Chapman–Enskog Velocity Distribution for Tracer Diffusion

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The Chapman–Enskog method is used to obtain an approximate velocity distribution function for tracer diffusion in dilute hard-sphere mixtures. Different ratios of the mass of the tracer to that of the excess component (including the well-known limiting cases of the Lorentz and the Rayleigh models) are considered and the corresponding diffusion coefficients are also evaluated. A comparison with the recent results of Tompson and Loyalka for both the diffusion coefficients and the distribution functions provides a perspective on the usefulness and nature of the approximate method.

1. INTRODUCTION

The ability to provide explicit expressions for the transport properties of dilute gases and gas mixtures in terms of the intermolecular forces is perhaps one of the greatest achievements of kinetic theory. The calculational procedures are nowadays fairly standard topics, which may be found, for instance, in the monographs by Chapman and Cowling[1] and Ferziger and Kaper.[2] But one must always bear in mind that a long period existed between the derivation of the Boltzmann equation[3] and the appearance of a general (albeit approximate) method to solve it. This method was derived independently by Chapman[4] and Enskog.[5] Thus, prior to 1917, only in a few particular cases had the transport properties been investigated. These include the gas composed of Maxwell molecules, the model considered by Lorentz[6] to describe electronic transport in metals, and the Rayleigh piston.[7] A common feature of these three models

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is that one may obtain the exact velocity distribution functions and transport coefficients and hence they provide the appropriate framework to test the accuracy of approximate results. Such tests have been conducted for the transport coefficients,[1,2] which usually constitute the interesting quantities, but to my knowledge very little, if anything, has been done concerning the distribution functions. It is the major aim of this paper to carry out an explicit comparison between the "exact" velocity distribution functions for tracer diffusion in dilute binary hard-sphere gas mixtures (for various ratios of the mass of the tracer to that of the excess component) and the Sonine polynomial expansion that approximates the same functions within the context of the Chapman–Enskog method at the Navier–Stokes level. These velocity distribution functions are apparently of interest in several problems of rarefied gas dynamics and particle transport. The "exact" results are taken from a recent paper by Tompson and Loyalka[8] in which they generalize the pioneering effort of Pidduck,[9] who, already in 1915 and long before the age of electronic computers, numerically solved the Boltzmann equation and computed very accurately the self-diffusivity.

The paper is organized as follows. In the next section I recall the main steps in the Chapman–Enskog method for a dilute binary hard-sphere gas mixture up to the Navier–Stokes level and later consider the specific case of tracer diffusion. This is followed in Section 3 by the outline of the method to transform the integral equation appropriate for tracer diffusion to a system of linear equations for the Sonine coefficients. The paper ends in Section 4 with a discussion of the numerical results and some concluding remarks.

2. CHAPMAN–ENSKOG INTEGRAL EQUATIONS FOR DILUTE BINARY MIXTURES

2.1. General Case

In the case of binary mixtures and in the absence of an external outside field the two single-particle distribution functions $f_i(\mathbf{r}, \mathbf{v}_i, t)(i = 1, 2)$ obey a set of two coupled nonlinear Boltzmann equations of the form

$$\left(\frac{\partial}{\partial t} + \mathbf{v}_1 \cdot \frac{\partial}{\partial \mathbf{r}}\right) f_1(\mathbf{r}, \mathbf{v}_1, t) = J_{11}(f_1 f_1) + J_{12}(f_1 f_2) \tag{1}$$

$$\left(\frac{\partial}{\partial t} + \mathbf{v}_2 \cdot \frac{\partial}{\partial \mathbf{r}}\right) f_2(\mathbf{r}, \mathbf{v}_2, t) = J_{21}(f_2 f_1) + J_{22}(f_2 f_2) \tag{2}$$

where

$$J_{ij}(f_i f_j) = \iint \theta(\mathbf{v}_{ji} \cdot \hat{k})(\mathbf{v}_{ji} \cdot \hat{k}) \, \sigma_{ij}^2$$

$$\times [f_i(\mathbf{r}, \mathbf{v}_i', t) f_j(\mathbf{r}, \mathbf{v}_j', t) - f_i(\mathbf{r}, \mathbf{v}_i, t) f_j(\mathbf{r}, \mathbf{v}_j, t)]$$

$$\times d\hat{k} \, d\mathbf{v}_j \qquad (i, j = 1, 2)$$

Here $f_i(\mathbf{r}, \mathbf{v}_i, t)$ is the average number of hard spheres of component i (with diameter σ_i and mass m_i) at the position $\mathbf{r}$ with velocity $\mathbf{v}_i$ at time t; $\mathbf{v}_{ji} = \mathbf{v}_j - \mathbf{v}_i$ is the relative velocity of two spheres with velocities $\mathbf{v}_j$ and $\mathbf{v}_i$, respectively, $\hat{k}$ is a unit vector directed along the line of centers from the sphere of component j to the sphere of component i upon collision, θ is the Heaviside step function, and $\sigma_{ij} = \frac{1}{2}(\sigma_i + \sigma_j)$. Here $\mathbf{v}_i'$ and $\mathbf{v}_j'$ are the velocities of the restituting collision, which are connected to those of the direct collision $\mathbf{v}_i$ and $\mathbf{v}_j$ by the relations

$$\mathbf{v}_i' = \mathbf{v}_i + 2M_{ji}(\mathbf{v}_{ji} \cdot \hat{k}) \, \hat{k}$$
$$\mathbf{v}_j' = \mathbf{v}_j - 2M_{ij}(\mathbf{v}_{ji} \cdot \hat{k}) \, \hat{k} \qquad (3)$$

where $M_{ij} = m_i/m_i m_j$. Defining the mass ratio $\mu = m_1/m_2$, one then has $M_{12} = \mu/(1 + \mu)$ and $M_{21} = (1 + \mu)^{-1}$.

The molecular fluxes and the transport coefficients for binary mixtures (up to the Navier–Stokes level) can be directly obtained from Eqs. (1) on the basis of the Chapman–Enskog method. Since the procedure is well known and easily available, I only state here the form of the approximate functions up to that level (and the associated linear integral equations) that arise in the method. For all details of the derivations, see Ferziger and Kaper[2] or Chapman and Cowling.[1]

To first order in the gradients of the local number densities n_1 and n_2, local hydrodynamic velocity $\mathbf{u}$, and local temperature T defined by

$$n_i(\mathbf{r}, t) = \int f_i(\mathbf{r}, \mathbf{v}_i, t) \, d\mathbf{v}_i \qquad (i = 1, 2) \qquad (4a)$$

$$\rho(\mathbf{r}, t) \, \mathbf{u}(\mathbf{r}, t) = \sum_{i=1}^{2} \int f_i(\mathbf{r}, \mathbf{v}_i, t) \, m_i \mathbf{v}_i \, d\mathbf{v}_i \qquad (4b)$$

and

$$\frac{3}{2} n(\mathbf{r}, t) \, k_B T(\mathbf{r}, t) = \sum_{i=1}^{2} \int f_i(\mathbf{r}, \mathbf{v}_i, t) \cdot \frac{1}{2} m_i V_i^2 \, d\mathbf{v}_i \qquad (4c)$$

where $\rho = \rho_1 + \rho_2$ is total mass density, $\rho_i = m_i n_i$ $(i = 1, 2)$ is the mass density of species i, $n = n_1 + n_2$ is the total number density, $\mathbf{V}_i(\mathbf{r}, t) = \mathbf{v}_i - \mathbf{u}(\mathbf{r}, t)$

is the peculiar velocity of species i, and k_B is Boltzmann's constant, one approximates the distribution $f_i(\mathbf{r}, \mathbf{v}_i, t)$ by $f_i^{(1)}(\mathbf{r}, \mathbf{v}_i, t)$ as follows:

$$f_i(\mathbf{r}, \mathbf{v}_i, t) \approx f_i^{(1)}(\mathbf{r}, \mathbf{v}_i, t)$$
$$= f_i^{(0)}(\mathbf{r}, \mathbf{v}_i, t)[1 + \phi_i(\mathbf{r}, \mathbf{v}_i, t)] \qquad (i = 1, 2) \qquad (5)$$

Here

$$f_i^{(0)} \equiv f_i^{(0)}(\mathbf{r}, \mathbf{v}_i, t)$$
$$= n_i(\mathbf{r}, t) \left(\frac{m_i}{2\pi k_B T(\mathbf{r}, t)}\right)^{3/2} \exp \frac{m_i V_i^2(\mathbf{r}, t)}{2 k_B T(\mathbf{r}, t)} \qquad (i = 1, 2) \qquad (6)$$

are local Maxwellians and $\phi_i(\mathbf{r}, \mathbf{v}_i, t)$ can be written in the form

$$\phi_i(\mathbf{r}, \mathbf{v}_i, t) = -\frac{1}{n}\left[\mathbf{A}_i(\mathbf{V}_i) \cdot \frac{\partial}{\partial \mathbf{r}} \log T + \mathbb{B}_i(\mathbf{V}_i) : \frac{\partial \mathbf{u}}{\partial \mathbf{r}} + \sum_{j=1}^{2} \mathbf{D}_i^j(\mathbf{V}_i) \cdot \mathbf{d}_j\right]$$
$$(i = 1, 2) \quad (7)$$

where the functions $\mathbf{A}_i$, $\mathbb{B}_i$, and D_i^j are solutions to the following integral equations:

$$\sum_{j=1}^{2} \frac{n_i n_j}{n^2} I_{ij}(\mathbf{A}) = -\frac{f_i^{(0)}}{n}\left(\frac{m_i V_i^2}{2 k_B T} - \frac{5}{2}\right)\mathbf{V}_i \qquad (i = 1, 2) \qquad (8a)$$

$$\sum_{j=1}^{2} \frac{n_i n_j}{n^2} I_{ij}(\mathbb{B}) = -\frac{f_i^{(0)} m_i}{n k_B T}\left(\mathbf{V}_i \mathbf{V}_i - \frac{1}{3} V_i^2 \square\right) \qquad (i = 1, 2) \qquad (8b)$$

$$\sum_{j=1}^{2} \frac{n_i n_j}{n^2} I_{ij}(\mathbf{D}^k) = -\frac{f_i^{(0)}}{n_i}\left(\delta_{ik} - \frac{\rho_i}{\rho}\right)\mathbf{V}_i \qquad (i, k = 1, 2) \qquad (8c)$$

in which $\square$ is the unit tensor, the operator I_{ij} is defined by

$$I_{ij}(F) = \frac{1}{n_i n_j} \iint \theta(\mathbf{V}_{ji} \cdot \hat{k})(\mathbf{v}_{ji} \cdot \hat{k})$$
$$\times \sigma_{ij}^2 f_i^{(0)} f_j^{(0)}(F_i' + F_j' - F_i - F_j) \, d\hat{k} \, d\mathbf{v}_j \qquad (9)$$

and F_i' stands for $F_i(\mathbf{V}_i')$. Since the integral operators I_{ij} are isotropic in velocity space, it follows that the $\mathbf{A}_i$, $\mathbb{B}_i$, and $\mathbf{D}_i^k$ are also isotropic tensors in velocity space, i.e. $(i = 1, 2)$,

$$\mathbf{A}_i(\mathbf{V}_i) = A_i(V_i)\,\mathbf{V}_i \qquad (10a)$$

$$\mathbb{B}_i(\mathbf{V}_i) = B_i(V_i)(\mathbf{V}_i \mathbf{V}_i - \tfrac{1}{3} V_i^2 \square) \qquad (10b)$$

$$\mathbf{D}_i^k(\mathbf{V}_i) = D_i^k(V_i)\,\mathbf{V}_i \qquad (k = 1, 2) \qquad (10c)$$

Also, the requirement that the n_i, $\mathbf{u}$, and T in Eq. (6) are the true local number densities, hydrodynamic velocity, and temperature, respectively, imposes certain subsidiary conditions on the functions $\mathbf{A}_i$ and $\mathbf{D}_i^j$ that assure the uniqueness of the solution, namely

$$\sum_{i=1}^{2} \int f_i^{(0)} m_i V_i^2 A_i \, d\mathbf{v}_i = 0 \tag{11a}$$

and

$$\sum_{i=1}^{2} \int f_i^{(0)} m_i V_i^2 D_i^k \, d\mathbf{v}_i = 0 \qquad (k = 1, 2) \tag{11b}$$

On the other hand, uniqueness of the solution of Eq. (8c) requires in addition

$$\sum_{j=1}^{2} \frac{\rho_j}{\rho} D_i^j = 0 \qquad (i = 1, 2) \tag{11c}$$

The diffusion driving forces $\mathbf{d}_i$ $(i = 1, 2)$ appearing in $\phi_i(\mathbf{r}, \mathbf{v}_i, t)$ [cf. Eq. (7)] reduce in the absence of external forces to

$$\mathbf{d}_i = \frac{\partial}{\partial \mathbf{r}} \left(\frac{n_i}{n} \right) + \left(\frac{n_i}{n} - \frac{\rho_i}{\rho} \right) \frac{\partial}{\partial \mathbf{r}} \log p \qquad (i = 1, 2) \tag{12a}$$

where the hydrostatic pressure $p = n k_B T$. Because

$$\sum_{i=1}^{2} \frac{n_i}{n} = \sum_{i=1}^{2} \frac{\rho_i}{\rho} = 1$$

it follows from Eq. (12a) that

$$\mathbf{d}_1 = -\mathbf{d}_2 \tag{12b}$$

2.2. Tracer Diffusion

Let us now assume that we have a binary mixture in which one of the components, say component 1, is present in tracer concentration, i.e., $n_1 \ll n_2 = n$ or $\nu = n_1/n_2 \ll 1$. Further, in order to study tracer diffusion, we also assume that mechanical equilibrium has been established (so that $\partial p/\partial \mathbf{r} = 0$) and that the only nonuniformity in the mixture is due to a concentration gradient. Under these circumstances, neglecting all the terms

which are of $O(v)$ or higher with respect to those which are of $O(1)$ as $v \to 0$, reduces the set of integral equations (8) to the set

$$I_{12,1}^{\text{tr}}(\mathbf{D}^1) = -\frac{n}{n_1^2} f_1^{(0)} \mathbf{V}_1 \tag{13a}$$

$$I_{21,1}^{\text{tr}}(\mathbf{D}^1) + \frac{n}{n_1} I_{22}^{\text{tr}}(\mathbf{D}^1) = \frac{f_2^{(0)}}{n_1} \mathbf{V}_2 \tag{13b}$$

where

$$I_{ij,l}(F) = \frac{1}{n_i n_j} \iint \theta(\mathbf{V}_{ji} \cdot \hat{k})(\mathbf{V}_{ji} \cdot \hat{k}) \, \sigma_{ij}^2 f_i^{(0)} f_j^{(0)}$$

$$\times (F_l' - F_l) \, d\hat{k} \, d\mathbf{v}_j \qquad (i, j, l = 1, 2) \tag{14}$$

and the superscript tr indicates that we only retained terms of $O(1)$ in the limit as $v \to 0$.

Notice that Eq. (13a) is decoupled from Eq. (13b), implying that, for tracer diffusion, it is as if the excess component 2 was always in (local) thermal equilibrium, although, as should be clear from Eq. (13b), this is certainly not the case. Such decoupling is the origin of the agreement in the values of tracer diffusion coefficients computed from seemingly different models, as has been discussed elsewhere.[10,11] For our purposes suffice it to say that Eq. (13a) is the dimensional version of Eq. (2) in the paper by Tompson and Loyalka[8] and will be the basis of the subsequent analysis. In fact, their $\hat{\phi}_d(c)$ is related to our D_1^2 by

$$\hat{\phi}_d(c) = \left(\frac{m_2 \pi}{m_1}\right)^{1/2} \frac{\sigma_{12} \rho^2}{n^2 m_2^2} D_1^2(c) \tag{15}$$

And of course it follows from the subsidiary condition (11c) that D_1^2 may be easily determined once D_1^1 has been found from the solution to Eq. (13c).

To close this subsection and for the sake of completeness, note that the diffusion coefficient as defined in Eq. (4) of Tompson and Loyalka[8] is thus given in terms of our $D_1^2(c)$ as

$$D_{12} = -\frac{4}{3} \frac{\rho^2}{n_2^2 m_1 m_2} \left(\frac{2k_{\text{B}} T}{\pi m_1}\right)^{1/2} \int_0^\infty c^4 D_1^2(c) \, e^{-c^2} \, dc \tag{16}$$

3. VELOCITY DISTRIBUTION FUNCTION FOR TRACER DIFFUSION

Except for two particular limiting cases, namely the Lorentz model ($m_1 = $ finite, $m_2 \to \infty$, so that $\mu \to 0$) and the Rayleigh model ($m_1 \Rightarrow \infty$,

$m_2 = $ finite, so that $\mu \to \infty$), no closed-form analytical solutions to Eq. (13a) may be obtained for arbitrary μ. In the Lorentz model (super-script L)

$$D_1^{1L}(V_1) = \frac{n}{n_1 V_1 \pi \sigma_{12}^2} \tag{17}$$

whereas in the Rayleigh model (superscript R)

$$D_1^{1R}(V_1) = \frac{3}{8} \left(\frac{m_1}{m_2} \right)^{1/2} \frac{n}{n_1 \pi \sigma_{12}^2} \tag{18}$$

These results are obtained after appropriate expansions of the collision operator $I_{12,1}^{tr}$ are performed and the above limits of μ are taken.[10,11] On the other hand, the case $\mu = 1$ was first solved numerically by Pidduck[9] and later reexamined by Pekeris,[12] who used a somewhat different numerical strategy. Very recently, Tompson and Loyalka[8] generalized the numerical approach of Pidduck for arbitrary μ and reported numerical values of the dimensionless velocity distribution function $\hat{\phi}_d(c)$ for selected values of μ.

I here follow a different route, more akin to the spirit of the Chapman–Enskog procedure. In this procedure, the function D_1^1 is expanded in a convenient complete set of orthonormal polynomials, the Sonine poly-nomials, so that

$$D_1^1(V_1) = \frac{m_1}{k_B T} \sum_{r=0}^{\infty} d_{1,r}^{(1)} S_{3/2}^{(r)} \left(\frac{m_1 V_1^2}{2 k_B T} \right) \tag{19}$$

where $S_{3/2}^{(r)}(x)$ is the Sonine polynomial of order r and index $3/2$, and $d_{1,r}^1$ are referred to as Sonine coefficients. We now take, as usual, the so-called Nth Enskog approximation, i.e., we let the index r in the summation appearing in Eq. (19) rum from $r = 0$ to $r = N - 1$. Substituting this Nth Enskog approximation in Eq. (13c), multiplying both sides of the resulting equation with

$$S_{3/2}^{(p)} \left(\frac{m_1 V_1^2}{2 k_B T} \right) \frac{m_1 \mathbf{V}_1}{2 k_B T}$$

and subsequently integrating over $\mathbf{v}_1$ leads to the following set of N linear equations for the coefficients $d_{1,r}^{(1)}[N]$ $(r = 0, 1,..., N - 1)$, in the Nth Enskog approximation,

$$\sum_{r=0}^{N-1} d_{1,r}^{(1)}[N] \, d_{pr} = \frac{3 k_B T}{m_1} \frac{n}{n_1} \delta_{p0} \qquad (p = 0, 1,..., N - 1) \tag{20}$$

Table I. Values of $-\hat{\Phi}_d(c)$ Computed by Tompson and Loyalka (TL) and in the Present Work for Selected Values of Inverse Mass Ratio μ^{-1}

c	$\mu^{-1}=0.1$		$\mu^{-1}=0.2$		$\mu^{-1}=0.5$		$\mu^{-1}=1.0$		$\mu^{-1}=2.0$		$\mu^{-1}=5.0$		$\mu^{-1}=10.0$	
	TL	Present	TL	Present	TL	Present	TL	Present	TL	Present	TL	Present	TL	Present[a]
0.01	4.0068	4.0069	2.1400	2.1401	1.0428	1.0429	0.7078	0.7079	0.5654	0.5654	0.4944	0.4999	0.4733	0.4520
0.05	4.0067	4.0068	2.1399	2.1400	1.0426	1.0427	0.7075	0.7076	0.5647	0.5648	0.4929	0.4905	0.4703	0.4500
0.10	4.0065	4.0066	2.1396	2.1397	1.0421	1.0422	0.7066	0.7066	0.5628	0.5629	0.4882	0.4861	0.4613	0.4437
0.20	4.0056	4.0057	2.1385	2.1385	1.0401	1.0402	0.7028	0.7028	0.5555	0.5555	0.4709	0.4698	0.4295	0.4200
0.30	4.0040	4.0041	2.1366	2.1366	1.0368	1.0368	0.6966	0.6967	0.5438	0.5439	0.4455	0.4453	0.3881	0.3857
0.40	4.0019	4.0020	2.1339	2.1340	1.0322	1.0323	0.6884	0.6884	0.5287	0.5288	0.4159	0.4161	0.3457	0.3465
0.50	3.9991	3.9992	2.1305	2.1306	1.0264	1.0265	0.6782	0.6783	0.5111	0.5112	0.3851	0.3853	0.3067	0.3078
0.60	3.9957	3.9958	2.1264	2.1265	1.0196	1.0196	0.6666	0.6666	0.4919	0.4920	0.3551	0.3552	0.2728	0.2730
0.70	3.9918	3.9919	2.1216	2.1217	1.0117	1.0118	0.6537	0.6537	0.4719	0.4720	0.3272	0.3272	0.2439	0.2436
0.80	3.9872	3.9873	2.1162	2.1162	1.0030	1.0031	0.6399	0.6399	0.4517	0.4518	0.3018	0.3018	0.2195	0.2193
0.90	3.9821	3.9822	2.1100	2.1101	0.9935	0.9936	0.6255	0.6255	0.4318	0.4319	0.2789	0.2790	0.1989	0.1990
1.00	3.9765	3.9765	2.1033	2.1034	0.9834	0.9834	0.6107	0.6107	0.4125	0.4126	0.2585	0.2586	0.1815	0.1817
1.10	3.9702	3.9703	2.0960	2.0961	0.9727	0.9727	0.5957	0.5958	0.3940	0.3941	0.2403	0.2403	0.1666	0.1667
1.20	3.9635	3.9635	2.0881	2.0882	0.9615	0.9616	0.5807	0.5808	0.3764	0.3765	0.2240	0.2241	0.1538	0.1538
1.30	3.9562	3.9562	2.0797	2.0798	0.9500	0.9501	0.5659	0.5660	0.3598	0.3599	0.2096	0.2096	0.1427	0.1427
1.40	3.9484	3.9484	2.0709	2.0709	0.9383	0.9383	0.5514	0.5514	0.3442	0.3442	0.1966	0.1967	0.1331	0.1331
1.50	3.9401	3.9401	2.0615	2.0616	0.9263	0.9264	0.5372	0.5372	0.3295	0.3295	0.1850	0.1851	0.1246	0.1247
1.60	3.9313	3.9314	2.0518	2.0518	0.9142	0.9143	0.5233	0.5234	0.3157	0.3158	0.1746	0.1747	0.1171	0.1173
1.70	3.9221	3.9221	2.0416	2.0417	0.9021	0.9021	0.5099	0.5099	0.3028	0.3029	0.1652	0.1653	0.1105	0.1105
1.80	3.9124	3.9125	2.0312	2.0312	0.8900	0.8901	0.4969	0.4970	0.2907	0.2908	0.1567	0.1568	0.1045	0.1045

1.90	3.9023	3.9024	2.0204	2.0204	0.8779	0.8780	0.4844	0.4845	0.2794	0.2795	0.1490	0.1490	0.0992	0.0992
2.00	3.8918	3.8919	2.0093	2.0093	0.8659	0.8660	0.4724	0.4724	0.2688	0.2689	0.1419	0.1420	0.0943	0.0944
2.10	3.8809	3.8810	1.9979	1.9980	0.8541	0.8541	0.4608	0.4608	0.2589	0.2589	0.1355	0.1355	0.0900	0.0901
2.20	3.8696	3.8697	1.9863	1.9863	0.8423	0.8424	0.4496	0.4497	0.2495	0.2496	0.1296	0.1297	0.0859	0.0860
2.30	3.8580	3.8581	1.9746	1.9746	0.8308	0.8308	0.4389	0.4390	0.2407	0.2408	0.1242	0.1242	0.0823	0.0823
2.40	3.8460	3.8461	1.9626	1.9627	0.8194	0.8194	0.4286	0.4287	0.2325	0.2325	0.1192	0.1193	0.0789	0.0789
2.50	3.8337	3.8338	1.9505	1.9506	0.8082	0.8082	0.4187	0.4188	0.2247	0.2248	0.1146	0.1147	0.0758	0.0759
2.60	3.8212	3.8212	1.9383	1.9383	0.7972	0.7972	0.4093	0.4093	0.2174	0.2174	0.1103	0.1104	0.0729	0.0731
2.70	3.8083	3.8084	1.9260	1.9260	0.7864	0.7864	0.4002	0.4002	0.2105	0.2105	0.1063	0.1064	0.0703	0.0704
2.80	3.7952	3.7952	1.9136	1.9136	0.7758	0.7759	0.3914	0.3914	0.2039	0.2040	0.1026	0.1027	0.0678	0.0678
2.90	3.7818	3.7818	1.9011	1.9011	0.7655	0.7655	0.3830	0.3830	0.1977	0.1978	0.0992	0.0992	0.0655	0.0653
3.00	3.7682	3.7683	1.8886	1.8887	0.7554	0.7554	0.3749	0.3749	0.1919	0.1919	0.0959	0.0960	0.0633	0.0633
3.10	3.7544	3.7544	1.8761	1.8761	0.7455	0.7455	0.3671	0.3672	0.1864	0.1864	0.0929	0.0930	0.0613	0.0615
3.20	3.7403	3.7404	1.8635	1.8636	0.7358	0.7358	0.3596	0.3597	0.1811	0.1811	0.0901	0.0900	0.0594	0.0598
3.30	3.7261	3.7262	1.8510	1.8510	0.7263	0.7264	0.3524	0.3525	0.1761	0.1762	0.0874	0.0874	0.0576	0.0578
3.40	3.7118	3.7118	1.8385	1.8385	0.7171	0.7171	0.3455	0.3455	0.1714	0.1714	0.0848	0.0849	0.0559	0.0556
3.50	3.6972	3.6973	1.8260	1.8260	0.7080	0.7081	0.3388	0.3389	0.1668	0.1669	0.0825	0.0826	0.0543	0.0538
3.60	3.6826	3.6826	1.8135	1.8136	0.6992	0.6992	0.3324	0.3324	0.1625	0.1626	0.0802	0.0803	0.0528	0.0529
3.70	3.6678	3.6678	1.8011	1.8012	0.6906	0.6906	0.3262	0.3262	0.1584	0.1585	0.0781	0.0779	0.0514	0.0524
3.80	3.6528	3.6529	1.7888	1.7888	0.6821	0.6822	0.3202	0.3202	0.1545	0.1546	0.0760	0.0759	0.0501	0.0512
3.90	3.6378	3.6379	1.7765	1.7765	0.6739	0.6740	0.3144	0.3144	0.1508	0.1508	0.0741	0.0742	0.0488	0.0485
4.00	3.6227	3.6228	1.7643	1.7643	0.6659	0.6659	0.3088	0.3088	0.1472	0.1473	0.0723	0.0728	0.0476	0.0452
4.50	3.5463	3.5464	1.7044	1.7046	1.6283	0.6284	0.2835	0.2836	0.1316	0.1360	0.0643	0.0658	0.0423	0.0353
5.00	3.4690	3.4693	1.6468	1.6473	1.5922	0.5948	0.2619	0.2662	0.1207	0.6094	0.0581	0.0520	0.0381	0.0718
5.50	3.3917	3.3924	1.5900	1.5920	0.5561	0.5655	0.2434	1.0393	0.1132	88.537	0.0532	2.9812	0.0347	0.9364
6.00	3.3118	3.3166	1.5308	1.5414	0.5283	0.5835	0.2272	48.275	0.1042	5355.3	0.0497	−196.9	0.0318	8.3097

[a] In this case $N = 45$.

where

$$d_{pr} \equiv [S_{3/2}^{(p)}(C^2)\, \mathbf{C},\, S_{3/2}^{(r)}(C^2)\, \mathbf{C}]_{12}' \tag{21}$$

are the so-called bracket integrals defined as

$$[F, G]_{12}' = \int G_1 I_{12,1}(F)\, d\mathbf{v}_1 \tag{22}$$

and $I_{12,1}$ is given by Eq. (14). Analytical results for d_{pr} have been recently derived by Lindenfeld and Shizgal,[13] which yield

$$d_{pq} = 2 \left[\frac{2k_B T(m_1 + m_2)}{m_1 m_2} \right]^{1/2} \sigma_{12}^2 \sum_{t=0}^{x} \sum_{s=0}^{x-t} \sum_{m=0}^{x-t-s} \sum_{n=0}^{1} \sum_{r=0}^{1-n}$$

$$\times \frac{4^t(r+s+t+n+1)!}{(t+n+1)!\, r!\, s!} \frac{\Gamma(p+q-2s-2t-m-r-n+1/2)}{(p-m-s-t)!\,(q-m-s-t)!\,(1-r-s)!\, m!}$$

$$\times \left\{ \frac{(2t+n+1)!}{2n!\,(2t+1)!} - 2^{n-1} \frac{(t+n+1)!}{t!\, n!} \right\} M_{12}^{1+t-r-n} M_{21}^{p+q+n-2m-2s-t}$$

$$\times (M_{12} - M_{21})^{m+r+2s} \tag{23}$$

where $x = \min(p, q)$. This allows us in principle to solve Eq. (20) for the $d_{1,r}^{(1)}$ and upon using the results in the Nth Enskog approximation to Eq. (19) (i.e., with $0 \leqslant r \leqslant N-1$ in the summation), we finally get $D_1^1(V_1)$. Once $D_1^1(V_1)$ is known, it is straightforward to obtain $\hat{\phi}_d(c)$ and D_{12} through Eqs. (10c), (11c), (15), and (16). We thus see that our basic task is the actual solution of the system of linear equations (20) for a given N. And it should be clear that although the algebra may be performed by hand, beyond $N = 2$ or 3 it is much more practical to use a standard numerical algorithm to get the desired answer. This I have done, and, with the aid of the subroutine MATIN2 of the CERN computer library, solved Eqs. (20) for N up to 50 and different μ's. The results of the computations for $\hat{\phi}_d(c)$ and D_{12} are shown in Tables I–IV, some of which also include, for comparison, corresponding results of Tompson and Loyalka.[8]

4. DISCUSSION

A simple analysis of the results in Tables I and II shows that, for $\mu^{-1} \leqslant 1$, our approximate solution for $-\hat{\phi}_d(c)$ [as obtained after using Eqs. (11c), (15), and (20)] is a very good representation of the actual solution to Eq. (13a) over a wide range of values of c ($0.01 \leqslant c \leqslant 4.50$) already for $N = 10$. Increasing the number of polynomials indeed improves the

Table II. Convergence of the Approximate $\hat{\phi}_d(c)$ to the Exact Solution in Terms of the Number N of Sonine Polynomials [cf. Eq. (19)] for Two Values of μ^{-1}

	$-\hat{\Phi}_d(c)$							
	$\mu^{-1} = 0.5$				$\mu^{-1} = 10.0$			
c	10	20	30	50	10	20	30	45
0.01	1.0428	1.0429	1.0429	1.0429	0.3578	0.4219	0.4469	0.4520
0.10	1.0421	1.0422	1.0422	1.0422	0.3549	0.4161	0.4391	0.4437
0.50	1.0265	1.0265	1.0265	1.0265	0.2939	0.3083	0.3081	0.3078
1.00	0.9834	0.9834	0.9834	0.9834	0.1834	0.1808	0.1817	0.1817
2.00	0.8660	0.8660	0.8660	0.8660	0.0950	0.0947	0.0943	0.0944
3.00	0.7554	0.7554	0.7554	0.7554	0.0655	0.0626	0.0631	0.0633
4.00	0.6662	0.6659	0.6659	0.6659	0.0996	0.0484	0.0515	0.0452
5.00	0.6025	0.5949	0.5948	0.5948	1.5902	0.5462	−0.044	0.0718
5.50	0.6667	0.5643	0.5647	0.5655	13.422	−3.543	−1.629	0.9364
6.00	−1.895	0.5410	0.5377	0.5835	−381.5	22.101	5.2920	8.3097

approximation for the higher values of c, but the price to be paid is that the CPU time required is also much greater. On the other hand, for $1 < \mu^{-1} \leqslant 10$, the approximate solution is good only for $0.50 \leqslant c \leqslant 3.40$ even when $N = 50$, and for smaller N it is only reasonable in a narrower range of c's. Note in particular the appearance of negative values for the distribution function, which of course make no physical sense. For higher values of μ^{-1} there are not enough data in the paper by Tompson and Loyalka[8] to compare with. However, on the basis of the limited available information (see Table III), it seems that the approximate solution

Table III. Comparison of Approximate $\hat{\phi}_d(c)$ with Corresponding Values in Tompson and Loyalka[8] (TL) for $\mu^{-1} = 238,0$

	$\hat{\phi}_d(c)$	
c	TL	Present
0.01	0.4535	0.1466
0.05	0.3934	0.1455
0.10	0.2946	0.1421
0.50	0.0727	0.0752
1.00	0.0365	0.0369
3.00	0.0122	0.0119
6.00	0.0061	−13.38

becomes much poorer in general both for $c < 0.50$ and $c > 3.40$ as μ^{-1} increases. Also, apart from running into some numerical troubles that already show up for $N = 50$, the increase in CPU time would make the calculation for bigger N prohibitively expensive. Concerning the diffusion coefficients, Table IV clearly indicates that the numbers obtained with $N = 10$ are within 1% of the exact answers, corroborating our earlier findings,[10,11] while of course if we take $N = 50$, we get practically the same results as Tompson and Loyalka for all the different μ's.

The facts just stated about the approximate values for $-\hat{\phi}_d(c)$ and D_{12} deserve some further elaboration. First of all, it should not be surprising that we get accurate values of D_{12} even when the approximation to $-\hat{\phi}_d(c)$ is not very accurate, due to the equivalence of the Sonine polynomial expansion [Eq. (19)] and the variational method of solution of the linear integral equation [Eq. (13a)], as exposed in Ferziger and Kaper.[2]

Table IV. Ratios of Diffusion Coefficients from Thompson and Loyalka[8] (TL) and Two Values of N to the First Enskog Approximation D_{12CE1} and the Lorentz Approximation D_{12Lor} for Selected μ^{-1} [a]

| | $D_C = D_{12}/D_{12CE1}$ | | | $D_L = D_{12}/D_{12Lor}$ | | |
| | | Present | | | Present | |
μ^{-1}	TL	$N = 50$	$N = 10$	TL	$N = 50$	$N = 10$
0.0718 (28/390)	1.0000	1.0002	1.0002	3.4139	3.4145	3.4145
0.1	1.0003	1.0003	1.0003	2.9314	2.9314	2.9314
0.2	1.0012	1.0011	1.0012	2.1669	2.1669	2.1669
0.5	1.0064	1.0064	1.0063	1.5402	1.5401	1.5401
1.0	1.0190	1.0190	1.0190	1.2733	1.2732	1.2732
2.0	1.0429	1.0429	1.0429	1.1286	1.1286	1.1286
5.0	1.0803	1.0803	1.0802	1.0456	1.0456	1.0455
10.0	1.1017	1.1017[b]	1.1013	1.0209	1.0209[b]	1.0206
50.0	1.1246	1.1246[b]	1.1229	1.0036	1.0036[b]	1.0021
100.0	1.1281	1.1280[b]	1.1259	1.0017	1.0016[b]	1.0000
238.0	1.1302	1.1300[b]	1.1277	1.0007	1.0005[b]	1.0000
∞	1.1318[c]			1.0000[c]		

[a] $D_{12CE1} = \dfrac{4}{3\pi(\mu\sigma_{12})^{1/2}} \left(\dfrac{2k_B T}{m_1}\right)^{1/2} \left[\dfrac{9}{64}(\mu\pi)^{1/2}(1+\mu)^{1/2}\right]$

and

$D_{12Lor} = \dfrac{2}{3\pi^{3/2}n\sigma_{12}^2}\left(\dfrac{2k_B T}{m_1}\right)^{1/2}$

[b] $N = 45$.
[c] Theoretical limit.

Second, the fact that Tompson and Loyalka find that for $\mu^{-1} \ll 1$ the first Enskog approximation to $-\hat{\phi}_d(c)$ is, relatively speaking, quite close to the exact solution is tied to the fact that in the limit $\mu^{-1} = 0$ one obtains the Rayleigh model. In this model the collision operator reduces to its Brownian motion form[14] and the first Sonine polynomial is the exact eigenfunction for diffusion $[-\hat{\phi}_d^R(c) = \frac{3}{8}\mu/\sqrt{\pi}]$. The Brownian motion form is obtained after an expansion of the collision operator in powers of μ^{-1}, keeping terms to $O(\mu^{-1})$ only, and thus it is no surprise that its eigenfunction is a good approximation also when $\mu^{-1} \ll 1$. A similar argument applies to the present results for $\mu^{-1} \leqslant 1$, since the Sonine polynomials are the proper eigenfunctions of the Rayleigh model. On the other hand, it is clear that it would require the infinite series of Sonine polynomials in Eq. (19) to represent the exact distribution function in the Lorentz model $[\mu = 0, -\hat{\phi}_d^L(c) = (\mu/\pi)^{1/2}/c]$, which explains why there is a poorer agreement between the present results and those of Tompson and Loyalka when $\mu^{-1} \gg 1$ and also suggests the source of the difficulty in matching the low-c values of the distribution function for these μ's.

It is important to stress that all the calculations reported in this paper (and also those by Pidduck,[9] Pekeris,[12] and Tompson and Loyalka[8]) are restricted to hard spheres. Nevertheless, by using the analytical results for the bracket integrals obtained by Lindenfeld and Shizgal[13] in the case of repulsive intermolecular interactions, one could perform similar studies for these other models as the one conducted here, simply by replacing the appropriate expressions for d_{pq} in Eqs. (20). The comparison with the exact solutions would be hampered, though, by the fact that, except in the case of Maxwell molecules, where the Sonine polynomials are the proper eigenfunctions and the exact solution for diffusion is thus well known, no study comparable to the one by Tompson and Loyalka exists to my knowledge for general repulsive models. We already know that the convergence of the Sonine polynomial expansion, as it manifests itself in the value of the diffusion coefficient, is slower for hard spheres than for any other repulsive interaction where the force $F \sim r^{-\alpha}$ with $5 \leqslant \alpha < \infty$. And, on the basis of this information and the analysis of the results of the present paper, it is not therefore unreasonable to expect that the approximate Chapman–Enskog velocity distribution function for tracer diffusion, expressed as a finite series of N Sonine polynomials (with a similar relationship between the required N, μ, and the range of c's where the accuracy would be as good as the one illustrated here for hard spheres) will provide, in the case of repulsive intermolecular potentials, a good representation of the actual distribution function.

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