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Boltzmann Equation and Gas–Surface Interaction

1.1. Introduction

According to kinetic theory, a gas in normal conditions (no chemical reactions, no ionization phenomena, etc.) is formed of elastic molecules rushing hither and thither at high speed, colliding and rebounding according to the laws of elementary mechanics. In this and the next section, the molecules of a gas will be assumed to be hard, elastic, and perfectly smooth spheres. Later we shall consider molecules as centers of forces that move according to the laws of classical mechanics and, starting with Chapter 6, more complex models describing polyatomic molecules.

The rules generating the dynamics of many spheres are easy to describe: Thus, for example, if no external forces, such as gravity, are assumed to act on the molecules, each of them will move in a straight line unless it happens to strike another molecule or a solid wall. The phenomena associated with this dynamics are not so simple, especially when the number of spheres is large. It turns out that this complication is always present when dealing with a gas, because the number of molecules usually considered is extremely large: There are about $2.7 \cdot 10^{19}$ in a cubic centimeter of a gas at atmospheric pressure and a temperature of 0°C .

Given the vast number of particles to be considered, it would of course be a hopeless task to attempt to describe the state of the gas by specifying the so-called microscopic state (i.e., the position and velocity of every individual sphere); we must have recourse to statistics. A description of this kind is made possible because in practice all that our typical observations can detect are changes in the macroscopic state of the gas, described by quantities such as density, bulk velocity, temperature, stresses, and heat flow, and these are related to some suitable averages of quantities depending on the microscopic state.

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The exact dynamics of N particles is a useful conceptual tool, but it cannot in any way be used in practical calculations because it requires a huge number of real variables (of the order of 10^{20}). This was realized by Maxwell and Boltzmann when they started to work with the one-particle probability density, or distribution function $P^{(1)}(\mathbf{x}, \boldsymbol{\xi}, t)$. The latter is a function of seven variables: the components of the two vectors \mathbf{x} and $\boldsymbol{\xi}$ and time t . In particular, Boltzmann wrote an evolution equation for $P^{(1)}$ by means of a heuristic argument, which we shall try to present in such a way as to show where extra assumptions are introduced.

Let us first consider the meaning of $P^{(1)}(\mathbf{x}, \boldsymbol{\xi}, t)$; it gives the probability density of finding one fixed particle (say, the one labeled by 1) at a certain point $(\mathbf{x}, \boldsymbol{\xi})$ of the six-dimensional reduced phase space associated with the position and velocity of that molecule. To simplify the treatment, we shall for the moment assume that the molecules are hard spheres, whose center has position \mathbf{x} . When the molecules collide, momentum and kinetic energy must be conserved; thus (Problem 1.2.2) the velocities after the impact, $\boldsymbol{\xi}'_1$ and $\boldsymbol{\xi}'_2$, are related to those before the impact, $\boldsymbol{\xi}_1$ and $\boldsymbol{\xi}_2$, by

$$\begin{aligned}\boldsymbol{\xi}'_1 &= \boldsymbol{\xi}_1 - \mathbf{n}[\mathbf{n} \cdot (\boldsymbol{\xi}_1 - \boldsymbol{\xi}_2)], \\ \boldsymbol{\xi}'_2 &= \boldsymbol{\xi}_2 + \mathbf{n}[\mathbf{n} \cdot (\boldsymbol{\xi}_1 - \boldsymbol{\xi}_2)],\end{aligned}\tag{1.2.1}$$

where \mathbf{n} is the unit vector along $\boldsymbol{\xi}_1 - \boldsymbol{\xi}'_1$. Note that the relative velocity

$$\mathbf{V} = \boldsymbol{\xi}_1 - \boldsymbol{\xi}_2\tag{1.2.2}$$

satisfies

$$\mathbf{V}' = \mathbf{V} - 2\mathbf{n}(\mathbf{n} \cdot \mathbf{V}),\tag{1.2.3}$$

that is, it undergoes a specular reflection at the impact. This means that if we split \mathbf{V} at the point of impact into a normal component \mathbf{V}_n , directed along \mathbf{n} and a tangential component \mathbf{V}_t (in the plane normal to \mathbf{n}), then \mathbf{V}_n changes sign and \mathbf{V}_t remains unchanged in a collision (Problem 1.2.4). We can also say that \mathbf{n} bisects the directions of \mathbf{V} and $-\mathbf{V}' = -(\boldsymbol{\xi}'_1 - \boldsymbol{\xi}'_2)$ (see Fig. 1.1).

Let us remark that, in the absence of collisions, $P^{(1)}$ would remain unchanged along the trajectory of a particle (see Problem 1.2.1). Accordingly we must evaluate the effects of collisions on the time evolution of $P^{(1)}$. Note that the probability of occurrence of a collision is related to the probability of finding another molecule with a center at exactly one diameter from the center of the first one, whose distribution function is $P^{(1)}$. Thus, generally speaking, in order

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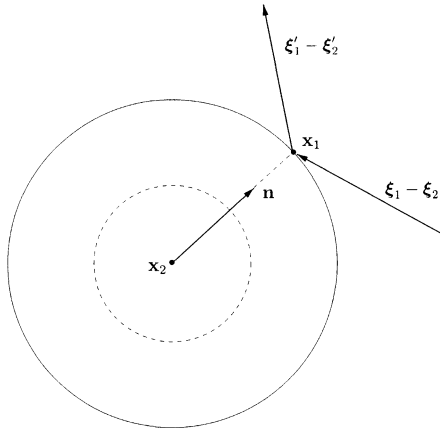


Figure 1.1. The directions of the relative velocities before and after the impact are bisected by the unit vector \mathbf{n} .

to write the evolution equation for $P^{(1)}$ we shall need another function, $P^{(2)}$, that gives the probability density of finding, at time t , the first molecule at \mathbf{x}_1 with velocity ξ_1 and the second at \mathbf{x}_2 with velocity ξ_2 ; obviously $P^{(2)} = P^{(2)}(\mathbf{x}_1, \mathbf{x}_2, \xi_1, \xi_2, t)$. Hence $P^{(1)}$ satisfies an equation of the following form:

$$\frac{\partial P^{(1)}}{\partial t} + \xi_1 \cdot \frac{\partial P^{(1)}}{\partial \mathbf{x}_1} = G - L. \tag{1.2.4}$$

Here $Ld\mathbf{x}_1d\xi_1dt$ gives the expected number of particles with position between \mathbf{x}_1 and $\mathbf{x}_1 + d\mathbf{x}_1$ and velocity between ξ_1 and $\xi_1 + d\xi_1$ that disappear from these ranges of values because of a collision in the time interval between t and $t + dt$, and $Gd\mathbf{x}_1d\xi_1dt$ gives the analogous number of particles entering the same range in the same time interval. Counting these numbers is easy, provided we use the trick of imagining particle 1 as a sphere at rest and endowed with twice the actual diameter σ and the other particles to be point masses with velocity $(\xi_i - \xi_1) = \mathbf{V}_i$. In fact, each collision will send particle 1 out of the above range and the number of the collisions of particle 1 will be the number of expected collisions of any other particle with that sphere. Since there are exactly $(N - 1)$ identical point masses and multiple collisions are disregarded, $G = (N - 1)g$ and $L = (N - 1)l$, where the lowercase letters indicate the contribution of a fixed particle, say particle 2. We shall then compute the effect of the collisions of particle 2 with particle 1. Let \mathbf{x}_2 be a point of the sphere such that the vector joining the center of the sphere with \mathbf{x}_2 is $\sigma\mathbf{n}$, where \mathbf{n} is a unit vector. A cylinder with height $|\mathbf{V} \cdot \mathbf{n}|dt$ (where we write just \mathbf{V} for \mathbf{V}_2) and base area $dS = \sigma^2 d\mathbf{n}$ (where $d\mathbf{n}$ is the area of a surface

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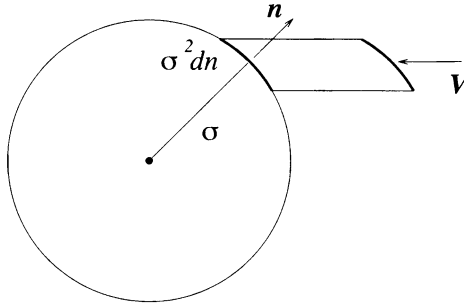


Figure 1.2. Calculation of the number of collisions between two molecules.

element of the unit sphere about \mathbf{n}) will contain the particles with velocity ξ_2 hitting the base dS in the time interval $(t, t + dt)$ (see Fig. 1.2); its volume is $\sigma^2 dn |\mathbf{V} \cdot \mathbf{n}| dt$. Thus the number of collisions of particle 2 with particle 1 in the ranges $(\mathbf{x}_1, \mathbf{x}_1 + d\mathbf{x}_1)$, $(\xi_1, \xi_1 + d\xi_1)$, $(\mathbf{x}_2, \mathbf{x}_2 + d\mathbf{x}_2)$, $(\xi_2, \xi_2 + d\xi_2)$, $(t, t + dt)$ occurring at points of dS is $P^{(2)}(\mathbf{x}_1, \mathbf{x}_2, \xi_1, \xi_2, t) d\mathbf{x}_1 d\xi_1 d\mathbf{x}_2 d\xi_2 \sigma^2 dn |\mathbf{V} \cdot \mathbf{n}| dt$. If we want the number of collisions of particle 1 with 2, when the range of the former is fixed but the latter may have any velocity ξ_2 and any position \mathbf{x}_2 on the sphere (i.e., any \mathbf{n}), we integrate over the sphere and all the possible velocities of particle 2 to obtain

$$L d\mathbf{x}_1 d\xi_1 dt = d\mathbf{x}_1 d\xi_1 dt \int_{R^3} \int_{B^-} P^{(2)}(\mathbf{x}_1, \mathbf{x}_1 + \sigma \mathbf{n}, \xi_1, \xi_2, t) |\mathbf{V} \cdot \mathbf{n}| \sigma^2 d\mathbf{n} d\xi_2, \tag{1.2.5}$$

where B^- is the hemisphere corresponding to $\mathbf{V} \cdot \mathbf{n} < 0$ (the particles are moving toward each other before the collision). Thus we have the following result:

$$L = (N - 1) \sigma^2 \int_{R^3} \int_{B^-} P^{(2)}(\mathbf{x}_1, \mathbf{x}_1 + \sigma \mathbf{n}, \xi_1, \xi_2, t) (\xi_2 - \xi_1) \cdot \mathbf{n} d\xi_2 d\mathbf{n}. \tag{1.2.6}$$

The calculation of the gain term G is exactly the same as the one for L , except for the fact that we have to integrate over the hemisphere B^+ , defined by $\mathbf{V} \cdot \mathbf{n} > 0$ (the particles are moving away from each other after the collision). Thus we have

$$G = (N - 1) \sigma^2 \int_{R^3} \int_{B^+} P^{(2)}(\mathbf{x}_1, \mathbf{x}_1 + \sigma \mathbf{n}, \xi_1, \xi_2, t) (\xi_2 - \xi_1) \cdot \mathbf{n} d\xi_2 d\mathbf{n}. \tag{1.2.7}$$

We thus could write the right-hand side of Eq. (1.2.4) as a single expression:

$$G - L = (N - 1) \sigma^2 \int_{R^3} \int_B P^{(2)}(\mathbf{x}_1, \mathbf{x}_1 + \sigma \mathbf{n}, \xi_1, \xi_2, t) (\xi_2 - \xi_1) \cdot \mathbf{n} d\xi_2 d\mathbf{n}, \tag{1.2.8}$$

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where now \mathcal{B} is the entire unit sphere and we have abolished the bars of absolute value in the right-hand side.

Equation (1.2.8), although absolutely correct, is not so useful. It turns out to be much more convenient to keep the gain and loss terms separated. Only in this way, in fact, can we insert in Eq. (1.2.4) the information that the probability density $P^{(2)}$ is continuous at a collision; in other words, although the velocities of the particles undergo the discontinuous change described by Eqs. (1.2.1), we can write

$$P^{(2)}(\mathbf{x}_1, \boldsymbol{\xi}_1, \mathbf{x}_2, \boldsymbol{\xi}_2, t) = P^{(2)}(\mathbf{x}_1, \boldsymbol{\xi}_1 - \mathbf{n}(\mathbf{n} \cdot \mathbf{V}), \mathbf{x}_2, \boldsymbol{\xi}_2 + \mathbf{n}(\mathbf{n} \cdot \mathbf{V}), t) \quad \text{if } |\mathbf{x}_1 - \mathbf{x}_2| = \sigma. \quad (1.2.9)$$

For brevity, we write (in agreement with Eq. (1.2.1))

$$\boldsymbol{\xi}'_1 = \boldsymbol{\xi}_1 - \mathbf{n}(\mathbf{n} \cdot \mathbf{V}), \quad \boldsymbol{\xi}'_2 = \boldsymbol{\xi}_2 + \mathbf{n}(\mathbf{n} \cdot \mathbf{V}). \quad (1.2.10)$$

Inserting Eq. (1.2.8) in Eq. (1.2.5) we thus obtain

$$G = (N - 1)\sigma^2 \int_{R^3} \int_{\mathcal{B}^+} P^{(2)}(\mathbf{x}_1, \mathbf{x}_1 + \sigma \mathbf{n}, \boldsymbol{\xi}'_1, \boldsymbol{\xi}'_2, t) |(\boldsymbol{\xi}_2 - \boldsymbol{\xi}_1) \cdot \mathbf{n}| d\boldsymbol{\xi}_2 d\mathbf{n}, \quad (1.2.11)$$

which is a frequently used form. Sometimes \mathbf{n} is changed into $-\mathbf{n}$ to have the same integration range as in L ; the only change (in addition to the change in the range) is in the second argument of $P^{(2)}$, which becomes $\mathbf{x}_1 - \sigma \mathbf{n}$.

At this point we are ready to understand Boltzmann's argument. N is a very large number and σ (expressed in common units, such as, e.g., centimeters) is very small; to fix the ideas, let us consider a box whose volume is 1 cm^3 at room temperature and atmospheric pressure. Then $N \cong 10^{20}$ and $\sigma \cong 10^{-8} \text{ cm}$. Then $(N - 1)\sigma^2 \cong N\sigma^2 \cong 10^4 \text{ cm}^2 = 1 \text{ m}^2$ is a sizable quantity, while we can neglect the difference between \mathbf{x}_1 and $\mathbf{x}_1 + \sigma \mathbf{n}$. This means that the equation to be written can be rigorously valid only in the so-called *Boltzmann–Grad limit*, when $N \rightarrow \infty$, $\sigma \rightarrow 0$ with $N\sigma^2$ finite.

In addition, the collisions between two preselected particles are rather rare events. Thus two spheres that happen to collide can be thought to be two randomly chosen particles and it makes sense to assume that the probability density of finding the first molecule at \mathbf{x}_1 with velocity $\boldsymbol{\xi}_1$ and the second at \mathbf{x}_2 with velocity $\boldsymbol{\xi}_2$ is the product of the probability density of finding the first molecule at \mathbf{x}_1 with velocity $\boldsymbol{\xi}_1$ times the probability density of finding the second molecule at \mathbf{x}_2 with velocity $\boldsymbol{\xi}_2$. If we accept this we can write (assumption of *molecular chaos*)

$$P^{(2)}(\mathbf{x}_1, \boldsymbol{\xi}_1, \mathbf{x}_2, \boldsymbol{\xi}_2, t) = P^{(1)}(\mathbf{x}_1, \boldsymbol{\xi}_1, t) P^{(1)}(\mathbf{x}_2, \boldsymbol{\xi}_2, t) \quad (1.2.12)$$

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for two particles that are about to collide, or

$$P^{(2)}(\mathbf{x}_1, \boldsymbol{\xi}_1, \mathbf{x}_1 + \sigma \mathbf{n}, \boldsymbol{\xi}_2, t) = P^{(1)}(\mathbf{x}_1, \boldsymbol{\xi}_1, t)P^{(1)}(\mathbf{x}_1, \boldsymbol{\xi}_2, t) \quad \text{for } (\boldsymbol{\xi}_2 - \boldsymbol{\xi}_1) \cdot \mathbf{n} < 0. \quad (1.2.13)$$

Thus we can apply this recipe to the loss term (1.2.4) but not to the gain term in the form (1.2.5). It is possible, however, to apply Eq. (1.2.13) (with $\boldsymbol{\xi}'_1, \boldsymbol{\xi}'_2$ in place of $\boldsymbol{\xi}_1, \boldsymbol{\xi}_2$) to the form (1.2.9) of the gain term, because the transformation (1.2.10) maps the hemisphere \mathcal{B}^+ onto the hemisphere \mathcal{B}^- .

If we accept all the simplifying assumptions made by Boltzmann, we obtain the following form for the gain and loss terms:

$$G = N\sigma^2 \int_{R^3} \int_{\mathcal{B}^-} P^{(1)}(\mathbf{x}_1, \boldsymbol{\xi}'_1, t)P^{(1)}(\mathbf{x}_1, \boldsymbol{\xi}'_2, t)|(\boldsymbol{\xi}_2 - \boldsymbol{\xi}_1) \cdot \mathbf{n}|d\boldsymbol{\xi}_2d\mathbf{n}, \quad (1.2.14)$$

$$L = N\sigma^2 \int_{R^3} \int_{\mathcal{B}^-} P^{(1)}(\mathbf{x}_1, \boldsymbol{\xi}_1, t)P^{(1)}(\mathbf{x}_1, \boldsymbol{\xi}_2, t)|(\boldsymbol{\xi}_2 - \boldsymbol{\xi}_1) \cdot \mathbf{n}|d\boldsymbol{\xi}_2d\mathbf{n}. \quad (1.2.15)$$

By inserting these expressions in Eq. (1.2.6) we can write the *Boltzmann equation* in the following form:

$$\frac{\partial P^{(1)}}{\partial t} + \boldsymbol{\xi}_1 \cdot \frac{\partial P^{(1)}}{\partial \mathbf{x}_1} = N\sigma^2 \int_{R^3} \int_{\mathcal{B}^-} [P^{(1)}(\mathbf{x}_1, \boldsymbol{\xi}'_1, t)P^{(1)}(\mathbf{x}_1, \boldsymbol{\xi}'_2, t) - P^{(1)}(\mathbf{x}_1, \boldsymbol{\xi}_1, t)P^{(1)}(\mathbf{x}_1, \boldsymbol{\xi}_2, t)] |(\boldsymbol{\xi}_2 - \boldsymbol{\xi}_1) \cdot \mathbf{n}|d\boldsymbol{\xi}_2d\mathbf{n}. \quad (1.2.16)$$

We remark that the expressions for $\boldsymbol{\xi}'_1$ and $\boldsymbol{\xi}'_2$ given in Eq. (1.2.1) are by no means the only possible ones. In fact we might use a different unit vector $\boldsymbol{\omega}$, directed as \mathbf{V}' , instead of \mathbf{n} . Then Eq. (1.2.1) is replaced by

$$\begin{aligned} \boldsymbol{\xi}'_1 &= \bar{\boldsymbol{\xi}} + \frac{1}{2}|\boldsymbol{\xi}_1 - \boldsymbol{\xi}_2|\boldsymbol{\omega}, \\ \boldsymbol{\xi}'_2 &= \bar{\boldsymbol{\xi}} - \frac{1}{2}|\boldsymbol{\xi}_1 - \boldsymbol{\xi}_2|\boldsymbol{\omega}, \end{aligned} \quad (1.2.17)$$

where $\bar{\boldsymbol{\xi}} = \frac{1}{2}(\boldsymbol{\xi}_1 + \boldsymbol{\xi}_2)$ is the velocity of the center of mass. The relative velocity \mathbf{V} satisfies

$$\mathbf{V}' = \boldsymbol{\omega}|\mathbf{V}|. \quad (1.2.18)$$

The Boltzmann equation is an evolution equation for $P^{(1)}$, without any reference to $P^{(2)}$. This is its main advantage. However, it has been obtained at the price of

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several assumptions; the chaos assumption present in Eqs. (1.2.12) and (1.2.13) is particularly strong and requires discussion.

The molecular chaos assumption is clearly a property of randomness. Intuitively, one feels that collisions exert a randomizing influence, but it would be completely wrong to argue that the statistical independence described by Eq. (1.2.12) is a consequence of the dynamics. It is quite clear that we cannot expect every choice of the initial distribution of positions and velocities of the molecules to give a $P^{(1)}$ that agrees with the solution of the Boltzmann equation in the Boltzmann–Grad limit. In other words molecular chaos must be present initially and we can only ask whether it is preserved by the time evolution of the system of hard spheres.

It is evident that the chaos property (1.2.12), if initially present, is almost immediately destroyed, if we insist that it should be valid everywhere. In fact, if it were strictly valid everywhere, the gain and loss terms, in the Boltzmann–Grad limit, would be exactly equal. As a consequence, there would be no effect of the collisions on the time evolution of $P^{(1)}$. The essential point is that we need the chaos property only for molecules that are about to collide, that is, those in the precise form stated in Eq. (1.2.13). It is clear then that even if $P^{(1)}$ as predicted by the exact dynamics converges nicely to a solution of the Boltzmann equation, $P^{(2)}$ may converge to a product, as stated in Eq. (1.2.11), only in a way that is in a certain sense very singular. In fact, it is not enough to show that the convergence is almost everywhere, because we need to use the chaos property in a zero measure set. However, we cannot try to show that convergence holds everywhere, because this would be false; in fact, we have just remarked that Eq. (1.2.11) is, generally speaking, simply not true for molecules that have just collided.

How can we approach the question of justifying the Boltzmann equation without invoking the molecular chaos assumption as an a priori hypothesis? Clearly, since $P^{(2)}$ appears in the evolution equation for $P^{(1)}$, we must investigate the time evolution for $P^{(2)}$; now, as is clear, the evolution equation for $P^{(2)}$ contains another function, $P^{(3)}$, which depends on time and the coordinates and velocities of three molecules and gives the probability density of finding, at time t , the first molecule at \mathbf{x}_1 with velocity ξ_1 , the second at \mathbf{x}_2 with velocity ξ_2 , and the third at \mathbf{x}_3 with velocity ξ_3 . In general if we introduce a function $P^{(s)} = P^{(s)}(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_s, \xi_1, \xi_2, \dots, \xi_s, t)$, the so-called *s-particle distribution function*, which gives the probability density of finding, at time t , the first molecule at \mathbf{x}_1 with velocity ξ_1 , the second at \mathbf{x}_2 with velocity ξ_2 , ... and the s th at \mathbf{x}_s with velocity ξ_s , we find the evolution equation of $P^{(s)}$ contains the next function $P^{(s+1)}$, till we reach $s = N$; in fact $P^{(N)}$ satisfies a partial differential equation called the Liouville equation. Clearly we cannot proceed unless we

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handle all the $P^{(s)}$ at the same time and attempt to prove a generalized form of molecular chaos, that is,

$$P^{(s)}(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_s, \boldsymbol{\xi}_1, \boldsymbol{\xi}_2, \dots, \boldsymbol{\xi}_s, t) = \prod_{j=1}^s P^{(1)}(\mathbf{x}_j, \boldsymbol{\xi}_j, t). \quad (1.2.19)$$

The task then becomes to show that, if true at $t = 0$, this property remains preserved (for any fixed s) in the Boltzmann–Grad limit. The discussion of this point is outside the scope of this book. The interested reader may consult Refs. 1–7.

There remains the problem of justifying the *initial chaos assumption*, according to which Eq. (1.2.19) is satisfied at $t = 0$. One can give two justifications, one of them being physical in nature and the second mathematical; essentially, they say the same thing, that is, it is hard to prepare an initial state for which Eq. (1.2.19) does not hold. The physical reason for this is that, in general, we cannot handle every single molecule, but rather we act on the gas as a whole, if we act at a macroscopic level, usually starting from an equilibrium state (for which Eq. (1.2.19) holds). The mathematical argument indicates that if we choose the initial data for the molecules at random, there is an overwhelming probability that Eq. (1.2.19) is satisfied for $t = 0$.^{1,3}

A word should be said about boundary conditions. When proving that chaos is preserved in the limit, it is absolutely necessary to have a boundary condition compatible (at least in the limit) with Eq. (1.2.19). If the boundary conditions are those of periodicity or specular reflection, no problems arise. In general, it is sufficient that the particles are scattered without adsorption from the boundary in a way that does not depend on the state of the other molecules of the gas.^{1,3}

Problems

- 1.2.1 Show that if there are no collisions (and no body forces), then $P^{(1)}$ satisfies

$$\frac{\partial P^{(1)}}{\partial t} + \boldsymbol{\xi}_1 \cdot \frac{\partial P^{(1)}}{\partial \mathbf{x}_1} = 0.$$

- 1.2.2 Show that Eqs. (1.2.1) hold. (Remark: Momentum and energy conservation imply $\boldsymbol{\xi}_1 + \boldsymbol{\xi}_2 = \boldsymbol{\xi}'_1 + \boldsymbol{\xi}'_2$ and $|\boldsymbol{\xi}_1|^2 + |\boldsymbol{\xi}_2|^2 = |\boldsymbol{\xi}'_1|^2 + |\boldsymbol{\xi}'_2|^2$ and, by definition, we have $\boldsymbol{\xi}'_1 = \boldsymbol{\xi}_1 - \mathbf{n}C$, where C is a scalar to be determined. . .).
- 1.2.3 Check that if we split the relative velocity \mathbf{V} at the point of impact into a normal component \mathbf{V}_n , directed along \mathbf{n} , and a tangential component

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\mathbf{V}_t (in the plane normal to \mathbf{n}), then \mathbf{V}_n changes sign and \mathbf{V}_t remains unchanged in a collision.

- 1.2.4 Show that if we transform from the variables ξ_1, ξ_2 to the variables \mathbf{V} (the relative velocity) and $\bar{\xi} = \frac{1}{2}(\xi_1 + \xi_2)$ (the velocity of the center of mass), the transformation has unit Jacobian.
- 1.2.5 Check, by a direct calculation, that the Jacobian of the transformation (1.2.1) is unity, if the collision occurs in a plane (i.e., ξ_1, ξ_2, ξ'_1 , and ξ'_2 have just two components, while the components of \mathbf{n} can be written $(\cos \theta, \sin \theta)$, where θ is a suitable angle).
- 1.2.6 Check that the transformation (1.2.1) actually maps the hemisphere \mathcal{B}^+ onto \mathcal{B}^- .
- 1.2.7 Find a relation between the angles formed by \mathbf{n} and ω with \mathbf{V} .
- 1.2.8 Give a reasonable definition of probability for the initial data in terms of $P^{(N)}$ and show that it attains a constrained maximum (the constraint being that $P^{(1)}$ is assigned) when $P^{(N)}$ is chaotic, that is, satisfies Eq. (1.2.19) (with $s = N$ and $t = 0$). (See Ref. 3.)

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In the previous section we discussed the Boltzmann equation when the molecules are assumed to be identical hard spheres. There are several possible generalizations of this molecular model; the most obvious is the case of molecules that are identical point masses interacting with a central force – a good general model for monatomic gases. If the range of the force extends to infinity, there is a complication due to the fact that two molecules are always interacting and the analysis in terms of “collisions” is no longer possible. If, however, the gas is sufficiently dilute, we can take into account that the molecular interaction is negligible for distances larger than a certain σ (the “molecular diameter”) and assume that when two molecules are at a distance smaller than σ , then no other molecule is interacting with them and the binary collision analysis considered in the previous section can be applied. The only difference arises in the factor $\sigma^2 |(\xi_2 - \xi_1) \cdot \mathbf{n}|$, which turns out to be replaced by a function of $V = |\xi_2 - \xi_1|$ and the angle θ between \mathbf{n} and \mathbf{V} (Refs. 1, 6, and 7). Thus the Boltzmann equation for monatomic molecules takes on the following form:

$$\frac{\partial P^{(1)}}{\partial t} + \xi_1 \cdot \frac{\partial P^{(1)}}{\partial \mathbf{x}_1} = N \int_{R^3} \int_{\mathcal{B}_-} [P^{(1)}(\mathbf{x}_1, \xi'_1, t) P^{(1)}(\mathbf{x}_1, \xi'_2, t) - P^{(1)}(\mathbf{x}_1, \xi_1, t) P^{(1)}(\mathbf{x}_1, \xi_2, t)] B(\theta, |\xi_2 - \xi_1|) d\xi_2 d\theta d\epsilon, \quad (1.3.1)$$

where ϵ is the other angle which, together with θ , identifies the unit vector \mathbf{n} .

The function $B(\theta, V)$ depends, of course, on the specific law of interaction between the molecules. In the case of hard spheres, of course,

$$B(\theta, |\xi_2 - \xi_1|) = \cos \theta \sin \theta |\xi_2 - \xi_1|. \quad (1.3.2)$$

In spite of the fact that the force is cut at a finite range σ when writing the Boltzmann equation, infinite range forces are frequently used. This has the disadvantage of making the integral in Eq. (1.3.1) rather hard to handle; in fact, one cannot split it into the difference of two terms (the loss and the gain), because each of them would be a divergent integral. This disadvantage is compensated in the case of power-law forces, because one can separate the dependence on θ from the dependence upon V . In fact, one can show^{1,6} that, if the intermolecular force varies as the n th inverse power of the distance, then (Problem 1.3.1)

$$B(\theta, |\xi_2 - \xi_1|) = \beta(\theta) |\xi_2 - \xi_1|^{\frac{n-5}{n-1}}, \quad (1.3.3)$$

where $\beta(\theta)$ is a nonelementary function of θ (in the simplest cases it can be expressed by elliptic functions). In particular, for $n = 5$ one has the so-called Maxwell molecules, for which the dependence on V disappears.

Sometimes the artifice of cutting the grazing collisions corresponding to small values of $|\theta - \pi/2|$ is used (angle cutoff). In this case one has both the advantage of being able to split the collision term and of preserving a relation of the form (1.3.3) for power-law potentials.

Since solving the Boltzmann equation with actual cross sections is complicated, in many numerical simulations use is made of the so-called variable hard sphere model in which the diameter of the spheres is an inverse power law function of the relative speed V (see Chapter 7).

Another important case is that of a mixture rather than a single gas. In this case we have n unknowns, if n is the number of the species, and n Boltzmann equations; in each of them there are n collision terms to describe the collision of a molecule with other molecules of all the possible species.³

If the gas is polyatomic, then the gas molecules have other degrees of freedom in addition to the translation ones. This in principle requires using quantum mechanics, but one can devise useful and accurate models in the classical framework as well. Frequently the internal energy E_i is the only additional variable that is needed, in which case one can think of the gas as of a mixture of species,³ each differing from the other because of the value of E_i . If the latter variable is discrete we obtain a strict analogy with a mixture; otherwise we have a continuum of species. We remark that in both cases, kinetic energy is not preserved by collisions, because internal energy also enters into the balance; this means that