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The Irreversibility of Microscopic Motions

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Abstract: People have long had a problem: the equations of motion that reflect the laws of physics are invariance under time inversion, while there always are irreversible processes for gases compose of microscopic particles. This article solves this problem. The point is that we should distinguish between the concepts of the equation of motion and motion. We also need to distinguish between the concepts of time-inverse motion and reverse motion. The former is anticlockwise, which is a frictional motion, while the latter is clockwise. For the single-particle motions in classical mechanics and in quantum mechanics, we present mathematical expressions for time-inversion motion and reverse motion, respectively. We demonstrate that single-particle motion is irreversible. The definition of the reversibility of two-particle collisions is given. According to the definition, the two-particle collision as a microscopic motion processes is irreversible. Consequently, for a gas consisting of a large number of particles colliding with each other, its movement should be irreversible, unless the condition of detailed balance is met. We give a physical explanation for the detailed balance, which does not concern the meaning of microscopic reversibility. The detailed balance means that after a pair of reciprocal collisions occur, the distribution function of the particles remains unchanged. Therefore, microscopic two-particle collision events are irreversible, but the statistical average of a large number of collision events makes it possible for the macroscopic process of a gas to be reversible. Conclusively, we clarify the microscopic mechanism of the irreversible process of gases.

Keywords: motion; equation of motion; irreversibility of motion; time-inverse motion; reverse motion; two-particle collision; detailed balance

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I. INTRODUCTION

A. The paradox of irreversibility

The motion of individual microscopic particles follows the laws of physics. The laws of physics are embodied in equations of motion, which are expressed as differential equations with derivative with respect to time. It is believed that the equations of motion are time-reversible.

A macroscopic gas is made up of a large number of microscopic particles. Since the equation of motion that every microscopic particle follows is time-reversible, people take it for granted that macroscopic processes should be reversible either. But in fact, we always see that irreversible processes happen. Therefore, people are faced with the fact that the laws of motion of microscopic particles are reversible in time, while the motion of macroscopic systems is irreversible [1–13]. It is also said that the movement of micro particles is symmetric with respect to time, but the movement of macro systems composed of a large number of micro particles is not [4,5].

This fact forms a paradox: "Classical mechanics itself is entirely symmetrical with respect to the two directions of time. The equations of mechanics remain unaltered when the time *t* is replaced by –*t*; if these equations allow any particular motion, they will therefore allow the reverse motion, in which the mechanical system passes through the same configurations in the reverse order. This symmetry must naturally be preserved in a statistics based on classical mechanics. Hence, if any particular process is possible which is accompanied by an increase in the entropy of a closed macroscopic system, the reverse process must also be possible, in which the entropy of the system decreases."[14]

We use (p_i, q_i) to represent the *i*-th generalized coordinate and generalized momentum. They follow Hamilton canonical equations:

$$\dot{p}_i = -\frac{\partial H}{\partial q_i}, q_i = \frac{\partial H}{\partial \dot{p}_i}. \tag{1}$$

Now, we make time inversion,

$$t \to -t. \tag{2}$$

Meanwhile, we take the following transformation,

$$p_i \to -p_i, q_i \to q_i. \tag{3}$$

Then, under the transformation Equations (2) and (3), the forms of Equation (1) remain unchanged. This is the time-reversal invariance of the equations of motion, and was called "the principle of dynamical reversibility" [13]. This seems that the movement of each particle should be time-reversible.

Consider that an isolated ideal gas is undergo a process that increases its entropy. At one moment, let the momentum of all molecules reverse, that is, the transformation of (2) and (3) are taken, then, from this moment on, each molecule still moves according to (1) in the reverse time direction. That is to say, the whole gas moves in the opposite time direction, i.e., it moves in the direction of decreasing entropy. But such a process is practically impossible. The second law of thermodynamics negates the possibility of such a process. This argument is known as the Loschmidt paradox [2,13,15,16]. The Loschmidt paradox can be stated quite simply: If all the laws of physics are time-reversal-symmetric, how can one prove a time-asymmetric law like the second "Law" of thermodynamics that states that the entropy of the Universe "tends to a maximum" [16].

In quantum mechanics (QM). There is the same paradox. "Time irreversibility is not a problem to be solved, ……Theoretically, in particular in the quantum case, realization of time irreversibility is difficult because the fundamental kinetic equations, including the Schrödinger equation and the Dirac equation, ensure that the dynamics are reversible in time." [17] Some ones believed that the microreversibility can be employed to provide a way to obtain the statistical cumulants [18].

Someone believed there was "no conflict between reversible microscopic laws and irreversible macroscopic behavior".[5] However, when he addressed this, he did not resolve the Loschmidt paradox.

People admit it is a problem and have been troubled by this paradox for more than one hundred years. Various efforts have been devoted to eliminate this problem. These efforts are speculating about the cause of the irreversibility of macroscopic processes from microscopic reversibility.

One view is that although every micro process is reversible, the statistical nature of a large number of micro processes can lead to the irreversibility of macro processes. For example, the law of motion of each micro particle is time-symmetrical, but the motion that evolves into a macroscopic gas is a diffusion equation which is temporally asymmetric [5]. However, it is difficult to transit from microscopic equations of motion to macroscopic equations, and there has been no successful solution so far. "There are many conceptual and technical problems encountered in going from a time-symmetric description of the dynamics of atoms to a time-asymmetric description of the evolution of macroscopic systems. This involves a change from Hamiltonian (or Schrödinger) equations to hydrodynamical ones, e.g., the diffusion equation. The problem of reconciling the latter with the former became a central issue in physics during the last part of the nineteenth century." [5] This is due to that "the microscopic details are usually unreachable, and a full description of the system is impossible." [19]

One view is that the irreversibility of thermodynamic processes arises because the initial state of thermodynamic systems is very special [3,10], such as at the initial moment the gas is confined to a specific region. In fact, this view is untenable. If the macroscopic gas is in another initial state, its motion process is still irreversible. The property that the motion of a gas is irreversible has nothing to do with its initial state.

Some ones think that there do not exist real isolated systems, and there are always various perturbations that more or less cause molecules to deviate slightly from their intended trajectories after collision. In this way, after multiple collisions, the molecule completely loses its memory. "In reality, it is impossible to produce a totally isolated system. There are always *external perturbations* present, such as radiation, sunspots or the variable gravitational influence of the surrounding matter." Thus, "the system loses its memory of the initial state after only a small number of collisions." [10] "In the forward direction, the macroscopic time development is stable with respect to perturbations but in the time-reversed direction, it is very unstable." This reason could not provide satisfactory explanation of the paradox, and was opposed by others [9]. As a matter of fact, even without external perturbation, an isolated system also follows the law of entropy increase. For instance, in deriving the Boltzmann H theorem, no external affection is considered.

Some people think that the walls with specific shapes and sizes have an effect on the state of a gas. It is well known that the irreversibility of thermodynamic processes is practically irrespective to the walls.

Prigogine [20] tried to give a mechanism of irreversibility, called "cascade mechanism". He thought that the variation of lower order correlations lead to higher order correlations, and the appearance of the higher order correlation were accompanied by a "directed flow". That was the mechanism of irreversibility. But he did not explain why there was no opposite directed flow in the higher order correlations, or, why the higher order correlations were anisotropic.

It was found, based on numerical simulations, that microscopic reversibility can lead to a state of time anisotropy. The corresponding mathematical proof is called the fluctuation theorem, [21,22] and the authors thought that it was the "first step toward understanding how macroscopic irreversibility arises from microscopically time-reversible dynamics". They addressed that "our new proof of how macroscopic irreversibility arises from time reversible microscopic dynamics is valid for all densities" and "time reversibility of the underlying equations of motion is the key component to proving these theorems."[16]

None of the above explanations correctly explains the irreversibility of thermodynamic processes. These explanations give different physical reasons for one physical problem. We think that if there are different interpretations for a physical phenomenon, and none of them can forcefully overturn the others, then, none of them is correct.

*Anyhow, the problem remains, and until 2002, "*there has been no real change in the situation."[8]

The Loschmidt's reasoning implicitly assumes that because the equation of motion that microscopic particles obey is time-reversible, the motion of the microscopic particle is necessarily time-reversible. This is also known as micro-reversibility, and this assumption is accepted by almost everyone. The time reversibility of the equations of motion is confirmed by transformations (2) and (3). People presuppose the micro reversibility and discuss with this premise the cause of the macro irreversibility. However, if the micro motion is reversible itself has not been demonstrated. If the micro motion is irreversible, this will inevitably have some consequences. For example, the absence of microscopic reversibility will lead to an asymmetry in the probability currents [23].

In order to solve this paradox, we have to clarify the relevant physical concepts. First, we should distinguish concepts of the equation of motion and specific motion. We must carefully study whether specific microscopic movements are reversible or not. If microscopic motion is irreversible, then it is not surprising that macroscopic motion is irreversible, and the so-called paradox disappears naturally. Secondly, when talking about the reversibility of specific motion, we must distinguish between reverse motion and time-inverse motion.

B. Distinguishing the concepts of reverse motion and time-inverse motion

For the motion of an individual particle and the motion of a system, we define the concepts of reverse motion and time-inverse motion, respectively.

The concepts for an individual particle is as follows.

Let a particle be in a state A, called the original initial state. Starting from the state A, the particle moves clockwise, passing through a series of intermediate states, and reaches an original final state B. This process is called the original movement process.

We take the state B as a new initial state, called the second initial state. Let us consider the following two processes, referred to as opposite processes.

Time-inverse movement process. Starting from the second initial state, the particle moves counterclockwise, in the opposite order, passing through each intermediate state in the original process, and returns to a final state that is just the original initial state A. Such a motion is called the time-inverse motion of the original process. This is a fictional movement, because in the real world, time always goes to the future.

Reverse movement process. Starting from the second initial state, the particle moves clockwise, in the reverse order, passing through each intermediate state in the original process, and returns to the original initial state A. Such a process is called the reverse movement process of the original process.

If the particle's states are described by momentum, the momentum direction in the opposite processes should be always opposite to that in the original process.

Suppose that one uses a camera to film the original process, and then play the video backwards. If the reverse process is the same as what the video playback shows, then the original process is said to be reversible. Note that when we play the video backwards, the time is playing into the future.

Although both the opposite processes describe the motion from the second initial state to the original initial state, the directions of time evolution are just opposite. The two processes have different mathematical expressions that will be given is Section II.

We turn to consider a macroscopic system composed of a large number of microscopic particles, such as a gas. The process that a macro system goes through is a macro process. The gas is in a macroscopic state at every macroscopic moment. We mark a macro state with a capital letter. There can be many micro states corresponding to a macro state. We mark a micro state with a lowercase Greek letter. At a certain micro moment , the gas is in a specific micro state α of a macro state A, denoted by $A\alpha$.

At the initial moment, the gas is in a macroscopic original initial state A and one of the specific microscopic original initial states α*. Starting from this original state* $A\alpha$*, the gas moves clockwise, passing through a series of intermediate states* $B\beta$*, and reaches a final state* $C\gamma$*, called the microscopic original final state. This process is called the original process.*

We take the $C\gamma$ *as a new initial state, called the second initial state. If the state* $C\gamma$ *is described by momentum of the microscopic particles, the momentum direction of every particle should be reversed to obtain the second initial state. We consider the following two opposite processes.*

Time-inverse movement process. Starting from the second initial state $C\gamma$*, the system moves counterclockwise, in the opposite order, passing through each intermediate state* $B\beta$ *in the original process, and returns to the original initial state* $A\alpha$*. We can image that a video recorder films the original process and then play the video rewind, although the playback is actually done clockwise. Such a motion is called the time-inverse motion of the original process. This is a fictional movement, because in the real world, time always goes to the future.*

Reverse movement process. Starting from the second initial state, the system moves clockwise, in the reverse order, passing through each intermediate macro state B in the original process, and returns to the macro original initial state A. Such a motion process is called the reverse movement process of the original process. If the reverse process can be realized, the original process is said to be reversible, otherwise it is irreversible.

In the reverse process, merely the intermediate macro states in the original process are retrieved in the opposite order without the requirement of the details of the micro states. This kind of reversibility, without resorting to microscopic details, is called reversibility in the macroscopic sense. In the time-inverse process and reverse process, the macro state at every macro moment should be same but the micro state can be different.

The reason why we make this distinction between the time-inversion process and the reverse process of a macroscopic system is that when people talk about the inverse process of a macro system, they actually mean the reverse process defined here, not the time-inversion process. The features of the reverse process are that it is clockwise and that merely the macroscopic states in the original process are required to retrieve in the opposite order, with no requirement the details of micro state. Some examples are given as follows.

An original process is that an ice cube dissolves in a cup of boiling water. Its imagined reverse process is impossible. "It is impossible to prepare a cup of lukewarm water in such a way that, one hour later, it will turn into an ice cube floating in boiling water." [24] First, the imagined reverse process is clockwise. Second, the imagined reverse process is not required to retrieve every intermediate micro state in the original process. It is merely required that every intermediate macro state is retrieved in the opposite order of the original process.

Evaporation and condensation are a pair of processes reverse to each other. "Since evaporation and condensation are in general thermodynamically reversible phenomena, the mechanism of evaporation must be the exact reverse of that of condensation, even down to the smallest detail." [25] Both the evaporation and condensation processes are in progress clockwise, and in the sense of macro states instead of micro states, they are mutually reversible processes. One of the processes does not mean a time-inverse process of the other.

People talk about the ideal perpetual motion machine of the second kind. This kind of perpetual motion machine is required to do a reversible cycle that is repeated over and over again. In each cycle there must be a reverse process which goes clockwise. Such a fictional machine always works clockwise. Moreover, people do not care the details of microscopic states in each cycle.

The envisaged Poincaré recurrences [7,10,26,27] are also clockwise processes.

Spin echo is also a clockwise process. It is regarded as the reverse process of the precession of a spin system [28–30].

There was a gedanken experiment [30]. The original process was that a system evolved clockwise starting from the moment $t=0$ until $t=T$. Then, at the moment $t=T$, the system started doing a reverse process until $t=2T$. Therefore, this reverse process was also carried out clockwise.

It the introduction of [16], when "the fundamental property of time reversible dynamics" was mentioned, time was supposed to go from 0 to *t*, and then to 2*t*. Time went clockwise throughout. Although the authors discussed reverse process, they did not take time inversion.

When computer numerical simulations of colliding particle systems are carried out, the reverse processes go in clockwise direction [10,32–34].

Any actually observable process is clockwise. The time-inverse processes are fictitious.

However, people sometimes confuse reverse motion with time-inverse motion, equating the two kinds of motion. That is to regard a clockwise reverse process as an anticlockwise process. Here are some examples.

Figure 4 in [3] envisaged an original motion and its reverse motion. The panels A-B in Figure4 "show athletes on a racetrack. At the first gunshot, they start running", which was the original process. Then, "at the second, they reverse and run back, ending up again in a line." The reverse process was shown by Figure 4D-F, going clockwise. But the author wrote the caption of the figure by "Reversing time".

In Figure 2.4 of [9], the author took time inversion $t \to -t$ at the moment $t=T$. Nevertheless, the system went on to the moment $t=2T$. That is to say, after time was inversed, time still went clockwise just as the original process.

In Ref. [10], the manipulation of $\boldsymbol{v} \to -\boldsymbol{v}$ was called *time reversal, but after the manipulation, the system actually still evolved clockwise, as shown by Figure 10.6 there.*

The confusion between clockwise and counterclockwise processes probably comes from the following thinking. If an original process of entropy increase is assumed to reverse, the assumed reverse process is necessarily accompanied by entropy decrease. People equate decreasing entropy with time inversion.

Let us review Loschmidt's reasoning. First, Loschmidt treated the differential equation (1) that particles' motion should obey as particles' motion, confusing the concepts of equation of motion and motion. Second, the Loschmidt's starting point was the time reversal of the equation of motion (1). That he did the transformation (2) meant to discuss the time-inverse motion. But in reality, time always points to the future. So, he confused time-inverse motion with reverse motion. What Loschmidt actually wanted to see was an increase in entropy as the gas moved clockwise, since he knew that it was impossible to reverse time in reality. What he expected was that the system would still move clockwise, but he could see the effect of reversing time. We will argue in subsection III.B that the outcome he envisaged is impossible.

The definition of reversible process of a particle's motion above only involves the motion itself, and does not involve its surrounding environment. When a particle undergoes an original process, its surroundings may also change, say, from an original initial state X to Y. Then, at the end of the reverse process, the external environment should return from the Y state to the original initial state X, that is, all external influences brought by the original process are eliminated. If the influence on the surroundings cannot be eliminated, then the *process is still irreversible. The same condition applies to a system. So, the conditions for an original process carried out by a system to be reversible are that after the reverse process of the system, not only must the system itself return to the original initial state, but the surroundings must also return to their original initial state.*

We will see in section II that the motion of an individual particle is irreversible. For a classical particle, its reverse motion at least needs us to prepare the initial state. Thus, the surroundings are unable to retrieve the initial state of the original process. For a quantum particle, the motion itself is irreversible.

For macroscopic matter such as gases, we should focus on the collision between particles

C. Collision systems

A macroscopic system is made up of a large number of microscopic particles. We roughly divide macro systems into two categories. The first category, called collision systems, is that the molecules composing the macro system collide with each other, such as ideal gases. Any system that does not belong to the first category is called a non-collisional system.

Non-collision systems are characterized by finite interactions between the particles that make up the system. The change in momentum caused by interactions between particles is continuous. The spatial coordinates of each particle can also change continuously. Hence, the Liouville equation applies to this category of systems. We give some examples of non-collisional systems. Harmonic and nonharmonic coupling systems are non-collision ones [35–42]. Spin systems [28–30] and spin glass [43,44] also belong to this category.

Another example is a system of one-dimensional identical particles [2,26,45], although collisions between the particles can occur. "Since the collisions between the molecules are elastic and the particles indistinguishable, we can allow the colliding molecules to move as if they passed through one another without collision."[45] In the Liouville equation of this system, the term with derivative of momentum does not appear. Thus, the momentum distribution does not change with time. Nevertheless, the spatial distribution of the particles can vary, tending to be uniformly distributed with time going. This system has essentially the same kinematic characteristics as a collision-free system. Indeed, in discussing the variation of the particle distribution of this system, collisions between particles were not taken into account [2]. Therefore, it is also classified as a collision-free system.

In general, because the non-collision systems satisfy the Liouville equation, their processes may be reversible, and it is possible to estimate the Poincaré recurrence time [26]. It is likely that the non-collision systems are not ergodic.

We will investigate the collision systems made up of a large number of molecules that frequently collide with each other. Such a system is called a gas. We mean the real molecules such as H, CO and so on, not hard ball model or any other ideal model. Only isolated systems are concerned. For the sake of simplicity, we make the following assumptions. The dimension of a gas is very much larger than that of a molecule in the gas, so that every molecule moves as if it is in an infinitely large space and we do not consider the boundary conditions of its motion. We also assume the case of one-component ideal gases composed of identical particles. Only elastic oscillations between particles are considered, regardless of the internal degrees of freedom of the particles. The gas is thin enough such that only two-particle collisions occur.

The macroscopic processes of a gas are generally irreversible except its quasi-static processes. The microscopic mechanism of the macroscopic motion of a gas must be hidden behind the collisions between particles. Therefore, it is necessary to take a closer look at the two-particle collision and its effects.

Some consequences of collisions between particles were investigated [46]. In a gas, the change of a particle's momentum is discontinuous due to its collision with other particles. As a result, in the phase space, the trajectory of a phase point is not continuous, and the phase function of the gas is not smooth. Due to this reason, one is actually unable to define a density current for the phase points. Consequently, the Liouville equation does not apply. All discussions based on the Liouville equation and on smooth phase functions are problematic. For example, the BBKGY method [7,27,47–57] deriving the Boltzmann equation from the Liouville equation is incorrect. The proof of Poincaré recurrence theorem assumes that the phase function is smooth [27], so that the proof procedure is incorrect. We do not negate the Boltzmann equation and Poincaré recurrence theorem themselves. Boltzmann himself has obtained the Boltzmann equation in his own way [58], without the need of the BBKGY method. Poincaré recurrence theorem itself may be correct, but a rigorous proof is still desirable.

The present work is going to more closely examine the collision process itself. One more consequence of a collision between particles is the collision causes a sudden change in momentum, which provides randomness to the final state after the collision. As a result, the microscopic process of collisions between particles is irreversible.

In Section II, we consider whether single-particle motion is reversible. To this end, the mathematical expressions for time-inverse motion and reverse motion are presented. The conclusion is that the motion of individual particles is essentially irreversible. Section III studies the irreversibility of the two-particle collision processes. We demonstrate that individual microscopic collision events are irreversible. Consequently, macro processes are generally irreversible. Nevertheless, when the number of particles in a gas is large enough to meet the condition of detailed balance, the quasi-static processes of a gas can be reversible. Section IV is our conclusion.

II. THE IRREVERSIBILITY OF INDIVIDUAL PARTICLE'S MOTION

We first distinguish between two concepts: the equation of motion that a particle obeys and the specific motion of the particle. The mathematical expressions corresponding to these two concepts are presented. We have a basic point of view: One physical concept should have a corresponding mathematical expression, and theoretical conclusion should be drawn from rigorous mathematical derivation. Two different concepts are of different mathematical expressions. Physical discussion cannot be clear without explicit mathematical expression and derivations.

First, the case of classical mechanics is studied. In classical mechanics, a particle can be any object that can be described by a massive point with no geometric size. It can be a micro particle, such as a molecule, or a macro object. Then, the case of quantum mechanics is studied.

A. Distinguishing equation of motion and specific motion

As mentioned in Introduction, people imply that the time reversibility of the equations of motion necessarily leads to the time reversibility of the motion of individual micro particles. That is to say, the motion of each particle can be carried out anticlockwise, since the form of the equation of motion that the particle obeys remain unchanged under time inversion.

An equation of motion expresses a physical law that the movement of particles must follow. The physical laws determine how the physical quantities of a particle, such as the coordinates, momentum, etc., vary with time. Equations of motion usually appear as differential equations. In classical mechanics, the most fundamental one is Newton's second law. It takes the form of

$$\frac{\mathrm{d}}{\mathrm{d}t}\boldsymbol{p}-\boldsymbol{F}=0\,. \tag{4}$$

This equation determines how a particle's moment should vary with time when it is subject to a force $\boldsymbol{F}$. Equation (4) is also the first equation in (1).

We assume that there is no friction in the force $\boldsymbol{F}$. This equation of motion is considered to be reversible in time or symmetrical with respect to time [7,9,16], i.e., under the transformation of (2) and (3), the form of (4) remains unchanged.

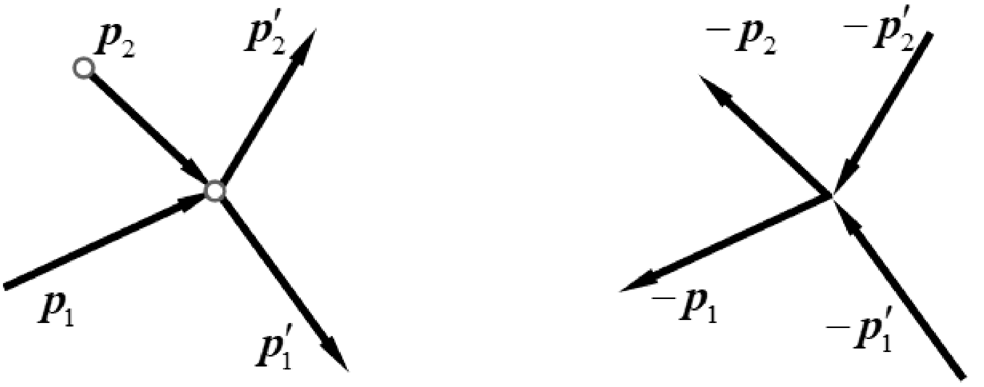
When we talk about the motion of a particle, we mean its specific motion process, or simply referred to as motion. In classical mechanics, it refers to the specific expression that shows that with time going, how a particle's physical quantities such as spatial coordinates, velocity, momentum, and energy, actually vary.

Suppose that the variation of a particle's momentum with time is known as

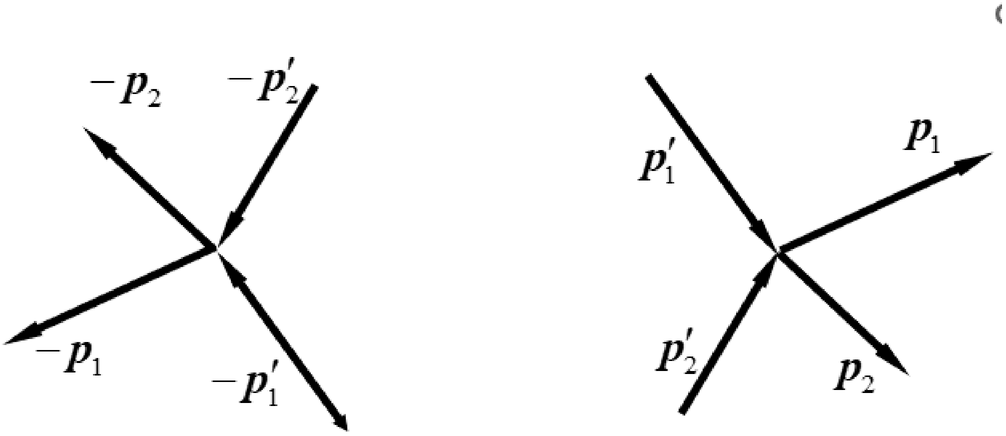
$$p = p(t)\,. \tag{5}$$

At any moment, the magnitude and direction of the momentum are explicitly known. Let time be inversed, $t \to -t$. Then, if the momentum expressed by Equation (5) satisfies $-p(-t) = p(t)$, we say that this motion is of time-reversal invariance, otherwise it is not.

Thus, we distinguish between the equation of motion and specific motion. Regarding the change in momentum of classical particles, the mathematical expression of the equation of motion is (4), while that of a specific motion is (5). A specific motion process can be illustrated by a picture. For instance, with the specific expression (5), a schematic diagram of momentum over time can be drawn. Figure 1 below is a schematic diagram for two-particle oscillations. The differential equation (4) cannot be represented graphically. What we actually see is the specific motion of the particle, the process represented by (5). Although the specific expression (5) certainly follows the laws of physics, it cannot be directly seen from (4) itself.



(a) Two-particle collision **(b) Time-inverse collision**



(c) Reverse collision (time forward) **(d) Reciprocal collision**

Figure 1. The sketches of the collisions of two free particles. (i) In classical mechanics, a particle with a momentum is represented by a line segment with an arrow. (a) The momenta of the particles before the collision are (p_1, p_2) and after the collision are (p_1', p_2'), respectively. The original collision process is denoted as $(p_1, p_2) \to (p_1', p_2')$. (b) The time-inverse collision of (a), $(-p_1', -p_2') \to (-p_1, -p_2)$. (c) The reverse collision of (a), $(-p_1', -p_2') \to (-p_1, -p_2)$. (d) The reciprocal collision of (a), $(p_1', p_2') \to (p_1, p_2)$. (ii) In QM, a plane wave with a momentum is

represented by a line segment with an arrow. (a) The scattering of two free particles having plane waves with momenta $(\boldsymbol{p}_1, \boldsymbol{p}_2)$. After the scattering, the two particles transit to the two plane waves with momenta $(\boldsymbol{p}'_1, \boldsymbol{p}'_2)$. The original transition process is denoted as $(\boldsymbol{p}_1, \boldsymbol{p}_2) \to (\boldsymbol{p}'_1, \boldsymbol{p}'_2)$. (b), (c), and (d) are respectively the time-inverse, reverse, and reciprocal transition processes of (a). The denotations of the (b), (c), and (d) are the same as those in the case of classical mechanics. Processes (b) and (c) look the same but the former is anticlockwise and the latter is clockwise. (a) and (d) are clockwise processes.

It is generally implicitly assumed that if the equation of motion (4) is time-reversible, then necessarily (5) is also temporally reversible. “The equations of classical mechanics are invariant under time reversal. Intuitively, this says that if a film of a sequence of events is run backward, what is seen on the screen appears to be physically possible.”[9] This is equating (4) and (5), which reflects that the two concepts, the equation of motion and the motion of particles, are confused.

The irreversibility of movement is occasionally mentioned. It was mentioned [1,2] that the irreversibility of single particle motion in an infinitely large system was trivial irreversibility. However, there was no conceptual distinction between motion and equations of motion.

Let a differential equation be integrated in some way so as to obtain the expression of the physical quantity with time. Such a relation is called the general solution of a differential equation. For example, the indefinite integral solution of Equation (4) results in a general solution:

$$\boldsymbol{p}(t) = \int \mathrm{d}t' \boldsymbol{F}(t') + C. \tag{6}$$

The process of finding a general solution is a purely mathematical operation without adding any physical factors.

So, does Equation (6) describe the specific motion of the particle? Or, is it equivalent to Equation (5)? The answer is no. this is because there is a pending constant in Equation (6), the value of which can only be determined by initial conditions. To set this constant is to add physical factors.

Physically, any specific motion of any particle has a starting point in time. From the Big Bang model, we know that our universe has a time beginning. Therefore, any movement that actually occurs in the universe has a starting point in time. Movement without a starting point of time does not exist. Few literature notices that specific motion should have initial conditions [6].

Hereafter, the initial time is denoted as t_0. When we mentioned time inversion above, we took $t \to -t$, which defaulted $t_0 = 0$. As $t_0 \neq 0$, time inversion should expressed as $t - t_0 \to -(t - t_0)$.

Mathematically, differential equations with derivative with respect to time are always solved under certain initial conditions. For example, the initial condition required to solve Equation (4) is

$$\boldsymbol{p}(t = t_0^+) = \boldsymbol{p}_0, t_0^+ = t_0 + 0^+. \tag{7}$$

A solution of the equation of motion that meets certain initial conditions is what describes the specific motion, so that is called a specific solution. For example, the specific solution of Equation (4) satisfying the initial condition (7) is

$$\boldsymbol{p}(t) = \int_{t_0}^{t} \mathrm{d}t' \boldsymbol{F}(t') + \boldsymbol{p}_0. \tag{8}$$

In Equation (8), the initial condition has already been used, i.e., the pending constant has been determined. Thus, Equation (8) clearly describes the specific process of movement, which is just Equation (5) that is required.

Above, we have tacitly assumed that time evolves clockwise from the initial moment t_0. So, we talk about the movement in the time range

$$t > t_0 . \tag{9}$$

The possible characteristics of the motion can be analyzed from the general solution of the equation of motion (6). For example, for a celestial body subject to gravitational action, there is a relationship between its radial and angular coordinates. The relationship may be elliptical, parabolic, or hyperbolic. When making such a qualitative analysis, the initial condition is not necessary, so that is usually ignored. But the qualitative analysis does not provide a specific orbit, because there is a coefficient called eccentricity to be determined by the initial condition. Therefore, analyzing the specific movement process needs the initial condition.

It is seen there are actually two elements for describing the motion of a particle: the differential equation (4) and the initial conditions and (7). The physical law (4) itself has only differential equations with no initial conditions.

Under different initial conditions, a differential equation may have different specific solutions, i.e., the details of the motion under different conditions may be different, reflecting different specific movement processes. These processes obey the same physical law. For example, imagine an object moving closer to the Earth from a distance. When approaching the Earth to a certain extent, it may fall to, may rotate around, and may move away from, the Earth. These three movements are different, and which one is achieved depends on the initial conditions of the motion of this object. However, these three possible specific motions follow the same physical law: objects move according to Newton's second law (4) under the gravitational pull of the Earth.

Therefore, we make it clear that equations of motion (4) cannot be equated with specific motion (5). The temporal inversion of Equation (4) does not determine the temporal inversion of the specific motion (5).

Only a specific solution (8) that meets the initial conditions describes a specific motion. So, is equation (8) temporally inverted or reversible? It seems not easy to give the answer directly from (8) itself. We do a further analysis below.

B. The equation of time-retarded motion of a particle

When we talk about the equation of motion (4), we are not clear whether time *t* points to the past or to the future. "The equations of motion in physics are by themselves insufficient to predict what goes on in the Universe. Those equations must be supplemented with the axiom of causality." [16] The so-called axiom of causality means "Only the past influences the present. The future will, in turn, be influenced by the present. The future *cannot* influence the present." [16] There is a close connection between the assumption of causality and the second law of thermodynamics [59].

That we talked about the initial conditions above referred to that time goes clockwise.

If a motion is carried out with time going to the future (past), i.e., in the clockwise (anticlockwise) direction, it is called time-retarded (time-advanced) motion, or in short, retarded (advanced) motion. The function that describes the retarded (advanced) movement is called retarded (advanced) function.

People always talk about the retarded motion if there is no additional word. For example, we have implicitly assumed that Equation (8) described a retarded motion in the time range (9). However, the solution (8) itself does not explicitly indicate that this is a retarded motion without the supplement of (9),

A physical concept should have its corresponding mathematical expression. The mathematical expression reflecting the time-retarded motion is the time step function $\theta(t-t_0)$. There have been few people, when they discussed the scattering theory and path integral in QM, noticed this point [60–63]. We established the differential equations satisfied by the time-retarded function and time-advanced function [64,65]. Here, we follow the same idea to establish the differential equations satisfied by the retarded and advanced functions corresponding to Equation (4).

To explicitly label a retarded motion, we attach a superscript R to the momentum, $\boldsymbol{p}^{\mathrm{R}}$ which is called a retarded solution. We think that the differential equation satisfied by the retarded solution $\boldsymbol{p}^{\mathrm{R}}$ is

$$\frac{\mathrm{d}}{\mathrm{d}t}\boldsymbol{p}^{\mathrm{R}}(t)-\theta(t-t_0)\boldsymbol{F}=\frac{\partial\theta(t-t_0)}{\partial t}\boldsymbol{p}_0\,. \tag{10}$$

Usually, the derivative of the step function is written as the Dirac delta function, $\frac{\partial\theta(t-t_0)}{\partial t}=\delta(t-t_0)$. We stress [64–67] that the rigorous result should be as follows:

$$\frac{\partial\theta(t-t_0)}{\partial t}=\delta(t-t_0)-\eta\theta(t-t_0)\,,\quad \eta\to 0^{+}\,. \tag{11}$$

The term with an infinitesimal η should not be discarded. It is because an infinitesimal term cannot be ignored compared to 0. The Dirac delta function itself is invariant with respect to the change of its argument's sign. Since the time step function $\theta(t-t_0)$ reflects time delay, this information should be retained after derivative with respect to of time. The term with the infinitesimal in Equation (11) reflects the delay in time. A careful discussion of (11) can be found in the appendix of Ref. [64].

Equation (10) also indicates that the force $\boldsymbol{F}$ acts at time $t>t_0$. Since only the motion in the time range $t>t_0$ is described, the retarded solution ought to have a time delay factor $\theta(t-t_0)$. We explicitly separate this factor:

$$\boldsymbol{p}^{\mathrm{R}}(t)=\theta(t-t_0)\boldsymbol{p}(t)\,. \tag{12}$$

Equation (12) is substituted into (10).

$$\theta(t-t_0)\left(\frac{\mathrm{d}}{\mathrm{d}t}\boldsymbol{p}(t)-\boldsymbol{F}\right)=\frac{\partial\theta(t-t_0)}{\partial t}(\boldsymbol{p}_0-\boldsymbol{p}(t))\,. \tag{13}$$

We let both sides of this equation be zero. That the left hand side is zero leads to Equations (4) and (9), and that the right hand side is zero gives the initial condition (7).

Equation (10) is called the equation of retarded motion. It contains both the equation of motion (4) and the initial condition (7). This form of Equation (10) is helpful to clearly recognize the physical meaning of retarded motion. It should be noted that Equation (8) satisfies equation (4) and the initial condition (7). Nevertheless, what really describes specific movements should be (12), for the time step function factor should not be ignored.

Combination of Equations (8) and (12) results in the solution of (10) to be

$$\boldsymbol{p}^{\mathrm{R}}(t)=\theta(t-t_0)\left(\int_{t_0}^{t}\mathrm{d}t'\boldsymbol{F}+\boldsymbol{p}_0\right). \tag{14}$$

This form of the solution makes us clearly discuss the reverse process of a specific motion, while Equation (4) itself does not.

Since there is a term of infinitesimal in Equation (11), the right side of Equation (10) is not invariant under inversion $t-t_0\to-(t-t_0)$. Therefore, the Equation (10) describing retarded motion does not guarantee that motion has invariance under time inversion.

In Introduction we mentioned that a distinction should be made between the concepts of time-inverse motion and reverse motion. Now, we write out the mathematical expressions for these two concepts.

C. The time-advance motion of a particle

The time-retarded motion above describes the motion in the time range Equation (9) starting from the initial moment t_0. Correspondingly, the time-advanced motion describes the motion, starting from the initial moment t_0, in the time range

$$t < t_0 . \tag{15}$$

That is to say, the motion goes anticlockwise starting from t_0.

The time-advance motion and aforementioned time-inverse motion have the same physical meaning, both being counterclockwise and describing the same physical processes. However, they are two concepts after all, and the corresponding mathematical expression should be different. We present the mathematical expressions.

Usually, when people discuss the time-inversion invariance of the equation of motion, they did inversion Equation (2). Then, after the transformations Equations (2) and (3), the equation of motion (4) remains unchanged. The time *t* after the transformation still points to the future, with defaults $t = 0$ as the initial moment. Such an approach is not conducive to discussing counterclockwise movement.

We do not take the time inversion (2). The equation of motion describing the anticlockwise motion of a particle is,

$$-\frac{\mathrm{d}}{\mathrm{d}t}\boldsymbol{p} - \boldsymbol{F} = 0; t < t_0 . \tag{16}$$

Here, the momentum is transformed according to Equation (3). Since we do not take the time inversion (2), the time *t* in Equation (16) varies anticlockwise. The initial moment is set as t_0. The form of Eq, (16) is convenient for discussing the anticlockwise motion.

Now, we are at the stage to describe the time-advanced motion in a way similar to that for time-retarded motion described above. We add a superscript A to momentum, $\boldsymbol{p}^{\mathrm{A}}$ which is called time-advanced momentum. It obeys the following differential equation:

$$\frac{\mathrm{d}}{\mathrm{d}t}\boldsymbol{p}^{\mathrm{A}}(t) + \theta(t_0 - t)\boldsymbol{F} = \frac{\partial \theta(t_0 - t)}{\partial t}\boldsymbol{p}_0 . \tag{17}$$

Naturally, the solution should have the form of

$$\boldsymbol{p}^{\mathrm{A}}(t) = \theta(t_0 - t)\boldsymbol{p}(t) . \tag{18}$$

This is substituted into Equation (17) and the resultant is

$$\theta(t_0 - t)(\frac{\mathrm{d}}{\mathrm{d}t}\boldsymbol{p}(t) + \boldsymbol{F}) = \frac{\partial \theta(t_0 - t)}{\partial t}(\boldsymbol{p}_0 - \boldsymbol{p}(t)) . \tag{19}$$

We let both side be zero. That the left hand side is zero results in Equation (16), and that the right hand side is zero leads to initial condition

$$\boldsymbol{p}(t = t_0^-) = \boldsymbol{p}_0, t_0^- = t_0 - 0^+ . \tag{20}$$

The specific solution satisfying both Equation (16) and the initial condition (20) is

$$\boldsymbol{p}(t) = -\int_{t_0}^{t} \mathrm{d}t' \boldsymbol{F}(t') + \boldsymbol{p}_0 . \tag{21}$$

The equation of advanced motion (17) contains both Equation (16) and the initial condition (20). It is useful for us to discuss counterclockwise movement. We regard the time-inverse motion and counterclockwise motion as synonym.

Let us examine that a particle first moves clockwise for a period of time and then moves counterclockwise.

When the particle moves clockwise, its momentum varies according to Equation (14). At the moment t_1, its momentum becomes $\boldsymbol{p}^{\mathrm{R}}(t_1)=\boldsymbol{p}_1$,

$$\boldsymbol{p}_1=\theta(t_1-t_0)\left(\int_{t_0}^{t_1}\mathrm{d}t'\boldsymbol{F}+\boldsymbol{p}_0\right). \tag{22}$$

After the moment t_1, the article moves anticlockwise, and the initial condition should be $\boldsymbol{p}(t_1)=-\boldsymbol{p}_1$. By Equations (18) and (21), the advanced momentum varies with time as follows:

$$\boldsymbol{p}^{\mathrm{A}}(t)=\theta(t_1-t)\left(-\int_{t_1}^{t}\mathrm{d}t'\boldsymbol{F}-\boldsymbol{p}_1\right). \tag{23}$$

We substitute Equation (22) into (23) and use $\theta(t_1-t)\theta(t_1-t_0)=\theta(t_1-t)$ to obtain

$$\boldsymbol{p}^{\mathrm{A}}(t)=-\theta(t_1-t)\left(\int_{t_0}^{t}\mathrm{d}t'\boldsymbol{F}+\boldsymbol{p}_0\right). \tag{24}$$

Comparing Equations (24) and (21), we know that in the time period $t_0\le t\le t_1$, the anticlockwise motion of the particle is strictly the inverse of the clockwise motion. In particular, the momentum at the "final moment t_0" of the counterclockwise motion (24) is just the negative sign of the momentum of the "initial moment t_0" of the clockwise motion (21). The condition is that the force $\boldsymbol{F}$ is the same at the same moment in the clockwise and counterclockwise time frames.

Therefore, if the initial condition $-\boldsymbol{p}_1$ of the advanced motion can be prepared, and the integrand $\boldsymbol{F}$ is finite and the integral can be done, this time-advanced process can be achieved, and the particle's momentum can reach $-\boldsymbol{p}_0$. An important postulation is that time can be inversed.

D. The reverse motion of a particle

Let us examine the reverse motion of the movement process (14). This means that at the moment t_1, the particle takes minus sign of (22), $-\boldsymbol{p}_1$, and then moves clockwise. We want to see if it moves in reverse order through each intermediate state of (14), and finally reaches the minus sign of its initial momentum, $-\boldsymbol{p}_0$. This reverse motion is a time-retarded one.

The initial condition of the reverse motion is $\boldsymbol{p}(t_1)=-\boldsymbol{p}_1$. Starting from the moment t_1, the particle moves in the way of

$$\boldsymbol{p}^{\mathrm{R}}=\theta(t-t_1)\left(\int_{t_1}^{t}\mathrm{d}t'\boldsymbol{F}-\boldsymbol{p}_1\right)=\theta(t-t_1)\left(\int_{t_1}^{t}\mathrm{d}t'\boldsymbol{F}-\int_{t_0}^{t_1}\mathrm{d}t'\boldsymbol{F}-\boldsymbol{p}_0\right). \tag{25}$$

The first integration in Equation (25) is divided into two parts, $\int_{t_1}^{t}\mathrm{d}t'=\int_{2t_1-t}^{t_1}\mathrm{d}t'+\int_{t_0}^{2t_1-t}\mathrm{d}t'$. Suppose that within the time period $t_1\le t\le 2t_1-t_0$, the force $\boldsymbol{F}$ meets the relationship

$$\boldsymbol{F}(t)=\boldsymbol{F}(2t_1-t),\quad t_1\le t\le 2t_1-t_0. \tag{26}$$

Then, we have

$$\int_{t_1}^{t} \mathrm{d}t'\boldsymbol{F} - \int_{2t_1-t}^{t_1} \mathrm{d}t'\boldsymbol{F} = 0\,. \tag{27}$$

It follows that

$$\boldsymbol{p}^{\mathrm{R}} = -\theta(t-t_1)\left(\int_{t_0}^{2t_1-t} \mathrm{d}t'\boldsymbol{F} + \boldsymbol{p}_0\right). \tag{28}$$

In this time period, the momentum changes strictly in reverse order over the time period $t_0 \le t \le t_1$. In particular, $\boldsymbol{p}^{\mathrm{R}}(2t_1 - t_0) = -\boldsymbol{p}(t_0)$, which is the minus sign of the original initial momentum $\boldsymbol{p}(t_0)$.

Thus, the condition that motion (14) is reversible is that the initial condition (22) can be prepared, and the force $\boldsymbol{F}$ satisfies the condition (26) and can be integrated over time.

For example, the earth-moon is regarded as an isolated two-body system, in which the earth is considered to be static and the moon rotates around the earth by the gravitational pull. Gravity meets the condition (26). If at a moment the momentum of the moon is reversed, the subsequent motion is the reverse motion. There is a premise that the initial condition of reverse motion can be realized. In fact, we know that the initial conditions of reversing the moon's momentum is unattainable. So, in reality, this reverse motion is impossible to achieve. The conclusion is that the motion of the moon around the earth is irreversible.

In general, when discussing an original process (14), there is no restriction on its initial condition. We always discuss a particle's motion when the initial condition (7) has been achieved.

By contrast, if we talk about a reverse motion of a known original motion process, its initial condition is not arbitrary, but is determined by the final state of the original motion and needs to be prepared by us. If the initial condition cannot be prepared, the original motion is irreversible. For example, an original motion is that, in a vacuum, a bullet is fired from the muzzle of a gun and reaches the target. No one can achieve the its reverse motion.

If, after the occurrence of the original process (14), there is a probability that the initial condition of the reverse process can be realized but the probability is less than 1, we think that the original motion process is still irreversible.

Even if we can prepare an initial condition, the surroundings are inevitably influenced in the course of the preparation. That is to say, the environment cannot return to the original initial state. In this case, we think that the original motion is still irreversible.

It is seen that the conditions for the reversibility of the motion of a particle are quite harsh. We can conclude that in classical mechanics, the motion of a particle is basically irreversible.

E. The motion of a particle in quantum mechanics is irreversible

In QM, the motion of microscopic particles with the property of wave-particle duality is described. The fundamental equations of motion, as well as the physical quantities, are different from those in classical mechanics. However, the idea of analyzing the time-inverse motion and reverse motion of a particle is consistent with that for classical mechanics presented above.

A fundamental physical quantity in QM is wave function $\psi(\boldsymbol{r},t)$. By the wave function, it is possible to calculate the expectations of some other physical quantities, such as particle density distributed in space, current density of particles, momentum, kinetic energy, energy, density of states, and so on.

The fundamental equations in QM are differential equations to solve wave functions, mainly the Schrödinger equation and Dirac equation. They have the following form.

$$\left(\mathrm{i}\hbar\frac{\partial}{\partial t} - H\right)\psi(\boldsymbol{r},t) = 0\,. \tag{29}$$

It the literature, the time inversion (2) is taken in (29), and subsequently, in the transformed equation, the time again points to the future and the solution becomes $\psi^*(\boldsymbol{r},t)$, the complex conjugate of the $\psi(\boldsymbol{r},t)$ [68]. Here, we do not take the time inversion (2), but simply retain Equation (29) unchanged, keeping in mind that the time therein can go anticlockwise. So, Equation (29) is the equation of motion for both the time-retarded and time-advanced motions.

The dependence of the wave function on time describes specific motion.

$$\psi=\psi(\boldsymbol{r},t) \tag{30}$$

The differential equation (29) tells us the fundamental law that a particle's motion must obey. From Equation (29) itself one is unable to see the specific motion described by Equation (30).

People think that since the equation of motion (29) has time inversion invariance, then the specific motion (30) of a particle should have either.

We stress that the equation of motion (29) and concrete motion (30) are two different concepts. Equation (29) indeed remains unchanged under time inversion, but this does not guarantee that the motion process described in (30) is reversible.

In order to solve a specific motion from Equation (29), an initial condition is required.

$$\psi(\boldsymbol{r},t=t_0^+)=\psi(\boldsymbol{r},t_0^+)\,. \tag{31}$$

Combination of Equations (29) and (31) results in the expression of the specific motion [64,65]:

$$\psi(\boldsymbol{r},t)=\exp(-\frac{\mathrm{i}}{\hbar}\int_{t_0}^{t}\mathrm{d}t'H(t'))\psi(\boldsymbol{r},t_0)\,. \tag{32}$$

The initial condition has been employed in the solution. Because Equation (29) is homogeneous one, the initial condition provides a factor in (29), instead of an additional term as that in Equation (8).

If the Hamiltonian H has a complete set of eigenfunctions $\{\varphi_n(\boldsymbol{r},t)\}$, the solution of Equation (29) can be written as the superposition of this complete set.

$$\psi(\boldsymbol{r},t)=\sum_n c_n\varphi_n(\boldsymbol{r},t)\,. \tag{33}$$

For example, the Hamiltonian of a free particle is

$$H=-\frac{\hbar^2}{2m}\nabla^2\,. \tag{34}$$

Its complete set of eigenfunctions and corresponding energies are

$$\varphi_k(\boldsymbol{r},t)=\frac{1}{(2\pi)^{3/2}}\mathrm{e}^{-\mathrm{i}(E(\boldsymbol{k})t/\hbar-\boldsymbol{k}\cdot\boldsymbol{r})},E(\boldsymbol{k})=\frac{\hbar^2\boldsymbol{k}^2}{2m}\,. \tag{35}$$

Equation (33) is the general solution of (29). From the general solution, one can analyze what features the wave function may have, but the real specific movement cannot be certain yet, unless the initial condition is known. When the expansion coefficient in (33) is determined by the initial conditions, (33) becomes a specific solution.

Thus, describing a specific motion of a particle requires two elements: the differential equation (29) and the initial conditions (31).

A differential equation can have different solutions subject to different initial conditions. Each specific motion has its own details. For the Hamiltonian (34) of a free particle, if the initial condition is a plane wave, the specific solution is either a single plane wave; If the initial condition is a wave packet, the particular solution is a traveling while collapsing wave packet.

Solution (29) does not clearly indicate that this is a retarded or advanced movement. Usually, it is always defaulted that this is a retarded motion.

Now, we explicitly discuss retarded motion, i.e., the motion in time range $t > t_0$ after the initial moment t_0. We add a superscript R to the wave function, $\psi^{\mathrm{R}}(\boldsymbol{r},t)$, to mark that this is a time-retarded wave function. The equation of motion satisfied by the $\psi^{\mathrm{R}}(\boldsymbol{r},t)$ is

$$(\mathrm{i}\hbar\frac{\partial}{\partial t}-H)\psi^{\mathrm{R}}(\boldsymbol{r},t)=\mathrm{i}\hbar\frac{\partial\theta(t-t_0)}{\partial t}\psi(\boldsymbol{r},t_0)\,. \tag{36}$$

Since $\psi^{\mathrm{R}}(\boldsymbol{r},t)$ is a time-retarded wave function, it is written in the form of

$$\psi^{\mathrm{R}}(\boldsymbol{r},t)=\theta(t-t_0)\psi(\boldsymbol{r},t)\,. \tag{37}$$

The factor $\theta(t-t_0)$ unambiguously indicates that time evolves toward the future [60–63].

After Equation (37) is substituted into (36), we achieve

$$\theta(t-t_0)(\mathrm{i}\hbar\frac{\partial}{\partial t}-H)\psi(\boldsymbol{r},t)=\mathrm{i}\hbar\frac{\partial\theta(t-t_0)}{\partial t}[\psi(\boldsymbol{r},t_0)-\psi(\boldsymbol{r},t)]\,. \tag{38}$$

We let both sides be zero. That the left hand side is zero leads to Equations (29) and (9) and that the right hand side is zero results in the initial condition (31). Thus, Equation (36) contains both the equation of motion and the initial condition.

It follows from the combination of Equations (32) and (37) that

$$\psi^{\mathrm{R}}(\boldsymbol{r},t)=\theta(t-t_0)\exp(-\frac{\mathrm{i}}{\hbar}\int_{t_0}^{t}\mathrm{d}t'H(t'))\psi(\boldsymbol{r},t_0)\,. \tag{39}$$

Note that the specific solution (32) satisfies the differential equation (29) and the initial condition (31). However, the solution that really describes the retarded movement should be (39).

With the preparation above, we are ready to respectively discuss the time-inverse motion and reverse motion.

The time-advanced wave function $\psi^{\mathrm{A}}(\boldsymbol{r},t)$ obeys the following equation.

$$(\mathrm{i}\hbar\frac{\partial}{\partial t}-H)\psi^{\mathrm{A}}(\boldsymbol{r},t)=\mathrm{i}\hbar\frac{\partial\theta(t_0-t)}{\partial t}\psi(\boldsymbol{r},t_0)\,. \tag{40}$$

In the expression of the $\psi^{\mathrm{A}}(\boldsymbol{r},t)$, there should be a time-advance factor.

$$\psi^{\mathrm{A}}(\boldsymbol{r},t)=\theta(t_0-t)\psi(\boldsymbol{r},t)\,. \tag{40}$$

Substitution of (41) into (40) leads to

$$\theta(t_0-t)(\mathrm{i}\hbar\frac{\partial}{\partial t}-H)\psi(\boldsymbol{r},t)=\mathrm{i}\hbar\frac{\partial\theta(t_0-t)}{\partial t}[\psi(\boldsymbol{r},t_0)-\psi(\boldsymbol{r},t)]\,. \tag{42}$$

We let both sides be zero. That the left hand side equal to zero results in the equation that the $\psi(\boldsymbol{r},t)$ satisfies:

$$(\mathrm{i}\hbar\frac{\partial}{\partial t}-H)\psi(\boldsymbol{r},t)=0;t<t_0\,. \tag{43}$$

The equation is the same as (29) but applies to past time. That the right hand side of (42) equals zero gives the initial condition

$$\psi(\boldsymbol{r},t=t_0^-)=\psi(\boldsymbol{r},t_0^-)\,. \tag{44}$$

Obviously, the solution of Equation (40) is

$$\psi^{\mathrm{A}}(\boldsymbol{r},t)=\theta(t_0-t)\exp(-\frac{\mathrm{i}}{\hbar}\int_{t_0}^{t}\mathrm{d}t'H(t'))\psi(\boldsymbol{r},t_0)\,. \tag{45}$$

We first let a particle move clockwise starting from the moment t_0. According to Equation (39), at t_1, the wave function is

$$\psi^{\mathrm{R}}(\boldsymbol{r},t_1)=\theta(t_1-t_0)\exp(-\frac{\mathrm{i}}{\hbar}\int_{t_0}^{t_1}\mathrm{d}t'H(t'))\psi(\boldsymbol{r},t_0)\,. \tag{46}$$

At this moment, we let the particle do time-inverse motion with the initial condition

$$\psi(\boldsymbol{r},t_1)=\psi^{\mathrm{R}}(\boldsymbol{r},t_1)\,. \tag{47}$$

Then, in the time period $t_0\le t\le t_1$, the advanced wave function is

$$\begin{aligned}\psi^{\mathrm{A}}(\boldsymbol{r},t)&=\theta(t_1-t)\exp(-\frac{\mathrm{i}}{\hbar}\int_{t_1}^{t}\mathrm{d}t'H(t'))\psi^{\mathrm{R}}(\boldsymbol{r},t_1)\\&=\theta(t_1-t)\theta(t_1-t_0)\exp(-\frac{\mathrm{i}}{\hbar}\int_{t_0}^{t}\mathrm{d}t'H(t'))\psi(\boldsymbol{r},t_0)=\psi^{\mathrm{R}}(\boldsymbol{r},t).\end{aligned} \tag{48}$$

We have used Equation (46). This shows that if the condition (47) is met, the wave function varies rigorously in the reversed order of the original motion. We mention again that the time-advanced motion is a fictional motion.

Now, we consider the reverse motion which is clockwise starting from the moment t_1. In Equation (39) the initial time is taken as t_1, and the initial condition is (46). Then, in the time range $t_1\le t\le 2t_1-t_0$,

$$\begin{aligned}\psi^{\mathrm{R}}(\boldsymbol{r},t)&=\theta(t-t_1)\exp(-\frac{\mathrm{i}}{\hbar}\int_{t_1}^{t}\mathrm{d}t'H(t'))\psi^{\mathrm{R}}(\boldsymbol{r},t_1)\\&=\theta(t-t_1)\theta(t_1-t_0)\exp(-\frac{\mathrm{i}}{\hbar}\int_{t_1}^{t}\mathrm{d}t'H(t'))\exp(-\frac{\mathrm{i}}{\hbar}\int_{t_0}^{t_1}\mathrm{d}t'H(t'))\psi(\boldsymbol{r},t_0).\end{aligned} \tag{49}$$

The second integration is divided into two parts: $\int_{t_0}^{t_1}\mathrm{d}t'=\int_{2t_1-t}^{t_1}\mathrm{d}t'+\int_{t_0}^{2t_1-t}\mathrm{d}t'$. The Hamiltonians in different time are assumed commutable. For a reversible motion, we expect that

$$\psi^{\mathrm{R}}(\boldsymbol{r},t)=\theta(t-t_1)\exp(-\frac{\mathrm{i}}{\hbar}\int_{t_0}^{2t_1-t}\mathrm{d}t'H(t'))\psi(\boldsymbol{r},t_0)=\psi^{\mathrm{R}}(\boldsymbol{r},2t_1-t)\,. \tag{50}$$

This requires that

$$\int_{t_1}^{t}\mathrm{d}t'H(t')+\int_{2t_1-t}^{t_1}\mathrm{d}t'H(t')=0\,, \tag{51}$$

i.e.,

$$H(t)=-H(2t_1-t)\,.. \tag{52}$$

This means that from t_1, the Hamiltonian has to change its sign. A Hamiltonian is kinetic energy plus potential energy. If a Hamiltonian changes its sign, it will become another system. Hence, Equation (52) is unattainable, and Equation (50) is either.

Let us see a simplest example, the case of a free particle moving as a plane wave. The Hamiltonian is (34), independent of time. Suppose that the initial condition is one of the planes (35). That is to say, at moment t_0, the wave function is

$$\varphi_{\boldsymbol{k}}(\boldsymbol{r},t_0)=\frac{1}{(2\pi)^{3/2}}\mathrm{e}^{-\mathrm{i}(E(\boldsymbol{k})t_0/\hbar-\boldsymbol{k}\cdot\boldsymbol{r})}. \tag{53}$$

At $t>t_0$, the wave function is

$$\begin{aligned}\varphi_{\boldsymbol{k}}^{\mathrm{R}}(\boldsymbol{r},t)&=\theta(t-t_0)\exp[\mathrm{i}(t-t_0)\frac{\hbar\boldsymbol{k}^2}{2m}\nabla^2]\varphi_{\boldsymbol{k}}(\boldsymbol{r},t_0)\\&=\theta(t-t_0)\frac{1}{(2\pi)^{3/2}}\mathrm{e}^{-\mathrm{i}(E(\boldsymbol{k})t/\hbar-\boldsymbol{k}\cdot\boldsymbol{r})}.\end{aligned} \tag{54}$$

Especially, the wave function at time t_1 is

$$\varphi_{\boldsymbol{k}}^{\mathrm{R}}(\boldsymbol{r},t_1)=\frac{1}{(2\pi)^{3/2}}\mathrm{e}^{-\mathrm{i}(E(\boldsymbol{k})t_1/\hbar-\boldsymbol{k}\cdot\boldsymbol{r})}. \tag{55}$$

We let the particle do reverse motion from the moment t_1. At this time, its wave vector is reversed. The initial condition of the reverse motion is

$$\varphi_{\boldsymbol{k}}(\boldsymbol{r},t_1)=\frac{1}{(2\pi)^{3/2}}\mathrm{e}^{-\mathrm{i}(E(\boldsymbol{k})t_1/\hbar+\boldsymbol{k}\cdot\boldsymbol{r})}. \tag{56}$$

If the original motion is reversible, in the time period $t_1\le t\le 2t_1-t_0$, the wave function should have a relationship

$$\varphi_{\boldsymbol{k}}^{\mathrm{R}}(\boldsymbol{r},t)=\varphi_{-\boldsymbol{k}}^{\mathrm{R}}(\boldsymbol{r},2t_1-t). \tag{57}$$

The wave function on the right hand side is that within the time period $t_0\le t\le t_1$, but the wave vector has a minus sign. However, by the initial condition (56), the wave function after the time t_1 is

$$\begin{aligned}\varphi_{\boldsymbol{k}}^{\mathrm{R}}(\boldsymbol{r},t)&=\theta(t-t_1)\exp[\mathrm{i}(t-t_1)\frac{\hbar\boldsymbol{k}^2}{2m}\nabla^2]\varphi_{\boldsymbol{k}}^{\mathrm{R}}(\boldsymbol{r},t_1)\\&=\theta(t-t_1)\frac{1}{(2\pi)^{3/2}}\mathrm{e}^{-\mathrm{i}(E(\boldsymbol{k})t/\hbar+\boldsymbol{k}\cdot\boldsymbol{r})}.\end{aligned} \tag{58}$$

Comparison of (58) and (54) demonstrates that (57) is not satisfied.

The conclusion is that in QM, the motion of particles is irreversible.

Hereafter, we discuss reverse motion which is clockwise. The time-inverse motion is purely fictional and will not be discussed anymore.

III. THE IRREVERSIBILITY OF TWO-PARTICLE COLLISION PROCESSES

We consider an ideal gas composed of a large number of molecules which collide with each other frequently. This is a collision system. We will only concern two-particle elastic collisions. Because of the collisions, energy and momentum transfer between molecules, which causes the rapid change of the microscopic state of the gas and moreover the change of the macroscopic state. So, examining whether the two-particle collision process is reversible is important. If it is reversible, the motion of the gas is either, otherwise the motion of the gas is not guaranteed to be reversible.

The collision is instant so that we actually do not know the details of the changes of the molecules' physical quantities during the collision [46]. The state of the two particles before the collision is called initial state, and that after the collision called final state. For a hard-sphere system, the dynamics is completely deterministic because the after-collision momenta are uniquely determined by the collision rule [34,35]. Even in this case, the momenta of the molecules before and after collisions are discontinuous.

Figure 1a is the schematic of the original process of two-particle collision. The two particles before the collision are called incident particles, the momenta of which are respectively $\boldsymbol{p}_1$ and $\boldsymbol{p}_2$. After the collision they are called outgoing particles, the momenta of which are respectively $\boldsymbol{p}_1'$ and $\boldsymbol{p}_2'$. The conservation of the total kinetic energy and total momentum is expressed as follows.

$$\frac{1}{2m}\boldsymbol{p}_1^2+\frac{1}{2m}\boldsymbol{p}_2^2=\frac{1}{2m}\boldsymbol{p}_1'^2+\frac{1}{2m}\boldsymbol{p}_2'^2 . \tag{59a}$$

$$\boldsymbol{p}_1+\boldsymbol{p}_2=\boldsymbol{p}_1'+\boldsymbol{p}_2' . \tag{59b}$$

Equations (59) are not differential equations, but they directly describe the motion of the two-particle collision. They are actually the solutions of equation of motion with given initial condition. The initial conditions are that the momenta $\boldsymbol{p}_1$ and $\boldsymbol{p}_2$ before the collision are known.

We write out Equation (59) referring to the original process Figure 1a. In Equations (59), the left (right) hand side represent the initial (final) state. We write from left to right. Once Equations (59) are put down, we can also write them from the right to left, i.e., to regard the right hand side as initial state and left hand side final state. Then, in this view, there can be three processes, as shown in Figure 1b–d. They are called the time-inverse process, the reverse process, and the reciprocal process of the original process Figure 1a, respectively. For Figure 1b,c, Equation (59b) has minus signs on both sides, so all the minus signs can be dropped. Figure 1d is obtained by exchanging the initial and final states of Figure 1a, so that is called the reciprocal process.

Note that our definitions for the processes in Figure 1 may differ from those in the literature. In the literature, Figure 1b is named as reverse collision [7,27] or time reverse collision [9]; Figure 1c is called inverse collision [69] or reverse collision [13,70]; Figure 1d is called opposite collision [58], restituting collision [69], inverse collision [7,9,11,13,27,52,70–72]. Since the time-inverse collision is purely fictitious, we will not discuss Figure 1b below.

A. Two-particle collision in classical mechanics

We first propose a definition of the reversibility of the collision process in Figure 1a. If the collision Figure 1a occurs, the reverse collision Figure 1c necessarily also occurs, that is, the probability of the occurrence of the reverse process Figure 1c is 1, then we say that the original collision Figure 1a is reversible; If the probability is less than 1, then the original collision is said to be irreversible. Let us analyze whether the probability of the reverse process occurring is equal to 1.

In one-dimensional space, Equation (59) contains two equations. The p_1 and p_2 of the incident particles are known. From (59), the two momenta of the final state can be uniquely solved. Therefore, the final state is uniquely determined. In particular, since the particles are identical, the solution is $p_1'=p_2, p_2'=p_1$, i.e., the two particles simply exchange their momenta. This case is as if no collision occurs, which was treated in [26,45]. That is why we classified one-dimensional identical particle systems as collision-free systems in subsection I.C.

In two-dimensional space, each momentum has two components, so Equation (59) contains three equations. There are four momentum components $(p_{1x}', p_{2y}'),(p_{2x}', p_{2y}')$ to be solved. Therefore, there is an uncertain quantity in the final state, e.g., the angle θ between $\boldsymbol{p}_1'$ and $\boldsymbol{p}_2'$ can vary in the range of 0~2π.

In three-dimensional space, each momentum has three components, so Equation (59) contains four equations. There are six momentum components $(p_{1x}', p_{1y}', p_{1z}'), (p_{2x}', p_{2y}', p_{2z}')$ to be solved. Thus, there are two uncertain quantities of the two outgoing particles, e.g., the angles (θ, φ) between $\boldsymbol{p}_1'$ and $\boldsymbol{p}_2'$ can vary in the range of 4π solid angles. Therefore, the momenta of the outgoing particles have a distribution [73].

We consider the case of three-dimensional space. In Figure 1a, only a pair of specific outgoing momenta $\boldsymbol{p}_1'$ and $\boldsymbol{p}_2'$ are plotted. The probability of the occurrence of this pair $\boldsymbol{p}_1'$ and $\boldsymbol{p}_2'$ is denoted as a_{12}. It must be that $a_{12} < 1$, because there are other outgoing $\boldsymbol{p}_1'$ and $\boldsymbol{p}_2'$ pairs, as long as they meet Equation (59).

The reciprocal collision of Figure 1a is the exchange of $(\boldsymbol{p}_1, \boldsymbol{p}_2)$ and $(\boldsymbol{p}_1', \boldsymbol{p}_2')$ as in Figure 1d, that is to say, the initial state is $(\boldsymbol{p}_1', \boldsymbol{p}_2')$ and the final state $(\boldsymbol{p}_1, \boldsymbol{p}_2)$, the occurrence probability of Figure 1d is denoted as a_{21}. By classical mechanics, it is demonstrated that $a_{21} = a_{12}$ [52]. One may believe [50] that the $a_{21} = a_{12}$ reflects "principle of dynamic reversibility". This recognition is not right, because the reverse collision is not involved in proving $a_{21} = a_{12}$.

Now, assume that the collision process Figure 1a takes place. We examine if its reverse collision necessarily occurs, or the occurrence probability of Figure 1c is 1. In Figure 1c, the momentum of the incident particles are $-\boldsymbol{p}_1'$ and $-\boldsymbol{p}_2'$, and only a specific pair of outgoing momenta $-\boldsymbol{p}_1$ and $-\boldsymbol{p}_2$ is plotted. In fact, there can be whatever pairs of outgoing $-\boldsymbol{p}_1$ and $-\boldsymbol{p}_2$ as long as they meet Equation (59). Therefore, the occurrence probability of the specific collision in Figure 1c is certainly less than 1. By definition, the original collision in Figure 1a is irreversible. Similarly, the collision process in Figure 1c is also irreversible. It is concluded that in two-dimensional and three-dimensional space, the two-particle collision is irreversible.

Since individual microscopic collision events are irreversible, why can a frictionless quasi-static process of a macroscopic system composed of a large number of microscopic particles colliding with each other be reversible?

At every moment of a frictionless quasi-static process, the gas is in equilibrium state. Therefore, let us first review the concept of equilibrium. The definition of equilibrium is: "A macroscopic state which does not tend to change in time, except for random fluctuation." [32] When a system is in equilibrium, its macro parameters, such as volume, temperature, pressure, ect., do not change with time. If a macroscopic parameter such as pressure can be measured with an instrument, the measured value does not change with time. An equilibrium state is a macro state. There can be a huge number of micro states corresponding to this one macro state. In an equilibrium state, micro state changes vary rapidly. The change is caused by the collisions between molecules. The molecules' momenta follow Maxwell-Boltzmann distribution. The reason that the micro states changes while the macro state does not is that the distribution remains unchanged.

That the frequent collisions between molecules do not change the distribution is determined by the principle of detailed balance.

B. Detailed balance

From Boltzmann's *H* theorem [51], it can be shown that detailed balance is the sufficient and necessary conditions for a gas to reach equilibrium [15,52,72,74]. Here, we review the principle of detailed balance.

For the two-molecule collision in Figure 1a, the mathematical expression of the detailed balance is

$$f(\boldsymbol{p}_1) f(\boldsymbol{p}_2) = f(\boldsymbol{p}_1') f(\boldsymbol{p}_2') . \tag{60}$$

The $f(\boldsymbol{p})$ is the momentum distribution function of the gas. In equilibrium, it is the Maxwell-Boltzmann distribution.

We inspect the physical meaning of Equation (60). It reveals that for the two particles participating the collision, the product of the distribution of the initial state is equal to that of the final state. In Equation (60), the left hand side equals to the right hand side. On the other hand, the right hand side also equals to the left hand side. That is, not only the collision $(\boldsymbol{p}_1,\boldsymbol{p}_2)\to(\boldsymbol{p}_1',\boldsymbol{p}_2')$ in Figure 1a, but also its reciprocal collision $(\boldsymbol{p}_1',\boldsymbol{p}_2')\to(\boldsymbol{p}_1,\boldsymbol{p}_2)$ shown by Figure 1d, satisfies Equation (60).

The detailed balance tells us that a pair of collisions reciprocal to each other retains the distribution function unchanged. Suppose that in an equilibrium gas there are four molecules. The momenta of molecules 1 and 2 are $\boldsymbol{p}_1$ and $\boldsymbol{p}_2$, and those of 3 and 4 are $\boldsymbol{p}_1'$ and $\boldsymbol{p}_2'$, respectively. Let molecules 1 and 2 collide as in Figure 1a, $(\boldsymbol{p}_1,\boldsymbol{p}_2)\to(\boldsymbol{p}_1',\boldsymbol{p}_2')$. After the collision, two extra $\boldsymbol{p}_1'$ and $\boldsymbol{p}_2'$ molecules are generated and two $\boldsymbol{p}_1$ and $\boldsymbol{p}_2$ molecules are reduced. As a result, the distribution function of the gas may deviate from the equilibrium one. If, meanwhile, another collision between molecules 3 and 4 takes place as in Figure 1d, $(\boldsymbol{p}_1',\boldsymbol{p}_2')\to(\boldsymbol{p}_1,\boldsymbol{p}_2)$, then, the extra $\boldsymbol{p}_1'$ and $\boldsymbol{p}_2'$ are reduced and the reduced $\boldsymbol{p}_1$ and $\boldsymbol{p}_2$ are restored. This retrieves the equilibrium distribution.

It is seen that the occurrence of a pair of reciprocal collisions can keep the distribution function unchanged and this unchanged distribution is an equilibrium one. Conversely, if a gas is in equilibrium, when a collision of Figure 1a takes place, there must also a reciprocal collision of Figure 1d, although this pair of reciprocal collisions changes the microscopic state of the gas. Someone [50] thought that the detailed balance was a sufficient but not necessary condition for equilibrium, but it has been proved that the detailed balance was a sufficient and necessary condition [7,52].

As a comparison, we consider a pair of reverse collisions Figure 1a,c. Assume that there are four molecules. The momenta of molecules 1 and 2 are $\boldsymbol{p}_1$ and $\boldsymbol{p}_2$, and those of 3 and 4 are $-\boldsymbol{p}_1'$ and $-\boldsymbol{p}_2'$, respectively. Let molecules 1 and 2 collide as in Figure 1(a), $(\boldsymbol{p}_1,\boldsymbol{p}_2)\to(\boldsymbol{p}_1',\boldsymbol{p}_2')$, and 1 and 2 collide as in Figure 1c, $(-\boldsymbol{p}_1',-\boldsymbol{p}_2')\to(-\boldsymbol{p}_1,-\boldsymbol{p}_2)$. After this pair of collisions, four molecules, $\boldsymbol{p}_1'$, $\boldsymbol{p}_2'$, $-\boldsymbol{p}_1$, and $-\boldsymbol{p}_2$ are produced, and other four, $\boldsymbol{p}_1$, $\boldsymbol{p}_2$, $-\boldsymbol{p}_1'$, and $-\boldsymbol{p}_2'$ are reduced. Apparently, the momentum distribution function changes. Therefore, a pair of reverse collisions cannot retain the distribution unchanged.

For the detailed balance, we address the following points. Before doing so, we remind the distinguish between macro and micro infinitesimals in time and space [46]. The macro (micro) infinitesimal in time is called macro-instant (micro-instant). Macroscopic instruments can do measurements during macro-instant. Spatially, a macro subregion is a very small region but it still belongs to a macro one. A micro region can contain merely a small number of molecules.

(i) Detailed balance is achieved within a macro-instant.

When a gas is in equilibrium, a pair of reciprocal collisions Figure 1a,d occur within the same macro-instant but not the same micro-instant. Macroscopically, the pair of $(\boldsymbol{p}_1,\boldsymbol{p}_2)\to(\boldsymbol{p}_1',\boldsymbol{p}_2')$ and $(\boldsymbol{p}_1',\boldsymbol{p}_2')\to(\boldsymbol{p}_1,\boldsymbol{p}_2)$ occur simultaneously, but microscopically, they occur sequentially. The system is in equilibrium at every macro-instant.

(ii) Detailed balance is achieved in a macro region.

A pair of reciprocal collisions occurs within a macro subsystem but not in a micro region. This is also what equilibrium requires. "If a closed macroscopic system is in a state such that in any macroscopic subsystem the macroscopic physical quantities are to a high degree of accuracy equal to their mean values, the system is said to be in a state of *statistical equilibrium* (or *thermodynamic* or *thermal equilibrium*)." [14] Equilibrium is reached in any macro subsystem, while in a micros region, detailed balance cannot be reached.

Based on the discussion of (i) and (ii) above, detailed balance is achieved statistically in macro subsystems. The equilibrium refers to that in macro subregions and at macro-instant. Microscopically, the gas is nonequilibrium everywhere and every time. Micro states cannot be distinguished by instruments that measure macro parameters.

(iii) Detailed balance is independent of reverse collisions.

Detailed balance (60) ensures that in equilibrium, the pair of reciprocal collisions occurs, with no requirement of the reverse collision Figure 1c. The pair of reciprocal collisions takes place clockwise, irrespective to any anticlockwise process [72]. On the other hand, as mentioned above, a pair of reverse collisions does not guarantee the invariance of the momentum distribution function. Therefore, the discussing whether a macro process is reversible is not based on whether two-particle collisions are reversible.

Detailed balance itself also contains

$$f(-\boldsymbol{p}_1)f(-\boldsymbol{p}_2)=f(-\boldsymbol{p}_1')f(-\boldsymbol{p}_2')\,. \tag{41}$$

That is to say, the collision process Figure 1c and its reciprocal process also keep the momentum distribution unchanged in the case of equilibrium.

We imagine a picture of the angular distribution of molecular momentum in a gas in equilibrium. Since the number of molecules in the gas is sufficiently large, by detailed balanced, there must be many reciprocal collisions, all of which have the same values of the incident and outgoing momenta, but in different directions. We superimpose events in one figure. Figure 2a is a superposition of four events of Figure 1d, where the incident and outgoing particles are represented by dashed and solid lines, respectively. Figure 2b roughly illustrates the superposition of a large number of collision events. The angle between the momenta of the two incident particles evenly distributes within solid angle 0~4π, and that of the outgoing particles also does so. Since the number of particles is large enough, both are dense enough and the angular distribution is uniform.

Reversing the directions of the arrows for both the solid and dashed lines in Figure 2b leads to the schematic diagram of Equation (61). This is a superposition of schematic diagram of Figure 1c in all directions. This shows that for reciprocal collisions, as well as for reverse collisions, the momentum of the incoming and outgoing particles are uniformly distributed in all directions. This means that if there is a collision of Figure 1a, then there will be a reverse collision Figure 1c.

Therefore, although the detailed balance itself does not require the reverse process of a collision to appear, we believe that once the detailed balance is reached, then, in the equilibrium state, the reverse collision process of any collision also inevitably occur. That a pair of reverse collisions, Figures 1a,c occur in a macro-instant should be a by-product when an equilibrium state is reached.

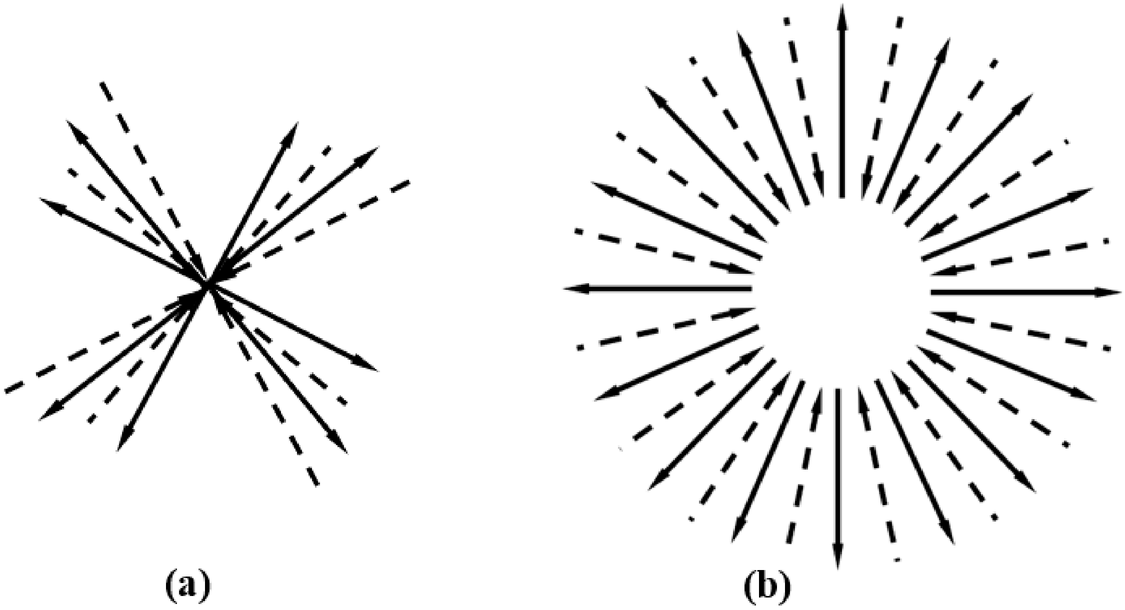


Figure 2. (a) The superposition of four Figure 1d in different directions. Incident and outgoing particles are represented by dashed and solid lines, respectively. (b) The superposition of a large number of similar collisions, which shows that in equilibrium, the momentum distribution is isotropic.

We conceive a situation that slightly deviates from detailed balance.

When Boltzmann derived the H theorem, he obtained the following inequality [13].

$$\ln\frac{f(\boldsymbol{p}_1)f(\boldsymbol{p}_2)}{f(\boldsymbol{p}_1')f(\boldsymbol{p}_2')}[f(\boldsymbol{p}_1)f(\boldsymbol{p}_2)-f(\boldsymbol{p}_1')f(\boldsymbol{p}_2')]\geq 0\,. \tag{62}$$

The equal sign holds only when the detailed balance (60) is reached. Suppose that the gas is very close to equilibrium, such that the momentum distribution of the two particles before the collision belongs to the equilibrium distribution with temperature T.

$$f(\boldsymbol{p}_1)\propto\exp(-\frac{\varepsilon(\boldsymbol{p}_1)}{k_{\mathrm{B}}T}),\, f(\boldsymbol{p}_2)\propto\exp(-\frac{\varepsilon(\boldsymbol{p}_2)}{k_{\mathrm{B}}T})\,. \tag{63}$$

After the collision, the distribution belongs to that with temperature $T+\Delta T$.

$$f(\boldsymbol{p}_1')\propto\exp(-\frac{\varepsilon(\boldsymbol{p}_1')}{k_{\mathrm{B}}(T+\Delta T)}),\, f(\boldsymbol{p}_2')\propto\exp(-\frac{\varepsilon(\boldsymbol{p}_2')}{k_{\mathrm{B}}(T+\Delta T)})\,, \tag{64}$$

where

$$\Delta T\ll T\,. \tag{42}$$

For an elastic collision (59), the total energy before and after the collision is denoted by ε, $\varepsilon=\varepsilon(\boldsymbol{p}_1)+\varepsilon(\boldsymbol{p}_2)=\varepsilon(\boldsymbol{p}_1')+\varepsilon(\boldsymbol{p}_2')$. We derive from Equation (62) that

$$-\frac{\varepsilon}{k_{\mathrm{B}}}(\frac{1}{T}-\frac{1}{T+\Delta T})(1-\exp[\frac{\varepsilon}{k_{\mathrm{B}}}(\frac{1}{T}-\frac{1}{T+\Delta T})])\mathrm{e}^{-\varepsilon/k_{\mathrm{B}}T}\geq 0\,. \tag{66}$$

No matter whether the two molecules become a hotter or cooler distribution after the collision, this expression is not less than zero. It is equal to zero only if $\Delta T=0$. This means that areas with slightly lower (higher) temperatures will increase (decrease) temperatures. Heat always flows from the hotter to the cooler area, making the temperature approach the same everywhere.

The isotropic distribution shown in Figure 2b is ideal only when the number of molecules in the gas approached infinity. In this equilibrium state the momentum distribution remains unchanged.

Therefore, a necessary condition for achieving detailed balance is that the number of molecules in the gas is sufficiently large. Although the molecule number in the actual gas is as high as the order of magnitude of Avogadro constant, it is not really infinity after all. So, even in every macro-instant, it is not guaranteed that for every two-particle collision, there always occur a corresponding reciprocal process. As a result, the momentum distribution of the molecule may deviate from the equilibrium distribution. This deviation is the fluctuation. Macro physical quantities are averages calculated by means of the distribution function. Therefore, they fluctuate around their average values. Obviously, the larger the molecule number, the smaller the fluctuation.

Now, consider a region in the gas which is macroscopically small enough, say, a submillimeter-scale region, the particle number in this region is much smaller than that of the whole gas. If in 1 m^3 there are $N \sim 10^{23}$ particles, then in 10^{-16} m^3 there are $N_1 \sim 10^7$ particles, such that $N_1 \ll N$. In such a small region fluctuation will be comparatively large. It is possible that the number of particles with momentum in a certain direction in a macro-instant is much greater than that with opposite momentum. If a pollen granule is positioned in this region, the molecular impact it receives is not isotropic, so that it suffers a net force. The pollen is subject to this force to move. This is the reason of Brownian motion, which reflects that in such a small area, detailed balance cannot be achieved.

Brownian motion also indicates that at a macro-instant, the number of particles entering and leaving the region is not always equal. That is to say, the density of particle numbers in this region is variable with times. The molecular number density in different small regions at a micro-instant are not the same. The density varies around its average value. The fluctuation in a gas actually embodies the non-equilibrium at micro-instant.

When the detailed balance is not achieved, the left and right side of Equation (60) are not equal. This mean that at least a collision of Figure 1a does not have its reciprocal collision at a macro-instant. Consequently, the momentum distribution function will change. The gas cannot tend to equilibrium. Rather, it is in a non-equilibrium state. As a result, the macroscopic state may change.

Now consider a case that an ideal gas expands into a vacuum, shown in Figure 3. Figure 3a shows that the gas is confined in the left half of a box by a partition. At the initial moment, the partition is removed and the gas begins to expand. The border line between the gas and vacuum is called frontline.

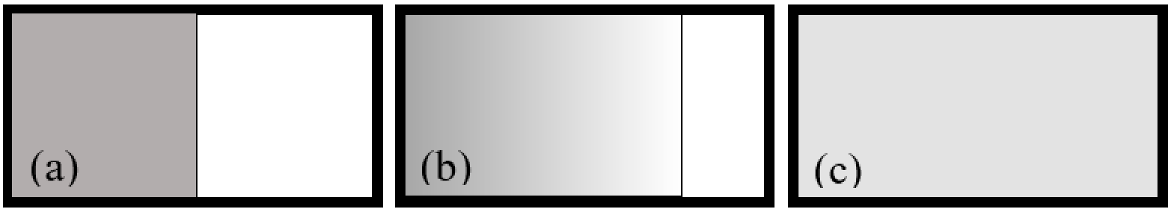


Figure 3. Schematic diagram of a gas expansion into vacuum. The dotted line indicates the border line between gas and vacuum, called frontline. (a) The gas is confine inside the left half box by a partition. At the initial moment, the partition is drawn and the gas starts expansion. (b) the gas expands to 3/4 box. (c) The gas is evenly distributed in the whole box, i.e., the equilibrium state is reached.

At the moment that the partition is just drawn, there is no particles on the right side of the frontline. Suppose that on the left side of the frontline, two particles moving rightward collide, as in Figure 1a, and after the collision, they enter the vacuum on the right side of the frontline. If a corresponding reciprocal collision of another two particle occurs as in Figure 1d, they also enter the vacuum. At this moment, since there are no particles on the right side of the frontline, there is no reverse collision in Figure 1c. Therefore, the molecules always enter the vacuum from the left side of the frontline. There is no mechanism for particles to immediately return to the left side of the frontline. The frontline moves rightward.

Assuming that at the moment in Figure 3b, the momenta of all molecules in the gas are reversed, will the frontline move leftward? The analysis is actually the same as that for Figure 3a. Since the right side of the frontline is a vacuum, the molecules on the left side of the frontline still enter the vacuum, and there is no a mechanism for particles return to the left of the frontline. The frontline continues moving rightward. This shows that Loschmidt's reasoning does not apply.

We next see the equilibrium state in Figure 3c. At every micro-instant, it is in a micro state. Every micro state in a macro state is equiprobable to appear. For a micro state in the macro state, when all the molecules' momentum directions are reversed, the resultant is still a micro state in this macro state. When a gas evolves from a non-equilibrium state to the equilibrium state of Figure 3c, it can be any of these micro states. Conversely, any micro state in Figure 3c can be the one, denoted as A, that is achieved by reversing all the molecule momentum directions of a micro state, denoted as B, the latter being achieved from a non-equilibrium state. Following Loschmidt's reasoning, we assume reversing all the molecular momentum in A to obtain state B, and with time going, the B will undergo a reverse process to go back to the original non-equilibrium state, such as Figure 1b. However, we know that such a process has never happened and we do not expect so. This again shows that Loschmidt's reasoning does not again.

On account of that the molecule number in the gas considered is not infinite, when there is a collision Figure 1a, the probability that its reverse collision Figure 1c is not zero. It seems that there is a nonzero probability for the reverse process of the gas to happen, say, from Figure 3c to Figure 3b. Nevertheless, this probability is so small that it is equivalent to impossibility. In Boltzmann's language, although the evolution from Figure 3b to Figure 3a or from Figure 3c to Figure3d "has a definite calculable (though inconceivably small) probability, which approaches zero only in the limiting case when the number of molecules is infinite." The time needed is so remote that "One may recognize that this is practically equivalent to *never*. …… If a much smaller probability than this is not practically equivalent to impossibility, then no one can be sure that today will be followed by a night and then a day." [58]

A frictionless quasi-static process is the exhibition of a series of equilibrium states. Therefore, such a process is reversible. However, this reversibility does not come from the reversibility of the motion of individual particles, nor from the reversibility of the two-particle collision. Rather, it is the statistical average effect of a large number of molecules colliding each other when the detailed balance is reached.

It is seen that macroscopic reversibility requires a large number of molecules in the gas. Usually, a gas contains molecules in the order of magnitude of the Avogadro constant, is very close to meeting this requirement.

In summary, the motion of microscopic particles is irreversible. Nevertheless, when the number of molecules that make up the gas is very large, the macro state of the gas can be in equilibrium when detailed balance is reached. The equilibrium state is the statistical average effect of the motion of a large number of microscopic molecules. Frictionless quasi-static processes are reversible.

C. Two-particle scattering in quantum mechanics

We have demonstrated in subsection II.E that single-particle motion in QM is irreversible.

We [65] rigorously derived the generalized scattering formula in QM. The state of particles before (after) the scattering is called the initial (final) state. For single-particle scattering, if the initial state is a plane waves of a free particle, $\mathrm{e}^{\mathrm{i}\boldsymbol{p}\cdot\boldsymbol{r}}$, after scattered by a scattering center, the final state is a complicated spherical wave function $\psi(\boldsymbol{r},t)$. This spherical wave has projected amplitudes on plane waves $\mathrm{e}^{\mathrm{i}\boldsymbol{p}'\cdot\boldsymbol{r}}$ in all directions.

We first consider the case that the two particles are both free before scattering, and then transit to two new plane waves after the scattering.

Suppose that two free particles with momenta $\boldsymbol{p}_1$ and $\boldsymbol{p}_2$ collide. The initial state is the product of two plane waves, $\mathrm{e}^{\mathrm{i}\boldsymbol{p}_1\cdot\boldsymbol{r}_1}\mathrm{e}^{\mathrm{i}\boldsymbol{p}_2\cdot\boldsymbol{r}_2}$. The final state $\psi(\boldsymbol{r}_1,\boldsymbol{r}_2;t)$ is complex, which can spread in all directions. If we intend to implement the reverse process of the scattering, we must prepare the $\psi(\boldsymbol{r}_1,\boldsymbol{r}_2;t)$ as the initial state for the reverse process, which is apparently impossible. So, this scattering process of two free particles in QM is irreversible.

Nevertheless, the $\psi(\boldsymbol{r}_1,\boldsymbol{r}_2;t)$ can be expanded by two-particle plane waves, i.e., it has project amplitude on every pair of plane wave $\mathrm{e}^{\mathrm{i}\boldsymbol{p}_1'\cdot\boldsymbol{r}_1}\mathrm{e}^{\mathrm{i}\boldsymbol{p}_2'\cdot\boldsymbol{r}_2}$. That is to say, there is a probability for the two particles with momenta $\boldsymbol{p}_1$ and $\boldsymbol{p}_2$ to transit to two plane waves with specific momenta $\boldsymbol{p}_1'$ and $\boldsymbol{p}_2'$. This probability is denoted as $w(\boldsymbol{p}_1,\boldsymbol{p}_2;\boldsymbol{p}_1',\boldsymbol{p}_2')$. In Figure 1, we use a piece of arrowed line to represent a plane wave with a momentum. Figure 1a is the sketch that the two $(\boldsymbol{p}_1,\boldsymbol{p}_2)$ plane waves transit to two new plane waves $(\boldsymbol{p}_1',\boldsymbol{p}_2')$, denoted as $(\boldsymbol{p}_1,\boldsymbol{p}_2)\to(\boldsymbol{p}_1',\boldsymbol{p}_2')$. Figure 1b–d are respectively the time-inverse transition, reverse transition, and reciprocal transition of Figure 1a. All of the transitions follow the total energy conservation and total momentum conservation (59). The transition probability of the reciprocal process is denoted as $w(\boldsymbol{p}_1',\boldsymbol{p}_2';\boldsymbol{p}_1,\boldsymbol{p}_2)$.

We have rigorously proved that [65]

$$w(\boldsymbol{p}_1,\boldsymbol{p}_2;\boldsymbol{p}_1',\boldsymbol{p}_2')=w(\boldsymbol{p}_1',\boldsymbol{p}_2';\boldsymbol{p}_1,\boldsymbol{p}_2) \tag{67}$$

The transition probability of the process Figure 1a, $(\boldsymbol{p}_1,\boldsymbol{p}_2)\to(\boldsymbol{p}_1',\boldsymbol{p}_2')$ is the same as that of Figure 1d $(\boldsymbol{p}_1',\boldsymbol{p}_2')\to(\boldsymbol{p}_1,\boldsymbol{p}_2)$. This conclusion is derived from the scattering theory in QM, so that it is always valid, irrespective to whether a system reaches detailed balance, as well as irrelevant to the properties of the whole gas [75].

The previous discussion about the two-particle collisions and detailed balance in classical mechanics is entirely applicable to the case here, as long as the two-particle collision in classical mechanics is replaced by the scattering transition of two free particles, $(\boldsymbol{p}_1,\boldsymbol{p}_2)\to(\boldsymbol{p}_1',\boldsymbol{p}_2')$, in QM. In particular, the detailed balance only concerns a pair of reciprocal scattering transition Figure 1a,d, and is irrelative to the reverse transition Figure 1c.

If a scattering transition Figure 1a occurs, the probability of the occurrence of its reverse process Figure 1c is equal to 1, then, the original process Figure 1a is said reversible. However, it is actually that $w(\boldsymbol{p}_1,\boldsymbol{p}_2;\boldsymbol{p}_1',\boldsymbol{p}_2')<1$. Similarly, the probability that the process Figure 1c happen is necessarily less than 1. Therefore, the process Figure 1a is irreversible.

It was believed that [51,52]

$$w(\boldsymbol{p}_1,\boldsymbol{p}_2;\boldsymbol{p}_1',\boldsymbol{p}_2')=w(-\boldsymbol{p}_1',-\boldsymbol{p}_2';-\boldsymbol{p}_1,-\boldsymbol{p}_2)\,. \tag{68}$$

This relationship means that the transition probabilities of the processes Figure 1a,b are the same. This was called detailed balance and seemed obtained from QM [76], the authors of which equated the time-inverse and reverse processes. We stress that in deriving scattering formulas [65], we always considered clockwise processes. We do not know how to include the clockwise and anticlockwise processes in one formulas. In Section II, it is seen that the retarded and advanced processes have to be studied separately. Therefore, we can prove Equation (67) but are unable to verify (68) by the scattering theory in QM.

We address three points here. First, we make it clear that detailed balance (60), but not (67), is a content in statistical mechanics. Equation (67) is proved by the scattering theory in QM. Second, Equation (60) is expressed by momentum distribution function, which involves all molecules in the gas, while (67) only concerns two molecules, irrespective to other molecules. Third, Equation (60) only applies to equilibrium states, while (67) is always correct for two-particle scattering, regardless of whether the whole gas reaches equilibrium.

In Ref. [51], Equation (68) is put down first. Then, with known Maxwell-Boltzmann distribution for equilibrium state, it is postulated that the numbers of the collision and reverse collision in unit time and unit phase space volume are the same so as to achieve (60). This procedure is different from that used by Boltzmann, who first obtained (60) for equilibrium state, and then derive Maxwell-Boltzmann distribution from Equation (60).

We turn to discuss the collision between two non-free particles. That is to say, before and after the collision, particles may be in bound states. A non-free particle is also called a bound particle. On account of the identity of particles, detailed balance should be written in the following form [11,13,15,74].

$$n_i n_j (1+\chi n_{i'})(1+\chi n_{j'}) = n_{i'} n_{j'} (1+\chi n_i)(1+\chi n_j), \quad \begin{cases} \chi = 0, \text{ Distinguishable particles} \\ \chi = +1, \text{ Bosons} \\ \chi = -1, \text{ Fermions} \end{cases} \tag{69}$$

In Equation (69), the n_i is the average number of particles in the energy state ε_i. From the left to right hand sides, Equation (69) represents that two particles in the energy levels ε_i and ε_j collide, and then transit to energy levels $\varepsilon_{i'}$ and $\varepsilon_{j'}$, respectively, denoted as $(i, j \to i', j')$. From the right to left hand side, Equation (69) refers to its reciprocal process, $(i', j' \to i, j)$. The transition probabilities of the two processes are denoted by $w(i, j \to i', j')$ and $w(i', j' \to i, j)$, respectively. It can be verified [65] that

$$w(i, j \to i', j') = w(i', j' \to i, j). \tag{70}$$

In the reciprocal courses, the total energy is conserved.

$$\varepsilon_i + \varepsilon_j = \varepsilon_{i'} + \varepsilon_{j'}. \tag{71}$$

Please note the difference of the two bound particles' collision and two free-particles' collision. A free particle has a momentum. Its state has an index momentum. In its revers motion, its momentum direction is opposite to that in its original motion. This direction reversion helps us distinguish the reverse and reciprocal motions, e.g., Figure 1c,d. In both original and reverse motions, its total energy and total momentum are conserved, see Equation (59).

A bound particle is in one of its discrete energy levels, and there is no momentum such a state index. Thus, a collision requires the conservation of total energy, see Equation (70), without the relationship of momentum conservation. In this case, there is no difference between reverse and reciprocal collisions.

It may be due to the identity of the reverse and reciprocal collisions of bound particles, some ones believed that the collisions are reversible. We reiterate the definition of reversibility of a process: if after an original process $(i, j \to i', j')$ occurs, the occurrence probability of the reverse process $(i', j' \to i, j)$ is less than 1, i.e., $w(i', j' \to i, j) < 1$, then the original process is irreversible. This is because the particles in the state (i, j) can also transit to states other than states (i', j') by collision, as long as Equation (71) is meet. The conclusion is that in any case, two-particle collisions are irreversible.

Messiah [77] thought that Equation (67) was a microreversibility relation. The author of Ref. [78] thought that Equation (67) meant the detailed balance. "This notion is based solely on the reversibility of the microscopic equation of motion. (Or, more technically, on the Hermitian nature of the scattering Hamiltonian.)" The detailed balance (69) only involves the distribution function, and has nothing to do with whether the equation of motion is reversible. Moreover, the two-particle scattering transition is irreversible. We emphasize that when deriving equation (67), we do not use the time inversion invariance of the microscopic equations of motion [65].

For the cases of two free particle collisions, that equilibrium is reached is not due to the reversibility of the collision, but form detailed balance (60). Similarly, in the case of bound particle collisions, equilibrium is neither due to the reversibility of the collisions, but due to (69). In the case of quantum statistics, detailed balance can be obtained by master equation, although in a form superficially different from (69) [9,11,53]. By the form from master equation, it is possible to define a "distance" measuring the violation of detailed balance [19].

IV. CONCLUSION

In this work, by careful analysis, we find that the motions of microscopic particles are irreversible.

We first distinguish between the concepts of equation of motion and specific motion. These two concepts have different mathematical expressions. An equation of motion is just a differential equation that embodies the laws of motion, which can be of invariance under time inversion, but it does not describe any specific motion. A specific motion is a specific solution solved from the equation of motion after considering the initial conditions. It represents the relationship between physical quantities over time and can be graphically illustrated.

We then distinguish between the concepts of time-inverse motion and reverse motion. The former is counterclockwise, which is a fictional movement, and the latter is clockwise. In both classical mechanics and quantum mechanics, we give mathematical expressions for time-inverse motion and reverse motion. The former is described by a time-advanced function, and the latter by a time-retarded function. From the mathematical derivation, we conclude that the single-particle motion process is irreversible.

A system consisting of a large number of molecules frequently colliding with each other is called a collision system. In such a system the microscopic mechanism that plays a decisive role is two-particle collision.

A careful analysis of the two-particle collision was carried out. Three cases are considered: two-particle collision in classical mechanics, the collisions of two free particles and two bound particles in quantum mechanics. For the cases of two free particle collisions, a distinction is made between reverse collision and reciprocal collision. This difference stems from the fact that there is a momentum index of the state of the particle. For the two bound particle collision, there is no difference between these two collisions, because there is no momentum index in the state of a particle.

We have defined the reversibility for the three cases of two-particle collisions. By definition, all these collision processes are irreversible.

The irreversibility of the microscopic two-particle collisions determines that, generally speaking, the macroscopic processes of gases are irreversible.

However, the occurrence of large number of collisions can make a gas reach detailed balance. The detailed balance means that the combination of a two-particle collision and its reciprocal collision retain the distribution function of the gas unchanged. This is the equilibrium state. The detailed balancing does not have the meaning of micro-reversibility. The prerequisite for achieving the detailed balance is that the number of molecules in the gas is sufficiently large.

In summary, every specific micro-process is essentially irreversible. The statistical nature of a large number of micro processes can lead to the reversibility of certain macro processes. Thereby, we explain the microscopic mechanism of why the processes of gases can be irreversible.

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