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DSMC SIMULATION OF HALF-SPACE SINGLE GAS IN THE PRESENCE OF AN ADSORBING SURFACE

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ABSTRACT

Steady one-dimensional flows of a gas in the presence of an adsorbing surface kept at constant and uniform temperature are studied by numerical solutions of the Boltzmann equation using the DSMC method. The phenomenological model proposed by Borgnakke and Larsen is used to describe the inelastic collisions dynamics for the gases with rotational degrees of freedom. The adsorption and desorption phenomena are modeled using the Langmuir model under equilibrium conditions. The additional equation for the evolution of the surface coverage in time is solved for the non-equilibrium case. The numerical simulations varying some input parameters are performed and the results are discussed.

INTRODUCTION

Gas flows induced by mass transfer of gaseous species onto (or from) solid surfaces can be found in many applications. One of the most important examples is the atmospheric BTEX concentration real-time monitoring [1] by a micro gas chromatograph, since the adsorption and desorption are the main processes operating in the gas chromatography. The BTEX group of molecules (Benzene, Toluene, Ethylbenzene and Xylenes) are, among volatile organic compounds, the most widely found in indoor air. The main sources of BTEX are the cleaning products, building materials and outdoor air supply [2]. The relative rates of adsorption and desorption onto and off the stationary phase inside the chromatographic column allows chemicals in samples to be separated. If the column conditions favor adsorption of a molecule, then the molecule adheres to the stationary phase for a time interval and so it becomes separated from the other sample chemicals. When the conditions favors desorption, the opposite process happens, and the chemicals are released into the mobile phase.

The consideration of a gas as a continuous medium imposes some conditions and, consequently, restricts the application of the hydrodynamic equations for the gas flow modeling. When a characteristic dimension of a gas flow is comparable to a molecular mean free path, then the continuous mechanics cannot be applied, but a modeling should be done at a microscopic level, that is, a gas must be considered as rarefied [3]. Besides, there is a narrow region close to the gas-solid surface interface, called Knudsen layer, where the mechanical interaction between gas molecules with the surface has to be evaluated by the microscopic approach *i.e.* by the kinetic theory of gases [4]. Although this layer is very thin, several mean free path lengths thick, the



macroscopic quantities calculated from the hydrodynamic equations may suffer strong jumps within this kinetic region. Typical value of the molecular mean free path for nitrogen at atmospheric pressure is about $\lambda_m \approx 10^{-8}$ m.

The present work aims the numerical investigation of the steady one-dimensional adsorption/desorption phenomena of single gases using the DSMC method. The binary inelastic collisions between gas molecules are described by the Borgnakke-Larsen model. The equilibrium state of adsorption and desorption processes is described by the Langmuir model. The additional equation considering non-equilibrium state is solved in the case, while the adsorption flux is not equal to the desorption flux. This work is the first step of a series of studies which aims to evaluate numerically the separation of benzene and toluene using the nitrogen as a carrier gas in a micro-column of a micro gas-chromatograph. The next version of the numerical code will solve a 2D mixture flow between two infinite parallel plates. The boundary conditions will be adsorption at the walls, prescribed mass flow rate at the inlet and open condition at the outlet. After that, different geometrical parameters could be simulated in order to check its influence in the separation.

PROBLEM STATEMENT AND BASIC EQUATIONS

It is considered the steady one-dimensional flow of a gas adsorbing onto an infinite solid planar surface kept at constant and uniform temperature T_w . This surface, located at $x=0$, separates the solid, which occupies the half-space $x < 0$, from the vapor phase, $x > 0$. Since the gap between quantized rotational energy levels is supposed to be much smaller than $\kappa_B T_w$, κ_B is the Boltzmann constant, vapor molecules behave as classical rigid rotators of average diameter a and mass m with $j=2$ (linear molecule) or $j=3$ (nonlinear molecule) rotational degrees of freedom. The vapor motion in the positive half-space is governed by the following steady and spatially one-dimensional Boltzmann equation:

$$v_x \frac{\partial f}{\partial x}(v, \varepsilon | x) = \int [f(v'_l, \varepsilon'_l | x) f(v', \varepsilon' | x) - f(v_l, \varepsilon_l | x) f(v, \varepsilon | x)] Q \varepsilon_l^\mu d^3 v_l \varepsilon_l \quad (1)$$

where $f(v, \varepsilon | x)$ is the distribution function of molecular velocity v and rotational energy ε at location x . The exponent μ takes the values 0 for $j=2$ and 0.5 for $j=3$. In Eq.(1), Q is defined as:

$$Q = \int_S d^2 \hat{e}' \int_0^{E-\varepsilon'} \varepsilon'^\mu d\varepsilon' \times \int_0^{E-\varepsilon'} \varepsilon_l'^\mu d\varepsilon_l' \frac{v_r'^2}{v_r} \sigma(E; \hat{e}' \circ \hat{e}; \varepsilon', \varepsilon_l' \rightarrow \varepsilon, \varepsilon_l) \quad (2)$$

where $\sigma(E; \hat{e}' \circ \hat{e}; \varepsilon', \varepsilon_l' \rightarrow \varepsilon, \varepsilon_l)$ is the differential cross section associated with a binary collision which produces a pair of molecules in the final states (v, ε) , (v_l, ε_l) from a pair of molecules in the initial states (v', ε') , (v_l', ε_l') . E is the conserved total energy in the center-of-mass reference frame.

Boundary Conditions

The boundary condition which describes adsorption/desorption ($x=0$), is presented in Eq.(3):

$$f_w(t, x, v) = \theta \frac{\tilde{n}_s^{(0)}}{\tau_a} \frac{1}{2\pi(RT_w)^2} \exp\left(-\frac{v^2}{2RT_w}\right) + [1 - (1 - \theta)\sigma] \left[(1 - \alpha) f(t, x, v - 2n(v' \cdot v)) + \frac{\alpha n_r}{(2\pi RT_w)^{3/2}} \right] \exp\left(-\frac{v^2}{2RT_w}\right) \quad (3)$$

where θ is the fractional surface coverage, $\tilde{n}_s^{(0)}$ is the number of active sites per unit area on a perfectly clean surface, experimentally obtained, τ_a is the residence time of an ad-atom, R is the specific gas constant, v is the distribution function of molecular velocity, σ is the probability of a molecule to be adsorbed upon hitting a free site, α is the accommodation coefficient and n_r is the density of reflected molecules.

The fractional coverage θ presented in Eq.(3) is obtained from the Langmuir theory [5], and it can be calculated under the equilibrium conditions according to Eq.(4):

$$\theta = \frac{bP}{1 + bP} \quad (4)$$



where b is the Langmuir constant, Eq.(5), and P is the pressure at the wall:

$$b = b_{\infty} \exp\left(\frac{E_d}{RT}\right) \quad ; \quad b_{\infty} = \frac{A}{k_{d\infty} \sqrt{2\pi RT}} \quad (5)$$

where E_d is the activation energy for desorption, A is the active unit area and $k_{d\infty}$ is the rate constant for desorption at infinite temperature. Another important parameter related to the adsorption/desorption phenomena is the average residence time of adsorption (τ_a):

$$\tau_a = \tau_0 \exp\left(\frac{E_d}{RT}\right) \quad ; \quad \tau_0 = \frac{1}{k_{d\infty}} \quad (6)$$

The rates of adsorption and desorption are obtained from Eq.(7) and Eq.(8), respectively [5].

$$R_a = \frac{AP}{\sqrt{2\pi m k_B T}} (1 - \theta) \quad (7)$$

$$R_d = k_{d\infty} \exp\left(\frac{E_d}{RT}\right) \theta \quad (8)$$

where, m is the molecular mass.

The boundary condition in the undisturbed far upstream vapor state, $x=\infty$, is described by the equilibrium Maxwellian distribution function [6]:

$$f_{\infty}(v, \varepsilon) = \frac{n_{\infty}}{(2\pi RT_{\infty})^{3/2}} \exp\left(-\frac{(v - u_{\infty})^2}{2RT_{\infty}}\right) \times \frac{\varepsilon^{j/2-1}}{\Gamma(j/2)(\kappa T_{\infty})^{j/2}} \exp\left(-\frac{\varepsilon}{\kappa T_{\infty}}\right) \quad (9)$$

where u_{∞} is the upstream bulk velocity and has two components, normal (x direction) and parallel (y direction) to the solid surface.

Dimensionless Properties

The results obtained in this work will be presented in its dimensionless form. The distance x is normalized by the mean free path λ , defined in Eq.(10). The temperature is normalized by the initial temperature at the wall. The density is normalized by the initial density at the wall. The velocity is normalized by $\sqrt{RT_w}$.

$$\lambda = \frac{1}{\sqrt{2\pi n_w d^2}} \quad (10)$$

NUMERICAL PROCEDURE

The adsorption-desorption boundary conditions are performed in the frame of the DSMC algorithm as follows: The residence time τ_0 and the activation energy for desorption E_d are input parameters and remain constant during the simulation.

- A. Compute the initial fractional coverage θ_0 , Eq.(4), using the initial gas pressure at wall $P_{w,0}$ and the Langmuir constant b , Eq.(5). For each particle hitting the solid surface ($x=0$) in each time step Δt it is performed the following:
 1. Solve Eqs.(1) and (2) with the boundary condition at the wall, Eq.(3);
 2. Calculate the new values of the gas macroscopic properties (pressure, temperature, density, velocity);
 3. Calculate the new value of the fractional coverage θ from the new value of pressure and temperature using Eq.(4).
- B. The steps 1, 2 and 3 stop when the simulation time achieves the maximum time of simulation, which is an input file. Then, the final value of fractional coverage θ is reached.

It is worth noting that, in general, pressure and thermal conditions may vary during the simulations, thus the fractional coverage θ varies until it establishes when the steady state flow regime is reached.



SIMULATIONS AND RESULTS

Some simulations varying the input parameters were performed in order to analyze the adsorption and desorption phenomena. Figure 1 presents the evolution of fraction coverage (θ) in time for different values of activation energy for desorption (E_d). As can be observed, the higher is the value of E_d , the higher is the converged value of θ . Figure 2 shows the fluxes at the wall (adsorption and desorption) and at the infinity for two of the different values of activation energy for desorption simulated. As can be seen, the adsorption and desorption rates are higher for smaller value of E_d , and consequently smaller values of θ . This is expected, since adsorption is proportional to $(1-\theta)$.

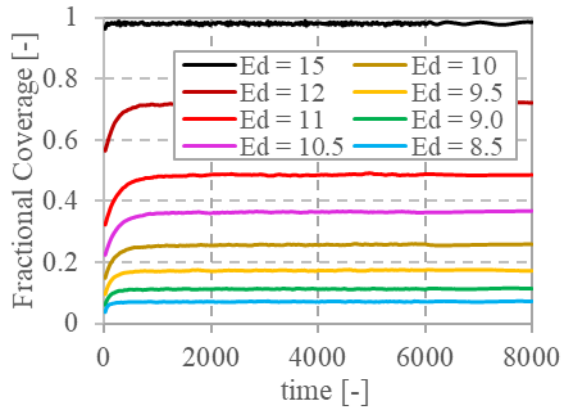


Figure 1: Variation of some macroscopic properties at the wall in function of time t .

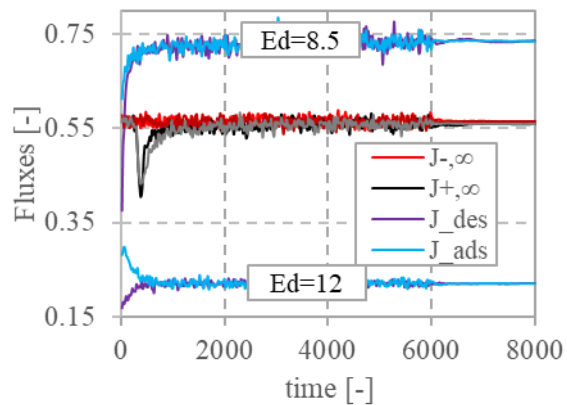


Figure 2: Variation of some macroscopic properties in function of the distance from the solid surface.

Conclusion

The presented results are just the preliminary ones and further development is needed to simulate the separation phenomena based on adsorption-desorption. However, as can be seen from the results, the presented adsorption-desorption model presented works properly for 1D flow, being an indication that it will work well also for 2D flows.

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