Preface

There exist in the market many excellent textbooks covering equilibrium statistical mechanics of liquids and dense gases. Why, then, yet another addition to the shelf? Is there any niche available for it to fill? This is perhaps a question to be answered by the reader rather than by the author. In any case, this book is not intended whatsoever to replace any of the good (some of them classical) texts on similar topics but, in the best scenario, to serve as a supplement to them. Despite the relatively small number of pages, some of the topics selected here are treated with more detail than in other books, but this is done at the expense of not addressing some other important topics. A delicate balance has been sought to have a piece of work that can be used as a textbook for a one-semester graduate-level course (perhaps by skipping some of the more advanced points), serving at the same time to the experienced researcher as a reference for some specific details.

Let me indulge myself in a little bit of personal recollection. Over more than 15 years, I had been producing, for personal use, handwritten lecture notes as a guide for (intermittent) teaching of graduate-level courses on equilibrium statistical mechanics in my university. When in the summer of 2012 Jarosław Piasecki invited me to be one of the speakers at the 5th Warsaw School of Statistical Physics (Kazimierz Dolny, June 2013), he informed me that speakers were expected to deliver six 45-min lectures to introduce a chosen subject belonging to statistical physics in a pedagogical way, inspiring further research. I decided to combine my experience as instructor of classical statistical mechanics and as researcher on simple models and approaches in liquid state theory to propose a series of lectures with the title "Playing with Marbles: Structural and Thermodynamic Properties of Hard-Sphere Systems." The lecture notes (slightly more than 90 pages long) were posted in October 2013 on the arXiv (http://arxiv.org/abs/1310.5578) and published by Warsaw University Press in the spring of 2014. This would have been the end of the story had Christian Caron, Executive Publishing Editor of Physics at Springer, not contacted me in January of 2014 to propose the extension of the Warsaw lecture notes (which he knew from the arXiv submission) to book length appropriate for the *Lecture Notes in Physics* series. After checking that there did not exist any copyright conflict with Warsaw University Press, and being aware that the lecture notes should be significantly enlarged, I accepted Christian's suggestion and presented a formal proposal. After about 2 years (much longer than anticipated!), the outcome is this monograph.

The aim of these lecture notes is to present an introduction to the equilibrium statistical mechanics of liquids and nonideal gases at a graduate-student textbook level, with emphasis on the basics and fundamentals of the field, but also with excursions into recent developments. The treatment uses classical (i.e., non-quantum) mechanics, and no special prerequisites are required, apart from standard introductory thermodynamics and statistical mechanics. Most of the content applies to any (short-range) interaction potential, any dimensionality, and (in general) any number of components. On the other hand, some specific applications deal with properties of fluids made of particles interacting via the hard-sphere potential or related potentials. Unavoidably, the selection of topics and the approach employed may be biased toward those aspects closer to the author's taste and expertise. My apologies if that bias turns out to be excessive.

While a large part of the content of this work is not that different from standard material found in well-established textbooks, some additional results published in specialized journals along the last few years are also covered. Moreover, the book includes original matter not published before, to the best of the author's knowledge. This can be found essentially as portions of Sects. 3.7–3.9, 4.5, 5.5, 6.9, 7.3, and 7.4.

An attempt has been made to preserve a pedagogical tone as much as possible. All the graphs (more than 70, many of them entirely new) have been specifically composed for the book with a uniform layout and aspect ratio. Nearly 30 tables are also included, not only for displaying diagrams or numerical values in an ordered way but also as summaries of equations and results that are obtained along the text but could be difficult to find when browsing through the pages. A list of exercises (adding to a total number higher than 200) is appended at the end of each chapter. In some cases they are just intended to fill gaps in the derivations of results presented in the text, thus stimulating the reader's self-study. In other cases, however, the exercises invite the reader to explore alternative or complementary views of the subjects under consideration.

One of the most difficult choices an author of a physics textbook must face concerns the choice of symbols and notation for mathematical and physical quantities. An imperfect balance has been attempted between avoiding repetition of symbols for different quantities as much as possible without, on the other hand, resorting to too many nonstandard, fancy, or awkward symbols. The non-exhaustive list of symbols included at the end of the front matter can alleviate the burden of this problem.

I am very much convinced that the student and the experienced researcher alike grasp more convincingly concepts, results, equations, or theories (maybe new to them) when they are able to associate faces with the names behind those concepts, results, equations, or theories. After all, science is made by beings as human (albeit with exceptional minds) as ourselves, and, therefore, the importance of the so-called human face of science cannot be overemphasized. Paying tribute to the scientists who have paved or are paving the way to the rest of us, knowing what they look like, and prompting our curiosity to know more about their scientific and personal lives (both usually being equally exciting) are issues that may perfectly belong in a "hard" monograph as much as in softer magazine articles or layman books. In agreement with that view, this book includes the photographs of more than 30 scientists, ranging from the second half of the nineteenth century to today. In some cases they are mentioned tangentially (if their main contributions overlap only partially with the content of this book), while in other cases those authors are frequently cited. Of course, not all those who have made relevant contributions to the field are represented, but the ones included here have certainly contributed to significant advances. I apologize for the absence of images of many other main contributors and practitioners.

The content of this book is organized into seven chapters. Chapters 1 and 2 present brief summaries of equilibrium thermodynamic and statistical-mechanical relations. They are mainly included to make the lecture notes as self-contained as possible and to unify the notation, but otherwise most of their content can be skipped by the knowledgeable reader.

Next, Chap. 3 describes the formal steps needed to derive the virial coefficients in the expansion of pressure in powers of density in terms of the pair interaction potential. Extensive use of diagrams is made, but several needed theorems and lemmas are justified by simple examples without formal proofs. Chapter 3 concludes with the discussion of approximate equations of state for (both one-component and multicomponent) hard-sphere fluids that are constructed by making use of the first few exact virial coefficients.

One of the core chapters of the book is Chap. 4, which starts with the definition of the reduced distribution functions and, in particular, of the radial distribution function $g(r)$ and the direct correlation function $c(r)$ and continues with the derivation of the main thermodynamic quantities in terms of $g(r)$. This includes the chemical-potential route, usually forgotten in textbooks.

Chapter 5 is perhaps a "side dish." Whereas one-dimensional systems can be seen as rather artificial, it is undoubtedly important, at least from pedagogical and illustrative perspectives, to derive their exact structural and thermophysical quantities and apply them to explicit model potentials.

The counterpart of Chap. 3 at the level of the radial distribution function makes most of Chap. 6, where the expansion of $g(r)$ in powers of density is worked out, again by diagrammatic manipulations justified with simple examples. The rest of Chap. 6 is devoted to the proposal of the hypernetted-chain and Percus–Yevick approximations, plus other approximate integral equations, and the issue of internal consistency among different thermodynamic routes in approximate theories.

Finally, Chap. 7 covers the analytical solutions of the Percus–Yevick approximation for hard spheres, sticky hard spheres, and their mixtures, derived as the simplest implementations of rational-function approximations for an auxiliary function defined in Laplace space. The latter approach is then applied to improve the Percus–Yevick solution for hard spheres and to circumvent the absence of an analytical solution of the Percus–Yevick approximation for square-well and square-shoulder potentials. Although such an approach is by now well established in the specialized literature, to the author's knowledge hardly other textbook on the subject includes the latter material.

Let me finish this already too long preface just by saying that I hope these lecture notes might be useful to students who want to be introduced to the exciting field of disordered condensed matter, to instructors who might find something profitable for their own courses, and to researchers who might need to have at hand a reference to quickly find a certain needed result.

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