

Moment Theory of Ion Motion in Electrodynamic Quadrupole Ion Traps

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OVERVIEW

Goal:

- To develop two-temperature moment theory for ion motion in devices where the electric field is time- and position-dependent, and subsequently apply the results to an ideal quadrupole ion trap

Methods:

- Starting from the Boltzmann equation, moment methods were used to develop a set of differential equations for average ion velocity and temperature
- Using analytical expressions for the trapping electric field, differential equations representing the first-order (momentum-transfer) approximation of the theory were written for the ion trap
- Mathcad code was developed to solve the differential equations and perform the calculations for various quantities of interest

Results:

- Solutions for the set of coupled differential equations directly provide average velocity and temperature (energy) for an ion ensemble as functions of time and of position in the apparatus
- Incorporating the ion velocity into the equation of continuity enables the time- and position-dependent ion number density to be determined
- Combining the above information enables metrics for the entire ion ensemble, such as effective temperature, to be determined as a function of time

INTRODUCTION

Many devices commonly used in analytical chemistry involve trace amounts of ions moving through dilute gases under the influence of external fields. The simplest devices to understand theoretically employ only an electrostatic field; examples include drift-tube mass spectrometers and ion mobility spectrometers. The theory of ion motion through gases when there are external fields that vary with both time and position is much less advanced, however¹. Such fields are present in several devices in common use such as field-asymmetric ion mobility spectrometers, linear RF multipole instruments, and ion trap devices.

The approach most often employed to understand ion motion in complicated electric fields is to use Newton's equations of motion to describe the motion of a single ion. For example, incorporating sinusoidal trapping fields into Newton's equations for pure quadrupole ion traps leads to a separate differential equation, the Mathieu equation, for ion motion in each direction in the apparatus². Recently, a kinetic theory (i.e., based on the Boltzmann equation) of radio frequency quadrupole ion traps was developed³. The advantage of using the Boltzmann equation is that the theory can treat collisions with the same level of sophistication and detail as is used to treat the external fields. The disadvantage is that the results are difficult to apply, except in special cases such as the Maxwell model of constant collision frequencies.

As an intermediary between the two approaches just described, the use of moments of the Boltzmann equation to provide an approximate kinetic theory has a long history⁴. The simplest approximation to the moment equations, known as momentum-transfer theory, has been extended to AC fields⁵. The inaccuracy of momentum-transfer theory is now known to be no more than 15-20% (and in most cases only a few percent) for electrostatic fields.

The purpose of this paper is to develop two-temperature moment theory⁶ for quadrupole ion traps. Solutions of the set of coupled differential equations resulting from the momentum-transfer approximation provide the average ion velocity and temperature as functions of time and of position in the apparatus. That information also enables the position-dependent ion number density and the effective temperature for the ion ensemble to be determined as a function of time.

THEORY

- The Boltzmann equation describes the effects of an applied electric field, E , and collisions, J , on the ion distribution function, $f(\mathbf{r}, \mathbf{v}, t)$, in 6D phase space

$$\left[\frac{\partial}{\partial t} + \mathbf{v} \cdot \nabla + \frac{q}{m} \mathbf{E}(\mathbf{r}, t) \cdot \nabla_{\mathbf{v}} \right] f(\mathbf{r}, \mathbf{v}, t) = J f(\mathbf{r}, \mathbf{v}, t)$$

change in $f(\mathbf{r}, \mathbf{v}, t)$ due to collisionless motion change in $f(\mathbf{r}, \mathbf{v}, t)$ due to collisions

- The moment equation is formed by multiplying the Boltzmann equation by any function, $\gamma(\mathbf{v})$, of the ion velocity, and then integrating over all velocities

$$\int \frac{d\mathbf{v}}{4\pi} n \bar{\gamma} + \nabla \cdot n \bar{\gamma} \mathbf{v} - \frac{q}{m} n \mathbf{E} \cdot \nabla_{\mathbf{v}} \bar{\gamma} = n J \bar{\gamma}$$

where the moment, $\bar{\gamma}$, is defined as

$$\bar{\gamma} = \bar{\gamma}(\mathbf{r}, t) = \frac{1}{n(\mathbf{r}, t)} \int f(\mathbf{r}, \mathbf{v}, t) \gamma(\mathbf{v}) d\mathbf{v}$$

and the ion number density, n , is

$$n = n(\mathbf{r}, t) = \int f(\mathbf{r}, \mathbf{v}, t) d\mathbf{v}$$

- The time derivative of n in the moment equation can be eliminated by using the equation of continuity (which is formed by setting $\gamma(\mathbf{v})=1$ to express ion conservation in the system)

$$\int \frac{d\mathbf{v}}{4\pi} \bar{\gamma} - \frac{q}{m} \mathbf{E} \cdot \nabla_{\mathbf{v}} \bar{\gamma} + x(T_{eff}) \bar{\gamma} = R(\bar{\gamma}) + [x(T_{eff}) \bar{\gamma} + J \bar{\gamma}]$$

$x(T_{eff})$, the collision frequency for momentum transfer, is a function of the effective temperature, T_{eff} , characterizing the COM collision energy. R is a functional involving a difference between: (1) $\bar{\gamma} \mathbf{v}$ and $\mathbf{v} \bar{\gamma}$, and (2) similar quantities containing a small gradient of $\bar{\gamma}$; thus, R is usually ~ 0 . The term in brackets is ~ 15 -20% of $x(T_{eff}) \bar{\gamma}$ in worst case.

- The first (momentum-transfer) approximation of the two-temperature moment theory for $\bar{\gamma}$ is obtained by setting $\gamma(\mathbf{v}) = \mathbf{v}$, neglecting the spatial gradients, and setting the RHS of the general moment equation to zero. Because x is a function of T_{eff} , another moment equation describing how the effective temperature changes must also be formed by setting $\gamma(\mathbf{v}) = \frac{1}{2} m v^2$.

$$\frac{d}{dt} \bar{\mathbf{v}} - \frac{q}{m} \mathbf{E} + x(T_{eff}) \bar{\mathbf{v}} = 0 \quad \bar{\mathbf{v}}(\mathbf{v}) = \mathbf{v}$$

$$\frac{d}{dt} T_{eff} - \frac{2q}{3k} \frac{M}{m+M} \mathbf{E} \cdot \bar{\mathbf{v}} + \frac{2m x(T_{eff})}{m+M} [T_{eff} - T] = 0 \quad T_{eff}(\mathbf{v}) = \frac{1}{2} m v^2$$

- Inserting the expressions for the electric fields in an ideal quadrupole ion trap

$$E_x = -\frac{U + V \cos(\Omega_{RF} t)}{r_0^2 + 2z_0^2} 2u \quad u = x, y \quad E_z = \frac{U + V \cos(\Omega_{RF} t)}{r_0^2 + 2z_0^2} 4z$$

and using the standard parameterized variables a_u and q_u

$$a_x = -2a_{x,y} = \frac{-16qU}{m(r_0^2 + 2z_0^2)\Omega_{RF}^2} \quad q_x = -2q_{x,y} = \frac{8qV}{m(r_0^2 + 2z_0^2)\Omega_{RF}^2}$$

then gives a system of differential equations, coupled through x , that can be solved for the four quantities, \bar{v}_x , \bar{v}_y , \bar{v}_z , and T_{eff} , each as a function of position and time. Note that the components of the average ion velocity may not be equated to the time derivative of the position du/dt for a single ion.

$$\frac{d}{dt} \bar{v}_u + \frac{\Omega_{RF}^2}{4} [a_u - 2q_u \cos(\Omega_{RF} t)] u + x \bar{v}_u = 0$$

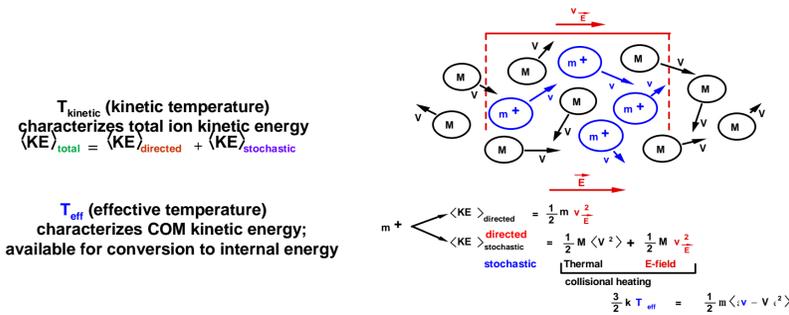
$$\frac{d}{dt} T_{eff} + \frac{m \Omega_{RF}^2}{6k} \sum_u [a_u - 2q_u \cos(\Omega_{RF} t)] u \bar{v}_u + \frac{2m x}{m+M} (T_{eff} - T) = 0$$

- The equation of continuity can then be solved by substituting the values obtained for \bar{v}_u to give the time- and position-dependent ion number density distribution, $n(x, y, z, t)$, and its standard deviations, $S_u(t)$.

$$n(x, y, z, t) = \frac{n_0}{(2p)^{3/2} s_x(t) s_y(t) s_z(t)} \exp\left(-\sum_u \frac{u^2}{2s_u^2(t)}\right)$$

m = ion mass M = neutral mass m = ion-neutral reduced mass = $\frac{mM}{m+M}$
 q = ion charge T = neutral temperature N = neutral number density
 J = Boltzmann collision operator
 U = amplitude of DC potential on ring electrode
 V = amplitude of AC potential with angular frequency Ω_{RF} , on ring electrode
 r_0 = radius of ring electrode z_0 = shortest distance between endcaps

RESULTS AND DISCUSSION



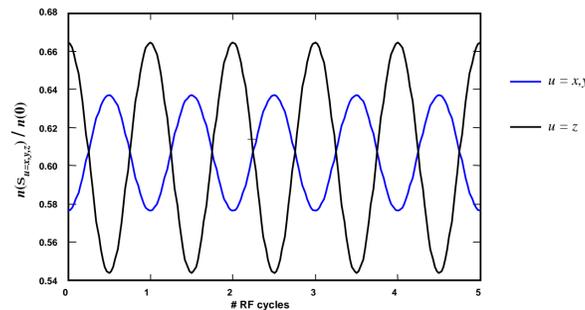
Two-temperature theory for ion transport through monatomic gases via electric fields

$$x(T_{eff}) = \left[\frac{4}{3} N \frac{M}{m+M} \left(\frac{8kT_{eff}}{pm} \right)^{1/2} \Omega^{(0,1)}(T_{eff}) \right]$$

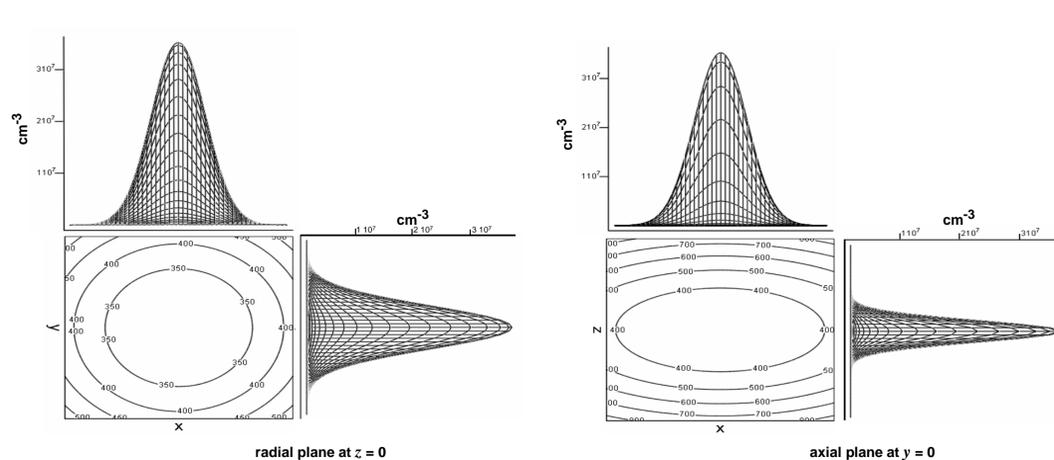
Collision frequency for momentum transfer in the context of two-temperature theory

$$x(T_{eff}) = \text{constant} \quad \text{ion-induced dipole collisions}$$

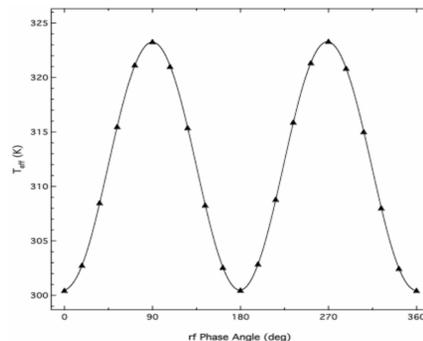
$$\Omega^{(0,1)}(T_{eff}) = \text{constant} \quad \text{rigid-sphere collisions}$$



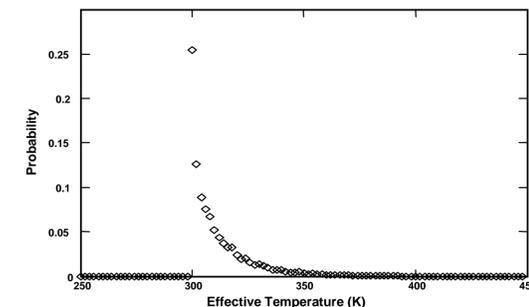
Time-dependence of the ion number density n in the radial plane at $z = 1s$ and in the axial plane at $x, y = 1s$ for the ion ensemble above.



T_{eff} contours with $a_x = 0$, $q_x = 0.20$, RF phase angle = $\pi/2$, $m = 100$ Da, $M = 4$ Da for the rigid-sphere model of ion-neutral interactions. The number density distribution for a population of 10^5 ions is also indicated at the top and side.



Time-dependence of T_{eff} over 1 RF cycle for the ion ensemble above. When averaged over the cycle, $T_{eff} = 311.6$ K.



T_{eff} probability distribution for the ion ensemble above when averaged over 1 RF cycle.

CONCLUSION

- The differential equations presented here, which do not appear to have been given previously, tend to complement those presented in previous ion trap studies. This is because of the difference in viewpoint between the present approach, which focuses on average behavior of an ion ensemble, and others that concentrate on the individual trajectories of single (or multiple) ions.
- The moment equations can be solved directly (ordinarily, by numerical means) for the average ion velocity and effective temperature as a function of position and time, and then used to determine the ion number density. However, they cannot reveal any positional or temporal information for a single ion (as is produced in the standard output from the widely used ion trap simulation program ITSIM⁷). Conversely, many individual ion trajectories must be simulated and the resulting data collected and post-processed outside that program to yield similar ensemble average and number density information.
- The differences between the results obtained with the different collision models are generally small for heavy ions in light gases; even significant differences in the collision frequency have only a small influence on the overall ion behavior in the trap. This reflects the facts that the collision frequencies for momentum transfer are small compared to the RF frequency, and that the transfer of energy from heavy ions to light neutrals is small in each collision.
- The results in first approximation are expected to be accurate, both by analogy with other cases for which the momentum-transfer theory has proven accurate and due to the good agreement obtained when compared with ITSIM simulations. However, should higher accuracy be desired, the two-temperature theory provides a series of successive approximations for further improving its accuracy.
- In future papers we expect to extend this work to include space charge effects by including Poisson's equation. We also intend to consider other devices including stretched quadrupole traps and linear traps.

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