# «Mass Spectrometry and its applied problems»

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## Introduction

Mass spectrometry (MS) is one of the main tools for detecting chemical or biological components, where gas dynamic interfaces play a crucial role for delivering ionized components from the atmosphere directly into the area with the lowered pressure. Optimization of similar interfaces is based on numerical modeling of gas flow, where governing equations are Navier-Stokes equations or non-stationary Euler equations.

However, various numerical models which are applied to the analysis of gas flow possess different advantages and limitations [1]. Usually numerical simulation of gas dynamic interfaces is based on a finite-volume scheme with unstructured triangular meshes [2, 3]. One alternative to this scheme are the numerical schemes based on particle methods, one of which is an approached known as 'Large particle method'.

An important feature of such methods is the approach to environment discretization, which treatsthe environment asa set of particles. Each particle is the carrier of attributes of the environment, such as density, velocity, kinetic energy and spatial coordinates [4].This study tests the applicability of 'Large particle model' to modeling of gas flow through highly under-expanded jet flow of neutral gas.

The analysis of the model's limitations is based on the following tests:

1. Modeling of Mach disk position as a function of the buffer gas pressure.
2. Knudsen number tests.
3. Local Mach number tests.

## Mach disk position tests

It is well known that the structure of Mach disk is determined by the ratio of ambient pressure to buffer gas pressure. Therefore,the position of Mach disk can be used for verifying 'Large particle model'. The aim of the tests described below is comparison of Mach disk position values derived from numerical simulation, and those obtained from experiments. The Mach disk position can be described by the following equation [5]:

$$L = 0.67 \cdot D \cdot \sqrt{\frac{P_0}{P_1}}$$

where $D$ – orifice,
$P_0$ – the ambient pressure at the entrance of the orifice,
$P_1$ – buffer gas pressure in the chamber,
$L$ – distance from the Mach disk to the exit from the orifice.

The expression is valid in the range [101325Pa – 6Pa], according to the experimental results by Ashkenas and Sherman [5].However Ashkenazi - Sherman model provides the overestimated value of Mach disk position under lower pressures. Evan and Moodi [6], also on the basis of experimental data, offered the corrected formula for calculation of Mach disk position under the lowered pressure:

$$L = 0.77\,D + 0.068\,(D^{1.35})\,(P_0/P_1)^{1/2}$$

Comparison of the three models is presentedon fig. 1. Mach disk position values, based on numerical simulation, coincide with experimental values for Ashkenazi-Sherman and Evan-Moodie in the range (5.3 – 1000) Pa. The border 5.3Pa corresponds to P0/P1 relation = 19118. Large particle model gives error of Mach dick position of about 18% at the pressure lower than 5.3Pa.

However it should be noted that the numerical scheme doesn't break when buffer gas pressure comes close to zero. This occurs because the numerical model complies with CFL condition.The essential divergence e of numerical and the experimental results is caused by the fact that Euler's equations aren't valid any more with the low pressure of buffer gas. It is connected to the fact that Euler's equations are correct only at Knudsen's numbers that do not exceed 1.

## Knudsen number tests

The nature of rarefied gas flow is characterized by the Knudsen number (Kn), which is the ratio of the molecular mean free path to the flow length scale, is used to be determined to degree of collision non equilibrium in gas flow.

The Knudsen number is $Kn = \lambda / dm$ [7], where $\lambda$ is mean free path, and dm – diameter of Mach disk.

$$\lambda = \frac{1}{\pi \cdot n \cdot d^2 \sqrt{2}}$$ , where n is density; $$n = \frac{P}{kT}$$ , where

$P$ is pressure (Pa), $T$ – temperature (K), $k$ – Boltzmanconst= $1.38 \cdot 10^{-23}$, and d – diameter of molecule [7]. Diameter of $N_2 = 3.2 \cdot 10^{-10}$ m has been used in current simulation.

Therefore calculation of Knudsen number distribution gives us the tool to define limitation of our model. The results of Knudsen number in our calculation is presented in table 1.

According to our calculation of distribution of Knudsen number, we can conclude that we reach the end of viscosity regime at about 5.3 Pa in out numerical tests. The pressure bellows 5.3 Pa corresponds to transient and free molecular regimes and large particle model is not valid in those pressure regimes.

## Local Mach number tests

The transition from viscosity regime to free molecular regime can be characterized by static temperature or velocity of gas flow. For the gas at thermodynamic equilibrium, the energy in each of the degrees of freedom has Boltzman distribution among molecules, so that the energy in each of the degrees of freedom can be characterized by a temperature [8]. Thus we can refer to translation temperature $T_{tr}$, rotational temperature Trot and vibration temperature $T_{vib}$. During the expansion of the jet, energy from different degrees of freedom of a molecule transforms into kinetic energy of the molecule moving in the stream.

## Local Mach number tests

As the collision frequency in the jet is reduced by the decrease in density, the exchange of energy among the various degrees of freedom slows down and ultimately stops, with the results that distribution within each degree of freedom remains fixed for the reminder of the gas expansion. The freezing of temperate was experimentally investigated by Fen and Andersen by time of flight mass-spectroscopy [9, 10]. They experimentally investigated velocity distribution in the jet and found out a value which they called the terminal Mach number MT and which is expressed as follows:

$M_T = 1.17 \cdot Kn_0^{(1-\gamma)/\gamma}$, where $Kn_0$ – orifice Knudsen number [9, 10].

MT shows the maximum value of velocity, which in principle can be achieved in a jet. When velocity of a jet reaches the maximum value gas density becomes so low that collision frequency is insufficient to continue the transformation of thermal energy (enthalpy) to streaming kinetic energy of the jet gas [10].

In case of nitrogen as buffer gas $Kn_0 = 1.5 \cdot 10^{-5}$, $\gamma = 1.4$, $N_2 = 3.5 \cdot 10^{-10}\,m$, then $M_T$ =27. It means that velocity of gas cannot be higher than 27 in terms of local Mach numbers.

Velocity of gas in term of Mach number ($V_{mach}$) can be estimated in alternative way asan ration of gas velocity and local velocity of sound:

$V_{mach} = \frac{V_{gas}}{c}$, $c = \sqrt{\frac{\gamma \cdot P}{\rho}}$, where $V_{gas}$ - velocity of gas (m/sec), $c$ - local velocity of sound, $\gamma$ - specific heat ration, $P$ - pressure, $\rho$ - density.

The local velocity of sound can dramatically change in a supersonic jet, because it is function of pressure and density. The next series of tests defined maximum value of the velocity in the term of local Mach numbers for different buffer gas pressure. Results of tests are presented in table 2.

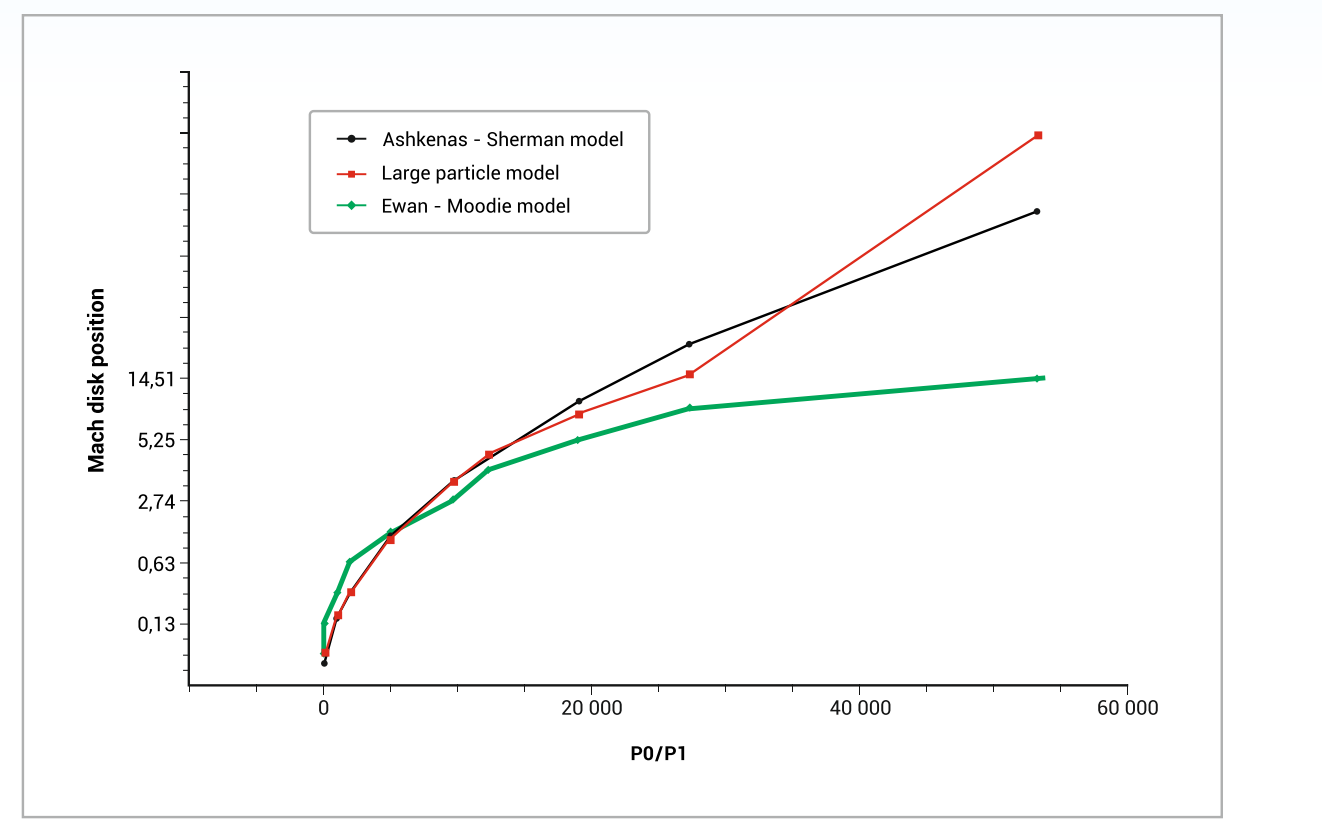
The evaluation of boundary between transient and free molecular regime, based on velocity of gas in term of Mach number, shows that our model reach free molecular regime about 2Pa. The range [1.97Pa - 5.3Pa] corresponded transient regime.

| Average pressure of buffer gas (Pa) | Knudsen number (max value in numerical field) |
|---|---|
| 5.3 | 0.73 |
| 1.9 | 1.67 |

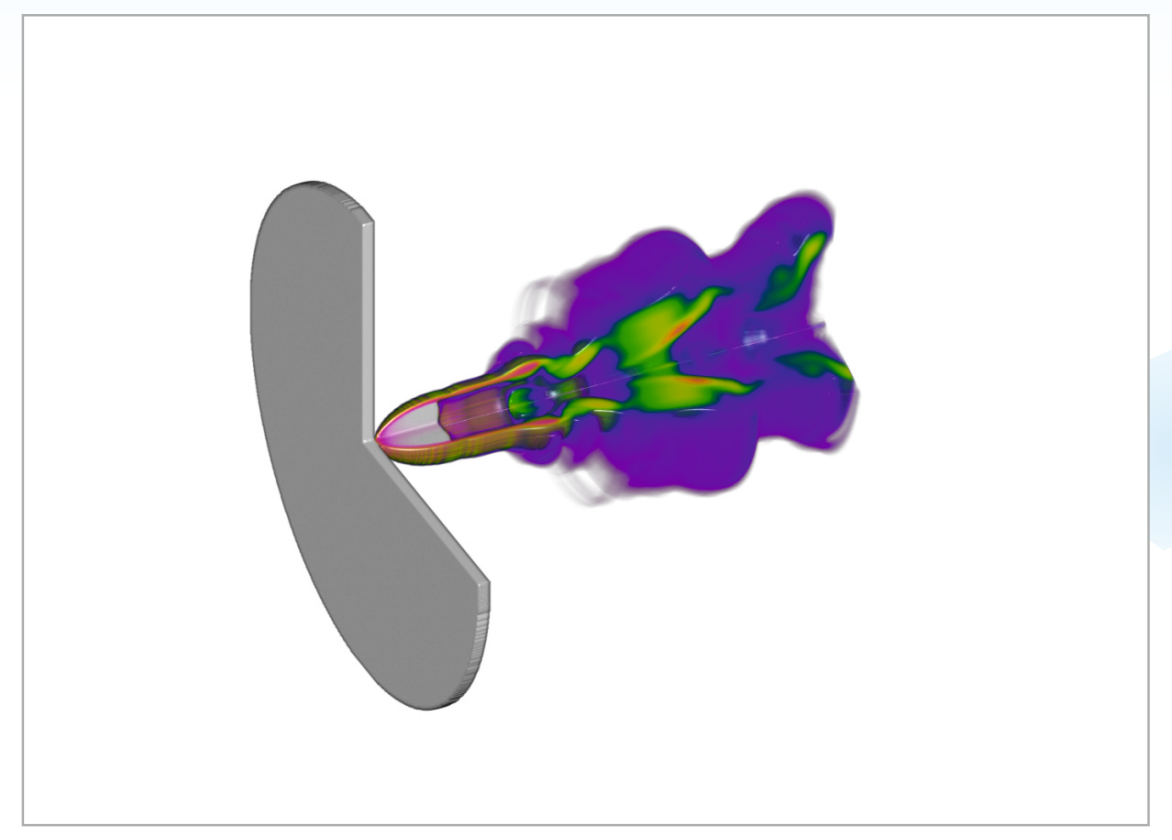
Table 1.

| Average pressure of buffer gas (Pa) | Maximum value of local Mach number |
|---|---|
| 10.4 | 18 |
| 5.7 | 20 |
| 3.85 | 22 |
| 1.97 | 26 |

Table 2.



Pic. 1. Comparison of three models.



Pic. 2. Example of Mach disk (velocity distribution).

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## Conclusions

In this work, we performed gas dynamic simulations for atmospheric pressure interface using Large particle model. Capability and limitation of model were checked by means of three tests. The first test based on behavior of Mach disk, where position of disk is function of buffer gas pressure.

Overall, the agreement between the experimental data and our numerical results was found to be very good. The second and third series of tests provides possibility to define limitation of Large particle model. Base on Fen & Anderson [9, 10] approach to estimation of transition from transient regime to free molecular regime we can conclude that pressure of about 1.9Pa is the pressure where transition regime comes to free molecular regime.

Combining Fennapproach and Knudsen number approach we can define that transformation from viscosity regime to transient molecular regime occurs at the pressure region from 5Pa to 1.9PA. Summarizing results of numerical modeling we can conclude that the Large particle model well works in the range [101325Pa - 5Pa].

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