LIFETIME OF IMMEDIATE ENVIRONMENT OF ATOMS IN A LENNARD–JONES LIQUID

N. N. Medvedev, A. Appelhagen, and A. Geiger

The nature of the relative motion of atoms in liquids determines many physical and chemical processes occurring in liquids. Computer simulation provides excellent possibilities for studying the mechanisms of these motions. The molecular dynamics method, which has already become standard in chemical physics (see, for example, [1]), gives us the coordinates and velocities of the atoms in the model under study at successive moments of time. A detailed analysis of this information allows us to study the fine details of the molecular motions, including those currently inaccessible to physical experiment. On the other hand, owing to the use of plausible interparticle interaction potentials and numerical solution of the equations of motion, computer simulation avoids the quite rough approximations inevitable in analytical treatments [2, 3].

Recently in [4] the time variation of the immediate environment of atoms was investigated in a molecular dynamics model of a Lennard–Jones liquid close to the triple point. It was shown that the structural characteristics of the immediate environment, defined by the topological (number of faces) and metric (volume) characteristics of the Voronoi polyhedra, vary rather rapidly. Their autocorrelation functions fall off to zero practically as the autocorrelation function of the modulus of the velocity of the atoms (in approximately one picosecond). On the other hand, a change in the geometric neighbors of the atom occurs significantly more slowly. After a time on the order of 4 picoseconds, half of the old geometric neighbors are preserved around each atom on the average (about seven atoms). Thus it was shown that the amplitudes of atomic motion after a few collisions are sufficiently large to change the appearance of the immediate environment, while real translations are due to slower diffusion processes.

In this paper, we have investigated in detail the process of the change in the atoms in the immediate environment in liquid argon at different temperatures and densities, and we derive quantitative parameters describing this change. By considering all pairs of nearest neighbors simultaneously, we can observe the "macroscopic" appearance of this process and determine the time of existence of their old nearest neighbors in a percolation cluster model.

The molecular dynamics models were obtained on an IBM RISC/6000 work station. We used a program based on the Verlet algorithm, maintaining a constant temperature by scaling the atomic velocities [5]. The parameters of the Lennard–Jones potential corresponded to argon ($\sigma = 3.405$ A, $\varepsilon = 119$ K), the integration step was dt = 0.002 picoseconds. Each model contained 500 atoms in a cube with periodic boundary conditions. The temperatures and densities of the studied models are presented in Table 1. In each thermodynamic state, the model first relaxed from the last configuration of the preceding state over the course of 10-20 thousand steps (the thermodynamic characteristics practically go the steady-state values in 1-2 thousand steps, but for a complete transition to the equilibrium state a somewhat longer time is needed), after which the molecular dynamics process was continued for 20-40 thousand more steps and we performed our analysis on these configurations. The self-diffusion coefficients (Table 1) were determined as usual from the slope of the time dependences of the mean-square atomic displacements.

For simple liquids, where there are no separate physical interactions between atoms, it is appropriate to determine the nearest neighbors using Voronoi polyhedra [4]. However, in our analysis this proved to be laborious (for a complete analysis of only one model, we need to calculate more than a million polyhedra). Therefore in order to save computer time, we use a very simple test. We consider atoms as nearest neighbors if they lie no more than $r_{max} = 1.6\sigma$ from the central atom. This distance approximately corresponds to the position of the first minimum in the radial distribution function; furthermore, the average number of nearest neighbors is close to the average number of geometric neighbors of the atom determined using Voronoi polyhedra.

TABLE 1. Parameters and Characteristics of the Models

No.	T*	ρ*	D [cm²/sec] × 10⁵	t_c, psec	⟨N(0)⟩	p_c^b
1	1.0	0.82	3.30	12.18 (0.82)	13.12 (0.07)	0.103 (0.011)
2	0.7	0.82	2.29	14.88 (1.01)	13.08 (0.03)	0.101 (0.015)
3	0.5	0.82	1.12	26.18 (1.38)	13.08 (0.03)	0.103 (0.011)
4	1.0	0.91	1.94	18.93 (1.22)	14.11 (0.07)	0.097 (0.014)
5	0.8	0.91	1.20	26.27 (1.13)	14.10 (0.05)	0.100 (0.012)
6	0.7	0.91	0.97	31.91 (2.12)	14.01 (0.06)	0.095 (0.025)
7	0.6	0.91	0.63	41.66 (0.85)	14.01 (0.04)	0.105 (0.013)

Notes. T* and ρ* are the reduced temperature and density; D) self-diffusion coefficient; t_c) critical time. ⟨N(0)⟩ is the average value of the number of nearest neighbors at time zero; p_c^b) is the critical fraction of preserved pairs of nearest neighbors at the moment the percolation cluster disappears (see text). Within the parentheses we give the mean-square deviations of the corresponding parameters upon averaging over eight independent zero times (start of the time clock).

At some moment of time chosen as the initial moment (zero time), for each atom of the model we store the positions of all of its nearest neighbors. Thus formally between each pair of nearest-neighbor atoms a bond is established, defining a neighborhood. As a result, for the given configuration of the model we obtain a network which can be called the "network of neighborhoods." We note that for a simple liquid, this network is close to the Delaunay network for the same configuration of the model [6]. Approximately 14 bonds converge at each vertex of the network, on the average. After the initial network of neighborhoods is obtained, we go on to consider subsequent configurations of the studied model. At each subsequent moment of time (every 40 molecular-dynamics steps), we again examine the network of neighborhoods. As a result of motion of the atoms, over the time that has passed some neighbors have gone beyond the limits of r_{max}, so the new network of neighborhoods is already different from the original one. Comparing the old network with the new network, we determine which bonds of the initial network have disappeared and thus determine the lifetime of these bonds, which is taken to be equal to the instantaneous time at which this configuration exists. Scanning the model over a sufficiently large time interval, we learn the lifetimes of all the pairs of nearest neighbors. We considered the effect of the size of the scanning step on the value of the lifetime of nearest neighbors. We found that if the scanning step is not greater than the interval of "kinetic" motion of the atoms, i.e., if it is less than the first zero in the autocorrelation function of the velocity (approximately 120 molecular-dynamics steps), then the results are practically independent of the specific scanning step size. We emphasize that in this paper, we neglect repeated approaches of neighbors; the immediate neighborhood is cut off only once.

For each time t from the zero time, bonds in the initial network of neighborhoods whose lifetime is less than the indicated time t are considered as broken bonds. Obviously, there exists some critical time t = t_c at which the cluster of remaining bonds is so depleted that it is decomposed into (finite) disconnected clusters. Following the terminology of percolation theory, let us call this time t_c the "critical time." It is in some sense a macroscopic characteristic of the system, since it indicates the moment at which the percolation cluster (penetrating the entire sample) disappears in the system. The presence of such a cluster means that if we were to have a model of macroscopic dimensions, then for the given fraction of
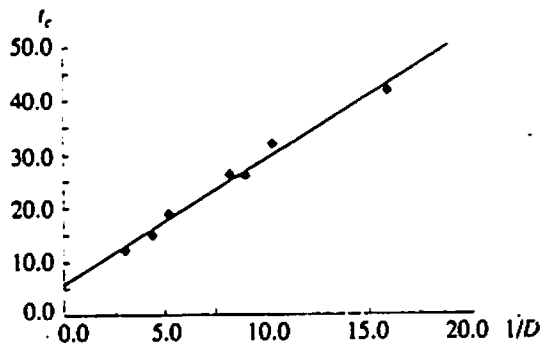
Fig. 1. Critical time t_c of the studied liquids vs. reciprocal self-diffusion coefficient, measured in $\text{Å}^2/\text{psec}$.
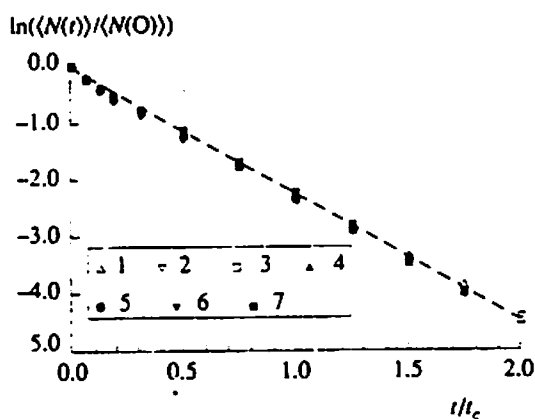

Fig. 2. Change in the relative number of "old" nearest neighbors over time in units of t_c. The numbering of the symbols corresponds to the numbering of the models in Table 1 (first column). The symbols are heavily superimposed on each other. Data was not obtained for some models for times close to $2t_c$.
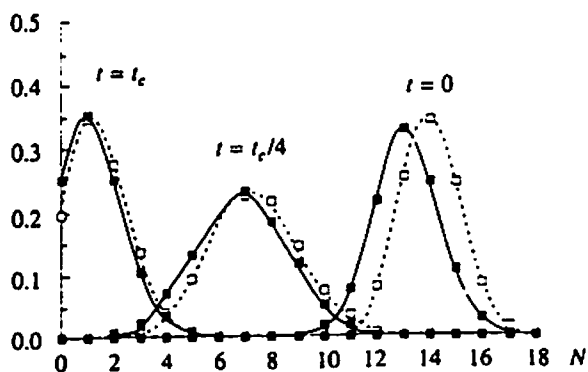

Fig. 3. Distribution of the number of "old" nearest neighbors at atoms at different moments of time. Solid line) for the most mobile of the studied liquids (No. 1 in Table 1); dashed line) for the least mobile liquid (No. 7).

intact bonds we would have a connected cluster, penetrating the entire macroscopic sample. Thus the time t_c means the moment of disappearance in the system of the macroscopic formation of atoms which have remained nearest neighbors up to this moment.

The values of t_c found for our models are presented in Table 1. The presented values for each model are the result of averaging over eight independent calculations (differing in the selection of different zero moments of time), as which we chose successive configurations of the model separated by 2000 molecular-dynamics steps (4 picoseconds). The mean-square deviations indicate that we have the values of the critical times to accuracy no worse than 6%. In Table 1, we also present the threshold fractions of intact bonds $p_c{}^b$. Within the error limits, which here are relatively high, they coincide for all the models and are approximately equal to 0.10. This is the typical order of magnitude for networks with high connectivity (see, for example, [7]).

In Fig. 1, we present the dependence of the critical time on the reciprocal self-diffusion coefficient. We see that all our models fit rather well on a single straight line:

$$t_c = \alpha + \beta/D, \tag{1}$$

where for measurement of the time in picoseconds and the self-diffusion coefficient in square angstroms per picosecond, $\alpha = 6.0$, and $\beta = 2.35$.

Knowing the lifetime of all the pairs of nearest neighbors, it is easy to determine how the average number of "old" neighbors for an atom decreases with time. Figure 2 illustrates the time dependence of the logarithms of the ratio $\langle N(t) \rangle / \langle N(0) \rangle$ in units of the critical time t_c. Here $\langle N(t) \rangle$ is the average (over all the atoms) number of nearest neighbors preserved up to time t; $\langle N(0) \rangle$ is the average number of neighbors for the zero-time configuration of this model. All the points fit very well on a single straight line. This means that in the considered interval, the immediate environments of the atoms decay exponentially with the same characteristic time

$$\tau = 0.452 t_c.$$

The value of τ can be given the meaning of the average lifetime of a neighbor in the immediate environment of a given atom. By virtue of Eq. (1), it also is a linear function of the reciprocal self-diffusion coefficient. At zero time, these distributions are close to the distributions for geometric neighbors determined from Voronoi polyhedra [8]. The fact that the distributions of the models do not coincide is due to some differences between the structures of the immediate environment of the atoms in a dense and less dense liquid.

At time $t_c/4$, seven neighbors still remain per atom on the average. At approximately this moment, the maximum width of the distribution occurs: a spread from 2 to 12 neighbors. At $t = t_c$, more than 20% of the atoms have completely lost all their old neighbors, while most of them only lose one. Moreover, there are atoms which keep four or even five neighbors. It is interesting to note that at nonzero times, the distributions for the different models match significantly better. Here the determining factor is probably not the structure of the immediate environment, but rather the rate of change in the old neighbors, which as we see is universal in units of t_c.

Thus we can say that not only the average (Fig. 2) but also the overall character of the change in the immediate environment (Fig. 3) is the same for all the models; i.e., it does not depend explicitly on either the temperature or on the density, but rather is determined by the average mobility of the atoms.

Let us emphasize that the observed fact of exponential decay of the immediate environment is nontrivial, although formally this law obviously is obtained assuming that the neighbors leave the immediate environment independently and that a common "sedentary lifetime" exists, similar to that postulated by the simple Frenkel model [2]. Our data are obtained from analysis of molecular-dynamics models, and in this sense the observed exponential decay is an experimental result, free from such assumptions. We also note that the neighbors do not leave the central atoms in the liquid in a jumpwise fashion [2]. A detailed consideration of the molecular-dynamics models allows us to say that atomic jumps, although they do occur, are not the determining factor in the overall picture of atomic motions. In [9], where this point was especially examined, it was shown that rapid translations to distances comparable with the size of an atom can be isolated as a separate type of motion only when the liquid goes to the glassy state.

REFERENCES

1. M. P. Allen and D. J. Tildesley, Computer Simulation of Liquids, Clarendon Press, Oxford (1987), p. 385.
2. Ya. I. Frenkel' [J. Frenkel], Physics of the Liquid State [in Russian], Nauka, Leningrad (1975).
3. R. Kapral, Adv. Chem. Phys., 48, 71-181 (1981).
4. N. N. Medvedev, Zh. Fiz. Khim., 66, No. 1, 152-154 (1992).
5. L. V. Woodcock, Chem. Phys. Let., 10, 257-259 (1971).
6. Yu. I. Naberukhin, V. P. Voloshin, and N. N. Medvedev, Mol. Phys., 73, No. 4, 917-937 (1991).
7. M. P. Hollewand and L. F. Gladden, J. Phys. Condens. Matter, 4, No. 26, 5757-5762 (1992).
8. N. N. Medvedev and Yu. I. Naberukhin, Zh. Strukt. Khim., 28, No. 3, 117 (1987).
9. H. Miyagawa, Y. Hiwatari, and S. Itoh, Progr. Theor. Phys., Supplement, 103, 47-60 (1991).