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Renormalization-group study of the dynamical viscosity of dilute solutions of self-avoiding polymer chains

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The first-order excluded-volume correction to the dynamical viscosity of dilute polymer solutions is studied within the path-integral formulation of the Kirkwood diffusion equation. The renormalization of the dynamical viscosity $[\eta(\Omega)]$ is explicitly performed in two limits: (a) zero frequency $\Omega=0$, and (b) $\Omega\neq 0$, large contour length L (or finite L and $\Omega\rightarrow\infty$). The effect of screening the hydrodynamic interaction by increasing the excluded-volume strength is predicted. The renormalization at the Ω-dependent renormalization point enabled us to derive the scaling law for the dynamical viscosity $[\eta(\Omega)]\approx\Omega^{-(d\nu-1)/d\nu}$ within the renormalization group.

I. INTRODUCTION

The transport properties of dilute polymer solutions have mainly been studied by using the Kirkwood diffusion equation.[1-4] Until recently, no efficient theoretical methods were available to treat this equation. Obtaining quantitative results from the Kirkwood diffusion equation required a number of approximations.

Because of the formal analogy between the Kirkwood diffusion equation and the Schrödinger equation, the powerful path-integral methods were applied to treat the former. In this way, the perturbation expansions of the transport quantities of dilute polymer solutions in powers of the excluded-volume strength and the hydrodynamic interaction are derived.[5-7]

The contribution of the excluded volume to the steady-state viscosity to the first order in $\epsilon=4-d$ (d is the space dimension) has previously been studied in Refs. 8–11 within the Kirkwood-Riseman formalism. The intrinsic dynamical viscosity has been considered by using the Langevin formalism in Refs. 12 and 13.

The excluded-volume effects on the dynamical viscosity are studied in[12,13] by carrying out the renormalization at zero frequency (the $\Omega=0$ renormalization point). This method is not efficient for studying the large-frequency limit of the dynamical viscosity.

In this article we study the dynamical intrinsic viscosity by using the path-integral formulation of the Kirkwood diffusion equation. The large-frequency behavior of the intrinsic viscosity is studied by carrying out the renormalization at the frequency-dependent renormalization point.

II. RENORMALIZATION-GROUP ANALYSIS OF THE DYNAMICAL VISCOSITY

The calculations of the dynamical viscosity to first order in the hydrodynamic interaction are given in Refs. 7, 14, and 15. The bare calculations are the basis for performing the renormalization-group (RG) analysis, which is different in Refs. 14, 15, and 7. In the present paper we consider the first-order excluded-volume correction to the dynamical viscosity. The same problem was considered in Refs. 12 and 13 on the basis of the Langevin formalism of polymer dynamics. The RG analysis is there the same as in Ref. 14.

The steady-state intrinsic viscosity $[\eta(0)]$ to the first-order of the excluded volume strength is obtained from Eqs. (A2) and (A4) of the Appendix as follows:

$$[\eta]=(N_A\zeta_0/12dM\eta_s)\times L^2[1+(2/\epsilon)\overline{v}_0L^{\epsilon/2}-\tfrac{13}{12}\overline{v}_0L^{\epsilon/2}+\cdots], \qquad (2.1)$$

where $\overline{v}_0=(d/2\pi l)^{d/2}v_0l^{-2}$ is introduced. Equation (2.1) coincides with the result obtained in the Kirkwood-Riseman formalism.[10,16]

Now we consider the renormalization of the intrinsic viscosity. The analysis of the divergences of the perturbation expansion of the intrinsic viscosity could give the prescription for the renormalization. It is expected that the excluded-volume singularities of the dynamical quantities belong to the universality class of the equilibrium excluded-volume problem. In this case, the dynamical exponent does not appear. The analysis of this problem is very difficult, and so far it has not been carried out. Under these circumstances we assume that the renormalization of L and v_0 in the dynamical perturbation expansion coincides with that in the equilibrium case.

The renormalization of L and v_0 to the first order in the excluded-volume strength is given by[17]

$$L'=L[1+(2/\epsilon)\overline{v}_0L^{\epsilon/2}+\cdots], \qquad (2.2)$$

$$v'=v_0[1-(8/\epsilon)\overline{v}_0L^{\epsilon/2}+\cdots]. \qquad (2.3)$$

From Eqs. (2.1)–(2.3) it follows that to the first order of the excluded-volume strength the monomer friction coefficient ζ_0 has to be renormalized as

$$\zeta'=\zeta_0[1-(2/\epsilon)\overline{v}_0L^{\epsilon/2}+\cdots]. \qquad (2.4)$$

Taking into account the first-order correction of the hydrodynamic interaction,[7] we obtain

$$\xi'=\xi_0[1-(2/\epsilon)\overline{v}_0L^{\epsilon/2}-(3/2\epsilon)\xi_0L^{\epsilon/2}+\cdots], \qquad (2.5)$$

where $\xi_0=(d/2\pi l)^{d/2}\zeta_0/(d\eta_s)$ is introduced.

Following our studies[6,7] we introduce the cutoff λ by demanding that Eqs. (2.2)–(2.5) remain finite in four dimensions. For this it is sufficient to modify the term $(2/\epsilon)L^{\epsilon/2}$ as follows: $(2/\epsilon)(L^{\epsilon/2}-\lambda^{\epsilon/2})$. In our opinion, this procedure can be performed in all orders of the perturbation expansion.

The renormalization group can be introduced by demanding that the physical quantities are invariant under the transformation of the cutoff,

$$f(L,\bar{v}_0,\xi_0,\bar{v}_0L^{\epsilon/2},\xi_0L^{\epsilon/2},\lambda) =f(L',\bar{v}',\xi',\bar{v}'(L')^{\epsilon/2},\xi'(L')^{\epsilon/2},\lambda') . \qquad (2.6)$$

The renormalization group describes the changes of the parameters L', $\bar{v}'$, and ξ' caused by the change of the cutoff.

For the dimensionless interaction constants $w=\xi'(\lambda')^{\epsilon/2}$ and $g=\bar{v}'(\lambda')^{\epsilon/2}$ we obtain the following differential equations of the RG:

$$\lambda' dw/d\lambda'=(\epsilon/2)w-w(g+\tfrac{3}{4}w)+\cdots . \qquad (2.7)$$

$$\lambda' dg/d\lambda'=\epsilon/2-4g^2+\cdots . \qquad (2.8)$$

Equation (2.8) has the nontrivial fixed point g^*. Eq. (2.7) has two nontrivial fixed points $w_1^*=\frac{2}{3}\epsilon$ and $w_2^*=\epsilon/2$. The solution of Eq. (2.7) is

$$w=4zw_0Q^{(\epsilon-2)/8}/[4z+w_0(Q^{3/4}-1)] , \qquad (2.9)$$

where $Q=1+(8/\epsilon)\bar{v}_0\lambda_m^{\epsilon/2}$, $\bar{v}_0=v_0l^{-2}(d/2\pi l)^{d/2}$, $z=\bar{v}_0L^{\epsilon/2}$ is the excluded-volume parameter, and λ_m is the final value of the parameter of the renormalization group.

The equations of the renormalization group (2.7) and (2.8) do not depend on the contour length L governing the infrared behavior of the perturbation expansion. Using the matching condition

$$\lambda_m=L' , \qquad (2.10)$$

with

$$L'/L=Q^{1/4} , \qquad (2.11)$$

enables one to include the information about the infrared behavior of the perturbation expansions into the RG equations. For the large L from Eq. (2.11) follows the scaling law for the effective parameter L',

$$L'\approx L\lambda_m^{(2\nu-1)/2\nu} , \qquad (2.12)$$

with $\nu=\frac{1}{2}+\epsilon/16$ being the critical exponent computed to order ϵ. Equations (2.10)–(2.12) give the power law

$$L'\approx L^{2\nu} . \qquad (2.13)$$

We note that the choice of the matching condition is not unique. In order to absorb the infrared singularities of the perturbation expansion into the parameters ζ, v, and L' of the ultraviolet renormalized theory it is sufficient to demand that $\lambda_m=\alpha L'$ with α being an arbitrary numerical factor. However, it is easy to see that using $\alpha\neq 1$ leads also to (2.9) with the quantities w, w_0, and v_0 changed as follows: $w\rightarrow w\alpha^{\epsilon/2}, \ldots$. The special value $\alpha=1$ corresponds to the renormalization with the minimal subtractions.

With increasing L and $v_0\neq 0$, the effective interaction constant w decreases, tending to the fixed point $\epsilon/2$. The consequence of this behavior of w is that the effective dynamic exponent $\nu_{\rm eff}^H$ defined by

$$[\eta]\approx L^{3\nu_{\rm eff}^H-1} \quad (d=3)$$

is smaller than the effective static exponent $\nu_{\rm eff}$. But the quantitative calculations for the parameter $z\approx 4.5$ and $w_0\approx 200$ yield $\nu_{\rm eff}-\nu_{\rm eff}^H\approx 0.003$, whereas the experimental finding is[18] $\nu_{\rm eff}-\nu_{\rm eff}^H\approx 0.02$. Taking into account the regular terms does not change this difference significantly, we note that the explanation of the inequality $\nu_{\rm eff}^H<\nu_{\rm eff}$ given above differs from that of Weill and des Cloizeaux, based on the blob model.

Taking into account the hydrodynamic interaction[7] we obtain the renormalized steady-state intrinsic viscosity as

$$[\eta]=\zeta(N_A/12dM\eta_s)(L')^2(1-\tfrac{13}{12}g+\tfrac{7}{6}w) , \qquad (2.14)$$

where the effective monomer friction coefficient ζ is defined by

$$\zeta=wd\eta_s(2\pi l/d)^{d/2}\lambda_m^{-\epsilon/2} . \qquad (2.15)$$

The effective interaction constant g is defined by

$$g=\bar{v}(L')^{\epsilon/2} \qquad (2.16)$$

with $\bar{v}=\bar{v}_0/Q$. By using g and w to the second order in ϵ, Eq. (2.14) gives $[\eta]$ to order ϵ^2. Eqs. (2.7)–(2.16) make it possible to study not only the scaling limit of $[\eta]$ but also the crossover behavior when g and w are not near to their fixed point values.

From Eq. (2.9) we predict the following effect. With increasing v_0 the effective interaction constant w tends to zero. This means that in the limit $v_0\rightarrow\infty$ the hydrodynamic interaction will be screened. As a result, the diffusion coefficient shows the Rouse behavior

$$D\approx kT/\zeta_0N .$$

This effect can be understood intuitively as follows. With increasing v_0 the polymer coil swells and the average monomer density within the coil decreases. For the solvent within the coil it becomes more difficult to move together with the coil, and consequently the draining increases. In accordance with the remark made above on the matching condition the use of $\alpha\neq 1$ does not influence the screening effect.

The observation of this effect depends on the relation between w_0 and z. Whereas in good solvents z can reach the value 4–5, the typical values of w_0 are not known. Since the draining effects have not been observed as far, w_0 is expected to be large. v_0 can be made greater by choosing the appropriate solvent and increasing the temperature.

The renormalization procedure described above can be designated as renormalization at the renormalization point $\Omega=0$. An analogous technique has been used to renormalize the dynamical viscosity in Refs. 14 and 15.

However, it is not efficient for studying the behavior of the dynamical viscosity at high frequencies. In Ref. 7, in connection with the investigation of the dynamical viscosity, the high-frequency behavior has been studied by using the frequency-dependent renormalization point. Here we extend this method in order to include the excluded-volume effects.

We start with Eqs. (A8) and (A9). The $1/\epsilon$ singularity renormalizes the contour length L and the monomer friction coefficient as follows:

$$L'=L[1+(2/\epsilon)\bar{v}_0 b^{-\epsilon/2}+\cdots], \tag{2.17}$$

$$\xi'=\xi_0[1-(2/\epsilon)\bar{v}_0 b^{-\epsilon/2}+\cdots]. \tag{2.18}$$

By taking the hydrodynamic interaction into account Eq. (2.18) is changed as follows:[7]

$$\xi'=\xi_0\left[1-(2/\epsilon)\bar{v}_0 b^{-\epsilon/2}-\frac{3}{2\epsilon}\xi_0 b^{-\epsilon/2}+\cdots\right]. \tag{2.19}$$

To ensure that Eqs. (2.17)–(2.19) remain finite for $d=4$ we modify the term $b^{-\epsilon/2}$ as follows: $b^{-\epsilon/2}-\lambda^{\epsilon/2}$.

In complete analogy to renormalization at the zero frequency, Eqs. (2.17)–(2.19) can be used to derive the differential equations of the renormalization group. It is remarkable that these equations coincide with that obtained for the zero frequency. The equations of the renormalization group (2.7) and (2.8), which are the equations of the ultraviolet renormalization, do not depend on the parameter L and Ω governing the infrared behavior of the perturbation expansion. The only difference from the previous case consists of the change of the matching condition. For both theta and good solvents, the matching condition for large Ω has to be chosen as

$$\lambda_m=(\zeta\Omega/2dkT)^{-1/2}, \tag{2.20}$$

where the effective monomer fricton coefficient scales as

$$\zeta=wd\eta_s(2\pi l/d)^{d/2}\lambda_m^{-\epsilon/2}. \tag{2.21}$$

From Eqs. (2.20) and (2.21) λ_m is obtained as

$$\lambda_m=[(2\pi l/d)^{d/2}wd\eta_s\Omega/2dkT]^{-2/d}. \tag{2.22}$$

Equations (2.21) and (2.22) give the effective monomer friction coefficient.

For large frequencies the dynamical viscosity behaves as

$$[\eta(\Omega)]\approx(L'/L)(\zeta/\Omega)^{1/2}, \tag{2.23}$$

where L' is given by Eq. (2.11). From Eqs. (2.11) and (2.21)–(2.23) we obtain the scaling law of the dynamical viscosity

$$[\eta(\Omega)]\approx\Omega^{-(d\nu-1)/d\nu}. \tag{2.24}$$

We note that the renormalization-group derivation of the scaling law (2.24) differs from the derivation based on the scaling arguments. The renormalized dynamical viscosity is obtained from Eqs. (A8) and (A9) by omitting the $1/\epsilon$ pole and replacing the bare quantities ζ_0, L, and $\bar{v}_0 b^{-\epsilon/2}$ by ζ, L', and g, respectively.

III. CONCLUSION

In the present paper we presented the study of the dynamical intrinsic viscosity of dilute polymer solutions in good solvents on the basis of the path-integral formulation of the Kirkwood diffusion equation. In carrying out the renormalization of the dynamical viscosity we stress the explicit calculation of the effective-interaction constant of the hydrodynamic interaction w, which is given to the first order in ϵ. For the first time, we predict the effect of the screening of the hydrodynamic interaction with increasing excluded-volume strength. In order to study the high-frequency behavior of the dynamical viscosity we apply the renormalization procedure at the Ω-dependent renormalization point.

APPENDIX

The dynamical intrinsic viscosity up to the first order of the excluded-volume strength is obtained within the path-integral formulation of the Kirkwood diffusion equation[6,7] as follows:

$$\begin{aligned}[\eta(\Omega)]^1=(N_A kT/M\eta_s)\int_0^\infty dt\int_0^t d\tau\, e^{-i\Omega t}\frac{1}{2}v_0 l^{-2}(2\pi)^{-d}\\
\times\int d^dq\int_0^L ds_1\int_0^L ds_2[2D_{(n)}^2(t)(Q_{s_1n}-Q_{s_2n})^2q_x^2\\
-2\lambda_{(n)}^{-1}D_{(n)}^2(\tau)(Q_{s_1n}-Q_{s_2n})^2D_{(k)}^2(t-\tau)\\
\times(Q_{s_1k}-Q_{s_2k})^2q_x^2q_y^2\\
+\lambda_{(k)}^{-1}D_{(k)}^2(t)(Q_{s_1k}-Q_{s_2k})^2\lambda_{(n)}^{-1}\\
\times(Q_{s_1n}-Q_{s_2n})^2q_x^2q_y^2]\exp(-q^2l|s_2-s_1|/2d),\end{aligned} \tag{A1}$$

where $D_0=kT/\zeta_0$, $\lambda_{(n)}=(d/l)(\pi n/L)^2$, $Q_{sk}=(2/L)^{1/2}\cos(\pi k/L)$ $(k=1,2,\ldots)$, and $Q_{s0}=L^{-1/2}$.

The steady-state viscosity is obtained to first order of the excluded-volume strength from (A1) as

$$[\eta]=(N_A\zeta_0/12dM\eta_s)L^2[1+2zI(\epsilon)], \tag{A2}$$

where $I(\epsilon)$ is given by

$$I(\epsilon)=1/[(2+\epsilon/2)(3+\epsilon/2)][6/\epsilon+(\epsilon/2)/(1+\epsilon/2)-(6+3\epsilon/2)/(8+2\epsilon)]\ , \tag{A3}$$

and the excluded-volume parameter $z=\bar{v}_0 L^{\epsilon/2}$ is introduced.

For small ϵ, $I(\epsilon)$ is obtained as

$$I(\epsilon)\approx 1/\epsilon-\tfrac{13}{24}\ , \tag{A4}$$

which coincides with the results obtained in Ref. 10.

For high frequencies the intrinsic viscosity is computed from (A1) as

$$[N_A \bar{v}_0 \zeta_0 L/(dM\eta_s)](i^{1/2}b)^{-1-\epsilon/2} I_2(\epsilon)\ , \tag{A5}$$

where $I_2(\epsilon)$ is given by

$$I_2(\epsilon)=\Gamma(1+\epsilon/2)\{3/2\epsilon-\tfrac{1}{4}-[-5/\epsilon+8(2)^{-\epsilon/2}/\epsilon+\tfrac{1}{2}]/(3-\epsilon/2)\}/[(1-\epsilon/2)(2-\epsilon/2)] \tag{A6}$$

and $b=[\zeta_0\Omega/(2dkT)]^{1/2}$ is introduced. For small ϵ, $I_2(\epsilon)$ is given by

$$I_2(\epsilon)=[1/\epsilon-\tfrac{5}{12}+8(\ln 2)/3]/4+O(\epsilon)\ . \tag{A7}$$

For high frequencies the dynamic viscosity is obtained up to first order of the excluded-volume strength as

$$\mathrm{Re}[\eta(\Omega)]=(N_A/4d\eta_s M)\zeta_0 L b^{-1} 2^{-1/2}\{1+\bar{v}_0 b^{-\epsilon/2}[1/\epsilon+8(\ln 2)/3-\tfrac{5}{12}-C-\pi/8)]\} \tag{A8}$$

$$-\mathrm{Im}[\eta(\Omega)]=(N_A/4d\eta_s M)\zeta_0 L b^{-1} 2^{-1/2}\{1+\bar{v}_0 b^{-\epsilon/2}[1/\epsilon+8(\ln 2)/3-\tfrac{5}{12}-C+\pi/8]\}\ , \tag{A9}$$

where C is the Euler number.

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