Creating thin layers at the contact surface of two nonmixing liquids

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Abstract. The paper presents the results of numerical simulation of processes aimed at production of nanostructures with the use of oil emulsions in water. The appropriate molecular models of water and oil, as well as the model of the substance which would sediment at the water – oil interface, are looked for. Such substance, after suitable solidification, would become the main component of the produced material. For the described simulations, the Molecular Dynamics method has been used throughout this paper.

Key words: thin layers, contact surface, nonmixing liquids.

1. Introduction

The design of new technologies, making it possible to manufacture the nano-structured materials is one of the most important tasks of the contemporary materials science [1]. The technologies, utilizing the emulsion droplets or bubbles as templates for producing nanostructures out of solid particles suspended in the liquid phase, seem very promising; work on developing such technologies is progressing fast [2]. It seems however conceivable, that even smaller structures could be obtained, if instead of solid particles a liquid film was utilized.

The researchers involved in production of nanomaterials concentrate on two aspects of the problem. The first is creation of a regular system consisting of bubbles or droplets in liquid [3–5]. In the next step the process of creating a sediment of particles is considered [6–8].

In the reported research we investigated the conditions necessary for producing a film at the interface of two nonmixing liquids. In our investigation we used emulsion consisting of oil droplets immersed in water. The third component was expected to create a thin layer at the contact surface of the liquids. After removing emulsion this third component was supposed to create a very regular, porous structure, which, when hardened, would produce the micro- or nanomaterial with very promising properties (Fig. 1).

The assumed diameters of the oil droplets were very small, therefore we treated all the liquids as ensembles of molecules and to simulate their behaviour we applied the Molecular Dynamics simulation technique. The motivation for using the MD method was building molecular models of substances, similar to realistic atomic systems. It was necessary to understand which properties of the system: polarity, atomic configuration and interactions, are important in the process. When looking for substances which would stay at the surface of an oil droplet, information on their molecular properties becomes essential. At the same time, knowing the molecular properties of the system, important for the process considered, it should be possible to create an adequate simplified model of the proposed substance, which in the next step might be useful for the mesoscopic methods. Such methods are necessary to describe the behaviour of emulsion of droplets with nano-particles attached at the interfaces, particularly interactions of droplets and creation of solid matrix of spheres built from nano-particles. Future mesoscopic simulations are possible using Lattice-Boltzmann Method (LBM) or Dissipative Particle Dynamics (DPD), recently introduced by Hoogerbrugge and Koelman [9]. Here, we limit our interest to small systems of several thousand molecules only. The constructed molecular model of sedimentation process might be an introduction to modelling larger systems of molecules, which could be useful for simulating mesoscale physical processes.

2. Method

The Molecular Dynamic simulation is a fully deterministic method, assuming that the investigated substances consist of molecules and the macroscopic behaviour of those substances, (evaporation, mixing, etc.) is determined by the intermolecular interactions.

To model the substances we used two types of interactions between molecules. All atoms interact with each other through the van der Waals forces, as described by the Lennard-Jones potential, given by the formula [10]:

$$U(r) = 4\varepsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^{6} \right] \tag{1}$$

where r is the distance between centres of mass of the molecules.

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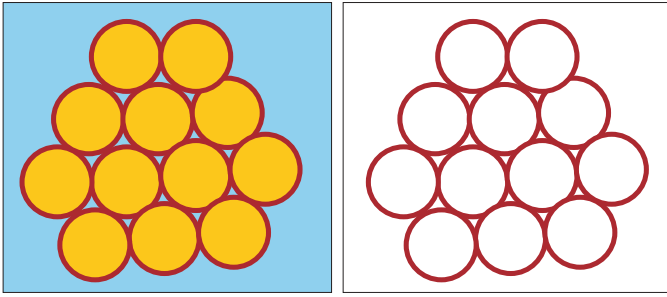
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Fig. 1. Structure of emulsion with the sediment on the contact surface and nanomaterial after removing the emulsion

The Lennard-Jones potential describes the attractive and repulsive interactions using two parameters: σ – "diameter of the molecule" and ε – "depth of the potential well". The molecules, which are electric dipoles or ions, interact also through the electrostatic forces via the Coulomb potential. The dynamics of the molecular motion is described by the Newton-Euler equations [10,11].

Difficulty of the problem is increased by the fact, that molecular interactions are not additive. To be able to obtain the solution, additivity of interactions is assumed, which in addition requires modification of interaction potentials (introduction of "effective potentials") [10]. Numerical implementation is then realized by solving huge system of pair-wise interactions. It is memory and CPU intensive task, limiting application of the method to small systems containing less than 106 molecules and evolution times in nanosecond range. In the following we present simulation results obtained with the shareware program "MOLDY" [12]. Moldy is a general-purpose molecular dynamics simulation program useful for a wide range of simulation calculations of atomic, ionic and molecular systems in the domain with periodic boundary conditions. In the presented simulations to maintain constant temperature of the system the method of velocity scaling was used.

A large majority of the simulations were calculated on the Mosix cluster in our Department, where a typical computational run of four thousands monoatomic molecules in a process lasting 100 picoseconds took about twenty hours.

3. Numerical modelling of emulsion

3.1. Modelling of water and oil. When modelling the process of formation of oil droplets in water we were looking for interactions between molecules, which would provide the expected separation of liquids. From macroscopic point of view the hydrophobic behaviour of oil molecules is responsible for this effect.

At the atomic level, the separation of liquids results from strong electrostatic dipolarization of water molecules and very weak polarization of oil molecules. Our model of water should therefore allow for the dipolarity of the molecules.
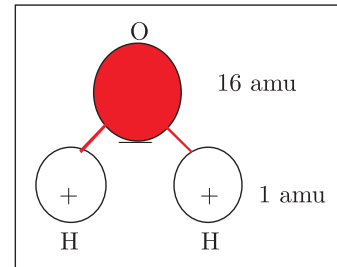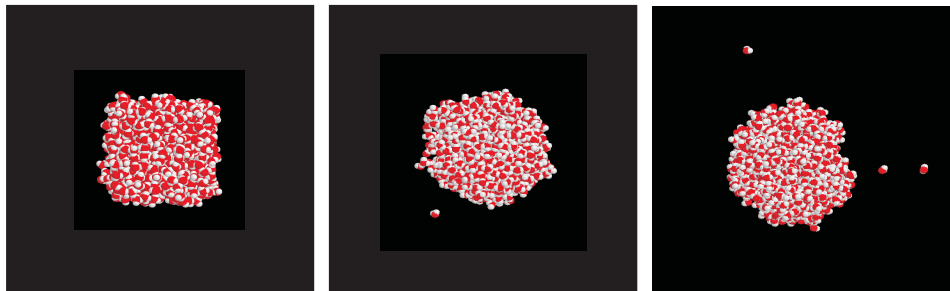

Fig. 2. Molecular model of water: TIPS2

Fig. 3. Water droplet (1000 molecules) in vacuum for times: t = 0, t = 8 ps and t = 40 ps
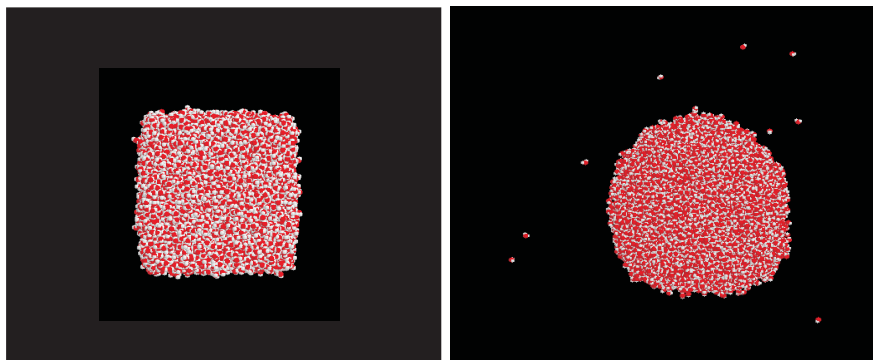

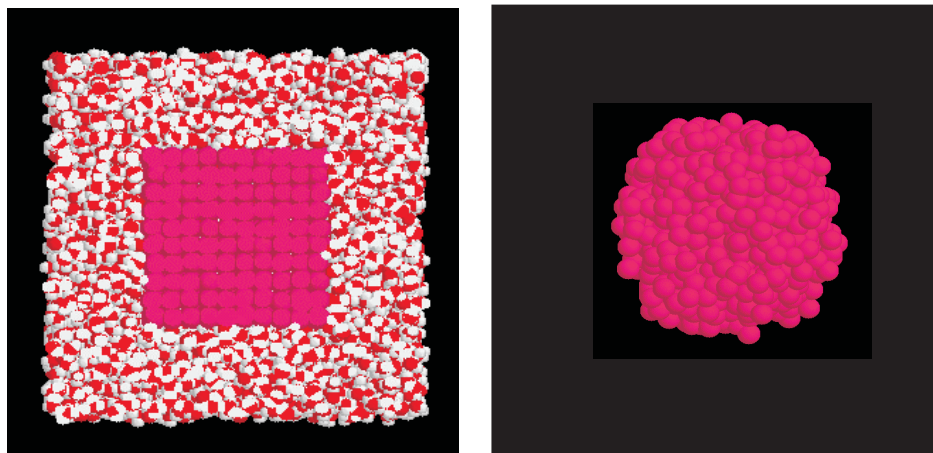Fig. 4. Water droplet in vacuum, 10648 molecules: t = 0 and t = 16 ps

Fig. 5. Oil droplet in water for t = 0 and t = 13 ps (here only oil molecules visible)
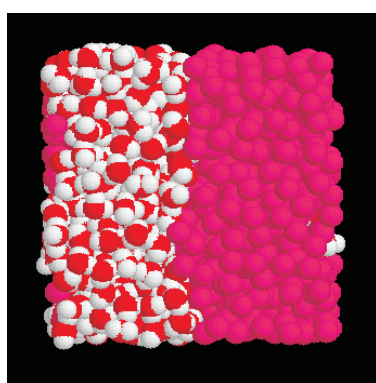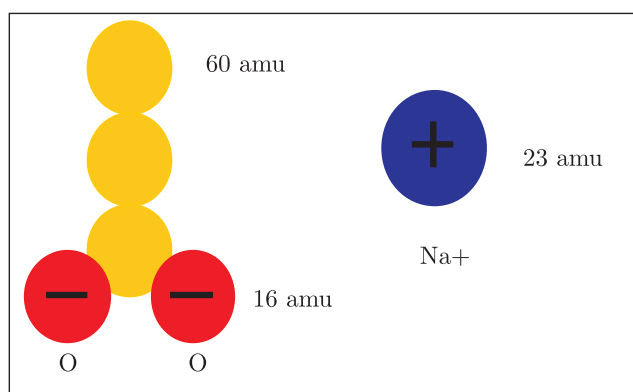

Fig. 6. Nonmixing layers of oil and water

Fig. 7. Molecular model of a surfactant

We used the well-known TIPS2 model of water [13] (Fig. 2). To test the behaviour of this model we placed in vacuum a droplet of water, consisting of 1000 molecules and having initially shape of a cube, and we observed the subsequent changes of its shape. Temperature of the water systems in the simulations was 300 K. After about 8 picoseconds the shape became nearly spherical. The diameter of this spherical droplet was about 3.8 nm. Some time later the expected beginning of evaporation could be seen (Fig. 3).

Similar process was also observed for larger droplet, consisting of 10648 molecules (Fig. 4). The diameter of this larger droplet was about 8.4 nm.

We tested also several other models of water, both simpler and more complex, with and without electric charges. However, only the presented TIPS2 model produced a stable, spherical droplet in vacuum, therefore we decided to use it in the later simulations.

The model of an oil molecule, which we accepted after some tests, was a relatively large sphere, consisting of single atom, having no electric charges and interacting with neighbours only via the Lennard-Jones potential. The attraction between such oil molecules was very weak.

To test the models of the two liquids together, 1000 oil molecules were placed in the central part of the cubic cell of water. Temperature of the system was 300 K, as before, and the pressure about 10^5 Pa . These conditions were compatible with experimental ones for the homogenisation process and were used for all subsequent simulations.

After 13 ps from the beginning of simulation the droplet of oil acquired a stable, spherical shape (Fig. 5). Water and oil molecules did not mix during the simulation even when, as in the next simulation, the contact surface between the liquids was plane (Fig. 6).

3.2. Modelling of emulsion with surfactant. The next problem to solve was the behaviour of the modelled liquids in contact with the third substance expected to create the film at the contact surface. As is well known, the properties of the surfactants enable their sedimentation between nonmixing liquids – oil and water. These properties, (widely used in chemical industry), follow from the specific atomic structure of surfactants. The molecule of a surfactant consists of two parts: hydrophobic and hydrophilic. Each part of the molecule attracts a suitable liquid, making the molecule stay at the contact surface.

To create the model of a surfactant we utilized the elements of water and oil molecules. The hydrophobic part

was built of an oil chain, and the hydrophilic part, similar in its structure to water, consisted of negative oxygen ions (Fig. 7). To neutralize the molecule electrically, positive sodium ions were immersed in water.

The first simulations were performed for a model of surfactant with short hydrophobic part, consisting of only one "atom" of oil. Such molecules of surfactant were placed at the surface between oil and water. During the simulation the surfactant did not stay at the interface and migrated into water. To improve stability of the configuration, a new model of surfactant, with longer, three-atomic oil chain was introduced. Such molecules of a surfactant produced a stable layer between oil and water (Fig. 8).

The obtained results indicate that, although molecules of oil in contact with water can be simulated using a "single-atom" model, for the surfactant we should use the more realistic model, with longer chain of oil "atoms".

4. Simulations with solid particles

4.1. Simulations with simple oil and carbon. When looking for solid particles which would stay at the surface between oil and water, several substances were tested and finally carbon molecule was selected. The used model of carbon atoms allowed for interactions via the Lennard-Jones potential only.

In the first simulation single carbon atoms were immersed in water (Fig. 9a). During the simulation these atoms migrated from water into oil and did not create any sediment at the contact surface. The interactions between oil and carbon molecules were then weakened and the simulation was repeated, still the results were the same. Carbon migrated into oil layer, as before, (Fig. 9b) only the time necessary for the process was longer.

For the next simulation, nanoparticles of soot – crystals consisting of 13 carbon atoms each – were used instead of single carbon atoms. The assumed interactions betweens atoms were the same as in the first simulation, where single carbon atoms were used.

Small number of such nanoparticles were placed initially in the water layer. After a while they created a sediment at the contact surface of liquids (Fig. 10a). Similar simulation for larger number of molecules confirmed the result; there was a general tendency to create the carbon sediment between oil and water. However, when the layer of water was thicker (Fig. 10b) some particles, placed initially far from the contact surface, created pellets inside water, which required obviously more time to move towards the interface than the simulation could offer. It seems probable, that the mechanism responsible for movements of particles as large as pellets, was that of Brownian motions.

4.2. Simulations of sedimentation at water-limonene interface. The process of removing oil droplets from inside the nanomaterial presents many technical difficulties. Looking for a substance easier to be re-

moved from the structure we decided to use limonene – an aromatic oil evaporating easily at room temperature [14]. A limonene molecule is close to being spherical, so we modeled it in simulations as a big, heavy sphere, interacting with other molecules only via the Lennard-Jones potential. The model of limonene was tested in a simulation with surfactant. A number of the surfactant molecules were initially dissolved in water; during the simulation all these molecules migrated to the contact surface between limonene and water and stayed there. The orientation of the surfactant molecules was "correct": the "oil chain" of each molecule was immersed in limonene and the ionic part was immersed in water (Fig. 11).

We tested also the interactions between limonene and nanoparticles of carbon. The results were similar to those for the first model of oil. They indicated, that the carbon particles placed close to the contact surface did create sediment, but the rest of them created larger pellets, staying permanently in water. Additional simulations were performed for smaller thicknesses of water layer. For layers only three particle diameters thick the sedimentation was complete (Fig. 12). This suggested, that the sedimentation was strongly influenced by the force gradients close to the interface.

5. Conclusions

The reported research was aimed at finding substances, which would sediment at the surface of oil droplets in water-oil emulsion. The tool used for this purpose was Molecular Dynamics simulation technique, which proved to be very efficient in this respect. The models of liquid and solid substances were investigated. Among liquids, the surfactants containing long-chain molecules appeared satisfactory. Among solids, carbon was good enough, provided that it appeared in complexes of at least 13 atoms each (forming elementary crystals of soot).

For the future: looking for a model of real mesoscopic emulsion with particles at the surface, it is necessary to create a simplified representation of the proposed molecular models of the substances. On the other hand, building a structure of spheres containing nano-particles one needs to solve mesoscopic problem of external forces and to analyse stability of such configuration.

Appendix

Parameters of the Lennard-Jones potential

In the following table, the parameters of the Lennard-Jones potential used in the presented simulations are given. To calculate parameters for interactions between atoms of two different species the known Lorentz-Berthelot rules [10] were used:

$$\varepsilon_{ij} = \sqrt{\varepsilon_i \varepsilon_j}, \qquad (A1)$$

$$\varepsilon_{ij} = \frac{\sigma_i + \sigma_j}{2}, \qquad (A2)$$
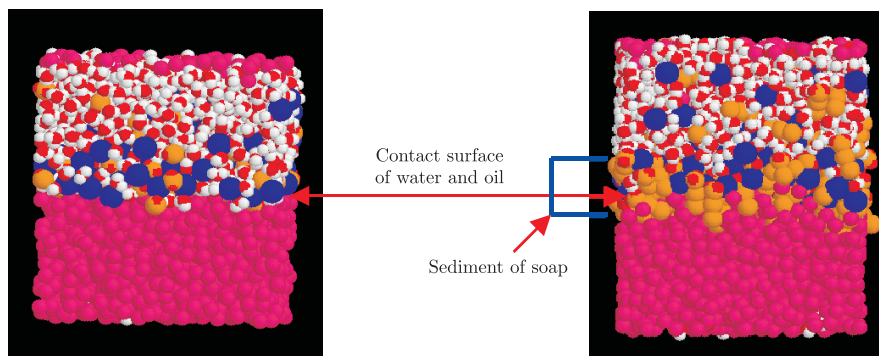
Fig. 8. Surfactant at the contact surface of emulsion: left – the short chain model: soap molecules mixed with water, right – the long chain model: soap molecules creating the sediment
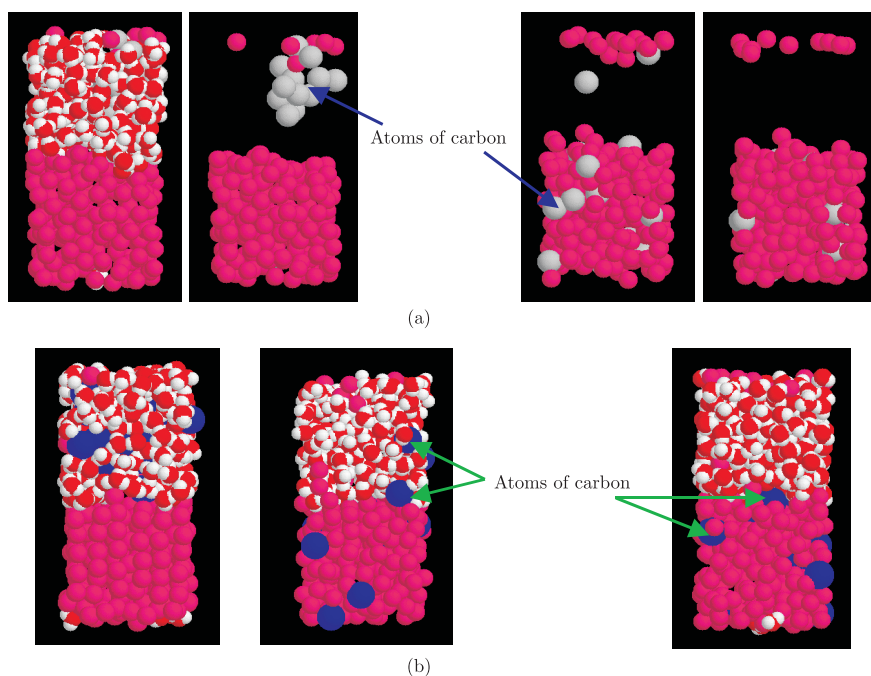

Fig. 9. Carbon dissolved in oil: (a) the first model (grey atoms, water molecules invisible), t = 224 ps, carbon molecules migrate from water to oil; (b) the model after diminishing oil-water interaction potential (blue atoms), t = 500 ps, carbon molecules still migrate into oil
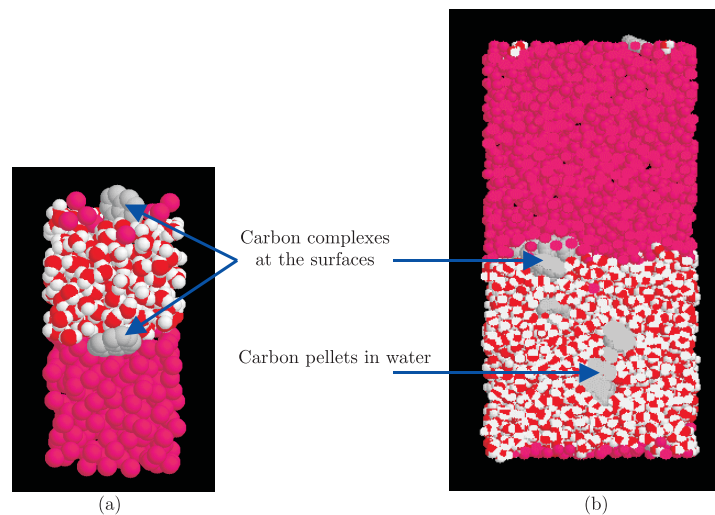

Fig. 10. Nanoparticles of carbon adsorbed in a layer between oil and water (a) and carbon pellets observed in water (b), migrating into the interface
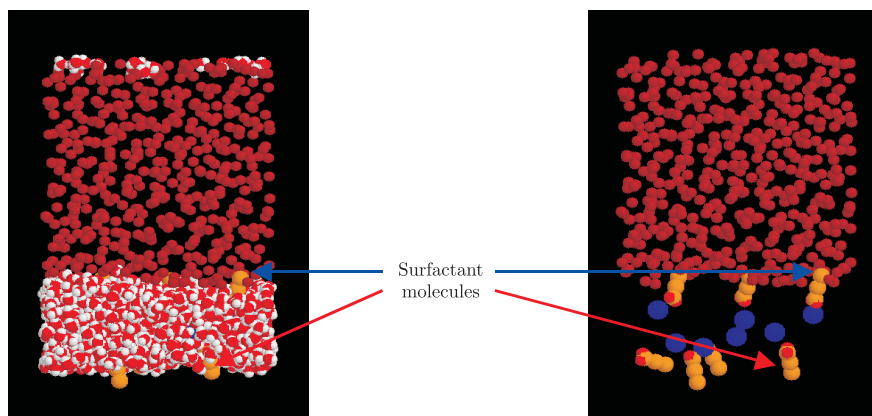
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Fig. 11. Surfactant at the contact surface of limonene and water (left – all three substances shown, right – molecules of water invisible): t = 300 ps
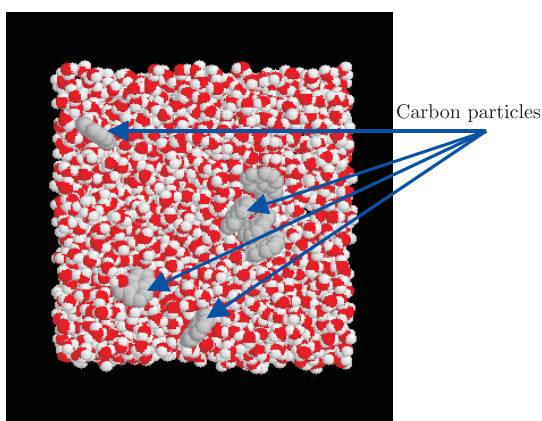

Fig. 12. Carbon particles at the contact surface of limonene and water (limonene invisible): t = 100ps

Here ε_i, σ_i are parameters for the same atoms and ε_{ij}, σ_{ij} are parameters for interactions between atoms of i and j species.

Table 1
Parameters of the Lennard-Jones potential for the used models of molecules

Interacting molecules	ε (kJ/mol)	σ (nm)
Oxygen – Oxygen	0.51799	0.32407
Oil – Oil	0.051799	0.32407
Limonene – Limonene	0.28777	0.7136
Sodium – Sodium	0.95178	0.32407
Carbon – Carbon	0.4257	0.335

REFERENCES

[1] J.C.T. Eijkel and A. van den Berg, "Nanofluidics: what is it and what can we expect from it?", *Microfuidics and Nanofluidics* 1, 249–267 (2005).

[2] G. Brenn, "Emulsions with nanoparticles for new materials", in *Scientific Report of EMMA Project*, Graz University of Technology, TU Graz, 2005.

[3] P. Garstecki, "Formation of bubbles and droplets in microfluidic systems", *Bull. Pol. Ac.: Tech.* 53, 361–372 (2005).

[4] S. Tcholakova, N.D. Denkov, D. Sidzhakova, I.B. Ivanov, and B. Campbell, "Interrelation between drop size and protein adsorption at various emulsification conditions", *Langmuir* 19 (14), 5640–5649 (2003).

[5] S. Błoński, P. Korczyk, and T.A. Kowalewski, "Analysis of turbulence in a micro-channel emulsifier", *Int. J. Thermal Scs*, doi:10.1016/ j.ijthermalsci. 2007.01.028 (2007).

[6] K.D. Danov, P.A. Kralchevsky, K.P. Ananthapadmanabhan, and A. Lips, "Particle-interface interaction across a nonpolar medium in relation to the production of particle-stabilized emulsions", *Langmuir* 22, 106–115 (2006).

[7] A.B. Subramaniam, M. Abkarian, and H.A. Stone, "Controlled assembly of jammed colloidal shells on fluid droplets", `www.nature.com/naturematerials`, (2005).

[8] P.A. Kralchevsky, K. Nagayama, and K. Nagayama, *Particles at Fluid Interface and Membranes*, Elsevier Science, New York, 2001.

[9] P.J. Hoogerbrugge and J.M.V.A. Koelman, "Simulating microscopic hydrodynamic phenomena with dissipative particle dynamics", *Europhys. Lett.* 19, 155–160 (1992).

[10] M.P. Allen and D.J. Tildesley, *Computer Simulation of Liquids*, Clarendon Press, Oxford, 1987.

[11] D. Frenkel and B. Smit, *Understanding Molecular Simulation*, Academic Press, 2002.

[12] K. Refson, "Moldy: a portable molecular dynamics simulation program for serial and parallel computers", *Comput. Phys. Commun.* 126(3), 309–328 (2000).

[13] W.L. Jorgensen, "Revised TIPS model for simulations of liquid water and aqueous solutions", *J. Chem. Phys.* 77, 4156–4163 (1982).

[14] Ch. Shin and G.G. Chase, *Nanofibers from Recycle Waste Expanded Polystyrene Using Natural Solvent*, Springer-Verlag, 2005.