LETTER TO THE EDITOR

The dynamic exponent of the diffusion coefficient of a long polymer chain in good solvents

S Stepanow

Technische Hochschule 'Carl Schorlemmer' Leuna-Merseburg, Sektion Physik, 4200 Merseburg, GDR

Abstract. The path integral formulation of polymer dynamics proposed by the author enables one to obtain perturbation expansions for the transport quantities in powers of the excluded volume and the hydrodynamic interactions. The renormalisation-group analysis of the perturbation expansion of the diffusion coefficient gives, to first order of $\varepsilon = 4 - d$ (d is the space dimension), the dynamic exponent ν_D ($D \sim N^{-\nu_D}$) $\nu_D = \frac{1}{2} + \frac{1}{20}\varepsilon$.

Dynamical scaling (de Gennes 1979) predicts that the dynamical exponents are expressed through the static exponent ν. This prediction does not agree, however, with experiment. For example, for the diffusion coefficient dynamical scaling gives $\nu_D = \nu = 0.588$, whereas experimentally $\nu_D = 0.54$–0.56. Weill and des Cloizeaux (1979) explained this discrepancy by the argument that the mean reciprocal radius converges more slowly to the asymptotic limit ($N \to \infty$) than the radius of gyration. As a result, the experimental studies measure an effective exponent. The true dynamic exponent, however, coincides with ν in accordance with the prediction of de Gennes.

The explanation of Weill and des Cloizeaux, which is based on the Kirkwood formula for the diffusion coefficient, is approximate and cannot be considered as the final solution of the problem. A better consideration is possible in the framework of the perturbation expansions of the transport quantities. The path integral formulation of the dynamics of one polymer chain in solution proposed by the author (Stepanow 1983, 1984) enables one to obtain the perturbation expansions of the transport quantities in powers of the excluded volume and the hydrodynamic interactions. In this paper we study the diffusion coefficient in good solvents on the basis of the perturbation expansion.

The idea of path integral formulation consists of the following. The Kirkwood diffusion equation is a Fokker–Planck equation, which is the differential equation for Markovian processes. The transition probability for these processes is, indeed, a path integral. Here, we use the formalism proposed for the Fokker–Planck equation by Langouche *et al* (1979). The generating functional $Z(j, j^*)$ plays an important role in this formalism. We have shown (Stepanow 1984) that the dynamic quantities, such as the inelastic scattering function, diffusion coefficient and intrinsic viscosity, can be expressed through $Z(j, j^*)$. In this way we obtain the Feynman-like perturbation expansions for the dynamic quantities in powers of the excluded volume strength v_0 and the hydrodynamic interaction. In general, the perturbation series diverge logarithmically in four dimensions. These divergences appear as a consequence of the continuous chain which breaks down at the length $\lambda \sim l$ (l is the statistical segment

length). Using λ as a cutoff, which eliminates the interaction on lengths smaller than λ, we transform the infinities to logarithms $\ln(L/\lambda)$ (L is the arc length of the chain). In θ-conditions, the excluded volume strength will become zero and the series in powers of the hydrodynamic interaction still remains. The expansion parameter for the hydrodynamic interaction is conveniently chosen as follows: $\xi = (d/2\pi l)^{d/2}(\zeta z/\eta)l/d$. ζ is the friction coefficient, η the solvent viscosity, and d the space dimension. The contribution of the hydrodynamic interaction, to first order in ξ, to the diffusion coefficient (the Kirkwood term) contains the logarithmic singularity (see equation (3)) in four dimensions. The straightforward calculation which was performed by the author shows that the second-order contribution is regular. It is to be expected that the next terms in the expansion in powers of ξ are also regular. Then, the perturbation expansion in powers of ξ will have the form

$$\tfrac{3}{4}\xi L^{-1}\ln(L/\lambda) + L^{-1}f(\xi).$$

In the asymptotic limit the Kirkwood term leads. In d dimensions, the expansion parameter changes to $\xi l^{\varepsilon/2} N^{\varepsilon/2}$ ($\varepsilon = 4 - d$). Expanding $N^{\varepsilon/2}$ in powers of ε we represent the contribution of the hydrodynamic interaction for small ε as follows

$$[(d-1)/d]\xi(2/\varepsilon)L^{-l+\varepsilon/2} + L^{-1}(f_0(\xi) + \varepsilon f_1(\xi)\ln(N) + \ldots). \tag{1}$$

The functions f_0 and f_1 can be evaluated by means of perturbation theory. In the vicinity of four dimensions, the first term in (1) remains leading for large L. The Kirkwood term is also leading in three dimensions if we break off expansion (1) after the first terms and then put $\varepsilon = 1$.

Now we investigate the contribution of the excluded volume interaction to the diffusion coefficient. The diagrams contributing to D up to v_0^2 are given by Stepanow (1984, § 9). For the evaluation of ν_D to first order of ε the main logarithms of these diagrams are necessary. The result is

$$\zeta_D/kT = 1/N + [(d-1)/d]\xi L^{-1}\ln(L/\lambda)(1 - v_0\ln(L/\lambda) + 3v_0^2\ln^2(L/\lambda)) \tag{2}$$

The factor $(d/2\pi l)^{d/2}l^{-2}$ is absorbed in v_0. The transition to d dimensions is carried out by the change $\ln(L/\lambda) \to (2/\varepsilon)(L^{\delta/2} - \lambda^{\varepsilon/2})$.

The aim of the renormalisation is the absorbtion of the logarithms produced by the excluded volume on the right-hand side of equation (2) in the parameters of the theory. We suppose that these logarithms change only the chain length L and the excluded volume strength v_0. Equation (2) gives to first order of v_0

$$L' = L(1 + v_0\ln(L/\lambda)). \tag{3}$$

The term $3v_0^2\ln^2(L/\lambda)$ in (2) contributes to L' in the second order of v_0 and also changes v_0 in the term $-v_0\ln(L/\lambda)$. We write the equation for the effective interaction in the form

$$v = v_0(1 - \beta v_0\ln(L/\lambda)), \tag{4}$$

β is a constant which will be fixed below. Equations (3) and (4) can be regarded as a change of the parameter L and v_0 due to the change of the cutoff from λ to L. We arrive at the concept of the renormalisation group if we carry out this change step by step. Performing the infinitesimal transformation we obtain the following differential equations

$$\lambda' \partial \ln L'/\partial\lambda = v \qquad \lambda' \partial v/\partial\lambda' = -\beta v^2. \tag{5}$$

The integration of equations (5) with the boundary conditions

$$v(\lambda) = v_0, \qquad L'(\lambda) = L \qquad \text{and} \qquad \lambda' = L', \qquad v(\lambda') = v$$

gives

$$v = v_0/(1 + \beta v_0 \ln(L'/\lambda)) \tag{6}$$

$$L' = L(1 + \beta n_0 \ln(L'/\lambda))^{1/\beta}. \tag{7}$$

The comparison of the expansion of $1/L'$ with the expression in brackets on the right-hand side of equation (2) yields $\beta = 5$. In d dimensions equations (6)–(7) are

$$v = v_0/[1 + +(10/\varepsilon)v_0 L'^{\varepsilon/2}]$$

$$L' = L[1 + (10/\varepsilon)v_0 L'^{\varepsilon/2}]^{1/5}. \tag{8}$$

In the asymptotic limit equation (8) gives

$$L' = \left(\frac{10}{\varepsilon}v_0\right)^{2\nu D/5} L^{2\nu_D}$$

where the dynamic exponent ν_D is obtained as

$$\nu_D = \tfrac{1}{2} + \varepsilon/20$$

with $\nu_D = 0.55$ for $d = 3$. The equation (2) gives after renormalisation for the diffusion coefficient in d dimensions

$$\zeta_D/kT = 1/N + [(d-1)/d]\xi(2/\varepsilon)L'^{-1+\varepsilon/2}. \tag{9}$$

It can be easily proved that for small ε equation (9) reproduces the perturbation limit in the approximation employed.

In this work we deal for the first time with the theory of the diffusion coefficient on the basis of the perturbation expansion. The renormalisation group analysis of the perturbation series in the vicinity of four dimensions enables us to obtain the dynamic exponent of the diffusion coefficient. The exponent is calculated up to first order in ε. It does not coincide with the static exponent as predicted by the dynamical scaling of de Gennes (1979). The reason for this discrepancy probably consists in the different character of the perturbation expansions. The dynamical scaling approach deals with the Kirkwood formula for the diffusion coefficient which produces the perturbation expansion in powers of the interaction energy. This is a consequence of the pre-averaging of the hydrodynamic interaction. Our perturbation expansion is in fact an expansion in powers of the excluded volume force. Although, the value 0.55 for ν_D obtained in the first order of ε agrees well with experiment, we do not know how the ε^2-correction alters this result. The evaluation of ν_D in the same order as the static exponent requires much more effort.

References

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