A path-integral approach to the collisional Boltzmann gas

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Abstract: Collisional effects are included in the path-integral formulation that was proposed in one of our previous paper for the collisionless Boltzmann gas. In calculating the number of molecules entering a six-dimensional phase volume element due to collisions, both the colliding molecules and the scattered molecules are allowed to have distributions; thus the calculation is done smoothly and no singularities arise.

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1 Introduction

In our previous works, we proposed a path-integral approach to the collisionless Boltzmann gas\cite{1}\cite{2}. It is assumed in the approach that there are continuous and discontinuous distribution functions in realistic Boltzmann gases: continuous distribution functions are produced by continuous distribution functions that exist previously and discontinuous distribution functions are caused by boundary effects. (Boundaries can block and reflect molecules in such a way that distribution functions become discontinuous in the spatial space as well as in the velocity space.) To treat these two kinds of distribution functions at the same time, a different type of distribution function, called the solid-angle-average distribution function, is introduced as

\[ f(t, r, v, \Delta \Omega) = \frac{1}{\Delta \Omega} \int f(t, r, v) d\Omega, \]  

(1)

where \(\Delta \Omega\) represents one of the solid angle ranges in the velocity space defined by the investigator and \(f(t, r, v)\) is the “ordinary” distribution function. By letting each of \(\Delta \Omega\) be adequately small, the newly employed distribution function is capable of describing gas dynamics with any desired accuracy. Provided that collisions in a Boltzmann gas can be neglected, the solid-angle-average distribution function is found to be

\[ f(t, r, v, \Delta \Omega) = \frac{1}{\Delta \Omega} \int_{\Delta S_1} \frac{f^{cl}(t_0, r_0, v, \Omega_0) \cos \alpha |dS_0|}{|r - r_0|^2} U_{r_0r} \]  

\[ + \frac{1}{\Delta \Omega} \int_{\Delta S_2} \eta(t_0, r_0, v, \Omega_0)|dS_0| U_{r_0r}, \]  

(2)

where, referring to Fig. 1, \(\Delta S_1\) is an arbitrarily chosen virtual surface within the effective cone defined by \(-\Delta \Omega\) at the point \(r\), \(\Delta S_2\) stands for all boundary surfaces within the effective cone, \(\eta\) is the local emission rate of boundary surface (acting like a surface-like molecular source), \(r_0\) represents the position of \(dS_0\), \(\Omega_0\) is the solid angle of the velocity but takes the direction of \((r - r_0)\), \(t_0\) is the local time defined by \(t_0 = t - |r - r_0|/v\), \(\alpha\) is the angle between the normal of \(dS_0\) and the vector \(r - r_0\), \(f^{cl}\) is the continuous part of the distribution function existing previously, and \(U_{r_0r}\) is the path-clearness step function, which is equal to 1 if the path \(\overline{r_0r}\) is free from blocking otherwise it is equal to 0.

The objective of this paper is to include collisional effects in the path-integral formalism.
According to the conventional wisdom collisions can be analyzed by the method developed by Boltzmann long ago, in which it is understood that there is a symmetry between the ways molecules enter and leave a phase volume element. Peculiarly enough, this well-accepted understanding includes actually hidden fallacies, which can briefly be summarized as follows. In terms of studying collisions in a Boltzmann gas, there are two issues that are supposedly important. The first one is related to how many collisions take place within a phase volume element and during a certain time; the second one is related to how the scattered molecules will, after collisions, spread out over the velocity space and over the spatial space. These two issues involve different physics and have to be formulated differently. If the molecules leaving a phase volume element is of interest, one needs to take care of only the first issue; whereas if the molecules entering a volume element is of interest, one needs to concern oneself with both the issues aforementioned. This imparity simply suggests that the time-reversal symmetry, though indeed exists for a single collision between two molecules, cannot play a decisive role in studying collective effects of collision.

In the present paper we formulate the collisional effects partly in an unconventional way. In deriving how many molecules make collisions, the standard method is employed without much discussion; but, in formulating how scattered molecules enter a six-dimensional phase volume element, which is an absolute must for the purpose of this paper, a rather different and slightly sophisticated approach is introduced.

In sec. 2, general considerations concerning basic collisional process are given. It is pointed out that only the scattering cross section in the center-of-mass frame is well defined and can be employed in our studies. Sec. 3 gives a formula that describes how a molecule, when moving along its path, will survive from collisions. Sec. 4 investigates how molecular collisions create molecules that enter a specific phase volume element. In the investigation, both the colliding molecules and the scattered molecules are allowed to have distributions. (Otherwise, singularities will arise, as Ref. 3 reveals.) Sec. 5 includes all the collisional effects in a complete path-integral formulation. In Sec. 6, approximation methods are introduced to make the new formulation more calculable and an application of the method is demonstrated. Sec. 7 offers a brief summary.

Throughout this paper, to make our discussion as simple as possible, it is assumed that molecules of interest are all identical, but distinguishable, perfectly rigid spheres and they move freely when not making collisions.
2 General considerations of collision

Firstly, we recall general features of binary collisions in terms of classical mechanics. Consider two molecules: one is called molecule 1 and the other molecule 2. Let \( v_1 \) and \( v_2 \) label their respective velocities before the collision. The center-of-mass velocity and the velocity of molecule 1 relative to the center-of-mass are before the collision

\[
\mathbf{c} = \frac{1}{2}(v_1 + v_2) \quad \text{and} \quad \mathbf{u} = \frac{1}{2}(v_1 - v_2).
\] (3)

Similarly, the center-of-mass velocity and the velocity of molecule 1 relative to the center-of-mass are after the collision

\[
\mathbf{c}' = \frac{1}{2}(v'_1 + v'_2) \quad \text{and} \quad \mathbf{u}' = \frac{1}{2}(v'_1 - v'_2).
\] (4)

The conservation laws of classical mechanics tell us that

\[
\mathbf{c} = \mathbf{c}' \quad \text{and} \quad |\mathbf{u}| = |\mathbf{u}'| = u.
\] (5)

Fig. 2 schematically illustrates the geometrical relationship of these velocities. Note that, for the collision defined as above the final velocities of the two molecules, such as \( \mathbf{u}' \), \( v'_1 \) and \( v'_2 \), cannot be completely determined unless the impact parameter of the collision is specified at the very beginning[4].

At this point, mention must be made of one misconception in that the usual derivation of the Boltzmann equation gets involved[3]. In an attempt to invoke the time-reversal symmetry of molecular collision, the standard treatment in textbooks[5] defines the scattering cross section in the laboratory frame in such a way that

\[
\tilde{\sigma}(v_1, v_2 \rightarrow v'_1, v'_2)dv'_1dv'_2\]

represents the number of molecules per unit time (per unit flux of type 1 molecules incident upon a type 2 molecule) emerging after scattering with respective final velocities between \( v'_1 \) and \( v'_1 + dv'_1 \) and between \( v'_2 \) and \( v'_2 + dv'_2 \).

If a close look at expression (6) is taken, we may find that the value of \( \tilde{\sigma} \) in it is ill-defined. As Fig. 2b clearly shows, the molecules of type 1, namely the ones with the velocities \( v'_1 \) after the collisions, will spread out over a two-dimensional surface in the velocity space (forming a spherical shell.
with diameter 2u) rather than over a three-dimensional velocity volume as suggested by the definition. Because of this seemingly small fault, the value of $\bar{\sigma}$ actually depends on the size and shape of $d\mathbf{v}'_1$ and cannot be treated as a uniquely defined quantity theoretically and experimentally.

Another type of scattering cross section, which is elaborated nicely in textbooks of classical mechanics and suffers from no difficulty, is in terms of the relative velocities $\mathbf{u}$ and $\mathbf{u}'$, as shown in Fig. 3. It is defined in such a way that the area element

$$dS = \sigma(\Omega_{\mathbf{u}'})d\Omega_{\mathbf{u}'}$$

(7)

represents the number of molecules per unit time (per unit flux of type 1 molecules with the relative velocity $\mathbf{u}$ incident upon a type 2 molecule) emerging after scattering with the final relative velocity $\mathbf{u}'$ pointing in a direction within the solid angle range $d\Omega_{\mathbf{u}'}$. Note that the definition (7), in which the center-of-mass velocity $\mathbf{c}$ or $\mathbf{c}'$ becomes irrelevant, makes good sense in the center-of-mass frame rather than in the laboratory frame.

Before finishing this section we turn to discussing how collisions can generally affect the solid-angle-average distribution function $f(t, \mathbf{r}, \mathbf{v}, \Delta\Omega)$ defined by (4). In view of that gas dynamics of the Boltzmann gas develops along molecular paths, as shown by (3), we believe that collisional effects should also be investigated and formulated in terms of molecular paths. Fig. 4 illustrates that there are two types of processes. On one hand, a molecule that would reach $\mathbf{r}$ with the velocity $\mathbf{v}$ at time $t$ may suffer from a collision and become irrelevant to the distribution function; on the other hand, an “irrelevant” molecule may collide with another molecule and then become relevant. It should be stressed again that there is no symmetry between the two types of processes. For the first type of process, we only need to investigate what happens to a single molecule. If a collision takes place with it, we know that the molecule will depart from its original path, which is sufficient as far as our formulation is concerned. For the second type of process, we need to know: (i) how many collisions take place within the effective cone; (ii) how the scattered molecules spread out over the phase space. As stressed in the introduction, the second issue is particularly essential because of that the distribution function is nothing but the molecular density per unit phase volume, in other words we must concern ourselves with the scattered molecules “around” the phase point $(\mathbf{r}, \mathbf{v})$, rather than the scattered molecules “at” the phase point $(\mathbf{r}, \mathbf{v})$.

In the next two sections, we will formulate the two processes respectively.
Since the collisions are assumed to take place in terms of classical mechanics all the calculations can be done without analytical difficulty.

3 The surviving probability

Consider a molecule moving along a spatial path where many other molecules make their own motions. If \( P(\tau) \) denotes the probability that the molecule survives a time \( \tau \) without suffering a collision and \( w(\tau)d\tau \) denotes the probability that the molecule makes a collision between time \( \tau \) and time \( \tau + d\tau \), we must have a simple relation

\[
P(\tau + d\tau) - P(\tau) = -P(\tau)w(\tau)d\tau,
\]

which yields

\[
\frac{1}{P} \frac{dP}{d\tau} = -w(\tau).
\] (9)

Therefore, the surviving probability associated with a molecule moving from \( r_0 \) to \( r \) with the velocity \( v \) can be expressed formally by

\[
P(r_0, r; v) = \exp(-\int_l w(\tau)d\tau),
\]

where \( l \) represents the path along that the molecule will move if no collision takes place. For the Boltzmann gas under consideration, whose molecules are assumed to be free from forces except in collisions, the path of a molecule is nothing but the segment of straight line linking up the two points.

The surviving probability defined by (10) can be evaluated by the standard approach\[5\]. To make this paper complete, we include the evaluation in what follows. Suppose that the molecule encounters a molecular beam with the velocity \( v_1 \) at the path element \( dl \). In terms of the molecular beam, the molecule has the speed \( 2u = 2|u| \), in which \( u = (v - v_1)/2 \), and it occupies the volume with respect to the beam

\[
2u\sigma(\Omega_{u'})d\Omega_{u'}d\tau,
\]

where \( \sigma(\Omega_{u'}) \) and \( \Omega_{u'} \) are defined in (7) and illustrated by Fig. 3. The molecular density of the colliding beam is

\[
f(\tau, r_l, v_1)d\nu_1,
\] (12)
where \( r \) is the position of the path element \( dl \). Thus, the total collision probability can be written as

\[
wd\tau = d\tau \int_{\Omega_{\Omega'}} 2uf(\tau, r_l, v_1)\sigma(\Omega_{\Omega'})d\Omega_{\Omega'}dv_1.
\]

(13)

In terms of (13), the surviving probability (10) becomes

\[
P(r_0, r; v) = \exp \left[ -\int_t^{\tau} \int_{\Omega_{\Omega'}} 2uf(\tau, r_l, v_1)\sigma(\Omega_{\Omega'})d\Omega_{\Omega'}dv_1d\tau \right],
\]

(14)

where \( d\tau \) is the time period during that the molecule passes the path element \( dl \). The formula (14) describes how collisions make the number of molecules along a certain path decrease. The method employed has nothing particularly new in comparison with that employed by the textbook treatment. Before changing our subject, one thing worth mentioning. In deriving (14), we had luck not to be concerned with how the scattered molecules spread out over the phase space. It is readily understandable that the same luck will not be there in the next section.

4 The creation probability

We now study the process in which collisions make molecules give contributions to the solid-angle-average distribution function \( f(t, r, v, \Delta\Omega) \).

It should be mentioned that in this section, unlike in the last sections, \( v' \) and \( v'_1 \) represent the velocities of colliding molecules while \( v \) and \( v_1 \) represent the velocities of scattered molecules.

The see how the scattered molecules spread out over the six-dimensional phase space, we consider a relatively small six-dimensional volume element as

\[
\Delta r \cdot \Delta v = \Delta r \cdot v^2 \Delta v \Delta\Omega.
\]

(15)

In (15) \( \Delta r \) is chosen to enclose the point \( r \) in \( f(t, r, v, \Delta\Omega) \), \( \Delta v \) to enclose the speed \( v \) in \( f(t, r, v, \Delta\Omega) \); and \( \Delta\Omega \) is just the finite velocity solid-angle-range \( \Delta\Omega \) in \( f(t, r, v, \Delta\Omega) \). The discussion below will be focused on molecules that really enter, after collisions, this six-dimensional volume element.

Note that in Fig. 5a each point in the spatial volume \( \Delta r \) defines an effective cone, within which physical events may make impact on the distribution function at the point. This means that the entire effective cone, with
respect to the spatial volume element $\Delta r$, must be slightly larger than the one defined solely by $r$, as shown by Fig. 5b. Fortunately, we will, in the end of formulation, let

$$\Delta r \to 0$$  \hspace{1cm} (16)

and thus the actual entire effective cone is only academically larger. On this understanding, we will not distinguish between the entire effective cone and the effective cone defined solely by the single point $r$.

Look at molecular collisions taking place within the effective cone shown in Fig. 6. Note that Fig. 6a, while coming to one’s mind immediately, is not an appropriate picture to manifest the collision process affecting the distribution function at the point $r$ since both the colliding molecules and scattered molecules in it have no true distributions. (Ref. 3 analyzes the situation and brings out that such mental picture will finally lead to singularities.) In Fig. 6b, the velocity distributions of all colliding molecules and scattered molecules are explicitly illustrated. Our task here is to formulate the relationship between the distribution functions of colliding molecules and the scattered molecules (including their velocity distributions and spatial distributions).

We divide the entire effective cone into many individual regions, denoted by $(\Delta r_i)_i$. It is obvious that within each of the regions collisions can generate a certain number of molecules that will finally enter the phase volume defined by (13). Let $n_{cl}^i$ denote the number of such molecules. In what immediately follows, it is assumed that the generated molecules suffer no further collisions. The entire contributions of all collisions to the distribution function $f(t, r, v, \Delta \Omega)$ can then be expressed by

$$f_{cl}(t, r, v, \Delta \Omega) = \frac{1}{\Delta r \cdot \Delta v} \sum_i n_{cl}^i,$$ \hspace{1cm} (17)

in which $i$ runs all the divided regions within the effective cone. For later use, we wish to rewrite (17) as

$$f_{cl}(t, r, v, \Delta \Omega) = \frac{1}{\Delta \Omega} \sum_i \frac{n_{cl}^i}{v^2(\Delta r)_i(\Delta v)_i}.$$ \hspace{1cm} (18)

The advantage of (18) over (17) is that $(\Delta r)_i$ and $(\Delta v)_i$ in (18) may be chosen to be different for different $i$ as long as the molecular number of $n_{cl}^i$ is counted up accordingly. (Of course, all velocity directions of the molecules have to be within the solid angle range $\Delta \Omega$.)
Now, consider a small, much smaller than $\Delta \Omega$, solid angle range $\Delta \Omega_0$ at a point $r_0$ towards the point $r$, as shown in Fig. 7a ($r_0$ is within the effective cone). It is easy to see that if collisions take place at $r_0$, the scattered molecules having velocities within $\Delta \Omega_0$ will spread out over the spatial volume element
\[
\Delta r \approx |r - r_0|^2 v \Delta \Omega_0 \Delta t,
\] (19)
as shown in Fig. 7b. Accordingly, they will spread out over the velocity volume element
\[
\Delta v \approx v^2 \Delta v \Delta \Omega_0,
\] (20)
as shown in Fig. 7c. Since $\Delta \Omega_0$ is much smaller than $\Delta \Omega$ (the latter one is finite), a molecule having a velocity within $\Delta \Omega_0$ can be regarded as one having a velocity within $\Delta \Omega$. Thus, by letting $(\Delta r)_i$ in (18) be equal to $\Delta r$ of (19) and letting $(\Delta v)_i$ in (18) be equal to $\Delta v$ in (20), expression (18) becomes
\[
f^{cl}(t, r, v, \Delta \Omega) = \frac{1}{\Delta \Omega} \int \lim_{(\Delta \Omega_0, \Delta v, \Delta t) \to (0, 0, 0)} \frac{\rho^{cl}(r_0) dr_0}{v^2 \Delta v |r - r_0|^2 \Delta \Omega_0 \Delta t},
\] (21)
where the integral is over the entire effective cone defined by $r$ and $-\Delta \Omega$ and $\rho^{cl}$ is the local density (per unit spatial volume) of the molecules that are “emitted” from $r_0$ due to collisions and finally enter the speed range $\Delta v$ and the solid-angle range $\Delta \Omega_0$ during the time $\Delta t$.

To determine the density $\rho^{cl}$, we have two tasks. One is to derive the collision rate at $r_0$ and the other is to derive what fraction of the scattered molecules emerge with velocities within the range $\Delta v \Delta \Omega_0$. The first task can be accomplished in a well-known way while the second one cannot.

As discussed in the last section, a specific molecule with the initial velocity $v'$ that collides with a beam of molecules with the initial velocity $v'_1$ occupies a volume with respect to the beam
\[
2u \Delta t \sigma(\Omega_u) d\Omega_u,
\] (22)
where $\Omega_u$ is the solid angle of the scattered relative velocity $u = (v - v_1)/2$. The number of “such specific” molecules within $dv' dr_0$ is
\[
f(t_0, r_0, v') dv' dr_0.
\] (23)
The density of the molecules with $v'_1$ is characterized by
\[
f(t_0, r_0, v'_1) dv'_1.
\] (24)
Therefore, the number of all collisions within the spatial volume $dr_0$ within the time $\Delta t$ is

$$dr_0 \int dv' \int dv'_1 \int d\Omega_u f(v')f(v'_1)2u\sigma(\Omega_u)\Delta t. \quad (25)$$

We now evaluate the probability that the molecules expressed by (25) enter the velocity range $\Delta v\Delta \Omega_0$. Note that the integration of $dv'dv'_1$ is carried out in the laboratory frame while the integration of $d\Omega_u$ is in the center-of-mass frame, which makes the evaluation quite difficult. For this reason, we make the integration conversion as

$$\int dv' \int dv'_1 \cdots = \int dc' \int d\Omega_u \int u^2du\|J\| \cdots, \quad (26)$$

where $u = u'$ is understood and $\|J\|$ represents the Jacobian between the center-of-mass frame and the laboratory frame

$$\|J\| = \frac{\partial(v',v'_1)}{\partial(c',u')}. \quad (27)$$

Equation (4) tells us that the Jacobian is equal to 8.

By making use of (25) and (26), the distribution function $f^{cl}$ expressed by (21) becomes

$$f^{cl}(t,r,v,\Delta \Omega) \approx \frac{1}{\Delta \Omega} \int_{-\Delta \Omega}^{\Delta \Omega} dr_0 \int dc' \int d\Omega_u \int \int_{\Delta v\Delta \Omega_0} u^2du \|J\| \cdot \frac{1}{v^3\Delta v|r-r'|^2\Delta \Omega_0} 2u\sigma(\Omega_u)f(t_0,r_0,c'-u')f(t_0,r_0,c'+u'). \quad (28)$$

In regard to expression (28), some observations are made. As mentioned in Sec. 2, if two molecular beams with definite velocities $v'$ and $v'_1$ collide with each other the scattered molecules will spread out only over a two-dimensional spherical surface in the velocity space, which implies that difficulty arises if the velocity distributions of scattered molecules are of concern. Whereas, in this expression, all the colliding molecules are allowed to have distributions, the value of $u' = u$ is allowed to vary and therefore the scattered molecules explicitly spread out over the velocity space (as well as over the spatial space). Furthermore, by using the notation

$$\int \int_{\Delta v\Delta \Omega_0} \cdots \cdots, \quad (29)$$
we have ensured that only the scattered molecules of relevance are taken into account.

In Fig. 8, which is drawn for scattered molecules in the velocity space, we are concerned only with molecules that finally enter the range $\Delta v \Delta \Omega_0$. Allowing $u$ to vary a little bit, we may let the scattered molecules fill out the velocity range. Namely, we have

$$\int \int_{\Delta \Omega_0 \Delta v} u^2 d\Omega_u du (\cdots) \approx v^2 \Delta v \Delta \Omega_0 (\cdots),$$  
(30)

where $(\cdots)$ represents other factors that have been treated as constants in terms of the infinitesimally small range of $\Delta v \Delta \Omega_0$.

Inserting (30) into (28) and taking the limits $\Delta \Omega_0 \to 0$ and $\Delta v \to 0$, we finally arrive at

$$f^{cl}(t, r, v, \Delta \Omega) = \frac{1}{v \Delta \Omega} \int_{-\Delta \Omega}^{\Delta \Omega} dr_0 \int dc' \int d\Omega_u' \frac{\|J\|}{|r - r_0|^2} 2u\sigma(\Omega_u)f(t_0, r_0, c' - u')f(t_0, r_0, c' + u'),$$  
(31)

where $t_0 = t - |r - r_0|/v$ and the integration

$$\int d\Omega_u' \cdots$$  
(32)

is over the entire solid angle ($0 \to 4\pi$). Note that $u$, $u'$ and $u$ in the integrand of (31) have to be determined skillfully. First use $c = c'$ and $v = v(r - r_0)/|r - r_0|$ to determine $u$, then use $u = |u|$ and $\Omega_u$ to determine $u'$, as shown in Fig. 9.

We have directly formulated the contribution to the solid-angle-average distribution function from collisions. It should be noted that the formulation can be done only under the condition that the velocity solid-angle range $\Delta \Omega$ is finite: if both $\Delta \Omega$ and $\Delta \Omega_0$ in the formulation were assumed to be infinitesimally small, the limiting processes concerning the two quantities would not be in harmony with each other. This shows again that the introduction of the solid-angle-average distribution function is a must to the gas dynamics of Boltzmann gas.

5 Complete formulation

The complete formulation for the collisional Boltzmann gas is now in order. In Fig. 10, we have depicted a piece of boundary and some collisions taking
place within the effective cone. As said before, all these events can directly contribute to the solid-angle-average distribution function.

We then use the following sum to represent the total distribution function

\[ f(t, r, v, \Delta \Omega) = f(i) + f(ii) + f(iii), \]  

(33)

where \( f(i) \), \( f(ii) \) and \( f(iii) \) represent the contributions from the existing continuous distribution function, from the piece of boundary and from the collisions respectively. For simplicity, no other types of distribution functions are assumed to exist within the effective cone.

As has been illustrated in Sec. 3, a molecule that makes its motion towards the point \( r \) may suffer a collision with other molecules. The involved surviving probability \( P \) has been defined by (14). By taking the probability into account, the first term in (2) becomes

\[ f(i)(t, r, v, \Delta \Omega) = \frac{1}{\Delta \Omega} \int_{\Delta S_1} \frac{f_{ct}(t_0, r_0, v, \Omega_0) \cos \alpha |dS_0|}{|r - r_0|^2} P(r_0, r, v_0), \]  

(34)

where \( v_0 \) in \( P \) take the value of \( v \) and points to the direction of \((r - r_0)\).

By taking the same effect into account, the second term in (2) can be expressed by

\[ f(ii)(t, r, v, \Delta \Omega) = \frac{1}{\Delta \Omega} \int_{\Delta S_2} \frac{\eta(t_0, r_0, v, \Omega_0) dS_0}{|r - r_0|^2 v^3} P(r_0, r, v_0). \]  

(35)

A rather detailed discussion on the molecular emission rate \( \eta \) has been included in Ref. 1. Here, we content ourselves with pointing out that the rate \( \eta \) satisfies the normalization condition at the surface element \( dS_0 \). If no molecular absorption and production by the surface element are assumed, the following expression holds

\[ \int \eta(t, r, v_1, \Omega_1) d\Omega_1 dv_1 = \int v_2 f(t, r, v_2, \Omega_2) |\cos \theta| v_2^2 d\Omega_2 dv_2, \]  

(36)

in which \( \theta \) is the angle between the velocity \( v_2 \) and the normal of \( dS_0 \). \( \Omega_1 \) points to an outward direction of \( dS_0 \) and \( \Omega_2 \) points to an inward direction of \( dS_0 \). The concrete relation between \( \eta(t, r, v) \) and \( f(t, r, v) \) must, of course, be ultimately determined by experimental data.

In obtaining (31) for the distribution function created by collisions, further collisions were excluded. To include possible further collisions, the
contribution expressed by (31) needs to be modified as

\[
 f_{(iii)}(t, \mathbf{r}, v, \Delta \Omega) = \frac{1}{v \Delta \Omega} \int_{\Delta \Omega} d\mathbf{r}_0 \int d\mathbf{c}' \int d\Omega_{\mathbf{u}'}
 \frac{||J||}{|\mathbf{r} - \mathbf{r}_0|^2} 2u\sigma(\Omega_{\mathbf{u}'}) f(t_0, \mathbf{r}_0, \mathbf{c}' - \mathbf{u}') f(t_0, \mathbf{r}_0, \mathbf{c}' + \mathbf{u}') P(\mathbf{r}_0, \mathbf{r}, \mathbf{v}_0),
\]  

(37)

where the integration of \(d\mathbf{r}_0\) is over the entire effective cone defined by \(\mathbf{r}\) and \(-\Delta \Omega\), \(|\mathbf{v}_0| = v\) and takes the direction of \((\mathbf{r} - \mathbf{r}_0)\), \(\mathbf{u}'\) is defined by \(u = |\mathbf{c} - \mathbf{v}_0|\) and \(\Omega_{\mathbf{u}'}\).

In these formulas, the probability \(P\) should be set to be zero at the very beginning if there is physical blocking along the path \(\mathbf{r}_0\).

Equations (33)-(37) constitute a complete set of integral equations that describe the collisional Boltzmann gas defined in this paper. The formulation proves in a theoretical way an obvious intuition that the distribution function at a spatial point can directly be affected by physical events taking place at other, even remote, points in view of the fact that a molecule can freely pass any distance in a certain probability. In this sense, the picture here is more “kinetic” than that associated with the Boltzmann equation, in which physical events have to make their influence region by region (like what happen in a continuous medium).

Another comment is about the famous \(H\)-theorem. If the involved distribution function is initially nonuniform in the spatial space and non-Maxwellian in the velocity space, the resultant distribution function given by the formalism will approach the uniform Maxwellian. Though such explicit proof has not been achieved yet, we believe that this must be the case by noticing a general discussion stating that as long as a statistical process is a Markoffian one the \(H\)-theorem must hold true[7].

6 Approximation and application

Although the formulation offered in the previous section is formally complete, there still exist difficulties that hinder one from performing calculation for a realistic gas. Unlike the solution for the collisionless Boltzmann gas, given by (34), the equation system in the last section, namely (33)-(37), is an integral-equation set. Without knowing the entire history of the distribution function \(f(t)\), the integrals in the system cannot be evaluated accurately.

Fortunately, there are situations for which adequate approximations can be introduced and meaningful results can be obtained. In what follows, we
first deal with weakly collisional gases and then give some discussion on how the consideration can apply to more general cases.

If the density of a Boltzmann gas is relatively low, by which we imply that the mean free path of molecules is not too short comparing with the length scale of the system or that the mean free time is not too short comparing with the time scale of the phenomena of interest, we may apply the following iterating procedure to calculate the distribution function.

Firstly, we assume that the system can be treated as a collisionless Boltzmann gas and the collisionless formulation can directly applied. Namely, we have the zeroth-order solution

\[
 f^{[0]}(t_0, \mathbf{r}_0, \mathbf{v}_0, \Omega_0) = \frac{1}{\Delta \Omega} \int_{\Delta S_1} f^{ct}(t_0, \mathbf{r}_0, \mathbf{v}, \Omega_0) \cos \alpha |dS_0| \frac{1}{|\mathbf{r} - \mathbf{r}_0|^2}.
\]

Then, we can construct the first-order distribution function by inserting the zeroth-order solution into all right sides of the equations (33)-(37), which yields

\[
 f^{[1]}(i) = \frac{1}{\Delta \Omega} \int_{\Delta S_1} f^{ct}(t_0, \mathbf{r}_0, \mathbf{v}, \Omega_0) \cos \alpha |dS_0| P^{[0]}(\mathbf{r}_0, \mathbf{r}, \mathbf{v}_0)
\]

\[
 f^{[1]}(ii) = \frac{1}{v^3 \Delta \Omega} \int_{\Delta S_2} \eta(t_0, \mathbf{r}_0, \mathbf{v}, \Omega_0) |dS_0| P^{[0]}(\mathbf{r}_0, \mathbf{r}, \mathbf{v}_0).
\]

and

\[
 f^{[1]}(iii) = \frac{1}{v \Delta \Omega} \int_{-\Delta \Omega} d\mathbf{r}_0 \int d\mathbf{c} \int d\mathbf{u}' \int d\Omega_{\mathbf{u}'} \frac{2u\sigma(\Omega_{\mathbf{u}'})f^{[0]}(t_0, \mathbf{r}_0, \mathbf{c}' - \mathbf{u}')f^{[0]}(t_0, \mathbf{r}_0, \mathbf{c}' + \mathbf{u}')P^{[0]}(\mathbf{r}_0, \mathbf{r}, \mathbf{v}_0).
\]

In all the first-order formulas, the surviving probability is defined as

\[
 P^{[0]}(\mathbf{r}_0, \mathbf{r}; \mathbf{v}_0) = \exp \left[ -\int_{\mathbf{v}_1} \int_{\Omega_{\mathbf{u}^*}} 2u\sigma(\Omega_{\mathbf{u}'})f^{[0]}(\tau, \mathbf{r}_1, \mathbf{v}_1) d\Omega_{\mathbf{u}'} d\mathbf{v}_1 d\tau \right].
\]

In equations (42) and (43), \( f^{[0]} \) is the total zeroth-order distribution function, namely \( f^{[0]} = f^{[0]}(i) + f^{[0]}(ii) \).

Along this line, we can formulate higher-order solutions for dilute gases.

If the gas of interest is rather dense, the approximation method presented
above may not work effectively. One wishes, however, to point out that for
the regions near boundaries, where the distribution function suffers from
most irregularities and collisions between molecules have no enough time
to erase such irregularities, the introduced method should still make sense.
In view of this, it is expected that a hybrid method will be developed, in
which the approach here and other effective approaches, such as the ordinary
fluid theory, can be combined into one scheme so that more practical gases
become treatable.

To illustrate the application of our approximation scheme, we investigate
a gas leaking out of box through a small hole. For simplicity, we assume,
referring Fig. 11, that the zeroth-order solution of the leaking gas is con-
fined to a “one-dimensional thin pipe” (shaded in the figure), which can be
expressed by

\[ f^{[0]} = \begin{cases} 
C_0 \exp \left[ -mv_x^2/(2\kappa T) \right] & \text{(inside the pipe)} \\
0 & \text{(outside the pipe)} 
\end{cases} \tag{44} \]

and then we try to determine the collisional effects of the distribution func-
tion.

Note that the distribution function expressed by (44) is kind of special so
that the formula (42) should be slightly modified. For this purpose, we write
the differential collision probability as (the subindex \( x \) of \( v_x \) is suppressed)

\[ [f(v')\Delta Sdx_0dv'] [f(v'_1)dv'_1] [2u\sigma(\Omega_u)d\Omega_u], \tag{45} \]

where \( \Delta S \) is the cross area of the pipe. By making the variable transfor-
mation, we obtain

\[ \int_0^\infty dv' \int_0^\infty dv'_1 \cdots = \int_0^\infty dc' \int_{-\infty}^{+\infty} du' ||J|| \cdots \]

\[ = \int_0^\infty dc' \int_0^\infty u^2 du4(u^2)^{-1} \cdots. \]

In a way similar to that has been presented in the last section, we finally
arrive at

\[ f^{[1]}[(\Delta \theta)_i] = \frac{\Delta S}{v(\Delta \theta)_i} \int_{-\Delta \theta}_i dx_0 \int_0^\infty dc' \frac{8\sigma(\Omega_u)}{|u| - r_0^2} f^{[0]}(c' + u') f^{[0]}(c' - u'), \tag{46} \]

where \( (\Delta \theta)_i \) is the polar angle range set by the investigator (the azimuthal
angle range is irrelevant in the case).
The formula (46) can be calculated easily with a computer. Referring to Fig. 11b, we set

\[ v = 1, \quad r_\perp = 1, \quad \frac{m}{2\kappa T} = 1, \]

let \((\Delta \theta)_i\) be the interval

\[ \left[ 0.4\pi - 0.52 + \frac{i}{50}, 0.4\pi - 0.5 + \frac{i}{50} \right] \]

and notice \(\sigma(\Omega_u)\) is constant. The numerical results are listed as the following: (normalized by \(f[(\Delta \theta)_0]\))

\[
\begin{align*}
    f[(\Delta \theta)_0] &= 1.00000e + 00 \\
    f[(\Delta \theta)_5] &= 5.23910e - 01 \\
    f[(\Delta \theta)_{10}] &= 2.01786e - 01 \\
    f[(\Delta \theta)_{15}] &= 5.03200e - 02 \\
    f[(\Delta \theta)_{20}] &= 4.76340e - 03 \\
    f[(\Delta \theta)_{25}] &= 5.11013e - 05.
\end{align*}
\]

(47)

7 Summary

In this paper, we have proposed a complete mathematical scheme to deal with the Boltzmann gas. The scheme has many new features. In addition to those given in Ref. 1, some related to treating collisional effects are the following.

Firstly, collisional effects are investigated in the full velocity-and-position space. In particular, a six-dimensional volume element is explicitly defined and a calculation concerning molecules entering the volume element is directly performed.

Secondly, both the colliding molecules and scattered molecules are allowed to have distributions. In other words, we consider the full and collective behavior of collisions, in which the time-reversal symmetry existing for a collision of two molecules plays almost no role.

Thirdly, the treatment in this approach is consistent with the previous approach to the collisionless Boltzmann gas in the sense that all the formulas are given in terms of what happens along molecular paths.

Finally, the resultant formulas of this approach are, in many practical situations, calculable by means of today’s computer.

It is believed that this approach will be developed further so that a better understanding of complicated fluid phenomena can be achieved.
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Figure captions

1. A physical surface and a virtual surface within the effective cone defined by \( r \) and \( \Delta \Omega \).

2. A collision between two molecules. (a) The molecular velocities before the collision. (b) The molecular velocities after the collision.

3. The scattering cross section in the center-of-mass frame. (a) Solid angles and relative velocities. (b) The relation between the cross section and solid angle range.

4. Two types of collision processes.

5. Effective cones. (a) For a single spatial point. (b) For a given spatial volume.

6. (a) A mental picture in which two molecular beams collide with each other. (b) A mental picture in which both colliding molecules and scattered molecules have distributions.

7. (a) A solid angle range \( \Delta \Omega_0 \) towards the point \( r \). (b) The distribution of scattered molecules in the spatial space. (c) The distribution of scattered molecules in the velocity space.

8. The velocity distribution of scattered molecules in the center-of-mass frame and in the laboratory frame.

9. Relations between various essential vectors in the formulation.

10. Contribution to the solid-angle-average distribution function from different sources.

11. A gas leaking out of a container through a small hole.
Figure 4

Figure 5

Figure 6
Figure 7

Figure 8

Figure 9
