Boltzmann’s $H$-theorem and time irreversibility

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Abstract

It is shown that the justification of the Boltzmann $H$-theorem needs more than just the assumption of molecular chaos and the picture of time irreversibility related to it should be reinvestigated.

It is well-known that while the Newtonian formalism is time reversible the kinetic equations, based almost entirely on the Newtonian formalism, are time irreversible. This paradox has served as a serious topic for the century-long debate. Recent studies of non-equilibrium phenomena, such as those related to turbulence, transport and chaos, constantly remind us that a good understanding of time irreversibility is of crucial importance in terms of knowing the game nature plays. Keeping those things in mind, we shall here concern ourselves with explication and implication of time irreversibility in classical physics. It will be shown that the Boltzmann $H$-theorem and the picture of time irreversibility related to it involve mathematical problems.

According to the standard theory[1], the evolution of dilute gas consisting of hard sphere balls (referred to as particles hereafter) is described by the Boltzmann equation

\[
\frac{\partial f_1}{\partial t} + \mathbf{v}_1 \cdot \frac{\partial f_1}{\partial \mathbf{r}} + \frac{\mathbf{F}}{m} \cdot \frac{\partial f_1}{\partial \mathbf{v}_1} = \int \int d\mathbf{v}_2 d\Omega u \sigma(f'_1 f'_2 - f_1 f_2). \tag{1}
\]

To show the time irreversibility of it, the theory introduces a function[2]

\[
H(t) = \int \int d\mathbf{r} d\mathbf{v}_1 f_1(\mathbf{r}, \mathbf{v}_1, t) \ln f_1(\mathbf{r}, \mathbf{v}_1, t), \tag{2}
\]

which can be recognized as a form of negative entropy. By substituting (1) into (2), the time derivative of $H(t)$ is, with external forces neglected,

\[
\frac{dH}{dt} = -\int \int d\mathbf{r} d\mathbf{v}_1 \left( \mathbf{r} \cdot \frac{\partial f_1}{\partial \mathbf{r}} \right) [\ln f_1 + 1]
+ \int \int \int d\mathbf{r} d\mathbf{v}_1 d\mathbf{v}_2 d\Omega u \sigma(f'_1 f'_2 - f_1 f_2) [\ln f_1 + 1]. \tag{3}
\]
On the premise of that the distribution function vanishes for large $r$ and $v_1$, called the null boundary condition herein, we arrive at

$$\frac{dH}{dt} = \int \int \int \int d\mathbf{r}d\mathbf{v}_1d\mathbf{v}_2d\Omega u\sigma (f'_1 f'_2 - f_1 f_2) [\ln f_1 + 1].$$  \hspace{1cm} (4)

Since $f_2, f'_1$ and $f'_2$ describe the same gas, three other formulas similar to (4) can also be obtained; thus $dH/dt$ finally becomes

$$\frac{dH}{dt} = \frac{1}{4} \int \int \int \int d\mathbf{r}d\mathbf{v}_1d\mathbf{v}_2d\Omega u\sigma (f'_1 f'_2 - f_1 f_2) \ln \frac{f_1 f_2}{f'_1 f'_2} \leq 0,$$  \hspace{1cm} (5)

which is always less than zero except for gases that are in equilibrium. This conclusion, called the Boltzmann $H$-theorem, was, and still is, regarded as a great triumph of the Boltzmann theory, since it explained, rather generally, macroscopic time irreversibility in terms of microscopic laws.

Notice that the derivation above specifically identifies particle-to-particle collisions as a mechanism responsible for time irreversibility. Interestingly, this identification, supposed to reveal the very secret of nature, confused, and continues to confuse, many scientists. The main reason lies in that the time irreversible $H$-theorem is, as has just shown, based on the properties of the Boltzmann collisional operator, while the Boltzmann collisional operator itself is based on the time reversibility of the Newtonian formalism.

To make things more perplexing, an explicit theorem in textbooks, while based also on the Newtonian formalism and null boundary condition, tells us a different story[3]. The theorem, called the $\rho - S$ theorem in this paper, goes as follows. The entropy of a gas system is defined as

$$S = -k \int d\Gamma \rho \ln \rho,$$  \hspace{1cm} (6)

where $\rho$ is the grand distribution of the system in the grand phase space, $\Gamma$-space. Differentiating $S$ with respect to time yields

$$\frac{dS}{dt} = -k \int d\Gamma (\ln \rho + 1) \frac{\partial \rho}{\partial t}.$$  \hspace{1cm} (7)

Substituting Liouville’s theorem $\partial \rho/\partial t + [\rho, H] = 0$ into (7), we finally get, after a few mathematical steps,

$$\frac{dS}{dt} = 0,$$  \hspace{1cm} (8)
which literally means that interactions between particles themselves, no matter what kinds of forms they take, are not responsible for time irreversibility. This theorem, though less popular than the Boltzmann one, is by no means surprising since it presents nothing but the time reversibility of Newtonian mechanics.

The conflict between the two theorems above has been known for quite long[4]. To resolve the difficulty, the conventional wisdom invoked the assumption of molecular chaos. It is widely believed that with help of molecular chaos the Boltzmann theory is justified at least in the practical sense[5]. However, being exposed to many interesting phenomena of gas dynamics, we are convinced that the Boltzmann theory needs more than just the assumption of molecular chaos.

Let’s first look at the time reversibility in mechanics. Consider two identical particles (still distinguishable according to classical physics). The initial and final velocities of them are denoted by $v_1, v_2$ and $v’_1, v’_2$ respectively. The usual concept of time reversibility states that if the collision $v_1, v_2 \rightarrow v’_1, v’_2$ is physically possible, then the inverse collision $-v’_1, -v’_2 \rightarrow -v_1, -v_2$ is also physically possible, which is trivial and we discuss it no more.

Then, we study the time reversibility concerning beam-to-beam collisions, from which the Boltzmann collisional operator is derived. To our great surprise, the time reversibility of this type does not exist at all: there is neither an intuitive one, nor a mathematical one.

Figure 1: A candidate for time reversibility of beam-to-beam collision: (a) the original collisions; and (b) inverse collisions imagined.

Intuitively, we may consider two pictures sown in Fig. 1. Fig. 1a shows that two particle beams at two definite velocities collide and the particles
produced by the collisions diverge in the position and velocity space. Fig. 1b illustrates the opposite process, in which different converging beams collide and the produced particles form two beams, each of which has one definite velocity. In no need of discussion, we all find that the first picture makes sense in statistical mechanics, while the second one does not.

In standard textbooks, the following mathematical definition of time reversibility has been employed[1]:

\[
\sigma(v_1, v_2 \rightarrow v'_1, v'_2) = \sigma(v'_1, v'_2 \rightarrow v_1, v_2),
\]

where the cross section \(\sigma(v_1, v_2 \rightarrow v'_1, v'_2)\) is defined in such a way that, after collisions between a beam of type-1 particles at \(v_1\) and a type-2 particles at \(v_2\),

\[
N = \sigma(v_1, v_2 \rightarrow v'_1, v'_2)dv'_1dv'_2
\]

represents the number of type-1 particles emerging between \(v'_1\) and \(v'_1 + dv'_1\) per unit incident flux and unit time, while the type-2 particle emerges between \(v'_2\) and \(v'_2 + dv'_2\); and the cross section \(\sigma(v'_1, v'_2 \rightarrow v_1, v_2)\) is defined in the same manner.

![Figure 2: Constraints on the final velocities of scattered particles. (a) \(v_1\) and \(v_2\) predetermine \(c\) and \(u = |u|\). (b) \(v'_1\) and \(v'_2\) have to fall on the shell \(S\) of diameter \(u\).](image)

An unfortunate fact with the time reversibility (9) is that the cross section in it is mathematically ill-defined. For the collisions between two beams with \(v_1\) and \(v_2\) respectively, the energy and momentum conservation laws imply that \(v'_1\) and \(v'_2\) satisfy

\[
v'_1 + v'_2 = v_1 + v_2 \equiv 2c \quad \text{and} \quad |v'_2 - v'_1| = |v_2 - v_1| \equiv u,
\]

where \(c\) is the center-of-mass velocity and \(u\) is the relative speed. Fig. 2a shows that \(c\) and \(u\) are determined by \(v_1\) and \(v_2\), while Fig. 2b shows that \(c\)
and $u$ impose constraints on $v'_1$ and $v'_2$. Referring to the figures, we find that $v'_1$ and $v'_2$ must fall on a spherical shell $S$ of diameter $u = |u|$ in the velocity space, called the energy-momenta shell herein. By adopting this notion, two misconcepts associated with (10) can be unveiled immediately. The first is that after $dv'_1$ is specified, specifying $dv'_2$ in (10) is a work overdone. The second is that the cross section should be defined in reference to an area element on the energy-momenta shell rather than in reference to an arbitrary velocity volume element. If we insist on doing the latter, the resultant ‘cross section’ can equal any value from zero to infinity, depending on how $dv'_1$ encloses the shell and how $dv'_1$ approaches zero. To see it, imagine that $dv'_1$ is a cylinder centered on and perpendicular to the shell. When $dv'_1$ becomes slimmer and slimmer, $\sigma \to 0$; when $dv'_1$ becomes shorter and shorter, $\sigma \to \infty [6]$.

The above discussion has shown that, the immediate problem is not that we cannot build up a theorem that produces the time irreversibility assumed by the existing formalism but that we cannot build up a theorem that produces the time reversibility assumed by the existing formalism; and the problem is that of mathematics and has nothing to do with how do we employ subtle physical assumptions.

It is now in order to return to our original subject and comment on physical mechanisms responsible for time irreversibility. According to information theory, the increase of entropy represents the destruction of information. For a classical gas, the information contained is nothing but the aggregate of all initial conditions. Whenever and wherever some of the initial conditions are erased, mechanisms of time irreversibility must be at work. Armed with this concept, we realize that chaos theory, as well as some analyses concerning averaging molecular motions, indeed promises to account for time irreversibility to some degree. Nevertheless, for purposes of this paper, boundary effects will be the subject of our discussion.

In view of that the $\rho - S$ theorem is time reversible and the null boundary condition related to it is just an assumption, it is arguable that time irreversibility may arise from realistic interaction between boundaries and particles.

Examine the situation in Fig. 3a, where a cuboid box with perfectly flat walls is stationary and all particles in it move with a definite speed $v$ rightward or leftward. To make the examination simpler, let all particles be rather small (or, the gas be rather dilute) so that particle-to-particle collisions are presumably negligible. Under these we find, if particle-to-boundary collisions are assumed to be perfectly elastic, the system will remain in the
original state for quite long; whereas, if realistic boundary conditions are allowed to apply, the system will approach its equilibrium rather realistically. In Fig. 3b, a particle colliding with the boundary loses its memory of initial condition, at least partly, and spreads with various velocities according to a statistical law, in which fluctuation and dissipation must get involved[7]. By setting the temperature $T$ of the walls uniform and such that $3\kappa T/2 = mv^2/2$, it is seen that the gas entropy increases with no macroscopic energy exchange between the gas and boundary.

![Diagram of particle movement](image1)

![Diagram of boundary collision](image2)

Figure 3: (a) Particles move rightward or leftward inside a box. (b) Schematic of how a particle collides with a boundary.

The relevance of the aforementioned effect can be verified quantitatively. For a dilute gas, we can simulate the relaxation process with help of certain empirical laws of particle-to-boundary collisions. It is very easy to see that while the $H$-theorem predicts much longer relaxation times for such gas ($\tau \propto f^{-2}$) the undeterministic boundary specification may yield results consistent with those observed in nature.

Our discussion also suggests that after colliding with a boundary a particle has to be regarded as part of particle beam in view of that the later motion of it can be known only in probability. As has been revealed, if such a beam meets with other beams, the consequent collisions should, in turn, be considered as being of time irreversibility.

More investigations reveal more interesting things[8, 9], of which one is that realistic boundaries can not only erase information, but, in many cases, create information. It is no wonder that so many striking phenomena in fluid experiments occur around boundaries.

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