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DYNAMICAL SCALING EXPONENT z FOR POLYMER CHAINS IN A GOOD SOLVENT

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Résumé. — L'exposant dynamique z d'une chaîne polymérique isolée dans un bon solvant est obtenu à l'ordre $\varepsilon = 4 - d$ pour le modèle de Rouse et Zimm. Dans la limite où les interactions hydrodynamiques sont absentes, on trouve $z = 4 - \varepsilon/4 + \dots$ en accord avec le résultat $z = 2 + 1/\nu$ du développement phénoménologique de de Gennes. L'accord cesse hors de cette limite, les valeurs de z sont respectivement $4 - 5\varepsilon/4 + \dots$ et d , comme le confirment de récents résultats expérimentaux qui s'écartent des prédictions phénoménologiques.

Abstract. — The dynamical exponent z for a single polymer chain in a good solvent is obtained to order ε ($= 4 - d$) for the bead and spring (Rouse-Zimm) model. In the free-draining limit $z = 4 - \varepsilon/4 + \dots$, a result in agreement with a phenomenological prediction that $z = 2 + 1/\nu$ due to de Gennes. In the non-free draining limit, $z = 4 - 5\varepsilon/4 + \dots$, which disagrees with de Gennes' prediction that $z = d$ for this limit, but which is consistent with recent experimental work which finds departures from the phenomenological predictions.

A central question in the study of polymer dynamics is the determination of the spectrum of relaxation rates for a single polymer chain in a good solvent [1]. One is particularly interested in the interplay between hydrodynamic interactions, which are induced by flow fields associated with the motion of a monomer unit, and excluded volume interactions.

There have been considerable advances in elucidating the static (equilibrium) behaviour of such polymer chains. It is believed [2] that universal properties are described by the usual Landau-Ginzburg-Wilson isotropic n -vector model [3] in the limit $n \rightarrow 0$. For example, the mean square end-to-end distance of an N link chain behaves as $\langle (\mathbf{R}_1 - \mathbf{R}_N)^2 \rangle \sim N^{2\nu}$ with, in an $\varepsilon = 4 - d$ expansion,

$$2\nu = 2\nu(n=0) = 1 + \varepsilon/8 + O(\varepsilon^2).$$

The exponent ν is universal and does not depend on, say, the strength of the excluded volume forces, but does depend crucially on the dimensionality.

Dynamical aspects of polymer chains in solution are described in terms of the exponent z . For example, the

characteristic times τ of the internal relaxation modes behave with a power law dependence on N , viz. $\tau \sim N^{zv}$. The translational diffusion coefficient D of the chain [4] is given by $D \sim N^{(2-z)\nu}$. In this letter, we present an $O(\varepsilon)$ calculation of z . In the so-called free-draining limit, where the hydrodynamic interactions are neglected, the excluded volume forces can be handled by an ε expansion and it is found that $z = 4 - \varepsilon/4 + \dots$. This result is consistent with the conjecture of de Gennes [4] that in this limit $z = 2 + 1/\nu$. Unfortunately, the free draining limit is not realizable in practice, for the hydrodynamic interactions always dominate the dynamics. Even in the absence of excluded volume effects the relaxation times τ in the non-free draining limit cannot be given in closed form [1]. However, near four dimensions we are also able to treat the hydrodynamics by means of an ε expansion. Our final result for z in the presence of excluded volume effects is $z = 4 - 5\varepsilon/4 + \dots$, which disagrees with de Gennes' conjecture [4] $z = d$ whether or not excluded volume forces are present.

The bead-spring (Rouse-Zimm) [5] model is described by the equations of motion

$$\dot{R}_{i\alpha} = \sum_{m\beta} D_{i\alpha, m\beta} \{ R \} \left[- \frac{\partial U \{ R \}}{\partial R_{m\beta}} + f_{m\beta}(t) \right], \quad (1)$$

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where $\mathbf{R}_j(t)$ is the position vector of the j th bead ($j = 1, 2, \dots, N$) and $\alpha = 1, \dots, d$ labels the Cartesian component. $U\{R\}$ is the potential energy of a configuration $\{\mathbf{R}_j\}$ and $\mathbf{f}_j(t)$ represents the effects of random collisions with solvent molecules. The distribution function of this random force is taken as Gaussian. The tensor D is given by

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

where γ is the friction coefficient [6] and $T\{R\}$ is the Oseen tensor, generalised to d -dimensions, whose form in k -space is given in eq. (19), and which incorporates the long-range hydrodynamic interactions. In the free-draining limit $T\{R\} = 0$. The potential energy $U\{R\} = U_0\{R\} + U_1\{R\}$ is given by

$$(k_B T)^{-1} U\{R\} = (2b^2)^{-1} \sum_{j=1}^{N-1} \times \\ \times |\mathbf{R}_{j+1} - \mathbf{R}_j|^2 + \frac{1}{2} \sum_{\mathbf{k} \neq \mathbf{j}} V_k e^{i\mathbf{k} \cdot (\mathbf{R}_i - \mathbf{R}_j)}, \quad (2)$$

where the first term, U_0 , represents harmonic forces between neighbouring beads and the second, U_1 , is the excluded volume term. In the actual calculation we shall take $V_k = V = \text{constant}$, which implies a delta function self-interaction.

The time evolution of the polymer configuration distribution function $P[\{R\}; t]$ is governed by the operator [7] (sums over repeated indices implied)

$$A = \sum \left(k_B T \frac{\partial}{\partial R_{m\beta}} - \frac{\partial U\{R\}}{\partial R_{m\beta}} \right) D_{l\alpha, m\beta} \{R\} \frac{\partial}{\partial R_{l\alpha}}, \quad (3)$$

according to

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

where $Z = \int d\{R\} \exp(-U\{R\}/k_B T)$ is the ordinary partition function. The characteristic relaxation times of the system are the inverse of the eigenvalues λ_n ,

$$A v_n \{R\} = -\lambda_n v_n \{R\}, \quad (5)$$

as any function of configuration $X\{R\}$ relaxes according to

$$\langle X\{R_0\} \rangle_t = \langle X \rangle_{\text{eq}} + \\ + \sum_{n=1}^{\infty} X_n v_n \{R_0\} \exp(-\lambda_n t),$$

where $\{R_0\}$ symbolizes here the configuration at $t = 0$ and

$$X_n \equiv \int Z^{-1} \exp(-U/k_B T) X\{R\} v_n \{R\} d\{R\}.$$

If excluded volume and hydrodynamic interactions are neglected ($V_k = 0$ in (2) and $T\{R\} = 0$) the system of eq. (1) or (3) with $A \rightarrow A^{(0)}$ is directly soluble in terms of the normal (Rouse) coordinates

$$R_{j\alpha} = N^{-1/2} \rho_{0\alpha} + \sqrt{2} N^{-1/2} \times \\ \times \sum_{q=1}^{N-1} \rho_{q\alpha} \cos(q\pi(j-1/2)/N). \quad (6)$$

In these coordinates $A^{(0)}$ becomes diagonal, i.e.

$$A^{(0)} = \sum_{q=0}^{N-1} \sum_{\alpha} A_{q\alpha}^{(0)},$$

and the eigenfunctions of $A_{q\alpha}^{(0)}$ are Hermite polynomials in the argument $\sqrt{\omega_q} \rho_{q\alpha}$ with, for $q \geq 1$,

$$A_{q\alpha}^{(0)} H_{j(q\alpha)}(\sqrt{\omega_q} \rho_{q\alpha}) = -\lambda_{j(q\alpha)}^{(0)} H_{j(q\alpha)}(\sqrt{\omega_q} \rho_{q\alpha}), \\ \lambda_{j(q\alpha)}^{(0)} = (\gamma k_B T) 2j(q\alpha) \omega_q, \quad (7) \\ \omega_q = b^{-2}(1 - \cos q\pi/N), \quad j(q\alpha) = 0, 1, \dots, \infty.$$

The ground state, $j(q\alpha) = 0$ all $q \geq 1$, corresponds to the equilibrium state. Note that the center-of-mass motion separates out completely; we have

$$A_{0\alpha}^{(0)} = (\gamma k_B T) \partial^2 / \partial \rho_{0\alpha}^2$$

which corresponds to motion of the whole chain. The dynamics of the center-of-mass motion corresponds to diffusion of a particle with diffusion constant $\gamma k_B T/N$. For the free-draining limit ($T\{R\} = 0$) generally, this result is recovered for any

$$U\{R\} = U\{\mathbf{R}_i - \mathbf{R}_j\},$$

by summing (1) over all beads. Note that for a long Rouse chain, $\lambda_{1(q\alpha)}^{(0)} \approx (\gamma k_B T) q^2 \pi^2 / b^2 N^2$, which means that the internal relaxation times

$$\tau_q^{(0)} (\equiv \lambda_q^{-1}) \sim (\gamma k_B T / b^2)^{-1} (N / \pi q)^2.$$

The aim of this letter is to discover the modifications of the power law when excluded volume and hydrodynamic interactions are present. Our technique is to do first order perturbation theory in the excluded volume and hydrodynamic interactions in four dimensions, followed by the usual renormalization group technique of exponentiating the logarithms. We consider first the *free-draining limit*.

In this case we set $T\{R\} = 0$. Write $A = A^{(0)} + A^{(1)}$ with

$$(\gamma k_B T)^{-1} A^{(1)} \equiv \\ \equiv - \sum_{\mathbf{k}} \sum_{ij} i k_{\alpha} V_k \exp[i\mathbf{k} \cdot (\mathbf{R}_i - \mathbf{R}_j)] \partial / \partial R_{i\alpha}, \quad (8)$$

and $\lambda_n = \lambda_n^{(0)} + \delta\lambda_n$, with $\delta\lambda_n$ to first order in a perturbation expansion in $A^{(1)}$ just given by

$$\delta\lambda_n = - \int Z^{-1} \exp(-U_0/k_B T) v_n^{(0)} A^{(1)} v_n^{(0)} d\{R\}. \quad (9)$$

Here $(k_B T)^{-1} U_0 = \sum_q \omega_q \rho_{q\alpha}^2$, corresponding to the first term of (2) and $v_n^{(0)}$ are the unperturbed eigenfunctions of eq. (7). We consider the typical state with the $(q\alpha)$ oscillator once excited, namely

$$v_n^{(0)} \propto H_1(\sqrt{\omega_q} \rho_{q\alpha}).$$

$A^{(1)}$ can be expressed in terms of the Rouse coordinates $\{\rho_{q\alpha}\}$, and evaluation of (9) directly yields

$$(\gamma k_B T)^{-1} \delta\lambda_{1(q\alpha)} = -\frac{2}{N} \sum_{\mathbf{k}l j} \times \\ \times k_\alpha^2 V_k \cos \frac{q\pi}{N} (l - 1/2) Q_q(lj) \exp[-k^2 B_N(lj)], \quad (10)$$

where

$$B_N(lj) \equiv \frac{1}{2N} \sum_{q=1}^{N-1} \frac{Q_q(lj)^2}{\omega_q}, \quad (11)$$

and

$$Q_q(lj) \equiv [\cos q\pi(l - 1/2)/N - \cos q\pi(j - 1/2)/N].$$

The main contributions to $B_N(lj)$ come from the small q region. Furthermore, for a long chain we can assume $l, j, |l - j| \gg 1$. Going over to the continuum limit one finds $B_N(lj) = b^2 |l - j|/2$.

At this point in the analysis the dimensionality of space begins to play a role. When $d > 4$ the integrals over $\mathbf{k}$ and then the sums over l and j in (10) can be performed without divergences occurring. One finds that $\delta\lambda_{1(q\alpha)} \sim N^{-2}$ so that the characteristic relaxation times remain $\tau_q \sim N^2$ in the presence of excluded volume interactions. The power law is not modified, although particular amplitudes will be affected. For $d < 4$, the power law is modified strongly (e.g. $\delta\lambda \sim N^{1/2} \lambda^0$ in $d = 3$) and standard perturbation theories are not justified. In the special dimensionality $d = 4$ the leading correction is logarithmic. Specifically, one finds for large N

$$(\gamma k_B T)^{-1} \delta\lambda_{1(q\alpha)} = \\ = -2 K_4 b^{-6} (\pi^2 q^2/N^2) V \ln(N/\pi q) + \dots, d = 4, \quad (12)$$

where the dots symbolise terms which are weaker than logarithmic. In evaluating (10) we used

$$\sum_{\mathbf{k}} = K_d \int k^{d-1} dk.$$

One therefore has a relaxation time spectrum

$$\tau_q = \tau_q^{(0)} (1 + 2 K_4 V b^{-4} \ln(N/\pi q)). \quad (13)$$

The special choice $V_0 = V_0(\varepsilon)$ for obtaining exponents in $d = 4 - \varepsilon$ dimensions can be found as follows. The equilibrium exponents are believed to be given by the $n \rightarrow 0$ limit of an ordinary isotropic

n -vector model. In the formalism adopted here, equilibrium averages are ground state expectation values ($V_0 \{R\} = 1$). Perturbation theory to first order in V for the end-to-end distance yields

$$\langle (R_{N\alpha} - R_{1\alpha})^2 \rangle = \langle (R_{N\alpha} - R_{1\alpha})^2 \rangle_0 - \\ - \langle (R_{N\alpha} - R_{1\alpha})^2 \beta U_1 \rangle_{0c}. \quad (14)$$

where U_1 is the excluded volume term and $\langle \rangle_{0c}$ implies a cumulant average in the unperturbed system. One finds

$$\langle (\Delta R_\alpha)^2 \rangle = b^2 N(1 + 2 K_4 V b^{-4} \ln N) \\ \approx b^2 N^{2\nu}, \nu = 1/2(1 + \varepsilon/8) + O(\varepsilon^2), \quad (15)$$

which yields the special value $2 K_4 V_0 b^{-4} = \varepsilon/8$. Hence for the relaxation times we have

$$\tau_q \sim (\gamma k_B T/b^2)^{-1} (N/\pi q)^{2+\varepsilon/8}, \quad N \rightarrow \infty, \quad (16)$$

which implies via the definition $\tau_q \sim N^{zv}$ that $z = 4 - \varepsilon/4 + O(\varepsilon^2)$. This is one of our central results. The $O(\varepsilon)$ expression agrees with the phenomenological prediction of de Gennes [4]

$$z = 2 + 1/\nu = 4 - \varepsilon/4 + O(\varepsilon^2).$$

If the phenomenological argument is correct to all orders in ε it means that no new dynamical exponent is required in the free draining limit, that is, z is completely determined by equilibrium exponents. This situation usually arises when there are conservation laws present (cf. Model B [8]). As noted above, there is a kind of conservation law for the center-of-mass motion in that the form it takes is independent of $U \{R\}$. The decoupling of center-of-mass motions from internal motions is removed when hydrodynamical interactions are included, as in the *non-free draining limit*, to which we now turn.

The non-free draining limit is experimentally much more important than the free-draining limit. Perturbation expansions in the Oseen tensor $T \{R\}$ can also be formally constructed. If we neglect excluded volume interactions temporarily we have the perturbation

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

Diagonal matrix elements yield a shift in $\delta\lambda_n$ in the unperturbed (Rouse) eigenvalue $\lambda_n^{(0)}$, where

$$\delta\lambda_n = k_B T \sum Z_0^{-1} \int \exp(-U_0/k_B T) \times \\ \times \frac{\partial v_n^0}{\partial R_{m\beta}} T_{l\alpha, m\beta} \frac{\partial v_n^0}{\partial R_{l\alpha}} d \{R\}. \quad (17)$$

Z_0 is the partition function appropriate to $U_0 \{ R \}$. If we take the typical state with one excited mode,

$$v_n^{(0)} \propto H_1(\sqrt{\omega_q} \rho_{q\alpha}),$$

we find by direct computation that

$$\begin{aligned} \delta\lambda_{1(q\alpha)} &= k_B T(2\omega_q) \frac{2}{N} \times \\ &\times \sum_{lm} \cos \frac{q\pi(l-1/2)}{N} \cos \frac{q\pi(m-1/2)}{N} \\ &\times \sum_k \frac{(d-1) \exp(-k^2 B_N(lm))}{d\eta k^2}, \quad (18) \end{aligned}$$

where we have used the form for the Oseen tensor in k space

$$T_{\alpha\beta}(\mathbf{k}) = \frac{1}{\eta k^2} \left(\delta_{\alpha\beta} - \frac{k_\alpha k_\beta}{k^2} \right) \quad (19)$$

which is valid for general dimensionality. In first order only $T_{\alpha\alpha}(\mathbf{k})$ enters the calculation. We find once again that $d = 4$ is the special dimensionality. When $d > 4$ the hydrodynamical interactions do not appear to modify the power law for relaxation times, while for $d < 4$ the first order correction (18) strongly dominates the unperturbed eigenvalue. In $d = 4$ we find

$$\delta\lambda_{1(q\alpha)} = \frac{3}{2} k_B T(2\omega_q) K_4(\eta b^{d-2})^{-1} \ln(N/\pi q), \quad (20)$$

plus convergent terms. This means that for large N a typical relaxation time goes like

$$\tau_q = \tau_q^{(0)} \left[1 - \frac{3}{2} K_4(\eta b^2)^{-1} \ln(N/\pi q) \right].$$

Since it is believed [1, 4, 9] that in the absence of excluded volume forces $\tau_q \sim N^{d/2}$, one can deduce that the special value of $(\eta b^2)^{-1}$ which allows such exponentiation must be $\varepsilon/3$. (This value for $(\eta b^2)^{-1}$ could presumably be established directly by going to next order in perturbation theory in $T \{ R \}$).

The validity of this typical renormalization group technique for what is essentially only a problem in hydrodynamics was checked by applying it to a similar problem which is, however, also exactly soluble. The *pre-averaged* Oseen tensor [1, 9], for which

$$\begin{aligned} T_{1\alpha, m\beta} &= \delta_{\alpha\beta} \frac{d-1}{d-2} (2\pi)^{-d/2} d^{-1} (\eta b^{d-2})^{-1} \times \\ &\times \frac{1}{|l-m|^{(d-2)/2}}, \quad (21) \end{aligned}$$

is such that the eigenvalues of the A associated with it can be calculated analytically for all d (in the absence of excluded volume forces) and again they have the

power law dependence $\tau_q \sim N^{d/2}$. It is easy to show from the exact solution that there does indeed exist a value of $(\eta b^{d-2})^{-1} = \varepsilon/3 + O(\varepsilon^2)$, for which exponentiation of the expansion about $d = 4$ yields the correct power law dependence for τ_q . Notice that the pre-averaged Oseen tensor (which is obtained from the full Oseen tensor $T \{ R \}$ by assuming that the bead positions $\{ R_{j\alpha} \}$ in it are Gaussian random variables and averaging over them) and first-order perturbation theory on the full Oseen tensor yield the same logarithmic corrections (in first order) to the eigenvalues (but not the eigenvectors), thereby at least recovering the result $\tau_q \sim N^{2-\varepsilon/2}$ to $O(\varepsilon)$.

We are now in a position to put together the effects of excluded volume and hydrodynamics. The excluded volume interaction V is again supposed of $O(\varepsilon)$. Hence in a first-order calculation of its effects on the non-free draining eigenvalues, we can, correct to $O(\varepsilon)$, just use the Rouse free-draining eigenfunctions of (7) rather than the non-free draining ones, as the two sets of eigenfunctions differ only by terms of $O(\varepsilon)$. In other words, the perturbations from $T \{ R \}$ and U_1 do not mix to $O(\varepsilon)$ and we can use the previously established special values V_0 and $(\eta b^2)^{-1}$. Thus to $O(\varepsilon)$ we have for the case of both excluded volume and hydrodynamic interactions at the special values of the constants,

$$\tau_q = \tau_q^{(0)} [1 + (\varepsilon/8) \ln(N/\pi q) - (\varepsilon/2) \ln(N/\pi q)], \quad (22)$$

where the logarithms arise separately from the two perturbations. On exponentiating $\tau_q \sim (N/q)^{2-(3/8)\varepsilon}$. This result implies $\tau_q \sim N^{zv}$ with

$$z = 4 - 5\varepsilon/4 \neq d = 4 - \varepsilon.$$

As noted above, the value $z = d$ has been suggested by de Gennes [4] on the basis of phenomenological arguments.

A consequence of the failure of de Gennes' prediction is that the hydrodynamic radius R_H will not have the same exponent describing its N dependence as the end-to-end distance. This can be seen as follows. On the basis of scaling [4] one expects a characteristic wave-number dependent relaxation rate Γ_k of the form $\Gamma_k = \tau^{-1} f(kN^v)$ where $\tau \sim N^{zv}$. Such a rate can be determined by measurements of the polymer's dynamic structure factor $S(\mathbf{k}, t)$ [10]. At long wavelengths $\Gamma_k \sim Dk^2$ so that the translational diffusion coefficient $D \sim N^{(2-z)v}$. One refers to the quantity

$$R_H \sim N^{(z-2)v/(d-2)}$$

as the hydrodynamic radius ($D \sim kT/\eta R_H^{d-2}$ according to Stokes law in d -dimensions). The de Gennes prediction yields $R_H \sim N^v \sim N^{0.6}$ ($d = 3$), while we find $R_H \sim N^{3v/4} \sim N^{0.45}$. While we do not take the numerical estimate seriously, we note that it deviates in the right direction from the phenomenological prediction as seen in the recent experiments of Adam

and Delsanti [10] who quote $R_H \sim N^{0.55}$ with an uncertainty of ± 0.02 in the exponent. The phenomenological statement that the equilibrium and hydrodynamical radii are proportional is appealing, but evidently incorrect.

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