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]. Another alternative to this scheme are the numerical schemes based on particle methods, one of which is an approach known as Large Particle Method (LPM).

An important feature of such methods is the approach to environment discretization, which treats environment as set of particles. Each particle in the model has the 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 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 value derived from numerical simulation, and those obtained from experiments. The Mach disk position can be described by the following equation (5):

\[ L = \frac{0.67 \cdot D \cdot P_i}{P} \]

where \( D \) – orifice; \( P_i \) – the ambient pressure at the entrance of the orifice; \( P \) – 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 \([0.03 \text{ Pa} \approx 60 \text{ cm}]\), according to the experimental results by Ainskern and Sherman [3] However, Ainskern–Sherman model provides the overestimated value of Mach disk position under lower pressures. Evan and Mook [3] also on the basis of experimental data, offered the corrected formula for calculation of Mach disk position under the lowered pressure:

\[ L \approx 0.77 \cdot D \cdot (0.0068 + 0.099 P) \]

Comparison of the models is presented in Fig. 1. Mach disk position values, based on numerical simulation, coincide with experimental values for Ainskern–Sherman and Evan-Mook in the range (0.3 – 1000) Pa. The border 5.3 Pa corresponds to 0.5 in relation 19.18. Large particle model gives error of Mach disk position of about 18% at the pressure lower than 5.3 Pa.

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 the condition. The essential divergence 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 determine degree of collision non-equilibrium in gas flow.

The Knudsen number is given by:

\[ Kn = \frac{\lambda}{L} \]

where \( \lambda \) is the mean free path, and \( L \) – diameter of Mach disk.

\[ \lambda = \frac{2 \cdot \sqrt{2} \cdot m \cdot \sqrt{ \frac{2 \cdot k \cdot T \cdot M}{\pi \cdot \rho \cdot \lambda} } }{P} \]

where \( P \) is pressure, \( T \) – temperature, \( M \) – Boltzmann constant \( 8.61 \times 10^{-5} \), and \( d \) – diameter of molecule. Diameter of 7.0–3.3 × 10^–5 mm has been used in current simulation.

Therefore calculation of Knudsen number distribution gives 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 our numerical tests. The pressure below 5.3 Pa corresponds to transient and free molecular 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 Boltzmann distribution among molecules, so that the energy in each of the degrees of freedom can be characterized by a temperature \( T \). Thus we can refer to translation temperature \( T_r \), rotational temperature \( T_v \) and vibrational temperature \( T_\text{vibr} \). 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
At the collision frequency in the jet is reduced by the decreases in density, the exchange of energy among the various degrees of freedom slows down and ultimately stops, with the rate that distribution within each degree of freedom remains fixed for the reminder of the gas expansion. The freezing of temperature was experimentally investigated by Pen and Anderson by times of flight mass spectrometry [8, 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:

\[ MT = 1.7 \cdot Kn^{1/2} \]

where \( Kn \) - critical Knudsen number [10].

MT shows the maximum value of velocity which in principle can be achieved in a jet. When velocity of jet gets to the maximum value gas becomes so low that collision frequency is insufficient to continue the transformation of thermal energy [9] or [10].

In case of nitrogen as buffer gas \( MT = 5.10^{-5^{1/2}} \) and \( 1.4 \cdot 10^{-5^{1/2}} \). Then \( MT \approx 10^{-5} \) if velocity of gas cannot be higher than \( 27 \) in terms of local Mach numbers.

Velocity of gas in term of Mach number \( \frac{v}{c} \) can be estimated in alternative expression of gas velocity and local velocity of sound:

\[ \frac{v}{c} = \frac{v}{\sqrt{T_r \cdot \rho \cdot \lambda}} = \frac{v}{c} \cdot \sqrt{T_r \cdot \rho \cdot \lambda} \]

\[ \frac{v}{c} = \frac{v}{\sqrt{T_v \cdot \rho \cdot \lambda}} = \frac{v}{c} \cdot \sqrt{T_v \cdot \rho \cdot \lambda} \]

\[ \frac{v}{c} = \frac{v}{\sqrt{T_\text{vibr} \cdot \rho \cdot \lambda}} = \frac{v}{c} \cdot \sqrt{T_\text{vibr} \cdot \rho \cdot \lambda} \]

where \( c \) = local velocity of sound, \( v \) = local velocity of sound, \( \lambda \) = local mean free path.

The local velocity of sound can dramatically change in a supercritical jet, because it is a function of pressure and density. The next set of tests defined maximum value of the velocity in the term of local Mach numbers for different buffer gas pressures. 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 37 Pa. The range [37 Pa – 5.3 Pa] corresponded transition regime.

Conclusions
In this work, we performed gas dynamic simulations for atmospheric pressure interface flow using Large particle model. Capability and limitation of model were checked by means of three tests. The first test looked at 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 tests of plates provides possibility to define limitation of Large particle model. Based on Pen and Anderson [8] approach to estimation of transition from transient regime to free molecular regime we can conclude that pressures of about 0.1 Pa is the pressure where transition regime comes to free molecular regime.

Golding-Fenn approach and Knudsen number approach we can define that transition from viscosity regime to transient molecular regime occurs at the pressure region from 5 Pa to 1.3 Pa. Summarizing results of numerical modeling we can conclude that the large particle models works in the range [0.03 Pa – 5.3 Pa].

Literature