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# First-principle proof of the modified collision boundary conditions for the hard-sphere system

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ABSTRACT

A fundamental issue lying at the foundation of classical statistical mechanics is the determination of the collision boundary conditions that characterize the dynamical evolution of multi-particle probability density functions (PDF) and are applicable to systems of hard-spheres undergoing multiple elastic collisions. In this paper it is proved that, when the deterministic $N$-body PDF is included in the class of admissible solutions of the Liouville equation, the customary form of collision boundary conditions adopted in previous literature becomes physically inconsistent and must actually be replaced by suitably *modified collision boundary conditions*.



## 1. Introduction

In this paper we intend to point out a critical aspect which characterizes the statistical treatment of the classical dynamical system (CDS) associated with closed systems of hard-sphere particles, i.e., in which the number of particles $N$ is constant. This depends on the choice of the collision boundary conditions (CBC) which characterize the $N$-body probability density functions (PDFs) for these systems. Since the latter depend in turn on the prescription of the admissible class of $N$-body PDFs, such a choice has a precise physical motivation. In this paper we point out that the traditional viewpoint adopted in the literature since Boltzmann and Grad rules out "de facto" both deterministic and partially deterministic PDFs among the admissible particular solutions for the statistical description of hard-sphere systems. In view of the fundamental nature of the involved physical considerations, it appears astonishing that the very existence of such a type of physical restriction on the class of admissible PDFs has (apparently) gone unnoticed in the past.

For a start it is worth setting the issue in the proper historical perspective, which is related to the foundations of classical statistical mechanics (CSM) itself. Indeed, there is a wide consensus in the literature about the equation established by Ludwig Boltzmann in 1872 [1–5] as being one of the pillars of the kinetic theory of gases. This is the famous Boltzmann kinetic equation dealing with the statistical behavior of the CDS known as Boltzmann–Sinai CDS (and here referred to in a short-way as $S_N$-CDS [6–8]). Such a CDS is associated with the ensemble $S_N$ of $N$ identical smooth hard spheres of constant diameter $\sigma > 0$ which are immersed in a bounded sub-set $\Omega_1$ of the Euclidean configuration space $\mathbb{R}^3$ having a stationary, connected boundary $\partial\Omega_1$. By assumption $S_N$-CDS satisfies the impenetrability condition, i.e., all particles are mutually impenetrable as it is the boundary $\partial\Omega_1$. Furthermore, the same particles are subject to hard collisions that are instantaneous, i.e., occur only at a discrete set of collision times $\{t_i \in I \equiv \mathbb{R}, i \in \mathbb{N},\}$ and elastic, i.e., conserve the total kinetic energy of the interacting particles. Collision events can involve respectively one, two or more particles simultaneously, the first case corresponding to unary collisions between a single particle and the boundary. The remaining cases correspond, instead, to binary and multiple collisions, occurring respectively between two particles and to more particles interacting among themselves and possibly also with the boundary at the same collision time. Instead, in the collisionless time subset, denoted as $\bar{I}$, i.e., in all open time intervals defined between two consecutive collision times $I_i = ]t_i, t_{i+1}[$, for all $i \in \mathbb{N}$, the motion of all particles is assumed inertial. The main properties of the $S_N$-CDS were summarized in Ref. [9]. Thus, in standard notation, we shall label by $\mathbf{x} = (\mathbf{r}, \mathbf{v})$, $(\mathbf{x}, t)$, $\mathbf{r} = (\mathbf{r}_1, .., \mathbf{r}_N)$ and $\mathbf{v} = (\mathbf{v}_1, .., \mathbf{v}_N)$ respectively the $N$-body state, the corresponding extended state and the configuration and velocity vectors, whereas $\mathbf{x}_i \equiv (\mathbf{r}_i, \mathbf{v}_i)$ identifies the $i$-th particle

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Newtonian state, while $\mathbf{r}_i \equiv (r_{i1}, r_{i2}, r_{i3})$ and $\mathbf{v}_i \equiv (v_{i1}, v_{i2}, v_{i3})$ its center-of-mass position and velocity vectors expressed in terms of Cartesian components. Respectively, $\mathbf{x}$ and $\mathbf{x}_i$ span the vector spaces $\Gamma_N \equiv \Omega_N \times U_N = \prod_{i=1,N} \Gamma_{1(i)}$ and $\Gamma_{1(i)}$, with the latter being the $i$-th particle phase-space $\Gamma_{1(i)} = \Omega_{1(i)} \times U_{1(i)}$. Here, $\Omega_N \equiv \prod_{i=1,N} \Omega_{1(i)}$ and $U_N \equiv \prod_{i=1,N} U_{1(i)}$ are the $N$-body configuration and velocity spaces, with $\Omega_{1(i)} \equiv \Omega_1 \subset \mathbb{R}^3$ and $U_{1(i)} \equiv \mathbb{R}^3$ being the corresponding Euclidean spaces for the $i$-th particle. Furthermore, we shall denote by $\widehat{\Gamma}_N \equiv \widehat{\Omega}_N \times U_N$ and $\overline{\Gamma}_N \equiv \overline{\Omega}_N \times U_N$ the subsets of phase-space in which respectively particles are impenetrable, and no collisions occur (collisionless subset). In particular, $\widehat{\Omega}_N$ and $\overline{\Omega}_N$ denote the subsets of the $N$-body configuration space in which either

$$\Theta^{(N)}(\mathbf{r}) \equiv \prod_{i=1,N} \Theta_i(\mathbf{r}) = 1, \tag{1}$$

or the equation

$$\overline{\Theta}^{(N)}(\mathbf{r}) \equiv \prod_{i=1,N} \overline{\Theta}_i(\mathbf{r}) = 1 \tag{2}$$

are satisfied identically. Here, letting $\mathbf{r}_{ij} = \mathbf{r}_i - \mathbf{r}_j$, $\Theta_i(\mathbf{r})$ and $\overline{\Theta}_i(\mathbf{r})$ denote respectively

$$\Theta_i(\mathbf{r}) \equiv \Theta\left(\left|\mathbf{r}_i - \frac{\sigma}{2}\mathbf{n}_i\right| - \frac{\sigma}{2}\right) \prod_{j=1,i-1} \Theta\left(|\mathbf{r}_i - \mathbf{r}_j| - \sigma\right), \tag{3}$$

$$\overline{\Theta}_i(\mathbf{r}) \equiv \overline{\Theta}\left(\left|\mathbf{r}_i - \frac{\sigma}{2}\mathbf{n}_i\right| - \frac{\sigma}{2}\right) \prod_{j=1,i-1} \overline{\Theta}\left(|\mathbf{r}_i - \mathbf{r}_j| - \sigma\right), \tag{4}$$

while $\Theta(y) = \begin{cases} 1 & y \geq 0 \\ 0 & y < 0 \end{cases}$ and $\overline{\Theta}(y) = \begin{cases} 1 & y > 0 \\ 0 & y \leq 0 \end{cases}$ identify the weak and strong Heaviside theta-functions, while $\mathbf{n}_i$ is the inward unit vector orthogonal to the boundary at the point of contact of the $i$-th hard sphere (i.e., at $\mathbf{r}_i - \frac{\sigma}{2}\mathbf{n}_i$). As a basic consequence, it is possible to show (see Ref. [9]) that for all $t, t_o \in \overline{I}$ the flow generated by the CDS onto the phase-space $\widehat{\Gamma}_N$ is globally realized in terms of the time-evolution operator $T_{t_o,t}$, via a bijection of the form

$$T_{t_o,t} : \mathbf{x}(t_o) \equiv \mathbf{x}_o \to \mathbf{x}(t) \equiv \chi(\mathbf{x}_o, t_o, t) \equiv T_{t_o,t}\mathbf{x}_o, \tag{5}$$

with inverse

$$T_{t,t_o} : \mathbf{x} \equiv \mathbf{x}(t) \to \mathbf{x}(t_o) = \mathbf{x}_o = \chi(\mathbf{x}, t, t_o) \equiv T_{t,t_o}\mathbf{x}_o. \tag{6}$$

To determine the time-evolution also at all collision times $t_i \in \{t_i\}$, let us introduce the states before and after collisions $\mathbf{x}^{(-)}(t_i)$ and $\mathbf{x}^{(+)}(t_i)$ (i.e., the incoming and outgoing states) in terms of the limits

$$\mathbf{x}^{(-)}(t_i) \equiv \lim_{t \to t_i^{(-)}} \mathbf{x}(t), \tag{7}$$

$$\mathbf{x}^{(+)}(t_i) \equiv \lim_{t \to t_i^{(+)}} \mathbf{x}(t). \tag{8}$$

Then, the time evolution of the $S_N$-CDS at an arbitrary $t_i$ is determined via suitable collision laws which uniquely prescribe $\mathbf{x}^{(+)}(t_i)$ in terms of $\mathbf{x}^{(-)}(t_i)$ (or vice versa).

For the $S_N$-CDS, the Boltzmann equation provides a kinetic description, i.e., a statistical treatment of single-particle dynamics in which the 1-body state $\mathbf{x}_1$ is prescribed in statistical sense in terms of the reduced 1-body phase-space probability density function (PDF) $\rho_1^{(N)}(\mathbf{x}_1, t)$. The latter, in turn, is uniquely related to the corresponding $N$-body PDF $\rho^{(N)}(\mathbf{x}, t)$ which is associated with the whole $S_N$-CDS (see for example Grad, 1958 [2]). Indeed, for $s = 1, N-1$, the reduced $s$-body PDF $\rho_s^{(N)}(\mathbf{x}^{(s)}, t)$ which depends only on the reduced $s$-body state $\mathbf{x}^{(s)} \equiv (\mathbf{x}_1, .., \mathbf{x}_s)$ is prescribed in terms of $\rho^{(N)}(\mathbf{x}, t)$ and is defined as

$$\rho_s^{(N)}(\mathbf{x}^{(s)}, t) = \overline{F}_s\{\rho^{(N)}(\mathbf{x}, t)\}, \tag{9}$$

with $\overline{F}_s$ being the linear operator

$$\overline{F}_s = \int_{\Gamma_N} d\mathbf{y} \rho^{(N)}(\mathbf{y}, t) \overline{\Theta}^{(N)}(\mathbf{r}) \prod_{i=1,s} \delta(\mathbf{y}_i - \mathbf{x}_i), \tag{10}$$

and denoting $\mathbf{y} \equiv (\widehat{\mathbf{r}}_i, \widehat{\mathbf{v}}_i)$, $\delta(\mathbf{y}_i - \mathbf{x}_i) = \delta(\widehat{\mathbf{r}}_i - \mathbf{r}_i)\delta(\widehat{\mathbf{v}}_i - \mathbf{v}_i)$. Here, $\delta(\mathbf{r}_i - \mathbf{r}_i(t))$ and $\delta(\mathbf{v}_i - \mathbf{v}_i(t))$ are the 3-dimensional Dirac-deltas in Cartesian components, i.e., $\delta(\widehat{\mathbf{r}}_i - \mathbf{r}_i) = \prod_{j=1,3} \delta(\widehat{r}_{ij} - r_{ij})$ and $\delta(\widehat{\mathbf{v}}_i - \mathbf{v}_i) = \prod_{j=1,3} \delta(\widehat{v}_{ij} - v_{ij})$.

Thanks to such an identification, the Boltzmann and Grad statistical approaches actually lead to the same form of the Boltzmann equation in the so-called Boltzmann–Grad limit [2]. Indeed, in its original derivation the Boltzmann equation applies to rarefied systems of hard spheres, for which the distance between interacting particles is considered much smaller than the relevant macroscopic scale lengths so that, in this sense, *the colliding particles are effectively treated as point-like* (see related discussion in Ref. [9]). As a result, the dynamical evolution of $\rho_1^{(N)}(\mathbf{x}_1, t)$ is determined by mutual particle collisions through the introduction of the so-called Boltzmann collision operator in which interacting particles are treated *as having the same position* [3,4]. As shown in Ref. [9] this feature actually rules out from the functional class of admissible solutions [for the Boltzmann equation] all PDFs which, as far as their spatial dependence is concerned, are expressed in terms of distributions.

However, several important theoretical problems remain to be solved regarding the statistical description of the $S_N$-CDS. A critical issue concerns the prescription of the so-called "collision boundary conditions" (CBC), i.e., the behavior of the $N$-body PDF across collision events. The latter generally include unary collisions between a single sphere with the fixed boundary and binary or multiple collisions occurring among particle themselves and/or among particles and the same boundary. Hence, the meaning of "collision boundary conditions" must be intended here in a wide sense, for the statistical treatment of hard spheres interacting both with the rigid boundary of the system and among themselves.

In this paper we point out, based on physical considerations, that the customary approach adopted in this regard by Boltzmann and Grad [2,3] as well as Enskog [10] should be actually modified to accommodate for the inclusion of modified collision boundary conditions (MCBC), to be invoked for the time evolution of the $N$-body PDF across collisions events. We show that such a choice is actually necessary in order to develop a consistent statistical description of the $S_N$-CDS in which, contrary to the Boltzmann, Enskog and Grad approaches, a subset or all of the particles, or some suitable phase-functions of $S_N$, can possibly be described, in a suitable sense, deterministically. In such a case the $N$-body PDF is generally realized by means of a distribution. Indeed, both the requirements appear justified on physical grounds by the necessity of extending the original Boltzmann theory to the treatment of real systems characterized by these properties. A related fundamental problem lies in the statistical description of systems formed by a finite number $N$ and finite size $\sigma$ of hard spheres. As realized already by Enskog [10,11], the issue is expected to be relevant especially in the case of dense or locally-dense gases or fluids [12–14], such as environmental and biological fluids [15–17] granular flows [18,19] and tracer-particle dynamics [20–22].