Application of molecular dynamics for modeling processes in microfluidic devices

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Abstract. The article considers the possibility of using the molecular dynamics (MD) as part of multi-level models for describing processes in microfluidic devices. Much attention is paid to issues related to the use of MD to describe processes at a gas-solid interface.

1. Introduction

Microfluidics (microhydrodynamics) is an interdisciplinary science that studies the behavior of liquids and gases moving along narrow channels inside sealed miniature microchips. Microfluidics is based on microfluidic modules, which allow controlling micro-, nano- and even picoliter volumes of liquids. It is important for operations such as sample preparation, transportation, mixing, separation, detection, dosing, etc. The advantages of microfluidic technologies are caused by the fact, that reactions take place in bounded systems, where contamination is excluded, and the volumes of reagents are minimal. As a result, not only traditional studies can be performed in a miniature format, but also analyzes that were previously unrealizable [1].

The key features of microfluidic devices include [2]:
1. Sufficiently large linear dimensions that impede the use of methods based on the micro approach.
2. Large influence of surface processes on the result of work, increasing with decreasing channel radius.
3. Significant imbalance in most processes, which limits the use of methods based on the macro approach.

Thus, when modeling the operation of microfluidic devices, several conflicting requirements must be taken into account. It makes modeling based on a single-level approach almost impossible.

In this work, it is proposed to use the MD method for modeling processes at the micro-level (primarily at the gas-solid interface), to obtain initial data for larger-scale models such as simulation models and systems of differential equations describing chemical processes and mass transfer. An example of such a model was previously considered by the authors in [3].

2. The relationships between micro and macro approaches

Macroscopic models of the flow of gases use kinetic coefficients (viscosity, thermal conductivity, mean free path, etc.) as input parameters. For the bulk component of the flow, these parameters can be
determined with sufficient accuracy based on equations of state and well-known experimental data. However, with a decrease of the geometric dimensions of the channel under study, the proportion of near-surface flows increases, therefore, the significance of errors associated with the inaccuracy of setting boundary conditions increases [4]. The interaction of the gas phase with the wall material in real physical systems is complicated by such phenomena as physical and chemical adsorption, so penetration of gas particles into the surface material and possibly knocking out of surface nanoparticles, accommodation coefficients [5,6] for such systems are a priori unknown, but can be determined on the basis of experimental data (which is possible only for a limited range of temperatures and pressures), or obtained as a result of simulation modeling of the system at the microlevel. A similar approach is found in [7,8].

Since it is proposed to use combined models (quasi-gas-dynamic (QGD) with molecular dynamics as subgrid), the final limitations of this approach will be caused by three factors: 1) limitations of the MD method; 2) limitations of the QGD method; 3) the stability of the solution of QGD equations with the introduction of the calculated MD corrections. And, if the first two factors are studied theoretically [9-11], the third requires a more detailed analysis, which is not included in the scope of this work.

3. Molecular dynamics model

In the molecular dynamics, the behavior of an ensemble of particles is calculated by solving the system of motion equations from classical mechanics:

\[
\frac{d^2 \vec{r}_i}{dt^2} = \frac{\vec{F}_i}{m_i},
\]  

where

\[
\vec{F}_i = -\nabla U(\vec{r}_1, ..., \vec{r}_N) = \sum_{j=1,N}^N \left( \frac{\vec{r}_{ij}}{|\vec{r}_{ij}|} \right) F\left(|\vec{r}_{ij}|\right), \quad \vec{r}_{ij} = \vec{r}_j - \vec{r}_i.
\]

The sets of configurations obtained by calculations based on the molecular dynamics method are distributed according to some statistical function, for example, corresponding to the microcanonical distribution [12].

To implement the interaction between the particles of the system in this work, the Lennard-Jones 6-12 pair interaction potential (PLD) is used:

\[
U(r) = 4\varepsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^{6} \right], \quad r = |\vec{r}_{ij}|,
\]

where \(\varepsilon\) is the depth of the potential well in the equilibrium state, \(\sigma\) is the characteristic van der Waals diameter of the molecule, \(r\) is the distance between the centers of the particles [13,14].

When studying the flow of a two-component gas mixture near the surface, it is necessary to take into account interactions between different types of particles. The PLD coefficients for such interactions are calculated according to the Berthelot-Lorentz rule [15].

\[
\varepsilon_{AB} = \sqrt{\varepsilon_A \cdot \varepsilon_B}; \quad \sigma_{AB} = 0.5(\sigma_A + \sigma_B).
\]

Here, the indices A and B correspond to different types of particles.

Periodic boundary conditions are usually used to increase the effective volume of the modeling domain and smooth out the influence of boundary conditions in molecular dynamics models [16].

Parameters of the model used in the work are mentioned below:

- interaction on Lennard-Jones potential 6-12;
- number of carrier gas particles in the model cell is equal to 8192;
- periodic boundary conditions (PBC) along the X and Y axes (parallel to the surface), elastically reflecting the boundary along the Z-axis.

Figure 1 shows a visualization of a model cell.
The plan of the experiment is mentioned below:

1. in the zone of generation of test particles, a particle is initiated with a given energy parameter and angle of incidence \( \alpha \) (relative to the normal to the surface);
2. the calculation of the trajectories of motion of all particles in the system;
3. when the particle reaches the region of the adsorbed state, the countdown of the retention time begins (if the particle falls into this region several times, the times are summed up);
4. the simulation ends when the test particle reaches the upper boundary of the simulation cell;
5. the surface is defined by a set of spherical particles interconnected and equilibrium points by elastic interaction potentials.

In the numerical experiments (NE) discussed in this article the surface is a three-layer structure. The first layer is continuous, acting as the lower boundary of the modeling cell. Particle distributions in the second and third layers form a periodic structure, schematically shown in Figure 2.

**Figure 1.** Visualization of a model cell.

**Figure 2.** Schematic representation of the surface structure of a simulation cell.

Processing Results are mentioned below:
• the experiment is carried out from $10^2$ to $10^5$ times;
• distributions of the output data are constructed depending on the angle of incidence and the initial particle energy.

The output of the experiment: 1) retention time (in the adsorbed state); 2) particle return time; 3) the angle of return (relative to the normal to the surface); 4) total energy.

4. Modeling results

One of the key parameters for modeling the operation of microfluidic devices using methods based on the macro-approach is the average retention time of particles in the adsorbed state. Figure 3 shows the result of calculating this value depending on the angle of incidence of the particle in the surface layer at a temperature of 300 K and the initial energy of the test particles equal to the average kinetic energy of thermal motion. Model carrier gas particles have argon parameters, test particles have CO$_2$ parameters. The system pressure is equal to 1 bar. The number of particles of the carrier gas is 131072.

![Figure 3](image)

**Figure 3.** Dependence of the average particle retention time near the surface on the angle of incidence.

Each point of this curve was obtained by averaging the results of 200 numerical experiment with the same initial energy distributions, but with different initial positions of the test particle relative to the surface.

Based on the shape of the dependence, it is possible to distinguish ranges of angles at which the longest retention of the test particle near the surface occurs. It is also worth noting an increase in the standard deviations of the results at angles to the normal close to zero and 90 degrees, however, this effect requires additional analysis.

The experiment was repeated for a temperature range from 270K to 340K in increments of 10 degrees. The results are shown in Figure 4.

The figure shows the decrease in retention time with increasing temperature. This effect is expected and explained by the authors as a result of an increase in the mobility (average kinetic energy) of the particles entering the model system, as well as an increase in the mean free path. The presence of
distinguished angles at which the time spent near the surface is increased may be due to uneven terrain.

Figure 4. Dependence of the retention time on temperature and angle.

5. Conclusion
There is proposed a scenario for using the molecular dynamics to obtain the parameters of macro models describing processes in microfluidic systems.

The possibility of calculating the retention time of particles near the surface depending on the temperature and angle of incidence is shown.

It is worth noting that, within the framework of the considered approach, it is possible to calculate a fairly wide range of parameters, for example, accommodation coefficients, which are the initial data for models based on the macro approach. It’s worth noting, that the proposed approach can take into account, within the framework of the proposed approach, the influence of surface topology parameters at the nanoscale (in particular, nanopore parameters), which is a significant difficulty in the framework of the macro-approach.

6. References
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