A Monte Carlo simulation of ion transport at finite temperatures

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Abstract
We have developed a Monte Carlo simulation for ion transport in hot background gases, which is an alternative way of solving the corresponding Boltzmann equation that determines the distribution function of ions. We consider the limit of low ion densities when the distribution function of the background gas remains unchanged due to collision with ions. Special attention has been paid to properly treating the thermal motion of the host gas particles and their influence on ions, which is very important at low electric fields, when the mean ion energy is comparable to the thermal energy of the host gas. We found the conditional probability distribution of gas velocities that correspond to an ion of specific velocity which collides with a gas particle. Also, we have derived exact analytical formulae for piecewise calculation of the collision frequency integrals. We address the cases when the background gas is monocomponent and when it is a mixture of different gases. The techniques described here are required for Monte Carlo simulations of ion transport and for hybrid models of non-equilibrium plasmas. The range of energies where it is necessary to apply the technique has been defined. The results we obtained are in excellent agreement with the existing ones obtained by complementary methods. Having verified our algorithm, we were able to produce calculations for Ar\textsuperscript{+} ions in Ar and propose them as a new benchmark for thermal effects. The developed method is widely applicable for solving the Boltzmann equation that appears in many different contexts in physics.

1. Introduction

Non-equilibrium plasmas are used in a broad range of applications that include plasma etching \cite{1,2}, biomedical applications \cite{3,4}, nanotechnologies \cite{5,6} and microdischarges \cite{7}. Development of devices based on non-equilibrium plasmas is quite expensive and cannot be based on empirical methods; therefore predictive accurate models have to be developed \cite{1,8}.

Ion transport coefficients are used as input parameters in both fluid and hybrid models of plasmas \cite{1,9–13} relevant for the applications mentioned above. Indirectly, transport coefficients can be used to verify the completeness and the absolute magnitude of the cross sections in the sets \cite{1,9} that are to be used in Monte Carlo (MC) and particle-in-cell models of plasmas \cite{14,15}. There is a critical shortage of data for ions in most gases that are interesting for applications \cite{16}.

In addition, there is a pressing need to have both accurate and efficient algorithms for simulation of ion motion. For example, even in hybrid models, which were developed to take into account the non-local transport of electrons, more and more frequently ions and even fast neutrals are treated by a MC technique \cite{13,17–19}. The procedure developed in the present paper is quite general for all externally driven particles in background gases that are at non-zero temperatures. We primarily focus on ions because they have energies close to the thermal energy over a wider range of reduced electric fields, although the same effects of the motion of background particles exist for electrons and neutral particles.

The standard theory of ion transport is well established and is now standard in textbooks \cite{20}. More recently, some important developments have been achieved, which include application of transport theory to gas-filled ion traps \cite{21}, radiofrequency–current-driven transport of ions \cite{22,23},...
general discussions of transport in crossed electric and magnetic fields [24] and transport data and cross sections [25].

1.1. Boltzmann equation and the distribution function

In the following we will consider ions that are driven by an external electric field through the neutral background gas. Their transport coefficients can be easily calculated once the distribution function is known. The latter is determined by the Boltzmann equation (BE) [26] for ion–neutral gas collisions, which reads

$$\frac{\partial f(x, v, t)}{\partial t} + v \nabla_x f(x, v, t) + \frac{E_x}{m} \nabla_v f(x, v, t) = \int \sigma_d(\theta) |v - u| \left[ f(x, v', t) F(u') - f(x, v, t) F(u) \right] \, d\Omega \, du.
$$

(1)

Here $f(x, v, t)$ and $F(u)$ are the distribution functions of ions and of the neutral gas, respectively, $m$ is the mass of ions, $d\Omega = \sin \theta \, d\theta \, d\psi$ is the solid angle and $\sigma_d((v - u)|\theta)$ is the total differential cross section for ion–neutral gas collisions. The angle $\theta$ denotes the angle of rotation of the relative velocity of collision particles before and after the collision. The postcollision velocities $v'$ and $u'$ are determined by the momentum and energy conservation laws from the precollision velocities $v$ and $u$. The external force is denoted by $E_x$. In (1) we assume that the neutral gas is homogeneous and that its distribution function does not significantly change due to collisions with ions.

The collision integral of the BE (right-hand side of (1)) is a functional that depends on the distribution functions of both ions and the background gas and also depends on the total cross section for their collisions. Since realistic cross sections are almost always complicated functions of the relative velocity ion–neutral gas, direct solution of the BE is often quite complicated, apart from some model cross sections. Instead of solving the BE an alternative route to determine the ion distribution function and their transport parameters (e.g., the mean energy, the drift velocity, the diffusion coefficients) is by an MC simulation where one simulates real physical processes and follows the temporal evolution of ions. Since the initial conditions for ions are arbitrary, the system should evolve for some time until the stationary regime is achieved, when the distribution function of ions becomes time independent. After the system has relaxed, it is quite a simple task to directly sample all ion properties in a simulation. Due to the stochastic nature of the MC method, an average over many uncorrelated measurements is necessary.

The first attempt to apply a MC simulation for ions in gases was made by Wannier [27]. Here we will briefly describe the technique. In the simulation we follow the evolution of a certain number of ions that collide with the background gas. For low ion densities, the interaction among ions is usually neglected and only the interaction with the host gas is taken into account. Different atomic processes between ions which collides with host particles are taken into account through the set of cross sections. The total cross section defines the collision frequency $\nu(v)$, which is a function of the ion velocity $v$. The time between successive collisions of an ion with host particles is stochastically determined knowing the collision frequency. Since for low densities of host gases, the ion mean free path is much larger than the thermal de Broglie wavelength (we consider not very low temperatures), the ion propagates between collisions according to the laws of classical mechanics. Consequently, quantum mechanics is contained only in the cross sections. The act of collision with a host particle is treated using the conservation laws and also the information from the differential cross sections about possible anisotropies of the direction of an ion after the collision. More details about the MC technique one can find, for example, in the review [28].

When calculating properties of ions that move in a neutral host gas using MC simulation [29] or momentum transfer theory [30], it is very often assumed that the particles of the neutral gas are at rest. This is a reasonable approximation when the mean ion energy significantly exceeds the thermal gas energy. Then the collision frequency takes a simple form (see equation (6) below). However, this approximation is not justified for low electric fields, when the mean ion energy is comparable to the thermal energy. In this case the motion of the host gas particles should be taken into account and the collision frequency has to be calculated more accurately, taking into account the thermal motion of gas particles. At this point we want to emphasize that in MC simulations we only follow the evolution of ions in time, since it is assumed that their motion does not significantly change the distribution function of the background gas particles, i.e. gas heating effects are neglected. All properties of the host gas particles are determined by their distribution function. If, however, there is a significant gas heating due to current flow, which is relevant for higher current discharges, the background gas may be at a considerably higher temperature. This would only extend the need to apply our technique but in that case the calculation of the temperature would have to be done in a self-consistent manner according to the experimental conditions.

One of the first papers that addressed the question of thermal effects of the background gas was that of Lin and Bardsley [31]. They used an approximate treatment and sampled the velocities of the host gas directly from the gas distribution function when an ion collided with a host particle. This procedure is not entirely correct, since during the process of MC simulation, at the moment when an ion of velocity $v$ collides with a gas particle of velocity $u$ is not only a function of the gas distribution function, but also depends on the cross section and the relative velocity (see (18) below). Using the gas distribution function for sampling the gas velocities is an approximation that leads to systematic errors in the results, as we demonstrate explicitly in an example; see section 3.1 and figure 6 below. The most dramatic consequences of wrong sampling of the background gas velocities are the absence of equilibration at vanishing electric field as well as the wrong ratio between the diffusion coefficient and mobility.

The rest of the paper is organized in the following way. In section 2 we derive and analyse an explicit expression for the collision frequency. We derive an asymptotic formula for the collision frequency which is valid for large ion velocities.
with respect to the background gas thermal velocity. In section 3 we emphasize a proper way of sampling velocities of the background gas, define the corresponding probability functions and propose the rejection methods for sampling background gas velocities from that distribution. The rejection methods depend on the specific form of cross section and we consider the two most common cases. In section 4 we describe the procedure for thermal gas effects in the case of mixtures and benchmark results are given in section 6, which is followed by the conclusions.

2. Collision frequency

The collision frequency for an ion of velocity \( v \) in a neutral background gas is [26]

\[
\nu(v) = n \int \sigma(|v - u|)|v - u|F(u) \, du,
\]

where \( n \) is the gas density and \( \sigma(|v - u|) \) is the total cross section for ion–neutral gas scattering processes as a function of relative velocity, obtained by integrating the total differential cross section introduced in (1) over the solid angle. Having in mind that the collision frequency should be calculated for many different ion velocities and that the form of cross sections is in general a complicated expression, one needs to be able to calculate (2) very efficiently. In addition, one should be aware that ions have thermal energies for a very wide range of reduced fields covering most practical discharges.

In principle, equation (2) is a simplification in the sense that at this point we deal with the total cross section. However, the point that (2) contains the total cross section rather than the differential present in (1) is due to the fact that the angular dependence in \( \sigma^d(|v - u|, \theta) \) could be integrated out from quantities that do not depend on the postcollision velocities. While the BE (1) does depend on the latter, and we have to deal with the differential cross section, the collision frequency does not and we could deal with the total cross section. The angular dependence determined by \( \sigma^d \) is taken into account later for the kinematics, when the angle of scattering is determined. In some systems when the force is not central, a more complex form of dependence on the vector of the relative speed may be required. However, the complex form of interaction is often not found in the species used for processing plasmas. In this paper we use the model of anisotropy proposed by Phelps [32] for argon ions, which is not as detailed as using the complete differential cross section but is sufficiently simple to be applied in plasma modeling and yet reproduces all the important features of ion transport with high accuracy. However, our approach is not limited to that simplified approach and one could use arbitrary differential cross sections.

Different approaches for the calculation of the collision frequency can be found in the literature. In [33] calculation of the integral in (2) is performed by numerical integration using an MC integration technique. While being simple, this technique is not a very efficient algorithm, and its accuracy could be improved at the expense of efficiency. Another approach is proposed in [34] where the authors treat the problem in a mean field-like approach. They define the mean relative velocity, which becomes the argument of the cross section. Taking the cross section outside the integral, the remaining integral in (2) is easily calculated. In this paper we have set out to find an accurate and efficient algorithm which may be used for MC simulations of ions (as well as electrons). In doing so we should remember that most cross sections are defined numerically at a limited number of points and that linear interpolation between those points is often used. Using this, we have developed an MC simulation which is used to propose benchmark calculations for ion motion in their parent gas at non-zero temperatures.

Explicit calculation of the collision frequency (2) is only possible for specific cross sections and gas velocity distribution functions. In the following we will assume that the background gas is in equilibrium at temperature \( T \), so is described by a Maxwell velocity distribution function (MVDF)

\[
F(u) = \frac{1}{(\pi w^2)^{3/2}} \exp\left(-\frac{u^2}{w^2}\right),
\]

where the most probable gas thermal velocity is \( w = (2kT/M)^{1/2} \), \( M \) is the mass of the gas particle, \( k \) is the Boltzmann constant and \( T \) the temperature. After angular integration, expression (2) transforms into

\[
\nu(v) = \frac{n}{\sqrt{\pi w^4}} \int_0^{+\infty} dx \sigma(x)x^2 \times \left\{ \exp\left[-\frac{(x-v)^2}{w^2}\right] - \exp\left[-\frac{(x+v)^2}{w^2}\right] \right\}.
\]

A similar expression may be derived for the ion velocity identically equal to zero, but this case is not encountered in realistic simulations and will not be considered explicitly here. One can alternatively determine \( \nu(0) \) as the limiting case \( v \to 0 \) of (4).

It is possible to convert the integral of the type (4), to give the following expression for the collision frequency when ion velocities are much greater than the thermal gas velocity (see the appendix for details):

\[
\nu(v) = n\sigma(v)v \left(1 + \frac{w^2}{v^2} \frac{\sigma(v)_v}{4\sigma(v)} + \cdots \right).
\]

We see that the first-order correction is proportional to the square of the ratio \( w/v \), which determines the criterion for importance of the thermal background gas motion. The collision frequency for cold gas \( (w = 0) \) is a special case of (5), when we obtain

\[
\nu(v) = n\sigma(v)v.
\]

This formula is very widely used in MC simulations, for example in [29, 35, 36] even though it is not applicable at low ion energies and at non-zero temperatures. Here we mention that the range of applicability of the previous expressions for the collision frequency is the same as for the standard transport theory with well isolated single collisions. At very
high pressures multiple collisions may become important and treatment of such processes requires additional assumptions.

For further evaluation of (4) we need a specific form of the cross section. Realistic cross sections are always tabulated as functions of incident ion energies (or velocities) or relative energies (velocities). In principle it could be argued that the cross sections are often tabulated as constant values in narrow energy bins so the solution for a constant cross section may be sufficient. However in the low-energy limit the cross sections often increase rapidly and application of a constant cross section may require application of a large number of energy bins. At the same time usually the data for the low energy limit of mobilities is available and thus one needs accurate and efficient schemes for calculation in this energy range. Thus we assume quite generally that the cross section, given as a function of the relative ion–neutral velocity x, may be expressed as

\begin{equation}
\sigma(x) = \begin{cases} 
\sigma_i^2 \left( \frac{x}{v} \right)^2 + \sigma_0^2 \left( \frac{x}{v} \right) + a_i^0, & 0 \leq x \leq x_1 \\
\sigma_i^2 \left( \frac{x}{v} \right)^2 + \sigma_i^1 \left( \frac{x}{v} \right) + a_i^2, & x_1 \leq x \leq x_2 \\
\sigma_i^2 \left( \frac{x}{v} \right)^2 + \sigma_i^1 \left( \frac{x}{v} \right) + a_i^0, & x_{i-1} \leq x \leq x_i \\
\varepsilon & 
\end{cases}
\end{equation}

This expansion is merely a polynomial expansion used for tabulation of the data in the code extending the usually implemented procedure to use constant cross sections in each of the energy bins. This expansion allows three terms all of which may provide analytic solutions later to facilitate the speed of implementation. The expansion is intended to be used in (2) and here x is the relative velocity while v is the velocity of the ion.

Taking into account (7) we can define integrals which originate in (4) as

\begin{equation}
I_j^\pm(v, w, x_0, x_1) = \int_{x_0}^{x_1} dx \frac{x^{2+j}}{\sqrt{\pi}w^2 v^{2j}} \exp \left[ - \left( x \pm \frac{v}{w} \right)^2 \right],
\end{equation}

with j = 0, 1, 2. These integrals can be calculated analytically, and in terms of the variables \(a_i^\pm = (x_i \pm v)/w\) they read

\begin{align*}
I_0^\pm(v, w, x_0, x_1) &= \frac{1}{4} \left(2 + \frac{w^2}{v^2}\right) \left[ \text{erf}(a_i^\pm) - \text{erf}(a_0^\pm) \right] \\
&+ \frac{1}{2\sqrt{\pi}} \frac{w^2}{v^3} a_0^0 \exp(-a_i^0) - \frac{1}{2\sqrt{\pi}} \exp(-a_i^0),
\end{align*}

\begin{align*}
I_1^\pm(v, w, x_0, x_1) &= \frac{1}{4} \left(2 + 3 \frac{w^2}{v^2}\right) \left[ \text{erf}(a_i^\pm) - \text{erf}(a_0^\pm) \right] \\
&+ \frac{1}{2\sqrt{\pi}} \frac{w^2}{v^3} \left[ \frac{3}{v} + \frac{w^2}{v^2} a_0^0 + \frac{3}{v^3} w^3 (1 + a_0^2) \right] \\
&+ \frac{1}{2\sqrt{\pi}} \exp(-a_i^2) \left[ \frac{3}{v} + \frac{w^2}{v^2} a_0^2 + \frac{3}{v^3} w^3 (1 + a_0^4) \right].
\end{align*}

Now, the collision frequency (4) can be easily calculated as

\begin{equation}
v(v) = \sum_{j=0}^{\infty} n j a_j \left[ I_j^+(v, w, x_1, x_{i+1}) - I_j^-(v, w, x_i, x_{i+1}) \right].
\end{equation}

We note that this sum is made over all values of the index i, i.e. for all relative velocities x, but in practical applications the situation is different. Integrals (8) are homogenous functions of their arguments of order zero, and we will now consider some of their general properties. Under the conditions \(v \geq 6w\), \(x_0 = 0, x_1 = \infty\), the integrals satisfy

\begin{equation}
I_1^+, I_2^+, I_2^- \ll 10^{-20},
\end{equation}

\begin{equation}
I_1^-, I_2^- \approx 1.
\end{equation}

Also, under the conditions \(v \geq 6w, x_0 \geq v + 6w, x_1 \geq x_0\), the integrals satisfy

\begin{equation}
I_0^-, I_1^-, I_2^- < 2 \times 10^{-16}.
\end{equation}

In other words, the integrals decrease very rapidly as v increases. For double precision when the machine accuracy is \(~10^{-16}\) and a given ion velocity \(v \geq 6w\), it is enough to integrate over the relative velocities up to \(v + 6w\). Moreover, because of (13) and (14), the expansion (5) converges very rapidly. For ion velocities which are less than \(6w\) similar consideration can be made. One can conclude that the upper limit for integration in (8) should be at most 12w.

2.1. Constant cross section

For a constant cross section \(\sigma_0\), from (4), (7) and (9) we obtain the collision frequency for hard sphere scattering (which was previously found and used in [37]):

\begin{equation}
v(v) = n \sigma_0 w \left( \frac{v}{w} + \frac{w}{2v} \right) \text{erf} \left( \frac{v}{w} \right) + \frac{1}{\sqrt{\pi}} \exp \left[ - \left( \frac{v}{w} \right)^2 \right].
\end{equation}

Either using (5) or expanding the previous equation for small ratio \(w/v\), the collision frequency (16) may be approximated by

\begin{equation}
v(v) \approx n \sigma_0 v \left( 1 + \frac{w^2}{2v^2} \right).
\end{equation}
One can note that, according to (5), in the case of a constant cross section, only the first-order power law correction exists.

### 2.2. Realistic cross sections

Calculations of the collision frequency are also done for a realistic cross section [32] for $\text{Ar}^+$ ions in their parent gas. In figure 1 we show the collision frequency calculated using different methods. The exact calculation using the functional form of the cross section from [32] in the definition (2) and the calculation based on equation (12) are essentially identical on the scale of the figure. We can see that the approximate formula from [34] (the dashed line) should be improved further (toward the solid line). Formula (6) for the cold gas approximation (the dashed–dotted line) is obviously inaccurate. However, it could be resolved by the analytic correction in (5) (for illustration, the correction is showed $v > 2w$). The relative difference between the exact formula (4) and formula (5) is less than $1.3 \times 10^{-3}$ for $v > 2w$, and less than $7.2 \times 10^{-6}$ for $v > 6w$. Having in mind that the relative difference between the exact formula and the cold gas approximation (6) even at $v = 18w$ is greater than $10^{-3}$ and increases with decreasing $v$, we may conclude that the corrected form of the calculation is necessary. For the large $v/w$ limit and in order to save computational time the analytic form (5) of the correction term is very useful and sufficiently accurate for all practical purposes.

The main point of this paper is to provide a technique to treat thermal collisions and then to provide benchmark results to test other codes. Thus we do not offer detailed discussions on the ion transport in argon and we do not discuss relative merits of different sources or experimental data or the subsequent analysis as we could add very little to that which is provided in [20, 32] and other relevant papers.

### 3. Gas velocity distribution in collisions with ions

When ions collide with gas particles, special attention must be given to the statistical properties of gas particles which collide with a particular ion. Naively, one would think that statistical properties of gas particles which collide with an ion of a given velocity are independent of that velocity and of the cross section. This is not entirely correct, as we already explained in the introduction. However, it has been customary in the literature [36, 38] to sample gas velocities directly from the gas velocity distribution function for use in MC simulations. This leads to inaccuracy, especially for small energies of particles.

The error in sampling velocities from the gas velocity distribution function $F(u)$ and from applying them in the collision kinematics may be small or compensated for by other effects. Still, this is a systematic error and one can never be sure how big the uncertainty is and whether it may become important under certain circumstances. We will see later that such a procedure leads to results that are obviously wrong: at zero field and when the gas is described by the MVDF, the mean ion energy is smaller than the gas thermal energy and the ratio $eD_I/(kT_I)$ is not equal one, as it should be (see figure 6).

While most authors use the cold gas approximation and study mainly higher energies, some have attempted to obtain a more accurate method of calculating the distribution function of the collision frequency in their calculations [33, 34, 37].

The probability density per unit time for the collision of an ion of velocity $v$ with a gas of velocity $u$ is given by

$$p(v, u) = \frac{n\sigma (|v| - |u|)}{v(v)} F(\nu(v)), \quad (18)$$

where $F(u)$ is the gas velocity distribution function and $v(v)$ is the collision frequency, see equation (2). This is a conditional probability. The velocity of the gas particle $u$ depends on the ion velocity $v$ as well as on the total cross section.

A randomly chosen gas velocity should be chosen according to the probability density given by (18). The method for the gas velocity sampling generally depends on the shape of the cross section. A possible way to do it is to use the rejection method [39] which is easy for implementation, but is often not efficient. Nevertheless, it is very hard to develop an efficient and quite general method for sampling for a wide range of possible cross section shapes, so the rejection method is very often the method of choice. For some special cases, like the constant cross section, one could furthermore transform equation (18), which we consider in the next subsection.

Two different implementations of the rejection method for (18) are obvious. The first one is as follows. Let $q_{\text{max}}$ be the maximum of $\sigma (|v - u|)/|v - u|$ for all allowed $v$ and $u$ (which are specified at the beginning of the simulation). This maximum can be chosen as

$$q_{\text{max}} = \sqrt{27u^2 + 6v^2 + v^2} \cdot \max_{v, u} \sigma (|v - u|). \quad (19)$$

The sampled velocity $u'$ from the MVDF is accepted as the background velocity if

$$\sigma (|v - u'|)|v - u'| > rq_{\text{max}} \quad (20)$$
Figure 2. Probability density of the sampled gas velocity \( u \): the case of zero ion velocity \( v = 0 \) is shown by a dashed line, the case \( v = w \) is shown by a dotted line. MVDF is represented by a solid line. When one samples gas velocities in an approximate way from MVDF, on average one always samples smaller velocities than by using the correct formula, which does not lead to the thermalization of ions at vanishing electric field, as confirmed in the next section.

Figure 3. Probability density of the azimuthal angle \( \theta \) in the case \( v = 0 \), dashed line; \( v = w \), dotted line; \( v = 5w \) or \( w = 5v \), solid line; \( v = 2w \) or \( w = 2v \), dashed-dotted line.

Angular distribution may also be obtained from expression (18). It is easy to see that the polar angle distribution is uniform, but the azimuthal angle distribution normalized by \( \sin \theta \) is nonuniform. Azimuthal angular dependence for a given ion velocity \( v \) and gas velocity \( V \) is

\[
p(\theta) = \frac{3wV (v^2 + V^2 - 2vV \cos \theta)^{1/2}}{(v + V)^3 - |v - V|^3},
\]

where \( \cos \theta = vV/(vV) \). In figure 3 we see that the uniform (isotropic) normalized azimuthal angle distributions correspond to the case of zero ion velocity and also to the case when ion velocity is much higher than the thermal velocity of the background gas. In the case \( v = w \) we have the highest anisotropy and angles closer to \( \pi \) are more probable. As the ratio \( v/w \) increases or decreases the angular distribution approaches the uniform case. Had we sampled the gas velocity from the gas velocity distribution function, we would have obtained uniform azimuthal distribution, since the gas velocity distribution function is uniform in space. We may conclude that all deviations made by not using the probability density (18) lead to systematic errors, both in magnitudes of sampled gas velocities and azimuthal distributions.

3.1. Constant cross section

In this subsection we will practically demonstrate artifacts of not using expression (18) for determination of background gas velocities when they collide with an ion of a given velocity.

In the case of a constant cross section \( \sigma \), expression (18) can be integrated analytically, and the probability density per unit time for the collision of an ion of velocity \( v \) with a gas of velocity \( u \) is

\[
p_\infty(v, u) = \frac{n\sigma_0}{v(v)} 4\exp\left(-\frac{u^2}{w^2}\right) \frac{u}{w} \left(3\frac{u^2}{w^2} + \frac{v^2}{w^2}\right), \quad (21)
\]

\[
p_{\infty}(v, u) = \frac{n\sigma_0}{v(v)} 4\exp\left(-\frac{u^2}{w^2}\right) \frac{u^2}{w^2} \left(\frac{u^2}{w^2} + 3\frac{v^2}{w^2}\right), \quad (22)
\]

where \( p_{\infty}(v, u) \) applies for velocities \( v < u \) and \( p_{\infty}(v, u) \) for \( v > u \) and \( v(v) \) for constant cross section is given by (16).

In figure 2 we show the probability density of the sampled gas velocities for two different ion velocities in comparison with the standard MVDF. We see that, with an increasing ion velocity, we approach the MVDF. For ion velocities of the order of the thermal gas velocity \( w \) and smaller, sampled gas velocities are considerably shifted toward higher velocities (with respect to the MVDF).

4. Mixtures of gases

If the background gas of density \( n \) is a mixture of \( k \) gases with relative densities \( \alpha_i, \sum_{i=1}^{k} \alpha_i = 1 \), the collision frequency (4) becomes

\[
v(v) = \sum_{i=1}^{k} \alpha_i v_i(v), \quad (24)
\]

\[
v_i(v) = n \int \int \sigma_i (|v - u|) |v - u| F_i(u) \, du, \quad (25)
\]

where \( F_i(u) \) is the gas velocity distribution (which has the same functional form for all gas components if the background gas is in equilibrium; the difference is only in the value of the thermal velocity due to different masses) and \( \sigma_i \) is the ion-neutral cross section of the component \( i \). Expression (25) can
be easily calculated having in mind the previously described procedure for a pure background gas.

Probability density per unit time for collisions of ions of velocity \( v \) with a gas particle of velocity \( u \) is given by

\[
p(v, u) = \sum_{i=1}^{k} w_i \frac{n_{ci} (|v - u| |v - u| F_i(u))}{v(v)} ,
\]

(26)

\[
w_i = \frac{\alpha_i v_i(v)}{v(v)} .
\]

(27)

Sampling a uniform number in accordance with weighting factors \( w_i \), we first determine the constituent of the mixture with which the ion of velocity \( v \) collides, and then we sample the velocity \( u \) of that constituent from the appropriate probability density [39]. Using the equations from this subsection and the results from the rest of the paper it is a straightforward procedure to consider thermal gas effects in mixtures of background gases.

5. Some details of an MC simulation

In this section we provide some details of an MC simulation that is intended to be used as a solver for the BE (1). While the procedure is well known and documented in the literature [28], some details are in order. First we derive the expressions for collision kinematics, since we have not found compact and simple formulae in the literature that are valid for particle collisions of arbitrary masses and inelastic processes. We then briefly describe the procedure of the simulation.

5.1. Collision kinematics

We consider two particles of masses \( m \) and \( M \) which collide. We assume that they have velocities \( v \) and \( V \), respectively with respect to the laboratory coordinate system with \( e_x, e_y \), and \( e_z \). Assuming momentum is conserved during the collisions, the postcollision velocities are

\[
v' = v - \frac{M}{m + M} (g - g'),
\]

(28)

\[
V' = V + \frac{m}{m + M} (g - g'),
\]

(29)

where

\[
g' = g' e_x' = v' - V' = \sqrt{(v - V)^2 - \frac{2E}{\mu} e_x'}.
\]

(30)

\[
\mu = \frac{MM}{m + M},
\]

(31)

\[
v_z = \frac{me + MV}{m + M},
\]

(32)

\[
g = v - V,
\]

(33)

while \( E \) is the inelastic threshold. In the case of isotropic scattering \( e_x' \) is the isotropic unit vector which in simulation may be chosen using the algorithm proposed in [40].

In the case of anisotropic scattering let \( \chi \) and \( \psi \) denote the azimuthal and polar angles of the relative particle velocity after collision with respect to the velocity before collision, see figure 4. We have \( gg' = gg' \cos \chi \). While the polar angle is completely undetermined in the simulation it is determined by the differential cross section. In the simulation, it is obtained as a solution of the equation

\[
\int_0^{\pi} \sigma^d(v, \chi) \sin \chi d\chi = r,
\]

(34)

where \( r \) is a uniform random number from \([0, 1]\), and \( \sigma^d(v, \chi) \) is the differential cross section.

Having the angles \( \psi \) and \( \chi \), it is not a difficult task to determine \( g' \) as a function of the angles and the relative velocity before the collision \( g \). Using that the unit vectors orthogonal to \( e_x = (g_x, g_y, g_z)/g \) are \( e_1 = (g_x, g_y, g_z, -g_x^2)/(gg_z) \) and \( e_2 = (-g_y, g_x, 0)/g_z \), we have \( h = ge_1 + g \sin \psi e_2 \), and \( g' = g' \cos \chi e_x + g' \sin \chi e_y \), see figure 4.

Therefore, the postcollision velocities read

\[
v' = v - \frac{M}{m + M} \left( g - \frac{g'}{g} (h \sin \chi + g \cos \chi) \right),
\]

(35)

\[
V' = V + \frac{m}{m + M} \left( g - \frac{g'}{g} (h \sin \chi + g \cos \chi) \right),
\]

(36)

where \( h \) has components

\[
h_x = (g_x g_z \sin \psi - gg_z \cos \psi)/g \rho,
\]

(37)

\[
h_y = (g_y g_z \sin \psi + gg_z \cos \psi)/g \rho,
\]

(38)

\[
h_z = -g \rho \sin \psi,
\]

(39)

\[
g \rho = \sqrt{g_x^2 + g_y^2}.
\]

(40)

Equivalent expressions for the case of purely elastic scattering \((E = 0)\) can be found in [28].
In order to solve the BE (1) and determine the distribution function of ions $f(x, v, t)$ one follows the evolution of an ion (or certain number of them). Once the ions relax one performs measurement of their velocities and positions, from which one produces the required information (such as the energy, the diffusion coefficients and the distribution function, etc) that has to be averaged over many uncorrelated measurements.

In the following we consider a single ion. Knowing the collision frequency (2) as a function of the ion velocity $v$, one (stochastically) determines the time of its evolution before a collision with the neutral gas particle takes place. The evolution between collisions is purely classical, determined a collision with the neutral gas particle takes place. The probability density that an ion that starts evolution at moment $t = 0$ will suffer a collision with a background gas particle after the time $t$ is given by [28]

$$p(t) = v(t) \exp \left[ - \int_0^t dt' v(t') \right]. \quad (41)$$

Once the probability density for a collision is known, the time for ion evolution is fully determined. The most direct way to determine $t$ is by solving the equation

$$\int_0^t dr' \, p(r') = r, \quad (42)$$

where $r$ is a uniform random number from $[0, 1]$. Since the ion velocity is a function of time, integration of the previous equation is possible. In practice one often applies different methods for sampling $t$ from (41). One of the most important ways, so-called the null-collision method [41], is the simplest rejection method [39]. After the time of free evolution $t$ the ion collides with a gas particle. At that moment we do need the velocity $u$ of the gas particle that collides with the ion having velocity $v(t)$ and that is determined by the probability density (18). The method for sampling $u$ from (18) is described in section 3. Knowing the precollision velocities, we determine the postcollision velocities as described in the previous subsection. Since we do not follow the evolution of gas particles, we actually need only the ion velocity after the collision.

The above procedure of evolution of a single ion and its collision with a gas particle is repeated over many collisions until the required precision of results is obtained. The flowchart is given in figure 5.

6. Results of MC simulation

We have developed a new MC simulation code for ion transport in a background gas in an external electric field using the methods described in the previous sections. The code was required to pass all the benchmark test calculations that are available for a zero gas temperature. We implemented in the code a procedure for collision frequency calculation and for sampling the gas velocity as described in this paper. The number of benchmark results that could be used to test the non-zero gas temperature calculations that are available in this literature is very small. Thus we have tried to produce new values while at the same time repeating the available benchmark results.

There are several sources for benchmark calculations for ions [29, 42], but we found that only [43] does not use the cold gas approximation while providing a range of results that may be used to test the code.

Numerical results of simulations in the case of a constant cross section for two ion–gas mass ratios are presented in table 1. There we compare our results with the BE results of White et al [43]. In the case of a small ion–gas mass ratio and a constant cross section the MC simulation takes a long time because of very slow relaxation of ion transport properties (very inefficient energy transfer from the ion to the gas particle in elastic scattering because of the low mass ratio), and our results are less accurate than those for equal masses. Nevertheless, our results are in excellent agreement with those from the numerical solution of the BE [43].

In figure 6 we show results from the simulation for different electric fields. We applied different sampling procedures for the background gas: from the correct formula (18) and directly from the gas velocity distribution function (which is assumed to be MVDF). One can see that thermal equilibrium (at zero field) cannot be achieved when the background velocities are not sampled in a proper way: the mean ion energy is lower than the thermal energy $kT/2$ and the characteristic energy $eD_f/\mu$ is lower than $kT$.

In figure 7 we show results for reduced mobilities for Ar$^+$ ions in their parent gas using a set of cross sections from [32]. One can see that measured values at 293 K [44] are in excellent agreement with our calculated values, while measured values at
Table 1. Results for the ions with a hard sphere cross section model for $m_{\text{gas}} = 4$ amu, $T = 293$ K, $E/n = 1$ Td, $\sigma_0 = 6 \times 10^{-20}$ m$^2$. The first column contains the results for $T = 0$ for comparison.

| $m_{\text{ion}} = m_{\text{gas}}$ | $m_{\text{ion}} = 10^{-4}m_{\text{gas}}$ |
|-----------------------------------|------------------------------------------|
| $T = 0$                           | $T = 293$ K                              |
| Results from [43]                 | Results from [43]                        |
| $\varepsilon$ (eV)                | 0.01962 0.04271 0.04271                  | 0.7332 0.73324 0.73324 |
| $W$ (10$^2$ ms$^{-1}$)            | 7.270 3.367 3.368                       | 56.27 56.187 56.187 |
| $nD_L$ (10$^{22}$ (ms$^{-1}$)     | 0.233 0.885 0.884$^a$                   | 155 158.27 158.27 |
| $nD_T$ (10$^{22}$ (ms$^{-1}$)     | 0.338 0.894 0.894$^a$                   | 315 313.20 313.20 |
| $T_L$ (10$^2$ K)                  | 0.5664 3.074 3.074                      | 56.70 56.717 56.717 |
| $T_T$ (10$^2$ K)                  | 0.8762 3.220 3.220                      | 56.72 56.727 56.727 |

$^a$ Note an error of a factor 10 in the original data from [43].

Figure 6. Mean ion energy, drift velocity, longitudinal and transverse diffusion coefficient and transverse diffusion coefficient over mobility as a function of reduced electric field for a hard sphere model for $m_{\text{ion}} = m_{\text{gas}} = 4$ amu, $T = 293$ K, $\sigma_0 = 6 \times 10^{-20}$ m$^2$ for different sampling procedures of velocity of background gas: from expression (18)—solid line; from MVDF—dashed line. In the third figure, the upper curve corresponds to $nD_T$ and the lower to $nD_L$, i.e. $D_T > D_L$ is satisfied.

77 K [45] are slightly lower than calculated. This may indicate the need to make some small adjustments to the cross section in the low energy limit. We should mention that measurements of Basurto et al [46] agree very well with those of Helm and with our calculations.

In table 2 we tabulate the results for Ar$^+$ ions in their parent gas which may be used as benchmark results for verification of MC codes or other techniques which take into account thermal effects of the background gas. We should mention that relative differences between results for two choices of parameters $m = 2$ and $m = 2.3$ (defined in [32]) are less than one per cent, and only the results for $m = 2$ are presented here.

In [34] an approximate calculation of the collision frequency was carried out in an attempt to properly include the thermal collisions. The difference in the collision frequency is appreciable, as can be seen in figure 1, although it is an improvement on the cold gas approximation. If we compare our results with the data from the analytic formula for the drift velocity given in [34], the differences are up to 10% in the low $E/n$ range. Results for the hard sphere for $T = 0$ K are included in table 1. These values are only for 1 Td and the mean energy would differ even more at lower $E/n$. The mobility already differs by a factor of two. As for argon, the effect of $T = 0$ approximation can be estimated by comparing 77 and 293 K results. The mean energy will continue to decrease going toward zero and the difference in mobility under those conditions in the case of argon could be as large as 30%.
One can see that the mobilities decrease with increasing temperature.

7. Conclusions

We have developed an accurate and efficient algorithm for calculating the collision frequency in the case when thermal motion of background gas cannot be neglected for a Maxwellian velocity distribution of the background gas particles. This is required for low energy simulations of ion transport using an MC technique or for implementation of hybrid and particle-in-cell codes [35, 47]. Exact formulae are derived for very general cross section dependences on relative velocity. Also, an analytic form of the correction terms in the collision frequency was found, in the case of a large ratio of ion–gas thermal velocities. It was emphasized that sampling of the gas velocity for a given ion velocity (in MC simulations) should be done using an appropriate probability of collisions. Explicit analytic formulae are obtained in the case of a constant cross section, and it was shown that the velocity distribution function of the gas particles which collide with an ion of a given velocity is significantly different from a Maxwell distribution. The results of our MC simulation for ion transport are in excellent agreement with the numerical solution of the BE and may be used as a benchmark for ion transport properties.

In a recent attempt to provide the data for some gases where data were lacking and to go beyond the basic Langevin theory, Nanbu and coworkers have defined the theory in terms of collision probabilities [48–50] rather than cross sections. It may be worth including the currently proposed technique together with their approach, especially since that theory is non-conservative collisions [16, 57, 58].

It is worth noting that so far very accurate numerical techniques for solutions of the BE have been used to study ion transport [20, 51, 52]. Application of MC simulations have not been as widespread for ions as they have been for electrons. This to some degree is due to the problems in representing thermal collisions which are important over a much broader range of \( E/n \). The present technique has already been applied in simulations of the transport of thermal ions [16, 53]. At the same time Boltzmann techniques mostly use interaction potentials to communicate the results to the scientific community. While it is possible to convert interaction potentials to cross sections, it is difficult and may not lead to unique results [54]. Plasma modelers may also have difficulty in appreciating the applicability of certain sets of data for potentials over a wide range of mean energies and values of \( E/n \). Thus it seems better to apply MC simulations to convert the transport data to cross sections as such codes may be directly compatible with plasma models or even more directly applicable to build hybrid models that treat ion transport by MC simulations [13, 17–19, 55, 56].

In general all MC techniques for modeling swarms [57, 58] and discharges would benefit from implementing our procedure. The same is true for hybrid codes [59], particle-in-cell MC models [60] and calculation of the data for global models [61]. Special cases where it is important to include proper treatment of collision frequency in the limit of thermal energies are, for example, modeling of the afterglow or flowing afterglow [62–65] for various applications, the border between the sheath and the bulk of glow discharges (both in direct and in radiofrequency–current regimes), microwave discharges, high and atmospheric pressure discharges [66, 67] including plasmas for medical applications, coronas [68] and gaseous elementary particle detectors [69]. While the surprising behavior of plasma bullets [70] and motion of ionization fronts implies high field regions, these have to be modeled within the field-free background, and for relaxation of the distribution function one needs to implement a technique similar to the one presented in this paper. Thermalization of charged particles in gases, dielectrics, living tissue and atmosphere is of special importance for emerging applications.

The technique described here has been applied in a number of situations during the preparation of this paper. Several publications dealing with different problems were published. While most of them cover the thermal region relatively slightly [16, 53, 71], the results indicate that the code has passed all other tests including those for reactive collisions, for anisotropic collisions and tests against hard sphere benchmarks for very different mass ratios. The code has also been used to show that for ions there are kinetic phenomena dictated by non-conservative collisions [16, 57, 58].

An additional test came from recent studies of thermalization of positrons and positronium [72] where direct sampling of the relative velocity from the gas distribution function proved to give incorrect limits, most importantly the mean energy. Only when the procedure described in this paper is employed have the correct limits been achieved [72, 73]. Thus the present results will prove useful in modeling of the effects of positrons in positron emission tomography and positron therapy [74].

The proposed procedure, while somewhat more complex than the basic MC procedure of [31], is not significantly more demanding in terms of computation time. The only difference is the sampling of the background velocities using the distribution (18). In general the need for data for modeling of plasmas including the low energy limit [57, 58, 75, 76] shows that this procedure should be implemented in all the MC codes when accurate data are required, including the ability to represent spatial and temporal dependences of the field. It is
opportune to note that the procedure in [31] or the cold gas approximation become sufficiently accurate at energies that are several times larger than the thermal energy, in the case of ions in their parent gas. The reason why the problem with the sampling was not found some years ago was that only a few studies were made that focused on very low energies and also because the statistics of simulations were too poor to note the effects.

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**Appendix**

Consider an integral of the form

\[ I = \frac{1}{\sqrt{\pi}} w \int_{-\infty}^{\infty} f(x) \exp \left[ -\left( \frac{x - v}{w} \right)^2 \right] \, dx. \]  

(A1)

Let \( f(x) \) be a function which is continuous and repeatedly differentiable at \( x = v \), and furthermore the integral in (A1) converges. We transform this integral by the substitution \( t = (x - v)/w \):

\[ I = \frac{1}{\sqrt{\pi}} \int_{-\infty}^{\infty} f(v + wt) \exp \left( -t^2 \right) \, dt. \]  

(A2)

After expanding the function \( f(v + wt) \) into a Taylor series

\[ f(v + wt) = \sum_{n=0}^{\infty} \frac{(wt)^n}{n!} f^{(n)}(v), \]  

(A3)

using the formula

\[ \int_{-\infty}^{+\infty} \exp \left( -t^2 \right) = \Gamma \left( n + \frac{1}{2} \right). \]  

(A4)

we obtain the final formula

\[ I = \sum_{n=0}^{\infty} \frac{(w)^n}{4^n n!} f^{(2n)}(v). \]  

(A5)

In the limit of vanishing \( w \), the integral (A1) can be calculated directly using a representation of the delta function

\[ \delta(v) = \frac{1}{\sqrt{\pi}} \lim_{w \to 0} \exp \left( -\frac{v^2}{w^2} \right). \]  

(A6)

When one wants to calculate an integral of the form

\[ I' = \frac{1}{\sqrt{\pi}} w \int_{0}^{\infty} f(x) \exp \left[ -\frac{(x - v)^2}{w^2} \right] \, dx \]  

(A7)

the situation is different. It is hard to obtain a general formula for integral \( I' \), but it is possible to calculate it in cases when the condition \( v \gg w \) holds. In that case the main contribution to \( I' \) comes from points \( x \) which are in vicinity of \( v \), so the lower limit in integral (A7) can be replaced by minus infinity, and \( I' \) is equal to the integral \( I \) up to the exponentially vanishing term:

\[ I' = I + O \left[ \exp \left( -\frac{v^2}{w^2} \right) \right]. \]  

(A8)
