

Self-Diffusion in Dense Fluids

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The time-dependent solutions to the low-order BBGKY hierarchy are examined for the case of interdiffusion of two mechanically identical isotopes. In order to effect a closure directed at evaluation of the pair-distribution-function perturbations and the self-diffusion constant D , we invoke a dynamical superposition approximation, and a truncated expansion in inverse powers of the initial composition fluctuation wavelength. The potential feasibility of this general approach to calculation of dense-fluid transport properties is illustrated by explicit numerical calculations for the dense fluid of rigid spheres, using in addition a pair-space local equilibrium assumption. Although the resulting pair-distribution-function perturbations seem to be in accord with physical intuition, cumulative errors in the approximation sequence render the self-diffusion coefficients predicted at variance with other calculations. Systematic improvements of the present scheme are outlined.

I. INTRODUCTION

THE recent availability of exact autocorrelation-function expressions for linear transport coefficients¹ has stimulated interest in the general area of irreversible statistical mechanics. Though this constitutes an elegant reformulation of the microscopic basis of hydrodynamic behavior for simple fluids, for example, the evaluation of relevant autocorrelation functions appears generally no less a formidable task than solution of the many-body dynamics from which they arose. Only in the case of dilute gases, to which the soluble two-body problem applies, can complete calculations actually be performed. The autocorrelation results, however, then represent no fundamental advance over the older Hilbert-Enskog approach to solution of the Boltzmann equation.²

In the case of dense fluids (i.e., liquids), one of the earliest attempts to develop a systematic transport theory was Kirkwood's generalization of Brownian-motion theory,³ utilizing kinetic equations of the Fokker-Planck type to describe motion of small sets of particles. Here, and in Rice's more recent modifications,⁴ the intractible many-body dynamics are transferred to a friction constant ζ , whose evaluation then constitutes the major challenge for that approach.

It is not the intent of the present paper to develop a critique of the Kirkwood-Rice scheme. Instead, we offer an exploratory analysis of the reduced Liouville equations (the BBGKY hierarchy) with a view toward providing an alternative and distinct approach

to transport in liquids. We wish to draw attention, therefore, to an independent set of merits and drawbacks.

The following development has largely resulted from a desire to construct a time-dependent analog of the closed and self-consistent Born-Green-Yvon superposition integrodifferential equation for determination of the *equilibrium* pair distribution function,⁵ which is historically important for equilibrium liquid state theory. Thus, we apply a time-dependent generalization of the well-known Kirkwood superposition approximation⁶ to aid in deduction of a closed set of equations. Throughout the analysis it is assumed that the equilibrium distribution functions are available in sufficient accuracy from some suitable independent source.

Having once obtained perturbed singlet and pair distribution functions from a self-consistently closed set of equations the corresponding flows (of matter, momentum, energy, etc.) may then immediately be written down.⁷ Rather than developing the corresponding general linear transport theory involving several simultaneous flows, we have elected to focus attention on just the self-diffusion process in a fluid of spherical structureless molecules. We trust that the corresponding loss of generality is adequately counterbalanced by increased readability. It is our intention to return to the other transport process in due course.

In order to introduce irreversibility in the Kirkwood-Rice scheme after starting with the mechanically reversible Liouville equation, the notion of time smoothing proved useful. We remark in passing here that in the present approach irreversibility is *not* ensured by

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¹ M. S. Green, *J. Chem. Phys.* **20**, 1281 (1952); **22**, 398 (1954); R. Kubo, *J. Phys. Soc. Japan* **12**, 570 (1957); H. Mori, *Phys. Rev.* **112**, 1829 (1958); **115**, 298 (1959).

² S. Chapman and T. G. Cowling, *The Mathematical Theory of Nonuniform Gases* (Cambridge University Press, New York, 1952).

³ J. G. Kirkwood, *J. Chem. Phys.* **14**, 180 (1946).

⁴ S. A. Rice and A. R. Allnatt, *J. Chem. Phys.* **34**, 2144 (1961).

⁵ J. G. Kirkwood, E. K. Maun, and B. J. Alder, *J. Chem. Phys.* **18**, 1040 (1950); J. G. Kirkwood, V. A. Lewinson, and B. J. Alder, *J. Chem. Phys.* **20**, 929 (1952); see also T. L. Hill, *Statistical Mechanics* (McGraw-Hill Book Company, Inc., New York, 1956), Chap. 6.

⁶ J. G. Kirkwood, *J. Chem. Phys.* **3**, 300 (1935).

⁷ We assume here, and in the following, that the particles of the system interact only through pairwise-additive potentials.

passage to the infinite system size limit, coupled with the initial time ensemble dispersion. The kinetic equations thus have both the desired relaxing solutions as well as the "time-reversed" exponentially growing solutions. There is, however, never any problem in identifying the solution corresponding to the initial conditions of experimental interest, and which therefore exhibits the standard hydrodynamical behavior of relaxation to equilibrium.

The modelistic and dynamical basis of our calculation is outlined in the following section. Symmetry arguments are invoked to identify the relevant perturbations to the singlet and pair distribution functions, and dynamical equations are deduced for these perturbations. The general method for effecting closure is then discussed, and Secs. IV and V illustrate the approach by application to the rigid-sphere model for dense fluids.

II. DISTRIBUTION FUNCTION PERTURBATIONS

The dynamical system with which we are concerned consists of $N = 2M$ classical structureless particles interacting in pairs with potential $v(\mathbf{r})$. These particles are divided into M A 's and M B 's which are mechanically identical, but which it is convenient to distinguish as "isotopes." These particles are confined to a rectangular box with volume V , to which periodic boundary conditions apply.

We suppose that a rectangular coordinate system has been aligned parallel to the container sides and that the container length along the x direction is L . Consider the following quantity which measures a sinusoidal A - B composition fluctuation:

$$S(k) = \sum_{j=1}^M [\sin(kx_j) - \sin(kx_{M+j})],$$

$$k = 2n\pi/L, \tag{1}$$

where x_j stands for the x component of position of Particle j , and n is some small integer.⁸ As the N particles move about under thermal motion, $S(k)$ will vary about zero, reflecting instantaneous composition fluctuations in the system.⁹

The regression of a fluctuation in $S(k)$ is exactly the diffusive process in which we are interested. To prepare a system for observation of diffusion, we may either pick from an equilibrium ensemble members for which $S(k)$ exhibits a preassigned value, or alternatively, a weak external potential which adds a term to the Hamiltonian proportional to $S(k)$ may be utilized to produce a new ensemble with time-independent com-

position variation in space. For this latter circumstance, the phase space probability becomes:

$$[Q(\beta, \sigma)]^{-1} \exp(-\beta E - \sigma S), \tag{2}$$

where β has its usual meaning,

$$E = \sum_{j=1}^N \left(\frac{p_j^2}{2m} \right) + \sum_{j < k=1}^N v(r_{jk}),$$

$$Q = \int \cdots \int \exp(-\beta E - \sigma S) d\mathbf{r} d\mathbf{p}, \tag{3}$$

and the external potential energy is $\sigma S/\beta$. We assume that σ is sufficiently small that the resulting composition fluctuation with wavenumber k is proportional to σ . When σ is suddenly reduced to zero (at time $t=0$) the diffusion begins to smooth out the composition variations.

The system's time evolution is represented by the normalized phase-space probability function $f^{(N)}(\mathbf{r}, \mathbf{p}, t)$, which satisfies the Liouville equation ($t > 0$):

$$\frac{\partial f^{(N)}}{\partial t} + \sum_{j=1}^N \left\{ \frac{\mathbf{p}_j}{m} \cdot \nabla_{\mathbf{r}_j} + \mathbf{F}_j \cdot \nabla_{\mathbf{p}_j} \right\} f^{(N)} = 0, \tag{4}$$

where \mathbf{F}_j is the force exerted on Particle j by its neighbors. In the customary fashion, we are concerned with lower order functions $f^{(n)}$ obtained from $f^{(N)}$ by integration over the remaining dynamical variables:

$$f^{(n)}(\mathbf{r}_1 \cdots \mathbf{r}_n, \mathbf{p}_1 \cdots \mathbf{p}_n, t)$$

$$= \int f^{(N)}(\mathbf{r}, \mathbf{p}, t) d\mathbf{r}_{n+1} \cdots d\mathbf{r}_N d\mathbf{p}_{n+1} \cdots d\mathbf{p}_N.$$

In this article, we have occasion to utilize only the leading members ($n=1, 2, 3$) of this hierarchy. The singlet reduced distribution function satisfies a dynamical equation obtained from (4) by integration over positions and momenta of $N-1$ particles:

$$[\partial f^{(1)}(\mathbf{r}_1, \mathbf{p}_1, t) / \partial t] + \mathbf{p}_1 \cdot \nabla_{\mathbf{r}_1} f^{(1)}(\mathbf{r}_1, \mathbf{p}_1, t)$$

$$= \sum_{j=2}^N \int [\nabla_{\mathbf{r}_1} v(r_{1j})] \cdot \nabla_{\mathbf{p}_1} f^{(2)}(\mathbf{r}_1, \mathbf{r}_j, \mathbf{p}_1, \mathbf{p}_j, t) d\mathbf{r}_j d\mathbf{p}_j \tag{6}$$

in which explicit use has been made of the pairwise additivity of the interaction. The analogous pair distribution function equation is similarly found to be:

$$\frac{\partial f^{(2)}(12, t)}{\partial t} + \sum_{j=1}^2 \left\{ \frac{\mathbf{p}_j}{m} \cdot \nabla_{\mathbf{r}_j} - [\nabla_{\mathbf{r}_i} \sum_{\substack{l=1 \\ (l \neq j)}}^2 v(r_{jl})] \cdot \nabla_{\mathbf{p}_i} \right\} f^{(2)}(12, t)$$

$$= \sum_{j=1}^2 \sum_{l=3}^N \int [\nabla_{\mathbf{r}_i} v(r_{il})] \cdot \nabla_{\mathbf{p}_i} f^{(3)}(12l, t) d\mathbf{r}_l d\mathbf{p}_l. \tag{7}$$

The next task is to decide what forms are appropriate for the nonequilibrium perturbations to the $f^{(1)}$ and $f^{(2)}$ functions under the diffusion process. After sufficient time has elapsed that the system has returned

⁸ The convention that all A 's precede B 's in the numbering has been adopted here.

⁹ Note that these fluctuations are not coupled to pressure fluctuations (sound waves) because the A 's and B 's are mechanically the same.

to complete homogeneity ($t \rightarrow \infty$), the distribution functions will have adopted the standard equilibrium forms:

$$f_A^{(1)}(\mathbf{r}, \mathbf{p}, t = \infty) = f_B^{(1)}(\mathbf{r}, \mathbf{p}, t = \infty) = f(p) \\ = \frac{\exp(-\beta p^2/2m)}{V(2\pi mkT)^{\frac{3}{2}}}$$

$$f_{\alpha\beta}^{(2)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{p}_1, \mathbf{p}_2, t = \infty) = f(p_1)f(p_2)g^{(2)}(r_{12}, N/V), \\ \alpha, \beta = A, B. \quad (8)$$

Here, $g^{(2)}$ is the equilibrium pair correlation function (at density N/V) which approaches unity at large r_{12} .¹⁰

If no means were available for distinguishing the isotopes A and B , the outward appearance of the system for *all* times would be that of a system at equilibrium. Thus the perturbed distribution functions for finite t must be subject to the restraints:

$$\frac{1}{2}[f_A^{(1)}(\mathbf{r}, \mathbf{p}, t) + f_B^{(1)}(\mathbf{r}, \mathbf{p}, t)] = f(p), \\ \frac{1}{4} \sum_{\alpha, \beta = A, B} f_{\alpha\beta}^{(2)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{p}_1, \mathbf{p}_2, t) = f(p_1)f(p_2)g^{(2)}(r_{12}, N/V), \quad (9)$$

stating that *total* singlet and pair densities are in equilibrium.

For negative times, while the sinusoidal external field is still on, the equilibrium concentrations of the two species are

$$C_{A,B}(\mathbf{r}, t < 0) = M \int f_{A,B}^{(1)}(\mathbf{r}, \mathbf{p}, t < 0) d\mathbf{p} \\ = (M/V)[1 \mp \sigma \sin(kx)], \quad (10)$$

where the upper sign refers to A , the lower to B . Precisely at $t=0$, the momentum distribution has the Maxwell-Boltzmann form shown in Eq. (8), but as diffusion gets underway perturbations in this distribution develop over a very short period of time (in typical liquids, roughly 10^{-12} sec). Thereafter, local steady states are established, modulated secularly only by the over-all hydrodynamic relaxation.

The wave vector k has been assumed small, so we should expect that subsequent to the quick initial induction period for the distribution-function perturbations to develop, the concentrations should obey the macroscopic differential equation for diffusion, Fick's law:

$$d/dt[C_{A,B}(\mathbf{r}, t)] = D\nabla^2 C_{A,B}(\mathbf{r}, t) \quad (t \gg 0). \quad (11)$$

Integrating, we find for t well past the induction period:

$$C_{A,B}(\mathbf{r}, t) = (M/V) \{1 \mp \sigma \exp[-Dk^2(t-t_0)] \sin(kx)\}; \quad (12)$$

the concentration spatial variation of course decays in time, but maintains its pure sinusoidal form. t_0 is a

¹⁰ For present purposes it is permissible to disregard the deviation of $g^{(2)}(r_{12})$ of order N^{-1} from unity at large r_{12} in our closed system.

time lag characteristic of (and comparable in length to) the rapid momentum-perturbation induction.

The simple separation of spatial and temporal dependence for the initial sinusoidal composition fluctuation is a crucial point, and allows us to simplify the coupled $f^{(1)}$ and $f^{(2)}$ integrodifferential equations. Thus by looking at these equations for the given initial conditions and at times long after the external field has been removed, we can reasonably expect to find but a single hydrodynamic relaxation underway, i.e., all distribution-function perturbations have the same exponentially decaying time dependence. Since it is essential in the following to consider the way in which this single remaining relaxation depends upon wave vector k , it must be recognized that both D and t_0 are possibly k dependent, so that the relevant time dependence involves the factor

$$\exp\{-k^2 D(k)[t-t_0(k)]\}, \quad (13)$$

in which both D and t_0 have expansions in even orders of k :

$$D(k) = D_0 + D_1 k^2 + D_2 k^4 + \dots, \\ t_0(k) = t_{00} + t_{01} k^2 + t_{02} k^4 + \dots. \quad (14)$$

The diffusive flows of course occur only in the x direction and since the system is fluid, the distribution functions must exhibit rotational symmetry about the x axis. Furthermore, the A 's and B 's have been handled from the outset in a manner inducing a reflection symmetry in the plane $x=L/2$. The singlet distribution functions therefore must be invariant to the operation consisting of:

$$(a) \quad x \rightarrow L-x, \\ (b) \quad p_x \rightarrow -p_x, \\ (c) \quad A, B \rightarrow B, A. \quad (15)$$

The singlet functions will exhibit perturbations varying spatially with wave vector k [i.e., as $\sin(kx)$ or $\cos(kx)$], with momentum dependence whose even or odd symmetry is dictated by (15), and all decaying exponentially according to the single secular relaxation time; the most general permissible form therefore is found to be:

$$f_{A,B}^{(1)}(\mathbf{r}, \mathbf{p}, t) = f(p) (1 \mp \sigma \exp\{-k^2 D(k)[t-t_0(k)]\}) \\ \times [\sin(kx)[1 + \sum_{n=1}^{\infty} k^{2n} \chi_n(p_x, p)] \\ + \cos(kx) \sum_{n=1}^{\infty} k^{2n-1} \phi_n(p_x, p)]. \quad (16)$$

The functions χ_n are even and the ϕ_n odd with respect to change in sign of p_x . By formal retention of momentum perturbations of all orders in k , in a manner analogous to the expansions (14), it will in principle be possible to encompass the full wavelength range of

composition fluctuation regression in the long-time limit.

The pair probabilities may be similarly delineated. They are also cylindrically symmetric about the x axis, and must be invariant to:

$$\begin{aligned} (a) \quad & x_1, x_2 \rightarrow L - x_1, L - x_2, \\ (b) \quad & p_{1x}, p_{2x} \rightarrow -p_{1x}, -p_{2x}, \\ (c) \quad & A, B \rightarrow B, A. \end{aligned} \tag{17}$$

Because the pair functions reduce to a product of singlet functions when the two particles are far removed from one another, it is convenient to factor the perturbed singlet functions out of each $f^{(2)}$, which then adopt the standard form¹¹:

$$\begin{aligned} f_{\alpha\beta}^{(2)}(12, t) = & f_{\alpha}^{(1)}(1, t) f_{\beta}^{(1)}(2, t) g^{(2)}(\mathbf{r}_{12}) \\ & \times (1 + \sigma \exp\{-k^2 D(k)[t - t_0(k)]\}) \\ & \times \left\{ \cos\left[\frac{1}{2}k(x_1 + x_2)\right] \sum_{n=1}^{\infty} k^{2n-1} h_{n,\alpha\beta}(\mathbf{r}_{12}, \mathbf{p}_1, \mathbf{p}_2) \right. \\ & \left. + \sin\left[\frac{1}{2}k(x_1 + x_2)\right] \sum_{n=1}^{\infty} k^{2n} l_{n,\alpha\beta}(\mathbf{r}_{12}, \mathbf{p}_1, \mathbf{p}_2) \right\}, \end{aligned} \tag{18}$$

which is entirely analogous to Eq. (16). The perturbation functions $h_{n,\alpha\beta}$ and $l_{n,\alpha\beta}$ possess cylindrical symmetry about the x axis for simultaneous rotation of all three argument vectors. In addition, the second of Restraints (9) requires

$$\begin{aligned} \sum_{\alpha,\beta} h_{n,\alpha\beta}(\mathbf{r}_{12}, \mathbf{p}_1, \mathbf{p}_2) &= 0, \\ \sum_{\alpha,\beta} l_{n,\alpha\beta}(\mathbf{r}_{12}, \mathbf{p}_1, \mathbf{p}_2) &= 0, \end{aligned} \tag{19}$$

for each $n \geq 1$. Each h_n and l_n should vanish rapidly as r_{12} increases.

It proves useful to decompose the pair perturbations into separate components each possessing definite symmetry under simultaneous sign change of x_{12}, p_{1x}, p_{2x} . Reference to standard form (18) shows that Condition (17) permits one to write:

$$\begin{aligned} h_{n,AA} &= \eta_n + \zeta_n + \psi_n, \\ h_{n,AB} &= -\eta_n + \zeta_n - \psi_n, \\ h_{n,BA} &= -\eta_n - \zeta_n + \psi_n, \\ h_{n,BB} &= \eta_n - \zeta_n - \psi_n, \end{aligned} \tag{20}$$

where the $\eta_n(\mathbf{r}_{12}, \mathbf{p}_1, \mathbf{p}_2)$ are symmetric with respect to simultaneous sign change of the three vectors' x components, and the ζ_n and ψ_n are antisymmetric. Analogously, we may write the following representation for the perturbations l_n :

$$\begin{aligned} l_{n,AA} &= \nu_n + \tau_n + \omega_n, \\ l_{n,AB} &= \nu_n - \tau_n - \omega_n, \\ l_{n,BA} &= -\nu_n + \tau_n - \omega_n, \\ l_{n,BB} &= -\nu_n - \tau_n + \omega_n \end{aligned} \tag{21}$$

where now the ν_n and τ_n are even, and the ω_n odd.

We are now in a position to substitute the perturbed distribution functions (16) and (18) into the reduced Liouville equation (6) for $f_A^{(1)}$.¹² Under the integrals containing the pair functions, elementary trigonometric identities may be used to extract $\sin(kx_1)$ or $\cos(kx_1)$ factors, which each nonvanishing term of the left-hand member of the equation already contains. Since these two functions are orthogonal over V , one obtains two independent equations from their coefficients, and in each the common time-dependence factor (13) may be cancelled. The resulting time-independent equation from coefficients of $\sin(kx_1)$ is:

$$\begin{aligned} -k^2 D(k) \left[1 + \sum_{n=1}^{\infty} k^{2n} \chi_n(p_{1x}, p_1) \right] - \frac{k p_{1x}}{m} \sum_{n=1}^{\infty} k^{2n-1} \phi_n(p_{1x}, p_1) \\ = -2M \int d\mathbf{r}_2 d\mathbf{p}_2 f(p_2) g^{(2)}(\mathbf{r}_{12}) [\nabla_{r_1} v(\mathbf{r}_{12})] \left\{ -\sin\left[\frac{1}{2}k(x_2 - x_1)\right] \sum_{n=1}^{\infty} k^{2n-1} \right. \\ \left. \times \left[\nabla_{p_1} \zeta_n(12) - \frac{\beta \mathbf{p}_1}{m} \zeta_n(12) \right] + \cos\left[\frac{1}{2}k(x_2 - x_1)\right] \sum_{n=1}^{\infty} k^{2n} \left[\nabla_{p_1} \nu_n(12) - \frac{\beta \mathbf{p}_1}{m} \nu_n(12) \right] \right\}, \end{aligned} \tag{22}$$

and from the coefficients of $\cos(kx_1)$:

$$\begin{aligned} -k^2 D(k) \sum_{n=1}^{\infty} k^{2n-1} \phi_n(p_{1x}, p_1) + \frac{k p_{1x}}{m} \left[1 + \sum_{n=1}^{\infty} k^{2n} \chi_n(p_{1x}, p_1) \right] = -2M \int d\mathbf{r}_2 d\mathbf{p}_2 f(p_2) g^{(2)}(\mathbf{r}_{12}) [\nabla_{r_1} v(\mathbf{r}_{12})] \\ \cdot \left\{ \cos\left[\frac{1}{2}k(x_2 - x_1)\right] \sum_{n=1}^{\infty} k^{2n-1} \left[\nabla_{p_1} \zeta_n(12) - \frac{\beta \mathbf{p}_1}{m} \zeta_n(12) \right] + \sin\left[\frac{1}{2}k(x_2 - x_1)\right] \sum_{n=1}^{\infty} k^{2n} \left[\nabla_{p_1} \nu_n(12) - \frac{\beta \mathbf{p}_1}{m} \nu_n(12) \right] \right\}. \end{aligned} \tag{23}$$

¹¹ Since σ is regarded as a small parameter, consistent with linearity of the transport process being discussed, the terms of order σ^2 in Eq. (18) are ignored.

¹² The same results would be obtained from the $f_B^{(1)}$ dynamical equation.

Of the entire set of pair perturbations appearing in the representations (20) and (21), only the ζ_n and ν_n remain in these last two equations.

If the remaining trigonometric functions in Eqs. (22) and (23) are expanded, there occurs in these equations, respectively, only even and odd powers of k , and again separate equations result from the individual coefficients. The lowest order in k is the first power, in Eq. (23), and it leads to the following relation:

$$(\dot{p}_{1x}/m) = -2M \int d\mathbf{r}_2 d\mathbf{p}_2 f(\dot{p}_2) g^{(2)}(\mathbf{r}_{12}) [\nabla_{\mathbf{r}_1} v(\mathbf{r}_{12})] \cdot [\nabla_{\mathbf{p}_1} \zeta_1(12) - (\beta \mathbf{p}_1/m) \zeta_1(12)]. \tag{24}$$

The terms of order k^2 in Eq. (22) yield:

$$D_0 + \frac{\dot{p}_{1x}}{m} \phi_1(\dot{p}_{1x}, \dot{p}_1) = -M \int d\mathbf{r}_2 d\mathbf{p}_2 f(\dot{p}_2) g^{(2)}(\mathbf{r}_{12}) [\nabla_{\mathbf{r}_1} v(\mathbf{r}_{12})] \cdot \left\{ (x_2 - x_1) \left[\nabla_{\mathbf{p}_1} \zeta_1(12) - \frac{\beta \mathbf{p}_1}{m} \zeta_1(12) \right] - 2 \left[\nabla_{\mathbf{p}_1} \nu_1(12) - \frac{\beta \mathbf{p}_1}{m} \nu_1(12) \right] \right\}. \tag{25}$$

Finally, we consider the result of the k^3 terms in Eq. (23):

$$-D_0 \phi_1(\dot{p}_{1x}, \dot{p}_1) + \frac{\dot{p}_{1x}}{m} \chi_1(\dot{p}_{1x}, \dot{p}_1) = -M \int d\mathbf{r}_2 d\mathbf{p}_2 f(\dot{p}_2) g^{(2)}(\mathbf{r}_{12}) [\nabla_{\mathbf{r}_1} v(\mathbf{r}_{12})] \cdot \left\{ 2 \left[\nabla_{\mathbf{p}_1} \zeta_2(12) - \frac{\beta \mathbf{p}_1}{m} \zeta_2(12) \right] - \frac{1}{4} (x_2 - x_1)^2 \left[\nabla_{\mathbf{p}_1} \zeta_1(12) - \frac{\beta \mathbf{p}_1}{m} \zeta_1(12) \right] + (x_2 - x_1) \left[\nabla_{\mathbf{p}_1} \nu_1(12) - \frac{\beta \mathbf{p}_1}{m} \nu_1(12) \right] \right\}. \tag{26}$$

These last three equations, giving exact restraints between possible perturbations to the singlet and pair probability functions, are a sufficient set to consider for present purposes out of the infinite set implied by Eqs. (22) and (23).

In order to develop the necessary equations for determination of the pair perturbation functions appearing in the three restraint Eqs. (24)–(26), we must examine the dynamical Eq. (7) for the pair probabilities. In doing so of course one requires some knowledge of the $f^{(3)}$'s. In analogy with Eq. (18) for the pair probabilities, one may write:

$$f_{\alpha\beta\gamma}^{(3)}(123, t) = f_{\alpha}^{(1)}(1, t) f_{\beta}^{(1)}(2, t) f_{\gamma}^{(1)}(3, t) g^{(3)}(123) \times (1 + \sigma \exp\{-k^2 D(k)[t - t_0(k)]\}) \{ (12) + (13) + (23) + \cos[\frac{1}{3}k(x_1 + x_2 + x_3)] \sum_{n=1}^{\infty} k^{2n-1} h_{n,\alpha\beta\gamma}^{(3)}(123) + \sin[\frac{1}{3}k(x_1 + x_2 + x_3)] \sum_{n=1}^{\infty} k^{2n} l_{n,\alpha\beta}^{(3)} \gamma(123) \}, \tag{27}$$

thereby defining specifically triplet perturbation $h_{n,\alpha\beta}^{(3)}$ and $l_{n,\alpha\beta}^{(3)}$. $g^{(3)}(123)$ is the equilibrium triplet correlation function at density N/V . For compactness we have let (ij) stand for the h_n and l_n sums shown explicitly in Eq. (18), and so the specific triplet perturbations $h_n^{(3)}$ and $l_n^{(3)}$ should vanish unless all three particles are close. Although we do not do so, it would be possible to display representations of these triplet perturbations similar to, but more complicated than, the previous pair perturbation Eqs. (20) and (21), in terms of cylindrically symmetric functions of specific reflection parity.

III. CLOSURE-PRODUCING APPROXIMATIONS

It is the primary objective of this paper to calculate the macroscopic self-diffusion constant D_0 , and because this quantity occurs in at least two of the restraint conditions (24)–(26), these latter are accorded a central role in our approach. It then becomes necessary to evaluate the low-order ζ and ν pair perturbations, equations for which may be obtained by substitution of forms (18) and (27) for $f^{(2)}$ and $f^{(3)}$ into Eq. (7). It is obvious, however, that the resulting appearance of unknown triplet perturbations limits usefulness. Therefore we make a “dynamical superposition approximation,” equivalent to neglect of these triplet perturbations,

$$h_{n,\alpha\beta\gamma}^{(3)}(123) \cong 0, \tag{28}$$

$$l_{n,\alpha\beta\gamma}^{(3)}(123) \cong 0.$$

For the time being, we carry along the exact equilibrium triplet correlation function $g^{(3)}$.¹³

The irrelevant pair perturbations ($\eta_n, \psi_n, \tau_n, \omega_n$) may be eliminated by adding together the $f_{AA}^{(2)}(12, t)$ and $f_{AB}^{(2)}(12, t)$ dynamical equations. Substantially the same operations may then be followed that led to Restraint Conditions (24)–(26). We do not reproduce tedious details except to remark that the equilibrium Born–Green–Yvon integrodifferential equation,

$$\nabla_{\mathbf{r}_1} w(\mathbf{r}_{12}) = \nabla_{\mathbf{r}_1} v(\mathbf{r}_{12}) + (N/V) \int [\nabla_{\mathbf{r}_1} v(\mathbf{r}_{13})] [g^{(3)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3)/g^{(2)}(\mathbf{r}_{12})] d\mathbf{r}_3, \tag{29}$$

$$w(\mathbf{r}_{12}) = -\beta^{-1} \ln g^{(2)}(\mathbf{r}_{12}),$$

¹³ Several recent studies have begun to reveal the nature of deviations of this function from the standard Kirkwood superposition product of $g^{(2)}$'s. See, for example: E. Helfand and F. H. Stillinger, Jr., *J. Chem. Phys.* **37**, 2646 (1962); B. J. Alder, *Phys. Rev. Letters* **12**, 317 (1964).

may be utilized to effect intermediate reductions. The equation deduced from the coefficients of terms proportional to the first power of the wave vector k is:

$$\begin{aligned} & \frac{\mathbf{p}_1}{m} \cdot \nabla_{r_1} \zeta_1(12) + \frac{\mathbf{p}_2}{m} \cdot \nabla_{r_2} \zeta_1(12) + \nabla_{r_1} w(r_{12}) \cdot [\nabla_{p_1} \phi_1(1) - \nabla_{p_1} \zeta_1(12) + \nabla_{p_2} \zeta_1(12)] \\ & = 2M \int d\mathbf{r}_3 d\mathbf{p}_3 f(p_3) \left\{ \left[\frac{g^{(3)}(123)}{g^{(2)}(12)} - g^{(2)}(13) \right] \nabla_{r_1} v(r_{13}) \cdot \left[\nabla_{p_1} \zeta_1(13) - \frac{\beta \mathbf{p}_1}{m} \zeta_1(13) \right] - \frac{g^{(3)}(123)}{g^{(2)}(12)} \nabla_{r_2} v(r_{23}) \cdot \frac{\beta \mathbf{p}_2}{m} \zeta_1(13) \right\}. \end{aligned} \quad (30)$$

From the coefficients of k^2 it likewise follows that:

$$\begin{aligned} & -\frac{p_{1x} + p_{2x}}{2m} \zeta_1(12) + \frac{\mathbf{p}_1}{m} \cdot \nabla_{r_1} \nu_1(12) + \frac{\mathbf{p}_2}{m} \cdot \nabla_{r_2} \nu_1(12) + \nabla_{r_1} w(r_{12}) \cdot \nabla_{p_1} \chi_1(1) \\ & \quad + \frac{x_2 - x_1}{2} \nabla_{r_1} w(r_{12}) \cdot \nabla_{p_1} \phi_1(1) - \nabla_{r_1} w(r_{12}) \cdot \nabla_{p_1} \nu_1(12) - \nabla_{r_2} w(r_{12}) \cdot \nabla_{p_2} \nu_1(12) \\ & \quad = 2M \int d\mathbf{r}_3 d\mathbf{p}_3 f(p_3) \left(\frac{g^{(3)}(123)}{g^{(2)}(12)} \nabla_{r_2} v(r_{23}) \cdot \left(-\frac{\beta \mathbf{p}_2}{m} \right) \left[\frac{x_2 - x_3}{2} \zeta_1(13) + \nu_1(13) \right] \right. \\ & \quad \left. + \left[\frac{g^{(3)}(123)}{g^{(2)}(12)} - g^{(2)}(13) \right] \nabla_{r_1} v(r_{13}) \cdot \left\{ \frac{x_2 - x_3}{2} \left[\nabla_{p_1} \zeta_1(13) - \frac{\beta \mathbf{p}_1}{m} \zeta_1(13) \right] + \nabla_{p_1} \nu_1(13) - \frac{\beta \mathbf{p}_1}{m} \nu_1(13) \right\} \right). \end{aligned} \quad (31)$$

Finally, the third pair perturbation equation with which we deal is obtained from coefficients of k^3 :

$$\begin{aligned} & -D_0 \zeta_1(12) + \frac{\mathbf{p}_1}{m} \cdot \nabla_{r_1} \zeta_2(12) + \frac{\mathbf{p}_2}{m} \cdot \nabla_{r_2} \zeta_2(12) + \frac{p_{1x} + p_{2x}}{2m} \nu_1(12) - \nabla_{r_1} w(r_{12}) \\ & \quad \cdot \left\{ -\nabla_{p_1} [\phi_2(1) - \frac{1}{2} x_{12} \chi_1(1) - \frac{1}{8} x_{12}^2 \phi_1(1)] + \nabla_{p_1} \zeta_2(12) \right\} - \nabla_{r_2} w(r_{12}) \cdot \nabla_{p_2} \zeta_2(12) \\ & \quad = 2M \int d\mathbf{r}_3 d\mathbf{p}_3 f(p_3) \left\{ \frac{g^{(3)}(123)}{g^{(2)}(12)} \nabla_{r_2} v(r_{23}) \cdot \left(-\frac{\beta \mathbf{p}_2}{m} \right) + \left[\frac{g^{(3)}(123)}{g^{(2)}(12)} - g^{(2)}(13) \right] \right. \\ & \quad \left. \times \nabla_{r_1} v(r_{13}) \cdot \left(\nabla_{p_1} - \frac{\beta \mathbf{p}_1}{m} \right) \right\} \left[\zeta_2(13) - \frac{1}{8} x_{23}^2 \zeta_1(13) + \frac{1}{2} x_{23} \nu_1(13) \right]. \end{aligned} \quad (32)$$

Unlike the situation regarding equilibrium distribution functions which may be indexed by the number of particles to which they refer, the perturbation functions must be indexed both by particle number and their order in wave vector k . The restraints and dynamical equations couple the functions in this two-dimensionally infinite array of functions. To close the set of functional equations at a manageable level of complication in equilibrium requires only terminating a one-dimensional sequence (as accomplished by the Kirkwood superposition approximation). Roughly speaking we now require a truncation scheme equivalent to retention only of one corner of the square function array, namely the corner with both indices small.

The simplest recipe which one might at first sight be tempted to try would be simultaneous use of Eqs. (24), (25), and (30), in which ν_1 is disregarded, so the unknowns are ζ_1 , ϕ_1 , and D_0 . The last of these then would be evaluated by setting $p_{1x} = 0$ in (25). We remark, however, that $\zeta_1(12)$ may be separated into two parts, respectively, even and odd under $x_{12} \rightarrow -x_{12}$

(momenta unchanged); only the latter is constrained by (24), whereas it is the former which determines D_0 and ϕ_1 in (25). Thus D_0 , ϕ_1 , and the spatially odd part of ζ_1 are undetermined to the extent of a common numerical factor, since their equations are linear and homogeneous.¹⁴

Consequently a somewhat more elaborate approach is warranted. Notice that Restraint (26) contains the product of D_0 and ϕ_1 , as well as ζ_1 linearly, so its use would serve to avoid the homogeneity difficulty. We propose therefore to work with Restraints (24) and (26) and the three pair perturbation equations (30), (31), and (32).

The pair perturbations retained, ζ_1 , ν_1 , and ζ_2 , are difficult to handle computationally, since they depend on three vector variables each. Although it is not absolutely mandatory in the face of the approximations already made, it is nevertheless very convenient to introduce yet another class of simplifications, which

¹⁴ This difficulty in working just in lowest order in wave vector k has been noticed before: G. Klein and I. Prigogine, *Physica* **19**, 89 (1953); R. E. Nettleton, *J. Chem. Phys.* **23**, 1560 (1955).

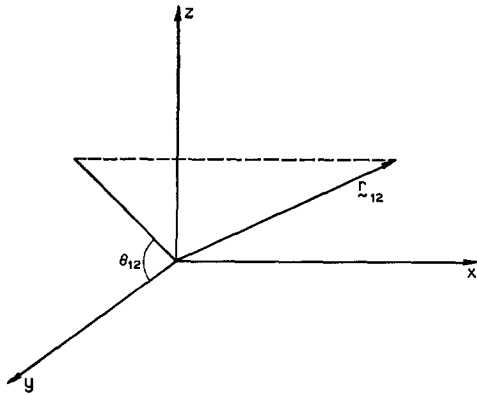


FIG. 1. Cartesian coordinate system and polar angle used in "local equilibrium" form of the pair perturbations, Eqs. (33)–(35).

should apply well to the case of interest, namely, dense fluids. In view of the high density and resulting high collision rate, it seems appropriate to suppose that the perturbed pair distribution functions exhibit Maxwellian momentum distributions about some locally shifted value of mean momentum. Since we are only interested in the linear region of the transport phenomenon, this is equivalent to the assumption that ζ_1 , ν_1 , and ζ_2 may be written as linear functions of momentum components. Since ζ_1 is odd under simultaneous sign change of its three argument x components, the appropriate linear form is:

$$\begin{aligned} \zeta_1(12) \cong & z^{(0)}(\mathbf{r}_{12}) + p_{1x} z_1^{(e)}(\mathbf{r}_{12}) + p_{2z} z_2^{(e)}(\mathbf{r}_{12}) \\ & + (p_{1y} \cos\theta_{12} + p_{1z} \sin\theta_{12}) z_1^{(0)}(\mathbf{r}_{12}) \\ & + (p_{2y} \cos\theta_{12} + p_{2z} \sin\theta_{12}) z_2^{(0)}(\mathbf{r}_{12}); \quad (33) \end{aligned}$$

θ_{12} is the angle¹⁵ of projection of \mathbf{r}_{12} into the y - z plane as shown in Fig. 1, so that ζ_1 is invariant to simultaneous rotation about the x axis of \mathbf{r}_{12} , \mathbf{p}_1 , \mathbf{p}_2 . Each z function is cylindrically symmetric about the x axis also, and has x_{12} parity, even or odd, denoted respectively by Superscript (e) or (0). Equation (33) may be thought of as the leading set of terms in a complete multiple power series expansion of ζ_1 in the six momentum components, and the terms quadratic or higher order in these variables should gain in relative importance as density decreases. The linear expression for ν_1 corresponding to (33) is:

$$\begin{aligned} \nu_1(12) \cong & n^{(e)}(\mathbf{r}_{12}) + p_{1x} n_1^{(0)}(\mathbf{r}_{12}) + p_{2z} n_2^{(0)}(\mathbf{r}_{12}) \\ & + (p_{1y} \cos\theta_{12} + p_{1z} \sin\theta_{12}) n_1^{(e)}(\mathbf{r}_{12}) \\ & + (p_{2y} \cos\theta_{12} + p_{2z} \sin\theta_{12}) n_2^{(e)}(\mathbf{r}_{12}), \quad (34) \end{aligned}$$

in which the same cylindrical symmetries and superscript conventions apply. Finally, the ζ_2 "local equilibrium" expression is:

$$\begin{aligned} \zeta_2(12) \cong & \tilde{z}^{(0)}(\mathbf{r}_{12}) + p_{1x} \tilde{z}_1^{(e)}(\mathbf{r}_{12}) + p_{2z} \tilde{z}_2^{(e)}(\mathbf{r}_{12}) \\ & + (p_{1y} \cos\theta_{12} + p_{1z} \sin\theta_{12}) \tilde{z}_1^{(0)}(\mathbf{r}_{12}) \\ & + (p_{2y} \cos\theta_{12} + p_{2z} \sin\theta_{12}) \tilde{z}_2^{(0)}(\mathbf{r}_{12}). \quad (35) \end{aligned}$$

When (33) is substituted into the first restraint condition (24), one finds:

$$1 = (2M\beta/V) \int d\mathbf{r}_{2g}^{(2)}(\mathbf{r}_{12}) [\partial v(\mathbf{r}_{12}) / \partial x_1] z^{(0)}(\mathbf{r}_{12}), \quad (36)$$

so that only the leading term in the ζ_1 "local equilibrium" expression remains. Inserting both (33) and (34) in the second restraint (25),

$$\begin{aligned} D_0 + \frac{p_{1x}}{m} \phi_1(p_{1x}, p_1) = & -\frac{M}{V} \int d\mathbf{r}_{2g}^{(2)}(\mathbf{r}_{12}) \frac{\partial v(\mathbf{r}_{12})}{\partial x_1} \\ & \cdot [(x_2 - x_1) z_1^{(e)}(\mathbf{r}_{12}) - 2n_1^{(0)}(\mathbf{r}_{12})] \left(1 - \frac{\beta p_{1x}^2}{m}\right). \quad (37) \end{aligned}$$

Set $p_{1x}=0$ in this last expression to obtain a formal relation for D_0 :

$$\begin{aligned} D_0 = & -(M/V) \int d\mathbf{r}_{2g}^{(2)}(\mathbf{r}_{12}) [\partial v(\mathbf{r}_{12}) / \partial x_1] \\ & \times [(x_2 - x_1) z_1^{(e)}(\mathbf{r}_{12}) - 2n_1^{(0)}(\mathbf{r}_{12})]. \quad (38) \end{aligned}$$

This result has no present computational interest, since we do not evaluate $z_1^{(e)}$ or $n_1^{(0)}$, however, it does show that Eq. (37) implies

$$\phi_1(p_{1x}, p_1) = -\beta D_0 p_{1x}, \quad (39)$$

which is fully consistent with our local equilibrium assumption.¹⁵

Finally, the third restraint (26), upon use of (39), leads to:

$$\begin{aligned} D_0^2 + \frac{1}{m\beta} \chi_1(p_{1x}, p_1) = & -\frac{M}{mV} \int d\mathbf{r}_{2g}^{(2)}(\mathbf{r}_{12}) \frac{\partial v(\mathbf{r}_{12})}{\partial x_1} \\ & \times \left[\frac{(x_2 - x_1)^2}{4} z^{(0)}(\mathbf{r}_{12}) - (x_2 - x_1) n^{(e)}(\mathbf{r}_{12}) - 2\tilde{z}^{(0)}(\mathbf{r}_{12}) \right]. \quad (40) \end{aligned}$$

Obviously χ_1 must be momentum independent in the present approximation. Going back to Eq. (16) for the appropriate form of $f^{(1)}$ time dependence, one sees that a constant χ_1 modifies the amplitude of the sinusoidal concentration variation for a given diffusive current (i.e., ϕ_1). This must therefore reflect wavelength dependence of $D(k)$, and in order that Eq. (16) for $f^{(1)}$ be consistent with Fick's law (11), we must have:

$$\chi_1 = -D_1/D_0, \quad (41)$$

¹⁵ Since the direction of diffusive flow in our isotropic system relative to the Cartesian coordinate system could initially have been arbitrary, ϕ_1 generally must have the form of a product of a scalar function of p_1 , times the only available vector, \mathbf{p}_1 itself. With our initial conditions therefore, the exact form of ϕ_1 must be $\phi(p_1) p_{1x}$, of which (39) represents the first term in a multiple momentum component series expansion.

upon neglect of ϕ_3 . In the Appendix the last ratio is estimated to be $m\beta D_0^2$, and accordingly Eq. (40) becomes:

$$D_0^2 = -\frac{M}{2mV} \int d\mathbf{r}_2 g^{(2)}(\mathbf{r}_{12}) \frac{\partial v(\mathbf{r}_{12})}{\partial x_1} \left[\frac{(x_2 - x_1)^2}{4} z^{(0)}(\mathbf{r}_{12}) - (x_2 - x_1) n^{(e)}(\mathbf{r}_{12}) - 2\bar{z}^{(0)}(\mathbf{r}_{12}) \right]. \quad (42)$$

Equations (36) and (42) are two of our working relations, and so clearly we need to determine $z^{(0)}$, $n^{(e)}$ and $\bar{z}^{(0)}$. The requisite formulas may be obtained by inserting local equilibrium approximations (33), (34), and (35) into the pair perturbation Eqs. (30), (31), and (32). The resulting expressions contain terms through quadratic order in momentum components. If we examine separately the coefficients of p_{1x} and p_{2x} in Eq. (30), we obtain, respectively, the following homogeneous integrodifferential equations for $z^{(0)}(\mathbf{r}_{12})$:

$$\frac{\partial z^{(0)}(\mathbf{r}_{12})}{\partial x_1} = -\frac{2\beta M}{V} \int d\mathbf{r}_3 \left[\frac{g^{(3)}(123)}{g^{(2)}(\mathbf{r}_{12})} - g^{(2)}(\mathbf{r}_{13}) \right] \frac{\partial v(\mathbf{r}_{13})}{\partial x_1} z^{(0)}(\mathbf{r}_{13}); \quad (43)$$

$$\frac{\partial z^{(0)}(\mathbf{r}_{12})}{\partial x_2} = -\frac{2\beta M}{V} \int d\mathbf{r}_3 \frac{g^{(3)}(123)}{g^{(2)}(\mathbf{r}_{12})} \frac{\partial v(\mathbf{r}_{23})}{\partial x_2} z^{(0)}(\mathbf{r}_{13}). \quad (44)$$

In a similar manner two equations may also, respectively, be obtained from p_{1x} and p_{2x} coefficients in Eq. (31),

$$\frac{\partial n^{(e)}(\mathbf{r}_{12})}{\partial x_1} - \frac{1}{2} z^{(0)}(\mathbf{r}_{12}) = -\frac{2\beta M}{V} \int d\mathbf{r}_3 \left[\frac{g^{(3)}(123)}{g^{(2)}(\mathbf{r}_{12})} - g^{(2)}(\mathbf{r}_{13}) \right] \frac{\partial v(\mathbf{r}_{13})}{\partial x_1} \left[\frac{(x_2 - x_3)}{2} z^{(0)}(\mathbf{r}_{13}) + n^{(e)}(\mathbf{r}_{13}) \right]; \quad (45)$$

$$\frac{\partial n^{(e)}(\mathbf{r}_{12})}{\partial x_2} - \frac{1}{2} z^{(0)}(\mathbf{r}_{12}) = -\frac{2\beta M}{V} \int d\mathbf{r}_3 \frac{g^{(3)}(123)}{g^{(2)}(\mathbf{r}_{12})} \frac{\partial v(\mathbf{r}_{23})}{\partial x_2} \left[\frac{(x_2 - x_3)}{2} z^{(0)}(\mathbf{r}_{13}) + n^{(e)}(\mathbf{r}_{13}) \right]. \quad (46)$$

The analogous equations containing ζ_2 , which follow by the same procedure from Eq. (32) are:

$$\frac{\partial \bar{z}^{(0)}(\mathbf{r}_{12})}{\partial x_1} + \frac{1}{2} n^{(e)}(\mathbf{r}_{12}) - D_0 \bar{z}_1^{(e)}(\mathbf{r}_{12}) = -\frac{2M\beta}{V} \int d\mathbf{r}_3 \left[\frac{g^{(3)}(123)}{g^{(2)}(12)} - g^{(2)}(13) \right] \frac{\partial v(\mathbf{r}_{13})}{\partial x_1} \left[\bar{z}^{(0)}(\mathbf{r}_{13}) - \frac{x_{23}^2}{8} z^{(0)}(\mathbf{r}_{13}) + \frac{x_{23}}{2} n^{(e)}(\mathbf{r}_{13}) \right] \quad (47)$$

$$\frac{\partial \bar{z}^{(0)}(\mathbf{r}_{12})}{\partial x_2} + \frac{1}{2} n^{(e)}(\mathbf{r}_{12}) - D_0 \bar{z}_2^{(e)}(\mathbf{r}_{12}) = -\frac{2M\beta}{V} \int d\mathbf{r}_3 \frac{g^{(3)}(123)}{g^{(2)}(12)} \frac{\partial v(\mathbf{r}_{23})}{\partial x_2} \left[\bar{z}^{(0)}(\mathbf{r}_{13}) - \frac{x_{23}^2}{8} z^{(0)}(\mathbf{r}_{13}) + \frac{x_{23}}{2} n^{(e)}(\mathbf{r}_{13}) \right]. \quad (48)$$

Solution of these pair perturbation equations is to be carried out subject to the vanishing at large r_{12} of each perturbation function.

In view of the appearance in Eqs. (47) and (48), respectively, of $\bar{z}_1^{(e)}$ and $\bar{z}_2^{(e)}$, the announced scheme of working just with the perturbations $z^{(0)}$, $n^{(e)}$, and $\bar{z}^{(0)}$ appears to be violated. However, our approximations thus far have been designed to describe dense fluids, for which D_0 is very small by comparison with its dilute gas values. It therefore seems appropriate and consistent to regard the third terms in the left members of each of Eqs. (47) and (48), since they contain the factor D_0 , as being negligible. Henceforth we drop these terms.

The six equations, (43)–(48), for calculation of just the three desired perturbations $z^{(0)}$, $n^{(e)}$, and $\bar{z}^{(0)}$ of course amount to an overdetermination. If each of the separate approximations used so far were in fact exact, (43) and (44) would necessarily possess a common solution, and the same would apply in turn to (45)–(46)

and (47)–(48). For the purpose of performing the exploratory hard-sphere calculation in the next section, attention is confined just to the three equations (43), (45), and (47). Equation (36) fixes the normalization of $z^{(0)}$, which then provides an inhomogeneous term in $n^{(e)}$ Eq. (45); these two functions in turn do the same for $\bar{z}^{(0)}$ Eq. (47). The three perturbation functions so determined may then be substituted into Eq. (42) to find the dense fluid self-diffusion constant D_0 .

IV. RIGID SPHERES

The rigid-sphere model is a convenient testing ground for the method so far outlined for several reasons. First, only a single variable thermodynamic parameter, the reduced density, affects the transport process in a nontrivial fashion. Secondly, the singular character of the interaction reduces the dimensionality of quadratures that are required in the theory. Also, the equilibrium pair distribution functions are relatively well

known. Finally, calculated D_0 values may be compared with estimates based on electronically computed molecular dynamics for this interaction.¹⁶

Since deviation of the equilibrium triplet correlation function $g^{(3)}$ from the superposition product of $g^{(2)}$'s should not be very severe,¹⁷ we introduce this simplification into Eqs. (43), (45), and (47) to obtain:

$$\frac{\partial z^{(0)}(\mathbf{r}_{12})}{\partial x_{12}} = -\frac{2\beta M}{V} \int d\mathbf{r}_3 [g^{(2)}(r_{23}) - 1] g^{(2)}(r_{13}) \frac{\partial v(r_{13})}{\partial x_{13}} z^{(0)}(\mathbf{r}_{13}), \tag{49}$$

$$\begin{aligned} \frac{1}{2} z^{(0)}(\mathbf{r}_{12}) + \frac{\partial n^{(e)}(\mathbf{r}_{12})}{\partial x_{12}} &= -\frac{2\beta M}{V} \int d\mathbf{r}_3 [g^{(2)}(r_{23}) - 1] g^{(2)}(r_{13}) \frac{\partial v(r_{13})}{\partial x_{13}} \\ &\quad \times \left[-\frac{x_{23}}{2} z^{(0)}(\mathbf{r}_{13}) + n^{(e)}(\mathbf{r}_{13}) \right]; \end{aligned} \tag{50}$$

$$\begin{aligned} \frac{\partial \bar{z}^{(0)}(\mathbf{r}_{12})}{\partial x_{12}} - \frac{1}{2} n^{(e)}(\mathbf{r}_{12}) &= -\frac{2M\beta}{V} \int d\mathbf{r}_3 [g^{(2)}(r_{23}) - 1] g^{(2)}(r_{13}) \frac{\partial v(r_{13})}{\partial x_{13}} \\ &\quad \times \left[z^{(0)}(\mathbf{r}_{13}) - \frac{x_{23}^2}{8} z^{(0)}(\mathbf{r}_{13}) + \frac{x_{23}}{2} n^{(e)}(\mathbf{r}_{13}) \right]. \end{aligned} \tag{51}$$

Unit lengths are selected equal to the collision diameter of the spheres. The hard-sphere interaction converts the space integrals in the last three equations to integrals over the surface $r_{13}=1$, due to the formal identity for hard spheres

$$g^{(2)}(r) [dv(r)/dr] = -(1/\beta) \delta(r-1) g^{(2)}(1+). \tag{52}$$

The homogeneous equation (49) may then be integrated with respect to x_{12} between some arbitrary lower limit (but outside of contact) and infinity to give, after some manipulation,

$$-z^{(0)}(r, u) = \int_{-1}^{+1} dv k(r, u, v) z^{(0)}(1, v), \tag{53}$$

where $z^{(0)}$ is reckoned to be a function of radial distance r , and u the cosine of the angle relative to the

x axis ($u=x/r$). The kernel in (48) is:

$$\begin{aligned} k(r, u, v) &= \frac{2M}{V} g^{(2)}(1) v \int_u^\infty dx' \int_0^{2\pi} d\phi \{g^{(2)}[r_{23}(u, v, x', \phi)] - 1\}, \\ r_{23}(u, v, x', \phi) &= [(x')^2 - u^2 + 2 - 2x'v - 2(1-u^2)(1-v^2) \cos\phi]^{\frac{1}{2}}. \end{aligned} \tag{54}$$

Setting $r=1$ in Eq. (48), we obtain an homogeneous integral equation over a finite interval, which is relatively easy to handle numerically. The odd (in u) function $z^{(0)}(1, u)$ therefore is presumably an eigenfunction corresponding to eigenvalue -1 . In view of the set of approximations we have been forced to make, though, it is by no means assured that kernel $k(1, u, v)$ possess either rigorously odd eigenfunctions or precisely -1 as an eigenvalue. We recognize, however, that it would have been possible at an earlier state in its derivation to have antisymmetrized the pair perturbation functional equation (before introducing any approximations), so that *after* use of approximations, Eq. (53) would instead have contain the antisymmetrized kernel:

$$k^{(0)}(r, u, v) = \frac{1}{2} [k(r, u, v) - k(r, -u, v)]. \tag{55}$$

For the purposes of numerical analysis, therefore, we examine the modified homogeneous integral equation,

$$-\lambda z^{(0)}(1, u) = \int_{-1}^{+1} dv k^{(0)}(1, u, v) z^{(0)}(1, v), \tag{56}$$

whose solutions are necessarily and rigorously odd. The deviation of λ from $+1$ for the physically acceptable eigenfunction $z^{(0)}(1, u)$ constitute a measure of the error in our approximations.

The hard-sphere version of the restraint (36), by which the eigenfunction must be normalized, is:

$$1 = \frac{4\pi M}{V} g^{(2)}(1) \int_{-1}^{+1} du u z^{(0)}(1, u). \tag{57}$$

Integration of Eq. (50) with respect to x_{12} , supplemented by a partial integration, yields:

$$\begin{aligned} -n^{(e)}(1, u) &= (u/2) z^{(0)}(1, u) \\ &\quad + \int_{-1}^{+1} dv [K(1, u, v) z^{(0)}(1, v) + k(1, u, v) n^{(e)}(1, v)], \end{aligned} \tag{58}$$

where

$$\begin{aligned} K(1, u, v) &= \frac{2M}{V} g^{(2)}(1) v \int_u^\infty dx' \int_0^{2\pi} d\phi (x' - \frac{1}{2}v) \\ &\quad \times \{g^{(2)}[r_{23}(u, v, x, \phi)] - 1\}. \end{aligned} \tag{59}$$

Since (58) is an inhomogeneous equation, it is not subject to the eigenvalue shift difficulty, but it is still

¹⁶ B. J. Alder and T. Wainwright, "Molecular Dynamics by Electronic Computers," in *Transport Processes in Statistical Mechanics*, edited by I. Prigogine (Interscience Publishers, Inc., New York, 1958), p. 97.

¹⁷ B. J. Alder, Ref. 13.

possible that the even parity of $n^{(e)}(1, u)$ with respect to u might have been destroyed by the approximations. Therefore we again modify the correct behavior; in (58) K and k are to be replaced by

$$K^{(e)}(1, u, v) = \frac{1}{2}[K(1, u, v) + K(1, -u, v)],$$

$$k^{(e)}(1, u, v) = \frac{1}{2}[k(1, u, v) + k(1, -u, v)]. \quad (60)$$

Henceforth, then, we consider

$$-n^{(e)}(1, u) = (u/2)z^{(0)}(1, u)$$

$$+ \int_{-1}^{+1} dv [K^{(e)}(1, u, v)z^{(0)}(1, v) + k^{(e)}(1, u, v)n^{(e)}(1, v)] \quad (61)$$

in place of Eq. (58).

The third integral equation required in the subsequent hard-sphere numerical calculation is obtained from Eq. (51) in an exactly similar way. The antisymmetrization and partial integration operations finally lead to:

$$-\tilde{z}^{(0)}(1, u) + \frac{1}{2}un^{(e)}(1, u) + \frac{1}{3}u^2z^{(0)}(1, u)$$

$$= \int_{-1}^{+1} dv [k^{(0)}(1, u, v)\tilde{z}^{(0)}(1, v) - K^{(0)}(1, u, v)n^{(e)}(1, v)$$

$$+ \mathfrak{K}^{(0)}(1, u, v)z^{(0)}(1, v)]. \quad (62)$$

The kernel $k^{(0)}$ has already been defined in Eq. (55) and:

$$K^{(0)}(1, u, v) = \frac{1}{2}[K(1, u, v) - K(1, -u, v)],$$

$$\mathfrak{K}^{(0)}(1, u, v) = \frac{1}{2}[\mathfrak{K}(1, u, v) - \mathfrak{K}(1, -u, v)]; \quad (63)$$

$$\mathfrak{K}(1, u, v) = \frac{2M}{V}g^{(2)}(1)v \int_u^\infty dx' \int_0^{2\pi} d\phi \left(-\frac{v^2}{8} + \frac{vx'}{2} - \frac{x'^2}{2} \right)$$

$$\times \{g^{(2)}[r_{23}(u, v, x', \phi)] - 1\}. \quad (64)$$

After having solved integral equations (56), (61), and (64) in sequence, the self-diffusion constant may be obtained from the hard-sphere version of Eq. (42):

$$D_0^2 = \frac{2\pi M g^{(2)}(1)}{V\beta m} \int_0^1 du \left[-\frac{u^3}{4}z^{(0)}(1, u) + u^2n^{(e)}(1, u) \right. \\ \left. + 2u\tilde{z}^{(0)}(1, u) \right]. \quad (65)$$

V. NUMERICAL ANALYSIS

The basic input, required by the scheme outlined in the last section for calculation of rigid-sphere pair perturbations and self-diffusion coefficients, is the equilibrium rigid-sphere pair correlation function $g^{(2)}$. On the basis of its performance in yielding reliable fluid-phase thermodynamic functions, and of its analytic tractability, we elected to employ the solution to the

approximate Percus-Yevick¹⁸ integral equation for $g^{(2)}$. The required values for this function (at steps of 0.01 in reduced distance up to 6.00) were easily obtained from Wertheim's¹⁹ explicit algebraic expressions for the Laplace transform of $g^{(2)}$, at each of six densities employed.

Next, the kernels k, K, \mathfrak{K} were computed from the $g^{(2)}$ results. In doing so, it proved possible to disregard the fluctuations of $g^{(2)}$ about one for distances greater than 6.00. Weddle's seven-point formula was used for the x' integration with a step length of 0.01 for $x' < 2$ and 0.05 for $x' > 2$; the 20-point Gaussian quadrature formula was used for the variable ϕ .²⁰ The values of $g^{(2)}$ required were obtained from interpolation into the relevant table of $g^{(2)}$ values by means of Newton's interpolation formula through third differences.²⁰ In anticipation of further use of the 20-point Gauss formula in the integral equations themselves, as well as in the $z^{(0)}$ normalization and D_0^2 integrals, the kernel variables $-1 < v < 1$ were given successively the values dictated by this quadrature formula.

The $z^{(0)}$ eigenvalue equation consequently was handled as a nominally 20x20 matrix eigenvalue problem. Kernel symmetry, however, reduced this (as was the case for the other two perturbation integral equations) to a 10x10 matrix problem. The $z^{(0)}$ eigenfunction of interest corresponds to the maximum eigenvalue; these were obtained through use of the relevant SHARE programs on the Murray Hill IBM 7094 computer. After having normalized $z^{(0)}$ according to Eq. (57), the functions $n^{(e)}$ and $\tilde{z}^{(0)}$ were computed in turn from the associated 10x10 linear arrays.

Six densities were considered. They corresponded to the following multiples of V_0 (the close-packed volume): $V/V_0 = 1.500, 1.550, 1.600, 1.767, 2.000, 3.000$. The first three of these values may actually involve first fluid metastable with respect to crystallization, but the Percus-Yevick $g^{(2)}$'s are oblivious to this possibility, and these high densities were included in view of the bias of the approximations in the foregoing theory.

Figure 2 displays the computed values of the contact pair perturbation $z^{(0)}(1, u)$, vs angle $\cos^{-1}u$, for three of the densities. The strong peak in the "forward" direction (0°) indicates the tendency for A-B sphere pairs to accumulate in the head-on collision configuration, resulting from their opposed flows, before they have a chance to get out of one another's way. Figure 3 shows for $V/V_0 = 1.600$, in addition to $z^{(0)}$, the higher-order contact pair perturbations $n^{(e)}(1, u)$ and $\tilde{z}^{(0)}(1, u)$. Qualitatively, this case was typical for all of the densities examined.

¹⁸ J. K. Percus and G. J. Yevick, Phys. Rev. **110**, 1 (1958).

¹⁹ M. S. Wertheim, J. Math. Phys. **5**, 643 (1964); $g^{(2)}$ calculations carried out in the same fashion as done for the present transport theory have independently been reported: G. J. Throop and R. J. Bearman, J. Chem. Phys. **42**, 2408 (1965).

²⁰ J. B. Scarborough, *Numerical Mathematical Analysis* (The Johns Hopkins Press, Baltimore, Maryland, 1962).

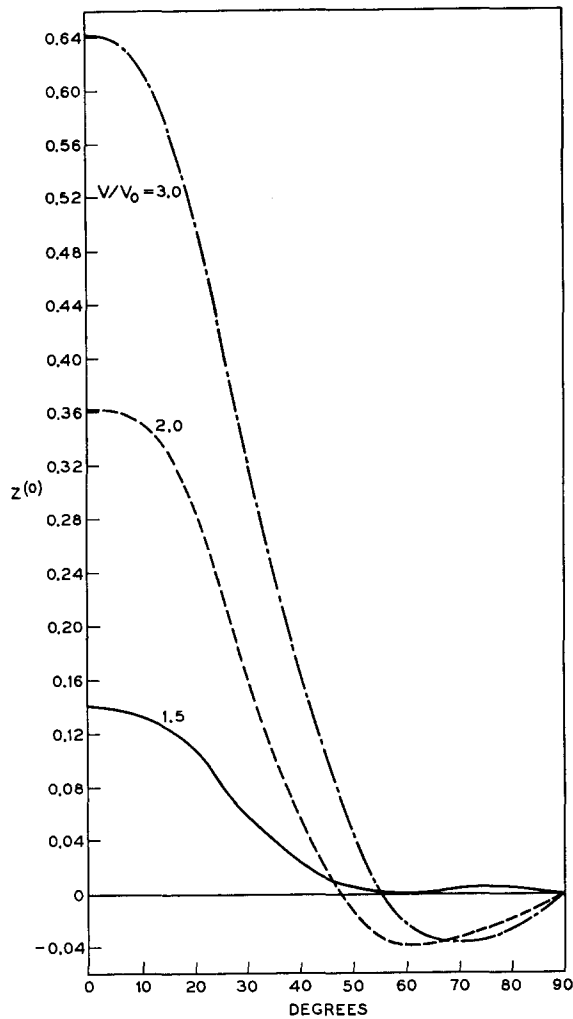


FIG. 2. Contact pair perturbations $z^{(0)}(1, u)$ for three of the six densities studied numerically. The abscissa represents angle $\cos^{-1}u$ (0° is in the flow direction).

Beside the obvious tendency of the $z^{(0)}$ to peak in the forward direction, there is another feature of this set of solutions which also seems to be in agreement with one's intuitive picture of transport in dense fluids. Clearly, as the fluid is compressed toward the close-

TABLE I. $z^{(0)}$ homogeneous integral equation eigenvalues (λ) and the predicted self-diffusion constant (D_0) values for the six densities considered in the rigid-sphere computation. The Enskog prediction for D_0 , Eq. (66), has been included for comparison. Diffusion constants are in units $a/(m\beta)^{1/2}$, where a is the rigid-sphere diameter.

V/V_0	λ	D_0	D_0 (Enskog)
3.000	0.6637	0.285	0.227
2.000	1.2398	($\pm 1.22i$)	0.103
1.767	1.6205	1.23	0.076
1.600	2.0698	0.465	0.058
1.550	2.2492	0.393	0.051
1.500	2.4555	0.356	0.046

packed limit, it becomes increasingly difficult for a sphere to escape from the momentary cage formed by its neighbors. Indeed, in the close-packed limit, no diffusion at all is permitted on purely geometric grounds in the presence of any concentration gradient. It is therefore not surprising that the flow perturbation $z^{(0)}$, defined in terms of unit concentration gradient, declines in magnitude as the density increases.

Table I collects the diffusion constant results, and shows, as well, the eigenvalue obtained during solution of the homogeneous $z^{(0)}$ equation. Included for com-

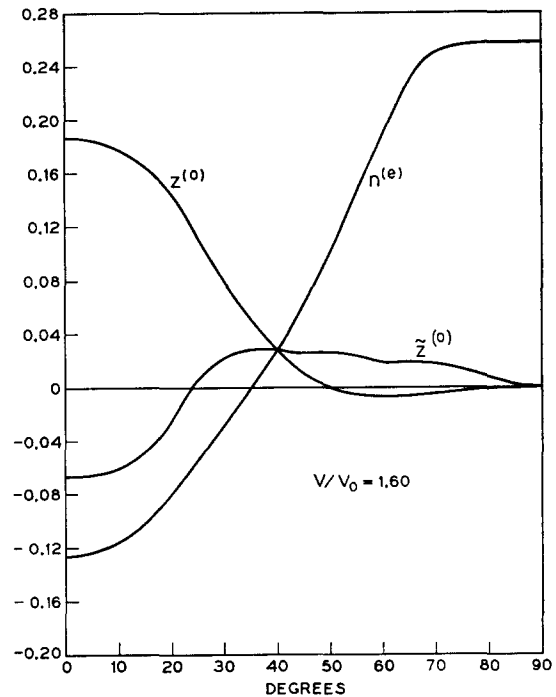


FIG. 3. The three contact pair perturbation functions, $z^{(0)}(1, u)$, $n^{(e)}(1, u)$, and $\tilde{z}^{(0)}(1, u)$ for $V/V_0 = 1.600$.

parison are the values predicted by the Enskog theory,

$$D_0 = \left[\frac{3}{8(\pi)^{1/2} N a^3 g^{(2)}(a)/V} \right] \frac{a}{(m\beta)^{1/2}}, \quad (66)$$

for rigid spheres of diameter a .

VI. COMMENTARY

In spite of the physically reasonable behavior of the perturbation $z^{(0)}$ already noted, the numbers entered into Table I are not quantitatively impressive. The eigenvalue λ , which would have been precisely unity if the theory were exact clearly deviates by roughly a factor of two in both directions from this desired value. Assuming in addition that the Enskog value is substantially accurate, the predicted D_0 values are far off the mark, in one instance becoming imaginary [i.e., D_0^2 in Eq. (65) was found to be negative]. One is therefore apparently confronted with a case of con-

siderable sensitivity of the central transport coefficient expression, Eq. (65), to errors that have accumulated during the approximate calculation. Since it is our belief that the general approach advocated in this paper has basic merit, it becomes necessary to suggest the various ways in which the relatively crude first level of approximation used above might profitably be sharpened to improve numerical results.

We note in passing that the rigid-sphere model constitutes a relatively severe test of, especially, the present transport theory. If the molecular pair interactions on the contrary were weak, so that pair encounters implied only small deflections from linear trajectories, the dynamical superposition approximation would have been essentially exact.

There are several areas in which the stringency of the approximations actually employed in the rigid-sphere D_0 numerical calculation could conceivably be relaxed:

- (1) Use of more accurate $g^{(2)}$'s than provided by the Percus-Yevick integral equation;
- (2) Avoidance of the superposition approximation for the equilibrium $g^{(3)}$;
- (3) Improvement of the dynamical superposition approximation;
- (4) Extension of the local equilibrium approximation to include pair perturbations quadratic in momentum components;
- (5) Inclusion in the theory of terms of higher order in the wave vector k , to permit direct evaluation of D_1 .

The first of these categories has been tested at $V/V_0=1.600$ by modifying slightly the input $g^{(2)}$ so as to conform with the presumably accurate pair correlation function obtained by Alder in molecular-dynamic investigations.¹⁷ The eigenvalue λ decreased slightly (from 2.0698 to 2.0425) but D_0 more than doubled in value (changing from 0.465 to 0.98). Quite aside from the fact that the D_0 result becomes even worse, it is clear that this quantity displays considerable sensitivity to the input $g^{(2)}$. Indeed, our experience has been that the various integral terms in Eq. (65) for D_0^2 tend to cancel one another, so that resultant error is amplified percentagewise. By implication, it would seem probable that the calculation is similarly sensitive to error in the equilibrium superposition approximation used to eliminate $g^{(3)}$. These equilibrium distribution function errors naturally increase in magnitude as density increases.

With regard to (3) above, it should be noted that one has no assurance that the steady-state flow pattern in the phase space of three particles, as predicted by dynamical superposition, is necessarily divergence free. It would eventually be valuable to impose at least this triplet flow conservation condition in quantitative rectification of the low-order calculation presented in this article. Of course it need hardly be mentioned that

computational difficulty increases with each suggested extension.

There are potentially two aspects of self-diffusion wherein the *form* of the present theory, as distinct from its *adaptability* to computation, may lead to important insights. Both are connected with the fact that equilibrium pair and triplet distribution functions, as input functions, will in the last analysis control the behavior of the transport phenomenon. Thus, the manner in which the decay of $g^{(2)}(r, N/V)-1$ to zero decreases as one increases density from the dilute gas limit may be connected with the apparent nonanalyticity of transport coefficients in density.²¹ For a similar reason, the very long-range tail that $g^{(2)}-1$ develops under critical conditions for substances with attractive intermolecular forces, also may suffice in the present context to clarify the anomalous behavior reported for self-diffusion coefficients at the critical point.²²

The conclusion to be drawn from the exploratory program outlined in this paper, we believe, is that qualitative (but not yet quantitative) feasibility has been demonstrated for construction of dense-fluid flow perturbations and transport coefficients directly from the low-order reduced Liouville equations.

APPENDIX

Under the local equilibrium assumption for the pair distribution function perturbations, χ_1 was related to D_1 , which then required elimination. We shall now investigate the character of D_1 for the stochastic process examined at length by Nelkin and Ghatak.²³

Consider the diffusive spreading of an initial delta-function concentration profile, which at arbitrary time t is denoted by $\Delta(\mathbf{r}, t)$. Then initially

$$\Delta(\mathbf{r}, t=0) = \delta(\mathbf{r}) = [1/(2\pi)^3] \int d\mathbf{k} \exp(i\mathbf{k} \cdot \mathbf{r}). \quad (A1)$$

For t greater than the induction times $t_0(k)$ for all wavelengths,

$$\Delta(\mathbf{r}, t) = [1/(2\pi)^3] \times \int d\mathbf{k} \exp\{-k^2 D(k)[t-t_0(k)] + i\mathbf{k} \cdot \mathbf{r}\}. \quad (A2)$$

Unit normalization is maintained at all times by (A2) automatically:

$$\begin{aligned} \int \Delta(\mathbf{r}, t) d\mathbf{r} &= [1/(2\pi)^3] \int d\mathbf{r} d\mathbf{k} \\ &\times \exp\{-k^2 D(k)[t-t_0(k)] + i\mathbf{k} \cdot \mathbf{r}\} \\ &= \int d\mathbf{k} \exp\{-k^2 D(k)[t-t_0(k)]\} \delta(\mathbf{k}) \\ &= 1. \end{aligned} \quad (A3)$$

²¹ K. Kawasaki and I. Oppenheim, Phys. Rev. **139**, A1763 (1965).

²² J. D. Noble and M. Bloom, Phys. Rev. Letters **14**, 250 (1965).

²³ M. Nelkin and A. Ghatak, Phys. Rev. **135**, A4 (1964).

The inverse to Fourier transform (A2) may be manipulated as follows:

$$\begin{aligned} \exp\{-k^2 D(k)[t-t_0(k)]\} &= \int d\mathbf{r} \exp(-i\mathbf{k}\cdot\mathbf{r}) \Delta(\mathbf{r}, t) \\ &= \int d\mathbf{r} \frac{\sin k r}{k r} \Delta(\mathbf{r}, t) \\ &= \sum_{n=0}^{\infty} \frac{(-1)^n k^{2n}}{(2n+1)!} \int d\mathbf{r} r^{2n} \Delta(\mathbf{r}, t) \\ &= \sum_{n=0}^{\infty} \frac{(-1)^n k^{2n}}{(2n+1)!} \langle r^{2n} \rangle_t, \quad (\text{A4}) \end{aligned}$$

to introduce the spatial moments $\langle r^{2n} \rangle_t$ at time t of the concentration packet. Now if the left hand member at the beginning of (A4) is expanded as a power series in k^2 [referring to Eqs. (14) in the text] and corresponding terms compared, we find:

$$\begin{aligned} D_0 &= \lim_{t \rightarrow \infty} (1/6t) \langle r^2 \rangle_t, \\ t_0 &= \lim_{t \rightarrow \infty} [t - (1/6D_0) \langle r^2 \rangle_t], \\ D_1 &= \lim_{t \rightarrow \infty} [\frac{1}{2} D_0^2 (t - 2t_0) - (1/120t) \langle r^4 \rangle_t]. \quad (\text{A5}) \end{aligned}$$

The statistics of Brownian paths executed by diffusing molecules are complex, even for rigid spheres. We suppose, however, that there exists an equivalent simpler stochastic process, whose parameters are chosen to reproduce the correct D_0 , and which will suffice to estimate D_1 . We choose the Nelkin-Ghatak process, which postulates a velocity-independent molecular collision rate, with randomization of velocities (according to the Maxwell distribution) after each collision. The successive spatial moments for this process have been computed,²³ and the leading members of the sequence are:

$$\begin{aligned} \langle r^2 \rangle_t &= (6/m\beta\alpha^2) [\tau - 1 + \exp(-\tau)], \\ \langle r^4 \rangle_t &= (120/m^2\beta^2\alpha^4) [\frac{1}{2}\tau^2 - 3 + (\tau^2 + 3\tau + 3) \exp(-\tau)], \\ \tau &= \alpha t, \end{aligned} \quad (\text{A6})$$

where α is the collision rate. After inserting these values in (A5), one obtains

$$-D_1/D_0 = m\beta D_0^2, \quad (\text{A7})$$

which was quoted in the text just before Eq. (40).

Mass-Spectrometric Studies of Reactions in Flames. II. Quantitative Sampling of Free Radicals from One-Atmosphere Flames*

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Direct mass spectrometric sampling studies of one-atmosphere flames are described. A simple model of the sampling process is summarized which accounts for the effects and results obtained. Stable product analysis and evidence for appreciable temperature dependence of fragmentation patterns are shown. Quantitative sampling of the free radicals H, O, OH, and Cl from the burnt gas region of one-atmosphere flames is demonstrated, with direct observation of excess free-radical concentrations in the reaction zones of these flames.

I. INTRODUCTION

THE first paper¹ in this series described the relationship between aerodynamic molecular-beam formation and the problem of the direct mass-spectrometric sampling of systems at atmospheric pressure and above. Since the publication of that paper, considerable theoretical and experimental work on the free jet expansion and aerodynamic molecular beams has been reported. Now a rather simple model of the sampling process can

be formulated which accounts for the observed effects and gives a quantitative history of the sampling process. In this paper, we summarize this model and present data on the sampling of reactive species from one-atmosphere flames.

II. BEAM FORMATION FROM HIGH-PRESSURE SOURCES

Starting from a stagnant condition, the gas to be sampled is accelerated as it approaches the sampling orifice, and reaches the speed of sound near the throat of the orifice. At this point, the pressure has dropped by as much as 15%–20%. From the sonic condition, the

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¹ F. T. Greene, J. Brewer, and T. A. Milne, *J. Chem. Phys.* **40**, 1488 (1964).