between neighbouring beads and the second, $U_1$, is the excluded volume contact potential. The effects of random collisions with solvent molecules are represented by the force $f_j(t)$ whose distribution function is taken to be Gaussian. The tensor $D$ is given by

$$D_{\alpha\beta} = \gamma \delta_{\alpha\beta} + T_{\alpha\beta} \{R\},$$

where $\gamma$ is the mobility of a bead and $T\{R\}$ is the Oseen tensor in $d$-dimensions by

$$T_{\alpha\beta} = \sum_k \frac{1}{\eta k^2} \left( \delta_{\alpha\beta} - \frac{k_{\alpha} k_{\beta}}{k^2} \right) e^{i\theta R_{k\alpha}}, \quad (3)$$

where $\eta$ is the viscosity of the solvent.

The polymer configuration distribution function $P\{R\};t$ evolves according to

$$\dot{\rho} = A\rho, \quad \rho = Z^{-1} \exp(-U\{R\}/k_B T)\rho,$$  \hspace{1cm} (4)

where $Z = \int d\{R\} \exp(-U\{R\}/k_B T)$ is the usual partition function and the operator $[8] A$ is given by

$$A = \sum \left( k_B T \frac{\partial}{\partial R_{\alpha\beta}} - \frac{\partial U\{R\}}{\partial R_{\alpha\beta}} \right) D_{\alpha\beta} \{R\} \frac{\partial}{\partial R_{\alpha\beta}}.$$ \hspace{1cm} (5)

The characteristic relaxation times of the system are then the inverse of the eigenvalues $\lambda_n$ of $A$.

$$Av_n\{R\} = -\lambda_n v_n\{R\}.$$ \hspace{1cm} (6)

The ground state, $\lambda_0 = 0$, $v_0$ corresponds to the equilibrium state.

If excluded volume and hydrodynamic interactions are neglected ($V = 0$, $T\{R\} = 0$) $A \rightarrow A^{(0)}$ can be diagonalized by use of normal (Rouse) coordinates, $\{p_q\}$,

$$R_j = N^{-1/2} p_0 + \sqrt{2} N^{-1/2} \times \sum_{\alpha=1}^{N-1} p_\alpha \cos \left[ \frac{\alpha\pi}{N} (j - 1/2) \right]. \quad (7)$$

The eigenfunctions of

$$A^{(0)} = \sum_{q=1}^{N-1} \frac{\partial}{\partial p_q},$$

are products of Hermite polynomials in the argument $\sqrt{\omega_q p_q}$ with, for $q \geq 1$,

$$\lambda_n^{(0)} = \gamma k_B T \frac{\partial^2}{\partial \rho_{0q}^2}, \quad \omega_q = -\lambda_n^{(0)} H_{\alpha q} H_{\alpha q} \sqrt{\omega_q p_q}, \quad (8)$$

where $\omega_q = N^{-1} \sum_{\alpha=1}^{N-1} (1 - \cos \frac{\alpha\pi}{N})$.

It is important to note that the centre-of-mass motion separates out; $A^{(0)} = \gamma k_B T \frac{\partial^2}{\partial \rho_{0q}^2}$ corresponds to the motion of the whole chain which diffuses like a particle with diffusion coefficient $D = \gamma k_B T/N$. In the free-draining limit ($T\{R\} = 0$) this result is generally true for any $U\{R\} = U(R_q)$ as may be shown by summing (1) over all beads. However, hydrodynamic interactions modify $D$. For a long Rouse chain we have for the first Rouse mode

$$\lambda_1^{(0)} \approx \gamma k_B T \left( q \pi / N \right)^2$$

and so for the internal relaxation times

$$\gamma^{(0)} \approx (\gamma k_B T)^{-1} \left( N \pi / q \right)^2.$$

Hydrodynamic and excluded volume interactions can be handled by perturbation theory from the Rouse solution. We write $A = A^{(0)} + A^{(1)} + A^{(2)} + A^{(3)}$, where

$$A^{(1)} = -(\gamma k_B T) \sum_{k,n,l} ik_n \exp[i\theta k \cdot R_{kj}] \frac{\partial}{\partial R_{kn}}$$

and

$$A^{(2)} = \sum \left\{ k_B T \frac{\partial}{\partial R_{\alpha\beta}} T_{\alpha\beta} \frac{\partial}{\partial R_{\alpha\beta}} - \frac{\partial U_0}{\partial R_{\alpha\beta}} T_{\alpha\beta} \frac{\partial}{\partial R_{\alpha\beta}} \right\}, \quad (10)$$

$$A^{(3)} = -\sum \left\{ \frac{\partial U_1}{\partial R_{\alpha\beta}} T_{\alpha\beta} \frac{\partial}{\partial R_{\alpha\beta}} \right\}, \quad (11)$$

and $\lambda_n = \lambda_n^{(0)} + \delta \lambda_n$ where $\delta \lambda_n$ is given by first order perturbation theory as

$$\delta \lambda_n = \sum_{i=1}^{3} \frac{\partial \lambda_n^{(0)}}{\partial \theta_i} \delta \theta_i,$$

and

$$\delta \lambda_n^{(0)} = -\int Z_0^{-1} \exp(-U_0/k_B T) v_0^{(0)} A^{(0)} v_0^{(0)} d\{R\},$$

$Z_0$ being the partition function appropriate to $U_0\{R\}$; here $U_0 = k_B T \sum_{q} \omega_q \rho_{0q}^2$ and $v_0^{(0)}$ are the unperturbed eigenfunctions of (8).

For the smallest eigenvalues (longest times) a
typical state is the \( g_\alpha \) oscillator once excited and all other oscillators in their ground states i.e.

\[
t_\alpha^{(0)} \propto H_1(\sqrt{\omega_\alpha \rho_\alpha}) .
\]

The \( A^{(0)} \) may be expressed in terms of the Rouse coordinates \( \{ p \} \) to evaluate the configurational integrals of eq. (12), e.g. for \( A^{(1)} \) one obtains

\[
\delta \lambda_{1(\alpha \sigma)}^{(1)} = - (\gamma k_B T) \frac{2}{N} \frac{q^2}{N} (l-1/2) Q_{\alpha}(l) \exp[-k^2 B_{\alpha}(l)] , \tag{13}
\]

where

\[
B_{\alpha}(l) = \frac{1}{2N} \sum_{q=N-1}^{N} \frac{Q_{\alpha}(l)q^2}{\omega_\alpha q} .
\]

and

\[
Q_{\alpha}(l) = \left[ \cos \frac{q\pi}{N} (l-1/2) - \cos \frac{q\pi}{N} (j-1/2) \right].
\]

The main contribution to \( B_{\alpha}(l) \) is from the small \( q \) region and for \( N \gg 1 \) we can assume \( l, j, |l-j| \gg 1 \) and obtain in the continuum limit

\[
B_{\alpha}(l) = b^2 |l-j|/2 .
\]

We evaluate the sum over \( k \) in (13) in \( d \)-dimensions \((d < 4)\) and the sums over \( l \) and \( j \) to obtain

\[
\delta \lambda_{1(\alpha \sigma)}^{(1)} = - \left( \gamma k_B T \right) \frac{2^4}{N} \frac{1}{b^d+2} \frac{(N)}{N} \Gamma \left( \frac{6-d}{2} \right) \cos \left( \frac{dn}{4} \right) \cos \left( \frac{dn}{4} \right) V^d .
\tag{14}
\]

Similarly, for \( A^{(2)} \) and \( A^{(3)} \) we obtain

\[
\delta \lambda_{1(\alpha \sigma)}^{(2)} = 2 k_B T \omega_\alpha \left( \frac{2}{N} \right) \frac{1}{b^d+2} \frac{2^4(1-d)}{(4-d)(2-d)} \frac{N}{(4-d)(2-d)} \Gamma \left( \frac{6-d}{2} \right) \cos \left( \frac{4-d}{4} \right) \gamma \eta b^{d-2} ,
\tag{15}
\]

and \( \delta \lambda_{1(\alpha \sigma)}^{(3)} = 0 \) [9]. From now on we shall refer to \( \lambda_{1(\alpha \sigma)} \) as \( \lambda \).

The mean translational diffusion coefficient \( D \) is given to first order by the Kirkwood [10] expression

\[
D = \frac{k_B T}{N} \left[ 1 + \frac{1}{16 \pi \eta \gamma N} \sum_{i} \left\langle \frac{1}{R_{ij}} \right\rangle \right] .
\]

Generalizing this result to \( d \)-dimensions we obtain

\[
D = \frac{k_B T}{N} \left[ 1 - \frac{2^4(1-d)}{(6-d)(4-d)(2-d)} \frac{1}{N} \Gamma \left( \frac{6-d}{2} \right) \gamma \eta b^{d-2} \right] ,
\tag{16}
\]

which suggests that excluded volume is irrelevant for \( d > 4 \).

The dynamics will be characterized by the mobility \( \gamma_p \). To lowest order \( \gamma_p = g^{-1} \gamma_{p-1} \) and so by Einstein’s law of diffusion \( D_p = g^{-1} D_{p-1} \) and also

\[
\lambda_p = \frac{\gamma_p k_B T}{\left\langle L_p^2 \right\rangle} \left( \frac{q^2}{N} \right)^2 = g^{-2} \lambda_{p-1} .
\]

We note that the viscosity of the solvent, \( \eta \), is unaffected by the blocking procedure. A dimensionless quantity which governs the dynamics is

\[
\left[ \gamma_p \eta \left\langle L_p^2 \right\rangle \right]^{-1} = g^{-2} \left[ \eta \left\langle L_{p-1}^2 \right\rangle \right]^{-1} ,
\]

which suggests hydrodynamic interactions become irrelevant for \( d > 4 \).

From Gabay and Garel [3] we have the approximate recursion relations correct to first order

\[
D = \frac{k_B T}{N} \left[ 1 - \frac{2^4(1-d)}{(6-d)(4-d)(2-d)} \frac{1}{N} \Gamma \left( \frac{6-d}{2} \right) \gamma \eta b^{d-2} \right] ,
\tag{16}
\]
which remain true in the presence of hydrodynamic interactions.

From section 2 we obtain approximate recursion relations for $\gamma_p$ and $\tau_p$ (or $\lambda_p$) correct to first order

\[ \gamma_{p+1} = \frac{D_p + 1}{k_B T g} \left[ 1 + \frac{2^2(1 - d)}{(4 - d)(2 - d)} \frac{1}{\gamma_p} \left\{ \frac{2^2 d}{\gamma_p} \right\} \right] \]

Note that the same recursion relation for $\gamma_p$ is obtained by using (20) instead of (19), and writing for $\gamma_p$ the equivalent expression

\[ \lambda_{p+1} = g^{-2} \lambda_p \left( 1 - \frac{2}{\gamma_p} \lambda_p + \frac{3}{2} \frac{\lambda_p}{\gamma_p} \right) \]

and (19), correct to $O(\varepsilon)$

\[ \lambda_{p+1} = g^{-2} \lambda_p \left( 1 - \frac{2}{\gamma_p} \lambda_p + \frac{3}{2} \frac{\lambda_p}{\gamma_p} \right) \]

Note that the same recursion relation for $\beta_p$ is obtained by using (20) instead of (19), and writing for $\beta_p$ the equivalent expression

\[ \beta_p = \left( 1 + \frac{2}{\gamma_p} \right) g^{-2} \frac{\lambda_p}{\gamma_p} \]

We now look for fixed points of $\alpha$ and $\beta$. We have of course the trivial fixed point $\alpha = 0$, $\beta = 0$ for all $p$, which gives Gaussian, free-draining behaviour. There are three non-trivial fixed points of (21) and (22)

\[ \alpha = \frac{e^2}{16} \ln g, \quad \beta = 0; \]

\[ \alpha = 0, \quad \beta = \frac{e^2}{3} \ln g; \]

where $\gamma_i$ are the associated eigenvalues. The fixed points of (25) and (26) are unstable and correspond to the free-draining limit with excluded volume, and to the non-draining limit without excluded volume respectively. The fixed point of (27) is stable and corresponds to excluded volume and hydrodynamic interactions both being included.

\[ \lim_{p \to \infty} \left( \frac{D_{p+1}}{D_p} \right) = g^{-1 + 3\varepsilon/8} \]
and from (23)

$$\lim_{p \to \infty} \left< \frac{L_{p+1}^2}{L_p^2} \right> = g^{1+\epsilon/8},$$

which with $D \sim g^{2-\alpha v}, \left< L^3 \right> \sim g^{2v}$ gives

$$z = 4 - \epsilon.$$  \hfill (29)

From (24) we have

$$\lim_{p \to \infty} \left( \frac{\lambda_{p+1}}{\lambda_p} \right) = g^{-2+\epsilon/4},$$

which with $\tau \sim g^{2v}$ also gives $z = 4 - \epsilon$. The exponents $z$ and $v$ for the other fixed points (25), (26) are calculated in the same way and are given in Table I.

<table>
<thead>
<tr>
<th>Fixed point</th>
<th>$\alpha_\infty$</th>
<th>$\beta_\infty$</th>
<th>Description</th>
<th>$v$</th>
<th>$z$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$e^2 \ln g$</td>
<td>$\alpha_0$</td>
<td>$\beta_0$</td>
<td>Free-draining limit, $\alpha_0 = \alpha_0(e)$, $\beta_0 = \beta_0(e)$.</td>
<td>$1/2 (1 + \epsilon/8)$</td>
<td>$4 - \epsilon/4$</td>
</tr>
<tr>
<td>$0$</td>
<td>$\alpha_0$</td>
<td>$\beta_0$</td>
<td>non-draining limit, no excluded volume</td>
<td>$1/2$</td>
<td>$4 - \epsilon$</td>
</tr>
<tr>
<td>$e^2 \ln g$</td>
<td>$\alpha_0$</td>
<td>$\beta_0$</td>
<td>non-draining limit, with excluded volume</td>
<td>$1/2 (1 + \epsilon/8)$</td>
<td>$4 - \epsilon$</td>
</tr>
<tr>
<td>$e^2 \ln g$</td>
<td>$\alpha_0$</td>
<td>$\beta_0$</td>
<td>with excluded volume</td>
<td>$1/2$</td>
<td>$4 - \epsilon$</td>
</tr>
</tbody>
</table>

Our direct R.G. calculation may be compared to the method of Jasnow and Moore [5] who using the notation of section 2 did perturbation theory in four dimensions. Exponents were then determined by exponentiating the logarithms for a special choice (in our notation) of the initial parameters $\alpha_0 = \alpha_0(e)$, $\beta_0 = \beta_0(e)$. The use of special values $\alpha_0(e)$, $\beta_0(e)$ is referred to as the removal of slow transients [11]. Jasnow and Moore determined $\alpha_0(e)$ and $\beta_0(e)$ by a matching procedure to $O(e)$. They obtained

$$\beta_0(e) = 2 \epsilon/3 + O(e^2)$$

in the absence of excluded volume ($\alpha_0 = 0$), which removes the slow transients in the approach to the fixed point of eq. (26). They then used the same value $\beta_0(e) = 2 \epsilon/3$ in the presence of excluded volume with $\alpha_0 = \epsilon/8$ to determine $z$. However, this value of $\beta_0(e)$ does not remove the slow transients in the approach to the fixed point of eq. (27) and so does not give the correct coefficients of the logarithms nor the correct exponent for the non-draining case with excluded volume. This point would become clear if the matching to find $\alpha_0(e)$, $\beta_0(e)$ were done by going to next order in perturbation theory. A further remark should be made here. Included in the definition of $\alpha$ and $\beta$ is a factor $g^{e^2}$ so that the recurrence relations contain factors like $\epsilon^{-1} g^{e^2}$. In 4 dimensions these appear as $\frac{1}{2} \ln g$ which leads to the special values of $\alpha_0$, $\beta_0$ being $2/(\epsilon \ln g)$ times the fixed point values $\alpha_\infty$, $\beta_\infty$.

4. Concluding remark. — Our calculation agrees with the phenomenological predictions of de Gennes [4] and is compatible with des Cloizeaux's result of $z \geq 3$ for $N \to \infty$ [6], but differs from the experimental results of Adam and Delsanti [12] who obtain $z = 2.85 \pm 0.05$. We think this discrepancy may be due to corrections to scaling.

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References

[8] See section 34 of Ref. [1].
[9] It is interesting to note that if the pre-averaged Oseen tensor (see Ref. [1]) is used, this term is not identically zero.