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Theory of transport in liquids. II. Viscosity

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The BBGKY hierarchy is analyzed to construct a theory of viscosity in liquids. The approach is an elaboration of a previous theory of self-diffusion. The results reduce to Chapman-Enskog theory at low density and represent a generalization of Enskog theory at high density. The whole analysis is carried out within the framework of Navier-Stokes hydrodynamics; quadratic and cubic contributions to the nonequilibrium correlation functions do not affect the coefficient of viscosity.

I. INTRODUCTION

Attempts to employ the time-dependent Bogoliubov-Born-Green-Kirkwood-Yvon (BBGKY) hierarchy as a basis for an approximate theory of transport phenomena in fluid systems slightly displaced from equilibrium have met with limited success.[1-4] The two principal objectives of such an approach are to develop an internally consistent theory of transport that circumvents the problems of N-body dynamics and to develop practical approximate methods for computing transport coefficients and nonequilibrium correlation functions.

One important shortcoming of these efforts has been a basic inconsistency between the theories as constructed and the domain of nonequilibrium behavior to which they are presumed applicable. In the Navier-Stokes hydrodynamics, which we exclusively consider, one treats effects linear in the system gradients or equivalently, the wave vector that characterizes a displacement. However, most previous attempts to analyze the hierarchy have required detailed knowledge of portions of the correlation functions quadratic and cubic in the system gradients.[1-3] A second difficulty has been the theories' failure to reduce to the Chapman-Enskog results at low density. Another problem is that treatment of a decaying self-diffusive wave and of steady-state self-diffusion, which should ultimately lead to equivalent formulations, fail to do so.[1,2] Since the formal justification for the various approaches must be considered suspect, it is understandable that little numerical analysis of the final equations has been attempted. In fact, because of the failings of these theories, the idea of using the BBGKY hierarchy as the foundation of a theory of transport in the Navier-Stokes domain has fallen into disfavor.

Here we attempt to revive interest in this idea by concentrating on the first major goal of this approach—the development of an internally consistent treatment. We have recently shown that a treatment of the hierarchy for the case of self-diffusion can be given which only requires consideration of terms linear in the system gradients.[4] Furthermore the approach reduces naturally to Chapman-Enskog theory at low density.

We shall extend our arguments to discuss shear viscosity. The present formulation is general and should admit of later application to treatments of thermal conductivity and bulk viscosity. Our expression for the shear viscosity is rather complicated; we can demonstrate that when simplified, our results contain those of Enskog dense-fluid theory. This suggests that our formalism might be approximated in ways that achieve the second goal of developing practical computational techniques.

In Sec. II we discuss construction of asymptotic solutions to the BBGKY hierarchy. The major emphasis is on a modification of the familiar Bogoliubov approach to the kinetic theory of gases.[5] As previously indicated,[4] the imposition of dynamical superposition leads to a closed set of equations. The evolution is governed by a nondynamical operator composed of two parts. There is an effective Liouville operator in which the potential of mean force replaces the ordinary intermolecular potential and a specific nonlocal interaction which can couple with the free-particle streaming. This latter feature is important and greatly modifies the results. This point was not fully appreciated in our previous treatment of self-diffusion[4]; hence a modification of the theory is presented in Appendix B. As we rely upon a modification of the Bogoliubov technique to extract asymptotic solutions, these suffer from a problem due to the singular nature of the basic equations. There are long-range correlations in the nonequilibrium contribution to the two-particle reduced distribution function in a limited region of phase space. No equilibrium property is affected nor do these correlations affect the integrals which determine the transport properties.

In Secs. III and IV we apply our formalism to Navier-Stokes hydrodynamics. Our treatment is demonstrated to be consistent with general statistical-mechanical theories of transport, at least to lowest order in a wave-vector expansion of the nonequilibrium correlation functions. We consider shear viscous flow and develop expressions for the coefficient of viscosity and for determining the linear term in a wave-vector expansion of the correlation functions. The relationship to Chapman-Enskog theory and to Enskog dense-fluid theory is also demonstrated. Section V deals with a summary of the theory, a comparison with previous approaches, and consideration of its extension to the problems of thermal conductivity and bulk viscosity.

II. GENERAL THEORY

We limit discussion to a fluid system of N structureless particles interacting via a short-range pair potential $u(r)$. The particles are confined in a volume V to which periodic boundary conditions are applied. The system is slightly displaced from equilibrium so that linear nonequilibrium thermodynamics is applicable. Macroscopically the temporal and spatial behavior can be of many forms. We consider the evolution of a system prepared so that a single independent orthonormal function (IOF) of wave vector $\vec{k}$ is the only nonequilibrium displacement.[6,7] There are a limited number of such functions corresponding to each $\vec{k}$. In a one-component system there are five—two shear waves perpendicular to $\vec{k}$, two sound waves traveling in the $+\vec{k}$ and $-\vec{k}$ directions, and a thermal (or entropy) wave. The IOF have the property that each decays independently to equilibrium without exciting any other; the relaxation time is $(Gk^2)^{-1}$ where G is the generalized diffusion coefficient specific to the IOF under consideration. Their general functional form is

$$\Delta x(\vec{r},t)=\Delta x_0 e^{i\vec{k}\cdot\vec{r}} f(t)\,,\qquad f(t)=\exp[(-Gk^2+i\omega)t]\,, \tag{2.1}$$

where Δx_0 is the specific combination of thermodynamic and velocity displacements which describe the IOF; ω, the frequency of oscillation, is equal to $\pm ck$ for the sound waves and zero otherwise.

Our procedure is to use (2.1) as the basis for postulating forms for the asymptotic behavior of the low-order reduced distribution function (RDF), $F_n\{n\}$. We assume that

$$F_n\{n\}=V^{-n}\prod_{i=1}^{n}\varphi(i)g_n\{n\}\Big(1+\sum_{i=1}^{n}\sigma_1(i)+\sum_{1\le i<j\le n}\sigma_2(ij)+\cdots+\sigma_n(1,\ldots n)\Big)\,, \tag{2.2}$$

where $\varphi(i)$ is the Boltzmann factor, g_n is the equilibrium n-particle correlation function (in a fluid $g_1=1$), and $\sigma_n\{n\}$ is the nonequilibrium perturbation function; $\sigma_n\{n\}$ has the cluster property that it is only nonzero when all n particles are close together. Using (2.1), we introduce specific forms for the σ_n,

$$\sigma_n\{n\}\equiv f(t)\exp(i\vec{k}\cdot\vec{R}_n)v_n(\{\vec{p}_i\},\{\vec{r}_{ij}\};\vec{k})\,, \tag{2.3}$$

where $\vec{R}_n$ is the center of mass of the n-particle group,

$$\vec{R}_n=\Big(\sum_{i=1}^{n}\vec{r}_i\Big)\Big/n\,.$$

The $v_n\{n\}$ may be expanded in powers of k,

$$v_n\{n\}=V_n+ikW_n-k^2X_n\cdots\,. \tag{2.4}$$

The V_n have already been determined from general statistical-mechanical considerations.[7] Our emphasis is on the W_n which are the Navier-Stokes terms. These are needed to determine the transport coefficients; it is, however, equally important to show that the higher-order terms, X_n, are unnecessary. In a one-component system the v_n are invariant under exchange of any pair of particles; they are also restricted by the symmetry of the IOF to which they refer.

In order to find equations determining the v_n, we examine the first two equations of the BBGKY hierarchy[8]:

$$\Big(\frac{\partial}{\partial t}+\vec{p}_1\cdot\nabla_1\Big)F_1(1)=(N-1)\int d\vec{\xi}_2\nabla_1u(12)\cdot\vec{\partial}_1F_2(12)\,,$$
$$\Big(\frac{\partial}{\partial t}+\vec{p}_1\cdot\nabla_1+\vec{p}_2\cdot\nabla_2-\nabla_1u\cdot\vec{\partial}_{12}\Big)F_2(12)=(N-2)\int d\vec{\xi}_3\sum_{i=1}^{2}\nabla_iu(i3)\cdot\vec{\partial}_iF_3(123)\,, \tag{2.5}$$

where $\vec{\partial}\equiv\nabla_p$ and $d\vec{\xi}\equiv d\vec{p}\,d\vec{r}$. Using (2.2) these become

$$\left(\frac{\partial}{\partial t}+L_1\right)\sigma_1(1)=J_1(1;2)[\sigma_1(2)+\sigma_2(12)] \ , \tag{2.6a}$$

$$\left(\frac{\partial}{\partial t}+L_2\right)\sigma_2(12)=\hat{\theta}_{12}\sum_{i=1}^{2}\sigma_1(i)+J_2(12;3)\left(\sigma_1(3)+\sum_{i=1}^{2}\sigma_2(i3)+\sigma_3(123)\right)+\sum_{i\neq j}^{2}J_1(i;3)[\sigma_2(j3)+\sigma_3(123)] \ , \tag{2.6b}$$

where

$$L_1=\vec{p}_1\cdot\nabla_1,\quad L_2=\vec{p}_1\cdot\nabla_1+\vec{p}_2\cdot\nabla_2-\hat{\theta}_{12},\quad \hat{\theta}_{12}=\nabla w\cdot\vec{\partial}_{12} \ , \tag{2.7}$$

with $w=-\ln g(12)$ the potential of mean force and

$$J_1(1;2)=\rho\int d\vec{\xi}_2\,\varphi(2)g(12)\nabla_1 u(12)\cdot(\vec{\partial}_1-\vec{p}_1) \ ,$$

$$M(12;3)=\rho\int d\vec{\xi}_3\,\varphi(3)\frac{g(123)}{g(12)}\times\sum_{i=1}^{2}\nabla_i u(13)\cdot(\vec{\partial}_i-\vec{p}_i) \ , \tag{2.8}$$

$$J_2(12;3)=M(12;3)-J_1(1;3)-J_1(2;3) \ .$$

To this point our treatment of the nonequilibrium hierarchy differs from earlier work only in its generality.[1-4]

Most previous attempts at solving (2.6) have relied upon direct substitution of the asymptotic forms (2.3).[1,3] A more satisfactory procedure is to *construct* the formal solution to (2.6) and then determine *under what conditions* our postulated forms are consistent with the formal solution. This can indeed be done. No change occurs in the equation for v_1; however the equation for v_2 is much altered.

The formal solution to (2.6a) is

$$\sigma_1(1;t)=O_t\,\sigma_1(1;t=0)+\int_0^t ds\,O_s J_1(1;2)[\sigma_1(2;t-s)+\sigma_2(12;t-s)] \ , \tag{2.9}$$

where $O_t=\exp(-tL_1)$. After introducing (2.3) and performing the time integration, we obtain

$$[-k^2G+i\vec{k}\cdot\vec{p}_1+i\omega]v_1(1;\vec{k})=J_1(1;2)[e^{i\vec{k}\cdot\vec{r}_{21}}v_1(2;\vec{k})+e^{i\vec{k}\cdot\vec{r}_{21}/2}v_2(12;\vec{k})] ; \tag{2.10}$$

this result is identical to that obtained by direct substitution of (2.3) into (2.6a).

We now seek an asymptotic solution to (2.6b) which takes into account the singular nature of this equation. This singularity is due to the free-particle streaming which takes place whenever particles are outside the range of interaction and which can introduce long-range correlations among particles initially well separated.[9] To isolate the singularity, we have decomposed the integral operators which occur in (2.6b) into two classes; $J_2(12;3)$ is specifically short range and vanishes when $r_{12}\to\infty$. The terms which involve $J_1(i;3)$ may be long range if $\sigma_2(j3)$ or $\sigma_3(123)$ have long-range contributions; they must therefore be handled with the Liouville operator L_2 which causes the singularity. By means of this separation we can construct an iterative scheme which affords the possibility of being soluble and handling exactly the significant mathematical peculiarities of the hierarchy.

In order to proceed we assume that $\sigma_3(123)$ is a short-range function of the interparticle coordinates; this is preparatory to truncating the hierarchy by means of dynamical superposition in which $\sigma_3(123)\equiv 0$. Then a formal solution to (2.6b) is

$$\sigma_2(12;t)=\mathcal{S}_t\sigma_2(12;0)+\int_0^t d\tau\,\mathcal{S}_\tau\left[\hat{\theta}_{12}\sum_{i=1}^{2}\sigma_1(i;t-\tau)+J_2(12;3)\left(\sigma_1(3;t-\tau)+\sum_{i=1}^{2}\sigma_2(i3;t-\tau)\right)+M(12;3)\sigma_3(123;t-\tau)\right] ; \tag{2.11}$$

both $\sigma_2(12;0)$ and the bracketed expression in the integral are short-range functions of r_{12}. The operator $\mathcal{S}_t=\exp(-t\hat{L})$ is not the simple dynamical operator $\mathcal{O}_t\equiv\exp(-tL_2)$. Instead $f(12;t)=\mathcal{S}_t f(12;0)$ is the solution of the associated integrodifferential equation

$$\left(\frac{\partial}{\partial t}+\hat{L}\right)f(12;t)=0 \ , \tag{2.12a}$$

$$\hat{L}f(12)=L_2 f(12)-\sum_{i\neq j}^{2}J_1(i;3)f(j3) \ . \tag{2.12b}$$

The solutions to this equation have certain similarities to those of a modified Vlasov equation[10]; furthermore our approach has common features with other recent treatments of the hierarchy.[11] The evolution operator $\mathcal{S}_t$ has some of the properties of the dynamical operator $\mathcal{O}_t$; the evolution of $f(12;t)$ into its asymptotic form occurs during an effective interaction time $t_{\text{int}}(\vec{r},\vec{p})$. This time is generally short, $\sim l/s$, where l is the range of interaction [now a bit larger than the range of $w(r)$ because of the integral term in (2.12b)] and s is the mean thermal speed of the molecules.[12]

But for a vanishingly small set of phase points t_{int} is much less than either the hydrodynamic time $(k^2G)^{-1}$ or the sound propagation time $(kc)^{-1}$. We therefore simplify (2.11); the first term on the right-hand side is zero and the upper limit in the second is arbitrary. We denote this limit as t^*. Introducing (2.3) we find the result

$$v_2(12)=\int_0^{t^*} d\tau f(-\tau)e^{-i\vec{k}\cdot\vec{R}_2}\mathcal{S}_\tau e^{i\vec{k}\cdot\vec{R}_2}\Theta(12) \tag{2.13}$$

where

$$\Theta(12)=\sum_{i\neq j}^{2}\left[\hat{\theta}_{12}e^{i\vec{k}\cdot\vec{r}_{ij}/2}v_1(i)+J_2(12;3)e^{i\vec{k}\cdot\vec{r}_{3j}/2}v_2(i3)\right.$$
$$\left.+J_2(12;3)e^{i\vec{k}\cdot(\vec{r}_{31}+\vec{r}_{32})/2}v_1(3)+M(12;3)e^{i\vec{k}\cdot(\vec{r}_{31}+\vec{r}_{32})/6}v_3(123)\right]. \tag{2.14}$$

The singular nature of the equation manifests itself as follows. For $|\vec{r}_{12}-(\hat{p}_{12}\cdot\vec{r}_{12})\hat{p}|<l$ while $r_{12}>l$, particles initially greatly separated would collide if the presence of intervening particles were ignored. An inconsistency arises since $v_2(12)$ need not approach zero as $r_{12}\to\infty$; the integral in (2.13) may be nonzero between t_0 and t_0+t_{dur} since $\mathcal{S}_\tau\Theta(12)$ might be nonzero during that time span (t_0 is the time at which interaction begins and t_{dur} is the duration of the interaction). This problem is not as serious as it appears. First, the normalization

$$\int d\vec{\xi}_2F_2(12)=F_1(1) \tag{2.15}$$

remains valid; there is an anomalous contribution of order $V^{-2/3}$ which is negligible. Second, no equilibrium property is affected. Third, the transport properties are not affected as the resultant integrals all contain factors of $u(r_{12})$. Finally, the derivation of (2.13) remains valid. The term $\mathcal{S}_t*\sigma_2(12;0)$ would evolve to $e^{-i\vec{k}\cdot\vec{R}_2}\mathcal{S}_t*\times e^{i\vec{k}\cdot\vec{R}_2}v_2(12)$ which is zero since $\mathcal{S}_t*v_2(12)=0$. This follows from (2.13); for the region of phase space being considered the limits on that integral are t_0 and t_0+t_{dur}. Thus $\mathcal{S}_t*e^{i\vec{k}\cdot\vec{R}_2}v_2(12)$ means that contributions to the integral are to be determined for times greater than t_0+t^*. The integral is then zero since these are times after which interaction has ceased, i.e., when $\mathcal{S}_\tau\Theta(12)$ is again zero.

As we introduced a nonlocal operator in (2.12) to determine an asymptotic solution to this problem, one might question the value of using an iterative scheme. However (2.12) is much simpler than the exact equation. It is independent of $g_3(123)$, and it is susceptible to Fourier analysis. At the same time the effect of the medium is introduced in two ways, through the appearance of the potential of mean force in L_2 and through nonlocal contributions to $\hat{L}$. These latter effects introduce the correspondence with a modified Vlasov equation,[10] a point which we will pursue in a future paper devoted to approximate solution of (2.12) for hydrodynamically interesting situations.

III. ANALYSIS OF k-INDEPENDENT TERMS

We now consider specific aspects of the nonequilibrium problems posed by a shear wave, a sound wave, and a thermal wave. We shall show that the k-independent terms in (2.4), V_n, which have previously been determined from general considerations, are solutions to (2.10) and (2.13).

To demonstrate that this approach is consistent with previous work, consider the k^0 terms in (2.10) and (2.13); using (2.4) these are

$$J_1(1;2)[V_1(2)+V_2(12)]=0, \tag{3.1a}$$

$$V_2(12)=\int_0^{t^*} d\tau\,\mathcal{S}_\tau\,\Xi_0(12), \tag{3.1b}$$

where

$$\Xi_0(12)=\nabla_1w\cdot\vec{\partial}_{12}[V_1(1)+V_1(2)]$$
$$+J_2(12;3)\Big(V_1(3)+\sum_{i=1}^{2}V_2(i3)\Big)$$
$$+M(12;3)V_3(123). \tag{3.2}$$

The general statistical-mechanical theory[7] for construction of the phase-space analogs of the IOF can be used to show that for a shear wave

$$V_1(1)=\vec{\epsilon}\cdot\vec{p}_1,\quad V_2(12)=0,\quad V_3(123)=0, \tag{3.3}$$

where $\vec{\epsilon}$ is a unit vector perpendicular to $\vec{k}$. Then $\Xi_0(12)=0$ and (3.1) is immediately satisfied. For the thermal wave we find that

$$V_1(1)=\frac{p_1^2}{2m}-\frac{3}{2\beta}-\frac{\alpha T}{\beta},\quad V_2(12)=-\left(\frac{\partial \ln g_2(12)}{\partial\beta}\right)_P ,$$

$$V_3(123)=-\left(\frac{\partial Z}{\partial\beta}\right)_P,\quad Z=\ln g_3(123)-\sum_{i<j}^{3}\ln g_2(ij), \tag{3.4}$$

while for the sound wave we have

$$V_1(1)=\frac{p_1^2}{2m}-\frac{3}{2\beta}+\frac{\kappa C_v}{\beta\alpha V}-\left(\frac{C_pC_vT}{mN(C_p-C_v)}\right)^{1/2}\frac{\vec{k}\cdot\vec{p}_1}{k},$$

$$V_2(12)=-\left(\frac{\partial \ln g_2(12)}{\partial\beta}\right)_{S,N},\quad V_3(123)=-\left(\frac{\partial Z}{\partial\beta}\right)_{S,N}. \tag{3.5}$$

In these expressions we have specifically exhibited the mass and temperature dependence; α is the coefficient of thermal expansion, κ is the isothermal compressibility, C_p and C_v are the constant-pressure and constant-volume heat capacities, and S is the entropy. Since the integral operator $J_1(1;2)$ from (2.8) is an odd function of $\vec{r}_{12}$, the forms for V_n immediately satisfy (3.1a). By direct substitution we find, for both thermal and sound waves,

$$\Xi_0(12)\equiv\frac{1}{m}\left(\vec{p}_{12}\cdot\nabla_1V_2(12)+\rho\int dr_3\sum_{i\neq j}^{2}\vec{p}_i\cdot\nabla_iu(i3)g(i3)V_2(j3)\right)$$

$$=\hat{L}\,V_2(12)\,. \tag{3.6}$$

Then the right-hand side of (3.1b) is

$$V_2-\mathcal{S}_t*V_2(12) \tag{3.7}$$

in both cases; since $V_2(12)$ is a short-range function of r_{12}, $\mathcal{S}_t*V_2(12)=0$ and (3.1b) is satisfied.

IV. APPLICATION TO SHEAR VISCOUS FLOW

Here we limit the analysis to consider shear waves for which $G=\eta/m\rho$, η being the shear viscosity. In (3.3) we specified the k^0 terms in the nonequilibrium RDF, V_n. Analysis of the linear and quadratic terms in k requires the diadic $\vec{\epsilon}\vec{n}$ and the triadic $\vec{\epsilon}\vec{n}\vec{n}$, where $\vec{n}$ is the unit vector parallel to $\vec{k}$. By introducing these second- and third-rank tensors, we make certain the hydrodynamically significant terms are properly considered when we treat (2.12) and (2.15). We may express $\vec{\epsilon}\vec{n}$ in terms of its orthogonal tensor invariants

$$\vec{\epsilon}\vec{n}=\underline{E}_s+\underline{E}_a\,, \tag{4.1}$$

where $\underline{E}_s$ is a symmetric tensor of zero trace and $\underline{E}_a$ is an antisymmetric tensor. Similarly, $\vec{\epsilon}\vec{n}\vec{n}$ is composed of three orthogonal tensor invariants

$$\vec{\epsilon}\vec{n}\vec{n}=\frac{1}{10}\sum_\alpha\sum_\beta(4[\vec{1}_\alpha\vec{1}_\beta\vec{1}_\beta]-\vec{1}_\beta\vec{1}_\alpha\vec{1}_\beta-\vec{1}_\beta\vec{1}_\beta\vec{1}_\alpha)\epsilon_\alpha+\sum_\alpha\sum_\beta\sum_\gamma(3[\vec{1}_\alpha\vec{1}_\beta\vec{1}_\gamma]+\vec{1}_\gamma\vec{1}_\alpha\vec{1}_\beta-\vec{1}_\beta\vec{1}_\gamma\vec{1}_\alpha)\Gamma_{\alpha\beta\gamma}+\sum_\alpha\sum_\beta\sum_\gamma\vec{1}_\alpha\vec{1}_\beta\vec{1}_\gamma\Lambda_{\alpha\beta\gamma}; \tag{4.2}$$

the $\vec{1}_\alpha$ are a set of space-fixed orthogonal unit vectors and

$$\Gamma_{\alpha\beta\gamma}=\tfrac{1}{6}(\epsilon_\alpha n_\beta-n_\alpha\epsilon_\beta)n_\gamma-\tfrac{1}{12}(\epsilon_\alpha\delta_{\beta\gamma}-\epsilon_\beta\delta_{\alpha\gamma}),$$

$$\Lambda_{\alpha\beta\gamma}=\tfrac{1}{3}(\epsilon_\alpha n_\beta n_\gamma+n_\alpha\epsilon_\beta n_\gamma+n_\alpha n_\beta\epsilon_\gamma)-\tfrac{1}{15}(\epsilon_\alpha\delta_{\beta\gamma}+\epsilon_\beta\delta_{\alpha\gamma}+\epsilon_\gamma\delta_{\alpha\beta})\,. \tag{4.3}$$

The first term in (4.2) transforms as the vector $\vec{\epsilon}$, the second has an antisymmetric component, and the third is totally symmetric. Since $\vec{\epsilon}\cdot\vec{n}=0$ there are only two terms in the diadic and three in the triadic instead of the maximum allowable, three and seven, respectively. In the subsequent analysis we only need that part of the triadic which transforms vectorially. In addition we also employ the vector portions of $\underline{E}_s\vec{n}$ and $\underline{E}_a\vec{n}$ which are

$$\underline{E}_s\vec{n}=\frac{1}{20}\sum_\alpha\sum_\beta[3(\vec{1}_\alpha\vec{1}_\beta+\vec{1}_\beta\vec{1}_\alpha)\vec{1}_\beta-2(\vec{1}_\beta\vec{1}_\beta\vec{1}_\alpha)]\epsilon_\alpha\cdots,$$

$$\underline{E}_a\vec{n}=\frac{1}{4}\sum_\alpha\sum_\beta(\vec{1}_\alpha\vec{1}_\beta-\vec{1}_\beta\vec{1}_\alpha)\vec{1}_\beta\epsilon_\alpha+\cdots. \tag{4.4}$$

We can now construct the most general forms for k^1 terms of the low-order RDF,

$$W_1=\underline{E}_s:\underline{P}B(\tfrac{1}{2}p^2),\quad \underline{P}=\vec{p}\vec{p}-\tfrac{1}{3}p^2\underline{I},$$
$$W_2=\underline{E}_s:\underline{S}(12)+\underline{E}_a:\underline{A}(12), \tag{4.5}$$

where $\underline{P}$ and $\underline{S}$ are traceless symmetric tensors and $\underline{A}$ is an antisymmetric tensor. Similarly, we write that part of the k^2 terms which transforms vectorially,

$$X_1=\vec{\epsilon}\cdot\vec{p}\,C(\tfrac{1}{2}p^2)+\cdots,\quad X_2=\vec{\epsilon}\cdot\vec{T}(12)+\cdots. \tag{4.6}$$

Dynamical superposition is also introduced to ensure closure of the Eqs. (2.12) and (2.15) by requiring $W_3 \equiv 0$ and $X_3 \equiv 0$.

We employ these forms to obtain both constraints on $\underline{S}(12)$ and $\underline{A}(12)$ and an expression for the transport coefficient G. Using (2.4) and substituting into (2.10), we find two equations linear in k. That conjugate to $\underline{E}_s$ is

$$\underline{P}_1 = J_1(1;2)\underline{S}(12), \tag{4.7}$$

and that conjugate to $\underline{E}_a$ is

$$O = J_1(1;2)\underline{A}(12). \tag{4.8}$$

Of the three terms quadratic in k only the equation conjugate to $\vec{\epsilon}$ is of immediate interest; it is

$$\vec{p}_1[G + \tfrac{1}{5}p_1^2 B(\tfrac{1}{2}p_1^2)] = J_1(1;2)[\vec{\Upsilon}(12) + \tfrac{3}{20}\underline{S}(12)\cdot\vec{r}_{12} + \tfrac{1}{4}\underline{A}(12)\cdot\vec{r}_{12}]. \tag{4.9}$$

In order to compute G we take the scalar product of this equation with $\vec{p}_1\varphi(1)$ and integrate over $\vec{p}_1$. Using the definition of $J_1(1;2)$ in (2.8), we obtain

$$G + \frac{1}{15}\int d\vec{p}\,\varphi(p)p^4 B(\tfrac{1}{2}p^2) = \rho\int d\vec{p}_1\,d\vec{\xi}_2\,P_2(12)\,u_1(r_{12})[\tfrac{1}{3}\vec{r}_{12}\cdot\vec{\Upsilon}(12) + \tfrac{1}{20}\vec{r}_{12}\cdot\underline{S}(12)\cdot\vec{r}_{12} + \tfrac{1}{12}\vec{r}_{12}\cdot\underline{A}(12)\cdot\vec{r}_{12}], \tag{4.10}$$

where

$$P_2(12) = \varphi(1)\varphi(2)g(r_{12}), \quad u_1 = (1/r)(du/dr). \tag{4.11}$$

Since the two-particle RDF is symmetric in the exchange of particles, $X(12)$ and therefore $\vec{\Upsilon}(12)$ must also be symmetric; the term $\vec{r}_{12}\cdot\vec{\Upsilon}(12)$ is thus antisymmetric and integrates to zero. As $\underline{A}$ is an antisymmetric tensor $\vec{r}_{12}\cdot\underline{A}\cdot\vec{r}_{12}=0$. Introducing a Sonine polynomial[13] expansion for B

$$B(\tfrac{1}{2}p^2) = \sum_{j=0} b_j S^{(j)}_{5/2}(\tfrac{1}{2}p^2), \tag{4.12}$$

the final result is

$$\frac{\eta}{\rho} = G = -b_0 + \frac{\rho}{20}\int d\vec{p}_1\,d\vec{\xi}_2\,P_2(12) \times u_1(r_{12})\vec{r}_{12}\cdot\underline{S}(12)\cdot\vec{r}_{12}. \tag{4.13}$$

The significant feature of this result is that terms linear in the k expansion of the nonequilibrium perturbation to the RDF's (i.e., the W_n) are sufficient to calculate η.

Formal solutions for $\underline{S}(12)$ and $\underline{A}(12)$ can be obtained after introducing the dynamical superposition approximation. It is convenient to express $\underline{S}(12)$ as

$$\underline{S}(12) = \sum_{j=0} b_j\,\underline{s}_j(12) + \tfrac{1}{2}\underline{s}_v(12). \tag{4.14}$$

Substituting (2.4), (3.3), (4.5), and (4.12) in (2.13), we obtain the k^1 equation conjugate to $\underline{E}_s$

$$\underline{s}_j(12) = \int_0^{t^*} d\tau\,\mathcal{S}_\tau\,[\hat{\theta}_{12}\underline{z}_j(12) + \hat{Q}\underline{s}_j(12)], \tag{4.15}$$

where

$$\underline{z}_j(12) = \underline{P}_1 S^{(j)}_{5/2}(\tfrac{1}{2}p_1^2) + \underline{P}_2 S^{(j)}_{5/2}(\tfrac{1}{2}p_2^2), \quad j>0,$$
$$\underline{z}_v(12) = \tfrac{1}{2}(\vec{r}_{12}\vec{p}_{12} + \vec{p}_{12}\vec{r}_{12}) - \tfrac{1}{3}(\vec{r}_{12}\cdot\vec{p}_{12})\underline{I}, \tag{4.16}$$

$$\hat{Q}f(12) \equiv J_2(12;3)[f(13) + f(23)]. \tag{4.17}$$

The equations conjugate to $\underline{E}_a$ can be formed from (4.15) by replacing $\underline{s}_j(12)$ by $\underline{A}(12)$ and $\underline{z}_j(12)$ by zero. These equations then have the solution $\underline{A}(12)=0$, which also satisfies the constraint (4.8). The set of equations (4.7), (4.13), and (4.15), is sufficient to solve the Navier-Stokes problem we have posed. While complete numerical solution of these equations appears beyond the scope of present technology, they comprise the solution of the BBGKY hierarchy when shear viscous flow is the only nonequilibrium displacement. The only limitation to the derivation has been dynamical superposition. We shall now demonstrate that the set of equations reduce to Chapman-Enskog theory at low density and represent a generalization of Enskog theory at high density. The simplifications which are introduced to establish the correspondence at high density will perhaps suggest ways to employ this formalism to improve upon Enskog's theory.

In order to express our results in a more familiar form, we multiply (4.7) by $\underline{P}_1 S^{(k)}_{5/2}(\frac{1}{2}p_1^2)\varphi(1)$ and integrate over $\vec{p}_1$ to obtain

$$10\delta_{k,0} = \tfrac{1}{2}\rho D_{kv} + \rho\sum_{j=0} b_j D_{kj}. \tag{4.18}$$

After a little rearrangement, we find the alternative forms

$$D_{kj} = -\frac{1}{2}\int d\vec{p}_1\,d\vec{\xi}_2\,P_2(12)[\nabla_1 u\cdot\vec{\partial}_{12}\underline{z}_k(12)]:\underline{s}_j(12), \tag{4.19a}$$

$$= \frac{1}{2}\int d\vec{p}_1\,d\vec{\xi}_2\,\underline{z}_k(12):\{\nabla_1 u\cdot\vec{\partial}_{12}P_2(12)\underline{s}_j(12)\},$$

$$j = v, 0, 1 \ldots. \tag{4.19b}$$

The integral in (4.13) involves the analogous quantities D_{vk} and D_{vv}. The presence of the factor $\nabla_1 u(12)$ ensures that the long-range correlations in the $\underline{s}_j(12)$ discussed in Sec. II do not affect the results. In the limit of low density one finds that $D_{kj} = D_{jk}$ and that $D_{kv} = -D_{vk}$, relationships which need not hold at higher densities. Then in terms of $\Lambda \equiv D^{-1}$, we find that the viscosity is

$$\eta = -10\Lambda_{00} + \frac{\rho}{2}\sum_j (\Lambda_{0j} D_{jv} - D_{vj}\Lambda_{j0}) + \frac{\rho^2}{40}\sum_j \sum_k (D_{vj}\Lambda_{jk} D_{kv} - D_{vv}) . \quad (4.20)$$

At low density, only the first term contributes. Furthermore the iterative term in (4.15), $\hat{Q}\underline{s}_j(12)$, may be neglected and $\mathcal{S}_t \to \mathcal{O}_t = \exp(-tL_2)$ so that

$$\lim_{\rho \to 0} D_{kj} = \frac{1}{2}\int d\vec{p}_1\, d\vec{p}_2\, d\vec{b}\, \varphi(1)\varphi(2) \times |p_{12}|\underline{z}_k(12): [\underline{z}_j^*(12) - \underline{z}_j(12)], \quad (4.21)$$

where $\vec{b}$ is the impact parameter and $\underline{z}_j^*(12) = \mathcal{O}_t * \underline{z}_j$; this is precisely the Chapman-Enskog dilute-gas result.

The correspondence with Enskog dense-fluid theory is made by taking the zeroth approximation to (4.20)

$$\eta = -\frac{10}{D_{00}}\left(1 + \frac{\rho}{20}(D_{v0} - D_{0v}) + \frac{\rho^2}{400}(D_{00}D_{vv} - D_{0v}D_{v0})\right). \quad (4.22)$$

The next simplification is to truncate (4.15) by dropping the iterative term $\hat{Q}\underline{s}_j(12)$ yielding

$$\underline{s}_j(12) = \int_0^{t*} d\tau\, \mathcal{S}_\tau \hat{\theta}_{12} \underline{z}_j(12), \quad j = 0, v . \quad (4.23)$$

In Appendix A we show that by limiting consideration to hard spheres of diameter σ and approximating the operator $\mathcal{S}_{t*}\hat{\theta}$ by hard-sphere dynamics, we obtain the Enskog result[14]:

$$\eta/\eta_0 = [1/g(\sigma)](1 + 0.8a + 0.7712a^2), \qquad a = \tfrac{2}{3}\pi\sigma^3\rho\, g(\sigma_+) . \quad (4.24)$$

There is a slight difference in the a^2 term because Enskog's result includes a full Sonine polynomial calculation of Λ_{00}. To perform this calculation in the present formalism requires using (4.20) and evaluating the D_{jv} which are nonzero.

Employing (4.19a) would appear to be the most natural way to treat the hard-sphere problem with greater accuracy. However because of the difficulties in treating the discontinuities which occur in the hard-sphere limit (see Appendix A), (A1) or (A4) are more convenient. A calculation based upon (A4), which incorporates the approximation (4.23), will allow us to assess the importance of the nonlocal nature of $\hat{L}$. Preliminary work shows that this equation is similar to a modified Vlasov equation, but with some differences, a point that will be pursued in future work. Should we wish to proceed beyond the use of (4.23), we could base a computation on (A1) and obtain a measure of the importance and speed of convergence of the iterative contributions to our solution. As our approximate approach can be related to Enskog dense-fluid results, we have a plausible starting point. So far our use of the formalism has been limited to hard-sphere systems; applications to systems with nonsingular potentials are being studied.

V. SUMMARY

Our major result is demonstrating that the BBGKY hierarchy can be used to develop a theory for shear viscosity in dense fluids. For several reasons our approach is a significant advance over previous attempts to apply the hierarchy along with dynamical superposition to transport phenomena. First of all, the hydrodynamic problem is completely specified by knowledge of the linear terms in a wave-vector expansion; hence Burnett and super-Burnett (quadratic and cubic) contributions to the low-distribution functions are unnecessary.[1-3] Secondly, our analysis reduces directly to the Chapman-Enskog results at low density. Thirdly, Enskog dense-fluid theory is obtained from a simplified version of the present formalism. Finally, we have applied the BBGKY hierarchy to a transport process other than self-diffusion.

Our analysis is based upon a number of specific considerations. We imposed prescribed asymptotic forms for the perturbation functions (2.2) and (2.3). In order to construct a well-defined iterative procedure for solving the second hierarchy equation, it was necessary to base our analysis on an integrodifferential equation rather than a dynamical operator. In this way we could properly treat the singular nature of the hierarchy equation itself. After imposing dynamical superposition we considered only the Navier-Stokes domain and finally obtained a closed set of equations from which we could determine the viscosity of a dense fluid. One residual problem remained; in a very limited region of phase space there are long-range correlations in the nonequilibrium part of the two-particle probability densities. These affect neither the viscosity nor any equilibrium property. They appear to be inherent to any method based upon decomposition of the dynamics into that of clusters of particles since they arise from the free-particle streaming which occurs after such clusters separate.

The current theory differs from our earlier treatment of self-diffusion in the formulation of the iterative scheme and the emphasis on the nonlocal operator $\hat{L}$ instead of the Liouville operator

L_2. We summarize the revised equations for self-diffusion in Appendix B.

Our approach is essentially equivalent to formulating the solution to a doublet kinetic equation; it thus retains a structural similarity with kinetic theories of the singlet distribution function which focus upon ways of constructing a collision operator applicable to a dense-fluid system.[15-17] A common feature between these theories and ours is that in the hydrodynamic limit the doublet perturbation functions are functionals of the singlet perturbation functions; i.e., W_2 is determined by W_1 through (4.15). In all the theories the separation of time scales into a hydrodynamic period and an interaction period plays a central role. It is the methods of affecting closure and of treating effects due to the medium which differ. Severne's theory requires no closure but leads to a result involving a complicated and quite intractable collision operator.[15] The Rice-Allnatt approach[16] uses Enskog closure and develops the theory in terms of a friction coefficient which is, in general, very difficult to evaluate. Schrodt and Davis[17] have coupled ideas from these treatments and obtain a tractable kinetic equation which yields reasonable numerical results. Our method used dynamical superposition which is less restrictive than Enskog closure. However, the imposition of the asymptotic forms (2.2) and (2.3) is a great limitation; the kinetic equations may contain a more extensive class of solutions than those we have assumed. Our final equations are complicated, but they may perhaps be approximated in ways which more accurately include medium effects than either Enskog theory or the recent work of Schrodt and Davis. The close relationship with a modified Vlasov equation is encouraging.

It is also worthwhile to compare our treatment with Gross's new approach to the nonequilibrium problem.[18] Both theories are inherently nonlocal. Gross imposes a restrictive functional form on the nonequilibrium portion of the full N-particle distribution, in contrast with our more conventional idea of specifying the form of the lower-order distribution functions. The Gross treatment formulated with a truncation at the two-body level leads to the exact initial conditions on the time-dependent triplet distribution function being satisfied.[19] Our treatment accomplishes this in a different way; in Sec. III we constructed the k-independent terms to satisfy the requirements of a general statistical-mechanical theory of the initial-value problem.[7] This leads to the correct value for the sound velocity as does Gross's method.[20] The difference between the two approaches is still considerable. Our method is specific to hydrodynamics, incorporates whatever exact information about the perturbation functions is available, and imposes closure by neglecting triplet correlations of order k in the wave-vector expansion. Gross restricts the form of the full distribution function and obtains the exact short-time dependence as a consequence.

The application of our method to the problems of thermal conductivity λ and bulk viscosity η_v creates two difficulties which do not arise in the treatment of shear viscosity or self-diffusion. From Sec. III we note that for the two transport problems already considered $V_2 = V_3 = 0$; unfortunately this is not true for the remaining transport coefficients. Arguments similar to those given in Sec. IV lead to equations for the perturbation functions analogous to (4.14) where the term corresponding to $\underline{s}_v$ is determined by an extremely complicated function corresponding to $\underline{z}_v$ which depends upon V_2 and V_3. To proceed we cannot employ dynamical superposition in its simplest form since that requires (incorrectly) that $V_3 = 0$. Instead we would drop nonequilibrium triplet correlations only at the linear terms in the wave-vector expansion. A more serious problem may arise in the treatment of the equations analogous to (4.10). A central feature of our approach is that only Navier-Stokes terms, $O(k)$, need be kept to compute D and η. Preliminary analysis indicates there may be difficulties in obtaining a similar result for λ or η_v since it is not immediately obvious how terms corresponding to $\vec{r}_{12} \cdot \vec{T}(12)$ can be eliminated. The complexity of this problem may best be gauged by recognizing that in our treatment the Burnett, $O(k^2)$, terms do not contribute to D or η because of the requirements of continuity and conservation of momentum, respectively. To obtain the same feature in the case of λ and η_v we must ensure conservation of energy which is not easily formulated for the problem at hand.

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APPENDIX A

The integrals D_{kj} all contain a factor $g(r)u'(r)$ which for hard-sphere potentials may be written as $-\delta(r-\sigma_+)g(\sigma_+)$. This suggests that evaluation of (4.19a) at contact would be the convenient procedure in the hard-sphere problem. While this can be done, there are numerous pitfalls in passing to the hard-sphere limit since at contact, $P_2(12)$, $\nabla_1 u(12)$, and $\underline{s}_j(12)$ are all discontinuous.[21] To circumvent this difficulty we note that only the immediate region about $r=\sigma$ contributes to the integral, and we may substitute $g(r)u'(r)$ by $g(\sigma_+)e^{-u(r)} \times u'(r)$. Hence, for hard spheres only, (4.19b) is

$$D_{kj} = \tfrac{1}{2} g(\sigma_+) \langle \underline{z}_k(12) : [\nabla_1 u(12) \cdot \vec{\partial}_{12} P_2^0(12) \underline{s}_j(12)] \rangle , \tag{A1}$$

where $P_2^0 = \varphi(1)\varphi(2)e^{-u}$ and the angular brackets signify integration over $\vec{p}_1$ and $\vec{\xi}_2$.

To analyze this expression, we transform to a resolvent operator formalism in which case the solution to (4.23) is

$$\underline{s}_j = \lim_{\epsilon\to 0} G_2 \theta \underline{z}_j = \lim_{\epsilon \to 0} [\epsilon G_2 - 1 + G_2(L_0 - \hat{R})] \underline{z}_j , \tag{A2}$$

where $G_2 = (\epsilon + \hat{L})^{-1}$, $L_0 = \vec{p}_1 \cdot \nabla_1 + \vec{p}_2 \cdot \nabla_2$, and $\hat{R}f(12) = J_1(1;3)f(23) + J_1(2;3)f(13)$. Then using the identity

$$\nabla_1 u \cdot \vec{\partial}_{12} = (\epsilon + L_0) - (\epsilon + L_2) - \nabla_1 V \cdot \vec{\partial}_{12} , \tag{A3}$$

with $V = w - u$, we obtain after some manipulation,

$$D_{kj} = \tfrac{1}{2} g(\sigma_+)(d_1 + d_2 + d_3) , \tag{A4}$$

$$d_1 = \int d\vec{p}_1\, d\vec{p}_2\, d\vec{b}\, \varphi(1)\varphi(2) |p_{12}| (\underline{z}_k : G_2 \hat{\theta} \underline{z}_j)_{r=l} ,$$

$$d_2 = \sigma \int d\vec{p}_1\, d\vec{p}_2\, d\vec{\Omega}\, \varphi(1)\varphi(2)(\underline{z}_k : [\vec{r} \cdot \vec{\partial}_{12}\, \underline{z}_j])_{r=\sigma} ,$$

$$d_3 = - \int d\vec{p}_1\, d\vec{p}_2 \int_0^l d\vec{r}\, \varphi(1)\varphi(2) \times (\{\underline{s}_j : [\vec{p}_{12} \cdot \nabla_{12} + \nabla_1 V \cdot (\vec{p}_{12} - \vec{\partial}_{12})] \underline{z}_k\} + \underline{z}_k : \hat{R} \underline{s}_j) , \tag{A5}$$

where l is the range of the interaction. To make the connection with Enskog's dense-fluid theory, we ignore both nonlocal effects and the soft part of the potential of mean force whereupon $l = \sigma$ and hard-sphere dynamics prevails. Thus $d_3 = 0$ and the computation of d_1 and d_2 is quite simple. The results are

$$D_{00} = -32\sqrt{\pi}\sigma^2 g(\sigma) ,$$
$$D_{v0} = -D_{v0} = \tfrac{16}{3}\pi\sigma^3 g(\sigma) , \tag{A6}$$
$$D_{vv} = -\tfrac{32}{3}\sqrt{\pi}\sigma^4 g(\sigma) .$$

Substituting these results into (4.22) yields the Enskog formula (4.24).

APPENDIX B

In our previous treatment of self-diffusion we did not account for the coupling between the free-particle streaming and a specific part of the nonlocal interaction. In terms of the analysis we have given here, the quantity $\vec{X}(12)$ is

$$\vec{X}(12) = \sum b_j \vec{x}_j(12) , \tag{B1}$$

with the b_j defined by Eq. (22) of Ref. 4. The equations determining the $\vec{x}_j(12)$ may be generated from (4.15) by making the following replacements

$$\hat{L}\underline{s}_j(12) \to L_2 \vec{x}_j(12) - J_1(2;3)\vec{x}_j(13) ,$$
$$\underline{s}_j(12) \to \vec{x}_j(12) , \tag{B2}$$
$$\underline{z}_j(12) \to \vec{y}_j(1) = \vec{p}_1 S_{3/2}^{(j)}(\tfrac{1}{2}p_1^2) ,$$
$$\hat{Q}\underline{s}_j(12) \to J_2(12;3)\vec{x}_j(13) .$$

The matrix elements Q_{kj} which must be calculated are then given by

$$Q_{kj} = -\rho \int d\vec{p}_1\, d\vec{\xi}_2\, \vec{y}_j(1) \cdot [\nabla_1 u \cdot \vec{\partial}_{12} P_2(12) \vec{x}_j(12)] , \tag{B3}$$

instead of Eq. (24) of Ref. 4. For hard spheres the analogs to (A1) and (A4) are formed by making the replacements (B2). In the event nonlocal effects and the soft part of the potential of mean force are ignored, we may easily compute the Q_{kj}; the result for Q_{00} is

$$Q_{00} = 8\sqrt{\pi}\rho\sigma^2 g(\sigma_+) . \tag{B4}$$

Since, from Eq. (25) of Ref. 4, $D = 3/Q_{00}$, this is again equivalent to Enskog's dense-fluid theory.

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