

## Cooperative Diffusion Constant of Semidilute Polymer Solutions

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A renormalization-group theoretical result for the concentration dependence of the cooperative diffusion constant of semidilute polymer solutions is given. The result satisfactorily explains the recent experimental result by Wiltzius *et al.* This is the first application of the renormalization-group theory to semidilute-solution transport properties.

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Renormalization-group theoretical approaches have been very successful in explaining the macroscopic properties of polymer solutions.<sup>1-6</sup> However, there has been no renormalization-group theory of transport properties of semidilute solutions where overlap of chains is important. There is even no renormalization-group theoretic calculation of the concentration derivative at zero concentration of transport properties (e.g., the Huggins coefficient). The reason is that so far there is no tractable method to take into account the hydrodynamic screening effect which is presumably crucial to eliminate divergences in the transport coefficients.<sup>7</sup>

In this Letter we show that, within the Kirkwood-Riseman scheme,<sup>8</sup> we can straightforwardly and consistently extend our method for obtaining transport coefficients<sup>5,9</sup> for the dilute solution to the semidilute solution. We calculate the cooperative diffusion constant  $D_{\text{coop}}$  which appears in the hydrodynamic description of the fluctuation of the monomer number density field  $\rho$  as

$$\partial\rho/\partial t = D_{\text{coop}}\Delta\rho. \quad (1)$$

Our lowest-nontrivial-order calculation gives results in good agreement with the recent experimental result of Wiltzius *et al.*<sup>10</sup>

The cooperative diffusion coefficient can be written as<sup>11</sup>

$$D_{\text{coop}} = s(\partial\pi/\partial c)/N, \quad (2)$$

where  $\pi$  is the osmotic pressure,  $c$  is the polymer number density,  $N$  is the degree of polymerization, and  $s$  is the sedimentation coefficient defined by

$$\bar{\mathbf{v}} = s\bar{\mathbf{f}}_m, \quad (3)$$

with  $\bar{\mathbf{v}}$  being the velocity of the center of mass of a

polymer, and  $\bar{\mathbf{f}}_m$  the external force per monomer.

Since we know the osmotic compressibility, which is in good agreement with experiments,<sup>3,4,12</sup> we have only to calculate the sedimentation coefficient. We use the (suitably modified) Kirkwood-Riseman formalism to this end.

In the Kirkwood approximation,<sup>8</sup> we assume that the relaxation time of the solvent velocity field is much faster than that of the polymer conformations (i.e., the fluid faithfully follows the motion of polymers without delay). Thus we use the stationary solution to the linearized Navier-Stokes equation in a closed container,

$$-\eta_0\Delta\bar{\mathbf{u}} = -\nabla p + \rho(\bar{\mathbf{r}})\bar{\mathbf{f}}(\bar{\mathbf{r}}) \quad (4)$$

where  $\bar{\mathbf{u}}$  is the solvent velocity field,  $\eta_0$  is the solvent viscosity,  $p$  is the pressure,  $\rho(\bar{\mathbf{r}})$  is the monomer-number-density field, and  $\bar{\mathbf{f}}$  is the force exerted on the solvent by the monomers. The general solution to (4) with the incompressibility condition  $\nabla \cdot \bar{\mathbf{u}} = 0$  is

$$\bar{\mathbf{u}}(\bar{\mathbf{r}}) = \bar{\mathbf{u}}_0(\bar{\mathbf{r}}) + \int d^d r' \bar{\mathbf{T}}(\bar{\mathbf{r}} - \bar{\mathbf{r}}')\rho(\bar{\mathbf{r}}')\bar{\mathbf{f}}(\bar{\mathbf{r}}'), \quad (5)$$

where  $\bar{\mathbf{u}}_0$  is a solution to (4) with  $\bar{\mathbf{f}} = \bar{\mathbf{0}}$  (the corresponding homogeneous equation) and  $\bar{\mathbf{T}}$  is the Oseen tensor given by

$$\bar{\mathbf{T}}(\bar{\mathbf{r}}) = (2\pi)^{-d} \int d^d k \frac{1}{\eta_0 k^2} \left[ 1 - \frac{\bar{\mathbf{k}}\bar{\mathbf{k}}}{k^2} \right] e^{i\bar{\mathbf{k}} \cdot \bar{\mathbf{r}}}, \quad (6)$$

with  $d$  being the spatial dimensionality. Notice that  $\bar{\mathbf{u}}_0$  is necessary to satisfy the boundary condition. Let  $\zeta_0$  be the (bare) friction constant for a monomer. Then, following Kirkwood,<sup>8</sup> we have

$$\rho(\bar{\mathbf{r}})\bar{\mathbf{f}}(\bar{\mathbf{r}}) = \zeta_0\rho(\bar{\mathbf{r}})[\bar{\mathbf{v}}(\bar{\mathbf{r}}) - \bar{\mathbf{u}}(\bar{\mathbf{r}})], \quad (7)$$

where  $\vec{v}(\vec{r})$  is the velocity of the monomer at  $\vec{r}$ . Combining (5) and (7), we get

$$\rho(\vec{r})\vec{f}(\vec{r}) = \zeta_0\rho(\vec{r})[\vec{v}(\vec{r}) - \vec{u}_0(\vec{r})] - \zeta_0\rho(\vec{r}) \int \vec{T}(\vec{r} - \vec{r}')\rho(\vec{r}')\vec{f}(\vec{r}')d^d r', \quad (8)$$

which is essentially the Kirkwood-Riseman equation.<sup>8</sup> However, note that  $\vec{u}_0$  is *not* the unperturbed flow field (which is zero in our problem) but a mathematical device to satisfy the boundary condition of the system under consideration.

In a sedimentation experiment in a *closed* container, there is no net flow (especially in our case where the volume fraction of polymers is negligibly small). Therefore on the average  $\vec{u}$  must vanish. Thus from (5) we can approximately determine  $\vec{u}_0$  in the bulk as

$$\vec{u}_0(\vec{r}) = - \int d^d r' \vec{T}(\vec{r} - \vec{r}') \langle \rho(\vec{r}') \vec{f}(\vec{r}') \rangle, \quad (9)$$

where  $\langle \rangle$  denotes an ensemble average.<sup>13</sup> Since the unperturbed flow is zero in our present problem, (9) is different from the unperturbed flow. With (9) we can solve (8) iteratively to obtain [putting  $\vec{v}(\vec{r}) = \vec{v}$ ],

$$\rho(\vec{r})\vec{f}(\vec{r}) = \zeta_0\rho(\vec{r})[1 - \zeta_0 \int \vec{T}(\vec{r} - \vec{r}')\delta\rho(\vec{r}')d^d r']\vec{v} + \dots, \quad (10)$$

where  $\delta\rho(\vec{r}) = \rho(\vec{r}) - \rho_0$ , with  $\rho_0$  being the average monomer number density. Now the second term of (10) is finite due to the subtraction in  $\delta\rho(\vec{r})$ . This subtraction comes from (9), i.e., from the correct consideration of the boundary condition. From (10) we finally get, using the definition (3) (note that  $\int \rho \vec{f} d^d r = \vec{f}_m \int \rho d^d r$ , because internal forces among polymer elements cancel each other),

$$s = \zeta_0^{-1} + \rho_0^{-1}(1 - d^{-1}) \int d^d r \vec{T}(\vec{r})S(\vec{r}), \quad (11)$$

where  $S(\vec{r}) = \langle \delta\rho(\vec{r})\delta\rho(0) \rangle$ , for which we need the zeroth-order result to get  $s$  to order  $\epsilon$  ( $= 4 - d$ ).

In the above solution,  $\vec{T}$  is the bare Oseen tensor instead of the screened Oseen tensor. The introduction of the hydrodynamic screening was originally to remove the divergence in transport coefficients.<sup>7</sup>

However, as we have seen, if we start from Eq. (4), correct consideration of the boundary condition can remove the unphysical divergence. One might think that if we consider an infinitely big system we need not worry about the boundary. Notice, however, that no matter how far away the boundary is, its effect is decisive; because of the impenetrable wall there is no net flow in our present problem. The arguments by Batchelor<sup>14</sup> and de Gennes<sup>11</sup> are essentially the same as ours, though they are not as straightforward and explicit as ours. Also the argument by Yamakawa<sup>15</sup> and by Pyun and Fixman<sup>16</sup> is analogous (but, note that  $u_0$  is not necessarily the mean fluid velocity).

The formula (11) can easily be calculated to order  $\epsilon$ , and we have the formula for the osmotic pressure,<sup>4</sup> so that we get the renormalized result for the monodisperse system as

$$\frac{D_{\text{coop}}(c)}{D_{\text{coop}}(0)} = (1+X)^{-(3/8)\epsilon} \frac{Z}{1+Z} \frac{1}{1-(1+Z)^{-3/4}} \left\{ 1 + \left[ \left( 1 + \frac{\epsilon}{8} \frac{Z}{1+Z} \right) X + \frac{\epsilon}{4} \frac{Z}{1+Z} \left( \frac{\ln(1+X)}{X} - 1 \right) \right] \right. \\ \left. \times \exp \left[ \frac{\epsilon}{4} \frac{Z}{1+Z} \left[ \frac{1}{X} - \left( \frac{1}{X^2} - 1 \right) \ln(1+x) \right] \right] \right\}, \quad (12)$$

where  $X = [16(1+Z)/(8+9Z)]cB_2$ , with  $B_2$  being the osmotic second virial coefficient, and  $Z$  the parameter describing the crossover between the Gaussian and the self-avoiding limit which has been introduced in the dilute-solution theory.<sup>5,17</sup> From (12) we get

$$D_{\text{coop}}(c)/D_{\text{coop}}(0) = 1 + Kc + \dots,$$

with

$$Kc = \left[ \exp \left( \frac{\epsilon}{8} \frac{Z}{1+Z} \right) - \frac{3}{8} \epsilon \frac{Z}{1+Z} \frac{1}{1-(1+Z)^{-3/4}} \right] X. \quad (13)$$

$D_{\text{coop}}(0)/D_{\text{coop}}(c) = \xi_H/R_H$ , where  $\xi_H = 6\pi\eta D_{\text{coop}}(c)/kT$  and  $R_H$  is  $\lim_{c \rightarrow 0} \xi_H$ , is plotted against  $X$  and against  $Kc$  in Figs. 1 and 2, respectively, with the experimental results by Wiltzius *et al.*<sup>10</sup> Although not shown, the recent experimental results by Makita and Nemoto<sup>18</sup> also agree with the results shown in the fig-

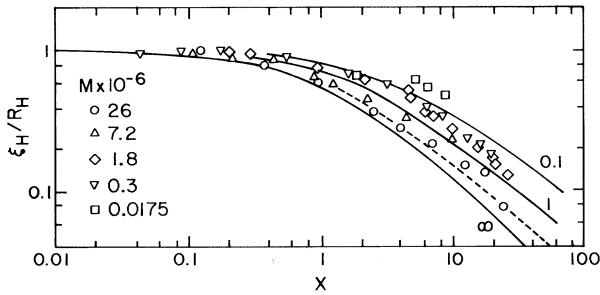


FIG. 1.  $\xi_H/R_H$  vs  $X$ , where  $R_H$  is the hydrodynamic radius in the infinite dilute limit,  $\xi_H$  is the effective hydrodynamic radius,  $X$  is approximately equal to  $16B_2c/9$ , with  $B_2$  being the osmotic second virial coefficient, and  $M$  denotes the molecular weight. The numbers beside the curves denote the value of the crossover parameter  $Z$ ;  $Z = \infty$  is the self-avoiding limit and  $Z = 0$  is the theta limit. However, since the theoretical results for the osmotic pressure for smaller  $Z$  are not reliable, the curves for  $Z = 0.1$  and  $1$  should not be taken seriously. The broken line is the theoretical result augmented with the best estimate of exponents at  $Z = \infty$ . Experimental results for polystyrene in toluene are taken from Wiltzius *et al.* (Ref. 10). Recent results by Makita and Nemoto (Ref. 18) are in good agreement with these.

ure. As suggested by Wiltzius *et al.*, the spread of experimental data in Fig. 1 is due to the crossover effect. They suggested in Fig. 2 that there is a universal curve almost independent of the crossover effect. Our result shows that the spread of curves is greatly reduced for  $Kc \leq 4$  ( $X \leq 10$ ), but there is no universal curve. In any case the agreement of our result *without* any adjustable parameter and the experimental result due to Wiltzius *et al.*<sup>10</sup> is satisfactory, especially when we take into account that our result is due to the lowest-nontrivial-order calculation. As is shown in the figures, if we use the best estimates of exponents, agreement of our results with experimental results becomes almost perfect in the high-molecular-weight limit.

One might think that the hydrodynamic screening of the Oseen tensor is necessary in (11). However, the physical origin of the screening is the out-of-phase motion of the solvent and polymers, so that in the long-wavelength limit, there should not be any hydrodynamic screening. Thus the formula (11) is more reasonable than the corresponding formula with the screening.<sup>19</sup>

In summary, we have extended the Kirkwood-Riseman scheme to the semidilute regime of polymer solutions. Within this formalism, the lowest-nontrivial-order renormalized perturbation calculation of the cooperative diffusion constant successfully explains the recent experiments. This implies,

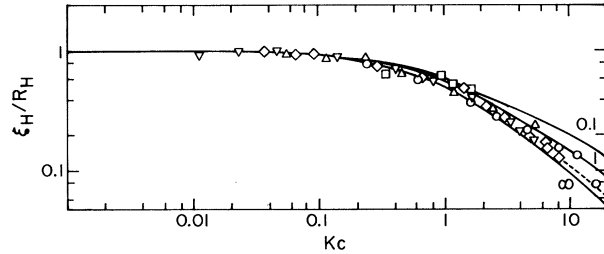


FIG. 2.  $\xi_H/R_H$  vs  $Kc$  [Eq. (13)]. Experimental results for polystyrene in toluene are taken from Wiltzius *et al.* (Ref. 10). Symbols are as in Fig. 1. The numbers beside the curves denote the value of  $Z$ . For  $Z$  between  $1$  and  $\infty$ , there is almost a universal curve. The broken line is the theoretical result augmented with the best estimate of exponents at  $Z = \infty$ .

along with other results so far obtained, that the statistical physics of polymer solutions provides one of the best fields for the quantitative application of renormalization-group theory.

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<sup>19</sup>In the short-wavelength limit, there must be hydrodynamic screening because the chain cannot faithfully follow the solvent velocity field. However, the transport coefficients are essentially determined by the long-wavelength modes, so that the effect of the screening on the cooperative diffusion constant must be small.