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Computer "Experiments" on Classical Fluids. III. Time-Dependent Self-Correlation Functions

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Molecular dynamics experiments made on a system of 864 particles interacting through a Lennard-Jones potential for various high-density states are used to study the self-correlation in classical fluids. The self-diffusion constant is computed and interpreted in terms of a hard-sphere model. The memory-function formalism is used to give a simple phenomenological fit for the computed velocity autocorrelation function and for the self-intermediate-scattering function. A detailed comparison is made with the various existing theories for the latter quantity.

I. INTRODUCTION

This paper is devoted to the phenomenological description of the self-motion of atoms in liquids.

We would like to interpret for instance the self-diffusion coefficient and the incoherent scattering of neutrons in simple liquids. In order to establish

such a phenomenological description, we need some experimental material. We shall use that provided by molecular dynamics experiments on Lennard-Jones molecules, inspired by the work of Rahman.[1] The advantage of these "experiments" is that they are more complete, generally more precise, and better controlled than the corresponding experiments on argon and other simple substances. The similarity of the Lennard-Jones fluid with argon is well known as far as equilibrium properties are concerned.[2-4] We shall see that the same is true for the self-diffusion constant. We may hope to get a very good understanding of time-dependent properties of simple liquids by the study of the Lennard-Jones fluid.

In Sec. II we review the theoretical framework in which the results will be interpreted. This is the memory function approach which constitutes a generalization of hydrodynamics for finite wavelengths and frequencies.[5-9] This formalism has the advantage of providing interpolation formulas in which the known limits can be conveniently included. In particular, through this formalism, one can easily use the fact that time expansions can be derived through a repeated use of the equations of motion.[10,11]

In Sec. III we discuss in detail how the various quantities – velocity autocorrelation function, self-diffusion constant, time-dependent self-correlation functions – are calculated, and we give estimates of the precision which can be hoped for.

The results are then displayed in Secs. IV–VI. The self-diffusion constant is first examined. A simple empirical formula, valid at high density, shows that its dependence on temperature is linear. This formula can be used to interpolate our data and to demonstrate that a very good agreement is obtained with the self-diffusion coefficient measured in the case of argon.[12] We may try to compare these results with the diffusion constant of hard spheres. A quantitative agreement cannot be reached because a hard-sphere model neglects the effect of the duration of the collision. But a slight modification to that model can be made to include this effect, and an excellent agreement is then reached.

The variety of the velocity autocorrelation functions obtained in Sec. IV seems to preclude a simple analysis. There the memory function formalism turns out to be useful. With a simple form of the memory function depending on three parameters only, it is possible to fit very precisely these various autocorrelation functions. This memory function, which is interpreted as a generalization of the friction coefficient, nonlocal with respect to time, is composed of two parts, one of short range in time, characteristic of the two-body collision, and the other, effective at large times, which is connected with the collective response of the neighbors to the self-motion.

Sec. V contains the description of the self-intermediate-scattering function or of its Fourier transform, which is proportional to the differential cross section for incoherent neutron scattering. We may pursue the memory function approach. Various relaxation time approximations lead to results which are not precise enough to represent the computer data. The same can be said of the well-known Gaussian approximation,[10] and of a recent approximation due to Lebowitz, Percus, and Sykes.[13] Both approximations lead to similar results, which are better than those provided by the relaxation-time approximations. They both require the complete knowledge of the velocity autocorrelation function. A further improvement, as is well known,[1] can be obtained by considering the corrections to the Gaussian approximation. We introduce a two-parameter approximation for that correction with the help of which excellent results are produced. Another approach, almost as good and more closely related both to experiment and to the physical description of the situation, consists in generalizing to finite k's the memory function introduced in order to describe the velocity autocorrelation function. This can be made at the expense of introducing one more parameter which may be interpreted as measuring the range of the many-body motion accompanying the self-motion.

II. MEMORY FUNCTION FORMALISM FOR SELF–CORRELATION FUNCTIONS

The probability density of a particular particle labeled by i is

$$\rho_i(r, t) = \delta(\vec{r} - \vec{r}_i(t)) \ , \tag{1}$$

with, on average, for a homogeneous system in equilibrium,

$$\langle \rho_i(r, t) \rangle = 1/V \ , \tag{2}$$

where V is the total volume of the system.

The Van Hove function[14] $G_s(r, t)$, which gives the probability density for having the particle at $\vec{r}$ at time t, when it was at the origin at time $t = 0$, is, with this notation,

$$G_s(r, t) = V \langle \rho_i(r, t) \rho_i(0, 0) \rangle \ . \tag{3}$$

Its spatial Fourier transform, the so-called intermediate scattering function is given by

$$F_s(k, t) = \langle \rho_{ik}(t) \rho_{i-k}(0) \rangle \ . \tag{4}$$

There we have introduced the Fourier transform of the probability density for particle i:

$$\rho_{ik}(t) = e^{-i \vec{k} \cdot \vec{r}_i(t)} \ . \tag{5}$$

Let us introduce the Fourier-Laplace transform of the intermediate scattering function:

$$\tilde{F}_s(k, \omega) = \int_0^\infty dt \, e^{i\omega t} F_s(k, t) \ . \tag{6}$$

As is well known, the cross section for incoherent neutron scattering is given in terms of the function $S_S(k, \omega)$:

$$S_S(k, \omega) = (1/2\pi) \int_{-\infty}^{+\infty} dt \, e^{i\omega t} F_S(k, t)$$

$$= (1/\pi) F_S'(k, \omega) , \qquad (7)$$

where the real part is denoted by a prime. The intermediate scattering function can be expanded in Taylor series. We write this expansion as

$$F_S(k, t) = 1 - \omega_{0S}^2 \frac{t^2}{2} + \omega_{0S}^2 \omega_{1S}^2 \frac{t^4}{4!} - \omega_{0S}^2 \omega_{2S}^4 \frac{t^6}{6!} . \qquad (8)$$

The application of the equations of motion enables us to calculate the coefficients

$$\omega_{0S}^2 = k_B T k^2/m , \qquad (9)$$

$$\omega_{1S}^2 = 3\omega_{0S}^2 + \Omega_0^2 , \qquad (10)$$

$$\omega_{2S}^4 = \langle \dot{a}_{iz}^2 \rangle (m/k_B T) + 15\omega_{0S}^2 \Omega_0^2 + 15\omega_{0S}^4 . \qquad (11)$$

The constant Ω_0^2 can be calculated from the radial distribution function $g(r)$, and the pair potential $V(r)$, by

$$\Omega_0^2 = (\rho/3m) \int d\vec{r} \, g(r) \nabla^2 V(r) . \qquad (12)$$

It can be obtained in some cases from the isotopic separation coefficient. $\dot{a}_{iz}$ is the time derivative of the z component of the acceleration felt by the ith particle.

The behavior of $\tilde{F}_S(k, \omega)$ for small values of k and ω is known. It is described by the equation of transport for the density of labeled particles. If D is the self-diffusion constant, it is given by

$$\tilde{F}_S(k, \omega) \simeq 1/(-i\omega + Dk^2) . \qquad (13)$$

This corresponds for small k's and large times to

$$F_S(k, t) = e^{-k^2 Dt} . \qquad (14)$$

Equation (13) can be generalized, by writing

$$\tilde{F}_S(k, \omega) = 1/[-i\omega + \tilde{M}_S(k, \omega)] . \qquad (15)$$

This equation defines the so-called memory function $\tilde{M}_S(k, \omega)$. Divided by k^2, this quantity is a diffusion coefficient generalized for finite values of k and ω. Written with time variables, Eq. (15) exhibits the causal character of the memory function

$$\frac{\partial}{\partial t} F_S(k, t) + \int_0^t d\tau \, M_S(k, \tau) F_S(k, t - \tau) = 0 . \qquad (16)$$

Using the known expansion (8) for $F_S(k, t)$, we can write the small-time expansion for the memory function:

$$M_S(k, t) = \omega_{0S}^2 [1 - \tfrac{1}{2} (\omega_{1S}^2 - \omega_{0S}^2) t^2 + \cdots] . \qquad (17)$$

The function

$$m_S(k, t) = M_S(k, t)/\omega_{0S}^2 \qquad (18)$$

is normalized to 1 for $t = 0$. The t^4 term in the expansion of $F_S(k, t)$, which is known, is to be included as a condition on the small-time behavior of $m_S(k,t)$. This may not be convenient. A more transparent way of taking this knowledge into account is provided by extending the above memory function formalism to the self-current-current correlation function.

Let us consider the current of particle i; its kth Fourier component is given by

$$\vec{J}_{ik} = \vec{v}_i \rho_{ik} . \qquad (19)$$

Let us define the self-current-current correlation function as

$$C_S(k, t) = - \frac{d^2 F_S(k, t)}{dt^2}$$

$$= \langle \vec{k} \cdot \vec{J}_{ik}(t) \vec{k} \cdot \vec{j}_{i-j}(0) \rangle \qquad (20)$$

and introduce the function

$$c_S(k, t) = C_S(k, t)/\omega_{0S}^2 , \qquad (21)$$

which is normalized to 1. Its small-time expansion is obtained from (8)

$$c_S(k, t) = 1 - \omega_{1S}^2 \frac{t^2}{2!} + \omega_{2S}^4 \frac{t^4}{4!} \cdots . \qquad (22)$$

ω_{1S}^2, which appeared in the fourth order in $F_S(k, t)$, now comes in the second order. It is obvious from (20), (21), and (9) that

$$\lim_{k \to 0} c_S(k, t) = (m/k_B T) \langle v_{iz}(t) v_{iz}(0) \rangle , \qquad (23)$$

which is the normalized velocity autocorrelation function $f(t)$.

Let us introduce a memory function $\tilde{\mathfrak{N}}_S(k, \omega)$ by

$$\tilde{c}_S(k, \omega) = 1/[-i\omega + \tilde{\mathfrak{N}}_S(k, \omega)] . \qquad (24)$$

We must take into account the fact that $C_S(k, t)$ is the second time derivative of $F_S(k, t)$. This condition can be written as

$$F_S(k, t) = 1 - \int_0^t d\tau \, (t - \tau) C_S(k, \tau) . \qquad (25)$$

As $F_S(k, \infty) = 0$, the following two conditions are obtained:

$$\int_0^\infty d\tau \, C_S(k, \tau) = 0 , \qquad (26)$$

$$\int_0^\infty d\tau \, \tau C_S(k, \tau) = -1 . \qquad (27)$$

From this, one gets the small-ω behavior of $\tilde{C}_S \times (k, \omega)$:

$$\tilde{c}_S(k, \omega) = (1/\omega_{0S}^2) \int_0^\infty dt \, e^{i\omega t} C_S(k, t)$$

$$= 0 - (i\omega/\omega_{0S}^2) + O(\omega^2) . \qquad (28)$$

From (28) and (24) it follows that

$$\tilde{\mathfrak{N}}_S(k, \omega) = (\omega_{0S}^2/-i\omega) + \tilde{N}_S(k, \omega) , \qquad (29)$$

where $\tilde{N}_S(k, \omega)$ is regular at small ω. Taking the

Fourier transform of (29),

$$\mathcal{M}_S(k, t) = \omega_{0S}^2 \, \epsilon(t) + N_S(k, t) \, , \tag{30}$$

where $\epsilon(t)$ is the Heaviside distribution and $N_S(k, t)$ tends to zero when t tends to infinity. Using (24) written in time variables, one gets the small-time expansion

$$N_S(k, t) = \omega_{1S}^2 - \omega_{0S}^2 - \tfrac{1}{2}(\omega_{2S}^4 - \omega_{1S}^4)t^2 \, . \tag{31}$$

We introduce, as above, the normalized memory function

$$n_S(k, t) = N_S(k, t)/(\omega_{1S}^2 - \omega_{0S}^2) \, . \tag{32}$$

The normalized current-current correlation function is therefore given by

$$\tilde{c}_S(k, \omega) = [- i\omega + \omega_{0S}^2/- i\omega + (\omega_{1S}^2 - \omega_{0S}^2)\tilde{n}_S(k, \omega)]^{-1} \, . \tag{33}$$

From this expression, the normalized velocity autocorrelation function is obtained by taking the $k \to 0$ limit:

$$\tilde{f}(\omega) = [- i\omega + \Omega_0^2 \tilde{n}_S(0, \omega)]^{-1} \, . \tag{34}$$

$\Omega_0^2 n_S(0, t) = N_S(0, t)$ is the memory function for the velocity autocorrelation function. It was first introduced by Berne, Boon, and Rice.[7] It is identical with the generalized friction coefficient of Forster, Martin, and Yip.[8] From (33) $\tilde{F}_S(k, \omega)$ is obtained by multiplication by ω_{0S}^2/ω^2. It is seen that $\tilde{F}_S(k, \omega)$ is given now by an expression which exhibits all the coefficients of the small-time expansion of $F_S(k, t)$ up to the fourth.

The hydrodynamic relation (13) imposes a supplementary condition

$$\frac{mD}{kT} = \lim_{\omega \to 0} \lim_{k \to 0} \tilde{c}_S(k, \omega)$$

$$= \tilde{f}(0)$$

$$= [\Omega_0^2 \tilde{n}_S(0, 0)]^{-1} \, . \tag{35}$$

The aim of developing such a formalism lies in the hope that the memory functions $m_S(k, t)$ and especially $n_S(k, t)$ are simpler objects than $F_S(k, t)$ itself and can therefore be more easily approximated. It is also apparent that even a rough approximation on $n_S(k, t)$ (as the relaxation-time approximation) may give a rather correct $S_S(k, \omega)$ since its first four moments are automatically included. Once these memory functions are known they can be used as ingredients for obtaining approximations for the coherent scattering. One can write, for instance, for the coherent scattering an expression similar to (15). The replacement of the normalized memory function appearing in this expression by $m_S(k, t)$ is simply Kerr's approximation,[15] as is easily seen if one uses a recent formulation of that approximation due to Nelkin.[16] One can, of course, generalize

that type of approximation to the current-current correlation functions.

III. COMPUTATIONAL TECHNIQUE

The computer experiments were performed using the technique described in Ref. 2 which is derived from Rahman's work.[1] We consider a system of 864 particles of mass m enclosed in a cubic box with periodic boundary conditions, interacting through a Lennard-Jones potential

$$V(r) = 4\epsilon \left[(\sigma/r)^{12} - (\sigma/r)^6 \right] \, . \tag{36}$$

We choose σ, ϵ, and $(m\sigma^2/48\epsilon)^{1/2}$, respectively, as length, energy, and time units. We integrate the equations of motion of the system for a time $\mathcal{T}$ corresponding to at least 1200 integration steps starting with initial equilibrium configurations. We take the value 0.032 for the time increment. This corresponds to 10^{-14} sec in the case of argon. Several states, shown in Table I, were considered. In each computation, the positions and velocities were recorded for time intervals $d = 0.128$. Thus, at least 300 configurations were in our possession.

The normalized velocity autocorrelation function at time t is calculated as

$$f(t) = (m/3k_B T)\langle \vec{v}_i(0) \cdot \vec{v}_i(t) \rangle \, , \tag{37}$$

where the average is made both on the 864 particles labeled by i and on the $(\mathcal{T} - t)/d + 1$ possible choices for the origin of time.

The error on the normalized velocity autocorrelation function is of two types, numerical and statistical. The first is negligible as compared to the second. To estimate the latter one some care is necessary: All the elements appearing in (37) are not statistically independent. Only after some typical relaxation time τ does the correlation tend to disappear. Explicating this viewpoint Zwanzig[17] has given the following estimate for the error $\delta f(t)$ on normalized autocorrelation functions:

$$\delta f(t) \simeq \pm \left(\frac{\tau}{(\mathcal{T} - t)N} \right)^{1/2} |f(t) - 1| \, . \tag{38}$$

Typically $\tau/\mathcal{T} \simeq \frac{1}{50}$. Then $\delta f(t) = \pm 0.004 \, |f(t) - 1|$. The comparison of two normalized autocorrelation functions obtained at the same temperature and density with different initial configurations confirms this estimate.

The diffusion constant D is calculated either with the help of (35) written here in the usual Kubo form

$$D = (k_B T/m) \int_0^\infty f(t) dt \tag{39}$$

or by considering the large-time behavior of the mean-square displacement of a particle:

$$\lim \langle [r_i(0) - r_i(t)]^2 \rangle = 6Dt + C \quad \text{as } t \to \infty, \tag{40}$$

where C is a constant. Both methods give consistent results with a similar uncertainty which is of

TABLE I. In this table, we give for the various states listed in columns 1 and 2 the values of Ω_0^2 as given by Eq. (12), of the diffusion constant [column 4: values obtained from molecular dynamics; column 5, use of approximation (49); column 6, hard-sphere model, formula (50)], and the values of A_0 [coefficient of the large time term in the memory function defined by Eq. (52)]. T and ρ are in Lennard-Jones reduced units.

ρ	T	Ω_0^2	D_{MD}	D	D_{HS}	A_0
0.85	0.76	5.98	0.0048	0.0052	0.0045	0.88
0.85	1.08	7.17	0.0078	0.0080	0.0080	0.42
0.85	1.273	7.73	0.0095	0.0097	0.0096	0.25
0.85	2.145	10.25	0.0182	0.0175	0.0179	−0.22
0.85	2.81	11.95	0.0245	0.0244	0.024	−0.31
0.85	4.70	16.20	0.040	0.040	0.038	−0.45
0.8442	0.72	5.68	0.0047	0.0051	0.0047	0.85
0.8244	0.820	5.68	0.0065	0.0068	0.0067	0.55
0.8244	0.824	5.68	0.0067	0.0069	0.0068	0.52
0.75	0.88	4.69	0.010	0.0112	0.0101	−0.08
0.75	1.12	5.32	0.014	0.0140	0.0143	−0.27
0.75	1.30	5.76	0.017	0.0160	0.0172	−0.36
0.75	2.04	7.41	0.026	0.0245	0.026	−0.52
0.75	3.81	10.75	0.046	0.045	0.045	−0.62
0.75	5.09	12.91	0.059	0.059	0.060	−0.68
0.65	1.43	4.51	0.026	0.0257	0.027	−0.75
0.65	1.827	5.15	0.031	0.032	0.034	−0.67
0.65	3.67	7.92	0.058	0.060	0.059	−0.82
0.65	5.09	9.83	0.077	0.081	0.079	−0.85
0.40	2.00	2.56	0.076			−1.59
0.30	1.62	1.66	0.095			−2.39
0.30	1.92	1.76	0.11			−1.87

the order of 5%. It should be noticed that if there exists a long tail of the velocity autocorrelation function decreasing very slowly in time[18] and of an amplitude corresponding to the noise level (a fraction of the percent), its contribution to the diffusion constant would not be taken into account and the quoted error could be larger.

From its definition (3) the self-correlation function $G_S(r,t)$ is given by

$$G_S(r,t) = (1/4\pi r^2 \Delta r)\langle N(\vec{r}_i(t) - \vec{r}_i(0) - \vec{r})\rangle, \quad (41)$$

where $N(\vec{X} - \vec{r})$ is equal to 1 if the distance X lies between r and $r + \Delta r$, and to zero otherwise. One can also calculate the $2l$th moment of the self-correlation defined by

$$\langle r^{2l}(t)\rangle = \langle [r_i(t) - r_i(0)]^{2l}\rangle . \quad (42)$$

From its moments, $G_S(r,t)$ can be reconstructed through the expansion

$$G_S(r,t) = \left(\frac{\beta}{\pi}\right)^{3/2} e^{-\beta r^2}[1 + \sum_{l=1}^{\infty} a_l L_l^{1/2}(\beta r^2)], \quad (43)$$

where

$$\beta = \tfrac{3}{2}\langle r^2\rangle \quad \text{and} \quad L_l^{1/2}(\beta r^2) \quad (44)$$

is a Laguerre polynomial obeying the condition

$$\int d\vec{r}\, e^{-\beta r^2} L_l^{1/2}(\beta r^2)L_{l'}^{1/2}(\beta r^2) = \delta_{ll'} \cdot \frac{2\pi}{\beta^{3/2}} \frac{\Gamma(l+\tfrac{3}{2})}{l!} . \quad (45)$$

When the coefficients a_l are related to the moments

through the formula

$$\beta^l \langle r^{2l}\rangle = 2 \frac{\Gamma(l+\tfrac{3}{2})l!}{\Gamma(\tfrac{1}{2})} \sum_{j=0}^{l} (-1)^j \frac{a_j}{j!(l-j)!}, \quad (46)$$

it follows from the choice of β, as given by (44), that $a_1 \equiv 0$.

The convergence of the series is fairly rapid: The moment of order 10 gives a contribution of the order of 10^{-3}, much less than the statistical error on $G_S(r,t)$ which is of the order of 1%.

From this moment expansion, the spatial Fourier transform can be obtained without computation as

$$F_S(k,t) = e^{-k^2/4\beta}\left[1 + \sum_{l=2}^{\infty} \left(\frac{k^2}{4\beta}\right)^l \frac{a_l}{l!}\right] . \quad (47)$$

The validity of this expression can be tested by calculating directly $F_S(k,t)$ through its definition (4). Because of the periodic boundary conditions one should take for $\vec{k}$ one of the reciprocal vectors of the box in which the system is enclosed. The direct computation of $F_S(k,t)$ implies a triple average: an average over all vectors $\vec{k}$ having a length between k and $k + \Delta k$, and, as above, averages over the possible values of the origin of time and over the 864 particles. We thus obtain a confirmation of the results obtained through the moment expansion: The difference between the two sets of values for $F_S(k,t)$ is less than 0.01.

In order to make a direct comparison with experiment, it is necessary to calculate the self-dynami-

cal form factor $S_S(k, \omega)$ through the Fourier transform $S_S(k, \omega)$. It is necessary to extrapolate the moments (46) for very large values of the time. The main contribution comes from the second moment $\langle r^2(t) \rangle$ which is fitted by the linear form (40). The very large time contribution of the next moment may play a little role and we estimate it by the following extrapolation:

$$\frac{3\langle r^4(t) \rangle}{5 \langle r^2(t) \rangle} - 1 \simeq C \frac{t_c}{t} e^{-(t_c/t-1)} . \tag{48}$$

The error on $S_S(k, \omega)/S_S(k, 0)$ is of the order of 0.01 and may reach 0.02 for small values of ω.

IV. DIFFUSION CONSTANT

The diffusion constant obtained through the molecular dynamics calculation, given in Table I, can be summarized except at low density ($\rho < 0.65$) through the empirical formula

$$D = 0.006423 \, T/\rho^2 + 0.0222 - 0.0280\rho. \tag{49}$$

As can be seen from Table I, this simple expression represents quite well the data within the precision of the computation, except at very low temperature ($T < 1$) where it appears to overestimate the computer results by at least 5%. It should be noticed that the first term in (49) contributes about 90% of the total value of the diffusion constant. That is to say that the diffusion constant of the Lennard-Jones liquid is nearly proportional to the temperature. We shall now investigate whether the hard-sphere model, so successfully designed to explain the equilibrium structure of simple liquids,[19] can be extended to study the self-diffusion. Let us first recall that the hard-sphere model at equilibrium is based on the very near coincidence between the structure factor of the liquid at density ρ and temperature T and that yielded by the Wertheim-Thiele[20] solution of the PY equation for the hard-sphere gas of diameter a at the same density ρ, when it is required that the heights of their first peak be the same. This requirement fixes the only parameter of the hard sphere, i.e., the packing fraction $\eta = \frac{1}{6}\pi\rho a^3$. Should the exact hard-sphere solution be used, this agreement would remain except for a slight renormalization of the packing fraction.

In order to extend this model to the study of the diffusion constant, we shall recall that this quantity is given, for a hard-sphere gas of diameter a and packing fraction η, by

$$D = a(T)^{1/2} C(\eta)/(z(\eta) - 1) . \tag{50}$$

There $z(\eta)$ is the compressibility factor $p/\rho k T$. It can be written as[21]

$$z(\eta) = 1 + 2\eta \, (2 - \eta)/(1 - \eta)^3 . \tag{51}$$

This expression summarizes the known computer

results[22] within the statistical accuracy. In Enskog's approximation $C(\eta) = (\frac{1}{3}\pi)^{1/2}\frac{1}{16}$. At high density there is a deviation from Enskog's expression. Alder and Wainwright[18] have deduced the "exact" $C(\eta)$ from their computations on the hard-sphere gas that we denote $C_A(\eta)$. In terms of (50), the simplest way to interpret our data would be the following: Let us consider the same hard-sphere model as described above that fits the structure factor of the Lennard-Jones fluid with the Wertheim-Thiele expression. The values of the packing fraction η thus obtained are fed into (50): This leads to values of the diffusion constant which have the right order of magnitude but are 25% smaller than the corresponding ones for the Lennard-Jones fluid. The use of values for the diameter and the packing fraction corresponding to "exact" structure factors for the hard-sphere gas still increases the discrepancy. This discrepancy is qualitatively understandable. When we interpret the Lennard-Jones results with the help of a hard-sphere gas, we neglect the duration of the collision, which, in real liquids, turns out to be of the same order of magnitude as the time between collisions. The effect of the collision time is reflected in the shape of the velocity autocorrelation function; it has a Gaussian appearance for small t in the case of the real fluid, where the collision time is finite, whereas it looks like an exponential in the case of a hard-sphere gas. Assuming that the properties at larger times of the velocity autocorrelation function are mainly determined by the collision with other particles and that they are the same in the two cases, it is clear that the area under the curve, which is equal to the diffusion constant, is larger in the first case. In any case it is necessary to improve (50) so as to allow for the finite duration of collisions. The data of Table I are then used to determine $C(\eta)$. It is not obvious that such a fit is possible, but it happens to be so. Moreover, it turns out that $C(\eta)$ is proportional to the Alder-Wainwright[18] factor $C_A(\eta)$.

The factor $C_A(\eta)$ is plotted in Fig. 1, and the results obtained using (50) with $C(\eta)$ taken as 1.28 $C_A(\eta)$ are shown in Table I. We see that a very good agreement is obtained. We thus possess a semi-empirical relation linking the packing fraction obtained from the analysis of the structure factor with the diffusion constant.

The comparison with experimental data on argon[12] shows an excellent agreement between the computed diffusion constants and the experimental ones. Within the 5% experimental error, and an error of the same magnitude on the molecular dynamics computation represented by (49), we find the agreement illustrated by Table I. We see that the Lennard-Jones potential provides us with an excellent description not only of the equilibrium properties of argon but also of some of the transport proper-
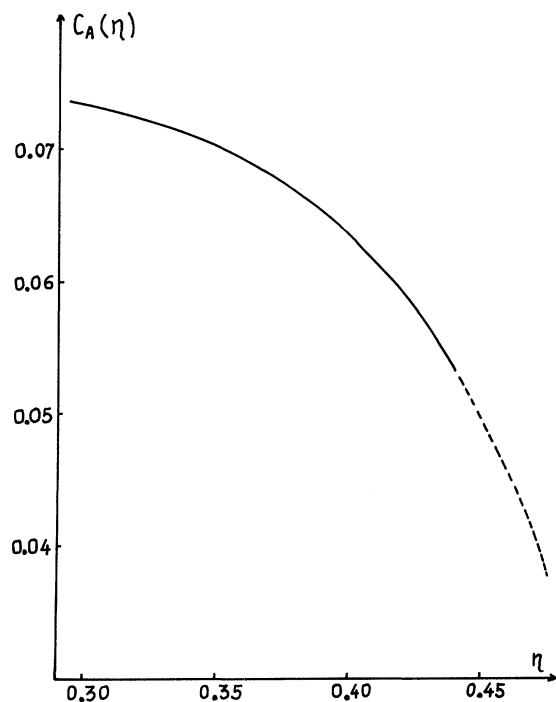
FIG. 1. $C_A(\eta)$: value of the factor $C(\eta)$ defined by (49) as a function of the packing fraction η for hard spheres. The straight line is taken from Alder and Wainwright (Ref. 18). The dotted line is extrapolated.

ties. The same would apply to other rare gases where the law of corresponding states applies as far as the diffusion constant is concerned.

The case of liquid metals[23] is different. It is true that if the diffusion constant obtained for the Lennard-Jones potential near triple point is scaled by assuming that the reduced triple-point parameters are the same for liquid metals as for the Lennard-Jones liquids, a value correct within about 20% is obtained for the diffusion constant of metals. Given the experimental values of the diffusion constant, if (50) is applied with the same factor $C(\eta)$ as in the case of the Lennard-Jones potential, it leads to values of the packing fraction of the order of 0.475 at the melting point as in the case of argon and of the Lennard-Jones fluid. (0.475 is the value of the packing fraction at crystallization when the Percus-Yevick approximation is used for the hard-sphere structure factor. It corresponds to $\eta = 0.49$ if the "exact" hard-sphere solution is used.)

It is known, on the other hand, that, experimentally, the packing fraction obtained from x-ray or neutron scattering is generally not that high in the case of liquid metals: If it is equal to 0.47 in the case of lead,[24] it is only 0.45 in the case of sodium[25] and aluminum[26] and even gets down to 0.44 in the case of calcium[27] and zinc.[28] We thus see that the hard-sphere model for diffusion described above,

where the packing fraction is deduced from the height of the main peak of the structure factor, cannot be applied to liquid metals near triple point: They have, as compared to argon, a normal diffusion constant; however, they exhibit a much less marked short-range order as shown by a low value of the main peak of the structure factor.

V. VELOCITY AUTOCORRELATION FUNCTION

In Figs. 2–4 are represented normalized velocity autocorrelation functions obtained for various values of the temperature for the densities $\rho = 0.85$, 0.75, and 0.65, respectively. At high density and low temperature, the autocorrelation function has a structure which has been observed and described by Rahman.[1] As time increases, this function decreases down to a negative dip followed by a plateau, at negative level, that persists for a substantial amount of time. When the temperature rises, this structure is less pronounced. The first negative minimum is less deep and the level of the plateau tends to rise. It becomes positive at high temperature. When the density is lower, it is seen from Fig. 3 that the velocity autocorrelation function remains positive, even when the temperature is low, and that the temperature dependence is weak.

We may try to get some qualitative insight on the velocity autocorrelation function by repeating the kind of analysis made by Alder and Wainwright[29] in the case of hard disks. We look at the correlation between the velocity of a given particle at time zero
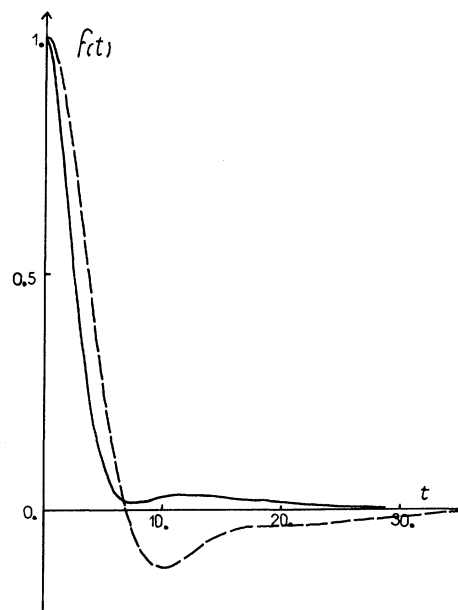

FIG. 2. Normalized velocity autocorrelation function $f(t)$ for density $\rho = 0.85$. Solid line: $T = 4.70$; dashed line: $T = 0.76$. The time units are equal to 0.128 reduced units, i.e., 4.10^{-14} sec for argon.
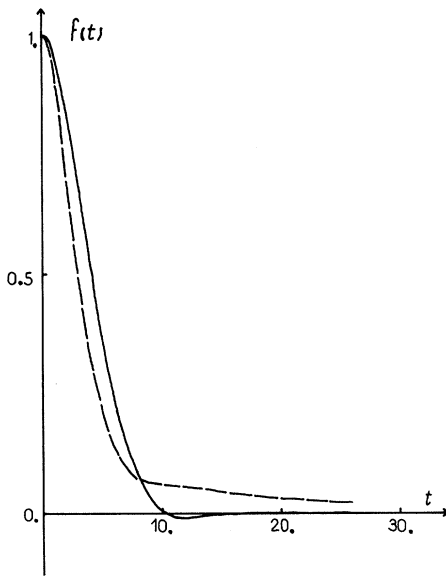
FIG. 3. Same as Fig. 2 for $\rho = 0.75$. Solid line: $T = 1.12$; dashed line: $T = 5.09$.

and that of the neighboring particles at some later time t. The precision of our calculation is admittedly not high: We do not detect correlations below a level of about 5%.

In all the cases that we have considered ($\rho = 0.75$, $T = 3.81$; and $\rho = 0.8442$, $T = 0.722$), we find that the only effect that we observe is the following: There is a positive correlation between the velocity of the distinguished particle and that of the particles which were initially in the forward direction of that distinguished particle. This correlation remains at a significant level as long as the velocity autocorrelation function remains at a significant level. We emphasize that this does not exclude a collective motion, in the form of a backflow pattern such as observed by Alder and Wainwright, in the case of the dense hard-sphere gas. It only means that this kind of correlation is below the 5% level. We shall in fact provide some evidence in Sec. VI for collective effects in the gaslike states. The observed correlation produces, on the average, a retarded current in the direction of the initial motion of the distinguished particle. In the general vicinity of the triple point, where, owing to strong cohesive effects, the motion of the distinguished particle is on the average reversed after a short time, this current gives rise to a retarded positive friction; that is, the memory function is positive for large times. At higher temperatures or lower densities, on the other hand, where the initial motion of the distinguished particle tends to persist for large times, the current pattern of the neighboring particles enhances this forward motion. The memory function, interpreted as a generalized friction co-

efficient is, in that case, negative for large times.

We shall now give a simple and very exact parametric representation of the velocity autocorrelation function. In order to do this, we shall consider the memory function formalism used in Sec. II. We may hope — and indeed it turns out to be so — that the memory function is somewhat simpler than the velocity autocorrelation function itself: We know, for instance, that a simple exponential memory function leads to an autocorrelation function which may present oscillations and be in rough agreement with the computer results.[7] In principle, Eq. (34) can be used to determine the normalized memory function $n_S(0, t)$ once $f(t)$ is known. This leads to a function which has a Gaussian-like short-time behavior and an extended tail at a few percent level.[30] The slowly varying part of the memory function is positive for states not far from the triple point and negative if the temperature is substantially higher or the density lower. It is tempting to interpret the Gaussian-like part of this generalized friction coefficient as describing the two-body encounter, and the long time part as produced by an accompanying motion of the medium, which according to the state reduces or enhances the self-motion. The tail of the memory function is responsible for the plateau region in the velocity autocorrelation function and cannot be neglected if a correct description of that long-time region is required.[7,8,31]

In order to fit the memory function we have just described, we choose the following three-parameter form:

$$N_S(0, t) = \Omega_0^2 e^{-B_0 t^2/2} + A_0 t^4 e^{-\alpha_0 t} . \qquad (52)$$

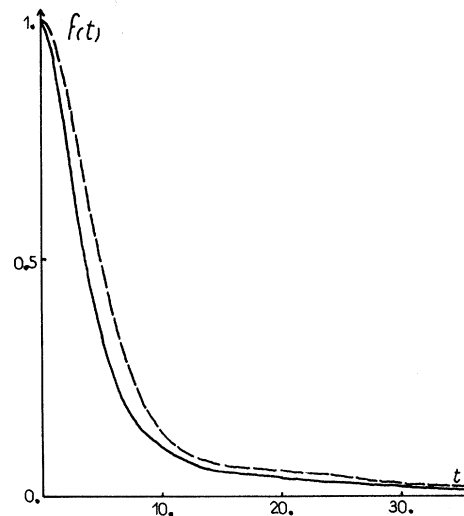This form is chosen so as to give the correct $t = 0$

FIG. 4. Same as Fig. 3 for $\rho = 0.65$. Solid line: $T = 1.43$; dashed line: $T = 5.09$.

limit and such that only its first term contributes at short times. Substituting into (34) we can thus obtain the small-time expansion of the normalized autocorrelation function as

$$f(t) = 1 - \frac{\Omega_0^2 t^2}{2!} + \Omega_0^2 (\Omega_0^2 + B_0) \frac{t^4}{4!} + O(t^6) . \qquad (53)$$

Comparing with (11), it is seen that

$$\langle \ddot{a}_{iz}^2 \rangle = \Omega_0^2 (\Omega_0^2 + B_0) . \qquad (54)$$

We have used Eqs. (32) and (34) to calculate the velocity autocorrelation function and to adjust, through a least-squares fit, the three parameters B_0, A_0, and α_0. The error on the fit is negligible for small times and is of the order of 0.01 at larger times. A little information is lost through the fit since the statistical error on the normalized velocity autocorrelation function has been seen to be less than 0.005.

The diffusion constant can be calculated, using (35). We obtain

$$D = \frac{kT}{m} \left[\Omega_0^2 \left(\frac{\pi}{2B_0} \right)^{1/2} + \frac{24A_0}{\alpha_0^5} \right]^{-1} . \qquad (55)$$

The error on this quantity is of the order of 3%, less than the statistical error. It should be noticed that the contribution to the diffusion constant of the tail of the memory function may reach 30% of the total.

It is found that, for all states considered in Table I, B_0 depends only on the temperature. This dependence turns out to be linear. Specifically, one gets

$$B_0 = 1.65 + 10.43 T . \qquad (56)$$

The time decay of the large-time part of the memory function is also very simple. For all states considered in Table I, α_0 depends only on the density. Its behavior can be accurately described through the simple formula

$$\alpha_0 = 4.12 - 2.61 \rho . \qquad (57)$$

The amplitude A_0 of the large-time term has a more complicated behavior. It can be, in principle, obtained from (55), when the other constants are known: Ω_0^2 and D are calculated directly (see Table I) and B_0 and α are obtained from (56) and (57), respectively. It should be noticed, however, that A_0 is then given as the difference of two terms which are of the same magnitude; one of these terms contains the diffusion constant which is known only within 5%. We found it useful therefore to give in Table I the results of the direct determination of A_0 through the fitting procedure we have described above.

It is seen that A_0 varies rapidly with temperature in the liquid region and tends to be very weakly temperature dependent at high temperature. The long-time part of the memory function thus depends

practically only on the density at high temperature. On the other hand, we see that, when the temperature increases, the short-time part of the memory function (52) becomes more and more like a delta function. Since we note that except at very low temperature Ω_0^2 is linear in $T^{1/2}$, the strength of this delta function, which is proportional to $\Omega_0^2 B_0^{-1/2}$, depends on the density and very weakly on the temperature. For high values of the temperature, the memory function thus depends little on the temperature and appears to resemble the memory function which is expected in the case of the hard-sphere gas.

VI. ANALYSIS OF $F_S(k,t)$ AND $S_S(k,\omega)$

We now investigate various representations of the intermediate scattering function $F_S(k, t)$ or equivalently of its Fourier transform, the self-dynamical structure factor $S_S(k, \omega)$.

We measure the accuracy of the various approximations for $F_S(k, t)$ by calculating the root-mean-square deviation δ with respect to the value $F_S^c(k,t)$, computed from the molecular dynamics data as explained in Sec. III:

$$\delta = [(1/\mathcal{T}) \int_0^{\mathcal{T}} ((F_S^c(k, t) - F_S(k, t))^2 dt]^{1/2} , \qquad (58)$$

where $\mathcal{T}$ has been taken equal to 8.96 reduced-time units.

In Tables II and III we give results of such a computation for the seven approximations studied below. They are shown for various values of k. Two typical examples are given: one near triple point ($\rho = 0.8442$, $T = 0.722$), and the other at lower density and higher temperature ($\rho = 0.65$, $T = 1.827$). We shall refer to these two examples as case I and case II, respectively. We have made the same kind of tables for the other states of Table I: The numbers

TABLE II. For case I ($\rho = 0.8442$, $T = 0.722$), we give the deviation of the approximate $F_S(k, t)$ from the exact one, for various values of k, as measured by 100 δ, where δ is given by (58). The headings of the columns refer to the various approximations of Sec. VI. ME: density-density memory function of exponential form [(Eq. 61)]. NE: current-current memory function of exponential form [Eq. (65)]. NG: same with Gaussian form [Eq. (68)]. G: Gaussian approximation. CG: corrected Gaussian approximation as defined by (73). LPS: Lebowitz-Percus-Sykes (Ref. 13) approximation. NC: current-current memory function using the corrected form (81). k is in Lennard-Jones reduced units [the k unit is equal to (3.405 Å)$^{-1}$].

k	ME	NE	NG	G	GC	LPS	NC
2.5	1.2	0.7	0.9	1.0	0.15	0.4	0.5
5.0	2.7	1.4	2.6	2.2	0.3	0.9	1.1
7.5	2.8	1.4	1.8	1.7	0.2	1.2	0.5
12.5	2.0	0.8	0.8	0.8	0.3	1.5	0.2
25.	1.6	1.2	0.7	0.1	0.1	1.4	0.2

TABLE III. Same as Table II for case II ($\rho = 0.65$, $T = 1.827$

k	ME	NE	NG	G	GC	LPS	NC
1.14	0.12	0.4	0.8	0.3	0.03	0.2	0.06
2.3	0.3	0.8	2.4	1.0	0.18	1.2	0.5
4.6	1.3	0.8	2.5	1.1	0.12	1.1	0.7
11.4	1.9	1.4	0.12	0.3	0.07	0.6	0.3
22.9	1.6	1.4	0.1	0.06	0.05	0.3	0.1

are very similar to those quoted in those two tables, and more or less lie inbetween.

It may turn out that δ is smaller than the average statistical error, which is of the order of 0.004. In that case the "experimental" results are, on the average, approximated better than they deserve from a statistical standpoint, and then the precision reached is partly illusory. On the other hand, the error may be small on the average, but unacceptably large for some values of the time variable. A more detailed investigation is therefore necessary. Since we are especially interested in giving a phenomenological representation of real experiments, we shall make those tests on $S_S(k, \omega)$ and consider, with Nijboer and Rahman,[11] the following quantities:

$$\Sigma(k) = \pi k^2 D S_S(k, 0) , \qquad (59)$$

$$\Delta(k) = \omega_{1/2}/(k^2 D), \qquad (60)$$

where $\omega_{1/2}$ is the half-width at half-height of $S_S(k, \omega)$. These two quantities are equal to one in the hydrodynamical limit. $\Sigma(k)$ is given for case I and case II in Tables IV and V, respectively. $\Delta(k)$ for the same case is given in Tables VI and VII.

We should note that the state considered in case I is very near to the one considered by Nijboer and Rahman,[11] who have studied in detail the state $\rho = 0.838$, $T = 0.714$. The potential they have is not a Lennard-Jones potential, but an exponential-6 potential which is quite similar. For $k = 6.8$, these authors obtain $\Sigma = 0.98$, $\Delta = 0.915$, when we obtain $\Sigma = 1.00$, $\Delta = 0.88$. The agreement is therefore

excellent. In comparing with Nijboer and Rahman's work, it should be taken into account that their diffusion constant is 8% larger than ours.

We now study various approximations for $S_S(k, \omega)$.

A. Relaxation-Type Approximation

In order to parametrize the function $S_S(k, \omega)$, it is natural to try a simple relaxation-time approximation for either of the normalized memory functions $m_S(k, t)$ and $n_S(k, t)$ as defined by (17) and (32). These functions may be given an exponential or Gaussian form.

1. Exponential Approximation to $m_S(k, t)$

The memory function

$$m_S(k, t) = e^{-t/\tau_m(k)} \qquad (61)$$

has been used by Chung and Yip.[9] It leads to an exponential velocity autocorrelation function of the Langevin type with

$$\tau_m(0) = mD/(k_B T). \qquad (62)$$

Using (61), (18), and (15) we get a simple analytical form for the self-dynamical form factor:

$$S_S(k, \omega) = \frac{\omega_{0S}^2}{\pi \tau_m(k)} \frac{1}{(\omega^2 - \omega_{0S}^2)^2 + \omega^2/\tau_m^2(k)} . \qquad (63)$$

We note that, in case I, the hydrodynamic frequency Dk^2 stays, up to high values of k, much smaller than the kinetic frequency ω_{0S}. Thus the hydrodynamic behavior persists for a substantial range of k. Comparison with exact results shows that this is so, and that this persistence of the hydrodynamic behavior is confirmed by the fact that $\tau_m(k)$ stays constant in the low-k region.

It is seen from (63) that for high values of k such that $\omega_{0S} \tau_m(k) > \frac{1}{2}$, there exist self-diffusion waves corresponding to an oscillatory behavior of $F_S(k, t)$. Since these oscillations are not present in the "exact" $F_S(k, t)$, they can be considered as a defect of the model.

In this approximation only the trivial second moment of $S_S(k, \omega)$ is taken into account explicitly.

TABLE IV. Ratio $\Sigma(k)$ of the self-dynamical form factor at zero frequency to its hydrodynamical limit [Eq. (59)] for case I. Same headings as in Table II; in the last column labeled by E are given the exact results.

k	ME	NE	NG	G	GC	LPS	NC	E
2.5	0.99	1.00	0.98	0.98	1.00	1.01	1.00	1.00
5.0	1.01	1.01	0.94	0.91	1.00	1.04	0.99	1.01
7.5	0.96	0.98	0.92	0.87	0.98	1.08	0.98	1.00
10.0	0.92	0.96	0.94	0.87	0.96	1.14	0.99	0.98
12.5	0.91	0.98	0.99	0.89	0.95	1.21	1.01	0.99
15.6	0.96	1.05	1.12	0.96	1.02	1.31	1.07	1.03
18.7	1.06	1.15	1.21	1.06	1.10	1.43	1.15	1.10
21.8	1.19	1.25	1.34	1.19	1.20	1.51	1.26	1.21
25.0	1.33	1.36	1.49	1.30	1.32	1.64	1.37	1.32

TABLE V. Same as Table IV for case II.

k	ME	NE	NG	G	GC	LPS	NC	E
1.14	1.04	1.06	1.02	1.01	1.03	1.02	1.03	1.03
2.29	1.16	1.17	1.08	1.12	1.17	1.11	1.14	1.16
4.57	1.55	1.51	1.32	1.42	1.51	1.42	1.45	1.50
6.86	1.86	1.86	1.68	1.76	1.86	1.81	1.80	1.86
9.14	2.23	2.24	2.13	2.14	2.22	2.23	2.19	2.23
11.4	2.62	2.62	2.62	2.54	2.59	2.67	2.60	2.62
17.1	3.66	3.67	3.92	3.60	3.61	3.78	3.66	3.65
22.9	4.75	4.77	5.24	4.69	4.70	4.91	4.74	4.73

The success of the fit rests on the adjustment, for each k of the function $\tau_m(k)$ which is theoretically not known and from which we learn little about the system. This is a heavy price to pay, considering the mediocrity of the results shown in Tables II and III. The function $\tau_m(k)$ is given by

$$\tau_m(k) = \tau_m(0)/\Sigma(k) . \qquad (64)$$

It can therefore be obtained from Tables IV and V.

2. Exponential Approximation to $n_S(k,t)$

We use the memory function

$$n_S(k,t) = e^{-t/\tau_n(k)} \qquad (65)$$

in conjunction with formula (33). This corresponds to the Berne-Boon-Rice[7] memory function when k is equal to zero. Then we have

$$\tau_n(0) = k_B T/m D \Omega_0^2 . \qquad (66)$$

In this approximation the fourth moment of $S_S(k,\omega)$ is correct: A fit of the experimental material using this approximation will provide a determination of Ω_0^2. The error is less than in the preceding approximation by roughly a factor of 2, but it is still too large to fit our data in a satisfactory manner.

Against this approximation, it can be said that, as in the preceding case, it depends on an unknown and apparently uninteresting function of k. This function can be obtained from Tables IV and V through the use of the formula

$$\tau_n(k) = \frac{\tau_n(0)\,\Sigma(k)}{1 + 2\omega_{0S}^2/\Omega_0^2} . \qquad (67)$$

3. Gaussian Approximation to $n_S(k,t)$

As a variant to the preceding approximation we may choose a Gaussian memory function

$$n_S(k,t) = e^{-Bt^2/2} . \qquad (68)$$

This corresponds to the Singwi-Tosi[31] Gaussian memory function for the velocity autocorrelation function:

$$n_S(0,t) = e^{-B_0 t^2/2} . \qquad (69)$$

If this last memory function is taken seriously, then its small-time expansion is obtained in terms of the self-diffusion coefficient [using (35)]:

$$B_0 = \frac{\pi}{2}\left(\frac{mD\Omega_0^2}{kT}\right)^2 . \qquad (70)$$

From (11) and (54), the t^6 term in the expansion of $F_S(k,t)$ can be expressed as

$$\omega_{2S}^4 = \Omega_0^2(\Omega_0^2 + B_0) + 15\omega_{0S}^2\Omega_0^2 + 15\omega_{0S}^4 . \qquad (71)$$

On the other hand, using the small-time expansion of (68) with (33), (20), and (71) it is easily seen that

$$B = \frac{B_0 + 3\omega_{0S}^2(3 + 2\omega_{0S}^2/\Omega_0^2)}{1 + 2\omega_{0S}^2/\Omega_0^2} . \qquad (72)$$

We see that, in contrast with the two approximations mentioned above, no arbitrary function of k is introduced here. The results, however, are not quite as good as in the preceding approximation

TABLE VI. Ratio $\Delta(k)$ of the half-width at half-height of $S_S(k,\omega)$ to its hydrodynamical limit [Eq. (60)] for case I.

k	ME	NE	NG	G	GC	LPS	NC	E
2.5	1.02	1.00	1.03	1.01	0.97	0.97	0.99	0.97
5.0	1.03	0.97	1.09	1.04	0.92	0.93	0.96	0.89
7.5	1.14	1.00	1.14	1.11	0.91	0.85	0.93	0.88
10.	1.31	1.04	1.16	1.22	0.99	0.78	0.94	0.96
12.5	1.44	1.06	1.15	1.32	1.15	0.74	1.05	1.08
15.6	1.45	1.05	1.13	1.49	1.35	0.79	1.19	1.34
18.7	1.32	1.01	1.07	1.35	1.30	0.83	1.16	1.29
21.8	1.19	1.02	1.01	1.20	1.18	0.80	1.10	1.17
25.	1.06	1.05	0.86	1.09	1.07	0.75	1.05	1.07

TABLE VII. Same as Table VI for case II.

k	ME	NE	NG	G	GC	LPS	NC	E
1.14	0.99	0.96	1.00	1.03	1.00	1.00	1.00	1.00
2.3	0.95	0.91	1.01	0.99	0.94	1.01	0.96	0.94
4.6	0.84	0.75	0.96	0.86	0.78	0.87	0.83	0.79
6.9	0.76	0.64	0.80	0.74	0.68	0.70	0.71	0.68
9.	0.63	0.56	0.64	0.63	0.60	0.57	0.61	0.59
11.4	0.54	0.50	0.52	0.55	0.53	0.49	0.53	0.52
17.1	0.38	0.45	0.34	0.40	0.40	0.37	0.40	0.39
22.9	0.29	0.38	0.25	0.31	0.31	0.29	0.31	0.31

for $n_S(k, t)$.

The present approximation has clearly two important defects: The memory function (69) is, as we have seen in Sec. V, an oversimplification and the value of B_0 given by (70) may be substantially wrong; although the high-k limit of B given by (72) is correct, the perfect-gas limit of the memory function $n_S(k, t)$ is not of the Gaussian form (68). We shall see later on how these two defects can be remedied.

B. Gaussian Approximation and Its Improvement

The well-known Gaussian approximation consists in truncating the expansion (47) to its first term:

$$F_S(k, t) = \exp\left[-\tfrac{1}{6}k^2\langle r^2(t)\rangle\right]$$
$$= \exp\left[-\omega_{0S}^2 \int_0^\infty d\tau\,(t-\tau)f(\tau)\right]$$
$$= \exp\left(-\frac{2\omega_{0S}^2}{\pi}\int_0^\infty d\omega\,\tilde{f}'(\omega)\,\frac{\cos\omega t - 1}{\omega^2}\right).$$

This approximation requires more than the preceding ones, since it involves the complete velocity autocorrelation function. It has the advantage of being correct for small and large values of k, and of giving exactly the small time expansion of $F_S \times (k, t)$ including the t^6 term.[10,11] It is therefore not surprising that this approximation is fairly good, as may be seen from Tables II-VII. Its main defect has been pointed out by Nijboer and Rahman. For intermediate values of k, $S_S(k, \omega)$ as yielded by the Gaussian approximation is less sharply defined than it should be: $\Sigma(k)$ is too small, and the reduced half-width at half-height $\Delta(k)$ is too large. Another drawback of this approximation is that only $F_S(k, t)$ is expressed in a simple form which is not directly appropriate to discuss the experimental data.

In order to improve the Gaussian approximation we shall take into account the first non-Gaussian correction in the expansion (47). Since it is known that the next terms in that expansion play a minor role,[11] we limit ourselves to the first term, which will be treated approximately. For all values of the time the approximation (48) will be used, so that the self-intermediate-scattering function is given by

$$F_S(k, t) = \exp\{-\tfrac{1}{6}[k^2\langle r^2(t)\rangle]\}$$
$$\times\left[1 + \frac{k^4\langle r^2(t)\rangle^2}{72}\frac{Ct_c}{t}\exp-\left(\frac{t_c}{t}-1\right)\right].$$
$$(73)$$

It is clear that the correction term introduced is not correct for short times: It should behave like t^8,[32] whereas the approximate form varies as $t^3\exp[-(t_c/t - 1)]$. This does not have too serious consequences, however, since the main contribution of the correction term comes about at times of the order of t_c. The fits obtained using (73) are quite good: The errors, as measured by (58), are never larger than the estimated statistical error.

We have not given any table containing the values of C and t_c obtained through this fitting procedure because, owing to the statistical errors, they behave in no sense as smooth functions of ρ and T and prove to be useless as far as interpolation to neighboring thermodynamic states is concerned. We have therefore accepted some increase in the error (by a factor of 2 at most) in order to devise some simple, although somewhat arbitrary, interpolating formula. Since it appears that the density dependence of C and t_c is weak, we neglect it altogether and fit all the high-density data through

$$C = 0.14\,e^{-0.233\,T}, \qquad (74)$$
$$t_c = 8.2\,e^{-0.457\,T}. \qquad (75)$$

We emphasize that these formulas have obvious defects: The high-temperature limit is clearly wrong and all density dependence has been neglected. They represent no more than a simple device introduced in order to represent $F_S(k, t)$ at high-density with an error less than 0.01.

C. Lebowitz-Percus-Sykes Approximation

Lebowitz, Percus, and Sykes[13] have recently presented a kinetic equation for the one-particle density, given that the other particles of the system are in thermal equilibrium. This equation is a part of a hierarchy. To close up this hierarchy an approximation is made so as to obtain a correct behavior for small times. This approximation re-

quires the knowledge of the velocity autocorrelation function, or, equivalently, of its memory function $N_S(0, t)$. Lebowitz, Percus, and Sykes (L. P. S.) then succeed in solving analytically the approximate kinetic equation and obtain the following expression for $\tilde{F}_S(k, \omega)$:

$$\tilde{F}_S(k, \omega) = \frac{1}{\tilde{N}_S(0, \omega)} \ \Phi\left(\frac{\omega_{0S}^2}{\tilde{N}_S^2(0, \omega)} - \frac{i\omega}{\tilde{N}_S(0, \omega)}, \ \frac{\omega_{0S}^2}{\tilde{N}_S^2(0, \omega)}\right),$$

(76)

where

$$\Phi(a, x) = (e^x/x^a) \int_0^x dt \, e^{-t} t^{a-1} .$$

(77)

The integral in this last expression is the incomplete gamma function $\gamma(a, x)$. Putting $t = xe^{-u}$, expanding the exponential in (77), and integrating over a term by term, the following expression, useful for numerical calculations, is obtained:

$$\Phi(a, x) = \sum_{n=0}^{n=\infty} x^n \left(\prod_{j=0}^{j=n} (a+j)\right)^{-1} .$$

(78)

It is easy to see from (76), (77), and (78) that the correct behavior is obtained both in the hydrodynamic and in the perfect-gas limit. The second and fourth moments of $\tilde{F}_S(k, \omega)$ are correct. The sixth moment is only correct for low and high k's: Carrying out explicitly the small-time expansion of $F_S(k, t)$, as defined by (8), it is seen that

$$\omega_{4S}^2 = \Omega_0^2 (\Omega_0^2 + B_0) + 10\omega_{0S}^2 \Omega_0^2 + 15\omega_{0S}^4 .$$

(79)

This expression, when compared to the exact result (71), proves to be incorrect.

It is seen from Tables II–VII that the results obtained with the L. P. S. approximation are about as precise as those obtained with the Gaussian approximation, except at high k's, where they are substantially worse, owing probably to the error introduced by (79).

D. Memory Function Approach

We wish, in this section, to return to the type of approach already considered at the beginning of this section: Namely, we want to find a simple approximation to the memory function $N_S(k, t)$. Once this memory function is known, the self-dynamical structure factor $S_S(k, \omega)$ can be obtained, as seen in Sec. II, through

$$S_S(k, \omega) = \frac{\omega_{0S}^2}{\pi} \ \frac{\tilde{N}_S'(k, \omega)}{\omega^2 \tilde{N}_S'^2(k, \omega) + [\omega^2 - \omega_{0S}^2 - \omega \tilde{N}_S''(k, \omega)]^2} .$$

(80)

We shall assume that $N_S(k, t)$ can be written in the form

$$N_S(k, t) = (2\omega_{0S}^2 + \Omega_0^2) e^{-Bt^2/2} [1 - \omega_{0S}^4 t^4 \varphi(\omega_{0S}t)]$$
$$+ A t^4 e^{-\alpha t} .$$

(81)

This reduces to the memory function (52) for the velocity autocorrelation function when k is zero and gives the correct $t = 0$ limit as seen from (31). The unknown quantities in (81) are chosen as follows: (i) B is given by (72). This ensures that the sixth moment of $S_S(k, \omega)$ is correct. (ii) Since the results turn out to be rather insensitive to the choice of α, it is taken equal to α_0 for all values of k. (iii) The k dependence of A is approximated by

$$A = A_0 e^{-(k\lambda_c/2\pi)^2} ,$$

(82)

where λ_c is a length which remains to be determined.

The function $\varphi(\omega_{0S}t)$ is to be defined by the requirement that the correct high-k limit is obtained: In that limit the memory function reduces to

$$N_S(k, t) \simeq 2\omega_{0S}^2 e^{-3u^2/2} [1 - u^4 \varphi(u)] ,$$

(83)

with $u = \omega_{0S}t$. It should be equal to the memory function of the perfect gas $2\omega_{0S}^2 n(u)$, where $n(u)$ is normalized, i.e., $n(0) = 1$. This memory function is easily obtained from (33), since the normalized self-current-current correlation function $C_S(k, t)$ is equal to $(1 - u^2) e^{-u^2/2}$ in the high-k limit. The perfect-gas memory function $n(u)$ decreases more rapidly than $e^{-3/2u^2}$ for small u's, vanishes for $u \simeq 1.24$, and shows thereafter strongly damped oscillations. The correction $\varphi(u)$ displaces the frequency spectrum of the memory function towards higher frequencies. When this correction is neglected $\tilde{N}_S(k, 0)$ is therefore overestimated, in the perfect-gas limit, by a factor easily shown to be $2/\sqrt{3} \simeq 1.15$. In view of the relation

$$\Sigma(k) = \tilde{N}_S(k, 0)/\tilde{N}_S(0, 0) ,$$

(84)

which follows from (59) and (80), it is seen that, in the same situation, $\Sigma(k)$ is overestimated by the same factor. This defect of the Gaussian memory function for high k's, already mentioned in Sec. VI A, can be seen from Tables IV and V.

The correction term $\varphi(u)$ can be written as a series expansion

$$\varphi(u) = C_0 + C_2 u^2 + \cdots .$$

(85)

The coefficients of this series can be obtained from the small-time expansion of $n(u)$. We get in this way $C_0 = \frac{1}{4}$, $C_2 = \frac{1}{10}$, etc. It appears, however, that the convergence is very slow for a range of values of u around 1 where the memory function is not yet negligibly small. Since we decide, for the sake of simplicity, to keep $\varphi(u)$ in the form of (85) with only the first two terms different from zero, we determine their coefficients C_0 and C_2 in a different way: We require that $\tilde{n}(0)$ be correctly given and that the first zero of $n(u)$ be located at the right place. We then obtain $C_0 = 0.7258$, $C_2 = -0.1876$.

Given the assumptions made above, the calculation of $S_S(k, \omega)$ through (80) requires the knowledge of the velocity autocorrelation as described by the parameters B_0, A_0, and α_0, and the determination of the parameter λ_c. This parameter has the character of a correlation length for the tail term of the memory function. We suggest that it is related to the spatial extent of the collective motion accompanying the motion of the distinguished particle, as observed by Alder and Wainwright[29] in the hard-disk gas. Fitting the "experimental" $F_S(k, t)$ with the help of (80) and (81), we obtain λ_c. It turns out to be of the order of 0.5 for case I and more generally for all states in the immediate neighborhood of the triple point, where the constant A_0 is positive and rather large. On the other hand, for the states like that of case II, where the temperature is higher and eventually the density lower, and for which A_0 is clearly negative, λ_c is found to be of the order of 2. In the transition region where A_0 is small in magnitude, the tail term plays a minor role. If we try to determine λ_c in that case, the error is very large and nothing definite can be said.

We see that the correlation length is, when A_0 is negative, four times larger than near the triple point, and that, in the first case, many more particles should be involved in the mechanism producing the large-time tail of the memory function. This agrees very well with the picture proposed by Alder and Wainwright[29] to which we have already alluded: For those states where the attraction plays a minor role, a moving particle develops around itself a correlated motion involving many neighbors which may correspond to the backflow pattern observed by Alder and Wainwright. Near the triple point, on the other hand, where the density is very high and the cohesive effects are very strong, such a collective motion does not exist. Only the nearest neighbors play a role. They tend

to act so as to reverse the initial motion.

We see from Tables II–VI that the memory function approximation (80) and (81) gives a fit to the computed data, which although not perfect, is clearly better than the Gaussian and Lebowitz-Percus-Sykes approximation. The price to pay for this improvement is the necessity of introducing one more parameter, the correlation length λ_c which may be given a physical interpretation. The memory function approximation is, on the other hand, not so good as the corrected Gaussian approximation studied in Sec. VI B where two parameters are needed instead of one as in the present case.

The great advantage of the approximation we have just defined is that it yields the simple form (80) for the dynamical structure factor $S_S(k, \omega)$ which is the observable quantity. The comparison with the results from neutron scattering experiment is thus quite direct.

In view of this comparison, we find it useful to give a discussion of the sensitivity of the results to the various parameters so far introduced. The aim of this discussion is to determine what can be practically obtained from an analysis of neutron scattering experiments.

It is clear that for $k \gg 2\pi/\lambda_c$, the role of the tail of the memory function is negligible. As already shown by Nijboer and Rahman,[11] high-k measurement will provide Ω_0^2 and, with possibly less precision, B_0.

Information on the remaining parameters will be obtained from observation at lower k's. It turns out, however, that the results are very insensitive to the range α_0 of the tail term of $N_S(k, t)$ as long as the total area of this tail, proportional to A_0/α_0^5, remains constant when α_0 is varied. This means that the neutron scattering results will not provide complete information about the long-time part of the velocity autocorrelation function. Fortunately α_0 depends only on the density, as we have seen in Sec. V. It may be hoped that it depends little on the details of the interaction and that when it comes to analyzing experiment, the value (57) may be a good estimate.

Near the triple point (case I), the results depend sensitively on the value of λ_c. We have plotted in Fig. 5 the values of $\Sigma(k)$ obtained for several values of λ_c differing by about 30%. With precise measurements, it should be possible to determine the spatial extent of the many-body correlation accompanying the self-motion, as measured by λ_c. Such a determination would be very interesting in case II, where λ_c should be large. There the precise determination of this quantity appears to be quite difficult, as may be seen from Fig. 6. Very precise measurements, extending to as low values of k as is feasible, could at least give a lower limit to the value of λ_c.
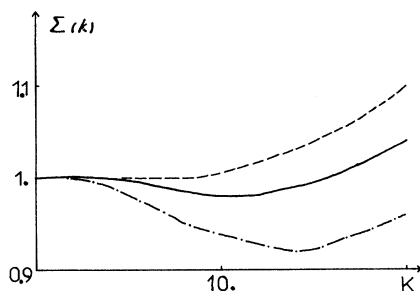

FIG. 5. Ratio $\Sigma(k)$ of the self-dynamical form factor at zero frequency to its hydrodynamical limit for case I with the memory function (81)-(82). Solid line: $\lambda_c = 0.46$; dashed line: $\lambda_c = 0.31$; dash-dot-line: $\lambda_c = 0.69$.
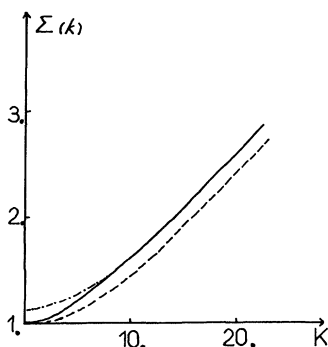
FIG. 6. Same as Fig. 5 for case II. Solid line: $\lambda_c = 2$; dashed line: $\lambda_c = 0$; dash-dot line: $\lambda_c = +\infty$.

VII. CONCLUSIONS

We have analyzed the precise and plentiful material provided by the computer experiments on self-correlations in fluids, and we have shown that it can be understood in terms of a rather simple memory function.

A similar analysis is presently being carried out[33] for the total current-current correlation of the transverse currents and for the total dynamical structure factor, quantities which have been computed with some details and precision in the neighborhood of the triple point.

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