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Dynamic behavior of pairs of atoms in simple liquids

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The microscopic dynamic behavior of some simple liquids has been investigated by observing the time evolution of the separation between members of pairs of atoms. The distribution function for this process was calculated in molecular-dynamics studies of several states of two model fluids: Lennard-Jones and simulated rubidium. The overall features of the results are described quite well by a simple model in which the distribution of pair separations satisfies Smoluchowski's equation with a potential of mean force. The model uses a nonlinear time scale determined from the single-particle motion.

I. INTRODUCTION

In this article we consider a distribution function which describes the relative motion of two atoms in a fluid. This distribution—the probability that two atoms are separated by $\vec{r}$ at time t, given that they were separated by $\vec{r}_0$ at time zero—was introduced by Oppenheim and Bloom[1] in their analysis of nuclear magnetic relaxation in fluids. Subsequently the same distribution has been considered in theories describing several other effects, including depolarized light scattering[2] and collision-induced absorption.[3] I have evaluated this time-dependent pair-distribution function for the fluid states listed in Table I. I have found that these results are described fairly well by a simple model which relates the evolution of the distribution to the radial distribution function and the single-particle motion.

In the theories mentioned above, the function to be considered here determines only one of three contributions, with the other two involving three- and four-body correlations. At low densities the contribution of the two-body correlations dominates. However at liquid densities the three contributions seem to be of comparable magnitude, with significant cancellations occurring between them. (See Ref. 4 for a recent discussion of this situation.) Hence a complete theory for these effects must involve more than a treatment of the pair dynamics.

On the other hand, I feel that an examination of the pair dynamics alone is of intrinsic interest. Molecular dynamics allows one to "measure" the time-dependent pair-distribution function *per se*. The analysis presented in this article is not an effort to explain, for example, nuclear magnetic relaxation; rather, I am using the pair dynamics as a tool for analyzing the properties of the liquids which have been simulated.

A fundamental difficulty with the microscopic physics of liquids is that there is no simple, natural way to describe a fluid on a microscopic level. This is apparent in contrast to a solid, which can be described by specifying its deviation from a perfect lattice. For a fluid there is no equally obvious manner of description. Certain averaged quantities are known to be useful ways to characterize a fluid's behavior; two outstanding examples are the dynamic structure factor and the velocity autocorrelation function.[5] But these known quantities do not comprise a complete description of all one might want to know about a fluid. Many potentially important characteristics of a liquid are simply not described by any of the standard functions.

For example, consider the hypothesis that some simple liquid is made up of quasimolecules—fairly long-lived groups of atoms which maintain a local structure as they move along together. Since these molecules could support short-ranged coherent modes, quasimolecular behavior would probably have an appreciable effect on, for example, the dynamic structure factor. But the dynamic structure factor alone does not allow one to determine whether anomalous behavior is the result of quasimolecular structure or of some other mechanism. The quasimolecules would not have an unambiguous signature in any of the quantities which are generally used as statistical descriptions of atomic motion in liquids.

A common feature of many of these known quantities (a feature which limits their usefulness in many situations) is that they measure *absolute* motion of the atoms. The reference frame in which the motion is measured may be defined microscopically, but is generally not moving along with the fluid in any microscopically defined way. The time-dependent pair-distribution function introduced by Oppenheim and Bloom measures the *relative* motion of the atoms. One might hope that some effects which cannot easily be seen in the conventional correlation functions and distributions would be readily apparent from this distribution.

Quantitative definitions and a simple theoretical model for the behavior of the distribution function are presented in Sec. II. There we also present our molecular dynamic results for two fluids: Lennard-Jones and simulated rubidium. The model does quite a good job of characterizing the overall features of the distribution function. It also provides a convenient starting place for examing some less obvious aspects of this property of a liquid.

II. QUANTITATIVE RESULTS

The basic function we are interested in is defined by

$$g_2(\vec{r}_0;\vec{r},t)=\langle\delta(\vec{r}_0-\vec{r}^{\,0}_{12})\delta(\vec{r}-\vec{r}^{\,t}_{12})\rangle/\langle\delta(\vec{r}_0-\vec{r}^{\,0}_{12})\rangle\,, \qquad (1)$$

where $\vec{r}^{\,t}_{12}$ is the relative coordinate $\vec{r}^{\,t}_1-\vec{r}^{\,t}_2$ of atoms 1 and 2 at time t. The average is over a stationary initial ensemble, ideally a canonical ensemble but in practice the ensemble characterizing molecular-dynamics experiments. The integral of g_2 over a volume in $\vec{r}$ gives the probability that the relative coordinate $\vec{r}^{\,t}_{12}$ is in that volume at time t, given that $\vec{r}^{\,0}_{12}=\vec{r}_0$. The distribution is normalized to $\delta(\vec{r}-\vec{r}_0)$ at $t=0$, and its integral over all $\vec{r}$ is unity for all times. Its dependence is on the magnitudes of $\vec{r}$ and $\vec{r}_0$ and on the angle between them.

A crude approximation for g_2 is found by assuming that the two atoms are diffusing with no correlation between their motions. In that case it is easy to show that

$$\frac{\partial}{\partial\tau}g_2=\nabla^2 g_2\,, \qquad (2)$$

where ∇^2 operates on the $\vec{r}$ dependence and

$$\tau=2Dt\,. \qquad (3)$$

Here D is the diffusion constant for *single*-particle motion; the factor of 2 arises because the coordinate $\vec{r}$ is the relative coordinate. Our model is obtained by improving on this in two ways.

First note that the static solution to Eq. (2) is found by making g_2 constant in $\vec{r}$. But the true static solution should be proportional to the equilibrium probability for finding a pair separated by $\vec{r}$, that is, the radial distribution function $g(r)$. This suggests that the uncorrelated diffusion should be replaced by diffusion in an effective interatomic potential $U(r)$ which has $g(r)=e^{-\beta U}$ as its equilibrium distribution. U is the familiar potential of mean force, which was already introduced into this context by Oppenheim and Bloom.[1] We take the motion in the potential U to be diffusive, replacing Eq. (2) with Smoluchowski's equation

$$\frac{\partial}{\partial\tau}g_2=\nabla^2 g_2+\vec{\nabla}\cdot[g_2\vec{\nabla}\beta U(r)]\,, \qquad (4)$$

where $\beta=1/k_BT$ and the potential is

$$U=-\beta^{-1}\ln g(r)\,. \qquad (5)$$

The remaining difficulty with the model is that it necessarily gives incorrect results at small time. For example, consider the behavior at large relative coordinate. In that case the atoms *are* moving with no correlation and g_2 is determined by the distribution function for single-particle motion. But the model as represented by Eqs. (3)–(5) would give a correct result at large distance only if the single-particle motion were itself exactly diffusive. The model would therefore misrepresent the initial kinetic spread of g_2. We correct this shortcoming by introducing a nonlinear t to τ relationship which is reminiscent of the Gaussian approximation for single-particle motion.[5] This comprises our second improvement on the primitive diffusion picture: Eq. (3) is replaced by

$$\tau=\tfrac{1}{3}\langle|\vec{r}^{\,0}_1-\vec{r}^{\,t}_1|^2\rangle\,, \qquad (6)$$

where $\langle|\vec{r}^{\,0}_1-\vec{r}^{\,t}_1|^2\rangle$ is the mean-squared distance moved by a single atom in time t.

The model is now represented by Eqs. (4)–(6). For large t the model incorporates diffusive relaxation to the expected static solution. For large interatomic separations it gives the same results as would be obtained by using the Gaussian model for the uncorrelated single-atom motions. Finally, it is not difficult to show that it properly represents the exactly calculable small time kinetic relaxation, which depends nontrivially on $\vec{r}_0$. The model therefore includes all of the "obvious" features of g_2.

The model can also be obtained more formally by making some explicit (but uncontrolled) approximations to an exact equation for the distribution function. However, since the model is presented here as a heuristic device intended to relate the single-particle motion to the evolution of the pair-distribution function, we feel that the simple physical argument presented above is more relevant.

As input to Eqs. (5) and (6) we need the radial distribution function $g(r)$ and the single-particle mean-squared displacement. These were evaluated from the molecular-dynamics coordinates, which will be discussed below. Because $g(r)$ is available only in tabular form, any solution to the equations of the model must be done numerically.

For economy of presentation, and to facilitate numerical solution of the equations of the model, it is convenient to reduce the number of variables occurring in g_2. One way to do this is to introduce spherical harmonic moments, integrating over the solid angles $\hat{r}$ and $\hat{r}_0$ with a Legendre polynomial $P_l(\hat{r}\cdot\hat{r}_0)$. This defines

$$\gamma_l(r_0;r,t)=(4\pi)^{-1}\int d\hat{r}_0 d\hat{r}\, P_l(\hat{r}\cdot\hat{r}_0)g_2(\vec{r}_0;\vec{r},t)\,. \qquad (7)$$

Spherical harmonics with $m\neq 0$ vanish because g_2 is cylindrically symmetric around $\vec{r}_0$. Yet another reduction of the description can be made by defining moments

$$R_{nl}(r_0;t)=\int_0^\infty dr\, r^2(r-r_0)^n\gamma_l(r_0;r,t)\,. \qquad (8)$$

It is trivial to derive a model equation for γ_l from Eq. (4). This can be solved numerically for a given $g(r)$.

These distribution functions were calculated from molecular-dynamics data for three states of simulated liquid rubidium and two states of the Lennard-Jones fluid. The rubidium simulation was based on the potential of Price and co-workers.[6] The states we used are listed in Table I. The $T^*=0.98$ Lennard-Jones state is rather strongly supercooled.[7] The molecular-dynamics procedure, simulating the motion of 250 atoms with cubical periodic boundary conditions, is described elsewhere.[8] We used an integration algorithm introduced by Tsai.[9]

The various fluids which we examined showed no remarkable differences in the overall behavior of g_2. The time scale varies but is always related to that of the single-particle motion (as determined by the model). There is some slight dependence on the state and the interatomic potential beyond that expected from the model (such as a tendency of the relative coordinate to oscillate), but these differences are on a level beyond that which we wish to discuss in this paper. Certainly the differences are not as apparent as one might have thought they could be. Because of this essential similarity among the five fluids, we have chosen to present results for only one representative case, the $T^*=1.32$ Lennard-Jones fluid. The discussion in this article holds equally for the four other fluids.

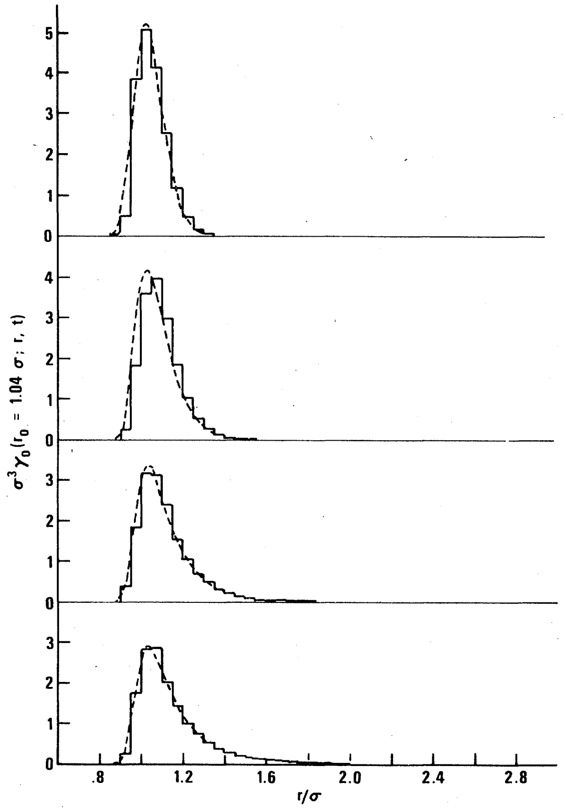

FIG. 1. Distribution function describing the distance between the members of a pair of atoms in the $T^*=1.32$, $n^*=0.95$ Lennard-Jones fluid. The initial separation r_0 corresponds to the first maximum of the radial distribution function $g(r)$. The histogram represents the molecular-dynamics results and the dotted line represents the model. The time scale is set by assuming the argon atomic mass for the atoms. Each curve represents γ_0 at a given time. Starting at the top, the times, in units of 1.45×10^{-13} s, are 1, 2, 5, and 9.9. The time unit is approximately a collision time: the first zero of the velocity autocorrelation function is at $1.4\times1.45\times10^{-13}$ s.

TABLE I. Molecular-dynamics states.

Potential	ϵ/k_B (K)	σ (Å)	$T^*=kT/\epsilon$	$n^*=n\sigma^3$
Lennard-Jones	···	···	0.98	0.950
Lennard-Jones	···	···	1.32	0.950
Rubidium	393	4.480	0.88	0.951
Rubidium	393	4.480	1.12	0.951
Rubidium	407	4.482	1.49	0.855

Results of the molecular dynamics and of the model are presented in Figs. 1–5. It is evident that the overall features of the results are represented surprisingly well by such a simple model.

Generally the evolution of g_2 is characterized by a relaxation toward certain favored separations [the peaks of $g(r)$]. Atoms initially separated by a distance corresponding to a peak of $g(r)$ tend to retain that separation for a relatively long time, whereas those initially not in a favored position soon lose their initial separation. This behavior is described quite well by the model. In addition we saw no tendencies in the angular behavior beyond the diffusive evolution expected from the model.

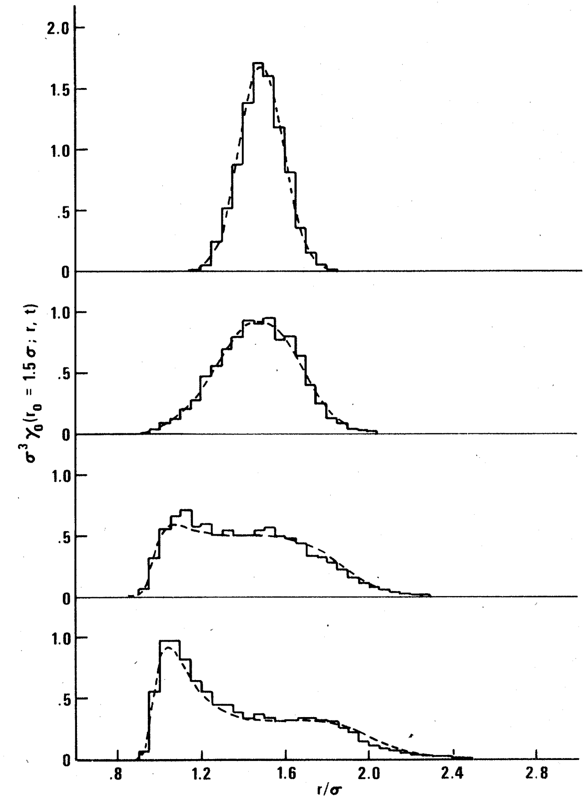

FIG. 2. Same as Fig. 1, except that the initial separation corresponds to the first minimum of $g(r)$.

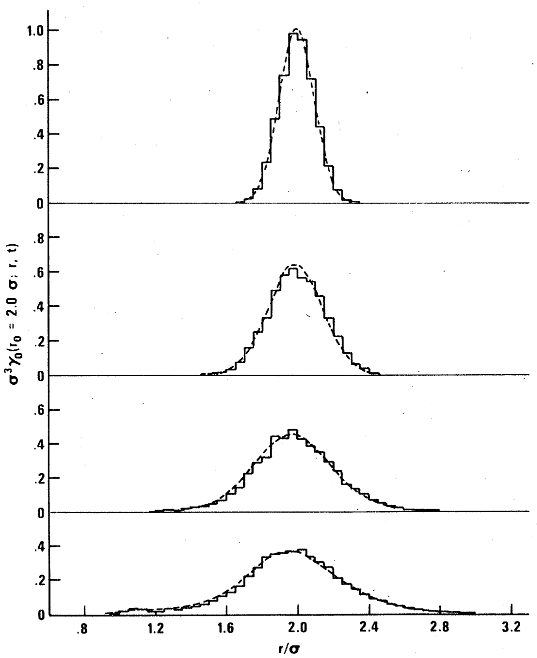

FIG. 3. Same as Fig. 1, except that the intial separation corresponds to the second maximum of $g(r)$.

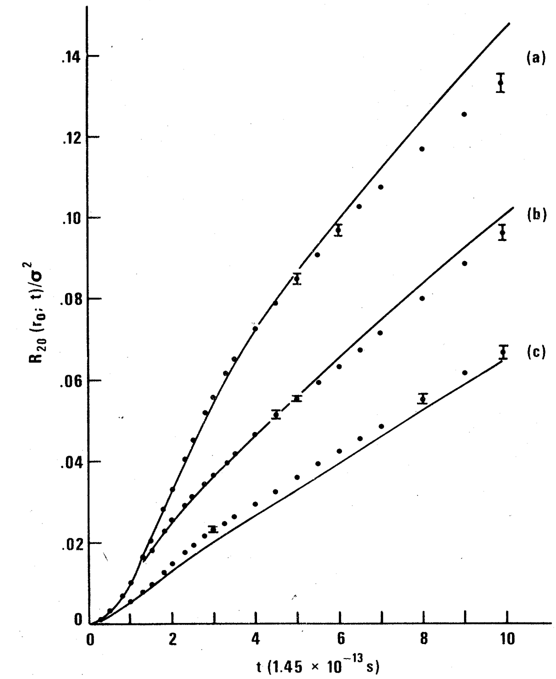

FIG. 4. Mean-squared changes in the separation of a pair of atoms for the three cases shown in Figs. 1–3. See Eq. (8) in the text. Curves (a), (b), and (c) correspond to $r_0/\sigma = 1.5$, 2.0, and 1.04, respectively (Figs. 2, 3, and 1, respectively). Error bars show some typical statistical errors.

III. DISCUSSION

The features of g_2 represented by the model are essentially those features which one would naively expect the distribution to show. So while it is sur-

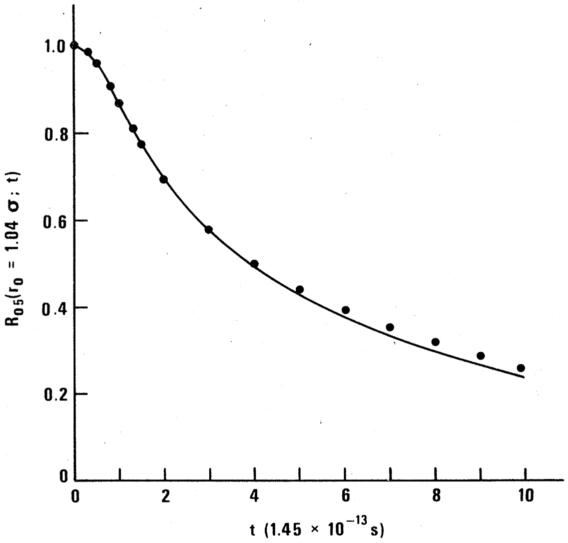

FIG. 5. $l = 5$ spherical harmonic moment R_{05} for the case shown in Fig. 1. See Eqs. (7) and (8) in the text.

prising that the model works as well as it does, this agreement between the model and the molecular-dynamics results means that g_2 shows no remarkable behavior at the level of precision which we are considering here. This information is useful in two ways.

First, there was a possibility that the behavior would *not* be what one would expect (that is, the model would not fit the molecular-dynamics results at all). For example, the fact that the model does work for the fluids we considered allows us to answer unambiguously the question of whether there are quasimolecules in any of these fluids. If a liquid had this structure, the motion of a single atom would be largely a result of the motion of the quasimolecule which contains the atom. The relative motion of a pair would result from dissolution of a quasimolecule (at least for long times, after those pairs which were not "bound" into the same quasimolecule had separated). Thus the time evolution of g_2 would occur on a different time scale from that of the single-particle motion. We found that in the liquids we examined the long-time decay of g_2 is determined by the single-particle self-diffusion constant. It is therefore clear that there are no quasimolecules of the sort we imagined above. We can similarly conclude that, because of the quality of the results we obtained with this simple model, there are no other outstanding anomalies which would be hidden from analyses using fixed reference frames.

Second, the less trivial aspects of the behavior of pairs of atoms in a fluid can now be more sensibly discussed in the context of the model. Processes with more coherent, systematic dynamics will appear as differences between the actual behavior and the essentially diffusive evolution predicted by the model. We are investigating some suggestions of such differences.

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