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ON GASEOUS SELF-DIFFUSION IN CAPILLARIES

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ON GASEOUS SELF-DIFFUSION IN CAPILLARIES

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ABSTRACT

The self-diffusion of a gas in a capillary has been re-examined using a density distribution which gives the same transport at the end and mid-point of the tube. This density function is chosen to be linear through the tube with effective discontinuities at the ends. Previous calculations in the limit of infinite mean free path have shown such a distribution to be reasonably reliable. The calculation reported here determines the limiting slope of the diffusion transport with increasing a/λ for right circular cylindrical capillaries of arbitrary length to radius ratio. The results are similar to those obtained previously by Pollard and Present, and Hiby and Pahl, but are believed to be more reliable. Theoretical predictions are compared with experimental data of Visner and seem to account satisfactorily for the observed decrease of the self-diffusion coefficient with increasing pressure. It is apparent that results from considerations of self-diffusion cannot be applied directly to flow at finite pressure.

ON GASEOUS SELF-DIFFUSION IN CAPILLARIES

INTRODUCTION

The problem of gaseous self-diffusion in capillary tubes has been examined by Pollard and Present(1) and Hiby and Pahl(2). The approach in both of these works is essentially identical except that Hiby and Pahl use a model consisting of a "bent-line" and hope in this way to eliminate any confusion resulting from the end effects apparent with short capillaries. Both of these works treat the diffusion of a very low concentration of molecules of a species A through a relatively much larger concentration of "fixed" molecules of species B. No pressure gradient is permitted and hence no bulk streaming of the gas need be considered; the principal function of the gas B is to maintain a finite free path, λ, for molecules of type A independent of the position of these molecules in the system. In essence, both approaches start from equations (24) and (25) of Pollard and Present which determine the transport through a cross-section midway down the tube and differ only in the interpretation of the numbers n_1 and n_2 in equation (25). In Pollard and Present's treatment these numbers refer to the number density of molecules of type A in bulbs at the ends of the capillary, and it is assumed that no density gradient exists in this region; in Hiby and Pahl's treatment, these numbers refer to the number density of molecules of type A required to give the correct emission from the walls terminating a short capillary segment. The two treatments are formally identical; this point is discussed in more detail in Appendix B of the report K-992 by W. H. Eberhardt(3).

In order to make the calculation tractable, Hiby and Pahl expand the exponentials in the integrals of equations (24) and (25) and keep only terms of order a/λ, where a is the tube radius*. They are then able to express the transport in terms of tabulated complete elliptic integrals and two integrals for which they give an approximate analytic function.

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* Hiby and Pahl's equation (3) contains an error in that the factor 1/2 should not be present. If this factor is eliminated, the terms of their equation (4) depending on a/λ vanish. However, if the equation used to obtain (3) is carried one step farther, their equation (4) results. Hence, by a fortuitous cancellation of errors, their results are still applicable.

In both of these approaches, the number density of molecules of type A is assumed to vary linearly with distance down the tube, and the density gradient is equated to $\frac{n_1 - n_2}{2L}$, where 2L is the length of the tube. It is easy to show under conditions where gas-phase collisions may be neglected, that such an assumption leads to a calculated transport midway down the tube which is twice as great as that entering and leaving the tube[3]. In K-992 this difficulty was avoided by the introduction of an effective density discontinuity, δn, at each end of the tube, but the assumption of a linear gradient

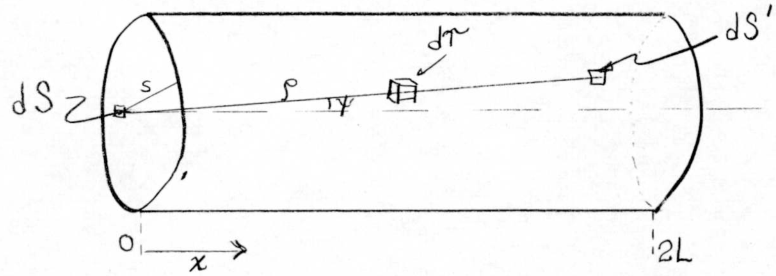
$$\frac{dn}{dx} = \frac{n_1 - n_2 - 2\delta n}{2L}$$

was maintained. The adjustable parameter, δn, was evaluated by calculating the transport at the ends of the tube and also at the center in terms of this parameter, equating the two values, and solving for δn. The assumption of a density distribution of this form is equivalent to that of the "extrapolated-boundary technique", and a physical justification for it is also provided in K-992. Furthermore, the more rigorous approaches of Clausing[4] and DeMarcus[5] lead to a collision density which is very nearly linear and described by very nearly the same slope as determined in K-992.

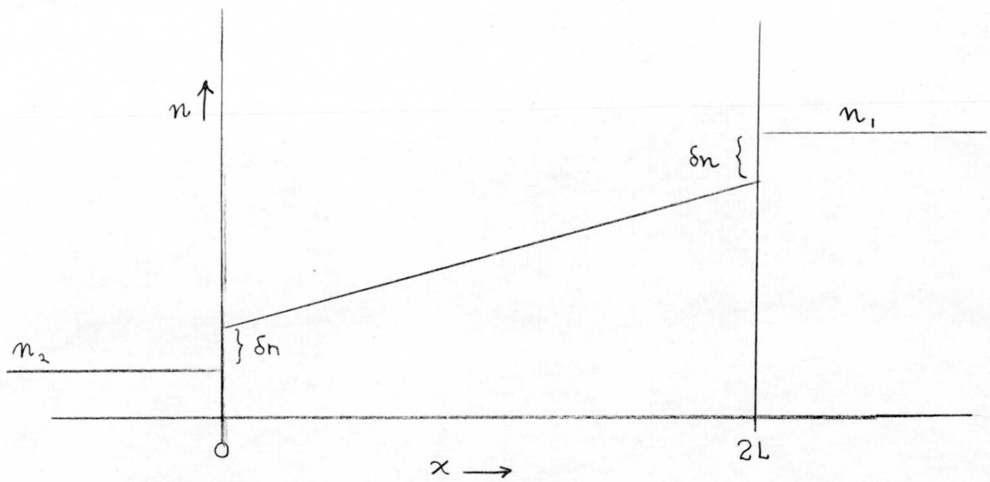
In this report the problem of self-diffusion is examined from the same starting point as Pollard and Present except that the density function is chosen to be linear with an effective discontinuity at both ends. As in the problem of long free paths, the density discontinuity is evaluated so that the transport calculated at the ends of the tube is the same as that at the midpoint.

DETAILS OF THE CALCULATION

The coordinate system of Pollard and Present is taken over directly to this problem:



The tube is taken to be of a radius a and length 2L. The density of molecules of type A is represented by the following sketch:



The calculation is first carried through for the element dS situated in the cross-section at the midpoint of the tube, i.e., x = L. The net number of molecules (of type A) crossing this cross-section per second from left to right is calculated as follows:

From the walls of the tube:

$$N_w = - \frac{1}{2} \bar{v} \iint dS \int_{\psi_o}^{\pi-\psi_o} n(x) \cos\psi \sin\psi \, e^{-\frac{s}{\lambda \sin\psi}} d\psi$$

$$= - \frac{1}{2} \bar{v} \frac{dn}{dx} \iint dS \int_{\psi_o}^{\pi-\psi_o} s \cos^2\psi \, e^{-\frac{s}{\lambda \sin\psi}} d\psi$$

$$= - \bar{v} \frac{dn}{dx} \iint dS \int_{\psi_o}^{\pi/2} s \cos^2\psi \, e^{-\frac{s}{\lambda \sin\psi}} d\psi$$

From gas collisions within the tube:

$$N_g = - \frac{1}{2\lambda} \bar{v} \iint dS \left\{ \int_{\psi_o}^{\pi-\psi_o} \cos\psi \sin\psi \, d\psi \int_o^{\frac{s}{\sin\psi}} n(x) \, e^{-\rho/\lambda} d\rho \right.$$

$$\left. + \int_o^{\psi_o} + \int_{\pi-\psi_o}^{\pi} \cos\psi \sin\psi \, d\psi \int_o^{\frac{L}{|\cos\psi|}} n(x) \, e^{-\rho/\lambda} d\rho \right\}$$

$$= - \bar{v}\lambda \frac{dn}{dx} \iint dS \left\{ \int_o^{\psi_o} \cos^2\psi \sin\psi \left[1 - \left(1 + \frac{L}{\lambda \cos\psi}\right) \right] e^{-\frac{L}{\lambda \cos\psi}} d\psi \right.$$

$$\left. + \int_{\psi_o}^{\pi/2} \cos^2\psi \sin\psi \left[1 - \left(1 + \frac{s}{\lambda \sin\psi}\right) \right] e^{-\frac{s}{\lambda \sin\psi}} d\psi \right\}$$

From the gas entering the ends of the tube:

$$N_e = -\frac{\bar{v}}{2}(n_1 - n_2) \iint dS \int_0^{\psi_0} \sin\psi \cos\psi e^{-\frac{L}{\lambda\cos\psi}} d\psi.$$

In these expressions, the integration over ϕ has already been carried out and the symmetry of the problem introduces only the gradient of the density function. The total transport is obtained by adding these three terms and is most conveniently expressed in terms of the dimensionless parameter

$$W = -\frac{N}{\frac{1}{4}\bar{v}(n_1 - n_2)\pi a^2}.$$

In evaluating the integrals the exponentials are expanded to a sufficiently high power in a/λ , and only the terms to the first order in this parameter are retained. Thus, the transport is written as $W = W_o + \frac{a}{\lambda} W_1$, and for convenience the notation $\xi = \frac{\delta n}{n_1 - n_2}$ and $\eta = a/\lambda$ is introduced. Also following the notation of Hiby and Pahl[2], the geometrical parameter $B = \frac{L}{2a}$ is used*.

The following results are obtained:

$$W_o = \left\{1 + \frac{2}{3B} + \frac{2}{3B^2} - \frac{2}{3B}(1 + B^2)\sqrt{1 + B^2}\right\}$$
$$+ \xi\left\{\frac{4}{3B}(1 + B^2)\sqrt{1 + B^2} - \frac{4}{3B} + \frac{8}{3}B^2 - 4B\sqrt{1 + B^2}\right\}$$

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* In K-992, a parameter $b = \frac{4a}{2L} = \frac{2a}{L} = \frac{1}{B}$ is used. In that report the length, L, stands for the entire tube length; in this report and those of Hiby and Pahl, and Pollard and Present, L stands for the half-length.

$$W_1 = \left\{- 2B + \frac{8B}{3\pi} I_3 + \frac{16B^2}{3\pi} I_4 + \frac{8}{3\pi B} (I_5 - I_6)\right\}$$

$$+ \xi \left\{- 4B - \frac{16B}{3\pi} I_3 + \frac{64B^2}{3\pi} I_4 - \frac{16}{3\pi B} (I_5 - I_6)\right\} .$$

The integrals I_3 to I_6 are defined by Hiby and Pahl; I_3 and I_4 are expressed in terms of complete elliptic integrals, and an approximate analytic expression is given for I_5 and I_6 valid over the range $1 \leq B \leq 10$. In terms of these functions W_1 may be written as

$$W_1 = 2\left\{- B + \frac{20}{9\pi} B^2 \sqrt{1 + B^2} (K - E) + \frac{8}{9\pi} \sqrt{1 + B^2} E + \frac{4}{3\pi B} (I_5 - I_6)\right\}$$

$$+ 4\xi\left\{- B + \frac{52}{9\pi} B^2 \sqrt{1 + B^2} (K - E) - \frac{8}{9\pi} \sqrt{1 + B^2} E - \frac{4}{3\pi B} (I_5 - I_6)\right\}$$

where $\frac{1}{3\pi} (I_5 - I_6) \cong \frac{7}{192} - \frac{1}{16} \ln B - \frac{1}{8} \ln 2 - \frac{0.03}{\pi B^2}$ and K and E are complete elliptic integrals of the parameter $k^2 = \frac{1}{1 + B^2}$ and are tabulated in Jahnke and Emde.

A similar calculation is carried through for $x = 0$. Here the absence of symmetry introduces the entire density function but aside from changes in the limits of integration, the formulation of the problem is identical with that above. The results are as follows:

$$W'_o = \left\{1 + \frac{1}{3B} + \frac{8}{3} B^2 - \frac{1}{3B} (1 + 4B^2) \sqrt{1 + 4B^2}\right\}$$

$$-\xi\left\{\frac{2}{3B} - \frac{8}{3} B^2 + \frac{2}{3B} (2B^2 - 1) \sqrt{1 + 4B^2}\right\}$$

$$W'_1 = \left\{- 4B - \frac{32}{3\pi} B\, I'_3 + \frac{224}{3\pi} B^2\, I'_4 + \frac{4}{3\pi B} (I'_5 - I'_6)\right\}$$

$$+\xi\left\{\frac{64}{3\pi} B\, I'_3 - \frac{256}{3\pi} B^2\, I'_4 - \frac{8}{3\pi B} (I'_5 - I'_6)\right\}$$

or in terms of the elliptic integrals,

$$W'_1 = 4\left\{-B + \frac{40}{9\pi}B^2\sqrt{1+4B^2}\,(K'-E') + \frac{4}{9\pi}\sqrt{1+4B^2}\,E' + \frac{1}{3\pi B}(I'_5 - I'_6)\right\}$$
$$+ 8\xi\left\{\frac{32}{9\pi}B^2\sqrt{1+4B^2}\,(K'-E') - \frac{4}{9\pi}\sqrt{1+4B^2}\,E' - \frac{1}{3\pi B}(I'_5 - I'_6)\right\}$$

where $\frac{1}{3\pi}(I'_5 - I'_6) = \frac{7}{192} - \frac{1}{16}\ln B - \frac{3}{16}\ln 2 - \frac{0.03}{4\pi B^2}$.

In the above formulas a prime has been attached to integrals for which the parameter $k^2 = \frac{1}{1 + 4B^2}$, i.e., B is replaced by 2B. This change results from a change in the limits of integration.

The expression for the transport through the center, $W = W_o + \eta W_1$, is now equated to that through the end, $W' = W'_o + \eta W'_1$ and the resultant equation used to eliminate $\xi = \frac{\delta n}{n_1 - n_2}$ from the transport. This expression for the transport is then differentiated with respect to $\eta = a/\lambda$ and evaluated at $\eta = 0$; this process gives the limiting slope at zero pressure. The zero pressure transport probability is determined with $\eta = 0$ and is identical with that given in K-992 and is very close to the more rigorous values given in references 4 and 5.

TABLE I

EFFECTIVE DENSITY DISCONTINUITY AND LIMITING SLOPE AS A FUNCTION OF THE GEOMETRICAL PARAMETER, B = L/2a

B	Limiting Slope, $a/\lambda = 0$	Density Discontinuity, $\frac{\delta}{n_1 - n_2}$ $a/\lambda = 0$	$a/\lambda = 0.1$
0	0	0.5000	0.5000
0.25	-0.220	0.3717	0.3463
0.50	-0.325	0.2405	0.2262
1	-0.453	0.3570	0.3177
2	-0.611	0.1064	0.0975
3	-0.723	0.0798	0.0716
6	-0.939	0.0463	0.0397

In presenting the results for the limiting slope, the transport may be written as

$$W = W_o \left(1 - K \frac{2a}{\lambda}\right)$$

to allow comparison with the results of Hiby and Pahl. The integrals $I_5 - I_6$ were evaluated numerically for $B = 1/4$, $1/2$, and 1, and the formula given by Hiby and Pahl was used for $B > 1$. The dependence of K on B is shown in figure 1. This figure also contains points calculated by Hiby and Pahl for comparison. It is apparent that the refinements introduced here do not change the results obtained by Hiby and Pahl significantly as far as K is concerned although the low pressure permeability itself is affected strongly.

Table I contains the limiting slopes upon which figure 1 is constructed and also values of the fractional density discontinuity $\xi = \frac{\delta n}{n_1 - n_2}$ at $a/\lambda = 0$ and 0.1. As might be anticipated, ξ decreases as a/λ increases.

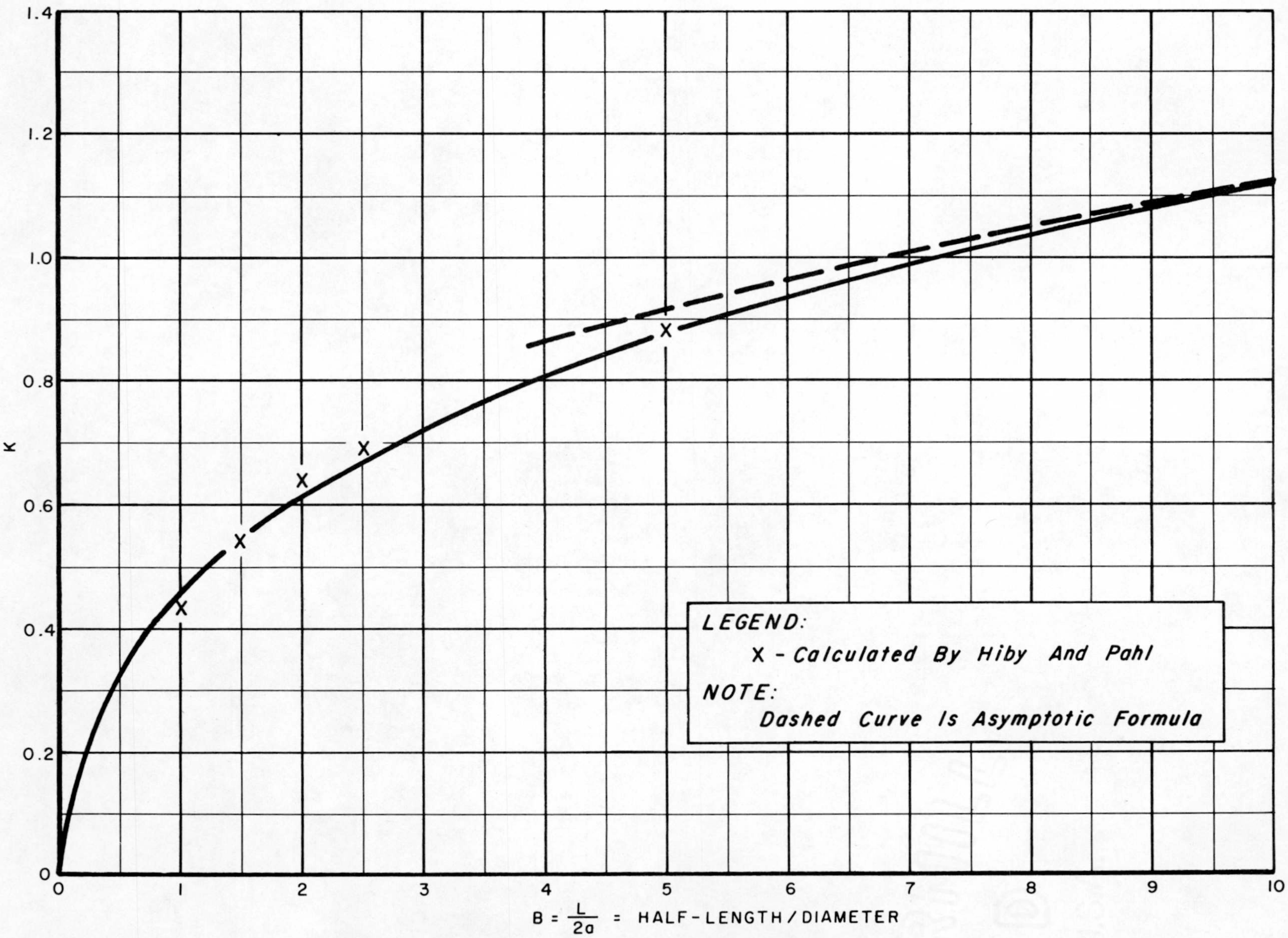
AN ASYMPTOTIC EXPANSION FOR K

Although the complicated nature of the expression for K does not allow a simple algebraic expression, it is possible to develop such as expression for large values of B. Expansions of the elliptic integrals are given in Jahnke and Emde and lead to the following expression for K to second order in 1/B:

$$K = \frac{\left(3 \ln 2 - \frac{9}{8} + \frac{3}{2}\ln B\right) + \frac{1}{B}\left(1 + \ln 2\right) - \frac{1}{B^2}\left(1 + \frac{5}{4}\ln 2 - \frac{0.157}{\pi} + \frac{1}{128} - \frac{9}{8}\ln B\right)}{4\left(1 + \frac{7}{24B} - \frac{5}{4B^2}\right)}$$

$$= \frac{\left(0.2387 + \frac{3}{8}\ln B\right) + \frac{1}{B}(0.4233) - \frac{1}{B^2}\left(0.4561 - \frac{9}{32}\ln B\right)}{\left(1 + \frac{7}{24B} - \frac{5}{4B^2}\right)}$$

This expression is also plotted in figure 1.



DEPENDENCE OF K ON B = $\frac{L}{2a}$

$$W = W_0 \left(1 - K \frac{2a}{\lambda}\right)$$

FIGURE 1

COMPARISON WITH EXPERIMENT

The only data which are suitable for comparison with the results derived here are those obtained by Visner for the self-diffusion of xenon through glass capillaries[6]. Visner studied three sets of capillaries with L/a of 66, 9.8, and 2.8. His results for the lowest pressures are shown in figure 2 in which solid lines are drawn as calculated a priori from the theory given here and Visner's experimental data are indicated. The ordinate is $D/\bar{v}a$ which is equal to WB. The agreement between theory and experiment seems adequate in the region for which the theory is applicable, particularly for the shorter capillaries. The scatter of experimental points for the long capillary makes comparison difficult although the theoretical curve seems to describe the low pressure measurements with reasonable success. Inspection of figure 2 shows that the first order expansion in terms of a/λ extends to larger values of a/λ for the short than for the long capillaries; this result might also have been anticipated intuitively.

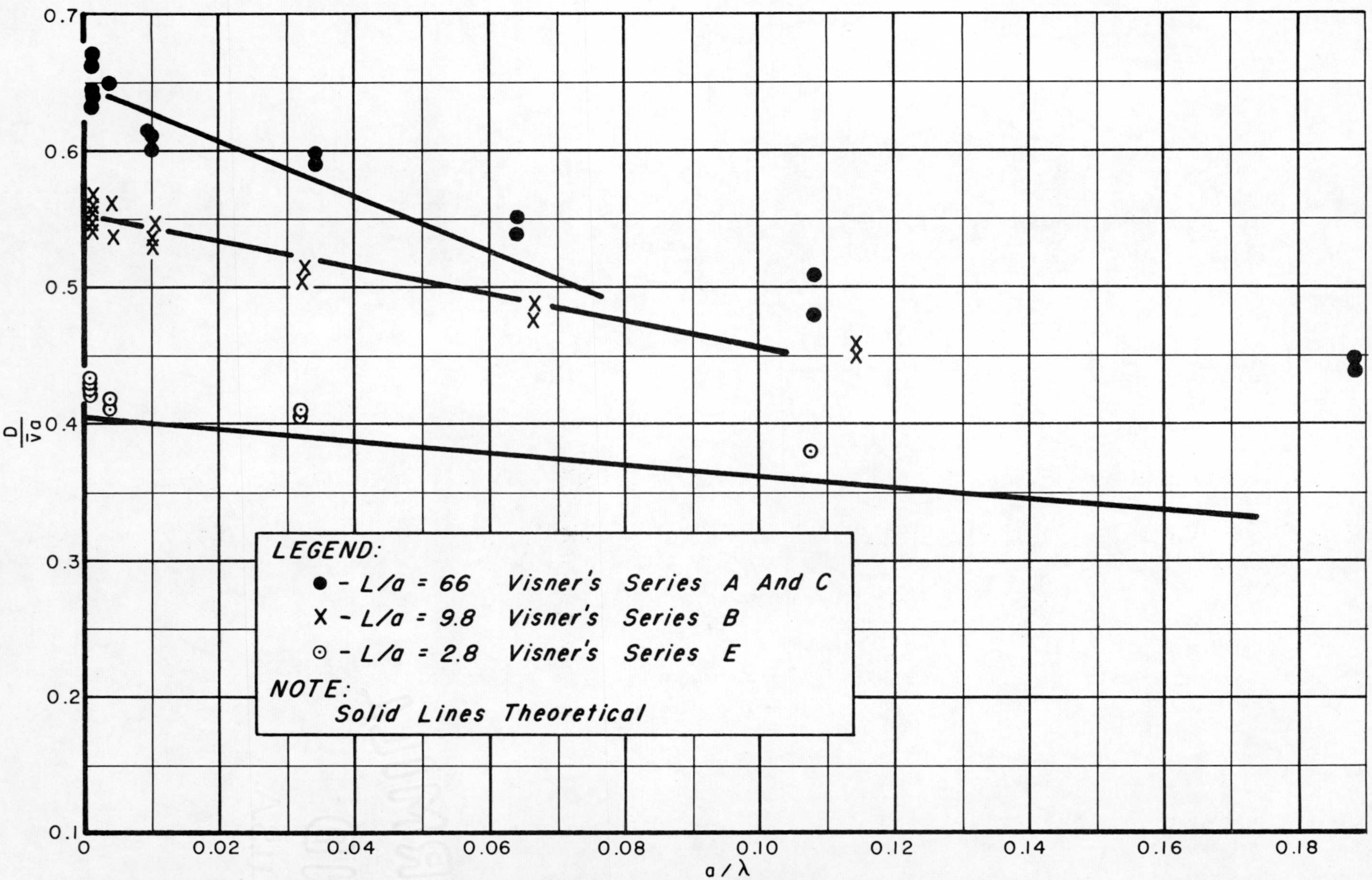
DISCUSSION

Although the calculation described here provides a necessary refinement to the previous approaches to the problem, it does not attempt to include some of the more difficult aspects required to give a complete solution. In particular two large assumptions are implied:

(1) the gas molecules leave a collision isotropically, i.e., there is no persistence of direction on collision, and

(2) the gas in the bulbs outside the capillary is not affected by the presence of the capillary.

Hiby and Pahl have made some estimates of these effects, which, although far from rigorous, suggest the value of K should be increased by a value +0.45 to +0.60. Thus, the calculation reported here presents the <u>hindering</u> of diffusion by foreign gas and does not take into account any possible enhancement which might result from persistence of direction on collision.



COMPARISON OF CALCULATED AND EXPERIMENTAL SELF-DIFFUSION COEFFICIENTS FOR XENON IN GLASS CAPILLARIES

FIGURE 2

The case of the orifice leads to particularly distressing results since in this problem all effects must be outside the flow system and the value of κ calculated here must vanish. However, Hiby and Pahl estimate $\kappa = 0.33$ for isotropic scattering and -0.12 for persistence of direction on scattering. These values of κ result from a consideration of the change in angular distribution of the molecules near the orifice; such a change is not considered in the treatment reported here.

It is difficult to reconcile the results of Hiby and Pahl on velocity persistence with the self-diffusion measurements of Visner. From the agreement of the results derived here and Visner's experimental data, it appears that isotropic scattering is sufficient to account for the phenomena at low pressures and nonisotropic scattering should be only a second-order effect.

Furthermore, the experimental fact that self-diffusion coefficients <u>decrease</u> as a/λ increases, whereas specific flow coefficients <u>increase</u> implies that the treatment of the self-diffusion problem cannot be taken over directly to the interpretation of specific flow measurements, but that a more correct approach must be used at the outset.

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