Dynamic scaling of dilute polymer solutions[a)]

J. A. Marqusee and J. M. Deutch

Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

(Received 15 July 1980; accepted 26 December 1980)

Dynamic scaling relations are presented for the diffusion coefficient and intrinsic viscosity for dilute polymer solutions in d dimensions. The functional integration description of Adler and Freed is used with the correct d-dimensional hydrodynamic interaction and assumptions of power law dependence to obtain the scaling relations. Recursion relations for the exponents are determined in the asymptotic region of large N by an interdimensional scaling argument.

I. INTRODUCTION

For the past several years there has been great interest in employing scaling theories to the dynamic properties of dilute polymer solutions. De Gennes and co-workers have developed scaling arguments in analogy to magnetic critical phenomena for both static and dynamic properties.[1–3] More recently Freed and co-workers[4–6] have developed a different scaling approach based on the functional integration description of polymer configuration and motion. For static properties, Kosmas and Freed[4] construct scaling relationships and introduce an interdimensional argument to determine the power law dependence of static properties as a function of the excluded volume parameter v and the number of monomer units in the chain N, Adler and Freed[5] (hereafter denoted AF) have extended this analysis, in an interesting way, to the dynamics of dilute polymer chains. For the diffusion coefficient D and the intrinsic viscosity $[\eta]$, AF obtain the result in *theta solvents*, for all dimensions d,

$$D \propto \frac{k_B T}{\eta_0 l} N^{-1/2}, \quad [\eta] \propto \frac{N_A}{M} N^{3/2} l^3, \tag{1.1}$$

where k_B is Boltzmann's constant, T the absolute temperature, η_0 the solvent viscosity, N_A Avogedro's number, M the chain molecular weight, and l the Kuhn statistical segment length.

In a good solvent AF obtain the results, for $2 < d \leq 4$,

$$D \propto \frac{k_B T}{\eta_0 l} N^{-\nu_d} (v l^{-d})^{-(2\nu_d - 1)/(4-d)} \tag{1.2}$$

and

$$[\eta] \propto \frac{N_A}{M} l^3 N^{3\nu_d} (v l^{-d})^{3(2\nu_d - 1)/(4-d)} . \tag{1.3}$$

Here the exponent ν_d is the Flory exponent obtained in a variety of ways[4,7,8] to be

$$\nu_d = \frac{3}{d+2}, \quad 1 \leq d \leq 4 ,$$
$$= \tfrac{1}{2}, \quad d \geq 4 . \tag{1.4}$$

For $d \geq 4$, in a good solvent, AF conclude that D and $[\eta]$ behave like the theta solvent, Eq. (1.1).

As remarked by AF, they have adopted in their analysis a form for the hydrodynamic interaction $\mathbf{T}(r)$ which is valid in three dimensions. The principal purpose of this paper is to demonstrate the modifications to the AF results that arise from use of the correct d-dimensional hydrodynamic interaction. In particular, we find in a *theta solvent* for $2 < d \leq 4$, in the large N limit, the result

$$D \propto \frac{k_B T}{\eta_0} \frac{N^{(2-d)/2}}{l^{d-2}}, \quad [\eta] \propto \frac{N_A}{M} N^{d/2} l^d , \tag{1.5}$$

while for $d \geq 4$,

$$D \propto \frac{k_B T}{\xi N}, \quad [\eta] \propto \frac{N_A}{M} \frac{\xi}{\eta_0} l^2 N^2 . \tag{1.6}$$

In a good solvent we find the following results are not inconsistent with our recursion relations for the exponents for $2 < d \leq 4$:

$$D \propto \frac{k_B T}{\eta_0} \frac{N^{-(d-2)\nu_d}}{l^{d-2}} (v l^{-d})^{(d-2/4-d)[1-2\nu_d]} \tag{1.7}$$

and

$$[\eta] \propto \frac{N_A}{M} N^{d\nu_d} l^d (v l^{-d})^{d(2\nu_d - 1)/(4-d)} , \tag{1.8}$$

while for $d \geq 4$, we obtain the results Eq. (1.6).

It is not surprising that our results [Eqs. (1.5)–(1.8)] agree with the AF results [Eqs. (1.1)–(1.3)] for $d = 3$ since for this dimensionality AF employed the appropriate form for $\mathbf{T}$. However, these results differ from those of AF for all cases where $d \neq 3$.

Our results can be reproduced by the following simple physical argument. For $d \leq 4$, we expect a hydrodynamic description to be necessary so we assume the validity of Stokes Law, for $d > 2$[9]

$$D \propto k_B T / \eta_0 R^{d-2} \tag{1.9}$$

and the Einstein expression for the intrinsic viscosity of a dilute suspension of spheres of radius R,

$$[\eta] \propto R^d / M , \tag{1.10}$$

with R of the form

$$R = l N^{\nu_d} . \tag{1.11}$$

For $d > 4$, hydrodynamics does not dominate, and we expect the simple result Eq. (1.6) for a Rouse free draining chain. Note that this physical argument leads to the proper units for D and $[\eta]$ as a function of dimensionality in contrast to the AF results.

Thus in good solvents for $2 < d \leq 4$, the predicted power

---

[a)] Supported in part by the National Science Foundation.

0021-9606/81/084261-05$01.00

law dependence N may be viewed as arising from the behavior of the *static* polymer end-to-end distance R. AF point out that replacement of this static length R by an appropriate dynamical scaling length R_H does not change their conclusions. Similarly we find that modification of our analysis to introduce a dynamical length does not change the results summarized above.

II. SUMMARY OF THE ADLER AND FREED METHOD

The static properties of a polymer chain with a configuration $\{\mathbf{r}\}$ are determined by the free energy functional[10]

$$(k_BT)^{-1}F[\{\mathbf{r}\},L,l,v]=\frac{3}{2l}\int_0^L ds\left(\frac{\partial\mathbf{r}(s)}{\partial s}\right)^2$$

$$+\frac{v}{2l^2}\int_0^L ds\int_0^L ds_0\,\delta[\mathbf{r}(s)-\mathbf{r}(s_0)]\ , \qquad (2.1)$$

where L is the length of the polymer. Kosmas and Freed have shown that the scaling of the distance along the polymer s and the position of a point on the polymer $\mathbf{r}(s)$ by

$$s'=(b/l)s\ ,\quad b>0\ ,\quad \mathbf{r}'(s')=(b^{1/2}/l)\mathbf{r}(s)\ , \qquad (2.2)$$

leads to the homogeneity relation for the free energy.

$$F[\{\mathbf{r}\},L,l,v]=F[\{\mathbf{r}'\},Nb,1,b^{(d-4)/2}vl^{-d}]\ , \qquad (2.3)$$

where $N=L/l$.

The dynamic properties are governed by the diffusion equation for the probability distribution $P(\{\mathbf{r}\},t)$[11]

$$\frac{\partial P}{\partial t}(\{\mathbf{r}\},t)=\int_0^L\frac{ds}{L}\int_0^L\frac{ds_0}{L}\frac{\delta}{\delta\mathbf{r}(s)}\cdot\left[\mathbf{1}\,\delta(s-s_0)k_BTl/\xi+\frac{k_BT}{\eta_0}\mathbf{T}[\mathbf{r}(s)-\mathbf{r}(s_0)]\right]$$
$$\cdot\left[\frac{\delta}{\delta\mathbf{r}(s_0)}+\frac{1}{k_AT}\frac{\delta}{\delta\mathbf{r}(s_0)}F[\{\mathbf{r}\},L,l,v]\right]P(\{\mathbf{r}\},t)\ , \qquad (2.4)$$

where ξ/l is the friction coefficient per unit length. AF assume $\mathbf{T}(r)$ to be the Oseen tensor

$$\frac{1}{\eta_0}\mathbf{T}(\mathbf{r})=\frac{1}{8\pi\eta_0}\frac{1}{r^2}\left[\mathbf{1}+\frac{\mathbf{r}\mathbf{r}}{r^2}\right] \qquad (2.5)$$

in all dimensions, although it is only correct in three dimensions. Using the above Oseen tensor and the static scaling leads to the time scaling

$$t'=\frac{k_BT}{\eta_0 l^3}b^{3/2}t\ . \qquad (2.6)$$

Scaling the diffusion equation [Eq. (2.4)] by the variable transformation Eq. (2.2) and Eq. (2.6) yields an equivalent diffusion equation in which the set of parameters that govern the dynamics are transformed as follows:

$$\{k_BTl/\xi,\ k_BT/\eta_0,\ L,\ l,\ v\}$$
$$\to\{\eta_0 lb^{1/2}/\xi,\ 1,\ Nb,\ 1,\ b^{(d-4)/2}vl^{-d}\}\ . \qquad (2.7)$$

Setting $b=N^{-1}$ leads to $\eta_0 lN^{-1/2}/\xi\to 0$ for large N and the AF result that the monomer friction coefficient is irrelevant in all dimensions.

The scaling relations for the diffusions coefficient D and the intrinsic viscosity $[\eta]$ are determined by applying the static and dynamic scaling to their equilibrium autocorrelation definitions.

The diffusion coefficient[12] is defined as

$$D=\frac{1}{3}\int_0^\infty dt\langle\mathbf{V}(t)\cdot\mathbf{V}(0)\rangle\ , \qquad (2.8)$$

where

$$\mathbf{V}(t)=\frac{1}{L}\int_0^L ds\frac{\partial}{\partial t}\mathbf{r}(s,t) \qquad (2.9)$$

and $\langle\cdots\rangle$ is the equilibrium average. Substitution of the transformed variable t', r', s' leads to the AF result, for large N, that $D\sim N^{-1/2}$ in theta solvents in all dimensions and in good solvents above four dimensions. While in good solvents for $d<4$, the same analysis leads to the result

$$D=\text{const}\frac{k_BT}{\eta_0 l}N^{-\omega_d}(vl^{-d})^{-(2\omega_d-1)/(4-d)}\ . \qquad (2.10)$$

This exponent ω_d is determined by an interdimensional scaling argument to be equal to the static exponent ν_d for the root mean square end-to-end distance R. This interdimensional argument consists of equating the power law dependence for v and N of a confined polymer in d dimensions to a polymer in $d-1$ dimensions when the size of the polymer is large compared to the confinement distance. AF solve the resulting first-order difference equation for ω_d by assuming the polymer is Rouse-like ($\omega_1=1$) in one dimension.

The intrinsic viscosity[13] is defined as

$$[\eta]=\frac{N_A}{Mk_BT\eta_0}\int_0^\infty dt\langle J(t)\cdot J(0)\rangle\ , \qquad (2.11)$$

where

$$J(t)=-\frac{k_BT}{L}\int_0^L ds\,r_x(s,t)\frac{\delta}{\delta r_y(s,t)}F[\{\mathbf{r}\},L,l,v]\ . \qquad (2.12)$$

In theta solvents and good solvents above four dimensions AF find, $[\eta]\sim N^{-3/2}/M$. While in good solvents below four dimensions,

$$[\eta]=\text{const}\frac{N_A}{M}l^3N^{3\omega_d'}(vl^{-d})^{[3(2\omega_d'-1)/(4-d)]} \qquad (2.13)$$

and ω_d' is determined to be equal to ν_d by an interdimensional argument similar to the diffusion case.

III. MODIFIED SCALING

The scaling of the hydrodynamic interaction used by AF for $d\neq 3$ is incorrect. Linear hydrodynamics predicts that the Oseen tensor in Fourier space is

$$\frac{1}{\eta_0}\mathbf{T}(\mathbf{k}) = \frac{1}{\eta_0 k^2}\left[\mathbf{I} - \frac{\mathbf{kk}}{k^2}\right] \tag{3.1}$$

in all dimensions.[9]

Thus in coordinate space

$$\frac{1}{\eta_0}\mathbf{T}(\mathbf{r}) \propto \frac{1}{\eta_0 r^{d-2}} , \tag{3.2}$$

so that the appropriate scaling is

$$\mathbf{T}(\mathbf{r}') = \left(\frac{b^{1/2}}{l}\right)^{2-d} \mathbf{T}(\mathbf{r}) . \tag{3.3}$$

As a result, two possible time scalings emerge in the diffusion Eq. (2.4). If we scale so the hydrodynamic interaction is fixed (as AF do) we obtain

$$t' = \frac{k_B T}{\eta_0}\left(\frac{b^{1/2}}{l}\right)^d t . \tag{3.4}$$

This leads to the set of parameters in Eq. (2.4) transforming as

$$\begin{aligned} &\{k_B T l/\xi, k_B T/\eta_0, L, l, v\} \\ &\quad \to \{\eta_0 b^{(4-d)/2}\, l^{(d-2)}/\xi, 1, Nb, 1, b^{(d-4)/2} v l^{-d}\} . \end{aligned} \tag{3.5}$$

By examining the behavior for large N, with $b = N^{-1}$, this scaling is seen to be appropriate for $d < 4$, so that the monomer friction coefficient or more explicitly the draining constant becomes irrelevant.

Alternatively, one may also fix the monomer friction coefficient and obtain the time scaling

$$t'' = \frac{k_B T}{\xi}\frac{b^2}{l^2} t \tag{3.6}$$

which leads to the transformation

$$\begin{aligned} &\{k_B T l/\xi, k_B T/\eta_0, L, l, v\} \\ &\quad \to \{1, \xi b^{(d-4)/2}\, l^{(2-d)}/\eta_0, Nb, 1, b^{(d-4)/2} v l^{-d}\} \end{aligned} \tag{3.7}$$

which is seen to be the appropriate scaling for $d > 4$. In this case both the excluded volume interaction and the hydrodynamic interaction become irrelevant. As is shown in the next section, the consequence of this scaling is that the polymer has unperturbed Rouse-like behavior above four dimensions.

IV. DIFFUSION COEFFICIENT AND INTRINSIC VISCOSITY

A. Diffusion coefficient

Employing the time scaling equation (3.4) for $d > 4$ and the static scaling with $b = N^{-1}$, we obtain

$$D = \frac{k_B T}{\xi} N^{-1} F_D(v l^{-d} N^{(4-d)/2}, \xi N^{(4-d)/2} l^{(2-d)}/\eta_0) . \tag{4.1}$$

For large N both the excluded volume interaction and the hydrodynamic interaction are irrelevant. Thus in the asymptotic region of large N, the diffusion coefficient exhibits free draining Rouse type behavior,

$$D = \frac{k_B T}{\xi} N^{-1} F_D(0) , \quad d > 4 . \tag{4.2}$$

Using the time scaling equation (3.3) for $d \le 4$, we obtain

$$D = \frac{k_B T}{\eta_0} N^{(2-d)/2} l^{2-d} F_D(v l^{-d} N^{(4-d)/2}, \eta_0 l^{d-2} N^{(d-4)/2}/\xi) . \tag{4.3}$$

Note that for $d = 4$, the N dependence of Eq. (4.3) and Eq. (4.1) match. For $d < 4$ the monomer friction coefficient is irrelevant for large N; i.e., $\eta_0 l^{d-2} N^{(d-4)/2}/\xi \to 0$. Thus Eq. (4.3) reduces to a two-parameter scaling equation. In theta solvents where $v = 0$, we immediately obtain the nonfree draining Rouse–Zimm behavior

$$D = \frac{k_B T}{\eta_0} N^{(2-d)/2} l^{(2-d)} F_D(0) . \tag{4.4}$$

In good solvents where the excluded volume interaction is present and $v l^{-d} N^{(4-d)/2} \gg 1$, we assume a new power law dependence for N to emerge. Assuming $F_D(v l^{-d} N^{(4-d)/2})$ scales as $\sim (v l^{-d} N^{(4-d)/2})^x$ yields the scaling relation

$$\begin{aligned} D &= \mathrm{const}\,\frac{k_B T}{\eta_0} N^{(2-d)/2} l^{(2-d)} (v l^{-d} N^{(4-d)/2})^x \\ &= \mathrm{const}\,\frac{k_B T}{\eta_0} N^{-\omega_d} l^{(2-d)} (v l^{-d})^{(d-2-2\omega_d)/(4-d)} , \end{aligned} \tag{4.5}$$

where $\omega_d = [d - 2 - (4 - d)x]/2$ is the new dynamic exponent for N.

An equation for the exponent ω_d can be obtained by the same interdimensional scaling argument employed by AF. Consider a polymer confined between two infinite planes a distance a apart. The scaling relation for the confined polymer must reduce to the unconfined result [Eq. (4.5)] as $a \to \infty$. Assuming there is only one length that characterizes the polymer for diffusion R leads one to the scaling relation for the confined polymer in d dimensions

$$D = \frac{k_B T}{\eta_0} N^{-\omega_d}\, l^{(2-d)} (v l^{-d})^{(d-2-2\omega_d)/(4-d)} g_D(a/R) , \tag{4.6}$$

where $g(\infty) = \mathrm{const}$. In the limit $(a/R) \to 0$ the scaling behavior of the confined polymer should be equivalent to the scaling behavior of the unconfined polymer in $(d - 1)$ dimensions. We assume a power law dependence for the scaling function $g_D(x)$ in this limit; $g_D(x) \sim x^y$. Equivalent results are obtained by assuming R is the static end-to-end distance, or a dynamic length [See Appendix] defined by a Stokes–Einstein relation

$$D = \mathrm{const}\,\frac{k_B T}{\eta_0 R_D^{d-2}} . \tag{4.7}$$

The dependence of the static end-to-end distance on N and v is

$$R \sim N^{\nu_d} v^{(2\nu_d - 1)/(4-d)} . \tag{4.8}$$

Proceeding with the static definition of R, the scaling law for the confined polymer in d dimensions in the limit $(a/R) \to 0$ becomes

$$D_d \sim N^{-\omega_d} v^{(d-2-2\omega_d)/(4-d)} N^{-\nu_d y} v^{-y(2\nu_d - 1)/(4-d)} . \tag{4.9}$$

Equating powers of N and v in Eq. (4.9) with the powers in Eq. (4.5) for $d - 1$ dimensions results in

$$\begin{aligned} &\omega_{d-1} = \omega_d + \nu_d y , \\ &\frac{d - 3 - 2\omega_{d-1}}{5 - d} = \frac{d - 2 - 2\omega_d}{4 - d} - \frac{y(2\nu_d - 1)}{4 - d} . \end{aligned} \tag{4.10}$$

We eliminate y from the above equations and obtain the first-order difference equation for ω_d:

$$\frac{d-3-2\omega_{d-1}}{5-d}=\frac{d-2-2\omega_d}{4-d}-\frac{\omega_{d-1}-\omega_d}{\nu_d}\frac{2\nu_d-1}{4-d}\,. \tag{4.11}$$

A unique solution can be constructed by fixing the value of ω_d for a specific dimension. Note that this difference equation differs from that obtained by AF.

In our view the type of analysis employed here, and by AF, cannot yield an unambiguous boundary for the interdimensional difference equation. Indeed for our result, Eq. (4.11), various consistant possibilities emerge for different assumed boundary conditions. For example, if we employ, as AF do, the boundary condition of Rouse behavior in one dimension, $\omega_1=1$, Eq. (4.11) leads to Rouse behavior in all dimensions. But we do not expect hydrodynamic interactions to be irrelevant for $2<d\leq 4$ and, indeed, note that

$$\omega_d=(d-2)\nu_d\,,\quad 2<d\leq 4 \tag{4.12}$$

is an acceptable solution, although not unique.

B. Intrinsic viscosity

Using the time scaling Eq. (3.4) for $d>4$ and the definition of the intrinsic viscosity Eq. (2.10) with $b=N^{-1}$ results in

$$[\eta]=\frac{N_A}{M}\frac{\xi}{\eta_0}l^2N^2F_\eta(vl^{-d}N^{(4-d)/2},\,\xi N^{(4-d)/2}l^{(2-d)}/\eta_0)\,. \tag{4.13}$$

As in the diffusion case, both the excluded volume and the hydrodynamic interactions are irrelevant above four dimensions, and we obtain the free draining Rouse behavior

$$[\eta]=\frac{N_A}{M}\frac{\xi}{\eta_0}l^2N^2F_\eta(0)\,,\quad d>4\,. \tag{4.14}$$

For $d\leq 4$, we apply the time scaling equation (3.3) and set $b=N^{-1}$ to obtain

$$[\eta]=\frac{N_A}{M}N^{d/2}l^dF_\eta(vl^{-d}N^{(4-d)/2})\,, \tag{4.15}$$

where the friction coefficient has been ignored for large N. In theta solvents, Eq. (4.15) reduces to the Rouse–Zimm result

$$[\eta]=\frac{N_A}{M}N^{d/2}l^dF_\eta(0)\,. \tag{4.16}$$

Note that the factor $l^dN^{d/2}$ is the d-dimensional volume of a chain in theta solvent.

In good solvent where the excluded volume interaction is present we expect a new power law. Assuming the scaling function $F_\eta(vl^{-d}N^{(4-d)/2})$ has a power law for when $vl^{-d}N^{(4-d)/2}\gg 1$, we obtain

$$[\eta]=\text{const}\frac{N_A}{M}N^{d/2}l^d(vl^{-d}N^{(4-d)/2})^x \tag{4.17}$$

and we define an exponent

$$\bar{\omega}_d=d/2+x(4-d)/2 \tag{4.18}$$

to describe N dependence. The same argument may be constructed to determine $\bar{\omega}_d$ as was employed for ω_d. The scaling length may be defined by the static end-to-end distance or a dynamic length defined by

$$[\eta]=\text{const}\,R_\eta^d/M\,. \tag{4.19}$$

Both definitions yield recursion relations for $\bar{\omega}_d$ that give the same results. Using the static end-to-end distance we obtain the difference equation

$$\frac{2\bar{\omega}_{d-1}-d+1}{5-d}=\frac{2\bar{\omega}_d-d}{4-d}+\frac{(\bar{\omega}_{d-1}-\bar{\omega}_d)}{\nu_d}\frac{(2\nu_d-1)}{4-d}\,. \tag{4.20}$$

If the chain is assumed Rouse-like in one dimension then it is Rouse-like in all dimensions. However, the expected solution

$$\bar{\omega}_d=d\nu_d\,,\quad 2<d\leq 4 \tag{4.21}$$

is consistent with the recursion relation.

V. CONCLUSION

We have presented scaling relations and explicit power laws for the diffusion coefficient and intrinsic viscosity of dilute polymer solutions. The analysis is based on AF method for the path integral representation of a polymer's dynamic and static properties. Our work differs from theirs in the treatment of the hydrodynamic interaction. AF assume the three-dimensional representation of the hydrodynamic interaction is valid in all dimensions. This leads them to incorrect results for $d\neq 3$.

Our results for $d\leq 4$ may also be obtained by the simple hydrodynamic argument stated in the introduction and for $d>4$ by assuming the polymer exhibits Rouse behavior. Through our scaling analysis we have found, in contradiction to AF, that the monomer friction coefficient is the controlling factor for the dynamics above four dimensions, while the hydrodynamic interaction is irrelevant. This leads to the free draining Rouse behavior.

The physical reason that the hydrodynamic interaction is unimportant above four dimensions may be understood by considering the picture Debye and Bueche[14] have given for the motion of a polymer. They demonstrate that the fluid inside a polymer in three dimensions moves with the same velocity as the polymer itself. That the difference between the fluid velocity and the polymer velocity decays to zero within a "shielding length"

$$K^{-1}\propto(C^*\xi/\eta_0)^{1/2}\,, \tag{5.1}$$

where C^* is the concentration of monomers within a polymer coil. In three dimensions K^{-1} is much smaller than the size of the polymer. This leads to the picture of a polymer as a sphere that obeys Stokes law. If we generalize this argument to d dimensions, one sees that the ratio of the size of polymer to the "shielding length" in the large N limit changes abruptly at four dimensions

$$\begin{aligned}R/K&\propto R(C^*\xi/\eta_0)^{1/2}\\&\sim N^{[(2-d)\nu_d+1]/2}\,.\end{aligned} \tag{5.2}$$

Thus, above four dimensions the polymer is much more porous, the fluid flows freely through it, and one should expect free draining Rouse behavior.

An alternative way of understanding why the hydrodynamic interaction is irrelevant above four dimensions, is to compare the direct frictional force $\mathbf{F}_f$ relative to the hydrodynamic force $\mathbf{F}_H$ acting on a typical polymer bead. In a uniform velocity field $\mathbf{v}_0$,

$$\mathbf{F}_f \sim \xi \mathbf{v}_0 \tag{5.3}$$

and

$$\mathbf{F}_H \sim \frac{1}{\eta_0} \int \mathbf{T}(\mathbf{r}-\mathbf{r}')\rho(r')\,d\mathbf{r}' \cdot \mathbf{v}_0 \,. \tag{5.4}$$

For a Gaussian distribution of neighboring segments,

$$\rho(r) \sim \langle R^2 \rangle^{-d/2} \exp[-dr^2/2\langle R^2 \rangle] \,, \tag{5.5}$$

one finds

$$\mathbf{F}_H \sim \eta_0^{-1} N^{1-(d-2)\nu_d} \,. \tag{5.6}$$

For $\nu_d = \frac{1}{2}$, the classical value, there is an abrupt transition at $d=4$, where the hydrodynamic force is dominated by the frictional force for large N.

Recent experimental work[15] has found that $D \sim N^{-0.54}$ rather than $D \sim N^{-0.6}$, the result inferred here, and also by other authors.[2,3,5] It has been speculated that this discrepancy between theory and experiment arises from an anomalous value[16] for the dynamic exponent z or because the asymptotic region of large N has not been experimentally reached.[17,18] The exponent z is related to the diffusion coefficient by $D \sim N^{(2-z)\nu_d}$. We have selected the values

$$\begin{aligned} z &= d \,, \quad d \le 4 \,, \\ &= 4 \,, \quad d \ge 4 \,, \end{aligned} \tag{5.7}$$

but the interdimensional scaling argument does not eliminate the possibility of an anomalous dynamic exponent, since the solutions to Eq. (4.11) and Eq. (4.20) are not unique.

In summary, the significance of what has been demonstrated here is that correct application of the AF dynamic scaling arguments leads to inferred results for the chain length dependence of D and $[\eta]$ that are consistent with the essential physics as a function of dimensionality. The essential physics is as follows. Above four dimensions the excluded volume and hydrodynamic interaction effects become irrelevant for large N. Between two and four dimensions, in a good solvent for large N, Stokes law for D and the Einstein law for $[\eta]$ contain the essence of the sophisticated dynamic scaling argument where the sphere size is associated with the mean end-to-end distance $R \sim N^{\nu d}$.

APPENDIX

Using the dynamic length R_D [Eq. (4.7)] we derive an equivalent alternative recursion relation for ω_d. The N and v dependence of R_D is

$$R_D \sim N^{-\omega_d/(2-d)} v^{(d-2-2\omega_d)/(4-d)(2-d)} \,. \tag{A1}$$

Employing this in Eq. (4.6) and comparing powers of N and v in the limit $a/R_D \to 0$, we obtain

$$\begin{aligned} &\omega_d - y\omega_d/(2-d) = \omega_{d-1} \,, \\ &\frac{d-2-2\omega_d}{4-d} - \frac{y(d-2-2\omega_d)}{(4-d)(2-d)} = \frac{d-3-2\omega_{d-1}}{5-d} \,. \end{aligned} \tag{A2}$$

Eliminating y yields the recursion relation for ω_d

$$\frac{(d-2-2\omega_d)}{\omega_d(4-d)} = \frac{(d-3-2\omega_{d-1})}{(5-d)\omega_{d-1}} \,. \tag{A3}$$

The solution of Eq. (A3) is

$$\frac{d-2-2\omega_d}{\omega_d(4-d)} = \text{const} \,, \tag{A4}$$

where the constant is determined by the boundary condition for ω_d. The results for Eq. (A4) are identical to the results for the recursion relation derived from the static length [Eq. (4.11)].

---

[1] M. Daoud, J. P. Cotton, B. Farnoux, G. Tannink, G. Sarma, H. Benoit, R. Duplessix, C. Picot, and P. G. de Gennes, Macromolecules **8**, 804 (1975).

[2] P. G. de Gennes, Macromolecules **9**, 587 (1976); **9**, 594 (1976).

[3] P. G. de Gennes, *Scaling Concepts in Polymer Physics* (Cornell University Press, Ithaca, 1979) and references therein.

[4] M. K. Kosmas and K. F. Freed, J. Chem. Phys. **69**, 3647 (1978).

[5] R. S. Adler and K. F. Freed, J. Chem. Phys. **70**, 3119 (1979).

[6] R. S. Adler and K. F. Freed, J. Chem. Phys. **72**, 4186 (1980). This article extends the work in Ref. 5 to concentration dependent dynamic properties. Our results apply in an analogous way in this region.

[7] P. J. Flory, *Principles of Polymer Chemistry* (Cornell University Press, Ithaca, 1953).

[8] S. F. Edwards, Proc. Phys. Soc. London **85**, 613 (1965).

[9] Because linear hydrodynamics may not be valid in two dimensions, we restrict results to $d > 2$. Where expressions are evaluated for two dimensions, it should be interpreted as the extrapolated value from above. It should be noted that the scaling analysis employed here with linear hydrodynamics is unable to obtain the expected logarhythmic divergences in two dimensions. That is why we restrict attention to $d > 2$.

[10] K. F. Freed, Adv. Chem. Phys. **22**, 1 (1972).

[11] H. Yamakawa, *Modern Theory of Polymer Solutions* (Harper and Row, New York, 1976). The factors of L have been introduced so that the equation has the proper units.

[12] R. Kubo, Rep. Prog. Phys. **29**, 255 (1966).

[13] W. H. Stockmayer, W. Gobush, Y. Chikahisa, and D. K. Carpenter, Discuss. Faraday Soc. **49**, 182 (1970); B. U. Felderhof, J. M. Deutch, and U. M. Titulaer, J. Chem. Phys. **63**, 740 (1975); R. S. Alder, J. Chem. Phys. **69**, 2849 (1978).

[14] P. Debye and A. Bueche, J. Chem. Phys. **16**, 573 (1948).

[15] M. Adam and M. Delsanti, Macromolecules **10**, 1229 (1977).

[16] M. Daoud and G. Jannink, J. Phys. (Paris) **39**, 331 (1978).

[17] G. Weill and J. des Cloizeaux, J. Phys. (Paris) **40**, 99 (1979).

[18] A. Z. Akcasu and C. C. Han, Macromolecules **12**, 276 (1979).