Molecular chaos

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The issues of reversibility and molecular chaos in a rarefied gas are discussed under conditions for which the behavior of the quantum atoms or molecules of the gas is nearly classical. Following the philosophy of the "correspondence principle," it is initially conjectured that the process of collapse of wave functions corresponds to exponentially diverging trajectories of classical particles. There then follows an investigation of a self-consistent picture in which binary collisions lead not only to Maxwellization of the distribution function but also to a mechanism that maintains definite geometrical sizes of wave packets. © *1995 American Institute of Physics.*

1. INTRODUCTION

It is well known that Boltzmann derived a kinetic equation from the hypothesis of molecular chaos, i.e., from the assumption that there are no correlations in the motion of particles before they collide. It was this hypothesis that ultimately led to the famous H theorem, i.e., to the essential irreversibility of gas kinetics. The question of how it was possible to obtain irreversibility on the basis of the reversible equations of dynamics remained somewhat obscure for a long time. It has now become generally accepted that irreversibility comes about through the exponential divergence of trajectories in phase space. Let us explain what is going on here.

Let $\lambda = 1/n\sigma$ be the mean free path and n the density of the gas molecules, and σ be the scattering cross section. As diameter of an atom, we take $a = \sqrt{\sigma}$. It is easy to see that a small perturbation δv of a gas molecule leads over a path $\sim\lambda$ to a change in the impact parameter of the scattering of the scale $\lambda(\delta v/v)$, where v is the velocity of the molecule. Accordingly, after scattering, the direction of the velocity will be perturbed by an amount of order $(\lambda/a)(\delta v/v)$. Each subsequent scattering multiplies the perturbation by the factor λ/a, so that on the average the perturbation increases with time as $\exp(At/\tau)$, where $A = \lambda/a$, $\tau = \lambda/v_T$, $v_T = \sqrt{T/m}$ is the mean thermal velocity, T is the temperature (in energy units), and m is the mass of the molecule. By virtue of the instability, initially close trajectories in the phase space of any molecule diverge in accordance with an exponential law. For $A = \lambda/a \gg 1$, just a few collisions are sufficient to ensure that initially close trajectories finish up in widely separated (on intermolecular scales) regions of space.

Now suppose that we have an ensemble of completely identically prepared isolated systems. By analogy with quantum theory, such an ensemble can be called pure. It is clear that all representatives of such an ensemble evolve in exactly the same manner and moreover are completely time-reversal invariant. A completely different picture arises when the systems are not isolated from the external world. In the case of a gas, lack of isolation means simply the possibility of inelastic collisions of the gas molecules with the walls. The inelastic collisions lead to forces of viscous friction of the gas on the walls. These forces give rise to an additional damping of sound waves, and in accordance with the fluctuation–dissipation theorem the surface layer of the gas must generate additional acoustic noise. Such noise makes essentially no contribution to the energy balance of the gas, but it leads to small relative displacements of the gas molecules, i.e., to a kind of loss of phase coherence. The binary collisions rapidly increase, in accordance with the law $\exp(At/\tau)$, the perturbations in time. As a result, the ensemble of systems becomes, as it were, "mixed:" its individual representatives evolve along different trajectories in phase space. Accordingly, such an ensemble can be described only statistically, and the time reversibility disappears completely.

We now attempt to describe such a gas from the point of view of quantum mechanics. In the case of a pure ensemble, the quantum description does not present fundamental difficulties—it is merely necessary to write down the Schrödinger equation for the complete system and then attempt to solve it in one way or another. However, interaction of such a system with the environment must radically change the picture of the evolution.

If we use the famous "correspondence principle," we must postulate that even weak incoherence must have a strong effect on the evolution of the system. For each individual molecule, this evolution takes the form of a succession of scatterings. If the external influence on the scattered waves is to be sufficiently strong, it must be assumed that the phases of the individual scattered waves "lose coherence" and the particle enters only one of the scattered waves. Such a process is known as "collapse" of the wave function ψ. In the different representatives of the statistical ensemble, the collapses are different, following the probability principle $\sim|\psi|^2$. It is through the collapses that the pure quantum ensemble is transformed into a mixed ensemble. A regular approach to the description of such irreversible mixed ensembles has yet to be sufficiently developed, and therefore we use here some approximate methods, relying to a large degree on qualitative considerations. Our main assumption is that each molecule or atom of the gas must be ascribed a wave function in the form of a certain compact wave packet. Our task is to describe the translational motion of such pack-

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ets, their scattering off each other, and the maintaining of definite sizes and shapes of the wave packets.

2. WAVE PACKETS

It is natural to begin the description of the gas in terms of wave packets by considering an isolated packet. It is natural to suppose that the size and shape of the wave packets must be determined by the natural processes of interaction between the molecules. However, it is convenient to begin with some preassigned canonical form of a wave packet, for which we take a function of the form

$$\psi=\exp\{ik_0x-x^2/2\Lambda^2\}. \tag{1}$$

For simplicity, we restrict ourselves here to the one-dimensional case. In Eq. (1), Λ characterizes the dimension of the wave packet along the x axis, and k_0 is some averaged wave number.

By a Fourier transformation with respect to x, it is easy to find the shape of the packet in the space of wave numbers:

$$\psi_k=\exp\{-(k-k_0)^2\Lambda^2/2\}. \tag{2}$$

Here $v_0=\hbar k_0/m$ characterizes the velocity of the wave packet. We assume that the velocity distribution of the wave packets is Maxwellian with temperature T_*:

$$F(v_0)=B\exp\{-mv_0^2/2T_*\}, \tag{3}$$

where B is a normalization factor.

If the square of the wave function (2) is multiplied by the distribution function (3) and the result is averaged over v_0, we obtain an expression for the diagonal elements of the density matrix:

$$\rho(k,k)=B_1\exp\{-\hbar^2k^2/2mT\}, \tag{4}$$

where the temperature T is determined by the relation

$$T=T_*+\hbar^2/2m\Lambda^2. \tag{5}$$

The relation (5) can be interpreted as follows: T is the true temperature of the free particle, T_* is an auxiliary quantity corresponding to the temperature of the moving wave packets, and $\hbar^2/2m\Lambda^2$ is, as it were, twice the "internal" energy of a wave packet. This energy is positive, so that the wave packet spontaneously decays with time, and there must be some external factor that maintains the equilibrium size of the packet. As we shall see, this is realized by successive collapses of wave functions.

In the three-dimensional case, it is natural to assume that the wave function of a packet is equal to the product of functions of the form (1) along the directions x,y,z. The corresponding wave packet will have a spherically symmetric envelope with a "filling" in the form of a plane wave with wave vector $\mathbf{k}_0$.

3. COLLAPSES AND RANDOM WAVE FUNCTIONS

We consider a rarefied gas under conditions for which the behavior of the molecules or atoms of the gas is nearly classical. More precisely, we assume that $a^3n=a/\lambda\ll 1$, where $a=\sqrt{\sigma}$ is the quantity that characterizes the molecular diameter. In addition, we shall assume $\sqrt[3]{n}\lambda_B\ll 1$, where $\lambda_B=\hbar/mv_T$ is the de Broglie wavelength.

We assume that in the initial state at $t=0$ the wave functions of the molecules take the form of wave packets of the type (3) but only in three dimensions. We choose some test particle and follow its evolution. We assume that the packet width Λ is not very small, namely, $\Lambda^2\gg\lambda\lambda_B$. In this case, the quantum-mechanical spreading of the wave packet during the mean free time $\tau=\lambda/v_T$ is not greater than Λ.

In time τ, a packet with mean velocity v_T successively covers one region after another with a total volume of order $\Lambda^2\lambda$. In this volume, there are $N=n\Lambda^2\lambda$ particles. We shall assume that $N\gg 1$. One can say that during the time τ the wave packet we are considering undergoes $N\gg 1$ scatterings and that the scattered waves occupy a volume $\sim\lambda^3$. During subsequent intervals of time of order $\sim\tau$, the waves are rescattered, so that an extremely complicated picture of the wave field is created. If the system we consider is isolated, i.e., is not subject to any perturbations from outside, the corresponding intricately organized wave function corresponds to a coherent state. Although this state is very unstable and delicate, it must be reversible in time: If the time is reversed at any instant t, the system must return to the initial state. This means that in the time-reversed system all the previously outgoing scattered waves must be transformed into incoming waves that, moreover, are so finely "tuned" that they can ultimately "coalesce" into the original wave packets at $t=0$. Accordingly, it must be assumed that in any steady picture of a coherent state, at $t\gg\tau$, outgoing and incoming waves are equally present.

We now suppose that the gas we are considering begins to interact with the environment through inelastic collisions of the gas molecules with the walls, which have the same temperature T as the gas. As we know, the walls create thermal noise that propagates with the speed of sound into the interior. This noise will certainly lead to destruction of the delicate picture of the coherent state. Above all, the noise destroys the phase coherence of the previously incoming waves, so that only the scattered outgoing waves remain. This circumstance by itself leads to destruction of the reversibility. However, the disturbance of the environment is in fact considerably stronger, and this can be explained as follows.

As we have established above, the initial wave packet creates N scattered waves over its mean free path. A weak external perturbation can slightly disturb the phase coherence between the waves, and the microscopic particle itself, being indivisible, can be present in only one of these waves. However, the phases of individual sections of the selected scattered wave can also be put slightly out of phase, so that the particle can find itself in only one of the small sections of the scattered wave. There is a collapse of the wave function into a new wave packet. It is difficult to say at which precise instant the collapse occurs, but if one goes back into the past along the trajectory of a newly formed packet it will be possible to find the small volume in which scattering occurred. Thus, from the point of view of the subsequent evolution of the wave packet this collapse can be nominally referred to the time of scattering.

Suppose that before the collapse the wave vector of the packet was $\mathbf{k}_i$, and after the collapse it is $\mathbf{k}_f$. One can say that a particle with velocity $\hbar \mathbf{k}_i/m$ has been scattered into the velocity direction $\hbar \mathbf{k}_f/m$. This process is purely random, so that a wave function in the form of a set of wave packets is also random. If the choice of the probabilities of formation of the packets follows a law $\sim|\psi|^2$, the statistical description of the processes of scattering and collapse automatically leads to a Boltzmann equation with transition probabilities calculated in accordance with the rules of quantum theory.

For us, great interest attaches to the dynamics of the wave packets. We consider the history of a wave packet of an arbitrarily chosen test particle. The trajectory of such a packet will have the form of a broken line consisting of straight sections with an average length λ; the random deflections are determined by the scattering probabilities. After each of the deflections, there is a collapse of the wave function to a form close to (1). To obtain a qualitative picture, the process of the discrete collapses can be replaced by continuous collapse. In addition, it is convenient to make a restriction to the one-dimensional case and consider the collapses in a coordinate system moving together with the packet (in each of the segments of the trajectory, a new system of coordinates is needed).

In this approximation, the collapse can be described by a factor of the type $A(t)\exp\{-x^2t/2b^2\tau\}$, by which it is necessary to multiply the wave function of the particle. By b we have here denoted the width of the collapsing form factor. During the time t there are t/τ collapses with total form factor $\exp\{-x^2t/2b^2\tau\}$, and the factor $A(t)$ takes into account the normalization of the wave function. In the approximation of continuous collapsing, the Schrödinger equation for the wave function of the test particle takes the form

$$i\hbar \frac{\partial \psi}{\partial t} = -\frac{\hbar^2}{2m}\frac{\partial^2 \psi}{\partial x^2} - i\frac{\hbar x^2}{2b^2\tau}\psi + i\hbar\gamma\psi, \tag{6}$$

where $\gamma = \dot{A}/A$.

We seek a steady solution of this equation in the form $\psi = \exp\{-i\omega t - x^2/2\Lambda^2\}$, and we choose γ in such a way that the frequency ω is real. Substituting this expression for ψ in Eq. (6), we obtain

$$\Lambda^{-2} = (1-i)\Lambda_0^{-2}, \quad \omega = \gamma = \frac{\hbar^2}{2m\Lambda_0^2}, \quad \Lambda_0^2 = \sqrt{\frac{2\hbar b^2\tau}{m}}. \tag{7}$$

As yet we do not know the width b of the packet corresponding to the very beginning of the collapse. If we assume approximately $b \simeq \Lambda_0$, then we obtain

$$\Lambda^{-2} = (1-i)\Lambda_0^{-2}, \quad \Lambda_0 = \sqrt{2\hbar\tau/m} = \sqrt{2\lambda\lambda_B}. \tag{8}$$

In other words, the steady width of the packet is of the order of the geometric mean value of λ and λ_B.

As we see, in the model of continuous collapse, $|\psi|^2 = \exp\{-x^2/\Lambda^2\}$ keeps a constant shape, i.e., all molecules of the gas are ascribed packets of the same shape, and the entire difference between them resides in the different values of their velocities $v_0 = \hbar k_0/m$. If $k_0\Lambda \gg 1$, the wave packet (1) differs little from a plane wave. Accordingly, the probabilities of scattering due to binary interactions of the particles can be calculated in the plane-wave approximation.

4. SUCCESSIVE COLLAPSE

The model of continuous collapsing is too simplistic. It is therefore of interest to consider the more realistic case of successive collapses. However, here too it is sensible to make some simplifications. First of all, we represent the trajectory of a test particle in the form of a certain broken curve. It is convenient to rectify this line and lay it out along the x axis, ignoring certain fine details in the behavior of the wave packets near the points of scattering. Further, it can be assumed approximately that the successive scatterings do not occur in accordance with the law of chance but at points precisely separated by the distance λ. Finally, we ignore the changes in the velocities of the particles on the transition from one segment of free motion to another, setting in (1) $k_0 = mv_T/\hbar$, where $v_T = \sqrt{T/m}$. In addition, we retain for the moment the width of the packet b in each of the collapses as a free parameter.

Thus, we arrive at a problem of periodic collapse, so that it is sufficient to consider only one transition, when the wave function undergoes the collapse (1) with $\Lambda = b$ and $k_0 = mv_T/\hbar$ at $t=0$ and arrives at the subsequent collapse at $t = \lambda/v_0$.

It is readily verified that the Schrödinger equation for a free particle has a solution of the form

$$\psi = \Lambda^{-1}\exp\{-i\omega t + ik_0x - (x-v_0t)^2/2\Lambda^2\}, \tag{9}$$

where $\omega = \hbar^2k_0^2/2m$, $v_0 = \hbar k_0/m$, and Λ^2 is a linear function of the time:

$$\Lambda^2 = b^2 + i(\hbar/m)t. \tag{10}$$

We have here chosen the initial value $\Lambda = b$ at $t=0$. It is this solution that describes the evolution of the wave function after the collapse at $t=0$. By means of (10), it is easy to find the mean value $\langle (x-v_0t)^2\rangle$, which we denote by Λ_a^2:

$$\lambda_a^2 = b^2 + \hbar^2t^2/m^2b^2. \tag{11}$$

Using this expression, we can obtain the mean value $\langle \Lambda_a^2\rangle$ with respect to the time over the interval $\Delta t = \tau$:

$$\langle \Lambda_a^2\rangle = b^2 + \hbar^2\tau^2/3m^2b^2. \tag{12}$$

By means of the relation (11), we can represent the wave function (9) in the form

$$\psi = \Lambda^{-1}\exp\{-i\omega't + ik_0'x' - x'^2/2\Lambda^2\}, \tag{13}$$

where we have introduced the notation

$$\omega' = \omega - k_0v_0, \quad x' = (x_0 - v_0t),$$

$$k_0' = k_0 + \frac{\hbar t}{2mb^2\Lambda_a^2}x'. \tag{14}$$

As we see, the wave vector k_0' depends linearly on x' due to the dispersion of the de Broglie waves.

We now consider the energy balance near the second collapse at $t=\tau$. Before the collapse, the particle energy can be calculated by means of the wave functions (9) or (13). It is

$$E=\frac{\hbar^2 k_0^2}{2m}+\frac{\hbar^2}{4mb^2}. \tag{15}$$

Here the first term describes the kinetic energy of a packet moving with velocity $v_0=\hbar k_0/m$, while the second corresponds to the "internal" energy of a packet at rest. We find the energy immediately after the collapse. We assume that the collapse occurred near the point x_0. It can be taken into account by an additional factor $\exp\{-(x'-x_0)^2/2b^2\}$ of the wave function (13). We first find the energy $E(x_0)$ of the collapsed state using the standard rules of quantum mechanics: $E(x_0)=\langle\psi_0^* H\psi_0\rangle$, where H is the Hamiltonian, and ψ_0 is given by the expression (13) with the additional factor $\exp\{-(x'-x_0)^2/2b^2\}$.

To avoid complicating the calculations, it is convenient to consider the case $b^2\ll\Lambda_a^2$, where Λ_a^2 is calculated in accordance with (12) at $t=\tau$. We then obtain

$$E_0\simeq\frac{\hbar^2}{2m}\left\{k_0^2+\frac{1}{2b^2}+\frac{2k_0}{b}\frac{x_0}{\Lambda_a}+\frac{x_0^2}{b^2\Lambda_a^2}\right\}. \tag{16}$$

Here the first two terms in the brackets correspond to the energy of the particle before the second collapse.

If the collapse probabilities were distributed in accordance with the law $|\psi|^2$, i.e., as $\exp\{-x^2/\Lambda_a^2\}$, then the energy (16) would be

$$\frac{\hbar^2}{2m}\left\{k_0^2+\frac{1}{b^2}\right\}.$$

In other words, the second collapse would add an energy $\hbar^2/4mb^2$ equal to the "internal" energy before the collapse. However, such an increase in the energy cannot occur, since otherwise the collapses would monotonically increase the particle energy. In each elementary collision, the momentum is conserved simply by virtue of the matching of the phases of the colliding and scattered waves in the center-of-mass system of the particles. To conserve the energy on the average, it must be assumed that the collapses deviate weakly from the law $|\psi(x_0)|^2$: The collapses must occur more frequently in the region $x_0\leqslant 0$, i.e., in the part of the wave packet in which the local momentum is somewhat smaller.

Suppose the mean value $\langle x_0\rangle$ is nonzero and negative, while $\langle x_0^2\rangle$ before the collapse is, as before, equal to $\Lambda_a^2/2$. We agree to call $\alpha=-\langle x_0\rangle/\Lambda_a$ the asymmetry parameter. To ensure that the energy conservation law is satisfied on the average, α must be equal to

$$\alpha=-\langle x_0\rangle/\Lambda_a=1/4k_0 b. \tag{17}$$

In order of magnitude, $\alpha\simeq\sqrt{\lambda_B/\lambda}$. Just such an asymmetry of the collapse is necessary[1] to explain the experiments of Sokolov *et al.*[2,3]

It must be emphasized once more that the collapses occur through the disturbance of the intricately organized coherent states. We have nominally said that the collapses occur at times immediately after the scattering. However, in reality the scattering itself can be established only by continuation into the past of the state that arose as a result of the collapse. There arises a kind of reverse correlation that need not end at the previous scattering and can extend over two or a few preceding scatterings. Thus, the collapses can be regarded as processes that are extended in time and enhanced by the binary interactions of the particles. Therefore, the models of continuous and discrete collapsing are merely two limiting simplified approaches to the description of the real process.

5. CONCLUSIONS

In this paper, we have considered qualitatively the wave functions of atoms or molecules of a gas under conditions when their behavior does not differ strongly from classical behavior. By analogy with a classical gas, one may suppose that because of interaction of the gas with the walls, i.e., with the external environment, intricately organized coherent states cannot exist for long in it. The loss of coherence is similar to the collapse of wave functions during ordinary measurements in quantum systems. One can say that the binary collisions of the molecules organize a constantly active mechanism of self-measurement. It appears that this process can be described rigorously but not easily. Therefore, we have used a qualitative approach based on a notion of the mechanism of collapse of wave functions under conditions when multiple scattering must create very intricately organized coherent states. Such an approach shows that the wave functions of the molecules are transformed into wave packets whose size and shape are determined by the actual mechanism of the binary collisions. It appears that each wave packet is prevented from spreading by a mechanism of "squeezing" of the packet that takes place at the rate of the binary collisions. The collisions of such packets with one another can be described by standard quantum theory, and the resulting relaxation process is described by the Boltzmann equation. Thus, with allowance for the collapsing of the wave functions the quantum description of gas kinetics does not differ that strongly from the classical description.

The processes of irreversible evolution of complex quantum systems considered here are analogs of the classical chaotic systems of Poincaré discussed by Prigogine and Petrovsky[4,5] in the framework of a somewhat different mathematical approach.

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