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To whom it may be concern

PhD Dissertation examination report on
New materials for studies on nanostructures and spatio-temporal patterns self-organized by surface phenomena
presented by Richard Julius Gotthard Löffler

PhD candidate Richard Löffler submitted a well-written dissertation on complex self-propelled systems, which is a very attractive topic related to my own research activities. The dissertation focuses on the life-like phenomena of both condensed and soft matter driven by surface and interface forces. It is known that far-from-equilibrium systems can exhibit interesting behaviour such as self-propulsion and self-organisation, nevertheless the author presents not only new experimental setups and new results for the commonly studied systems (camphor boats), but also introduces the novel systems not yet described in the literature (the mixture of camphor and camphene). However, all the data presented are purely experimental. The originality and quality of this dissertation is supported by the fact, that the results were already published in two impacted journals (Molecules IF 4.411 and Physical Chemistry Chemical Physics IF 3.676) and as a peer-reviewed conference paper (in all cases with the PhD candidate as a first author).

The dissertation consists of 171 pages. It is well organized and clearly structured into six chapters. In the first introductory chapter (Preamble I), the most relevant terms related to the active matter are outlined. The most significant works in the field of self-propelled objects from recent years are introduced with the aim to highlight the importance of this research.

The second chapter (Part 1: Camphor boats) focuses on a development of an improved setup for experiments with camphor. There is/was an extensive research on camphor pills and boats and one can find a lot of papers and books related to this simple chemical system. There are also various setups and various aims of camphor boats studies. However, the author of this dissertation focuses on the setup as follows: camphor pills glued to the rectangular boat with a U-shape profile from the front view. The boat was attached by a plastic arm (which was glued to the middle of a Petri dish on one side) and the circular trajectory of the boat was studied.

The author performed many experiments where he changed the position of the camphor pill in the boat. He analysed the positions of a boat in the Petri dish in time and then evaluated angular velocities. Several modes of motions were observed and defined (continuous, intermittent, vibratory and inversive) and then compared. It was concluded that this improved setup solved some previous problems and thanks to the arm it enabled a circular movement of boats in Petri dishes, however for further studies still further improvements are needed. To be able to perform several tens of experiments under the same conditions and get statistically significant data, the pills and boats must be prepared more precisely, for example by using 3D printing, as the author suggests. In present work, for each kind of boat 1-3 experiments were performed, which is sufficient considering the length of experiments (several hours). Anyway, the parallelisation could help as well.

The third chapter (Part 2: Hybrid material) describes a novel hybrid material consisting of camphor, camphene and polypropylene. This semi-soft substance has intriguing properties. It can be easily formed into various shapes, and it is able to self-propel on the air/water interface. The author performed admirable number of experiments where the shapes of self-propelling objects from this new compound were changed (from marbles, via rods to more complicated shapes). Further, he changed the composition of pills and evaluated the motion parameters such as speed or the position of the pill in the Petri dish. Fascinating phenomena resembling collective behaviour were shown in Petri dishes containing large number of rods or marbles. As a side result of this research, the foam material with interesting hydrophobic properties offering several potential applications was discovered. In my opinion, this chapter is the key part of the presented dissertation. While the Part 1 presents a variation of other experiments with an improved experimental setup and Part 3 is also based on previous published data, the Part 2 brings the information about completely novel material and the results are the discoveries of author of this thesis. Moreover, two papers related to these results were already published.

The fourth chapter (Part 3: Self-propelled droplets) is related to the droplet systems. In the first part of this chapter, the author describes the observation, how the dyes can affect the behaviour of droplets, namely what kind of behaviour can be observed in paraffin and paraffin/camphor droplets in dependence on the Oil Red O concentrations. The experimental analysis of interfacial dynamics of these systems was performed. These results are valuable for everyone working on droplet systems and using various colorants or other additives. Although in some control experiments the behaviour of pure and coloured droplets does not differ at all, under specific conditions, the differences can be significant, as the author nicely highlighted. The second part of this chapter is also related to the study of the dye effects on droplet behaviour, but in a different droplet system – ethyl salicylate droplets mixed with paraffin floating in the aqueous solution of sodium dodecyl sulfate. This work was performed in collaboration with Shinpei Tanaka from Hiroshima University. The new results which are described in this dissertation are remarkable, namely the experiments with two kinds of droplets – coloured by Oil Red O and Sudan Black. The hypotheses are based on sound arguments and supported by surface and interface tensions measurements. Also, the systems

where one kind of droplets is hunting the other droplets were not described in literature yet and this approach opens a new direction in the multiple droplet systems studies.

The fifth chapter is dedicated to conclusions and outlook to the future, the experimental procedures are described in the sixth chapter. The thesis contains the list of all abbreviations and references. I very appreciate the supplementary movies uploaded to YouTube. Of course, I have not seen all of them in the full length (they take almost 6 hours in total), anyway they are very useful and supportive for the readers of this dissertation. The description of individual movies and the experimental conditions directly on YouTube would be even more useful.

The dissertation is written well, with occasional minor grammatical and spelling mistakes. The figures and graphs are clear with an appropriate description in both the legend and the main text. Only rarely, it is possible to find the wrong numbering (e.g. page 34 - number of tables 0.1 and 0.2 instead of II.1 and II.2). I dislike the graphs in Part 3, where the author included the titles of graphs (apparently from Excel with the underlined words – see for example Figure IV.42). The author explains all experimental conditions and results in details, however in some parts this approach is excessive (and maybe even annoying for a reader). For example, sections 3.2.3.1 - 3.2.3.6 describe the same type of experiments – the solid pill with a diameter 4 mm and height 1 mm moving on the water surface in a Petri dish, the pills differ in the composition (weight ratios of camphene, camphor a polypropylene). These experiments are described by the same type of texts, figures and graphs, even some sentences are repetitive. Even the errors in some sentences repeat ("the distance between the pill center and the dish center was always larger than XX mm" instead of dish wall). For the reader it is hard to orient in these chapters. Everything is clear later by a simple sentence "The results presented in Section III. 3.2.3.1 to III. 3.2.3.6 indicate that the self-propelled motion of pills made of camphene-camphor-polypropylene plastics is independent of the component weight ratio." In my opinion, one well-arranged figure and/or table comparing all the experiments confirming the independency of the behaviour on pill composition would save the reader's time and energy. I have uncovered only one factual error (related to my own papers) - the PhD candidate writes that the decanol droplets follow the gradients of sodium decanoate, however decanol droplets follow the gradients of salts or hydroxides (page 11). Regardless the comments summarized above I state that the thesis is a high-quality work, and these points are just minor forgivable shortcomings.

In summary, this work provides a valuable original contribution to development and characterization of self-propelled systems consisting of solid, semi-soft and liquid materials. The dissertation contains many comments related to the future work and the work in progress is mentioned as well. Based upon what is contained in the thesis, I augur that Mr Löffler has a most productive research career ahead of him since he is well prepared to make further contributions to the fields of complex systems and artificial life research.

Questions that might be put to the PhD candidate Richard Löffler include:

1. To justify the importance of such interdisciplinary research and where does Mr Löffler see the self-propelled systems and their applications in a decade from now.

2. The author uses the term “fork” in his dissertation (page 34). Can he explain this term (and other terms used for the description of nonlinear behaviour) and use it also in the context of results presented in the other parts of his dissertation?
3. As the author states, “camphor consists of white, translucent crystals at room temperature, delivered by chemical suppliers as small granules often times in bigger clumps” (page 35). Is the author familiar with the laboratory and industrial synthesis of camphor? Can he (as a chemist) explain the ways of camphor production and how the quality of product can be controlled?
4. Part 2 describes a large number of experiments on Petri dishes. However, the Petri dishes differed in their size and the author has not explained why he was not consistent and why he has not performed all experiment under the same conditions. Since he used different Petri dishes and the same volume of water, the experiments differed in the depth of water pool. Can the author discuss the data from literature, namely how the depth of aqueous solutions affects the behaviour of droplets and solid particles, and compare these data with his experimental observations.
5. The author performed a set of experiments with camphor/camphene/polypropylene pills varying in the composition. The distances between the pill centre and the dish wall varied. Can the author suggest any explanation why and suggest a type of experiments where the effects of meniscus can be studied.
6. The author states (page 109) that “Oil red O as expected is not a surfactant, but it does seem to be a liquid-phase interfactant”. The term "interfactant" is usually used in the context of adsorption to the solid surfaces, could the author discuss the idea of a "liquid-phase interfactant"?
7. In chapter IV. 2.2, the author discusses the differences between Oil Red O and Sudan IV, however the experiments in this dissertation were performed by using Sudan Black. Can the author discuss the differences between Sudan IV and Sudan Black and if his hypotheses described for Sudan IV are valid also for Sudan Black?
8. Although the work should focus on nanostructures, this word was used only in the title of this dissertation. Can the author discuss his work in the context of nano-world studies?

I declare that I have reviewed the thesis and based upon this thesis, published works and other Mr Löffler’s activities (active contribution to scientific gatherings such organising and co-organising of workshops and conferences, namely artificial life related), I recommend this thesis very strongly and without any reservation for the oral examination. I believe this doctoral dissertation meets the conditions specified in Article 187 of Act of July 20, 2018 Law on Higher Education and Science (Journal of Laws of 2018, item 1668, as amended).

Yours sincerely,

Jitka Čejková 

Prague, 25 August 2021