PHYSICAL REVIEW B VOLUME 19, NUMBER 12 15 JUNE 1979

# Diffusion coefficients of $^{124}$Sb, $^{113}$Sn, $^{110m}$Ag, and $^{195}$Au in liquid copper

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(Received 15 November 1978)

Measurements of the diffusion coefficient of $^{124}$Sb, $^{113}$Sn, $^{110m}$Ag, and $^{195}$Au in liquid copper are made using a shear-cell device which provides accurate data. The experimental diffusion coefficient is given by $D_i = CD_i^E$, where $D_i^E$ is obtained using Enskog's theory and $C$ is a correction factor accounting for dynamical correlation effects. $C$ is a function of the fluid density and of the relative mass and size of the solute with respect to the solvent. The data show that among the solutes smaller in size and mass than the solvent, those of larger mass and smaller size tend to diffuse more rapidly than predicted by Enskog's theory. For solutes larger and heavier than the solvent, the diffusion coefficient tends to increase with their mass and size.

## I. INTRODUCTION

In view of their prominent role in metallurgical phenomena such as nucleation and growth processes during the solidification of alloys, it is of primary importance to have a good knowledge of diffusion coefficients in liquid metals. In contrast to the work done in solids, impurity diffusion has not been studied extensively in liquid metals because of the inherent experimental difficulties namely: (i) diffusion into the container has to be avoided, which explains why most of the data published in the literature are concerned with metals of low melting temperature and of low vapor pressure; (ii) the control of sample purity is made difficult by the high reactivity of liquids and the large diffusion coefficients of impurities; and (iii) temperature and concentration gradients may induce convection currents so that the experiments must be conducted in small-diameter samples, thereby reducing the accuracy of the measurements and increasing spurious surface effects.

Among the different methods used for measuring diffusion coefficients in liquid metals, the most common is the capillary-reservoir technique.[1] A capillary container, sealed at one end, is filled with the dilute liquid alloy and immersed in a much larger vessel containing a large volume of the pure host liquid metal. The profile of the solute concentration along the capillary, when fitted to the appropriate solution to Fick's second law, provides a value of the solute diffusion coefficient. Large experimental corrections[2] must be made however because of the following points: (i) solute diffusion occurs during heating and cooling from the diffusion temperature; (ii) large solute segregation may occur during the nonuniform solidification of the sample, as was emphasized by Nachtrieb[2]; and (iii) since the accumulation of solute atoms at the open end of the capillary is usually prevented by stirring the reservoir liquid, convection currents are induced in the vicinity of the open end of the capillary. Corrections to the length of the sample must be made, which lead to a rather large uncertainty in the measurements. In the experiments described in Sec. II of the present paper, a shear cell is used, eliminating most of these uncertainties and corrections.

From a theoretical point of view, self-diffusion and impurity diffusion in liquid metals are qualitatively well understood. Enskog's theory of dense fluids[3] has been corrected by Alder *et al.*[4,5] to account for dynamical correlations. Hence the diffusion coefficient $D_i$ of species $i$ in a liquid is usually written $D_i = D_i^E C_{AW}$, where $D_i^E$ is the diffusion coefficient calculated according to Enskog's theory and $C_{AW}$ is a correlation factor accounting for these correlations. After a computer simulation, Alder *et al.* showed that $C_{AW}$ depends on the fluid density and on the relative mass and size of the solute with respect to the solvent. Using this type of approach, Protopapas *et al.*[6] have been able to calculate the self-diffusion coefficients of a number of liquid metals. Despite its phenomenological character, this theory accounts fairly well for the experimental values of self-diffusion coefficients and their variation with temperature.

On a more fundamental footing, the detailed calculations of the velocity autocorrelation function by Resibois[7] agree with the computer calculation of Alder *et al.* Since most of his work is concerned with self-diffusion however, we shall give in Sec. IV an interpretation of our results in the framework of the Enskog theory, corrected according to the model of Protopapas *et al.* for self-diffusion.

## II. EXPERIMENTAL PROCEDURE

In order to avoid most of the drawbacks presented by the capillary-reservoir technique, a shear cell has been constructed to determine the diffu-

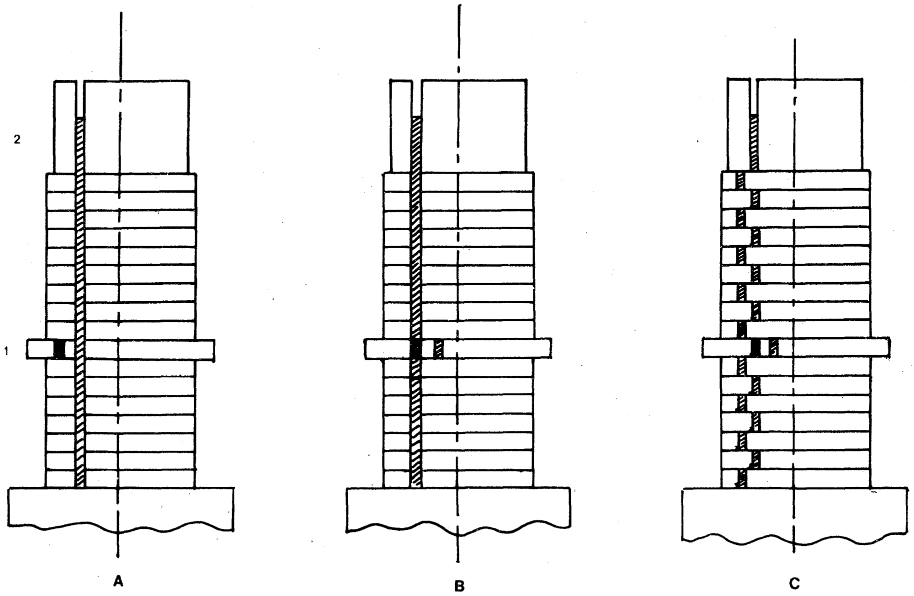

FIG. 1. Schematic representation of the shear cell: (1) intermediate disk with radioactive alloy; (2) filling reservoir: A, configuration of the cell during the heating of the system; B, the radioactive isotope is put into contact with the long capillary; C, at the end of the diffusion run, each capillary is sectioned into 20 beads.

sion coefficients of radioisotopes in liquid copper (Fig. 1). The cell consists of a stack of 20 disks, 4 mm thick and 42 mm in diameter, in which two holes of 1.5 mm in diameter are bored. The mechanical arrangement of the system makes it possible to rotate the disks with respect to one another, from outside the furnace. A typical experiment proceeds as follows.

(a) Both capillaries are initially filled with a solid rod of pure (99.999%) copper supplied by the Materials Research Corp. Two short pieces of a dilute alloy of copper with the radioactive solute are inserted in two holes bored in an intermediate disk located in the middle of the stacking. During the initial stage of the experiment, no contact is allowed between this alloy and the long capillaries of pure copper.

(b) When it is appropriately filled with pure copper and the radioisotopes, the shear cell is introduced in a furnace and heated with a graphite resistor under helium atmosphere. The temperature gradient along the cell is smaller than 2 K $\mathrm{cm}^{-1}$. Therefore no thermally induced convection currents are expected in the capillaries, as the critical gradient is about 500 $\mathrm{K\,cm}^{-1}$ for the geometry used in the present experiment.

(c) When the desired temperature is obtained in the furnace, the intermediate disk is rotated from outside the furnace until a perfect contact is ensured between the thin layer of radioactive alloy and the two halves of each capillary. This operation accurately determines the beginning of the diffusion run.

(d) At the end of the diffusion run each disk is rotated with respect to its neighbors; this operation takes place at the diffusion temperature and determines the end of the diffusion run. Hence each capillary is sectioned into 20 beads which are subsequently extracted from the disk and whose radioactivity is measured using a standard NaI-Tl analyzer.

The theoretical solute concentration $c_\alpha(x,t)$ along each capillary is given by the solution to Fick's equation

$$\frac{\partial c_\alpha}{\partial t} = D_\alpha \frac{\partial^2 c_\alpha}{\partial x^2} \tag{1}$$

in an infinite medium, with the initial condition

$$c_\alpha(x,0) = c_0 \Theta(x+h)[1-\Theta(x-h)], \tag{2}$$

where $2h$ is the thickness of the intermediate disk in which the alloy of initial concentration $c_0$ is inserted, and $\Theta(x)$ is the step function.

The diffusion coefficients of radioisotopes in liquid copper are obtained by a least-square fitting of the experimental concentration profile to the solution of Eq. (1):

$$c(x,t) = \frac{c_0}{2}\left[\operatorname{erf}\left(\frac{h-x}{2\sqrt{Dt}}\right) + \operatorname{erf}\left(\frac{h+x}{2\sqrt{Dt}}\right)\right]. \tag{3}$$

## III. EXPERIMENTAL RESULTS

In order to investigate the influence of the parameters pertaining to solute atoms (mass, size, valence, etc.) on their diffusion coefficient in copper, a systematic program of measurements has been planned. The diffusion coefficient of some impurities belonging to the copper, silver, and gold series of the Periodic Table have been measured in a fairly large temperature range. In

TABLE I. Diffusion coefficient of $^{110m}$Ag in liquid Cu.

| $T$ (K) | 1423 | 1463 | 1523 | 1610 | 1721 | 1825 | 1925 |
|---|---|---|---|---|---|---|---|
| $t$ ($10^3$ sec) | 7.2 | 7.2 | 7.8 | 1.8 | 3.6 | 2.4 | 2.4 |
| $D$ ($10^{-5}$ cm$^2$ sec$^{-1}$) | 3.42 | 3.65 | 4.48 | 4.76 | 5.95 | 7.0 | 7.65 |
|  | 3.45 | 3.70 | 4.49 | 5.15 | 5.97 |  |  |

TABLE II. Diffusion coefficient of $^{113}$Sn in liquid Cu.

| $T$ (K) | 1383 | 1458 | 1515 | 1548 | 1666 | 1773 |
|---|---|---|---|---|---|---|
| $t$ ($10^3$ sec) | 7.8 | 6.6 | 5.52 | 3.00 | 3.60 | 2.70 |
| $D$ ($10^{-5}$ cm$^2$ sec$^{-1}$) | 2.85 | 4.00 | 4.38 | 5.51 | 6.11 | 7.56 |
|  | 2.92 | 4.10 | 4.48 | 5.57 | 6.12 | 7.90 |

TABLE III. Diffusion coefficient of $^{124}$Sb in liquid Cu.

| $T$ (K) | 1373 | 1413 | 1443 | 1473 | 1513 | 1573 | 1613 | 1673 | 1718 | 1773 | 1838 |
|---|---|---|---|---|---|---|---|---|---|---|---|
| $t$ ($10^3$ sec) | 3.6 | 3.6 | 1.8 | 3.6 | 2.7 | 2.7 | 1.92 | 3.6 | 2.7 | 2.7 | 2.7 |
| $D$ ($10^{-5}$ cm$^2$ sec$^{-1}$) | 4.08 | 4.15 | 4.92 | 4.42 | 4.90 | 5.52 | 5.60 | 6.35 | 6.69 | 7.20 | 7.30 |
|  | 4.12 | 4.23 |  | 4.54 | 4.97 |  | 6.26 |  | 6.85 |  | 7.85 |

TABLE IV. Diffusion coefficient of $^{195}$Au in liquid Cu.

| $T$ (K) | 1373 | 1406 | 1473 | 1523 | 1603 | 1663 | 1673 | 1728 | 1823 |
|---|---|---|---|---|---|---|---|---|---|
| $t$ ($10^3$ sec) | 6.9 | 6.5 | 7.2 | 7.5 | 7.2 | 7.5 | 6.9 | 5.4 | 5.4 |
| $D$ ($10^{-5}$ cm$^2$ sec$^{-1}$) | 3.34 | 3.45 | 3.80 | 4.39 | 4.95 | 5.20 | 5.40 | 5.33 | 6.53 |
|  | 3.36 | 3.46 | 3.86 | 4.40 | 4.97 | 5.20 |  | 5.85 | 6.71 |

TABLE V. Values of the exponent $n$ and of coefficients $A$ and $B$ for the diffusion of $^{124}$Sb in liquid copper, according to Eq. (4), in the temperature range 1356–1700 K.

| $n$ | $\frac{1}{2}$ | 1 | 2 | 2.38 | $-1$ |
|---|---|---|---|---|---|
| $A$ (cm$^2$ sec$^{-1}$ K$^{-n}$) | $6.42\times10^{-6}$ | $8.2\times10^{-4}$ | $2.65\times10^{-11}$ | $1.3\times10^{-12}$ | $-0.192$ |
| $B$ (cm$^2$ sec$^{-1}$) | $-1.99\times10^{-4}$ | $-7.38\times10^{-5}$ | $-1.09\times10^{-15}$ | 0 | $1.78\times10^{-4}$ |

Tables I–IV we report measurements of the diffusion coefficient of $^{110m}$Ag, $^{113}$Sn, $^{124}$Sb, and $^{195}$Au in liquid copper, from 1373–1900 K. For each run, the values of the diffusion coefficient measured in the two independent capillaries are given, showing that the reproducibility of the experiments is fairly good.

The temperature dependence of the diffusion coefficient $D$ can be expressed through different laws. As $D$ increases relatively slowly with temperature, this temperature dependence can be represented by different power laws in the temperature range explored. In Table V, for instance, we report calculated values of $A$, $B$, and $n$ leading to good fits of the experimental data for $^{124}$Sb in Cu to a power law of the type

$$D = AT^n + B. \tag{4}$$

In order to make a comparison between the diffusion coefficients of the four isotopes investigated in the present work, we write the impurity diffusion coefficient as

$$D = A'(T - T_m) + B', \tag{5}$$

where $T_m = 1356$ K is the melting temperature of pure copper and we give values of $A'$ and $B'$ in Table VI for $^{110m}$Ag, $^{113}$Sn, $^{124}$Sb, and $^{195}$Au.

In Fig. 2 our experimental results are compared with those given by Henderson and Yang[8] for the self-diffusion coefficient in liquid copper, by Ejima and co-workers[9] for Sb and Ag and with the data obtained by Kado and Ohno[10] for Ag. Although the diffusion coefficients obtained in the preceding investigations are of the same order of magnitude as those obtained in the present work, the marked discrepancy between the different data can be traced to the difference in the experimental technique used to measure $D$. Since our experimental method is free of many of the drawbacks of the capillary-reservoir technique, we shall use our results in the following discussion.

## IV. INTERPRETATION OF THE EXPERIMENTAL RESULTS

The discussion of our experimental results will be based on the following scheme.

(i) From the theory of transport phenomena in dense gases and liquids derived from the Enskog theory,[3] we can get a crude estimation of the diffusion coefficient $D_i^E$ of an impurity in a liquid metal.

(ii) It is well known however that dynamical correlations, which are neglected in this estimation, play an important role in determining the diffusivity of a given atom. These correlations, usually calculated using molecular dynamics, depend on the density of the fluid and on the mass and size of the solute relative to solvent atoms. These correlations are expressed as the ratio $C$ of the true diffusion coefficient to the diffusion coef-

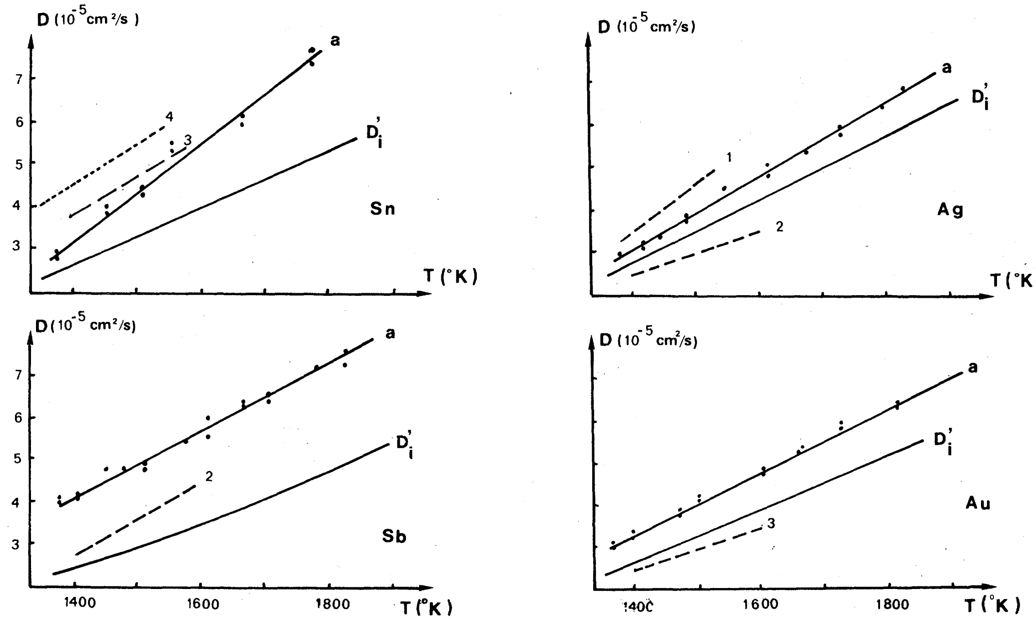

FIG. 2. Experimental data obtained for the diffusion coefficient of Ag, Sn, Sb, Au, plotted against temperature [solid line (a)]. $D_i'$ is the Enskog diffusion coefficient corrected for density [Eq. (12) in the text]. Curve (1) represents the experimental data published in Ref. 10, curves (2) and (3) correspond to data of Ref. 9, and curve (4) refers to the self-diffusion coefficient measured in Cu (Ref. 8).

ficient obtained using the Enskog theory. Therefore we calculate $D_i^E$ and thus obtain an experimental value for the correction factor $C$.

### A. Enskog's diffusion coefficient $D_i^E$

The hard-sphere model has been developed by Protopapas and co-workers to calculate self-diffusion coefficients in a number of liquid metals,[6] shear viscosity coefficients of pure liquids[11] and of binary alloys.[12] The starting point of the calculation is the Enskog approximation, extended to binary hard-sphere liquids by Thorne.[3,13,14] As in our experiments $n_i$ the number density of solute atoms, is very small with respect to $n_s$, the number density of solvent atoms, the diffusion coefficient $D_i^E$ of the solute is given by

$$D_i^E = \frac{3}{8 n_s g_{is}(\sigma_{is}) \sigma_{is}^2} \left( \frac{kT}{2\pi\mu} \right)^{1/2}, \tag{6}$$

where $\mu = m_i m_s / m_i + m_s$ is the reduced mass, $\sigma_i$ and $\sigma_s$ are the hard-sphere diameters of solute and solvent atoms, respectively, $\sigma_{is} = \frac{1}{2}(\sigma_i + \sigma_s)$, and $g_{is}(\sigma_{is})$ is the value of the pair-correlation function $g_{is}(r)$ for different atoms evaluated at contact of the hard spheres. Therefore in a binary mixture we have to evaluate $\sigma_i$, $\sigma_s$, and $g_{is}(\sigma_{is})$ in order to compare Eq. (6) with the experimental data.

In the theory of Protopapas and co-workers, the hard-sphere diameter $\sigma$ is chosen as an average distance of closest approach of the atoms in the fluid. As the temperature increases, the energy of the collision increases and $\sigma$ decreases according to the simple law

$$\sigma = \sigma_0 [1 - 0.112 (T/T_m)^{1/2}]. \tag{7}$$

In this expression, $T_m$ is the melting temperature and $\sigma_0$ is the distance at which the interatomic potential assumes its minimum value; in principle $\sigma_0$ can be chosen to give a good fit to the first peak of the structure factor[15] as measured by x-ray or neutron scattering. Using a simple model to calculate $\sigma$, Protopapas and co-workers show that in a pure metal a reasonable value of $\sigma_0$ is given by

$$\sigma_0 = 1.0878 n_m^{-1/3}, \tag{8}$$

where $n_m$ is the number density of the liquid at its melting temperature. According to this model, we calculate the hard-sphere diameters $\sigma_i(T)$ and $\sigma_s(T)$ of pure solute and pure solvent and we assume that these (functions of $T$) remain unaltered after alloying.

Owing to the lack of an experimental determination of $g_{is}(\sigma_{is})$ in the binary alloys investigated in the present paper, we must evaluate this quantity using a specific model. In liquid mixtures, Bertucci and Flygare[14] make use of a phenomenological radial distribution function at contact which is a linear combination of $g_{is}^c$ taken from the scaled-particle theory[16] and $g_{is}^v$ given by the Lebowitz solution of the Percus-Yevick equation for mixed hard spheres.[17] In the present paper we prefer to use the expression of $g_{is}$ given by Protopapas and Parlee,[12] relevant to infinite dilution:

$$g_{is}(\sigma_{is}) = \frac{(2 - y_s)}{(2 + y_s)(1 - y_s)^3} \left[ 1 + y_s \left( \frac{2\sigma_i - \sigma_s}{\sigma_i + \sigma_s} \right) \right], \tag{9}$$

where $y_s = \frac{1}{6}\pi n_s \sigma_s^3$ is the packing fraction of the pure host metal. This expression of $g_{is}$ is shown in Ref. 12 to satisfy almost exactly the Carnahan-Starling equation of state for binary hard-sphere liquids.

TABLE VI. Coefficients $A'$ and $B'$ defined in Eq. (5) for the diffusion of $^{110m}$Ag, $^{113}$Sn, $^{124}$Sb, and $^{195}$Au in liquid copper.

| | $^{110m}$Ag | $^{113}$Sn | $^{124}$Sb | $^{195}$Au |
|---|---|---|---|---|
| $A'$ ($10^{-8}$ cm$^2$ sec$^{-1}$K$^{-1}$) | 8.5 | 12.0 | 8.2 | 7.3 |
| $B'$ ($10^{-5}$ cm$^2$ sec$^{-1}$) | 2.87 | 2.73 | 3.82 | 3.11 |

### B. Correction factor to the Enskog diffusion coefficient

The discrepancy between $D_i^E$ and the experimental data can be traced to many-body correlations in the liquid phase. These correlations have been shown by Alder and co-workers,[4,5] using molecular-dynamics simulation, to depend strongly on the density of the fluid and on the relative mass and size of the solute atom with respect to the solvent. Therefore, we write the diffusion coefficient of species $i$ in the solvent as

$$D_i = D_i^E C(v/v_0, \Delta M, \Delta\sigma), \tag{10}$$

where $v/v_0 = \pi\sqrt{2}/6y_s$, $\Delta M = m_i - m_s$, and $\Delta\sigma = \sigma_i - \sigma_s$.

In the correction factor $C$, it is possible to separate the variation with density which we write $C_1(v/v_0)$ from the dependence on the mass and size of the solute atom $C_2(\Delta M, \Delta\sigma)$. In pure fluids, $C_1(v/v_0)$ has been extensively studied by Alder *et al.*[4] who showed that $C_1$ varies very rapidly with $v/v_0$ in the high-density region, relevant to liquid metals. In view of the very large dilution of the alloys used in the present work, we may assume that $C_1(v/v_0)$ for the alloy is correctly approximated by the value obtained by Alder for the host metal at the same temperature. Actually, we used the interpolation formula given by Bertucci and Flygare[14] to calculate $C_1$:

$$C_1\left(\frac{v}{v_0}\right) = -3.5\left(\frac{v}{v_0}\right)^2 + 13.45\left(\frac{v}{v_0}\right) - 11.72. \tag{11}$$

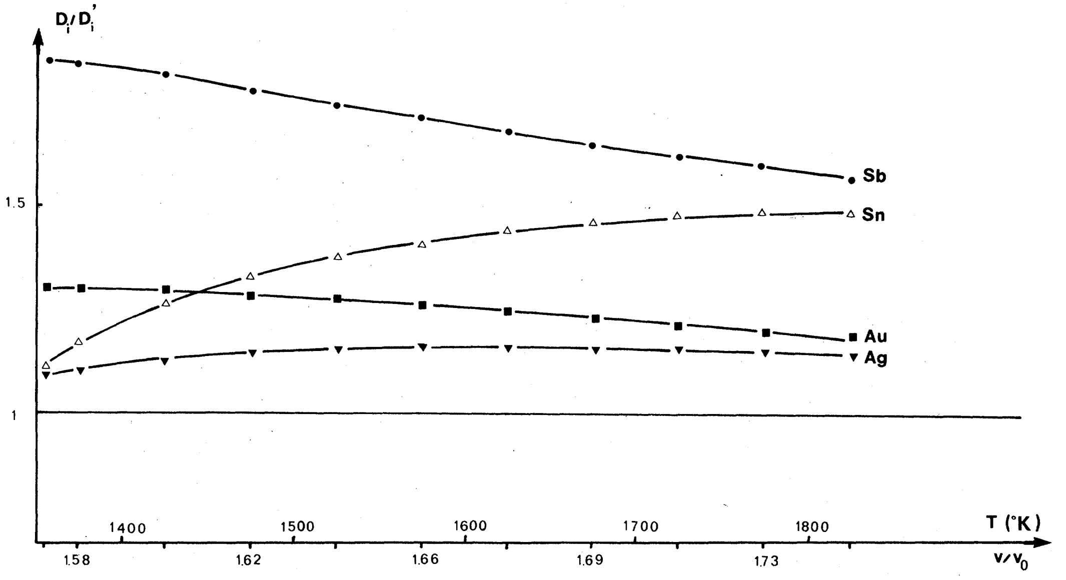

FIG. 3. Ratio $D_i/D_i'$ of the measured diffusion coefficient $D_i$ to the coefficient $D_i'$ corrected from Enskog's theory for density effects.

Using Eq. (8) to calculate $\sigma_0$ for each atom of the binary mixture, we obtain $\sigma_s(T)$ and $\sigma_i(T)$ from Eq. (7), $g_{is}(\sigma_{is})$ from (9), and the diffusion coefficient

$$D_i' = D_i^E C_1(v/v_0) \qquad (12)$$

corrected by $C_1$ from the value $D_i^E$ given by the Enskog theory.

The calculated values of $D_i'$ are given in Fig. 2 for the four solute atoms Ag, Au, Sn, Sb and compared with the experimental data. This comparison provides an estimation of the correlations due to the fact that the diffusing species are different from the solvent in size, mass and chemical nature. In order to study these correlations we report in Fig. 3 the ratio $D_i/D_i'=C_2(\Delta M, \Delta\sigma)$, where $D_i$ is the experimental value of the diffusion coefficient and $D_i'$ is calculated using Eq. (12), in the temperature range 1356–1823 K, corresponding to the density range $v/v_0=1.57$–$1.75$. The following contributions to $C_2(\Delta M, \Delta\sigma)$ are exhibited by Fig. 3.

(a) $C_2$ increases with the mass of the solute atom. A similar dependence of the dynamic correlations on the solute mass has also been observed by molecular dynamics by Alder *et al.*[4,5] (for solutes of mass smaller than that of the host metal) and by Toukubo *et al.*[18] in Lennard-Jones fluids. Qualitatively, it is easy to understand this effect since at large densities, the correlations are dominated by the backscattering effect. The larger the mass of the diffusing species, the smaller the backscattering. The diffusion coefficient of solute atoms of larger mass than the solvent is therefore larger than one would expect from a pure Enskog theory, even corrected by the factor $C_1$ of the host metal.

(b) $C_2$ increases with the size of the solute atoms, their mass being kept roughly constant [$C_2(\text{Sb}) > C_2(\text{Sn}) > C_2(\text{Ag})$]. While this dependence of $C_2$ on $\sigma$ is the reverse of the dependence found by Alder *et al.*[4,5] for impurities smaller than the solvent, it is in agreement with the results obtained by Toukubo *et al.*[18] in Lennard-Jones fluids. It is plausible to argue that solutes of large size may favor the onset of the hydrodynamic regime of the dynamical correlations. In order to confirm this point, it would be very interesting to perform molecular-dynamics calculations on hard-sphere systems with solute atoms larger than the solvent.

## V. CONCLUSION

We have reported measurements of the diffusion coefficient of some solute atoms in liquid copper, using a shear-cell device which provides accurate data. From a comparison between experimental data and theoretical calculations based on hard-sphere models, two correlation regimes are apparent, namely, (i) for particles smaller in size and mass than the solvent, the predictions of the computer simulation are in agreement with the experimental data, i.e., solutes of large mass and small size have a tendency to diffuse more rapidly and, (ii) solutes larger and heavier than the solvent diffuse faster than predicted by Enskog's theory. The observed effect increases with the difference in mass and size of the solute relative to the solvent. In order to understand this point, it would be very interesting to perform computer simulation calculations on such systems.

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