Condensed Matter Physics, 2013, Vol. 16, No 4, 40101: 1–5

http://www.icmp.lviv.ua/journal

Foreword

Advances in liquid state theory

This special issue is a collection of papers coming from different research groups from different countries about recent advances in the area of theoretical description and computer simulations of fluids. All these papers, however, have been submitted to this particular journal with the dedication to Prof. Myroslav Holovko on the occasion of his 70th birthday. Myroslav Holovko[1] is one of the leading Ukrainian scientists, well-known to the liquid state research community due to his important and influential contributions.

Myroslav Holovko graduated from the Pedagogical Institute of the city of Ivano-Frankivsk in 1965 as a teacher of physics. All his following life, scientific growth and mature research, however, ocurred in Lviv, the center of industry, science and culture of the Western Ukraine. After graduation, Myroslav entered the Ph.D. program in theoretical physics at the Faculty of Physics at Lviv University and was supervised by Prof. Ihor Yukhnoskii, the founder and leader of the contemporary Lviv School of statistical physics. A particular constellation of stars occurred at the moment of their meeting that benefited both of them — the maestro met a brilliant hard-working student while the student found an intelligent, creative and scientifically ambitious mentor. Myroslav completed his Ph.D. studies in 1970 defending his dissertation "Towards the statistical theory of equlibrium systems of charged particles with complex electrostatic structure" [1]. The dissertation was an extended version of his first published work co-authored with Yukhnovskii in the Ukrainian Physical Journal [2] devoted to the evaluation of the screened potentials of interactions between particles with complex electrostatic structure in fluid systems mimicking electrolyte solutions. Methodologically, the early works of Myroslav were based on the method of collective variables applied to the calculation of the statistical sum (partition function) and the pair distribution function for many-particle systems with electrostatic interactions of Yukhnovskii [3–6].

After his Ph.D. defence, Holovko was employed as a researcher in the newly founded department of statistical theory of condensed systems (STECS) that belonged to the Bogoliubov Institute of Theoretical Physics (ITP) of the Academy of Sciences of Ukraine. Science was cheap in those days, especially in the former Soviet Union, prior to the technological (computer) revolution; all one needed was a plentiful supply of sheets of paper and pencils to write and to dream. Myroslav, had been brought up in the spirit of entirely analytic calculations, still he accepted the value of numerical methods. The memory tapes and programming cards were frequent in the surrounding of his co-workers. The line of research of the cluster expansions for the ion-dipole model of electrolyte solutions lasted till the mid of seventies, reaching numerical results and analysis of the third and fourth virial coefficients of the ion-ion potential of the mean force, see e.g. [7–9]. However, Myroslav felt unsatisfied with the account of short-range part of inter-particle interactions via functional differentiation in this type of cluster expansions; he looked forward to more efficient developments and planned new research lines in this direction.

[1]Note that there are two methods for transliterating Holovko from the Cyrillic to the Roman alphabet, yielding Golovko and Holovko. Both methods have been used in Myroslav's publications, especially in his early ones when the influence of the former Soviet Union was heavy. For consistency, we have used Holovko exclusively throughout this essay since this is the preferred method in Ukraine.

The seventies were marked not only by new ideas; two important things happened: Myroslav married and obtained a new inspiration and guide in Natalka, and, on the other hand, he started to write a book with Yukhnoskii. After a few years of hard work, the book was published in 1980 [10] and soon became a bestseller in the area of statistical physics of fluids. The process of writing was really hard and heavy; one of the favorite "novels" of Myroslav at that time was the voluminous book of J. Hirschfelder et al. [11]. If one examines the contents of the Yukhnoskii and Holovko book in more detail, it gives perfect and comprehensive insight into the evolution of the theory of fluids and state of the art up to the summer of 1979. Two points of view are explained throughout their book, one starting from the method of collective variables and the description of screening and other cooperative long-range effects, with a great many results, and the second that has a description of short-range interactions contributions as a starting point and then takes into account the long-range correlations yielding, for example, the optimized cluster expansions. This second type of construction of the theory is well described in parallel to the first, and illustrated for different systems, e.g., ionic and dipole models as well as for ion-molecular mixtures. Interesting extensions to interfacial phenomena are given as well. During that decade, the first generation of students entered his orbit and became his co-workers for years, V.S. Vysochanskyj, M. Habashi, I. Kuryliak, Yu. Kalyuzhnyi, E. Sovjak, A. Trokhymchuk, I. Protsykevych, A. Kovalenko, A. Popov, V. Grouba, and O. Pizio.

In general terms, the theory of electrolyte solutions was the principal focus of interest of Holovko at the end of the seventies and the entire eighties. Optimized cluster expansions, analytic solutions of the mean spherical approximation for ion, dipole, ion-dipole models, the resulting thermodynamics at different conditions, ion and ion-dipole mixtures in a neutralizing backround, solutions of site-site integral equations, and interfacial phenomena were explored in great detail. Some new analytic solutions of integral equations for fluids of molecules with internal structure were obtained and explored. We would like to cite just a few works by Holovko and co-workers to give a flavor of activity of his group in that period of time [12–19]. In the meantime, Myroslav defended his habilitation work (second and higher doctoral thesis) at the ITP in 1980 and received an important promotion. Taking into account the extraordinary scientific performance and achievements of the STECS department during several years, the Academy of Sciences of Ukraine decided to transform it into the division of statistical physics of the ITP with three departments, and Myroslav was designated as the chief of the newly formed department of the theory of solutions.

During the late eighties, different research groups focused their attention in the statistical mechanics of associating fluids [20–24], i.e., in which particles can form bonds upon certain conditions. The association potential is strongly attractive but acts only in a quite narrow range, i.e., it can be viewed as a shell permitting, for example, an overlap of cores that formally determine the diameter of the particles. The shell-like associative potential also can be located precisely over the repulsive core inducing the formation of clusters. In another set of models, the associative potential is a localized attraction between imaginary points on the repulsive cores of the respective particles and, as a result, it is an angle-dependent attraction. The geometry of interaction can be chosen to permit only a certain type of clusters, e.g., dimers, chains and branched chains or networks. The theory of Wertheim [21–24] for chemical association starts from the decomposition of the Mayer function into the non-associative (non-bonding) and associative (bonding) contributions. The combined cluster series for the pair correlation functions were developed such that the contribution of the bonding term of the interparticle interaction is given in terms of the activity expansion while the nonbonding part of interaction is taken into account by using common type density expansion. The classification of the diagrams of such cluster expansions leads to the matrix-type multi-density integral equation that contains the density of non-bonded particles, or in other words monomers, and the densities of bonded partciles in different bonding states. The mass action law that determines the relation between non-bonded and bonded particles as well as a set of closure relations for the partial correlation functions completes the statement of the problem in the multi-density integral equation approach. In addition, Wertheim laid the fundamentals of a multidensity version of thermodynamic perturbation expansions for associating fluids that is most frequently called nowadays the statistical associating fluid theory.

Myroslav profoundly analyzed the aformentioned developments, rapidly understood the arising possibilities and brought his own ideas into the area, especially into the theory of electrolyte solutions. In particular, he and his co-workers proposed an associative extension of the mean spherical approximation complemented by the mass action law, and obtained the analytic solution of this model and reformulated the optimized cluster expansions in the multidensity formalism. Systematic research of the effects of association of ions provided a successful description of 2-2 electrolyte solutions and of highly non-symmetric electrolytes. The principal contributions describing these developments are highly cited [25–30]. In the nineties, a second wave of Myroslav's students, Yu. Duda, T. Sokolovska, M. Fedotova, E. Vakarin, and V. Kapko, shared his philosophy of research and grew to maturity.

Systems with Coulomb inter-particle interactions attracted the attention of Myroslav throughout his career. Developments in the application of the concepts of association to model electrolyte solutions without and with explicit solvent permitted him to obtain a set of important results in understanding the phase behavior of such mixtures, the temperature dependence of the capacitance of electric double layer, osmotic and activity coefficients, electric conductivity and dielectric permittivity [31–36].

The theory of homogeneous associating fluids inspired progress in the study of their inhomogeneous counterparts. The first works in this area [37–39] were performed by using Henderson-Abraham-Barker approach [40]. Later, these efforts were extended and resulted in the development of the density functional approaches for associating fluids in contact with energetically homogeneous and heterogeneous solid surfaces and in micropores [41–45]. On the other hand, Holovko and co-workers proposed the application of associative treatment of strong interparticle interaction for the problem of description of fluids confined in disordered porous media [46, 47] as well as investigated the relation between the aggregation of species in homogeneous and inhomogeneous associating fluids and percolation [48–50].

Most recently, the scientific interests of Holovko and his laboratory focused in three important topics. All of them in some way reflect his devotion to strict mathematical conditions in the theory of complex fluids and permanent desire to obtain novel results permitting further applications. In particular, dissatisfaction by intrinsic problems arising due to the application of the replica trick in the theory of fluids in random porous media lead him to the development of scaled particle type approach in this area [51–53].

On the other hand, novel rigorous relations for the charge profile of ions in contact with solid surface and related systems have been obtained in the series of works by Holovko and co-workers [54–58] that complement the contact value theorem for the density profile of Henderson and Blum [59, 60].

Finally, one of the recent projects pushed forward by Myroslav in his laboratory is the implementation of different techniques for the description of nematic fluids. His focus is in an adequate description of the microscopic structure, thermodynamics, and phase behavior of these systems [61–63] as well in studying this type of fluids at solid surface [64]. Myrolav's department is not entirely focused on preserving the purity of theoretical developments, objects of study determine techniques that are used. Holovko actively participates in and inspires the use of numerical and computer simulation methods. Also, he knows experimental methods and appreciates experimental results. Recently, several works based on classical molecular dynamics for the modelling of cation hydrolysis [65, 66], *ab initio* molecular dynamics and dissipative particle dynamics have come out from the department of the theory of solutions or in other words made by Holovko and his young team, M. Druchok, T. Patsahan, I. Kravtsiv, V. Shmotolokha.

Myroslav's scientific achivements are recognized by world-wide community that works in soft matter physics, chemical physics, and theoretical physical chemistry. He participates in several scientific councils, editorial boards and, besides, was elected recently as a corresponding member of the National Academy of Sciences of Ukraine. What are the fundamentals of his success is both difficult and easy to say. He had an extraordinary teacher, a group of good students, but most importantly he had fallen in love with statistical physics in his youth, kept and is keeping this strong devotion to science with self-discipline and enjoying his work. He is lucky to work in the demanding and creative atmosphere of the Condensed Matter Physics Institute. His talent, mildness, modesty and patience attracts beginners in their careers. Also these features are multiplied by talent and profoundness in research that makes collaboration with him a real pleasure.

On behalf of the Editorial Board of this journal and personally, we wish Myroslav Holovko continued good health, new ideas and results. It is our pleasure to express our gratitude to the contributors of this special issue for their interesting articles and we do not doubt that the reader will enjoy all of them.

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