INTUITION INTERPRETATION OF SELF-DIFFUSION MECHANISM
IN LIQUID ARGON BY MOLECULAR DYNAMICS

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ABSTRACT

To get an intuitive understanding of the self-diffusion mechanism in liquids, molecular dynamics simulation analysis was performed on liquid argon composed of 864 atoms just above the melting point. Examining the histograms of root-mean-square displacements at several time intervals, we found a few abnormal fast atom movements, indicating a jump diffusion mechanism. About 20% of the self-diffusion coefficient originates from the jump mechanism, which occurs about 1.25 times per one hundred atomic oscillations; the residual part comes from Brownian-like movement of a cage-forming atomic group composed of an atom and its nearest neighbor atoms.

I. INTRODUCTION

The essential feature of atomic and ionic behavior in several types of liquids, including molten salts, can be understood with an intuitive interpretation of self-diffusion mechanisms. For this purpose, a computer simulation analysis by molecular dynamics of more than several hundred particles is one of the most direct and effective methods, although even the molten alkali halides could not effectively be analyzed by the pair potential approximation (1).

As an initial try, liquid argon just above the melting point was chosen because argon is the simplest monoatomic liquid and has the most reliable information on interatomic forces, which are, to a high degree of accuracy, approximated by a pair potential form. This means a central force approximation can be used and provides an easier condition for the molecular dynamics experiments (2,3). The condition of melting point was chosen as the densest atom-packed state, most significantly characterizing the normal liquid state, even though the rather dense conditions will be present in the super-cooled liquids.

Rahman already tried an ambitious examination of the self-diffusion mech-
anism in argon by this method (4), where he considered the primary and higher order polyhedra formed by neighbor atoms and their local fluctuations. This idea has some qualitative relation to that of Swalin (5). However, one of the authors had declared that it could not be denied that the jump diffusion might occur by the passage through interstices prepared by the normal fluctuations of local atom-packing density, in the monoatomic liquids including pure metallic liquids (6) and alkali halide melts (7), even near their melting points.

Therefore, several new examinations were performed again, and a realistic diffusion mechanism in liquid argon was revealed.

II. MOLECULAR DYNAMICS CALCULATION OF LIQUID ARGON AT MELTING POINT

The conditions of the calculation are as follows:
(A) the number of argon atoms: 864 particles,
(B) interaction force: Lennard-Jones type 6-12 potential,

\[ \phi(r) = 4\epsilon \left( \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^{6} \right) \]

where \( \epsilon = 119 \) K and \( \sigma = 0.34 \) nm,
(C) temperature: 87 K, just above melting point, not far from triple point (83.8 K, 1.435 g/cm³),
(D) density: 1.418 g/cm³,
(E) length of basic cube: 3.43 nm,
(F) time of step for integral with periodic boundary condition: 0.005 psec, and
(G) total integral step: 2500.

III. PHENOMENOLOGICAL ANALYSIS OF SELF-DIFFUSION COEFFICIENT

The phenomenological self-diffusion coefficient, \( D_{\text{total}} \) was calculated by the conventional method (3) from the following relation with the mean-square displacements \( \langle (R(t) - R(t_0))^2 \rangle \): 

\[ W(t) = \frac{1}{3} \langle (R(t) - R(t_0))^2 \rangle \approx 2D_{\text{total}}(t - t_0) \]

which was taken from 1.7 x 10⁶ samples per 0.005 psec interval for the time of \( t_0 < t < 7.5 \) psec.
The delay time, $\tau_0$, in the above was 1.055 psec. $D_{total}$ was $1.96 \times 10^{-5}$ cm$^2$/sec, which was sufficiently in agreement with the experimental values (8,9).

It is doubtful that the microscopic self-diffusion coefficient is equivalent to the macroscopically measured one, considering complex semi-microatomic mass movements, for example.

IV. SUBSTANTIAL ANALYSIS OF SELF-DIFFUSION MECHANISM

To get an intuitive understanding of the self-diffusion mechanism of atoms, the following examination was performed using the root-mean-square displacements:

$$\Delta R_i(t_0, \Delta t) = \sqrt{(R_i(t_0 + \Delta t) - R_i(t_0))^2}$$

after several time intervals, $\Delta t$, from several initial times, $t_0$ for all 864 atoms.

The histograms of $\Delta R_i(t_0, \Delta t)$ are shown for the intervals of $\Delta t = 0.2, 0.3, 0.4, 0.5,$ and $0.6$ psec in Fig. 1 and $\Delta t = 0.5, 1.0, 2.0, 3.0, 4.0, 6.0,$ and $12.0$ psec in Fig. 2. These curves in Figs. 1 and 2 reflect the straight distance of movement from the initial position of each atom after the time interval, $\Delta t$, independently of its paths. The curves in Fig. 1 in general look like the natural results after simple random walks. However, in the curves for the intervals longer than 1.0 psec in Fig. 2, abnormally elongated tails near the horizontal axis were found. The position of $r_1$ shows the nearest neighbor atom distance. These tail parts would originate from some abnormal displacement mechanism, such as "jumping," according to the following two reasons:

(1) Several projection charts were drawn of atomic movements included in the 0.58-nm-thick slab inside the basic cube, presenting the two-dimensional trajectories of about 140 atoms onto the x-y plane. For example, the chart of 0.5-psec interval had shown only small curved trajectories of about 0.03 to 0.1 nm length with no apparent abnormality. However, as shown in Fig. 3(b), the chart of 1.0 psec interval included two or three abnormal trajectories having a nearly straight line and being about 0.3 nm or longer. These long trajectories might be understood as the jump movement of some atoms passing through the side of many irregularly oscillating atoms.

(2) In 1959, an effective structural model (6) of monoatomic liquids, including van der Waals and pure metallic liquids, was proposed. This model suggested a high feasibility of jumping through the interstices of the atom cage formed by an average of 10.8 atoms surrounding an atom, even just above the melting point.
A simplified picture with rigid-sphere atoms is shown in (a), (b), and (c) of Fig. 4, for which a quasi-face-centered-cubic arrangement was used to help the intuitive understanding. Figure 4(a) shows schematically the jump mechanism. In Fig. 4(b), solid-line circles represent the average position determined by the rigid-sphere atoms of effective radii placed in the quasi-(100) plane; if four central atoms were moved to the positions of the dotted-line circles, the other shaded atom would pass through this plane freely. Figure 4(c) shows the side view of the above mechanism. If the shaded atom could move straight for more than about 0.2 nm, there is a high probability that it would jump out of the cage. (The velocity of gas-like free movement is about 0.23 nm/psec at this temperature.)

With the above consideration, the number of atoms that have jumped in the time intervals of $\Delta t = 2, 3, 4, \text{or } 6 \text{ psec}$ was estimated from the number of atoms that have moved farther than the threshold distances of 0.22, 0.225, 0.23, or 0.24 nm, respectively, shown by vertical arrows in Fig. 2. The accounted number of "jumped" atoms is shown in Table 1.

The oscillation frequency, $\nu_m$, of atoms near the melting point, $T_m$, was assumed to be estimated by Lindemann's formula (10):

$$\nu_m = 2.8 \times 10^{12} T_m^{1/2} M^{-1/2} V_m^{-1/3}$$

where M represents the atomic weight and $V_m$ the atomic volume at $T_m$. In the case of argon, $\nu_m$ is $1.335 \times 10^{12}$ per sec and the oscillation period of atoms is 0.75 psec. From Table 1, the jump frequency is estimated to be 1.25

The self-diffusion coefficient, $D_{\text{jump}}$, as a result of jumping can be calculated (11) from

$$D_{\text{jump}} = \frac{1}{6} (\text{jump frequency}) (\text{displacement})^2$$

The displacement by single jump can, on the average, be considered nearly equal to the mean interatomic distance (0.375 nm). Therefore,

$$D_{\text{jump}} = \frac{1}{6}(1.335 \times 10^{12} \text{sec}^{-1} \times 1.25\%)(0.375\text{nm})^2 = D_{\text{total}} \times 20\%$$

The residual part of the self-diffusion coefficient will be originated from the Brownian-like movement of an atomic group consisting of a central atom and the surrounding cage atoms:

$$D_{\text{total}} = D_{\text{jump}} + D_{\text{Brownian-like}}$$
The number of cage atoms is estimated to be about 10.8 atoms from the radial distribution function at the melting point (12,6).

From the Langevin's relation of Brownian motion:

\[ D_{\text{Brownian-like}} = \tau_0 \times \frac{kT}{M^*} \]

where \( \tau_0 = 1.055 \) psec, as shown in Section II, and the effective mass, \( M^* \), is calculated as

\[ M^* = 8.10 \times 10^{-22} \text{g} \cdot \text{s} = 12.2 \text{atoms} \times M_{\text{Ar}} \]

This is consistent with the above prediction: 10.8 + 1 = 11.8 atoms. Although this coincidence may be fortuitous with respect to the above crude estimations, it seems that the essential feature of the self-diffusion mechanism is a little more revealed by the above analysis.

V. CONCLUSION

Using molecular dynamics simulation, the self-diffusion mechanism in liquid argon just above the melting point has been analyzed for a very short time scale. The essential mechanism was divided into two parts. One was the jumping process of an atom passing through its surrounding atom cage, with a jumping frequency of about 1.25 times per one hundred oscillations of the central atom. This process will contribute about 20% to the total self-diffusion coefficient. The second process was a Brownian-like movement of an atom with its cage as a whole (the effective mass of 12.2 Ar atoms).

These approaches for analysis of self-diffusion mechanisms apply to liquid argon at higher temperatures, to pure metallic liquids, and also to ionic liquids starting as molten alkali halides.
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Table 1. Jump probability of atoms in liquid argon near melting point. (87.0K, 1.418gr/cm$^3$)

| time-interval $\Delta t$(psec) | threshold distance D (nm) | jumped atoms $N_j$ | $\frac{N_j}{N_{tot}}$ (%) | $\frac{N_j}{N_{tot}}$ (%) average: |
|---------------------------------|---------------------------|--------------------|---------------------------|----------------------------------|
| 2                              | >0.22                     | 28.5               | 3.30                      | 1.24                             |
| 3                              | >0.225                    | 43.7               | 5.06                      | 1.26                             |
| 4                              | >0.23                     | 57.9               | 6.70                      | 1.26                             |
| 6                              | >0.24                     | 87.2               | 10.09                     | 1.26                             |

Fig. 1 Histogram of root-mean-square displacements at several time intervals in liquid argon.
Fig. 2 Histogram of root-mean-square displacements at several time intervals in liquid argon.
Fig. 3 Trajectories of argon atoms inside a slab of 0.58 nm thickness in the time intervals of (a) 0.5 psec and (b) 1.0 psec.
Fig. 4 Schematic figures of jump-diffusion mechanism in liquid argon assuming quasi face-center-cubic arrangements.