are 27.3–29.1 dyn/cm, and the extrapolation to infinite molecular weight shown in Figure 3 yields a value of 29.9 dyn/cm at this temperature. A similar discrepancy appears at other temperatures, since Roe estimated a theoretical value of 45.9 dyn/cm at 20°, while linear extrapolation of our data to 20° yields 39.0–39.3 dyn/cm. (It should be emphasized that this extrapolated value, which refers to a hypothetical liquid state, is of doubtful significance.)

Roe[8] and Wu[20] have noted that MacLeod's exponent, *i.e.*, the slope of a log–log plot of surface tension *vs.* density, is lower for several polymers than the usual value (near 4) found for simple liquids. Their results for poly(isobutylene), however, indicated that this is not a general effect. The present results for poly(styrenes) are also consistent with a "normal" MacLeod's exponent (slopes of 3.8–4.1 are obtained depending on whether values for the various samples are plotted separately or all data are combined).

LeGrand and Gaines[1] attempted to relate the molecular weight dependence of surface tension to variations in glass transition temperatures by a crude free volume argument. Their expression for the slope of the γ *vs.* $M^{-2/3}$ plot was based on the premise (among others) that T_g is linearly related to $1/M$. This simple relation is not accurately obeyed by our materials. There is some uncertainty in the assignment of a $T_{g\infty}$, as well as the already noted difficulties with the T_g's of the experimental samples. Depending on these assignments, and which sample is considered, it is possible to calculate predicted slopes of 175–540, using eq 4 of ref 1. The slope of the line in Figure 3 is 366; because of the variation of $d\gamma/dT$ with molecular weight, the slopes at other temperatures would have somewhat different values, in the range 320–340. Hence we find, as before, that the results of this crude argument are qualitatively consistent with experiment, but cannot be used for quantitative correlation. The present results suggest that this difficulty is related at least as much to the qualitative nature of the free-volume relation for bulk properties as to our attempt to relate it to the surface tension.

Acknowledgment. We are indebted to D. G. LeGrand for many helpful discussions.

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(20) S. Wu, *J. Colloid Interfac. Sci.*, 31, 153 (1969).

Separation by Flow

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ABSTRACT: Dilute solutions of finite size particles undergoing Brownian motion and flowing through a capillary have average velocities which depend on the particle size. Thus one can obtain a separation of particles of different sizes due to fluid flow. The elution volumes of suspended particles or polymer molecules are derived for various tube geometries. Following Taylor, the effects of diffusional broadening of the volume elution peak for finite size particles are discussed and a criteria for separation is given. It is found that particles very similar in size can always be separated. A scheme for separation by flow on a continuous basis is proposed.

I. Introduction

An isolated polymer molecule flowing down the inside of a thin capillary and undergoing Brownian motion will have an average velocity greater than that of the solvent. This is because the center of the particle (assumed to be a rigid sphere) cannot get any closer to the walls of the capillary than its radius. It therefore samples only those solvent velocities away from the walls. Since the solvent velocity is larger, the farther the distance from the wall, larger molecules will have larger average velocities than smaller molecules.

Suppose we now introduce particles of two different sizes simultaneously at the top of the column. The average distance between these particles will increase linearly with time as they flow through the tube because they have different average velocities. On the other hand the peak widths of the distribution of particle distances about their mean value for each kind of particle increases as the square root of time. This is a characteristic of particle diffusion. It therefore follows that by waiting for sufficiently long periods of time the separation between peaks can be made large compared to the width of the peaks. The particles therefore separate into two groups.

The purpose of this paper is to place the above ideas on a firm quantitative foundation.

Calculations of average velocity (and elution volume) of particles in right circular cylinders and parallel plates have been published.[1] Also, preliminary calculations showing the connection of the concept of separation by flow to gel permeation chromatography have been made.[2]

We will, in section IIA, derive formulas for the velocity of a polymer molecule as a function of both its size and the geometry of the tube through which it flows, as well as of its placement in the tube. The main conclusion of this section is that the velocity of the center of mass of a molecule in a general velocity field is approximately that which the fluid would have at the location occupied by the center of mass were the polymer molecule not there. In section IIB the average velocity and the elution volume in both circular cylinders and parallel plates are calculated. In IIC the dispersion in the elution volume peak due to diffusion and to the

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(1) E. A. DiMarzio and C. M. Guttman, *J. Polym. Sci., Part B*, 7, 267 (1969).

(2) E. A. DiMarzio and C. M. Guttman, *Bull. Amer. Phys. Soc.*, 14, 424 (1969).

smearing effect of the shear gradient is calculated in the limits of Fickian and Knudsen diffusion. It is found that the width of the peak spreads as the square root of t for both regimes. In section IIIA we show that two different size molecules can, in principle, always be separated no matter how small the difference. Criteria of resolution are given. In IIIB a variation of the theory is used to suggest an instrument to separate particles on a continuous basis. In sections IV, V, and VI the possible applications and limitations of the theory are discussed.

II. Theory of Separation by Flow in One Tube

A. Evaluation of Polymer Velocity. Retardation Effect. If we put a polymer molecule into a fluid moving through a tube of uniform cross section, the polymer will have a velocity, $\vec{v}_p$, which in general will be a function of its position in the tube. It is this velocity, $\vec{v}_p$, we now seek to evaluate. Unfortunately, the theoretical evaluation of $\vec{v}_p$ for realistic models of polymers larger than a fluid particle has not yet been performed. However, calculations of $\vec{v}_p$ exist for dilute suspensions of hard spheres.[3] In addition, experimental measurements of $\vec{v}_p$ on impermeable spheres have been made.[4] The results of these experiments and of the model calculations as well as the calculations presented here are qualitatively similar. That is, one finds that the velocity of the polymer not too close to the wall of the tube is that of the fluid at the center of mass of the polymer minus a quantity independent of the distance from the wall but dependent on the size of the polymer and on the curvature of the velocity field.

The derivation of the formula for $\vec{v}_p$ for the so-called free draining model has been sketched out by us[1] and will now be redone here in a more complete way.

The model we assume for our calculations is that given by Debye in his classic 1948 paper.[5] The polymer molecule is considered as rigid and permeable to the solvent. Further, the solvent fluid velocity profile is assumed unchanged by the presence of the polymer. To find the velocity of the polymer we follow the technique used by Debye. The only difference is that in our case the molecule sees not only a linear component of shear field but also higher components.

We now consider a polymer molecule immersed in a fluid whose velocity, $\vec{v}_f(x,y,z)$, has in general components in all directions; $v_f^x(x,y,z)$, $v_f^y(x,y,z)$, $v_f^z(x,y,z)$ are the x, y, and z components of fluid velocity, respectively.

Now, if we consider the polymer as rigid, then the most general motion it may have is described by a rotation around its center of mass plus a translation of the center of mass. Then the velocity of the ith bead of a N-beaded polymer, $\vec{u}_i$, is given by

$$\vec{u}_i = \begin{cases} \omega_y z_i' - \omega_z y_i' + v_{p,x} \\ \omega_z x_i' - \omega_x z_i' + v_{p,y} \\ \omega_x y_i' - \omega_y x_i' + v_{p,z} \end{cases} \tag{1}$$

where $\vec{v}_p$ is the velocity of the center of mass of the polymer, $\vec{\omega}$ is the angular velocity around that center of mass, and x_i', y_i', and z_i' are the x, y, and z components of the vector $\vec{r}_i'$, the vector distance from the center of mass of the polymer to its ith bead.

Since we assume the only force on the macromolecule is a viscous one, the force $\vec{F}_i$ on the ith bead is simply

$$\vec{F}_i = f[\vec{u}_i - v_f(x_c + x_i', y_c + y_i', z_c + z_i')] \tag{2}$$

where f is the microscopic coefficient of friction and x_c, y_c, and z_c are the x, y, z coordinates of the center of mass of the polymer in the laboratory system. For simplicity of notation let us rewrite $\vec{v}_f(x_c + x_i', y_c + y_i', z_c + z_i')$, the velocity of the fluid at the position of the ith bead as $\vec{v}_{f,i}$.

$$\vec{v}_{f,i} \equiv \vec{v}_f(x_c + x_i', y_c + y_i', z_c + z_i'). \tag{3}$$

Now, in the steady state (neglecting inertial terms) the average moment of the force about the center of mass is zero as is the net force acting on the center of mass.[5] Thus

$$\sum_i \vec{F}_i = 0 \tag{4a}$$

$$\vec{M} = \sum_i \vec{r}_i' \times \vec{F}_i = 0 \tag{4b}$$

If we assume the particle is spherically symmetric, then all the moments in which the power of at least one of the variables x_i', y_i', z_i' is odd, will vanish; thus

$$\begin{gathered} \sum x_i' = \sum y_i' = \sum z_i' = 0 \\ \sum x_i'y_i' = \sum x_i'z_i' = 0, \text{ etc.} \end{gathered} \tag{5}$$

We then obtain

$$\begin{aligned} F_x/f &= \Big[Nv_{p,x} - \sum_i v_{f,i}^x\Big] = 0 \\ F_y/f &= \Big[Nv_{p,y} - \sum_i v_{f,i}^y\Big] = 0 \\ F_z/f &= \Big[Nv_{p,z} - \sum_i v_{f,i}^z\Big] = 0 \end{aligned} \tag{6a}$$

$$\begin{aligned} M_x/f &= \omega_x\Big(\sum_i[(y_i')^2 + (z_i')^2]\Big) - \sum_i(y_i'v_{f,i}^z - z_i'v_{f,i}^y) = 0 \\ M_y/f &= \omega_y\Big(\sum_i[(z_i')^2 + (x_i')^2]\Big) - \sum_i(z_i'v_{f,i}^x - x_i'v_{f,i}^z) = 0 \\ M_z/f &= \omega_z\Big(\sum_i[(x_i')^2 + (y_i')^2]\Big) - \sum_i(x_i'v_{f,i}^y - y_i'v_{f,i}^x) = 0 \end{aligned} \tag{6b}$$

For present purposes we consider the velocity of a fluid in a tube of fixed cross section. If the x axis in the laboratory coordinate system is assumed to be parallel to the tube axis, the fluid velocity, $\vec{v}_f$, will have only a component in the x direction; further, for an infinitely long tube the assumption of lamellar flow causes the fluid velocity to depend only on the y and z position of the fluid particles. That is

$$\begin{gathered} v_f^x = v_f^x(y,z) \\ v_f^y = v_f^z = 0 \end{gathered} \tag{7}$$

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(3) J. Happel and H. Brenner, *A. I. Ch. E. J.*, **3**, 506 (1957).

(4) H. L. Goldsmith and S. G. Mason, *J. Colloid Sci.*, **17**, 448 (1962).

(5) P. Debye, *J. Chem. Phys.*, **14**, 636 (1946).

We immediately obtain from eq 6 independent of tube geometry

$$v_{\mathrm{p},x} = \sum_i v_{\mathrm{f},i}{}^x/N$$

$$v_{\mathrm{p},y} = 0$$

$$v_{\mathrm{p},z} = 0 \qquad \text{(8a)}$$

$$\omega_x = 0$$

$$\omega_y = +\sum_i z_i' v_{\mathrm{f},i}{}^x \Big/ \sum_i [(x_i')^2 + (z_i')^2]$$

$$\omega_z = -\sum_i y_i' v_{\mathrm{f},i}{}^x \Big/ \sum_i [(x_i')^2 + (y_i')^2] \qquad \text{(8b)}$$

Two tube cross sections of interest for which the velocity profile of the fluid is known are the parallel plates and circular cylinder. For parallel plates the fluid velocity is simply

$$v_{\mathrm{f}}{}^x = \frac{1}{2\eta}\frac{\partial p}{\partial l}(z_0{}^2 - z^2) \qquad (9)$$

where $\partial p/\partial l$ is the pressure per unit length (head), η the fluid viscosity, and z_0 is half the distance between plates.[6] Notice that here we have taken the z direction perpendicular to the plates. Then

$$v_{\mathrm{f},i}{}^x = \frac{1}{2\eta}\frac{\partial p}{\partial l}\,[z_0{}^2 - z_{\mathrm{c}}{}^2 - 2z_{\mathrm{c}}z_i' - (z_i')^2] \qquad (10)$$

Now, from eq 5, 8, and 10 we obtain

$$v_{\mathrm{p},x} = \frac{1}{2\eta}\frac{\partial p}{\partial l}\left[z_0{}^2 - z_{\mathrm{c}}{}^2 - \sum_i (z_i')^2/N\right]$$

$$v_{\mathrm{p},y} = 0$$

$$v_{\mathrm{p},z} = 0 \qquad \text{(11a)}$$

$$\omega_x = 0$$

$$\omega_y = -\frac{z_{\mathrm{c}}}{\eta}\frac{\partial p}{\partial l}\left[\sum_i (z_i')^2 \Big/ \sum_i \{(z_i')^2 + (x_i')^2)\}\right] = -\frac{z_{\mathrm{c}}}{2\eta}\frac{\partial p}{\partial l}$$

$$\omega_z = 0 \qquad \text{(11b)}$$

Our model thus predicts no radial force on the polymer. However, if $\Sigma_i x_i$ were unequal to zero, a force would exist.

For circular cylinders the fluid velocity is[6]

$$v_{\mathrm{f}} = \frac{1}{4\eta}\frac{\partial p}{\partial l}(y_0{}^2 + z_0{}^2 - y^2 - z^2) \qquad (12)$$

Then the fluid velocity at the ith bead is

$$v_{\mathrm{f},i} = \frac{1}{4\eta}\frac{\partial p}{\partial l}[y_0{}^2 + z_0{}^2 - y_{\mathrm{c}}{}^2 - z_{\mathrm{c}}{}^2 - 2y_{\mathrm{c}}y_i' - 2z_{\mathrm{c}}z_i' - (y_i')^2 - (z_i')^2] \qquad (13)$$

Thus, eq 5, 8, and 10 yield

$$v_{\mathrm{p},x} = \frac{1}{4\eta}\frac{\partial p}{\partial l}\left[y_0{}^2 + z_0{}^2 - y_{\mathrm{c}}{}^2 - z_{\mathrm{c}}{}^2 - \sum_i \frac{(y_i')^2 + (z_i'^2)}{N}\right]$$

$$v_{\mathrm{p},y} = 0$$

$$v_{\mathrm{p},z} = 0 \qquad \text{(14a)}$$

$$\omega_x = 0$$

$$\omega_y = -\frac{z_{\mathrm{c}}}{2\eta}\frac{\partial p}{\partial l}\sum_i (z_i')^2 \Big/ \left[\sum_i \{(x_i')^2 + (z_i')^2\}\right] = -\frac{z_{\mathrm{c}}}{4\eta}\frac{\partial p}{\partial l}$$

$$\omega_z = \frac{y_{\mathrm{c}}}{2\eta}\frac{\partial p}{\partial l}\sum_i (y_i')^2 \Big/ \left[\sum_i \{(x_i')^2 + (z_i')^2\}\right] = +\frac{y_{\mathrm{c}}}{4\eta}\frac{\partial p}{\partial l} \qquad \text{(14b)}$$

One observes that the angular velocity is identical with that obtained by Debye, and is one-half of the shear gradient. The velocity of the center of mass of the polymer, $v_{\mathrm{p},x}$, differs from the fluid velocity, v_{f}, by a constant. Thus, the only effect of the quadratic term in the velocity of the fluid is to retard the macromolecule. For a spherically symmetrical particle the last term in the brackets of the expression for $v_{\mathrm{p},x}$ is just two thirds the radius of gyration s, squared.[7] Thus

$$2\sum_i (z_i')^2/N = 2s^2/3 \qquad (15)$$

One notices that the retardation term is twice as large for circular cylinders as for parallel plates. This arises because the shear field for a circular cylinder has two quadratic components of equal magnitude. There is quadratic variation along the tangential direction as well as the radial direction. At first sight it is surprising that the tangential variation is as large as the radial, but if we transform to a coordinate system centered at the particle, the result is easily derived.

The fact that $v_{\mathrm{p},y} = v_{\mathrm{p},z} = 0$ means that there is no component of velocity perpendicular to the direction of fluid flow.

Equations 11 and 14 are very simple results. We will now show that they have a validity beyond our model. Happel and Byrne[8] have derived a relation for the slip at the axis of a cylindrical tube of radius r_0 for rigid impermeable spheres of radius s. They obtain

$$\left[\frac{v_{\mathrm{f}} - v_{\mathrm{p}}}{v_{\mathrm{f}}}\right]_{r=0} = \frac{2}{3}\left(\frac{s}{r_0}\right)^2 \qquad (16)$$

This relation is identical with ours if we identify the radius of the sphere with the radius of gyration of the molecule. Equation 16 has been confirmed experimentally by Goldsmith and Mason.[4] Further, they evaluated the quantity

$$\frac{v_{\mathrm{f}} - v_{\mathrm{p}}}{\frac{2}{3}v_{\mathrm{f}}\left(\frac{s}{r_0}\right)^2} \qquad (17)$$

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(6) W. E. Langlois, "Slow Viscous Flow," The Macmillan Co., New York, N. Y., 1964.

(7) P. J. Flory, "Principles of Polymer Chemistry," Cornell University Press, Ithaca, N. Y., 1953.

(8) J. Happel and B. J. Byrne, *Ind. Eng. Chem.*, **46**, 1181 (1954).

off the axis and found a behavior (Figure 3 of their paper) which is very much like that which we would predict by use of eq 12 and 14. For values of $0 < r_c/r_0 < 0.5$ our formulas give results which are within experimental error. r_c is, of course, the distance from the axis to the particle. For $0.5 < r_c/r_0$ there seem to be systematic deviations of the experimental data from our predictions. The deviations are such that the experimental retardation effect is less than the predicted value. Since the retardation effect is a small perturbation on the velocity to begin with, we expect that a small error in its estimation will be of little consequence.

On the basis of the above remarks we will assume eq 11 and 14 to be accurate statements of particle velocities down tubes or between plates and we will use them in subsequent derivations. However, when the radius of the polymer molecules approaches the radius of the cylinder (characteristic dimension of the capillary), we cannot expect the formula to be valid. Experimental results[4] suggest that if this ratio is less than 0.5 we can safely use eq 11 and 14.

B. Evaluation of Average Velocity. Elution Volume. Because of entropy forces a polymer molecule will tend to maintain its shape as it flows down the tube. That is to say, if we deform a polymer molecule from its spherical shape by means of an external force, a restoring force is set up by the polymer which acts in a direction so as to restore the shape. It is for this reason that the center of mass of the polymer molecule cannot approach too closely the walls of the tube down which it flows. We are thus led to define an effective radius, a, for the polymer. In appendices A and B we show that this radius is related to the radius of gyration, s, by

$$a = \frac{3}{\sqrt{\pi}}\, s \tag{18}$$

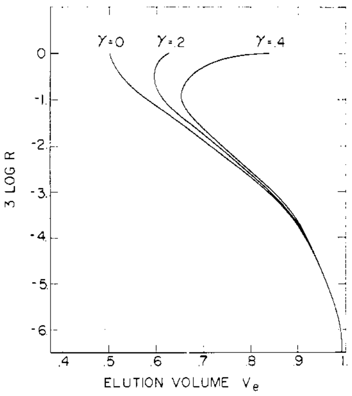

Figure 1. A plot of the normalized elution volume *vs.* the logarithm of the effective particle volume for a circular cylinder is shown. The effect of varying γ, the parameter relating to the magnitude of the retardation effect, is seen to be small below $R = 0.4$.

If Brownian motion in a direction perpendicular to the axis of the tube is allowed, then the center of mass of the polymer molecule will sample every possible horizontal position in the tube with equal probability, except for the fact that it cannot be closer than a distance, a, to the wall. We obtain then for $\langle v_p \rangle$, the average velocity of the polymer, in a circular cylinder

$$\langle v_p \rangle = u_0 \int_0^{r_0 - a} \left[1 - \left(\frac{r_c}{r_0}\right)^2 - \gamma\left(\frac{a}{r_0}\right)^2\right] r_c\, dr_c \Big/ \int_0^{r_0 - a} r_c\, dr_c$$

$$\langle v_p \rangle = u_0\left[1 - \frac{(1 - a/r_0)^2}{2} - \gamma\left(\frac{a}{r_0}\right)^2\right] \quad \text{circular cylinders} \tag{19}$$

where

$$u_0 = \frac{\partial p}{\partial l}\frac{r_0^2}{4\eta}$$

We have let r_0 be the radius of the cylinder and r_c the distance from an axis down the center of the tube to the particle center of mass. It should be noted that u_0 as defined in eq 19 is the maximum velocity of the fluid in the tube. The γ in eq 19 is defined by

$$\gamma a^2 = 2s^2/3 \tag{20}$$

From eq 18 we see that for flexible polymer molecules $\gamma = 2\pi/27$. However, in general, γ is a function of the shape of the particle as well as the density distribution within the particle. For this reason we retain γ as a parameter. In a similar manner we obtain for parallel plates

$$\langle v_p \rangle = u_0\left[1 - \frac{(1 - a/z_0)^2}{3} - \frac{\gamma}{2}\left(\frac{a}{z_0}\right)^2\right] \quad \text{plates} \tag{21}$$

where for parallel plates

$$u_0 = \frac{\partial p}{\partial l}\frac{z_0^2}{2\eta}$$

The elution volume, V_e, is the fluid volume flow rate, Q, times the time needed for passage of the polymer through the capillary, t. Thus, for a tube of length l

$$V_e = Qt = Ql/\langle v_p \rangle \tag{22}$$

We obtain then

$$V_e = \frac{\pi l r_0^2}{2\left[1 - \dfrac{(1 - R)^2}{2} - \gamma R^2\right]} \quad \text{circular cylinders} \tag{23}$$

$$V_e = \frac{z_0 l}{\dfrac{3}{4}\left[1 - \dfrac{(1 - R)^2}{3} - \dfrac{\gamma}{2}R^2\right]} \quad \text{plates} \tag{24}$$

In eq 23, $R = a/r_0$, while in eq 24 it is $R = a/z_0$. Thus, the elution volume is equal to the elution volume of solvent times a factor which is a function only of R and the geometry of the capillary.

In Figure 1 the effect of varying γ on the elution volume of a circular cylinder is given; for convenience we have let $\pi l r_0^2$ equal 1 in this figure. We have plotted V_e *vs.* 3 log R in the figure since R^3 is nearly proportional to the so-called hydrodynamic volume of the polymer.[9] We pointed out previously[1] that the features of the curves given here are similar to the log hydrodynamic

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[9] B. H. Zimm and W. H. Stockmayer, *J. Chem. Phys.*, 17, 1301 (1949).

volume *vs.* volume elution curves of Grubisic, *et al.*,[10] found experimentally for a gel permeation chromatography (gpc) column. However, it is not the purpose of this paper to derive the relationship of this mechanism of separation to gpc. That will be done in a later paper.[11] We wish to emphasize here the similarity of the curves for $R < 0.2$. Clearly for this region we have an insensitivity to γ in the V_e *vs.* 3 log R plots.

In Figure 2 we have plotted V_e *vs.* 3 log R for three different cross sections of tubes; we have normalized all the curves to $V_e = 1$ for $R = 0$. In this plot we see that although the parallel plates result is different from the others, the shape of the curves show a general insensitivity to cross section for smaller R's.

Neglecting the retardation effect ($\gamma = 0$), the ratio of maximum to minimum elution volume is 2 for circular cylinders and 1.5 for parallel plates. It is interesting to compute this ratio for tubes of various other cross sections. This is done by computing the ratio of maximum velocity to average velocity. We obtain, for a square cross section 2.5, for an elliptical cross section 2.0 (independent of the eccentricity of the ellipse), and for equilateral triangles 2.2. Thus, one might expect the effect of different cross section on volume elution is a small one.

C. Dispersion in the Elution Volume Peak Due to Diffusion. (1) Fickean Diffusion. Taylor had addressed himself to the problem of dispersion of soluble matter in solvent flowing through a circular cylinder.[12] Aris has extended the results to cylinders of arbitrary cross section.[13] Their problem is identical with ours except for one factor: the size of the molecule. They assumed that the soluble matter is made up of point particles, while we assume our soluble matter is made up of particles of finite size.

In order to solve the diffusion problem for finite size particles accurately one would need to write down a diffusion equation which includes angular diffusion terms as well as translational diffusion. Although angular and translational diffusion have been treated separately,[14] we are not aware of a treatment of the combination which is appropriate to our system. Accordingly, we will assume that the translational diffusion equation alone is adequate to our problem. Of course, many experimental tests of the translational diffusion equation are made on systems in which the suspended particles are large compared to solvent molecules.[15] Thus, the wealth of experimental confirmations of the validity of the ordinary translational diffusion equation is also an argument for the validity of our assumption. The above statement must be modified if the molecule is in a high shear field, for then there are orientation effects on the polymer and one does not in general expect a decoupling of rotational and translational diffusion.[16]

We now review briefly the work of Taylor and Aris for point particles. The diffusion equation appropriate to the problem as given by Taylor is

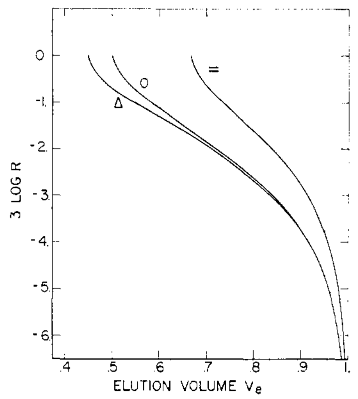

Figure 2. A plot of the normalized elution volume *vs.* the logarithm of the effective particle volume (with $\gamma = 0$) for various tube geometries is shown. Notice the general shape of the curve is insensitive to the geometry.

$$D\nabla^2 C = \frac{\partial C}{\partial t} + \vec{v} \cdot \vec{\nabla} C \tag{25}$$

where C is the concentration of solute particles, $\vec{v}$ is their velocity, D their diffusion constant, and t time. Equation 25 is a generalization of the ordinary diffusion equation to a moving medium. Its validity becomes obvious when one recognizes that the right-hand side of eq 25 is the derivative moving along with the particle (material derivative). Alternatively, if one transforms variables so that the origin of the new coordinate system translates along with the particle, then the ordinary diffusion equation is obtained from eq 26 at the origin of the new system.

We will work in the context of the circular cylinder problem for which the particle and thus the fluid velocity is

$$\begin{aligned} v_f^x &= u_0[1 - (r_c/r_0)^2] \\ v_f^y &= 0 \\ v_f^z &= 0 \end{aligned} \tag{26}$$

where u_0 is again the maximum fluid velocity in the cylinder and r_c and r_0 have been defined in section II but now are applied to point particles. Then the main result of Taylor and Aris can be described as follows. Suppose we define C_m to be the mean concentration over the cross-sectional area whose normal is parallel to the axis of the cylinder. Then in the limit of long time C_m is found to obey a diffusion equation

$$K\frac{\partial^2 C_m}{\partial x''^2} = \frac{\partial C_m}{\partial t} \tag{27}$$

$$K = D + \frac{u_0^2 r_0^2}{192D} \tag{28}$$

The coordinate system of eq 28 is chosen in the works of Aris and Taylor to move along with the mean velocity of the solute particles (which is that of the fluid). D is the molecular diffusion coefficient.

For polymers, or particles of finite size, we have again eq 25, where now C is the concentration of the polymer

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(10) Z. Grubisic, P. Rempp, and H. Benoit, *J. Polym. Sci., Part B*, **5**, 753 (1967).

(11) E. A. DiMarzio and C. M. Guttman, to be published.

(12) G. Taylor, *Proc. Roy. Soc.* (London), **A219**, 186 (1953).

(13) R. Aris, *ibid.*, **A235**, 67 (1956).

(14) L. D. Fava, *Phys. Rev.*, **119**, 53 (1960).

(15) A. Einstein, "Investigations on the Theory of Brownian Motion," Dover Publications, New York, N. Y., 1956.

(16) H. L. Frisch and R. Simha in "Rheology," Vol. I, Academic Press, New York, N. Y., 1956, Chapter 14.

and $\vec{v}$ is its velocity. Then in the context of the circular cylinder problem we have for the polymer velocity

$$\begin{aligned} v_{p,x} &= u_0[1 - (r_c/r_0)^2 - \gamma R^2] \\ v_{p,y} &= 0 \\ v_{p,z} &= 0 \end{aligned} \tag{29}$$

The boundary condition for point particles was that the normal gradient at the surface was zero, but because of the finite size of the particles it is now generalized to

$$\frac{\partial C}{\partial r_c} = 0 \tag{30}$$

at $r_c = r_0 - a$.

Let us now choose a coordinate system which moves along with the velocity that the polymer has at $r_c = r_0 - a$.

$$\begin{aligned} x_c' &= x_c - u_0\left[1 - \left(\frac{r_0 - a}{r_0}\right)^2 - \gamma R^2\right]t \\ t' &= t \end{aligned} \tag{31}$$

Equation 25 becomes in this new system

$$D\nabla^2 C = \frac{\partial C}{\partial t} + u_0\left(\frac{r_0 - a}{r_0}\right)^2\left[1 - \left(\frac{r_c}{r_0 - a}\right)^2\right]\frac{\partial C}{\partial x_c'} \tag{32}$$

Equations 30 and 32 together with the initial ($t = 0$) conditions completely specify the problem. Taylor and Aris solved it for the special case of a equals zero. We wish to point out that their solution is valid also for the a unequal to zero case if we replace the quantities r_0 and u_0 whenever they appear in eq 32 by r_0' and u_0' defined by

$$\begin{aligned} r_0' &= r_0 - a \\ u_0' &= u_0\left(\frac{r_0 - a}{r_0}\right)^2 \end{aligned} \tag{33}$$

Upon such a substitution into eq 32 we obtain, in place of eq 28 for point particles, eq 34 for C_m, now considered to be the mean concentration of polymer over the area perpendicular to the axis of the tube

$$K\frac{\partial^2 C_m}{\partial x_c''^2} = \frac{\partial C_m}{\partial t}$$

where

$$K = D + \frac{u_0^2 r_0^2}{192D}\left(1 - \frac{a}{r_0}\right)^6 \tag{34}$$

The double prime coordinate system again moves with the mean velocity of the polymer, which is now *not* that of the fluid.

One can get an estimate of the time required for eq 28 and 34 to become valid by calculation of the exact first and second moments of the mean concentration C_m. This is readily done for parallel plates using the formalism of Aris. Our result is, if we assume a narrow slug (thin disk) of material distributed uniformly over the cross sectional area at time $t = 0$

$$m_1 = \int_{-\infty}^{+\infty} x''C_m\, dx'' = 0 \tag{35}$$

$$\begin{aligned} m_2 &= \int_{-\infty}^{\infty} (x'')^2 C_m\, dx'' \\ &= 2t\left(D + \frac{8u_0'^2 z_0'^2}{\pi^6 D}\right) + \\ &\frac{16u_0'^2 z_0'^2}{\pi^8 D^2}\left[\sum_{m=1}^{\infty}\left\{\exp\left(-Dt\left(\frac{m\pi}{z_0}\right)^2\right) - 1\right\}m^{-8}\right] \end{aligned} \tag{36}$$

In eq 36, u_0' and z_0' are defined by

$$\begin{aligned} z_0' &= z_0 - a \\ u_0' &= u_0\left(\frac{z_0 - a}{z_0}\right)^2 \end{aligned} \tag{37}$$

Because of the m^{-8} factor only the leading term of the expansion need be retained. Since the solution to eq 34 is the Gaussian distribution, and since the second moment of this Gaussian distribution is exactly that part of eq 36 which is proportional to t, we expect that eq 34 will hold when

$$\frac{2t\left(D + \dfrac{8u_0'^2 z_0'^2}{\pi^6 D}\right)}{\dfrac{16u_0'^2 z_0'^4}{\pi^8 D^2}} > \frac{\pi^2 tD}{z_0'^2} \gg 1 \tag{38}$$

The time obtained from this expression is roughly several times the time required for material to diffuse across the tube. Therefore, one is justified in the use of eq 34 after such a time, at least insofar as the evaluation of the second moment of C_m.

(2) Non-Fickean Diffusion. All of the above results were derived when the mean free path of a diffusing molecule is small compared to the transverse dimensions of the capillary. It is only in this limit that eq 26 is valid.[17] For particles whose size is comparable to capillary dimensions a much more complicated view of the diffusion process is demanded. However, we will now show that eq 34 remains valid, in a slightly modified form, even when the particle has very long mean free paths. Thus, for both short and long mean free paths, the functional form of eq 34 is the same. Furthermore, it can be shown that the validity of eq 34 requires only that the particle samples the transverse dimensions of the capillary ergotically.

We will work in the context of the parallel plate problem and point particles. The generalization to other geometries and to finite size particles will be obvious. Let us assume that the particle makes n transitions per unit time in the following manner. A particle jumps to a place z_i, x_i from a place z_{i-1}, z_{i-1} and then flows along with the fluid velocity for fixed time, $1/n$. It then instantaneously jumps to a new place z_{i+1}, x_{i+1}, and so on. To simplify the mathematics we will assume that the particle either jumps along the direction of flow or perpendicular to it with equal probability.

Now the particle can travel down the tube, *i.e.*, in the x direction, in two ways. First, it can move from x_i to

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[17] M. C. Wang and G. E. Uhlenbeck, *Rev. Mod. Phys.*, **17**, 331 (1945).

x_{i+1} during the ith jump. This distance of traveling in the x direction we call Δx_i^{jump}. Then

$$\Delta x_i^{\text{jump}} = x_i - x_{i-1}$$

Second, it travels in the x direction due to the fact it flows in the x direction between jumps for a time $1/n$. Thus the particle jumps to the position (x_i, z_i) and flows for a time $1/n$ a distance Δx_i^{flow}

$$\Delta x_i^{\text{flow}} = \frac{1}{n} u_0\left[\frac{1}{3} - \left(\frac{z_i}{z_0}\right)^2\right] \tag{39}$$

In eq 39 our coordinate system is again moving with the average particle velocity and we are ignoring size effects since we can now correct for these later, trivially.

Now, if we wish to know the average distance traveled down a tube in the ith step $\langle \Delta x_i \rangle$, we must compute

$$\langle \Delta x_i \rangle = \langle \Delta x_i^{\text{flow}} \rangle + \langle \Delta x_i^{\text{jump}} \rangle \tag{40}$$

To compute $\langle \Delta x_i^{\text{jump}} \rangle$ we need to know $f(\Delta x_i^{\text{jump}})$, the probability density that a particle will jump Δx_i^{jump} in the x direction. For our purposes here we only need weak restrictions on $f(\Delta x_i^{\text{jump}})$

$$\int f(\Delta x_i^{\text{jump}})\,\mathrm{d}(\Delta x_i^{\text{jump}}) = \frac{1}{2}$$

$$\int (\Delta x_i^{\text{jump}}) f(\Delta x_i^{\text{jump}})\,\mathrm{d}(\Delta x_i^{\text{jump}}) = 0$$

$$\int (\Delta x_i^{\text{jump}})^2 f(\Delta x_i^{\text{jump}})\,\mathrm{d}(\Delta x_i^{\text{jump}}) \equiv \langle x_0^2 \rangle \tag{41}$$

The first equation allows jumps along the flow direction to be as likely as jumps across the flow direction. The second equation states that a jump backward in the x direction is as likely as one forward. The third equation simply defines our symbol for the second moment of the function $f(x)$.

We now proceed to compute $\langle \Delta x_i^{\text{flow}} \rangle$. We assume that $P(z_i)\mathrm{d}z_i$, the probability of the ith jump being made to $(z_i \pm \mathrm{d}z_i/2)$ from any other position, is a constant independent of z. That is, it is as probable to jump to one z position as any other. Then

$$P(z_i) = \frac{1}{4z_0} \tag{42}$$

Then we define $\mathcal{P}(\Delta x_i^{\text{flow}})\mathrm{d}(\Delta x_i^{\text{flow}})$ as the probability that a particle flows a distance $(\Delta x_i^{\text{flow}} \pm [\mathrm{d}(\Delta x_i^{\text{flow}})]/2]$. Now these two probabilities are identical since a particle which gets to z_i must, by assumption, flow a distance Δx_i^{flow}. Thus

$$\mathcal{P}(\Delta x_i^{\text{flow}})\mathrm{d}(\Delta x_i^{\text{flow}}) = P(z_i)\mathrm{d}z_i$$

and

$$\mathcal{P}(\Delta x_i^{\text{flow}}) = P(z_i)\frac{\mathrm{d}z_i}{\mathrm{d}\Delta x_i^{\text{flow}}} = \frac{n}{4u_0}\left(\frac{1}{3} - \frac{\Delta x_i^{\text{flow}}}{u_0}n\right)^{-1/2} \tag{43}$$

Now, one can easily show

$$\langle \Delta x_i^{\text{flow}} \rangle = 0$$

$$\langle (\Delta x_i^{\text{flow}})^2 \rangle = \frac{2}{45}\left(\frac{u_0}{n}\right)^2 \tag{44}$$

We then obtain for $\langle \Delta x_i \rangle$ and $\langle \Delta x_i^2 \rangle$

$$\langle \Delta x_i \rangle = 0$$

$$\langle \Delta x_i^2 \rangle = \langle x_0^2 \rangle + \frac{2}{45}\left(\frac{u_0}{n}\right)^2 \tag{45}$$

Imagine that a time t has elapsed so that nt steps have occurred. We can now use the central limit theorem to obtain the statistical behavior of the variable

$$X = \sum_{i=1}^{nt} \Delta x_i \tag{46}$$

We have

$$\langle X \rangle = 0$$

$$\langle X^2 \rangle = nt\langle \Delta x_i^2 \rangle = 2t\left(\frac{n\langle x_0^2 \rangle}{2} + \frac{u_0^2\langle x_0^2 \rangle}{90n\,\frac{\langle x_0^2 \rangle}{2}}\right) \tag{47}$$

And, if we define $n\langle x_0^2 \rangle/2 = D$, then we obtain

$$\langle X^2 \rangle = 2t\left(D + \frac{u_0^2\langle x_0^2 \rangle}{90D}\right) \tag{48}$$

Further, we know from the central limit theorem that the distribution function for X is Gaussian, and it is, in fact, the solution to the equation

$$\left(D + \frac{u_0^2\langle x_0^2 \rangle}{90D}\right)\frac{\partial^2 C_{\mathrm{m}}}{\partial X^2} = \frac{\partial C_{\mathrm{m}}}{\partial t} \tag{49}$$

Equation 49 is identical with eq 28 except that the term $\langle x_0^2 \rangle/90$ replaces $r_0^2/192$.

Aris has shown that the effective diffusion coefficient for flow down a cylinder of arbitrary cross section is always given by

$$K = D + k_1 u_0^2/D \tag{50}$$

where k_1 is a constant dependent on only the cross-sectional geometry. The derivation was made on the assumption of Fickean diffusion. We have shown that even for Knudsen-like diffusion a similar relation still holds.

III. Separation by Flow as a Useful Tool

The question naturally arises as to whether the separation by flow phenomenon is of any practical use. In the last analysis this can be answered only by construction of a working instrument based on the phenomenon. Nevertheless, there are considerations and calculations presented here which lead us to expect that separation by flow will become a useful tool in the near future.

A. Some Design Considerations for a Single Circular Cylinder. We shall now show that if a cylinder is made long enough, then separation of molecules on the basis of size would always occur no matter how similar the molecules are. The average distance traveled by molecule i down a tube in time t is $\langle v_{\mathrm{p}} \rangle_i t$; then the distance between peak centers for two substances 1 and 2 is

$$d_{12} = \left|\langle v_{\mathrm{p}} \rangle_1 - \langle v_{\mathrm{p}} \rangle_2\right| t \tag{51}$$

Because of diffusion, the elution volume peaks become spread out in time. But as is always the case for diffusion, the width of the peaks are proportional to $\sqrt{t}$ rather than t. Thus, if one waits for a long enough time, either by using a long tube or equivalently by recycling through one tube, one can always separate the two materials.

(1) Figure of Merit, *M*. We seek to calculate the separation efficiency of a single tube of fixed length and cross section. A measure of the efficiency of the separation process is given by M, the ratio of the sum of the spatial breadths of the two elution volume peaks (or more exactly the sum of the square roots of the second moments of the peaks) to the spatial separation between the two elution volume peaks

$$M = \frac{\sqrt{2K_1t} + \sqrt{2K_2t}}{|\langle v_p\rangle_1 - \langle v_p\rangle_2|\, t} \tag{52}$$

where

$$K_1 = D_1 + u_0^2r_0^2(1 - R_1)^6/192D_1$$

$$K_2 = D_2 + u_0^2r_0^2(1 - R_2)^6/192D_2$$

In the above equations D_i is the molecular diffusion constant for molecule i, R_i is, as before, the ratio of the radius, a_i, of molecule i to the radius of the tube, r_0, and u_0 is the maximum fluid velocity in the tube. We assume for all further considerations that R_1 and R_2 are less than 0.2 so that we may let $\gamma = 0$. Then for tubes of fixed length, eq 52 becomes with the use of $l = u_0t/2$ and eq 19

$$M = \frac{\sqrt{4K_1/u_0} + \sqrt{4K_2/u_0}}{l^{1/2}|(1 - R_1)^2 - (1 - R_2)_2|} \tag{53}$$

If we are interested in separating particles close to each other in size and properties, then for cases of interest, R_1 and R_2 as well as D_1 and D_2 are assumed to be nearly the same. Thus, K_1 and K_2 are nearly the same as are their derivatives with respect to u_0.

Now each tube of finite length, l, and cross section, r_0, has an upper and lower limit for flow rate beyond which the separation phenomenon is ineffective. The lower limit exists because molecular diffusion in a direction parallel to the tube axis causes a smearing out of the elution volume peaks for very slow flow. The upper limit exists because the effective diffusion constant discussed in section IIC is proportional to the square of the velocity; thus the larger the velocity, the larger the contribution to the effective diffusion coefficient. Physically, the latter broadening arises from the smearing out of polymer due to the quadratic velocity gradient; that is, material near the walls travels slowly compared to material near the center of the tube. Diffusion in the direction normal to the length of the tube helps to minimize this effect.

We shall define the criteria of resolution by the condition $M = {}^1/_4$; that is, for $M \leq {}^1/_4$, we, in general, expect separation. One can show, for broadening that is Gaussian, that with $M = {}^1/_4$ one obtains separate well-defined peaks for each kind of particle even when the ratio of total numbers of particles within the peaks is as great as 100:1. With these criteria and eq 53 we obtain for the two limiting velocities above and below which there is no separation

$$u_0 = \frac{96\delta D}{r_0^2(1 - R)^6}\left(1 \pm \sqrt{1 - \frac{r_0^2(1 - R)^6}{48\delta^2}}\right)$$

where

$$\delta = \{(1 - R_1)^2 - (1 - R_2)^2\}^2 l/256 \tag{54}$$

and $R = (R_1 + R_2)/2$.

(2) Conditions for Optimum Separation. Now the most effective separation occurs when M is a minimum. For fixed l and R's then we minimize eq 53 under the assumptions stated above with respect to u_0; we obtain u_m, the value of u_0 which minimizes M, as

$$u_\mathrm{m} = 8\sqrt{3}D/r_0(1 - R)^3 \tag{55}$$

where D and R refer to either particle 1 or particle 2. Notice that if K_1 is evaluated at $u_0 = u_\mathrm{m}$ we have as the optimum effective diffusion coefficient

$$K_1 = 2D \tag{56}$$

Now with this best value of u_m we can search for the smallest difference between particle sizes that can be separated for a given l and r_0. Using as our criteria of separation $M = {}^1/_4$ with $u_0 = u_\mathrm{m}$, we obtain from eq 53 for the smallest difference between particle radii, $a_1 - a_2$, that can be separated

$$a_1 - a_2 = \frac{4}{(3)^{1/4}}r_0\left(\frac{r_0}{l}\right)^{1/2}(1 - R)^{3/2} \tag{57}$$

for $a_1 > a_2$.

For example, consider a cylinder 1 cm long and 1 μ in radius. Then we get

$$(a_1 - a_2) = \frac{4}{3^{1/4}} \times 10^{-6}\ \mathrm{cm}$$

$$\cong 300\ \text{Å} \tag{58}$$

This means that molecules whose radii are about 300 Å different from each other can be just barely separated from each other in this tube. If one considers tubes of sizes that can be produced by etching fission fragment tracks in insulators[18] ($r_0 = 100$ Å and $l = 10^{-2}$ cm), then use of eq 57 would result in a separation capability of 3 Å. This suggests the usefulness of these materials to separate small molecules; however, at these dimensions the concepts of size and continuous flow become indefinite. It is obvious from the above that the separation capabilities of a single tube are large.

One seeks not only to separate but also to obtain significant quantities of materials. There exists a competition between the effectiveness of the separation and the amount of flow. Effective separation requires long narrow tubes which is exactly the condition for small flow. From eq 57 we obtain

$$(a_1 - a_2)^2 = \frac{16}{\sqrt{3}}\frac{r_0^3}{l}(1 - R)^3 \tag{59}$$

The flow through a circular cylinder is

$$Q = \frac{\pi\Delta p}{8\eta}\frac{r_0^4}{l} \tag{60}$$

where Δp is the pressure head.

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[18] R. L. Fleischer, R. B. Price, and R. M. Walker, *Sci. Amer.*, 30 (June 1969).

If we seek to adjust r_0 and l to maximize flow for a given separation, we have

$$Q = \frac{\pi\Delta p r_0}{8\eta}\frac{(a_1 - a_2)^2}{(1 - R)^3}\frac{\sqrt{3}}{16} \tag{61}$$

so that for a given separation capability one can make Q as large as one desires by making the tube long enough. However, the lengths required are prohibitively large. If one seeks to make the flow 10^3 times as large as it was for the case of $r_0 = 10^{-4}$ cm, and $l = 1$ cm, then, from eq 59 we would need to have $r_0 = 10^{-1}$ cm, $l = 10^9$ cm. For an increase in flow of ten times, l would have to be increased to 10^3 cm and so on.

For parallel plates there is no advantage whatsoever to increasing the length of the tube because the flow varies as z_0^3/l and the r_0^3/l dependence of eq 59 is changed to z_0^3/l.

It appears that one will always have small flow through tubes of reasonable separation capability. We can thus expect that large quantities of material can be obtained only by using many tubes in parallel.

We are naturally led to the more general problem of determining the separation characteristics of a large number of tubes connected in series and in parallel in some as yet unspecified way. This problem is a difficult one because it involves calculation of flow properties at junctures of tubes. This general problem will be discussed in a future paper[11] in which we will attempt to establish the connection between separation by flow in combination of tubes and gel permeation chromatography.

B. An Instrument for Continuous Separation by Flow. (1) Velocities of Particles under Both Head and Shear. Let us calculate flow properties for molecules between parallel plates when we have simultaneously both a pressure head and a shear gradient. We will use Figure 3 to aid in visualization. The applied pressure differential is from top to bottom along the x axis. The front plate moves to the right along the y axis with a constant velocity u_{y0}. We immediately obtain for the velocity of the fluid at a point x, y, z in the fluid

$$v_f^x = u_{x0}[1 - (z/z_0)^2]$$
$$v_f^y = \frac{u_{y0}}{2}\left[\left(\frac{z}{z_0}\right) + 1\right]$$
$$v_f^z = 0 \tag{62}$$

where u_{x0} and u_{y0} are the maximum velocities of the fluid in the x and y directions, respectively.

Using the development in section IIA, the velocity of the fluid at the ith bead of the polymer is

$$v_{f,i}^x = \frac{u_{x0}}{z_0^2}[z_0^2 - z_c^2 - 2z_c z_i' - (z_i')^2]$$

$$v_{f,i}^y = \frac{u_{y0}}{2z_0}[z_0 + z_c + z_i'] \tag{63}$$

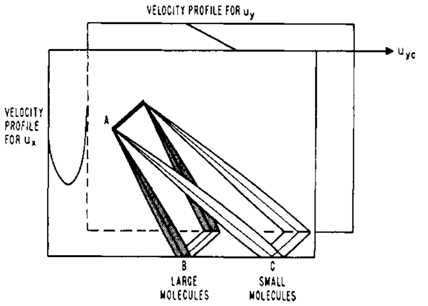

Figure 3. A model for an instrument for continuous separation by flow. Here the larger molecules have a larger component of velocity, u_x, in the x direction than the smaller molecules. In the y direction both molecules have the same velocity. Therefore, if one injects continuously a solution of molecules of two different sizes at A one will separate continuously at B and C as indicated in the figure. The separation between plates has been exaggerated compared to the spreading produced by diffusion in order to display the fluid velocity profile.

Using eq 6 for the total force and moment on a molecule, we obtain for the translational and rotational velocities of the polymer molecule whose center of mass is at x_c, y_c, and z_c

$$v_{p,x} = \frac{u_{x0}}{z_0^2}\left[z_0^2 - z_c^2 - \sum_i (z_i')^2/N\right]$$

$$v_{p,y} = \frac{u_{y0}}{2z_0}(z_0 + z_c)$$

$$v_{p,z} = 0 \tag{64a}$$

$$\omega_x = -\frac{u_{y0}}{2z_0}\left(\sum_i (z_i')^2\right)\bigg/\left[\sum_i \{(y_i')^2 + (z_i')^2\}\right] = -\frac{u_{y0}}{4z_0}$$

$$\omega_y = -\frac{2u_{x0}}{z_0^2}z_c\left(\sum_i (z_i')^2\right)\bigg/\left[\sum_i \{(z_i')^2 + (x_i')^2\}\right] = -\frac{u_{x0}z_c}{z_0^2}$$

$$\omega_z = 0 \tag{64b}$$

As before there is no force on the polymer molecule tending to push it toward the center of the plates. One should note that the velocity in the x direction is identical with that obtained for fixed parallel plates and thus is independent of the flow in the y direction. Similarly, the velocity in the y direction is independent of flow in the x direction. We again assume as we did in section IIB that Brownian motion makes all positions available to the polymer molecule. Thus we have as before

$$\langle v_p^x\rangle = \int_{-(z_0-a)}^{z_0-a} v_{p,x}\,\mathrm{d}z_c\bigg/\int_{-(z_0-a)}^{z_0-a}\mathrm{d}z_c \tag{65}$$

$$\langle v_p^y\rangle = \int_{-(z_0-a)}^{z_0-a} v_{p,y}\,\mathrm{d}z_c\bigg/\int_{-(z_0-a)}^{z_0-a}\mathrm{d}z_c \tag{66}$$

Integration yields

$$\langle v_p^x\rangle = u_{x0}\left[1 - \frac{\left(1 - \frac{a}{z_0}\right)^2}{3} - \gamma\left(\frac{a}{z_0}\right)^2\right] \tag{67}$$

$$\langle v_p^y\rangle = \frac{u_{y0}}{2} \tag{68}$$

One observes that the average particle velocity in the x direction, $\langle v_p^x \rangle$, is a function of particle size while that in y direction, $\langle v_p^y \rangle$, is not. Thus the velocity vectors of two different size particles always have different directions.

(2) Peak Breadth. The above equations when multiplied by t give the location of the peak of the distribution function. We need also to know the breadth of the distribution of particles. Thus we must consider the associated diffusion problem.

We will allow diffusion to occur only along the three coordinate directions (orientations) and we will as in section IIC assume n jumps per second with the particle flowing along with the fluid between jumps. Again we assume for the jumping process a uniform probability distribution in the z direction. Now it is obvious that diffusion in the y direction does not affect the diffusion in the x direction. In considering diffusion in the x direction then we need consider only the jumps in the x and z directions just as before. Since a jump in the x direction is as equally likely as one in the z direction, we have the same result as obtained previously in section IIC for the net diffusion coefficient in the x direction. The net diffusion coefficient is the quantity multiplying $2t$ on the right-hand side of eq 36.

$$K^x = D + k_x u_{x0}^2 z_0^2/D, \; k_x = 8/\pi^6 \tag{69}$$

In like manner diffusion in the x direction has no effect on the net diffusion coefficient in the y direction. We need then only know the result for the effective diffusion coefficient due to parallel plates under shear. Thus the net diffusion coefficient in the y direction is

$$K^y = D + k_y u_{y0}^2 z_0^2/D \tag{70}$$

where k_y is given in appendix D. The diffusion equation for the mean concentration averaged over a line perpendicular to the plate is

$$\frac{\partial C_m}{\partial t} = K^x \frac{\partial^2 C_m}{\partial x_c^2} + K^y \frac{\partial^2 C_m}{\partial y_c^2} \tag{71}$$

The above was all for point particles. For particles of finite size one uses the modifications discussed at the end of Appendix D.

(3) Model for Continuous Separations. We are now in a position to discuss a model for continuous separation. Under the combined influence of a pressure gradient and a perpendicular shear gradient, molecules move from top to bottom and from left to right in Figure 3. The y (horizontal) component of velocity is the same independent of size but the x (vertical) component is larger the larger the molecule as shown in eq 67. Large molecules, then, will travel a more vertical path than small molecules. If we introduce a solution of two sizes of molecules continually (at a constant rate) at point A (see Figure 3) large molecules will move along the path AB and small molecules along the path AC. This model is the basis of continuous separation by flow.

Now, if the length of the sheet in the x direction is l and that in the y direction is much greater than l, then the time, t_i, it takes for the ith polymer to travel the distance l in the x direction, that is, to come out of the bottom of the system of parallel plates, is

$$t_i = l/\langle v_p^x \rangle_i \tag{72}$$

The distance in the y direction molecule i travels in that time, $\langle y_i \rangle$, is then

$$\langle y_i \rangle = \frac{l}{\langle v_p^x \rangle_i} \langle v_p^y \rangle_i \tag{73}$$

We are interested in diffusional broadening. Let us first obtain the solution to eq 71 when we introduce continually material at the origin. If a δ function of material is introduced at the origin ($x = 0$, $y = 0$) at time t_0 we have as the Green function for plates infinite in both the x and y directions

$$C_m = \frac{C_0 \exp\left\{\dfrac{-[x - \langle v_p^x \rangle (t - t_0)]^2}{4K^x(t - t_0)} - \dfrac{[y - \langle v_p^y \rangle (t - t_0)]^2}{4K^y(t - t_0)}\right\}}{4\pi(t - t_0)(K^x)^{1/2}(K^y)^{1/2}} \qquad t > t_0 \tag{74}$$

$$= 0 \qquad t < t_0$$

If we now imagine material to be introduced continually at a constant rate at the origin, then the total concentration, $C_{m,T}$, at any point is simply the integral over all the sources

$$C_{m,T} = \int_{-\infty}^{t} C_m \, dt_0 \tag{75}$$

One can easily show by a change of variables that $C_{m,T}$ is independent of t. This means that eq 75 is the time independent steady state solution. We now can evaluate any of the various moments we desire by integration of eq 75 over space. Of interest are the moments in the y direction at fixed x ($x = l$) because they are measures of the distribution of particles in the emerging liquid. The variance is of particular interest.

$$\langle (\Delta y_i)^2 \rangle = \frac{\int_{-\infty}^{+\infty} (y_i^2 - \langle y_i \rangle^2) C_{m,T} \, dy}{\int_{-\infty}^{+\infty} C_{m,T} \, dy} \tag{76}$$

In performing the above integrations it is convenient to invert the order of integration. We obtain

$$\langle (\Delta y_i)^2 \rangle = 2t_i \left[K^y + 3K^x \left(\frac{\langle v_p^y \rangle_i}{\langle v_p^x \rangle_i} \right)^2 \right] \times \left[1 + \frac{2K^x}{\langle v_p^x \rangle_i l} \right] \tag{77}$$

The factor multiplying $2t_i$ on the right-hand side of eq 77 defines a new effective diffusion coefficient.

In the above treatment we allowed back-diffusion across the $x = l$ line. In reality, this could not occur because we would collect the material as it crossed the line. The proper boundary condition for this situation is an absorbing boundary along $x = l$. Thus, the above treatment is valid only when K^x is small compared to $\langle v_p^x \rangle l$.

(4) Criteria of Resolution. We can now look in detail at a criteria of resolution in the y direction. We shall consider the separation of particles near each other in most properties and size; thus D_i, a_i, and K_i^x

and K_i^y and their derivatives are nearly the same. We shall again define M, the criteria of resolution, as

$$M = \frac{\sqrt{\langle(\Delta y_1)^2\rangle} + \sqrt{\langle(\Delta y_2)^2\rangle}}{d_{12}} \tag{78}$$

In the above equation $\sqrt{\langle(\Delta y_i)^2\rangle}$ is the broadening in the y direction for particle i; d_{12} is the distance between particles 1 and 2

$$d_{12} = l\langle v_{\text{p}}^y\rangle \left(\frac{1}{\langle v_{\text{p}}^x\rangle_1} - \frac{1}{\langle v_{\text{p}}^x\rangle_2}\right) \tag{79}$$

It would not appear unduly difficult to tap off separately solutions emerging 0.2 cm apart along the $x = l$ line. Accordingly, we choose $d_{12} \geq 0.2$ cm. Furthermore, we notice that for R_1 and R_2 near each other and small, we have for d_{12}

$$d_{12} = \frac{3}{4} l \frac{u_{y0}}{u_{x0}}(R_1 - R_2) \tag{80}$$

The ratio of velocities is fixed once one decides on the geometry of the system and on the size of the particles to be separated. Thus

$$\frac{u_{y0}}{u_{x0}} \cong \frac{4d_{12}}{3l(R_1 - R_2)} = \xi \tag{81}$$

Then only one of the velocities is free to vary independently. For M we now have

$$M^2 = \frac{12l}{d_{12}^2}\left[\frac{D}{u_{x0}}\left(1 + \frac{27}{16}\xi^2\right) + \frac{u_{x0}z_0^2}{D}\left(k_y\xi^2 + \frac{27}{16}\xi^2 k_x\right)\right] \tag{82}$$

The best separation occurs for M a minimum. Thus minimizing M with respect to u_{x0} for fixed l, ξ, d_{12}, R_1 and R_2 we have u_{xom}.

$$u_{\text{xom}} = \frac{D\left(1 + \frac{27}{16}\xi^2\right)^{1/2}}{z_0\xi\left(k_y + \frac{27}{16}k_x\right)^{1/2}} \tag{83}$$

If we use as before $M = 1/4$ as a criteria for resolution, then eq 82 and 83 yield

$$\xi\left(1 + \frac{27}{16}\xi^2\right)^{1/2}\left(k_y + \frac{27}{16}k_x\right)^{1/2} = \frac{d_{12}^2}{384lz_0} \tag{84}$$

One can for fixed l and z_0 vary d_{12} in eq 84 so that it goes through two distinct regimes, $\xi < 1$ and $\xi > 1$. The regime of $\xi < 1$ is of no interest since it yields poor separation; this is because the velocity in the y direction is smaller than that in the x direction and the particle peaks tend to bunch on each other (notice the extreme case of $\xi = 0$; here there is no separation of particles along the y direction). Thus, we are only interested in $\xi > 1$. Then eq 84 yields approximately

$$\xi = 0.095d_{12}/(lz_0)^{1/2} \tag{85}$$

where we have used the values of k_x and k_y given in appendix D. This equation coupled with eq 81 yields

$$R_1 - R_2 = 14\left(\frac{z_0}{l}\right)^{1/2} \tag{86}$$

Let us consider parallel plates with $z_0 = 10^{-3}$ cm and $l = 10$ cm. Then $a_1 - a_2 = 1.4 \times 10^{-4}$ cm and $d_{12} > 0.9$ cm. Thus, particles of radii differing by 1.4 μ can be separated in such an instrument as long as one adjusts ξ so that the particles come out further than 1 cm apart. For another instrument let $z_0 = 10^{-4}$ cm and $l = 100$ cm. Then, $a_1 - a_2 = 140$ Å and $d_{12} > 0.9$ cm.

In practice one cannot continue to shear two parallel plates for any length of time because we run out of plate area. It seems reasonable to wrap the plates around a cylinder so that one has two concentric cylinders with the fluid between them. Relative rotation of the cylinders shear the fluid while a pressure head along the cylinder forces fluid through them. As long as the separation between the cylinders is small compared to their radii, the above parallel plate analysis holds with minor modification.

IV. Discussion of Results

Most of the results have been discussed along with their derivation in the body of the paper. We wish only to stress three points.

From eq 23 and 24 we observe that the elution volume peak is a function only of the effective radius of the particle and of the geometry of the tube. It is independent of both viscosity of the fluid and the diffusion coefficient of the molecules. It also does not depend on the pressure head and the flow rate through the tube. If we flow different molecules through the same tube then the only pertinent variable is the effective radius. We have already pointed out[1] that the effective radius cubed of a polymer is nearly proportional to its hydrodynamic volume. Presumably then we have a method of characterizing molecules on the basis of hydrodynamic volume alone. In appendix A we show that the elution volume of a rigid rod depends only on its effective radius which is one-quarter of its length. Previous investigators have shown that the hydrodynamic volume of rigid rods is nearly proportional to the cube of the length.[19] Thus for the rigid rods also the only pertinent variable for volume elution is hydrodynamic volume.

The dependence of the peak width (variance) on the various parameters is given in eq 28, 36, and 50. The interesting aspect is the dependence on the inverse of the diffusion coefficient D in one of the two terms in the sum. This term is the dominant one for many situations of interest.[12] Thus, the larger the diffusion coefficient, the smaller the spreading in the elution volume peak.

The validity of the concept of separation by flow is independent of the detailed assumptions used in deriving the specific formulas. It is, for example, not necessary for us to have a quadratic dependence of fluid velocity in a circular cylinder. All that is required is that we have on the average a larger velocity toward the center that at the boundary of the tube. It is not necessary even to have Brownian motion. All that is needed is a mechanism whereby the particles sample various levels

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(19) J. G. Kirkwood and P. L. Auer, *J. Chem. Phys.*, **19**, 281 (1951).

in the tube. Turbulence for example might replace Brownian motion as the mode of sampling.[19a]

V. Some Unsolved Problems

It is known that a deformable particle migrates toward the center of the tube under the action of the flow field while a rigid particle does not.[4] One expects that a particle is deformed more in large shear fields than in small. We know then that our formulas are less valid for large flow rates than for small. It is desirable to obtain a quantitative estimate of the inward force resulting from deformation of the shape of the molecule by large shear fields.

Our theory is an independent particle theory and is strictly valid therefore only in the limit of zero concentration. The extension of the theory to finite concentrations is desirable. The problem of rigid spheres strung out evenly on the axis of a circular cylinder has been recently solved[20] but the analogous off axis problem apparently has not.

Other kinds of hydrodynamic interactions have been neglected by us. The effect of walls has not been taken properly into account. This can be serious either when the particle is close to a wall or when the characteristic size of the particle is a substantial fraction of that of the tube. The simple problem of a sphere rotating under the effect of a linear shear field near a surface has never been solved. This indicates that much remains to be done in this area.

A real polymer molecule is neither free draining nor impermeable to solvent. We have discussed the two extremes in the text because it is these which can be solved. In section IIA we showed that these extremes give the same results and we expect that the intermediate situation therefore would be no different, but we cannot be sure.

In appendix B we derived an expression for a when a polymer molecule is near a flat surface. Its value then is valid only when the molecule is small compared to the tube. In general, a is dependent on tube size both because of the conformational aspect of the problem and because the shear field is not linear. A treatment of this problem along the lines of appendices A and B is obiously possible.

The problem of the coupling of rotational to translational diffusion has never been solved for dense systems. Its solution is certainly a prerequisite to the proper treatment of a small particle of nonpsherical shape in a spacially varying velocity field. Additionally, we are interested in the case when the mean free path of the particles is a substantial fraction of the tube diameter. Thus, generalization of the Fickean diffusion to account for rotations is only a first step.

The effects of variation in cross section of the capillary should be investigated. One is tempted to use an adiabatic approach but this method would obviously fail when inertial effects of the Navier-Stokes equations become nonnegligible.

Also, in this connection, it is known that entrance effects would give an initial distribution across the capillary for the particles which is not necessarily uniform.[21]

Adsorption effects must be considered. This treatment neglected adsorption. It is important to know how much can occur without masking the separation by flow phenomena.

VI. Application to Real Systems

A. Connection with Gel Permeation Chromatography. We believe there is a casual connection between separation by flow and gel permeation chromatography. This will be developed in detail in a later paper, but for now we wish only to describe what we think are three highly relevant points. First, according to Benoit, *et al.*,[22] the elution volume of a given experimental gpc column is a function only of the hydrodynamic volume of the molecules being separated. Dependence of elution volume on hydrodynamic volume alone is also a property of separation by flow. Indeed, it was an attempt to explain the observations of Benoit that led us to the separation by flow concept.

Second, the variance in elution volume in gpc columns has the same qualitative dependence on the diffusion coefficient and flow rate as implied by the second term of eq 50.[23] The variance is smaller the larger the diffusion coefficient and also it is linear in flow rate both for gpc and for separation by flow.

Third, a model in which only the phenomena of separation by flow is operative has elution volume behavior which, as near as we can presently tell, is identical in all of its essential features with that of a gpc column. This model consists of banks of parallel capillary tubes stacked upon one another with a region between each bank sufficient to allow mixing of molecules. Each bank, for example, can be viewed as a membrane riddled with holes (circular cylinders) of two different sizes and the region between membranes allows molecules to sample the tubes of different cross section. A given molecule during its traverse through the stack of membranes then has the opportunity to sample both large and small cylinders. Large cylinders are necessary to give high flow rates, and small cylinders are necessary to give large separation capabilities. This model will be treated in detail in our later paper.[11]

B. Separation of "Large" Particles. Although we have framed our discussion in the context of separation of polymer molecules, the concepts should be applicable to other particles as well. Viruses and colloidal paint particles are possibilities. The only major restriction to quantitative application of the equations would seem to be that the particles be small enough to suffer Brownian motion during their traverse. This means that the particle should be able to move across the diameter of the tube under the influence of Brownian motion several times during its traverse through the tube. A characteristic quantity is obviously

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[19a] Note Added in Proof. G. K. Batchelor, A. M. Binnie, and O. M. Phillips [*Proc. Phys. Soc.* (London), **B68,** 1095 (1955)] have discussed the question of the effect of particle size on the average velocity under conditions such that turbulence causes the transverse sampling of fluid velocities. They calculated average velocity as a function of particle size, and displayed experimental data taken on pipes of 2-in. i.d. which confirmed their predictions.

(20) H. Wang and R. Skalak, "Viscous Flow in a Cylindrical Tube Containing a Line of Spherical Particles," Office of Naval Research Contract No. N00014-67-A-0108-0003, July 1967.

(21) R. L. Whitmore, *Proc. Intern. Congr. Rheol., 4th, Providence, R.I.*, 69 (1965).

(22) H. Benoit, Z. Grubisic, P. Rempp, D. Decker, and J. G. Zilliox, *J. Chem. Phys.*, **63,** 1507 (1966).

(23) J. G. Hendrickson, *J. Polym. Sci.*, **6,** 1903 (1968).

$$\frac{r_0^2}{Dt} = \frac{r_0^2 l}{Du_0} \tag{87}$$

When this number is of the order of one or less, then Brownian motion is operative. An estimate of D can be gotten from Einstein's formula

$$D = \frac{kT}{6\pi\eta a} \tag{88}$$

We also require lamellar flow. This means that the Reynolds number

$$R_e = \frac{\rho r_0 u_0}{\eta} \tag{89}$$

where ρ is the density, should be small. Equations 87 and 89 provide us with an estimate of the region of validity of the derived formulas. Of course, as discussed before, the phenomenon of separation of flow may be operative well beyond these limits even though the quantitative expressions no longer apply.

C. Use of a Bed of Impermeable Beads. If one packs a column with impermeable glass beads, then the region between beads can be viewed as a set of highly connected channels through which fluid can flow. There should therefore be separation on the basis of size. If one places three spheres in mutual contact with each other, then the pin cushion triangle which is the intersection of the surface of the spheres with the plane going through their centers has dimensions on the order of one-fifth the radius of the spheres. From Figure 2 we see then that the radii of particles in the range of effective separation are about 1/50th of the radius of the glass beads.

Apparently, a bed of impermeable glass beads has been used previously as a separation column. Pedersen[24] has observed the fractionation of proteins in such a column and has suggested that separation in this system may be caused by flow. He suggests that the larger particles flow faster than smaller ones in analogy to the faster rate of flow of blood cells (compared to plasma) through blood vessels; but he does not develop the idea any further. However, we propose that particle separation can occur in a bed of beads through the separation by flow mechanism alone. Effects other than the separation by flow mechanism are operative in the flow of blood cells through blood vessels.[20,25] In particular, the tubular pinch effect seems to dominate the flow of blood in blood vessels. In this effect Brownian motion is incidental; the effect exists for large particles in the absence of Brownian motion. In our flow mechanism Brownian motion (or turbulence) is essential. Also, in the tubular pinch effect, no part of the particles comes near the surface. There is a region lining the inside of the capillary of approximately one particle diameter which is completely free of particles (and any part of the particles). But in our effect the edge of the molecule comes up to and touches the inside surface of the capillary. That is to say, we have no layer of exclusion in the sense used by Pedersen. We should also point out that the pinch effect is thought not to exist at low particle Reynolds numbers[25] while "separation by flow" exists at all particle Reynolds numbers.[25a]

Acknowledgment. The authors wish to thank one of the reviewers for pointing out an error in the derivation of the effective radius a in appendix B.

Appendix A

Average Velocity of Thin Rigid Rods Flowing between Parallel Plates. The solution of this problem is useful in its own right. Also, the insight gained in solving it will enable us to solve approximately the more complicated problem for flexible polymers. If we define ρ to be the probability that the center of the (thin) rigid rods is at z, then the average velocity is

$$\langle v_p \rangle = \int_0^{z_0} v_p \rho \, dz \Big/ \int_0^{z_0} \rho \, dz \tag{A1}$$

In eq A1 we used the symmetry of the situation to set the lower limit of the integral at zero. In order to compute ρ, we assume that the time required to sample various angles by rotational diffusion is small compared to the tumble time due to the shear field. Thus, ρ is determined in the equilibrium limit and is porportional to the phase volume available to the rod. The phase space involved is, of course, that due to angular rotation; a rigid rod centered at a distance less than half its length from the surface has its angular freedom diminished by this fact.

If we define φ to be the angle that the rod makes with the z axis, then the minimum allowed angle φ_0 is given by the condition $\cos \varphi_0 = (z_0 - z)/L$, where $2L$ is the length of the rod and z the location of its center. The fraction of solid angle, ρ, available to the rod is

$$\rho = \int_{\varphi_0}^{\pi/2} \sin \varphi \, d\varphi \Big/ \int_0^{\pi/2} \sin \varphi \, d\varphi = \frac{z_0 - z}{L} \qquad z_0 - L \leq z \leq z_0 \tag{A2}$$

$$\rho = 1 \qquad 0 \leq z \leq z_0 - L$$

Equation A2 is valid if L is less than z_0. For L greater than z_0 we have

$$\rho = \frac{z_0 - z}{L} \qquad L > z_0 \tag{A3}$$

Using eq A1, A2, A3, and 11 with the retardation effect absent ($\gamma = 0$) we obtain for $\langle v_p \rangle$

$$\langle v_p \rangle = u_0\left[1 - \frac{\left(1 - \frac{L}{2z_0}\right)^2}{3}\right] - \frac{u_0(L/z_0)^2}{12} \qquad 0 \leq L \leq z_0 \tag{A4}$$

$$\langle v_p \rangle = \frac{5}{6}u_0 \qquad z_0 \leq L$$

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[24] K. O. Pedersen, *Arch. Biochem. Biophys., Suppl.* 1, 157 (1962).

[25] H. L. Goldsmith and S. G. Mason, *Proc. Intern. Congr. Rheol., 4th,* 85 (1965).

[25a] NOTE ADDED IN PROOF. In the above model of gpc the small cylinders represent the beads of a gpc column and allow for flow through (within) the beads, while the large cylinders represent the region between beads. It is these smaller cylinders that are imagined to have radii approximately 10–100 times larger than the radii of the particles being separated. Thus in the smaller cylinders there is separation by flow. The large cylinders, having radii an order of magnitude larger than the small tubes, do not contribute appreciably to the separation by flow effect.

We now seek to compare this exact result with the result of a method which uses the idea of an effective radius, a, of a particle. The probability, ρ, of the particle being at some point in space is one or zero depending on whether or not the center of the particle is a distance, a, from the wall. a is defined so that the exact configurational integral is the same as that obtained by assuming the particle has complete internal freedom throughout the restricted range allowed for its center. Thus, we have

$$\int_{-z_0}^{z_0} \rho \, \mathrm{d}z = \rho_0(2z_0 - 2a) \tag{A5}$$

where ρ_0 is the value of the probability in the absence of a surface. Use of eq A2 for ρ gives immediately for rigid rods

$$a = \frac{L}{2} \tag{A6}$$

If we now calculate $\langle v_{\mathrm{p}} \rangle$ we obtain, of course

$$\langle v_{\mathrm{p}} \rangle = u_0\left[1 - \frac{(1 - a/z_0)^2}{3}\right] \tag{A7}$$

Equations A7 and A4 are identical whenever the effective radius is small compared with the characteristic dimensions, z_0, of the plates. We expect then that the method of effective radius is valid as long as the radius is small compared to tube dimensions. Its great advantage is that if can be used for molecules with a large number of internal degrees of freedom. Using the same general method for prolate ellipsoids as we have for the rods, one obtains for the effective radius of an ellipsoid in the presence of the wall

$$a = \beta + \frac{\alpha}{2} - \frac{\beta^2 \ln\left(\dfrac{\alpha + \sqrt{\alpha^2 - \beta^2}}{\beta}\right)}{\sqrt{\alpha^2 - \beta^2}} \tag{A8}$$

where α and β are the semi minor axes and $\alpha > \beta$.

The above derived concept of the effective radius requires only the evaluation of thermodynamic phase integrals. Giddings, *et al.*,[26] and Casassa and Tagami[27] have evaluated these phase integrals for various geometries in a different context and their results are directly applicable.

Appendix B

The Calculation of the Effective Size of a Flexible Polymer Molecule. In this appendix we estimate the effective radius of a flexible polymer molecule using procedures developed in appendix A. Our procedure is as follows. We calculate the total phase space available to a polymer which is constrained to have all of its segments on one side of a plane. (This plane is arbitrarily chosen to be the $z = 0$ plane.) Thus, we have for the partition function

$$Z = \int_0^{h/2} \mathrm{d}z_0 \int_0^{h/2} \mathrm{d}z \int_{-h/2}^{h/2} \mathrm{d}x_0 \int_{-h/2}^{h/0} \mathrm{d}x \int_{-h/2}^{h/2} \mathrm{d}y_0 \int_{-h/2}^{h/2} \mathrm{d}y \, W(N, x, y, z, x_0, y_0, z_0) \tag{B1}$$

where x, y, and z are the coordinates of the first segment of the polymer at x_0, y_0, and z_0 are the coordinates of the last segment. The parameter h is taken to be much greater than any other distance parameter in the integral and is taken to approach infinity. Thus, there are no walls at, for example, $x = h/2$; the only surface is, as described above, at $z = 0$. For convenience and so we may write explicit volumes and areas h is left to seem finite.

In eq B1, W is given, for a N-beaded polymer of segment length, l, by

$$W = \frac{q^N}{\left(\frac{2}{3}\pi l^2 N\right)^{3/2}}\left[\exp\left(\frac{-(x - x_0)^2 - (y - y_0)^2 - (z - z_0)^2}{\frac{2}{3}l^2 N}\right) - \exp\left(\frac{-(x - x_0)^2 - (y - y_0)^2 - (z + z_0)^2}{\frac{2}{3}l^2 N}\right)\right] \tag{B2}$$

Equation B2 is normalized so that far from the surface

$$\int W \, \mathrm{d}x \, \mathrm{d}y \, \mathrm{d}z = q^N$$

$$\langle r^2 \rangle = Nl^2 \tag{B3}$$

It has been shown in a previous work[28] that near a boundary one correctly counts the conformations of a polymer molecule by adding a source point and the negative of its mirror image.

We may now estimate the partition function from another point of view. Because of the depletion of polymer conformation due to the surface, Z is not equal to q^N times the volume available to one end of the molecule but rather

$$Z = (V - A \cdot a)q^N \tag{B4}$$

where A is the area of the xy plane near $z = 0$ (thus $A = h^2$) and V is the volume on one side of the surface (thus $V = h^3/2$). Equation B4 may be viewed as the defining equation for a, the effective radius of the particle.

Equation B4 and B1 together enable us to calculate a. The integration over x, y, x_0, y_0 in eq B1 is easily performed and we obtain

$$\frac{Z}{Aq^N} = \int_0^{h/2} \int_0^{h/2} \frac{(\exp[-3(z - z_0)^2/2l^2N] - \exp[-3(z + z_0)^2/2l^2N])\mathrm{d}z_0\mathrm{d}z}{(2\pi l^2 N/3)^{1/2}} \tag{B5}$$

If we shift to the variables

$$u = z - z_0$$

$$v = z + z_0$$

$$\frac{\partial(u,v)}{\partial(z,z_0)} = 2 \tag{B6}$$

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(26) J. C. Giddings, E. Kucera, C. P. Russell, and M. N. Myers, *J. Phys. Chem.*, 72, 4397 (1968).

(27) E. F. Casassa and Y. Tagami, *Macromolecules*, 2, 14 (1969).

(28) E. A. DiMarzio, *J. Chem. Phys.*, 42, 2101 (1965).

we then have

$$\frac{Z}{Aq^N} = \frac{1}{2}\int_{v=0}^{h/2}\int_{u=-v}^{+v}\left[\frac{\exp(-3u^2/2l^2N)}{(2\pi l^2N/3)^{1/2}} - \frac{\exp(-3v^2/2l^2N)}{(2\pi l^2N/3)^{1/2}}\right]\mathrm{d}u\mathrm{d}v + \frac{1}{2}\int_{v=h/2}^{h}\int_{-(h-v)}^{h-v}\left[\frac{\exp(-3u^2/2l^2N)}{(2\pi l^2N/3)^{1/2}} - \frac{\exp(-3v^2/2l^2N)}{(2\pi l^2N/3)^{1/2}}\right]\mathrm{d}u\mathrm{d}v = \frac{1}{2}\int_0^{h/2}\operatorname{erf}\left(\frac{v}{\sqrt{\frac{2l^2N}{3}}}\right)\mathrm{d}v - \frac{1}{2}\int_0^{h/2}\frac{2v\exp(-3v^2/2l^2N)}{(2\pi l^2N/3)^{1/2}}\,\mathrm{d}v + \frac{1}{2}\int_{h/2}^{h}\operatorname{erf}\left(\frac{h-v}{\sqrt{\frac{2l^2N}{3}}}\right)\mathrm{d}v - \frac{1}{2}\int_{h/2}^{h}\frac{2(h-v)\exp(-3v^2/2l^2N)}{(2\pi l^2N/3)^{1/2}}\,\mathrm{d}v = \int_0^{h/2}\operatorname{erf}\left(\frac{v}{(2l^2N/3)^{1/2}}\right)\mathrm{d}v - \frac{1}{2}\left(\frac{2l^2N}{3\pi}\right)^{1/2} \quad \text{(B7)}$$

Using eq B4 and writing V in the form

$$V = A\int_0^{h/2}\mathrm{d}v$$

we obtain

$$a = \int_0^{\infty}\operatorname{erfc}\left(\frac{v}{(2l^2N/3)^{1/2}}\right)\mathrm{d}v + \frac{1}{2\sqrt{\pi}}\left(\frac{2l^2N}{3}\right)^{1/2} \quad \text{(B8)}$$

where we have now let h go to infinity.

Performing the integration in eq B8 by parts, we obtain

$$a = \frac{3}{2\sqrt{\pi}}\left(\frac{2l^2N}{3}\right)^{1/2} \quad \text{(B9)}$$

In terms of the end-to-end length $\sqrt{\langle r^2\rangle}$ and radius of gyration s

$$a = \left(\frac{3}{2\pi}\right)^{1/2}\sqrt{\langle r^2\rangle} = \frac{3}{\sqrt{\pi}}\,s \quad \text{(B10)}$$

Appendix C

Average Velocity of Particles in a Triangular Tube. We wish here to compute the average velocity of particles in tubes of an equilateral triangular cross section. For simplicity, we have assumed that the particles of interest are small compared to the tube size so there is no retardation effect. Thus the velocity of the particle is the fluid velocity at its center of mass. In triangular tubes the fluid velocity is[6]

$$v_f^x = (u_0/4h^3)(h - y)(y - \sqrt{3}z + 2h)(y + \sqrt{3}z + 2h) \quad \text{(C1)}$$

where u_0 is the maximum velocity and h is one-third of the height of the triangle. The coordinate system perpendicular to the tube axis is shown in Figure 4. The solid lines in this figure refer to the tube cross section.

The average velocity for a particle of radius a then is given by

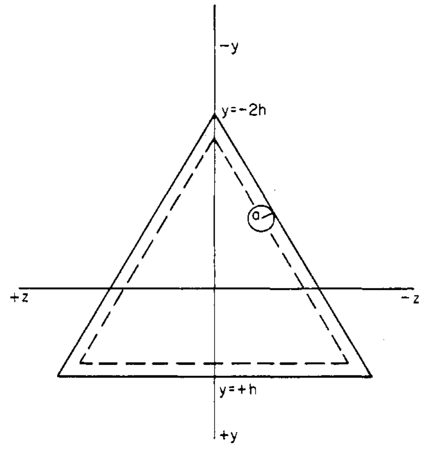

Figure 4. Coordinate system and schematic for triangular tube integration. Outside triangle shows pipe cross section; it is bounded by the lines $y = +h$, $y = -\sqrt{3}z - 2h$, and $y = \sqrt{3}z - 2h$. The inside dashed triangle shows the area available to the center of mass of a particle of radius a (shown by the circle); the dashed triangle is bounded by the lines $y = h - a$, $y = -\sqrt{3}z - 2(h - a)$, and $y = \sqrt{3}z - 2(h - a)$.

$$\langle v_p^x\rangle = 2\int_{-\sqrt{3}h+\sqrt{3}a}^{0}\int_{-2(h-a)-\sqrt{3}z}^{h-a} v_f^x\,\mathrm{d}y\mathrm{d}z/A \quad \text{(C2)}$$

where

$$A/2 = \int_{-\sqrt{3}h+\sqrt{3}a}^{0}\int_{-2(h-a)-\sqrt{3}z}^{h-a}\mathrm{d}y\mathrm{d}z$$

The limits on the above integration are those of the dashed triangle in Figure 4; the center of the particle is not allowed outside the dashed triangle. The result of the integration is

$$\langle v_p^x\rangle = \frac{u_0}{2\sqrt{3}A}\left[\left(-\frac{y^5}{20} + \frac{y^4}{4}(h - 2a) - \frac{y^3}{3}\left(6ha - \frac{3}{2}a^2\right) - \frac{y^2}{2}(3ha^2 - 2a^3) + y\left(\frac{7}{4}a^4 - 4ha^3\right)\right)\right]_{y=a}^{y=3h-2a} \quad \text{(C3)}$$

The plot of this function if given in Figure 2.

Appendix D

Evaluation of the Effective Diffusion Coefficient under Pure Shear. We seek to solve eq 26 when the velocity

$$v_f^x = v_f^x = 0$$

$$v_f^x = \frac{u_{y0}z}{2z_0} \quad \text{(D1)}$$

field is pure shear. We have chosen our coordinate system so that the velocity at $z = 0$ is zero. If we assume that there is no variation in the x direction (or if we integrate over the x variable) then our problem has only the two spacial variables, y, z. We now wish to

$$D\left(\frac{\partial^2C}{\partial y^2} + \frac{\partial^2C}{\partial z^2}\right) = \frac{\partial C}{\partial t} + \frac{u_{y0}z}{2z_0}\frac{\partial C}{\partial y} \quad \text{(D2)}$$

$$\left.\frac{\partial C}{\partial z}\right|_{\pm z_0} = 0,\; C(y,z,t = 0) = \delta(y)\delta(z) \quad \text{(D3)}$$

show that the concentration averaged over the z direction obeys the ordinary diffusion equation with a new effective diffusion coefficient. Following Aris, eq D2 and D3 can be solved by a method of moments. Multiply eq D2 by y^n and integrate. In obtaining eq D4 we

$$Dn(n-1)C_{n-2} + D\frac{\partial^2 C_n}{\partial z^2} = \frac{\partial C_n}{\partial t} - \frac{u_{y0} z n C_{n-1}}{2z_0}$$

$$C_n = \int_{-\infty}^{+\infty} y^n C \, \mathrm{d}y \tag{D4}$$

used the fact that C and $\partial C/\partial y$ approach zero at large y faster than y^{-n}. This set of equations is nicely coupled because it allows us to evaluate C_n in terms of C_{n-1} and C_{n-2} only. If we now multiply eq D4 by z^m and integrate over z we obtain

$$Dm(m - l)C_{n,m-2} + Dn(n-1)C_{n-2,m} - \frac{\mathrm{d}C_{n,m}}{\mathrm{d}t} =$$

$$Dmz_0^{m-1}C_n(z_0,t)[(-1)^{m+n} + 1] - \frac{u_{y0}n}{2z_0} C_{n-1,m+1}$$

$$C_{n,m} = \int y^n z^m C \, \mathrm{d}y \, \mathrm{d}z \tag{D5}$$

In deriving eq D5 one uses

$$\left.\frac{\partial C_n}{\partial z}\right|_{\pm z_0} = 0, C_n(z) = (-1)^n C_n(-z),$$

$$C(y,z,t) = C(-y,-z,t) \tag{D6}$$

We seek the quantity $C_{2,0}$ which is the second moment in y of the mean value in z. From eq D5 we obtain

$$\frac{\mathrm{d}C_{2,0}}{\mathrm{d}t} = 2DC_{0,0} + \frac{u_{y0}}{z_0}C_{1,1} \tag{D7}$$

By use of eq D7 we avoid having to solve eq D4 for C_2. We will now solve eq D4 for C_0 and C_1 and then use eq D7 to evaluate $C_{2,0}$. The equation for C_0 is

$$D\frac{\partial^2 C_0}{\partial z^2} = \frac{\partial C_0}{\partial t}, \left.\frac{\partial C_0}{\partial z}\right|_{\pm z_0} = 0, \ C_0(z,0) = \text{const} \tag{D8}$$

C_0 is obviously a constant for all z,t. This can be seen also on physical ground if one realized that eq D8 describes the temperature distribution in a rod that is perfectly insulated and has constant initial temperature distribution. C is normalized so that $C_{0,0} = 1$. We obtain

$$C_0(z,t) = \frac{1}{2z_0} \tag{D9}$$

The equation for C_1 is

$$D\frac{\partial^2 C_1}{\partial z^2} - \frac{\partial C_1}{\partial t} = -\frac{u_{y0}z}{4z_0^2} \tag{D10}$$

$$\left.\frac{\partial C_1}{\partial z}\right|_{\pm z_0} = 0, \ C_1(z,0) = 0 \tag{D11}$$

We pick as the solution to eq D10

$$C_1 = \sum_{k=0}^{\infty} A_k(t) \sin\left[\frac{(2k+1)\pi z}{2z_0}\right] \tag{D12}$$

$$A_k(0) = 0$$

The argument of the sine is half integer at $z = z_0$ so that the gradient of C_1 is automatically zero on the boundary. Also C_1 is an odd function as required by eq D6. If we substitute eq D12 into eq D10 the left-hand side is nothing more than a Fourier expansion for the right hand side. We obtain

$$DA_k(t)\left[\frac{(2k+1)\pi}{2z_0}\right]^2 + \frac{\mathrm{d}A_k(t)}{\mathrm{d}t} = \frac{2u_{y0}(-1)^k}{[(2k+1)\pi]^2} \tag{D13}$$

These equations can be immediately solved for $A_k(t)$. Equation D12 becomes

$$C_1 = \sum_{k=0}^{\infty} \frac{8u_{y0}(-1)^k z_0}{[(2k+1)\pi]^4 D}\left[1 - \exp\left(-D\left[\frac{(2k+1)\pi}{2z_0}\right]^2 t\right)\right] \sin\left[\frac{(2k+1)\pi z}{2z_0}\right] \tag{D14}$$

We now calculate $C_{1,1}$ from eq D14 and use eq D7 to obtain

$$C_{2,0} = 2t\left(D + \frac{32u_{y0}^2 z_0^2}{D\pi^6}\sum_{k=0}^{\infty}\frac{1}{(2k+1)^6}\right) - \frac{256u_{y0}^2 z_0^4}{D^2\pi^8}\sum_{k=0}^{\infty}\frac{\left[1 - \exp\left(-D\left[\frac{(2k+1)\pi}{2z_0}\right]^2 t\right)\right]}{(2k+1)^8} \tag{D15}$$

Notice also that $C_{0,0} = 1$, $C_{n,0} = 0$ n odd. This means that eq D2 and D3 give for large time the same first four y moments for the mean concentration (averaged over the z direction) as

$$K^y \frac{\partial^2 C_m}{\partial y^2} = \frac{\partial C_m}{\partial t}$$

$$K^y = D + \frac{32u_{y0}^2 z_0^2}{D\pi^6} \tag{D16}$$

In eq D16 we have retained only the leading term in the sum over k. k_4 is thus equal to $32/\pi^6 \cong 1/30$ while k_x is from eq 36 approximately equal to 1/120.

The above was for point particles. One can proceed just as in eq D1 to D16 for particles of radius a. One obtains the same equations except that

$$u_{y0} \longrightarrow u_{y0}\left(1 - \frac{a}{z_0}\right)$$

$$z_0 \longrightarrow z_0 - a \tag{D17}$$