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An historical approach to the effects of elastic collisions in radiofrequency devices and recent developments

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ABSTRACT

After an historical review of several approaches to predict the spatial and energy distributions of ions confined in a Paul trap and subjected to collisions with neutrals, the paper focuses on the temporal invariance method. Two improvements of this method are studied. The first one is used to probe the shape of the equilibrium distribution around a given value of the dynamic state of the ion. The second one is an enhancement to compute the solution by the Monte Carlo technique: a large increase of the performances of the variance reduction is achieved for light buffer gases (He and Ne) by using a control model of the tested device.

The application to the computation of the equilibrium distribution of Cs^+ ions subjected to collisions with He, Ne and Ar shows that the distribution is not Gaussian, even with the lightest buffer gas atom, and the magnitude of the tail of the distribution dramatically increases with the collisional atom mass. In addition, the possibility to extend the studies to other confinement devices is discussed if the efficiency obtained by means of the use of a control model is increased.

1. Introduction

The dynamic stabilization of ions in two-dimensional radio frequency quadrupole electric fields originated with the mass filter [1–3], followed by the confinement of ions in 3D quadrupole electric fields by means of 3D ion traps [4–6]. The latter has revolutionized mass spectrometry and enables among other important investigations in the field of atomic physics and frequency standards [7,8].

The ion trap, denoted as the Paul trap, the name of its inventor [9], possesses a quadrupolar electric configuration due to a hyperbolically shaped ring mounted between two hyperbolic rotationally symmetric end-caps. The $\vec{Oz}$ axis passes through the centre of the two end-caps: it is a rotational symmetry axis. The plane of symmetry of the trap passes through the centre of the ring in which two orthogonal axes $(\vec{Ox}, \vec{Oy})$ define with $\vec{Oz}$ an orthonormal frame. To satisfy the Laplace equation the same potential must be applied to the two end-caps, while an opposite potential is applied to the ring. The confinement of an ion (*i.e.* the maximal amplitude of ion trajectory is finite in all directions) is impossible by applying a constant potential. However, the confinement is achieved by adding a periodically oscillating RF potential to a DC component of the quadrupole potential. This periodic oscillation is denoted as a "micro metric oscillation". According to the dimensions of the trap, the amplitude and the frequency of the confinement voltage and the mass-over-charge ratio of the ion, the latter can have a stable and quasi-periodic motion in each direction. The motion frequencies are discrete, the lowest one in each of the three directions is the secular frequency of the motion [10–14].

In most applications of Paul traps, ions undergo interactions with gas atoms/molecules. These may be residual but may also be introduced intentionally to "thermalize" the ions or to be used in the process of collision-induced dissociation (or CID) [15]. The collisions disturb the motion of an individual ion and therefore alter the statistical properties of the population to which it belongs. They contribute to limiting the temporal duration of confinement of an ion which is manifested by a loss rate for the ion population. Thus a precise knowledge of the ion position and velocity distributions is of great concern.

2. Historical approach

The influence of collisions is a topic that was immediately addressed by different approaches. The first of them was to model the trap as a potential well [16]. This model explains that the equilibrium temperature depends on the ion mass (m_i) to the collisional gas mass (m_g) ratio, with a law of energy W of the form $\exp(-\alpha(m_i, m_g)W/kT)$. The results were used to qualitatively explain the process

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of collisional cooling. However, the fact that the equilibrium is not thermodynamic is important in explaining that in a real trap (*i.e.* limited by electrodes) the ion lifetime can increase with the density of the buffer gas. Indeed, Dawson and Wetten have first observed that a light gas can act to stabilize the motion of a heavier ion: the trapping of mercury ions has been shown in the presence of neon at different pressures [17]. The sensitivity of the evolution equations to the ion velocity in presence of collisions requires taking into account a more realistic model.

In 1972, Andre and Schermann [18] proposed to model the ion evolution by a discrete Markov process with constant temporal steps corresponding to the zero phase of the applied micro metric potential, under the assumption of "rare impacts". This assumption is valid for neutral gas densities low enough such that the probability of more than one collision between two successive instants of the Markov process can be neglected (*i.e.* for pressures higher than 10^{-3} Torr in the usual traps). This model allowed (1) to calculate the energy and spatial properties of ions in traps with low energy pseudo-potential depth, (2) to show that the distribution of these properties is Gaussian only under the assumption of the adiabatic approximation and with a neutral to ion mass ratio close to zero and (3) to explain the effect of collisional cooling by the favourable influence of a light buffer gas on the energy distribution of ions subjected to collisions with the residual gas. The confinement time of the ions in the presence of residual and buffer gases was also studied [19], and the results qualitatively agreed with those of an experimental work carried out in parallel [20].

This model is based on solving integro-differential equations of large dimensions involving heavy computing resources at that time, which limited its use. However this approach by the Markov process is important as (1) it is an algorithmic method not involving hypothesis on the nature of the solution and (2) the method has been validated by experiment. So it can be a reference method.

Subsequently, André and Vedel proposed an approach of the equilibrium solution of the ion cloud based on the invariance of the statistical properties of the ion state at specific confinement times [21–24]. This method involves building a bilinear functional form ψ of the function g, denoted as test function and h denoted as unknown function. Whatever g (with respect to sommability condition), this generating functional form cancels when h is equal to the probability density of the ion state. In practice, this method requires the knowledge of a general formulation of the solution (typically we look for the probability density within a family of functions of m parameters, limited to Gaussian functions if $m = 2$) and its resolution uses Monte Carlo methods for the computation of integrals. The accuracy achieved depends directly on n_{ech} the number of samples ε_k for $k = 1, \ldots, n_{ech}$ of sequence e_k. This method allowed the study of equilibrium solutions under the effect of elastic collisions, but in principle, its scope can be extended to other types of binary interactions. For instance, the problem of weak space charge, which is one of the causes of performance limitation of the traps, was addressed by considering that the effect of other ions results in a superposition of a weak potential to the confinement potential [23]. The use of this method was also proposed to study the "laser cooling" [25].

More recently, combining analytical and Monte Carlo treatments, DeVoe proposed to describe the spatial distribution for confined ions colliding with several buffer gases in terms of a Tsallis distribution [26]. He concludes that the spatial distribution is non-Gaussian, except for He buffer gas.

3. Further developments

As with any resolution technique using Monte Carlo methods, the actual scope is limited by the available computing resources and also by the performance of the methods using variance reductions. However, the temporal variance method cannot yet address the issue of a finite-dimensional trap, so the question of confinement duration can only be solved qualitatively.

In fact, the temporal invariance method was limited to configurations of perfect traps (whose trajectories are solutions of Mathieu equations) to find the probability density within families of Gaussian functions (*i.e.* with two dependent parameters). But, it is known that solutions are Gaussian in few cases. Moreover, it is interesting to study the real trap anharmonicities as they can have positive and negative effects according to the trap operating mode [27].

Other traps exist for which ion trajectories are more complex. This is the case of cylindrical traps [28,29] and the Linear Quadrupole Ion Trap (LQIT) or 2D ion trap [30–36] which has the advantage over the Paul trap in reducing the space charge at a constant number of ions. Papers report the investigations about confinement and effects of the collisions upon confinement properties of an LQIT. For instance, Song et al. [37] have shown experimentally the efficiency of confinement and a size reduction of the main domain of stability with the increase of the pressure (at few 10^{-3} Torr) using a Rectilinear Ion Trap (RIT), an ion trap with planar electrodes [38,39].

To extend the temporal invariance method to these devices, it would be necessary to use realistic ion trajectory calculation taking into account the accurate shape, size, and relative positioning of the electrodes, with programs such as SIMION [40] or CPO [41], but with a large increase in computation time, making it prohibitive to use Monte Carlo methods, unless the efficiency of the variance reduction technique can reduce this handicap.

The main objective of this paper is to propose improvements in treatment of temporal invariance method by (1) seeking adapted test functions, (2) using correlations of real trajectories with those of a control model, enabling one to reduce the number of samples ε for a given precision and to search for solutions such as "disturbed Gaussian", belonging to families based on more than two parameters. As first application, we precise the shape of the dynamical state density of Cs^+ ion colliding with different neutral buffer gases He, Ne and Ar.

A glossary is provided and the major mathematical developments are given in Appendix. The probability theory used in this article is referred in [42,43].

4. Temporal invariance method

4.1. Determination of the functional equation for a pure infinite-dimension trap

The ion state at instant t is a random vector denoted as $\vec{S}_t$ the components of which in the orthonormal system (Ox, Oy, Oz) are expressed by:

$$\text{either} \quad \vec{S}_t = [X_t, Y_t, Z_t, \dot{X}_t, \dot{Y}_t, \dot{Z}_t]$$

$$\text{or} \quad \vec{S}_t = [\vec{U}_t, \dot{\vec{U}}_t] \text{ with } \vec{U}_t = [X_t, Y_t, Z_t] \text{ and } \dot{U}_t = [\dot{X}_t, \dot{Y}_t, \dot{Z}_t]$$

The value of $\vec{S}_t$ for a sample ε is the vector $\vec{s}_t$, the components of which are expressed by:

$$\text{either} \quad \vec{s}_t = [x_t, y_t, z_t, \dot{x}_t, \dot{y}_t, \dot{z}_t]$$

$$\text{or} \quad \vec{s}_t = [\vec{u}_t, \dot{\vec{u}}_t] \text{ with } \vec{u}_t = [x_t, y_t, z_t] \text{ and } \dot{\vec{u}}_t = [\dot{x}_t, \dot{y}_t, \dot{z}_t]$$

For simplification, if $\vec{S}$ and $\vec{S}''$ are random vectors which take values in $\vec{s}$ and $\vec{s}''$), if $(\vec{s}'', d\vec{s}'')$ is the elementary domain of $\vec{S}''$, we will use the notation $E(g(\vec{S})/\vec{s}'')$ for the expectation of $g(\vec{S})$ subjected to the occurrence of the events $\{\vec{S}'' \in (\vec{s}'', d\vec{s}'')\}$.

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