Referee Report (RR) on Ph.D. Thesis "New Materials for Studies on Nanostructures and Spatio-Temporal Patterns Self-Organized by Surface Phenomena" Submitted by Richard Julius Gotthard Loeffler

Author of the RR: Adam Gadomski, Professor of Physics

UTP University of Science & Technology, Group of Modeling of Physicochemical Processes, Institute of Mathematics & Physics, al. S. Kaliskiego 7/421, PL-85796 Bydgoszcz

E-mail: agad@utp.edu.pl

Phone: +48523408697; Fax: +48523408643

REPORT

The ph.d. dissertation entitled "New Materials for Studies on Nanostructures and Spatio-Temporal Patterns Self-Organized by Surface Phenomena" presented by Richard J.G. Loeffler concerns with complex self-propelled motions resulting from underlying surface and interface involving phenomena.

The Author has focused on indroducing new materials and experimental setups useful for studies on self-propelled active matter. Essentially, three main types of the experiment have been carried out.

The first type of the experiment can be viewed under the heading of rotational camphor boat in which the main focus has been on its long term motion on a water surface, depending on various diffusion distances achievable upon different placements of the camphor pills underneath the boat's bottom.

The second type of the experiment can be termed as hybrid materials, with the camphor-camphene wax and the camphor-camphene-polypropylene plastic matching the perfect-material conditions due to extreme easiness in forming different shapes of the self-propelled objects on water surfaces.

The third type of the experiment designed by the Author of the dissertation has concentrated on examining the collective motions on water surface of self-propelled droplets designed by the Author by dissolving of surface-active camphor in paraffin oil. In addition, it has been discovered by the Author that the dye oil red O can express a significant effect on the interfacial tension between the droplet and the water phase.

In spite of the preamble, designated as chap. 1 of the dissertation, the most crucial parts of the work are presented in detail as chapters 2, 3 and 4. The contents of these three chapters are presented in the qualitative order of a phase transition: from condensed via a semi-soft to soft-matter, thus toward the most elastic and/or plastic soft phase, which is the most tractable material for shaping it to desirable shapes.

In chap. 2, a circular motion of the boat with the camphor pill glued to the bottom's boat has been fairly well examined. The strategy has been to identify four types of motion resulting from gluing the camphor pill slightly or more distinctly deviated from the geometrical center of the rectangular bottom of the boat.

The types of motion have been named: continuous, intermittent, vibrational and inversive (prone to reversed motion). The system under inspection has, however, missed very precise and much more exact than offered analysis of the passages between the domains of the type of motion, pointed out by qualitative data collected in Tables 1 and 2. This type of shortage has been mainly attributed to imperfections in designing and manufacturing the boat as a whole, in mounting the pills in strict locations, in having the pills devoid of being glued, in manufacturing the pills in extremely controllable and structure-designable ways, etc.

This overall, makes an unavoidable impression that the system under study is very much controlled in a qualitative way by the diffuse distance of the pill location(s) from the center. The rule is that the motion of the boat becomes the less unpredictive the more slightly from the geometrical center the dissolving and interface-tension changing pill is mounted. If the distance of interest becomes more apparent, the systems tends to behave more regularly and less complex.

The question posed by the present reviewer is: How the irregular but circular motion of the boat becomes readily intermittent or discontinuous in terms of the relevant system's distances, and their relationships? To be more precise, the relevant distances of interest here are the following: The diameter of the Petri dish; the diffuse distance measured from the geometrical center, and finally, the distance viewed as the length and/or width of the boat. The first distance describes the principal boundary condition here (in general: whether absorbing or reflecting, or mixed? In a computer simulation, one could prescribe a periodic boundary condition as well. The second distance varies along the length of the boat; it can also vary along its width, thus along both distances, in fact. The size of the boat can always be viewed by its aspect ratio, that means, by its quotient between length and width. These all distance involving relationships can be carefully examined against the type of motion. It turns out that it does not happened in detail to the present study. As a consequence, the question appears: Why the Author postponed such a dimensional analysis of the examined system? Could he prove that it is not useful or unproductive? Why he did not resort to a simple computer simulation when he was left with certain technological manufacturing oriented difficulties summarized in the conclusions to chap. 2?

In chap. 3, a step toward lowering the stiffness of the material under examination has reasonably been taken. The concerns has been on camphor and camphene pills; as previously, the shapes and characteristic sizes of the pills have not been decisively taken into account to model the system pretending to mimic a corresponding life-like system. More quantitative measure, see eqs (2)-(5) have, however, been taken into consideration. The circular motion has been examined in the way similar to that considered in chap. 2. Also, many shapes such as rod-like, crescent, ellipse-like spoon- or fork-like, or others, have been examined upon the corresponding circular motions, provided that the rotating object have been made from the composition of wax-like camphor and camphene. Certain probability distributions have been derived from the system's behavior, also those, revealing collective motions, characteristic of more than two self-propelled objects, wherein the self-propulsion comes out from respective changes of the object(s) vs. water surface tension. The speeds of the objects and the diffuse distances are derived from the system's behavior , also in terms of certain radial-density-like functions, showing up an expected course and logic of the behavior of the complex system under study. Many interesting spatio-temporal patterns, such as collective behaviors of rods, have been uncovered. A hydrophobic polymer product as a byproduct has been identified during the series of the experiments, and explicitly proposed as a novel useful material for further studies of the type. Its structure has been carefully enough characterized by means od electron micrographs. Certain further applications, e.g. toward superhydrophobicity of the with-polypropylene-dopped material, have been sketched for future studies on self-propelling realizations. The contents of the chap. 3, have been improved considerably when compared to their counterpart contained in chap. 2.

In chap. 4, self-propelled elastic-plastic and wax-like droplets have been addressed. A multitude of collective behaviors of droplets, dopped with red oil O, sudan black B or alike, have been disclosed and captured with camera in different contrastive colors and time frames. Changes over interfacial tensions in course of time have been disclosed. However, their quantitative drops in time have not been reported or attempted to fit to capture the overall complex collective behavior. The question is why the Author likely left it for another study? In turn, the mechanism for collective droplet behavior for the so-called active droplets has been proposed in terms of a few stages pointing inversive, vibrational collective motions, and the corresponding clustering, as it is sometimes observed in living cells involving systems; the ring formation, as a nonlinear phenomenon, has also been reported. The overall studies performed in chap. 4 are mostly qualitative but they express a good enough feeling and outreach of the experimenter; for the present reviewer less chemical peculiarities, and more theoretical, thus on proposing a modeling framework argumentation, might be of help in comprehending the details of the studies.

Moreover, the chap. 5 includes conclusions and outlook to the future, and it is sufficiently well-done, involving three types of sub-systems presented. Of help are also details gathered in chap. 6 which reveals the details of the experiments (co-)performed by the Author of the dissertation under evaluation. The survey of the experimental methods is characteristic of the examination of physical chemistry fundamentals. Of great usefulness is of course the list of movies constituting the body of chap. 7. Chap. 8 represents the literature (138 items) used the dissertation throughout. It is done properly as it involves well-updated literature data. A certain question mark can be put on the number of papers published by the Candidate, being, however, honestly revealed on page *iv* at the beginning of the text.

Except of rather general quests addressed to the Author of this dissertation, which remains to be discussed, I cannot provide any serious objections that can even slightly downgrade the overall pretty good quality of the dissertation written by Richard Loeffler. An exception would perhaps be about using the notion of nanostructures in the title of the dissertation, the notion itself not elaborated exhaustively enough within the work presented (the studied objects are mainly macroscopic, aren't they?); conceptually, the current reviewer may propose to get a further insight from a special issue of BioSystems (2008) Volume 94, Issue 3 "Bio(nano)materials with structure-property relationship" (with a plausible inclusion of the term 'function', characteristic of active matter).

By mentioning only qualitatively that within the text one might find certain typographical errors, or alike (see, chap. 5 or the preamble, thus chap. 1), I can state that the ph.d.

dissertation has been sufficiently well-written and has been prepared in an accurate way for the evaluation. As a consequence of it, my final reception of the thesis is fairly affirmative, and in general, positive.

In the light of the above, let me recommend Mr. Richard Loeffler’s dissertation for further procedural and formal steps to follow. It enables me to confirm that the reviewed dissertation fulfills the conditions of Polish Law of Science of July 20, 2018 (article 187) “Law of Higher Education and Science”, and therefore, it should be send without any great doubt for further procedural steps to be materialized in full.

Bydgoszcz, August 20th, 2021.

Adam Gadomski

/Adam Gadomski/