

A parallelized tool to calculate the electrical mobility of charged aerosol nanoparticles and ions in the gas phase.

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Abstract

Electrical Mobility is a transport property that describes a particle behavior in the gas phase. When dealing with the free molecular regime, ascertaining the shape of a nanoparticle or an ion directly from measurements of mobility becomes quite difficult as the particle no longer can be assumed to have spherical shape. Here we propose an efficient parallelized tool, IMoS, that makes use of all-atom models to calculate the mobility of nanoparticles in a variety of gases. The program allows for different types of calculations that range from the efficient Projection Approximation algorithm to the 4-6-12 Lennard-Jones potential Trajectory Method. It also includes a diffuse inelastic simulation that achieves Millikan's predicted 1.36 value over PA. When compared to experimental results, the error of the most efficient calculations is shown to be approximately 2% on average.

Keywords: mobility, IMoS, aerosol, ion, nanoparticle, Trajectory Method, Hard Sphere scattering, EHSS

1. Introduction

Electrical mobility of charged particles in the gas phase is a well-known technique that allows charged particles to be separated by means of an electric field. The mechanism of separation is, in reality, quite simple as it involves using the electric field E and the drag of the particle to reach a drift velocity (terminal velocity), v_d , for which a property of the ion, electrical mobility K , can thus be inferred:

$$v_d = KE \quad (1)$$

While empirically obtaining the mobility of a charged particle can be done effortlessly; assigning a particle shape to this mobility K is quite difficult without proper tools, except when the charged particle is of spherical shape. However, as aerosol scientists begin to study ions and nanometer-sized particles more in detail in the free molecular, non-spherical shapes begin to be more common and thus assigning a spherical shape and a mobility diameter to a charged particle below 100nm is no longer ideal. In fact, the area vs. volume ratio is quite important when considering effects of contamination, optical properties or chemical reactions, and thus a more accurate way of establishing a relation between mobility and shape is necessary.

In this technical note, we present an enhanced numerical tool that allows the user to calculate the mobility of all-atom structures of ions and small nanoparticles with ease in the free molecular regime. This tool has been labeled Ion Mobility Spectrometry Suite (IMoS). IMoS has been redefined to have a parallelized interface for ease of use that can be employed as a learning tool to calculate and understand mobility. It also includes a non-interface version that may be used to submit batches of calculations to a supercomputer. It comes with a comprehensive manual that explains how mobility is obtained and provides detailed examples of how to run its different methods of calculation. A brief explanation of the methods is provided below and results of how the calculation performs are provided in the supplementary information which includes the manual. The software is free to use and may be downloaded from www.imospedia.com.

2. Methods and Discussion

Figure 1 shows the interface of IMoS. In it, the ion and nanoparticle can be loaded and plotted. A series of different methods and gas selections are provided as choices. The calculation of mobility that IMoS performs is based on Mason-Schamp's first approximation of the two-temperature theory[1]:

$$\langle K \rangle_I = \frac{3}{16} \frac{ze}{n} \left(\frac{2\pi}{\mu k_b T_{eff}} \right)^{\frac{1}{2}} \frac{1}{\bar{\Omega}_{T_{eff}}(1,1)} \quad (2)$$

Here ze is the charge of the ion, n is the gas density, $\mu = mM / (m + M)$ is the reduced mass, with m the mass of the gas and M the mass of the ion/nanoparticle, k_b is the Boltzmann constant, T_{eff} is the effective temperature and $\bar{\Omega}_{T_{eff}}(1,1)$ is the Collision Cross Section (CCS). The effective temperature takes into

account the effects of strong fields and is calculated as: $T_{eff} = T + mv_d^2/3k_b$. Under most instances, i.e. when the electric field is low, the second term of T_{eff} accounts for less than 1% in the calculation.

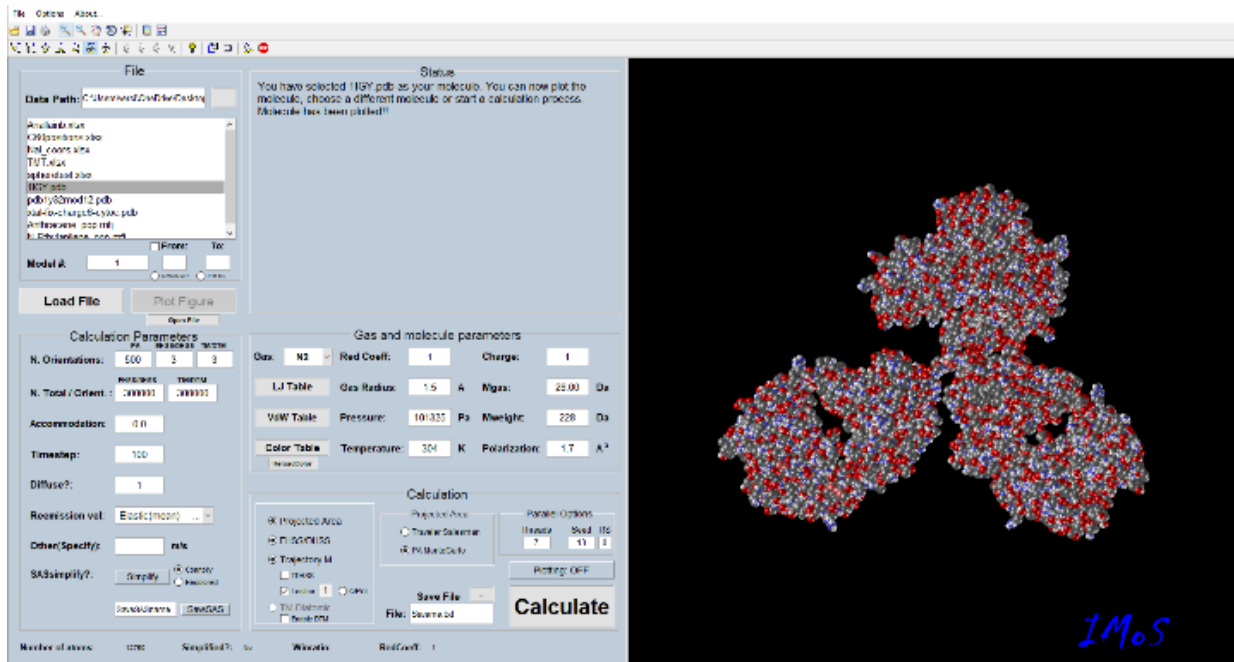


Figure 1. IMoS interface with an Immunoglobulin plotted.

The most important part of the code involves calculating $\bar{\Omega}_{T_{eff}}(1,1)$ directly, or a related quantity using different approximations, obtaining the mobility only once the solution for the CCS is obtained. The CCS is a very complicated parameter that measures the interaction between the charged nanoparticle and the gas molecules in the free molecular regime. This interaction can depend on the size of the gas molecule compared to the charged nanoparticle, their mass, their relative velocity and the potential interaction between them. In what follows, a brief explanation of the most important CCS calculations performed in IMoS is presented, including the Projection Approximation (PA), the Elastic/Diffuse Hard Sphere Scattering (EHSS/DHSS), and the Trajectory Method (TM)[2-7]. The degree of accuracy of the calculation is directly proportional to the computational time.

2.1 Projection Approximation (PA)

As the name suggests, CCS is directly related to area of interaction between gas and ion. In its most simple definition, this area is equivalent to the projected area of the combination of gas and ion. In short, the gas ion footprint is projected at random angles onto a plane and the area of the shadow is calculated[8, 9]. The average area over all orientation is then calculated and is directly related to the CCS of the ion in the gas of choice as shown in Figure 2. For this calculation to work, the Van der Waals (VdW) radii of the atoms in the molecule as well as radii of the gas have to be provided. The area of the all-atom structure with the addition of the gas molecule is calculated using either a MonteCarlo algorithm or a Traveler Salesman (TS) algorithm. The PA method gives rough estimates of CCS for all but the smallest ions in very light gases. The error varies, generally being below 40%, but could be as high as 300% for small highly charged ions in very polarizable gases such as CO₂ or N₂. If the reason for the deviation from experimental results is known, e.g. due to diffuse reemission, one can attempt to multiply the resulting value of PA value by a correction factor, ξ , to obtain a more accurate result $\Omega = \xi \cdot PA$. The PA has the advantage of being the most efficient calculation. In IMoS, the only method that is parallelized is the MonteCarlo algorithm while TS is reserved for plotting.

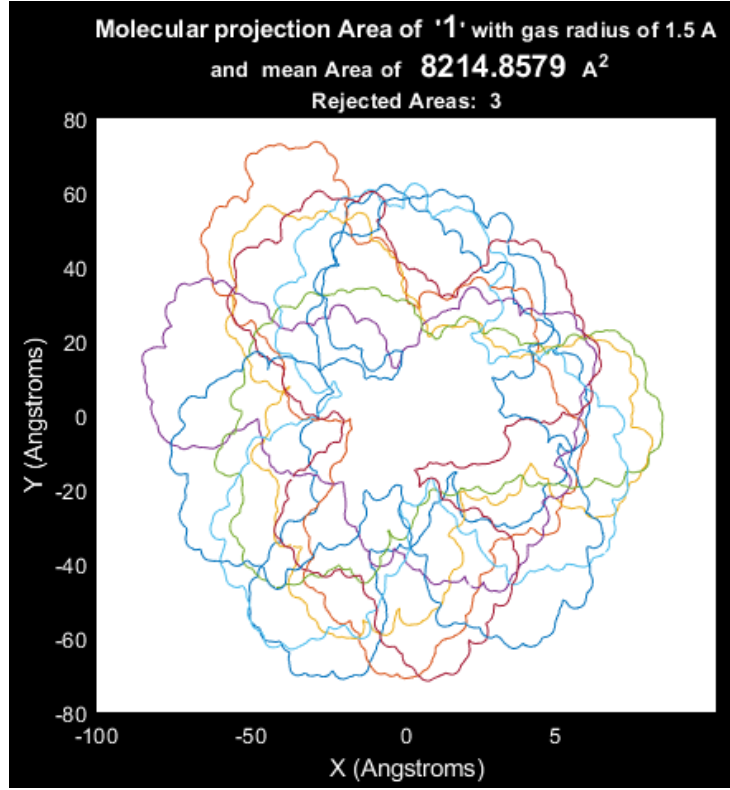


Figure 2. Average Projected Area of a Y-shaped immunoglobulin.

2.2 Elastic/Diffuse Hard-Sphere Scattering (EHSS/DHSS)

The calculation involving the mobility and $\bar{\Omega}_{T_{eff}}(1,1)$ corresponds to a calculation of the momentum exchange (momentum transfer) or drag force, i.e. how much does the buffer gas restrict the motion of an ion that is accelerated due to the presence of an electric field. In order to calculate that momentum exchange, the algorithm simulates the trajectories of different gas molecules and calculates the momentum transfer, Δp , of each as:

$$\Delta p \sim m(\vec{g}_f - \vec{g}_i) \quad (3)$$

where \vec{g}_i and \vec{g}_f are the initial and final relative velocities. Correcting for the effect of the reduced mass on the algorithm, and knowing the total time τ_t that N_t gas molecules take to collide with the ion, one can calculate the total drag as [10]:

$$\vec{F}_D = \left(1 + \frac{m}{M}\right)^{-\frac{1}{2}} \frac{N_t m}{\tau_t} (\vec{g}_f - \vec{g}_i) \quad (4)$$

Finally, the drag is related to the mobility through the drift velocity, the field and charge,

$$ze\vec{E} = \vec{F}_D \rightarrow KE = KF_D/ze = v_d \quad (5)$$

or

$$K = \frac{ze}{F_D} v_d \quad (6)$$

The calculation is repeated for 3 perpendicular orientations. The final result is then averaged, and the mobility obtained with the above formula. The CCS can then be inferred through the Mason-Schamp approximation. While this calculation slightly differs from other types of ion mobility calculations, it yields

equivalent results. Given that initial and final relative velocities are not assumed equal, an advantage of using this approach to the calculation is that it allows for the study of inelastic collisions.

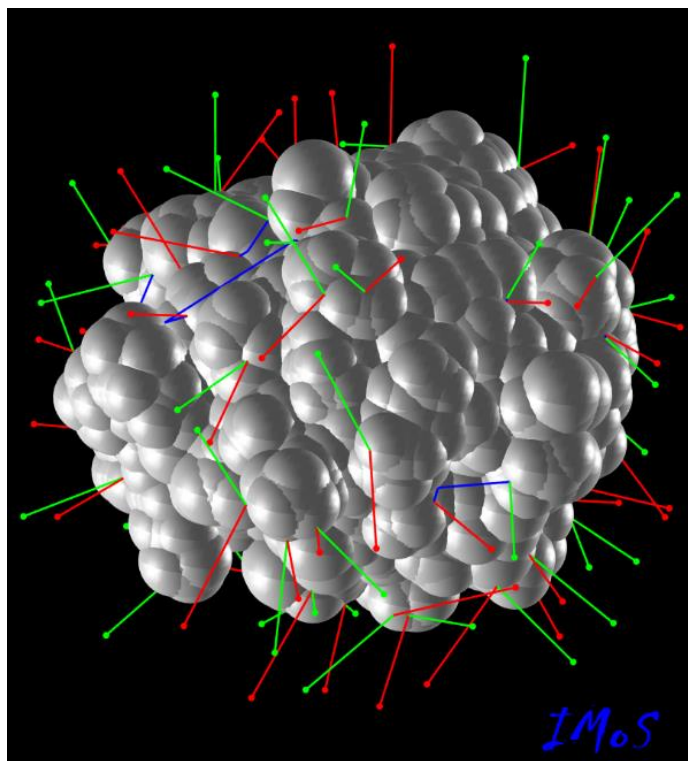


Figure 3. EHSS/DHSS of Cytochrome C ion. Red are incoming gas molecules; green are reemitted gas molecules and blue are partially scattered molecules that collide more than once with the ion.

The EHSS/DHSS method calculates the trajectories as if they were rectilinear not considering any interaction potential and thus using the VdW of gas and ion to study the collision, i.e. using a hard sphere potential. Upon collision with the ion, the gas molecule is reemitted, checks for secondary collisions (scattering) until the gas molecule leaves the domain and the momentum transfer is calculated. A schematic of the process is shown in Figure 3. The original Exact Hard Sphere Scattering only allowed elastic and specular collisions to occur[11]. However, IMoS allows the user to choose an accommodation parameter that specifies that a portion of the collisions may be regarded as inelastic and may be re-emitted diffusely. The program works as follows. The accommodation parameter has a value between 0 and 1[2, 3]. This parameter only establishes the percentage of gas molecules that are accommodated. For example, choosing 0.9 establishes that 90% of the gas molecules will be accommodated while 10% will follow an elastic and specular collision. The selected 90% may be chosen to be reemitted diffusely or not using a secondary parameter, labeled diffuse. When diffuse is chosen, the gas molecules are reemitted at a random angle within a semi-sphere at the point of contact. The re-emission speed of the 90% accommodated molecules may also be chosen. The program allows for plenty of different choices for this velocity, including being reemitted elastically or being reemitted at the surface temperature. The reemission velocity may be chosen randomly from a Maxwellian distribution or it may be chosen to always be the mean of a particular distribution. For example, if accommodation is chosen to be 0.91 with diffuse reemission and velocity from a Maxwell distribution at the surface temperature, the resulting value for a sphere would be expected to be the characteristic 1.3573 from the Millikan oil experiments[12, 13]. Due to scattering from the 9% that undergo specular and elastic collisions, a better approximation for non-spherical ions is to choose an accommodation of 1 and a velocity coming from a distribution at 92% energy of that of Maxwell which more closely yields the 1.36 value for non-spherical ions. Figure 4 shows how two different gas molecules

may have different types on interaction with an atom, where one can gas could have a more elastic re-emission while a heavier ion could have a more elastic one[4].

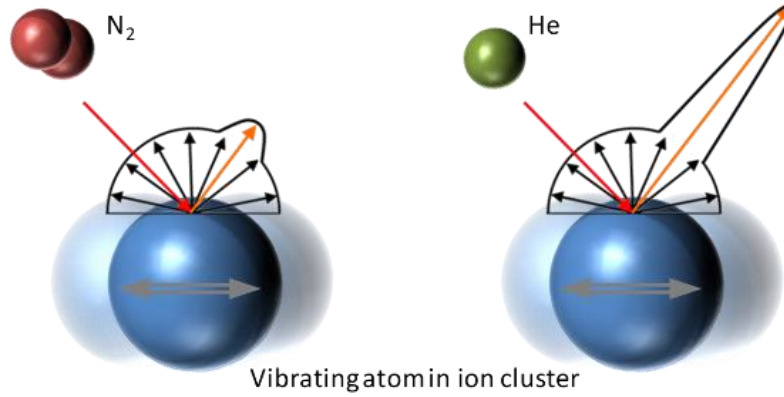


Figure 4. Comparison between a largely diffuse collision and a largely specular collision on a vibrating atom inside a cluster.

In all, EHSS should only be used for small ions in light gases, yielding similar results to PA, and DHSS should be used for singly charged large particles for which $\Omega \sim 1.36 \cdot PA$ is expected with negligible contribution from interaction potentials. Even under diatomic nitrogen, the $1.36 \cdot PA$ will not hold for very small ions where it seems that the collisions become slightly more elastic. At the same time, for those small sizes, the ion-induced dipole potential becomes quite important and may increase the CCS value even by a factor of two. For these cases, a trajectory method should be employed.

2.3 Trajectory Method / Diatomic Trajectory method (TM/DTM)

The trajectory method follows the logic of the EHSS/DHSS but allows interaction potentials between atoms/charges and the gas molecules. IMoS allows many different types of potentials to be used. Among the different trajectory methods there are two that are the most important, the Trajectory Diffuse Hard Sphere Scattering (TDHSS) which utilizes a $(4-\infty)$ potential and the Trajectory Method Lennard Jones (TMLJ) which uses a $(4-6-12)$.

The TDHSS method is very similar to EHSS/DHSS but adds an ion-induced dipole potential between charges and the gas molecule. Since the gas and ion are hard spheres, one can add inelastic/diffuse collisions to TDHSS in the same way as they are done in the EHSS/DHSS and therefore VdW's radii for atoms and gas must still be provided. For TDHSS, the reemission velocity for those gas molecules that are accommodated should come from a distribution rather than the mean of the distribution. The main reason for this choice is that since there is an attraction potential, lower velocities will lead to more scattering that higher velocities which affects the overall result. TDHSS works well for nanoparticles in diatomic nitrogen gas, in particular for those that are heavily charged. For ions that are smaller than 1.3nm in diameter, TDHSS performs poorly as it seems that smaller ions undergo more elastic collisions (accommodation should be lower). A good estimate for ions in the 0-300Å² range of CCS is to set the accommodation coefficient to 0.48 to yield a value close to the TMLJ.

The TMLJ composes the set of algorithms that employ a 4-6-12 potential. It follows the same principles as previous trajectory methods, but the potential is now given by[14]:

$$\Phi(x, y, z) = 4\epsilon \sum_{i=1}^n \left[\left(\frac{\sigma}{r_i} \right)^{12} - \left(\frac{\sigma}{r_i} \right)^6 \right] - \frac{\alpha}{2} \left(\frac{ze}{n} \right)^2 \left[\left(\sum_{i=1}^n \frac{x_i}{r_i^3} \right)^2 + \left(\sum_{i=1}^n \frac{y_i}{r_i^3} \right)^2 + \left(\sum_{i=1}^n \frac{z_i}{r_i^3} \right)^2 \right] \quad (7)$$

$r_i = (x_i, y_i, z_i)$ is the relative distance between each of the n atoms (and/or charges) and the gas molecule, with α being the polarizability of the buffer gas, and ϵ and σ are the Lennard-Jones(L-J) gas-atom

parameters corresponding to well-depth and zero potential crossing, respectively. The aforementioned potential is then used to calculate the acceleration of the gas molecule and its trajectory until the gas molecule leaves the domain and the angle of deflection recorded for each gas molecule. If the L-J potentials are optimized correctly, TMLJ yields some of the most accurate results available for numerical CCS and mobility. The optimization of L-J parameters can be done straightforward if empirically accurate information is available. IMoS allows to change the L-J parameters quite easily through a tabulated list. Each different gas requires a different set of L-J parameters. IMoS includes optimized parameters for C, H, O, N and F in He and N₂ and has general values for other atoms. Even when L-J parameters are not exactly known for a small fraction of the atoms, the calculations may still be reliable for large ions, in particular when the unknown atoms are not on the surface. The error is approximately 2% on average for TMLJ calculations in N₂ and He with optimized L-J parameters. A cartoon of the soft interaction when using an all-energy interaction 4-6-12 potential is shown in Figure 5.

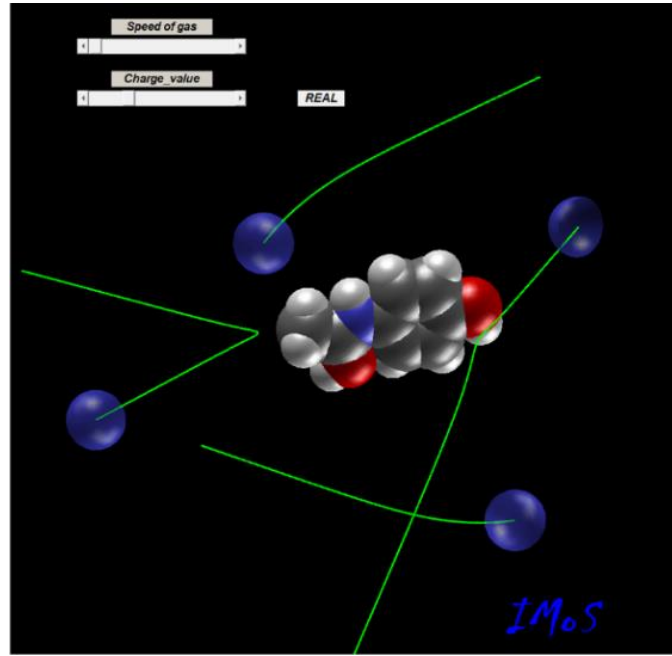


Figure 5. IMoS cartoon of the TMLJ 4-6-12 potential interaction.

For N₂ gas, IMoS offers the possibility of adding an ion quadrupole potential together with gas orientation averaging. The quadrupole moment is obtained by placing one negative charge of 0.4825e on each nitrogen and one positive charge of 0.965e in the center of the molecule. In such a way, the quadrupole potential can be expressed as[15]:

$$\Phi_{IQ}(x, y, z) = \sum_{j=1}^3 \sum_{i=1}^n z_i z_j e^2 / r_{ij}^3$$

The index j denotes three different N₂ charges (where 2 is the center charge) and index i indicates the charges on the ion. The orientation of the N₂ molecule is taken into account by assuming an appropriate weighted impact parameter. The ion quadrupole potential could have an effect on very small molecules. Given the high computational cost of adding the ion-quadrupole potential, the ion quadrupole should be considered only if its effect has the same order of magnitude as the rest of the potential interaction.

A final method considered in IMoS is that of the diatomic trajectory method (DTM). This method takes into account the moment of inertia of the N₂ molecule together with a 4-∞ potential and conserves not only linear momentum but also angular momentum of the gas molecule. Similarly to TDHSS, the re-emission

may be chosen to be elastic/inelastic and specular/diffuse depending on the choice of accommodation. The results from DTM follow the same trend as those of TDHSS although the resulting CCS may be larger due to augmented effective size of the gas molecule. Rotation and scattering effects due to the diatomic nature seem to be increasingly important for very small ion sizes (in particular, smaller than the gas molecule). The DTM subroutine is not parallelized and hence its performance falls behind the other subroutines specified above.

3. Conclusions

IMoS, a parallelized tool for enhanced electrical mobility and CCS calculations, has been greatly improved to include a more user-friendly interface and a dynamic environment. The program is intended to be used for both professional and academic interest and comprises some of the most up to date methods in electrical mobility calculations. There are different degrees of accuracy vs. efficiency in the different algorithms that IMoS can run. The most efficient but less accurate is the Projected Area Algorithm. The EHSS/DHSS algorithm is still a very efficient algorithm that uses a hard-sphere potential, takes into account scattering and allows for inelastic collisions. The most accurate algorithm but also the most computationally expensive is the Trajectory Method. IMoS allows for many different kinds of TM methods that use different potentials, ranging from a simple 4- ∞ potential that allows for inelastic collisions to a 4-6-12 potential with an ion quadrupole potential. IMoS may be downloaded and used for free when employed for academic interest.

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