Estimation of parameters of gas diffusion in models of microtransfactions of different type by the method of molecular dynamics

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Abstract. Estimation of gas transport parameters in organic nano-porous materials, such as kerogens, is important for understanding the fundamentals of the processes that co-produce natural gas. In this regard, the description and numerical parameterization of the processes of transfer of components of natural gas occurring at the micro level in organic nano-porous materials is of interest both from fundamental and practical points of view, including the search for possible ways to optimize the yield of natural gas and boost recoil. The purpose of this study is to study the methods of molecular modeling and the molecular dynamics of the mechanisms of gas transport in structures that mimic organic nano-porous materials, and the numerical evaluation of mass transfer parameters.

1. Introduction

Computer simulation methods have long shown their effectiveness in the study of the fundamental properties of physical systems, as well as in applied studies of mass transfer, diffusion / convection in complex systems [1–3]. To correctly solve diffusion / convection problems using computational physics methods based on solving differential equations for continuous media, as a rule, knowledge of such physical constants describing the properties of a simulated medium, such as diffusion coefficients, thermal expansion, etc., and their depending on the parameters of the system. These coefficients are usually obtained from experimental data. However, in some cases, obtaining experimental data is difficult or impossible. This applies, in particular, to the study of mass transfer processes in nanostructures at high pressures and temperatures, which correspond in particular to the natural conditions of gas mass transfer processes in kerogen. In this case, at the first step, other methods of computational physics can be applied, in particular, the molecular dynamics method (MD, [4]), which makes it possible to make sufficiently accurate estimates of the macroscopic parameters of gas diffusion processes on scales of the order of nanometers; n The use of MD allows one to analyze diffusion processes in structures and study the effect of dynamic mobility of molecules.

The obtained estimates of diffusion coefficients can be further used to refine the diffusion parameters of gas in nanostructures that mimic kerogen, for computer simulation of shale gas transport processes on a macroscopic scale, and to refine models describing shale gas transport processes. In particular, this applies to estimates of effective coefficients within the Pore-Network Model, for studying shale gas transport processes on a macroscopic scale, using grid methods (such as the finite element method).
These models can be used in problems of rational nature management, in studying the development processes of shale deposits, many of which in the Russian Federation are concentrated in the Arctic zone. This applies, among other things, to the Kuonamian kolumplex of sediments in Yakutia, which, according to some experts, are of interest from the point of view of ease of exploration and production.

In the long term, due to the gradual exhaustion of traditional sources of hydrocarbons, there is an increase in the interest of the extractive industry to the deposits of shale hydrocarbons, many of which are located in the Russian Federation in the Arctic zone. Despite the fact that currently the development of shale deposits in the Russian Federation has no economic justification, monitoring and scientific research in the field of the extraction of hard-to-recover hydrocarbons are also necessary in order not to become in terms of technologies that may become relevant in the future in 20-50 years. This also applies to Yakutia, whose GRP is currently largely dependent on the extraction of minerals.

2. Materials and methods

2.1. Preparing of the structures

The original software BiLayer was used to build structures that simulate the gaps between the sheets of graphene, as well as structures that mimic the organic polymer. As a structure imitating the gap between the sheets of graphene, we used a structure with a size of 1.7 nm · 1.7 nm (in the X, Z plane) containing 836 carbon atoms. The structure of graphene is presented in Fig. 2. Periodic boundary conditions were used with regard to chemical bonds, and the MD OPLS force field was used [6–8].

The distance between the sheets (size of the periodic cell in the direction of the OY axis) varied from 0.5 nm to 19.5 nm (Figure 3, a). As a structure imitating the gap between the sheets of organic polymer, we used a structure with a size of 1.7 nm · 1.7 nm (in the X, Z plane), in which amino acid residues (a.k.o.) were added, supplemented with NH2 and C-OOH, while the position of the C-alpha atom was fixed in space to limit the drift of the molecule.

Figure 1. Graphene structure in periodic boundary conditions (blue lines).
Three models were used that mimic the surface acid / alkaline, hydrophilic and hydrophobic. The residues Glu and Arg were chosen as the amino acid residues, and the acid a.k. and alkaline a.k.o. respectively, Gln as a hydrophilic a.k.o, Trp as a hydrophobic a.k.o. (Figure 4). For each of the systems (Graphene, acid / alkaline, hydrophilic and hydrophobic surfaces), 38 structures were created with the distance between the walls from 0.5 nm to 19.5 nm with a step of 0.5 nm. The type of structure simulating the organic polymer Arg / Glu with a distance between the walls of 5 nm is shown in Figure 3, b. In this work, the molecules of methane and carbon dioxide included in the composition of natural gas were used as a model gas.

Since the presence of a graphene sheet does not have a significant effect on the diffusion of gas molecules, to accelerate the calculations, models simulating acid / alkaline, hydrophilic, and hydrophobic surfaces without the presence of a graphene sheet were also constructed. Amino acid residues were placed in a triangular grid, while the average area per 1 a.k. was 0.4 nm². When preparing the structure, molecules a.k. aligned along the OY axis and rotated at a random angle in the XZ plane.

The prepared structures were then supplemented with structures obtained in the simulation of the gas phase (this process is described in more detail in Section 1.2). Figure 5 shows the structure model for the gap between the sheets of graphene. The periodic cell is highlighted in blue, supplemented with periodic images along the OX and OY axes.

The distance between the sheets (the size of the periodic cell in the direction of the OY axis) varied from 0.5 nm to 19.5 nm; in total, 38 structures were prepared for each system. During the simulation,
amino acid residues supplemented with NH2 and C-OOH groups, imitating an organic polymer, were fixed in space due to the application of a harmonic potential with a stiffness constant of 1000 kJ / (mol · nm2) to C-alpha atoms a.k.

Figure 3. Models of molecules imitating organic polymer with acidic (a), basic (b), hydrophilic (c) and hydrophobic (d) properties.

2.2. Modelling of electrostatic interactions
Since the existence of electrons in the system is not explicitly taken into account in the MD method, the nonuniformity of the charge distribution is described by using partial charges for each atom and the Coulomb interaction energy between atoms is described by a standard expression. The calculation of the partial charges of atoms in the system is a separate fundamental point of molecular modeling, since these characteristics of atoms can have a significant impact on the dynamic behavior of the molecular system.

Different works use different partial charges corresponding to atoms of methane and carbon dioxide molecules, and the difference can reach 300% [6, 9, 10]. The problem is that when simulating gas transport under conditions that simulate natural conditions in kerogen, in this case, the parameters of the force fields selected for correct reproduction of the physical characteristics of the gas under normal conditions can give distortions. Therefore, to estimate the Coulomb interactions in the system, quantum chemical calculations were performed using the Firefly Gamess software [11]. The partial charges of atoms were estimated using the unrestricted Hartree-Fock method, the 6-31G * basis, and the Mulliken method. The calculation results are shown in table 1.

Table 1. Quantum-chemical calculations of the partial atom charges for methane and carbon dioxide molecules.

| Molecule | Atom | Partial charge, e |
|----------|------|-------------------|
| CH4      | C    | 0.660             |
|          | H    | 0.165             |
| CO2      | C    | 0.892             |
|          | O    | -0.446            |

To prepare a periodic cell corresponding to the gas volume, molecular dynamics calculations were performed. Computational experiments were carried out in the Gromacs software package [12] version 4.6.7. The OPLS force field was used [6, 8], the minimization of the energy of the collected systems was carried out by the method of conjugate gradients. Then the system was subjected to multi-stage relaxation. The main parameters of modeling:

- Solving the equations of motion using the stochastic dynamics method with constant temperature control: τt = 1 ps;
- Integration step: 0.2-0.5 fs;
• Temperature: 300K and 353 K;
• Barostat: Berendsen with constant barostating $\tau = 5$ ps;
• Pressure: 1 bar and 178.57 bar;
• Cutoff radius of non-valent interactions: 1.8 nm;
• The lengths of the connections and angles were not fixed.
• The initial atomic velocities were determined using a random number generator using the Maxwell distribution.

Figure 4. Model of the crack with methane gas between graphene layers under periodic boundary conditions (indicated with blue lines).

MD calculations were carried out for periodic cells containing 27,000 gas molecules under conditions of 300 K at $T = 300$ K, the results of the calculations are given in Table 2.

Table 2. Calculated diffusion coefficients in pure gas phase.

| System                          | Calculated diffusion coefficient, cm$^2$/s |
|---------------------------------|-------------------------------------------|
| CH$_4$, Temperature 300K, Pressure 178 bar, OPLS forcefield. | $83.9 \pm 0.1 \times 10^{-5}$ |
| CH$_4$, Temperature 353K, Pressure 178 bar, OPLS forcefield. | $153.9 \pm 1.7 \times 10^{-5}$ |

A total of 2 calculations were made with a total path length of 22 ns. For analysis, we used the data of the last 1 ns trajectories. As can be seen, with increasing temperature and pressure, the gas phase density and diffusion coefficient change. For further modeling of the conditions characteristic of the gas state in the kerogen, the simulation parameters were used: an integration step of 0.2 fs, a pressure of 178 bar, a temperature of 353 K. In the calculations of the diffusion of gases in model cracks, a model of methane was used.
3. Results
As a result of the calculations, an analysis was made of the diffusion coefficients of gas molecules in each system (Figure 6). As can be seen, with increasing the distance to the walls to about 0.8 nm, the graph reaches a plateau, and the difference in the diffusion coefficient in the thickness becomes insignificant and does not exceed the values of the standard deviation (on average 1.5 - 2.7 • 10^-5 cm^2 / s) however, it remains understated for the graphene system.

At the same time, the data near the border, on the contrary, are overestimated for the graphene system, and for the system from a.k. Trp simulating a hydrophobic organic polymer, the calculated diffusion coefficient is underestimated.

The results of the analysis of the energy of non-valent interactions of gas molecules with the walls are shown in Figure 7. As you can see, the total interaction energy decreases with the size of the system, and the interaction energy with the walls simulating a polymer is much stronger than in the graphene system to a distance of about 3 -5 nm, which may explain the underestimated values of the diffusion coefficient near the walls. As can be seen from Figure 8, a significant contribution to this effect is made by the partial Coulomb interaction potential, which is explained in particular by the fact that in the models of graphene used in the MD methods, the partial charge on the carbon atom is 0 and, thus, the Coulomb interaction between gas molecules and the wall is not taken into account. It can be seen that the expected contribution of Coulomb interactions is most significant in a system that mimics an acid / alkaline surface, and then decreases in the series: hydrophilic and hydrophobic surfaces.

It can also be noted here that in the case of using more polar molecules in the composition of the gas mixture (for example, carbon dioxide or water molecules), we can expect an additional enhancement of the role of Coulomb interactions on the rate of diffusion processes.

Figure 5. Estimated effective diffusion coefficient values for different systems.
Figure 6. Calculated total energy of non-bonded interactions (a) and contribution of the Coulomb interaction energy (b).

4. Conclusion

Thus, in the course of the work, the structures of the gaps between the planes of pure carbon (graphene) and organic polymer were constructed, quantum-chemical calculations were performed to refine the force fields for non-standard system nodes, including methane and carbon dioxide molecules. Complexes of structures with a model gas were prepared (the methane model was used) and protocols were developed for simulating the diffusion of gases along the gap using the molecular dynamics method.

It is shown that in systems imitating an organic polymer, the processes of diffusion of gases near the system’s boundary differ markedly from similar processes in the system, in which the crack...
boundary is described by the graphene model, which can be explained as a contribution of Lennard-Jones interactions with atoms other than carbon, and the contribution of Coulomb interactions.

The results can be used to refine macroscopic models of gas transport using grid methods (such as the Pore-Network Model and the finite element method) to study the transport processes of shale gas in kerogen.

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References

[1] Akkutlu I.Y. et al. Multiscale model reduction for shale gas transport in a coupled discrete fracture and dual-continuum porous media // J. Nat. Gas Sci. Eng. 2017.
[2] Kou R., Alafman S.F.K., Akkutlu I.Y. Multi-scale Analysis of Gas Transport Mechanisms in Kerogen // Transp. Porous Media. 2017. Vol. 116, № 2. P. 493–519.
[3] Riewchotisakul S., Akkutlu I.Y. Adsorption-Enhanced Transport of Hydrocarbons in Organic Nanopores // SPE J. Society of Petroleum Engineers, 2017. Vol. 21, № 06. P. 1960–1969.
[4] Berendsen H.J.C. et al. Molecular dynamics with coupling to an external bath // J. Chem. Phys. 1984. Vol. 81, № 8. P. 3684.
[5] Antonov M.Ju. et al. Ocenka profilej potenciala srednej sily metodom umbrella sampling dlja transmembrannogo perenosja molekuly vody. // Matematicheskie zametki SVFU. 2014. Vol. 21, № 3. P. 95–105.
[6] Kaminski G.A. et al. Evaluation and Reparametization of the OPLS-AA Force Field for Proteins via Comparison with Accurate Quantum Chemical Calculations on Peptides // J. Phys. Chem. B. American Chemical Society, 2001. Vol. 105, № 28. P. 6474–6487.
[7] Jorgensen W.L., Maxwell D.S., Tirado-Rives J. Development and Testing of the OPLS All-Atom Force Field on Conformational Energetics and Properties of Organic Liquids // J. Am. Chem. Soc. 1996. Vol. 118, № 45. P. 11225–11236.
[8] Jorgensen W.L., Tirado-Rives J. The OPLS [optimized potentials for liquid simulations] potential functions for proteins, energy minimizations for crystals of cyclic peptides and crambin // J. Am. Chem. Soc. 1988. Vol. 110, № 6. P. 1657–1666.
[9] Martin M.J., Siepmann J.I. Transferable Potentials for Phase Equilibria. 1. United-Atom Description of n-Alkanes. American Chemical Society, 1998.
[10] Sigfridsson E., Ryde U. Comparison of methods for deriving atomic charges from the electrostatic potential and moments // J. Comput. Chem. John Wiley & Sons, Ltd, 1998. Vol. 19, № 4. P. 377–395.
[11] Gordon M., Schmidt M. Advances in electronic structure theory: GAMESS a decade later. 2005. P. 1167–1189.
[12] Hess B. et al. GROMACS 4: Algorithms for Highly Efficient, Load-Balanced, and Scalable Molecular Simulation // J. Chem. Theory Comput. American Chemical Society, 2008. Vol. 4, № 3. P. 435–447.