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Large Energy Behavior of the Velocity Distribution for the Hard-Sphere Gas

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The initial-value problem for the Boltzmann–Lorentz equation for hard spheres at zero temperature is shown to be ill defined, the general solution depending on an arbitrary function. The uniqueness of the solution can be obtained by imposing the conservation of the number of particles (Carleman's type of condition does not suffice). The linearized Boltzmann equation for hard spheres is then analyzed, as it occurs in Enskog's method for calculating transport coefficients. It is demonstrated that in the case of viscosity and diffusion it is necessary to add supplementary conditions to obtain the uniqueness of the solution. The nonuniform character of Enskog's expansion and violation of positivity in the large velocity region are exhibited.

KEY WORDS: Hard-sphere gas; Boltzmann equation; Boltzmann–Lorentz equation; Chapman–Enskog developments.

1. INTRODUCTION

In this paper, we study some questions related to the kinetic theory of the hard-sphere gas.

There has been recently much interest in exact solutions in kinetic theory.[(1)] Most efforts have been directed toward solutions for the space-independent problem.[3] These are rather exceptional nonequilibrium situations, as in gases typical nonequilibrium processes are basically space

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[3] Nevertheless Bobylev[(2)] has already pointed out that once a solution of the nonlinear kinetic model is known, a centrosymmetric inhomogeneous solution can be constructed by the method of Nikolski'i.

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dependent—one may cite (among others) plane shock waves [a still formidable problem of kinetic theory at nonvanishing and positive $(M - 1)$, M Mach number], Couette flows, heat conduction around some heated or cooled bodies, and so on. In these inhomogeneous situations the Chapman–Enskog theory yields a method for "solving" the kinetic problem in the limit where the macroscopic quantities have small variations on distances of the order of the mean free path.

The nature of the approximation involved by the Chapman–Enskog theory is largely unknown, with the noticeable exception of the perfect Lorentz gas with fixed hard-sphere scatterers.[3] However, none of the problems considered in the present article appear in this model. Actually, the particle velocity has a constant modulus therein, so that no trouble may come from the large velocity region. And our analysis shows that it is precisely at large energies that restrictions must be imposed on distribution functions in order to make the method of Enskog's expansion well defined.

Indeed, in the Chapman–Enskog theory the computation of transport coefficients for gases requires the solution of linear integral equations. In Section 2 we show that the uniqueness of solution of these equations poses rather subtle problems because of the existence of slowly (powerlike) decaying solutions at large velocities.

To give an idea of these difficulties we consider in detail in the forthcoming part of this introduction the diffusion at zero temperature within the Boltzmann–Lorentz theory, which presents a simple evolution problem with a nonunique solution for Cauchy data. To introduce this question we give first the equations of Boltzmann and Boltzmann and Lorentz for hard spheres.

The full nonlinear Boltzmann equation for hard spheres is

$$\left(\frac{\partial}{\partial t} + \mathbf{v}\cdot\frac{\partial}{\partial \mathbf{r}}\right) f(\mathbf{r},\mathbf{v},t) = \frac{\sigma^2}{4}\int d\hat{n}\int d\mathbf{v}_1 |\mathbf{v}-\mathbf{v}_1| \times\left[f\left(\mathbf{r}, \frac{\mathbf{v}+\mathbf{v}_1}{2} - \frac{|\mathbf{v}-\mathbf{v}_1|}{2}\hat{n}, t\right) \times f\left(\mathbf{r}, \frac{\mathbf{v}+\mathbf{v}_1}{2} + \frac{|\mathbf{v}-\mathbf{v}_1|}{2}\hat{n}, t\right) - f(\mathbf{r},\mathbf{v}_1,t) f(\mathbf{r},\mathbf{v},t)\right] \tag{1.1}$$

where $f(\mathbf{r}, \mathbf{v}, t)$ is the time-dependent density in the position–velocity space $(\mathbf{r}, \mathbf{v})$, σ is the sphere diameter, and $\hat{n}$ a vector running freely on a unit sphere.

This equation has as steady uniform solution the equilibrium Maxwell distribution

$$f^{\mathrm{eq}}(v) = n\left(\frac{m}{2\pi kT}\right)^{3/2}\exp\left(-\frac{mv^2}{2kT}\right) \tag{1.2}$$

where $v = |\mathbf{v}|$, n is the number density of the spheres, m their mass, T is the temperature, and k is the Boltzmann constant.

We shall be mainly concerned with the linearized Boltzmann equation, since this is what is needed for computing transport coefficients. Let $\delta f = (f - f^{\mathrm{eq}})$ be a small deviation of f near its equilibrium form as given by Eq. (1.2). Let us put

$$\delta f(\mathbf{v}) = f^{\mathrm{eq}}(v)\,\psi\left[\mathbf{v}\left(\frac{m}{2kT}\right)^{1/2}\right]$$

and introduce the dimensionless velocity

$$\mathbf{c} = \mathbf{v}\left(\frac{m}{2kT}\right)^{1/2}$$

Expanding now the right-hand side of (1.1) around f^{eq} to first order in δf, one gets the linearized collision term in the form

$$n\sigma^2\left(\frac{2\pi kT}{m}\right)^{1/2} f^{\mathrm{eq}}(v)\left[J^B\psi\right](\mathbf{c})$$

where J^B is the linear integral operator defined with the dimensionless quantities as

$$\begin{aligned}\left[J^B\psi\right](\mathbf{c}) = \frac{1}{4\pi^2}\int d\hat{n}\int d\mathbf{c}_1 e^{-c_1^2}|\mathbf{c}-\mathbf{c}_1| \\ \times\left[\psi\left(\frac{\mathbf{c}+\mathbf{c}_1}{2} + \frac{|\mathbf{c}-\mathbf{c}_1|}{2}\hat{n}\right) + \psi\left(\frac{\mathbf{c}+\mathbf{c}_1}{2} - \frac{|\mathbf{c}-\mathbf{c}_1|}{2}\hat{n}\right)\right. \\ \left. -\psi(\mathbf{c}_1) - \psi(\mathbf{c})\right]\end{aligned} \tag{1.3}$$

Hilbert[4,5] found a simpler expression for J^B by performing the $\hat{n}$ integral in (1.3)

$$\left[J^B\psi\right](\mathbf{c}) = \frac{1}{\pi}\int d\mathbf{c}_1 e^{-c_1^2}K^B(\mathbf{c},\mathbf{c}_1)\psi(\mathbf{c}_1) - \left[1 + \left(2c + \frac{1}{c}\right)I(c)\right]e^{-c^2}\psi(c) \tag{1.4a}$$

where

$$K_B(\mathbf{c},\mathbf{c}_1) = \frac{2}{|\mathbf{c}-\mathbf{c}_1|}\exp\left(\frac{|\mathbf{c}\times\mathbf{c}_1|^2}{|\mathbf{c}-\mathbf{c}_1|^2}\right) - |\mathbf{c}-\mathbf{c}_1| \tag{1.4b}$$

and where

$$I(c) = e^{c^2} \int_0^c dx\, e^{-x^2}, \qquad c = |\mathbf{c}| \tag{1.4c}$$

Consider now the Boltzmann–Lorentz kinetic theory describing the diffusion of dilute tagged hard spheres in a gas of mechanically identical particles at equilibrium. Let $f_s(\mathbf{r}, \mathbf{v}, t)$ be the density of these tagged hard spheres. Its evolution obeys the equation

$$\left(\frac{\partial}{\partial t} + \mathbf{v} \cdot \frac{\partial}{\partial \mathbf{r}} \right) f_s(\mathbf{r}, \mathbf{v}, t) = \left[C^{\mathrm{BL}} f_s \right](\mathbf{r}, \mathbf{v}, t) \tag{1.5a}$$

where

$$\begin{aligned} \left[C^{\mathrm{BL}} f_s \right](\mathbf{r}, \mathbf{v}, t) = \frac{\sigma^2}{4} \int d\hat{n} \int d\mathbf{v}_1 |\mathbf{v} - \mathbf{v}_1| \\ \times \left\{ f_s\left(\mathbf{r}, \frac{\mathbf{v} + \mathbf{v}_1}{2} - \hat{n} \frac{|\mathbf{v} - \mathbf{v}_1|}{2}, t \right) f^{\mathrm{eq}}\left(\frac{\mathbf{v} + \mathbf{v}_1}{2} + \hat{n} \frac{|\mathbf{v} - \mathbf{v}_1|}{2} \right) \right. \\ \left. - f_s(\mathbf{r}, \mathbf{v}, t) f^{\mathrm{eq}}(v_1) \right\} \end{aligned} \tag{1.5b}$$

The notations being the same as in Eqs. (1.1) and (1.2).

The linear operator C^{BL} can be put in the Hilbert form. For that purpose let us introduce the function χ by

$$f_s(\mathbf{v}) = n_s \left(\frac{m}{2\pi k T} \right)^{3/2} \exp\left(-\frac{m v^2}{2kT} \right) \left[1 + \chi(\mathbf{c}) \right]$$

with n_s being the tagged spheres number density, and $\mathbf{c} = \mathbf{v}(m/2kT)^{1/2}$, so that

$$\left[C^{\mathrm{BL}} f_s \right](\mathbf{v}) = n_s \sigma^2 (2\pi k T/m)^{1/2} f^{\mathrm{eq}}(v) \left[J^{\mathrm{BL}} \chi \right](\mathbf{c})$$

where

$$\left[J^{\mathrm{BL}} \chi \right](\mathbf{c}) = \frac{1}{\pi} \int d\mathbf{c}_1 e^{-c_1^2} K^{\mathrm{BL}}(\mathbf{c}, \mathbf{c}_1) \chi(\mathbf{c}_1) - \left[1 + \left(2c + \frac{1}{c} \right) I(c) \right] e^{-c^2} \chi(\mathbf{c}) \tag{1.6a}$$

and

$$K^{\mathrm{BL}}(\mathbf{c}, \mathbf{c}_1) = \frac{1}{|\mathbf{c} - \mathbf{c}_1|} \exp\left(\frac{|c \times c_1|^2}{|c - c_1|^2} \right) \tag{1.6b}$$

$I(c)$ being defined in (1.4c).

The proof of existence of a unique solution at any time of either Eq. (1.1) or (1.5) is very difficult. A great achievement in this field is the theory of Carleman[6] developed for the spatially homogeneous version of the Boltzmann equation. In what follows we shall illustrate on an example the difficulties involved in this sort of problem.

Consider the Boltzmann–Lorentz equation (1.5) when the function f_s does not depend on $\mathbf{r}$. Let us assume furthermore that the temperature in f^{eq} is zero. Whence Eq. (1.5) takes the explicit form

$$\frac{\partial}{\partial t} f_s(\mathbf{v},t) = \frac{n\sigma^2}{4} \int d\hat{n} \int d\mathbf{v}_1 |\mathbf{v}-\mathbf{v}_1| \times \left[f_s\left(\frac{\mathbf{v}+\mathbf{v}_1}{2} - \hat{n}\frac{|\mathbf{v}-\mathbf{v}_1|}{2}, t \right) \delta\left(\frac{\mathbf{v}+\mathbf{v}_1}{2} + \hat{n}\frac{|\mathbf{v}-\mathbf{v}_1|}{2} \right) - \delta(\mathbf{v}_1) f_s(\mathbf{v},t) \right] \tag{1.7}$$

δ being the Dirac distribution.

Consider now the evolution of the isotropic part of f_s, i.e., of

$$\varphi(v,t) = \frac{1}{4\pi} \int d\hat{v}\, f_s(\mathbf{v},t)$$

A direct calculation gives from (1.7)

$$\frac{\partial}{\partial t} \varphi(v,t) = n\pi\sigma^2 \left[\frac{2}{v} \int_v^\infty dx\, x\varphi(x,t) - v\varphi(v,t) \right] \tag{1.8}$$

A similar equation was considered by Aizenman and Bak[7] in a problem of reacting polymers. The equation (1.8) can be solved explicitly.

Put

$$\varphi(v,t) = \frac{1}{v} \exp(-n\pi\sigma^2 vt) \tilde{\Gamma}(v, n\pi\sigma^2 t)$$

which defines a new function $\tilde{\Gamma}$. From Eq. (1.8) $\tilde{\Gamma}$ is the solution of

$$\frac{\partial}{\partial \tau} \tilde{\Gamma}(v,\tau) = 2e^{v\tau} \int_v^\infty dx\, e^{-x\tau} \tilde{\Gamma}(x,\tau) \tag{1.9}$$

where τ is the dimensionless time $\tau \equiv n\pi\sigma^2 t$. Differentiating Eq. (1.9) once with respect to v and twice with respect to τ, one gets

$$\frac{\partial^4}{\partial \tau^3 \partial v} \tilde{\Gamma} = \tau \frac{\partial^3}{\partial \tau^3} \tilde{\Gamma} \tag{1.10}$$

Equation (1.10) can be solved with respect to v

$$\frac{\partial^3}{\partial \tau^3} \tilde{\Gamma}(v,\tau) = \alpha(\tau) e^{v\tau}$$

where α is an arbitrary function of τ. Integrating now with respect to τ and choosing the integration constants in such a way that $\tilde{\Gamma}$ satisfies Eq. (1.9), one obtains the general solution of Eq. (1.8) in the form

$$\varphi(v,t) = \frac{1}{v}\frac{\partial^2}{\partial v^2}\left\{\exp(-n\pi\sigma^2 vt)\left[\int_v^\infty dx\int_x^\infty dy\, y\varphi(y,0) + \int_0^{n\pi\sigma^2 t} d\tau\,\alpha(\tau)\exp(v\tau)\right]\right\} \tag{1.11}$$

Aizenman and Bak discuss a particular case of this solution corresponding to

$$\alpha(\tau) = \tfrac{1}{2}\exp(a\tau), \qquad a > 0$$

If one thinks to the origin of the problem [i.e., Eq. (1.8)], the form of the solution (1.11) is quite surprising, because the value of $\varphi(v,t)$ at time t does not depend only on $\varphi(v,0)$, but also on an arbitrary function α. This is unusual, because the equation of evolution for φ is first order in time.

The fact that the evolution governed by Eq. (1.8) is ill-defined is a consequence of allowing a too large function space containing all the solutions (1.11). Here the supplementary condition to be imposed on $\varphi(v,t)$, making the solution unique, is the conservation of the number of particles, that is the norm $\int_0^\infty dv\, v^2\, \varphi(v,t)$ must be independent of t.

This condition is not obvious, since it is usually claimed that the conservation of the number of particles is a consequence of the kinetic equation, rather than a supplementary condition.

It is to be noted here that Cornille and Gervois[8] have already shown that conservation of energy was a restricting condition on isotropic homogeneous solutions of the linearized Boltzmann equation, eliminating power-like ($\sim v^{-6}$) decaying distributions. Hauge and Praestgard[9] have also considered the possibility of solutions of the linearized Boltzmann equation with algebraic tails.

Indeed, the explicit solution (1.11) allows one to understand why the conservation law is not a simple consequence of the original equation (1.8). Take $\alpha(\tau) = \delta(\tau - \tau_0)$, where δ is the Dirac distribution. This yields a solution of (1.8) of the form

$$\varphi_\delta(v,t) = (n\pi\sigma^2)^2\theta(t-t_0)\frac{(t-t_0)^2}{v}\exp\left[-n\pi\sigma^2 v(t-t_0)\right] \tag{1.12}$$

where θ is the step function. The norm of this solution (as defined previously) is

$$\int_0^\infty dv\, v^2\varphi_\delta(v,t) = \theta(t-t_0)$$

It is obviously not a constant. The usual argument showing the conservation of the norm from (1.8) fails here because

$$\frac{\partial}{\partial t}\int_0^\infty dv\, v^2\varphi_\delta(v,t) = \delta(t-t_0) \neq \int_0^\infty dv\, v^2 \frac{\partial}{\partial t}\varphi_\delta(v,t) = 0$$

so that multiplying Eq. (1.8) by v^2 and integrating with respect to v one gets zero on the right-hand side, although the left-hand side is not the time derivative of the norm of φ_δ, because the t derivation and the v integration do not commute for φ_δ.

If one *imposes* that $\int_0^\infty dv\, v^2\, \varphi(v,t)$ is constant, then this implies $\alpha = 0$, so that requiring that the number of particles is conserved at any time makes the solution of (1.8) unique.

To show this let us notice first that

$$\int_0^\infty dv\, v \frac{\partial^2}{\partial v^2}\left[e^{-v\tau}\int_v^\infty dx \int_x^\infty dy\, y\varphi(y,0)\right]$$
$$= -\int_0^\infty dx \int_x^\infty dy\, y\varphi(y,0) = \int_0^\infty dv\, v^2\varphi(v,0)$$

Thus to keep constant the norm of φ, one must have from (1.11)

$$\int_0^\infty dv\, v \frac{\partial^2}{\partial v^2}\left[e^{-v\tau}\int_0^\tau d\tau_1 e^{v\tau_1}\alpha(\tau_1)\right] = 0, \qquad \forall \tau$$

Integrating by parts, one finds

$$\int_0^\tau d\tau_1 \alpha(\tau_1) = 0 \qquad \forall \tau$$

Thus α vanishes almost everywhere for positive times.

It is of interest to notice that Carleman's type of condition *does not* imply the uniqueness of solution of (1.8). Roughly speaking in theorems of Carleman's type the uniqueness of solution is established for continuous velocity distributions decaying faster than some fixed power v^{-x}, at large velocities ($v \to \infty$). In the present case this condition is equivalent to making the integral of the right-hand side of Eq. (1.8) vanish with the measure $v^2 dv$. One can verify that this is satisfied whenever φ is continuous and decays faster than v^{-4} at $v \to \infty$. As shown before, this implies $\int_0^\infty dv\, v^2\, \partial\varphi/\partial t = 0$, but not $(\partial/\partial t)\int_0^\infty dv\, v^2\varphi(v,t) = 0$. And the previous example shows that a solution of Carleman's type exists for (1.8) with a nonconserved norm. It would be of interest to understand why this Carleman type condition is not sufficient to guarantee the uniqueness for our particular model.

In what follows, we shall be concerned with the solution of the Boltzmann equation in the form needed for the Enskog expansion. For that purpose we shall give some details on this to make our point as clear as possible.

In the Enskog expansion the Boltzmann equation is solved by iteration.[4] The expansion is made in the limit of small gradients of temperature $T(\mathbf{r},t)$, velocity $u(\mathbf{r},t)$, and density $n(\mathbf{r},t)$. The lowest-order solution has the local equilibrium form

$$f^{(0)}(\mathbf{r},\mathbf{v},t) = n(\mathbf{r},t)\left[\frac{m}{2kT(\mathbf{r},t)}\right]^{3/2}\exp\left[-\frac{m(\mathbf{v}-\mathbf{u}(\mathbf{r},t))^2}{2kT(\mathbf{r},t)}\right] \tag{1.13}$$

As a consequence of the local conservation laws, the quantities n, $\mathbf{u}$, T satisfy the Euler fluid equations at the lowest order in the gradients, and one has

$$\left(\frac{\partial}{\partial t}+\mathbf{v}\cdot\frac{\partial}{\partial \mathbf{r}}\right)f^{(0)}(\mathbf{r},\mathbf{v},t) = \left[\frac{1}{T}\left(\frac{2kT}{m}\right)^{1/2}\left(C^2-\frac{5}{2}\right)\mathbf{C}\cdot\frac{\partial T}{\partial \mathbf{r}} + 2\mathbf{C}^0\mathbf{C}:\nabla\mathbf{u}^s\right]f^{(0)}(\mathbf{r},\mathbf{v},t) \tag{1.14}$$

where $\mathbf{C}=(m/2kT)[\mathbf{v}-\mathbf{u}(\mathbf{r},t)]$, $\mathbf{C}^0\mathbf{C}$ is the traceless tensor defined from $\mathbf{CC}$ as

$$\mathbf{C}^0\mathbf{C} = \mathbf{CC} - \frac{\mathbb{1}}{3}(\mathrm{Tr}\mathbf{CC})$$

$\mathbb{1}$ being the unit tensor, and $\nabla\mathbf{u}^s$ is the symmetric rate of strain tensor with Cartesian components

$$(\nabla\mathbf{u}^s)_{ij} = \frac{1}{2}\left(\frac{\partial u_i}{\partial r_j}+\frac{\partial u_j}{\partial r_i}\right)$$

The free streaming operator acting on the local equilibrium distribution, as given by (1.14), gives a source term for the first-order perturbation to $f^{(0)}$. This first-order perturbation reads

$$f^{(1)} = f^{(0)}\psi$$

where ψ satisfies an integral equation wherein the inhomogeneous part is computed from the right-hand side of (1.14)

$$\sqrt{\pi}\, n\sigma^2[J^B\psi] = \frac{1}{T}\left(C^2-\frac{5}{2}\right)\mathbf{C}\cdot\frac{\partial T}{\partial \mathbf{r}} + 2\mathbf{C}^0\mathbf{C}:\nabla\mathbf{u}^s\left(\frac{m}{2kT}\right)^{1/2} \tag{1.15}$$

J^B being the linear integral operator already introduced in (1.4a).

The usual way[5] of solving this kind of integral equation is by means of spectral theory.[(12)] This is questionable (see Uhlenbeck and Ford[(13)] and

[4] A good modern exposition of the Chapman–Enskog method can be found in Ref. 10.

[5] With the noticeable exception of Pekeris and co-workers.[(5,11)]

references given therein), as the recourse to spectral theory implies severe restriction on the function space. That is, integrals such as $\int d\mathbf{v}\, f^{(0)}\psi^2$ must converge, although the square of a distribution function has no physical meaning, contrary to the squared modulus of solutions of wave equations in quantum mechanics.

As we shall see in what follows the condition imposed to get a unique solution for (1.15) is of Carleman's type. However, the exact situation is rather complicated. In the case of the heat conductivity term the algebraic decay of ψ at large velocities (in short-algebraic tail in ψ) is excluded by the integral equation itself, a fact which does not appear in the analysis of Pekeris and Alterman.[11] But the situation is completely different for the shear viscosity contribution, and for the self-diffusion in the Boltzmann–Lorentz equation. The algebraic tails in the corresponding contributions to ψ and χ must be eliminated by an extra assumption, that does not result from the kinetic equation itself or from Enskog's method.

From the conceptual point of view this need of supplementary assumptions is difficult to accept. As will appear in our analysis, the distribution functions with algebraic tails are solutions of the homogeneous part of (1.15) and these solutions cannot be eliminated by an Enskog condition ($\equiv$ no contribution of $f^{(1)}$ to the hydrodynamic moments) when they depend on higher spherical harmonics of velocity as they do not contribute to the hydrodynamic moments. Whence it is possible that steady solutions of the (nonisotropic) Boltzmann equation exist with algebraic tails in higher spherical harmonics. This kind of solution could be obtained for instance in a perturbative approach. Indeed, this violates the H theorem. To reconcile the two points of view it is possible that the steady solutions of this kind have *necessarily* negative parts, so that the H theorem cannot be applied to them: it assumes that distribution functions are positive, and one has to take their logarithm. This view is reinforced by the fact that perturbations with algebraic tails heavily dominate the zeroth-order Maxwell–Boltzmann distribution at large velocities. As the sign of this perturbation is certainly not constant, owing to its angular dependence, there are regions in the velocity space wherein the total distribution is negative at large velocities.

Nevertheless one must recognize, that, even if one eliminates algebraic tails in the solution of (1.15), the perturbation of the velocity distribution dominates at large velocities. This is to be shown in this paper, where we shall compute the *exact* large-energy behavior of the solution of (1.15). This shows that the Enskog expansion is not uniform, contrary to the assumption of Chapman and Cowling.[14] It remains thus to show that the Chapman–Enskog expansion, together with some assumptions eliminating algebraic tails, yields finally positive velocity distributions. This is presumably a difficult task.

2. CALCULATION OF TRANSPORT COEFFICIENTS: ANALYSIS OF ENSKOG'S METHOD

2.1. Self-Diffusion

The self-diffusion process can be analyzed by applying Enskog's method to the Boltzmann–Lorentz equation (1.5). The basic idea is again to assume that the velocity distribution of diffusing particles becomes rapidly thermalized by the host hard-sphere gas (after a time of the order of mean free time), whereas their number density $n_s(\mathbf{r}, t)$ relaxes to equilibrium on a much longer time scale. Consequently, the zeroth-order approximation to the solution of (1.5) is written as

$$f_s^{(0)}(\mathbf{r}, \mathbf{v}, t) = n_s(\mathbf{r}, t)\left(\frac{m}{2\pi kT}\right)^{3/2}\exp\left(-\frac{mv^2}{2kT}\right) \tag{2.1}$$

where T is the temperature of the host fluid. The local equilibrium state $f_s^{(0)}$ is invariant under collisions and yields a vanishing current density

$$\mathbf{j}^{(0)}(\mathbf{r}, t) = \int d\mathbf{v}\, \mathbf{v} f_s^{(0)}(\mathbf{r}, \mathbf{v}, t) \equiv 0$$

The conservation of the number of particles implies that within this approximation the number density n_s does not depend on time. The free streaming term in Eq. (1.5), calculated at local equilibrium (2.1), reduces thus to $\mathbf{v} \cdot (\partial/\partial \mathbf{r}) f_s^{(0)}$, and is to be balanced by the lowest-order effect of collisions involving the first Enskog correction $f_s^{(1)}$. The function $f_s^{(1)}$ satisfies the inhomogeneous equation

$$\mathbf{v} \cdot \frac{\partial}{\partial \mathbf{r}} f_s^{(0)}(\mathbf{v}) = [C^{\mathrm{BL}}] f_s^{(1)}(\mathbf{v}) \tag{2.2}$$

supplemented with the condition

$$n_s^{(1)}(\mathbf{r}, t) = \int d\mathbf{v}\, f_s^{(1)}(\mathbf{r}, \mathbf{v}, t) \equiv 0 \tag{2.3}$$

Putting

$$f_s^{(1)}(\mathbf{v}) = f_s^{(0)}(\mathbf{v}) \chi(\mathbf{c})$$

with $\mathbf{c} = (m/2kT)^{1/2} v$, and using Eqs. (1.5b), (1.6) one finds

$$\frac{1}{n_s} \mathbf{c} \cdot \frac{\partial}{\partial \mathbf{r}} n_s = \sqrt{\pi}\, n\sigma^2 [J^{\mathrm{LB}} \chi](\mathbf{c}) \tag{2.4}$$

Equation (2.4) can be greatly simplified owing to the rotational invariance of the operator J^{LB}. A convenient representation of χ is

$$n_s \chi(\mathbf{c}) = \frac{1}{(\pi n \sigma^2)^{1/2}} \mathcal{D}(c) \hat{c} \cdot \frac{\partial}{\partial \mathbf{r}} n_s \tag{2.5}$$

The correction $f_s^{(1)}$ satisfies then the subsidiary condition (2.3), and Eq. (1.6a) together with the relation

$$\int d\hat{c}_1(\hat{c}\cdot\hat{c}_1)K^{\mathrm{BL}}(\mathbf{c},\mathbf{c}_1) \underset{c>c_1}{=} \frac{4\pi}{c}\left[\frac{1}{c_1}+\left(1-\frac{1}{c_1^2}\right)I(c_1)\right] \tag{2.6}$$

leads to an integral inhomogeneous equation for the scalar function $\mathfrak{D}$

$$4\int_0^c dx\left[x_1(x^2-1)I(x)\right]e^{-x^2}\mathfrak{D}(x)+4\left[c+(c^2-1)I(c)\right]$$
$$\times\int_c^\infty dx\, e^{-x^2}\mathfrak{D}(x)-\left[c^2+(c+2c^3)I(c)\right]e^{-c^2}\mathfrak{D}(c)=c^3 \tag{2.7}$$

It will be convenient to define a new function E as

$$E(c)=\int_c^\infty dx\, e^{-x^2}\mathfrak{D}(x) \tag{2.8}$$

Taking the derivative with respect to c (hereafter denoted by a prime) of both sides of Eq. (2.7) one finds a second-order differential equation

$$\left\{\left[c^2+(c+2c^3)I(c)\right]E'(c)\right\}'+4c^2\left[1+2cI(c)\right]E(c)=3c^2 \tag{2.9}$$

when $c\to 0$

$$I(c)=c+\tfrac{2}{3}c^3+0(c^5)$$

so that the asymptotic form of (2.9) in this limit reads

$$\left[2c^2E'(c)\right]'+4c^2E(c)=3c^2 \tag{2.10}$$

with a general solution

$$\tfrac{3}{4}+(1/x)\left[\alpha_1\cos(\sqrt{2}\,x)+\alpha_2\sin(\sqrt{2}\,x)\right]$$

where α_1, α_2 are constants. A direct calculation of the limit $c\to 0$ of both sides of Eq. (2.7) shows that α_1 must vanish if $\mathfrak{D}$ obtained from (2.8) is to satisfy the integral equation (2.7). The constant α_2 remains, however, arbitrary, which means that there exists a one-parameter family of solutions of Eq. (2.7), and thus of Enskog's equations (2.2) and (2.3). In order to further clarify this unsatisfactory situation let us turn now to the asymptotic analysis of Eq. (2.9) for $c\to\infty$. As

$$I(c) \underset{c\to\infty}{\simeq} \frac{\sqrt{\pi}}{2}e^{c^2}$$

the large velocity behavior of $E(c)$ is governed by the equation

$$\left\{(c+2c^3)e^{c^2}E'(c)\right\}'+8c^3e^{c^2}E(c)=\frac{6}{\sqrt{\pi}}c^2 \tag{2.11}$$

whose general solution has the asymptotic form

$$-\frac{3}{2\sqrt{\pi}}\frac{1}{c}e^{-c^2}+\frac{1}{c^2}\left[a_1+a_2e^{-c^2}\right] \tag{2.12}$$

where a_1, a_2 are constants. The first term corresponds to a solution of the inhomogeneous equation (2.11), whereas the remaining two terms describe the large c asymptotics of the solutions of the homogeneous equations

$$\left[c^2+(c+2c^3)I(c)E_0'(c)\right]'+4\left[c^2+2c^3I(c)\right]E_0(c)=0 \tag{2.13}$$

The condition at $c=0$ determines solutions of (2.13) up to a multiplicative constant, fixing the ratio a_1/a_2. We have analyzed Eq. (2.13) by a method of numerical integration establishing the following result:

$$\text{if}\quad E_0(0)=1,\qquad \text{then}\quad E_0(c)\underset{c\to\infty}{\simeq}(1.55\pm 0.01)c^{-2}$$

Hence, any nonzero solution of Eq. (2.13), regular at $c=0$, has the asymptotic behavior

$$E_0(c)\underset{c\to\infty}{\simeq}a_1c^{-2}\qquad\text{with}\quad a_1\neq 0$$

[see Eq. (2.12)]. This means that the large velocity behavior of the first Enskog correction $f_s^{(1)}$ is in general given by

$$f_s^{(1)}\simeq\frac{1}{v^3}\left(\frac{2a_1}{n\pi^2\sigma^2}\right)\left(\hat{v}\cdot\frac{\partial n_s}{\partial \mathbf{r}}\right) \tag{2.14}$$

Such a slow, powerlike decay is incompatible with the existence of a finite current density of diffusing particles.

It is only when

$$|\mathbf{j}^{(1)}|=\left|\int d\mathbf{v}\,\mathbf{v}f_s\right|<\infty \tag{2.15}$$

that one finds $\mathbf{j}^{(1)}=D(\partial n_s/\partial\mathbf{r})$, with a finite self-diffusion coefficient

$$D=\frac{4}{3n\sigma^2}\left(\frac{2\pi kT}{m}\right)^{1/2}\int_0^\infty dc\,c^3e^{-c^2}\mathfrak{D}(c)$$

It is, however, to be stressed that the condition (2.15) must be added to Enskog's equations (2.2) and (2.3) in order to make them represent a well-defined problem (i.e., leading to a unique solution for $f^{(1)}$). Of course, one could think of more restrictive requirements, as for example those used in the spectral theory approach. There is thus an element of arbitrariness in the original formulation of the theory. Condition (2.15) is of Carleman's type, as it is equivalent to assuming that the distribution $f_s^{(1)}$ decays for large velocities faster than v^{-4}. It represents the existence of the self-diffusion coefficient D (and the uniqueness of the solution to Enskog's equation). One could say that in order to make Enskog's method well defined the existence of transport coefficients must be assumed.

When $a_1 = 0$, Eq. (2.12) yields the exact asymptotic behavior of $E(c)$ at $c \to \infty$

$$E(c) \simeq -\frac{3}{2\sqrt{\pi}}\,\frac{1}{c}\,e^{-c^2} \tag{2.16}$$

The corresponding large velocity form of $f_s^{(1)}$ reads

$$f_s^{(1)}(v) \underset{v\to\infty}{\simeq} -\frac{3}{\pi n^2\sigma^2}\,f^{\text{eq}}(v)\left(\hat{v}\cdot\frac{\partial}{\partial \mathbf{r}}\,n_s\right)$$

For sufficiently weak gradients of density $f_s^{(1)}$ is thus small (in the large velocity region) compared to the local equilibrium term $f_s^{(0)}$. We shall show in the next section that this is no longer the case when Enskog's expansion is applied to other transport processes.

2.2. Heat Conductivity

The internal energy flow in a gas can be characterized by the heat current density

$$\mathbf{q}(\mathbf{r},t) = \int d\mathbf{v}\big[\mathbf{v}-\mathbf{u}(\mathbf{r},t)\big]\,\frac{m}{2}\,\big[\mathbf{v}-\mathbf{u}(\mathbf{r},t)\big]^2 f(\mathbf{r},\mathbf{v},t)$$

According to Enskog's expansion the lowest-order contribution comes here from the first correction $f^{(1)}$, as the local equilibrium distribution $f^{(0)}$ does not contribute to $\mathbf{q}$. The heat conduction term in $f^{(1)}$ is conveniently written as

$$f_{\text{hc}}^{(1)} = f^{(0)}\psi_{\text{hc}} \tag{2.17}$$

where

$$\psi_{\text{hc}}(\mathbf{C}) = \frac{1}{(\pi n\sigma^2)^{1/2}}\,\mathscr{C}(c)\,\frac{1}{T}\left(\hat{c}\cdot\frac{\partial T}{\partial \mathbf{r}}\right)$$

[see Eq. (1.15)]. The corresponding heat current obeys Fourier's law

$$\mathbf{q}^{(1)}(\mathbf{r},t) = \kappa\,\frac{\partial T(\mathbf{r},t)}{\partial \mathbf{r}}$$

with the heat conductivity coefficient given by

$$\kappa = \frac{4k}{3\pi\sigma^2}\left(\frac{2kT}{m}\right)^{1/2}\int_0^\infty dc\,c^5 e^{-c^2}\mathscr{C}(c) \tag{2.18}$$

It is convenient to define a new function B as

$$B(c) = \int_c^\infty dx\,e^{-x^2}\mathscr{C}(x) \tag{2.19}$$

Inserting then Eq. (2.17) into Eq. (1.15) and using formula (1.4) together with the relation

$$\int d\hat{c}_1(\hat{c}\cdot\hat{c}_1)K^B(\mathbf{c},\mathbf{c}_1) \underset{c>c_1}{=} 4\pi\left\{\frac{1}{3}c_1 - \frac{1}{15}\frac{c_1^3}{c^2} + \frac{2}{c}\left[\frac{1}{c_1} + \left(1 - \frac{1}{c_1^2}\right)I(c_1)\right]\right\}$$

one obtains an integral equation of the form

$$\begin{aligned}&\left[c^2 + (c + 2c^3)I(c)\right]B'(c) + \left[8c - \tfrac{4}{15}c^5 + 8(c^2-1)I(c)\right]B(c)\\ &\quad - \int_0^c dx\left[8x - \tfrac{4}{15}x^5 + 8(x^2-1)I(x)\right]B'(x)\\ &\quad - \tfrac{4}{3}c^2\int_0^c dx\, x^3B'(x) - \tfrac{4}{3}c^3\int_c^\infty dx\, x^2B'(x) = c^5 - \tfrac{5}{2}c^3 \end{aligned}\tag{2.20}$$

The possibility of deriving from (2.20) a fourth-order differential equation for function B has been exploited by a number of authors.[11,12] We shall show later on that one can do even better, reducing the problem to solving a second-order equation. However, it will be sufficient for the present purposes to consider simply the relation obtained by taking the first derivative of Eq. (2.20) with respect to c. One gets then

$$\begin{aligned}&\left\{\left[c^2 + (c + 2c^3)I(c)\right]B'(c)\right\}' + \left[-\tfrac{4}{3}c^4 + 8c^2 + 16c^3I(c)\right]B(c)\\ &\quad - \tfrac{8}{3}c\int_0^c dx\, x^3B'(x) - 4c^2\int_c^\infty dx\, x^2B'(x) = 5\left(c^4 - \tfrac{3}{2}c^2\right)\end{aligned}\tag{2.21}$$

Equations (2.20) and (2.21) should be supplemented with Enskog's condition (no contribution from $f^{(1)}$ to the mean velocity)

$$\int_0^\infty dc\, c^3B'(c) = 0 \tag{2.22}$$

Indeed, one can verify, that the function of the form $a_1e^{-c^2}$, where a_1 is any constant, is a solution of the homogeneous equation associated with (2.20). Enskog's condition serves thus for fixing the constant a_1 in the solution of the inhomogeneous integral equation (2.20).

Equations (2.21) and (2.22) imply that the asymptotic behavior of $B(c)$ for $c\to\infty$ is described by the equation

$$\left[c^3e^{c^2}B'(c)\right]' + 8c^3e^{c^2}B(c) = \left(5/\sqrt{\pi}\right)\left(c^4 - \tfrac{3}{2}c^2\right)\tag{2.23}$$

whose general solution is

$$\left(-\frac{5}{2\sqrt{\pi}}ce^{-c^2} + a_1e^{-c^2} + 2a_2e^{-c^2}\int_1^c dx\,\frac{e^{x^2}}{x^3}\right)$$

where a_1, a_2 are constants. When $a_2 \neq 0$,

$$B(c) \underset{c\to\infty}{\simeq} \frac{a_2}{c^4} \tag{2.24}$$

which leads to a slow, powerlike decay of the first Enskog correction according to the formula

$$f_c^{(1)}(\mathbf{v}) \underset{v\to\infty}{\simeq} \frac{1}{v^5} \frac{8ka_2}{m\pi^2\sigma^2}\left(\mathbf{v} \cdot \frac{\partial T}{\partial \mathbf{r}}\right)$$

The situation seems thus to be analogous to that encountered in the study of self-diffusion. However, the structure of the inhomogeneous term in Eq. (2.21) rules out $a_2 \neq 0$. This fact, which may appear as a miraculous coincidence, can be demonstrated owing to the relation

$$\int_0^\infty dc\left(c^4 - \tfrac{3}{2}c^2\right)e^{-c^2} = 0 \tag{2.25}$$

This "orthogonality" property can be used in a straightforward way to evaluate a_2. Indeed, one can check that the left-hand side of Eq. (2.21), when multiplied by e^{-c^2}, can be written as a derivative $L'(c)$ with

$$\begin{aligned} L(c) = e^{-c^2}\Big\{ &\left[c^2 + (c + 2c^3)I(c)\right]B'(c) \\ &+ \left[\tfrac{8}{3}c^3 + 4c^4 I(c)\right]B(c) + \frac{4}{3}\int_0^c dx\, x^3 B'(x) \\ &+ 2\left[c - I(c)\right]\int_c^\infty dx\, x^2 B'(x)\Big\} \end{aligned} \tag{2.26}$$

Equation (2.25) implies the relation

$$\lim_{c\to\infty} L(c) = \lim_{c\to 0} L(c) \tag{2.27}$$

and the asymptotic behavior (2.24) yields a simple result

$$\lim_{c\to\infty} L(c) = \lim_{c\to\infty} 4c^4 e^{-c^2} I(c) B(c) = 2\sqrt{\pi}\, a_2 \tag{2.28}$$

In order to calculate the right-hand side of (2.27) one has to examine the small-c behavior of $B(c)$. When $c \to 0$, Eq. (2.20) takes the asymptotic form

$$-4\int_0^c dx\, x^3 B'(x) + 4c^3 B(c) + 3c^2 B'(c) = \left(2\alpha - \tfrac{15}{4}\right)c^3 \tag{2.29}$$

where $\alpha = \int_0^\infty dx\, x^2 B'(x)$, which gives a second-order differential equation

$$\left[c^2 B'(c)\right]' + 4c^2 B(c) = \left(2\alpha - \tfrac{15}{4}\right)c^2$$

with a general solution

$$\left[-\frac{15}{16} + \frac{\alpha}{2} + \frac{1}{c}\left(\alpha_1 \cos 2c + \alpha_2 \sin 2c\right)\right]$$

The behavior $B(c) \simeq \alpha_1/c$ being incompatible with Eq. (2.29) we conclude that $B(c)$ is regular at the origin. Hence, $\lim_{c\to 0} L(c) = 0$, and Eqs. (2.27) and (2.28) imply that $a_2 = 0$. This permits us to establish the exact velocity behavior of B as

$$B(c) \underset{c\to\infty}{\simeq} -\frac{5}{2\sqrt{\pi}} c e^{-c^2} \tag{2.30}$$

Enskog's correction $f_{\text{hc}}^{(1)}$ is correspondingly given by

$$f_{\text{hc}}^{(1)}(v) \underset{v\to\infty}{\simeq} -\frac{5m}{2n\pi\sigma^2 kT^2} v^2 f^{(0)}(v)\left(\hat{v}\cdot\frac{\partial T}{\partial \mathbf{r}}\right) \tag{2.31}$$

There is thus no need here to introduce extra conditions to guarantee the uniqueness of the solution for $f_{\text{hc}}^{(1)}$.

Enskog's method in the case of heat conductivity represents a well-defined problem. However, a new difficulty appears.

In the presence of an arbitrary small but fixed gradient of the temperature field $f_{\text{hc}}^{(1)}$ dominates over $f^{(0)}$ for sufficiently big velocities (unless $\mathbf{v}\cdot\partial T/\partial\mathbf{r} = 0$). It follows that Enskog's representation of the solution to Boltzmann's equation as $f \simeq f^{(0)} + f^{(1)}$, violates the positivity requirement $f \geqslant 0$, because $f^{(1)}$ takes both negative and positive values (depending on the sign of the scalar product $\mathbf{v}\cdot\partial T/\partial\mathbf{r}$).

It is very hard to see how one could get rid of this unsatisfactory feature of Enskog's method. It might happen that the situation is different for smooth pair potentials with a divergent total cross section. This is, however, an open question.

Let us finally notice that the possibility of writing Eq. (2.21) in the form

$$L'(c) = 5\left(c^4 - \tfrac{3}{2}c^2\right)e^{-c^2} \tag{2.32}$$

permits us to reduce the problem of determining the function B to solving a second-order differential equation. Indeed, using the regularity of B at the origin one finds from (2.32),

$$L(c) = -\tfrac{5}{2}c^3 e^{-c^2}$$

which is equivalent to

$$\begin{aligned}\left[B'(c) + 2cB(c)\right]cI''(c) - 8\int_0^c dx\, x^2 B(x)&\\ + 8\left[I(c) - c\right]\int_c^\infty dx\, xB(x) = -5c^3&\end{aligned} \tag{2.33}$$

Defining function Γ by

$$\Gamma(c) = B(c) - 2\int_c^\infty dx\, xB(x) \tag{2.34}$$

one finds from (2.33) (by taking the derivative with respect to c)

$$\left[cI''(c)\Gamma'(c)\right]' - 8cI(c)\Gamma(c) = -15c^2 \tag{2.35}$$

Once the second-order equation (2.35) is solved one obtains the general form of $B(c)$ from the formula

$$B(c) = e^{-c^2}\int_0^c dx\, e^{x^2}\Gamma'(x) + B(0)e^{-c^2} \tag{2.36}$$

This remark may be of some use for the numerical study of Eq. (2.20), based up to now on the fourth-order differential equation, found first by Pekeris and Alterman.[11]

2.3. Shear Viscosity

The momentum current density in a fluid is described by the pressure tensor

$$\mathbb{P}(\mathbf{r},t) = m\int d\mathbf{v}\left[\mathbf{v}-\mathbf{u}(\mathbf{r},t)\right]\left[\mathbf{v}-\mathbf{u}(\mathbf{r},t)\right]f(\mathbf{r},\mathbf{v},t)$$

The local equilibrium contribution to $\mathbb{P}$ follows the perfect gas law

$$\mathbb{P}^{(0)} = nkT\mathbb{1}, \qquad \mathbb{1} = \text{unit tensor}$$

The dependence of $\mathbb{P}$ on the gradients of the velocity field is determined (to the lowest order) by the first correction $f^{(1)}$. Taking into account the structure of Eq. (1.15) it is convenient to write the viscous term in $f^{(1)}$ as

$$f^{(1)}_{\text{visc}} = f^{(0)}\psi_{\text{visc}}$$

with

$$\psi_{\text{vis}}(\mathbf{c}) = -\frac{1}{n\sigma^2\sqrt{\pi}}\left(\frac{m}{2kT}\right)^{1/2}\mathcal{G}(c)(\mathbf{c}^0\mathbf{c} : \nabla\mathbf{u}^s) \tag{2.37}$$

The contribution to the pressure tensor corresponding to $f^{(1)}_{\text{visc}}$ has the form predicted by Newton's law

$$\mathbb{P}^{(1)} = -2\mu\nabla^0\mathbf{u}^s$$

where $\nabla^0\mathbf{u}^s$ is the traceless rate of strain tensor and the shear viscosity coefficient μ is given by

$$\mu = \frac{4(2mKT)^{1/2}}{15\pi\sigma^2}\int_0^\infty dc\, c^6 e^{-c^2}\mathcal{G}(c) \tag{2.38}$$

Inserting formula (2.37) into Eq. (1.15), and using Eq. (1.4), one finds an inhomogeneous integral equation for the scalar function $\mathcal{G}$

$$-\frac{1}{\pi}\int d\mathbf{c}_1\, c_1^2 e^{-c_1^2} P_2(\hat{c}\cdot\hat{c}_1) K^B(\mathbf{c},\mathbf{c}_1)\mathcal{G}(c_1) + \left[c^2+(c+2c^3)I(c)\right]e^{-c^2}\mathcal{G}(c) = 2c^2 \tag{2.39}$$

where $P_2(\nu)=\frac{1}{2}(3\nu^2-1)$ is the second Legendre polynomial. The formula

$$\frac{1}{\pi}\int d\hat{c}_1\, P_2(\hat{c}\cdot\hat{c}_1)K^B(\mathbf{c},\mathbf{c}_1) \underset{c>c_1}{=} \frac{6}{(cc_1)^3}\left[c_1(-c^2+c_1^2-6) + \left(c^2-\tfrac{2}{3}c^2c_1^4+2c_1^4-5c_1^2+6\right)I(c_1)\right] - \frac{4}{35}\frac{c_1^4}{c^3}+\frac{4}{15}\frac{c_1^2}{c} \equiv k(c,c_1) \tag{2.40}$$

permits to transform further Eq. (2.39). One gets

$$-\int_0^c dx\, x^4 k(c,x)e^{-x^2}\mathcal{G}(x) - \int_c^\infty dx\, x^4 k(x,c)e^{-x^2}\mathcal{G}(x) + \left[c^2+(c+2c^3)\right]I(c)e^{-c^2}\mathcal{G}(c) = 2c^2 \tag{2.41}$$

Defining functions

$$\alpha(c) = -\tfrac{4}{35}c^2+6c^3-36c+(12c^4-30c^2+36)I(c)$$

$$\sigma(c) = \tfrac{4}{15}c^5-6c+(-4c^2+6)I(c)$$

one can then rewrite (2.41) as

$$\int_0^c dx\left[\alpha(x)+c^2\sigma(x)\right]xc^{-x^2}\mathcal{G}(x) + \int_c^\infty dx\left[\alpha(c)+x^2\sigma(c)\right]xe^{-x^2}\mathcal{G}(x) - \left[e^2+(c+2c^3)I(c)\right]c^3e^{-c^2}\mathcal{G}(c) = -2c^5 \tag{2.42}$$

When $c\to 0$, Eq. (2.42) can be asymptotically replaced by

$$4\int_0^c dx\, x^6 e^{-x^2}\mathcal{G}(x) - 5c^5e^{-c^2}\mathcal{G}(c) = (-5-4\mu_1+2\mu_3)c^5 \tag{2.43}$$

where

$$\mu_i = \int_0^\infty dx\, x^i e^{-x^2}\mathcal{G}(x), \qquad i=1,3$$

Equation (2.43) implies that $\mathcal{G}(c)$ is regular at $c=0$, and satisfies then the relation

$$\mathcal{G}(0) = 1+\tfrac{4}{5}\mu_1-\tfrac{2}{5}\mu_3 \tag{2.44}$$

This conclusion is consistent with the assumption μ_1, $\mu_3<\infty$, made when writing Eq. (2.43). [One can show by a more thorough analysis that $\mathcal{G}$ must be regular at $c = 0$ if it is to satisfy Eq. (2.42).]

It is convenient here to introduce a new function H related to $\mathcal{G}$ by

$$H(c) = \int_c^{\infty} dx\, x \int_x^{\infty} dy\, y e^{-y^2} \mathcal{G}(y) \tag{2.45}$$

so that

$$cH''(c) - H'(c) = c^3 e^{-c^2} \mathcal{G}(c)$$

From Eq. (2.42) one obtains a fourth-order differential equation for H, which can be written in a compact form as

$$\left[cH''(c + H''(c)\right]'' + \left\{\left[16c^2 I'(c) - (1/c)(cI''(c))'\right]H'(c)\right\}' + 16\left[-c^2 + cI''(c)\right]H(c) = 60c^2 \tag{2.46}$$

Let us study the asymptotic form of (2.46) when $c \to \infty$. Using the formula

$$I(c) \underset{c\to\infty}{\simeq} \frac{\sqrt{\pi}}{2} e^{c^2}$$

we find the equation

$$\left[c^3 e^{c^2} H''(c)\right]'' + 6\left[c^3 e^{c^2} H'(c)\right]' + 16 c^3 e^{c^2} H(c) = \frac{30c^2}{\sqrt{\pi}} \tag{2.47}$$

Supposing that

$$H(c) \underset{c\to\infty}{\simeq} c^a e^{-c^2} \tag{2.48}$$

one verifies, that the asymptotic behavior reproducing the inhomogeneity in Eq. (2.47) is given by

$$H(c) = \frac{15}{14\sqrt{\pi}} \frac{1}{c} e^{-c^2} \tag{2.49}$$

In principle, any solution of the homogeneous equations associated with (2.47) can be added to (2.49). Hypothesis (2.48) leads to the dominant term in the left-hand side of Eq. (2.47) proportional to

$$(a^2 + 6a + 12)c^{a+3}$$

The coefficient of c^{a+3} vanishes for $a = -3 \pm i\sqrt{3}$, leading to the asymptotic behavior

$$(1/c^3)\left[a_1 \cos(\sqrt{3}\log c) + a_2 \sin(\sqrt{3}\log c)\right]e^{-c^2} \tag{2.50}$$

where a_1, a_2 are constants.

Assuming then that $H(c) \simeq c^b$, $c \to \infty$, one obtains the dominant contribution to the left-hand side of (2.47) proportional to

$$(b^2 + 2b + 4)c^{b+3} e^{c^2}$$

giving rise to the remaining two possibilities, corresponding to $b = -1 \pm i\sqrt{3}$. We thus arrive at the formula

$$H(c) \underset{c\to\infty}{\simeq} \frac{15}{14\sqrt{\pi}} \frac{1}{c} e^{-c^2} + \left(\frac{a_1}{c^3} e^{-c^2} + \frac{\tilde{a}_1}{c} \right) \cos\left(\sqrt{3} \log c\right)$$

$$+ \left(\frac{a_2}{c^3} e^{-c^2} + \frac{\tilde{a}_2}{c} \right) \sin\left(\sqrt{3} \log c\right) \qquad (2.51)$$

Let us now find out whether we have enough conditions to fix the constants $a_1, \tilde{a}_1, a_2, \tilde{a}_2$. Now, H (as $\mathcal{G}$) must be regular at the origin, and equation (2.44) is equivalent to

$$H(0) = \tfrac{5}{4} - H''(0) - \tfrac{5}{12} H^{iv}(0) \qquad (2.52)$$

Moreover, by a straightforward calculation one verifies that if the function $\mathcal{G}$, calculated form (2.45), is to satisfy the integral equation (2.42) then $H'(0) = H'''(0) = 0$. Hence, if $H(0)$ and $H''(0)$ were known, one could construct a Taylor series for $H(c)$ near $c = 0$. This means that we need two complementary conditions to fix the solution $H(c)$. However, Enskog's method does not yield such conditions, and thus it represents for viscous phenomena an ill-defined problem. The situation is quite analogous here to the one encountered in the self-diffusion problem. Again, assuming the existence of the transport coefficient (viscosity μ) determines $H(c)$ in a unique way, yielding two supplementary conditions:

$$\tilde{a}_1 = \tilde{a}_2 = 0$$

which eliminate distributions whose slow decay at infinity is incompatible with the convergence of the integral in (2.38). The precise large-velocity behavior of $H(c)$ is then readily deduced from (2.51) to be that given by Eq. (2.49). The corresponding formula for Enskog's correction $f^{(1)}_{\text{visc}}$ reads

$$f^{(1)}_{\text{visc}}(\mathbf{v}) \underset{v\to\infty}{\simeq} -\frac{15m}{7\pi\sigma^2 kTn} v f^{(0)}(v)(\hat{v}^0\hat{v} : \nabla \mathbf{u}^s)$$

Similarly to the case of thermal conductivity the above asymptotic form $f^{(1)}_{\text{visc}}$ shows the nonuniform character of Enskog's expansion and violation of the positivity requirement in the large-velocity region.

3. CONCLUSION

We have studied the linearized Boltzmann kinetic equation for hard spheres, as it has to be solved for computing transport coefficients. We have shown that this gives generally ill-defined problems, with the noticeable exception of the case of heat conductivity. This kind of problem does not seem to have been considered before. We have mainly used the differential equations equivalent to the linearized Boltzmann equation, as did Pekeris and co-workers. The possibility of deriving these differential equations was already remarked by Boltzmann himself. As he did not have at his disposal the Hilbert representation, his derivation has been a fantastic "tour de force."

We have shown that, by adding some extra assumptions, it is possible to get well-defined values for the transport coefficients. These assumptions are needed to eliminate algebraic tails in the velocity space. One would prefer to deduce the absence of such algebraic tails from the kinetic theory itself. We suggested in the Introduction that this could result from the requirement of positiveness for the distribution function. However, this is certainly not easy to fulfill. In particular the perturbation expansion involved in Chapman–Enskog theory does in general introduce velocity distribution negative somewhere in the velocity space, where the algebraic tails are dominant. Whence it seems important to know whether, in strongly nonequilibrium situations, as in strong shock wave for instance, such algebraic tails could be excited or not. One cannot also a priori exclude their appearance in the presence of external fields.

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