Phys. A: Math. Gen. 1984, 17, 211.
(5) Daoud, M.; Cotton, J. P. J. Phys. (Les Ulis, Fr.) 1982, 43, 531.
(6) Birshtein, T. M.; Zhulina, E. B. Polymer 1984, 25, 1453.
(7) Huber, K.; Burchard, W.; Fetters, L. J. Macromolecules 1984, 17, 541.
(8) Miyake, A.; Freed, K. F. Macromolecules 1983, 16, 1228.
(9) (a) Weil, G.; des Cloizeaux, J. J. Phys. (Les Ulis, Fr.) 1979, 40, 99. (b) Akcasu, A.; Han, C. C. Macromolecules 1979, 12, 276.
(10) Witten, T.; Pincus, P. Macromolecules 1986, 19, 2509.
(11) (a) Klein, J. Nature (London) 1980, 288, 248. (b) Hadziioannou, G.; Patel, S.; Granick, S.; Tirrel, M. J. Am. Chem. Soc., in press.

Least-Draining Limit of Linear Flexible Chain Molecules

J. J. H. Mulderije and H. L. Jalink*

Department of Physical and Macromolecular Chemistry, Gorlaeus Laboratories, University of Leiden, 2300 RA Leiden, The Netherlands. *Received May 9, 1986*

ABSTRACT: A theoretical study has been made to decide whether in the so-called non-free-draining limit of a linear flexible chain without excluded volume the inner region of the chain domain is asymptotically nondrained. To this end the average velocity perturbation field of the solvent medium resulting from a single chain in uniform translation, and observed from the center of mass, is calculated with the bead–string model of Kirkwood and Riseman. Only the asymptotic limit for a large number of segments is considered. In the approximation obtained, the average fluid velocity relative to the stationary molecule and at the center of mass is 3.6% of the unperturbed velocity whereas at a radial distance beyond which on the average half of the segments is present the relative velocity in the equatorial plane is 36% of the unperturbed velocity. Average perturbation fields have also been calculated as observed from the middle and end segments of the chain. These fields are markedly different. It is concluded that words like "the nondraining limit" and "the impermeable limit", which long have been widely used, refer to a hydrodynamical condition that for unbranched flexible polymers is never obtained. We suggest the use of terms like "the least-draining limit" or "limit of smallest drain".

Introduction

Ever since its introduction by Kirkwood and Riseman[1] (KR) in 1948, the spaced bead–string model in conjunction with the Oseen hydrodynamic interaction between the beads has appeared in theories on the intrinsic viscosity $[\eta]$ and the friction coefficient f of dilute polymer solutions.[2] In this model two limiting states are discerned, the "free-draining limit", and its opposite, the "non-free-draining case", cautiously named so by Yamakawa in his monograph.[2] The latter limit is all-important because the behavior of real polymer solutions usually conforms to this limit.

The term "non-free-draining" leaves open the question whether the solvent in the interior of the chain domain is immobilized with respect to the chain. Over many years, however, terms like "the nondraining limit" and "the impermeable limit" have been in vogue.[3] The idea of a chain molecule being nondrained for high degrees of polymerization was suggested by the results obtained by Debye and Bueche[4] in their calculation of $[\eta]$ and f using a sphere of uniform segment density. They introduced the concept of hydrodynamical shielding and the "shielding length" L ($L = [\eta_0/\nu\zeta]^{1/2}$, ν is the bead density and ζ is the friction coefficient of a bead).[5] For large values of the "shielding ratio" σ ($=R_s/L$, with R_s the radius of the sphere), $[\eta]$ and f approach values that hold for impermeable spheres of radius R_s. Apparently, there is exclusion of flow lines from the interior of the sphere in these cases.

It is a well-known result of the KR theory for the bead string model that for large values of nr_b/R_g ($r_b = \zeta/6\pi\eta_0$ is the bead radius, n is the total number of beads, and R_g is the radius of gyration of the chain), $[\eta]$ and f become independent of ζ. Besides, the average drift velocities of the beads vanish $\sim n^{-1/2}$ (Θ state). From these results, Kirkwood and Riseman concluded that the interior segments of a long flexible chain are likewise hydrodynamically shielded.

Evaluation of the shielding ratio for the chain will only fortify this opinion. Making use of the spherically symmetric Gaussian approximation for the segment distribution[2]

$$\nu(r) = n\left(\frac{3}{2\pi R_g^{\,2}}\right)^{3/2} \exp\left(-\frac{3r^2}{2R_g^{\,2}}\right) \qquad (1)$$

in which $R_g^{\,2} = nb^2/6$, b being the distance between the segment beads, we consider the succession of shells of varying segment density. Thus we obtain

$$\sigma_{ch} = \int_0^\infty \frac{dr'}{L(r')} = \left(\frac{\zeta}{\eta_0}\right)^{1/2} \int_0^\infty \{\nu(r')\}^{1/2}\, dr' = \left(\frac{3\zeta}{2b\eta_0}\right)^{1/2}\left(\frac{n}{\pi}\right)^{1/4} \qquad (2)$$

It is seen that σ_{ch} increases with $n^{1/4}$, as it does for a sphere of uniform segment density.

Flory[6] was very definite in the matter, writing "once ζ/η_0 is great enough to exclude the flow lines from the interior region of the molecule". These words suggest that ζ/η_0 might be raised at will independent of the bead density. This cannot be true, however. Accordingly as the real chain bears more side groups, it becomes stiffer. Consequently we have to assume a greater value for the bead–bead distance of the equivalent statistical chain, which has free rotation of segments. As one bead has to represent a larger section of the chain, the size of the beads increases and their number decreases. In this way, while ζ/b is slowly varying, the value of the well-known draining parameter h (eq 27) will decrease through the factor $n^{1/2}$, rather than increase.

Whatever the thickness of the real chain, when the chain statistics is Gaussian or not very different, the segment density in a point defined with respect to the center of

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Table I
Ratio of the Hydrodynamic Radius (R_h) to the Radius of Gyration (R_g) and Parent Data for Two Narrow Distribution Polymers in the Θ Solvents Cyclohexane, *trans*-Decalin, and Methyl Acetate[a]

polymer	solvent	Θ, °C	$10^{-3}M$	$s_0\bar{M}_w^{-1/2}$, 10^{-15} s	$D_0\bar{M}_w^{-1/2}$, 10^{-4} cm²/s	ref	$R_g\bar{M}_w^{-1/2}$, 10^{-9} cm	ref	$\bar{v}_p$, mL/g	ρ, g/mL	η, 10^{-3} g/(cm·s)	R_h/R_g
PS	CH	35		1.50		13	2.90	16; 17	0.934	0.765	7.69	0.75
		34.5		1.51 ± 0.01		14	2.90		0.934	0.765	7.62	0.75
		35.4		1.50 ± 0.01		15	2.90		0.934	0.765	7.58	0.76
		35			1.37 ± 0.1	18	2.90				7.69	0.74
		35	179.3[b]		1.34	19	2.90				7.69	0.75
		35			1.38 ± 0.04	20	2.90				7.69	0.73
		35	179.3[b]		$D_0 = (3.23 \pm 0.02) \times 10^{-7}$	21	2.90				7.69	0.74
		34.5			1.309	22	2.90				7.62	0.78
		35			1.24 ± 0.05	23	3.1 ± 0.3	23			7.61	0.77
	tD	20.5	179.3[b]		$D_0 = 1.11 \times 10^{-7}$	24	$R_g = 1.30 \times 10^{-6}$	24			21.1	0.70
		20.5			4.60 ± 0.08	25	2.80	26			21.1	0.79
	MAc	43	179.3[b]		$D_0 = 8.65 \times 10^{-7}$	27	$R_g = 1.34 \times 10^{-6}$	27			3.03	0.66
PαMS	CH	38		2.00		28	2.96 ± 0.05	29	0.882	0.760	7.30	0.67
		34.5		1.80		30	2.90	31[c]	0.886	0.766	7.60	0.71
	tD	9.5		0.39		30	2.83	31[c]	0.894	0.878	25.9	0.66

[a] Relationships used: $R_h = f/6\pi\eta$; $f = M(1 - v_p\rho)/s_0N_A$; $f = RT/D_0N_A$; N_A is the Avogadro number. [b] NBS 705 Standard. [c] Same polymer batches as under ref 30.

mass, and therefore not necessarily on the chain, always decreases with $n^{-1/2}$ and so ultimately vanishes. The same applies to the volume fraction of segments. Therefore, exclusion of flow lines, if it is realized, cannot result from a material filling of the interior region. When a segment is taken as the reference point, then to the R_g scale the average segment density vanishes also everywhere with $n^{-1/2}$, except at distances that are vanishingly small with respect to R_g (cf. eq 69).

The theoretical results and the discussions by the aforesaid authors have given rise to the view that the domain of a long flexible chain is largely nondrained. This view has survived to the present, as appears from remarks in recent literature.[8-11]

The state for large n has also been characterized as containing "no draining effect".[12] This is to say that for a solution in the Θ state $[\eta]/n^{1/2}$ and $f/n^{1/2}$ are independent of n. No doubt these characteristics are correct. However, they do not require the absence of draining, because they arise as soon as the average draining pattern is approaching its asymptotic profile (Figure 1, curve 1), the remaining draining making the friction smaller than in case of complete exclusion of flow lines. This smaller friction, too, is a draining effect. A strong indication for partial draining of the long flexible chain is the established fact that the radius of the friction-equivalent impermeable sphere, the hydrodynamic radius R_h, is smaller than R_g. R_h is calculated from sedimentation coefficients (s_0) or diffusion coefficients (D_0) valid at infinite dilution. Literature data about these coefficients and the radii of gyration for two narrow distribution polymers in three Θ solvents are collected in Table I. The ratio R_h/R_g is in the last column. R_h/R_g is seen to be considerably smaller than 1, although it is larger than the corrected KR value (=0.676, eq 39). This has been known for several years from data that did not include sedimentation coefficients.[32]

In 1977 the porous sphere model was taken up again in semiemperical calculations of $[\eta]$ and f for given polymer–solvent systems. Mijnlieff and Wiegel[7] postulated a Gaussian distribution for the permeability and established its relationship with the segment density by experiment. For the Θ system PαMS ($M = 3 \times 10^6$) in cyclohexane in sedimentation flow they calculated the drift velocity of the center of mass to be 12% of the particle velocity. An extrapolation for $n \rightarrow \infty$ was not made, however.

It was two results of the KR theory that elicited the view that linear chain molecules are asymptotically nondrained. Lest this theory be blamed for producing a result that is disproved by experiment, the KR model comes first in an attempt to decide whether for $n \rightarrow \infty$ the draining of the inner region of a chain vanishes, as it does, on the average, close to a segment.

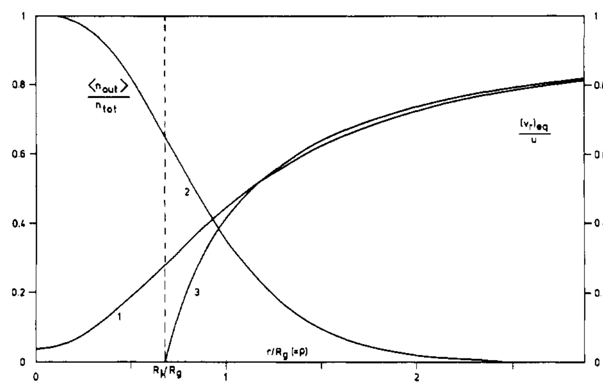

Figure 1. Average draining and extension of the linear freely jointed chain in the limit of least draining and observed from the center of mass: (1) ratio of the average relative solvent velocity in the equatorial plane to the unperturbed velocity; (2) average number fraction of segments outside the sphere of radius r/R_g; (3) ratio of the relative solvent velocity in the equatorial plane to the unperturbed velocity for the friction equivalent sphere. (R_g is the radius of gyration of the chain; R_h is the radius of the equivalent sphere).

Average Perturbation Field Observed from the Center of Mass

Let the origin 0 of rectangular axes 1, 2, 3 be in the center of mass of a freely jointed chain of point forces $\mathbf{F}_k$ at distances $\mathbf{r}_k$ from 0 (k = 1, 2, ..., n). For the application of Gaussian statistics to be allowed, each force is supposed to represent the action of several monomer units of a real chain. The Stokes dimension of the segments may be ignored, because the resulting additional perturbation is of the order S_k^{-3} (cf. eq 4) and because its ratio to a representative dimension of the chain (e.g., R_g) vanishes with $n^{-1/2}$. Let the chain be at rest and the unperturbed solvent velocity be $\mathbf{u}$ in the positive direction of axis 3. We require the average velocity perturbation at distance $\mathbf{R}$ from 0 resulting from the combined action of all segments.

The distribution of the forces generates a perturbation

$$\mathbf{v}_p(\mathbf{R},\{\mathbf{r}_n\}) = \sum_{k=1}^{n} \boldsymbol{T}(\mathbf{R},\mathbf{r}_k)\cdot\mathbf{F}_k(\{\mathbf{r}_n\}) \quad (3)$$

in which $\{\mathbf{r}_n\}$ indicates the forces to be dependent on the coordinates of all segments. The Oseen tensor is[1,2]

$$\boldsymbol{T}(\mathbf{R},\mathbf{r}_k) = \frac{1}{8\pi\eta S_k}\left(\boldsymbol{I} + \frac{\mathbf{S}_k\mathbf{S}_k}{S_k^2}\right) \tag{4}$$

with

$$\mathbf{S}_k = \mathbf{r}_k - \mathbf{R} \tag{5}$$

Forces $\mathbf{F}_k$ are proportional to the drift velocities $\mathbf{w}_k$. It is recalled that $-\mathbf{w}_k$ is the fluid velocity at $\mathbf{r}_k$ that would be observed in the absence of segment k. Defining $\zeta = F_k/w_k$ as the friction coefficient of a segment, we have

$$\mathbf{v}_{\mathrm{p}}(\mathbf{R},\{\mathbf{r}_n\}) = \zeta\sum_{k=1}^{n} \boldsymbol{T}(\mathbf{R},\mathbf{r}_k)\cdot\mathbf{w}_k(\{\mathbf{r}_n\}) \tag{6}$$

Let $P(\{\mathbf{r}_n\})$ be the multivariate distribution function of the segments to be in $\{\mathbf{r}_n\}$. The average perturbation in $\mathbf{R}$ is then given by

$$\langle\mathbf{v}_{\mathrm{p}}(\mathbf{R})\rangle = \zeta\sum_{k}^{n}\int \ldots \int \boldsymbol{T}(\mathbf{R},\mathbf{r}_k)\cdot\mathbf{w}_k(\{\mathbf{r}_n\})P(\{\mathbf{r}_n\})\,\mathrm{d}\{\mathbf{r}_n\} \tag{7}$$

$P(\{\mathbf{r}_n\})$ may be factorized in a conditional distribution function and the singular distribution function for $\mathbf{r}_k$

$$P(\{\mathbf{r}_n\}) = P(\{\mathbf{r}_{n,\neq k}\}|\mathbf{r}_k)P_k(\mathbf{r}_k) \tag{8}$$

Equation 7 thus becomes

$$\langle\mathbf{v}_{\mathrm{p}}(\mathbf{R})\rangle = \zeta\sum_{k}^{n}\int \boldsymbol{T}(\mathbf{R},\mathbf{r}_k)\cdot\langle\mathbf{w}_k(\mathbf{r}_k)\rangle P_k(\mathbf{r}_k)\,\mathrm{d}\mathbf{r}_k \tag{9}$$

with

$$\langle\mathbf{w}_k(\mathbf{r}_k)\rangle = \int \ldots \int \mathbf{w}_k(\{\mathbf{r}_n\})P(\{\mathbf{r}_{n,\neq k}\}|\mathbf{r}_k)\,\mathrm{d}\{\mathbf{r}_{n,\neq k}\} \tag{10}$$

Since we have no expression for the conditional drift velocity $\langle\mathbf{w}_k(\mathbf{r}_k)\rangle$, we approximate the average of the product by using the product of the averages

$$\langle\mathbf{v}_{\mathrm{p}}(\mathbf{R})\rangle \approx \zeta\sum_{k}^{n}\langle\boldsymbol{T}_k(\mathbf{R})\rangle\cdot\langle\mathbf{w}_k\rangle \tag{11}$$

in which

$$\langle\boldsymbol{T}_k(\mathbf{R})\rangle = \int \boldsymbol{T}(\mathbf{R},\mathbf{r}_k)P_k(\mathbf{r}_k)\,\mathrm{d}\mathbf{r}_k \tag{12}$$

and

$$\langle\mathbf{w}_k\rangle = \int \langle\mathbf{w}_k(\mathbf{r}_k)\rangle P_k(\mathbf{r}_k)\,\mathrm{d}\mathbf{r}_k \tag{13}$$

We now derive $\langle\boldsymbol{T}_k(\mathbf{R})\rangle$. The distribution function for segment k with respect to the center of mass is[2]

$$P_k(\mathbf{r}_k) = \left(\frac{3}{2\pi\langle r_k^2\rangle}\right)^{3/2}\exp\left(-\frac{3r_k^2}{2\langle r_k^2\rangle}\right) \tag{14}$$

with

$$\langle r_k^2\rangle = \frac{nb^2}{3}\left\{1 - \frac{3k(n-k)}{n^2}\right\} \tag{15}$$

Occasionally the use of continuous variables for the segment order is more efficient. With $x = 2(k/n) - 1$ ($-1 \leq x \leq 1$) and the use of $nb^2 = 6R_g^2$, eq 14 becomes

$$P_x(\mathbf{r}_x) = \{\pi R_g^2(x^2 + \tfrac{1}{3})\}^{-3/2}\exp\left\{-\frac{r_x^2}{R_g^2(x^2+\tfrac{1}{3})}\right\} \tag{16}$$

Since in the region of integration a singularity is present at $S_k = 0$, we take this point as the origin of polar coordinates S_k,θ,ϕ with $\mathbf{R}$ as polar axis and $\phi = 0$ in the plane containing $\mathbf{R}$ and axis 3.

To establish the angular-dependent part of $\langle\boldsymbol{T}_k(\mathbf{R})\rangle$, we also introduce rectangular auxiliary axes 1′, 2′, 3′ through the same origin, with axis 3′ in the direction of $\mathbf{R}$ and axis 1′ in the plane containing $\mathbf{R}$ and axis 3. The components of S_k in this system are

$$S_{k1}' = S_k\sin\theta\cos\phi$$
$$S_{k2}' = S_k\sin\theta\sin\phi$$
$$S_{k3}' = S_k\cos\theta \tag{17}$$

Use is also made of the cosine relation

$$r_k^2 = R^2 + S_k^2 - 2RS_k\cos(\pi - \theta) \tag{18}$$

After transformation of $P_x(\mathbf{r}_x)\,\mathrm{d}\mathbf{r}_x$ to the polar coordinates, integration with respect to ϕ, θ, and S_k gives the components of $\langle\boldsymbol{T}_k'(\mathbf{R})\rangle$. For the sake of brevity and an easy reading of the following equations for small ξ, we use the second moment function in addition to the error function

$$\mathrm{erf}\,\xi \equiv \frac{2}{\pi^{1/2}}\int_0^{\xi} e^{-t^2}\,\mathrm{d}t$$

$$\mathrm{smf}\,\xi \equiv \frac{2}{\pi^{1/2}}\int_0^{\xi} t^2 e^{-t^2}\,\mathrm{d}t$$

Thus we obtain

$$\langle\boldsymbol{T}'(\mathbf{R})\rangle_{ii} = \frac{1}{8\pi\eta R}\left(\mathrm{erf}\,\gamma^{1/2}R + \frac{\mathrm{smf}\,\gamma^{1/2}R}{\gamma R^2}\right) \quad (i = 1, 2) \tag{19}$$

$$\langle\boldsymbol{T}_k'(\mathbf{R})\rangle_{33} = \frac{1}{4\pi\eta R}\left(\mathrm{erf}\,\gamma^{1/2}R - \frac{\mathrm{smf}\,\gamma^{1/2}R}{\gamma R^2}\right) \tag{20}$$

$$\langle\boldsymbol{T}_k'(\mathbf{R})\rangle_{ij} = 0 \qquad (i \neq j) \tag{21}$$

Here $\gamma = 3/[2\langle r_k^2\rangle]$.

Return to the laboratory system is achieved by means of an ordinary matrix transformation comprising a rotation around axis 2′, which lines up axis 3′ with axis 3. The angle of rotation satisfies $\cos\alpha = R_3/R$. A second rotation through β around axis 3 makes axes 1′ and 2′ coincide with axes 1 and 2, respectively. This angle fulfills $\sin\alpha\cos\beta = R_1/R$ as well as $\sin\alpha\sin\beta = R_2/R$. We further change k for the parameter x and introduce symbols

$$\rho = R/R_g \qquad g_x = (x^2 + \tfrac{1}{3})^{1/2} \tag{22}$$

This yields

$$\langle\boldsymbol{T}(\mathbf{R},x)\rangle = \frac{1}{8\pi\eta R}\left\{A_1(\rho,x)\boldsymbol{I} + A_2(\rho,x)\frac{\mathbf{RR}}{R^2}\right\} \tag{23}$$

in which

$$A_1 = \mathrm{erf}\,\frac{\rho}{g_x} + \left(\frac{g_x}{\rho}\right)^2\mathrm{smf}\,\frac{\rho}{g_x} \tag{24}$$

$$A_2 = \mathrm{erf}\,\frac{\rho}{g_x} - 3\left(\frac{g_x}{\rho}\right)^2\mathrm{smf}\,\frac{\rho}{g_x} \tag{25}$$

Since the average drift velocity $\langle\mathbf{w}_k\rangle$ is proportional and antiparallel with $\mathbf{u}$, we introduce the reduced drift velocity $\phi_k = -\langle w_k\rangle/u$ to become $\phi(x)$ in the continuous variable. We recall that $\phi(x)$ is the solution of the integral equation

$$\phi(x) = 1 - h\int_{-1}^{1}\frac{\phi(t)}{|x-t|^{1/2}}\,\mathrm{d}t \tag{26}$$

resulting from the KR theory. h is the draining parameter

$$h = \frac{n^{1/2}\zeta}{(12\pi^3)^{1/2}\eta b} = \frac{n\zeta}{6(2\pi^3)^{1/2}\eta R_g} \quad (27)$$

Our approximation in going from (9) to (11) is similar to the one made by Kirkwood and Riseman to obtain (26). The asymptotic solution of (26), valid for large h, is

$$\psi(x) = h^{-1} \lim_{h\to\infty} h\phi(x) = \frac{(1-x^2)^{-1/4}}{\pi h 2^{1/2}} \quad (28)$$

which is due to Kurata and Yamakawa[33] in continuation of a mathematical analysis by Auer and Gardner.[34]

Since only this asymptotic solution is known in explicit form and since the asymptotic limit interests us most, we calculate only the average flow pattern for $n \to \infty$.

Meanwhile eq 11 has changed into

$$\langle v_p(\mathbf{R})\rangle = \frac{\eta\zeta}{2}\left[\int_{-1}^{1}\langle \boldsymbol{T}(\mathbf{R},x)\rangle\psi(x)\,dx\right]\cdot\mathbf{u} \quad (29)$$

With (23), (22a), (28), and (27), this becomes

$$\langle \mathbf{v}_p(\rho)\rangle = -\frac{3}{8\rho\pi^{1/2}}\left[\int_{-1}^{1}\left\{A_1(\rho,x)\boldsymbol{I} + A_2(\rho,x)\frac{\rho\rho}{\rho^2}\right\}\times (1-x^2)^{-1/4}\,dx\right]\cdot\mathbf{u} \quad (30)$$

A_1 and A_2 start from $\rho = 0$ as follows:

$$A_1(\rho,x) = \frac{8}{3\pi^{1/2}}\left\{\frac{\rho}{g_x} - \frac{2}{5}\left(\frac{\rho}{g_x}\right)^3 + \frac{9}{70}\left(\frac{\rho}{g_x}\right)^5 - ...\right\} \quad (31)$$

$$A_2(\rho,x) = \frac{8}{15\pi^{1/2}}\left\{\left(\frac{\rho}{g_x}\right)^3 - \frac{3}{7}\left(\frac{\rho}{g_x}\right)^5 + ...\right\} \quad (32)$$

The average solvent velocity relative to the center of mass is $\mathbf{u} + \langle \mathbf{v}_p(\rho)\rangle$. We calculated its value for the equatorial plane. In this plane $\rho \perp \mathbf{u}$, so we have

$$\langle \mathbf{v}_p(\rho)\rangle_{eq} = -\frac{3}{8\pi^{1/2}}\frac{\mathbf{u}}{\rho}\int_{-1}^{1}A_1(\rho,x)(1-x^2)^{-1/4}\,dx \quad (33)$$

Single and double integrations were done with a programmable hand-held calculator. Curve 1 in Figure 1 shows $\langle v_{rel}\rangle_{eq}/u = 1 + \langle v_p\rangle_{eq}/u$ as a function of ρ.

For large ρ we expect the perturbation field of the chain to approach that due to the equivalent sphere. The perturbation caused by a sphere of radius a is given by[35]

$$\mathbf{v}_p(\mathbf{R}) = -\frac{3}{4}\frac{a}{R}\left\{\left(1 + \frac{1}{3}\frac{a^2}{R^2}\right)\boldsymbol{I} + \left(1 - \frac{a^2}{R^2}\right)\frac{\mathbf{RR}}{R^2}\right\}\cdot\mathbf{u} \quad (R \geq a) \quad (34)$$

so in the equatorial plane

$$\{\mathbf{v}_p(\mathbf{R})\}_{eq} = -\frac{3}{4}\frac{a}{R}\left(1 + \frac{1}{3}\frac{a^2}{R^2}\right)\mathbf{u} \quad (35)$$

For the equivalent sphere we have to substitute $a = R_h$. The theoretical value for R_h/R_g, consistent with the present model, is established as follows:

The friction coefficient of the chain is given by

$$f = \sum_k^n \langle F_k\rangle/u \quad (36)$$

which in the KR theory for very large n becomes

$$f = \frac{n\zeta}{2}\int_{-1}^{1}\psi(x)\,dx \quad (37)$$

With (28) and (27) and changing to $x = \sin\phi$, we obtain

$$f/\eta = 3\pi^{1/2}R_g\int_{-\pi/2}^{\pi/2}(\cos\phi)^{1/2}\,d\phi \quad (38)$$

With $R_h = f/6\pi\eta$ it follows that

$$R_h/R_g = 0.676 \quad (39)$$

Curve 3 in Figure 1 shows $(v_r)_{eq}$ for the equivalent sphere.

The preasymptotic values for (24) and (25) are given by

$$A_1 = 1 + \frac{1}{2}\left(\frac{g_x}{\rho}\right)^2 + \mathcal{O}(e^{-\rho^2}/\rho) \quad (40)$$

$$A_2 = 1 - \frac{3}{2}\left(\frac{g_x}{\rho}\right)^2 + \mathcal{O}(e^{-\rho^2}/\rho) \quad (41)$$

Using (22a), (39), and the relationship

$$\int_{-1}^{1}x^2(1-x^2)^{-1/4}\,dx = \frac{3}{5}\int_{-1}^{1}(1-x^2)^{-1/4}\,dx \quad (42)$$

we derive from (30)

$$\langle \mathbf{v}_p(\mathbf{R})\rangle = -\frac{3}{4}\frac{R_h}{R}\left[\left\{1 + \frac{7}{15}\frac{R_g^2}{R^2} - \mathcal{O}(e^{-\rho^2}/\rho)\right\}\boldsymbol{I} + \left\{1 - \frac{7}{5}\frac{R_g^2}{R^2} + \mathcal{O}(e^{-\rho^2}/\rho)\right\}\frac{\mathbf{RR}}{\mathbf{R}^2}\right]\cdot\mathbf{u} \quad (43)$$

Comparison with eq 34 shows that the perturbation due to the chain converges to that by the equivalent sphere with respect to terms $\mathcal{O}(R^{-1})$. As a result of its larger expansion it does not converge with respect to terms $\mathcal{O}(R^{-3})$ but is a little stronger. Figure 1 shows that for $R/R_g > 1.2$ $\langle \mathbf{v}_p\rangle$ for the chain is slightly larger than for the sphere.

We also calculated the average fraction of the number of segments found outside the sphere with radius ρ.

$$\langle n(R)\rangle_{out}/n = 4\pi\sum_{k=1}^{n}\int_R^\infty r_k^2 P_k(r_k)\,dr_k \quad (44)$$

with $P_k(r_k)$ given by (14).

Replacing the summation over k by integration with respect to x (making the substitution $x = \tan\phi/3^{1/2}$ in eq 16), we obtain from eq 44

$$\langle n(\rho)\rangle_{out}/n = 1 - \text{erf}\,\frac{\rho 3^{1/2}}{2} + 2(3\pi)^{-1/2}e^{-3\rho^2}\int_0^{3/2\rho}e^{t^2}\,dt \quad (45)$$

This function is shown in curve 2.

Average Perturbation Field Observed from the Middle and End Segments

With the use of eq 28 in our calculations for $n \to \infty$, we introduced a zero drift velocity for the segments. We should refind this result when we calculate the average perturbation field observed from a segment. It further will be interesting to know how rapidly $\langle v_{rel}\rangle$ increases upon withdrawing from the chain.

The analysis is similar to that in the previous section. Let again the chain be at rest and the unperturbed solvent move with velocity $\mathbf{u}$ in the positive direction of axis 3. Segment k is at the origin. Let $\mathbf{S}_l$ be the vector from segment k to segment l, and let $\mathbf{S}$ be a vector from k to a vacant point. The perturbation in $\mathbf{S}$ resulting from a particular distribution of segments now reads

$$\mathbf{v}_p(\mathbf{S},\{\mathbf{S}_{n,\neq k}\}) = \zeta \sum_{l=1}^{n} \boldsymbol{T}(\mathbf{S},\mathbf{S}_l)\cdot\mathbf{w}_l(\{\mathbf{S}_{n,\neq k}\}) \qquad (46)$$

with the Oseen tensor

$$\boldsymbol{T}(\mathbf{S},\mathbf{S}_l) = \frac{1}{8\pi\eta Q_l}\left(\boldsymbol{I} + \frac{\mathbf{Q}_l\mathbf{Q}_l}{Q_l^2}\right) \qquad (47)$$

and

$$\mathbf{Q}_l = \mathbf{S}_l - \mathbf{S} \qquad (48)$$

By introducing the multivariate distribution function $P(\{\mathbf{S}_{n,\neq k}\})$, to be factorized as follows:

$$P(\{\mathbf{S}_{n,\neq k}\}) = P(\{\mathbf{S}_{n,\neq k,l}\}|\mathbf{S}_l)P_l(\mathbf{S}_l) \qquad (49)$$

we may change the expression for the average perturbation $\langle \mathbf{v}_p(\mathbf{S})\rangle$ =

$$\zeta\sum_{l=1}^{n} \int \cdots \int \boldsymbol{T}(\mathbf{S},\mathbf{S}_l)\cdot\mathbf{w}_l(\{\mathbf{S}_{n,\neq k}\})P(\{\mathbf{S}_{n,\neq k}\})\ \mathrm{d}\{\mathbf{S}_{n,\neq k}\} \qquad (50)$$

to

$$\langle \mathbf{v}_p(\mathbf{S})\rangle \approx \zeta \sum_{l=1}^{n} \int \boldsymbol{T}(\mathbf{S},\mathbf{S}_l)\cdot\langle \mathbf{w}_l(\mathbf{S}_l)\rangle P_l(\mathbf{S}_l)\ \mathrm{d}\mathbf{S}_l \qquad (51)$$

We have no expression for $\langle \mathbf{w}_l(\mathbf{S}_l)\rangle$ and therefore preaverage with respect to $\mathbf{S}_l$

$$\langle \boldsymbol{T}_l(S)\rangle = \int \boldsymbol{T}(\mathbf{S},\mathbf{S}_l)P_l(\mathbf{S}_l)\ \mathrm{d}\mathbf{S}_l \qquad (52)$$

$$\langle \mathbf{w}_l\rangle = \int \langle \mathbf{w}_l(\mathbf{S}_l)\rangle P_l(\mathbf{S}_l)\ \mathrm{d}\mathbf{S}_l \qquad (53)$$

to obtain

$$\langle \mathbf{v}_p(\mathbf{S})\rangle \approx \zeta \sum_{l=1}^{n} \langle \boldsymbol{T}_l(\mathbf{S})\rangle\cdot\langle \mathbf{w}_l\rangle \qquad (54)$$

For $\langle w_l\rangle$ we have $\phi(y) = -\langle w_l\rangle/u$ in the continuous parameter $y = 2(l/n) - 1$. The derivation is analogous to that of $\langle \boldsymbol{T}_k(\mathbf{R})\rangle$, eq 12.

The distribution function for $P_l(\mathbf{S}_l)$ is

$$P_l(\mathbf{S}_l) = \left(\frac{\lambda}{\pi}\right)^{3/2} e^{-\lambda S_l^2} \qquad (55)$$

in which

$$\lambda = 3(2b^2|k - l|)^{-1} = (2R_g^{\,2}|x - y|)^{-1} \qquad (56)$$

The result of the derivation is

$$\langle \boldsymbol{T}_l(\mathbf{S})\rangle = \frac{1}{8\pi\eta S}\left\{B_{1l}(\lambda^{1/2}S)\boldsymbol{I} + B_{2l}(\lambda^{1/2}S)\frac{\mathbf{SS}}{S^2}\right\} \qquad (57)$$

$$B_{1l} = \operatorname{erf} \lambda^{1/2}S + \frac{\operatorname{smf} \lambda^{1/2}S}{\lambda S^2} \qquad (58)$$

$$B_{2l} = \operatorname{erf} \lambda^{1/2}S - 3\frac{\operatorname{smf} \lambda^{1/2}S}{\lambda S^2} \qquad (59)$$

with smf ξ defined above eq 19.

From (54), (57), (28), and (27), writing $\sigma \equiv S/R_g$, we obtain for the flow field at very large n

$$\langle \mathbf{v}_p(\sigma)\rangle = -\frac{3}{8\pi^{1/2}\sigma}\left[\int_{-1}^{1}\left\{B_1(\sigma,x,y)\boldsymbol{I} + B_2(\sigma,x,y)\frac{\sigma\sigma}{\sigma^2}\right\} \times (1 - y^2)^{-1/4}\ \mathrm{d}y\right]\cdot\mathbf{u} \qquad (60)$$

Since in the region of integration a singularity occurs at $x = y$, a series expansion of $\langle \mathbf{v}_p(\sigma)\rangle$ in powers of σ^2 is not possible. However, assuming $x \neq y$, we may evaluate the following limits

$$\lim_{\sigma\to 0} B_1/\sigma = {}^8\!/\!_3(2\pi|x - y|)^{-1/2} \qquad (61)$$

$$\lim_{\sigma\to 0} B_2/\sigma = 0 \qquad (62)$$

Substitution in (60) yields

$$\lim_{\sigma\to 0} \langle \mathbf{v}_p(\sigma)\rangle = -\frac{1}{\pi 2^{1/2}}\left[\int_{-1}^{1}|x - y|^{-1/2}(1 - y^2)^{-1/4}\ \mathrm{d}y\right]\mathbf{u} \qquad (63)$$

It follows on the grounds of eq 26 and 28 that

$$\lim_{\sigma\to 0} \langle \mathbf{v}_p(\sigma)\rangle = -\mathbf{u} \qquad (-1 \le x \le 1) \qquad (64)$$

So, on the average $\langle \mathbf{v}_r(0)\rangle = 0$ in agreement with the requirement stated in the beginning of this section. The solvent does not slip along the chain and the contour of the chain is nondrained.

As before we will consider the pattern of the average perturbation in the equatorial plane. For this plane $\sigma\cdot\mathbf{u} = 0$, so that substitution of (58a), using (56b), in (60) gives

$$\langle \mathbf{v}_p(\sigma)\rangle_{eq} = -\frac{3}{8\pi^{1/2}}\frac{\mathbf{u}}{\sigma}\int_{-1}^{1}\left\{\operatorname{erf}\frac{\sigma}{(2|x - y|)^{1/2}} + \frac{4|x - y|}{\sigma^2}\operatorname{smf}\frac{\sigma}{(2|x - y|)^{1/2}}\right\}(1 - y^2)^{-1/4}\ \mathrm{d}y \qquad (65)$$

Numerical calculations have been done for $x = 0$ and $x = \pm 1$ and for a range of values of σ. To improve upon the reliability of calculating the ratio of small numbers the integrals have been transformed and the factors σ^{-1} and σ^{-3} removed. This is shown in the Appendix. Curves 4 and 5 in Figure 2 show $\langle v_r\rangle_{eq}/u = 1 + \langle v_p\rangle_{eq}/u$ as a function of σ for $k = n/2$ ($x = 0$) and $k = 1$ or n ($x = \pm 1$). The initial course of $\langle v_r\rangle$ from the origin for $x = \pm 1$ is proportional to $\sigma^{1/2}$, so the initial slope of curve 5 is infinitely large.

Curves 4 and 5 should be appraised against the extension of the chain observed from the middle or end segments. The average fraction of the total number of segments found outside the sphere with radius S centered on segment k is given by

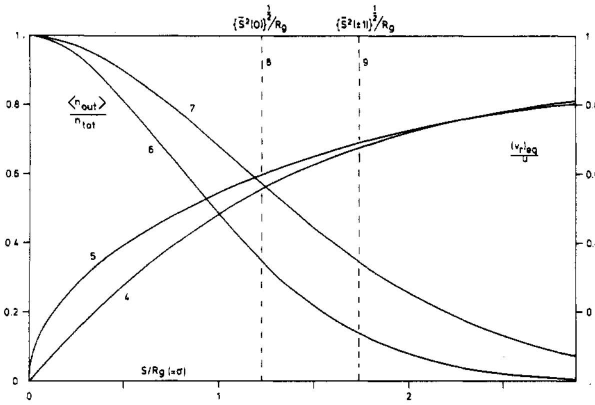

Figure 2. Average draining and extension of the freely jointed chain observed from the middle and end segments: (4) $\langle v_{rel}\rangle_{eq}/u$ observed from the middle segment; (5) same as curve 4, except observed from an end segment; (6) average fraction of total number of segments outside the sphere with radius S/R_g centered on the middle segment; (7) same as curve b, except for a sphere centered on an end segment; (8) reduced root-mean-square segment distance from the middle segment; (9) same as curve 8, except from an end segment.

$$\langle n(S,k)\rangle_{\text{out}}/n = 4\pi \sum_{l=1}^{n} \int_S^\infty (S')^2 P_{kl}(S')\,dS' \quad (66)$$

Here $P_{kl}(S')$ is given by (55).

After changing to the variables σ, x, and y, eq 66 can be developed to the following expression:

$$\langle n(\sigma,x)\rangle_{\text{out}}/n = \frac{1}{2}\left[(1 + x - \sigma^2)\left\{1 - \text{erf}\,\frac{\sigma}{2^{1/2}(1+x)^{1/2}}\right\} + (1 - x - \sigma^2)\left\{1 - \text{erf}\,\frac{\sigma}{2^{1/2}(1-x)^{1/2}}\right\} + \left(\frac{2}{\pi}\right)^{1/2}\sigma\{(1+x)^{1/2}e^{-\sigma^2/[2(1+x)]} + (1-x)^{1/2}e^{-\sigma^2/[2(1-x)]}\}\right] \quad (67)$$

For $x = 0$ and $x = \pm 1$ this function is shown by curves 6 and 7. Vertical lines 8 and 9 indicate the root-mean-square distances of all other segments from the middle segment ($x = 0$) or the end segments ($x + \pm 1$). These distances follow from the mean-square distance between segments k and l, which is $|k - l|b^2$, and are given by

$$\overline{S^2}(x) = \tfrac{3}{2}(1 + x^2)R_g^{\,2} \quad (68)$$

Comparison of Segment Density Distributions for $n \rightarrow \infty$

The average segment density distribution, observed from the center of mass, is given by (14) after summation over k. This density decreases everywhere with $n^{-1/2}$.

When a segment (k) is taken as the reference point the segment density is given by (55) after summation over l. With continuous variables this density is found to be given by

$$\bar{\nu}(\sigma,x) = \left(\frac{3}{2n}\right)^{1/2}\frac{3}{\pi b^2\sigma}\left\{2 - \text{erf}\,\frac{\sigma}{2^{1/2}(1+x)^{1/2}} - \text{erf}\,\frac{\sigma}{2^{1/2}(1-x)^{1/2}}\right\} \quad (-1 \le x \le 1) \quad (69)$$

In our figures to a scale, in which R_g is the unit of distance, $\bar{\nu}$ again vanishes everywhere with $n^{-1/2}$, except in $\sigma = 0$. Here the value is infinite.

Discussion

In the approximation obtained by using eq 11 the fluid near the center of mass (Z) is nearly immobilized with respect to the chain (curve 1). In Z $\langle v_r\rangle/u$ is as small as 0.036. At the level of R_h, however, the value is 0.28. Since on the average $^2/_3$ of the total number of segments is outside the sphere with radius R_h (curve 2), we conclude that the greater part of the chain domain is partially drained, even for $n \rightarrow \infty$. This conclusion may be drawn already from the single ratio (39). For, quite generally, if the chain were nondrained up to R_g, then on the grounds of Stokes' relation the friction coefficient would be more than a factor R_g/R_h larger than the observed value.

Close to the chain the hydrodynamical shielding is greater than that for the center of mass and is greatest for the middle segment. However, for a volume element at distance $\sigma = 0.1$ from this segment the average shielding is already smaller than at the same distance from the center of mass. This is due to the occasionally peripheral position of a segment, even of the middle segment.

We considered only $\langle \mathbf{v}_r(\mathbf{R})\rangle$. What about the fluctuations $\mathbf{v}_r(\mathbf{R}) - \langle \mathbf{v}_r(\mathbf{R})\rangle$ for the real chain? These may be as large as $-\langle \mathbf{v}_r(\mathbf{R})\rangle$, when the chain passes through $\mathbf{R}$, up to a considerable fraction of $\mathbf{u} - \langle \mathbf{v}_r(\mathbf{R})\rangle$, when between lobes of higher segment density there is a passage of lower density roughly in the direction of $\mathbf{u}$.

In conclusion we give as our opinion that terms like the "nondraining limit", the "impermeable limit" or even "no-draining effect" refer to a hydrodynamical condition which for linear flexible chains is never obtained. These terms should be avoided and words like "the least-draining limit" or "limit of smallest drain" be used instead.

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Appendix (Eq 65)

For given values of x ($-1 \le x \le 1$) and α ($\alpha = \sigma/\sqrt{2} \ge 0$) we require evaluation of the integrals

$$I_1(x,\alpha) = \alpha^{-1}\int_{-1}^{1}(1 - y^2)^{-1/4}\,\text{erf}\,\frac{\alpha}{|x - y|^{1/2}}\,dy \quad (1')$$

and

$$I_2(x,\alpha) = \alpha^{-3}\int_{-1}^{1}(1 - y^2)^{-1/4}|x - y|\int_0^{\alpha(|x-y|)^{-1/2}} q^2 e^{-q^2}\,dq\,dy$$

The evaluation offers some difficulty for small values of α. We divide the area of integration in four parts ($I_i = \sum_{j=1}^{4} I_{ij}$; $i = 1, 2$) as follows:

$$I_{11}:\quad -1 \le y \le x,\quad 0 < q < \alpha(1 + x)^{-1/2}$$

$$I_{12}:\quad -1 \le y \le x,\quad \alpha(1 + x)^{-1/2} < q < \alpha(x - y)^{-1/2}$$

$$I_{13}:\quad x < y \le 1,\quad 0 < q < \alpha(1 - x)^{-1/2}$$

$$I_{14}:\quad x < y \le 1,\quad \alpha(1 - x)^{-1/2} < q < \alpha(y - x)^{-1/2}$$

The subintegrals for I_1 are the following:

$$I_{11} = \left[\int_{-1}^{x}(1 - y^2)^{-1/4}\,dy\right]\cdot\alpha^{-1}\,\text{erf}\,\frac{\alpha}{(1 + x)^{1/2}}$$

For small α this should be expanded in powers of α.

For I_{12} we transform to the variable t through $q = \alpha(x - t)^{-1/2}$ and then obtain

$$I_{12} = \frac{2}{\alpha\pi^{1/2}}\int_{-1}^{x}(1 - y^2)^{-1/4}\int_{\alpha(1+x)^{-1/2}}^{\alpha(x-y)^{-1/2}} e^{-q^2}\,dq\,dy = \pi^{-1/2}\int_{-1}^{x}(1 - y^2)^{-1/4}\int_{-1}^{y} e^{-\alpha^2/(x-t)}(x - t)^{-3/2}\,dt\,dy$$

This is finite also for $\alpha = 0$.

$$I_{13} = \left[\int_{x}^{1}(1 - y^2)^{-1/4}\,dy\right]\cdot\alpha^{-1}\,\text{erf}\,\frac{\alpha}{(1 - x)^{1/2}}$$

I_{14} we transform with $q = \alpha(t - x)^{-1/2}$

$$I_{14} = \frac{2}{\alpha\pi^{1/2}}\int_{x}^{1}(1 - y^2)^{-1/4}\int_{\alpha(1-x)^{-1/2}}^{\alpha(y-x)^{-1/2}} e^{-q^2}\,dq\,dy = \pi^{-1/2}\int_{x}^{1}(1 - y^2)^{-1/4}\int_{y}^{1} e^{-\alpha^2/(t-x)}(t - x)^{-3/2}\,dt\,dy = \pi^{-1/2}\int_{x}^{1} e^{-\alpha^2/(t-x)}(t - x)^{-3/2}\int_{x}^{t}(1 - y^2)^{-1/4}\,dy\,dt$$

which is finite for $\alpha \ge 0$.

Similarly we obtain for I_2

$$I_{21} = \left[\int_{-1}^{x}(1 - y^2)^{-1/4}(x - y)\,dy\right] \times \alpha^{-3}\left\{\frac{\pi^{1/2}}{4}\,\text{erf}\,\frac{\alpha}{(1 + x)^{1/2}} - \frac{\alpha}{2(1 + x)^{1/2}}e^{-\alpha^2/(1+x)}\right\}$$

which can be expanded in α^2 ($x > 1$).

$$I_{22} = \alpha^{-3}\int_{-1}^{x}(1-y^2)^{-1/4}(x-y)\int_{\alpha(1+x)^{-1/2}}^{\alpha(x-y)^{-1/2}} q^2e^{-q^2}\,dq\,dy = \frac{1}{2}\int_{-1}^{x}(1-y^2)^{-1/4}(x-y)\times\int_{-1}^{y}(x-t)^{-5/2}e^{-\alpha^2/(x-t)}\,dt\,dy \qquad (\alpha \geq 0)$$

$$I_{23} = \left[\int_{x}^{1}(1-y^2)^{-1/4}(y-x)\,dy\right]\times \alpha^{-3}\left\{\frac{\pi^{1/2}}{4}\,\mathrm{erf}\,\frac{\alpha}{(1-x)^{1/2}} - \frac{\alpha}{2(1-x)^{1/2}}e^{-\alpha/(1-x)}\right\}$$

$$I_{24} = \alpha^{-3}\int_{x}^{1}(1-y^2)^{-1/4}(y-x)\int_{\alpha(1-x)^{-1/2}}^{\alpha(y-x)^{-1/2}} q^2e^{-q^2}\,dq\,dy = \frac{1}{2}\int_{x}^{1}(1-y^2)^{-1/4}(y-x)\int_{y}^{1}(t-x)^{-5/2}e^{-\alpha^2/(t-x)}\,dt\,dy = \frac{1}{2}\int_{x}^{1}e^{-\alpha^2/(t-x)}(t-x)^{-5/2}\times\int_{x}^{t}(1-y^2)^{-1/4}(y-x)\,dy\,dt \qquad (\alpha \geq 0)$$

An algorithm, based on the Romberg method, was developed for the evaluation of integrals of the kind

$$\int_{a}^{b} f_1(t)\int_{a}^{t} f_2(t')\,dt'\,dt$$

It was written out in a program for the HP-41C hand-held calculator and used for the evaluation of I_{12}, I_{14}, I_{22}, and I_{24} for various values of x and α.

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References and Notes

(1) Kirkwood, J. G.; Riseman, J. *J. Chem. Phys.* **1948**, *16*, 565.
(2) Yamakawa, H. *Modern Theory of Polymer Solutions*; Harper & Row: New York, 1971; Chapter 6.
(3) For example: Zimm, B. H.; Kilb, R. W. *J. Polym. Sci.* **1959**, *37*, 19. Hearst, J. E. *J. Chem. Phys.* **1962**, *37*, 2547. Pyun, C. W.; Fixman, M. *J. Chem. Phys.* **1965**, *42*, 3838. Yamakawa, H.; Tanaka, G. *J. Chem. Phys.* **1970**, *55*, 3188. Fujita, H.; Taki, N.; Norisuye, T.; Sotobayashi, H. *J. Polym. Sci., Polym. Phys. Ed.* **1977**, *15*, 2255. Jones, G.; Caroline, D. *Chem. Phys.* **1979**, *37*, 187.
(4) Debye, P.; Bueche, A. M. *J. Chem. Phys.* **1948**, *16*, 573.
(5) Let the positive z direction be downward. Above the plane $z = 0$ (i.e., for $z < 0$) a liquid flows in the x direction with a uniform gradient in the negative z direction and $v = v_0$ at $z = 0$. Below $z = 0$ there is a uniform distribution of flow-resisting beads. Then the average flow velocity at a depth z in the x direction satisfies the relation $v = v_0e^{-z/L}$.
(6) Flory, P. J. *Principles of Polymer Chemistry*; Cornell University Press: Ithaca, NY, 1953; p 607.
(7) Wiegel, F. W.; Mijnlieff, P. F. *Physica* **1977**, *89A*, 385. Mijnlieff, P. F.; Wiegel, F. W. *J. Polym. Sci., Polym. Phys. Ed.* **1978**, *16*, 245.
(8) Ullman, R. *Macromolecules* **1981**, *14*, 746.
(9) Tanaka, G. *Macromolecules* **1982**, *15*, 1028.
(10) Barret, A. J. *Macromolecules* **1984**, *17*, 1566.
(11) Douglas, J. F.; Freed, K. F. *Macromolecules* **1984**, *17*, 2354, footnote 23.
(12) Yamakawa, H. *J. Chem. Phys.* **1970**, *53*, 436.
(13) Cowie, J. M.; Bywater, S. *Polymer* **1965**, *6*, 197.
(14) Mulderije, J. J. H. *Macromolecules* **1980**, *13*, 1207.
(15) Vidaković, P.; Allain, C.; Rondelez, F. *Macromolecules* **1982**, *15*, 1571.
(16) Yamamoto, A. et al. *Polymer J. (Tokyo)* **1971**, *2*, 799.
(17) Mays, J. W.; Hadjichristidis, N.; Fetters, L. J. *Macromolecules* **1985**, *18*, 2231.
(18) King, T. A.; Knox, A.; Mc Adam, J. P. G. *J. Polym. Sci., Polym. Symp.* **1974**, *No. 44*, 195.
(19) Gulari, E. et al. *Polymer* **1979**, *20*, 347.
(20) Han, C. C. *Polymer* **1979**, *20*, 259.
(21) Han, C. C.; Akcasu, A. Z. *Polymer* **1981**, *22*, 1165.
(22) Pritchard, M. J.; Caroline, D. *Macromolecules* **1981**, *14*, 424.
(23) Novotny, V. J. *J. Chem. Phys.* **1983**, *78*, 183.
(24) Nose, T.; Chu, B. *Macromolecules* **1979**, *12*, 590.
(25) Tsunashima, Y.; Nemoto, N.; Kurata, M. *Macromolecules* **1983**, *16*, 1184.
(26) Fukuda, M. et al. *J. Polym. Sci.* **1974**, *12*, 871.
(27) Kubota, K.; Abbay, K. M.; Chu, B. *Macromolecules* **1983**, *16*, 137.
(28) Abe, M. et al. *Bull. Chem. Soc. Jpn.* **1968**, *41*, 2330.
(29) Mijnlieff, P. F.; Coumou, D. J. *Colloid Interface Sci.* **1968**, *27*, 553.
(30) Noda, I.; Mizutani, K.; Kato, T. *Macromolecules* **1977**, *10*, 618.
(31) Kato, T. et al. *Macromolecules* **1970**, *3*, 777.
(32) For a summary of results until 1981 see: Schmidt, M.; Burchard, W. *Macromolecules* **1981**, *14*, 210.
(33) Kurata, M.; Yamakawa, H. *J. Chem. Phys.* **1958**, *29*, 331.
(34) Auer, P. L.; Gardner, C. S. *J. Chem. Phys.* **1955**, *23*, 1545; **1955**, *23*, 1546.
(35) Landau, L. D.; Lifshitz, E. M. *Fluid Mechanics*; Addison-Wesley: Reading, MA, 1959.