Statement

regarding a PhD thesis on the topic: "*Molecular modeling of phase transitions at the water-alkane interface: role of surfactants and curvature*", presented by **Stoyan Iliyanov Iliev** for awarding the educational and scientific degree "**doctor**" in professional direction 4.2. Chemical Sciences (Theoretical Chemistry – Computational Chemistry)

by Natasha Trendafilova, IGIC-BAS, Prof. Dr. (retired)

Stoyan Iliyanov Iliev graduated from the Faculty of Chemistry and Pharmacy at Sofia University "St. Kliment Ohridski" in 2020 with full honors and a professional qualification "Master of Computer Chemistry - Computational Chemistry". In the same year, he was enrolled as a full-time PhD student in the doctoral program "Theoretical Chemistry - Computational Chemistry" at the Physical Chemistry Department with scientific supervisors Prof. Dr. Anela Ivanova and Academician Prof. DSc. Nikolai Denkov. In 2023, with the decision of the Faculty Council of the Faculty of Chemistry and Pharmacy (Protocol No. 26/21.07.2023) and an electronic report from the Dean of the Faculty of Chemistry and Pharmacy (No. 70-07-545/24.07.2023), Stoyan Iliev was dismissed with the right of defense. The PhD thesis was discussed and directed for defense by the council of the Physical Chemistry Department of the Faculty of Chemistry and Pharmacy of Sofia University, held on September 2, 2024.

The report on the fulfillment of the minimum national requirements under Art. 2b of the Act on Development of the Academic Staff in the Republic of Bulgaria for professional direction 4.2. Chemical Sciences (Theoretical Chemistry - Computational Chemistry), clearly shows that Stoyan Iliyanov Iliev fulfills and exceeds the minimum national requirements for awarding the educational and scientific degree "doctor". In the attached Declaration of Authorship, Stoyan Iliev declares that the presented PhD thesis is own original work, prepared during his studies in the doctoral program "Theoretical Chemistry - Computational Chemistry". In addition, the procedure for checking the originality of the PhD thesis, by using a specialized plagiarism prevention system, integrated into the e-learning environment at Sofia University, did not register plagiarism.

The structure, volume and content of Stoyan Iliev's PhD thesis meet the requirements of the Act on Development of the Academic Staff in the Republic of Bulgaria and the additional criteria for the acquisition of the educational and scientific degree "doctor" at Faculty of Chemistry and Pharmacy of Sofia University, for professional direction 4.2. Chemical Sciences. The PhD thesis is written in 114 pages and has the following structure: Introduction, Literature review, Computational methods, Results and discussion, Conclusion, Contributions and References, citing 72 titles. The Abstract (Autoreferat) correctly reflects the content of the PhD thesis.

The Literature review presents the experimental and theoretical studies on the subject known to date, which have provoked Stoyan Iliev's interest in upgrading and developing the theoretical models and computational procedures. The PhD thesis text and the illustrative material (62 figures, 49 equations and 17 tables) give a clear idea of the conducted research volume, the constructed structural models, the used computational methods and the inferred dependencies.

The topic of the PhD thesis is relevant and significant for the science, since the conducted theoretical studies open up possibilities to predict and control the properties of alkane-containing systems by preliminary studying the thermodynamic and structural characteristics of their supramolecular formations and the possible phase transitions between them. The topic also has specific practical significance, especially for the petroleum and pharmaceutical industries, where solid-state systems, composed of normal alkanes, have applications.

The main goal of the research, described in the Soyan Iliev's PhD thesis, is the theoretical study of phase transitions at the water-alkane interface, with an emphasis on the role of surfactants and curvature. Through competent and comprehensive molecular modeling, the hexadecane model system has been investigated in detail at molecular level. The behavior of hexadecane after freezing was studied. Two models have been proposed to describe the freezing process of hexadecane-containing systems, in which it is known that a transient rotator phase may exist. The effect of the surfactant on the freezing process and on the type of the ordered phase obtained, was evaluated. Comprehensive molecular dynamics simulations were performed with the pre-validated CHARMM36 force field. Basic thermodynamic characteristics, such as enthalpy and density profiles, are investigated.

A major contribution of the PhD thesis is the development of an original computational protocol for conducting classical atomistic molecular dynamics simulations of hexadecane-containing systems, in which transitions from a regular hexadecane lattice to an isotropic liquid (melting) and from an isotropic liquid to an ordered state (freezing) are successfully modeled and reproduced. With the thus proposed protocol, the freezing mechanism of bulk hexadecane and of hexadecane in contact with water at interface stabilized with a long-chain surfactant has been elucidated. In agreement with experimental literature data, upon freezing, the formation of intermediate, polycrystalline rotator phases was established. Procedures for the structural analysis of polycrystalline model phases, composed of quasi-linear molecules, have been proposed, with the help of which, structural analysis of the hexadecane crystallites in the frozen model systems has been made. An assumption has been made about the most likely sequence in which interphase transitions occur during the crystallization of hexadecane.

The computational protocol used in the PhD thesis overcomes the shortcomings of other approaches by allowing systems to freely transition from solid to liquid when heating the system and *vice versa* when cooling. The structural analyzes carried out are independent of the coordinate system and allow the analysis of polycrystallite structures. The combination of three structural parameters used distinguishes all the five possible rotator phases and the triclinic crystal.

The most significant research results have been published in three scientific papers in international journals of the Q1 category with a high impact factor (*Journal of Colloid and Interface Science*, 2023, IF: 9.9 (6 citations already noted), *Molecules* 2023, IF: 4.6 and *Colloids and Surfaces A: Physicochemical and Engineering Aspects* 2024, IF: 5.2). Research results have been presented at 7 scientific forums in the country or abroad.

Conclusion. The model theoretical studies presented in the PhD thesis of Stoyan Iliyanov Iliev were conducted at a high theoretical level, correctly and comprehensively. They are an undeniable contribution to the study of phase transitions at the water-alkane interface and the clarification of the role of surfactants and curvature.The results are described in a convincing way, with precise terminology, they are discussed with reason and understanding, which is indisputable proof of the in-depth knowledge and excellent theoretical training of Stoyan Iliev, which contributed to the successful implementation of the research in this advanced for the modern science topic.

The analysis of the PhD thesis, the scientific publications and results obtained give me sufficient reason and occasion, without hesitation to give my positive assessment by voting "**yes**" for the awarding of the educational and scientific degree "**doctor**" to **Stoyan Iliyanov Iliev** in professional direction 4.2. Chemical Sciences (Theoretical Chemistry–Computational Chemistry).

November, 2024

Sofia Natasha Trendafilova