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Review of doctoral thesis of Mr. Richard Löffler, M.Sc:

"New materials for studies on nanostructures and spatiotemporal patterns self-organized by surface phenomena"

The research described in reviewed thesis is a contribution to the field of "complex systems" – a term meaning today coupled nonlinear dynamical systems of complicated cooperative behavior, including those mimicking selected aspects of living matter. Accordingly, this work contains extensive experimental characteristics of dynamical systems in which particles, subject to gradients of interfacial tensions, are set into self-organized motion of various degree of complexity.

The dissertation was prepared under the common supervision of Prof. Dr. hab. Jerzy Górecki from the Institute of Physical Chemistry of the Polish Academy of Sciences and Prof. Dr. Martin M. Hanczyc from the University of Trento in Italy, who are very experienced researchers in both experimental realization and modeling of such dynamical chemical systems. The research was conducted in the Institute of Physical Chemistry in Warsaw, at the University of Trento, as well as at the University of Hiroshima in Japan. The entire thesis, including all attachments, counts 171 pages, and includes 138 literature references.

Regarding the essential content of the dissertation, only the first dozen or so pages are devoted to a synthetic description of the current state of knowledge, based on literature references, while vast majority of the thesis (covering pages from 18 to 160) is devoted to the description of own research, done by Mr. Löffler, and this point should be emphasized. In the construction of the work, the author, somewhat unusual, adopted such a sequence that a detailed description of the preparation of the materials and interfacial tension measurement methods was placed only at the end of the work, but I find this acceptable.

The above-mentioned introductory part of the thesis, although ending already on p. 17, is essentially a sufficient, synthetic introduction to its main issues. Nevertheless, I have some comments about the content of chapter 1.6 which very briefly describes theoretical approaches to the described systems. In my opinion, this section should be a bit more extensive. I pose a specific question in this matter at the end of this review.

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As also mentioned above, the research described in this thesis is essentially experimental, with quantitative treatment applied only to statistical and methodological analysis of data. This means further that the interpretation of results, aimed at explaining the systems' dynamics, has the character of rather preliminary hypotheses of qualitative nature. Their verification, also due to the complexity of the systems and the complicated interplay of forces operating in them, would require in the future appropriate theoretical treatment. Nevertheless, it should be emphasized that Mr. Löffler in each case tried to formulate a relevant mechanistic explanations.

Mr. Löffler has performed numerous successful experiments with "hard matter" and "soft matter" dynamical systems. I may imagine that they required a lot of effort, time, precision, patience, but also ingenuity in planning experiments of increasing complexity, both in terms of system design and its dynamic behavior. Undoubtedly, Mr. Löffler showed experimental skill and inventiveness in this matter. A great help for the reviewer in recognizing and understanding the dynamics of the studied systems are the video recordings, to which links are given in the pdf version of the thesis. These images were by Mr. Löffler also analyzed using the FFMPEG and ImageJ software in order to obtain their more quantitative characteristics, including the distribution of particle speeds, positions, as well as directions of their motion.

The essential content of the dissertation is divided into three main groups of investigations, according to the type of self-propelled system studied.

In the **first part**, which refers to the dynamics of "hard matter" systems, the author's optimization of the construction of the well-known "camphor boat" is described, which aimed to avoid the role of boundary effects in a system of limited size (Petri dish), so that it was possible to study the influence of various parameters on the nature of the "boat" possible motions. In this experimental setup, when the plastic frame with attached piece of camphor was rigidly connected to the axis of rotation, fixed in the center of Petri dish, effectively 1-dimensional space for rotary motion was available. Of particular importance here was the "diffusion distance", understood as distance between camphor boat edge and closest camphor perimeter. Graphical and tabular collections of results reveal the following modes of motion: deterministic continuous, intermittent (meaning periodic bursts of motion separated by long quiescent states), vibratory and inversive regimes (the latter one meaning the bursts of motion in reversed directions). Quite logically, when the system's symmetry was only slightly broken, its resulting dynamics became relatively complex, while stronger deviations from symmetry resulted in more predictable dynamic responses. Indeed, such modification of the camphor boat allowed for better control of its dynamics, which in a traditional, simple experiment seems to be rather random.

The **second part** of the dissertation shows an **innovative modification** of the camphor (still hard matter) system in the direction of making a material more plastic, which eventually turned out to be a kind of wax, prepared at elevated temperature from camphor and chemically similar camphene, which means the production of a material of a hybrid nature. Both camphor and camphene pills are self-propelled, but the ability of the hybrid phase to form easily almost any shape, as well as possibility of using various proportions between camphor and camphene, opened the way to the investigations of the role of these factors in the dynamics of the system formed on liquid layer in Petri dish. One of important conclusions was that by changing the camphor/camphene ratio, it is possible to control the character of motion. It also appeared that the hybrid system showed a synergistic increase in the speed of motion, compared to pure camphor. Particularly impressive are the results of experiments with groups of such hybrid particles, which in the course of evolution of their trajectories form clusters resembling bacterial colonies. Results were described in terms of the radial distribution function. I have the impression that the mechanism of such a strong mutual cooperation of those camphor-camphene particles can not only be due to interfacial tension effects, but arise also from purely chemical interactions between chemically related species. Results of these experiments and their analysis are described in Ref. [2] (*Phys. Chem. Chem. Phys.,* IF ≈ 3.7) on the list of publications related to the thesis.

In the next stage of the development of these experiments, the hybrid system was **enriched with polypropylene**. This modification increased the plastic properties of particles and extended the duration of action of such dissipative systems, as well as reduced the sensitivity of its evolution to the proportion between camphor and camphene. The self-propelled objects could be prepared in the form of pills or rods, in which polypropylene skeleton moderated the transport of camphor and camphene molecules from the interior of the rod towards its surface. Both simple and complex modes of motion were observed, including rotational modes. In addition, the formation of polypropylene foam was found, which, as Mr. Löffler mentioned, may be of interest for chemists working in the field of "materials science", who look for new functional materials. These results are described in an extensive publication denoted as Ref. [3] (*Molecules,* IF ≈ 4.4) on the list of three publications, related to this thesis.

To summarize, these first two parts of the dissertation are an interesting development of the well-known idea of the "camphor boat" by introducing innovative modifications to its design, as well as thanks to quantitative analysis of images of motion.

In the **third part** of the work, instead of the solid phase, the self-propelled, **liquid droplets (soft-active matter)** were designed, the dynamics of which might probably resemble the motions of coacervates in the so-called "primordial soup" or any other kind of aqueous phase. Here, the preparation of the liquid particle consisted in dissolving camphor in paraffin oil which means that camphor remained the species powering the motion of the droplet.

Furthermore, in order to allow observation of the movements of the transparent drop prepared in this way, a suitable dye, oil red O, used for this purpose also earlier by other researchers, was added to every droplet. Placed on the liquid surface, such soft objects showed not only translations as a whole, but also changes in shape (referred to as "morphing"), rapid "explosive" splitting and coalescence, depending on experimental conditions (e.g. on camphor concentration). It should be emphasized that Mr. Löffler had noticed effect of the dye on the decrease in local interfacial tension, which on one hand could be considered a nuisance, but on the other hand this indicator induced additional, complex dynamics of the studied system. Somewhat disturbing drift of the system's characteristics over time indicates that perhaps in these conditions there is a contribution from some slowly occurring, uncontrolled processes. I understand that only physical changes were assumed, but isn't it possible that also side chemical processes occur, like slow degradation, e.g. oxidation of some components of the system with oxygen from the air, dissolved in water? Perhaps conducting such experiments with liquids deaerated with nitrogen or argon and (and also kept in the inert atmosphere), could provide some clue as to the nature of the processes involved? Another possibility would be to conduct these experiments in various, fixed ambient temperatures. The role of temperature, although often complex, is also often a source of valuable diagnostic information. The above experiments are described in Ref. [1] (*Proceedings of the 2018 Conference on Artificial Life*) from the list of publications related to this thesis.

Since the essential source of driving force also for the droplet dynamics are the gradients of surface tension, its measurements for different phase boundaries were performed. These results, together with obtained adsorption isotherms, give the experimental presentation a really much-needed quantitative character. Some difficulties are caused by the influence of dyes on the surface tension, but these complex effects probably cannot be unambiguously interpreted now, based on current data.

The **further part** of the dissertation results from a collaboration with Japan, in consequence of which it was proposed to study the dynamics of liquid droplets with alkyl salicylates, dissolved in paraffin and moving on the layer of a surfactant. Specifically, the task of Mr. Löffler was to study the influence of two dyes: oil red O and Sudan black B on the dynamics of droplets containing ethyl salicylate (ES) dissolved in paraffin and placed on a layer of the surfactant (SDS) solution. It must be admitted that the dynamic structures obtained also in this series of experiments are spectacular, visually stunning: they really give the impression of almost "living" systems, including, among others, the formation of chains and agglomeration of droplets into a strictly packed "two-dimensional crystalline" phase, depending on the experimental conditions. An additional analysis concerned with the long-time behavior of such systems, in which the formation of dimers or trimers of droplets was observed. At the same time, however, a certain influence of the dye becomes in this case evident: oil red O increases the activity of droplets, while Sudan black B decreases it.

The consequence of this dye-dependent activity of droplets led further to next ingenious experiments with several droplets, each containing one or another dye. For example, red droplets are able to surround and encapsulate blue droplets. Also in this part of the work, measurements of interfacial tension were carried out and attempts were made to explain their correlation with the system's dynamics. It was definitely not an easy task, and the same concerns with the reviewer. The author uses here suggestions from the literature (the very laconic summary of which in the dissertation is not entirely clear to me) and on this basis he develops his extended proposal for a 7-stage process of creating and destroying ring structures of droplets. This mechanism contains various assumptions and also alternative suggestions for the processes taking place. Obviously local changes of interfacial tension gradients play again a fundamental role, in competition with capillary attraction supposed to be responsible for the aggregation of droplets. The author shows how the ring of droplets can form, expand and finally split, breaking the symmetry, which opens space for local enhanced transport of surface active species. Although it is a qualitative and in places variant proposal, I think that at this stage of research is quite acceptable, as the starting point for eventual further analysis, including also theoretical treatment.

Last but not least, at the end of his thesis, Mr. Löffler describes extremely impressive experiments, which show how in the system of red droplet of decanol and blue ES droplet placed on pure water surface, the "predator – prey" competition develops, on some level of generality analogous to that occurring in non-linear kinetic systems of Lotka-Volterra type. Video recordings show how one droplet is “chasing” the other one. Anyone looking for essentially universal schemes of behavior in various dynamical systems will appreciate not only the stunning visual effect, but also the intellectual aspect of this phenomenon. I understand that these results are being prepared for publication.

Thus, the reviewed dissertation constitutes a detailed description and preliminary mechanistic analysis of numerous carefully prepared and elaborated experiments of potential interest for every researcher who investigates dynamics of droplets, also interpreted as the precursors of life or as working “liquid robots”. In final conclusions, the perspectives for further work are outlined, in the area of both dynamical droplet systems and fabricating higher-order hybrid materials. Noteworthy, the analysis of the literature clearly shows that the subject of such dynamical systems has been intensively studied, not only in the teams of the above-mentioned both supervisors, but also, e.g. in Japan and the USA.

Please allow me a little personal reflection. For me, as a chemist who once received a very classical education in this field, and later extended it by exploration of nonlinear dynamics in chemistry, the research described in this dissertation is another proof that there is a fundamental difference between looking at a phenomenon and the ability to perceive its essence and significance, just as in the seemingly random dripping of a drop of tap water, one can perceive deterministic chaos, if the observer is intellectually prepared for that. Although every classical chemist is familiar with the concept of interfacial tension, not everyone is aware of the importance of its implications for the dynamics of various complex systems, not to mention its possible role even in the origin of life. That is why I consider this work to be of also high educational value, both for classical chemists and for all scientists dealing with pattern formation in nature.

From the formal side, the work is very carefully prepared, written in an understandable way and, if I can assess it as a person who is not a native speaker – correctly in English. In any case, I had no problems with understanding the content of the work. Of course, in a work of such a large volume, it is difficult to avoid minor misprints. However, their number is small, and I mention them only out of my reviewing duty.

Before my final conclusion, I would like to address a few comments and questions to Mr. Löffler that I hope to discuss during the doctoral defense.

A. Essential remarks:

1. In the introduction to the dissertation, in chapter 1.6, the author presents (in my opinion, a bit too concisely) outline theoretical approaches to the self-organized motion of the type described in his work. The equations given there refer to dynamics of surface concentrations, of, e.g. camphor, driven by diffusion and also other physical/chemical processes. However, in these equations I do not see the explicit description of the fluid convection. Therefore, my question is, whether the modelling of this type of systems could be or was already performed with the Navier-Stokes equation? It is generally possible to couple the calculations of the motion of a viscous liquid with the progress of diffusion and/or other molecular transports in this phase. For some of the studied systems, two-dimensional spatial model should be sufficient, but for modeling of, e.g. (SDS + ES) system the third spatial dimension would probably be necessary, making the calculations more advanced and computer-time consuming.

2. My minor remark is related to the sentence about "transformation of chemical into kinetic energy" as a mechanism of self-propelled motion. I think it is useful to express this idea explicitly in terms of basic physical concepts of potential and kinetic energy, as, e.g. "the transformation of *potential* energy into kinetic energy, with "chemical energy" understood as coming from the difference in chemical potentials of species that not necessarily have to undergo strictly chemical transformation (as in this work), but can be, e.g. only inhomogeneously distributed at the interface, giving rise to local gradients of interfacial tension".

3. In the evolution of self-organized nonlinear dynamical systems, the competition between positive and negative feedback loops generally plays an essential role. Is it possible to indicate explicitly such feedbacks in the characteristics of the studied systems and their role as destabilizing/stabilizing the stationary state, meaning here the quiescent state of hydrodynamic system?

4. Could imposing temperature gradient in the studied systems, e.g. using Peltier plates in appropriate spatial arrangement, introduce a certain additional direction of order to the studied systems, making their evolution more deterministic?

5. The author uses the terms "surface tension" and "interfacial tension" in a way that may suggest that they are quantities of different meaning. I suppose that "surface tension" is reserved for the gas/liquid interface, but this also an interface. (p. 104)

6. What's the difference between "Marangoni convection" and "Marangoni flow" (p. 92)? Also, I think that when the species is transported not only along the fluid surface, but also into the bulk, the Rayleigh-Bénard convection, caused by local density gradients, can contribute to the overall convective transport, but perhaps in this case density gradients are too small to compete or cooperate with interfacial tension gradients?

7. What does "reverse" mode mean (p. 24) ? It was listed as one of observed dynamical modes, but apparently not explicitly discussed later.

8. The formula for interfacial tension shown on p. 152 is probably wrong. If β is a dimensionless shape factor, the correct formula should read:

$$\gamma = \frac{\Delta\rho g R_0^2}{\beta} \quad [\mathrm{N/m}]$$

Could this mistake affect the calculations of the interfacial tension in the thesis?

B. Formal remarks:

1. The chemical formulas on p. 36 are drawn inconsistently, i.e. according to different conventions; the peripheral methyl group CH_3 is either explicitly shown (as for camphene) or is not shown at the end of the bond with carbon atom (as for the camphor molecule on the same page). Both conventions are in principle acceptable, but it is good to use only one of them in the same work. The same point refers to structural formulas of Sudan black B and ethyl salicylate on p. 107

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2. It is a good custom, both in doctoral dissertations and in scientific publications, to compose the caption under the drawing so that it becomes fully characterized without reaching for the text. Thus, if each image of the system's dynamics contained all relevant parameters, their immediate correlation would facilitate the analysis (cf. Figures II.2 and II.3 as an example).

The above questions and comments in no way affect my essentially **positive opinion** about the doctoral thesis submitted for this review.

Concluding, in my opinion, from both the essential and formal point of view, the doctoral dissertation of Mr. Richard Löffler meets the criteria specified in Article 187 of the Act of July 28, 2018 (Law on Higher Education and Science, Polish Journal of Laws of 2018, item 1668, with amendments). This carefully prepared thesis evidently contains elements of scientific novelty, supported by 3 valuable publications and on this basis I recommend further stages of the procedure of obtaining by Mr. Löffler a Ph.D. degree.

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