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Bilinear Hydrodynamics and the Stokes-Einstein Law*

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The autocorrelation function of the density of a tagged particle is studied using the Mori formalism. The variables used are the collective conserved variables, the tagged-particle density, and bilinear products thereof. The case of point particles is considered in two dimensions, and, in three dimensions, self-diffusion by a particle of arbitrary size is treated. It is found that the bilinear-hydrodynamic approach automatically separates the self-diffusion coefficient of the tagged particle into a nonhydrodynamic part, and a hydrodynamic part which resembles the Stokes-Einstein law. In two dimensions, it is found that the mean-square displacement of a particle increases as $t\ln t$, and that certain natural redefinitions of the diffusion and friction coefficients leave Einstein's law invariant. In three dimensions, for a large particle, the Stokes-Einstein law is reproduced. The relation between the well-known $t^{(-3/2)}$ "tails" on correlation functions, and the Stokes-Einstein law, is discussed.

I. INTRODUCTION

Stokes[1] has calculated the force on a sphere in uniform motion through a continuum which obeys the laws of linearized Navier-Stokes hydrodynamics, and which sticks to the sphere at its surface. The result is

$$\vec{F} = -6\pi\eta R\vec{p}/m, \tag{1}$$

where $\vec{p}$ is the momentum of the sphere, m is the mass, and R is the radius, while η is the coefficient of shear viscosity of the continuum. The friction coefficient of Brownian-motion theory ξ is defined by the relation

$$\vec{F} = -(\xi/m)\vec{p}\,; \tag{2}$$

thus, we have Stokes law

$$\xi = 6\pi\eta R. \tag{3}$$

Einstein's law[2] relates the diffusion coefficient D of a Brownian particle to the friction coefficient

$$D = k_B T/\xi, \tag{4}$$

where k_B is Boltzmann's constant and T is the absolute temperature. The combination of Eqs. (3) and (4) yields the Stokes-Einstein law[2]

$$D = k_B T/6\pi\eta R, \tag{5}$$

which relates the diffusion coefficient of a Brownian sphere to the viscosity of the solvent, the radius of the sphere, and known constants. From a molecular point of view, the Brownian-motion conditions for which Eqs. (1)–(5) ought to be valid correspond to the motion of a large heavy particle through a dense solvent of small light molecules. More precisely, the mass of the heavy particle must be large compared to the mass of a solvent particle and its radius must be large compared to the distance between solvent particles. It is indeed true[3] that solutions of macromolecules in small-molecule solvents appear to obey the Stokes-Einstein law.

Remarkably enough,[4] the Stokes-Einstein law also seems roughly correct for particles which should not obey Brownian-motion assumptions. For example, the law works reasonably well for relating the self-diffusion coefficient of a constituent particle of a pure liquid to the shear-viscosity coefficient of the liquid. The wide range of usefulness of the Stokes-Einstein law has provoked numerous attempts to derive the law using molecular arguments. Such attempts have met with varying degrees of success, and have utilized different theoretical approaches. For example,[5] attempts to derive the Stokes-Einstein law have been made utilizing the correlation-function expression for the friction coefficient $\xi = \int_0^\infty \langle FF(t)\rangle\, dt/k_B T$. In the following, we shall present a new approach to the problem, based upon the principles of generalized hydrodynamics.

In order to introduce our approach, it is necessary to present a definition of the self-diffusion coefficient. Let $n^i(\vec{r}, t)$ be the density of the ith particle in an N-particle system (we can let $i=1$). For point particles,

$$n^1(\vec{r}, t) = \delta(\vec{r} - \vec{r}_1(t)), \tag{6}$$

where $\vec{r}_1(t)$ is the center-of-mass position of particle 1 at time t. Equation (6) must be modified for large Brownian particles, but we shall defer the discussion of this question to Sec. V. The spatial Fourier transform of $n^1(\vec{r}, t)$ is $n^1_{\vec{k}}(t)$,

$$n^1_{\vec{k}}(t) = \int e^{i\vec{k}\cdot\vec{r}} n^1(\vec{r}, t)\, d\vec{r} = e^{i\vec{k}\cdot\vec{r}_1(t)}. \tag{7}$$

Mori's identity[6] allows the calculation of the Laplace transform of the autocorrelation function of $n^1_{\vec{k}}(t)$,

$$\int_0^\infty e^{-st}\langle n^1_{\vec{k}}(t)\, n^1_{-\vec{k}}(0)\rangle\, dt \equiv S^1(\vec{k}, s) = [s + k^2 D(\vec{k}, s)]^{-1}, \tag{8}$$

where $\langle\ \rangle$ denotes an equilibrium-ensemble average, k is the magnitude of $\vec{k}$, and $S^1(\vec{k}, s)$ is defined by Eq. (8). $D(\vec{k}, s)$ is given by

$$D(\vec{k}, s) = m^{-2}\tfrac{1}{3}\int_0^\infty e^{-st} \times\langle (1-P_L)\vec{p}^{\,1}_{-\vec{k}} \cdot \{\exp[(1-P_L)i\mathfrak{L}t](1-P_L)\vec{p}^{\,1}_{\vec{k}}\}\rangle\, dt, \tag{9}$$

where

$$\vec{p}^{\,1}_{\vec{k}} \equiv \vec{p}_1\, e^{i\vec{k}\cdot\vec{r}_1}, \tag{10}$$

$\vec{p}_1$ is the momentum of particle 1, P_L is the Mori projection operator onto the variable n^1,

$$P_L A_{\vec{k}} = \langle n^1_{\vec{k}} A_{-\vec{k}}\rangle n^1_{\vec{k}} \tag{11}$$

for an arbitrary variable A, and $\mathfrak{L}$ is the classical Liouville operator. We define $D(\vec{k}, s)$ as the wave-vector- and frequency-dependent self-diffusion coefficient of particle 1. From Eqs. (7) and (8), we can easily see that

$$\int_0^\infty e^{-st}\langle |\vec{r}_1(t) - \vec{r}_1(0)|^2\rangle\, dt = d(-\nabla^2_{\vec{k}} S^1(\vec{k}, s))_{k=0}, \tag{12}$$

where d is the dimensionality. If D is independent of $\vec{k}$ and s, Eqs. (8) and (12) yield the usual result

$$\langle |\vec{r}_1(t) - \vec{r}_1(0)^2|\rangle = 2dD(0,0)t. \tag{13}$$

We introduce the dimensionality at this point because we intend to discuss self-diffusion in both two and three dimensions.

The theory which is to follow is based on two ideas. The first idea is that, since the Stokes law follows from hydrodynamics, a microscopic calculation of $S^1(\vec{k}, s)$ [and thus, via Eq. (8), of $D(\vec{k}, s)$] which correctly includes hydrodynamic effects should also include the Stokes law. The second idea is that it should be possible, via the Zwanzig-Mori[6,7] theories of generalized hydrodynamics, to correctly calculate the hydrodynamic effects upon the autocorrelation function of any dynamical variable (n^1 in our case) by using the variable of interest, plus the hydrodynamic conserved variables, and all possible products thereof, as a complete set of variables.

Thus, we apply the Zwanzig-Mori[6,7] formalism to the calculation of $S^1(\vec{k}, s)$ [and thus $D(\vec{k}, s)$], using as variables n^1 and the collective conserved variables.[8] Bilinear products of n^1 with the collective conserved variables play an important role. The resulting $D(\vec{k}, s)$, for particles of all sizes, has a hydrodynamic part of Stokes-Einstein law form. Since we calculate $D(\vec{k}, s)$, and not just $D(k=0, s=0)$, we are also able to discuss deviations from Eq. (13), $\langle \Delta\vec{r}^{\,2}(t)\rangle \propto t$; this discussion is of particular interest for two dimensions, where we shall see that the physical meaning of the much discussed[9] infinite-diffusion coefficient [$D(k=0, s=0)=\infty$] is that $\langle |\Delta\vec{r}(t)|^2\rangle \propto t\ln t$ for large t. Finally, we shall show how our general expression for $D(\vec{k}, s)$ reduces to the Stokes-Einstein law for a large Brownian particle.

II. GENERALIZED HYDRODYNAMICS

Mori's identity for the set of variables Q is[6]

$$\int_0^\infty e^{-st}\langle \dot{Q}(t)Q^*\rangle\, dt = -\mathcal{T}^{-1}(s)\int_0^\infty e^{-st}\langle Q(t)Q^*\rangle\, dt, \tag{14}$$

where

$$\mathcal{T}^{-1}(s) = \left(-\langle \dot{Q}Q^*\rangle + \int_0^\infty e^{-st}\langle \dot{Q}(t)\dot{Q}^*\rangle^\dagger\, dt\right)\langle QQ^*\rangle^{-1}, \tag{15}$$

$\langle QQ^*\rangle$ is the matrix whose ij element is $\langle Q^i Q^{*j}\rangle$,

$$\langle \dot{Q}(t)\dot{Q}^*\rangle^\dagger \equiv \langle (1-P)\dot{Q}^*[e^{(1-P)i\mathcal{L}t}(1-P)\dot{Q}]\rangle, \quad (16)$$

and P is the projection operator onto the set of variables Q. If $\langle \dot{Q}(t)\dot{Q}^*\rangle^\dagger$ decays rapidly on the time scale of interest, we may replace $\mathcal{T}^{-1}(s)$ by its $s=0$ value[6] and inverse Laplace transform Eq. (14) to obtain

$$\frac{d}{dt}\langle Q(t)Q^*\rangle = -\mathcal{T}^{-1}(s=0)\langle Q(t)Q^*\rangle, \quad (17)$$

a set of coupled linear equations which is easily solved.

We wish to construct the equations to calculate $S^1(\vec{k},s)$. For small k, the hydrodynamic-conserved variables[9] are the most slowly varying variables of the system. These variables are[8] the number density

$$n_{\vec{k}} = \sum_{j=1}^{N} e^{i\vec{k}\cdot\vec{r}_j} \quad (18)$$

and the momentum density

$$\vec{p}_{\vec{k}} = \sum_{j=1}^{N} \vec{p}_j e^{i\vec{k}\cdot\vec{r}_j}. \quad (19)$$

In Eqs. (18) and (19) we have left implicit the time dependence of the molecular properties, and we shall continue to do so. In order to perform the self-diffusion calculation, we also include the conserved tagged particle density $n^1_{\vec{k}}$ defined in Eq. (7). We shall denote $n_{\vec{k}}$, $\vec{p}_{\vec{k}}$, and $n^1_{\vec{k}}$ as $L_{\vec{k}}$. We shall ignore fluctuations in the energy density; as discussed in an earlier paper,[10] this should not affect the general structure of our results. One should note that the original derivation of the Stokes law[1] also ignores temperature (energy) fluctuations. Equations (7), (18), and (19) are appropriate for a system in which all the particles have essentially the same size (radius a) and for which $ka \ll 1$. In Sec. V we shall modify them for a system in which a large, Brownian particle is embedded in a fluid of small bath particles. The system considered here consists of N-point particles in a volume V in the thermodynamic limit (N, $V\to\infty$, N/V fixed).

If we include the $L_{\vec{k}}$, and all products thereof, in our set $Q_{\vec{k}}$, for small k, the operator $(1-P)$ in Eq. (16) will remove[6] all the slowly varying parts of $\langle \dot{Q}(t)\dot{Q}^*\rangle^\dagger$, which is then rapidly decaying, and Eq. (17) will be valid. Thus we should be able to use Eq. (17), with the above-mentioned set of variables, to perform a small-k small-s (long-time) calculation of $S^1(\vec{k},s)$ which includes hydrodynamic effects.

The set of bilinear products of the $L_{\vec{k}}$ which are characterized by wave vector $\vec{k}$, i.e., $L_{\vec{k}+\vec{k}'}L_{-\vec{k}'}$, shall be denoted by $B_{\vec{k},\vec{k}'}$. As discussed by Kawasaki,[11] and in an earlier paper,[10] the components of $\vec{B}$ are slowly varying for small k, and for $k' < k_c$, where $\vec{k}_c$ is the cut-off wave vector; for pure liquids, we expect $(ak_c) \ll 1$, where a is the particle radius. In this paper, as in Ref. 10, we shall limit our set $Q_{\vec{k}}$ to consist of the linear variables $L_{\vec{k}}$ and the bilinear variables $B_{\vec{k},\vec{k}'}$. The trilinear and higher nonlinear variables should not yield important contributions to our results.

III. DERIVATION OF EQUATIONS

A. General Remarks

We now derive the coupled equations necessary for the calculation of the correlation function, $\langle n^1_{\vec{k}}(t)n^1_{-\vec{k}}\rangle$. The derivation proceeds as in Ref. 10. First note that the variable, $n^1_{\vec{k}+\vec{k}'}n^1_{-\vec{k}'}$, is identical to $n^1_{\vec{k}}$, and is hence superfluous. The next important simplification is that the variables $n_{\vec{k}}, \vec{p}_{\vec{k}}, n_{\vec{k}+\vec{k}'}n_{-\vec{k}'}, \vec{p}_{\vec{k}+\vec{k}'}\vec{p}_{-\vec{k}'}, n_{\vec{k}+\vec{k}'}\vec{p}_{-\vec{k}'}$, and $\vec{p}_{\vec{k}+\vec{k}'}n_{-\vec{k}'}$ are unnecessary for the calculation of the autocorrelation function of $n^1_{\vec{k}}$. As discussed in Ref. 10, the Euler equations for n^1 [those resulting from the first term on the right-hand side of Eq. (15)] may be schematically written

$$\frac{d}{dt}\langle n^1_{\vec{k}}(t)n^1_{-\vec{k}}\rangle = \frac{\langle \dot{n}^1_{\vec{k}}L_{-\vec{k}}\rangle}{\langle L_{\vec{k}}L_{-\vec{k}}\rangle}\langle L_{\vec{k}}(t)n^1_{-\vec{k}}\rangle$$
$$+\sum_{\vec{k}'}^{\vec{k}_c} \frac{\langle \dot{n}^1_{\vec{k}}B^{cc}_{-\vec{k},\vec{k}'}\rangle}{\langle B^{cc}_{\vec{k},\vec{k}'}B^{cc}_{-\vec{k},\vec{k}'}\rangle}\langle B^{cc}_{\vec{k},\vec{k}'}(t)n^1_{-\vec{k}}\rangle$$
$$+\sum_{\vec{k}'}^{\vec{k}_c} \frac{\langle \dot{n}^1_{\vec{k}}B^{sc}_{-\vec{k},\vec{k}'}\rangle}{\langle B^{sc}_{\vec{k},\vec{k}'}B^{sc}_{-\vec{k},\vec{k}'}\rangle}\langle B^{sc}_{\vec{k},\vec{k}'}(t)n^1_{-\vec{k}}\rangle, \quad (20)$$

where B^{sc} and B^{cc} are bilinear products of single-particle linear variables (n^1) with collective linear variables, and of collective linear variables with collective linear variables, respectively. The order in N, the number of particles, of the various static averages in Eq. (20), is

$$\langle \dot{n}^1_{\vec{k}}L_{-\vec{k}}\rangle, \langle \dot{n}^1_{\vec{k}}B^{cc}_{-\vec{k},\vec{k}'}\rangle, \langle \dot{n}^1_{\vec{k}}B^{sc}_{-\vec{k},\vec{k}'}\rangle \propto O(1), \quad (21a)$$

$$\langle L_{\vec{k}}L_{-\vec{k}}\rangle, \langle B^{sc}_{\vec{k},\vec{k}'}B^{sc}_{-\vec{k},\vec{k}'}\rangle \propto O(N), \quad (21b)$$

$$\langle B^{cc}_{\vec{k},\vec{k}'}B^{cc}_{-\vec{k},\vec{k}'}\rangle \propto O(N^2). \quad (22)$$

Thus, Eq. (20) becomes

$$\frac{d}{dt}\langle n^1_{\vec{k}}(t)n^1_{-\vec{k}}\rangle \propto O\left[\frac{1}{N}\langle L_{\vec{k}}(t)n^1_{-\vec{k}}\rangle + \frac{1}{N}\sum_{\vec{k}'}^{\vec{k}_c}\langle B^{sc}_{\vec{k},\vec{k}'}(t)n^1_{-\vec{k}}\rangle\right.$$
$$\left.+\frac{1}{N^2}\sum_{\vec{k}'}^{\vec{k}_c}\langle B^{cc}_{\vec{k},\vec{k}'}(t)n^1_{-\vec{k}}\rangle\right]. \quad (23)$$

It is also necessary to use the result

$$M \equiv \sum_{\vec{k}'}^{\vec{k}_c} \approx N(ak_c)^d, \quad (24)$$

since a is on the order of the interparticle spacing for dense systems. We therefore see that the only term on the right-hand side of Eq. (23), which does not disappear in the thermodynamic limit is the B^{sc} term. Thus, since the Euler $\mathcal{T}^{-1}$ matrix elements are the dominant off-diagonal[10] terms, for small k, k', and for point particles, we need consider only the variables $n^1_{\vec{k}}, n^1_{\vec{k}+\vec{k}'}\, n_{-\vec{k}'}, n_{\vec{k}+\vec{k}'}\, n^1_{-\vec{k}'}$, $n^1_{\vec{k}+\vec{k}'}\, \vec{p}_{-\vec{k}'}$, and $\vec{p}_{\vec{k}+\vec{k}'}\, n^1_{-\vec{k}'}$. This simplification arises because we are interested only in one-particle dynamics, and does not hold for two-component systems of arbitrary concentration.

B. Euler Equations, General Discussion

Although the derivation of the coupled equations for the variables of interest $(n^1_{\vec{k}}, B^{sc}_{\vec{k},\vec{k}'})$ is analogous to the derivation in Ref. 10, we shall discuss the derivation of our equations in some detail from this point. This is done to facilitate later comparison with the case of a Brownian particle. In order to determine the Euler coefficients $\langle \dot{Q}Q^*\rangle\langle QQ^*\rangle^{-1}$ we first consider the matrix $\langle QQ^*\rangle$. We define new bilinear variables[10] $B^{sc\prime}_{\vec{k},\vec{k}'}$, which are orthogonal to $n^1_{\vec{k}}$ in the sense that $\langle n^1_{\vec{k}} B^{sc\prime}_{-\vec{k},\vec{k}'}\rangle = 0$. These variables are

$$(n^1_{\vec{k}+\vec{k}'}\, \vec{p}_{-\vec{k}'})' = n^1_{\vec{k}+\vec{k}'}\, \vec{p}_{-\vec{k}'}, \tag{25}$$

$$(n^1_{\vec{k}+\vec{k}'}\, n_{-\vec{k}'})' = n^1_{\vec{k}+\vec{k}'}\, n_{-\vec{k}'} - g(\vec{k}')n^1_{\vec{k}}, \tag{26}$$

where

$$g(\vec{k}) = 1 + (N-1)\langle e^{i\vec{k}\cdot\vec{r}_{12}}\rangle\,; \tag{27}$$

$(\vec{p}_{\vec{k}+\vec{k}'}\, n^1_{-\vec{k}'})'$ and $(n_{\vec{k}+\vec{k}'}\, n^1_{-\vec{k}'})'$ are obtained from the above by the substitution, $\vec{k}' \to -\vec{k}-\vec{k}'$. The quantity $\langle e^{i\vec{k}'\cdot\vec{r}_{12}}\rangle$ is of order a^3/V away from the critical point, and thus $g(\vec{k}') \approx 1$ $(Na^3 \approx V$ for dense systems).

We order the variables $n^1_{\vec{k}}$, then $(n^1_{\vec{k}+\vec{k}'}\, \vec{p}_{-\vec{k}'})'$, $(\vec{p}_{\vec{k}+\vec{k}'}\, n^1_{-\vec{k}'})'$, $(n^1_{\vec{k}+\vec{k}'}\, n_{-\vec{k}'})'$, $(n_{\vec{k}+\vec{k}'}\, n^1_{-\vec{k}'})'$ for a given $\vec{k}'$, then the $B^{sc\prime}$ for a different $\vec{k}'$, and so on. The matrix $\langle QQ^*\rangle$ is seen, from Eqs. (21) and (22) to consist of a 1×1 block of order 1 in the upper-left-hand corner, and successive 4×4 diagonal blocks which may be of order N. Of course, there are no linear-nonlinear terms by construction. It is easy to see that the coupling elements between $B^{sc\prime}$ of different $\vec{k}'$ are of order 1. It is now possible to expand in powers of $1/N$ to obtain the result that the inverse, $\langle QQ^*\rangle^{-1}$, consists of diagonal blocks of order 1 and $1/N$, and off-diagonal elements of order $(1/N^2)$.

Using similar considerations, we find that the matrix $\langle \dot{Q}Q^*\rangle$ has a zero in the upper-left-hand corner, 4×4 diagonal blocks which may be of order N, off-diagonal elements between bilinear variables of different k' of order 1, and linear-bilinear coupling coefficients of order 1. We may now schematically write out the Euler equations

$$\frac{d}{dt}\langle n^1_{\vec{k}}(t) n^1_{-\vec{k}}\rangle = \left(\frac{1}{N} + \frac{M}{N^2}\right)\sum_{\vec{k}'}^{\vec{k}_c}\langle B^{sc\prime}_{\vec{k},\vec{k}'}(t) n^1_{-\vec{k}}\rangle, \tag{28a}$$

$$\frac{d}{dt}\langle B^{sc\prime}_{\vec{k},\vec{k}'}(t) n^1_{-\vec{k}}\rangle = 1\,\langle n^1_{\vec{k}}(t) n^1_{-\vec{k}}\rangle + 1\,\langle B^{sc\prime}_{\vec{k},\vec{k}'}(t) n^1_{-\vec{k}}\rangle + \left(\frac{1}{N} + \frac{M}{N^2}\right)\sum_{\vec{k}''\neq\vec{k}'}^{\vec{k}_c}\langle B^{sc\prime}_{\vec{k},\vec{k}''}(t)\, n^1_{-\vec{k}}\rangle. \tag{28b}$$

In the coefficients of form $1/N + M/N^2$, the first term $1/N$ arises from the diagonal blocks in the matrices, and the second term M/N^2 is the only term to which the off-diagonal elements of the inverse $\langle QQ^*\rangle^{-1}$, contribute. The smallness of the off-diagonal coefficients is partially cancelled by their large multiplicity M, but from Eq. (24) we see that $M/N^2 \approx (1/N)(ak_c)^d \ll 1/N$, and thus we may ignore the contribution of the off-diagonal elements of $\langle QQ^*\rangle^{-1}$. We shall see later that this is not possible for a Brownian particle. It has already been shown in Ref. 10 that, for point particles, the coupling between bilinear variables of different k' is negligible for the L_k correlation functions. This coupling involves the only coefficients to which the off-diagonal elements between different k' in the matrix $\langle \dot{Q}Q^*\rangle$ contribute. It is therefore necessary to consider only the diagonal blocks of the matrices $\langle \dot{Q}Q^*\rangle$ and $\langle QQ^*\rangle^{-1}$ and the linear-bilinear terms in $\langle \dot{Q}Q^*\rangle$, in our treatment of the self-diffusion Euler equations for point particles.

C. Derivation of Euler Equations

We now write down the Euler equations. The necessary nonzero static averages are

$$\langle \dot{n}^1_{\vec{k}}(n^1_{-\vec{k}-\vec{k}'}\, \vec{p}_{\vec{k}'})'\rangle = (i\vec{k}/m)m\, k_B T, \tag{29}$$

$$\langle (n^1_{\vec{k}+\vec{k}'}\, \dot{n}_{-\vec{k}'})'(n^1_{-\vec{k}-\vec{k}'}\, \vec{p}_{\vec{k}'})'\rangle = -(i\vec{k}'/m)Nmk_B T, \tag{30}$$

$$\langle (n^1_{\vec{k}+\vec{k}'}\, \vec{p}_{-\vec{k}'})'(n^1_{-\vec{k}-\vec{k}'}\, \vec{p}_{\vec{k}'})'\rangle = Nm\, k_B T\, \overleftrightarrow{I}, \tag{31}$$

$$\langle (n^1_{\vec{k}+\vec{k}'}\, n_{-\vec{k}'})'(n^1_{-\vec{k}-\vec{k}'}\, n_{\vec{k}'})'\rangle = Ng(\vec{k}+\vec{k}'), \tag{32}$$

where $\overleftrightarrow{I}$ is the unit tensor. As we are considering systems away from the critical point, with $k, k' \ll 1/a$, we may always replace $g(\vec{k})$ by its zero-k value, which we shall write as g. With these results, and with the well-known properties of the equilibrium-momentum correlation functions, we obtain

$$\frac{d}{dt}\langle n^1_{\vec{k}}(t)n^1_{-\vec{k}}\rangle=\frac{i\vec{k}}{2mN}\cdot\sum_{\vec{k}'}^{\vec{k}_c}\langle[n^1_{\vec{k}+\vec{k}'}\vec{p}_{-\vec{k}'}+\vec{p}_{\vec{k}+\vec{k}'}n^1_{-\vec{k}'}]'(t)n^1_{-\vec{k}}\rangle, \tag{33a}$$

$$\frac{d}{dt}\langle[n^1_{\vec{k}+\vec{k}'}\vec{p}_{-\vec{k}'}]'(t)n^1_{-\vec{k}}\rangle=i\vec{k}\,k_BT\,\langle n^1_{\vec{k}}(t)n^1_{-\vec{k}}\rangle-i\vec{k}'\,\frac{k_BT}{g}\langle[n^1_{\vec{k}+\vec{k}'}n_{-\vec{k}'}]'(t)n^1_{-\vec{k}}\rangle, \tag{33b}$$

$$\frac{d}{dt}\langle[n^1_{\vec{k}+\vec{k}'}n_{-\vec{k}'}]'(t)n^1_{-\vec{k}}\rangle=-i\vec{k}'/m\cdot\langle[n^1_{\vec{k}+\vec{k}'}\vec{p}_{-\vec{k}'}]'(t)n^1_{-\vec{k}}\rangle. \tag{33c}$$

D. Dissipative Equations

We shall treat the dissipative coefficients as in Ref. 10. Off-diagonal dissipative coefficients are negligible with respect to Euler coefficients for small k and k'. We assume that the equations of motion may be expanded up to quadratic order in k and k'; this fundamental assumption of our method is discussed in Ref. 10. We define the diagonal-dissipative coefficients via the relations

$$(1-P)\dot{n}^1_{\vec{k}}=(i\vec{k}/m)\cdot(1-P)\vec{p}^{\,1}_{\vec{k}}, \tag{34}$$

$$\int_0^\infty dt-i\vec{k}\cdot\langle(1-P)\vec{p}^{\,1}_{-\vec{k}}[e^{(1-P)i\mathcal{L}t}(1-P)\vec{p}^{\,1}_{\vec{k}}]\rangle\cdot i\vec{k}\equiv mk_BT(-i\vec{k}\cdot\overleftrightarrow{D}_0\cdot i\vec{k}), \tag{35}$$

$$(1-P)\frac{d}{dt}n^1_{\vec{k}+\vec{k}'}n_{-\vec{k}'}=\frac{i(\vec{k}+\vec{k}')}{m}\cdot(1-P)\vec{p}^{\,1}_{\vec{k}+\vec{k}'}n_{-\vec{k}'}, \tag{36}$$

$$\int_0^\infty dt-i(\vec{k}+\vec{k}')\cdot\langle(1-P)(\vec{p}^{\,1}_{-\vec{k}-\vec{k}'}n_{\vec{k}})'[e^{(1-P)i\mathcal{L}t}(1-P)(\vec{p}^{\,1}_{\vec{k}+\vec{k}'}n_{-\vec{k}'})']\rangle\cdot i(\vec{k}+\vec{k}')\equiv Ngmk_BT[-i(\vec{k}+\vec{k}')\cdot\overleftrightarrow{D}_1\cdot i(\vec{k}+\vec{k}')], \tag{37}$$

$$(1-P)\frac{d}{dt}(n^1_{\vec{k}+\vec{k}'}\vec{p}_{-\vec{k}'})=\frac{i(\vec{k}+\vec{k}')}{m}\cdot(1-P)\vec{p}^{\,1}_{\vec{k}+\vec{k}'}\vec{p}_{-\vec{k}'}-\frac{i\vec{k}'}{m}\cdot(1-P)n^1_{\vec{k}+\vec{k}'}\overleftrightarrow{\sigma}_{-\vec{k}'}, \tag{38}$$

$$\dot{\vec{p}}_{\vec{k}}=\frac{i\vec{k}}{m}\cdot\overleftrightarrow{\sigma}_{\vec{k}}, \tag{38a}$$

$$\int_0^\infty dt\left\langle(1-P)\frac{d}{dt}(n^1_{-\vec{k}-\vec{k}'}\vec{p}_{\vec{k}'})'[e^{(1-P)i\mathcal{L}t}(1-P)\frac{d}{dt}(n^1_{\vec{k}+\vec{k}'}\vec{p}_{-\vec{k}'})']\right\rangle$$
$$\equiv Nmk_BT[-i(\vec{k}+\vec{k}')\cdot\underline{D}_2\cdot i(\vec{k}+\vec{k}')+i\vec{k}'\cdot\underline{\eta}_0\cdot-i\vec{k}'-i(\vec{k}+\vec{k}')\cdot\underline{\delta}\cdot i\vec{k}'+i\vec{k}'\cdot\underline{\delta}\cdot-i(\vec{k}+\vec{k}')]. \tag{39}$$

The quantities, $\overleftrightarrow{D}_0$ and $\overleftrightarrow{D}_1$ are "bare" self-diffusion tensors, and should be related to each other. For isotropic fluids these tensors are just equal to constants times the unit tensor, i.e., $\overleftrightarrow{D}_0=D_0\overleftrightarrow{I}$, etc. It is quite possible that the "bare" diffusion coefficients, D_0 and D_1, are smaller than the "ordinary" self-diffusion coefficient. The bilinear variable, $n^1_{\vec{k}+\vec{k}'}\vec{p}_{-\vec{k}'}$, has the property that

$$\sum_{k'=0}^{k'>\pi/a}n^1_{\vec{k}+\vec{k}'}\vec{p}_{-\vec{k}'}\approx\vec{p}^{\,1}_{\vec{k}}+\sum_{j\neq 1}\vec{p}_je^{i\vec{k}\cdot\vec{r}_j}\delta(\vec{r}_{1j}); \tag{40}$$

due to the nonsuperimposability of particles, the second term on the right-hand side of Eq. (40) may be ignored. Thus, if we had $k_c>\pi/a$, we would expect $(1-P)\vec{p}^{\,1}_{\vec{k}}\approx 0$, and thus $D_0\approx 0$, due to the projections orthogonal to the $n^1_{\vec{k}+\vec{k}'}\vec{p}_{-\vec{k}'}$ variables for all $\vec{k}'\leqslant\vec{k}_c$. Since the sum over $\vec{k}'$ in our equations is actually terminated at $k'=k_c\ll\pi/a$, it is not expected that $(1-P)\vec{p}^{\,1}_{\vec{k}}$ is actually zero, but it is still possible that $P\vec{p}^{\,1}_{\vec{k}}$ is large enough to reduce the bare diffusion coefficients from their ordinary values. Later, we shall see that D_0 is identically zero for a Brownian particle. The diffusion tetrad, $\underline{D}_2$, is more complicated than the diffusion tensors, but similar considerations hold.

The tetrad, $\underline{\eta}_0$, is the bare kinematic-viscosity tetrad, and should be similar to the usual kinematic-viscous tetrad; there is no particular reason why the microscopic stress tensor $\overleftrightarrow{\sigma}$, which determines the bare viscosity, should be significantly reduced from its usual value by the new projections which we have introduced. The tetrad $\underline{\delta}$ involves the time integral of a correlation function which vanishes at zero time, and may be very small.

We may now write down our complete set of equations. These equations are intended to describe self-diffusion in two and three dimensions for a pure liquid composed of point particles, in which energy fluctuations are negligible up to Navier-Stokes order. The equations are

$$\frac{d}{dt}\langle n^1_{\vec{k}}(t)n^1_{-\vec{k}}\rangle=\frac{i\vec{k}}{m}\cdot\frac{1}{2N}\sum_{\vec{k}'}^{\vec{k}_c}\langle[n^1_{\vec{k}+\vec{k}'}\vec{p}_{-\vec{k}'}+\vec{p}_{\vec{k}+\vec{k}'}n^1_{-\vec{k}'}]'(t)n^1_{-\vec{k}}\rangle-k^2D_0\langle n^1_{\vec{k}}(t)n^1_{-\vec{k}}\rangle, \tag{41a}$$

$$\frac{d}{dt}\langle[n^1_{\vec{k}+\vec{k}'}n_{-\vec{k}'}]'(t)n^1_{-\vec{k}}\rangle=-(i\vec{k}'/m)\cdot\langle[n^1_{\vec{k}+\vec{k}'}\vec{p}_{-\vec{k}'}]'(t)n^1_{-\vec{k}}\rangle-|\vec{k}+\vec{k}'|^2D_1\langle[n^1_{\vec{k}+\vec{k}'}n_{-\vec{k}'}]'(t)n^1_{-\vec{k}}\rangle, \tag{41b}$$

$$\begin{aligned}\frac{d}{dt}\langle[n^1_{\vec{k}+\vec{k}'}\vec{p}_{-\vec{k}'}]'(t)n^1_{-\vec{k}}\rangle={}&i\vec{k}k_BT\langle n^1_{\vec{k}}(t)n^1_{-\vec{k}}\rangle-(i\vec{k}'/g)k_BT\langle[n^1_{\vec{k}+\vec{k}'}n_{-\vec{k}'}]'(t)n^1_{-\vec{k}}\rangle\\&+[i(\vec{k}+\vec{k}')\cdot\underline{D}_2\cdot i(\vec{k}+\vec{k}')+i\vec{k}'\cdot\underline{\eta}_0\cdot i\vec{k}'-i\vec{k}'\cdot\underline{\delta}\cdot i(\vec{k}+\vec{k}')-i(\vec{k}+\vec{k}')\cdot\underline{\delta}\cdot i\vec{k}']\cdot\langle[n^1_{\vec{k}+\vec{k}'}\vec{p}_{-\vec{k}'}]'(t)n^1_{-\vec{k}}\rangle.\end{aligned} \tag{41c}$$

IV. SOLUTIONS

In this section we shall solve Eqs. (41) for $\langle n^1_{\vec{k}}(s)n^1_{-\vec{k}}\rangle$, and thus obtain [see Eq. (8)] $D(\vec{k},s)$, in two and three dimensions. We choose $\vec{k}\,||\,\hat{x}$, and we Laplace transform Eq. (41a), to obtain

$$\langle n^1_{\vec{k}}(s)n^1_{-\vec{k}}\rangle=\left(s+k^2D_0-\frac{ik}{2mN}\sum_{\vec{k}'}^{\vec{k}_c}\langle[n^1_{\vec{k}+\vec{k}'}p^x_{-\vec{k}'}+p^x_{\vec{k}+\vec{k}'}n^1_{-\vec{k}'}]'(s)n^1_{-\vec{k}}\rangle\langle n^1_{\vec{k}}(s)n^1_{-\vec{k}}\rangle^{-1}\right)^{-1} \tag{42}$$

D_0 is the nonhydrodynamic "microscopic" part of $D(\vec{k},s)$, and the third term on the right-hand side of Eq. (42) contains the part of $D(\vec{k},s)$ describable by bilinear hydrodynamics. Equation (42) is valid for two and three dimensions. In order to evaluate the hydrodynamic part of $D(\vec{k},s)$ it is necessary to express $[n^1_{\vec{k}+\vec{k}'}p^x_{-\vec{k}'}]'(s)$ and $[p^x_{\vec{k}+\vec{k}'}n^1_{-\vec{k}'}]'(s)$ in terms of $n^1_k(s)$.

A. Two Dimensions

There has been much recent discussion of the nature of self-diffusion in two dimensions, prompted[9] by Alder's computer experiments and various theories.[12] These predict an infinite diffusion coefficient $D(k=0,s=0)$. We shall now obtain an expression for $D(\vec{k},s)$ for point particles in two dimensions. In order to treat the $[n^1p^x]'$ and $[p^xn^1]'$ terms in Eq. (42), we introduce an (x',y') coordinate frame in which $\vec{k}'\,||\,\hat{x}'$. In the following, we shall omit the primes on the $B^{sc'}$, and we shall omit k subscripts whenever our meaning is obvious. We have

$$n^1p^x+p^xn^1=(n^1p^{x'}+p^{x'}n^1)\cos\phi-(n^1p^{y'}+p^{y'}n^1)\sin\phi, \tag{43}$$

where ϕ is the angle between $\vec{k}$ and $\vec{k}'$. The (x',y') coordinate system is the natural coordinate system for this problem. Since $\vec{k}'$ lies along the x' axis, as $k\to0$, $p^{x'}_{\vec{k}+\vec{k}'}n^1_{-\vec{k}'}$ represents a pure "longitudinal" ($p^{x'}$ is a function of x') mode, whereas $p^{y'}_{\vec{k}+\vec{k}'}n^1_{-\vec{k}'}$ represents a pure transverse mode. Equations (41) are simplified in the (x',y') system because $k'_{y'}=0$. We now introduce two simple approximations. We set $\underline{\delta}=0$, which clearly does not violate any important principle. Furthermore, we shall replace $\underline{\eta}_0$ by $\eta_0^{\parallel}I^{(4)}$ and $\eta_0^{\perp}I^{(4)}$ in the calculation for $n^1p^{x'},p^{x'}n^1$ and for $n^1p^{y'},p^{y'}n^1$, respectively, where $\eta_0^{\parallel}$ is the bare longitudinal viscosity, $\eta_0^{\perp}$ is the bare shear viscosity, and $I^{(4)}$ is the unit tetrad. This latter approximation may at most introduce a small numerical error in our results for D, and is of a trivial nature. We may now solve Eqs. (41) to obtain

$$\langle[n^1_{\vec{k}+\vec{k}'}p^{y'}_{-\vec{k}'}](s)n^1_{-\vec{k}}\rangle=ik^{y'}k_BT(s+|\vec{k}+\vec{k}'|^2D_2+k'^2\eta_0^{\perp})^{-1}\langle n^1_{\vec{k}}(s)n^1_{-\vec{k}}\rangle, \tag{44a}$$

$$\langle[p^{y'}_{\vec{k}+\vec{k}'}n^1_{-\vec{k}'}](s)n^1_{-\vec{k}}\rangle=ik^{y'}k_BT[s+k'^2D_2+|\vec{k}+\vec{k}'|^2\eta_0^{\perp}+(k^2_{y'}k_BT/mg)(s+k'^2D_1)^{-1}]^{-1}\langle n^1_{\vec{k}}(s)n^1_{-\vec{k}}\rangle; \tag{44b}$$

thus,

$$\begin{aligned}&-\sum_{\vec{k}'}^{\vec{k}_c}\langle[n^1_{\vec{k}+\vec{k}'}p^{y'}_{-\vec{k}'}+p^{y'}_{\vec{k}+\vec{k}'}n^1_{-\vec{k}'}](s)n^1_{-\vec{k}}\rangle\sin\phi\\&\quad=ikk_BT\langle n^1_{\vec{k}}(s)n^1_{-\vec{k}}\rangle\sum_{\vec{k}'}^{\vec{k}_c}\sin^2\phi\left[(s+|\vec{k}+\vec{k}'|^2D_2+k'^2\eta_0^{\perp})^{-1}+\left(s+|\vec{k}+\vec{k}'|^2\eta_0^{\perp}+k'^2D_2-\frac{k^2\sin^2\phi k_BT}{mg(s+k'^2D_1)}\right)^{-1}\right]\end{aligned} \tag{45}$$

where we have used the inverse transform

$$k'_y=-k\sin\phi. \tag{46}$$

The sums in Eq. (45) are performed via the substitution $\sum_{\vec{k}'}\to[V/(2\pi)^d]\int d\vec{k}'$. We then obtain the part of the "hydrodynamic" diffusion coefficient (times k^2) due to the $p^{y'}$ terms [see Eqs. (42) and (43)]

$$\left(\frac{ik}{2mN}\right)\sum_{\vec{k}'}^{\vec{k}_c}\sin\phi\,\langle[n^1_{\vec{k}+\vec{k}'}p^{y'}_{-\vec{k}'}+p^{y'}_{\vec{k}+\vec{k}'}n^1_{-\vec{k}'}](s)n^1_{-\vec{k}}\rangle\langle n^1_{\vec{k}}(s)n^1_{-\vec{k}}\rangle^{-1}=\frac{k^2k_BT}{8\pi\rho(\eta_0^\perp+D_2)}\ln\frac{s+2k_c^2(\eta_0^\perp+D_2)}{s+k^2(\eta_0^\perp+D_2)}\,. \tag{47}$$

As k, $s\to 0$, the region of interest, k^{-2} times the right-hand side of Eq. (47) becomes infinite. Using the same techniques as above, it is easy to see that the $n^1p^{x'}$ and $p^{x'}n^1$ contribution to D remains finite for k, $s\to 0$. Thus, for small k, s,

$$S^1(\vec{k},s)=\left(s+k^2D_0+k^2\frac{k_BT}{8\pi\rho(\eta_0^\perp+D_2)}\ln\frac{s+2k_c^2(\eta_0^\perp+D_2)}{s+k^2(\eta_0^\perp+D_2)}\right)^{-1} \tag{48}$$

and, via Eq. (8),

$$D(\vec{k},s)=D_0+\frac{k_BT}{8\pi\rho(\eta_0^\perp+D_2)}\ln\frac{s+2k_c^2(\eta_0^\perp+D_2)}{s+k^2(\eta_0^\perp+D_2)}\,. \tag{49}$$

The second term on the right-hand side of Eq. (49) is the hydrodynamic part of D, and D_0 is the microscopic part of D. Note that it is actually inconsistent to retain D_0, as we have kept only the "divergent" part of the hydrodynamic contribution to $D(\vec{k},s)$, and we have discarded hydrodynamic contributions of the order of D_0. However, we retain the microscopic D_0 for illustration.

B. Discussion of Two-Dimensional Result

Equation (49) shows that $D(\vec{k},s)$ is indeed infinite in two dimensions as k, $s\to 0$, in agreement with numerous other theories.[12] The differences between our theory and the other theories is discussed in Ref. 10. Reasonably enough, $D(\vec{k},s)$ has precisely the same form as the $\vec{k}$- and s-dependent shear viscosity $\eta(\vec{k},s)$ discussed in Ref. 10. An inverse Laplace transform of Eq. (49), via comparison with Eq. (9), yields the $p^1_{\vec{k}}$ autocorrelation function

$$(m^{-2})\langle p^1_{\vec{k}}(t)p^1_{-\vec{k}}\rangle^\dagger=2D_0\delta(t)+[k_BT/8\pi\rho(\eta_0^\perp+D_2)]\times(e^{-k^2(\eta_0^\perp+D_2)t}-e^{-2k_c^2(\eta_0^\perp+D_2)t})t^{-1}, \tag{50}$$

which has a t^{-1} tail for $k\to 0$. One might be tempted to neglect D_2 with respect to η_0 in Eqs. (47)–(50), as we expect $D_2\leq D$, $\eta_0\sim\eta$, and usually $\eta\gg D$. "Usually," however, means in three dimensions, and the relative magnitudes of D_2 and η_0 in two dimensions are unclear.

The discussion of the Stokes-Einstein ideas in Sec. I was appropriate for three dimensions, and sheds little light upon the results obtained above. Nonetheless, we may try to make connection between our results and macroscopic hydrodynamics in two dimensions. First note that, for small k, s, the hydrodynamic part of $D(\vec{k},s)$ dominates the microscopic part; we have the interesting result that a hydrodynamic calculation for $D(\vec{k},s)$ is valid in two dimensions for a point particle! Next, let us try to find two-dimensional quantities analogous to the three-dimensional friction and diffusion constants. For the force on a "Brownian disk" in uniform motion with velocity $\vec{v}$, macroscopic hydrodynamics yields[13]

$$\vec{F}=4\pi\eta\vec{v}/\ln|\vec{v}| \tag{51}$$

for small v. By comparison with Eqs. (1) and (2), it seems natural to define the two-dimensional friction coefficient $\gamma^{(2)}$ by the relation

$$\vec{F}=\gamma^{(2)}\vec{v}/\ln|\vec{v}|\,; \tag{52}$$

i.e., $\gamma^{(2)}=4\pi\eta$. In order to redefine an appropriate two-dimensional diffusion coefficient $D^{(2)}$, we recall that in three dimensions $D=\langle|\Delta\vec{r}(t)|^2\rangle/6t$ for long times. With Eqs. (12) and (48) we may calculate $\langle|\Delta\vec{r}(t)|^2\rangle$ in two dimensions; the result is

$$\langle|\Delta\vec{r}(t)|^2\rangle=[k_BT/2\pi\rho(\eta_0^\perp+D_2)]t\ln t. \tag{53}$$

Equation (53) shows why D, when defined as $D=\langle|\Delta\vec{r}|^2(t)\rangle/6t$, is infinite in two dimensions; $\langle|\Delta\vec{r}|^2\rangle/t$ "blows up" as $\ln t$ for long times. Equation (53) suggests that a reasonable definition of a two-dimensional diffusion coefficient $D^{(2)}$ is

$$\langle|\Delta\vec{r}^2(t)|\rangle=4D^{(2)}t\ln t \tag{54}$$

or, via Eq. (53),

$$D^{(2)}=k_BT/8\pi\rho(\eta_0^\perp+D_2). \tag{55}$$

Thus, if we ignore D_2, and if we ignore the difference between bare and ordinary viscosities we find that an Einstein Law also holds in two dimensions,

$$D^{(2)}=k_BT/2\gamma^{(2)}\,; \tag{56}$$

if one makes certain natural redefinitions of the diffusion and friction coefficients upon passing from three to two dimensions, Einstein's law (except for a factor of $\frac{1}{2}$) remains invariant.

C. Three-Dimensional Calculation

Owing to the algebraic complications in the solution of Eqs. (41) caused by the third dimension, we shall treat the three-dimensional fluid as incompressible, i.e., we shall set $n=0$ in Eqs. (41). As we have seen in two dimensions, the only effect of compressibility is to eliminate the contribution of longitudinal modes (the $np^{x'}$ terms) to $D(\vec{k}, s)$. Thus, we may correct our calculated hydrodynamic part of $D(\vec{k}, s)$ by multiplying by a factor of $\frac{2}{3}$ (two transverse modes instead of three), and by setting $\underline{\eta}_0 = \eta_0^\perp I^{(4)}$. Equations (41) are now easy to solve, with the result

$$S^1(\vec{k}, s) = \left[s + k^2 D_0 + \frac{2}{3} \frac{k^2 k_B T}{m} \frac{1}{2N} \sum_{\vec{k}'}^{\vec{k}_c} \left(\frac{1}{s + k'^2 D_2 + |\vec{k} + \vec{k}'|^2 \eta_0^\perp} + \frac{1}{s + k'^2 \eta_0^\perp + |\vec{k} + \vec{k}'|^2 D_2} \right) \right]^{-1} . \tag{57}$$

Equation (57) may be combined with Eq. (8), to obtain, for small k and s,

$$D = D_0 + k_B T k_c / 3\pi^2 \rho (\eta_0^\perp + D_2) ; \tag{58}$$

the second term in Eq. (58) is the hydrodynamic part of D.

D. Discussion of Three-Dimensional Result

Equation (58) is correct to Navier-Stokes order (k^2), which is the order in k to which our theory may be used consistently. Thus, we see that, to order k^2, the self-diffusion coefficient in three dimensions may be considered frequency independent, i.e., the p^1 autocorrelation function [see Eq. (9)] may be considered to decay as a δ function in time. In order to reconcile this δ-function behavior of $\langle p^1_{\vec{k}}(t) p^1_{-\vec{k}} \rangle^\dagger$ with the previously[9,12] discussed evidence that the hydrodynamic part of D is associated with a $t^{-3/2}$ decay of $\langle p^1_{\vec{k}}(t) p^1_{-\vec{k}} \rangle$ for $k = 0$, we evaluate Eq. (57) for small k and s:

$$D(k, s) = D_0 + \frac{k_B T}{3\pi^2 \rho} \frac{1}{\eta_0^\perp + D_2} \times \left[k_c - \frac{\pi}{2(\eta_0^\perp + D_2)} \left(s + \frac{\eta_0^\perp D_2}{\eta_0^\perp + D_2} k^2 \right)^{1/2} \right] . \tag{59}$$

An inverse Laplace transform of Eq. (59) yields

$$m^{-2} \langle p^1_{\vec{k}}(t) p^1_{-\vec{k}} \rangle^\dagger = 2 D_0 \delta(t) + \frac{k_B T}{3\pi^2 \rho} \frac{1}{\eta_0^\perp + D_2} \times \frac{\pi^{1/2}}{4(\eta_0^\perp + D_2)^{1/2}} f(t), \tag{60}$$

where

$$\begin{aligned} f(t) &= t^{-3/2} \exp\left(\frac{-\eta_0^\perp D_2}{\eta_0^\perp + D_2} k^2 t \right) , & t &> \frac{\pi}{4k_c^2(\eta_0^\perp + D_2)} \\ f(t) &= 0, & t &< \frac{\pi}{4k_c^2(\eta_0^\perp + D_2)} . \end{aligned} \tag{61}$$

The hydrodynamic part of Eq. (60) indeed decays as $t^{-3/2}$ for times greater than the rather short ($k_c \gg k$) time, $\pi / 4k_c^2(\eta_0^\perp + D_2)$, and for $k = 0$. For finite k, the $t^{-3/2}$ tail is destroyed by a decaying exponential. Note that it is not the $s^{1/2}$ term alone in Eq. (59) which yields the $t^{-3/2}$ tail when $k = 0$. The $s^{1/2}$ term and the s-independent term (k_c) in the bracket in Eq. (59) combine to yield $t^{-3/2}$. Nonetheless, for $s \approx k^2$, as is appropriate for self-diffusion, and for $k \to 0$, we have $s^{1/2} \sim k$, and the $s^{1/2}$ term may be dropped as in Eq. (58). [Since the second term in the bracket in Eq. (59) is a "k^3" term, while our theory is appropriate to order k^2, Eq. (59) is not complete; we present Eq. (59) for illustration, with these reservations in mind.] This means that, for sufficiently small k, the hydrodynamic time scale becomes sufficiently long that even a $t^{-3/2}$ tail may be regarded as a delta function. Thus there is no need to include the $B_{\vec{k},\vec{k}'}$ as variables, in three dimensions, to obtain a useful expression for D up to Navier-Stokes order. Our reward for including the $B_{\vec{k},\vec{k}'}$ variables is the appearance of the explicit expression for the hydrodynamic part of $D(\vec{k}, s)$ in Eq. (58).

The hydrodynamic part of D [Eq. (58)] strongly resembles the Stokes-Einstein law $D_{\text{SE}} \equiv k_B T / 6\pi\eta R$. Recall that we expect $\eta \approx \eta_0^\perp \gg D_2$ in three dimensions, that $\rho\eta_0^\perp$ gives the "usual" $\eta_0^\perp$, and that we require $k_c = (\pi/a)c$, where a is the particle radius and $c < 1$. Thus

$$D = D_0 + 2c D_{\text{SE}} ; \tag{62}$$

in three dimensions, D may be written as the sum of a microscopic part and a hydrodynamic part of Stokes-Einstein form. Unlike our two-dimensional results, the microscopic and hydrodynamic parts of D enter into Eq. (62) on an equal footing; this is because hydrodynamics alone is not sufficient to describe the self-diffusion of point particles in three dimensions. Similarly, in contrast to the two-dimensional case, the cutoff wave vector (and hence the unknown parameter c) enters into the hydrodynamic parts of D.

We remark that the shear-viscosity coefficient η may also be written as in Eq. (62), with $\eta_0^\perp$ replacing D_0, and with trivial numerical changes. Similar considerations probably hold for the other transport coefficients. However, since $D_{\text{SE}} \approx D$, and since the other transport coefficients tend to be much larger than D, it appears that "long-time tails" should be most important for self-diffusion.

We may attempt an evaluation of the relative magnitudes of the hydrodynamic and nonhydrodynamic parts of D. The relevant quantity for this discussion is the ratio Z of the mean-square average of the Euler-equation [see Eq. (33a)] approximation for $\dot{n}^1$ to the mean-square average of the exact result $\dot{n}^{1}_{\vec{k}} = (i\vec{k}/m)\cdot\vec{p}^{1}_{\vec{k}}$:

$$Z = \frac{1}{N^2}\left\langle \sum_{\vec{k}'=0}^{\vec{k}_c} n^{1}_{\vec{k}+\vec{k}'} p^{x}_{-\vec{k}'} \sum_{\vec{k}''=0}^{\vec{k}_c} n^{1}_{-(\vec{k}+\vec{k}'')} p^{x}_{\vec{k}''} \right\rangle (m k_B T)^{-1}. \tag{63}$$

The condition for $D_0 = 0$ is $Z = 1$, for then the Euler equation must be exact, and D must have only a hydrodynamic (Stokes-Einstein) part. It is easy to see that

$$\langle n^{1}_{\vec{k}+\vec{k}'} p^{x}_{-\vec{k}'} n^{1}_{-\vec{k}-\vec{k}''} p^{x}_{\vec{k}''} \rangle = m k_B T \left[N \delta_{\vec{k}',\vec{k}''} + g(\vec{k}' - \vec{k}'')\right], \tag{64}$$

and so

$$Z = (1/N^2) M (N + Mg), \tag{65}$$

where we have set $g(\vec{k}' - \vec{k}'') = g(0)$, as discussed earlier, and M is defined in Eq. (24). We have already seen that $g \approx 1$ for point particles; the combination of Eqs. (24) and (65) now yields

$$Z = (a k_c)^d \ll 1. \tag{66}$$

Thus, Z is small, and we have no way to argue that D_0 should be small. For a three-dimensional point particle, both hydrodynamic and nonhydrodynamic processes contribute to self-diffusion. D does indeed have a Stokes-Einstein-law part in three dimensions, although that part does not comprise the whole of D. The separation of D into two parts occurs naturally via bilinear dynamics.

V. LARGE BROWNIAN PARTICLE

Thus far, we have considered self-diffusion in fluids composed of identical point particles. We shall now introduce the techniques necessary to treat the diffusion of a particle of arbitrary radius R through a solvent of identical small particles of radius $a\,(R \geq a)$. We shall show that in the limiting case $kR \ll 1$, $k_c R \gg 1$, our method yields the Stokes-Einstein law. This limiting case, which corresponds to the motion of a particle large on the microscopic scale ($k_c R \gg 1$), over distances large compared to the particle size ($kR \ll 1$), in a solvent of relatively small particles ($R \gg k_c^{-1} \gg a$), corresponds to conventional ideas of Brownian motion. The reproduction of the Stokes-Einstein law under the above-mentioned conditions is an important check on the validity of our approach.

It is necessary to modify the derivation of our equations to treat the case of arbitrary (not small) R. We shall assume that, despite the disturbing influence of the single large particle, the cutoff wave vector is still determined as in the point particle case. We now introduce the appropriate expressions for the linear hydrodynamic variables in the system of interest. The system consists of $N-1$ small particles of mass m and radius a, and one particle, denoted particle 1, of mass $\mathfrak{M}$ and radius $R\,(R \geq a)$. Instead of Eq. (6), $n^1(\vec{r}, t) = \delta(\vec{r} - \vec{r}_1)$, we have

$$n^1(\vec{r}, t) = (\tfrac{4}{3}\pi R^3)^{-1} S(\vec{r} - \vec{r}_1), \tag{67}$$

where S is the three-dimensional step function

$$\begin{aligned} S(\vec{r} - \vec{r}_1) &= 1, \quad |\vec{r}_1 - \vec{r}| < R, \\ S(\vec{r} - \vec{r}_1) &= 0, \quad |\vec{r}_1 - \vec{r}| > R. \end{aligned} \tag{68}$$

Similarly,

$$\vec{p}(\vec{r}, t) = \vec{p}_1 (\tfrac{4}{3}\pi R^3)^{-1} S(\vec{r} - \vec{r}_1) + \sum_{j \neq 1}^{N} \vec{p}_j \delta(\vec{r} - \vec{r}_j). \tag{69}$$

We shall not consider the variable $n(\vec{r}, t)$; the prescription given in Sec. IV for correcting the errors introduced by this omission is still valid.

The new definitions of the hydrodynamic densities changes their spatial Fourier transforms, the $L_{\vec{k}}$; viz.,

$$n^{1}_{\vec{k}} = e^{i\vec{k}\cdot\vec{r}_1} \chi(k), \tag{70}$$

$$\vec{p}_{\vec{k}} = \vec{p}_1 e^{i\vec{k}\cdot\vec{r}_1} \chi(k) + \sum_{j \neq 1}^{N} \vec{p}_j e^{i\vec{k}\cdot\vec{r}_j}, \tag{71}$$

where $\chi(k)$ is a cutoff function

$$\chi(k) = 3\left[(\sin kR - kR \cos kR)/(kR)^3\right]. \tag{72}$$

For $k = 0$, $\chi(k) = 1$, and for $k > \pi/R$, $\chi(k)$ decays to zero in damped oscillatory fashion. As we shall see, if $Rk_c \gg 1$, the presence of the function $\chi(k)$ removes the dependence of D on the more-or-less arbitrary cutoff wave vector $\vec{k}_c$. If $Rk_c \gg 1$, $\chi(k)$ terminates all sums over $\vec{k}'$ which enter our results at about $k' \approx \pi/R$.

According to Eqs. (70) and (71),

$$\begin{aligned} U_{\vec{k}',\vec{k}''} &\equiv \langle n^{1}_{\vec{k}+\vec{k}'} p^{x}_{-\vec{k}'} n^{1}_{-\vec{k}-\vec{k}''} p^{x}_{\vec{k}''} \rangle \\ &= m k_B T \chi(k + k') \chi(k + k'') \\ &\quad \times \{[N - 1 + (\mathfrak{M}/m)] \delta_{\vec{k}',\vec{k}''} + (\mathfrak{M}/m) \chi(k') \chi(k'') \\ &\qquad + (1 - \delta_{\vec{k}',\vec{k}''})(N - 1) \langle e^{i(\vec{k}' - \vec{k}'')\cdot\vec{r}_{12}} \rangle\}; \end{aligned} \tag{73}$$

we define

$$(N - 1) \langle e^{i(\vec{k}' - \vec{k}'')\cdot\vec{r}_{12}} \rangle \equiv h(\vec{k}' - \vec{k}''). \tag{74}$$

Since $n^{1}_{\vec{k}}$ is orthogonal to $n^1 p$ and $p n^1$, we may trivially obtain the inverse, $\langle QQ^* \rangle^{-1}$, from the inverse of $U_{\vec{k}',\vec{k}''}$, $U^{-1}_{\vec{k}',\vec{k}''}$. In Sec. III B we saw that for point particles $\langle QQ^* \rangle^{-1}$ could be obtained by regarding the off-diagonal elements of $\langle QQ^* \rangle$ as small with respect to the diagonal elements, and by writing the inverse as a convergent power series in $1/N$. The criterion for the validity of this procedure was that M, the number of wave vectors less than $\vec{k}_c$, times the magnitude of the off-diagonal elements of $\langle QQ^* \rangle$, was much less than N. For point particles, this meant $Mg \ll N$, which is indeed the case. According to Eq. (73), we require $Mh(\vec{k}'-\vec{k}'') \ll N$ for all R if we wish to obtain the inverse $\langle QQ^*\rangle^{-1}$ for a particle of arbitrary radius, via a power series expansion.

We may make a reasonable estimate of $h(\vec{k})$, via the assumption that the only effect of particle 1 upon the static structure of the fluid is the exclusion of solvent particles from a sphere of radius R about its center of mass. It is then easy to see that

$$h(\vec{k}'-\vec{k}'') \approx -(R^3/a^3)\,\chi(\vec{k}'-\vec{k}''). \tag{75}$$

As discussed above, the *effective* cutoff wave vector is about π/R for this problem if the actual $k_c \gg \pi/R$. Then Eq. (24), with $k_c \approx \pi/R$, yields $M \approx N(a^3/R^3)$, and Eq. (75) yields $Mh(\vec{k}'-\vec{k}'') \approx -N\chi(\vec{k}'-\vec{k}'')$. Therefore, for arbitrary $R \gg a$, we may not invert the matrix $\langle QQ^*\rangle$ using the technique developed for point particles.

Our alternative method of performing the inversion begins with the definition of the inverse

$$\sum_{\vec{k}''}^{\vec{k}_c} U_{\vec{k}',\vec{k}''}\, U^{-1}_{\vec{k}'',\vec{k}'''} = \delta_{\vec{k}',\vec{k}'''}\,. \tag{76}$$

Equations (73)–(76) may be combined to yield an equation for U^{-1},

$$mk_BT\left[N\chi^2(k')U^{-1}_{\vec{k}',\vec{k}'''} + \left(\frac{\mathfrak{M}}{m}\right)\chi^2(k')\sum_{\vec{k}''}^{\vec{k}_c}\chi^2(k'')U^{-1}_{\vec{k}'',\vec{k}'''} + \chi(k')\sum_{\vec{k}''\neq\vec{k}'}^{\vec{k}_c}\chi(k'')h(\vec{k}'-\vec{k}'')U^{-1}_{\vec{k}'',\vec{k}'''}\right] = \delta_{\vec{k}',\vec{k}'''}\,, \tag{77}$$

where we have used the condition $kR \ll 1$, which is true for all systems of interest, to justify neglect of k wherever it appears in the argument of the χ's, and we have used the condition $N \gg \mathfrak{M}/m$, 1, in the thermodynamic limit. Equation (77) is difficult to solve for arbitrary $h(\vec{k})$. However, we shall see that, under the approximation [Eq. (75)], an exact result for D may be obtained from Eq. (77), in the limit $Rk_c \gg 1$, without an actual calculation of U^{-1}. Thus, we shall employ Eq. (75) in all the manipulations of Eq. (77) which are to follow, with the intention of deriving a result valid for large particles. This approximation is the only addition which we shall make to our previously stated fundamental approximations in order to treat the case of arbitrary $R \geq a$; Eq. (75) should involve negligible error for $R \gg a$.

Since we do not wish to actually attempt an evaluation of U^{-1}, we now write down the equations appropriate for the description of self-diffusion by a particle of arbitrary radius $R \geq a$, proceeding as if U^{-1} is known. These equations (assuming U^{-1} is known) follow from the ideas presented for point particles, and from the form of our redefined $L_{\vec{k}}$ [Eqs. (70) and (71)]. It is easy to see that off-diagonal dissipative matrix elements coupling linear and bilinear variables $[O(k^2)]$ are negligible with respect to the Euler elements $[O(k)]$ for small k. Furthermore, off-diagonal dissipative matrix elements coupling bilinear variables of different $\vec{k}'$ vanish due to spatial isotropy as $k \to 0$. The off-diagonal dissipative matrix elements are therefore ignorable, and we obtain the equations,

$$\frac{d}{dt}\langle n^1_{\vec{k}}(t)n^1_{-\vec{k}}\rangle = i\vec{k}\cdot k_BT\,\frac{1}{2}\sum_{1}^{\vec{k}_c}\left(\sum_{2}^{\vec{k}_c}\chi^2(2)U^{-1}_{21}\right)\langle[n^1_{\vec{k}+\vec{k}_1}\vec{p}_{-\vec{k}_1} + \vec{p}_{\vec{k}+\vec{k}_1}n^1_{-\vec{k}_1}](t)n^1_{-\vec{k}}\rangle - k^2D_0\langle n^1_{\vec{k}}(t)n^1_{-\vec{k}}\rangle \tag{78a}$$

$$\begin{aligned}\frac{d}{dt}\langle[n^1_{\vec{k}+\vec{k}_1}\vec{p}_{-\vec{k}_1}](t)n^1_{-\vec{k}}\rangle = i\vec{k}k_BT\chi^2(1)\langle n^1_{\vec{k}}(t)n^1_{-\vec{k}}\rangle - [\vec{k}_1\cdot\underline{\eta}_0\cdot\vec{k}_1 + (\vec{k}+\vec{k}_1)\cdot\underline{D}_2\cdot(\vec{k}+\vec{k}_1) - (\vec{k}+\vec{k}_1)\cdot\underline{\delta}\cdot\vec{k}_1 - \vec{k}_1\cdot\underline{\delta}\cdot(\vec{k}+\vec{k}_1)]\\ \times Nmk_BT\chi^2(1)\sum_{3}^{k_c}U_{13}{}^{-1}\langle[n^1_{\vec{k}+\vec{k}_3}\vec{p}_{-\vec{k}_3}](t)n^1_{-\vec{k}}\rangle,\end{aligned} \tag{78b}$$

where we have written i instead of $\vec{k}_i$ whenever possible. Note that Eq. (78b) includes coupling between bilinear variables of different $\vec{k}'$.

In order to solve Eqs. (78) we shall make all the approximations which we made for the case of point particles in three dimensions, i.e., $\underline{\delta}=0$, $\underline{D}_2$ is treated as a scalar, $\underline{\eta}_0$ is replaced by $\eta_0^1 I^{(4)}$, and the hydrodynamic part of our result for D is multiplied by $\frac{4}{3}$ to correct for the effect of compressibility. In Sec. IV C we saw that D was independent of $\vec{k}$ and s to Navier-Stokes order for point particles, and we shall assume that this is also true for large particles. With these reasonable approximations in mind, we may now perform successive substitutions of Eq. (78b) into Eq. (78a) to obtain, for the self-diffusion coefficient of a particle of arbitrary $R \geq a$,

$$D=D_0+\frac{2}{3}\frac{k_BT}{m(\eta_0^\perp+D_2)}\Bigg[\sum_1^{\vec{k}_c}\Bigg(\sum_2^{\vec{k}_c}\chi^2(2)U_{21}{}^{-1}\Bigg)(k_1^2U_{11}{}^{-1}N)^{-1}-\sum_1^{\vec{k}_c}\Bigg(\sum_2^{\vec{k}_c}\chi^2(2)U_{21}{}^{-1}\Bigg)\sum_{3\neq1}^{\vec{k}_c}\frac{U_{13}{}^{-1}}{U_{11}{}^{-1}}(k_3^2U_{33}{}^{-1}N)^{-1}$$
$$+\sum_1^{\vec{k}_c}\Bigg(\sum_2^{\vec{k}_c}\chi^2(2)U_{21}{}^{-1}\Bigg)\sum_{3\neq1}^{\vec{k}_c}\frac{U_{13}{}^{-1}}{U_{11}{}^{-1}}\sum_{4\neq3}^{\vec{k}_c}\frac{U_{34}{}^{-1}}{U_{33}{}^{-1}}(k_4^2U_{44}{}^{-1}N)^{-1}+\cdots\Bigg]. \tag{79}$$

We now perform certain manipulations designed to allow the reduction of Eq. (79) to final form, in the limit $Rk_c \gg 1$, without an actual calculation of U^{-1}. The factor, $\sum_2^{\vec{k}_c}\chi^2(2)U_{23}{}^{-1}$, which appears in each term of the hydrodynamic part of Eq. (79), may be evaluated exactly in this limit by summing both sides of Eq. (77) over $\vec{k}_1$. The third term on the left-hand side is evaluated via the transformation $\sum_{\vec{k}} \to [V/(2\pi)^d]\int d\vec{k}$, the convolution theorem for Fourier transforms [Eq. (75)], and the property of the step functions $S^2(\vec{r})=S(\vec{r})$. The $k_c \gg 1$ condition is required for the use of the convolution theorem. The result is

$$\sum_2^{\vec{k}_c}\chi^2(2)U_{23}{}^{-1}=(M^{(2)}\mathfrak{M}k_BT)^{-1}, \tag{80}$$

where $M^{(2)}$, the "natural" measure of the importance of off-diagonal terms for this problem, is defined by the relation

$$M^{(2)}\equiv\sum_1^{\vec{k}_c}\chi^2(1). \tag{81}$$

For $Rk_c \gg 1$, $\chi^2(1)$ will cut off the sum in Eq. (81) at some value of $k_1 \ll k_c$, and $M^{(2)}$ will be independent of k_c, which may be set equal to ∞. $M^{(2)}$ is then about equal to our previously defined M with $\vec{k}_c \approx \pi/R$. Note that $\sum_1^{\vec{k}_c}\chi^2(1)U_{1j}{}^{-1}$ is independent of j, and thus we may extract a factor of $(M^{(2)}\mathfrak{M}k_BT)^{-1}$ from each term in the sum in Eq. (79).

Next, we note that the diagonal elements of U^{-1} are easily obtained. The corrections to the diagonal elements of U^{-1} which arise from the off-diagonal elements of U vanish, with respect to the $[U_{ii}]^{-1}$, in the thermodynamic limit; this may be seen from an iteration of Eq. (77). The correction terms, which are of the same order of magnitude for each matrix element, survive in the thermodynamic limit only if multiplied by a factor of M. Thus $U_{ii}{}^{-1}=[U_{ii}]^{-1}$ and, from Eq. (73),

$$U_{ii}{}^{-1}=[Nmk_BT\chi^2(i)]^{-1}. \tag{82}$$

The only remaining unknown quantities in Eq. (79) are the sums of form $\sum_{j\neq i}^{\vec{k}_c}U_{ji}{}^{-1}/U_{jj}{}^{-1}$. These sums may be evaluated by combining Eqs. (82) and (80), with the result

$$\sum_j^{\vec{k}_c}\frac{U_{ji}{}^{-1}}{U_{jj}{}^{-1}}=\frac{Nm}{M^{(2)}\mathfrak{M}}; \tag{83}$$

the restricted sums over j may be obtained by subtracting $U_{ii}{}^{-1}/U_{ii}{}^{-1}=1$ from Eq. (83). Note that the sum in Eq. (83) is independent of i. It follows that the terms in Eq. (79) form a geometric series, which may be summed, using the results above, to obtain

$$D=D_0+\frac{2}{3}\frac{k_BT}{m(\eta_0^\perp+D_2)}\frac{1}{N}\sum_i^{\vec{k}_c}\chi^2(i)k_i{}^{-2}. \tag{84}$$

For the large-particle limit, for which Eq. (84) has been derived, the $\sum_i$ is cut off by $\chi^2(i)$ before the cutoff wave vector is reached, and k_c may be set to infinity; the result is

$$D=D_0+k_BT/5\pi(\eta_0^\perp+D_2)\rho R. \tag{85}$$

Equation (84) also reproduces correctly the $Rk_c \ll 1$ form of D [Eq. (58)], which suggests that Eq. (84) may be more general than our derivation would indicate. Note that Eqs. (84) and (85) are very similar in form to Eq. (58), despite the added complexities in their derivation. For particles of all sizes, our method naturally divides D into microscopic and Stokes-Einstein parts. Furthermore, it is easy to see that D_0 is identically zero in this limit. Recall that the magnitude of D_0 was formulated, for the case of point particles, in terms of the quantity, Z [see Eq. (63) and related discussion]; if $Z=1$, $D_0=0$. For particles of arbitrary radius $R \geqslant a$,

$$Z=\mathfrak{M}k_BT\sum_{1,2,3,4}^{\vec{k}_c}\chi^2(2)U_{21}^{-1}U_{13}\chi^2(4)U_{43}^{-1}. \tag{86}$$

The sums over 1 and 2 are easily done, with the result

$$Z=\mathfrak{M}k_BT\sum_{3,4}^{\vec{k}_c}\chi^2(3)\chi^2(4)U_{34}^{-1}. \tag{87}$$

The sums in Eq. (87) are evaluated by multiplying both sides of Eq. (77) by $\chi^2(3)$, and summing over 1 and 3. We find that Z is exactly equal to one, if $Rk_c \gg 1$, and our final result for a large Brownian particle is

$$D=k_BT/5\pi\rho(\eta_0^\perp+D_2)R. \tag{88}$$

Equation (88) is almost identical to the Stokes-Einstein law, Eq. (5). Recall that we expect $\eta_0^\perp \approx \eta \gg D_2$ in three dimensions, and that $\rho\eta$, via our definitions, is equal to the usual η. Thus, the only difference between Eq. (88) and the Stokes-

Einstein law is a factor of $\frac{5}{6}$. To within the factor of $\frac{5}{6}$, we have shown that the Stokes-Einstein law follows naturally from a bilinear hydrodynamic theory, in the limit of a large diffusing particle. For such a particle, the cutoff wave vector does not enter our final result.

VI. DISCUSSION

Let us now summarize the major points of this paper. We have developed a theory capable of explicitly treating the Navier-Stokes hydrodynamic aspects of self-diffusion, by point and Brownian particles, in two and three dimensions. The theory is based upon sets of bilinear "hydrodynamic" equations. The variables employed are the tagged-particle density $n^1_{\vec{k}}$, the usual conserved variable densities, $L_{\vec{k}}$, and all bilinear products thereof. In the thermodynamic limit, the calculation of the autocorrelation function of the tagged-particle density involves only $n^1_{\vec{k}}$ itself and the bilinear variables of form $n^1_{\vec{k}+\vec{k}'} L_{-\vec{k}'}$. The calculation of $\langle n^1_{\vec{k}}(t) n^1_{-\vec{k}}\rangle$ via the solution of our equations automatically divides the self-diffusion coefficient into a Navier-Stokes hydrodynamic part plus a "microscopic" part; the Navier-Stokes hydrodynamic part of D has a Stokes-Einstein law form.

For the case of point particles in three dimensions, the microscopic part of D is not arguably small, and an unknown coefficient multiplies the Stokes-Einstein law in the hydrodynamic part of D. Thus Navier-Stokes hydrodynamics does not fully describe the self-diffusion of point particles in three dimensions; our results show the actual role of the Stokes-Einstein law for this case. The hydrodynamic part of D is associated with a $t^{-3/2}$ tail on the tagged-particle momentum autocorrelation function, for zero k. We have seen that, to Navier-Stokes order, the $t^{-3/2}$ tail may actually be treated as a δ function, and in fact the word tail may be misleading.

We have mentioned that the shear-viscosity coefficient, and probably the other transport coefficients as well, have hydrodynamic parts almost identical to the hydrodynamic part of D. Since D is usually the smallest of the ordinary transport coefficients, it appears that the hydrodynamic ($t^{-3/2}$) effects should be most important for diffusive processes. Also, note that the frequency dependence of D [see Eq. (59)] is only negligible for small k and s, and thus the transport coefficients of non-Navier-Stokes hydrodynamics (Burnett equations, etc.) may be significantly frequency dependent. The importance of bilinear effects for non-Navier-Stokes hydrodynamics has been noted by other authors.[14]

For the case of a large Brownian particle in three dimensions, the microscopic part of D vanishes. There exist no arbitrary coefficients in the hydrodynamic part of D, which is in fact equal to the Stokes-Einstein law D, modified by a factor of $\frac{1}{5}$ instead of the usual $\frac{1}{6}$, and by the replacement of the usual viscosity by a "bare" viscosity. Thus, with minor differences, our approach "derives" the Stokes-Einstein law for a large Brownian particle. The Stokes-Einstein law appears as the large-particle limiting form of an expression [Eq. (58) or (84)], valid for particles of all sizes, which in general is only partially described by the Stokes-Einstein law.

It is of interest to note that the Stokes-Einstein law follows naturally from the same equations which give rise to the $t^{-d/2}$ tails. Thus, as first noted by Widom,[15] there is no contradiction between the existence of the Stokes-Einstein law and a nonexponential decay of the momentum autocorrelation function; the two phenomena are, in fact, intimately related.

For two dimensions, we have obtained the usual t^{-1} behavior of the momentum autocorrelation function for point particles. Due to the singularities in the Navier-Stokes hydrodynamic part of D as $k, s \to 0$ resulting from the t^{-1} tails, the microscopic part of D is negligible in two dimensions. Furthermore, the unknown cutoff wave vector $\vec{k}_c$ does not enter our small k, s results in two dimensions, and thus Navier-Stokes hydrodynamics completely describes self diffusion in two dimensions at long times and small wave vectors. Since our results are complete even for point particles in two dimensions, it has been unnecessary to consider the limiting case of a Brownian particle.

Our equations predict that the mean-square displacement of a particle increases at $t \ln t$ for large t in two dimensions. We have seen that if we redefine D so as to be finite and time independent [Eq. (54)], and if we redefine the two-dimensional friction coefficient so as to be finite and velocity independent, then the redefined quantities obey the Einstein law (to within a factor of $\frac{1}{2}$).

There has been some speculation of late[16] concerning the transport coefficients which belong in the hydrodynamic part of the momentum autocorrelation function in two dimensions. It has been suggested that equations such as our Eq. (49), which contains the "bare" transport coefficients ($\eta_0^\perp$ and D_2), should actually contain the "dressed" viscosity, $\eta(k, s)$, which is calculated in Ref. 10. The t^{-1} behavior of the two dimensional "tails" would then be changed to $[t(\ln t)^{1/2}]^{-1}$.[16] Our results do not incorporate the above-mentioned idea. Although the theory presented here encompasses all the processes which give rise to the "dressed" $\eta(k, s)$ (see Ref. 10), the dressed viscosity enters nowhere into the self-diffusion results. However, it appears possible that the inclusion of triple products of hydrodynamic variables in our formalism converts η_0 into a dressed η.

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t-Matrix Calculations of the Ground-State Energies of Solid He^3 and Solid H_2

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The ground-state energies of solid He^3 and H_2 at various densities are calculated using a self-consistent method in the t-matrix formulation. The two-body equation of motion is solved by expanding the two-body wave function in terms of partial waves. The partial-wave expansion gives rise to a set of coupled differential equations which are solved numerically for the ground-state eigenfunctions. The calculations for He^3 are done using three different two-body potentials, the Lennard-Jones potential, the Beck potential, and the Frost-Musulin potential. The calculations for H_2 are done using the Mason-Rice two-body potential. A bcc structure is assumed for solid He^3, while an fcc structure is assumed for solid H_2. Exchange effects are neglected. Figures and tables are given which compare the present results with those of other authors.

I. INTRODUCTION

The ground-state properties of solid helium, which is well known to be the most characteristic quantum crystal, have been the subject of quite intensive theoretical and experimental activities in recent years. There exist a number of excellent expositions dealing with the behavior of solid He^3 among which one may mention the papers of Werthamer[1] and Guyer.[2] Here one can find a series of convincing arguments and figures exhibiting the rather unique character of He isotopes when compared with other solid rare-gas elements such as Ar, Ne, etc. The helium solid is more "quantum" than solid H_2 or D_2 even though the masses of the molecules of the latter solids are smaller than that of He, the kinetic energies larger, and consequently the excursions around