

From the molecules of resorcinolic lipids to alga *G. prisca* globular colonies in kukersite microfossils: a multiscale simulation study

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Abstract. *To understand the presence of globules in the kerogen of Estonian kukersite a multiscale simulation study is performed using the ESPResSo methodology and structures of known building blocks. It is demonstrated how these globules are formed due to the intermolecular interactions in these building blocks.*

Keywords: *Estonian kukersite kerogen, resorcinolic lipids, alga *G. prisca*, multiscale simulation, ESPResSo methodology.*

1. Introduction

The results of the research on Estonian kukersite kerogen up to the end of the last century have been generalized by Lille [1]. It has been concluded that the 5-alkyl-1, 3-dioxysubstituted benzene nucleus in the kerogen originates from the starting lipids of the kerogen formation. It was fully supported by the experimental study of alga *G. prisca* microfossils in the kukersite samples [2]. The role of alga *G. prisca* in the formation of kukersite has been reviewed by Lille [3].

The colloidal properties of kukersite were shown by Zalesky already in 1917 [4] and later by Fomina et al. [5] and Savest et al. [6]. These studies shed light upon the formation of colloidal particles in kukersite, while their presence has been supposed by many researchers.

The size of particles consisting of globular colonies *G. prisca* microfossils in kukersite ranges from 10 to 80 μm . The scanning and transmission electron microscopy (SEM and TEM, respectively) pictures demonstrate the size of the set of colonies up to 50 μm [2]. These colonies are comprised of concentric layers of alkylresorcinol building blocks formed around the voids of the microscopic image. This is understandable because in aqueous solution

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resorcinolic lipids spontaneously assemble into bilayer membranes [7]. Due to the attractive interactions between them, the membrane components are transformed into closed structures, i.e. vesicles [8]. Cellular organelles can be formed from the fusion of vesicles [9]. The elastic properties of lipid bilayers enable the formation of tilted and spherical bilayers ([10].

The size of the abovementioned building blocks corresponds roughly to that of the kukersite molecular model [11]. Hence we can classify kukersite as a lipid-based fuel. It should be noted that nowadays the cultivation of microalga is a sustainable candidate for biomass and oil production [12].

The aim of the present study is to gain an understanding of the globule formation process in the Ordovician Sea based on the kukersite molecular model.

In the study, the ESPResSo methodology (User Guide version 2016: setting up particles, interactions, system) was used [13].

2. Setting up particles

To simulate the behaviour of a system we used the coarse-grained model similar to that employed by Cooke et al. [14]. For simulation first we chose the combined groups of multiple atoms (beads). Considering the typical structural unit of resorcinolic lipids as a 0-substituted long chain 5-alkylresorcinol [15], we selected three groups of beads: one 1,3-oxygen-5-alkyl-substituted benzene ring and two alkyl-chain units consisting of 6-methylene and methyl-6-methylene units. A lipid molecule as a phenolic amphiphile consists of one hydrophilic and two hydrophobic beads. This 3-bead form is one particle (this is not the particle identified by electron microscopy). It is a cylinder with the length and diameter $l = d = 400$ nm, i.e. $0.4 \mu\text{m}$. These 3-bead forms are then connected to form a 5-alkylresorcinol-based polymer.

It is necessary to select the proper number of beads which allows for the use of the computationally acceptable simulation system necessary for the calculation of the experimentally determined set of colonies. We chose the calculation box of $12 \times 12 \times 12 \mu\text{m}$ consisting of 200 000 particles.

3. Setting up interactions

The Lattice Boltzmann method (LBM) as implemented in ESPResSo [16] was used. In addition, fene, kinetic, harmonic and four types of non-bonded interactions were calculated during 1000 time steps per $0.001 \mu\text{s}$.

4. Conducting simulations

To conduct simulations we used 20 processors, the number of particles was 2×10^5 and simulation time 1.0 μ s.

5. Results and discussion

The simulation resulted in globular colonies. One of these colonies is shown in Figure 1. However, from such pictures it is rather difficult to understand the internal structure of a colony. The cross-sections of a colony enable a much better understanding of its internal structure (Figs. 2–4).

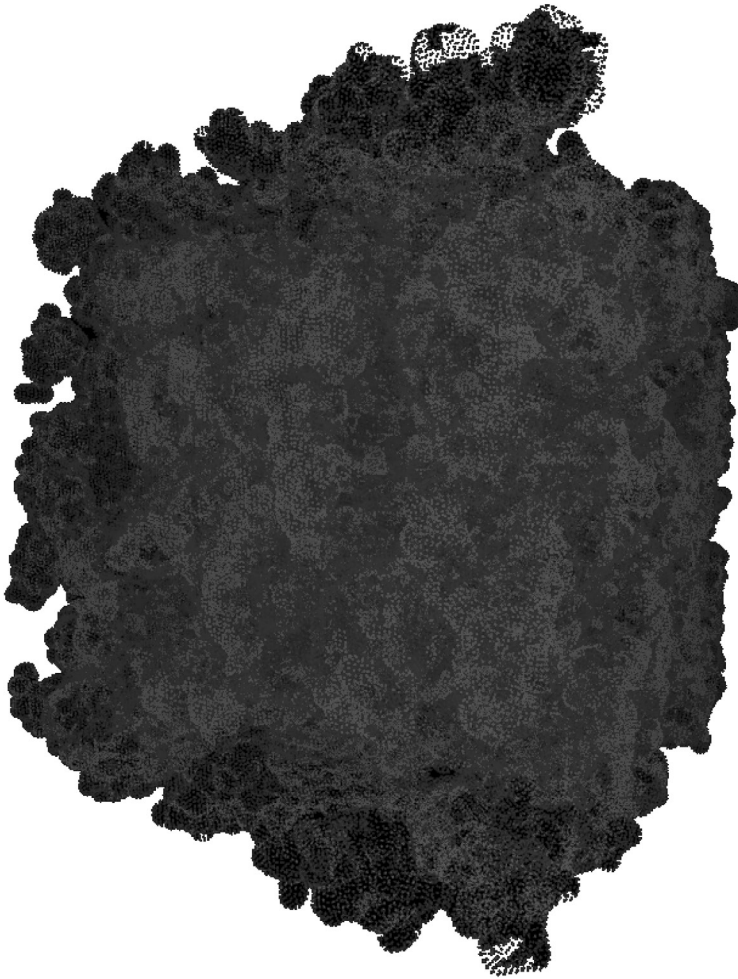


Fig. 1. Calculation box.

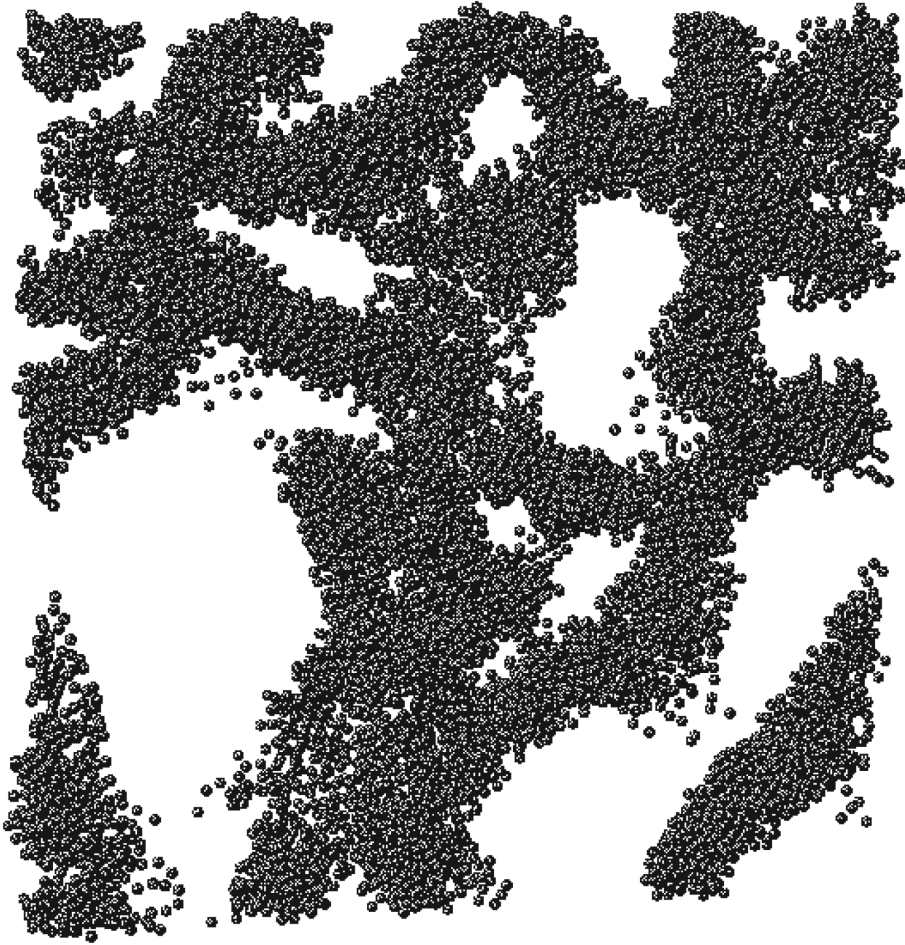


Fig. 2. Cross-sections of the YZ plane of the calculation box ($12 \times 12 \times 12 \mu\text{m}$).

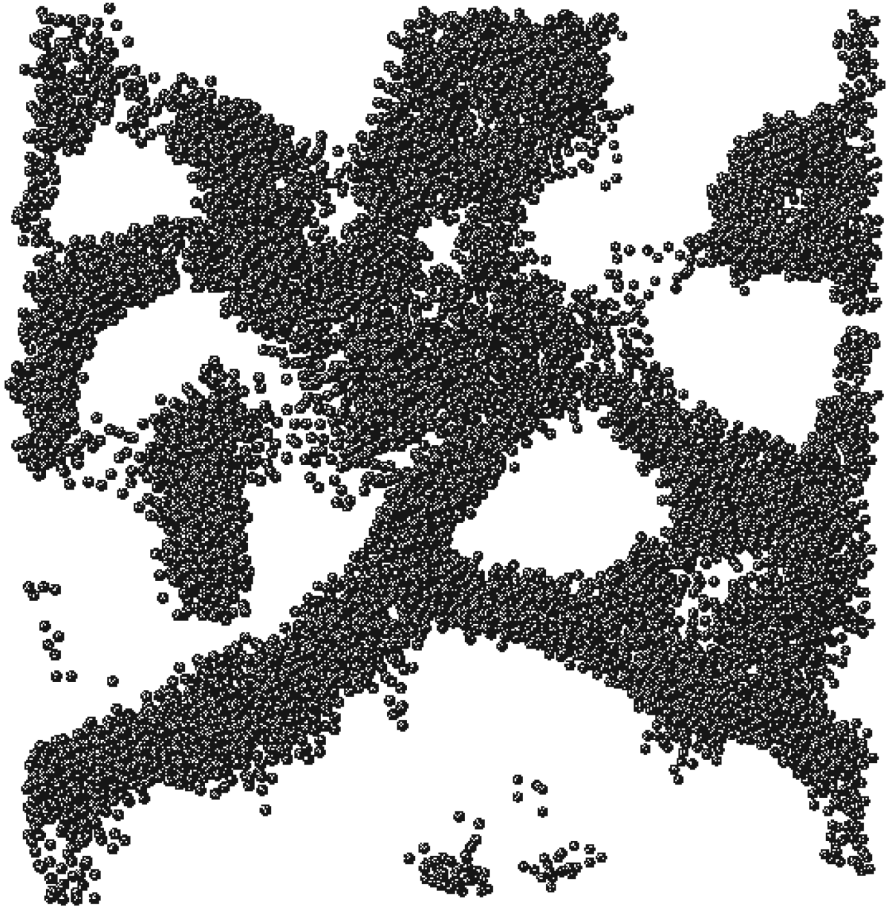


Fig. 3. Cross-sections of the XZ plane of the calculation box ($12 \times 12 \times 12 \mu\text{m}$).

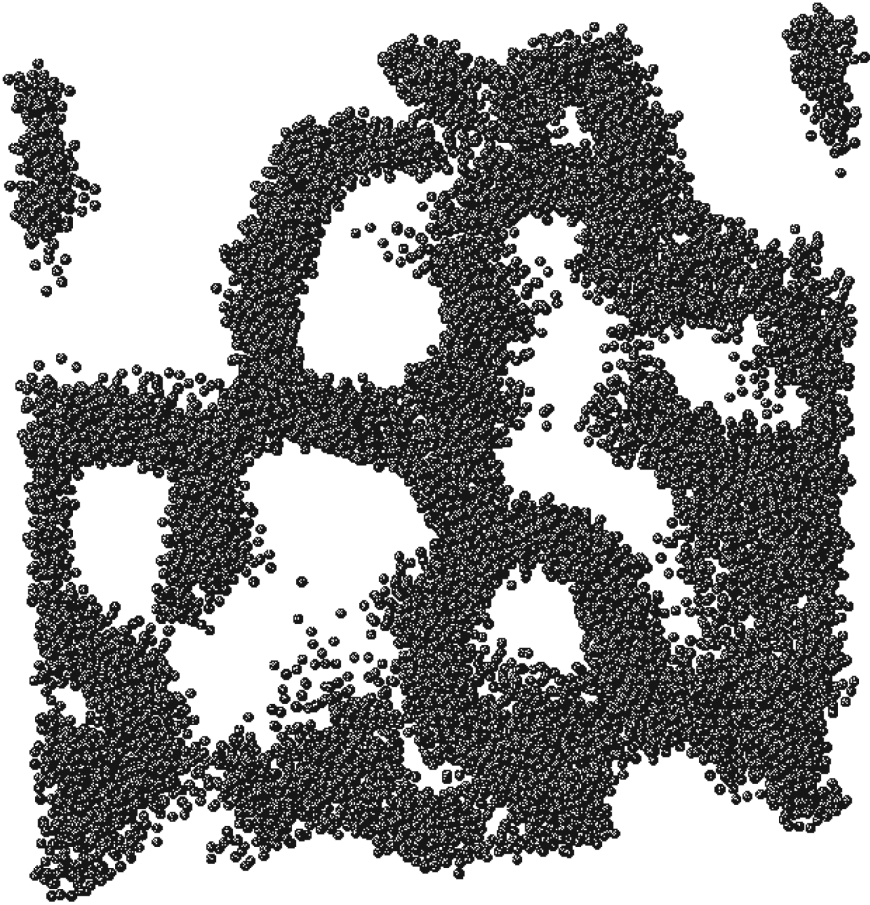


Fig. 4. Cross-sections of the XY plane of the calculation box ($12 \times 12 \times 12 \mu\text{m}$).

These pictures are quite similar to the microscopic images given by Zalesky already in 1917, see Figures 2 and 3 in [17]. Contrary to the electronic microscopy the bright field light microscopy shows dark objects on a bright background.

6. Conclusion

Globules are formed due to the intermolecular interactions between amphiphilic lipid components of kerogen.

REFERENCES

1. Lille, Ü. On the origin of 5-alkyl-1,3-benzenediols in the retort oil of Estonian kukersite. *Oil Shale*, 1999, **16**(3), 231–237.
2. Blokker, P., Van Bergen, P., Pancost, R., Collinson, M. E., De Leeuw, J. W., Sinninghe Damste, J. S. The chemical structure of *Gloeocapsomorpha prisca* microfossils: implications for their origin. *Geochim. Cosmochim. Ac.*, 2001, **65**(6), 885–900.
3. Lille, Ü. Current knowledge on the origin and structure of Estonian kukersite kerogen. *Oil Shale*, 2003, **20**(3), 253–263.
4. Zalessky, M. D. *Proc. Russian Acad. Sci.*, 1917, II, part 1 (in Russian).
5. Fomina, A. S., Pobul, L. J., Degtereva, Z. A. The Chemical Nature of Baltic Kukersite Oil Shale and Its Properties as A Chemical Raw Material. Tallinn: Estonian Acad. Sci., 1965 (in Russian, Summary in English).
6. Savest, N., Oja, V., Kaevand, T., Lille, Ü. Interaction of Estonian kukersite with organic solvents: A volumetric swelling and molecular simulation study. *Fuel*, 2007, **86**(1–2), 17–21.
7. Kozubek, A. Interaction of alkylresorcinols with proteins. *Acta Biochim. Pol.*, 1995, **42**(2), 241–246.
8. Reynwar, B. J., Illya, G., Harmandaris, V. A., Müller, M. M., Kremer, K., Deserno, M. Aggregation and vesiculation of membrane proteins by curvature-mediated interactions. *Nature*, 2007, **447**, 461–464.
9. Hettema, E. H., Gould, S. J. Cell biology: Organelle formation from scratch. *Nature*, 2017, **542**, 174–175.
10. Helfrich, W. Elastic properties of lipid bilayers: theory and possible experiments. *Z. Naturforsch. C*, 1973, **28**(11), 693–703.
11. Lille, Ü., Heinmaa, I., Pehk, T. Molecular model of Estonian kukersite kerogen as evaluated by ¹³C MAS NMR spectra. *Fuel*, 2003, **82**(7), 799–804.
12. Bekirogullari, M., Fragkopoulos, I. S., Pittman, J. K., Theodoropoulos, C. Production of lipid-based fuels and chemicals from microalgae: An integrated experimental and model-based optimization study. *Algal Res.*, 2017, **23**, 78–87.
13. Bereau, T., Hu, M., Diggins, P., Deserno, M. *Mesoscopic Membrane Simulations with Mbtools*. Carnegie Mellon University, Pittsburgh, PA, USA, 2012, pp. 14.
14. Cooke, I. R., Kremer, K., Deserno, M. Tunable generic model for fluid bilayer membranes. *Phys. Rev. E*, 2005, **72**(1), 011506.
15. Kozubek, A., Tyman, J. H. P. Resorcinolic lipids, the natural non-isoprenoid phenolic amphiphiles and their biological activity. *Chem. Rev.*, 1999, **99**(1), 1–26.
16. Cimrak, J., Gusenbauer, M., Schrefl, T. Modelling and simulation of processes in microfluidic devices for biomedical applications. *Comp. Math. Appl.*, 2012, **64**(3), 278–288.
17. Zalessky, M. D. On the marine Silurian sapropelite formed by blue-green algae. *Proc. Russian Acad. Sci.*, 1917, VI, **11**(1), 3–18 (in Russian).