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Diffusion in Simple Liquids

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The diffusion coefficient of various tracers (H_2, T_2, Ne, Ar, CH_4) in liquid nitrogen has been determined, using the capillary technique of Anderson and Saddington, in the temperature range $70 \leq T \leq 100$°K at constant pressure of 16 atm. The experimental results can be well described by the expression $D = A \exp(-B/T)$. The B values for the various tracers turn out to be equal within the experimental errors. The A values are also independent of the mass of the tracers (absence of isotopic effect) except for a small quantum effect, and proportional to some inverse power of the molecular parameters of the tracer. The features of the present experimental results are compared with the predictions of some theories. Models which emphasize the importance of hard-core collisions or the activated process in the liquid dynamics are found in disagreement with the experimental data.

INTRODUCTION

In recent years considerable efforts have been made to understand the dynamical behavior of simple liquids either from a theoretical point of view[1] or from an experimental point of view which takes advantage of the use of inelastic neutron scattering.[2]

The main problem is, of course, the structure of the distribution functions, and recently there has been some tendency to stress the importance of hard-core collisions in determining the static and dynamic behavior of simple liquids.[3-5] The diffusion coefficient is determined essentially by the long-time behavior of the distribution function.[2] However, considerable insight about correlations in liquids can be obtained by looking at the dependence of the diffusion coefficient in binary dilute solutions of simple liquids and using the principle of corresponding states. [A similar approach[6] has been used to study correlations in solids.] For this purpose very few experimental data are available in the literature,[7-11] and they are incomplete, as far as our problem is concerned, either because they are referred to a too small number of tracers,[7,8] or because of the complication of large quantum effects,[9-11] or because they do not analyze the temperature dependence completely, and solvents for which the corresponding-state principle does not apply properly[10,11] have been used. In any event, very interesting suggestions[10] have been made as far as the D dependence on the molecular parameters is concerned, and we thought it worthwhile to study them more extensively.

For this reason we have measured the diffusion coefficient of various tracers (H_2,T_2,Ne,Ar,CH_4)[12] in liquid N_2 in the temperature range 70–100°K at constant pressure of 16 atm. All these substances obey quite satisfactorily the corresponding-state principle both for equilibrium properties[13,14] and for transport properties,[15] with well-known sets of molecular parameters.[14]

APPARATUS

The capillary method of Anderson and Saddington adapted for low-temperature work[6,16] has been used. Since in one case (Ar-N_2) the solution was heavier than the pure solvent, whereas in the other cases the pure solvent was heavier than the solution, we used two different diffusing cells (A and B) in order to avoid convection currents due to gravitational effects. The apparatus A was of the same type used before.[7] The diffusion cell B is shown in Fig. 1. In this case particular efforts were made to reduce the volume of the capillary sampling line to a minimum, in order to avoid any loss of matter in the sampling process, as discussed later.

A block diagram of the whole apparatus is shown in Fig. 2.

The procedure, to carry out an experiment, was as follows:

(1) After having evacuated the system and closed the bath-capillary valve, the solution (N_2 + tracer) is condensed in the bath through the bath line.

(2) After closing the capillary-capillary line valve and opening the bath-capillary valve for a short time, a sample of the condensed solution (standard) is taken and then transferred with the Toepler pump into a sample vial.

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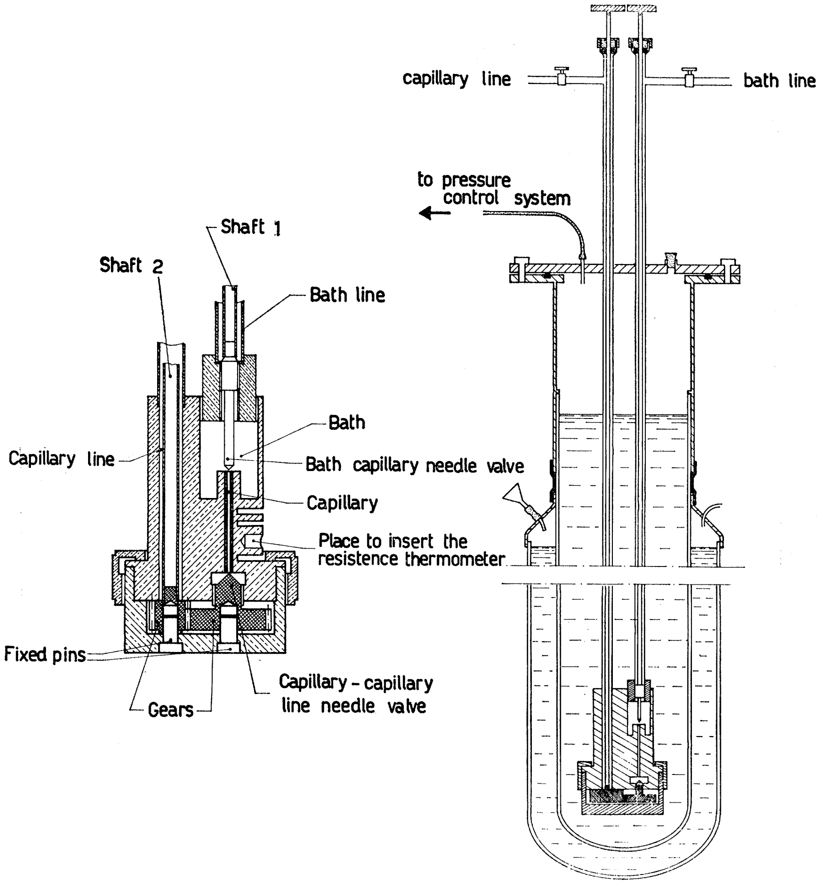

FIG. 1. Apparatus *B*. The movement of the bath-capillary needle valve is driven by the rotating shaft 1; that of the capillary-capillary line valve is driven by the rotating shaft 2 through the gears rotating on the fixed pins.

(3) Pure N_2 is liquefied in the capillary through the capillary line, fixing the pressure at the same level as for the solution in the bath. The pressures are read on the two pressure gauges with an error of ±0.5 atm. Then the capillary-capillary line valve is closed.

(4) The capillary-bath valve is opened. (At this step the diffusion period begins.)

(5) The capillary-bath valve is closed. (At this step the diffusion period ends; the time between steps 4 and 5 is the "diffusion time".)

(6) The pure N_2 in the capillary line is pumped off until a vacuum $\leq 10^{-3}$ mm Hg is reached.

(7) The sample enclosed in the capillary is transferred to a sample vial by means of the Toepler pump.

(8) Step 2 is repeated; thus it is possible to control the constancy of the bath concentration during the diffusion time.

In any transfer of samples from capillary to vials (see steps 2, 7, 8) care is taken so that the Toepler pumping

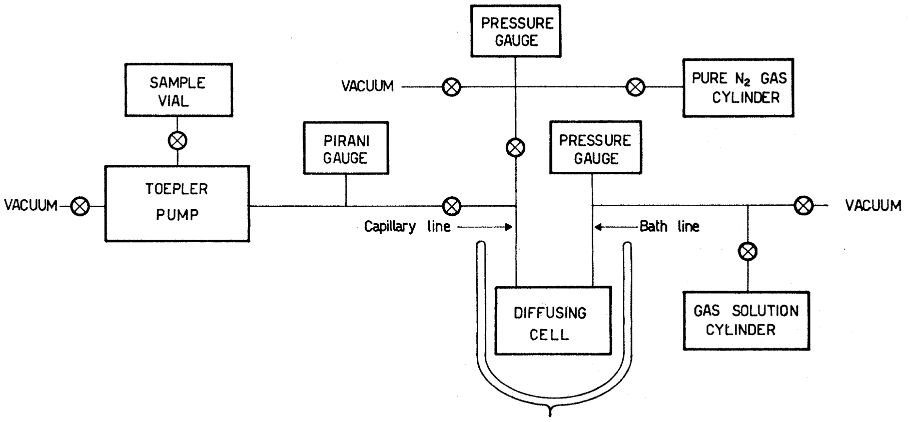

FIG. 2. Block diagram of the diffusion apparatus.

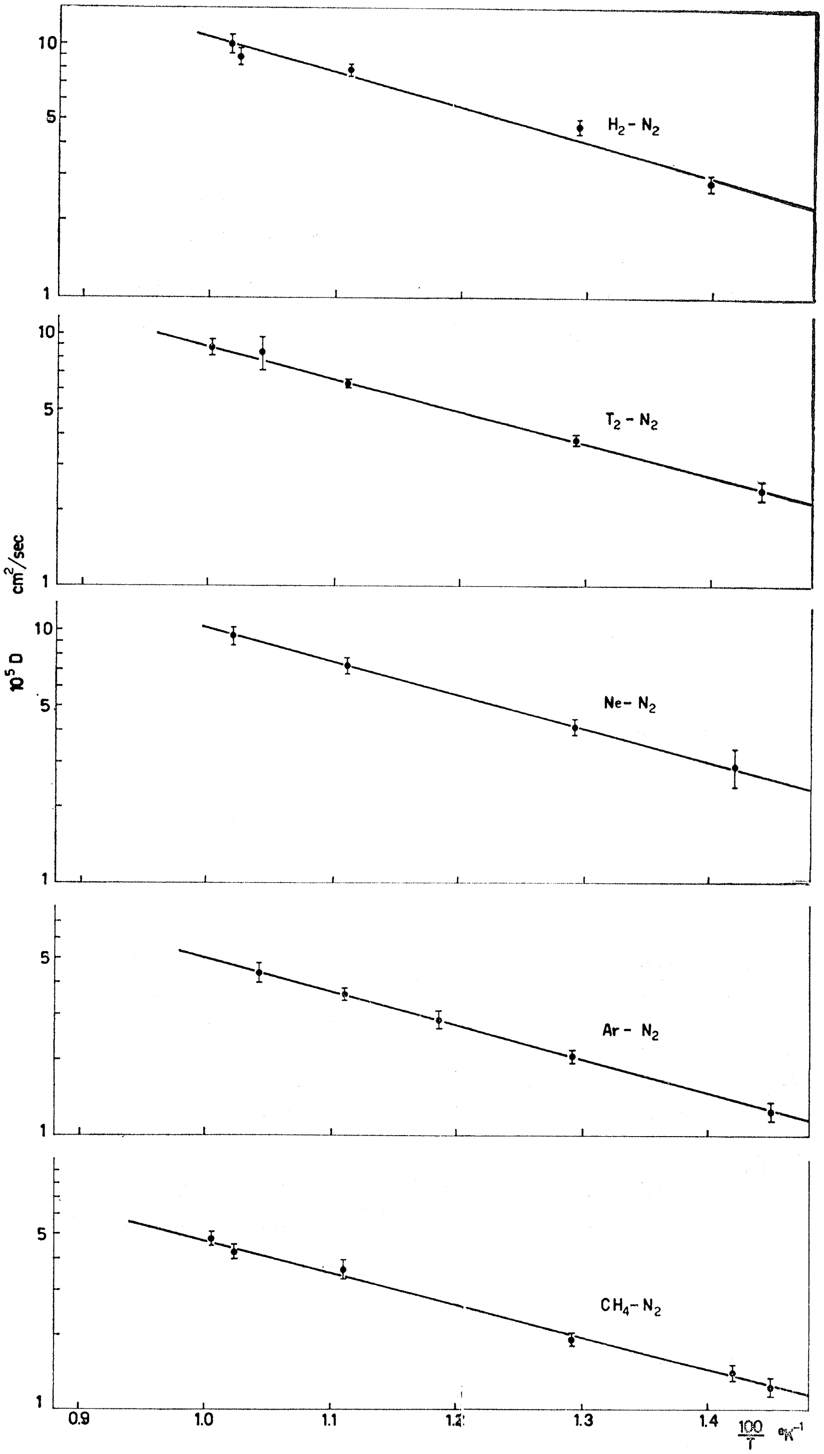

FIG. 3. Diffusion coefficient in liquid nitrogen of various tracers as a function of temperature at constant pressure of 16 atm.

continues until the gas left in the capillary line is at a pressure less than 10^{-2} mm Hg as read on the Pirani gauge. (The quantity of gas left is therefore less than 1/1000 of the gas transferred in the sample vial.) By means of the Pirani gauge it was also possible to check (after steps 1, 2, 6) that there were no leaks in the needle valves. The tracer concentration in the samples was determined by means of a G. M. internal gas counter[17] for the radioactive tracer and by means of a mass spectrometer for the stable elements (Ar,CH_4, Ne,H_2). The temperature control was achieved by regulating, with a Cartesian manostat, the pressure over

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[17] G. Cini-Castagnoli, A. Giardini, and F. P. Ricci, Nuovo Cimento **13**, 916 (1959).

the evaporating oxygen in the Dewar. The temperature was read on a Hg manometer and its constancy checked with a differential oil manometer. The temperature was constant in each run to better than 0.1°K. A copper resistance thermometer cemented to the diffusion cell was used to obtain a local temperature measurement.

EXPERIMENTAL RESULTS

The diffusion coefficient D can be evaluated by the well-known equation[7]

$$c_s-c_d/c_s-c_i=\frac{8}{\pi^2}\sum_{n=0}^{\infty}\left\{\frac{1}{(2n+1)^2}\exp\left[-\frac{(2n+1)^2\pi^2Dt}{4L^2}\right]\right\}$$

where L is the capillary length, t is the diffusion time, c_s is the concentration of standard samples (steps 2,8), c_d is the average concentration of the diffusion sample (see step 7), and c_i is the tracer concentration still present in the pure nitrogen. (For example, in the case of Ar, c_i is $<5\times10^{-4}$ as compared to $c_s\sim2\%$.) c_i is obtained by following steps 3 to 7 but omitting steps 4 and (of course) 5; i.e. with zero diffusion time.

For the T_2 the c_s concentration was $\sim10^{-6}\%$, whereas for the stable elements it was between 1–2%, so in any case we can speak in terms of dilute solutions.

The diameter d of the capillary was always 0.08 cm and the length 3.35 cm so that $d/L<0.03$.[18]

At each temperature the diffusion-coefficient measurement was repeated at least twice with different diffusing times (the diffusing time ranged from 4 000 to 14 000 sec) and the results always agreed within the experimental errors.

The errors in D were evaluated taking into account the error in the concentration determinations and that in the length of the capillary since the penetration of the needle valves gives rise to some uncertainty in L.[18]

The experimental results are summarized in Fig. 3 for CH_4-N_2, Ar-N_2, Ne-N_2, T_2-N_2 and H_2-N_2 systems. The full lines are least-squares fits of the experimental points[19] with the expression

$$D=Ae^{-B/T} \tag{1}$$

The A and B values are given in Table I. They were obtained together with their uncertainties, from the best-fit analysis.[19] We notice that although the uncertainties in the B values are quite small (a few percent), those in the A values are enhanced, according to the form of Eq. (1). Therefore also a small increase in the B uncertainty becomes quite large in A. In the case of H_2 the experimental results are less precise, because of the smaller sensitivity of the mass spectrometer to the heavier molecules. The A values will not be important in the following remarks, which are based mainly on the constancy of the B values (equal within a few percent).

TABLE I. Best-fit values of A and B in Eq. (1).

Tracer	(10^{-5} cm²/sec)	B(°K)
CH_4	94±8	298±6
Ar	112.5±3.0	310±5
Ne	204±8	301±4
T_2	172.5±12	296±6
H_2	232±47	309±16

We can compare the Ar–N_2 data with the older ones obtained by us[7] in a smaller temperature range. The agreement is satisfactory if one takes into account the different pressures at which the measurements are made.

We want to note that the expression of D in the form of Eq. (1) is just a fit to the experimental points. This fit is not enough to prove that the diffusion process is an activated one. Later in the discussion we will make clear why, in our opinion, the diffusion coefficient behaves like Eq. (1).

DISCUSSION

In analyzing the experimental data we must recall[7] that D, in the case of dilute binary solutions of liquids obeying the principle of corresponding states, must be a function of the variables ϵ_{11}, σ_{11}, m_1, ϵ_{12}, σ_{12}, m_2, T, p. Here ϵ_{ij} and σ_{ij} are the intermolecular force parameters between molecule i and molecule j. The subscript 1 refers to the solvent molecule; the subscript, 2 to the tracer.

The experimental results shown in Fig. 3 have some well-defined features.

(1) Within the experimental errors the B values of Table I (i.e. the temperature dependence of D) seem to be independent of the tracer molecular parameters. Therefore we must conclude that, at constant pressure, B must be of the form $B=f(\epsilon_{11},\sigma_{11},m_1)$ with f a function independent of the nature of the liquid. But since B must have the dimension of temperature, just by dimensional analysis one derives

$$B=C\epsilon_{11}/K \tag{2}$$

where K is Boltzmann constant and C a constant which does not depend upon the nature of the liquid but just on the pressure. In our case $C=3.05\pm0.06$; this value agrees very well also with that derived from self-diffusion in rare gases at the same pressure[20]. The validity of Eq. (2) was already pointed out in previous work,[7,9,21] but in the present case it has been verified in a wider range of temperature and with more tracers.

(2) There seems to be no dependence of D on the mass of the tracer molecule. This consideration, which

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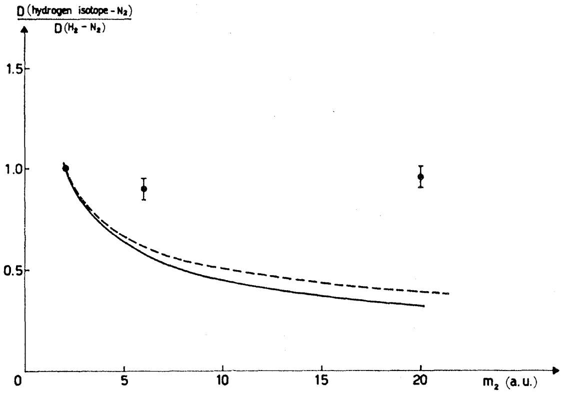

FIG. 4. Behavior of the diffusion coefficient as a function of the mass of the tracer. The value for $m=2$ has been taken as unity. The black points are experimental points deduced from the best fit of Fig. 3 and the experimental errors are shown. The full curve gives the behavior for D proportional to $1/\sqrt{m_2}$; the dashed curve, for D proportional to $1/\sqrt{\mu}=1/[2m_1m_2/(m_1+m_2)]^{1/2}$ (a.u. = atomic units).

in our opinion is of great importance, is suggested by a simple, although not rigorous, analysis of the series of H_2–N_2, T_2–N_2, Ne–N_2 results. In this case the various tracers differ only in their mass, except for the very small difference between the intermolecular potential parameters of Ne and H_2.[14] In Fig. 4 the D values for the tracers Ne, T_2, and H_2 are reported as a function of m_2 together with the curves showing the behavior under the hypothesis that $D\propto 1/\sqrt{m_2}$ and $D\propto 1/\sqrt{\mu}$ where μ is the reduced mass $2m_1m_2/(m_1+m_2)$. The points are normalized to that of H_2 at $m_2=2$ so that the curve in Fig. 4 is independent of temperature [see paragraph (1)] in the temperature range of our experimental data. The fact that Ne has molecular parameters slightly smaller than the hydrogens can explain why the experimental point is slightly higher ($\sim$15%) than the general trend exhibited from H_2 to T_2 values. However, this is a quite small correction as compared with the other curves and it is of the same order as the experimental errors.

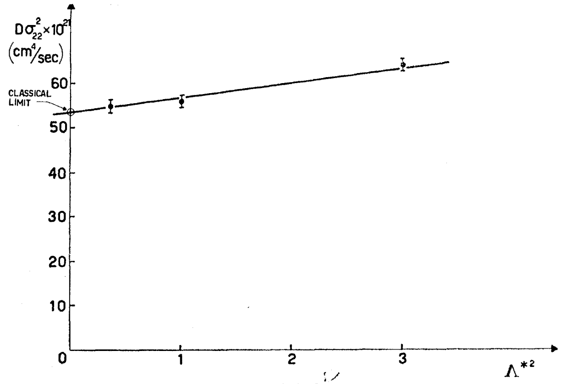

FIG. 5

FIG. 5. Diffusion coefficient at $T=90°K$ as a function of the quantum parameter in the case of H_2, T_2, and Ne tracers in liquid N_2. The experimental points are taken from the best fit of Fig. 3. The intercept with the ordinate axis, $\Lambda^*=0$, gives the diffusion coefficient of H_2 in N_2 if classical mechanics holds.

But some other points need to be considered if we want to be confident about the indications of Fig. 4. (a) We are comparing monoatomic molecules and diatomic ones. (b) The local density around different tracers can be different because of different perturbation of the impurity. (c) We must be careful about the possibility of describing the diffusion process without quantum effects.

As far as point a is concerned, the fact that we compare monoatomic molecules with diatomic ones is not a serious problem, as can be seen from the fact that the hydrogen isotopes fit well, both for equilibrium properties and for the viscosity at the same reduced temperature, the curve drawn for monoatomic substances as a function of the quantum parameter[9,14]; The same agreement holds for the transport properties in the gas phase[22] in the same range of precision as our experimental errors.

As far as point b is concerned, the only reason for a different local density around H_2, T_2, and Ne is the presence of quantum effects, since the parameters of the intermolecular potential of these tracers are practically equal. As far as we know, no measurements of partial molar volumes are available in the literature for such mixtures. However if we compare the equilibrium curves for the H_2-N_2[23] and Ne-N_2[24] systems, we can see that quantum effects must be very small. Moreover this effect, if present, would tend to enhance the diffusivity of H_2 tracer with respect to Ne tracers; therefore, it goes in the wrong direction if we would like to restore the classical $1/\sqrt{m_2}$ law.

As far as point c is concerned, we refer to the Hildebrand analysis[11] to show that the quantum deviations are of the same order as the experimental errors.

Using our Ne-N_2, T_2-N_2 and H_2-N_2 results, we draw in Fig. 5 a plot of the same type of Fig. 1 of Ref. 11 and we can see how for H_2 in liquid N_2 the quantum effect is less than 20%, compared with a factor of 2 for CCl_4 solvent. In fact the internal pressure in liquid N_2 is much smaller than in liquid CCl_4, and the importance of this quantum effect has been supposed to be proportional to the internal pressure of the solvent.[11] Moreover, we would like to mention that just these quantum effects explain the small D dependence on the tracer mass shown in Fig. 4. Therefore we can conclude that in first approximation these simple arguments support the indication that, as far as classical mechanics holds, D does not depend on the tracer mass. We would like to point out that such a feature also explains our previous results of diffusions in liquid hydrogen.[9] Certainly a

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[24] W. B. Street, Cryogenics 5, 27 (1965).

more rigorous analysis would be desirable but it seems to us that it would produce little change in the above conclusion.

(3) As far as the D dependence on ϵ_{ij} and σ_{ij} is concerned, the situation is less clear, since we do not have a group of tracers which differ among them only by the ϵ (or σ) values, in order to repeat the unambiguous analysis of point 2.

As mentioned before, Hildebrand and co-workers, just on the basis of the correlation of experimental data, suggest

$$D=(1/\sigma_{22}^2)f(\epsilon_{11},\sigma_{11},m_1,p,T). \qquad (3)$$

The check they used is to verify the constancy of $D\sigma_{22}^2$ for a group of tracers in a given solvent. This is just a tentative correlation, by no means the only possible one, and it is not based on a definite model. Moreover we do not understand how σ_{22} can have a definite meaning in a dilute solution where tracer-tracer interactions are negligible. In Table II our data are compared in Hildebrand's way and we can see how there seems to be a little discrepancy when ϵ_{12} changes significantly. Another check can be made if we write out Eq. (3) explicitly, taking into account the D dependence in Eq. (1) and the result of Eq. (2). We have, just by the dimensional analysis, that at constant reduced pressure $p^*=p\sigma_{11}^3/\epsilon_{11}=6\times10^{-2}$, for dilute binary solutions

$$D=1.4\frac{\sigma_{11}^3}{\sigma_{22}^2}\sqrt{\epsilon_{11}/m_1}\exp\left(-\frac{3.05\epsilon_{11}}{kT}\right), \qquad (4)$$

where we have used the Ar–N_2 data to deduce the number 1.4.

If, using Eq. (4), we are going to calculate the self-diffusion in Ar, in the temperature range $0.75\sim kT/\epsilon_{11}\leq1.04$ and at the reduced pressure of $p^*\sim6\times10^{-2}$, we find a discrepancy, independent of temperature of about a factor of 2 between the prediction of Eq. (4) and the experimental results.[20] Therefore we can conclude that Hildebrand's suggestion is a rather rough approximation. Our data show that in a phenomenological expression like Eq. (4) we must introduce a $(1/\epsilon_{12})^g$ dependence, where g is a positive number. However we will not attempt to find such a relationship, because it is meaningless unless it is suggested by a model.

In any case, as far as Fig. 5 is concerned we do not expect any change, since the comparison of Ne and H_2 involves very little change in molecular parameters. Therefore a first approximation such as Hildebrand's rule is satisfactory.

We want now to compare the features of our experimental results (as expressed in the preceding paragraphs) with some theoretical predictions. We start with the problem of the dependence of D on the mass of the tracer (isotopic effect).

TABLE II. Comparison between experimental results and Hildebrand's rule.

Tracer	σ_{22} (Å)	$10^{21}D\sigma_{22}^2$ (cm^4/sec)
Ar	3.42	44.0
CH_4	3.80	46.5
H_2(classical limit)	2.96	54.0

Models giving great importance to binary collisions, such as hard-sphere assemblies[25] or the improved versions using the square-well fluid model,[26,27] predict that D should go as $1/\sqrt{\mu}$, which is clearly in contradiction with our experimental results as shown in Fig. 4. The uncertainty in the meaning of binary collisions in a fluid at liquid density is certainly the most serious defect of the approach. In this respect it would be interesting to test the Rice-Alnatt theory[4], which supposes that it is possible to describe the basic dynamical event as a hard-core collision followed by a quasi-Brownian motion with time scales well separated. However, we prefer to await constant-density experiments, since the dependence on tracer mass in this theory is less severe than in the hard-sphere models, because of the relative importance of the hard-core and the soft part of the friction coefficient.

Also, models which consider the diffusion process as an activated one in which a particle jumps from one equilibrium site to another, flying over a barrier of height measured by the activation energy of the process,[28] are in disagreement with our data, because in that case it is to be expected that D will be proportional to $1/\sqrt{m_2}$. This disagreement raises doubts about the solid-like behavior of simple liquids,[29] except the small cage effect, as revealed by inelastic neutron scattering on liquid argon.[30]

On the other hand, a statistical-mechanical theory of the diffusion coefficients in binary liquid solutions developed by Bearman[31] following the definition of a mean frictional force satisfies the experimental result that D is independent of m_2.[32]

Finally if we consider the temperature dependence of the diffusion coefficient (i.e. paragraph 1), we can understand whether an Arrhenius law seems to be satisfied without involving an activated process, or the pseudoactivation energy is not dependent on the tracer

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molecular parameters, according to the model of Cohen and Turnbull,[33] who suggest that the fluidity of a liquid is given by the possibility of correlations in free volumes similarly to the Rice normal-mode analysis of diffusion in crystals.[34] In fact the pseudo-activation energy of the process should vary with the molecular parameters of the tracers only insofar as its diameter increases much over the diameter of the solvent molecule. Where the Cohen-Turnbull theory is very rough indeed is in the mechanism by which the diffusing molecule moves once the step has been made possible by the free-volume fluctuations. In this respect also the refinement by Naghizadeh[35] does not give any better improvement and leaves $D \propto 1/\sqrt{m_2}$.

Probably the free movement in the enlarged cage should be replaced by a quasi-Brownian motion, but this is not a simple change in the Cohen-Turnbull theory, since it will involve the condition under which a free-volume fluctuation is useful for the diffusive steps to start. Incidentally, we must point out that the discrepancies found[20] between self-diffusion data and the Cohen-Turnbull theory are mainly connected with the pre-exponential factor which is given by just those features of the model we do not rely on.

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Elementary Excitations in Classical Liquids*

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Collective dynamical variables in classical liquids, having the character of longitudinal and transverse phonons, are proposed. A variational argument is used to determine their frequency spectrum; the sound velocities of long-wavelength modes are determined by elastic moduli of the liquid. Their lifetimes are estimated, and turn out to be of the order of 10^{-13} sec for normal liquids, but much longer for highly viscous liquids (glasses).

I. INTRODUCTION

THE question to be discussed here is: Do there exist collective variables, in classical liquids, analogous to longitudinal and transverse phonons in solids? The answer to this question is a qualified "yes". A physically reasonable basis can be found for the construction of longitudinal and transverse phonons in classical liquids, and it is possible even to calculate their frequency spectrum. The physical existence of these phonons is more doubtful. Except for liquids at very low temperatures, e.g., in the glassy state, their lifetimes are expected to be very short.

In this paper, I discuss the mathematical and physical basis for the construction of phonons in liquids, and I give some estimates of their dispersion and lifetimes.

II. DEFINITIONS

The concept of an elementary excitation is very familiar in connection with the theory of solids and also the theory of superfluids. In solids, for example, the dynamical behavior of a lattice is usually discussed by means of normal modes of vibration; these are the longitudinal and transverse phonons. Internal electronic states are described by excitons. Excitations in superconductors are described by Cooper pairs. Excitations in liquid helium are described by longitudinal phonons and by rotons. And so on.

All these elementary excitations are used in what is essentially a quantum-mechanical way. That is, creation and annihilation operators, in the language of second quantization, are used to characterize states of excitation of a system from its quantum-mechanical ground state.

The same language could be used, in principle, to describe classical systems also (e.g., liquid xenon); but a quantum-mechanical description is extremely cumbersome because of the high degree of excitation involved. For classical liquids it seems far simpler to use a characteristically classical description in the first place.

But then what classical quantities correspond to elementary excitations in quantum mechanics? The following definition appears reasonable.

First, we recall that a characteristic property of any elementary excitation (in quantum mechanics and in the classical limit) is that it varies approximately periodically with time. Let A be some property of the system,

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