CONDENSED
MATTER
PHYSICS

Foreword

> All that doth flow we cannot liquid name
> Or else would fire and water be the same;
> But that is liquid which is moist and wet
> Fire that property can never get.
> Then 'its not cold that doth the fire put out
> But 'tis the wet that makes it die, no doubt.
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> *The poem "What is Liquid?"*
> *Margaret Cavendish,*
> *Duchess of Newcastle-upon-Tyne,*
> *English aristocrat, philosopher, poet and writer*
> *(1623 – 15 December 1673)*

What is Liquid?

Nowadays it is well accepted to divide matter into two major types – solids and fluids. A usual way to distinct between solid and fluid by analyzing the pictures obtained in diffraction experiments, namely, sharp Bragg reflections in the case of solids while diffuse rings in the case of fluids is not, generally speaking, entirely obvious. The atoms in glasses and amorphous solids do not possess an ordered arrangement as well. Fluids can be defined unambiguously as substances that flow under a shear stress, no matter how small. This distinction is not so evident, however, between liquids and gases that basically (although not exclusively) form the subset of fluids. The pioneering theory of van der Waals (1873) of the continuity of the gaseous and liquid states of matter yielded qualitative interpretation of the vapor-liquid equilibrium and the existence of a critical point. According to this theory, at temperatures below the critical temperature, the gaseous and liquid phases can coexist in equilibrium. Above the critical temperature, there is a single fluid phase, i.e., one can proceed continuously from low-density fluid to high-density fluid. It means that an equilibrium high-density fluid below the critical temperature, that according to van der Waals theory is a liquid, somehow differs from the fluid of exactly the same density but at temperature above the critical temperature. In fact, at temperatures above the critical temperature, the coexistence of fluid phases is not observed; this means that there is no difference between gas and liquid.

In their review article, written for *Reviews of Modern Physics* in 1976, after a century of effort since the work of van der Waals, Barker and Henderson asked a question *What is "liquid"*? They presented a unified account of the statistical mechanics of condensed phases and did their best to give a comprehensive survey of the many approaches to the theory of liquids, examining many possible extensions of the theories existing at that time. The question *What is "liquid"*? was just a paraphrase of the questions that were often asked by aliens in "Star Trek". As in the television series, with this question they were echoing the existing puzzlement in the theory of liquids. Curiously, exactly the same question had been documented even before the van der Waals work, more than three centuries ago as the title of the poem written by Margaret Cavendish[1], the poem that is used as an epigraph to this introduction.

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[1]Margaret Cavendish was a poet, philosopher, writer of prose romances, essayist, playwright and, some say, a tireless self-publicist. Her writing addressed a number of topics, including gender, power, manners, scientific method, and animal protection. Her romance, The Blazing World, is one of the earliest examples of science fiction. She rejected the Aristotelianism and mechanical philosophy of the seventeenth century. She criticized and engaged with the members of the Royal Society of London and the philosophers Thomas Hobbes, René Descartes, and Robert Boyle. The titles of some other poems by Cavendish that are relevant to the topic of this paper include "The World Made by Atomes", "A Warr

Despite some clear faults, the van der Waals theory had a potential to serve as the basis of a satisfactory theory. Unfortunately, this was not understood at the time, and nearly a century was wasted by attempting to adjust the van der Waals parameter a instead of refining the concept of an excluded volume. The beginning of a modern understanding of the liquid state in the direction originated by van der Waals occurred when the theory of hard-sphere fluid was formulated and when the computers and simulations were being developed. This made it possible to separate the questions of the appropriateness of a model for the intermolecular potentials and the accuracy of the theoretical approximations. In 1964 Longuet-Higgins and Widom published an important paper that indicated that the van der Waals theory was not merely an interesting pedagogical tool but was the basis of a useful theory. However, a real development of our understanding of the liquid state began in 1967 with two papers published in The *Journal of Chemical Physics* by Barker and Henderson and the review article in *Science* by Widom. This was continued by the already mentioned seminal article in *Reviews of Modern Physics* by Barker and Henderson (1976) and by a review article in *Science* by Chandler, Weeks, and Andersen (1983).

The idea of this special issue was derived a year ago. The year 2014 was a significant anniversary both generally and personally. Personally, it was 80 years since the oldest of us, Douglas Henderson, was born. More generally, it was a hundred years since another important paper in the theory of liquids by Ornstein and Zernike appeared. With this in mind, we felt it is timely for a collection of expert contributions to fill at least some of the gaps on the way to answer that magic question *What is "liquid"*? We are thankful for all colleagues who joined us in this project.

In total, we have collected thirteen contributions, which provide an insight into the selected developments, as well as some new concepts that emerged recently when studying the liquid matter. The issue is opened by a reminiscence of Douglas Henderson on the influence of Henry Eyring and John Barker upon his life and work, reminding all of us about these two outstanding scientists and fine men.

As it was already admitted, to a very great degree, the success of the Barker-Henderson perturbation theory was due to analytical results for the hard-sphere fluid widely used as the reference system in the theory of fluids. In a variety of applications of the perturbation theory, the main problem was to find a way to relate the hard-sphere reference to a particular fluid system of interest. In this connection, it is rather interesting to note the first article written by Myroslav Holovko, Taras Patsahan and Volodymyr Shmatolokha where among others, the analytical results are presented for thermodynamics of a hard-sphere fluid in a hard-sphere matrix, that were obtained within the scaled particle theory. These results are further used as the reference system in the framework of the Barker-Henderson perturbation theory to study the vapor-liquid coexistence in the Lennard-Jones fluid adsorbed into a hard-sphere porous media.

Within the content of the issue, there are two more contributions that concern an extension of the application of the Barker-Henderson perturbation theory, that originally was formulated for simple fluid, on the so-called complex fluid systems. Namely, the article by Taras Hvozd and Yuri Kalyuzhnyi that concerns generalization of the second-order Barker-Henderson perturbation theory for description of the vapor-liquid phase behaviour in a polydisperse mixture, and the article by Roman Melnyk towards combined application of the mean spherical approximation, second-order Barker-Henderson perturbation theory and Wertheim thermodynamic perturbation theory to study the structural properties and phase behaviour of the protein solutions.

The article by Søren Toxvaerd as well as the one by Andrij Trokhymchuk, Roman Melnyk and Ivo Nezbeda, both discuss the role of repulsive and attractive interactions in the fluid and liquid matter in general, and within the van der Waals theory, in particular. The results presented in these studies bring a new insight into the consequences of the short-range and long-range attractive forces for the physical properties of fluids, and ultimately could result in a revision of an existing common approach to the separation of pair interaction energy into two parts – a necessary attribute behind the perturbation theory methodology towards understanding the liquid state of matter.

The modern developments in our understanding of fluid state of matter show a tendency to rely more and more on the use of computer simulations machinery. Despite some controversy and scepticism

in the community from the point of view of the consequences for a future of the field, the applications of molecular dynamics and Monte Carlo to study the fluid systems, both simple and complex, have become today an essential attribute for each respectful research project. Regarding the case of simple fluids, this issue presents the article by Taras Bryk, Tullio Scopigno and Giancarlo Ruocco, where these authors apply the molecular dynamics simulations to obtain the autocorrelation functions of the energy, heat and entropy densities of the supercritical argon fluid. A nice correspondence of the long-wavelength region behavior of these time correlation functions with that predicted by hydrodynamics, enables the estimation of the wavenumber-dependent specific heats of this fluid system, which in the macroscopic limit perfectly agree with experimental data. Such an approach is a good example to promote the advantage of a combination of the theory and computer simulations, which in this particular case serves for the further understanding of the collective dynamics in the supercritical state of matter, which promises many interesting features observed recently in the scattering experiments.

The issue consists of five other contributions that concern the application of computer simulations in the field of fluid systems. Two of these articles form a pair and discuss the application of molecular dynamics simulations to the classical complex fluid system – pure water. The article by Tomaz Mohoric, Barbara Gribar-Lee and Vojko Vlachy is devoted to the application of the non-equilibrium molecular dynamics to the study of the structure of the SPC/E water under non-equilibrium conditions due to different temperatures for the translational and rotational degrees of freedom. By contrast, in the article by Edgar Galicia-Andres, Hector Dominguez and Orest Pizio, the authors have applied the constant pressure molecular dynamic simulation to investigate temperature trends of the microscopic structure of the same SPC/E water as well as TIP4P-Ew water model.

The other two contributions, that concern the application of computer simulations, are dealing with really complex fluid systems. Namely, the article by Dezso Boda, Gary Leaf, Jim Fonseca and Bob Eisenberg reports the application of Grand Canonical Monte Carlo simulations to the study of the energetics of ionic selectivity in the neuronal sodium channels. The results obtained in such a way show the key role that entropic hard-core excluded volume plays to distinguish between one or another ion, the issue of a primary importance to understand the mechanism of ion channels selectivity. In turn, in the article by Ivo Nezbeda, Jan Jirsak, Filip Moucka and William Smith, the authors have performed molecular dynamics simulations on pure liquid water, aqueous solutions of sodium chloride, and polymer solutions when these samples are exposed to a strong external electric field with the goal of gaining a molecular insight into the structural response to the field.

A rather distinct example of the application of computer simulations can be found in the article by William and Carol Hoover. This contribution is devoted to the Hamiltonian liquids and the so-called "Lyapunov instability" or the "sensitive dependence on initial conditions" that these systems display. Although Hamilton's equations are thoroughly time-reversible, the forward and backward Laputa instabilities can differ qualitatively. As an example, these authors consider the many-body inelastic collisions in two dimensions. Two mirror-image colliding crystallites can either bounce, or not, giving rise to a single liquid drop, or to several smaller droplets, depending upon the initial kinetic energy and the interparticle forces. The difference between the forward and backward evolutionary instabilities can be correlated with the dissipation and with the Second Law of Thermodynamics, providing an "Arrow of Time" that is illustrated for two small crystallites colliding so as to make a warm liquid.

Finally, there is one more contribution that was inspired by the slogan *What is "liquid"*? but will be printed in the forthcoming issue of *Condensed Matter Physics*. We are referring here to the article by Andriy Kovalenko, where this author and his colleagues are dealing with computations as well, but tribute is paid to another powerful tool of the statistical mechanics modelling in the world of molecular fluids – the Ornshtein-Zernike integral equation theory. In particular, the article discusses a rather promising application of this theory as an essential part of the multiscale methodology for chemical and biomolecular nanosystems in solutions. The author is arguing that for real systems, solving the three-dimensional reference interaction site model (3D-RISM) integral equations is far less computationally expensive than running the equivalent molecular computer simulations, which must be long enough to sample the relevant exchange and binding events in the sample system. As a result, the 3D-RISM integral equation theory, complemented with an appropriate closure relation, naturally yields the solvation structure around a solute (supra)molecule of an arbitrary shape in terms of 3D maps of correlation functions. The latter includes the density distributions of solvent interaction sites, and at once the solvation thermodynam-

ics analytically in terms of the correlation functions all with fully consistent account for the effects of chemical functionalities of all species in the solution.

All together, we hope that this special issue will be of interest and will provide new insights for those working in the front line of fluid and liquid state statistical physics modelling, as well as for those who are interested in new developments in condensed matter physics in general.

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