

## Molecular Transport in Liquids and Glasses

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## Molecular Transport in Liquids and Glasses

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We have derived, by using simple considerations, a relation between the diffusion constant  $D$  in a liquid of hard spheres and the "free volume"  $v_f$ . This derivation is based on the concept that statistical redistribution of the free volume occasionally opens up voids large enough for diffusive displacement. The relation is  $D = A \exp[-\gamma v^*/v_f]$ , where  $v^*$  is the minimum required volume of the void and  $A$  and  $\gamma$  are constants. This equation is of the same form as Doolittle's [J. Appl. Phys. **22**, 1471 (1951)] empirical relation between the fluidity  $\phi$  of simple hydrocarbons and their free volume. It has been shown [Williams, Landel, and Ferry, J. Am. Chem. Soc. **77**, 3701 (1955)] that the Doolittle equation also can be adapted to describe the abrupt decrease in molecular kinetic constants with decreasing temperature that accompanies the glass transition in certain liquids. Our result predicts that even the simplest liquids would go through this glass transition if sufficiently undercooled and crystallization did not occur. The problem of transport in actual simple and network liquids also is discussed.

It is shown that data on self-diffusion in some simple van der Waals liquids and liquid metals are described satisfactorily by our relation with  $v^*$  near the molecular volume for the van der Waals liquids and near the volume of the ion, corresponding to the highest valence state, for the metals.

## INTRODUCTION

**A** LIQUID may solidify (i.e., become sensibly rigid) by crystallizing or, in some cases, by undercooling to an amorphous rigid, i.e., glassy, state. The course of the fluidity  $\phi$  ( $\phi = 1/\eta$ ), where  $\eta$  is the coefficient of viscosity), as the liquid is cooled from the fluid to the glassy state, is represented schematically in Fig. 1. The apparent activation energy for fluid flow tends to increase as the temperature is lowered. In the simpler liquids this increase is almost imperceptible until the glass transition is approached. Then the fluidity decreases many orders of magnitude over a narrow temperature range (glass transition range), as shown in Fig. 1, to a value  $< 10^{-13}$  poise $^{-1}$  associated with rigid behavior. In the case of the network liquids, SiO<sub>2</sub>, B<sub>2</sub>O<sub>3</sub>, etc., the fluidity often is orders of magnitude lower than that of simple liquids even above the melting temperature, and the transition to the rigid state appears to be more gradual<sup>1</sup> (see also Fig. 1).

The factors which determine whether or not a liquid can be undercooled to the glassy state were discussed by the authors in an earlier paper.<sup>2</sup> The purpose of the present paper is to develop a simple explanation for the mobility of molecules in liquids and its striking decrease, implied by the fluidity behavior, in the glass transition region.

There are much fewer self-diffusion than fluidity data for liquids. In those liquids for which both kinds of data exist, the self-diffusion constant  $D$  is directly proportional to the fluidity. If, in addition, the molecules are nearly spherical, the proportionality constant is given approximately by the Stokes-Einstein rela-

tion,<sup>3,4</sup>

$$D = (kT/3\pi a_0)\phi, \quad (1)$$

where  $a_0$  is the diameter of a sphere having the volume of the molecule. It is not established whether or not this relation holds through the glass transition, but data on the kinetics of molecular reorientation processes in glasses suggest that it does. We shall assume throughout the subsequent discussion that  $D$  is proportional to  $\phi$ .

The fluidity of the simpler liquids exhibits certain noteworthy features. In the first place, it varies but little with temperature and from one liquid to another. Thus the fluidity usually falls between 500 and 50 poise $^{-1}$  and the corresponding diffusion coefficients between  $10^{-4}$  and  $10^{-5}$  cm<sup>2</sup> sec $^{-1}$ . On the basis of the transition state theory of diffusion<sup>5</sup> it would have to be supposed that a very large fraction of the molecules (e.g., 5 to 10%) is always in the activated state and that the entropy of activation for self-diffusion is negative.

The fluidity of liquids decreases markedly with increasing pressure. In fact, Batschinski<sup>6</sup> noted that the fluidity of many liquids is nearly independent of temperature at constant volume. This generalization appears to hold at relatively high specific volumes for simple van der Waals liquids.<sup>7</sup> However, the fluidity of "associated" liquids generally, or of van der Waals liquids at small volumes, varies markedly with temperature at constant volume.<sup>7,8</sup>

<sup>4</sup> N. H. Nachtrieb and J. Petit, J. Chem. Phys. **24**, 746 (1956).

<sup>5</sup> Glasstone, Laidler, and Eyring, *Theory of Rate Processes* (McGraw-Hill Book Company, Inc., New York, 1941), pp. 477-552.

<sup>6</sup> A. J. Batschinski, Z. physik. Chem. **84**, 644 (1913).

<sup>7</sup> P. W. Bridgman, *The Physics of High Pressure* (G. Bell and Sons, London, 1949), pp. 330-357.

<sup>8</sup> J. D. Mackenzie, J. Chem. Phys. **28**, 1037 (1958).

<sup>1</sup> For general review of the glass transition see (a) W. Kauzman, Chem. Revs. **43**, 219 (1948); (b) G. O. Jones, *Glass* (Methuen and Company, Ltd., London, 1956).

<sup>2</sup> D. Turnbull and M. H. Cohen, J. Chem. Phys. **29**, 1049 (1958).

<sup>3</sup> R. E. Hoffman, J. Chem. Phys. **20**, 1567 (1952).

From its pressure dependence alone one can infer that fluidity is closely connected with the average free volume per molecule  $v_f$  defined by

$$v_f = \bar{v} - v_0, \quad (2)$$

where  $\bar{v}$  is the average volume per molecule in the liquid and  $v_0$  is the van der Waals volume of the molecule. Indeed Batschinski had suggested that the fluidity increases linearly with free volume. The important role of free volume in molecular transport also was stressed in the "hole" theories of Frenkel<sup>9</sup> and of Eyring and his associates,<sup>10</sup> and Fox and Flory<sup>11</sup> attributed the glass transition to the falling of the free volume below some critical value.

Recently Doolittle<sup>12</sup> found that the fluidity of many simple hydrocarbon liquids can be represented satisfactorily by a relation having a form quite different from Batschinski's, as follows:

$$\phi = A \exp[-bv_0/v_f], \quad (3)$$

where  $b$  is a constant of order unity. It is evident that Doolittle's equation predicts an abrupt decrease in fluidity in a narrow temperature range when  $v_f$  becomes very small. Williams, Landel, and Ferry<sup>13</sup> have in fact shown that the relaxation times for a large number of glass-forming substances are described by the Doolittle equation in the glass transition range. They took the free volume to be

$$v_f = v_g[0.025 + \alpha(T - T_g)], \quad (4)$$

where  $v_g$  is the volume at the glass-transition temperature  $T_g$  and  $\alpha$  is the difference between the thermal expansion coefficients of the liquid and the glass. F. Bueche<sup>14</sup> developed an explanation for the glass transition based on the concept, also used earlier by Barrer,<sup>15</sup> that molecular transport in liquids, though requiring little activation relative to  $kT$ , occurs mainly through the cooperation of several degrees of freedom. In this paper<sup>16</sup> we shall present an interpretation of diffusion and the glass transition in molecularly simple liquids which we believe is considerably simpler than the earlier ones. Our derivation is based on the idea that molecular transport occurs by the movement of molecules into voids, with a size greater than some

<sup>9</sup> J. Frenkel, *Kinetic Theory of Liquids* (Clarendon Press, Oxford, 1946), pp. 93-247.

<sup>10</sup> H. Eyring, *J. Chem. Phys.* **4**, 283 (1936); Hirschfelder, Stevenson, and Eyring *ibid.* **5**, 896 (1937); see also reference 5.

<sup>11</sup> T. G. Fox and P. J. Flory, *J. Appl. Phys.* **21**, 581 (1950); *J. Phys. Chem.* **55**, 221 (1951); *J. Polymer Sci.* **14**, 315 (1954).

<sup>12</sup> A. K. Doolittle, *J. Appl. Phys.* **22**, 1471 (1951).

<sup>13</sup> Williams, Landel, and Ferry, *J. Am. Chem. Soc.* **77**, 3701 (1955).

<sup>14</sup> F. Beuche, *J. Chem. Phys.* **21**, 1850 (1953); *ibid.* **24**, 418 (1956); *ibid.* **30**, 748 (1959).

<sup>15</sup> R. M. Barrer, *Trans. Faraday Soc.* **38**, 322 (1942); *ibid.* **39**, 48 (1943).

<sup>16</sup> A preliminary account of this work was presented at the Cambridge, Massachusetts meeting of the American Physical Society, March, 1959 [M. H. Cohen and D. Turnbull, *Bull. Am. Phys. Soc. Ser. II*, **4**, 157 (1959)].

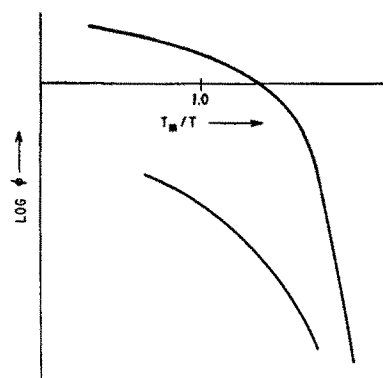


Fig. 1. Schematic representation of variation of fluidity ( $\phi$ ) of liquids with temperature. The upper curve represents simple van der Waals bonded liquids. The lower curve represents liquids bound by a continuous covalent network.  $T_m$  is the absolute melting temperature.

critical value, formed by redistribution of the free volume. This concept is analogous to that of molecular cooperation which underlies the treatments of Bueche and Barrer.

We do not propose to present here a statistical mechanical theory for liquids, but we hope that our considerations will serve to illuminate some of the main features of molecular transport in liquids and glasses.

#### TRANSPORT IN A LIQUID OF HARD SPHERES

Let us first consider molecular transport in a liquid consisting of hard spheres. In such a liquid the potential energy of a molecule is constant except that it becomes infinite upon intermolecular contact. The hard sphere model actually may approximate the behavior of simple liquids rather well. It has been shown (for example, see Vineyard<sup>17</sup>) that the potential between molecules is virtually flat in liquids of ordinary density if the force field around the molecule is spherically symmetric.

In such a system molecules move with the gas kinetic velocity  $u$  but most of the time are confined to a cage bounded by their immediate neighbors. Occasionally there is a fluctuation in density which opens up a hole within a cage large enough to permit a considerable displacement of the molecule contained by it. Such a displacement gives rise to diffusive motion only if another molecule jumps into the hole before the first can return to its original position. The correction for this correlation is similar to that deduced for crystals by Bardeen and Herring,<sup>18</sup> whose work shows that it is well within the error of the present considerations. Mangelsdorf<sup>19</sup> has pointed out that the validity of the Stokes-Einstein equation implies that, when a molecule

<sup>17</sup> G. H. Vineyard, *Liquid Metals and Solidification* (American Society for Metals, Cleveland, Ohio, 1958), pp. 1-48.

<sup>18</sup> J. Bardeen and C. Herring, in *Imperfections in Nearly Perfect Crystals*, edited by W. Shockley *et al.* (John Wiley & Sons, Inc., New York, 1952), pp. 261-289.

<sup>19</sup> P. Mangelsdorf (private communication).

moves, its cage is simultaneously in motion. Hydrodynamic considerations then show that the actual diffusion coefficient is  $\frac{3}{2}$  that computed relative to a stationary cage. This correction also lies within the limit of error of our present considerations.

Thus we treat diffusion simply as translation of a molecule across the void within its cage. In our view, diffusion occurs not as a result of an activation in the ordinary sense but rather as a result of redistribution of the free volume within the liquid. Our basic ideas are closely akin to those expressed in Rice's<sup>20</sup> normal mode analysis of diffusion in crystals.

We define the free volume  $v$  of a given molecule to be the volume within its cage less the volume of the molecule. The contribution of this molecule to the diffusion coefficient is

$$D(v) = ga(v)u, \quad (5)$$

where  $a(v)$  is roughly the diameter of the cage and  $g$  is a geometric factor.  $D(v)$  is zero unless  $v$  exceeds a critical volume  $v^*$  just large enough to permit another molecule to jump in after the displacement. Therefore the average diffusion coefficient is

$$D = \int_{v^*}^{\infty} D(v) p(v) dv, \quad (6)$$

where  $p(v)$  is the probability of finding the free volume between  $v$  and  $v+dv$ .

We must now find the average distribution of free volume  $p(v)$  for a system of hard spheres in which no energy change is associated with a redistribution of the free volume. The average free volume is

$$v_f = V_f/N, \quad (7)$$

where  $V_f$  is the total free volume and  $N$  the number of molecules. Let the total range of values of the free volume of a molecule be divided into small regions  $i$  having average value  $v_i$ . If  $N_i$  is the number of molecules having free volume in the  $i$ th region, we have

$$\gamma \sum_i N_i v_i = V_f \quad (8)$$

for the total free volume, and the total number of molecules is given by

$$\sum_i N_i = N. \quad (9)$$

Here  $\gamma$  is a numerical factor introduced to correct for overlap of free volume; it should lie between  $\frac{1}{2}$  and 1. The number of ways of redistributing the free volume without changing the  $N_i$  is

$$W = N! / \prod_i N_i! \quad (10)$$

If we require that  $W$  be a maximum for given  $N$  and

$V_f$ , we obtain in the usual way

$$N_i = \exp[-(\lambda + \beta v_i)], \quad (11)$$

where  $\lambda$  and  $\beta$  are Lagrangian multipliers. By obtaining  $\lambda$  and  $\beta$  from Eqs. (9) and (8), respectively, and passing to the continuum limit for the  $v_i$ , we obtain for  $p(v)$

$$p(v) = (\gamma/v_f) \exp[-\gamma v/v_f]. \quad (12)$$

Ordinarily,  $v^*$  is of order  $10v_f$ . Since  $D(v)$  is slowly varying, we may set it equal to  $D(v^*)$  and obtain

$$D = D(v^*) P(v^*). \quad (13)$$

Here  $P(v^*)$ , the total probability of finding a hole of volume exceeding  $v^*$ , is

$$P(v^*) = \int_{v^*}^{\infty} p(v) dv = \exp[-\gamma v^*/v_f]. \quad (14)$$

We finally obtain

$$D = ga^*u \exp[-\gamma v^*/v_f] \quad (15)$$

for the diffusion coefficient, where  $a^*$  approximately equals the molecular diameter. Equation (15) has the form found empirically by Doolittle for the fluidity of the simple hydrocarbons. To fit the experiments,  $\gamma v^*$  must be near the molecular volume, which is in accord with our model. Our result for the diffusion coefficient predicts that *liquids of even the simplest structure would go through the glass transition if sufficiently undercooled and crystallization did not occur*. Further we predict that  $D$  varies only as  $T^{\frac{1}{2}}(u \propto T^{\frac{1}{2}})$  at constant volume.

On our model the diffusion constant of impurities will be governed by molecular size. If the impurity molecule is smaller than the solvent molecule (but still very large compared with  $v_f$ ), it will diffuse at the same rate as the solvent since the diffusive transport is completed only by the jumping of a neighboring solvent molecule into the void. If the impurity molecule is larger than the solvent, the critical void for diffusion must be correspondingly larger; therefore, in this case the impurity should diffuse more slowly than the solvent.

#### INTERPRETATION OF EXPERIENCE

To test the applicability of our explanation to real liquids we have first to find an expression for the free volume. To do this we shall assume that the free volume is equivalent to the total thermal expansion at constant pressure; that is, the van der Waals volume  $v_0$  is taken to be independent of temperature. Then,

$$v_f = v_0 \left\{ \exp \left[ \int_{T_0}^T \alpha dT \right] - 1 \right\}, \quad (16)$$

where  $\alpha$  is the coefficient of thermal expansion and  $T_0$  is the temperature at which the free volume disappears. If we replace the coefficient of thermal expansion and

<sup>20</sup> S. A. Rice, Phys. Rev. **112**, 804 (1958).

TABLE I. Constants of Eq. (19) necessary to fit transport data on some simple liquids.<sup>a</sup>

Substance	Reference	Pressure range (atm.)	Temperature range °K	$g a^* u$ (cm <sup>2</sup> /sec)	$T_0$ °K	$\gamma v^*/\bar{v}_m$	$\gamma v^*/v_0$
Carbon tetrachloride	21	1-200	298-323	$1.49 \times 10^{-5} T^{\frac{1}{2}}$	80	0.75	0.86
2,3 dimethylbutane	22	...	175-308	$1.98 \times 10^{-5} T^{\frac{1}{2}}$	65	0.60	0.70
2,2 dimethylbutane	22	1-530	210-308	$1.98 \times 10^{-5} T^{\frac{1}{2}}$	90	0.58	0.665
<i>i</i> -butyl bromide	23, 24	...	110-135	...	86.5	0.60	0.69

<sup>a</sup> We took  $\alpha=0.0012$ ,  $a^*=7 \times 10^{-8}$  cm,  $g=1/6$ , and  $u=(3kT/m)^{\frac{1}{2}}$  in all cases ( $m$  is the mass of the molecule).

the molecular volume by their mean values,  $\alpha$  and  $\bar{v}_m$ , over the temperature range of interest, we obtain the following simpler approximate expression:

$$v_f = \alpha \bar{v}_m (T - T_0). \quad (17)$$

If the van der Waals volume is also independent of pressure, the pressure variation of  $v_f$  should be approximately as follows:

$$v_f = \alpha \bar{v}_m (T - T_0) - \beta \bar{v}_p \Delta P, \quad (18)$$

where  $\alpha$  and  $\bar{v}_m$  are evaluated at  $\Delta P=0$ ,  $\beta$  is the mean compressibility, and  $\bar{v}_p$  the mean molecular volume for the pressure increment  $\Delta P$ .

Substitution of (18) into Eq. (15) gives

$$D = g a^* u \exp \left[ \frac{-\gamma v^*}{\bar{v}_m \alpha (T - T_0) - \bar{v}_p \beta \Delta P} \right]. \quad (19)$$

It appears that the assumptions on which Eq. (19) is based are most likely to be fulfilled for molecularly simple liquids bound only by van der Waals forces. We shall show now how well the transport data for some of these liquids are fitted by the equation. Finally, we shall discuss the description of self-diffusion data on liquid metals.

### van der Waals Liquids

We have fitted the liquid state self-diffusion data of Watts *et al.*<sup>21</sup> on carbon tetrachloride and of McCall *et al.*<sup>22</sup> on two hexane isomers to Eq. (19) with the constants given in Table I. In this procedure  $\gamma v^*$  and  $T_0$  are the only disposable parameters. The fit to the data for 1-atmos pressure is well within the experimental scatter over the entire temperature range for all three compounds.

The measured effect of pressure increase on  $D$  in carbon tetrachloride<sup>21</sup> and 2,2 dimethylhexane<sup>22</sup> tends to be a little smaller than predicted by our equation with the compressibilities reported by Bridgman. However, the deviation is hardly outside the experimental scatter and is in the direction expected if the van der Waals volume decreases slightly with increasing

pressure. For example, McCall *et al.*<sup>22</sup> found that at 28°C a pressure increase of 530 atmos decreases  $D$  in 2,2-dimethylhexane by a factor of 2.0 which is to be compared with the factor 2.3 predicted by our equation.

Watts *et al.*<sup>21</sup> found that iodine, which has a molecular volume about one-third smaller than that of CCl<sub>4</sub>, diffuses in CCl<sub>4</sub> at a rate only 4% greater than the self-diffusion rate of CCl<sub>4</sub>. This result is in good accord with our prediction that the diffusion rate of impurity should equal that of the solvent when the size of the impurity molecule is equal to or somewhat smaller than that of the solvent molecule.

Also we have fitted our equation to data on the fluidity<sup>23</sup> and dielectric relaxation time<sup>24</sup> of undercooled *i*-butyl bromide. These data are of interest in that they extend well into the glass-transition range. As shown in Fig. 2, the data are quite satisfactorily described by an equation of the form of (24) with the constants given in Table I; in this case the pre-exponential term was treated as a disposable parameter. The agreement between the equation and the data would be still closer

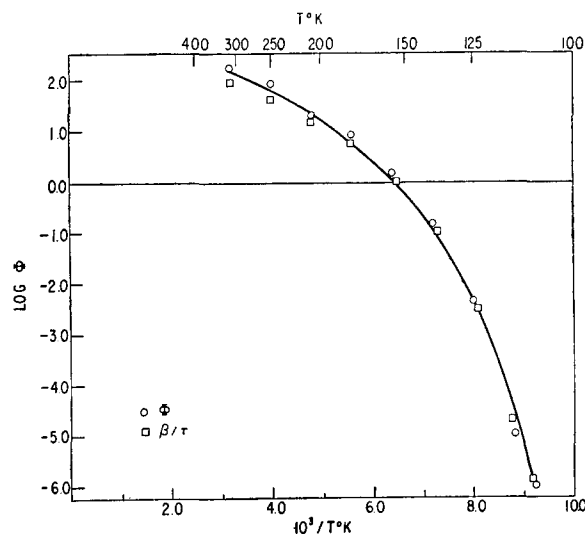


Fig. 2. Fit of Eq. (19) to fluidity<sup>23</sup> ( $\phi$ ) and dielectric relaxation time<sup>24</sup> ( $\tau$ ) data of Denney for *i*-butyl bromide.  $\beta$  is a scale factor. The equation of the solid curve, which has the same form as Eq. (19), is (in cgs units)  $f = 10^{3.1} \exp[(-0.6)/0.0012(T - 86.5)]$ .

<sup>21</sup> Watts, Alder, and Hildebrand, *J. Chem. Phys.* **23**, 659 (1955).

<sup>22</sup> McCall, Douglass, and Anderson, *Phys. Fluids* **2**, 87 (1959).

<sup>23</sup> D. J. Denney, *J. Chem. Phys.* **30**, 159 (1959).

<sup>24</sup> D. J. Denney, *J. Chem. Phys.* **27**, 259 (1957).

TABLE II. Constants of Eq. (19) necessary to fit the self-diffusion data on liquid metals.<sup>a</sup>

Metal	Reference	$\alpha \times 10^4$	$ga^*u$ (cm <sup>2</sup> /sec)	$\gamma v^*/\bar{v}_m$	$r^*$ (Å°)	Goldschmidt ion radius (Å°)	Atom radius (Å°)
Na	26	2.8	$2.16 \times 10^{-5} T^{\frac{1}{2}}$	0.236	1.22	0.95 (Na <sup>+</sup> )	1.9
Hg	3	1.8	$0.6 \times 10^{-5} T^{\frac{1}{2}}$	0.0935	0.75	1.1 (Hg <sup>++</sup> )	1.6
	4			0.103	0.775		
Ag	b	1.1	$0.76 \times 10^{-5} T^{\frac{1}{2}}$	0.312	1.04	1.13 (Ag <sup>+</sup> )	1.45
Pb	c, d	1.2	$0.64 \times 10^{-5} T^{\frac{1}{2}}$	0.133	0.92	0.84 (Pb <sup>++++</sup> )	1.75
Sn	25	1.0	$0.8 \times 10^{-5} T^{\frac{1}{2}}$	0.095	0.77	0.71 (Sn <sup>++++</sup> )	1.65
In	e	1.16	$0.81 \times 10^{-5} T^{\frac{1}{2}}$	0.115	0.81	0.81 (In <sup>+++</sup> )	1.65
Ga	4	1.08	$0.85 \times 10^{-5} T^{\frac{1}{2}}$	0.72	0.57	0.62 (Ga <sup>+++</sup> )	1.35

<sup>a</sup> We have set  $g=1/6$  and  $u=(3kT/m)^{\frac{1}{2}}$ . The critical void radius  $r^*$  was calculated with  $\gamma=1$ . The coefficients of thermal expansion are taken from *International Critical Tables* and *Liquid Metals Handbook*.

<sup>b</sup> Yang, Derge, and Kado, *Trans. Met. Soc. Am. Inst. Mining, Met., Petrol. Engrs.* **212**, 628 (1958).

<sup>c</sup> S. J. Rothman and L. D. Hall, *Trans. Am. Inst. Mining Met., Petrol. Engrs.* **206**, 199 (1956).

<sup>d</sup> J. Groh and G. von Hevesy, *Ann. phys.* **63**, 85 (1920).

<sup>e</sup> A. Lodding, *Z. Naturforschung* **11A**, 200 (1956).

if the van der Waals volume were permitted to decrease slightly with lowering temperature.

It appears that the magnitudes of the constants are reasonable in all cases. Thus, the volume  $v^*$  of the critical void is near the van der Waals volume  $v_0$  or, more specifically,  $0.66v_0 \leq v^* \leq 0.86v_0$  with  $\gamma=1$  and  $1.32v_0 < v^* < 1.7v_0$  with  $\gamma=\frac{1}{2}$ . Also the temperature  $T_0$ , which might be identified approximately with the glass-transition temperature  $T_g$ , is always near that which would be expected from the behavior of molecularly similar compounds; usually  $T_g$  for simple van der Waals liquids is  $\frac{1}{4}$  to  $\frac{1}{3}$  of the absolute normal boiling temperature.

We note also that the transport data for the fluid range at relatively high temperatures can be fitted approximately by setting  $T_0=0$  and taking a slightly different value for  $\gamma v^*$ . This results in a relation which is formally equivalent to that of Arrhenius.

### Liquid Metals

We have fitted the data on self-diffusion in liquid metals at 1 atmos pressure by Eq. (19). In these calculations we have set  $T_0=0$  so that  $\gamma v^*$  is the only disposable parameter. The required values of  $\gamma v^*$  for the different metals are given in Table II. In most cases the experimental variation of  $D$  with temperature is slightly smaller than predicted by our equation, but the deviations are well within the experimental scatter for all the metals excepting tin, for which our equation predicts a temperature coefficient about 30% larger than that found by Careri and Paoletti.<sup>25</sup>

It is evident that in liquid metals the volume  $v^*$  of the critical void is a much smaller fraction of the atomic volume than in van der Waals liquids. When we arbitrarily set  $\gamma=1$ , we find that  $v^*$  in a liquid metal is in most cases near the volume of the ion core. The radii  $r^*$  of the critical voids, calculated with  $\gamma=1$ , are com-

pared with the Goldschmidt radii  $r_i$  for the corresponding ion cores in columns 6 and 7 of Table II. Except for sodium (for which  $r^*/r_i \sim 1.3$ ) and mercury (for which  $r^*/r_i \sim 0.7$ ),  $r^*$  is very near the ion core radii corresponding to the highest valence state of the metal. Hoffman<sup>3</sup> and Nachtrieb *et al.*<sup>4,26</sup> had already noted that the Stokes-Einstein relation [Eq. (1)] could be made to hold for liquid metals by taking radii for the diffusing units near those of the corresponding ion core. Earlier, Eyring and associates<sup>5</sup> had suggested that, for liquid metal diffusion, it is only necessary that voids exist which will accommodate the ion cores.

Petit and Nachtrieb<sup>4</sup> found that the self-diffusion constants of gallium and mercury are relatively insensitive to pressure; for example,  $D$  decreases by about 25% for a pressure increase of  $10^4$  atmos. This variation is negligible compared with that (a factor of  $10+$  decrease of  $D$  for  $\Delta P \sim 10^4$  atmos) calculated from our Eq. (24) using the observed compressibilities.

However, we note that the compressibilities of metals are relatively insensitive to temperature and, according to Bridgman<sup>7</sup> and Kleppa,<sup>27</sup> increase only 10 to 20% upon melting. Further, the ratio  $\alpha/\beta$  is about 5 times greater for metallic than for van der Waals liquids. On the basis of this we suggest tentatively that the expansion of a liquid metal which occurs on heating is primarily due to the introduction of free volume while the contraction upon the application of pressure is largely due to a uniform shrinking of the electron gas, that is, in a liquid metal the temperature coefficient of  $v_0$  is small compared with that of the free volume whereas the reverse is true of the pressure coefficients. If these ideas are correct, we expect that the free volume change  $\Delta v:(\Delta P)$  upon the application of a pressure might be approximated by

$$\Delta v_f(\Delta P) = \bar{v}_p \Delta \beta \Delta P, \quad (20)$$

<sup>26</sup> R. E. Meyer and N. H. Nachtrieb, *J. Chem. Phys.* **23**, 1851 (1955).

<sup>27</sup> O. J. Kleppa, *J. Chem. Phys.* **17**, 668 (1949).

<sup>25</sup> G. Careri and A. Paoletti, *Nuovo Cimento* **2** [X], 574 (1955).

where  $\Delta\beta$  is the compressibility difference between the solid at 0°K and the liquid. Actually the pressure variation of self-diffusion in liquid mercury calculated from Eq. (19) with an estimated  $\Delta\beta$  in place of  $\beta$  is of the order of magnitude of that measured by Petit and Nachtrieb.<sup>4</sup>

We conclude that our explanation accounts qualitatively for the essential features of the atomic and molecular transport properties of simple van der Waals and metallic liquids. Indeed the model is in surprisingly

good quantitative agreement with experiment, and the values of the adjustable parameters  $\gamma v^*$  (Tables I, II) required are quite reasonable.

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## Local Steric Hindrances and Configurations of Linear Macromolecules in Solutions. I. Formulation\*

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The previous theory treating the analogous problem is developed to include rigorously the interactions between the atomic groups whose relative spatial configurations are determined by the rotational angles of two neighboring skeletal bonds. The mean-square end-to-end distances and/or the electric moments are calculated for isotactic- and syndiotactic-vinyl macromolecules as well as a few other macromolecules with similar structures. As a model for linear macromolecules is adopted, the discrete one whose each C—C bond is assumed to take only three rotational configurations (e.g., *trans*, *gauche*, and another *gauche*). In such a model the problem of taking all of the interactions between neighboring bonds into account is equivalent to that of a one-dimensional cooperative system. While the partition function of this system can be obtained easily, some techniques are required to find the mean quantities under consideration. Results obtained involve the task of evaluating the trace of a certain matrix of nine degrees. Numerical calculations by a computer and discussions of the results will be given in part II of this series.

### I. INTRODUCTION

**M**ANY experimental<sup>1-4</sup> and theoretical<sup>5-11</sup> investigations have been made on the properties of linear macromolecules with stereospecific structures in dilute solutions. Most of the theoretical investigations have calculated the mean dimensions and the electric moments since these quantities correlate closely to local isomeric structures of macromolecules and their deformations in the well-defined manner.

\* Preliminary results of this work have been published in the *Busseiron Kenkyu* **2-5**, 364 (1959).

<sup>1</sup> F. W. Peaker, *J. Polymer Sci.* **22**, 25 (1956).

<sup>2</sup> F. Ang, *J. Polymer Sci.* **25**, 126 (1957).

<sup>3</sup> F. Danusso and G. Moraglio, *J. Polymer Sci.* **24**, 161 (1957); *Makromol. Chem.* **28**, 250 (1958).

<sup>4</sup> Krigbaum, Carpenter, and Newman, *J. Phys. Chem.* **62**, 1586 (1958).

<sup>5</sup> Y. Suzuki and K. Suzuki, *Busseiron Kenkyu* **9**, 39 (1947).

<sup>6</sup> T. M. Birshtein and O. B. Ptitsyn, *Zhur. Fiz. Khim.* **28**, 213 (1954).

<sup>7</sup> R. S. Sack, *J. Chem. Phys.* **25**, 1087 (1956).

<sup>8</sup> S. Lifson, *J. Polymer Sci.* **27**, 573 (1958); *J. Chem. Phys.* **29**, 80, 89 (1958).

<sup>9</sup> M. V. Volkenstein, *J. Polymer Sci.* **29**, 441 (1958).

<sup>10</sup> K. Nagai, *Busseiron Kenkyu* **2-4**, 65 (1958).

<sup>11</sup> K. Nagai, *J. Chem. Phys.* **30**, 660 (1959).

The method of calculations is mainly that first proposed by H. Eyring.<sup>12</sup> Direct applications of his method give useful information but involve a limitation here mentioned. As an example, consider the configurations of isotactic polypropylene in solutions. As already mentioned in the previous article,<sup>11</sup> the probable rotational angles of two skeletal C—C bonds interposed between two neighboring substituted groups (which, following Lifson, we refer to as bond pairs) are  $T$  (*trans*,  $\theta=0^\circ$ )  $G$  (*gauche*,  $\theta=120^\circ$ ) or  $G'$  (another *gauche*,  $\theta=-120^\circ$ )  $T$ , if we choose adequately the relative position of each substituted group to the corresponding skeletal carbon atom. The probability of having  $TG$  followed by  $TG$  is very much larger than of having it followed by  $G'T$ , since  $GG'$  involved in the latter junction has a very high energy because of the steric hindrance between methylene groups. Consequently, the probable configuration of isotactic polypropylene seems to be the alternation of considerably long sequences of  $TG$  and those of  $G'T$  on a macro-

<sup>12</sup> H. Eyring, *Phys. Rev.* **39**, 746 (1932).