Ion Sources for Biomolecules with controlled Superposition of Electric and Pneumatic Fields

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ABSTRACT

As previously reported the design of advanced ion sources for collisionaly cooled biomolecules required the development of an advanced multi-physics simulation system GEMIOS (Gas and Electromagnetic Ion Optical Simulator). Recent research based on such GEMIOS simulations led to the creation of the term "electro-pneumatic ion optics" since the functionality of considered novel ion-optical devices is in fact based on the superposition of two vector fields and two scalar field. Specifically, and in contrast to state-of-the art devices, gas pressure and gas flow velocities are not considered as global quantities but true field solutions are obtained. As a result, collision frequencies and momentum transfer vary spatially. This allows the design a of new class of electro-pneumatic devices in which elements act as electrodes as well as nozzles or wings and in which the balance between electrical and collisional forces varies locally in a controlled fashion.

1. INTRODCTION

A principal and critical step in protein biomarker discovery is the creation of ions of large organic molecules performed in laser based ion sources called MALDI (matrix-assisted laser desorption/ionization) /SELDI (surface-enhanced laser desorption/ionization). Due to high laser pulse power densities one of the fundamental problems associated with MALDI ion sources are the substantial translational and internal temperatures of ejected ions which frequently results in molecular fragmentation and progressive unimolecular decay thereby limiting the available time for analysis.

It is know that the presence of background gases in MALDI ion sources can provide higher ion survivability. In addition, experimental results [1] have indicated improved ion transmission within gas-filled multipole ion guides. Although it is rather counter-intuitive to assume any positive consequence of a background gas within an ion-optical device the effect of increased ion transmission was explained by what is now called "collisional cooling". Deeper understanding of more complex combinations of gas-filled electric lenses and multipole ion guides has been limited by the fact that semi-analytical approximations are only possible for idealized cases such as 2D quadrupole with spatially constant pressure [2]. The design of current state-of-the art MALDI sources is typically only based on SIMION-like trajectory calculations and gas pressure is, at best, assumed to be a globally constant quantity.

2. METHODS

Various novel configurations of a MALDI source based on non-trivial electro-pneumatic element configurations were numerically investigated using the GEMIOS simulator. Such designs belong to a of new class of electro-pneumatic ion optical devices in which so called electro-pneumatic elements (EPEs) act as electrodes as well as nozzles or wings and in which collision frequencies and momentum transfer vary spatially in a controlled fashion. However, the ion dynamics resulting from the superposition of non-trivial electric and pneumatic fields is no longer easily imagined or calculated and simulations are required for realistic 3D electro-pneumatic configurations. GEMIOS's capability to provide electromagnetic field solutions and fluid dynamic field solutions has been essential to model such ion optical systems.

3. RESULTS

One of the fundamental aspects of classical charged particle optics is that governing fields are conservative. This, however, is no longer the case in electro-pneumatic ion optical systems. Ions can be cooled, or, depending on the average kinetic energy gain of ions between collision events in relation to the thermal energy of the gas, substantially heated by applied electric fields.

It has been shown that the GEMIOS simulator correctly predicts such drag induced ion temperatures and drift velocities as function of applied field strength according to two well known theoretical conjectures by Langevin and Wannier concerning ion mobility in rarified gases suggesting either a linear or a quadratic dependency. The simulator can also cover the transition between those two regions (Fig. 1).

The design of advanced ion sources typically needs to minimize these drag induced ion temperatures while maintaining sufficient control over the beam. However, these are in fact contradicting requirements and GEMIOS simulations have been used to determine possible design compromises.

As a first step, a simplified model of an ion source is illustrated in Fig. 2. The second element with the long hole may e.g. be imagined as an inlet into a vacuum system.

The gas flow field in such a configuration provides little support for ion guidance away from the sample spot since the gas flow velocity increases only in the immediate vicinity of and inside said hole. In addition, the shown configuration has very poor performance if operated only under electric field influence. Likewise, electro-pneumatic operation exhibit considerable ion losses.

Fig. 3 – Fig. 6 show an example of an advanced 5-EPE ion source coupled to a RF quadrupole ion guide. The gas flow field is substantially more complex compared to Fig. 2 and effectively supports the guidance of ions into the RF quadrupole. However, the pneumatic influence alone is insufficient for completely lossless quadrupole injection (Fig. 4). Conversely, assuming no ion-gas collision this system behaves like a classical ion-optical configuration and undisturbed, well-focussed trajectories are possible (Fig. 5). Such operational mode permits, of course, no collisional cooling of ions. However, the shown advanced configuration can be operated in electro-pneumatic mode in which at certain field values the superposition of the created electric and pneumatic fields achieves rapid ion cooling as well as efficient ion guidance and quadrupole injection as illustrated in Fig. 6. A prototype of an ion source based on this principle has been built and experimental results have confirmed its superior performance with respect to ion cooling and ion transmission.

References

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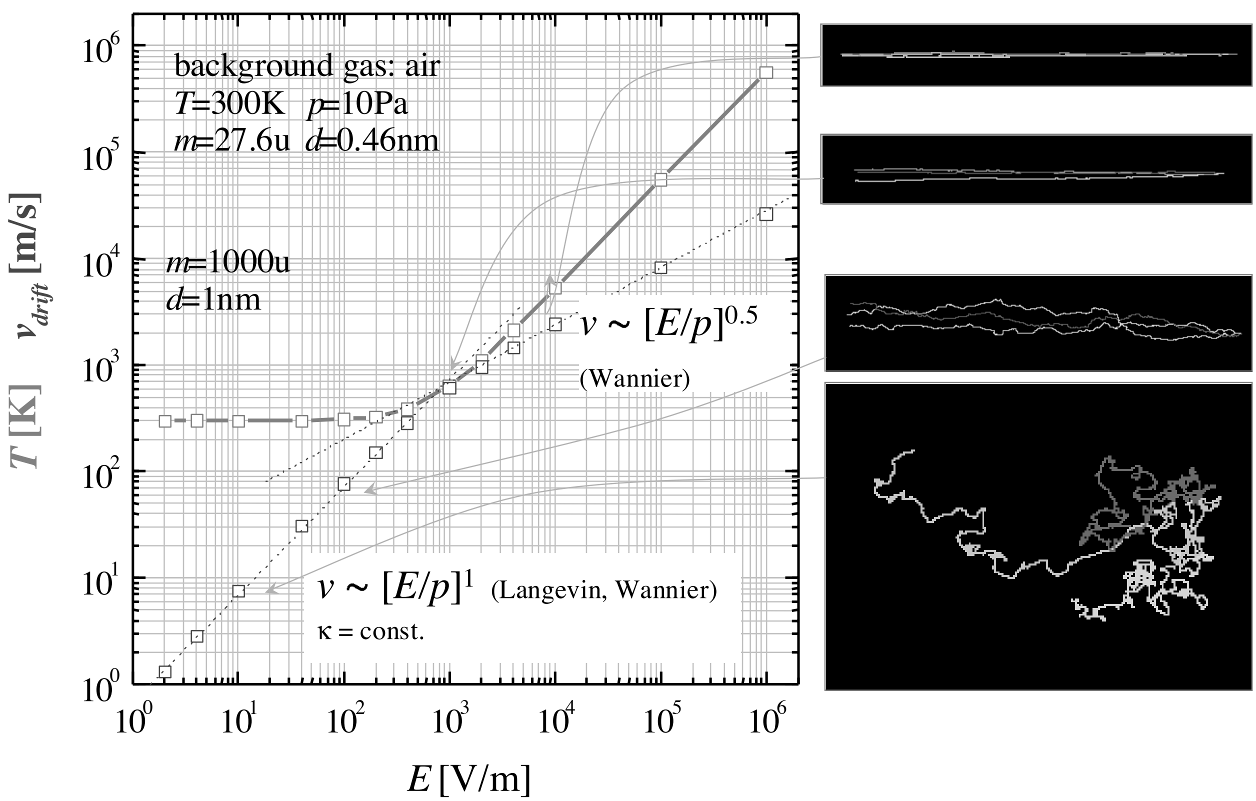

Fig.1: GEMIOS simulation of drag induced ion (d=1nm, m=1000u) temperatures and drift velocities in air at p=10Pa as function of applied electric field strength (replicating ion mobility theories by Langevin and Wannier) as well as corresponding characteristic ion trajectories illustrating the tradeoff between ion temperature and ion beam control

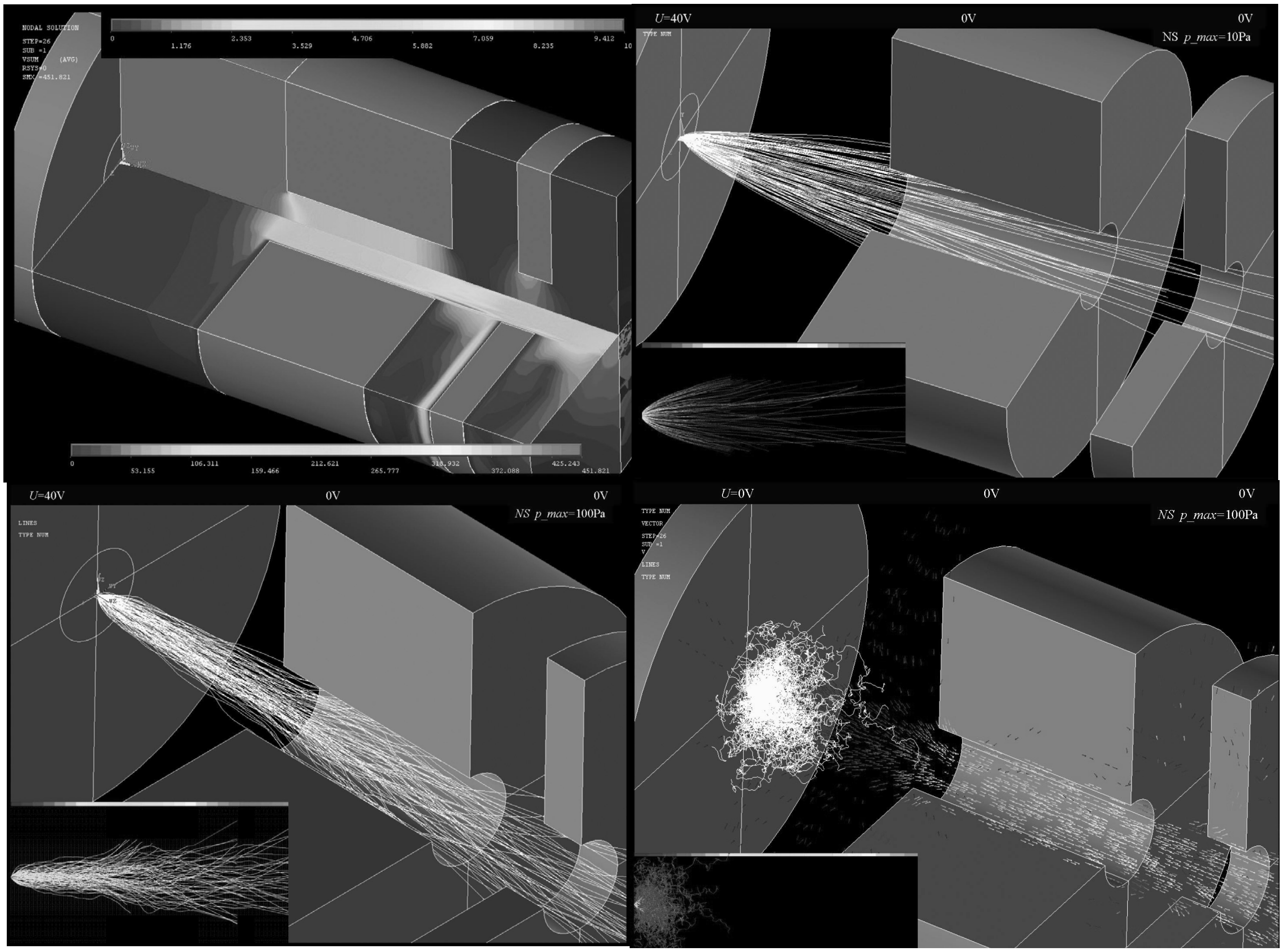

Fig. 2: Simplified model system of an ions source illustrating the influence of electric and pneumatic fields on the ion dynamics: upper left: Navier-Stokes solution for gas pressure and flow velocity; upper right: ion trajectories under electric-pneumatic field influence at p_{max}=10Pa, m_{ion}=1000u; lower left: ion trajectories under electric-pneumatic field influence at p_{max}=100Pa, m_{ion}=1000u; lower right: purely pneumatically dominated early stage of ion trajectories at p_{max} =100Pa, m_{ion}=1000u (no E-field)

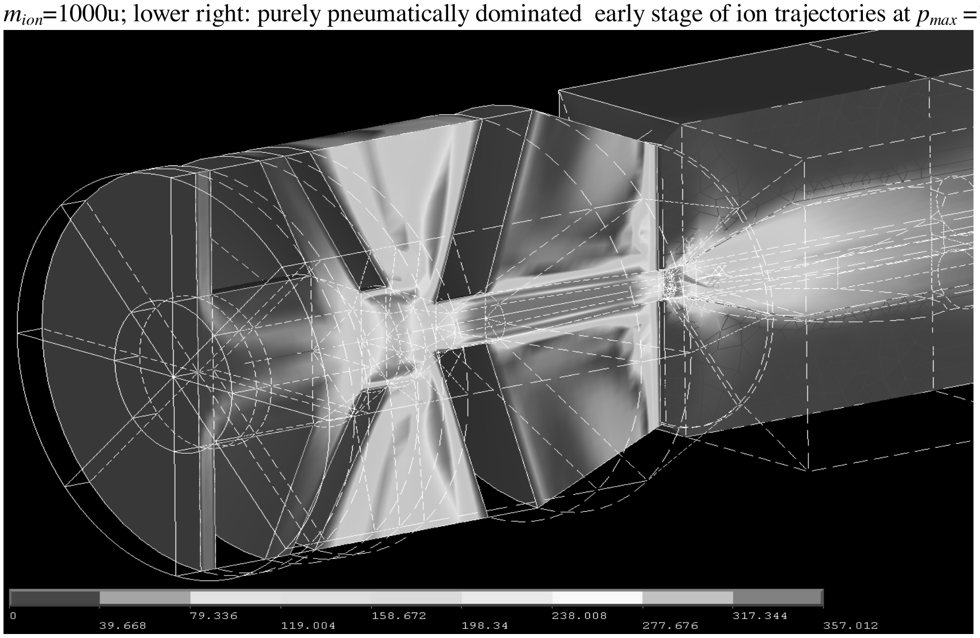

Fig. 3: Model system of an advanced 5-EPE ions source coupled to a RF quadrupole ion guide. Contour plot of Navier-Stokes solution of gas flow velocity magnitude $|v|$ at the center plane of the 3D model

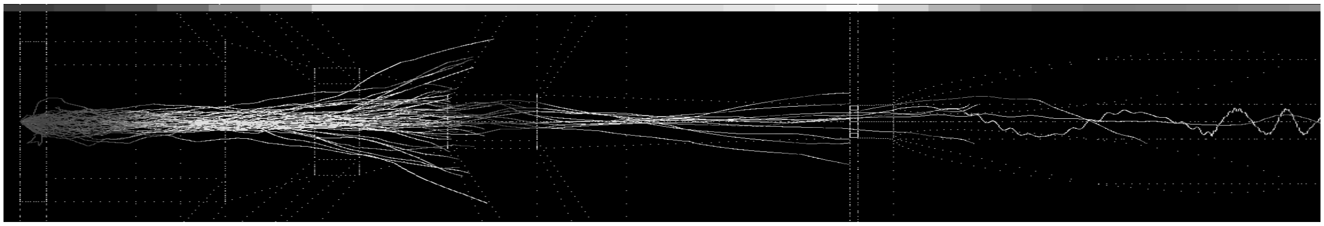

Fig. 4: GEMIOS simulation of ion trajectories in system as shown in Fig. 3: p_{max}=10Pa, m_{ion}=100u, v_0=600m/s + RND·400m/s, quadrupole: U_{AC_peak}=34V f=816kHz; no electric fields inside the source – purely pneumatically dominated: considerable ion losses

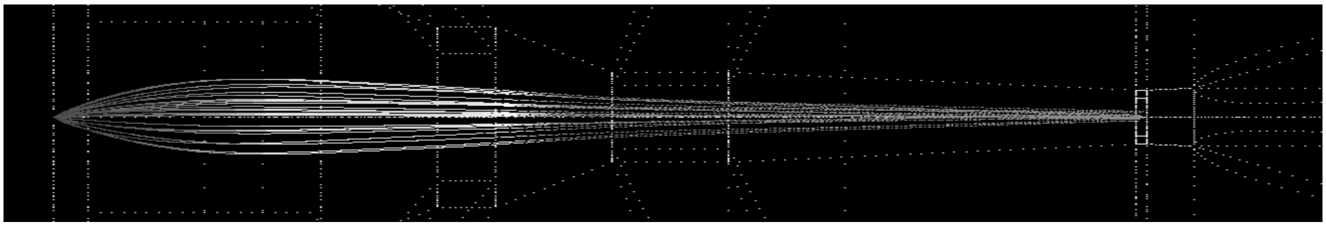

Fig. 5: Opposite to Fig 4: no collision (p_{max}=0Pa) but electric fields inside the source, m_{ion}=100u, v_0=600m/s + RND·400m/s, purely electric field dominated beam (here color indicates continuous acceleration toward the RF ion guide)

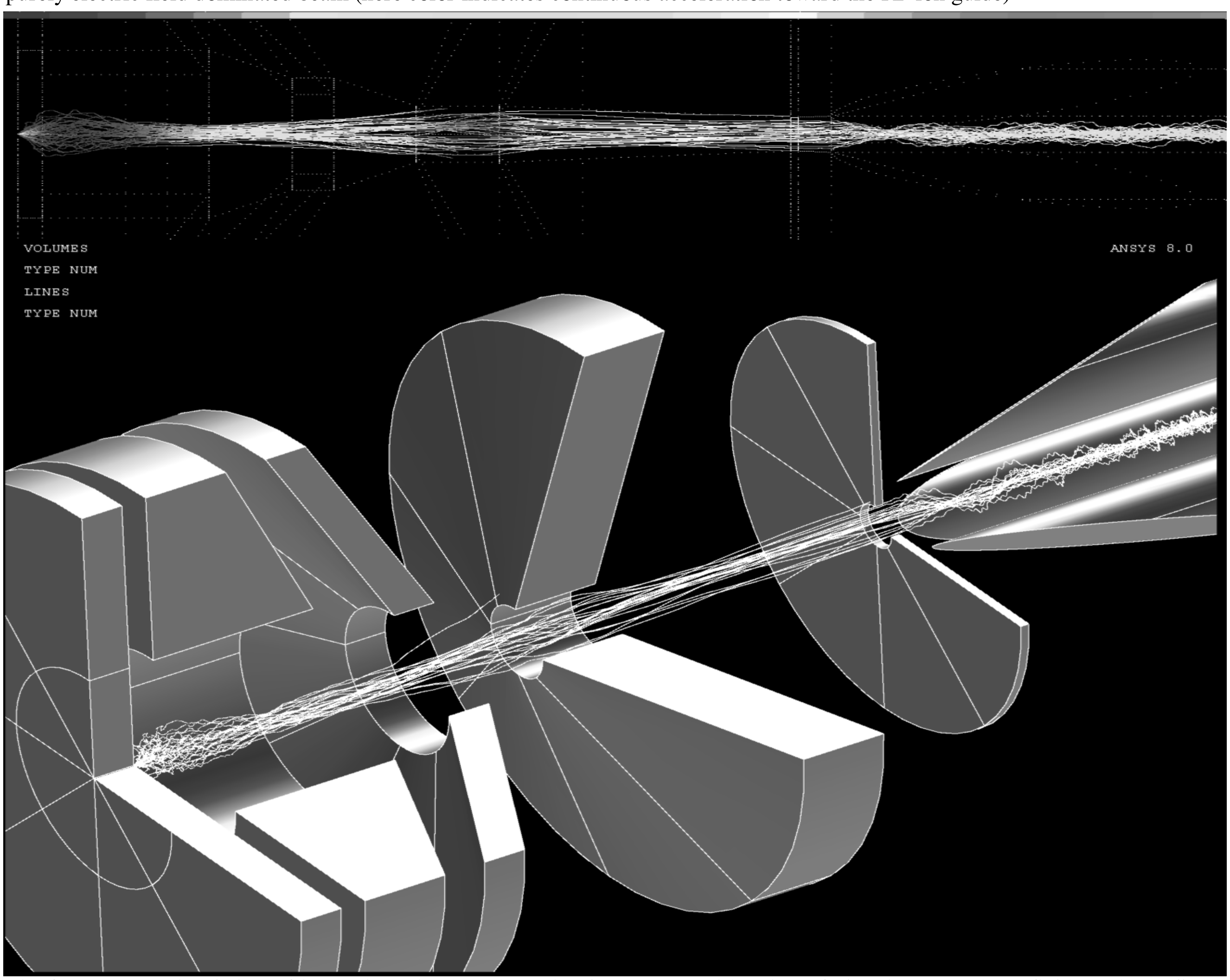

Fig.6: GEMIOS simulation of ion trajectories based on simultaneous consideration of electric DC and RF fields and gas flow fields; minimal ion losses and rapid ion cooling in source at optimal superposition conditions; m_{ion}=1000u, v_0=600m/s + RND·400m/s, U_{AC}=340V, f=816kHz, (OpenGL visualization via ANSYS)