$$f(t)=\frac{a+[(1-\gamma^2)t^2-\gamma^2(1-\gamma^2-a^2)]^{1/2}}{1-\gamma^2}-i\left[-\left(\frac{a+[(1-\gamma^2)t^2-\gamma^2(1-\gamma^2-a^2)]^{1/2}}{1-\gamma^2}\right)^2+1\right]^{1/2},\qquad \theta<t<1-a \tag{A11}$$

$$f(t)=\frac{a+i[-(1-\gamma^2)t^2+\gamma^2(1-\gamma^2-a^2)]^{1/2}}{1-\gamma^2}-i\left[-\left(\frac{a+i[-(i-\gamma^2)t^2+\gamma^2(1-\gamma^2-a^2)]^{1/2}}{1-\gamma^2}\right)^2+1\right]^{1/2},\quad |t|<\theta \tag{A12}$$

$$f(t)=\frac{a-[(1-\gamma^2)t^2-\gamma^2(1-\gamma^2-a^2)]^{1/2}}{1-\gamma^2}-i\left[\left(\frac{a-[(1-\gamma^2)t^2-\gamma^2(1-\gamma^2-a^2)]^{1/2}}{1-\gamma^2}\right)^2-1\right]^{1/2},\quad -(1+a)<t<-\theta \tag{A13}$$

$$f(t)=\frac{a-[(1-\gamma^2)t^2-\gamma^2-\gamma^2(1-\gamma^2-a^2)]^{1/2}}{1-\gamma^2}+\left[\left(\frac{a-[(1-\gamma^2)t^2-\gamma^2-\gamma^2(1-\gamma^2-a^2)]^{1/2}}{1-\gamma^2}\right)^2-1\right]^{1/2},\qquad t<-(1+a). \tag{A14}$$

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Generalization of Boltzmann's Kinetic Theory. The Lorentz Gas.

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We present in this paper a new formulation of the kinetics of the Lorentz gas, based on an analysis of statistically independent collisional events. We give a method in which the general collision operator is expanded in terms of functions of the density, and we carefully treat the μ^s approximation (μ is the density parameter and s is the dimensionality of the gas). The method is applied to the calculation of the self-diffusion coefficient.

INTRODUCTION

From the point of view of Boltzmann's early work in kinetic theory, one considers a particle of a gas at time t with velocity $\vec{v}(t)$ and evaluates the transition probabilities associated with the various possible binary collision processes. Molecular chaos (MC) is then assumed, wherein each collision is a random event having no correlation with the past history of the particle. One can then derive the increment $d\Pi(t)$ of the particle distribution function $f(\vec{v}, t)$ between times t and $t+dt$ in terms of these transition probabilities and $f(\vec{v}, t)$. The kinetic equation thus obtained is local in time, and in the case of the Lorentz gas, the successive deflections of the velocity vector constitute a Markov chain.

The concept of MC is introduced naturally when one considers an infinite dilute gas: Each molecule encountered by the test particle in a collision is a "new molecule" (never before encountered). In the case of a dense gas, the MC hypothesis must be relaxed and the past history of the particle (before the collision) must be taken into account. This can be done systematically by starting from the kinetics of the N interacting particles and then describing, by successive approximations, the evolution of the Gibbs ensemble, subject to given initial conditions. One either uses an appropriate expansion of the Green's function of the Liouville equation [binary collision expansion (BCE),[1] in the case of the neutral gas] or one postulates the existence of separate relaxation time scales for the various correlation functions entering the Bogoliubov-Born-Green-Yvon-Kirkwood (BBGYK) hierarchy. These approximations, whose statistical significance is not quite clear, depend fundamentally on the idea that there exists, as in thermodynamic equilibrium, an expansion of the statistical quantities in powers of the density. The inadequacy of this statement has been responsible for the difficulties encountered in recent years in the calculation of the transport coefficients (divergencies). Theoreticians have therefore been led to modify the above methods. It has been shown that the divergencies of the BCE theory can be removed by resuming appropriate subseries of divergent collision integrals.[2-5] An equivalent method is to construct convenient cluster expansions of the dynamical operators whose terms contain from the beginning the screening effect of the "virtual collisions" and are therefore not divergent.[6,7] Later on, these renormalization procedures have been shown to be equivalent, for obtaining a generalized kinetic equation of the gas, to a suitable solution of the first equations of the hierarchy.[8]

In this paper we propose to generalize the Boltzmann point of view, starting with the consideration of the statistically independent collision sequences in the gas (the simplest being the ordinary binary collision). These sequences contain all the various recollision processes. Moreover, we have been led to consider "virtual" sequences, which represent forbidden trajectories which are counted in the Boltzmann statistics and which must be removed. In order to obtain a systematic and complete classification of the collisional processes, we have introduced the notion of "topological collisional schemes" (TS) which contain real or virtual collision sequences and whose topology is defined by precise rules. In terms of these TS it has been possible to derive an expression for $d\Pi(t)$ which accounts for all possible independent collisional processes which can occur before t, and therefore to obtain the general non-Markovian kinetic equation of the gas. An approximate description of the kinetics is obtained by retaining in the general collision operator only those terms associated with the most probable collisional events (up to the desired approximation): This is the method used to proceed beyond the MC statement. Using the classification of the collisional processes with respect to their probability we obtain an expansion of the collision operator with respect to the density (the contribution of short-range and long-range collisions being carefully analyzed). The kinetic equations in the μ^s approximation are of special interest (μ being the customary density parameter and s the dimension of the space). We determine under what conditions the collision operators which enter these equations may be approximated by Markovian operators. As an application of the theory we present a calculation of the self-diffusion coefficient for the Lorentz gas of hard disks.

We limit ourselves, in this paper, to the case of the Lorentz gas. For simplicity, this gas will consist of point particles moving among an array of fixed hard spheres (or disks) with radius R, distributed in space with uniform density n. The state of a test particle will be represented by $\vec{\Omega}(t)$, where

$$\vec{\Omega}(t) = \{\vec{X}(t),\ \vec{v}(t)\},$$

and $\Omega(t)$ will denote the orientation of $\vec{v}(t)$. In the same manner $f(\Omega, t)$ will represent the marginal distribution of the velocity angles where

$$f(\Omega, t) = \int f(\vec{\Omega}, t)\, d\vec{X}.$$

I. BOLTZMANN APPROXIMATION

A. Fundamental Concept

The essential feature of the Boltzmann approximation is the consideration of the motion of a test particle in the gas as a stochastic process in which the elementary events are binary collisions with the individual scatterers, each collision being uncorrelated with the previous ones. As a consequence, $\Omega(t)$ is independent of the coordinates $\vec{X}_c$ of the scatterer with which the particle will eventually interact at time t. On the one hand, the probability $W(\vec{\Omega}\,|\,\vec{\Omega}', \vec{X}_c)d\Omega\, dt$ for a test particle in the state $\vec{\Omega}'$ to undergo a collision with an arbitrary scatterer c during t and $t+dt$ and leading to $\vec{\Omega}$, $\vec{\Omega}+d\Omega$ is given by

$$W(\vec{\Omega}\,|\,\vec{\Omega}', \vec{X}_c)d\Omega\, dt = n(\vec{X}_c)v dt\, \sigma(\vec{\Omega}, \vec{\Omega}')d\Omega\ ,$$

where $n(\vec{X}_c)$ is the particle distribution function (pdf) of the scattering centers (assumed to be uniform) and $\sigma(\vec{\Omega}\,|\,\vec{\Omega}')$ is the differential cross section for the collision. Introducing the normalized angular transition probability

$$\bar{\omega}(\vec{\Omega}'\,|\,\vec{\Omega}) = \sigma(\vec{\Omega}'\,|\,\vec{\Omega}')/\int d\Omega'\, \sigma(\vec{\Omega}'\,|\,\vec{\Omega})\ ,$$

we shall write

$$W(\vec{\Omega}'|\vec{\Omega},\vec{X}_c)=\nu(\vec{X}_c)\,\bar{\omega}(\vec{\Omega}'|\vec{\Omega})\ ,$$

where ν stands for the Boltzmann collision frequency. On the other hand, the probability that a particle will leave the state $\vec{\Omega}$ is

$$dt\int W(\vec{\Omega}'|\vec{\Omega},\vec{X}_c)\,d\Omega'\ .$$

By virtue of the statistical independence of $\vec{\Omega}(t)$ and $\vec{X}_c$ the probability increment $d\pi_B$ of $f(\vec{\Omega},t)$ between t and $t+dt$ takes the simple form

$$d\pi_B=dt\int d\Omega'\chi(\vec{\Omega}'|\vec{\Omega},\vec{X}_c)f(\vec{\Omega}',t)\ ,$$

where χ does not actually depend on $\vec{X}_c$ (uniform distribution of the scatterers) and is given by

$$\chi(\vec{\Omega}'|\vec{\Omega})=\nu[\bar{\omega}(\vec{\Omega}'|\vec{\Omega})-\delta(\vec{\Omega}-\vec{\Omega}')]\ .$$

The Chapman-Kolmogoroff equation which governs the process takes the well-known Boltzmann-Lorentz form

$$\frac{d}{dt}f(\vec{\Omega},t)=\int d\Omega'\,\chi(\vec{\Omega}'|\vec{\Omega})f(\vec{\Omega}',t)\ ,$$

where d/dt is the streaming operator: $\partial/\partial t+\vec{v}\cdot\partial/\partial\vec{X}$. The emission and absorption terms contained in χ may be represented by the diagrams of Fig. 1. In the diagrams which will be considered in this paper for describing the various collisional processes we will always find emission and absorption diagrams associated. Hence, it will be convenient to write only the emission diagrams in place of the two associated diagrams. With these definitions, the Boltzmann-Lorentz equation will be written as shown on Fig. 2.

B. Hard-Sphere and Hard-Disk Lorentz Gas.

a. *Hard-sphere case* ($s=3$). $\bar{\omega}(\vec{\Omega}'|\vec{\Omega})$ is uniform and therefore the vectors l_i which separate two successive encountered scatterers are statistically independent. An analytical solution can then be derived for the homogeneous and inhomogeneous Boltzmann equations.

b. *Hard-disk case* ($s=2$). $\bar{\omega}(\Omega'|\Omega)$ is not uniform, but the angular increments are independent. A simple expression for the characteristic function $\phi(\theta,t)$ of the angular process can then be obtained. Indeed, since the collisions are distributed in time according a Poisson law, we have

$$\phi(\theta,t)=\langle e^{i\theta\Omega(t)}\rangle=\textstyle\sum_j[(\nu t)^j/j\,!\,]e^{-\nu t}\psi_j(\theta)\ ,$$

where $\psi_j(\theta)$ is the characteristic function of the deflection after j collisions and $[(\nu t)^j/j\,!\,]e^{-\nu t}$ is the probability that j collisions have occurred before t. The statistical independence of the angular increments permits us to write

$$\psi_j(\theta)=[\psi(\theta)]^j\ ,$$

where $\psi(\theta)$ is the characteristic function of the angular deflection in the binary collision:

$$\psi(\theta)=\frac{1-2\theta\sin\pi\theta}{1-4\theta^2}\ . \tag{1}$$

Therefore we obtain

$$\phi(\theta,t)=e^{\nu t[\psi(\theta)-1]}\ . \tag{2}$$

FIG. 1. Emission and absorption diagrams.

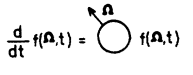


FIG. 2. Boltzmann-Lorentz equation.

II. GENERALIZATION OF BOLTZMANN STATISTICS

A. Preliminary Remarks

In the Boltzmann approximation, $\vec{\Omega}(t)$ and the coordinate $\vec{X}_c$ of the next-encountered scatterer are independent. This assumption, which expresses the MC in the case of the Lorentz gas, is equivalent to the statement that, at any point within the gas, the probability of a new collision is uniform in space and independent of the past history of the test particle. One then ignores the possibility that the particle may interact several times with the same scatterer and therefore that during a collision cycle, $\vec{\Omega}(t)$ and $\vec{X}_c$ are not independent. Moreover, the assumption of statistical independence of $\vec{\Omega}(t)$ and $\vec{X}_c$ leads to unphysical trajectories. To properly describe the evolution of $f(\vec{\Omega},t)$ we may proceed as follows: We start from the Boltzmann probability increment $d\pi_B$ at time t. In writing $d\pi_B$ we are stating that the particle has not previously interacted with scatterer c. However, among all the possible configurations of previously encountered scatterers, there will exist some configurations where particle trajectory has crossed c before time t; these configurations are forbidden. As an example, scheme (a) (see Fig. 3) may be obtained. In such configurations the past trajectory crosses c at least once. These crossings will be called "virtual collisions" and the corresponding configurations "virtual schemes." They are counted in the Boltzmann statistics and their probability must therefore be subtracted from $d\pi_B$. Due to the constraint imposed on the trajectory (namely, to have crossed c in the past), $\vec{\Omega}(t)$ and $\vec{X}_c$ are not independent during the cycle. This fact will be taken into account when we calculate the probability increment of $f(\vec{\Omega},t)$ between t and $t+dt$ due to the contribution of such virtual events. This increment will be expressed in terms of the probability $f(\vec{\Omega}',t-\tau)$ at the beginning of the cycle.

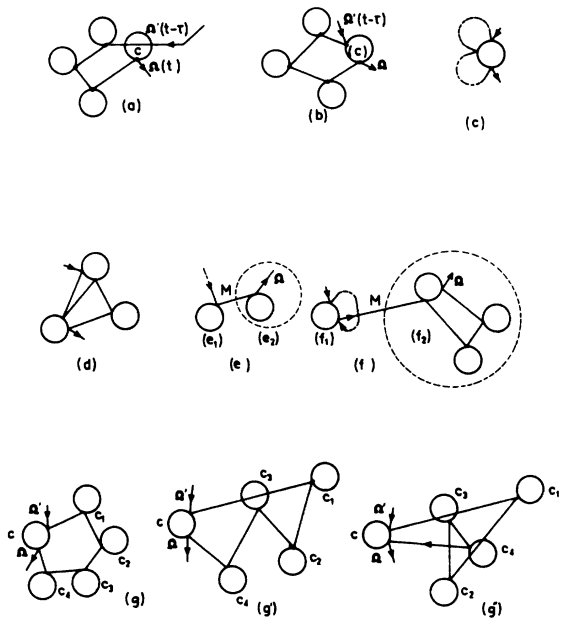


FIG. 3. (a) Forbidden scheme incorporated in the Boltzmann statistic. (b) Real scheme associated with scheme (a). (c) (d) Examples of collision schemes. (e) (f) Examples of disconnected schemes. (g) Arbitrary scheme. (g′) Example of forbidden trajectory obtained with (g). (g″) Scheme to be taken with a positive sign.

These considerations concerning the forbidden events included in the Boltzmann statistics may be formulated in the following equivalent way: Each new scatterer c may find itself anywhere in space with uniform probability except in a forbidden region ϵ constituted by the union of the past collision cylinders. When the center of c is found in ϵ, one then considers a virtual cycle of collisions whose probability will be subtracted from $d\pi_B$.

We shall now consider real recollisions with c. Indeed, to each virtual cycle of the above type, there corresponds a real cycle in which the initial virtual collision is replaced by a real one. As an example, to the virtual scheme (a) there corresponds the real scheme (b) (cf. Fig. 3). In scheme (b), as in (a), we obviously have to go back in time to the beginning of the cycle to find a variable $\vec{\Omega}'$ independent of $\vec{X}_c$.

We have accounted for all the possible collision events, any collision always being classified in one of three categories: (i) ordinary Boltzmann collisions (in which the scatterer has never been encountered before), (ii) collisions in the forbidden region, and (iii) real recollisions. To obtain the kinetic equation for the Lorentz gas we consider systematically all the interaction processes with several scatterers for which the successive collisions are not independent. The schemes (c) and (d) are examples of collision schemes more complicated than (a) and (b) (see Fig. 3). In scheme (c) we have three successive real collisions with scatterer c. In scheme (d) the paths into and out of the scheme do not pertain to the same scatterer. These examples, as well as those which will be considered in the following, are "connected"; i.e., it is impossible to divide them into two subschemes by means of a surface encircling one of the subschemes and cutting only one trajectory. A scheme such that such a surface exists will be called "disconnected." The schemes (e) and (f) are examples of disconnected schemes (cf. Fig. 3). We see that in (e) and (f) the global collisional process may be divided into two processes: f_1(or e_1) and f_2 (or e_2), which are statistically independent. At point M, $\vec{\Omega}(t)$ is independent of the coordinates of the scatterers present in f_2 (or e_2). It is therefore possible to relate $f(\vec{\Omega}, t)$ (at the end of the cycle) to $f(\vec{\Omega}, t-\tau)$ at point M.

B. Notion of "Topological Scheme"

Let us consider an arbitrary scheme, such as (g) (see Fig. 3). To evaluate the probability of such a configuration with a given initial collision on c, we have to sum the probabilities of all possible configurations of the c_i ($i = 1, 2, 3, 4$) which are compatible with a closed trajectory and with the transition $\vec{\Omega} \to \vec{\Omega}'$. If the c_i were sought in all space with a uniform pdf, taking account of the unique constraint mentioned above, we would obtain forbidden trajectories containing virtual collisions. An example is the configuration (g′) (Fig. 3).

The probability of configuration (g′) must be subtracted from the total probability of (g), the latter being computed by integrating over all the impact parameters compatible with the constraint which defines (g). Scheme (g′), whose probability enters into the collision integral with a minus sign, is defined by the previous constraint and by the fact that the trajectory *must* cross c_3. Evaluating the probability of (g′) by integration over the impact parameters we again find forbidden configurations containing two virtual collisions [for example, with c_3 and c_4, scheme (g″)]. The probability of (g'') must be subtracted from that of (g'), which means that it enters into the collision integral with a positive sign (see Fig. 3). Also, on generalizing, it is clear that we obtain the following rule: "The probability of a collision scheme enters into the collision integral with a plus or minus sign according to whether it contains an even or odd number of virtual collisions." (The initial collision is of course taken into account in computing this number.)

Returning to the initial scheme (g) we see that it generates a set of schemes whose probabilities must be affected by different signs. Therefore we are led to consider secondary schemes, in which the constraints imposed on the trajectory relative to

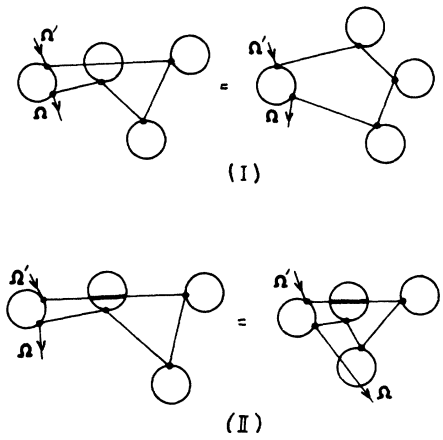


FIG. 4. Equivalent TS (I) are different from the TS(II), which bear one additional constraint.

the various scatterers are completely specified. We shall call them "topological schemes" (TS) and we define them as "collisional schemes which are completely defined by an ensemble of constraints imposed on the trajectory."

We wish to point out that the introduction of TS is also necessary in order for the paths into and out of a scheme to be defined unambiguously. Indeed, (g) generates configurations in which one or several c_i cross the paths into and out of the scheme. Such configurations must be considered separately, as new TS.

A TS will be represented by a graph which contains all the specified interactions (real or virtual) of the test particle with any scatterer. We shall adopt the following definitions: (i) A real collision will be denoted by a bold impact point on the scatterer. (ii) A virtual collision will be denoted by a bold line on the trajectory inside the scatterer.

As an example, the two upper TS of Fig. 4 are the same, but are different from the two lower TS, which bear an additional constraint. Scheme (g) (Fig. 3) generates, with their sign, the TS represented in Fig. 5.

Let us consider a particular virtual collision taking place in a TS. We may associate with this TS another TS in which this virtual collision is replaced by a real collision, the probability of these two TS being of the same order of magnitude. An example is provided by the graphs of Fig. 6, which contain the same number of constraints. Consequently, given a set of scatterers, this set generates an ensemble of TS whose probabilities will be classified according to the number of their real (or virtual) constraints.

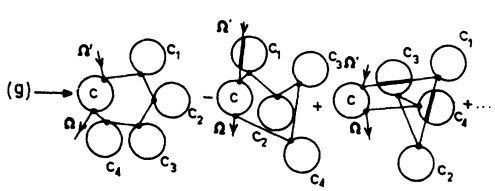


FIG. 5. TS generated by scheme (g) (Fig. 3).

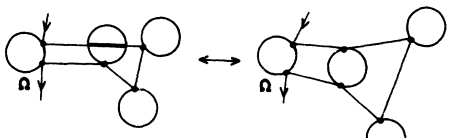


FIG. 6. Two TS of the same order of magnitude.

To evaluate the probability of an arbitrary TS, one has to integrate over the coordinates of the scatterers entering into the TS and compatible with the specified constraints, the order of the successive interactions with $\{1 \cdots j\}$ being preserved. It is important to note that any scatterer in the TS undergoes at least one real interaction.

The schemes shown in the above figures are of the emission type. We must also consider the corresponding absorption schemes (see Fig. 7).

We shall adopt the same convention as in Sec. I: Diagram (a) will represent the sum of both diagram (a) and (b) (see Fig. 7).

C. General Kinetic Equation for Lorentz Gas

1. *Derivation of Kinetic Equation*

Let us evaluate the probability increment $d\,\Pi_{\{j\}}$ of $f(\vec{\Omega}, t)$ between t and $t+dt$, due to the contribution of the connected TS characterized by the configuration $\{j\}$ (cf. Fig. 8).

The probability of the collision $\vec{\Omega}_1 \to \vec{\Omega}$ with c occuring between t and $t+dt$, not taking account of the past history of the particle, is $\nu dt W_B(\vec{\Omega}_1 | \vec{\Omega})$. This probability must be multiplied by the probability of finding a connected configuration before this collision, starting with the collision with c_0, the initial state being $\vec{\Omega}_0$. Therefore, we have

$$d\Pi_{\{j\}} = \mathrm{sgn}\{j\}\, \nu dt W_B(\vec{\Omega}_1 | \vec{\Omega})[\text{probability of finding configuration } \{j\} \text{ leading to } (\vec{\Omega}_0 \to \vec{\Omega}_1) \text{ transition, the time of flight of this configuration being between } \tau_j \text{ and } \tau_j + d\tau_j] \times f(\vec{\Omega}_0,\ t - \tau_j) d\Omega_0 d\tau_j ,$$

$\mathrm{sgn}\{j\}$ being + or − according to the even or odd

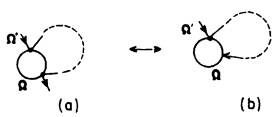


FIG. 7. Emission and absorption graphs.

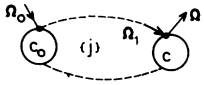


FIG. 8. Connected graph associated with the $\{j\}$ configuration.

number of virtual collisions contained in the TS.

Let us now write

$$\nu W_B(\vec{\Omega} \mid \vec{\Omega}_1)(\text{Probability of } \{j\} \text{ configuration})$$

$$= \nu W\{j\}\bar{\omega}(\vec{\Omega} \mid \vec{\Omega}_0, \{j\}), \tag{3}$$

where $W\{j\}d\tau_j$ is the total probability of encountering a configuration of $\{j\}$ whose time of flight is between τ_j and $\tau_j + d\tau_j$, and where $\bar{\omega}(\vec{\Omega} \mid \vec{\Omega}_0, \{j\})$ is the normed probability of deflection $\vec{\Omega}_0 \to \vec{\Omega}$ associated with this scheme. Thus, we may write

$$d\Pi_{\{j\}} = \mathrm{sgn}\{j\}\,\nu dt \int_0^\infty d\tau_j$$

$$\times \int d\Omega_0\, W\{j\}\bar{\omega}(\vec{\Omega} \mid \vec{\Omega}_0, \{j\}) f(\vec{\Omega}_0, t - \tau_j).$$

The total probability increment $d\Pi$ of $f(\vec{\Omega}, t)$ between t and $t + dt$ will be

$$d\Pi = \sum_{\{j\}} d\Pi_{\{j\}}\ , \tag{4}$$

the sum $\sum_{\{j\}}$ extending over all the possible connected TS. It is clear that taking account of a disconnected scheme would mean considering successive statistically independent collisional events, which is already done in a kinetic equation constructed with the above increment $d\Pi$.

Representing the probability defined by Eq. (3) by the graph of Fig. 9, we shall write the kinetic equation of the Lorentz gas in the form represented in Fig. 10, in which the Boltzmann term has been written apart. The top equation in Fig. 10 must be solved with given initial conditions, namely, the initial state of the particle and the initial correlations between the particle and the scatterers. We shall consider later the effect of these initial conditions.

2. Effect of Correlations between Scatterers

Up to now we have ignored the correlations between the scatterers. Thus we have been able to obtain the modifications of the Boltzmann kinetics which are due only to the "memory" of the past trajectory. It is particularly simple, in the case of hard spheres or disks, to take account of the correlations between the scatterers, these correlations being simply excluded-volume effects.

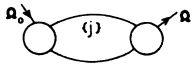


FIG. 9. Representation of the probability appearing in Eq. (3).

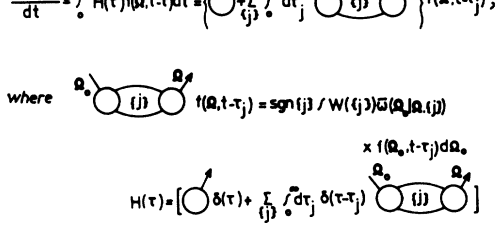


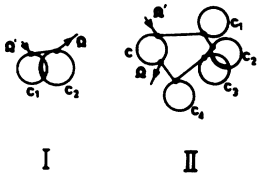
FIG. 10. Kinetic equation of the Lorentz gas.

It is clear that for an infinite system, the constraints due to the excluded volumes simply reconstraints due to the excluded volumes simply require that we subtract from the probability of the real collision events the probability of the events in which the scatterers overlap. Therefore, these forbidden events play exactly the same role as the above virtual collisions, and they generate TS subject to the rules previously given. The simplest TS in which this new type of virtual collision is to be found is represented in Fig. 11 (I). The graphic representation contains a bold line indicating that its probability must be computed by summing over all overlapping configurations of c_1 and c_2. (Let us note that this scheme satisfies the ordinary condition for being connected.) In the same way scheme (g) (cf. Fig. 3), considered above, gives rise to TS as represented in Fig. 11 (II), where the probability must be preceded by a minus sign.

III. PRINCIPLES OF A DENSITY EXPANSION OF COLLISION OPERATOR: EXPANSION WITH RESPECT TO CONSTRAINTS

A. Generalities

It is clear that the more complicated the structure of a TS, that is, the greater the number of constraints imposed on the trajectory, the lower will be the probability of this TS. Since this probability is a known function of the density parameter μ, it seems feasible to propose a simple density expansion of the collision operator based on the classification of the various TS according to the number of constraints which they contain. Unfortunately, the μ dependence of the various TS is quite complicated and is not determined solely by the number of constraints. The reason for this



I II

FIG. 11. (I) Simplest TS associated with excluded-volume effects. (II) TS generated by (g) (cf. Fig. 3) when considering excluded-volume effects.

complexity is that the different possible constraints have different weights. First, the constraints which result from the correlations between the scatterers are, in general, stronger than those which are due to the memory of the past trajectory of the particle. Second, when the separation between scatterers is of the order of R, the constraints will be weaker than for the case in which the separation is of the order of the mean free path.

Therefore, we shall not try to give a general classification of the TS, and we shall restrict ourselves to a study of the simplest TS classes.

For a given number of scatterers, it is clear that the most probable TS which may be constructed from them is the simple cycle (see Fig. 12). This TS contains only one constraint, namely, the closure of the cycle. If we now consider various simple cycles it is intuitively obvious that the probability of any cycle is only a slowly decreasing function of the number of scatterers j; roughly speaking, one can say that the successive collisions are free from constraints except for the last collision which closes the cycle. Therefore, we might be tempted to say that the first term of the expansion of the collision operator will be, after the Boltzman term, the sum of the set of all simple cycles. Actually, as mentioned above, we must incorporate into the same approximation the contribution of short-distance interactions, namely, the 3-body$\cdots(s+1)$-body interactions, as will be shown later. We shall now specify these considerations by evaluating the probabilities of some recollision diagrams.

B. Evaluation of Probability of Several TS

1. *Three-body Recollision (Simple Cycle)*

First we shall consider the simplest diagram, namely, the recollision between two disks in the two-dimensional case (cf. Fig. 13). Let us evaluate the probability $P(\Omega' \mid \Omega)d\Omega$ of the transition $(\Omega' \to \Omega, \Omega + d\Omega)$, being given the initial collision on disk 1 (characterized by angle φ). A particular configuration $\{1, 2\}$ will then be determined by the distance l between the scatterers. For a recollision at a distance between l and $l + dl$, the center c_2 of disk 2 lies on the surface element $d\Sigma$ defined by

$$d\Sigma = \psi(l, \theta)\, d\Omega\, R dl\,,$$

where θ represents the set of angles $\{\varphi, \Omega, \Omega'\}$ which characterize the configuration, and $\psi(l, \theta)$ is a measure of the allowed angular domain seen from c_2. The probability of finding c_2 in $d\Sigma$ is $nd\Sigma$. Furthermore, in order to calculate P we have to

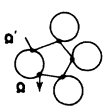


FIG. 12. Simplest cycle.

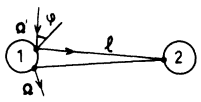


FIG. 13. Simplest two-dimensional recollision scheme.

take into account that disk 2 should be the first encountered scatterer, i.e., no other disk is to be found in the union S of the collision cylinders attached to the trajectories $1 \to 2$ and $2 \to 1$ ($S = S_1 \cup S_2 = S_1 + S_2 - S_1 \cap S_2$, S_1 and S_2 being the collision cylinders relative to the "forward" and "backward" trajectories). The probability of not finding any disk in S is

where $n = N/\Sigma$ and Σ equals the total surface of the system. S, like ψ, is a function of l and θ. Therefore $P(\Omega' \mid \Omega)d\Omega$ is given by

$$P(\Omega' \mid \Omega)d\Omega = \tfrac{1}{2}\int_0^\infty (dl/\lambda) e^{-n\,S(l,\theta)}\, d\Omega,$$

where $\lambda = (2Rn)^{-1}$ is the Boltzmann mean free path. For large l, $S(l, \theta)$ takes the form

$$S(l, \theta) = 2Rl\alpha(\theta), \quad \text{where } 1 \leq \alpha(\theta) < 2\,,$$

and $\psi(l, \theta)$ is such that

$$\psi(l, \theta) \sim R \quad \text{for } l \lesssim R,$$

$$\psi(l, \theta) = \beta(\theta)R/l \quad \text{for large } l,$$

where $\beta(\theta)$ is a normalized function ($\int d\Omega\, \beta = 1$). Let us now evaluate the total probability of recollision $W = \int P d\Omega$. Large values of l ($l \gg R$) dominate the integration (the integrand decreases as l^{-1} for large l if one ignores the shielding exponential which contributes only for $l \gg R$), and we can thus write

$$W = nR \int d\Omega \int_0^\infty dl\, \psi(l, \theta) e^{-nS(l,\theta)}$$

$$= \mu \int d\Omega\, \beta(\theta) \int_\mu^\infty \frac{dx}{x}\, e^{-2\mu x\, \alpha(\theta)}\,, \quad \text{with } x = \mu l/R.$$

The integration over x yields $\ln\mu^{-1}$ in the limit $\mu \to 0$. We then obtain

$$W = \mu \ln\mu^{-1}\,. \tag{5}$$

2. *General Form of Transition Probabilities*

In order to generalize this calculation to the case of any simple cycle we shall first give a general expression for the probability of an arbitrary TS containing j interactions. Let $l_1, \ldots, l_j, l_{j+1}$ be the distances between the successive neighboring scatterers. The elementary probability of the diagram may be written as

$$dp = \frac{dl_1}{\lambda}\frac{dl_2}{\lambda} \cdots \frac{dl_j}{\lambda}\, e^{-nS(\theta, l_1 \cdots l_j)}$$

$$\times\, C\{\Theta, l_1 \cdots l_j\}\, P(\Theta) d\Theta,$$

where Θ stands for the set of angles characterizing the configuration $(\vec{\Omega}_1, \cdots, \vec{\Omega}_{j-1})$, S is the union of the collision cylinders,

$$P(\Theta) = \prod_{k=1}^{j-1} \mathcal{P}(\vec{\Omega}_k | \vec{\Omega}_{k+1})$$

is the product of the probabilities of the successive angular deflections, and $C(\Theta, l_1 \cdots l_j)$ is a function which expresses the ensemble of the constraints defining the TS; $C = 1$ or 0 according to whether the constraints are satisfied or not. Finally a differential element like dl_k/λ is the unconditional probability of finding scatterer k in dl_k. It is convenient to use polar variables in the j dimensional space:

$$\left.\begin{matrix} l_1 \\ \cdot \\ \cdot \\ \cdot \\ l_j \end{matrix}\right\} \rightarrow \left\{\begin{matrix} \rho \\ \\ \\ (\alpha_1 \cdots \alpha_{j-1}) = \{\mathfrak{a}\} \end{matrix}\right. ,$$

where ρ and $\mathfrak{a}$ are, respectively, the radius vector and the set of polar angles for this space. In terms of these variables, we have

$$P = \int dp = \int_0^\infty \frac{\rho^{j-1} d\rho}{\lambda^j} e^{-nS(\rho, \Theta, \mathfrak{a})} \times P\{\Theta\} C\{\rho, \Theta, \mathfrak{a}\} \, d\Theta \, d'\mathfrak{a}, \qquad (6)$$

where $\rho^{j-1} d\rho \, d'\mathfrak{a}$ is the volume element in the frame of the l_k's. The functions $P\{\Theta\}$ and $C\{\rho, \Theta, \mathfrak{a}\}$ have no singularities and the integrand has a regular behavior when $\rho \to 0$, since the constraints are then associated with finite solid angles. When $\rho \to \infty$ the argument of the shielding exponential takes the form $n\rho R^{S-1} \bar{S}(A, \Theta)$, and the exponential *makes the integral converge in all cases.*

3. *Particular Case of Simple Cycle*

The effect of the constraint on the closing of the cycles may be expressed by writing $\vec{\Omega}_j$ and l_{j+1} as known functions of the previous random variables $l_1 \cdots l_j$, $\vec{\Omega}_1 \cdots \vec{\Omega}_{j-1}$, where the solid-angle element corresponding to Ω_j has the form

$$\Delta\Omega_j = H(l_{j+1}, \vec{\Omega}_{j+1}) d\Omega' \sim (R/l_{j+1})^{s-1} d\Omega' \quad \text{as } l_{j+1} \to \infty ,$$
$$\Delta\Omega_j \sim d\Omega' \quad \text{for } l_{j+1} \lesssim R , \qquad (7)$$

l_{j+1} being of the form

$$l_{j+1} = \rho F_j(\Theta, \mathfrak{a}) \quad \text{for large } l_k\text{'s.} \quad \text{(See Fig. 14.)}$$

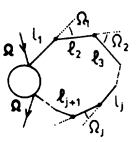


FIG. 14. Two-dimensional recollision cycle.

Therefore, the integrand in the general expression (6) for ρ takes the form, for large ρ,

$$\lambda^{-j} \rho^{j-s} d\rho \, e^{-nS} P(\Theta) C(\rho, \Theta, A) \, d\Theta \, d'\mathfrak{a} ,$$

from which it follows that, if $s - j > 1$, the integrand converges even in the absence of the shielding term e^{-nS}. Furthermore, the effective range of ρ in the calculation of the integral is of the order of R, i.e., those values for which $e^{-nS} \approx 1$. Accordingly, the dominant dependence on n of the integral is given by λ^{-j}, that is, we have

$$\Pi_j d\Omega' \sim \mu^j d\Omega', \quad s - j > 1 .$$

This case holds for $s = 3$, $j = 1$. If $s - j < 1$, the integral diverges in the absence of the shielding factor. As a result the important values of ρ in the integration (with the shielding factor) are such that $\rho \gg R$. In this range we can use the asymptotic form (7) of $\Delta\Omega_j$ and of the shielding factor nS.

Using the variable $x = \mu l/R$ we have

$$\Pi_j d\Omega' \sim \mu^{s-1} \int d\Theta \, d'\mathfrak{a} \int_\mu^\infty \frac{dx}{x^{s-j}} e^{-2x\bar{S}(\mathfrak{a}, \Theta)} \times \frac{\mathcal{P}\{\Omega_j[\Theta, \mathfrak{a}, (x/\mu)]\}}{F_j^{s-1}(\Theta, \mathfrak{a})} P(\Theta) \, d\Omega' , \qquad (8)$$

where the lower limit μ of the integral over x accounts for the modification of $\Delta\Omega_j$ when the last collision occurs at a short distance. μ appears in expression (8) in the μ^{s-1} factor, in the lower limit of the integral over x, and in the argument of the angular probability $\mathcal{P}(\vec{\Omega}_j)$. The latter dependence on μ is rather weak since this probability is, in general, a regular function with a value between 0 and 1 and Ω_j is also a regular function of the cycle's length. In a first approximation we will neglect the dependence of Π_j on μ through $\mathcal{P}(\vec{\Omega}_j)$. (This is equivalent to replacing this probability by some mean value independent of μ.) This approximation is no longer necessary in the case of hard spheres where the probabilities $\mathcal{P}(\vec{\Omega}_k)$ are uniform. Two cases are thus to be considered: (a) $s - j < 1$. The integral over x converges in the limit $\mu \to 0$, and

$$\Pi_j d\Omega' \sim \mu^{s-1} d\Omega' ;$$

(b) $s - j = 1$. The integral over x diverges for $\mu \to 0$. One then has

$$\int_\mu^\infty dx \cdots \sim \ln \mu^{-1}, \quad \Pi_j d\Omega' \sim \mu^{s-1} \ln \mu^{-1} .$$

Let us reformulate these results for the collision frequencies ν_{j+1} ($\nu_{j+1} = \Pi_j \times$ probability of the initial collision):

$$\text{If } s - j > 1, \ \nu_{j+1} \sim \mu^{j+1} \ (s = 3, \ j = 1, \ \nu_j \sim \mu^2) ;$$

If $s-j<1$, $\nu_{j+1}\sim\mu^s$

(For j sufficiently large, ν_j becomes independent of j);

If $j=s$, $\nu_{s+1}\sim\mu^s\ln\mu^{-1}$.

4. *Probability of Cycles Sum*

It is important to know whether the sum (over j) of the probabilities of the cycles is convergent. The central limit theorem answers this question in the case of hard spheres ($s=3$). The vectors $\vec{l}_j$ are then statistically independent and

$$\vec{L}=\sum_{i=1}^{j}\vec{l}_i$$

obeys a normal law in the limit of large j. This result remains valid when the angular deflection in a collision does not have uniform probability.[9] The distribution of $\vec{L}$ has the form

$$\varphi_s^j(\vec{L})=j^{-s/2}\lambda^{-s}e^{-L^2/j\Lambda^2},$$

where

$$\Lambda=\langle(\textstyle\sum_j l_\alpha l_j)\rangle^{1/2}$$

(α being a large enough arbitrary integer).

The probability of recollision with the initial scatterer (assumed to be in $\vec{L}=0$) is proportional to $\sum_j\varphi_s^j(\vec{L}=0)$. But

$$\textstyle\sum_j\varphi_s^j(0)\begin{cases}<\infty & \text{for } s>2,\\ =\infty & \text{for } s=2.\end{cases}$$

This sum converges only in the three-dimensional case; the probability of recollisions is then well defined and it is small if n is small. On the contrary, the sum diverges for a two-dimensional system. Then, by virtue of the well-known theorem on Markov chains, only the probability of first return is well defined, and it is unity. The probability of returning to the origin between τ and $\tau+d\tau$ is then

$$P_2(\tau)d\tau\sim\nu d\tau/\tau\quad(s=2).$$

5. *Mean Duration of Various Cyclic Diagrams*

In the three-dimensional case the probabilities of the cycles decrease as $j^{-3/2}$, and, therefore, a good approximation of the collision operator is obtained by retaining only the cycles containing a relatively small number of scatterers. The duration of these cycles ($\tau_j=\langle L_j/v\rangle$) can easily be evaluated by using the approximate probabilities given in Sec. III B 3. We then obtain

$$\tau_1=\langle L_1/v\rangle\sim\nu/v=\mu\nu^{-1}\quad(s=3),$$

$$\tau_2=\langle L_2/v\rangle\sim\nu^{-1}/\ln\mu^{-1},$$

$$\tau_{j>2}=\langle L_j/v\rangle\sim\nu^{-1},$$

where ν is the Boltzmann collision frequency.

In the two-dimensional case, on the contrary, the probability of first return is unity while the probability of any particular cycle is of the order of μ ($\mu\ll1$). It follows that a large number of cycles must be included in the reconstruction of the probability of first return, which enters the collision operator (the relevant domain of j would be of the order of μ^{-1}). This implies the contribution of cycles whose duration is much larger than ν^{-1}. Nevertheless, as we shall see later, the efficiency of the collision operators associated with large cycles becomes very low when j increases.

C. Effect of Initial Conditions

We suppose that the moving particles are "created" at $t=0$ with pdf $f^0(\vec{\Omega})$ and a given correlation with the scatterers. Let us first study the evolution of the joint probability $P(\vec{\Omega},t\,|\,\vec{\Omega}_0)$. For this we must consider that the distribution of the scatterers is inhomogeneous in a region around $\vec{x}=\vec{x}_0$ whose extension is of the order of the initial correlation length. Consequently, the transition probabilities of the collisional processes which take place in the vicinity of $\vec{x}=\vec{x}_0$ are modified (being space dependent). The kinetic equation for P may be written as

$$\frac{d}{dt}P(\vec{\Omega},t\,|\,\vec{\Omega}_0)=\int_0^t d\tau\,H(\vec{\Omega},\vec{\Omega}_0,\tau)\,P(\vec{\Omega},t-\tau\,|\,\vec{\Omega}_0),\tag{9}$$

where $H(\vec{\Omega},\vec{\Omega}_0,\tau)$ is the modified collision operator, when account is taken of the inhomogeneity of the medium. It is worth noting that, due to the dependence of H on $\vec{\Omega}_0$, Eq. (9) does not yield an equation for $f(\vec{\Omega},t)$ [$f(\vec{\Omega},t)=\int Pf^0(\vec{\Omega}_0)\,d\Omega_0$] by means of an averaging over the initial states. Nevertheless, it is clear that in the limit of long times, P becomes independent of $\vec{\Omega}_0$, the contribution of the collision schemes dependent on $\vec{\Omega}_0$ becoming negligible; we then recover the kinetic equation (see Fig. 10) for $f(\vec{\Omega},t)$.

It is instructive to consider the case for which the initial given correlation is that no particle is to be found inside the volume occupied by the hard spheres. This correlation is of the "excluded-volume" type as are the correlations between the spheres. Again, it is possible to take account of this initial correlation by considering forbidden TS, namely, those in which $\vec{x}_0$ is located inside one of the scatterers. A virtual scheme of this type is given in Fig. 15. Its topology is such that no "way in" can be defined, and, therefore, it does not appear in the classification of the above-defined TS. This new class of virtual schemes produces inhomogeneous terms in the kinetic equation for P. It is clear that the contributions of the term associated with the scheme of Fig. 15 is of the same order of magnitude as the contribution of the recollision scheme (cf. Fig. 16) which enters the colli-

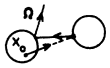


FIG. 15. Scheme associated with initial conditions of excluded volume.

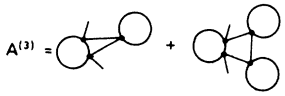


FIG. 17. Intersection of $\mathcal{T}_1^{(3)}$ and $\mathcal{T}_2^{(3)}$.

sion operator in the kinetic equation (see Fig. 10). We conclude that during the initial state of the evolution neglecting the propagation of the initial correlation introduces an error of the same order as that incurred by neglecting the recollision processes in the kinetic equation. This remark leads to the difficult question of the evaluation of a time autocorrelation function in the gas. We shall return later to this problem when we calculate the self-diffusion coefficient.

IV. KINETIC EQUATION IN μ^s APPROXIMATION

A. Derivation of Kinetic Equation

Taking account of all the simple cycles in the collision operator means that one retains terms up to the μ^s order. On the other hand, it is obvious that the probability of a configuration containing j neighboring scatterers (whose distances are of the order of R or of the range a of the interaction potential) is of the order of μ^j. Therefore we must, in the μ^s approximation, retain in the kinetic equation all the configurations with $j = s$ scatterers. In the case of hard spheres (or disks) this means that we keep all multiple recollision processes involving s scatterers. In the case of an arbitrary interaction potential (not of the hard-sphere type) the recollision concept is less clear, and it loses its meaning entirely when the potential range of several scatterers overlap. It is therefore necessary to introduce the total transition probabilities relative to the interaction of a particle with s scatterers. The probabilities of the large cycles ($l_j \gg R, a$) will be evaluated asymptotically in the limit of large l_j's, the limits of which are in general well defined.

Let us denote by $\mathcal{T}_1^{(s)}$ the set of diagrams which involve at most s scatterers and by $\mathcal{T}_2^{(s)}$ the set of the simple cycles. These two sets have a nonempty intersection A which for $s = 3$ is given in Fig. 17.

Since these diagrams must be counted only once, we will consider the sets

$$\Xi = \mathcal{T}_1 - A \quad \text{and} \quad \mathcal{T}_2.$$

$\mathcal{T}_2$ contains all the simple cycles and may be written as in Fig. 18, where we have explicitly shown the real and the virtual terms. The kinetic equation including Ξ will therefore be written as in Fig. 19.

The equation in Fig. 19 is the most general kinetic equation in the μ^s approximation. The last term contains the probability $G(\tau)$ that the particle returns to the initial scatterer between τ and $\tau + d\tau$ and after an arbitrary number of independent collisions. This probability may of course be expressed by means of the Green's function for the inhomogeneous Boltzmann equation. The collisions which occur in the cycle are, in the μ^s approximation, ordinary binary collisions. Furthermore, both initial and final interactions may be described by means of the usual binary collision operator T. T itself can be split into an emission and an absorption part:

$$T = T_R - T_V$$

(which are the "real" and the "virtual" parts in the usual terminology).

Writing explicitly the emission and the absorption parts of the real and virtual diagrams in the last term of the equation in Fig. 19, we obtain the four terms represented in Fig. 20 with their corresponding signs.

Grouping these four terms, we obtain the relation written in Fig. 21.

The "Markovianized" version of this equation is given in Fig. 22, where

$$\bar{G}_{\alpha,\beta} = \int_0^\infty d\tau\, G_{\alpha,\beta}(\tau)$$

is the probability that the particle will return to the initial scatterer, irrespective of the time. This last form is identical, except for the Ξ term, to the equation given by Cohen[1] and by Pomeau.[4] We shall now study the conditions of validity of this equation.

B. Validity of a Collision Operator Local in Time

The evolution of the gas is driven mainly by the ordinary binary collisions which are the most probable events. The relaxation time of an anisotropy in velocity space is therefore of the order of ν^{-1}. Consequently, the relative variation of this anisotropy during the duration τ_j of an arbitrary cycle will be of the order of $\nu\tau_j$. We thus conclude that a first condition of validity of the equation in Fig. 22 is $\nu\tau_j \ll 1$. An additional condition must be fulfilled in order to make a coherent approximation of the kinetic equation: The errors which result from an approximate calculation of the most probable diagrams in the collision operator must be

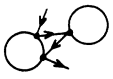


FIG. 16. Recollision scheme.

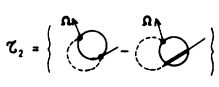


FIG. 18. Expression of $\mathcal{T}_2$.

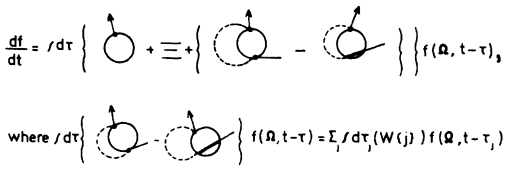


FIG. 19. Kinetic equation including Ξ.

negligible compared to the contribution of the most unprobable diagrams retained.

In particular, in the μ^s approximation, we have to account for the duration of the ordinary binary collisions whenever the interaction potential is not of the hard-sphere type.

1. *Three-Dimensional Markovian Kinetic Equation*

Let us first recall (Fig. 23) the μ dependence of the various relevant diagrams containing terms of the order of μ^2, $\mu^3 \ln \mu^{-1}$, and μ^3.

Considering the first criterion and using the results obtained on the time duration of the cycles (Sec. III B 5), we see that the diagrams with more than three scatterers provide non-Markovian contributions and therefore must be disregarded in the equation in Fig. 22. It is worth noting that these diagrams are negligible if we restrict ourselves to the $\mu^3 \ln \mu^{-1}$ approximation. We can thus approximate Ξ (see Fig. 24).

Considering, next, the second criterion, we remark that a Markovian approximation of the Boltzmann binary term is only valid if the range of the interaction potential is very short. In general, there is a non-Markovian contribution of the order of μ^2 if the potential range is of the order of the radius of the scatterers.

The Markovian kinetic equation for hard spheres is then given in (Fig. 25) with Ξ given in Fig. 24.

We point out that the contribution of distant collisions has a fairly simple form since it involves only three-body and four-body interactions. As for the Lorentz gas, the contribution of the non-Markovian cycles is small compared to that of the retained cycles, and therefore the equations in Figs. 22 and 24 are equivalent (they differ, however, from that given by Cohen and by Pomeau by the presence

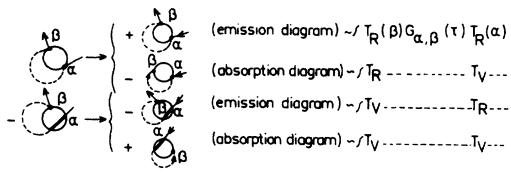


FIG. 20. Explicit form of the last term of the equation in Fig. 19.

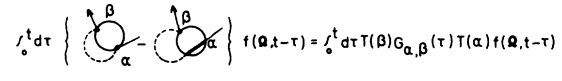


FIG. 21. Expression of the collision integral.

of the "short-distance operator" Ξ).

2. *Two-Dimensional Markovian Equation*

We consider the diagrams of Fig. 26. For this case, only the two-scatterer diagram is Markovian and it is much larger than Ξ. Therefore, the Markovian equation will be given, if it exists, in Fig. 27. However, one may doubt the validity of this equation. Since the probability of return on the initial scatterer has a probability equal to unity, one may ask if, over a long time, the set of large cycles does not play a decisive role in the kinetics (even though each of these cycles separately is of higher order).

Let us now consider the four cyclic contributions of Fig. 28.

The central limit theorem tells us that the probability of these configurations for large τ is such that

$$W_i(\vec{\Omega}, \vec{\Omega}', \tau) \sim \mu(d\tau/\tau) .$$

Furthermore, it is intuitively obvious that these probabilities tend to become isotropic, i.e., independent of $\vec{\Omega}$. It is shown in the Appendix that

$$\left| |W_i(\vec{\Omega}, \vec{\Omega}', \tau)| - |W_j(\vec{\Omega}, \vec{\Omega}_1', \tau)| \right| d\tau \sim \mu(d\tau/\tau)(1/\nu\tau) .$$

From this, it follows that the sum of the cycles

$$\nu \int [(W_1 - W_2) + (W_3 - W_4)] d\tau \sim \nu\mu \int_{\tau \sim 1/\nu}^{\infty} \frac{\nu\, d\tau}{\nu\tau} \frac{1}{\nu\tau} \sim \nu\mu$$

never causes any divergence in the kinetic equation and provides a regular contribution of the order of μ^2, i.e., smaller than the contribution resulting from the recollision term (Fig. 16). This ensures the consistency of the kinetic equation in two dimensions (Fig. 27).

We now give an explicit form of the equation for the marginal pdf $f(\Omega, t)$ in the approximation $\mu^2 \ln \mu^{-1}$. It may be written in terms of binary collision operators as

$$\frac{\partial f(\Omega, t)}{\partial t} = (T + T\bar{G}T) f(\Omega, t)$$

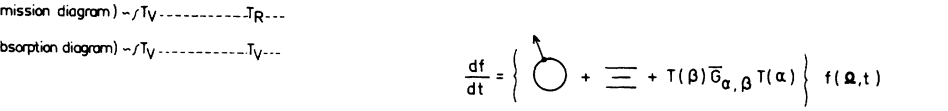


FIG. 22. Markovianized kinetic equation.

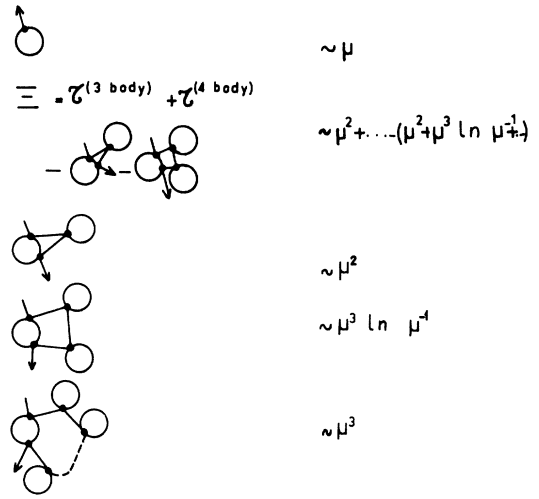


FIG. 23. μ dependence of the relevant diagrams (three dimensions).

or

$$\frac{\partial f}{\partial t} = (\nu[\Pi(R_\alpha)R_\alpha - I] + \nu'\{[\Pi(R_\alpha)R_\alpha - I] \times R(\Pi)[\Pi(R_\beta)R_\beta - I]\})f\,, \tag{10}$$

where $\nu' = \mu^2 \ln \mu^{-1}$, $R_{\alpha \text{ or } \beta}$ represents the rotation operators associated with the various rotations occurring in the process, $\Pi(R_{\alpha \text{ or } \beta})$ is the probability of rotations $R_{\alpha \text{ or } \beta}$. The intermediate rotation in the triple-collision term has been taken as $R(\Pi)$: This is due to the fact that the long-distance recollisions are dominant. It is interesting to write down the kinetic equation for the characteristic function $\phi(\theta, t)$ defined by

$$\phi(\theta, t) = \langle e^{i\theta\Omega(t)} \rangle\,.$$

The eigenfunctions of the rotation operators are of the form $e^{i\theta\Omega}$, and the Fourier transform of the collision operator is a function $K(\theta)$. Fourier transforming Eq. (10) we obtain

$$\frac{\partial}{\partial t}\,\phi(\theta, t) = K(\theta)\phi(\theta, t), \tag{11}$$

with

$$K(\theta) = \nu[\psi(\theta) - 1] + \nu'\{[\psi(\theta) - 1]e^{i\Pi\theta}[\psi(\theta) - 1]\}\,,$$

where $\psi(\theta)$ is the characteristic function of the angular deflection in the binary collision [given by Eq. (2)].

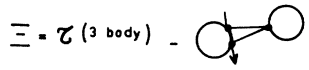


FIG. 24. Approximation for Ξ in the $\mu^3 \ln \mu^{-1}$ approximation.

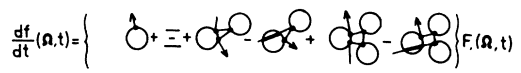


FIG. 25. Markovian kinetic equation for hard spheres.

The solution of Eq. (11) is

$$\phi(\theta, t) = e^{K(\theta)t}\phi(\theta, t = 0)\,,$$

which has the same form as in the Boltzmann approximation. This is due to the fact that the increments of $\Omega(t)$ resulting from the various collisional events (real or virtual) remain independent of Ω. This property does not survive in the three-dimensional gas.

C. Self-Diffusion Coefficient of Lorentz Gas

We start from the usual definition of the self-diffusion coefficient, namely,

$$D = \tfrac{1}{2} \lim \int_0^t \langle \vec{v}(t) \cdot \vec{v}(t - \tau) \rangle\, d\tau \quad \text{as } t \to \infty\,.$$

One way to calculate D is to evaluate the autocorrelation function in the limit of long times. Let $Q(\tau)$ be the asymptotic form of this function, which is stationary. It is "intuitive" that $Q(\tau)$ can be expressed in terms of the collision operator $H(\tau)$ of the kinetic equation Fig. (10), that is, without initial correlation terms. One thus writes

$$Q(\tau) = \langle \vec{v}(0) \cdot \vec{v}(\tau) \rangle = \vec{v}(0) \cdot [F(\vec{v}, \tau)\vec{v}(0)]\,,$$

where $F(\vec{v}, \tau)$ is the propagator of the kinetic equation (Fig. 10)[the distribution of $\vec{v}(0)$ is assumed to have reached its stationary isotropic form]. For simplicity we shall consider the two-dimensional gas. The Fourier transform of $F(\Omega, \tau)$ will be $\phi(\theta, \tau)$, the solution of a kinetic equation of the following form:

$$\frac{\partial}{\partial \tau}\,\phi(\theta, \tau) = \int_0^\tau dt'\, K(\theta, t')\phi(\theta, \tau - t')\,, \tag{12}$$

with initial condition $\phi(\theta, \tau = 0) = 1$. We then have

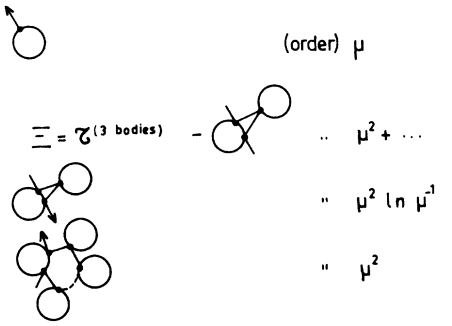


FIG. 26. Relevant diagrams in the two-dimensional case.

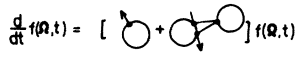


FIG. 27. Markovian kinetic equation in the two-dimensional case.

$$Q(\tau) = v^2[\cos\Omega(\tau)] = v^2\phi(\theta = 1, \tau) .$$

Laplace transforming Eq. (12) with respect to time, we obtain

$$\hat{\phi}(\theta, \epsilon) = [\epsilon - \hat{K}(\theta, \epsilon)]^{-1} ,$$

where $\hat{\phi}$ and $\hat{K}$ are the Laplace transforms of ϕ and K. We then have

$$D = \frac{1}{2}\int_0^{\tau\to\infty} d\tau \frac{1}{2\pi i}\int_{(\Gamma)} d\epsilon \frac{e^{\epsilon\tau}}{\epsilon - \hat{K}(1, \epsilon)}$$

$$= \frac{1}{2}\,\frac{1}{2\pi i}\int_{(\Gamma)} \frac{ds}{\epsilon[\epsilon - \hat{K}(1, \epsilon)]} ,$$

where (Γ) is the Bromwich contour in the ϵ plane (Fig. 29); such that $\mathrm{Re}(\epsilon) < 0$, but with all the singularities of $[\epsilon - \hat{K}(1, \epsilon)]^{-1}$ on the left of (Γ). The existence of (Γ) will be assumed, arguing that if $Q(\tau)$ has a regular behavior for $\tau \to \infty$, then all the singularities must be on the left of $\epsilon = 0$. Closing the contour on the right in this fashion, we find the unique pole $\epsilon = 0$ and we obtain

$$D = -\tfrac{1}{2}\,[1/\hat{K}(1, \epsilon = 0)] , \qquad (13)$$

where

$$\hat{K}(1, \epsilon = 0) = \int_0^\infty d\tau\, K(1, \tau)$$

is the "Markovianized" collision operator of the kinetic equation.

This result relies upon the use of the kinetic equation (Fig. 10) with no initial correlation terms. Due to the non-negligible effects of the propagation of an initial correlation state over times which are relevant in the calculation of D (cf. Sec. III),

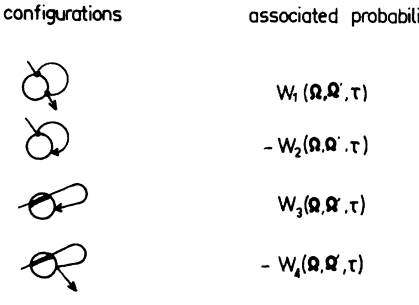


FIG. 28. Four cyclic contributions and their probabilities.

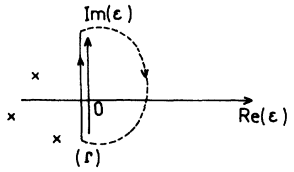


FIG. 29. Bromwich contour in the ϵ plane.

we should justify the use of the kinetic equation (Fig. 10) to obtain $Q(\tau)$. The justification of this procedure is a rather delicate question which we prefer not to treat here. Instead, we shall confirm expression (13) for D by calculating it without the intermediate evaluation of the time autocorrelation function. We have

$$D = \tfrac{1}{2}\lim_{t\to\infty}\langle \vec{X}(t)\cdot\vec{v}(t)\rangle = \tfrac{1}{4}\lim_{t\to\infty}\frac{d}{dt}\langle \vec{X}^2(t)\rangle .$$

We may therefore calculate D by means of an asymptotic evaluation of the inhomogeneous pdf $f(\vec{X}, \vec{v}, t)$, and we can safely ignore the initial correlations in the kinetic equation. Since the particular form of the initial condition is unimportant, we state that the particles start at $\vec{X} = 0$ with an isotropic distribution in velocity space:

$$f(\vec{X}, \vec{v}, t = 0) = \delta(\vec{X})\frac{\delta(|\vec{v}| - v_0)}{v_0}\frac{1}{2\pi} .$$

D may be written as

$$D = \lim_{t\to\infty}\tfrac{1}{2}\int \vec{X}\cdot\vec{v} f(\vec{X}, \vec{v}, t)\, d\vec{X}\, d\vec{v}$$

$$= \lim_{\epsilon\to 0}\tfrac{1}{2}\epsilon\int \vec{X}\cdot\vec{v}\hat{f}(\vec{X}, \vec{v}, \epsilon)\, d\vec{X}\, d\vec{v} ,$$

where $\hat{f}(\vec{X}, \vec{v}, \epsilon)$ is the time-Laplace transform of $f(\vec{X}, \vec{v}, t)$. In Fourier space, with respect to $\vec{X}$, the solution of the kinetic equation is

$$f_{\vec{K}}(\vec{v}, \epsilon) = f_{\vec{K}}(\vec{v}, t = 0)/[\epsilon + i\vec{K}\cdot\vec{v} - \hat{H}(\epsilon)] ,$$

where $\hat{H}(\epsilon)$ is the Laplace transform of the non-Markovian collision operator:

$$D = \lim_{\epsilon\to 0}\frac{\epsilon}{2}\int \vec{X}\cdot\vec{v}\, e^{i\vec{K}\cdot\vec{X}}\frac{f_{\vec{K}}(\vec{v}, t = 0)}{\epsilon + i\vec{K}\cdot\vec{v} - \hat{H}(\epsilon)}\, d\vec{X}\, d\vec{K}\, d\vec{v} ;$$

writing

$$\vec{X}\cdot\vec{v}\, e^{i\vec{K}\cdot\vec{X}} = -i\vec{v}\cdot\left(\frac{\partial}{\partial\vec{K}}\, e^{i\vec{K}\cdot\vec{X}}\right)$$

and integrating by parts over $\vec{K}$, we have

$$D = \lim_{\epsilon\to 0}\frac{i\epsilon}{2}\int e^{i\vec{K}\cdot\vec{X}}\vec{v}\circ\frac{\partial}{\partial\vec{K}}\frac{f_{\vec{K}}(\vec{v}, 0)}{\epsilon + i\vec{K}\cdot\vec{v} - \hat{H}(\epsilon)}\, d\vec{X}\, d\vec{K}\, d\vec{v} ,$$

where $f_{\vec{K}}(\vec{v}, 0)$ does not depend on $\vec{K}$.

Let ψ be the inverse of the operator $[\epsilon + i\vec{K}\cdot\vec{v}$

$-\hat{H}(\epsilon)]$. We have

$$[\epsilon + i\vec{K}\cdot\vec{v} - \hat{H}(\epsilon)]\psi = 1 .$$

Taking the derivative of this equation with respect to $\vec{K}$ we obtain $\vec{v}\cdot(\partial/\partial\vec{K})\psi = -i\vec{v}\cdot\psi\vec{v}\psi$, which yields

$$D = \tfrac{1}{2}\int e^{i\vec{R}\cdot\vec{X}}\vec{v}\cdot\psi\vec{v}\psi f_{\vec{R}}(\vec{v}, 0)\, d\vec{X}\, d\vec{K}\, d\vec{v} .$$

Integrating over $\vec{X}$ and $\vec{K}$, we find

$$D = \tfrac{1}{2}\int d\vec{v}\vec{v}\cdot\psi(\vec{K}=0)\vec{v}\psi(\vec{K}=0) f_{\vec{R}}(\vec{v}, 0)$$

$$= \tfrac{1}{2}\int d\vec{v}\vec{v}\frac{1}{\epsilon - \hat{H}(\epsilon)}\vec{v}\frac{1}{\epsilon - \hat{H}(\epsilon)} f_{\vec{R}}(\vec{v}, 0) .$$

Since $f_{\vec{R}}(\vec{v}, 0)$ is isotropic, we obtain

$$\frac{\epsilon}{\epsilon - \hat{H}(\epsilon)} f(\vec{v}, 0) = f(\vec{v}, 0) .$$

Therefore, in the limit $\epsilon \to 0$, we are left with

$$D = \tfrac{1}{2}\int d\vec{v}\vec{v}[1/-\hat{H}(\epsilon=0)]\vec{v} f_{\vec{R}}(\vec{v}, 0) .$$

Since $\vec{v}$ is an eigenfunction of H with eigenvalue $\hat{K}(\theta=1, \epsilon=0)$, we recover expression (13).

As an application, let us evaluate D in the hard-disk case and in the $\mu^2\ln\mu^{-1}$ approximation. From Eqs. (2), (11), and (13) we obtain

$$D = (v^2/\Lambda) ,$$

with

$$\Lambda = \tfrac{1}{2}[\tfrac{8}{3}\nu + (\tfrac{8}{3})^2\nu'] ,$$

which is the result given by Van Leeuwen and Weijland.[5] In the three-dimensional case the calculation, though more complicated, also leads to the results obtained by these authors (cf. Sec. V for the interpretation of some contributions).

V. COMPARISON BETWEEN BCE AND EXPANSION WITH RESPECT TO CONSTRAINTS

In BCE theory, the N-body Liouville operator is expanded in a series whose terms contain products of binary collision operators. If suitable resummations of divergent collision integrals are performed, this expansion leads to collision operators which it is instructive to compare to ours. For this, let us return to the general expression (6) for the transition probabilities. We may make a series expansion, in Eq. (6), of the screening exponential:

$$e^{-nS(\rho,\Theta,\alpha)} = \sum_p (-nS)^p/p! ,$$

and write for the contribution of the pth term

$$dW_p = \lambda^{1-j}\rho^{j-2}d\rho\,[-nS(\rho, \Theta, \alpha)]^p$$

$$\times[p(\Theta)/p!]C(\Theta, \rho, \alpha)d'\alpha\, d\Theta ; \qquad (14)$$

the convergence of the integral $\int dW_p$ results from the asymptotic behavior of the integrand ($\rho \to \infty$).

Two cases are to be considered:

(a) $dW_p < \infty$, which occurs if $dW_p < 1/\rho$ as $\rho \to \infty$. The terms containing $(-nS)^p$ may be interpreted as representing p "virtual collisions" in the sense of the BCE theory. Let us recall that, according to the terminology of BCE theory, a virtual collision represents the T_v part of the binary collision operator which does not change the orientation of the particle velocity (and which is proportional to the Boltzmann collision frequency ν). We shall call these collisions "free virtual collisions" to distinguish them from those which are introduced in our theory and whose physical significance is fundamentally different. A "free virtual collision" simply represents a part of the binary collision operator, the sum of all such collisions along a trajectory (between two real collisions) generating the screening exponential e^{-nS}. On the contrary, a virtual collision in the present theory expresses a topological constraint imposed on a recollision scheme or, in other words, represents a dynamical correlation, and any scatterer involved in one (or several) virtual collision must also make a *real interaction* within the test particle.

We shall use the graph of Fig. 30 (I) to represent a free virtual collision. The dotted line outside the graph means that no screening effect is taken into account on the trajectory (a continuous line being associated with a screening factor).

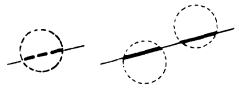
(b) $dW_p = \infty$ for $p > p_{\text{minimum}} = p_i$. The collision integrals being divergent for $p_i < p < \infty$, we conclude that there exists no series expansion of the transition probabilities in powers of the density. Nevertheless, it can be shown that $\sum_{p_i}^{\infty} dW_p$ can be written

$$\sum_{p_i}^{\infty} dW_p \simeq \sum_{\mu\to 0} \lambda^{1-j}\rho^{j-2}d\rho p(\Theta)C(\Theta, \rho, \alpha)d\Theta d'\alpha$$

$$\times\frac{(-nS)^{p_i}}{p_i!}e^{-nS} + \text{smaller terms} , \qquad (15)$$

where the "smaller terms" have an unknown analytical form. The dominant term in Eq. (15) yields a contribution of the order of $\mu^{p_i+j-1}\ln\mu^{-1}$ to $\int\sum_{p_i}^{\infty} dW_p$: It may be looked at as the result of a renormalization procedure performed on the series of divergent terms ($p > p_i$).

This dominant term may be considered to represent p_i free virtual collisions occuring together with screening effects along the trajectory. The graph of Fig. 30 (II) represents a term of this kind ($p_i = 2$)



I II

FIG. 30. (I) Free virtual collision (without screening effects). (II) Free virtual collisions (with screening effect).

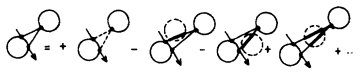


FIG. 31. Development of the recollision term including free virtual collisions.

in which the continuous line means that the screening is taken into account. Considering a three-dimensional gas, the interaction with two scatterers gives rise to the expansion given in Fig. 31 (corresponding to $p_i = 1$). The first term is the Choh-Uhlenbeck collision operator[10] which is proportional to μ^2: It is the nondivergent term of Eq. (14). The three following terms correspond to the renormalized expression in (15): They are of the order of $\mu^3 \ln \mu^{-1}$.

Beyond the approximation $\mu^{p+j-1} \ln \mu^{-1}$ it seems difficult (and probably untractable) to rebuild the transition probabilities through a BCE expansion, even in terms of renormalized virtual collisions.

CONCLUSION

We think that the consideration of the elementary collisional events leads to a clear description of the gas kinetics. Moreover, the classification of these events with respect to their probability yields a sound basis for an expansion of the general collision operator. Since these probabilities are well defined, the present theory is free from the divergencies which appear in the BCE. The theory is therefore free from the renormalization procedures which are needed in order to remove these divergencies and whose justification is not evident (actually, these renormalizations find a simple physical interpretation in our theory). In addition, serious difficulties occur in the framework of the BCE if one wants to go beyond the approximation of the cycles: They are caused by the nonanalyticity of the transition probabilities. The coherent treatment of the short- and long-distance collisions would also be difficult.

We shall make two remarks concerning the physics of the Lorentz gas:

(a) It would seem, at first sight, that the properties of the two-dimensional and the three-dimensional gas are quite different because the recollision with an arbitrary scatterer is a certain event in two dimensions but not in three dimensions. Actually, we have seen that the large cycles yield a normal contribution (of the order of μ^2) to the collision operator: This is due to the decreasing efficiency of the cycles with an increase in the number of scatterers (isotropization effect).

(b) In reference to the Markovian character of the gas kinetics, we have shown that, for small enough density ($\mu^3 \ln \mu^{-1}$ approximation), the collision operator may be assumed to be local in time (and in space) and that it contains no more than three-body and four-body interactions. For higher density one must take account, in the collision operator, of those cycles whose length is of the order of (or larger than) the Boltzmann mean free path. For these cycles, the kinetic equation is non-Markovian. This fact may be of special importance in the case of the ordinary gas in which the correlations are vehicled along very large distances by the weakly damped eigenmodes of the Boltzmann propagator.

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APPENDIX

We shall assume, for simplicity, that the $\vec{l}_i$ vectors are statistically independent (this assumption is convenient, but not essential, for the argument).

Let us consider a particle starting from the origin with velocity $\vec{v}_0$. The first collision occurs at M_1, and after this collision the distribution of the $\vec{l}_i$'s is isotropic. In a reference frame whose origin is in M_1 the particle distribution becomes normal after n collisions (n being large) and the probability of finding a particle in M is

$$P_n(\vec{L} - \vec{l}_1) = (1/2\pi n\lambda^2) e^{-(\vec{L}-\vec{l}_1)^2/n\lambda^2}.$$

The probability that $l_1 < |\vec{l}_1| < l_1 + dl_1$ is $e^{-l_1/\lambda} dl_1/\lambda$ and therefore

$$P_n(\vec{L}) \int_0^\infty (1/2\pi n\lambda^2)\, e^{-(\vec{L}-\vec{l}_1)^2/n\lambda^2} e^{-l_1/\lambda} dl_1/\lambda,$$

which, in the limit of large n, gives

$$P_n(\vec{L}) = \frac{1}{2\pi n\lambda^2} \int_0^\infty e^{-l_1/\lambda} \left(1 - \frac{(\vec{L}-\vec{l}_1)^2}{n\lambda^2}\right) dl_1$$

$$= \frac{1}{2\pi n\lambda^2} \left(1 - \frac{L^2}{n\lambda^2} + \frac{2L\cos\theta}{n\lambda} - \frac{2}{n}\right),$$

with $\theta = (\vec{L}, \vec{l}_1)$.

The probability of returning to O after the $(n+1)$th collision, with a velocity vector at angle θ, is

$$W(\theta, n+1)\, d\theta = \int P_n(L, \theta) e^{-L/\lambda} (2R/2\pi L) L\, dL\, d\theta,$$

$2R/2\pi L$ being the angle subtended by the scatterer located in O from point M. We obtain for $L \gg \lambda$

$$W(\theta, n+1) = \int_0^\infty \frac{1}{2\pi n}\left[1 - \frac{1}{n}\left(\frac{L^2}{\lambda^2} - \frac{2L}{\lambda}\cos\theta + 2\right)\right] \times e^{-L/\lambda}\frac{\mu}{2\pi}\, dL$$

$$= (\mu/4\pi^2 n)[1 - (2/n)(2 - \cos\theta)],$$

from which we easily deduce

$$W(\theta, t)\, dt \sim (\mu/4\pi^2)(\nu dt/\nu t),$$

$$|W(\theta, t)\, dt - W(\theta', t)\, dt| \lesssim \frac{\mu}{4\pi^2}\frac{4}{\nu t}\frac{\nu dt}{\nu t} \quad \text{for all } (\theta, \theta').$$

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