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COLLOIDS AND SURFACES A

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Preface

Ivan B. Ivanov: Remarkable figure in colloid science

This special edition of *Colloids and Surfaces A*: *Physicochemical & Engineering Aspects* is dedicated to Prof. Ivan B. Ivanov on the occasion of his 70th birthday, and honors his contributions to surface and colloid science. The papers in this issue were provided by his colleagues, friends, and by scientists who appreciate his achievements. Here, we make an attempt to briefly recount the story of his career as distinguished scientist, inspiring educator and enterprising administrator.

Ivan Boyanov Ivanov was born (1935) in Gorna Lipnitsa, a village near the old Bulgarian capital Tarnovo, where his father, a young medical doctor, had been dispatched in the beginning of his professional career. Ivan graduated the elite high school for foreign languages in Lovetch, where he studied French. After being admitted as a student of French philology in the University of Sofia, he changed his mind and subscribed chemical engineering in the Higher Institute of Chemical Technology.

After graduating in 1960, he became assistant professor in the Department of Physical Chemistry (University of Sofia). At that time, the department, whose history begins with the names of prominent scientists as Ivan Stranski and Rostislaw Kaischew (known for their studies on crystal nucleation and growth), was already a leading scientific center, where Alexei Scheludko was developing experimental research in the field of colloid chemistry and thin liquid films. Ivan Ivanov felt that the theory was his vocation. He became an external Ph.D. student of the academician P.A. Rehbinder in the Department of Colloid Chemistry at the Moscow State University. Under the supervision of Dr. G.A. Martynov, he worked on the statistical thermodynamics of gas adsorption on solid surfaces [1–6]. His Ph.D. Thesis, “Statistical Theory of Monomolecular Adsorption” was defended in Moscow in 1969. Since that time, the statistical mechanics and thermodynamics of interfaces and dispersions has become one of his basic research fields. Jointly with his Ph.D. student B.V. Toshev, he worked on the thermodynamics of thin liquid films [7–9] and clarified the relation between the thermodynamically defined film thickness and contact angle, and the respective quantities, which are measured experimentally. With C. Vassilieff, he proposed an approach for calculation of the van der Waals surface force in foam films [10–12].

The second main research area of I.B. Ivanov has been the physicochemical hydrodynamics of liquid films. According to the ideas by de Vries [13], Scheludko [14], and Vrij [15], the rupture of liquid films occurs through spontaneous growth of capillary waves. Stationary fluctuation waves are always present at the film surfaces, but when the film becomes sufficiently thin, these waves could grow spontaneously driven by the van der Waals attraction. For a given critical wave number and critical film thickness, the wave amplitude becomes so large that the two surfaces touch each other and the film breaks. The theoretical description of this complex process (including the effects of surfactants and film thinning) became one of the first serious achievements of I.B. Ivanov and coauthors in physicochemical hydrodynamics [16]. The theory of the critical thickness of film rupture was further elaborated by Ivanov, Radoev and coworkers [17,18], and brought to the state of complete agreement with the experiment, without the use of any adjustable parameters [19,20]. In addition, Ivanov et al. [21–23] established that another, different mechanism of film rupture could take place, due to solute transport across the liquid film, and the appearance of Marangoni instability.

Other important problem in physicochemical hydrodynamics, investigated by I.B. Ivanov, is the effect of surfactants on the rate of drainage of liquid films. This problem is closely related to the practically important issue about the hydrodynamic stability of foams and emulsions. The hydrodynamic flow drives the adsorbed surfactant molecules away from the film center, while

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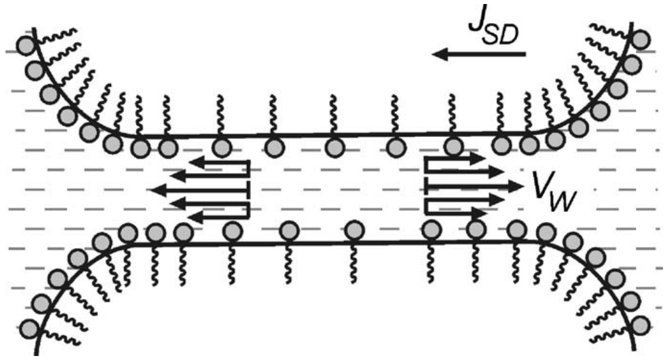

Fig. 1. Appearance of adsorption gradient in thinning foam and emulsion films, as a result of the viscous stress on the film surfaces. The dilution of the adsorption layers in the film center causes: (1) Marangoni effect, which decelerates the film thinning, and (2) surface diffusion of surfactant, which damps the Marangoni effect (the surface diffusion flux is denoted by J_{SD}). These effects were theoretically described, experimentally studied, and discussed from the viewpoint of foam and emulsion stability [24–30,39,40].

the gradient of adsorption (the Marangoni-Gibbs effect) tends to restore the equilibrium and thus opposes the film drainage [24–26], Fig. 1. The gradient of surfactant adsorption gives rise also to another effect—the *surface diffusion*, which was incorporated in the theoretical consideration [26] and a quantitative agreement with the experimental results was achieved. The effects of surface deformation and of the finite size of the emulsion drops and gas bubbles were also taken into account [27–30].

An interesting and important theoretical prediction appeared while Ivanov and Traykov analyzed the drainage of *emulsion* films. The calculations predicted [31] and the experiment confirmed [32] that the planar film between two drops should drain much faster when the surfactant is dissolved in the drop phase, in comparison with the case when the surfactant is in the outer (continuous) phase, Fig. 2. This discovery provided a hydrodynamic explanation [33] of the empirical *Bancroft rule*, which states "in order to have a stable emulsion, the surfactant must be soluble in the continuous phase". The hydrodynamic interpretation of the Bancroft rule was used to explain the chemical demulsification [33] and extended to the case of spherical emulsion drops [34].

I.B. Ivanov summarized his studies on liquid film drainage and stability in his second thesis "Physicochemical Hydrodynamics of Thin Liquid Films" for the higher degree *doctor habilis* (DSc). After the thesis defense (1976), he went for a two-year sabbatical period in the USA, in Columbia University (New York) and in the University of Rochester. There, jointly with R. Jain, C. Maldarelli, P. Somasundaran, K.P. Ananthapadmanabhan and E. Ruckenstein, he extended his survey on thin film hydrodynamics and surfactant adsorption [35–38]. At the end of this period, I.B. Ivanov wrote a detailed review article on the advance in liquid-film hydrodynamics [39], which became a basic reference in this area.

With his return to the University of Sofia in 1980, a turbulent period in the Ivanov's life began. First, he was elected Dean of the Faculty of Chemistry. The everyday problems of the faculty (150 educators and 900 students) occupied much of his time. Because the area of the thin liquid films was developing into a broad research field, he realized the necessity to collect and systematize the results of the various research groups into a single book. In 1981, I.B. Ivanov organized a symposium "Thin Liquid Films" in Sofia and initiated the preparation of the "thick book on thin films". Twenty-two scientists from eight countries supported the idea and the book, edited by I.B. Ivanov, appeared in

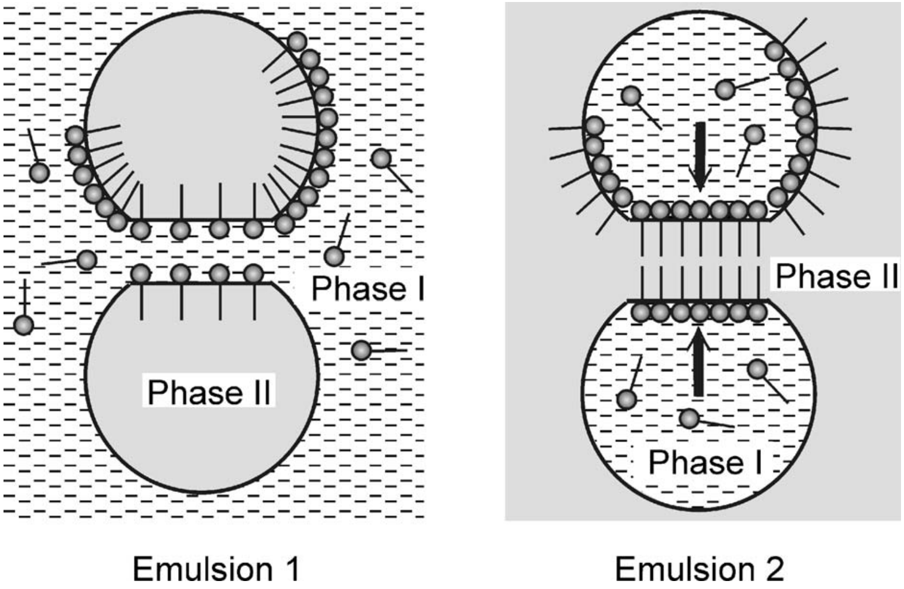

Fig. 2. Schematic presentation of the explanation of the Bancroft rule by considering the hydrodynamic stability of colliding emulsion drops [31–33]. When the surfactant is dissolved in the continuous phase (Emulsion 1) the thinning of the film between the drops is decelerated by the Marangoni effect. As a result, the lifetime of the emulsion film is much longer than the lifetime in the absence of surfactant and, hence, the emulsion is more stable. In contrast, if the surfactant is dissolved in the drops, the Marangoni effect disappears due to the convective flux of surfactant from the drop interior toward the film surfaces, and the lifetime of the emulsion is similar to that in the absence of surfactant (at negligible effect of disjoining pressure).

1988 [40]. In the meantime, a hot scientific debate arose within the Department of Physical Chemistry about the measurement procedures and magnitude of line tension at the periphery of foam films [41–51]. As a result, Ivanov left the Department and founded a new laboratory under the name "Laboratory of Thermodynamics and Physicochemical Hydrodynamics" (LTPH). In December 1999, it was renamed "Laboratory of Chemical Physics and Engineering" (LCPE). Several of his associates, A. Nikolov, C. Vassilieff, P. Kralchevsky, and E. Basheva followed him in this new undertaking.

The next years of I.B. Ivanov were devoted to stabilization and development of the new laboratory. Ivanov's talent to attract young capable researchers, to motivate them, and to secure research grants played a decisive role for his success. Thus, during the next years his research team grew and strengthened with the integration of C.D. Dushkin, A.S. Dimitrov, N.D. Denkov, D.N. Petsev, T.D. Gurkov, K.D. Danov, O.D. Velev, and T.S. Horozov, most of them being now known names in colloid science. In this period, the thermodynamic and mechanic theory of arbitrarily curved interfaces and liquid films was extended [52–55]; a model for the stabilization of Pickering emulsions was proposed [56], and a theoretical model for the surfactant adsorption from micellar solutions was developed [57,58]. I.B. Ivanov has always taken special care for the scientific development of his students and associates, starting from the formulation of important and feasible research problems (often comprising theory and experiment) and the assembly of appropriate research teams. Special attention has been paid to the international cooperation and to the exchange of visits, which was not always so easy during the Cold War years.

Close and fruitful cooperation was established with the group of Prof. Darsh T. Wasan in the Illinois Institute of Technology (IIT), Chicago. Alex Nikolov was invited in IIT to investigate the reason for the stepwise thinning of foam films, which was believed at that time to be due to a layer-by-layer destruction of a lamellar liquid crystal formed inside the film. I.B. Ivanov and coworkers were attracted to help for the theoretical explanation of this phenomenon. The experiments revealed that stepwise thinning is observed also when spherical particles, such as surfactant micelles or latex spheres, are present inside the liquid film. The results implied a new explanation of the observed effects, viz. colloid particle structuring in the thin films [59–63]. Analogous phenomenon was observed by Horn and Israelachvili [64,65] with solvent molecules between two smooth solid surfaces. These findings marked the discovery of a new component of disjoining pressure, termed *oscillatory-structural* surface force.

The political changes in Eastern Europe at the end of 1989, that are usually associated with the Fall of the Berlin Wall, found Ivanov in IIT Chicago, where he was spending a sabbatical year. On the background of the enthusiasm and euphoria from the democratic changes, he forecasted that difficult years are coming for the science in Bulgaria. His dark forecast was soon confirmed. Because of the economic difficulties and political instability, the development of science and higher education degraded to last priority of the new governments of Bulgaria. The miserable salaries and funds for science drove many of the leading and enterprising scientists away from the country. Research laboratories and institutes were either closed or functioned on the margin of existence. Purpose of life of the graduating students became to emigrate from the country at first opportunity. Within 10 years, Bulgaria lost almost 15% of its population and many young, highly educated fellows found their realization abroad.

Under these circumstances, I.B. Ivanov got profitable offers for full professorship in the USA. To a great surprise of his American colleagues, he declined all of them with the motive that he is returning back to Sofia to save his laboratory. The explanation he gave to his bewildered partners was "*you do not know how nice it is to feel needed*". His idea for the future of the science in Bulgaria was to keep alive "fireplaces" of science, which could serve as sources of revival of the scientific potential when better times come. The tool for realization of this idea was the involvement of the laboratory in international research projects, which would bring research funds in Bulgaria, instead of dispatching the scientists outside the country. And he began to fulfill this plan with the typical for him devotion, imagination, managerial skills, high standards ("good enough" is not enough), and deep involvement of his associates.

His search for projects was gratified with a first success in Japan. The old friend of Ivan, Dr. Mutsuo Matsumoto from Kyoto University, introduced him to Prof. Kuniaki Nagayama, who had just started a big "Protein Array Project", supported by the ERATO program of the Japanese Research and Development Corporation (JRDC). Prof. Nagayama and his colleagues had developed a new method for creation of ordered arrays of globular protein molecules by spreading of protein solution over the surface of mercury. The new method could find promising applications for creation of new organic materials and for analysis of the protein structure by electron diffraction from the protein array. The mercury-trough method was functioning well, but it remained unclear what is the force driving the ordering of the protein molecules into a two-dimensional crystal and how one could control efficiently this process. The clarification of this issue became the central task for the Ivanov's team within the project. Although the direction of JRDC had no practice to finance projects abroad, and the partnership with a laboratory in Bulgaria seemed risky at that time, the project agreement was signed in 1991. This act got publicity on the pages of *Nature* [66], where it was given as a good example for support of science in the transforming Eastern Europe.

Ivanov put forward the idea that the two-dimensional protein crystallization is driven by capillary forces, due to the overlap of the menisci formed around the protein molecules, when they are trapped in thin liquid layers, Fig. 3. Before that, lateral capillary forces have been studied only for floating particles, as an effect due to particle weight and buoyancy [67,68]. However, such gravity-controlled capillary forces are negligible for submicrometer colloidal particles and protein macromolecules. The project team established both theoretically [69,70] and experimentally [71,72] that a *lateral capillary force* could exist between very small particles (even of nanometer size), as an

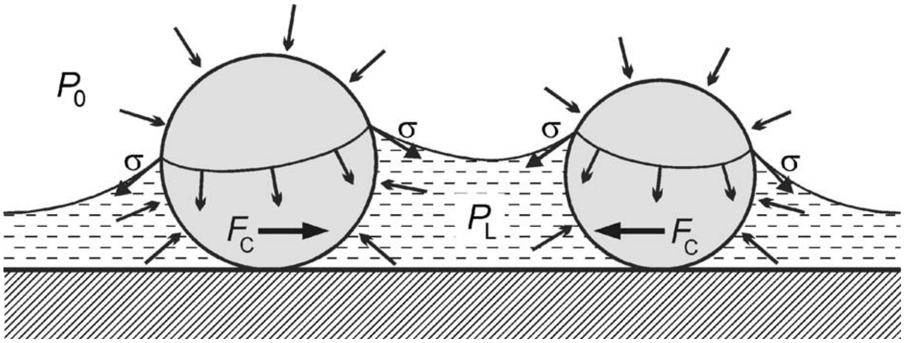

Fig. 3. Schematic presentation of the origin of the capillary forces between two colloidal particles trapped in a liquid film [69,70,73–75]. The deformation of the fluid interface around the particles leads to inclination of the three-phase contact line on the particle surface and a net attractive capillary force between the particles.

effect related to the wettability of the particle surface, rather than to the particle weight. In model experiments, the mechanism of two-dimensional crystallization, termed later *convective self-assembly* [72], was directly observed and explained, which led to the publication of a series of widely cited papers [73–75].

In the meantime, the Ivanov's laboratory organized the 9th international symposium on Surfactants in Solution (Chairmen I.B. Ivanov and K. Mittal, Varna, 1992) and started several other international projects, with partners from both academia and industry. Most of them were focused on the properties of foams and emulsions, and especially, on the effect of surfactants and surface forces on the interactions between drops or bubbles. The hydrodynamic and kinetic theories of bubble and drop interactions in foams and emulsions were refined and many interesting effects have been found [76–79]. For example, the non-equilibrium phenomena, *osmotic swelling* [80] and *cyclic dimpling* [81] in emulsion films were discovered and interpreted. With the participation of other colleagues from the laboratory and a new generation of Ph.D. students (K. Marinova, A. Hadjiiski, S. Tcholakova) an advance in the understanding of emulsification, protein-stabilized and Pickering emulsions has been achieved [82–86]. The charging of the interface between pure water and oil phases was investigated, and explained by spontaneous adsorption of hydroxyl ions [87]. It was established theoretically and experimentally [88] that the lifetime of emulsion drops as a function of the drop size exhibits a minimum due to the appearance of a liquid film between the drops upon collision. A new method, the film-trapping technique (Fig. 4), was developed for determination of the contact angles of micrometer-sized particles and biological cells [89–91]. The method has played an important role in the antifoam studies of the laboratory [91,92]. New series of experimental and theoretical studies on the surfactant adsorption and interfacial rheology has been started [93,94], including the development of several original experimental methods [95]. The results have been reported at numerous international meetings. Step by step, Ivanov's laboratory became one of the respected centers of colloid and surface science.

I.B. Ivanov has been an inspiring lecturer who draws the students' attention to the fascinating world of physical and colloid chemistry, provokes their curiosity, and awakes their striving for scientific knowledge. In 1984 he initiated a major of Chemical Physics and Theoretical Chemistry, which attracted many of the best students in the Faculty of Chemistry. Later, during the period 1992–1998 he was the engine of two successful European TEMPUS projects at master degree level, with the participation of universities from Belgium, Bulgaria, France, Germany, Greece, and UK. Most of the students educated in this major in Sofia had the opportunity to spend research periods in Western European academic and industrial laboratories. Many of these students graduated a Ph.D. level and continued their scientific careers in various countries in Europe, the USA, and Japan, thus disseminating the knowledge accumulated in Sofia. From the 22 graduated Ph.D. students of Professor Ivanov, currently 5 are full professors, 7 are associate professors, and most of the others are senior scientists in research institutes.

Instead of conclusion, let us mention the scientific philosophy of I.B. Ivanov, which has guided him in his long and successful research career. In the autumn of 1989, when he was leaving Sofia for a sabbatical year in USA, he was asked by his asso-

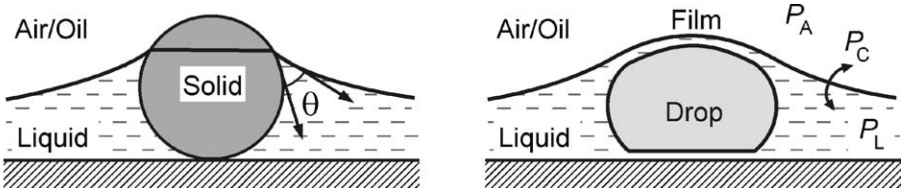

Fig. 4. Schematic presentation of particles trapped in liquid layers, as studied by the Film Trapping Technique (FTT). (A) The three-phase contact angle of micrometer-sized particles, θ, has been measured [89,90]. (B) The critical capillary pressure P_C leading to rupture of the microscopic film between the drop and the fluid interface has been experimentally determined [91].

ciates and students to leave a laboratory “constitution”, which he formulated in the following way:

> *Theory without experiment is useless.*
> *Experiment without theory is meaningless.*
> *Both are worthless without a new original idea.*

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