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Diffusion blocking in a frozen rigid-sphere fluid

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The diffusion and localization of a classical particle of diameter σ_0 in an environment of fixed spherical scatterers of diameter σ_1 in arbitrary dimensionality is considered by extending the self-consistent current relaxation theory for the Lorentz gas of a point particle and overlapping spheres. The variation of the diffusion coefficient with scatterer density n and diameter ratio $\delta=\sigma_0/\sigma_1$ is calculated analytically. Different factorization schemes are examined and compared. The overlapping $\delta=\infty$ and nonoverlapping $\delta=0$ Lorentz gas are discussed briefly as special cases. The critical density $n_c(\delta)$ in the (n,δ) phase diagram separating diffusive from localized behavior is established and good agreement with Monte Carlo results for the percolation density of hard-core disks is obtained.

I. INTRODUCTION

In the study of classical transport phenomena in fluids and disordered materials the Lorentz gas attracted a great deal of attention in recent years.[1,2] This model deals with a particle moving in a static environment of scatterers. One seeks an understanding and quantitative description of various dynamical properties of the tagged particle for a given average density n of scatterers, in particular, its velocity-autocorrelation function, diffusion coefficient, and Van Hove's self-correlation function.

There are several versions of the Lorentz gas[1] differing by the geometrical shape of the scatterers and by allowing the scatterers to either overlap or not. One of the models studied most extensively by computer simulations,[3–6] as well as theoretically,[7–15] is that of a point particle moving in a random array of spherical scatterers of a certain diameter σ which interact with the tagged particle through a hard-core potential and which are allowed to overlap otherwise. This model is known as the overlapping Lorentz gas (OVLG).

The interesting fact about this model is that it not only exhibits the expected diffusive behavior at low scatterer density, but the particle also may be trapped at high density, as first suggested by computer simulation results on two- and three-dimensional systems,[3] and later, by further investigation for two dimensions.[4,5] A self-consistent current relaxation theory[10] successfully explained this diffusion-localization transition at a critical density n_c of scatterers and yielded a linearly vanishing diffusion coefficient approaching n_c from below. Above n_c the theory showed that the particle was localized in a finite region of space, the extent of which was defined to be the localization length and found to diverge with an exponent 1/2 near n_c. Moreover, the theory provided a complete description of the system by also predicting the velocity autocorrelation and Van Hove's scattering function which was found to be in almost quantitative agreement with available simulation data.

The Lorentz gas of a tagged point particle and overlapping scatterers of diameter σ is equivalent to a system of point scatterers with a tagged particle of the same diameter σ.

In this work the more general situation of a tagged particle of diameter σ_0 and fixed hard-core scatterers of a diameter σ_1 will be considered. Then the OVLG is contained as the special case with $\sigma_1=0$, while the special case $\sigma_0=0$ of a tagged point particle represents the so-called nonoverlapping Lorentz gas[1] (NOVLG). Of particular interest is also the case of equal diameters of tagged particle and scatterers. The special case of the one-dimensional Lorentz gas,[8] which can be solved exactly, will not be discussed here.

For practical purposes one may imagine that the system is prepared in a computer-simulation experiment by generating a fluid containing a tagged particle. After equilibrium is reached the fluid particles are held fixed while the motion of the tagged particle in this static environment, which we refer to as the frozen liquid, is studied by solving Newton's equations of motion. The system of static scatterers is characterized, besides the average density n, by its static structure factor $s_{11}(q)$ at this density which is assumed to be known.

The present model is considerably richer than the Lorentz gas analyzed previously because one can study the dynamical properties of the tagged particle in their dependence on the diameter ratio $\delta=\sigma_0/\sigma_1$ as a new parameter in addition to the density n of scatterers. One can also investigate the effects of static correlations among the scatterers. Our analysis will focus on the behavior of the diffusion coefficient which will be calculated analytically. In Sec. II an extension of the classical self-consistent current relaxation theory to this model is presented. The results are discussed in Sec. III where it is shown that there exists a critical line $n_c(\delta)$ in the (n,δ) plane such that for a given diameter ratio δ, the particle is able to diffuse for scatterer densities $n<n_c(\delta)$, while it is localized for $n>n_c(\delta)$. Good agreement is obtained with Monte Carlo computer results[16,17] for the percolation density of hard disks. Furthermore, various factorization schemes for the current relaxation kernel are discussed, which, in general, are different but turn out to be equivalent in the case of the OVLG as well as the NOVLG.

II. SELF-CONSISTENT CURRENT RELAXATION THEORY

The theory outlined below is a generalization of the one presented recently[10] by incorporating several new effects.

First, the finite diameters σ_0 and σ_1 of the tagged particle and the scatterers will be taken into account. Secondly, the pair correlation $g_{01}(r)$ which is proportional to the probability of finding a scatterer at a distance r from the tagged particle will appear explicitly in the calculation. Third, the static correlations between the scatterers as described by the static structure factor $s_{11}(q)$ will be treated.

The main points of the theory may be summarized as follows: A formal, exact kinetic equation for the phase-space density-correlation function is set up. The two ingredients, free-particle motion and collisions, are incorporated from the outset. The kinetic equation, which for simplicity may be solved within a single relaxation-time approximation, yields the tagged-particle density propagator $\phi(q,z)$ for wave number q and frequency z. It may be cast in the form

$$\phi(q,z)=-\frac{1}{z+q^2D(q,z)}\ , \tag{1}$$

where $D(q,z)$ is a generalized diffusion coefficient which in the single relaxation-time approximation is entirely determined by the free-particle density-correlation function[10] and the single relaxation kernel $\mathscr{C}(z)$.

For small wave numbers $D(q,z)$ is related to the autocorrelation function of the velocity $\vec{v}_0$ of the tagged particle

$$\phi_{vv}(t)=\langle v_0^z(t)v_0^z\rangle \tag{2a}$$

by

$$D(z)=\lim_{q\to 0}D(q,z)=i\int_0^\infty dt\, e^{izt}\phi_{vv}(t)\ \ (\mathrm{Im} z>0)\ . \tag{2b}$$

The angle brackets in Eq. (2a) denote an average over scatterer configurations and velocity directions. Note that $v_0=|\vec{v}_0|$ is constant due to the elastic hard-core collisions. For $D(z)$ one obtains

$$D(z)=-\frac{v_0^2/d}{z+\mathscr{C}(z)}\ , \tag{2c}$$

where d is the dimension of space. Thus, $\mathscr{C}(z)$ is the velocity-relaxation kernel. It is generally frequency dependent and has both an imaginary and real part which describe friction as well as oscillation. The frequency dependence was found to be the crucial point of the diffusion-localization transition.[18,10,2] The zero-frequency limit of the spectrum of $\phi_{vv}(t)$ is the diffusion constant D, or

$$\lim_{z\to i0}D(z)=iD\ . \tag{2d}$$

In general, $\mathscr{C}(z)$ can be separated into two parts each of a different physical origin

$$\mathscr{C}(z)=i\nu+m(z)\ . \tag{3}$$

The first part arises from uncorrelated binary collisions between the tagged particle and a scatterer. It is frequency independent due to the nature of the instantaneous hard-core collisions and given by the collision frequency

$$\nu=n\sigma^{d-1}v_0g_{01}(\sigma)(2\pi^{(d-1)/2})/\Gamma((d+3)/2)\ , \tag{4}$$

where $\sigma=(\sigma_0+\sigma_1)/2$ and $g_{01}(\sigma)$ are the distance of the centers and the pair correlation at contact. As a function of the diameter ratio $\delta=\sigma_0/\sigma_1$ of tagged particle and scatterers, $g_{01}(\sigma)$ increases from $g_{01}(\sigma)=1$ for $\delta=\infty$ (OVLG) to $g_{01}(\sigma)=1/(1-\eta)$ for $\delta=0$ (NOVLG), where $\eta=nV_d(\sigma_1/2)^d$ is the packing fraction of scatterers and $V_d=\pi^{d/2}/\Gamma(1+(d/2))$ is the volume of the unit sphere. For arbitrary ratio δ the solution of the Percus-Yevick integral equation[19,20] in three dimensions and of the scaled-particle theory[21] in two and three dimensions[22] yields

$$g_{01}(\sigma)=\begin{cases}[1-(\sigma_1/\sigma)\eta/2]/(1-\eta)^2\ \ (d=2) & \text{(5a)}\\ [1+\eta+\eta^2-(\sigma_1/\sigma)\frac{3}{2}\eta(1+\eta)+(\sigma_1/\sigma)^2\frac{3}{4}\eta^2]/(1-\eta)^3\ \ (d=3)\ . & \text{(5b)}\end{cases}$$

An exact expression for $g_{01}(\sigma)$ was also derived for arbitrary ratio δ in two dimensions at close packing.[23]

Ignoring for the moment the second term $m(z)$ in Eq. (3), one obtains by inserting in Eq. (2c) the result of the Lorentz-Enskog kinetic theory

$$D_E(z)=-\frac{v_0^2/d}{z+i\nu}\ , \tag{6a}$$

which implies an exponential-decaying velocity-autocorrelation function and a diffusion coefficient

$$D_E=v_0^2/d\nu\ . \tag{6b}$$

The picture of uncorrelated binary collisions is expected to break down as the density of scatterers is increased. This is accounted for by the second frequency-dependent term on the right-hand side (rhs) of Eq. (3) which describes dynamically correlated collisions. The part $m(z)$ is essentially a force-autocorrelation function and thus a four-point correlation. It is approximated by factorizing it in a product of the tagged-particle and scatterer-density correlation functions. Thereby, the relaxation kernel is, in turn, expressed by the unknown tagged-particle propagator and, thus, one arrives at a closed nonlinear equation for the tagged-particle propagator.

There are several different ways of factorizations depending on whether one aims at a good approximation for short or long times. The results will generally be different and the quality of the approximation can be judged best by comparing with experimental results. One particular factorization will be discussed here; two others at the end of this section and their derivations are presented in the Appendix.

Employing a method similar to the one used in the theory of classical liquids[24,25] we obtain

$$\mathscr{C}(z)=i\nu+\frac{n}{d}\left[\frac{v_0^2}{d}\right]\sum_{\vec{k}}\frac{k^2h_{01}^2(k)}{s_{11}(k)}\phi(k,z)\ , \tag{7}$$

where $\sum_{\vec{k}} = \int d^dk/(2\pi)^d$ and $h_{01}(k)$ is the Fourier transform of $h_{01}(r) = g_{01}(r) - 1$. In Eq. (7) we restrict the selection of modes to only the tagged-particle density propagator $\phi(k,z)$ for simplicity. In general, there are also couplings to other tagged-particle modes[10], but it has been shown elsewhere[10,11] that it is only the density mode that is responsible for the diffusion-localization transition.

Since at present little information is available for the wave-number and frequency-dependent Van-Hove scattering function $\phi(q,z)$, or the velocity-correlation function $\phi_{vv}(t)$, we will discuss here mainly the diffusion coefficient, which may be evaluated analytically by employing a further approximation that is quite reasonable. For small frequency z the main contribution to the wave-number integral in Eq. (7) will come from the small wave-number regime. Therefore, the hydrodynamic approximation

$$\phi(k,z) \simeq -\frac{1}{z + k^2 D(z)} , \tag{8}$$

which is valid at small wave numbers may be inserted in Eq. (7). Then, using Eqs. (2c) and (6a), Eq. (7) can be cast into the form of a transcendental equation for $D(z)$

$$D(z)/D_E(z) = 1 - \frac{n}{d} \sum_{\vec{k}} \frac{k^2 h_{01}^2(k)}{s_{11}(k)} \left[\frac{1}{k^2 + z/D(z)} \right] . \tag{9}$$

The question of whether this equation describes a diffusion-localization transition can be answered by its small frequency properties. Assuming that D is finite, Eq. (9) reads for zero frequency,

$$D/D_E = 1 - \frac{n}{d} \sum_{\vec{k}} h_{01}^2(k)/s_{11}(k) . \tag{10}$$

The wave-number integral can be performed exactly by using the Ornstein-Zernike relations for fluid mixtures

$$h_{kj}(q) = C_{kj}(q) + \sum_i h_{ki}(q) n_i C_{ij}(q) , \tag{11}$$

where the subscripts denote the tagged particle and the fluid for $i = 0,1$, respectively, and $n_0 = 0$, $n_1 = n$ are the corresponding number densities. The result is quite simple,

$$D/D_E = 1 - [-1 - C_{00}(r=0)]/d , \tag{12}$$

expressing D/D_E in terms of the tagged-particle direct correlation function $C_{00}(r=0)$ at zero separation. Notice, incidentally, that the result of Eq. (12) is independent of the hard-core interaction potential, and one may surmise that it may be also valid for soft potentials.

Anticipating that the term in brackets in Eq. (12) increases with density as suggested by the explicit factor n in Eq. (10), one finds that D/D_E vanishes at a critical density n_c. Above this density the solution Eq. (12) is unphysical. Instead, as in the case of the OVLG,[10] one finds for $n > n_c$,

$$D(z) \simeq z l_0^2 + O(z^2) , \tag{13a}$$

for small frequency with the constant l_0 determined by

$$1 = \frac{n}{d} \sum_{\vec{k}} \frac{k^2 h_{01}^2(k)}{s_{11}(k)} \left[\frac{1}{k^2 + l_0^{-2}} \right] . \tag{13b}$$

The vanishing of the diffusion coefficient in Eq. (13a) implies a zero-frequency pole in the tagged-particle density propagator[18,10,2]

$$\phi(q,z) = -\frac{1}{z} \frac{1}{1 + q^2 l_0^2} + \phi_R(q,z) , \tag{14}$$

where $\phi_R(q,z)$ denotes the regular part. Thus, the spectrum exhibits an elastic $\delta(\omega)$ peak with form factor $f(q) = 1/(1 + q^2 l_0^2)$, where the length l_0 is a measure of the size of the localization region. From Eq. (13b) one finds that the localization length l_0 diverges with a square-root behavior with logarithmic corrections in two dimensions as the critical density is approached from above. In Sec. III the result for the diffusion coefficient in Eq. (12) will be discussed in more detail, together with the results obtained by employing two other factorization approximations.

Other factorization schemes. Two other factorization schemes shall be examined here. They differ from the one leading to Eq. (7), in the way that static correlations are approximated, and their derivation is given in the Appendix. These approximations have been discussed in a similar form in the case of the velocity-autocorrelation function of a hard-sphere fluid.[26,27] But instead of the particle propagators of the Enskog theory used by these authors, the self-consistent propagators will be used here since it was found[2,10,18] that a self-consistent theory can yield a diffusion-localization transition and provide a valid description below as well as above the critical density.

One particular factorization[26] is aimed at achieving a good approximation of the time-dependent current relaxation kernel $m(t)$ at short times by factorizing the normalized four-point correlation function in such a way that its value at time zero is maintained exactly as explained in the Appendix. This leads to the equation

$$D/D_E = 1 - \frac{n}{d} g_{01}(\sigma) \sum_{\vec{k}} h_{01}^{(0)}(k) h_{01}(k) , \tag{15a}$$

to be compared with Eq. (10) where $h_{01}^{(0)}(k)$ is the Fourier transform of the low-density pair-correlation function $h_{01}^{(0)}(r) = -1,0$ for $r < \sigma$ and $r > \sigma$, respectively. The wave-number integral in Eq. (15a) also can be performed exactly and one finds instead of Eq. (12)

$$D/D_E = 1 - (V_d/d) n \sigma^d g_{01}(\sigma) . \tag{15b}$$

It is interesting to note in passing that because of $\sum_{\vec{k}} h_{01}^{(0)}(k) h_{01}(k) = \sum_{\vec{k}} [h_{01}^{(0)}(k)]^2$ the static structure factor of the scatterers does not enter Eq. (15a) for D/D_E directly.

A different approximation[27] consists in factorizing the time-dependent four-point correlation function directly and this leads to

$$D/D_E = 1 - \frac{n}{d} g_{01}^2(\sigma) \sum_{\vec{k}} [h_{01}^{(0)}(k)]^2 s_{11}(k) . \tag{16a}$$

For the NOVLG, the wave-number integral can be performed exactly with the result

$$D/D_E=1-\frac{\eta/d}{1-\eta}\ . \tag{16b}$$

For a tagged particle of finite diameter the wave-number integral in Eq. (16a) is evaluated numerically in three dimensions by using the structure factor of the Percus-Yevick theory[20] (PY), and the results are presented in Sec. III, along with the results of Eqs. (15b) and (12).

III. RESULTS AND DISCUSSION

In order to evaluate D/D_E of Eq. (12) one needs to know the tagged-particle direct correlation function at zero separation. In three dimensions $C_{00}(r)$ is known analytically from the solution of the approximate PY integral equation,[20] but for the two-dimensional system no analytic solution is currently available. On the other hand, analytical results for the thermodynamical properties of rigid-sphere mixtures have been obtained within the scaled-particle theory[22] (SP) in one, two, and three dimensions and the method also can be generalized to arbitrary dimensions. In one dimension the scaled-particle theory is exact as is the PY theory, while in three dimensions both the PY and SP theories[19] yield the same thermodynamic properties.

By combining PY and SP theories, analytical expressions can be obtained for $C_{00}(r=0)$ in all dimensions. Using the Ornstein-Zernike relations, Eq. (11), and assuming $C_{ik}(r)=0$ for $r>\sigma_{ik}=(\sigma_i+\sigma_k)/2$, which is equivalent to the PY approximation, one can relate $C_{00}(r=0)$ to the pressure derivative with respect to density

$$C_{00}(r=0)=-\frac{\partial[\beta p(n_0,n_1)]}{\partial n_0}\ , \tag{17}$$

where $\beta=1/k_BT$; T is the temperature and p is the pressure. Using the results of the SP theory[22] for the pressure of a rigid-sphere fluid for $n_0=0$ and $n_1=n$, one finds

$$C_{00}(r=0)=\begin{cases}-\left[1+\delta\dfrac{2\eta}{1-\eta}+\delta^2\dfrac{\eta(1+\eta)}{(1-\eta)^2}\right]\dfrac{1}{1-\eta}\quad(d=2) & \text{(18a)}\\[2ex] -\left[1+\delta\dfrac{3\eta}{1-\eta}+\delta^2\dfrac{3\eta(1+2\eta)}{(1-\eta)^2}+\delta^3\dfrac{\eta(1+2\eta)^2}{(1-\eta)^3}\right]\dfrac{1}{1-\eta}\quad(d=3) & \text{(18b)}\end{cases}$$

where $\delta=\sigma_0/\sigma_1$ is the diameter ratio and η the packing fraction. Note in passing that the results

$$C_{00}(r=0)=\begin{cases}-1/(1-\eta)\quad(\sigma_0=0) & \text{(18c)}\\ -[1+nV_d(\sigma_0/2)^d]\quad(\sigma_1=0) & \text{(18d)}\end{cases}$$

corresponding to the NOVLG and OVLG, respectively, are exact in all dimensions. Furthermore, the small density expansion

$$C_{00}(r=0)=-[1+nV_d\sigma^d+O(n^2)] \tag{18e}$$

is in agreement with Eqs. (18a) and (18b) for $d=2$ and 3.

A. Overlapping Lorentz gas

The diffusion coefficient for the OVLG ($\sigma_1=0$) will be discussed first. Since, in this case there are no correlations between the scatterers, implying that $s_{11}(k)=1$, $h_{01}(k)=h_{01}^{(0)}(k)$, and $g_{01}(\sigma)=1$, the three approximations, Eqs. (10), (15a), and (16a), are equivalent. Inserting Eq. (18d) in Eq. (12) yields

$$D/D_E=1-n(\sigma_0/2)^dV_d/d\ . \tag{19}$$

D/D_E linearly decreases with density up to the critical reduced density $n_c^*=d/V_d$ and above this critical density of scatterers the particle is localized as discussed before. The value of the critical density is in agreement with results obtained earlier.[10,13] Although it is well known that the small density expansion of D/D_E leads to logarithmic contributions[7] with a leading term proportional to $n^{d-1}\ln(n)$ for $d\geq 2$, which was also confirmed by computer simulations,[3] the molecular-dynamics data[3–5] show an overall nearly linear decrease of D/D_E with increasing density, a behavior in good agreement with the result of Eq. (19). Moreover, it has been shown[10] that the logarithmic density term can be rederived within the present theory by including the coupling to other tagged-particle modes in Eq. (7). The critical density $n_c^*=4/9\pi$ for three dimensions is in good agreement with experimental results,[3,28] while $n_c^*=2/\pi$ for two dimensions is too high compared to the experimental result[4,29] $n_c^*\approx 0.37$.

B. Nonoverlapping Lorentz gas

For the NOVLG ($\sigma_0=0$), Eqs. (18c) and (12) lead to the simple result

$$D/D_E=1-\frac{\eta/d}{1-\eta}\ , \tag{20}$$

and the same result is also obtained by the two different factorization schemes leading to Eqs. (15b) and (16b). Equation (20) shows that D/D_E decreases for small density with the same slope as for the OVLG which is to be expected since for small density the difference between overlapping and nonoverlapping scatterers is irrelevant. But for increasing density D/D_E decreases faster than for the OVLG. The critical packing fraction where D/D_E vanishes linearly is $\eta_c=d/(d+1)$.

While there is no restriction to the density of scatterers for the OVLG, the upper limit in the nonoverlapping case is the density of close packing corresponding to the packing fraction η_0. Since in two dimensions the critical density $\eta_c=2/3$ is smaller than the close-packing density $\eta_0=(\pi/6)\sqrt{3}=0.907$, the theory predicts a diffusion-localization transition for a tagged point particle in a frozen hard-disk fluid at $\eta_c/\eta_0=0.735$. It is quite satisfying that the value of η_c is less than η_0 since for hard disks diffusion clearly has to stop finally at close packing even for a moving point particle.

In contrast, for the three-dimensional NOVLG the critical density $\eta_c = \frac{3}{4}$ is higher than the density $\eta_0 = (\pi/6)\sqrt{2} = 0.740$ of close packing. Thus, for a point particle moving in a frozen rigid-sphere fluid, the theory predicts a nonzero diffusion constant even at close packing. This result is also quite reasonable since even at the close packing density there are channels through which a point particle can move.

The same is also true in more than three dimensions as one can see by comparing the critical density $\eta_c = d/(d+1)$ with the density of close packing η_0, the former approaching unity while the latter decreases to zero with increasing dimensionality.[30] The fact that η_0 tends to zero with increasing dimensionality shows that in higher dimensions most of the space is not filled by hyperspheres and so localization of a point particle becomes increasingly more difficult.

The diffusion coefficient of the two- and three-dimensional Lorentz gas is shown in Figs. 1 and 2(a), respectively, as indicated by $\delta = 0$. For two dimensions D/D_E may be compared with the results of computer simulations.[5] Although the scattering in the data is considerable, the data seem to indicate that the critical density is somewhat higher than predicted.

C. Scatterers and particle of finite diameter

In the general case of a tagged particle and scatterers of diameter σ_0 and σ_1, respectively, the result for the diffusion constant, Eq. (12), together with Eqs. (18a) and (18b), is

$$D/D_E = \begin{cases} 1 - \dfrac{\eta/2}{1-\eta}\left[1 + \delta\dfrac{2}{1-\eta} + \delta^2\dfrac{1+\eta}{(1-\eta)^2}\right] & (d=2) \qquad \text{(21a)} \\[2ex] 1 - \dfrac{\eta/3}{1-\eta}\left[1 + \delta\dfrac{3}{1-\eta} + \delta^2\dfrac{3(1+2\eta)}{(1-\eta)^2} + \delta^3\dfrac{(1+2\eta)^2}{(1-\eta)^3}\right] & (d=3) \qquad \text{(21b)} \end{cases}$$

in two and three dimensions with $\delta = \sigma_0/\sigma_1$. As one expects, for a given density of scatterers, diffusion becomes more and more difficult with increasing size of the tagged particle. This is shown in Figs. 1, 2(a), and 2(b) for various diameter ratios δ. In Fig. 1, for the two-dimensional system, the result, Eq. (15b) for $\delta = 1$, also indicates the effect of the different approximations at intermediate values of δ.

The system of a tagged particle moving in a frozen fluid may be considered as the limiting case of zero mass ratio $m = m_0/m_1$ of a solvent fluid of mass m_1 and a solute tagged particle of mass m_0. For a three-dimensional hard-sphere system, computer simulations[31] have been performed for various mass and diameter ratios at several

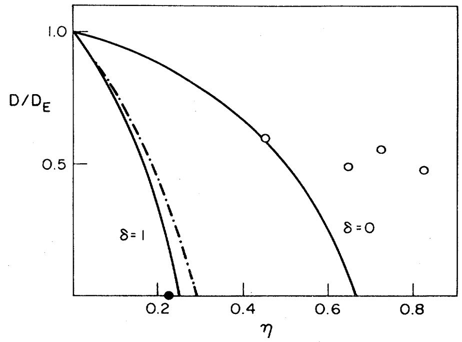

FIG. 1. Diffusion constant D divided by Enskog value D_E vs packing fraction η in two dimensions for diameter ratios $\delta = 0$ and $\delta = 1$. Solid curves, result of Eq. (21a); dash-dotted curve, Eq. (15b); open circles, molecular-dynamics data for NOVLG (Ref. 5); full circle, Monte Carlo result (Ref. 17).

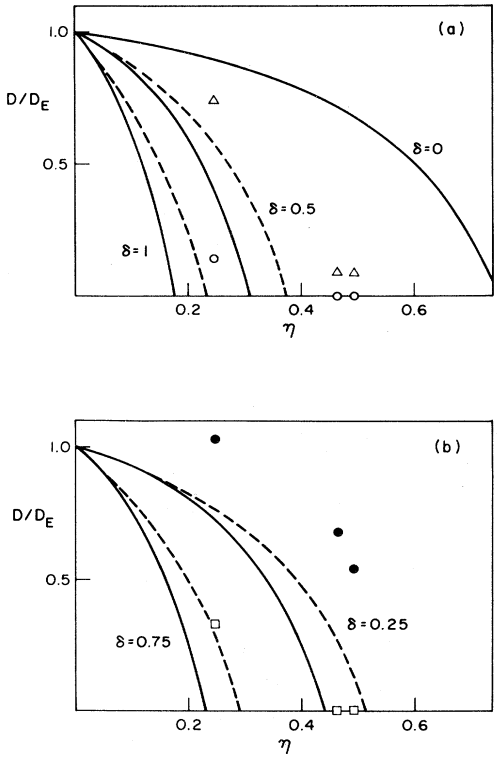

FIG. 2. (a) and (b) Diffusion constant D divided by Enskog value D_E vs packing fraction η in three dimensions for various diameter ratios δ. Solid curves, result of Eq. (21b); dashed curves, Eq. (16a); full circles, molecular-dynamics results extrapolated from data in Ref. 31 to zero mass ratio are shown for $\delta = 0.25$; triangles, $\delta = 0.5$; squares, $\delta = 0.75$; open circles, $\delta = 1$.

densities. Figures 2(a) and 2(b) show results obtained by extrapolating the data for mass ratios $m=1$, $\frac{1}{10}$, $\frac{1}{100}$, and $\frac{1}{5625}$ to $m=0$. The combined statistical error of the data and of the extrapolation is difficult to estimate, but the simulation results seem to indicate that the diffusion coefficient is larger than predicted. The diffusion coefficient resulting from Eq. (16a), also shown in Figs. 2(a) and 2(b), is generally larger than that predicted by Eq. (21b) for intermediate values of δ. The result of Eq. (15b) which lies between the curves corresponding to Eqs. (16a) and (21b) is not shown.

Since D/D_E decreases with increasing tagged-particle size, the critical density where diffusion is blocked will decrease also. The variation of the critical density $\eta_c(\delta)$ with the diameter ratio δ resulting from Eqs. (21a) and (21b), is shown in Figs. 3(a) and 3(b) together with the results of Eqs. (15b) and (16a). In the region below the critical line $\eta_c(\delta)$, the diffusion coefficient of the tagged particle is finite; in the region above this line the particle is localized. The small and large δ limits corresponding to the NOVLG with $\eta_c=d/(d+1)-\delta d^2/(d+1)+O(\delta^2)$ for $\delta\rightarrow 0$ and the OVLG with $\eta_c=d/\delta^d+O(\delta^{1-d})$ for $\delta\rightarrow\infty$ have been mentioned above. There is a qualitative change in increasing the dimension from $d=2$ to $d>2$. While for $d=2$ the particle at high density above η_c is localized for all size ratios δ, for $d\geq 3$ there is a critical size ratio δ_c, below which the particle can diffuse at all densities.[32] It may be accidental that δ_c at close packing is smaller than the smallest cross-section diameter $(2/\sqrt{3}-1)$ of channels in a close-packed array of spheres, as indicated by an arrow in Fig. 3(b), but the contrary would obviously be wrong.

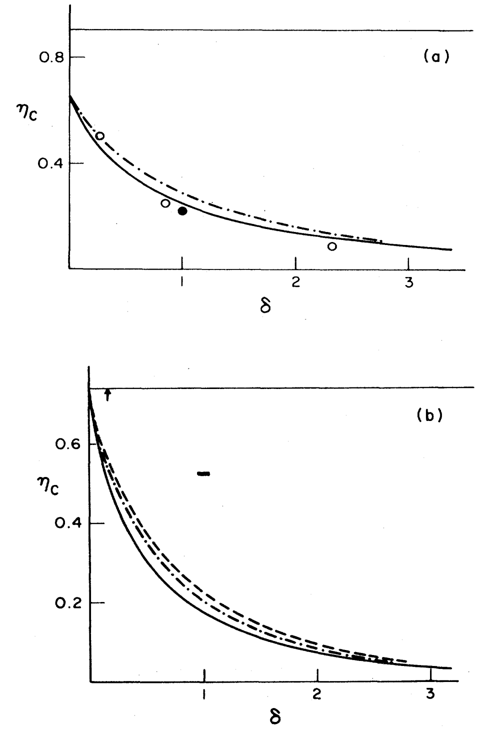

FIG. 3. Critical-packing fraction η_c vs diameter ratio $\delta=\sigma_0/\sigma_1$. Solid curves, result of Eq. (21); dash-dotted curves, Eq. (15b). (a) Two dimensions: Monte Carlo results for the percolation density; open circles (Ref. 16); full circle (Ref. 17); (b) Three dimensions: dashed curve, result of Eq. (16a); the bar indicates the glass-transition density of a hard-sphere fluid (Ref. 34).

The system of a tagged particle in a frozen fluid is related to percolation theory.[33] One can define that two scatterers of hard-core diameter σ_1 belong to the same cluster if the distance of their centers is smaller than $R=\sigma_1+\sigma_0$. For the two-dimensional system this implies that the tagged particle of diameter σ_0 cannot pass between them. The percolation density, defined as the density where the mean cluster size becomes infinite, will depend on $\delta=\sigma_0/\sigma_1$. Clearly, for $d=2$, diffusion is impossible above this percolation density and one may probably identify it as the critical density where D vanishes. Note that the above definition of a cluster contains the more familiar one of overlapping spheres for the special case $\sigma_1=0$. Results of two different Monte Carlo computer simulations[16,17] for the percolation density of a hard-disk system are shown in Fig. 3(a). Agreement with the prediction $\eta_c(\delta)$, especially Eq. (21a), appears to be quite good. For large ratio δ our results are somewhat too high, which we have already noted in the case of the OVLG, the $\delta\rightarrow\infty$ limit. Monte Carlo results for the three-dimensional system would be quite helpful.

For completeness we mention that the critical densities for equal sizes of tagged particle and scatterers resulting from Eqs. (21a) and (21b) are $\eta_c=0.253$ and 0.177 in two and three dimensions, respectively, which are 0.279 and 0.239 of close-packed densities. These critical densities should not be misinterpreted as the glass-transition densities of a rigid-sphere fluid since we consider here the model with fixed fluid particles. If the fluid particles are allowed to move they can be pushed away by a tagged particle, so one expects that its diffusion coefficient will be larger and, therefore, the glass-transition density should be larger than the one calculated for the present model. This is indeed the case as shown in Fig. 3(b).

IV. SUMMARY

An extension of the self-consistent current relaxation theory of the OVLG, to the more general model of a particle of diameter σ_0 moving in an environment of fixed hard-core scatterers of diameter σ_1, is accomplished by incorporating the static correlations among the scatterers. The diffusion constant is evaluated analytically and it is found that with increasing density it decreases faster than in the absence of correlations between the scatterers. The variation of the diffusion-localization transition with the diameter ratio $\delta=\sigma_0/\sigma_1$ is evaluated and good agreement with Monte Carlo results for the percolation density of a hard-disk system is obtained.

Various factorization schemes of the current relaxation kernel are examined. The close agreement of the results of these approximations [see Figs. 3(a) and 3(b)] suggests that the treatment of the static correlations is reasonable. Thus, the remaining discrepancies in comparison with experimental data are probably caused by the simple factorization of the dynamical four-point correlation function. In terms of collisional processes this factorization corresponds to considering only ring collisions. The inclusion of repeated ring collisions is expected to make diffusion more difficult. Moreover, it was shown elsewhere[15] that still other collision sequences, which may be called rattling collisions, since in the simplest case the particle collides several times with two scatterers, play an important role for the Lorentz gas. Further simulation results for the three-dimensional system are desirable. Also further molecular-dynamic experiments, especially for the NOVLG in two and three dimensions, would enable a more detailed analysis of dynamical correlations.

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APPENDIX: VARIOUS FACTORIZATION SCHEMES

The formal expression for the current relaxation kernel is

$$m(z)=\frac{1}{\Omega}\int d\vec{r}_{12}\int d\hat{v}_1\int d\hat{v}_2\hat{v}_1 m(12,z)\hat{v}_2\ , \qquad \text{(A1a)}$$

$$m(12,z) =(Q\mathscr{L}'_+f(1)\,|\,(Q\mathscr{L}_-Q-z)^{-1}\,|\,Q\mathscr{L}'_-f(2))\ , \qquad \text{(A1b)}$$

where $\hat{v}=\vec{v}/|\vec{v}|$ is a unit vector and Ω is the surface of the d-dimensional unit sphere. The tagged-particle phase-space distribution function is denoted by $f(1)=\delta(1-0)=\delta(\vec{r}_1-\vec{r}_0)\delta(\vec{v}_1-\vec{v}_0)$ and the projector Q projects onto the space orthogonal to $f(1)$. The two parts of the "pseudo"-Liouville operator $L_\pm=L_0+L'_\pm$ with $L_0=-i\vec{v}_0\cdot\vec{\nabla}_0$ and $L'_\pm=\sum_{n\neq0}^{N}T_\pm(0n)$, where

$$T_\pm(0n)=i\int d\hat{r}(\vec{v}_0\hat{r})\Theta(\mp\vec{v}_0\hat{r}) \times\delta(\hat{r}\sigma_{01}-\vec{r}_{0n})(b-1)\ , \qquad \text{(A2)}$$

describe free-streaming and binary collisions. In Eq. (A2) the operator b replaces the particle velocity $\vec{v}_0$ by $\vec{v}_0'=b\vec{v}_0=\vec{v}_0-2(\vec{v}_0\cdot\hat{r})\hat{r}$. The parentheses in Eq. (A1b) denote an ensemble average with $(A\,|\,B)=\langle A^*B\rangle$ over scatterers and particle configurations with fixed velocity v_0 of the particle. Observing that

$$L'_\pm f(1)=\sqrt{N}\,T_\pm(1\bar{2})f(1\bar{2})\ , \qquad \text{(A3)}$$

where

$$f(12)=\sum_{n\neq0}^{N}\delta(1-0)\delta(\vec{r}_2-\vec{r}_n)/\sqrt{N}$$

is a tagged-particle scatterer phase-space distribution, and integration over variables with a bar is implied, one is led to define $F_2(12)=Qf(12)$ and the four-point correlation function

$$G(12,34;z)=(F_2(12)\,|\,(QL_-Q-z)^{-1}\,|\,F_2(34))\ . \qquad \text{(A4a)}$$

Its value at time zero is denoted by

$$\tilde{G}(12,34)=(F_2(12)\,|\,F_2(34))\ , \qquad \text{(A4b)}$$

which can be expressed by static two- and three-particle correlation functions. Its inverse $\tilde{G}^{-1}$ is defined by $\tilde{G}^{-1}(12,\bar{3}\bar{4})\tilde{G}(\bar{3}\bar{4},56)=\delta(15)\delta(26)$. Also, a new projector P_2 may be defined by $P_2=|F_2)\tilde{G}^{-1}(F_2|$. Abbreviating the resolvent in Eq. (A1b) by $R_Q(z)=(QL_-Q-z)^{-1}$ and using Eq. (A3) one finds that $m(12,z)$ can be cast into three equivalent forms

$$m(12,z)=\begin{cases}(Q\mathscr{L}'_+f(1)\,|\,P_2R_Q(z)P_2\,|\,Q\mathscr{L}'_-f(2))\ , & \text{(A5a)}\\ (Q\mathscr{L}'_+f(1)\,|\,P_2R_Q(z)\,|\,Q\mathscr{L}'_-f(2))\ , & \text{(A5b)}\\ (Q\mathscr{L}'_+f(1)\,|\,R_Q(z)\,|\,Q\mathscr{L}'_-f(2))\ . & \text{(A5c)}\end{cases}$$

The approximation of factorizing the four-point correlations in Eq. (A5) by

$$G(12,34;t)\simeq\phi(13,t)s_{11}(24)\ , \qquad \text{(A6a)}$$

$$\tilde{G}(12,34)\simeq\delta(13)s_{11}(24)\ , \qquad \text{(A6b)}$$

where $\phi(13,t)$ is the tagged-particle phase-space correlation function and $s_{11}(24)$ is the static scatterer-structure factor, leads to three different results.

From Eq. (A5a) one finds with the notations

$$V_-(12,3)=(F_2(12)\,|\,QL'_-f(3))$$

and

$$V_+(1,23)=(QL'_+f(1)\,|\,F_2(23))$$

the result

$$m(12,z)\simeq V_+(1,\bar{3}\bar{4})\phi(\bar{3}\bar{6},z)s_{11}^{-1}(\bar{4}\bar{7})V_-(\overline{67},z)\ . \qquad \text{(A7a)}$$

Evaluating the static correlations $V_\pm$ exactly, which in general also requires the knowledge of the three-particle correlation function, leads to Eq. (7).

Equation (A5b) is approximated by this factorization by

$$m(12,z)\simeq g_{01}(\sigma)V_+(1,\bar{3}\bar{4})\phi(\bar{3}2,z)T_-(2\bar{4})\ , \qquad \text{(A7b)}$$

while from Eq. (A5c) one finds

$$m(12,z)\simeq g_{01}^2(\sigma)T_+(1\bar{3})\phi(12,z) \times s_{11}(\bar{3}\bar{4})T_-(2\bar{4})\ . \qquad \text{(A7c)}$$

In Eqs. (A7b) and (A7c) the fact that the collisions take place in a dense system is taken care of by an explicit factor of $g_{01}(\sigma)$ for each collision operator T. This leads to the formulas (15a) and (16a), respectively. In the case that the static correlations are trivial, i.e., at low density or for the OVLG, all three approximations in Eqs. (A7a)–(A7c) are equivalent. With respect to the static correlations the three approximations are, in general, different, but with respect to dynamical correlations, they have in common the fact that only ring collisions are considered.

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[1] E. H. Hauge, in *Théories Cinétiques Classiques et Relativstes,* Springer Lecture Notes in Physics, edited by G. Kirczenow and J. Marro (Springer, Berlin, 1974), Vol. 31, pp. 337; E. G. D. Cohen, in *Colloques Internationaux CNRS,* No. 236 (CNRS, Grenoble, 1974), pp. 269.

[2] W. Götze, in *Modern Problems in Solid State Physics,* edited by Yu. E. Lozovik and A. A. Maradudin (North-Holland, Amsterdam, 1983), Vol. 1.

[3] C. Bruin, Phys. Rev. Lett. 29, 1670 (1972); Physica (Utrecht) 72, 261 (1974).

[4] B. J. Alder and W. E. Alley, J. Stat. Phys. 19, 341 (1978); W. E. Alley and B. J. Alder, Phys. Rev. Lett. 43, 653 (1979).

[5] W. E. Alley, Ph.D. thesis, University of California, Davis, 1979 (unpublished).

[6] J. C. Lewis and J. A. Tjon, Phys. Lett. 66A, 349 (1978).

[7] J. M. J. van Leeuwen and A. Weyland, Physica (Utrecht) 36, 457 (1967); A. Weyland and J. M. J. van Leeuwen, *ibid.* 38, 35 (1968).

[8] A. Weyland, J. Math. Phys. 15, 1942 (1974).

[9] T. Keyes and J. Mercer, Physica (Utrecht) 95A, 473 (1979).

[10] W. Götze, E. Leutheusser, and Sidney Yip, Phys. Rev. A 23, 2634 (1981); 24, 1008 (1981); 25, 533 (1982).

[11] W. Götze and E. Leutheusser, Z. Phys. B 45, 85 (1981).

[12] M. H. Ernst and H. van Beijeren, J. Stat. Phys. 26, 1 (1981).

[13] E. Leutheusser, J. Phys. C 15, L295 (1982).

[14] A. J. Masters and T. Keyes, Phys. Rev. A 25, 1010 (1982); 26, 2129 (1982).

[15] E. Leutheusser, Phys. Rev. A (in press).

[16] G. E. Pike and C. H. Seager, Phys. Rev. B 10, 1421 (1974).

[17] W. G. Hoover, N. E. Hoover, and K. Hanson, J. Chem. Phys. 70, 1837 (1979).

[18] W. Götze, Solid State Commun. 27, 1393 (1978); J. Phys. C 12, 1279 (1979); Philos. Mag. B 43, 219 (1981).

[19] For a review, see J. A. Barker and D. Henderson, Rev. Mod. Phys. 48, 587 (1976).

[20] J. L. Lebowitz, Phys. Rev. 133, A895 (1964).

[21] H. Reiss, H. L. Frisch, and J. L. Lebowitz, J. Chem. Phys. 31, 369 (1959).

[22] J. L. Lebowitz, E. Helfand, and E. Praestgaard, J. Chem. Phys. 43, 774 (1965).

[23] M. A. Cotter and F. H. Stillinger, J. Chem. Phys. 57, 3356 (1972).

[24] W. Götze and M. Lücke, Phys. Rev. A 11, 2173 (1975); J. Bosse, W. Götze, and M. Lücke, *ibid.* 17, 434 (1978).

[25] Although the factorization presented here in Eq. (A7a) leading to Eq. (7) is formally similar to the one used in Ref. 24, one should keep in mind the different physical meaning due to the difference between the Liouville operator for a system interacting by a continuous potential and the hard-core pseudo-Liouville operator.

[26] P. Résibois, J. Stat. Phys. 13, 393 (1975).

[27] G. Mazenko and S. Yip, in *Statistical Mechanics,* edited by B. J. Berne (Plenum, New York, 1977), Vol. 6, Part B, pp. 181–231.

[28] J. Kertész, J. Phys. (Paris) Lett. 42, L393 (1981).

[29] S. W. Haan and R. Zwanzig, J. Phys. A 10, 1547 (1977).

[30] C. A. Rogers, *Packing and Covering* (Cambridge University Press, Cambridge, 1964).

[31] P. T. Herman and B. J. Alder, J. Chem. Phys. 56, 987 (1972); B. J. Alder, W. E. Alley, and J. H. Dymond, *ibid.* 61, 1415 (1974).

[32] Actually the results presented here are based on the static correlations corresponding to the fluid branch of the equation of state and are supposed to be applicable, at most, up to the density of random close packing (Ref. 34). In the case of an ordered solid the corresponding expressions for $g_{01}(\sigma)$, $p(n_0,n_1)$, etc., have to be used, which, however, seem generally to be unknown. The results for the case $\delta=0$, however, remain valid.

[33] For a review see D. Stauffer, Phys. Rep. 54, 1 (1979).

[34] C. A. Angell, J. H. R. Clarke, and L. V. Woodcock, in *Advances in Chemical Physics,* edited by I. Prigogine and S. A. Rice (Wiley, New York, 1981), Vol. 48, pp. 397–453.